Chemistry and Opportunities in a Global Society

Book of abstracts

14-16th July 2021

Building II

Campus of Gualtar

University of Minho

SOCIEDADE PORTUGUESA DE QUÍMICA

Universidade do Minho
Escola de Ciências

Title

Livro de resumos do XXVII Encontro Nacional da Sociedade Portuguesa de Química

Book of abstracts of the XXVII National Meeting of the Portuguese Chemical Society

Editors

Ana Paula Estevão

Luís Monteiro

Maria Manuela Raposo

Sílvia Pereira-Lima

Susana Costa

Edition

Sociedade Portuguesa de Química

Graphic design

Renato Gonçalves

Sílvia Pereira-Lima

Date

July 2021

ISBN

978-989-8124-33-3 (digital edition)

Recommended cataloging

Livro de resumos do XXVII Encontro Nacional da Sociedade Portuguesa de Química

Departamento de Química, Universidade do Minho, 2021 – 345 p.

ISBN 978-989-8124-33-3

This book was produced from the abstracts submitted directly by the authors, in accordance with the rules publicly disclosed in the event's announcements. Only small formatting changes were introduced that did not modify the scientific contents, which are the sole responsibility of the respective authors.

Scientific Committee

Artur Silva – UA - SPQ President - Chair

Susana Costa - UM, Coordinator

Ana Isabel Ricardo - UNL

Anthony Burke - UEv

Armando Silvestre - UA

Baltazar Castro - UP

Carlos Afonso - UL

Cristina Freire - UP

Fernanda Proença - UM

Mª Lurdes Cristiano - UAlg

Mª Isabel Ismael - UBI

Mário Berberan e Santos – UL

Joana Amaral - IPB

João Rocha - UA

João Paulo Crespo - UNL

João Rodrigues - UMa

Rui Fausto - UC

Verónica Zea-Bermudez - UTAD

National Organizing Committee

SPQ Executive Committee

Artur Silva - UA, President

Joaquim Faria - UP, Vice-President

Adelino Galvão - UL, General Secretary

SPQ Delegations

Susana Costa - UM, Braga delegation

Jorge Parola - UNL, Lisbon delegation

Amparo Faustino - UA, Aveiro delegation

Sara Pinto - UC, Coimbra delegation

Victor Freitas - UP, Porto delegation

SPQ Divisions

Mª Teresa Conceição, UL

Paula Branco, UNL

João Pedro Lopes, UL

Manuel Minas da Piedade, UL

Filipe Paz, UA

Mª Emília Sousa, UP

Mário Simões, UA

Pedro Góis, UL

José Câmara, UMa

SPQ Training Center

Fernanda Carvalho, UL

Tânia Coelho

SPQ Bulletin

Paulo Mendes, UEv

SPQ Groups

Isabel Malaquias, UA

Sílvia Carriço, UA

Eduardo Marques, UP

Celso Reis, IPATIMUP

Luís Carlos, UA

Cláudia Silva, UP

Anabela Valente, UA

Filipe Paz, UA

Nuno Candeias, GQEst

Mª Inês Dias, GQJ

Daniel Santos, UP

SPQ Secretariat

Cristina Campos

Leonardo Mendes

XXVII ENCONTRO NACIONAL Sociedade Portuguesa de Química

Local Organizing Committee UM

Susana Costa (coordinator)
Alice Carvalho
Ana Paula Estevão
Ana Paula Esteves
António Gil Fortes
Dulce Geraldo
Fernanda Proença
João Carlos Marcos
Luís S. Monteiro
Manuela Raposo
Manuela Silva
Mª José Alves
Renato Gonçalves
Rui Pereira
Sameiro Gonçalves
Sandra Barros
Sílvia Pereira-Lima

PREFACE

The XXVII edition of the National Meeting of the Portuguese Chemical Society (ENSPQ) will take place at the University of Minho, in Braga, from the 14th to the 16th of July 2021.

Under the theme “Chemistry and Opportunities in a Global Society”, this Meeting intends to demonstrate the vitality and diversity of the chemistry that is currently made in Portugal and in the world, with a varied scientific program with internationally and nationally renowned speakers.

Society was, and continues to be, shaken by an unprecedented pandemic with serious economic, social and health consequences, and it was necessary to adapt this Meeting to the moment we live in, with the adoption of a model that allows for in person and virtual attendance.

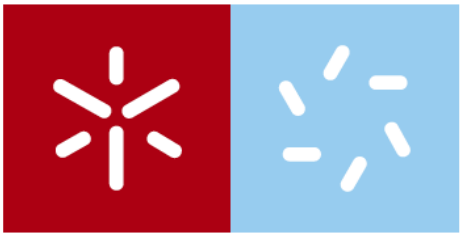
Despite the challenging conditions, the ENSPQ will be an excellent opportunity to regain some normality in the dissemination and sharing of science, so the entire national chemical community is invited to participate and (re)establish connections. In this context, the central role of Chemistry in dealing with societal challenges and opportunities is more pertinent than ever, and chemists are called to be part of the solution in areas such as the environment, energy, food, health and water, among many others.

And speaking of opportunities, enjoy the opportunity to visit Braga by taking a trip back in time into modernity. The city of Braga, a millenary city with an impressive Roman legacy and enormous beauty and heritage, lives hand in hand with entrepreneurship and a young spirit in areas as vital as culture, commerce and gastronomy.

Welcome everyone, in person or remotely!

Susana Costa (Coordinator of the XXVII ENSPQ)

Institutional Support



Universidade do Minho
Escola de Ciências

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

Sponsors

PLATINUM

Hovione

Bial
Keeping life in mind.

BRUKER
IO ANOS em PORTUGAL

BONDALTI
EVOLVING CHEMISTRY

SILVER

NORLEQ

Izasa Scientific
A Werfen Company

Grupo I.L.C.

thermo scientific
UNICAM
www.thermounicam.pt

COPPER

Qlabo
Quality Driven

ROTOQUIMICA
EQUIPAMENTO CIENTÍFICO DE LABORATÓRIO, LDA

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

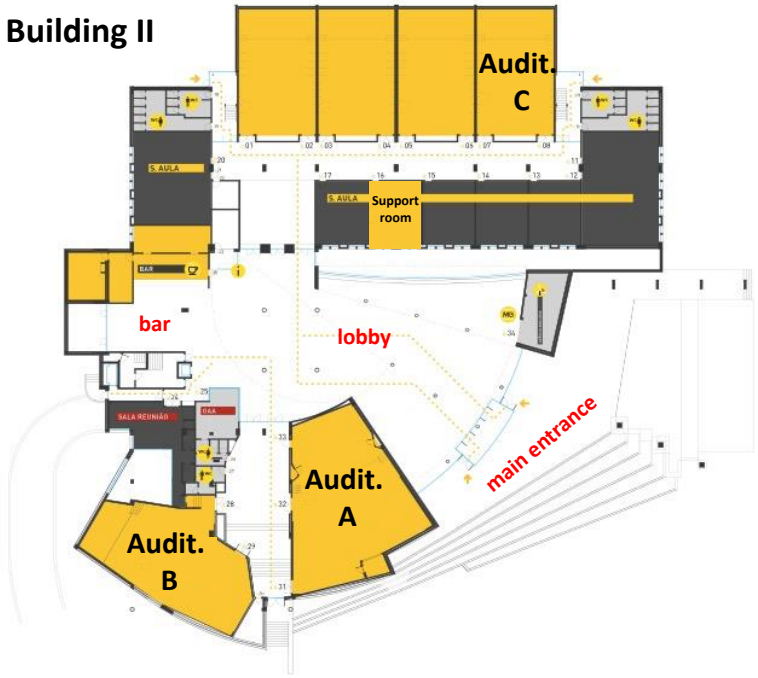
Scientific Programme

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

Important information

Venue

Building II, Campus of Gualtar, Braga



Access and stay at the venue

- Each delegate must wear the corresponding name badge at all times, during the meeting.
- The access of the delegates to the Auditoriums will be controlled in compliance with the maximum capacity allowed by the health authorities.
- Delegates must use facial mask, use alcohol-based hand sanitizer when entering the Auditoriums and in common circulation areas, comply with access and exit routes and sit only in marked seats. The sanitation of the auditoriums will take place during coffee and lunch breaks.
- Delegates participating in person can circulate between the auditoriums of the different sessions, although it is not advisable to ensure adequate levels of hygiene.
- In case of Covid-19 symptoms, please contact immediately a staff member to initiate the corresponding sanitary protocol.

Delegates presenting communications IN PERSON

Please contact a staff member 2 hours in advance at the reception/help desk to deliver your Powerpoint presentation in a flash drive (pen drive).

Delegates presenting communications REMOTELY

Please connect to the zoom link provided 15 min in advance to test audio (speaker and microphone, and headphones if applicable) and video (webcam) before the presentation.

Physical *vs* Virtual event

The meeting will take place in a physical venue and in a virtual platform, to allow attendance of delegates in person or remotely.
The physical Auditoriums A to C directly correspond to the virtual Auditoriums A to C.
In the same way as a physical event, the virtual event will allow delegates to attend sessions, hear and watch talks, ask/answer questions and network with other delegates and speakers.

During the presentations, delegates will be able to ask questions to the speakers using the chat. This process will be managed by the session chair.

Virtual posters

The posters will be always available for viewing at the virtual platform during the XXVII ENSPQ, to all registered participants.
There are no time slots allocated for **poster discussion** and delegates will be able to send messages/questions **at any time** to the poster presenters using the chat functionality, and the poster presenters will receive notifications to answer.

The meeting has a large number of oral presentations in parallel sessions, so all speakers are requested **not to exceed the maximum allocated times**, which already include scientific discussion:

- Plenary (**PL**) - **50 min**
- Keynote **(KN**) - **30 min**
- Invited Oral Communication (**OC)** - **20 min**
- Oral Communication (**O**) - **15 min**
- Flash Communication (**F**) - **6 min**
- Poster (**P**) - Always on display at the virtual platform

Meeting schedule

14th July (Wednesday)

9h30	**Opening ceremony** *Auditorium A*		
10h15	**PL1 - Ferreira da Silva Award** **Mário Nuno Berberan Santos** (IST-UL), *Auditorium A*		
11h05	*Coffee break / virtual posters*		
11h35	*Auditorium A* *Chair: I. Ismael*	*Auditorium B* *Chair: A. Silvestre*	*Auditorium C* *Chair: C. Silva*
	KN1 Salette Reis - UP	**KN3** Paula Ferreira - UM	**KN5** Sérgio Seixas Melo - UC
12h05	**OC1** Sónia Ventura - UA	**OC4** Mª Manuel Marques - UNL	**OC7** Filomena Barreiro - IPB
12h25	**OC2** Licínia Justino - UC	**OC5** Marta Correia-da-Silva - UP	**OC9** Rosa Perestrelo - UMa
12h45	*lunch*		
14h30	**PL2** **Christine Keating** (Penn State University, USA), *Auditorium A*		
15h20	*Auditorium A* *Chair: C. Afonso*	*Auditorium B* *Chair: J. Rodrigues*	*Auditorium C* *Chair: P. Gois*
	KN2 Eulália Pereira - UP	**KN4** Tiago Rodrigues - UL	**KN6** Lillian Barros - IPB
15h50	**OC3** Manuel Souto - UA	**OC6** Jaime Coelho - UL	**OC8** Ana Seca – UAc
16h10	**O1** Elsa Gonçalves - Hovione	**O5** Ana Gomes - UP	**O9** Rafael Rippel - UNL
16h25	*Coffee break / virtual posters*		
16h55	*Auditorium A* *Chair: M. A. Carvalho*	*Auditorium B* *Chair: J. C. Marcos*	*Auditorium C* *Chair: L. Monteiro*
	O2 Igor Reva - UC	**O6** Eva Monteiro - Bruker	**O10** Joana Azevedo - UP
17h10	**O3** Zhipeng Yu - UP	**O7** Joana Martins - UNL	**O8** Cláudia Braga - UL
17h25	**O4** Luís Branco - UNL	**O11** J. Valentine - UAlg	**O12** Alexander Beliaev -Bial
17h40	**Flash1-10 e 53** Cátia Lopes Rui Machado João Nunes Krzysztof Biernacki Mariana Velho André Pinto Mariana Martins Joana Nunes Joana Lopes Iwona Biernacka Maria Carpena	**Flash11-21** Lara Fidalgo Fátima Paiva-Martins Raquel Gonçalves Flávia Magalhães Pedro Varandas Sónia Pinto Shirley Sancha Bruno Gonçalves Alexandra Borges Dina Maciel André Luz	**Flash22-32** Luís Lema Rui Sousa Juliana Pereira Maria Barros Solange Magalhães Ana Fernandes Nathalia Foureaux Ouissal Assila Hugo Salazar Thainara Viana Márcia Silva

15th July (Thursday)

9h30	**PL3** **Christian Bochet** (University of Fribourg, Switzerland), *Auditorium A*		
10h20	*Auditorium A* *Chair: M. Berberan*	*Auditorium B* *Chair: J. Amaral*	*Auditorium C* *Chair: A. Ricardo*
	KN7 Nuno Silva - UA	**KN9** Goreti Sales - UC	**KN11** Cláudia Lopes - UA
10h50	**OC10** Elisabete Carreiro - UEv	**OC13** Nuno Candeias - UA	**OC16** Ana Lado Ribeiro - UP
11h10	*Coffee break / virtual posters*		
11h40	*Chair: J. Faria* Iberian Photocatalisys Association / White Book of Photocatalysis, Auditorium A		
12h00	**PL4** **Damià Barceló** (Catalan Institute for Water Research, Spain), *Auditorium A*		
12h50	*lunch*		
14h30	**PL5** **Pierre Dixneuf** (University of Rennes, France), *Auditorium A*		
15h20	*Auditorium A* *Chair: F. Proença*	*Auditorium B* *Chair: A. Burke*	*Auditorium C* *Chair: N. Candeias*
	KN8 Manuela Raposo - UM	**KN12** Luísa Martins - IST-UL	**KN10** Teresa Casimiro - UNL
15h50	**OC11** Luís Viegas - UC	**OC17** Ana Nunes - UNL	**OC14** Carolina Marques - UEv
16h10	**OC12** Mariana Fernandes - UTAD	**OC18** Joana Leal - UAlg	**OC15** Cândida Tomaz - UBI
16h30	**O13** Ivo Martins - UMa	**O17** Rafael Gomes - UL	**O15** Marta Andrade - Hovione
16h45	**O14** Sara Jorge - IST-UL	**O18** Gianluca Utzeri - UC	**O16** Beatriz Pires-Lima - UP
17h00	*Coffee break / virtual posters*		
17h30	**DEBATE - Public perception of Science in a pandemic** Moderator: Adriano Cerqueira Speakers: Miguel Castanho, Cecília Arraiano, David Marçal, Elsa Costa e Silva *Auditorium A*		
19h00	**SPQ Meeting**, *Auditorium A /Zoom link* https://us06web.zoom.us/j/89205764683?pwd=eUlIV0NFQXZ1cGZjVmlkU1Q5aikzdz09 **ID:** 892 0576 4683 / **access code**: 357051		

16th July (Friday)

9h30	**PL6** **Milo Shaffer** (Imperial College London, UK), *Auditorium A*		
10h20	*Auditorium A* *Chair: L. Cristiano*	*Auditorium B* *Chair: A. P. Estevão*	*Auditorium C* *Chair: R. Fausto*
	KN13 Fátima Montemor - IST-UL	**KN17** Mª Luz Sampaio - UNL	**KN15** Paulo Almeida - UBI
10h50	**OC19** Rui Pereira - UM	**OC23** Fernanda Carvalho - IST-UL	**OC21** Alice Carvalho - UM
11h10	*Coffee break / virtual posters*		
11h40	*Auditorium A* *Chair: V. Bermudez*	*Auditorium B* *Chair: F. Carvalho*	*Auditorium C* *Chair: M. M. Silva*
	KN14 Paulo Coelho - UTAD	**KN18** Manuel Monte - UP	**KN16** Cecília Arraiano - UNL
12h10	**PL7** **Tomás Torres** (Universidad Autónoma de Madrid, Spain), *Auditorium A*		
13h00	*lunch*		
14h30	**PL8** **Pierre Braunstein** (University of Strasbourg, France), *Auditorium A*		
15h20	*Auditorium A* *Chair: A. Galvão*	*Auditorium B* *Chair: S. Pereira-Lima*	*Auditorium C* *Chair: M. J. Alves*
	OC20 Helena Tomás - UMa	**OC24** João Paulo André - UM	**OC22** Susana Lopes - UC
15h40	**O19** Nuno Basílio - UNL	**O21** José Luís Araújo - UP	**O20** Ricardo Lopes - UL
15h55	**Flash33-42** Ana Ferreira Marlene Pacheco Rafaela Marques João Barbosa Ana Lima João Sarrato Roberto Aguado Rafael Castro Adriano Silva Inês Martins	**Flash54-62** Marlene Costa Javier Echave Mikel Anibarro-Ortega Mónica Honrado Rosa Pérez-Gregório Luís Cruz Carlos Guerreiro Samara Silva Stephany Rezende	**Flash43-52** Cátia Martins Catarina Cipriano Ana Francisca Silva André Campaniço Nuna Ramos Fernanda Carvalho Sofia Teixeira Rita Félix Elizabeth Lopes João Ravasco
17h10	*Coffee break / virtual posters*		
17h30	**Vicente de Seabra Medal** **Gonçalo Bernardes** (UL), *Auditorium A*		
18h15	**Closing ceremony** *Auditorium A*		

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

Full Programme

Wednesday, 14th July

8h30 **Registration**

9h30 **Opening Ceremony**
F. Vaz, Pro-Rector for Research and Projects of the University of Minho
N. Castro, Vice-President for Research and Inovation of the School of Sciences, University of Minho
A. Silva, President of Portuguese Chemical Society
S. P. Costa, Coordinator of the XXVII Meeting of the Portuguese Chemical Society
Auditorium A

10h15 **PL1 Ferreira da Silva Award – Mário Nuno Berberan e Santos** (IST, UL, PT)
DeLightful molecules: selected studies in physical photochemistry
Auditorium A

11h05 **Coffee break / Virtual poster session**

Session 1.A - Chair: I. Ismael
Auditorium A

11h35 **KN1 - S. Reis** (FF, UP, PT)
Key scientific and technological strategies for the development of drug delivery systems

12h05 **OC1 - S. Ventura** (CICECO, UA, PT)
Blue biorefinery: overviewing the processes, the materials and the applications

12h25 **OC2 - L. Justino** (FCT, UC, PT)
Structure, properties and applications of 8-hydroxyquinoline-5-sulfonate based materials

Session 1.B - Chair: A. Silvestre
Auditorium B

11h35 **KN3 - P. M. T. Ferreira** (CQ-UM, PT)
Dehydropeptide based nanostructures for biomedical applications

12h05 **OC4 - M. M. Marques** (FCT, UNL, PT)
Hypervalent iodine(III) mediated carbon-nitrogen and nitrogen-sulfur bond formation: innovating access to bioactive compounds

12h25 **OC5 - M. Correia-da-Silva** (CIIMAR, UP, PT)
Playing with chemical diversity to protect marine biodiversity

Session 1.C - Chair: C. Silva
Auditorium C

11h35 **KN5 - S. Seixas de Melo** (FCT, UC, PT)
Molecules at the museum

12h05 **OC7 - M. F. Barreiro** (CIMO, IPB, PT)
Encapsulation strategies for effective natural food ingredients

12h25 **OC9 - R. Perestrelo** (CQM, UMa, PT)
Establishment of putative geographical markers of apple ciders using HS-SPME/GC-MS combined with chemometric tools

12h45 **Lunch**

14h30 **PL2 – Christine Keating** (Penn State University, USA)
Liquid-liquid phase coexistence in polyelectrolyte solutions: experimental model systems for RNA compartmentalization
Chair: C. Afonso
Auditorium A

Session 2.A - Chair: C. Afonso
Auditorium A

15h20 **KN2 - E. Pereira** (FC, UP, PT)
Metal nanoparticles as scaffolds for biosensing and biocatalysis

15h50 **OC3 - M. Souto** (CICECO, UA, PT)
Electrically conductive metal-organic frameworks based on electroactive organic building blocks

16h10 **O1 - E. Gonçalves** (Hovione, PT)
Calorimetry of NBS addition to DMF: unstable or under studied?

Session 2.B - Chair: J. Rodrigues
Auditorium B

15h20 **KN4 - T. Rodrigues** (FF, UL, PT)
Machine learning for accelerating chemical biology

15h50 **OC6 – J. Coelho** (FC, UL, PT)
Developing data science tools for bioorthogonal chemistry

16h10 **O5 - A. Gomes** (FC, UP, PT)
Dual-action chimeric peptides and their ionic liquid conjugates as a novel approach to tackle skin infections

Session 2.C - Chair: P. Gois
Auditorium C

15h20 **KN6 - L. Barros** (CIMO, IPB, PT)
Development and application of natural ingredients in the food industry

15h50 **OC8 - A. Seca** (FCT, UAc, PT)
Secondary metabolites in edible species: looking beyond nutritional value

16h10 **O9 – R. Rippel** (FCT, UNL, PT)
Total synthesis of cernumidine

16h25 **Coffee break / Virtual poster session**

Session 3.A - Chair: M. A. Carvalho
Auditorium A

16h55 **O2 - I. Reva** (FCT, UC, PT)
Photochemistry of monomeric benzoxazole and isocyanophenol

17h10 **O3 - Z. Yu** (FE, UP, PT)
Highly dispersed noble metal-based carbon nitride as efficient electrocatalytic/photocatalytic hydrogen evolution

17h25 **O4 - L. C. Branco** (FCT, UNL, PT)
Ionic liquids and eutectic systems as functional materials for energy

Session 3.B - Chair: J. C. Marcos
Auditorium B

16h55 **O6 - E. Monteiro** (Bruker, PT)
Recent FT-IR trends in protein analysis and Biopharma

17h10 **O7 - J. N. Martins** (FCT, UNL, PT)
Light-activated membrane transport of arginine-rich peptides

17h25 **O11 – J. Valentine** (CMS, UAlg, PT)
Biodegradation potential of paracetamol by marine bacteria consortia

Session 3.C - Chair: L. Monteiro
Auditorium C

16h55 **O10 - J. Azevedo** (FC, UP, PT)
Development of a methodology for the determination of the reactivity of brandies used in wine fortification

17h10 **O8 - C. Braga** (FF, UL, PT)
Hypoxia-selective triazene prodrugs designed to address glioblastoma microenvironment

17h25 **O12 - A. Beliaev** (Bial, PT)
Synthesis of 4-phenylimidazoles in the discovery of potent, long-acting inhibitors of FAAH

17h40 **Flash session 1.A - Chair: M. A. Carvalho**
Auditorium A

F1 **C. S. D. Lopes** (FC, UL, PT)
Modeling halogen bonds in molecular dynamic simulation of active pharmaceutical ingredients

F2 **R. L. Machado** (FC, UP, PT)
Multi-composition biocompatible catanionic vesicles for the encapsulation and delivery of doxorubicin

F3 **J. C. F. Nunes** (CICECO, UA, PT)
Supported ionic liquid materials for L-asparaginase bioconjugation

F4 **K. Biernacki** (FC, UP, PT)
Molecular dynamics studies of dipeptide nano-pores as a membrane for gas storage and separation

F5 **M. F. G. Velho** (IST, UL, PT)
Conducting neutral bis(1,2-dithiolene) gold complex [Au(dspdt)2] with a unique crystal structure

F6 **A. Pinto** (CQ-VR, UTAD, PT)
Bio-inspired films based on Buxus sempervirens

F7 **M. B. M. S. Martins** (FC, UP, PT)
Binary Fe(III) and Mn(III) porphyrin materials with catalase-like activity

F8 **J. Nunes** (CQ-VR, UTAD, PT)
Sol-gel derived electrolytes for prototype ECDs

F9 **J. C. Lopes** (FE, UP, PT)
Visible light-driven photocatalytic synthesis of imines assisted by carbon nitride

F10 **I. Kuźniarska-Biernacka** (FC, UP, PT)
Application of coal fly ash in wastewater treatment

F53 **M. Carpena** (FFST, UVigo, SP)
A phenomenological approach to describe and characterize pro- and anti-oxidant activities with useful mechanistic contents

17h40 **Flash session 1.B - Chair: J. C. Marcos**
Auditorium B

F11 **L. Fidalgo** (FF, UL, PT)
Development of novel thiazole-based inhibitors: targeting necroptosis and RIPK1

F12 **F. Paiva-Martins** (FC, UP, PT)
Caffeic acid phenolipids in the protection of cell membranes from oxidative injuries. Interaction with the membrane phospholipid bilayer

F13 **R. C. R. Gonçalves** (CQ-UM, PT)
BODIPY-based probe for live-cell imaging of lysosomes in cancer cells

F14 **F. F. Magalhães** (CICECO, UA, PT)
Enzymatic production of polydopamine in aqueous biphasic systems

F15 **P. A. M. M. Varandas** (FC, UP, PT)
Fluorescent-lipid probes: advances towards bioconjugation by flow chemistry

F16 **S. C. S. Pinto** (CQ-UM, PT)
A fluorescent probe based on a BODIPY derivative to study cellular ingestion and internalization of solid lipid nanoparticles

F17 **S. Sancha** (FF, UL, PT)
Cytotoxic activity against HCT-116 colon carcinoma cells of amaryllydaceae-type alkaloids

F18 **B. M. F. Gonçalves** (FF, UL, PT)
ATP binding induces characteristic structural changes in the ABCG2 transport channel

F19 **A. Borges** (FC, UP, PT)
Effect of cyclodextrins on the acid-base equilibrium of pyranoanthocyanins

F20 **D. Maciel** (CQM, UMa, PT)
Exploring the behavior of ruthenium metallodendrimers as anticancer drugs

F21 **A. F. S. Luz** (FF, UL, PT)
Targeting necroptosis: discovery and optimization of novel RIPK1 inhibitors

17h40 **Flash session 1.C - Chair: L. Monteiro**
Auditorium C

F22 **L. Lema** (CQ-UM, PT)
Desenvolvimento de um sensor eletroquímico baseado em Pt-GO para quantificação de contaminantes fenólicos

F23 **R. P. C. L. Sousa** (CQ-UM, PT)
Heterocyclic thiosemicarbazone based on a bithienyl π-conjugated bridge for heavy metal cations detection

F24 **J. G. Pereira** (FF, UL, PT)
Preparation of aminals under mild conditions and their remarkable applications

F25 **M. A. Barros** (FE, UP, PT)
Photocatalytic degradation of tramadol using metal-free carbon nitride

F26 **S. Magalhães** (CIEPQPF, UC, PT)
Contribution of inland sources to microplastics increase in aquatic systems: The Portuguese case

F27 **A. C. Fernandes** (IST, UL, PT)
Conversion of plastic waste into value-added compounds using cheap and environmentally friendly catalysts

F28 **N. S. Foureaux** (CIMO, IPB, PT)
Optimization of SPE/HPLC analytical method for 17b-estradiol quantification in wastewater treatment plant (in)effluents using a surface response methodology

F29 **O. Assila** (CQ-UM, PT)
Box-Behnken design for optimization of Fenton-type reaction for water treatment using heterogeneous catalysts

F30 **H. Salazar** (CF-UM, PT)
Reusable polymer hybrid membranes for arsenite and arsenate dual-water remediation

F31 **T. Viana** (LAQV-REQUIMTE, UA, PT)
Recovery of technology-critical elements from complex aqueous mixtures through live seaweed: optimization by response surface methodology

F32 **M. Silva** (FE, UP, PT)
Recovery and purification of gold from a chloride multi-metal solution

Thursday, 15th July

9h30 **PL3 – Christian Bochet** (UFribourg, CH)
Probing and tuning photochemical reactions with isotopes
Chair: M. N. Berberan e Santos
Auditorium A

Session 4.A - Chair: M. N. Berberan e Santos
Auditorium A

10h20 **KN7 - N. J. Silva** (CICECO, UA, PT)
Development of 3D temperature tomography at the micro and nanoscale

10h50 **OC10 - P. E. Carreiro** (REQUIMTE-LAQV, UEv, PT)
Smart molecularly imprinted polymers for trace detection of dimethoate in olive oil

Session 4.B - Chair: J. Amaral
Auditorium B

10h20 **KN9 - M. G. F. Sales** (FCT, UC, PT)
Health monitoring by protein imprinted polymers

10h50 **OC13 - N. R. Candeias** (LAQV-REQUIMTE, UA, PT)
Deoxygenation of quinic acid towards new chirons for divergent syntheses

Session 4.C - Chair: A. Ricardo
Auditorium C

10h20 **KN11 - C. Lopes** (CICECO, UA, PT)
Providing solutions for clean water production and recycling of technological critical elements

10h50 **OC16 - A. R. L. Ribeiro** (FE, UP, PT)
How to reduce analytical interferences in removal studies of micropollutants?

11h10 **Coffee break / Virtual poster session**

Session 5 - Chair: J. Faria
Auditorium A

11h40 **Iberian Photocatalysis Association / White Book of Photocatalysis**
Speakers:
D. Almazán, President of the Iberian Photocatalysis Association.
C. G. Silva, Vice-President of the Iberian Photocatalysis Association and President of the Industrial Chemistry Group of SPQ.

12h00 **PL4 – Damià Barceló** (ICRA, SP)
Macro- and micro-plastic litter and increased COVID-19 based plastic pollution in the aquatic environment and landfills: treatment, environmental risks and policy solutions
Chair: J. Faria
Auditorium A

12h50 **Lunch**

14h30 **PL5 – Pierre Dixneuf**, (URennes, FR)
Ruthenium catalysts for green transformations: from alkenes metathesis to C-H bond functionalisations and useful ligands
Chair: M. F. Proença
Auditorium A

Session 6.A - Chair: M. F. Proença
Auditorium A

15h20 **KN8 - M. M. M. Raposo** (CQ-UM, PT)
Versatile π-conjugated heterocyclic molecules: design, synthesis and application in optoelectronics and energy

15h50 **OC11 - L. P. Viegas** (CQC, UC. PT)
In-Silico improvement of green chemical design

16h10 **OC12 - M. Fernandes (**CQ-VR, UTAD, PT)
The potential of the sol-gel process for the preparation of electrochromic devices

16h30 **O13 - I. Martins** (CQM, UMa, PT)
Nanohybrids and hybridplexes based on carbon dots and PAMAM dendrimer for bioimaging and gene delivery

16h45 **O14 - S. M. Jorge** (IST, UL, PT)
Improved water resistance and large conductivity enhancement of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) through cross-linking with an oxetane unit

Session 6.B - Chair: A. Burke
Auditorium B

15h20 **KN12 - L. M. D. R. S. Martins** (IST, UL, PT).
Design of efficient water-soluble catalysts for alkane and CO_2 activation

15h50 **OC17 - A. Nunes** (FCT, UNL, PT)
CO_2 utilization as a renewable carbon source towards the production of bio-based organic carbonates

16h10 **OC18 - J. F. Leal** (CCMAR, UAlg, PT)
Novel saccharinate-based compounds and their potential for multiple, but selective, applications

16h30 **O17 – R. F. A. Gomes** (FF, UL, PT)
Diversity-oriented synthesis of biomass derived furanic platforms aiming at drug discovery.

16h45 **O18 - G. Utzeri** (FCT, UC, PT)
Heptakis–aminocyclodextrin nanosponges for imidacloprid removal in aqueous media

Session 6.C - Chair: N. Candeias
Auditorium C

15h20 **KN10 - T. Casimiro** (FCT, UNL, PT)
Green molecularly imprinted polymers in API manufacturing

15h50 **OC14 - C. S. Marques** (LAQV-REQUIMTE, UEv, PT)
Exploring N-1,2,3-triazole-isatin-oxindole hybrids as promising inhibitors against two of the deadliest diseases worldwide

16h10 **OC15 - C. Tomaz** (CICS, UBI, PT)
Continuous beds: a promising tool for chromatographic purification of plasmid DNA for gene therapy and DNA vaccines

16h30 **O15 - M. M. Andrade** (Hovione FarmaCiência SA, PT)
Low-field benchtop NMR for solvent swap analysis

16h45 **O16 - B. L. Pires-Lima** (FC, UP, PT)
Probing heteroaromatic scaffolds in the melanostatin neuropeptide: a bioisosteric

approach using niacin as a pro surrogate

17h00	**Coffee break / Virtual poster session**

17h30	**Debate: Public perception of Science in a pandemic** Moderator: A. Cerqueira (RTP, Antena 1) Speakers: M. Castanho (FM, UL, PT), C. Arraiano, (ITQB, UNL, PT), D. Marçal (FCSH, UNL, PT), E. Costa e Silva (CECS, UM, PT) **Auditorium A**

19h00	**SPQ Meeting** Auditorium A / Zoom link https://us06web.zoom.us/j/89205764683?pwd=eUlIV0NFOXZ1cGZjVmlkU1Q5ajkzdz09 ID: 892 0576 4683 / access code: 357051

Friday, 16th July

9h30 **PL6 – Milo Shaffer** (ICL, UK)
Versatile and scalable nanocarbon chemistry, assembly, and application
Chair: M. L. Cristiano
Auditorium A

Session 7.A - Chair: M. L. Cristiano
Auditorium A

10h20 **KN13 - M. F. Montemor** (IST, UL, PT)
Functional nanofoams: paving the way for sustainable energy conversion

10h50 **OC19 - R. F. P. Pereira** (CQ-UM, PT)
Silk as a multifaceted source of inspiration for sustainable materials

Session 7.B - Chair: A. P. Estevão
Auditorium B

10h20 **KN17 - M. L. Sampaio** (FCSH, UNL, PT)
Women in Chemical Engineering: a majority within a minority

10h50 **OC23 - M. F. N. N. Carvalho** (IST, UL, PT)
2020: O ano em que a pandemia obrigou a rever o paradigma ensino/aprendizagem.

Session 7.C - Chair: R. Fausto
Auditorium C

10h20 **KN15 – P. Almeida** (CICS, UBI, PT)
(Thio)barbituric acid derivatives: the versatility of synthesis and biological diversity

10h50 **OC21 - M. A. Carvalho** (CQ-UM, PT)
2-Arylpurine derivatives as new promising antituberculosis agents

11h10 **Coffee break / Virtual poster session**

Session 8.A - Chair: V. Zea-Bermudez
Auditorium A

11h40 **KN14 – P. Coelho** (CQ-VR, UTAD, PT)
The use of light to induce a reversible color change.

Session 8.B - Chair: F. Carvalho
Auditorium B

11h40 **KN18 - M. J. Monte** (FC, UP, PT)
A poligamia intelectual dos químicos

Session 8.C - Chair: M. M. Silva
Auditorium C

11h40 **KN16 - C. Arraiano** (ITQB, UNL, PT)
The amazing new world of RNA

12h10 **PL7 – Tomas Torres-Cebada** (UAM, SP)
Can something that is called "Sub" be Superb? The case of Subphthalocyanines
Chair: V. Zea-Bermudez
Auditorium A

13h00 **Lunch**

14h30 **PL8 – Pierre Braunstein** (UStrasbourg, FR)
Phosphorus- and NHC-based assembling ligands for metallophilic interactions
Chair: A. Galvão
Auditorium A

Session 9.A - Chair: A. Galvão
Auditorium A

15h20 **OC20 - H. Tomás** (CQM, UMa, PT)
Dendrimers and DNA: a promising marriage

15h40 **O19 - N. Basílio** (FCT, UNL, PT)
Remotely controlled host-guest assemblies in aqueous solution

Session 9.B - Chair: S. Pereira-Lima
Auditorium B

15h20 **OC24 - J. P. André** (CQ-UM, PT)
"Química para Senhoras": As obras de Marie Meurdrac e Giuseppe Compagnoni

15h40 **O21 - J. L. Araújo** (FC, UP, PT)
"Química ao pé da letra": o encontro das palavras com o ensino e a divulgação da química

Session 9.C – Chair: M. J. Alves
Auditorium C

15h20 **OC22 - S. M. M. Lopes** (FCT, UC, PT)
Synthesis of novel chiral penta- and hexacyclic steroids

15h40 **O20 - R. M. R. M. Lopes** (FF, UL, PT)
Iminoboronate platforms for the targeted delivery of citotoxic and fluorogenic payloads into cancer cell lines

15h55 **Flash session 2.A - Chair: A. Galvão**
Auditorium A

F33 **A. C. Ferreira** (IST, UL, PT)
Methanation of CO_2 over Ni-Ce bimetallic oxides supported on SiO_2 aerogel.

F34 **M. Pacheco** (FC, UP, PT)
Preparation of photochromic nanomaterials through different synthetic routes for light-responsive textiles

F35 **R. T. Marques** (FC, UL, PT)
Mononuclear Fe(III) SCO complexes: how do solvates affect the magnetic behavior?

F36 **J. C. Barbosa** (CF-UM, PT)
A solid polymer electrolyte based on poly(vinylidene fluoride-co-hexafluoropropylene) combining ionic liquid and zeolite for room temperature lithium-ion battery applications

F37 **A. C. Lima** (FC, UGipuzkoa, SP)
Enzymatically crosslinked gelatine/alginate hydrogel-based inks applied in 3D printing

F38 **J. Sarrato** (FCT, UNL, PT)
New 3-ethynylaryl coumarin-based dyes for DSSC applications: synthesis, spectroscopic properties and theoretical calculations

F39 **R. Aguado** University of Coimbra, CQC, Department of Chemistry, Portugal.
Luminescent aqueous dispersions of lanthanide ions and gum arabic for coatings

F40 **R. C. Castro** (FF, UP, PT)
Determinação cinética de oxitetraciclina usando pontos quânticos de $AgInS_2$ e com recurso a ferramentas quimiométricas

F41 **A. S. Silva** (CIMO, IPB, PT)
Synthesis and characterization of yolk-shell magnetic nanoparticles prepared by a bottom-up approach for biomedical applications

F42 **I. Martins** (ISEL, IPL, PT)
Estudo de diferentes arquiteturas de superfície no âmbito da montagem de um imunosensor piezoeléctrico para determinação de ácido úrico em amostras de urina

15h55 **Flash session 2.B - Chair: S. Pereira-Lima**
Auditorium B

F54 **M. Costa** (FC, UP, PT)
Effects of the reactive moiety of phenolipids on their antioxidant efficiency in model emulsified systems

F55 **J. Echave** (FFST, UVigo, SP)
Eat your weeds: nutritional composition of edible Atlantic brown seaweeds

F56 **M. Añibarro-Ortega** (CIMO, IPB, PT)
Extração de aloeresina B a partir de Aloe vera com recurso a solventes alternativos: otimização do processo e avaliação de bioatividades

F57 **M. Honrado** (CIMO, IPB, PT)
Detection of species mislabeling in a plant sold as Nepeta cataria L.

F58 **R. Pérez-Gregório** (FC, UP, PT)
Interaction between peanut proteins and polyphenols: impact on protein digestibility and immunogenicity

F59 **L. Cruz** (FC, UP, PT)
Dendrimer-based polymers as new hosts for color tuning of anthocyanin-type guests

F60 **C. Guerreiro** (FC, UP, PT)
New insights into the oral interactions of different families of phenolic compounds: deepening the astringency mouthfeels

F61 **S. C. Silva** (CIMO, IPB, PT)
Spirulina (Artrhospira platensis) protein extract: techno-functional properties and potential application as a natural emulsifier

F62 **S. C. de Rezende** (CIMO, IPB, PT)
Innovative fat-reduced food solutions based on Pickering emulsions

15h55 **Flash session 2.C – Chair: M. J. Alves**
Auditorium C

F43 **C. D. F. Martins** (CQ-UM, PT)
Evaluation of a specific OFF-ON fluorescence reporter for Granzyme B activity

F44 **C. I. Cipriano** (FCT, UNL, PT)
Synthetic approach for the synthesis of a new family of phosphoglycoglycerols

F45 **A. F. G. Silva** (CQ-UM, PT)

Synthesis of the human neutrophil elastase inhibitor Ala-Ala-Pro-Val using microwave-assisted solid phase

F46 **A. Campaniço** (FF, UL, PT)
Expanding the chemical diversity of Azaaurones as a new chemical tool in the fight against Tuberculosis

F47 **N. L. P. Ramos** (CQ-UM, PT)
Synthesis and screening of antibacterial activity of 2,4,5-tri(hetero)arylimidazoles based on thieno[3,2-b]thiophene

F48 **M. F. N. N. Carvalho** (IST, UL, PT)
Camphorimine gold complexes active towards Gram-negative bacteria strains with high selectivity for Burkholderia contaminans

F49 **S. Teixeira** (CQ-UM, PT)
New hydrazone derivatives as promising antimalarial drugs

F50 **R. Félix** (FF, UL, PT)
Quenched activity-based probes as novel biochemical tools to analyse resistance to antibiotics

F51 **E. A. Lopes** (FF, UL, PT)
In silico approach to develop dual inhibitors of MDM2 and MDMX

F52 **J. M. J. M. Ravasco** (FF, UL, PT)
Chemically comprehensive predictive multivariate models for bioorthogonal metal-free cycloadditions

17h00 **Coffee break / Virtual poster session**

17h30 **Vicente de Seabra Medal**
Gonçalo Bernardes (FM, UL, PT)
Chair: J. Faria
Auditorium A

18h15 **Closing ceremony**
J. Faria, Vice-President of Portuguese Chemical Society
S. P. Costa, Coordinator of the XXVII Meeting of the Portuguese Chemical Society.
Auditorium A

List of Communications

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

Plenary Lectures

PL1-FSA *DeLightful molecules: selected studies in physical photochemistry.*
M. M. B. Santos, Instituto Superior Técnico - Universidade de Lisboa, Portugal.

PL2 *Liquid-liquid phase coexistence in polyelectrolyte solutions: Experimental model systems for RNA compartmentalization.*
C. Keating, Penn State University, USA.

PL3 *Probing and tuning photochemical reactions with isotopes.*
C. Bochet, University of Fribourg, Switzerland.

PL4 *Macro- and micro-plastic litter and increased COVID-19 based plastic pollution in the aquatic environment and landfills: treatment, environmental risks and policy solutions.*
D. Barceló, Catalan Institute for Water Research (ICRA) Institute of Environmental Assessment and Water Research, Spain.

PL5 *Ruthenium catalysts for green transformations: from alkenes metathesis to C-H bond functionalisations and useful ligands.*
P. Dixneuf, University of Rennes, France.

PL6 *Versatile and scalable nanocarbon chemistry, assembly, and application.*
M. Shaffer, Imperial College London, United Kingdom.

PL7 *Can something that is called "Sub" be Superb? The case of Subphthalocyanines.*
T. Torres-Cebada, Universidad Autónoma de Madrid, Spain.

PL8 *Phosphorus- and NHC-based assembling ligands for metallophilic interactions.*
P. Braunstein, University of Strasbourg, France.

VSM *Translational Chemical Biology.*
G. Bernardes, Instituto de Medicina Molecular, Faculdade de Medicina, Universidade de Lisboa, Portugal.

Online Pre-conferences

PCO1 *Technologies to upcycle plastic solid wastes into nanostructured carbon materials and their application in the removal of micropollutants.*
J. L. D. de Tuesta, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

PCO2 *Targeting N-terminal cysteines in bioconjugation.*
P. M. P. Gois, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

PCO3 *Exploring the environmental applications of microalgae: CO_2 capture and nutrients removal from wastewaters.*
A. L. Gonçalves, EPABE - Laboratório de Engenharia de Processos, Ambiente, Biotecnologia e Energia, Faculdade de Engenharia da Universidade do Porto, Portugal

PCO4 *Ionic liquid and water: the perfect duo to improve the extraction of high-value compounds from biomass.*
M. G. Freire, CICECO - Instituto de Materiais, Universidade de Aveiro, Portugal.

Keynotes

KN1 *Key scientific and technological strategies for the development of drug delivery systems.*
S. Reis, LAQV-REQUIMTE, Department of Chemical Sciences, Laboratory of Applied Chemistry, Faculty of Pharmacy, University of Porto.

KN2 *Metal nanoparticles as scaffolds for biosensing and biocatalysis.*
E. Pereira, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

KN3 *Dehydropeptide based nanostructures for biomedical applications.*
P. M. T. Ferreira, Centre/Department of Chemistry, University of Minho, Portugal.

KN4 *Machine learning for accelerating chemical biology.*
T. Rodrigues, Faculdade de Farmácia da Universidade de Lisboa, Portugal.

KN5 *Molecules at the museum.*
S. S. Melo, Department of Chemistry, University of Coimbra, Portugal.

KN6 *Development and application of natural ingredients in the food industry.*
L. Barros, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

KN7 *Development of 3D temperature tomography at the micro and nanoscale.*
N. J. Silva, CICECO - Instituto de Materiais, Universidade de Aveiro, Portugal.

KN8 *Versatile π-conjugated heterocyclic molecules: design, synthesis and application in optoelectronics and energy.*
M. M. M. Raposo, Centre/Department of Chemistry, University of Minho, Portugal.

KN9 *Health monitoring by protein imprinted polymers.*
M. G. F. Sales, BioMark@UC, Departamento de Engenharia Química da Faculdade de Ciências e Tecnologia da Universidade de Coimbra, Portugal.

KN10 *Green molecularly imprinted polymers in API manufacturing.*
T. Casimiro, CleanMIPTech group, LAQV-REQUIMTE, Chemistry Department, NOVA School of Science & Technology, NOVA University of Lisbon, Portugal.

KN11 *Providing solutions for clean water production and recycling of technological critical elements.*
C. Lopes, CICECO - Instituto de Materiais, Universidade de Aveiro, Portugal.

KN12 *Design of efficient water-soluble catalysts for alkane and CO_2 activation.*
L. M. D. R. S. Martins, Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Portugal.

KN13 *Functional nanofoams: paving the way for sustainable energy conversion.*
M. F. Montemor, Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Portugal.

KN14 *The use of light to induce a reversible color change.*
P Coelho, Centro de Química - Vila Real, Universidade de Trás-os-Montes e Alto Douro, Portugal.

KN15 *(Thio)barbituric acid derivatives: the versatility of synthesis and biological diversity.*
P. Almeida, CICS-UBI – Health Sciences Research Center University of Beira Interior, Portugal.

KN16 *The amazing new world of RNA.*
C. Arriano, Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Portugal.

KN17 *Women in Chemical Engineering: a majority within a minority.*
M. L. Sampaio, Instituto de História Contemporânea, Faculdade de Ciências Sociais e Humanas, Universidade Nova de Lisboa, Portugal.

KN18 *A poligamia intelectual dos químicos.*
M. J. Monte, CIQUP, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Portugal.

Invited Oral Communications

OC1 *Blue biorefinery: overviewing the processes, the materials and the applications.*
S. Ventura, CICECO - Instituto de Materiais, Universidade de Aveiro, Portugal.

OC2 *Structure, properties and applications of 8-hydroxyquinoline-5-sulfonate based materials.*
L. Justino, Department of Chemistry, University of Coimbra, Portugal.

OC3 *Electrically conductive metal-organic frameworks based on electroactive organic building blocks.*
M. Souto, Department of Chemistry, CICECO-Aveiro Institute of Materials, University of Aveiro, Portugal.

OC4 *Hypervalent iodine(III) mediated carbon-nitrogen and nitrogen-sulfur bond formation: innovating access to bioactive compounds.*
M. M. Marques, LAQV@REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal.

OC5 *Playing with chemical diversity to protect marine biodiversity.*
M. Correia-da-Silva, Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR), Universidade do Porto, Portugal.

OC6 *Developing data science tools for bioorthogonal chemistry.*
J. A. S. Coelho, CQE, Faculdade de Ciências da Universidade de Lisboa, Portugal.

OC7 *Encapsulation strategies for effective natural food ingredients.*
M. F. Barreiro, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

OC8 *Secondary metabolites in edible species: looking beyond nutritional value.*
A. Seca, Faculty of Sciences and Technology, University of Azores, Portugal.

OC9 *Establishment of putative geographical markers of apple ciders using HS-SPME/GC-MS combined with chemometric tools.*
R. Perestrelo, CQM – Centro de Química da Madeira, Universidade da Madeira, Portugal.

OC10 *Smart molecularly imprinted polymers for trace detection of dimethoate in olive oil.*
P. E. Carreiro, REQUIMTE-LAQV, IIFA, Universidade de Évora, Portugal.

OC11 *In-Silico improvement of green chemical design.*
L. P. Viegas, CQC, Centro de Química de Coimbra, Departamento de Química, Universidade de Coimbra, Portugal.

OC12 *The potential of the sol-gel process for the preparation of electrochromic devices.*
M. Fernandes, CQ-VR and Chemistry Department, University of Trás-os-Montes e Alto Douro, Portugal.

OC13 *Deoxygenation of quinic acid towards new chirons for divergent syntheses.*
N. R. Candeias, LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, Portugal.

OC14 *Exploring N-1,2,3-triazole-isatin-oxindole hybrids as promising inhibitors against two of the deadliest diseases worldwide.*
C. S. Marques, LAQV-REQUIMTE, University of Évora, Institute for Research and Advanced Studies, Portugal.

OC15 *Continuous beds: a promising tool for chromatographic purification of plasmid DNA for gene therapy and DNA vaccines.*
C. Tomaz, CICS - Centro de Investigação em Ciências da Saúde, Departamento de Química, Universidade da Beira Interior, Portugal.

OC16 *How to reduce analytical interferences in removal studies of micropollutants?.*
A. R. L. Ribeiro, Laboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Portugal.

OC17 *CO_2 utilization as a renewable carbon source towards the production of bio-based organic carbonates.*
A. Nunes, LAQV@REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Portugal.

OC18 *Novel saccharinate-based compounds and their potential for multiple, but selective, applications.*
J. F. Leal, Center of Marine Sciences, CCMAR, Gambelas Campus, University of Algarve, Portugal.

OC19 *Silk as a multifaceted source of inspiration for sustainable materials.*
R. F. P. Pereira, Centre/Department of Chemistry, University of Minho, Portugal.

OC20 *Dendrimers and DNA: a promising marriage.*
H. Tomás, CQM-Centro de Química da Madeira, MMRG, Universidade da Madeira, Portugal.

OC21 *2-Arylpurine derivatives as new promising antituberculosis agents.*
M. A. Carvalho, Centre/Department of Chemistry, University of Minho, Portugal.

OC22 *Synthesis of novel chiral penta- and hexacyclic steroids.*
S. M. M. Lopes, University of Coimbra, Coimbra Chemistry Centre and Department of Chemistry, Portugal.

OC23 *2020: O ano em que a pandemia obrigou a rever o paradigma ensino/aprendizagem.*
M. F. N. N. Carvalho, Centro de Química Estrutural e Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Portugal.

OC24 *"Química para Senhoras": As obras de Marie Meurdrac e Giuseppe Compagnoni.*
J.P. André, Centre/Department of Chemistry, University of Minho, Portugal.

Oral Communications

O1 *Calorimetry of NBS addition to DMF: unstable or under studied?*
E. Gonçalves, Hovione FarmaCiencia SA, R&D Center, Portugal.

O2 *Photochemistry of monomeric benzoxazole and isocyanophenol.*
I. Reva, CIEPQPF, Department of Chemical Engineering, University of Coimbra, Portugal.

O3 *Highly dispersed noble metal-based carbon nitride as efficient electrocatalytic/photocatalytic hydrogen evolution.*
Z. Yu, Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Portugal.

O4 *Ionic liquids and eutectic systems as functional materials for energy.*
L. C. Branco, LAQV-REQUIMTE, Departmento de Química da Faculdade de Ciências e Tecnologia, Univ. NOVA de Lisboa, Portugal.

O5 *Dual-action chimeric peptides and their ionic liquid conjugates as a novel approach to tackle skin infections.*
A. Gomes, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

O6 *Recent FT-IR trends in protein analysis and Biopharma.*
E. Monteiro, Bruker, Portugal.

O7 *Light-activated membrane transport of arginine-rich peptides.*
J. N. Martins, Laboratório Associado para a Química Verde (LAQV), Rede de Química e Tecnologia (REQUIMTE), Departament of Chemistry, NOVA School of Science and Technology (FCT-NOVA), Portugal.

O8 *Hypoxia-selective triazene prodrugs designed to address glioblastoma microenvironment.*
C. Braga, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

O9 *Total synthesis of cernumidine.*
R. Rippel, LAQV-REQUIMTE, NOVA School of Science and Technology, Portugal.

O10 *Development of a methodology for the determination of the reactivity of brandies used in wine fortification.*
J. Azevedo, LAQV – REQUIMTE - Laboratório Associado para a Química Verde - Faculdade de Ciências da Universidade do Porto, Portugal.

O11 *Biodegradation potential of paracetamol by marine bacteria consortia.*
J. Valentine, Centre of Marine Sciences, University of Algarve, Portugal.

O12 *Synthesis of 4-phenylimidazoles in the discovery of potent, long-acting inhibitors of FAAH.*
A. Beliaev, Bial, Portugal.

O13 *Nanohybrids and hybridplexes based on carbon dots and PAMAM dendrimer for bioimaging and gene delivery.*
I. Martins, CQM - Centro de Química da Madeira, MMRG, Universidade da Madeira, Portugal.

O14 *Improved water resistance and large conductivity enhancement of poly(3,4 - ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) through cross-linking with an oxetane unit.*
S. M. Jorge, Instituto de Telecomunicações, Instituto Superior Técnico, Portugal.

O15 *Low-field benchtop NMR for solvent swap analysis.*
M. M. Andrade*,* R&D, Process Chemistry Development, Hovione FarmaCiência SA, Portugal.

O16 *Probing heteroaromatic scaffolds in the melanostatin neuropeptide: a bioisosteric approach using niacin as a pro surrogate.*
B. L. Pires-Lima, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

O17 *Diversity-oriented synthesis of biomass derived furanic platforms aiming at drug discovery.*
R. F. A. Gomes, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

O18 *Heptakis–aminocyclodextrin nanosponges for imidacloprid removal in aqueous media.*
G. Utzeri, Coimbra Chemistry Centre, Department of Chemistry, University of Coimbra, Portugal.

O19 *Remotely controlled host-guest assemblies in aqueous solution.*
N. Basílio, LAQV/REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Portugal.

O20 *Iminoboronate platforms for the targeted delivery of citotoxic and fluorogenic payloads into cancer cell lines.*
R. M. R. M. Lopes, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

O21 *"Química ao pé da letra": o encontro das palavras com o ensino e a divulgação da química.*
J. L. Araújo, CIQUP, UEC, DQB, Faculdade de Ciências da Universidade do Porto, Portugal.

Flash Communications

F1 *Modeling halogen bonds in molecular dynamic simulation of active pharmaceutical ingredients.*
C. S. D. Lopes, CQE, Faculdade de Ciências, Universidade de Lisboa, Portugal.

F2 *Multi-composition biocompatible catanionic vesicles for the encapsulation and delivery of doxorubicin.*
R. L. Machado, CIQUP, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Portugal.

F3 *Supported ionic liquid materials for L-asparaginase bioconjugation.*
J. C. F. Nunes, Department of Chemistry, CICECO-Aveiro Institute of Materials, University of Aveiro, Portugal.

F4 *Molecular dynamics studies of dipeptide nano-pores as a membrane for gas storage and separation.*
K. Biernacki, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal

F5 *Conducting neutral bis(1,2-dithiolene) gold complex [Au(dspdt)2] with a unique crystal structure.*
M. F. G. Velho, Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa Portugal.

F6 *Bio-inspired films based on Buxus sempervirens.*
A. Pinto, CQ-VR and Chemistry Department, University of Trás-os-Montes e Alto Douro, Portugal.

F7 *Binary Fe(III) and Mn(III) porphyrin materials with catalase-like activity.*
M. B. M. S. Martins, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

F8 *Sol-gel derived electrolytes for prototype ECDs.*
J. Nunes, CQ-VR and Chemistry Department, University of Trás-os-Montes e Alto Douro, Portugal.

F9 *Visible light-driven photocatalytic synthesis of imines assisted by carbon nitride.*
J. C. Lopes, Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Department of Chemical Engineering, Faculty of Engineering, University of Porto, Portugal.

F10 *Application of coal fly ash in wastewater treatment.*
I. Kuźniarska-Biernacka, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

F11 *Development of novel thiazole-based inhibitors: targeting necroptosis and RIPK1.*
L. Fidalgo, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

F12 *Caffeic acid phenolipids in the protection of cell membranes from oxidative injuries. Interaction with the membrane phospholipid bilayer.*
F. Paiva-Martins, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

F13 *BODIPY-based probe for live-cell imaging of lysosomes in cancer cells.*
R. C. R. Gonçalves, Centre/Department of Chemistry, University of Minho, Portugal.

F14 *Enzymatic production of polydopamine in aqueous biphasic systems.*
F. F. Magalhães, CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Portugal.

F15 *Fluorescent-lipid probes: advances towards bioconjugation by flow chemistry.*
P. A. M. M. Varandas, LAQV, REQUIMTE, Department of Chemistry Sciences, Faculty of Pharmacy, University of Porto, Portugal.

F16 *A fluorescent probe based on a BODIPY derivative to study cellular ingestion and internalization of solid lipid nanoparticles.*
S. C. S. Pinto*,* Centre/Department of Chemistry, University of Minho, Portugal.

F17 *Cytotoxic activity against HCT-116 colon carcinoma cells of amaryllydaceae-type alkaloids.*
S. Sancha, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

F18 *ATP binding induces characteristic structural changes in the ABCG2 transport channel.*
B. M. F. Gonçalves, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

F19 *Effect of cyclodextrins on the acid-base equilibrium of pyranoanthocyanins.*
A. Borges, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

F20 *Exploring the behavior of ruthenium metallodendrimers as anticancer drugs.*
D. Maciel, CQM - Centro de Química da Madeira, MMRG, Universidade da Madeira, Portugal.

F21 *Targeting necroptosis: discovery and optimization of novel RIPK1 inhibitors.*
A. F. S. Luz, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

F22 *Desenvolvimento de um sensor eletroquímico baseado em Pt-GO para quantificação de contaminantes fenólicos.*
L. Lema*,* Centre/Department of Chemistry, University of Minho, Portugal.

F23 *Heterocyclic thiosemicarbazone based on a bithienyl π-conjugated bridge for heavy metal cations detection.*
R. P. C. L. Sousa, Centre/Department of Chemistry, University of Minho, Portugal.

F24 *Preparation of aminals under mild conditions and their remarkable applications.*
J. G. Pereira*,* Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

F25 *Photocatalytic degradation of tramadol using metal-free carbon nitride.*
M. A. Barros, Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Portugal.

F26 *Contribution of inland sources to microplastics increase in aquatic systems: the Portuguese case.*
S. Magalhães, Department of Chemical Engineering, CIEPQPF, University of Coimbra, Portugal.

F27 *Conversion of plastic waste into value-added compounds using cheap and environmentally friendly catalysts.*
A. C. Fernandes, Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Portugal.

F28 *Optimization of SPE/HPLC analytical method 17b-estradiol quantification in wastewater treatment plant (in)effluents using a surface response methodology.*
N. S. Foureaux*,* Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

F29 *Box-Behnken design for optimization of Fenton-type reaction for water treatment using heterogeneous catalysts.*
O. Assila, Centre/Department of Chemistry, University of Minho, Portugal.

F30 *Reusable polymer hybrid membranes for arsenite and arsenate dual-water remediation.*
H. Salazar*,* Center/Department of Physics, University of Minho, Portugal.

F31 *Recovery of technology-critical elements from complex aqueous mixtures through live seaweed: optimization by response surface methodology.*
T. Viana*,* Departament of Chemistry, LAQV-REQUIMTE, University of Aveiro, Portugal.

F32 *Recovery and purification of gold from a chloride multi-metal solution using strong basic anion exchange resins.*
M. Silva*,* REQUIMTE/LAQV, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Portugal.

F33 *Methanation of CO_2 over Ni-Ce bimetallic oxides supported on SiO_2 aerogel.*
A. C. Ferreira*,* Centro de Química Estrutural, Departamento de Engenharia e Ciências Nucleares, Instituto Superior Técnico, Universidade de Lisboa, Portugal.

F34 *Preparation of photochromic nanomaterials through different synthetic routes for light-responsive textiles.*
M. Pacheco*,* LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

F35 *Mononuclear Fe(III) SCO complexes: how do solvates affect the magnetic behavior?*
R. T. Marques*,* BioISI - Biosystems & Integrative Sciences Institute, Faculty of Sciences, University of Lisboa, Portugal.

F36 *A solid polymer electrolyte based on poly(vinylidene fluoride-co-hexafluoropropylene) combining ionic liquid and zeolite for room temperature lithium-ion battery applications.*

J. C. Barbosa, Center/Department of Physics, University of Minho, Portugal.

F37 *Enzymatically crosslinked gelatine/alginate hydrogel-based inks applied in 3D printing.*
A. C. Lima, Materials + Technologies' Group, Department of Chemical and Environmental Engineering, Faculty of Engineering – Gipuzkoa, University of the Basque Country, Spain.

F38 *New 3-ethynylaryl coumarin-based dyes for DSSC applications: synthesis, spectroscopic properties and theoretical calculations.*
J. Sarrato, LAQV-REQUIMTE, Departament of Chemistry, NOVA School of Science and Technology, FCT NOVA, Universidade NOVA de Lisboa, Portugal.

F39 *Luminescent aqueous dispersions of lanthanide ions and gum arabic for coatings.*
R. Aguado, University of Coimbra, CQC, Department of Chemistry, Portugal.

F40 *Determinação cinética de oxitetraciclina usando pontos quânticos de $AgInS_2$ e com recurso a ferramentas quimiométricas.*
R. C. Castro, LAQV, REQUIMTE, Departamento de Ciências Químicas, Laboratório de Química Aplicada, Faculdade de Farmácia da Universidade do Porto, Portugal.

F41 *Synthesis and characterization of yolk-shell magnetic nanoparticles prepared by a bottom-up approach for biomedical applications.*
A. S. Silva, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

F42 *Estudo de diferentes arquiteturas de superfície no âmbito da montagem de um imunosensor piezoeléctrico para determinação de ácido úrico em amostras de urina.*
I. Martins, ADEQ-ISEL/IPL- Área Departamental de Engenharia Química do ISEL/IPL, Portugal.

F43 *Evaluation of a specific OFF-ON fluorescence reporter for Granzyme B activity.*
C. D. F. Martins, Centre/Department of Chemistry, University of Minho, Portugal.

F44 *Synthetic approach for the synthesis of a new family of phosphoglycoglycerols.*
C. I. Cipriano, LAQV-REQUIMTE: Department of Chemistry, NOVA School of Science and Technology, FCT NOVA, Universidade NOVA de Lisboa, Portugal.

F45 *Synthesis of the human neutrophil elastase inhibitor Ala-Ala-Pro-Val using microwave-assisted solid phase.*
A. F. G. Silva, Centre/Department of Chemistry, University of Minho, Portugal.

F46 *Expanding the chemical diversity of azaaurones as a new chemical tool in the fight against Tuberculosis.*
A. Campaniço, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

F47 *Synthesis and screening of antibacterial activity of 2,4,5-tri(hetero)arylimidazoles based on thieno[3,2-b]thiophene.*
N. L. P. Ramos, Centre/Department of Chemistry, University of Minho, Portugal.

F48 *Camphorimine gold complexes active towards Gram-negative bacteria strains with high selectivity for Burkholderia contaminans.*
M. F. N N Carvalho, Centro de Química Estrutural e Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Portugal.

F49 *New hydrazone derivatives as promising antimalarial drugs.*
S. Teixeira, Centre/Department of Chemistry, University of Minho, Portugal.

F50 *Quenched activity-based probes as novel biochemical tools to analyse resistance to antibiotics.*
R. Félix, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

F51 *In silico approach to develop dual inhibitors of MDM2 and MDMX.*
E. A. Lopes, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

F52 *Chemically comprehensive predictive multivariate models for bioorthogonal metal-free cycloadditions.*
J. M. J. M. Ravasco, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

F53 *A phenomenological approach to describe and characterize pro- and anti-oxidant activities with useful mechanistic contents.*
M. Carpena, Nutrition and Bromatology Group, Faculty of Food Science and Technology, University of Vigo, Spain.

F54 *Effects of the reactive moiety of phenolipids on their antioxidant efficiency in model emulsified systems.*
M. Costa LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

F55 *Eat your weeds: nutritional composition of edible Atlantic brown seaweeds.*
J. Echave, Nutrition and Bromatology Group, Faculty of Food Science and Technology, University of Vigo, Spain.

F56 *Extração de aloeresina B a partir de Aloe vera com recurso a solventes alternativos: Otimização do processo e avaliação de bioatividades.*
M. Añibarro-Ortega*,* Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

F57 *Detection of species mislabeling in a plant sold as Nepeta cataria L.*
M. Honrado*,* Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

F58 *Interaction between peanut proteins and polyphenols: Impact on protein digestibility and immunogenicity.*
R. Pérez-Gregório*,* LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

F59 *Dendrimer-based polymers as new hosts for color tuning of anthocyanin-type guests.*
L. Cruz*,* LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

F60 *New insights into the oral interactions of different families of phenolic compounds: deepening the astringency mouthfeels.*
C. Guerreiro*,* LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

F61 *Spirulina (Artrhospira platensis) protein extract: techno-functional properties and potential application as a natural emulsifier.*
S. C. Silva*,* Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

F62 *Innovative fat-reduced food solutions based on Pickering emulsions.*
S. C. de Rezende*,* Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

Posters

P1 *Polyphenol extraction by deep eutectic solvent for valorisation of Portuguese green tea and their impact on chitosan-based films properties.*
T. F. P. Alves, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

P2 *Antioxidant profile of brown algae from the Iberian Peninsula sea.*
C. Rodrigues, REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Portugal.

P3 *Optimization of bioactive compounds with antioxidant activity of Sargassum muticum by microwave assisted extraction using the response surface.methodology.*
F. Chamorro, Nutrition and Bromatology Group, Faculty of Food Science and Technology, University of Vigo, Spain.

P4 *Antioxidant efficiency of chlorogenic acid in omega-3 enriched emulsified systems and correlation with their distribution.*
R. Lopes, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

P5 *Synthesis, insecticidal activity and encapsulation of carvacrol and thymol derivatives.*
M. S. T. Gonçalves, Centre/Department of Chemistry, University of Minho, Portugal.

P6 *Eugenol derivatives with potential inseticide activity.*
J. R. A. Coelho, Centre/Department of Chemistry, University of Minho, Portugal.

P7 *Synthesis of amino alcohols from eugenol and their biological evaluation against AGS cell line.*
A. G. Fortes, Centre/Department of Chemistry, University of Minho, Portugal.

P8 *Avaliação da composição nutricional e atividade antioxidante do caule e folhas de trapoeraba (Commelina erecta L.).*
L. V. Cavichi, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

P9 *Evaluation of the phenolic composition and bioactivities of plants from Asteraceae family.*
M. Barral-Martinez, Nutrition and Bromatology Group, Faculty of Food Science and Technology, University of Vigo, Spain.

P10 *Study of phenolic composition and biological properties of traditionally used plants Achillea millefolium, Calendula officinalis and Chaemelum nobile.*
P. Garcia-Oliveira, Nutrition and Bromatology Group, Faculty of Food Science and Technology, University of Vigo, Spain.

P11 *Polyphenols-rich functional foods in the prevention and management of type 2 diabetes mellitus.*
F. Campos LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

P12 *Anthocyanins-polysaccharides nanocomplexes for food application.*
I. Pereira, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

P13 *Changes in the secondary structure of lysozyme by interactions with gallic acid.*
D. Leithardt, CICS-UBI – Centro de Investigação em Ciências da Saúde, Universidade da Beira Interior, Portugal.

P14 *Understanding of the effect of successive exposure in astringency: oral interactions of a green tea flavanol extract.*
M. Jesus, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

P15 *Chemical composition and antimicrobial activity of the essential oil of winter savory (Satureja montana L.).*
J. S. Amaral, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

P16 *Phenolic compounds of propolis: optimization of extraction by response surface methodology recovery.*
A. Otmani, Laboratoire de Biochimie appliquée, Faculté des Sciences de la Nature et de la Vie, Université de Bejaia, Algeria.

P17 *Saponin-rich extracts as new natural emulsifiers.*
T. B. Schreiner, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

P18 *High-value biomolecules from Tetraselmis chuii and Chlorella vulgaris: production and extraction strategies.*
S. Hussen, Área Departamental de Engenharia Química, ISEL-IPL, Portugal.

P19 *Optimization of microwave-assisted extraction of bioactive compounds from coffee beans produced in Gorongosa, Mozambique.*
J. M. Fernandes, Área Departamental de Engenharia Química, ISEL-IPL, Portugal.

P20 *Biodegradation studies in seawater of a new polyphenolic antifouling agent.*
C. V. Boas, Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Portugal.

P21 *Synthesis of carbon dots composite materials and their use for the photodegradation of water contaminants.*
G. S. Catalão, Departamento de Engenharia Química, ISEL – Instituto Politécnico de Lisboa, Portugal.

P22 *Volatility and thermodynamic stability of Clopyralid.*
A. R. R. P. Almeida, Centro de Investigação em Química (CIQUP), Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

P23 *Gas-phase standard molar enthalpies of formation of some anthranilate derivatives.*
C. A. O. Silva, Centro de investigação em Química (CIQUP), Department of Chemistry and Biochemistry, Faculty of Sciences – University of Porto, Portugal.

P24 *Development of innovative materials for antibiotics removal.*
A. Saraiva, CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Portugal.

P25 *New strategies for the removal of cytostatics from urine.*
R. Francisco, CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Portugal.

P26 *Determination of sertraline antidepressant drug in aqueous effluents by SPE/HPLC-DAD.*
V. Machado, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

P27 *Effect of zeolite nanomaterials in methanogenic communities.*
J. F. Faria, Centre/Department of Chemistry, University of Minho, Portugal.

P28 *Complexos heterolépticos de cobre (I) como catalisadores da CuAAC.*
M. S. Viana, LAQV-REQUIMTE, Departamento de Química, NOVA School of Science and Technology (FCT NOVA), Portugal.

P29 *Heterogeneous photocatalysis and photo-Fenton as integrated water treatment.*
A. Torres-Pinto, Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Portugal.

P30 *Evaluation of a triphenylamine-derived thiosemicarbazone as an optical chemosensor for anions.*
Â. B. M. P. Leite, Centre/Department of Chemistry, University of Minho, Portugal.

P31 *Biodegradation potential of microplastics by bacteria recovered from the marine environment.*
N. F. de Villalobos, Centro de Ciências do Mar do Algarve, Universidade do Algarve, Portugal.

P32 *Optimization of SPME/GC-MS analytical method using response surface methodology for pesticides monitoring in aqueous matrices.*
F. Cáceres, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

P33 *Atmospheric deposition of microplastics in southern Portugal.*
I. M. Beltrán*, Centro de Ciências do Mar do Algarve, Universidade do Algarve,* Portugal.

P34 *Recovery of strategic metals from extreme acid mine drainage by combining solvent extraction methods and biological strategies.*
A. Nobahar*,* CCMAR, Centre of Marine Sciences, University of Algarve, Portugal.

P35 *Impact of interfering compounds on arsenic removal from water through polymer nanocomposite membranes.*
R. Abreu*,* Centre/Department of Chemistry, University of Minho, Portugal.

P36 *Natural polymer membranes for removal of volatile organic compounds.*
J. Teixeira*,* Centro de Física das Universidades do Minho e Porto, Universidade do Minho, Portugal.

P37 *Efficient and rapid delamination of waste printed circuit boards using microwave-assisted organic swelling.*
P. M. S. Sousa*,* REQUIMTE/LAQV, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, Portugal.

P38 This poster was withdrawn by the authors.

P39 *Sensing microplastics in aqueous suspensions using pyrene fluorescent probe.*
C. Q. V. da Costa*,* Center of Marine Science (CCMAR), University of Algarve, Portugal.

P40 *Marine pollutants: identifying microplastics through volatile and non-volatile degradation products obtained after a heat treatment.*
I. I. Afonso*,* Center of Marine Science (CCMAR), University of Algarve, Portugal.

P41 *Fenton-type heterogeneous catalysts based in zeolites for water treatment.*
B. L. C. Santos Centre/Department of Chemistry, University of Minho, Portugal.

P42 This poster was withdrawn by the authors.

P43 *Synthesis of α-enaminones from biomass – sustainable continuous flow hydrogenation of furfural-derived trans-diamino cyclopentenones.*
L. A. S. Cavaca*,* Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

P44 *Influence of DNA in pulp water absorption capacity.*
A.C.S. Ferreira*,* University of Coimbra, CQC and Department of Chemistry, Portugal.

P45 *Synthesis of DSPE-PEG2000-NH_2-D-amino acids conjugates to overcome the biofilm formation caused by Staphylococcus aureus.*
D. R. P. Loureiro*,* Department of Chemical Sciences, Laboratory of Organic and

Pharmaceutical Chemistry, Faculty of Pharmacy, University of Porto, Portugal.

P46 *A novel palladium-catalyzed synthetic route to obtain a key xanthonic chemical precursor of potential antitumor pyranoxanthones.*
A. Dias*,* Department of Chemical Sciences, Laboratory of Organic and Pharmaceutical Chemistry, Faculty of Pharmacy, University of Porto, Portugal.

P47 *Targeting chitinase 3-like 1 in pancreatic cancer: in silico identification of inhibitors from a DrugBank database and confirmation of growth inhibition effect in cell lines.*
S. Sousa*,* Laboratory of Organic and Pharmaceutical Chemistry/ Department of Chemical Sciences, FFUP - Faculty of Pharmacy, University of Porto, Portugal.

P48 *Click chemistry approach for the synthesis of new flavonoid derivatives with potential biological activities.*
D. Pereira*,* Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Portugal.

P49 *Oligonucleotide-modified AuNPs for the development of rapid tests for detecting single nucleotide polymorphisms.*
B. Ferreira*,* LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

P50 *Detection of immunoglobulins by nanoparticle tracking analysis.*
C. Machado*,* LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

P51 *Antimicrobial studies of a library of diarylpentanoids and their potential in the reversal of antibacterial resistance.*
F. Durães*,* Laboratory of Organic and Pharmaceutical Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Portugal.

P52 *Preliminary virtual screening studies to explore the potential of chemical-diverse in house families of compounds as inhibitors of SARS-CoV-2.*
F. Carvalhal*,* Laboratory of Organic and Pharmaceutical Chemistry/ Department of Chemical Sciences, FFUP - Faculty of Pharmacy, University of Porto, Portugal.

P53 *A new diarylpentanoid as potential disruptor of p53-MDM2/MDMX interactions.*
J. Moreira*,* Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Portugal.

P54 *Synthesis of chitosan conjugates with a potential as inhibitores of growth of human tumor cell lines.*
R. Lima*,* Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Portugal.

P55 *Bis-(thio)barbiturates as promising xanthine oxidase inhibitors for gout treatment.*
J. L. Serrano, CICS-UBI – Health Sciences Research Center University of Beira Interior, Portugal.

P56 *Synthesis of novel 1,2,3-triazole epicinchona compounds: applications from organocatalysis to biological activities.*
A. C. Amorim, Chiratecnics, LDA, University of Évora, Portugal.

P57 *Synthesis and biological evaluation of novel quinoline analogues against T. brucei and L. infantum parasites.*
A. Lopes, Centre/Department of Chemistry, University of Minho, Portugal.

P58 *Rational design of novel selective PI3K inhibitors for cancer therapy.*
V. Lobo, Centre/Department of Chemistry, University of Minho, Portugal.

P59 *Novel halochromic and antimicrobial azopyrimidine dyes: synthesis, colorimetric studies and biological assays.*
A. Dias, Centre/Department of Chemistry, University of Minho, Portugal.

P60 *Synthesis and antimicrobial activity of a new class of azoimidazoles.*
D. Dantas, Centre/Department of Chemistry, University of Minho, Portugal.

P61 *New highly fluorescent nucleobase analogues as biological tools: photophysical studies.*
S. Pêra, Centre/Department of Chemistry, University of Minho, Portugal.

P62 *Boosting antimicrobial activity of ionic fluoroquinolones by functionalization of mesoporous silica nanoparticles.*
L. Filipe, LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Portugal.

P63 *Evaluation of the potential application of a barbiturate squaraine dye as a fluorescent probe for HSA detection.*
V. S. D. Gomes, Centre of Chemistry-Vila Real, Department of Chemistry, University of Trás-os-Montes and Alto Douro, Portugal.

P64 *Biocompatible excipients to enhance the stability of avian immunoglobulin Y (IgY) antibodies, envisaging their use as biopharmaceuticals.*
C. A. S. Almeida, CICECO- Aveiro Institute of Materials, Chemistry Department, University of Aveiro, Portugal.

P65 *Surface active ionic liquids based on antimalarial drugs.*
A. T. Silva, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

P66 *The design of new Trofinetide® conjugates using constrained prolines.*
S. C. Silva-Reis, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

P67 *Indole alkaloid derivatives as P-glycoprotein inhibitors.*
D. S. P. Cardoso, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

P68 *The boron hot-spot methodology: peptide functionalization.*
R. Padanha, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

P69 *Metal ion-zeolite nanomaterials for chemodynamic therapy.*
S. D. C. Ferreira, Centre/Department of Chemistry, University of Minho, Portugal.

P70 *4,9-Diaminoacridines and 4-aminoacridines as dual-stage antiplasmodial hits.*
M. Fonte, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

P71 *First insights into the ability of silver camphorimine complexes to functionalize PCL coatings with anti-Candida activity.*
J. P. Costa, CQE Instituto Superior Técnico, Departamento de Engenharia Química, Universidade de Lisboa, Portugal.

P72 *Electrochemical cyanation of quinolizidine alkaloids.*
R. M. Durão, Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal.

P73 *Phase transition studies of 5-methyl-1H-benzotriazole.*
A. C. M. O. Lima, Centro de Investigação em Química, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Portugal.

P74 *Hybrid sol-gel materials doped with AgY and NaY zeolites.*
B. R. Gomes, Centre/Department of Chemistry, University of Minho, Portugal.

P75 *Pyranoflavylium salt incorporated in cellulose acetate films with glycerol as colorimetric pH-sensors for food packaging applications.*
V. Gomes, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

P76 *Solid polymer electrolytes based on HPMC and $Tm(CF_3SO_3)_3$.*
M. M. Silva, Center/Department of Química, University of Minho, Portugal.

P77 *Flavylium compounds meet cucurbiturils: a light responsive pseudo-rotaxane.*
A. Seco, Associated Laboratory for Green Chemistry - LAQV, REQUIMTE, Chemistry Department - NOVA School of Science and Technology, Portugal.

P78 *Development of hierarchical 1D/2D nanocomposites as electrocatalysts for the oxygen reactions in fuel cells.*
M. Rocha, Centro de Investigação em Química - CIQUP, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Portugal.

P79 *Thermotropic ionic liquid crystal phase behavior of double-tailed lysine-based surfactants.*
I. S. Oliveira, Centro de Investigação em Química - CIQUP, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Portugal.

P80 *Supramolecular photochemical control of fluid rheology.*
A. Camuenho, LAQV-REQUIMTE, FCT - Universidade NOVA de Lisboa, Portugal.

P81 *Characterization of coal fly ash applied in wastewater treatment.*
A. C. Santos, Earth Science Institute – Porto pole, Department of Geosciences, Environment and Spatial Plannings, Faculty of Sciences, University of Porto, Portugal.

P82 *Water-in-oil nanoemulsions as delivery systems of hydrophilic natural extracts: a stability and functionality study.*
G. Colucci, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

P83 *Modified nanostructured cobalt foams as electrocatalysts for the oxygen evolution reaction.*
M. Nunes, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

P84 *CuAl-LDH/g-C_3N_4 Nanohybrids for photocatalytic H_2 and O_2 generation via water splitting.*
H. Boumeriame, Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Portugal.

P85 *Amphiphilic carbon nanotubes for catalytic wet peroxide oxidation of 4 nitrophenol.*
F. F. Roman, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

P86 *Rhododendron ponticum as a possible candidate for the creation of biomimetic films inspired by plant leaves.*
R. Rua, CQ-VR and Chemistry Department, University of Trás-os-Montes e Alto Douro, Portugal.

P87 *Photoswitchable and pH-gated self-assembled nanostructures for controlled delivery of an antineoplastic agent.*
D. X. Moreira, CIQUP, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Portugal.

P88 *$Co_4(PW_9)_2$ POM "bulk"-deposition on MOF-74 derived nanocarbons to the synthesis of ternary OER electrocatalysts.*
D. M. Fernandes, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

P89 *Biodiesel production from residual edible oils catalyzed by ionic liquid hydrogen sulfate 1-butyl-3-methylimidazolium, [BMIM][HSO_4].*
F. M. Almeida, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

P90 *Silk-based polymer electrolytes incorporating glycerol, DMSO and LiTFSI.*
R. F. P. Pereira, Centre/Department of Chemistry, University of Minho, Portugal.

P91 *Additive manufacturing applied to the design of photocatalytic reactors.*
I. S. O. Barbosa, Laboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Portugal.

P92 *Valorization of used cooking oils through ionic liquid catalyzed biodiesel conversion processes.*
F. Monteiro, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

P93 *Light and pH-responsive cucurbit[8]uril-dithienylethene host-guest complexes.*
M. Colaço, Laboratório Associado para a Química Verde (LAQV), Rede de Química e Tecnologia (REQUIMTE), Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Portugal.

P94 *A different kind of aminal: challenges and insights.*
F. Leitão, LAQV-REQUIMTE, Departamento de Química, NOVA School of Science and Technology, Portugal.

P95 *Solid biopolymer electrolytes applied to diverse electrochemical systems.*
S. C. Barros, Center/Department of Química, University of Minho, Portugal.

P96 *Development and characterization of polysulfone dialysis membranes doped with human elastase inhibitors pilot study.*
R. Rebelo, Faculty of Sciences, University of Porto, Portugal.

P97 *Time-dependent self-assembly of Copper(II) coordination polymers and tetranuclear rings: new catalysts for oxidative functionalization of saturated hydrocarbons.*

I. F. M. Costa, Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Portugal.

P98 *Valorization of waste cooking oils through conversion processes catalyzed by choline hydroxide.*
Y. Gué, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

P99 *Natural materials based polymer blends for photoluminescent applications.*
B. D. D. Cruz, Centre/Department of Chemistry, University of Minho, Portugal.

P100 *Biopolymer films doped with Silver(I) coordination polymers against bacterial biofilms.*
T. A. Fernandes, Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico, Portugal.

P101 *Nanostructered biomimetic catalysts for solar light assisted redox reactions.*
M. P. Loureiro, LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

P102 *Poliuretanos microcelulares com propriedades de regulação térmica para calçado de segurança com propriedades de conforto incrementadas.*
H. M. Rafael, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

P103 *Direct ink writing of poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) as polymer binder for printed cathodes for energy storage system.*
R. Gonçalves, Centre/Department of Chemistry, University of Minho, Portugal.

P104 *Development of superparamagnetic yolk-shell nanoparticles as nanocarriers of antineoplastic drugs.*
H. T. Gomes, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

P105 *Cobalt-lanthanide bimetallic oxide nanofibers as catalysts for the selective hydrogenation of CO_2.*
J. F. Martinho, Centro de Química Estrutural, Departamento de Engenharia e Ciências nucleares, IST, Universidade de Lisboa, Portugal.

P106 *Evaluation of dicarboxymethyl cellulose efficiency in white wine protein stabilization.*
D. Gago, LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Portugal.

P107 *Sambucus nigra L. colour stabilization through microencapsulation studies.*
L. G. Teixeira, Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Portugal.

P108 *Self-assembly of 2-hydroxychalcones amphiphilic derivatives: a new approach for a drug-delivery system.*
R. Anastácio, Associated Laboratory for Sustainable Chemistry-Clean Processes and Technologies (LAQV), Network of Chemistry and Technology (REQUIMTE), NOVA School of Sciences and Technology, Portugal.

P109 *Synthesis of nanoparticles for controlled delivery of anticancer compound.*
T. I. de Menezes, Faculdade de Ciências da Universidade do Porto, Departamento de Química e Bioquímica, Portugal.

P110 *Coffee grounds as a valuable source for production of fluorescent carbon nanomaterials for nitroanilines detection.*
A. I. Costa, Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, Portugal.

P111 *A novel calixarene-carbazole capsule for fullerene complexation.*
P. D. Barata, Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, Portugal.

P112 *Antimicrobial activity of fruit packages coated with nanomaterials based in metal-ions zeolites.*
F. C. Rodrigues, Centre/Department of Chemistry, University of Minho, Portugal.

P113 *Production of sustainable polymers from the valorization of sugars and derivatives obtained by catalytic depolymerization of lignocellulosic materials.*
L. B. Silva, CQE - Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, Portugal.

List of Presenting Authors

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

Plenary Lectures

PL1	M. M. B. Santos	PL6	M. Shaffer
PL2	C. Keating	PL7	T. Torres-Cebada
PL3	C. Bochet	PL8	P. Braunstein
PL4	D. Barceló	MVS	G. Bernardes
PL5	P. Dixneuf		

Online Pre-conferences

PCO1	J. L. D. de Tuesta	PCO3	A. L. Gonçalves
PCO2	P. M. P. Gois	PCO4	M. G. Freire

Keynotes

KN1	S. Reis	KN10	T. Casimiro
KN2	E. Pereira	KN11	C. Lopes
KN3	P. M. T. Ferreira	KN12	L. M. D. R. S. Martins
KN4	T. Rodrigues	KN13	M. F. Montemor
KN5	S. S. Melo	KN14	P Coelho
KN6	L. Barros	KN15	P Almeida
KN7	N. J. Silva	KN16	C. Arriano
KN8	M. M. M. Raposo	KN17	M. L. Sampaio
KN9	M. G. F. Sales	KN18	M. J. Monte

Invited Oral Communications

OC1	S. Ventura	OC13	N. R. Candeias
OC2	L. Justino	OC14	C. S. Marques
OC3	M. Souto	OC15	C. Tomaz
OC4	M. M. Marques	OC16	A. R. L. Ribeiro
OC5	M. Correia-da-Silva	OC17	A. Nunes
OC6	J. A. S. Coelho	OC18	J. F. Leal
OC7	M. F. Barreiro	OC19	R. F. P. Pereira
OC8	A. Seca	OC20	H.Tomás
OC9	R. Perestrelo	OC21	M. A. Carvalho
OC10	P. E. Carreiro	OC22	S. M. M. Lopes
OC11	L. P. Viegas	OC23	M. F. N. N. Carvalho
OC12	M. Fernandes	OC24	J.P. André

Oral Communications

O1	E. Gonçalves	O12	A. Beliaev
O2	I. Reva	O13	I. Martins
O3	Z. Yu	O14	S. M. Jorge
O4	L.C. Branco	O15	M. M. Andrade
O5	A. Gomes	O16	B. L. Pires-Lima
O6	E. Monteiro	O17	R. F. A. Gomes
O7	J. N. Martins	O18	G. Utzeri
O8	C. Braga	O19	N. Basílio
O9	R. Rippel	O20	R. M. R. M. Lopes
O10	J. Azevedo	O21	J. L. Araújo
O11	J. Valentine	OC23	M. F. N. N. Carvalho

Flash Communications

F1	C. S. D. Lopes	F22	L. Lema	F43	C. D. F. Martins
F2	R. L. Machado	F23	R. P. C. L. Sousa	F44	C. I. Cipriano
F3	J. C. F. Nunes	F24	J. G. Pereira	F45	A. F. G. Silva
F4	K. Biernacki	F25	M. A. Barros	F46	A. Campaniço
F5	M. F. G. Velho	F26	S. Magalhães	F47	N. L. P. Ramos
F6	A. Pinto	F27	A. C. Fernandes	F48	M. F. N. N. Carvalho
F7	M. B.M.S. Martins	F28	N. S. Foureaux	F49	S. Teixeira
F8	J. Nunes	F29	O. Assila	F50	R. Félix
F9	J. C. Lopes	F30	H. Salazar	F51	E. A. Lopes
F10	I. K.-Biernacka	F31	T. Viana	F52	J. M. J. M. Ravasco
F11	L. G. Fidalgo	F32	M. Silva	F53	M. Carpena
F12	F. Paiva-Martins	F33	A. C. Ferreira	F54	M. Costa
F13	R. C. R. Gonçalves	F34	M. Pacheco	F55	J. Echave
F14	F. F. Magalhães	F35	R. T. Marques	F56	M. Añibarro-Ortega
F15	P. A. M. M. Varandas	F36	J. Barbosa	F57	M. Honrado
F16	S. C. S. Pinto	F37	A. C. C. Lima	F58	R. Pérez-Gregório
F17	S. Sancha	F38	J. Sarrato	F59	L. Cruz
F18	B. M. F. Gonçalves	F39	R. Aguado	F60	C. Guerreiro
F19	A. Borges	F40	R. C. Castro	F61	S. C. Silva
F20	D. Maciel	F41	A. S. Silva	F62	S. C. de Rezende
F21	A. F. S. Luz	F42	I. Martins		

Posters

P1	T. F. P. Alves	P39	C. Q. V. da Costa	P77	A. Seco
P2	C. Rodrigues	P40	I. I. Afonso	P78	M. Rocha
P3	F. Chamorro	P41	B. L. C. Santos	P79	I. S. Oliveira
P4	R. Lopes	P43	L. A. S. Cavaca	P80	A. Camuenho
P5	M. S. T. Gonçalves	P44	A.C.S. Ferreira	P81	A. C. Santos
P6	J. R. A. Coelho	P45	D. R. P. Loureiro	P82	G. Colucci
P7	A. G. Fortes	P46	A. Dias	P83	M. Nunes
P8	L. V. Cavichi	P47	S. Sousa	P84	H. Boumeriame
P9	M. Barral-Martinez	P48	D. Pereira	P85	F. F. Roman
P10	P. Garcia-Oliveira	P49	B. Ferreira	P86	R. Rua
P11	F. Campos	P50	C. Machado	P87	D. X. Moreira
P12	I. Pereira	P51	F. Durães	P88	D. M. Fernandes
P13	D. Leithardt	P52	F. Carvalhal	P89	F. M. Almeida
P14	M. Jesus	P53	J. Moreira	P90	E. R. F. P. Pereira
P15	J. S. Amaral	P54	R. Lima	P91	I. S. O. Barbosa
P16	A. Otmani	P55	J. L. Serrano	P92	F. Monteiro
P17	T. B. Schreiner	P56	A. C. Amorim	P93	M. Colaço
P18	S. Hussen	P57	A. Lopes	P94	F. Leitão
P19	J. M. Fernandes	P58	V. Lobo	P95	S. C. Barros
P20	C. V. Boas	P59	A. Dias	P96	R. Rebelo
P21	G. S. Catalão	P60	D. Dantas	P97	I. F. M. Costa
P22	A. R. R. P. Almeida	P61	S. Pêra	P98	Y. Gué
P23	C. A. O. Silva	P62	L. Filipe	P99	B.D.D. Cruz
P24	A. Saraiva	P63	V. S. D. Gomes	P100	T. A. Fernandes
P25	R. Francisco	P64	C. A. S. Almeida	P101	M. P. Loureiro
P26	V. Machado	P65	A. T. Silva	P102	H. M. Rafael
P27	J. F. Faria	P66	S. C. Silva-Reis	P103	R. Gonçalves
P28	M. S. Viana	P67	D. S. P. Cardoso	P104	H. T. Gomes
P29	A. Torres-Pinto	P68	R. Padanha	P105	J. F. Martinho
P30	A. B. M. P. Leite	P69	S. D. C. Ferreira	P106	D. Gago
P31	N. F. de Villalobos	P70	M. Fonte	P107	L. G. Teixeira
P32	F. Cáceres	P71	J. P. Costa	P108	R. Anastácio
P33	I. M. Beltrán	P72	R. M. Durão	P109	T. I. de Menezes
P34	A. Nobahar	P73	A. C. M. O. Lima	P110	A. I. Costa
P35	R. Abreu	P74	B. R. Gomes	P111	P. D. Barata
P36	J. Teixeira	P75	V. Gomes	P112	F. C. Rodrigues
P37	P. M.S. Sousa	P76	M. M. Silva	P113	L. B. Silva

Ferreira da Silva Award

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

DeLightful molecules: Selected studies in Physical Photochemistry

Mário N. Berberan e Santos

[1]iBB-Institute for Bioengineering and Biosciences, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal

[2]Associate Laboratory i4HB - Institute for Health and Bioeconomy at Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal

Email: mbs@tecnico.ulisboa.pt

After some general considerations, I will review my contributions in three partially overlapping areas of Physical Photochemistry: Excited-State Kinetics, Thermally Activated Delayed Fluorescence, and Electronic Energy Transfer.

Vicente de Seabra Medal

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

Translational Chemical Biology

Bernardes GJL[a,b]

a) Instituto de Medicina Molecular, Faculdade de Medicina da Universidade de Lisboa, Av. Prof. Egas Moniz, 1649-028 Lisboa, Portugal; b) Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Road, CB2 1EW Cambridge, UK

Email: gb453@cam.ac.uk

Our research uses chemistry principles to address questions of importance in life sciences and molecular medicine. This lecture will cover recent examples of emerging areas in our group in:

(i) methods developed for site-selective chemical modification of proteins at cysteine, disulfide, lysine and serine and their use to build stable and functional protein conjugates for in vivo applications
(ii) bioorthogonal cleavage reactions for targeted drug activation in cells
(iii) click-degraders, small molecules that can be covalently attached to RNA species through click-chemistry and can degrade them, that are akin to ribonucleases. Using click-degraders we developed meCLICK-Seq, a powerful method for the study of diverse aspects of cellular RNA methylation.

Acknowledgements: I thank the Fundação para a Ciência e Tecnologia and the Royal Society.

Plenary Lectures

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

Liquid-liquid phase coexistence in polyelectrolyte solutions: experimental model systems for RNA compartmentalization

Christine D. Keating[a]

a) Department of Chemistry, Pennsylvania State University, University Park, PA, USA

Email: keating@chem.psu.edu

Biological cells are highly organized with numerous subcellular compartments, many of which lack membranous boundaries. These membraneless organelles form by liquid-liquid phase separation, which is a common phenomenon in aqueous solutions of macromolecules. Solutes such as ions, small molecules, and biopolymers can become compartmentalized by partitioning between the phases (Figure 1). We are studying mechanisms for, and consequences of, this type of compartmentalization using a variety of simple model systems composed of phase-separating aqueous polyelectrolyte solutions. Through these types of studies, we hope to uncover underlying physiochemical mechanisms in cellular organization and to identify new avenues for biomimetic systems for applications in biotechnology and materials science.[1] For example, RNA can be accumulated within polymer-rich aqueous droplets, enhancing ribozyme reaction rates. Distinct physicochemical properties of adjacent phases within multiphase droplets can enable nucleic acid sorting, such as accumulating single-stranded versus double-stranded RNAs in different phases, and can impact binding thermodynamics.[1,2] Bioinspired compartmentalization by aqueous phase coexistence is of interest for understanding biological cells, their prebiotic ancestors, and their artificial analogues, and more generally for bioreactors.

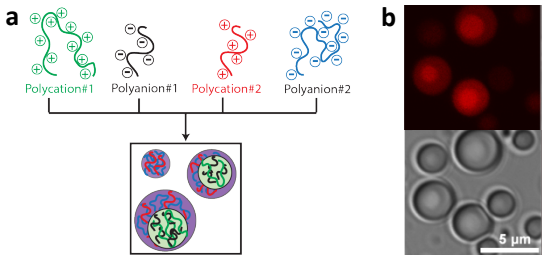


Figure 1: RNA compartmentalization within multiphase coacervate droplets formed by mixing two polycations and two polyanions. (a) Schematic of multiphase droplet production. (b) Fluorescently-labeled RNA oligonucleotides are accumulated preferentially in the interior coacervate phase.

Acknowledgements: We thank the National Science Foundation and NASA for financial support.

References:

1. a) Poudyal, R.; Pir Cakmak, F.; Keating, C. D.; Bevilacqua, P. C. *Biochemistry* **2018**, *57*, 2509-2519. b) Crowe, C. D.; Keating, C. D. *Interface Focus* **2018**, 8, 20180032.
2. a) Mountain, G. A. and Keating, C. D. *Biomacromolecules* **2020**, *21*, 630-640. b) Pir Cakmak, F.; Choi, S.; Meyer, M. O.; Bevilacqua, P. C.; Keating, C. D. *Nature Communications* **2020**, *11*, 5949.

Probing and tuning photochemical reactions with isotopes

Christian G. Bochet,[a]

a) Department of Chemistry, University of Fribourg, 9 chemin du Musée, CH-1700 Fribourg, Switzerland

Email: christian.bochet@unifr.ch

The use of isotopes to investigate reaction mechanisms is a classical tool in the hands of chemists since almost a century. Labelling a functional group with a stable (or unstable) isotope is routinely used to identify a particular site in a molecule, feeding labelled building blocks to an organism in order to elucidate biosynthetic pathways is now a very well established technique, and measuring kinetic isotope effects gives valuable information on rate determining steps and the nature of the reaction intermediate or transition state. Isotopes have also been used to create asymmetry,[1] a feature also called sometimes pseudochirality or cryptochirality. Very large isotope effects have also been used synthetically, in order to prevent the unwanted rupture of a particular bond.

On the other hand, the use of isotopes to probe photochemical reactions has been less popular, despite some very interesting work, among others, such as the impact of isotopes on the lifetime of excited states. In our early attempt to tune the rate of photolysis of protecting groups, we have observed a relatively large kinetic isotope effect in hydrogen abstraction reactions, something that we also exploited for synthetic purpose.[2]

In this contribution, we will mix two approaches, *i.e*. using isotopes to create a pseudochiral molecule *and* to generate a kinetic isotope effect in order to study the potential energy surface of a Norrish-type II photochemical reaction. This study may give hints on whether the Hammond Postulate, a valuable tool for thermal reactions, also applies to photochemical reactions.[3]

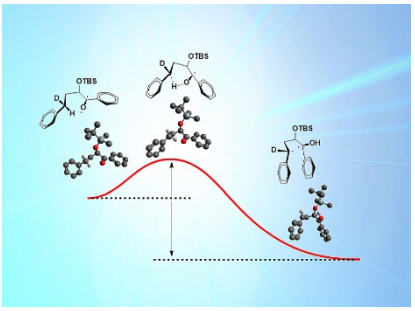


Figure 1: Studying a Norrish-Type II reaction using isotopes.

Acknowledgements: We thank the Swiss National Science Foundation for financial support.

References:

1. J. Haesler, I. Schindelholz, E. Riguet, C.G. Bochet, W. Hug, *Nature* **2007**, *446*, 526–529.
2. A. Blanc, C.G. Bochet, *Org. Lett.* **2007**, *9*, 2649–2651.
3. C.G. Bochet, F.M. Harvey, *Chem. Sci.* **2021**, *12*, 599–605.

Macro- and micro-plastic litter and increased COVID-19 based plastic pollution in the aquatic environment and landfills: treatment, environmental risks and policy solutions

Damià Barceló [a,b]

a) Institute of Environmental Assessment and Water Research, IDAEA-CSIC, C/ Jordi Girona 18-26, 08034 Barcelona, Spain
b) Catalan Institute for Water research, ICRA-CERCA, Emili Grahit 101, 17003, Girona, Spain

Email: dbcqam@cid.csic.es //dbarcelo@icra.cat

Plastic pollution is nowadays a global and ubiquitous problem being detected everywhere: marine environment , sand beaches, wastewaters, surface waters, soils, sludges, sediments, biota, food and air. The work plastic comes from the Greek term plastikos, which means that it can remain shaped in various systems. Global plastic production did hit approximately 348 million tonnes in 2017, being China the largest producer responsible of 27% of worldwide pollution. It is estimated that more than 8300 million tonnes of virgin plastic have been produced to date. Many consumers are not aware that plastic goods are usually made in petrochemical plants. According to the 2019 Centre for International Environmental Law Report, its production will contribute approximately to 850 million tons greenhouse emissions. Plastic is part of our daily life and worldwide we use 4 trillion plastic bags annually and 1 million plastic bottles every minute.

Plastics in the environment are divided into Macro-Plastics (with particles >2.5 cm), Meso-Plastic (with particles 2.5cm-5mm), Micro-Plastics (MPs) (with particles between micron- 5mm) and Nano-Plastics (with particles between 1-100nm). Macro-Plastics include everything identified as litter, such as plastic bags, bottles discarded fishing nets, plastic toys among other items and they can be usually observed. MPs are commonly invisible to the naked eye. particularly when mixed with sediment. Macro-Plastics enter the marine environment via rivers, poor waste management or being dumped into the marine waters.

MPs are directly released into the water or formed by degradation of Macro-plastics. In short, annually between 4 and 12 millions of tonnes of plastics are going into the oceans and most probably in 2050 will exceed the amount of fish. The amount of anthropogenic debris in the marine and coastal environments is steadily increasing with an estimation of 270,000 of plastic floating. In consequence international organizations, as well as NGOs recognize marine litter as a global issue of major concern. Plastic litter enters the marine environment from diverse points and diffuse sources and it can be transported through rivers long distances before being deposited in the bottom of seas. Few studies suggest that river litter can contribute up to 40% of all marine litter input, being estimated over 1.2-2.5 million tonnes of plastic every year.[1,2]

MPs are made from diverse molecules and correspond to diverse product types. MPs are composed of diverse suite of polymer type, being the most produced and consumed ones polypropylene (PP), low density polyethylene (LDPE), high density polyethylene (HDPE), polyvinyl chloride (PVC), polyurethane, polyethylene terephthalate (PET), polystyrene (PS) and polyamide (PA) are diverse and come from a multitude of sources, also they are in different sizes, colours, shapes and types of materials. MPs contain additives, i.e. phthalates and they can be as well a vector of organic contaminants and pathogens that can be ingested by organisms and introduced into the food web. Airborne fibrous MPs may enter our respiratory system with risk to the environment and humans.

Having said that, this presentation will cover in the first part different aspects of MPs and Macro-Plastic litter pollution in coastal waters, rivers, sediments and lakes. Case studies of MP pollution in several coastal environments, sediments and catchments of China, Saudi Arabia, India, Europe and Australia will be reported.[2,3,4] It is well-known that microplastics affect communities, biological diversity, and ecosystem processes will be reported. Microplastics increase the abundance of some taxa but decrease the abundance of some other taxa, indicating trade-offs among taxa and altered microbial community composition in both the natural environment and animals' gut. The alteration of community composition by microplastics is highly conserved across taxonomic ranks, while the alpha diversity of microbiota is often reduced or increased, depending on the microplastics dose and environmental conditions, suggesting potential threats to biodiversity. Biogeochemical cycles, greenhouse gas fluxes, and atmospheric chemistry, can also be altered by microplastics pollution. These findings suggest that microplastics may impact the U.N. Sustainability Development Goals (SDGs) to improve atmospheric, soil, and water quality and sustaining biodiversity.[5]

The last part of this lecture will discuss as well plastic litter and its increase use under Covid-19 outbreak. In this sense, the excessive use and consumption of single-use plastics (including personal protective equipment such as masks and

gloves) due to COVID-19 pandemic. This review aimed to provide an integrative and synthesized overview on the effects of COVID-19 on macroplastic pollution and its potential implications on the environment and human health in a long-term scenario; addressing the main challenges and discussing potential strategies to potentially overcome them. It emphasizes that future measures, involved in emergent health crisis or not, should reflect the balance between public health and environmental safety as they are both undoubtedly connected. Although the use and consumption of plastics significantly improved our quality of life, it is crucial to shift towards sustainable alternatives, such as bio-based plastics. Plastics should remain in the top of the political agenda in Europe and across the world, not only to minimize plastic leakage and pollution, but to promote sustainable growth and to stimulate both green and blue- economies.[6]

Landfilling and illegal waste disposal have risen to deal with the Covid-19 potentially infectious waste, particularly in developing countries. The intense use of such a disposal method drives us apart from the envisioned 2030 circular economy and environmental sustainability. It is estimated that 3.5 million metric tons of masks have been landfilled worldwide in the first year, which can generate up to 2.3 x 10^{21} microplastics of 7 μm in the coming year. This presentation addresses the challenges raised in the pandemic and post-pandemic scenarios on landfills; while discussing the potential environmental and health implications that might drive us apart from the 2030 UN sustainable goals. Also, it highlights some innovative mitigation technologies and improved management strategies that can pave the way to environmental recovery.[7]

MPs and macro litter pollution is nowadays in the radar not only of the scientific community but also of the public, the so-called citizen science. Media coverage helps to push such initiatives being complementary to scientific approaches. Such synergistic combination of academia, the public as well as policy actions should help to mitigate MP and macroplastics litter pollution in the next coming years. It is important to note that there are still many gaps in knowledge and we do not know well how plastics and MPs are transported and distributed and in what quantity. However, all these programs together with the modelling will allow us to know it soon. Monitoring and sampling systems also need to be improved especially in coastal areas and all existing programs will help. This is urgently needed in the next coming years due to the impact of plastic waste due to Covid-19 outbreak. Previous monitoring program will need to be repeated again to measure and evaluate in the field the real impact of plastic under almost two years of pandemic.

The detailed study of the strictly technological alternatives to the solution of this problem, show that they are not sufficient, and that in many cases they just transfer the problem of water to the generated sludge. More studies in these aspects are absolutely necessary, because although the number of publications is enormous, the gaps in knowledge are also enormous. Another solution that is expected to be developed and that could bring more definitive results is the degradation of MPs by microorganisms (fungi and bacteria). Many studies are being carried out, although the complexity of these studies means that progress in this field is slow. In this context, we would like to add few recommendations : (i) law and waste management strategies, such as exploring new removal technologies and avoid landfilling if this is economically feasible (ii) education, outreach and awareness, (iii) source identification, (iv)increasing monitoring and risk assessment to better understand the threat to biodiversity by reporting additional case studies where showing the impact of MP around the globe and (v) further innovative research lines like the development of bioplastics to replace SUPs in our daily life. In short, a greater awareness and responsibly of the general public, stakeholders, industries is needed. Discussions on this topic, particularly considering the excessive use of plastic, should start soon with the involvement of the scientific community, plastic producers and politicians in order to be prepared for the near future.

References:

1. Damià Barcelo and Yolanda Picó, Case studies of macro- and microplastics pollution in coastal waters and rivers: Is there a solution with new removal technologies and policy actions? *Case Studies in Chemical and Environmental Engineering,* 2 (2020) 100019.

2. Bianying Zhou, Jiaqing Wanga, Haibo Zhang, Huahong Shi, Yufan Fei, Shunyin Huang, Yazhi Tong, Dishi Wen, Yongming Luo, Damià Barceló, Microplastics in agricultural soils on the coastal plain of Hangzhou Bay, east China: Multiple sources other than plastic mulching film, *Journal of Hazardous Materials*, 368(2020)121814.

3. Gabriella F. Schirinzi , Marianne Köck-Schulmeyer , María Cabrera , Daniel González-Fernández , Georg Hanke , Marinella Farré , Damià Barceló, Riverine anthropogenic litter load to the Mediterranean Sea near the metropolitan area of Barcelona, Spain, *Science of the Total Environment*, 714 (2020) 136807

4. Yolanda Picó, Vasiliki Soursou , Ahmed H. Alfarhan , Mohamed A. El-Sheikh , Damià Barceló, First evidence of microplastics occurrence in mixed surface and treated wastewater from two major Saudi Arabian cities and assessment of their ecological risk, *Journal of Hazardous Materials*, 416 (2021)125747.

5. Evgenios Agathokleous, Ivo Iavicoli, Damià Barceló, Edward J. Calabrese, Ecological risks in a 'plastic' world: A threat to biological diversity? *Journal of Hazardous Materials,* 417 (2021)126035.

6. Ana L. Patricio Silva, Joana C. Prata, Tony R. Walker, Armando C. Duarte, Wei Ouyang,Damià Barceló, Teresa Rocha-Santos, Increased plastic pollution due to COVID-19 pandemic: Challenges and recommendations, *Chemical Engineering Journal*, 405 (2021)126683.

7. Ana L.P. Silva, Joana C. Prata, Armando C. Duarte, Amadeu M.V.M. Soares,Damià Barceló, Teresa Rocha-Santos, Microplastics in landfill leachates: The need for reconnaissance studies and remediation technologies, *Case Studies in Chemical and Environmental Engineering,* 3 (2021) 100072.

Ruthenium catalysts for green transformations: from alkenes metathesis to C-H bond functionalisations and useful ligands

Pierre H. Dixneuf

Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes, campus de Beaulieu 35042 Rennes, France,

Email: pierre.dixneuf@univ-rennes1.fr

Ruthenium(II) catalysts have been shown to contribute to green catalysis and sustainable chemistry and they have the advantages to be easy to make, stable with air and even operate in water under mildconditions. Many applications gathered in Rennes during the last 10 years will illustrate this point in the lecture.
Ruthenium-alkylidenes have been shown, since the pioneered work of Grubbs, to be efficient catalysts for alkene metathesis. The Rennes group has contributed to produce new alkene metathesis ruthenium catalysts and to apply them for the transformation of natural products such as terpenes[1] and to the building of monomers arising from plants to generate polyamides.[2]
Direct catalytic functionalizations of sp^2 and sp^3 C-H bonds are bringing revolutions in synthesis as they can replace with atom economy the classical, useful cross-coupling reactions arising from organometallics. The Rennes group has contributed not only to show applications with ruthenium(II) catalysts in the C-H functionalisation of imines, ketones, heterocycles,[3] but to explain the mechanism and the role of cocatalysts such as carboxylic acid in an autocatalytic process,[4] even operating in water.[5]
These concepts with Ru(II) catalysts will be applied to create new polydentate ligands or modify under mild conditions some ligands, such as by alkylation versus alkenylation of phosphine oxides[6] thus able to offer the best catalytic activities for a given reaction. When the action of Ru(II) catalysts will not be profitable enough, some Rh(I) catalysts will be used successfully to functionalyze C-H bonds of biaryl phosphines.[7,8]
The lecture will present several ways to create new polypyridines and polyfunctional functional phosphines via C-H bond functionalization and their uses to promote efficient catalytic transformations.

References:

1. H. Bilel, H. Naceur, C. Fischmeister, C. Bruneau, *Green Chem.*, **2011**, *13*, 1448
2. P. H. Dixneuf , C. Bruneau, C. Fischmeister, *Oil & Gas Sci. Technol.– Rev. IFP Energies nouvelles,* **2016**, 71, 19-40.
3. P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012,** 112, 5879.
4. E. Ferrer Flegeau, C. Bruneau, P. H. Dixneuf, and A. Jutand, *J. Am. Chem. Soc.* **2011**, *133*, 10161.
5. Bin Li, K. P. H. Dixneuf *Chem. Soc. Rev.* **2013,** 42, 5744.
6. Chang-Shen Wang, P. H. Dixneuf, J. F. Soulé*, ChemCatChem*, **2017,** 9, 3117.
7. Zhuan Zhang , P. H. Dixneuf, J.F. Soulé *Angew. Chem. Int. Ed.* **2019,** 58, 14110.
8. Zhuan Zhang, M. Cordier, P. H. Dixneuf, J. F. Soulé. *Org. Lett*. **2020,** 22, 5936

Versatile and scalable nanocarbon chemistry, assembly, and application

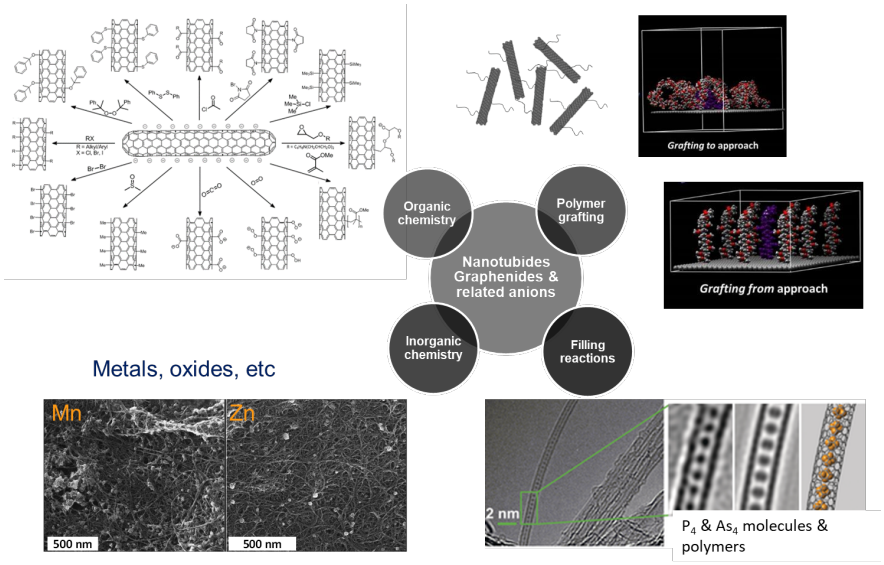
Milo S. P. Shaffer[a,]

a) Department of Chemistry and Department of Materials, Imperial College London.

Email: m.shaffer@imperial.ac.uk

Individual perfect nanocarbon structures have exceptional properties; the challenge is often how to exploit their potential in real macroscopic systems. Chemical functionalisation is critical to a wide range of nanocarbon technologies but needs to be versatile and applicable at scale. Existing approaches tend to rely on liquid phase reactions, often requiring damaging sonication or lengthy work up through filtration or centrifugation. The formation of individualized functionalised single wall nanotubes (SWNTs) and graphenes is a particular challenge.

One particularly promising approach, relies on reductive charging to form pure charged nanocarbon anions which can be redissolved, purified, or optionally functionalised, whist avoiding the damage typically associated with sonication and oxidation based processing. This simple system is effective for a host of nanocarbon materials including MWCNTs, ultralong SWCNTs, carbon blacks, graphenes, and related materials. The resulting nanocarbon ions can be readily chemically grafted for a variety of applications. The chemistry of these discrete nanions raises interesting fundamental questions, but is also practically useful. Dispersed nanocarbon related materials may form liquid crystal mesophases and can be assembled, by electrophoresis, cryogel formation, or direct cross-linking to form Joule heatable networks, protein nucleants, supercapacitor electrodes, and catalyst supports, particularly suited to combination with other 2d materials, such as layered double hydroxides. Comparative studies allow the response of nanocarbons with different dimensionalities to be assessed to identify fundamental trends and the most appropriate form for specific situations. The use of nanostructured materials often provides opportunities to simultaneously address otherwise conflicting materials property requirements, such as high ionic conductivity with high stiffness, or self-healing with high absolute strength.



Scheme 1: Examples of nanocarbon chemical transformations

Reference:

1. Clancy, Shaffer, et al, Charged Carbon Nanomaterials: Redox Chemistries of Fullerenes, Carbon Nanotubes, and Graphenes, Chem. Rev., **2018**, 118, 7363−7408.

Can something that is called “Sub” be Superb? The case of Subphthalocyanines

Tomás Torres

a) Department of Organic Chemistry, Universidad Autónoma de Madrid, c/ Francisco Tomás y Valiente 7, Cantoblanco, 28049 Madrid, Spain; b) IMDEA-Nanociencia, c/ Faraday 9, Campus de Cantoblanco, 28049 Madrid, Spain c) Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, Madrid, 28049, Spain.

Email: tomas.torres@uam.es

Subphthalocyanines (SubPcs) are well-known cone-shaped chromophores consisting on three 1,3-diiminoisoindole units assembled around a boron atom. As a result of their 14 pi-electron aromatic core and their tetrahedral geometry, SubPcs exhibit outstanding physical and optoelectronic properties (e.g., strong dipole moment, excellent light absorption in the 550-650 nm, rich redox features, and excellent charge transport capabilities), that have been skilfully used in variety of applied fields, such as molecular photovoltaics, among others [1,2]. SubPcs were used by us as non-fullerene acceptors in bulk heterojunctions (BHJ) solar cells [2g]. On the other hand as part of our systematic investigation in the preparation and study of novel SubPc-based D–A systems, we have used 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) as partner for SubPcs. Moreover, in the case of unsymmetrically substituted SubPcs (i.e., prepared by cyclotrimerization of a phthalonitrile with no C2v symmetry), they present inherent chirality and the corresponding couple of enantiomers can be isolated Columnar aggregates based on chiral SubPcs have been also prepared, giving rise to ferroelectric self-assembled molecular materials showing both rectifying and switchable conductivity [2a,i]. These chromophores have been incorporated in multicomponent systems showing a panchromatic response and allowing the tuning and controlling intramolecular FÖRSTER Resonance Energy Transfer for Singlet Fission [2j,k,l].

References:

1. a) Claessens, C. G. et al., Chem. Rev., 2014, 114, 2192–2277

2. a) Guilleme, J. et al., Angew. Chem. Int. Ed. 2015, 54, 2543-2547. b) Rudolf, M. et al. Chem. Sci. 2015, 6, 4141-4147. c) Cnops, K. et al. J. Am. Chem. Soc. 2015, 137, 8991−8997. d) J. Guilleme, J. et al , Chem. Commun., 2016, 52, 9793-9796. e) Guilleme, J. et al., Chem. Commun., 2016, 52, 9793-9796. f) Urbani, M. et al., Chem. Asian J. 2016, 11, 1223-12131. g) Duan, C. et al., Angew. Chem. Int. Ed. 2017, 56, 148–152. h) Winterfeld, K. A. et al., J. Am. Chem. Soc., 2017, 139, 5520–5529. i) A. V. Gorbunov, et al., Science Advances, 2017, 3, e1701017. j) Lavarda, G. et al. Angew. Chem. Int. Ed. 2018, 57, 16291-16295. k) J. Zirzlmeier, et al. Nanoscale 2020, 12, 23061-23068. l) Guzman, D. et al. Angew. Chem. Int. Ed. 2021, 60,1474–1481.

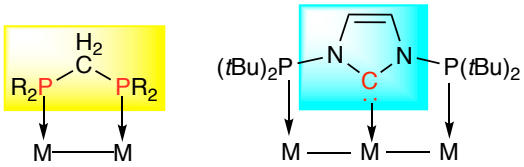
Phosphorus- and NHC-based Assembling Ligands for Metallophilic Interactions

Pierre Braunstein

University of Strasbourg – CNRS, Institute of Chemistry, 4 rue Blaise Pascal, 67081 Strasbourg (France)

Email: braunstein@unistra.fr

The formation and stabilization of metal-metal bonds in molecular compounds are known to be favored by supporting ligands. In particular, bi- or multidentate assembling ligands are well-suited to promote sometimes unexpected metal-metal bonding interactions.
Symmetrical short-bite diphosphine ligands of the dppm- or dppa-type[1] have been shown to promote non-covalent, metallophilic interactions[2] between d^{10} centres in heteropolynuclear complexes[3] and new short-bite functional *N*-Heterocyclic carbene (NHC) ligands have been recently applied to the stabilization of unusual metal chains.[4]



Functional NHC polydentate ligands are increasingly used in molecular design to enhance structural versatility and the catalytic, photophysical and magnetic properties of their metal complexes.[5]

Acknowledgements: We are grateful to the CNRS and the University of Strasbourg for continuous support and all the dedicated and talented coworkers and collaborators who were involved in this research topic and nd whose names appear in the references.

References

1. C. Fliedel, A. Ghisolfi, P. Braunstein, *Chem. Rev.* **2016**, *116*, 9237−9304.
2. S. Sculfort, P. Braunstein, *Chem. Soc. Rev.*, **2011**, *40*, 2741–2760.
3. P. Braunstein, A. A. Danopoulos, *Chem. Rev.* **2021**, in press.
4. P. Braunstein, A. A. Danopoulos, *Chem. Rev.* **2021**, in press. (b) P. Ai, K. Yu. Monakhov, J. van Leusen, P. Kögerler, C. Gourlaouen, M. Tromp, R. Welter, A. A. Danopoulos, P. Braunstein, *Chem. Eur. J.* **2018**, *24*, 8787–8796; (c) P. Ai, M. Mauro, L. De Cola, A. A. Danopoulos, P. Braunstein, *Angew. Chem. Int. Ed.* **2016**, 55, 3338 –3341.
5. See e.g. S. Hameury, P. de Frémont, P. Braunstein, *Chem. Soc. Rev.,* **2017**, *46*, 632–733; V. Charra, P. de Frémont, P. Braunstein, *Coord. Chem. Rev.* **2017**, *341*, 53–176; C. Fliedel, P. Braunstein, *J. Organomet. Chem.,* **2014**, *751*, 286–300; X. Ren, M. Wesolek, C. Bailly, L. Karmazin, P. Braunstein, *Eur. J. Inorg. Chem.* **2020**, 1073–1087; A. A. Danopoulos, P. Braunstein, J. Saßmannshausen, D. Pugh, J. A. Wright, *Eur. J. Inorg. Chem.* **2020**, 3359–3369.

Online

Pre-conferences

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

Materials chemistry and applications

Technologies to upcycle plastic solid wastes into nanostructured carbon materials and their application in the removal of micropollutants

Jose L. Diaz de Tuesta,[a] Fernanda F. Roman,[a] Adriano S. Silva,[a] Rui S. Ribeiro,[b] Octávia Vieira,[b] Adrián M.T. Silva,[b] Joaquim L. Faria,[b] Helder T. Gomes[a]

a) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; b) Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

Email: jl.diazdetuesta@ipb.pt

The world's plastics production has been increasing stiffly over the years. Accounting only 2019, the global production of plastics reached nearly 370 million metric tonnes, with ca. 15.7% of those produced in Europe.[1] Recent projections point towards a cumulative generation of plastic solid wastes (PSWs) of over 25,000 million metric tonnes by 2050.[2] Among these, 36.4% are expected to be discarded in landfills or in the environment; a similar fraction (36.4%) should be incinerated, and only 27.2% will be recycled.[2] These forecasts point out that PSWs are mismanaged, mainly because current technologies are unable to promote proper reusing/recycling of these materials.[3]

Proper waste management falls within the scope of upstream responses. However, several difficulties have been hindering waste plastic recycling, such as the lack of economic attractiveness of the resulting products.[4] Using waste plastics as feedstock for the production of added-value products and materials has been proposed as the boost needed to increase the attractiveness of plastics recycling. Among them are the preparation of carbon nanomaterials (CNs), such as carbon nanotubes or graphene, using PSWs as carbon precursors. This represents a new strategy for the valorisation of PSWs, consisting in the cracking of polymers that compose them and further synthesizing the CNs, using the resultant degradation gaseous products, by catalytic chemical vapour deposition (CCVD). However, most studies only report single pure polymers as model PSW to carry out a one-step process (pyrolysis and synthesis) without targeting applications of the resulting CNs.[5-7] The properties of the CNs obtained from PSWs could be fined tuned for specific applications, as demonstrated in a previous work.[8] These characteristics of the developed fine tuned CNs make them highly suitable for the removal of micropollutants, as will be shown in this talk.

Acknowledgements: This work was financially supported by project POCI-01-0145-FEDER-031439 (PLASTIC_TO_FUEL&MAT) funded by FEDER funds through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI), and by national funds (PIDDAC) through FCT/MCTES. The work was also partially funded by the Base Fundings - UIDP/50020/2020 of the Associate Laboratory LSRE-LCM and UIDB/00690/2020 of the Centro de Investigação de Montanha (CIMO) - by national funds through FCT/MCTES (PIDDAC).

References:

1. PlasticsEurope, Plastics – the Facts 2020, **2021**.
2. R. Geyer, J.R. Jambeck, K.L. Law, Production, use, and fate of all plastics ever made, *Sci. Adv.* **2017**, *3*, e1700782.
3. WWF, Solving plastic pollution through accountability, in, World Wildlife Fund, Gland, Switzerland **2019**.
4. Miranda M.N., Silva A.M.T., Pereira M.F.R., Microplastics in the environment: A DPSIR analysis with focus on the responses, *Sci Total Environ.* **2020**, *718*, 134968.
5. Panahi A.; Wei Z.; Song G.; Levendis Y.A.; *Ind. Eng. Chem. Res.* **2019**, *58*, 3009.
6. Jia J.; Veksha A.; Lim T.-T.; Lisak G.; *J. Clean. Prod.* **2020**, *258*, 120633.
7. Cai N.; Li X.; Xia S.; Sun L.; Hu J.; Bartocci P.; Fantozzi F.; Williams P.T.; Yang H.; Chen H.; *Energy Convers. Manag*. **2021**, *229*, 113794.
8. Diaz de Tuesta J.L., Machado B. F., Serp P., Silva A.M.T., Faria J.L., Gomes H.T., *Catal Today* **2019**, *356*, 205.

Chemistry in life sciences

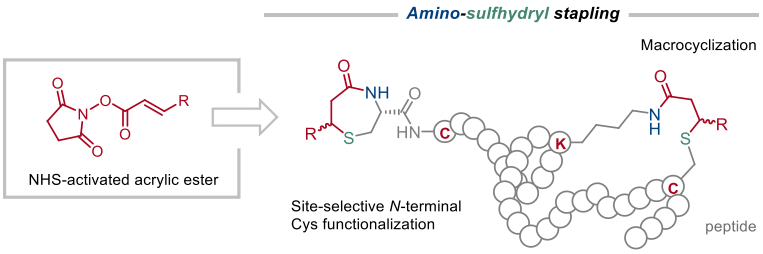
Targeting N-terminal cysteines in bioconjugation

Pedro M. P. Gois

a) Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Lisbon, Portugal

Email: pedrogois@ff.ulisboa.pt

Post-translational-modifications are part of Nature's "toolbox" devised to extend the range of protein functions and to control fundamental cellular processes. Appreciation for this strategy, have led chemical biologists to develop many different genetic and chemical methods to mimic Nature's proficiency to attach chemical handles onto proteins, though, the complex structure and marginal stability of proteins in vitro, still constitute a formidable challenge for bioconjugation. In recent years, a plethora of innovative chemical methods have been developed to selectively modify specific residues without disturbing protein's architecture or function. This synthetic "toolbox" greatly expanded in recent years, benefiting from the straightforward covalent functionalization of the thiol and ε-amino groups of cysteine and lysine residues. In this presentation will be discussed or most recent bioconjugation methods targeting these residues, namely at the N-terminal cysteines, and their use in the construction of bioconjugates. (**Scheme 1**).[1-5]



Scheme or Figure 1: Selected example of our recently developed amino-sulfhydryl stapling reaction.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support (iMed.ULisboa UIDB/04138/2020 and UIDP/04138/2020; PTDC/QUI-QOR/29967/2017); LISBOA-01-0145-FEDER-029967.

References:

1. Iminoboronates: A New Strategy for Reversible Protein Modification, P. M. S. D. Cal, J. B. Vicente, E. Pires, A. V. Coelho, L. F. Veiros, C. Cordeiro, P. M. P. Gois, J. Am. Chem. Soc. 2012, 134, 10299.
2. Iminoboronates are Efficient Intermediates for Selective, Rapid and Reversible N-Terminal Cysteine Functionalisation, H. Faustino, M. J. S. A. Silva, L. F. Veiros, G. J. L. Bernardes, P. M. P. Gois, Chem. Sci. 2016, 7, 5052-5058
3. Engineering Boron Hot Spots for the Site-Selective Installation of Iminoboronates on Peptide Chains, R. Russo, R. Padanha, F. Fernandes, L. F. Veiros, F. Corzana, P. M. P. Gois, Chem. Eur. J. 2020, 26, 15226 – 15231
4. Efficient Amino-Sulfhydryl Stapling on Peptides and Proteins Using Bifunctional NHS-Activated Acrylamides M. J. S. A. Silva, H. Faustino, J. A. S. Coelho, M. V. Pinto, A. Fernandes, I. Compañón, F. Corzana, G. Gasser, P. M. P. Gois, Angew. Chem. Int. Ed. 2021, 60, https://doi.org/10.1002/anie.202016936

Environment and water

Exploring the environmental applications of microalgae: CO_2 capture and nutrients removal from wastewaters

Ana L. Gonçalves[a]

a) LEPABE - Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

Email: algoncalves@fe.up.pt

The accumulation of carbon dioxide (CO_2) in the atmosphere, as well as the enrichment of water courses in nutrients are environmental issues associated with numerous impacts on ecosystems. Several attempts have been made to address these issues, but the cost and sustainability of current methodologies are still a concern. Cultivation of photosynthetic microorganisms, such as microalgae, appears as a sustainable solution because[1]: (i) they can effectively uptake CO_2 from different emission sources (e.g., atmosphere and exhaust gas emissions); (ii) they can assimilate nitrogen and phosphorus present in excess in wastewaters; and (iii) the resulting biomass can be processed into valuable products. Although the use of microalgae for these applications seems to be a valuable option, there are several aspects in need for improvement. Regarding CO_2 uptake, the low solubility of CO_2 in the liquid medium results in a reduced CO_2 utilisation efficiency by microalgae. On the other hand, high CO_2 concentrations may inhibit microalgal growth, also reducing their uptake efficiency.[2] In wastewater treatment using microalgae, some characteristics of the effluent (e.g., high colour and turbidity, high heavy metals content, etc.) may also limit microalgal growth and, hence, their bioremediation efficiency.[3] For this reason, optimisation of microalgal culturing conditions (either by modulating some operational parameters, using alternative microalgal species, or by studying novel photobioreactor configurations) should be addressed. In this presentation, the potential of microalgae for CO_2 capture and nutrients removal from wastewaters will be demonstrated, focusing on the main advances performed on the optimisation of microalgal biomass production.

Acknowledgements: This work was financially supported by: (i) Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology and Energy – LEPABE - funded by national funds through the FCT/MCTES (PIDDAC); and (ii) Project POCI-01-0145-FEDER-031736 – PIV4Algae - Process Intensification for microalgal production and Valorisation, funded by FEDER funds through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES.

References:

1. a) Hussain, F.; Shah, S. Z.; Ahmad, H.; Abubshait, S. A.; Abubshait; H. A.; Laref, A.; Manikandan, A.; Kusuma, H. S.; Iqbal, M. *Renew. Sust. Energy Rev.* **2021**, *137*, 110603. b) Razzak, S. A.; Ali, S. A. M.; Hossain, M. M.; deLasa, H. *Renew. Sust. Energy Rev.* **2017**, *76*, 379.
2. Chiu,S.-Y.; Kao, C.-Y.; Chen, C.-H.; Kuan, T.-C.; Ong, S.-C.; Lin, C.-S. *Bioresour. Technol.* **2008**, *99*, 3389.
3. Guldhe, A.; Kumari, S.; Ramanna, L.; Ramsundar, P.; Sigh, P.; Rawat, I.; Bux, F. *J. Environ. Manage.* **2017**, *203*, 299.

Chemistry in life sciences

Ionic liquid and water: the perfect duo to improve the extraction of high-value compounds from biomass

Mara G. Freire

CICECO-Aveiro Institute of Materials, Chemistry Department, University of Aveiro, Portugal

Email: maragfreire@ua.pt

Biomass is a source of high-value small organic compounds, such as phenolic compounds, terpenoids, flavonoids, among others. These compounds display a range of relevant biological activities, among which antioxidant, anti-inflammatory and antitumor features, being relevant compounds for application in food, cosmetic and nutraceutical products. Furthermore, most of these compounds can be obtained from the waste generated by agroforest and agrofood industries, thus contributing to the full valorization of feedstock in an integrated biorefinery perspective and, ultimately, contributing to a circular economy. However, most of these compounds, and particularly those with recognized health benefits, are of high cost due to the complex and multistep methods required for their extraction, purification and recovery. The extraction of these compounds from biomass is commonly carried out using volatile organic solvents, which recently have been combined with microwave and ultrasound-assisted methods to improve the extraction efficiency. On the other hand, a large interest was observed on the identification of promising solvents with greener credentials to replace volatile organic solvents, in which supercritical CO_2 extraction, ionic liquids (ILs) and deep eutectic solvents (DES) have been the most investigated. Among these solvents, in the past two decades, the number of studies comprising the application of ILs as alternative solvents to extract high-value compounds from biomass faced a significant increase.[1] In this field, mixtures of ILs and water stood out as solvents of low cost, low viscosity and high selectivity, performing better than pure ILs or pure water.[1] The high performance of IL-water solvents is due to two main molecular-level mechanisms that have been comprehensively investigated along the years, namely hydrotropy or micelles formation.[2]
In this lecture, relevant examples on the use of IL-water mixtures as greener solvents to improve the extraction of high-value compounds from biomass will be given, in which the recovery process and biological activities of the target compounds have been addressed as well. Supported on these promising examples a critical overview on the potential of these processes to reach the industrial level will be provided.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement.

References:

1. a) Passos, H.; Freire, M. G.; Coutinho, J. A. P. *Green Chem.* **2014**, *16*, 4786. b) Ventura, S. P. M.; Silva, F. A.; Quental, M. V.; Mondal, D.; Freire, M. G.; Coutinho, J. A. P. *Chem. Rev.* **2017**, *117*, 6984.
2. a) Faria, E. L. P.; Ferreira, A. M.; Cláudio, A. F. M.; Coutinho, J. A. P.; Silvestre, A. J. D.; Freire, M. G. *ACS Sust. Chem. Eng.* **2019**, *7*, 14143. b) Faria, E. L. P.; Shabudin, S. V.; Cláudio, A. F. M.; Valega, M.; Domingues, F. M. J.; Freire, C. S. R.; Silvestre, A. J. D.; Freire, M. G. *ACS Sust. Chem. Eng.* **2017**, *5*, 7344.

Keynotes

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

Materials chemistry and applications

Key scientific and technological strategies for the development of drug delivery systems

Salette Reis

LAQV-REQUIMTE, Department of Chemical Sciences, Laboratory of Applied Chemistry, Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal.

Email: shreis@ff.up.pt

Nanotechnology is a promising and emerging technology with great potential to improve the efficacy of bioactive compounds. Nanoparticles are nowadays widely used in various sectors such as nutrition, therapy, targeted drug delivery, among others. However, the clinical translation of nanomedicine is very limited. Thus, a complete understanding of the properties of nanocarriers and their interactions with the physiological interfaces is essential to design effective nanoformulations.
The rationale that guides the planning and development of a drug carrier and the most important parameters that should be considered during nanocarriers optimization for applications in nanomedicine will be highlighted. *In vitro* and *in vivo* assays usually performed in a pre-clinic stage will be also mentioned. Some case studies already developed will be discussed.

Materials chemistry and applications

Metal nanoparticles as scaffolds for biosensing and biocatalysis

E. Pereira

LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal

Email: eulalia.pereira@fc.up.pt

Localized surface plasmon resonance (LSPR) in metal nanoparticles imparts optical properties, such as high intensity absorption and scattering of visible light, enhancement of Raman spectra of molecules adsorbed to their surface, and fluorescence quenching/enhancement, that makes them excellent reporters in (bio)sensing applications. In addition, methods for surface modification of metal nanoparticles are now well established, allowing binding of biological molecules, and affording molecular recognition properties or enzymatic activities to the bionanoconjugates.
Our research team is studying these bionanoconjugates in biosensing and biocatalysis applications, in particular studying the effect of size/shape of nanoparticles (**Figure 1**). Selected examples will be presented including (i) the use of silver and gold nanostars in disposable platforms for Surface Enhanced Raman Spectroscopy (SERS);[1] (ii) gold nanoparticles for immunosensors; (iii) gold nanoparticles as activity modulators of enzymes.[2]

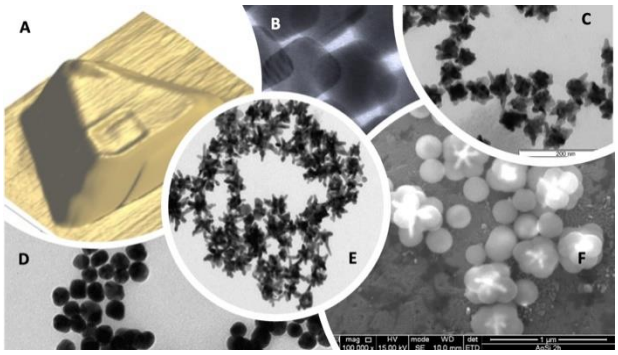


Figure 1: Selected examples of metal nanoparticles synthesized in our team: A) AFM image of one gold nanotriangle; B) TEM image of gold nanocubes: C) TEM image of gold nanostars; D) TEM image of spherical gold nanoparticles; E) TEM image of silver nanostars; F) SEM image of core-shell silver nanostars@silica.

Acknowledgements: The work was supported through the project UIDB/50006/2020 | UIDP/50006/2020, funded by FCT/MCTES through national funds, and through National Funds (FCT, Fundação para a Ciência e Tecnologia) through project PTDC/NAN-MAT/30589/2017.

References:

1. a) Oliveira M. J.; de Almeida M. P.; Nunes D.; Fortunato E.; Martins R.; Pereira E.; Byrne H. J.; Águas H.; Franco R. *Nanomaterials* **2019**, *9*, 1561; b) de Almeida M. P.; Leopold N.; Franco R.; Pereira E. *Frontiers in Chemistry* **2019**, *7*, 368.
2. a) Bessa L.J.; de Almeida, M. P.; Eaton P.; Pereira E.; Gameiro P. *Int. J. Environ. Res. Public Health* **2020**, *17*, 7891; b) Silveira C.M.; Zumpano R.; Moreira M.; de Almeida M. P.; Oliveira M. J.; Bento M.; Montez C.; Paixão I.; Franco R.; Pereira E.; Almeida G. *ChemElectroChem* **2019**, *6*, 4696; c) de Almeida M. P.; Quaresma P.; Sousa S.; Couto, S.; Gomes I.; Krippahl L.; Franco R.; Pereira E. *Phys. Chem. Chem. Phys.*, **2018**, *20*, 16761.

Chemistry in life sciences

Dehydropeptide based nanostructures for biomedical applications

P.J. Jervis, J.A. Martins, P.M.T. Ferreira

Centro de Química, Escola de Ciências, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

Email: pmf@quimica.uminho.pt

Nanometric structures obtained from the self-assembly of small peptide building blocks are being used as new functional materials for biological applications such as biosensing, tissue engineering, controlled drug delivery and theranostic.[1] Our research group, and others, have reported new dehydropeptides capable of self-assembly forming different types of nanostructures including hydrogels, nanoparticles and nanotubes.[2] The presence of a dehydroamino acid residue imparts increased proteolytic resistance, as well as different physical properties arising from the decreased structural flexibility of the dehydropeptide chain. In this communication, the recent results obtained by our research group in the synthesis, characterization and potential biomedical applications of dehydropeptide based nanomaterials will be presented and discussed (**Figure 1**).

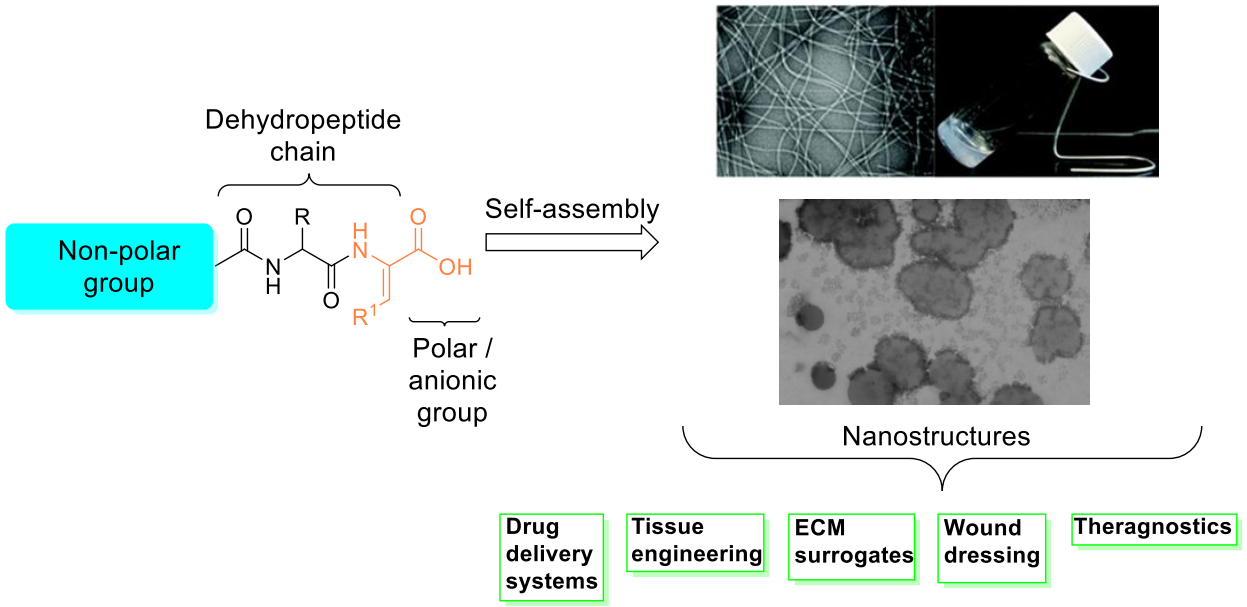


Figure 1: Dehydropeptide nanostructures for biomedical applications.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support in the framework of the Strategic Funding of CQUM (UID/QUI/00686/2019) and project PTDC/QUI-QOR/29015/2017 (POCI-01-0145-FEDER-029015).

References:

1. Fleming S, Ulijn R V. *Chem. Soc. Rev.* **2014**, 43, 8150.
2. a) Veloso S.R.S., Jervis P.J., Silva J.F.G., Hilliou L., Moura C., Pereira D.M., Coutinho P.J.G., Martins J.A., Castanheira E.M.S., Ferreira P.M.T. *Materials Science and Engineering: C* **2021**, 122, 111869. b) Jervis P.J., Amorim C., Pereira T., Martins J.A., Ferreira P.M.T. *Int. J. Mol. Sci.* **2021**, 22, 2528.

Chemistry in life sciences

Machine learning for accelerating chemical biology

T. Rodrigues

Faculdade de Farmácia da Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal

Email: tiago.rodrigues@ff.ulisboa.pt

Machine learning has seen numerous outstanding applications in the chemical sciences as consequence of the recent developments in data acquisition and storage, hardware capabilities and algorithms.[1] The automation of pattern recognition may thus bring benefits to chemistry by augmenting expert intuition and accelerating the development of high value chemical matter, either through proposing synthetic pathways to small molecules,[2] predicting properties,[3] among others.
In this talk, we discuss how we are using machine learning to deorphanize natural products with known anti-proliferative activity,[4,5] and harnessing statistical learning as leverage to augment knowledge and bringing discoveries from bench to clinic. We will also discuss and provide examples of how machine learning can be effectively employed in real-world, low data scenarios[6,7] and as an assistant to mitigate attrition in early chemical probe and/or drug lead discovery.[8]

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support (CEECIND/00684/2018).

References:

1. de Almeida F *et al. Nat Rev Chem* **2019**, *3*, 589-604.
2. Segler M. H. S.; Preuss M; Waller M. P. *Nature* **2018**, *555*, 604-610.
3. Meftahi N *et al*. *npg Comput. Mater.* **2020**, *6*, 166.
4. Rodrigues T *et al. Chem. Sci.* **2018**, *9*, 6899-6903.
5. Conde J *et al. ACS Cent. Sci.* **2021**, *7*, 868-881.
6. Reker D *et al. Cell Rep. Phys. Sci.* **2020**, *1*, 100247.
7. de Almeida F *et al. submitted.*
8. Lee K *et al.* arXiv: 2105.00267v1 **2021.**

Food and natural products

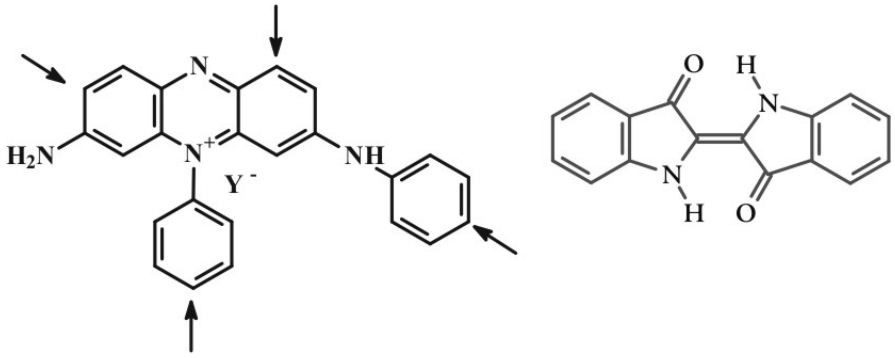
Molecules at the Museum

J. Sérgio Seixas de Melo,[a]

a) University of Coimbra, CQC, Department of Chemistry, 3004-535 Coimbra, Portugal

Email: *sseixas@ci.uc.pt*

Indigo and violet/purple, colours of the rainbow, are also associated to two timeless molecules: mauveine and indigo. Indigo, the oldest source of blue, and believed in many cultures to possess unique talismanic properties, is also found in the first organic-inorganic pigment produced by the Maya Civilization: Maya Blue.[1,2] Although initially extracted from *Indigofera* plants, the chemical synthesis of this fascinating blue dye by Adolf von Bayer in 1878 (started in 1865) is associated to the genesis of the German chemical industry. Mauveine is also associated with the birth of the chemical dye industry in Europe, with its synthetic discovery in 1856 by W. H. Perkin.[1,2] Despite the more than 165 years of Mauveine's synthesis, recent discoveries of new mauveine structures in historical samples have lead to different views on its original synthetic procedure.[3,4]



Scheme 1 Structures of Mauveine (left) and Indigo (right). In the case of Mauveine the arrows indicate the positions of the methyl groups found in the different structures and Y^- the counterion that can be a sulfate or an acetate anion.

Indigo is, nowadays, still in use to dye blue jeans and it gained a renewed interest as a molecule due to its remarkable photostability. The enormous impact these molecules have had in the history of science, makes them the title of this presentation. However, these two dyes, which are linked by their historical importance, are also remarkably stable. Some of the mechanisms behind this stability will also be addressed in this presentation, meant to be of interest to a broad community of chemists.

Acknowledgements: This work was carried out with the support of Centro de Química de Coimbra [FCT (Fundação para a Ciência e a Tecnologia) Ref. UIDB/00313/2020 and UIDP/00313/2020], and the COMPETE 2020 Operational Thematic Program for Competitiveness and Internationalization (Project "Hylight", 02/SAICT/2017, PTDC/QUI-QFI/31625/2017), co-financed by national funds through the FCT/MCTES, the European Union through the European Regional Development Fund (ERDF) under the Portugal 2020 Partnership Agreement.

References:

1. a) Seixas de Melo, J.S., *The Molecules of Colour*, in *Photochemistry*, A. Albini, E. Fasani, and S. Protti, Editors. 2018, RSC: London. p. 68-100. b) Seixas de Melo, J.S., *The molecules of colour and Art. Molecules with history and modern applications*, in *Photochemistry*, A. Albini and S. Protti, Editors. 2020, RSC: London. p. 196-216.c) Seixas de Melo, J.S., The molecules of colour. The real blue indigo: photostability mechanisms, new functional derivatives, and hybrids, in *Photochemistry*, S. Protti and C. Raviola, Editors. 2021, RSC: London. Vol. 49 (in press).
3. a) Cova, T.F.G.G., A.A.C.C. Pais, and J.S. Seixas de Melo,. Sci. Rep., **2017**. 7, 6806. b) Conceição Oliveira, M.; Dias, A.; Douglas, P.; Seixas de Melo, J. S., *Chem. Eur. J.* **2014,** *20*, 1808.
4. Plater M.J.; Raab, A. *J. Chem. Res.* **2015**, 39, 180.

Food and natural products

Development and application of natural ingredients in the food industry

L. Barros, C. Pereira, I.C.F.R. Ferreira

Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

Email: lillian@ipb.pt

Given the increasing awareness of consumers in what concerns healthy dietary habits, natural alternatives have been explored for artificial additives. In this context, plants and mushrooms are unquestionable sources of valuable compounds to be used as colouring, preservative, and bioactive compounds in food industry. The sustainable exploitation of these natural resources is of extreme importance and, therefore, efforts have been made to valorise bio-residues from food industry by recovering their compounds of interest to be included in natural additives formulation. Moreover, distinct techniques, such as maceration, ultrasound, or microwave-assisted extractions have been applied through optimized methodologies attempting to achieve an optimal extraction yield.

Thus, several compounds have been extracted from plants and mushrooms and applied in food matrices with different purposes. For example, betalains (*e.g.* gomphrenin II, gomphrenin III, isogomphrenin II, and isogomphrenin III) and anthocyanins (*e.g.* cyanidin, delphinidin, and malvidin derivatives) obtained from purple globe amaranth, rose, dahlia, centaurea, strawberry-tree, roselle, and blueberry have proved bioactive and colouring properties when incorporated in ice-cream, yogurt, and waffles.[1]

Moreover, phenolic acids (*e.g.* rosmarinic acid), flavonoids (e.g. quercetin derivatives), and ellagitannins (*e.g.* sanguiin H-10 and lambertianin) from mushrooms, wild strawberry, rosemary, mountain sandwort, and flowers of silva brava demonstrated bioactive properties when introduced in gelatin, yogurt, and cottage cheese.[2]

On the other hand, strawberry-tree, basil, lemon balm, sweet chestnut flowers, fennel, and German chamomile revealed to be great sources of preserving molecules with antioxidant and antimicrobial activity, such as flavonoids (*e.g.* catechin, and quercetin and luteolin derivatives), phenolic acids (*e.g.* rosmarinic, chicoric, lithospermic, caffeic, and caffeoylquinic acids), and hydrolysable tannins (*e.g.* trigalloyl-HHDP-glucoside), which were tested in loaf bread, cupcakes, yogurt, cheese, and cottage cheese.[3]

These natural extracts allowed promising results, leading to the development of natural alternatives to the massively used artificial additives.

Acknowledgements: The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support by national funds FCT/MCTES to CIMO (UIDB/00690/2020). To the European Regional Development Fund (ERDF) through the Regional Operational Program North 2020, within the scope of Project *Mobilizador* Norte-01-0247-FEDER-024479: ValorNatural® and Project GreenHealth - Digital strategies in biological assets to improve well-being and promote green health, Norte-01-0145-FEDER-000042. To FEDER-Interreg España-Portugal programme through the project TRANSCoLAB 0612_TRANS_CO_LAB_2_P.

References:

1. Roriz C.L. et al. *LWT* **2018**, *92*, 101.
2. Dias M.I. et al. *J. Funct. Foods* **2015**, *16*, 243.
3. Takwa S. et al. *LWT* **2018**, *88*, 47.

Materials chemistry and applications

Development of 3D temperature tomography at the micro and nanoscale

N.J.O Silva,[a]

a) CICECO – Aveiro Institute of Materials e Departamento de Física, Universidade de Aveiro, 3810-193 Aveiro, Portugal

Email: nunojoao@ua.pt

Devices capable of measuring temperature at the nanoscale are valuable in both fundamental and applied science, and find applications in micromachine or celular overheating, for instance[1]. Although they hold tremendous promise for many applications, their 2D resolution has been a limiting factor against their more widespread use. We are develping nanoprobes with tailored magnetic properties able to record critical information about temperature in 3D. Since this approach is based on magnetic properties, it will allow measurements in depth and in non-transparent media, complementing current optical nanothermometers.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia (PTDC/NAN-MAT/3901/2020, POCI-01-0145-FEDER-029460) and H2020-EU.1.1. - EXCELLENT SCIENCE - European Research Council (ERC Grant agreement ID: 865437) for financial support.

References:

1. Brites, C.D.S.; Lima, P.P.; Silva, N.J.O.; Millan, A.; Amaral, V.S.; Palacio, F.; Carlos, L.D. *Nanoscale* **2012**, 4, 4799.
2. Silva, R.O.; Pereira, R.A.; Silva, F.M.; Gaspar, V.M.; Ibarra, A.; Millan, A.; Sousa, F.L.; Mano, J.F.; Silva, N.J.O. *Mater. Horizon.* **2019**, 6, 524.

Materials chemistry and applications

Versatile π-conjugated heterocyclic molecules: design, synthesis and application in optoelectronics and energy

M. Manuela M. Raposo[a]

a) Centre of Chemistry, Campus of Gualtar, University of Minho, 4710-057 Braga, Portugal

Email: mfox@quimica.uminho.pt

Donor/acceptor π-conjugated heterocyclic molecules (D-π-A) are a versatile class of organic compounds with a wide range of applications in diverse areas such as medicinal, supramolecular, or materials chemistry due to their biological activity, as well their optoelectronic properties. Comprehensive work developed during the last years in this research group showed that the optical, thermal and electronic properties of donor/acceptor π-conjugated heterocyclic compounds could be tuned through functionalization of the heterocycles, changing its electronic nature or position on the heterocyclic system.[1] This increased the potential for several innovative applications, namely as nonlinear optical (NLO) and photochromic materials as well for dye sensitized solar cells (DSSCs) and organic light emitting diodes (OLEDs).[1,2]
Results from the research group exemplifying the innovative design, synthesis and evaluation of heterocyclic molecules (**Figure 1**) as nonlinear optical and photochromic materials, as well as organic components for DSSCs and OLEDs, will be presented and discussed.

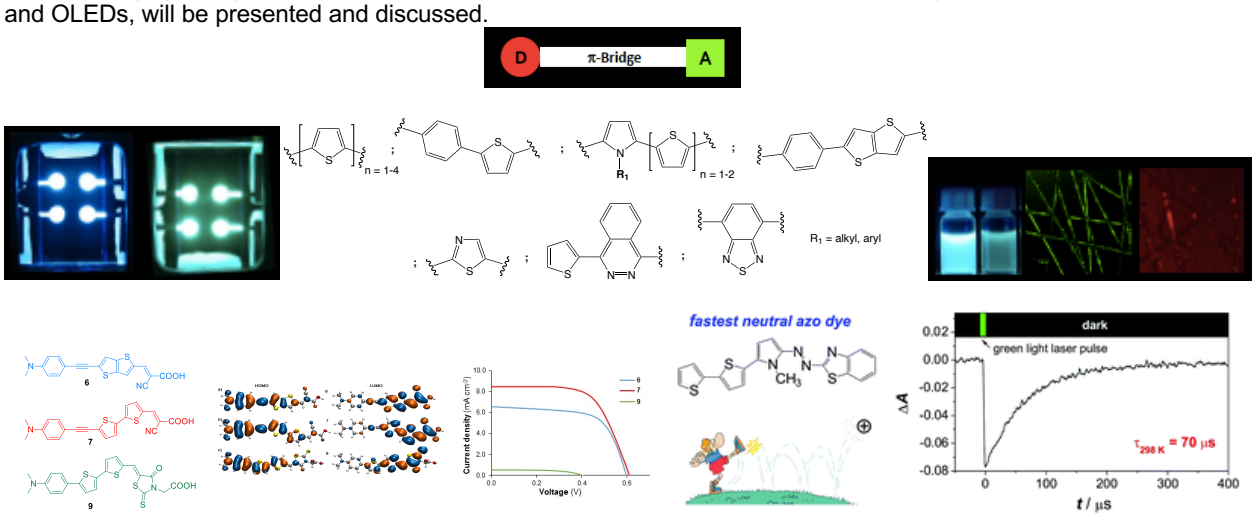


Figure 1: Donor/acceptor π-conjugated heterocyclic molecules for optoelectronic and energy applications.

Acknowledgements: The author acknowledge Fundação para a Ciência e Tecnologia - FCT (Portugal) for funding through CQUM (PEst-C/QUI/UI0686/2013, PEst-C/QUI/UI0686/2016, PEst-C/QUI/UI0686/2018 and UID/QUI/00686/2020) and PhD grants to M. C. R. Castro (SFRH/BD/78037/2011) and S. S. M. Fernandes (SFRH/BD/87786/2012). The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network and was purchased within the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT.

References:

1. a) Raposo, M. M. M.; Sousa, A. M. R. C.; Kirsch, G.; Cardoso, P.; Belsley, M.; Matos Gomes, E.; Fonseca, A. M. C. *Org. Lett.* **2006**, *8*(17), 3681-3684. b) Pina, J.; Seixas de Melo, J. S.; Batista, R. M. F.; Costa, S. P. G.; Raposo, M. M. M. *Phys. Chem. Chem. Phys*. **2010**, *12*(33), 9719-9725.
2. a) Castro, M. C. R.; Belsley, M.; Raposo, M. M. M. *Dyes Pigments* **2016**, *131*, 333-339. b) Fernandes, S. S. M.; Herbivo, C.; Aires-de-Sousa, J.; Comel, A.; Belsley, Raposo, M. M. M. *Dyes Pigments* **2018**, *149*, 566-573. c) Garcia-Amorós, J.; Castro, M. C. R.; Coelho, P.; Raposo, M. M. M.; Velasco, D. *Chem. Commun.* **2016**, *52*, 5132. d) Fernandes, S. S. M.; Belsley, M.; Pereira, A.; Ivanou, D.; Mendes, A.; Justino, L. L. G.; Belsley, M.; Burrows, H. D.; Raposo, M. M. M. *ACS Omega* **2018**, *3*(10), 12893-12904; e) Fernandes, S. S. M.; Pereira, A.; Ivanou, D.; Mendes, A.; Raposo, M. M. M. *Dyes Pigments* **2018**, *151*, 89-94; f) Pina, J.; Seixas de Melo J. S.; Batista, R. M. F.; Costa, S. P. G.; Raposo, M. M. M. *J. Org. Chem.* **2013**, *78*(22),11389-11395.

Chemistry in life sciences

Health monitoring by protein imprinted polymers

M.G.F. Sales

BioMark@UC, Departamento de Engenharia Química da Faculdade de Ciências e Tecnologia da Universidade de Coimbra, Rua Sílvio Lima, pólo II, 3030-790 Lisboa, Portugal; CEB, Centro de Engenharia Biológica da Universidade do Minho, Gualtar, Braga, Portugal.

Email: goreti.sales@eq.uc.pt

Health monitoring requires portable and inexpensive devices that can be used at the point-of-care (POC). Typically, biosensors are used for this purpose. These are compact devices that combine biorecognition and transduction elements in a single device. The biorecognition element is crucial to ensure selective and sensitive detection of the analyte. Various compounds can be used for this purpose, including antibodies. In this case, biosensors work similarly to an ELISA test, but with a different transduction mode. However, the production of natural antibodies in the laboratory remains complicated and expensive, requiring trained personnel and complex facilities/equipment, often involving the use of animals. In addition, antibodies in commercial solutions are difficult to handle because they are unstable to simple variations in temperature, pH, or ionic strength.
In contrast, protein imprinted polymers are synthetic "analogues" of natural antibodies that are capable of selectively binding a particular analyte; they also offer greater stability and lower cost than natural antibodies[1]. There are several ways to prepare protein imprinted polymers, typically using conventional molecular imprinting technologies[2]. Briefly, an imprinted polymer is made by growing a rigid polymeric network (of individual monomers and crosslinkers to precisely tailor a molecular shape in a 3D imprinted site) around a target molecule; the imprinted sites are created when the template exits the polymer matrix and theoretically matches the size and shape of the target. This technology is also compatible with low-cost substrates, such as cellulose[3] or cork[4].
Protein imprinted polymers have been used on several proteins that signal cancer[5], cardiovascular[6] or neurological diseases[7]. In this talk, several examples of these specific applications will be presented, along with their production in biosensing devices that can be used in POC and their intended application in extracellular vesicles, which is an emerging topic.

Acknowledgements: The author thanks the European Commission for funding the project MindGAP (FET-Open/H2020/GA829040).

References:

1. Cardoso A. R.; Frasco M. F.; Serrano V.; Fortunato E.; Sales M. G. F. *Biosensors* **2021**, *11*, 152.
2. Moreira F. T. C; Guerreiro J. R. L.; Brandão L.; Sales M. G. F. Synthesis of molecular biomimetics, Chapter 1 in Biomimetic Technologies, Principles and Applications, Woodhead Publishing, Series in Electronic and Optical Materials, 2015, Pages 3–31.
3. Khan M. A. R.; Vieira C. A.C.; Riu J.; Sales M. G. F. *Talanta*, **2021**, *224*, 121861.
4. Tavares A. P. M.; Sá H. H.; Sales M. G. F. *Journal of Electroanalytical Chemistry,* **2021**, *880*, 114922.
5. Carneiro L. P. T.; Ferreira N. S.; Tavares A. P. M.; Pinto A. M. F. R.; Mendes A.; Sales M. G. F. *Biosensors and Bioelectronics*, **2021**, *175*, 112877.
6. Ribeiro J. A.; Pereira C. M.; Silva A. F.; Sales M. G. F. *Analytica Chimica Acta*, **2017**, *981*, 41.
7. Pereira M. V.; Marques A. C.; Oliveira D.; Martins R.; Moreira F. T. C.; Sales M. G. F; Fortunato E. *ACS Omega*, **2020** 5, 12057.

Chemistry in life sciences

Green molecularly imprinted polymers in API manufacturing

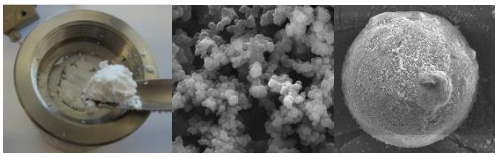
R. Viveiros, T. Casimiro

CleanMIPTech group, LAQV-REQUIMTE, Chemistry department, NOVA School of Science & Technology, NOVA University of Lisbon, Campus de Caparica, 2829-516 Caparica, Portugal

Email: teresa.casimiro@fct.unl.pt

During production of active pharmaceutical ingredients (APIs), reactive intermediates, catalysts, acids or bases are typically used. Due to their chemical structure and reactivity, some are recognized as being genotoxic such as sulfonates, alkylhalides, arylamines, epoxides, Michael-reactive acceptors, etc. These genotoxins can potentially end up at trace levels in final drugs posing in risk the human health. The pharma industry must comply with regulatory authorities EMA and FDA in terms of genotoxic impurity trace levels, thus a significant part of pharmaceutical industry costs are from purification processes. Different methodologies are used such as intensive recrystallization, membranes, chromatography or activated carbon powders, which unfortunately present some drawbacks such as lack of affinity and high cost. In recent years, affinity structures have gained increasing attention for chemical processes. Molecularly imprinted polymers (MIPs) are custom made materials with affinity for a specific target molecule and have high potential to be used as cost-efficient adsorption affinity devices in purification processes.[1,2]

MIPs are produced by combining molecular imprinting and supercritical fluid technologies, overcoming the disadvantages of conventional MIPs. Supercritical CO_2 is an alternative solvent, non-toxic, non-flammable and relatively cheap. Due to its strong solvent power, high diffusivity and low viscosity, provides an excellent medium to produce and process polymers. Polymers are obtained as ready-to-use free-flowing powders, pure, with homogeneous particles with controlled properties, without the need of any further purification, grinding or sieving. The MIP particles produced can be easily supported in membranes, scaffolds and as well as, produced as a layer at the surface of large core-shell beads for gravity-driven purification. In addition, these very robust polymeric affinity materials have been explored in other applications such as drug delivery devices, supercritical fluid chromatography, sensors etc.[3] including another application with high potentiality in API manufacturing, the use of MIPs as cheap plastic catalysts.



High-pressure reactor, MIP particles and large core-shell MIP-layered beads.

Acknowledgements: The authors would like to thank financial support from Fundação para a Ciência e Tecnologia, Ministério da Ciência, Tecnologia e Ensino Superior (FCT/MCTES), Portugal through project PTDC/EQU-EQU/32473/2017 (by national funds through FCT/MCTES, PIDDAC). The Associate Laboratory Research Unit for Green Chemistry - Clean Technologies and Processes - LAQV is financed by national funds from FCT/ MCTES (UIDP/QUI/50006/2020 and UIDB/QUI/50006/2020) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER – 007265).

References:

1. Viveiros R.; Dias F.M.; Maia L.B.; Heggie W.; Casimiro T., *J. Ind. Eng. Chem.*, **2017**, *54*, 341.
2. Viveiros R.; Bonifácio V.D.B.; Heggie W., Casimiro T., *ACS Sustain. Chem. Eng.*, **2019**, *7* 15445.
3. CleanMIPTech Group: https://sites.fct.unl.pt/clean-mip-tech/

Environment and water

Providing solutions for clean water production and recycling of technological critical elements

Lopes C,[a] Pereira E,[b] Trindade T [a]

a) Department of Chemistry and CICECO – Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal; b) LAQV-REQUIMTE - Associated Laboratory for Green Chemistry, University of Aveiro, Aveiro, Portugal

Email: claudia.b.lopes@ua.pt

Water is a vital resource for life, but according with the U. Nations, in 2017, an estimated 3 billion people worldwide lacked the ability to safely wash their hands at home – one of the cheapest, easiest, and most effective ways to prevent the spread of diseases like the coronavirus, and despite progress 2.2 billion of people throughout the world still lack access to safely managed water.
In addition to classical contaminants, technology-critical elements (TCE) which includes the rare-earth and the Pt-group elements, are emerging as inorganic water contaminants of significant concern due to their increasing use, poorly understood biogeochemical behaviour and potential toxicity. However, taking into consideration the supply risk and the relevance in developing new technologies,TCE are also among the elements classified by the European Commission as “Critical Raw Materials”.The development of technologies for TCE recycling from wastewaters and end-of-life products is point out as a crucial solution for decreasing the importation dependence of these elements and to secure their availability in near future.

Increasing attention has been given to carbon nanostructure materials for application in many fields. Carbon is the essential building block in many of the compounds and materials, due to its capability of having several oxidation states and/or coordination numbers. This makes carbon one of the few elements to have multiple numbers of allotropic forms like graphite, graphene, graphene oxide, carbon nanotubes, carbon nanofibers, carbon dots, among others.[1]
Among carbon materials, graphite-like nanoplatelets (GNPs) have attracted great attention in the past decade, as a viable and inexpensive material for many engineering applications. Our own interest in the preparation of magnetic nanomaterials as new adsorbents for water treatment applications led us to explore the preparation of magnetic composites based on graphite nanoplatelets, combining the sorption properties of GNPs with the magnetic properties of spinel-type nanoparticles, there by conferring ability for magnetic separation of the sorbents when exposed to an external magnetic gradient.
These hybrid nanostructures have been successfully applied to improve water quality by uptaking potential toxic elements like mercury and arsenic. Moreover, in line with the high demand of technology critical elements for high-tech applications, these hybrid nanostructures have been also applied in the recovery and recycling of some of these critical elements. One of these examples is a magnetic composite prepared with magnetite nanoparticles and exfoliated graphite, which has the ability to remove lanthanides (La, Eu and Tb) from aqueous solutions at low concentrations.[2]

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials (UIDB/50011/2020 & UIDP/50011/2020), financed by national funds through the FCT/MCTES and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. Cláudia B. Lopes acknowledges the costs resulting from the FCT hirings funded by national funds (OE), through FCT, I.P., in the scope of the framework contract foreseen in the numbers 4, 5, and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19.

References:

1. Cardoso C.E. D.; Almeida J.; Lopes C.B.; Trindade T.; Vale C.; Pereira E. *Nanomaterials.* **2019**, 9(6), 814.
2. Afonso E.; Carvalho L.; Pereira E.; Silva C.M.; Trindade T.; Lopes C.B.. *J. Hazard Materials.* **2019**, *380*, 120845.

Environment and water

Design of efficient water-soluble catalysts for alkane and CO_2 activation

L.M.D.R.S. Martins

Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico Av. Rovisco Pais,1049-001 Lisboa, Portugal

Email: luisammartins@tecnico.ulisboa.pt

Reimagining chemistry for a sustainable world encompasses the search for efficient catalytic processes for the activation of cheap and abundant molecules into high-added-value products.
Alkanes, although being the richest potential source of carbon, are mainly used as non-renewable fossil fuels, leading to environmental issues such as CO_2 formation. Carbon dioxide, in turn, is also a promising nontoxic low-cost carbon source for the development of sustainable chemistry since CO_2-based C1-chemicals can reduce the impacts of global warming and fossil depletion.
Herein, successful catalytic strategies for using inert carbon dioxide or alkanes as carbon feedstock for the syntheses of functionalized added-value organic compounds, namely alcohols (*e.g.*, methanol) or carboxylic acids (*e.g.*, acetic acid) are addressed.[1]
The catalysts are based on water-soluble metal complexes bearing C-scorpionate tris(pyrazol-1-yl)methane ligands (**Figure 1**).

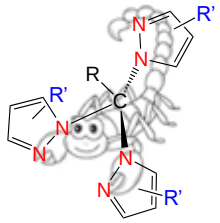


Figure 1: Schematic structure of C-scorpionate tris(pyrazol-1-yl)methanes $RC(R'pz)_3$ (pz = pyrazolyl; R = H or substituent at the methine carbon; R' = H or substituent at the pz ring) and comparison with a scorpion.

Unconventional systems and conditions of sustainable significance, including mechanosynthesis, the use of ionic liquids or supercritical fluids as reaction media and of microwave irradiation (as alternative energy source) are highlighted, and the preferable requirements for a prospective homogeneous or single site heterogeneous catalyst in the transformations of the above substrates are identified.

Acknowledgements: This research was funded by Fundção para a Ciência e a Tecnologia, Portugal, project UIDB/00100/2020 of the Centro de Química Estrutural.

References:

1. Martins, L. M. D. R. S. *Coord. Chem. Rev.*, **2019**, *396*, 89.

Materials chemistry and applications

Functional nanofoams: paving the way for sustainable energy conversion

M.F. Montemor,[a] P. Cid,[a] A. Mas,[a,b], M. Macatrão,[a] G. Carvalho,[a] K. Siwek,[a,b] S.Eugénio,[a,b] T.M.Silva[a,c]

a) Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av Rovisco Pais, 1049-001 Lisboa, Portugal; b) C2CNewCap, Paiã Park, 1675-078 Odivelas, Portugal; c) ISEL-Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, Lisboa, Portugal

Email: mfmontemor@tecnico.ulisboa.pt

Energy storage are central to implement the energetic transition and to support the electrification of the society. Presently, novel energy storage devices must possess tailored metrics, namely specific energy and specific power, while the volume and weight of the final device must fit the application requirements. The design of new nanostructured materials with well-defined properties is a powerful tool for this purpose, offering great surface to volume ratio, a critical parameter for the optimization of the device metrics. In this sense, electrodeposition has attracted immense attention as a method for the preparation of functional energy storage materials due to easy implementation, eco-friendliness, cost-effectiveness, fast synthesis and the ability to prepare novel materials at room temperature and atmospheric pressure. Modification of the deposition conditions can lead to a great variability of compositions and morphologies, allowing to choose those suitable for the desired application. Among them, metallic nanofoams present an extraordinary potential to enable a new generation of electrodes for energy storage materials. These materials present a porous microstructure with increased active surface area (**Figure 1**), a critical parameter for enhancing electrochemical activity of different devices, like supercapacitors. The simplicity of the production route allows variation at microstructural level, controlling the composition, porosity, size and shape of the deposits, along with compositional control, with the possibility of obtaining pure or composite materials in a one-pot synthesis, choosing the best combination for maximize their activity for energy storage[1,2]. Even more, as metallic materials, foams possess a great conductivity that makes them valuable as improved substrates for further deposition of new nanostructures as active metal compounds.
Properties that make metal foams a promising candidate for energy storage are also those required in other energy related applications as hydrogen production[3], CO_2 reduction or electrocatalysis for other water/air pollutants degradation. These structures are an open-door for the development of a new generation of improved materials to solve the actual environmental concerns.

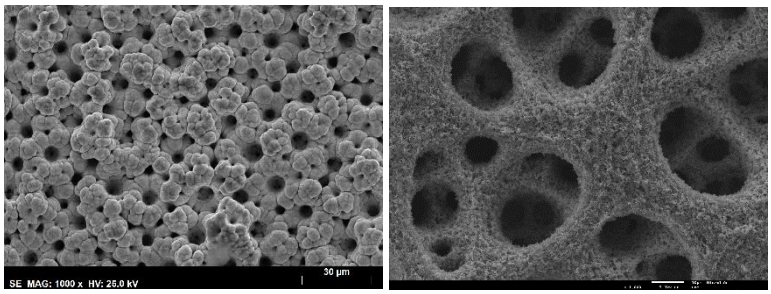


Figure 1: Metallic foams obtained under different conditions.

Acknowledgements: financial support of the projecst from Fundação para a Ciência e Tecnologia PTDC/QUI-ELT/28299/2017, PTDC/QUI-ELT/2075/2020, UIDB/00100/2021 and Baterias 2030, with the reference LISBOA-01-0247-FEDER-046109 co-funded by Operational Programme for Competitiveness and Internationalisation (COMPETE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

References:

1. Lange G.A.; Eugénio S.; Duarte R.G.; Silva T.M.; Carmezim M.J.; Montemor M.F. *J. Electroanal. Chem.* **2015**, *737*, 85-92.
2. Arévalo-Cid, P.; Adán-Más, A.; Silva, T. M.; Rodrigues, J. A.; Maçôas, E.; Vaz, M. F.; Montemor, M. F. *Materials Characterization* **2020**, 169
3. Siwek K.I.; Eugénio S.; Santos D.M.F.; Silva M.T.; Montemor M.F. *Int. J. Hydrogen Energ.* **2019**, *44*, 1701-1709.

Materials chemistry and applications

The use of light to induce a reversible color change

P. Coelho

Centro de Química - Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5000-801 Vila Real, Portugal

Email: pcoelho@utad.pt

The color of some compounds may be changed, reversibly, through the action of an external stimulus such as light. The phenomenon is based on a reversible photoisomerization between two molecules with different absorption spectra (**Scheme 1**). Many types of molecules show this behavior but only a few are really important. [1]

These dyes can be successfully dissolved in polymers providing colorless transparent materials that acquire an intense coloration when exposed to the sunlight (UV) and revert spontaneously to the initial state, in the absence of direct sunlight. The optimization of this process has allowed the industrial development of ophthalmic lenses that dark under sunlight.

The design of new efficient photochromic molecules involves the fulfillment of a series of requirements like an easy (short) synthesis, high sensibility towards the UV light, generation on intense coloration between 15-35 °C, quick fading in the dark, and above all, a high resistance to degradation. [2]

Scheme 1: Photochromic equilibrium

Acknowledgements: We acknowledge the FCT (Fundação para a Ciência e a Tecnologia) and FEDER (program COMPETE) for financial support through the research project PTDC/QUI-QOR/28532/2017.

References:

1. Towns A. Naphthopyran dyes, Phys. Sci. Rev. **2020**, 5, 20190085.
2. Graça V.; Sousa C. M.; Coelho P.J. Dyes Pigments **2021**, 192, 109388

Chemistry in life sciences

(Thio)barbituric acid derivatives: the versatility of synthesis and biological diversity

P. Almeida

CICS-UBI – Health Sciences Research Center University of Beira Interior, Av. Infante D. Henrique, 6200-506 Covilhã, Portugal

Email: paulo.almeida@ubi.pt

The easy ability to modify barbituric and thiobarbituric acids scaffold at N1, C2, N3 and, principally at C5 position, has been responsible for the versatility and for the so diverse biological activities of this pyrimidine heterocyclic scaffold [1 and references cited therein]. An excellent example of this versatility was demonstrated in our previous and ongoing experience with the easy C-5 enolization that allows the enol or enolate nucleophilic attack to electrophilic species, such as carbonyl groups (e.g., benzaldehydes or ketones) to afford different and so rich biological active derivatives like benzylidenes, benzisoxazoles, spiros and dimers as representative examples (Figure 1) [2].

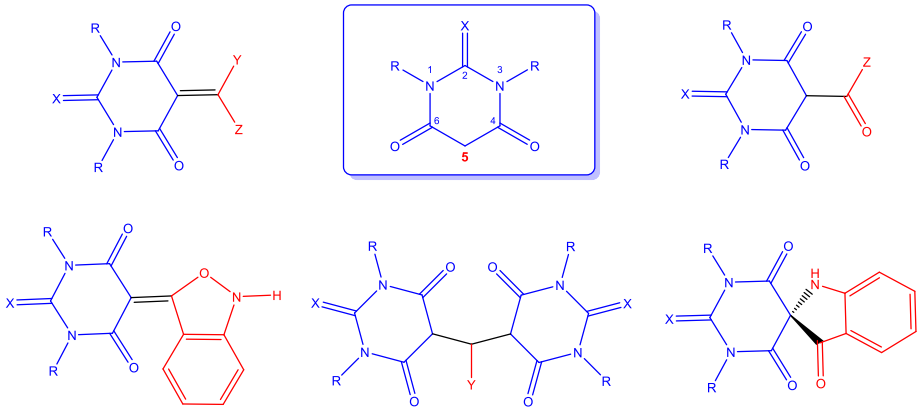


Figure 1: General structure of thio)barbiturates derivatives scaffolds. X is O or S; R is H, alkyl or aryl; Y and Z are, alkyl, aryl or heteroaryl.

Taking in mind this both versatility and biological diversity, this keynote will bring you to the magic world of (thio)barbiturates, other than their classical role as sedative-hypnotic drug, giving an overview of some advances in this domain in our research group, exemplified by illustrative examples.

Acknowledgements: This work is supported by funds from the Health Sciences Research Center (CICS-UBI) (UID/Multi/00709/2019) through National Funds by Fundação para a Ciência e Tecnologia (FCT). FEDER funds also support this work through the POCI-COMPETE 2020-Operational Programme Competitiveness and Internationalization in Axis I–Strengthening research, technological development and innovation (COMPETE 2020), project No. 007491)]. It is also acknowledged founding from C4- Cloud Computing Competences Center project (CENTRO-01-0145-FEDER-000019).

References:

1. Shafiq, N.; Arshad, U.; Zarren, G.; Parveen, S.; Javed, I.; Ashraf, A. *Curr. Org. Chem.* **2020**, *24(2)*, 129.
2. a) Figueiredo, J.; Serrano, J.L.; Cavalheiro, E.; Keurulainen, L.; Yli-Kauhaluoma, J.; Moreira, V.M.; Ferreira, S.; Domingues, F.C.; Silvestre, S.; Almeida, P. *Euro. J. Med. Chem.* **2018**, *143*, 829; b) Figueiredo, J.; Serrano, J.L.; Soares, M.; Ferreira, S.; Domingues, F.C.; Almeida, P.; Silvestre, S. *Euro. J. Med. Chem.* **2019**, *137*, 104964; c) Serrano, J.L.; Cavalheiro, E.; Barroso, S.; Romão, M.J.; Silvestre, S.; Almeida, P. *C. R. Chimie* **2017**, *20(11-12)*, 990; d) Serrano, J.L.; Soeiro, P.F.; Reis, M.A.; Boto, R.E.F.; Silvestre, S.; Almeida, P. *Mol. Divers.* **2020**, *24(1)*, 155; e) Soeiro, P.F.; Serrano, J.L.; Paixão, J.A.; Boto, R.E.F., Silvestre, S., Almeida, P. *Synthesis* **2020**, *52(14)*, 2065.

Chemistry in life sciences

The amazing new world of RNA

Cecília M. Arraiano

Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, 2780-157 Oeiras, Portugal

Email: cecilia@itqb.unl.pt

Biological processes can not be fully understood without a deep understanding of RNA metabolism. In 2006 and 2009 Nobel prizes were dedicated to research in the field of RNA and more recently the power of small RNAs and CRISPr technology has given a new perspective to Molecular Biology and led to another Nobel in 2020. Recently, RNA based vaccines against SARS-CoV2 RNA virus, have been successful in holding the COVID-19 pandemic crisis, and this brought new interest on RNA in the media.
Our laboratory has been focused in the study of RNA degradation mechanisms and the characterization of enzymes and RNA chaperones that mediate RNA decay. Namely we have studied RNase II family of ribonucleases in the maturation, degradation, and quality control of mRNAs and functional non-coding small RNAs, and we have extended our research to eukaryotes to further understand the role of RNases in global regulation and Disease. Our studies have been also applied to areas of Biotechnological interest and Health, and we have been involved in European Projects on Synthetic Biology to reprogram bacteria for biotechnology use. Recently we have characterized the mechanism of action of the two SARS-CoV2 ribonucleases which have shown to be prominent targets for the development of novel antiviral drugs.
The intent of this talk will be to refresh your knowledge on RNA and to encourage you to learn more about the AMAZING NEW WORLD OF RNA!

Culture and education

As mulheres na Engenharia Química: a maioria dentro da minoria

Women in Chemical Engineering: a majority within a minority

Maria da Luz Sampaio

Investigadora integrada do IHC - HTC FCSH da Universidade Nova de Lisboa. Projecto Pos- Doc (FCT) História do Ensino da Engenharia: 1910-1960. Lisboa Portugal

Email: mluzsampaio@gmail.com

The OECD Report (2018) presents a set of data about women in the world of technology and it shows that women are under-represented in ICT jobs, in top management careers or in academic careers. It also points out that on average, at age 15, only 0.5% of girls want to become ICT professionals, compared to 5% of boys, and that start-ups owned by women receive 23% less funding and are 30 % less likely to succeed compared to male-owned businesses. (OECD, 2018).[1]

To the warnings of international organizations we add in the last decades a number of gender studies focused on the social stereotypes that affect women and the difficulties in overcoming them. In recent decades, a wide spectrum of studies has been developed (Ferreira, 2010), (Klanovicz, 2011); (Covas, 2006) analyzing the economic, cultural and social impacts that weigh on women's options, gender asymmetries in different domains (Saavedra, 2014), (Teixeira, Casaca, 2020) and comparative studies in different countries. (Canel, Oldenziel Zachmann, 2005).

In Portugal, the historical analysis carried out about educational policies with a long-term framework, allow us to find trends in social change and the inclusion of new social groups. Thus was a process which we connected with changes in education policies and with technical and higher education program, with the creation of new technical schools in the XIX century and with new school and universities in the XX century that opened the path to a formative offer, in which the female student gained new opportunities in areas hitherto dominated by male elites such as engineering. We highlight that educational reforms launched after the establishment of the Republic in 1911[2] boosted engineering education, with the provision of five different courses: Mining Engineering, Civil Engineering, Electrotechnic Engineering, Mechanical Engineering, Chemical-Industrial Engineering.[3]

From the early days of the teaching of engineering that we found a preference of female students on Chemical Engineering, but it was only in the 1940s that we found the first groups of girls applying for teaching in chemical-industrial engineering. In the 1930s we found in FEUP – Faculty of Engineering of the University of Porto the enrollment of two students in chemical-industrial engineering and at IST – Instituto Superior Técnico in Lisbon, we found 11 students registered. In 1947, at FEUP six female students entered to Chemical Engineering for the first time and at IST (Lisbon) we found in same year four female students enrolled. [4] At FEUP, the number of female students enrolled tends to grow and in the academic year of 1962/63 and the data reveals 39 female students and 127 male students enrolled in the Faculty of Sciences for the three preparatory years.[5] This is followed by three years of specialization at the Faculty of Engineering, and in the same year we found one female student and 3 students graduated in Chemical Engineering. For these graduate students, the laboratory will be their central place, reserved and magical, where they do the analysis on raw materials, where they prepared solutions and refined processes that would be applied on an industrial scale.

In this period, we establish a relation between the success of chemical engineering is associated with the industrialization phase that Portugal experienced after the second world war. The country benefited from the signing of the OECD constitution pact (1948), and by the cooperation structures provided by the Marshall Plan. This opening was accompanied by the launch of the Development Plans (1953 to 1973) aimed at “accelerating the rate of growth of the national product, improving the standard of living of the Portuguese, guaranteeing employment and improving the balance of payments”.[6] In this context, the development of the chemical sector shows great dynamism. In the south, in the city of Barreiro, CUF – Companhia União Fabril – the most important national chemistry industrial project lives a phase of expansion and are launched new projects associated with the production of sulfuric acid, based on the introduction of a new technology: the contact process.[7] In Alfarrarede (Abrantes) in 1952, CUF installed the production of ammonia via electrolytic hydrogen with União Fabril de Azoto. In the north, we highlight a phase of industrial investments with the creation in 1944 of the Companhia Portuguesa do Cobre in the city of Porto, the installation of the unit of the EFA-ACEC in 1948 in Arroteia - Maia[8] dedicated to the production of electrical equipment production unit and the constitution of the CIFA – Companhia Industrial de Fibras Artificiais (Valongo) in 1949 dedicated to the production of viscose fabrics. At FEUP, the academic works carried out in the subject of Chemical Industries show the involvement of students in the study on Styrene, Wolframic Acid, the manufacture of Butyl Acetate, the production of

phosphoric acid, polyvinyl acetate from butyl acetate vinyl or even the production of alkyd resins,[9] among others, thus establishing an interaction between engineering education and the needs of the chemical sector.

The analysis of women's entry into Chemical Engineering requires a reflection on the social contexts that affected women in their training and professional paths. As an open field of analysis, this study demonstrates that, once graduated, these female students sought a place in the labor market compatible with their degree of specialization, however, they did not always manage to pursue a career in technology and business projects. In this study, we followed the careers of chemical engineering female students and we found that some became teachers in secondary or engineering schools, others in a smaller number, made their careers in company laboratories or joined the staff of their family companies. The social background of these students was a determining factor in their choices, by following the models transmitted by their families and their education achievements were possible due to receiving support from their families to continue their studies. We found that most of the students were daughters of army officers, engineers, writers, businessmen, most of them were from bourgeois families with progressive ideas and business and political connections.

In conclusion, and based on the registered data, we can say that Chemical Engineering was the women's option par excellence for specialized and higher education and is still one of the most chosen courses together with biological engineering or environmental engineering.[10] These students, when choosing chemical engineering, sought not only a place in the labor market but also to overcome the existing social barriers, challenging the generalized gender stereotypes in the technological sectors.

Acknowledgements: We are grateful for the support of the archives of IST - Instituto Superior Técnico (Lisbon) and FEUP - Faculty of Engineering of the University of Porto and also the FCT - FCT postdoctoral scholarship - SFRH/BPD/117829/2016 - dedicated to the project: History of Engineering Education: 1910-1960.

References:

1. OECD, Bridging the Digital Gender Divide, Include, Upskill, Innovate. OECD, 2018.
2. Decreto-Lei de 22 de março de 1911, que culminou na criação do IST Instituto Superior Técnico - (Instituto Técnico) em Lisboa, e a Universidade do Porto que oferecia cursos de ensino superior em engenharia. Ver: Matos, A. C. and M. L. Sampaio. The Portuguese Schools of Engineers and the Creation of National and International Networks of Experts." *Web of Knowledge: A Look into the Past, Embracing the Future*, edited by Sara Albuquerque, Teresa Ferreira, M. Fátima Nunes, Ana Cardoso de Matos, and António Candeias, 65–70. Faro: Sílabas & Desafios, 2019. http://dspace.uevora.pt/rdpc/bitstream/10174/25355/1/Proceedings%20WoK_v1.pdf
3. Decree-Law of March 22, 1911, which culminated in the creation of the IST Instituto Superior T cnico - (Technical Institute) in Lisbon, and the University of Porto that offered higher education courses in engineering. See: Matos, A. C. and M. L. Sampaio. 2019. http://dspace.uevora.pt/rdpc/bitstream/10174/25355/1/Proceedings%20WoK_v1.pdf
4. Lisboa. IST - Instituto Superior Técnico. Arquivo IST. Processos de discentes do IST.
5. U.P. Anuário da Universidade do Porto. Universidade do Porto. Porto 1946 – 1963.
6. Caeiro, J. M. C. "Os planos de fomento nacional no contexto do desenvolvimento económico nacional no pós guerra", Intervenção Social 31 (2005): 193–219.
7. Cruz, Isabel, A CUF e a indústria Química-uma narrativa e uma interpretação sobre capacidade endógena de realização, in Álvaro Ferreira da Silva (Coord.), O Arquivo Histórico CUF- Alfredo ad Silva : Um passado com Futuro, 2021:85-105.
8. Sampaio, M.L., Da Fábrica ao Museu: Identificação, Patrimonialização e Difusão da Cultura Técnico-Industrial, DGPC/ Caleidoscópio, 2017, 277.
9. FEUP. SDI. Arquivo FEUP. Trabalhos Académicos. Química Industrial. 1947 – 1969.
10. Portugal, "Dados e Estatísticas dos Cursos Superiores, 2020," accessed 10 April 2021, https://infocursos.mec.pt/dges.asp?code=1105&codc=9540&pg=1#.YIGoHehKg2w.

Additional Reading

- Bystydzienski, J. and S. Bird, eds. Removing Barriers, Women in Academic Science, Technology, Engineering, and Mathematics. Bloomington: Indiana University Press, 2006.
- Cannel, Annie, Ruth Oldenziel, and Karin Zachmann, eds. Crossing Boundaries, Building Bridges. Comparing the History of Women Engineers, 1870s - 1990s. Amsterdam: Taylor and Francis, 2005.
- Cova, Anne, Comparative Women's History: New Approaches, Columbia University Press, 2006.
- Klanovicz, L.. História, Gênero e Ciência: Mulheres Engenheiras no Sul do Brasil, Revista Venezolana de Estudios de la Mujer - Julio – Diciembre 2011. Vol. 16/N°37: 105-122.
- Matos, A. C. and M. L. Sampaio. The Portuguese Schools of Engineers and the Creation of National and International Networks of Experts. Web of Knowledge: A Look into the Past, Embracing the Future, edited by S. Albuquerque, T. Ferreira, M. de F tima Nunes, A. C. de Matos, and A. Candeias. Faro: S labas & Desafios, 2019. 65–70. http://dspace.uevora.pt/rdpc/bitstream/10174/25355/1/Proceedings%20WoK_v1.pdf.
- Saavedra, L., A. Araújo, and J. Oliveira. *Looking through glass walls: Women engineers in Portugal*. Women's Studies International Forum 45, 2014: 27–33.
- Teixeira, C. and Falcão S.. Assimetrias de género na(s) engenharia(s) em Portugal: Dinâmicas e Desafios. Faces de Eva: Estudos sobre a Mulher 43 2020: 61–82.

Culture and education

A poligamia intelectual dos químicos

Manuel J. S. Monte

Centro de Investigação em Química da Universidade do Porto (CIQUP). Faculdade de Ciências da Universidade do Porto (DQB-FCUP)

Email: mjmonte@fc.up.pt

Carl Djerassi (1923-2015) é mundialmente conhecido como o pai da pílula contraconceptiva, que teve um impacto muito significativo na libertação da mulher. Numa entrevista, em maio de 2010, Carl revelou que se considerava um "**polígamo intelectual**". Através deste epíteto, enfatiza, com o seu habitual sentido de humor, a entrega a fortes paixões que se estendem da Química às artes, com relevância para a dramaturgia. Haverá vários Químicos merecedores deste título, mas selecionei apenas mais três para esta comunicação. Um deles, **Roald Hoffmann**, está ligado a **Carl Djerassi** como co-autor do livro *Oxigénio*[1] levado a cena em diversos países, incluindo Portugal em 2006.

A ânsia de saber do russo **Mikhail Lomonosov** (1711-1765) levou-o da Universidade de São Petersburgo às iluminadas universidades alemãs de Marburgo e Friburgo, para aprofundar conhecimentos de química. A sua formação foi também complementada pelo estudo de várias outras disciplinas (física, geologia, filosofia, línguas e literaturas clássica e contemporânea). De regresso a uma Rússia arcaica, trouxe consigo a frescura do saber acumulado nos cinco anos de estudos na Alemanha, despoletando revoluções culturais nas ciências e na literatura russas. Construiu uma nova gramática e são-lhe atribuídas duas paternidades: a da Poesia e a da Ciência russas. As suas experiências levaram-no a formular a lei de conservação da massa (e da energia) e a refutar a Teoria do Flogisto, marcos da química moderna geralmente creditados a Antoine Lavoisier. O seu trabalho foi publicado em 1750 no artigo intitulado *Meditationes de caloris et frigoris causa*,[2] que terá chegado, muito provavelmente, ao conhecimento de Lavoisier.

Na contracapa do livro *The Same and Not the Same*,[3] pode ler-se: "Posicionada na encruzilhada entre as ciências físicas e biológicas, a Química trata não do infinitamente pequeno, nem do infinitamente grande, nem diretamente da vida. Por isso, é por vezes considerada pouco interessante, como acontece frequentemente às coisas que ficam no meio. Mas é precisamente neste terreno intermédio que existem os seres humanos e o Laureado com o Nobel [em 1981] **Roald Hoffmann** mostra [neste livro] que o mundo ao nível molecular é complexo e agitado, como as emoções do supostamente desapaixonado cientista que o explora". Esta centralidade da Química promove, naturalmente, encontros íntimos com outras ciências e com a filosofia e as artes. Autor de seis livros de poesia, Roald termina um dos seus poemas com os seguintes três versos: "Os homens (e as mulheres) não são / tão diferentes das moléculas / como julgam". Curiosamente, é um dos raros cientistas ocidentais que recebeu a medalha de ouro **Lomonosov** atribuída pela Academia das Ciências da Rússia.

Jorge Calado dispensa apresentação neste curto resumo. Os seus interesses sobre a ligação entre Arte e Ciência foram compartilhados durante longos períodos de convivência com **Roald Hoffmann** na Universidade de Cornell. Para quem saboreou a obra de arte, em formato de livro, *Haja Luz*!,[4] a justificação para a pertença ao clube dos polígamos intelectuais é óbvia.

Referências:

1. Carl Djerassi & Roald Hoffmann, *Oxigénio*, Editora UP (U.Porto Press), Porto (2005).
2. Mikhail Lomonosov, *Novi Commentarii Academiae Scientiarum Imperialis Petropolitanae*, 1, 230-244. (1747-1478), Russia (Publicado em 1750). Citado por Henry M. Leicester, *Chymia*, 5, 138-144 (1959).
3. Roald Hoffmann, *The Same and Not the Same*, Columbia University Press, New York, (1995).
4. Jorge Calado, *Haja Luz! – Uma História da Química Através de Tudo*, IST Press, Lisboa (2012).

Invited Oral Communications

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

Materials chemistry and applications

Blue biorefinery: overviewing the processes, the materials and the applications

Sónia P.M. Ventura

Aveiro Institute of Materials – CICECO, Chemistry Department, University of Aveiro, Campus Universitário de Santiago, 3810-193, Aveiro, Portugal

Email: spventura@ua.pt

Macroalgae and cyanobacteria are recognized as rich raw materials since they are composed of a large range of bioactive compounds. Included in the range of commercially interesting bioactive compounds are the pigments, which can be divided in three main categories, phycobiliproteins, chlorophylls and carotenoids/xanthophyll.[1] Over the years, all of which have been applied in different industries, including cosmetics, human food, and energy.
Macroalgae production requires simple conditions to produce large amounts of biomass, allowing for high yields of biomass production and pigments. Despite the high economical value of some of the ingredients accumulated in macroalgae cells, its commercialization has still not reached its maximum, due to the high costs of the downstream processes being applied up to date.[2] These are normally related with the processes' complexity, using large amounts of organic solvents or those using more sophisticated equipment and specialized human resources, compromising the compounds' sustainable and profitable commercialization. A critical overview focusing the pigments will be present, from the downstream processes to the applications being investigated, which include the use of these pigments in human food, biomedical materials, and energy devices.[3]

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES. his work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the Portuguese Foundation for Science and Technology/MCTES. S.P.M. Ventura acknowledges FCT for the contract IF/00402/2015. The authors acknowledge the financial support from project REFINECYANO - Valorização de pigmentos de cianobactérias pela aplicação do conceito de biorefinaria (PTDC/BTA-BTA/30914/2017) funded by FCT.

References:

1. Macário, I.P.E.; Ventura, S.P.M.; Gonçalves, F.J.M., Torres-Acosta, M.A.; Pereira, J.L. *ACS Sustainable Chem. Eng.* **2021**, DOI: 10.1021/acssuschemeng.1c00458
2. Martins, M; Ventura, S.P.M.; Sustainable Seaweed Technologies, **2020**, 287-311.
3. Frias, A.R.; Correia, S.F.H.; Martins, M.; Ventura, S.P.M.; Pecoraro, E.; Ribeiro, S.J.L.; André, P.S.; Ferreira, R.A.S.; Coutinho, J.A.P.; Carlos, L.D. *Advanced Sustainable Systems,* **2019**,3,1800134

Materials chemistry and applications

Structure, properties and applications of 8-hydroxyquinoline-5-sulfonate based materials

L.L.G. Justino, M.L. Ramos, S.M. Fonseca, T. Costa, R. Fausto, H.D. Burrows

CQC-IMS, Department of Chemistry, University of Coimbra, Rua Larga 3004-535, Coimbra, Portugal

Email: liciniaj@ci.uc.pt

The discovery by Tang and VanSlyke at Kodak in 1987 that tris(8-hydroxyquinoline) aluminium(III) (Alq3) could be used to build organic light emitting devices with high electroluminescent emission efficiency, fast response, low voltage drive, and simplicity of fabrication[1] has led to the use of this material in commercial organic light emitting diodes (OLEDs). Alq3 is a cost-efficient green light-emitting material and an excellent electron transport layer, which also finds applications as a component of solar cells. This has led to an increased interest in the research of Alq3 and related metal ion complexes to optimize their applications in optoelectronic devices and to investigate device degradation mechanisms in order to increase their lifetime.

Free 8-hydroxyquinoline (8-HQ) is a very weak fluorophore, due probably to ultrafast excited state intramolecular proton transfer leading to a nonfluorescent phototautomer.[2,3] In contrast, since this deactivation pathway is normally inhibited upon complexation, many of its coordination complexes show a strong enhancement of fluorescence intensity. This provides the basis for applications in devices such as OLEDs and sensors. In particular, turn-on sensors based on an increase of fluorescence have the potential for applications in imaging.

In recent years we have been interested in studying the interaction between a water soluble derivative of 8-HQ, 8-hydroxy-5-sulfoquinoline (8-HQS), and its potential for applications. This ligand has shown excellent chelating and interesting fluorescence properties with a variety of metals[4] and is a promising candidate for applications in OLEDs, sensing, and surface water remediation as a sorbent of toxic metals.

In the context of these applications, it is of major importance to characterize the structures and properties of the complex species formed between the metals and 8-HQS. Here we present a brief summary of some of our findings related with the characterization of some of the metal:8-HQS systems that we have studied in recent years. Results from spectroscopic, photophysical and computational studies, will be discussed.

Acknowledgements: The authors are grateful for funding from the Coimbra Chemistry Centre, which is supported by the Fundação para a Ciência e a Tecnologia (FCT), the Portuguese Agency for Science and Technology, through the projects CQC UIDB/00313/2020 and UIDP/00313/2020, and COMPETE Programme (Operational Programme for Competitiveness). The authors also thank the Laboratory for Advanced Computing at University of Coimbra for providing computing resources that have contributed to the research results reported (URL: https://www.uc.pt/lca) and the Rede Nacional de RMN (REDE/1517/RMN/2005), the Portuguese NMR Network, for providing access to the NMR spectroscopy facilities.

References:

1. Tang, C. W.; VanSlyke S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.
2. Bardez, E.; Devol, I.; Larrey, B; Valeur, B. *J. Phys. Chem. B* **1997**, *101*, 7786.
3. Park, S.-Y.; Gosh, P., Park, S. O.; Lee, Y. M.; Kwak, S. K.; Kwon, O.-H. *RSC Adv.* **2016**, *6*, 9812.
4. For example, a) Ramos, M. L.; Justino, L. L. G.; Barata, R.; Costa T.; Nogueira, B. A.; Fausto, R.; Burrows, H. D. *Dalton Trans.* **2017**, *46*, 9358. b) Ramos, M. L.; Justino, L. L. G.; Salvador, A. I. N.; Sousa, A. R. E.; Abreu, P. E.; Fonseca, S. M.; Burrows, H. D. *Dalton Trans.* **2012**, *41*, 12478.

Materials chemistry and applications

Electrically conductive metal-organic frameworks based on electroactive organic building blocks

G. Valente,[a] A. Paracana,[b] J. Rocha,[a] A. Rodríguez-Diéguez,[c] H. Alves,[b] M. Souto[a]

a) Department of Chemistry, CICECO-Aveiro Institute of Materials, University of Aveiro, Aveiro 3810-393, Portugal; b) Department of Physics, CICECO-Aveiro Institute of Materials, University of Aveiro, Aveiro 3810-393, Portugal; c) Departamento de Química Inorgánica, Universidad de Granada, 18071, Granada, Spain

Email: manuel.souto@ua.pt

Metal-Organic Frameworks (MOFs) have emerged in the past two decades as promising crystalline porous materials for gas storage and separation, catalysis, sensing, and many other applications.[1] Besides their inherent porosity, MOFs may also incorporate tunable electronic properties (electrical, optical or magnetic) which strongly depend on the selected building blocks, becoming very attractive for their implementation as integral components in electronic devices. [2] Although most MOFs are electrical insulators, in the last few years some examples of conductive MOFs exhibiting high charge mobility have been reported based on the incorporation of electroactive organic ligands.[3] In particular, electroactive organic ligands have received much interest due to their tunable electronic properties by molecular design, easy functionalization and possibility to modulate the MOFs electrical conductivity by chemical doping (Figure 1a).[3] In the first part of the presentation, I will show a family of electroactive tetrathiafulvalene (TTF)-based MOFs exhibiting structure-dependent redox-activity and electrical conductivity.[4] In the second part of the talk, I will present a detailed study on the electrical properties of a perylene-based MOF showing enhanced electrical conductivity upon iodine doping (Figure 1b),[5] paving the way for the implementation of such electroactive MOFs in electronic devices.

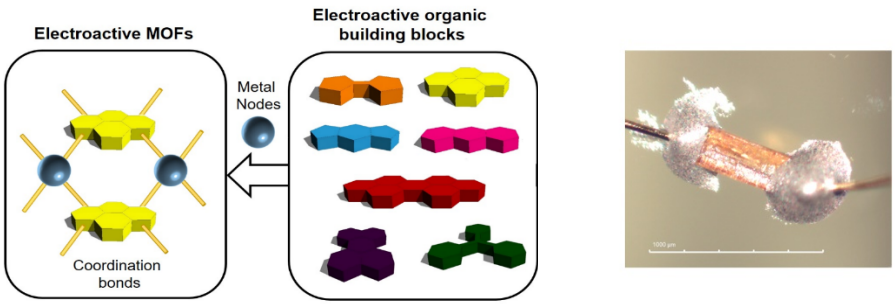


Figure 1: a) Schematic representation of the construction of MOFs based on electroactive organic building blocks. b) Two-contact probe device made from a single crystal of perylene-based MOF.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 and UIDP/50011/2020

References:

1. M. Dincă, J. Long, *Chem. Rev.* **2020**, *120* 8037.
2. M. D. Allendorf, R. Dong, X. Feng, S. Kaskel, D. Matoga, V. Stavila, Chem. Rev. **2020**, *120* 8581.
3. M. Souto, K. Strutynski, M. Melle-Franco and J. Rocha, *Chem. Eur. J.* **2020**, *26*, 10912.
4. a) M. Souto *et al. Chem. Sci.* **2018**, *9*, 2413. b) M. Souto *et al. J. Am. Chem. Soc.* **2018**, *140*, 10562. c) J. Castells-Gil *et al. Chem. Eur. J.* **2019**, *25*, 12636.
5. G. Valente *et al. unpublished results*.

Chemistry in life sciences

Hypervalent iodine(III) mediated carbon-nitrogen and nitrogen-sulfur bond formation: innovating access to bioactive compounds

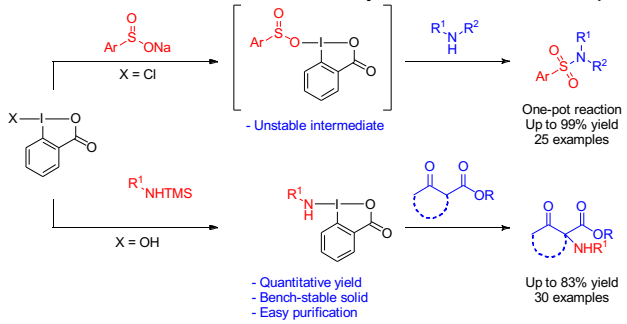
D. L. Poeira,[a] J. Macara,[a] A. C. R. Negrão,[a] H. Faustino,[b] J. Coelho,[b] Pedro Góis,[b] M. Manuel B. Marques[a]

a) LAQV@REQUIMTE, Chemistry Department, NOVA School of Science & Technology, Universidade Nova de Lisboa Campus de Caparica, 2829-516 Caparica, Portugal; b) Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003, Lisboa, Portugal

Email: mmbmarques@fct.unl.pt

Hypervalent Iodine reagents consist of compounds containing iodine in a higher oxidation state, generally iodine(III) or iodine(V). While iodine(V) compounds are typically oxidation reagents, iodine(III) compounds exhibit reactivity and chemical properties closer to those of transition metal complexes, acting as electrophilic synthons of normally nucleophilic groups – umpolung reactions.[1] Benziodoxoles and benziodoxolones are cyclic compounds containing an iodine(III) core, which have attracted much interest in the scientific community due to their increased stability when compared to the acyclic analogues.[2]

Our group has been investigating new benziodoxolone-derived reagents. We have disclosed new transfer reactions for the sulfonylation of amines and oxidative amination of α-ketones. These methods take advantage of the umpolung reactivity and group-transfer properties of iodine(III) compounds. We have combined hypervalent iodine chemistry with sulfinate salts to deliver a clean and mild transfer of sulfonyl groups to amines and anilines. Furthermore, hypervalent iodine reagents have been prepared and applied as transfer reagents of primary amines to deliver an oxidative amination reaction. (**Scheme 1**).[3] These methodologies were applied in the preparation of key functional groups in medicinal chemistry, such as sulfonamides and α-amino carboxylic acids, and will be presented herein.



Scheme 1: Benziodoxolone-mediated C-N and N-S bond formation.

Acknowledgements: We thank the FC&T for the fellowship SFRH/BD/116322/2016. This work was supported by the Associate Laboratory for Green Chemistry- LAQV which is financed by national funds from FCT/MCTES (UID/QUI/50006/2019) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER - 007265). The National NMR Facility is supported by FC&T (ROTEIRO/0031/2013 – PINFRA/22161/2016, co-financed by FEDER through COMPETE 2020, POCI, and PORL and FC&T through PIDDAC).

References:

1. a) Yusubov M. S.; Zhdankin V. V. *Curr. Org. Synth.* **2012**, *9*, 247.
2. Li Y. F.; Hari D. P.; Vita M. V.; Waser, J. *Angew. Chem.-Int. Ed.,* **2016**, *55*, 4436.
3. a) Poeira D. L.; Macara J.; Faustino H.; Coelho J. A. S.; Gois P. M. P.; Marques M. M. B. *Eur. J. Org. Chem.,* **2019**, *15*, 2695. b) Poeira D. L.; Negrão A. C.; Faustino H.; Coelho J. A. S.; Gomes C.; Gois P. M. P.; Marques M. M. B. *submitted* **2021**.

Chemistry in life sciences

Playing with chemical diversity to protect marine biodiversity

J.R. Almeida,[a] A.R. Neves,[a,b] D. Pereira,[a,b] C. Vilas Boas,[a,b] D. Resende,[a,b] V. Vasconcelos,[a] M. Pinto,[a,b] E. Silva,[c] E. Sousa,[a,b] H. Cidade,[a,b] M. Correia-da-Silva[a,b]

a) Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR), Universidade do Porto, Terminal de Cruzeiros do Porto de Leixões, Av. General Norton de Matos s/n 4450-208 Matosinhos, Portugal b) Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira nº 228, 4050-313, Porto, Portugal c) BioISI—Instituto de Biosistemas e Ciências Integrativas, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

Email: m_correiadasilva@ff.up.pt

Biofouling on ship hulls cause trans-global contamination of ecosystems with non-indigenous species, leading to marine biodiversity reduction. On the other hand, the antifouling paints in use are continuing leaching persistent, bioaccumulative and toxic substances into the oceans. Imposex in female gastropods, oysters malformations, *Nucella lapillus* extinction, and toxic impacts on juvenile salmon are some of the reported effects of biocide-based coatings. Due to the massive increase of ocean-related activities, marine environment biodiversity is at high risk.[1] The European Commission has been pushing member states to work harder on finding alternatives to biocide-based coatings, investing in harmless systems.

In the last years, we have been focusing on finding new eco-friendly and sustainable alternatives.[2] Nearly 200 chemical diverse compounds obtained by synthesis were screened against the adhesive larvae of the shell fouling organism *Mytillus galloprovincialis*, listed by the IUCN/SSC Invasive Species Specialist Group among the 100 "World's Worst" invaders.[2] Six xanthones, four flavonoids, four bile acids, and two gallates emerged with the necessary balance between the ability to discourage the attachment of mussels larvae and the low toxicity to fouler species (US Navy recommendations: EC_{50} values < 25 µg/mL and LC_{50}/EC_{50} > 15) and to nontarget organisms (< 10 % lethality to *Artemia salina* at 25 µM in contrast to the Econea biocide that caused 100 % lethality at the same concentration). Three xanthones, one bile acid, and two gallates also exhibited low potential to bioaccumulate (predicted octanol/water partition coefficient, LogKow, < 3) and were selected for incorporation and/or immobilization in coatings. Coatings-containing the selected compounds were highly effective against the adhesive larvae of the *M. galloprovincialis*[3] highlighting the potential of these new agents to replace biocide-based marine coatings.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia (FCT) for financial support through the strategic funding UIDB/04423/2020 and UIDP/04423/2020 (CIIMAR) and the project PTDC/AAG-TEC/0739/2014 (reference POCI-01-0145-FEDER-016793) supported through national funds provided by FCT and ERDF through the COMPETE - POFC programme and the RIDTI Project -9471 (2015-2017). This work is now being funded by the structured program of R&D&I ATLANTIDA - Platform for the monitoring of the North Atlantic Ocean and tools for the sustainable exploitation of the marine resources (reference NORTE-01-0145-FEDER-000040), supported by the North Portugal Regional Operational Programme (NORTE2020), through the European Regional Development Fund (ERDF). Neves AR, Pereira D, and Vilas-Boas C acknowledge FCT for the PhD grants SFRH/BD/114856/2016, SFRH/BD/147207/2019, and SFRH/BD/136147/2018, respectively.

References:

1. Price A. R. G.; Readman J. W.; Gee D. *European Environment Agency* **2013**, 265-278.
2. a) Almeida J. R.; Correia-da-Silva M.; Sousa E.; Antunes J.; Pinto M.; Vasconcelos V.; Cunha I. *Scientific Reports* **2017,** *7*, 42424. b) Neves A. R.; Almeida J. R.; Carvalhal F.; Camara A.; Pereira S.; Antunes J.; Vasconcelos V.; Pinto M.; Silva E. R.; Sousa E.; Correia-da-Silva M. *Ecotoxicol. Environ. Saf.* **2020,** *187*, 109812. c) Almeida J. R.; Palmeira A.; Campos A.; Cunha I.; Freitas M.; Felpeto A. B.; Turkina M. V.; Vasconcelos V.; Pinto M.; Correia-da-Silva M.; Sousa E., *Biomolecules* **2020,** *10* (8), 1126. d) Pereira D.; Gonçalves C.; Martins B.T.; Palmeira A.; Vasconcelos V.; Pinto M.; Almeida J.R.; Correia-da-Silva M.; Cidade H. *Mar. Drugs* **2021**, *19*, 5.
3. Vilas-Boas, C.; Carvalhal, F.; Pereira, B.; Carvalho, S.; Sousa, E.; Pinto, M. M. M.; Calhorda, M. J.; Vasconcelos, V.; Almeida, J. R.; Silva, E. R.; Correia-da-Silva, M. *Marine Drugs* **2020,** *18* (10), 489.

Chemistry in life sciences

Developing data science tools for bioorthogonal chemistry

J.A.S. Coelho,[a] J.M.J.M. Ravasco[b]

a) CQE, Faculdade de Ciências da Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal; b) iMed.ULisboa, Faculdade de Farmácia da Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal

Email: jaimeacoelho@edu.ulisboa.pt

Bioorthogonal reactions are widely used for probing and controlling biological functions through labelling, tracking and imaging of relevant biomolecules. Advances in the bioorthogonal toolbox have rendered these reactions more effective, selective and widespread, enabling the construction of innovative theragnostic and delivery systems for in vivo applications.[1]
Density functional theory (DFT) calculations have been performed to understand reaction kinetics by transition state searches and analysis of the free energy profiles of bioorthogonal cycloadditions.[2] Herein we show a complementary approach based on modern data analysis[3] by parametrizing the cycloaddition reagents and solvents (**Figure 1**).[4] In this approach we use chemically comprehensible, easy to calculate descriptors and the developed models are statistically robust and have good predictive skills.

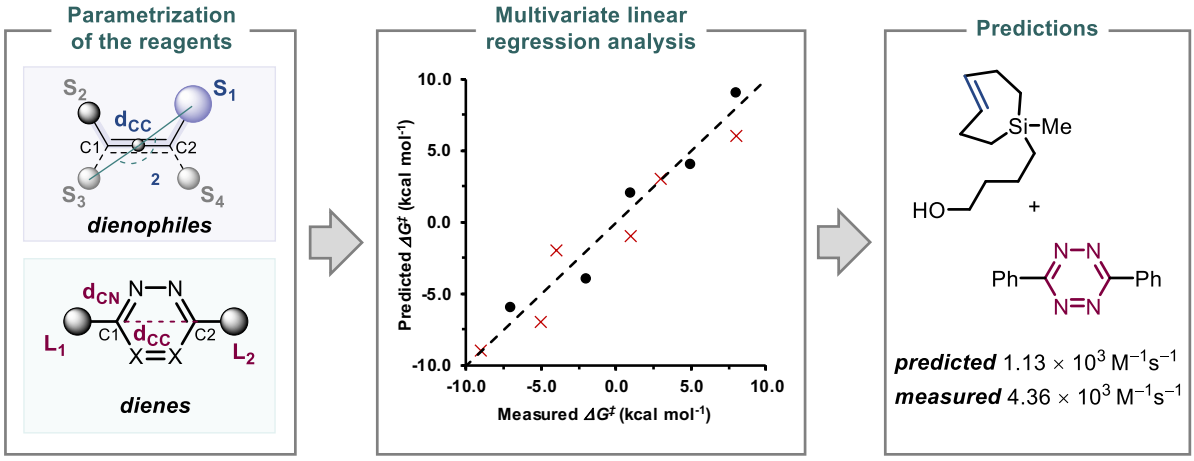


Figure 1: Workflow for Modeling Bioorthogonal Inverse-Electron Demand Diels–Alder Reactions.

Acknowledgements: We thank the Fundação para a Ciência e a Tecnologia for financial support (PTDC/QEQ-QOR/3644/2014, SFRH/BD/120829/2016, UID/DTP/04138/2019 and CEECIND/02383/2020).

References:

1. Devaraj, N. K., *ACS Cent. Sci.* **2018**, *4*, 952.
2. Liu, F., Liang, Y., Houk, K. N., *Acc. Chem. Res.* **2017**, 50, 2297.
3. Sigman, M. S., Harper, K. C., Bess, E. N., Milo, A., *Acc. Chem. Res.* **2016**, 49, 1292.
4. Ravasco, J. M. J. M., Coelho, J. A. S., *J. Am. Chem. Soc.* **2020**, 142, 4235.

Food and natural products

Encapsulation strategies for effective natural food ingredients

M.F. Barreiro

CIMO, Centro de Investigação de Montanha, Instituto Politécnico de Bragança, Campus Santa Apolónia, 5300-253 Bragança, Portugal.

Email: barreiro@ipb.pt

Natural-based ingredients are needed for different industrial fields, as they can help to overcome problems associated with the use of synthetic counterparts, including factors related to human health, and decrease petroleum dependency. Nevertheless, the successful application of this renewed generation of natural ingredients depends on the development of appropriate technologies to achieve products with the required technical specifications. Among them, encapsulation processes are being increasingly applied, contributing to attain product differentiation and enhance commercial value. Developing a microencapsulation process can present several constrains and challenges, as the raw materials and processes must be properly selected to avoid toxicity, conform applied legislation, and provide adequate performance to the produced systems. Furthermore, choosing technologies and processes able to reach high TRLs and perform end-use tests is of high relevance. In this context, this work aims to present an overview of micro/nanoencapsulation techniques with potential to be applied in the food sector by showing a set of practical case studies developed at CIMO and directed at solving constraints related with the direct use of natural ingredients (loss of bioactivity, solubility problem, mask odour and taste, solve problems of incompatibility, etc.), or intended to achieve target or controlled release. Examples will include applications in the fields of natural colorants, preservatives, and bioactives, and will focus the use of natural matrices and sustainable/green processes.

Acknowledgements: The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) and FEDER under Program PT2020 for the financial support to CIMO (UIDB/00690/2020).

Food and natural products

Secondary metabolites in edible species: looking beyond nutritional value

A.M.L. Seca,[a,b,c] M. Viveiros,[a] M.C. Barreto,[b]

a) Faculty of Sciences and Technology, University of Azores, Rua Mãe de Deus, 9500-321 Ponta Delgada, Portugal; b) cE3c—Centre for Ecology, Evolution and Environmental Changes/Azorean Biodiversity Group, University of Azores, Rua Mãe de Deus, 9500-321 Ponta Delgada, Portugal; c) LAQV-REQUIMTE, University of Aveiro, 3810-193 Aveiro, Portugal

Email: ana.ml.seca@uac.pt

Secondary metabolites are organic molecules of low molecular weight, biosynthesized by any living being using a wide range of biosynthetic pathways, known as secondary metabolism. It aims to produce molecules with specific functions that promote the adaptability and survival of the species. However, secondary metabolites are not molecules essential to life, as are the lipids, carbohydrates and amino acids involved in basic life functions.[1]
Scientific research dedicated to the isolation and identification of secondary metabolites and the evaluation of their potential in different applications has already shown that these small molecules can be used in the promotion of human well-being, such as on the preservation and improvement of the organoleptic quality of the food, their medicinal and cosmetic effects, and as environmentally friendly herbicidal and pesticide agents.[2]
Additionally, the research in this field is by no means complete. There are still many species, edible or not, whose profile in secondary metabolites is unknown and many other whose potential benefits to humanity have not yet been explored; and those in which some applications are already known, but the most relevant probably remains to be determined.
Thus, it remains pertinent to deepen the investigation on the isolation and identification of bioactive secondary metabolites, contributing so that the secondary metabolites present in a species are seen as an asset of that species, expanding the field of applications of the secondary metabolites and the species themselves, valuing them.
Secondary metabolites, isolated from edible genera, with potential application in the food, medicinal and cosmetic industries (Figure 1) will be presented and discussed.

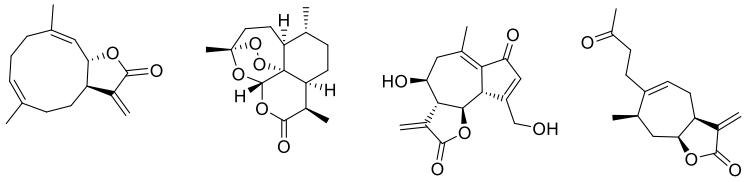


Figure 1: The chemical structure of some secondary metabolites with added-value.

Acknowledgements: This work was funded by FCT–Fundação para a Ciência e a Tecnologia, the European Union, QREN, FEDER, COMPETE, by funding the cE3c centre (UIDB/00329/2020) and the LAQV-REQUIMTE (UIDB/50006/2020) research units, and funded by the project MACBIOPEST (MAC2/1.1a/289), program Interreg MAC 2014–2020 co-financed by DRCT (Azores Regional Government).

References:

1. a) Adedeji A.A., Babalola O.O. *Planta* **2020**, *252*, 61. b) Zaynab M.; Fatima M.; Abbas S.; Sharif Y.; Umair M.; Zafar M.H.; Bahadar K. *Microb. Pathogen*. **2018**, *124*, 198.
2. a) Seca A.M.L.; Pinto D.C.G.A. *Int. J. Mol. Sci*. **2018**, *19*, 263. b) Ivănescu B.; Burlec A.F.; Crivoi F.; Roșu C.; Corciovă, A. *Molecules* **2021**, *26*, 3061. C) Korkina L.; Kostyuk V.; Potapovich A.; Mayer W.; Talib N.; De Luca, C. *Cosmetics* **2018**, *5*, 32.

Food and natural products

Establishment of putative geographical markers of apple ciders using HS-SPME/GC-MS combined with chemometric tools

A. Sousa,[a] J. Vareda,[a] S. Medina,[a,b] R. Pereira,[c] J.S. Câmara,[a,d] R. Perestrelo[a]

a) CQM – Centro de Química da Madeira, Universidade da Madeira, Campus da Penteada, 9020-105 Funchal, Portugal; b) Department of Food Science and Technology, Research Group on Quality, Safety and Bioactivity of Plant Foods, CEBAS (CSIC), Campus Espinardo, 30100 Murcia, Spain; c) Direção Regional de Agricultura, Divisão de Inovação Agroalimentar, Avenida Arriaga, n° 21A, Edificio Golden Gate, 9000-060 Funchal, Portugal; d) Departamento de Química, Faculdade de Ciências Exatas e Engenharia, Campus da Penteada, Universidade da Madeira, 9020-105 Funchal, Portugal

Email: rmp@staff.uma.pt

Apple cider is a traditional alcoholic beverage fermented from apple juice, with increasing consumption and production worldwide. Apples (*Malus domestica*) and their derivates, particularly cider, pose a significant impact in terms of global fruit cultivation, being the most ubiquitous and well-adapted fruit species in temperate regions.[1] In 2017, across Madeira Island, around 130 ha were dedicated to the production of 2000 tons of apples, corresponding to the production of 3328 hl of apple cider. Moreover, opposite to evidence in the remaining country, the cider-making by traditional process has never been discontinued in Madeira Island.[2] The traditional cider-making started with the harvest of selected apple varieties (e.g., Azedo, Branco, Calhau, Domingos, Festa, Rijo, Ribeiro, Vime and Verde apple varieties). Then, the apples are cleaned, crushed and pressing to obtain the fruit juice without solid parts. The fruit juice is submitted to a controlled fermentation (15 to 18 days) at 18 °C to obtain an ethanol content of 7–8% (v/v). Due to the edaphoclimatic and geographical characteristics associated with the organoleptic quality of the different endogenous varieties of cultivated apples, Madeira Island has all the natural conditions to produce excellent quality apple ciders.[1]

Currently, the food-quality programme of the European Union encourages food-origin protection through Protected Designation of Origin (PDO) and Protected Geographical Indication (PGI)) with the purpose of ensuring the quality of the final product.[3] Therefore, it is necessary to develop analytical tools to establish the authenticity and genuineness of food-derived products.

In the current work, headspace solid-phase microextraction followed by gas chromatography-mass spectrometry (HS-SPME/GC–MS) combined with chemometric tools was used to establish the volatile fingerprint of apple ciders produced in different geographical regions of Madeira Island, in order to define their typicity and to identify putative geographical markers. A total of 143 volatile organic compounds (VOCs) belonging to different chemical families have been identified, of which 28 were found in all apple ciders independently of geographical region. Esters, terpenic and furanic compounds presented, on average, the highest contribution for the total volatile fingerprint in cider produced in northern region of the Island, whereas alcohols, acids, volatile phenols, carbonyl compounds and lactones in cider from southern region. Forty-three VOCs revealed statistically significant differences ($p < 0.001$) between the target geographical regions, and 11 between northern and southern regions. A clear differentiation among cider-producing regions was observed on the developed partial least squares-discriminant analysis (PLS-DA) model. Two alcohols (1-hexanol, 1-octanol), 6 esters (methyl acetate, (*Z*)-3-hexen-1-ol acetate, ethyl hexanoate, ethyl nonanote, ethyl octanoate, isoamyl octanoate) and 1 terpenic compound (limonene), can be considered putative geographic markers due to their discriminatory ability. The results obtained recognize the specific and typical geographical characteristics of the cider, which will allow the forthcoming guarantee for the construction of a sustainable platform for the establishment of the authenticity and typicality of the regional cider.

Acknowledgements: This work was supported by FCT-Fundação para a Ciência e a Tecnologia through the CQM Base Fund—UIDB/00674/2020, and Programmatic Fund—UIDP/00674/2020, and by Madeira 14–2020 Program, to the Portuguese Mass Spectrometry Network (PROEQUIPRAM, M14-20 M1420-01-0145-FEDER-000008), by ARDITI—Agência Regional para o Desenvolvimento da Investigação Tecnologia e Inovação, through the projects M1420-01-0145-FEDER-000005—Centro de Química da Madeira—CQM$^+$ (Madeira 14–20 program).

References:

1. Sousa, A.; Vareda, J.; Pereira, R.; Silva, C.; Câmara, J. S.; Perestrelo, R. *Food Res. Int.* **2020**, *137*, 109550.
2. Perestrelo, R.; Silva, C. L.; Silva, P.; Medina, S.; Pereira, R.; Câmara, J. S. *Microchem. J.* **2019**, *148*, 643.
3. Medina, S.; Perestrelo, R.; Pereira, R.; Câmara, J. S. *Foods* **2020**, *9*, 1830.

Materials chemistry and applications

Smart molecularly imprinted polymers for trace detection of dimethoate in olive oil

P.E. Carreiro,[a] J.P.P. Ramalho, [a,b] J.C. Lima,[c] M.G. Silva,[c] A.M.C. Freitas,[d,e] M.J. Cabrita,[d,e] A.J. Burke.[a,b] R. Garcia[d,e]

a) REQUIMTE-LAQV, IIFA, Universidade de Évora, Colégio L.A. Verney, 7000 Évora, Portugal; b) Departamento de Química, Escola de Ciências e Tecnologia, Universidade de Évora, Colégio L.A. Verney, 7000 Évora, Portugal; c) LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal; d) MED- Instituto Mediterrâneo para a Agricultura, Ambiente e Desenvolvimento, IIFA, Universidade de Évora, Núcleo da Mitra, Ap. 94, 7006-554 Évora, Portugal; e) Departamento de Fitotecnia, Escola de Ciências e Tecnologia, Universidade de Évora, Núcleo da Mitra, Ap. 94, 7006-554 Évora, Portugal.

Email: betepc@uevora.pt

In recent decades, Molecularly Imprinted Polymers (MIPS) have had an important contribution to the development of more selective sample preparation methodologies for application in the previous step of pre-concentration/isolation focused on the analysis of pesticide residues in various food matrices, due to their simplicity in preparation and affinity achieved as a recognition element. Nowadays, food safety remains a major issue for the World Health Organization as the number of illnesses and deaths continues to rise due to food insecurity. Thus, to solve this problem, the development of innovative, straightforward and selective analytical methods is crucial.[1] Dimethoate was the target insecticide of this work, since it is mostly used to combat the olive fly pest, and thus the development of selective analytical methods for its detection in olive oil are essential. The main objective of this work is the synthesis and full characterization (FTIR, SEM, XRD) of three different MIP systems responsive to magnetic, photonic and dual-magnetic and photonic stimuli. Molecular recognition capacity of the MIP systems was evaluated and complemented with molecular modelling studies. MIPs were applied as sorbents in the molecularly imprinted solid phase extraction (MISPE) procedure enabling the extraction of dimethoate from spiked olive oil samples at levels similar to the maximum residue limits established by legislation (Figure 1).[2] All three MIP systems possess excellent recovery rates and promising properties for development of more advanced analytical methods for detecting trace amounts of dimethoate in olive oil.

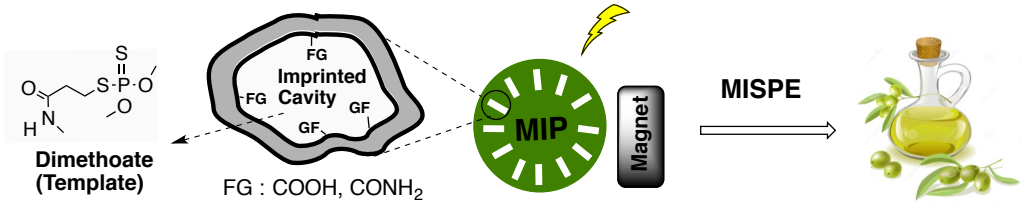


Figure 1: *Smart* MIPs systems for trace analysis of dimethoate in olive oil.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support under the Projects UIDB/50006/2020, UIDB/05183/2020 and PTDC/ASP-AGR/30097/2017.

References:

1. a) Arreguin-Campos, R.; Jiménez-Monroy, K.L.; Diliën, H.; Cleij, T.J.; van Grinsven, B.; Eersels, K. *Biosensors* **2021**, *11*, 46. b) World Health Organization (WHO). Fact Sheets on Food Safety. 2015. Available online: https://www.who.int/news-room/factsheets/detail/food-safety (accessed on 6 June 2021)
2. a) Garcia, R.; Carreiro, E. P.; Ramalho, J. P. P.; Burke, A. J.; Mirão, J.; Gomes da Silva, M. D. R.; Freitas, A. M. C.; Cabrita, M. J. *Food Chemistry,* **2018**, *254*, 309 b) Garcia, R.; Carreiro, E. P.; Ramalho, J. P. P.; Burke, A. J.; Lima, J. C.; Gomes da Silva, M. D. R.; Freitas, A. M. C.; Cabrita, M. J. *Analytica Chimica Acta*, **2018**, *1035*, 60-69; c) Garcia, R.; Carreiro, E. P.; Lima, J. C.; Silva, M. G.; Freitas, A. M. C.; Cabrita, M. J. *Foods* **2020**, *9(5),* 618.

Materials chemistry and applications

In-Silico improvement of green chemical design

L.P. Viegas

CQC, Centro de Química de Coimbra, Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal

Email: lpviegas@ci.uc.pt

Green Chemistry,[1] defined by IUPAC[2] as "the invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances", lays its foundations in 12 Principles. 'Design' is thus one of the key concepts in Green Chemistry for which the design of environmentally benign substances and processes plays a key role. The design procedure, whether one is referring to the planning of a synthetic route or to the determination of the environmental impact of a particular compound, requires reliable prediction of the associated molecular properties. The most refined tools for knowing the properties of molecules are those provided by quantum chemistry and calculated through computational chemistry. Here, we will show how we can use state-of-the-art computational chemistry tools to improve and solidify the 'benign-by-design' concept introduced at the onset of Green Chemistry.

First, we will show how our recently developed multiconformer transition state theory (MC-TST) protocol[3] can be used to predict accurate rate constants for OH-initiated bimolecular tropospheric degradation reactions of volatile organic compounds, enabling the theoretical design of hydrofluorocarbon replacements with the lowest possible tropospheric lifetimes and therefore offering solutions to the compliance of the Kigali Amendment to the Montreal Protocol[4].

Second, we will take a deep look into the quantum mechanical tunneling (QMT) phenomenon which, in recent years, has gained a clear importance in the understanding of rates and selectivities of chemical reactions. Specifically, we will analyze some cases[5] of hydrogen-atom and heavy-atom spin-forbidden QMT studied at the Laboratory for Molecular Cryospectroscopy and Biospectroscopy of CQC and demonstrate that non-adiabatic TST[6] can consistently predict reasonably accurate QMT rate constants for these elusive and not fully understood reactions. Such a tool will be invaluable for the prediction and creation of reactions where the application of tunneling control in chemical synthesis can lead to the creation of a larger molecular universe and to new green synthetic route designs, as the generation of species that are not accessible by conventional means will become possible.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support through the project UIDB/00313/2020.

References:

1. Anastas P. T.; Warner J. C. *Green Chemistry: Theory and Practice* (Oxford University Press, 1998).
2. Tundo P.; et al. *Pure Appl. Chem.* **2000**, *72*, 1207.
3. a) Viegas L. P. *J. Phys. Chem. A* **2018**, *122*, 9721. b) Viegas L. P. *Int. J. Chem. Kinet.* **2019**, *51*, 358. c) Viegas L. P. *Theor. Chem. Acc.* **2019**, *138*, 65. d) Viegas L. P.; Jensen F. *J. Phys. Chem. A* **2020**, *124*, 3460. e) Viegas L. P. *J. Phys. Chem. A* **2021**, *125*, 4499.
4. https://www.unep.org/news-and-stories/news/kigali-amendment-montreal-protocol-another-global-commitment-stop-climate
5. a) Nunes C. M.; Viegas L. P.; et al. *Angew. Chem. Int. Ed.* **2020**, *59*, 17622. b) Viegas L. P.; Nunes C. M.; Fausto R. *Phys. Chem. Chem. Phys.* **2021**, *23*, 5797. c) Roque J. P. L.; Nunes C. M.; Viegas L. P.; et al. *J. Am. Chem. Soc.* **2021** https://doi.org/10.1021/jacs.1c04329
6. Lykhin A. O.; et al. *Int. J. Quantum Chem.* **2016**, *116*, 750.

Materials chemistry and applications

The potential of the sol-gel process for the preparation of electrochromic devices

M. Fernandes

CQ-VR and Chemistry Department, University of Trás-os-Montes e Alto Douro (UTAD), 5000-811 Vila Real, Portugal

Email: msf@utad.pt

Energy is one of the most important vectors in wealth generation, economic growth, and social development. The last decades have witnessed a considerable growth in energy consumption and environmental concerns. Global challenges related to energy depletion, global warming, and climate awareness are hot topics debated daily. Today a great percentage of the world's population lives in urban areas, a proportion that is expected to increase. A sustainable development of the cities, including energy-efficient buildings is mandatory. Buildings are the largest energy consumer in the EU and one of the largest carbon dioxide (CO_2) emitters, being responsible for 40% of energy consumption and 36% of greenhouse gas (GHG) emissions. Buildings will play an essential role in the energy solution. About 10% of the total energy consumed in the building is related with windows. The replacement of conventional windows by smart windows, especially electrochromic windows (ECWs), will be highly beneficial. Electrochromic devices (ECDs) undergo reversible colouring and bleaching operations upon application of a small voltage (0-3 V). ECDs are composed of several layers along a sandwich multilayer configuration[1]. They comprise two outermost glass or plastic substrates, two transparent conductive oxide layers, an active EC electrode layer (EC1, usually tungsten oxide (WO_3)), an ion conductor (IC) (electrolyte/separator) layer, and ion storage (IS) layer (sometimes EC2). Usually, the deposition of high quality oxide layers is achieved by means of physical vacuum deposition, an expensive process responsible for the high price of ECWs, a critical aspect which has limited their widespread use. The sol-gel process [2] is a very attractive alternative for the fabrication of the various layers of an ECD[3]. The sol-gel method is a sustainable, clean, and fast chemical synthesis route that allows fabricating all the layers, with high quality, at a low price, with an easy experimental set-up, low processing temperature and employing classical coating techniques, such as, spin-coating, dip-coating, and spray-coating. The first all-sol-gel ECD was proposed by Judeinstein and Livage in 1988[4].
Here the works developed in recent years on IC layers for ECDs composed of sol-gel derived organic/inorganic biohybrid ormolytes based on a di-urethane cross-linked poly(epsilon-caprolactone) (PCL(530)/siloxane) matrix doped with lithium triflate[5a], a mixture of lithium triflate with ionic liquid[5a], and erbium salt[5b] and a β-diketonate complex[5c]. The structure, morphology, and thermal stability of the new electrolyte systems have been characterized. ECDs have been built with optimized electrolyte samples and their performance has been analyzed by means of UV/VIS and chronoamperometric measurements.

Acknowledgements: This work was funded by "SOLPOWINS – Solar-Powered Smart Windows for Sustainable Buildings" (PTDC/CTM-REF/4304/2020), OBTAIN-Objective Building Sustainability (NORTE-01-0145-FEDER-000084) projects, financed by the Foundation for Science and Technology (FCT) and FEDER, and NORTE2020, respectively, and by CQ-VR (UID/QUI/00616/2013 and UID/QUI/00616/2019). M. F. acknowledges FCT-UTAD for the contract in the scope of Decreto-Lei 57/2016 – Lei 57/2017.

References:

1. Granqvist, C.G., Arvizu, M.A., Pehlivan, I. B., Qu, H.-Y., Wen, R.-T., Niklasson, G.A. *Electrochim. Acta* **2018**, 259, 1170.
2. Brinker, C.J., Sherrer, G.W. Sol–gel Science: The Physics and Chemistry of Sol–gel Processing, Academic Press, San Diego, **1990**.
3. Fernandes, M.; de Zea Bermudez V. "Sol-gel Materials for Smart Electrochromic Devices". In *Chemical Solution Synthesis for Materials Design and Thin Film Device Applications*, Soumen Das; Sandip Dhara (Eds:) Cambridge, United States: Elsevier Inc., **2021**
4. Judeinstein P., Livage J., Zarudiansky A., Rose R. *Solid State Ionics* **1988**, 28, 1722.
5. a) Fernandes M.; Leones R.; Costa A.M.S.; Silva M.M.; Pereira S.; Mano J.F.; Fortunato E.; Rego R.; de Zea Bermudez V. *Electrochim. Acta* **2015**, 162, 226. b) Fernandes M.; Freitas V.T.; Pereira S.; Fortunato E., Ferreira R A.S.; Carlos L.D.; Rego R.; de Zea Bermudez V. *Sol. Energy Mater. Sol.f Cells* **2014**, 123, 203. c) Fernandes M.; Freitas V.; Pereira S.; Leones R.; Silva M.M.; Carlos L.D.; Fortunato E.; Ferreira R.A.S., Rego R., de Zea Bermudez V., *Energies* **2018**.

Chemistry in life sciences

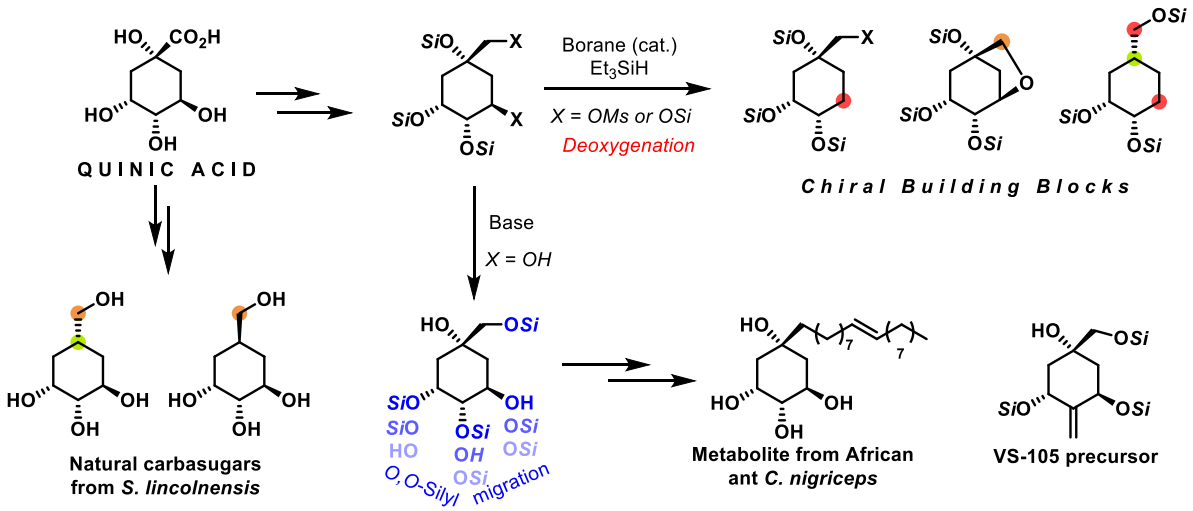
Deoxygenation of quinic acid towards new chirons for divergent syntheses

N.R. Candeias

LAQV-REQUIMTE, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal; Faculty of Engineering and Natural Sciences, Tampere University, 33101 Tampere, Finland;

Email: ncandeias@ua.pt

The shikimate pathway gives rise to the aromatic amino acids in plants and microorganisms. It also provides quinic acid as a secondary metabolite, which is taken by plants in the biosynthesis of a large number of aromatic compounds, and esters by condensation with hydroxycinnamic acids.[1] With a three-dimensional arrangement of secondary hydroxy groups and methylene units, quinic acid skeleton can greatly overlap with the functional groups to be adapted in the chiron strategy in total synthesis.[2] In this communication will be presented our efforts in increasing the synthetic value of this cyclitol either by: a) its direct use in the synthesis of natural carbasugars[3]; b) by creating chirons upon deoxygenation of quinic acid-derived silyl ethers[4]; or c) exploring *O*,*O*-silyl group migrations to create divergent synthesis routes[5].



Acknowledgements: The Academy of Finland (Decisions 326487, 326486, and 326416) and Fundação para a Ciência e Tecnologia (PTDC/QUI-QOR/1131/2020 and CEE-CINST/2018) are acknowledged for financial support.

References:

1. Candeias, N. R.; Assoah, B.; Simeonov, S. P. *Chem. Rev.*, **2018**, *20*, 10458.
2. a) Barco A.; Benetti S.; Risi C.; Marchetti P.; Pollini, G. P.; Zanirato, V. *Tetrahedron: Asymmetry* **1997**, *8*, 3515. b) Mulzer, J.; Drescher, M.; Enev, V. *Curr. Org. Chem*. **2008**, *12*, 1613.
2. Holmstedt, S.; Candeias, N. R. *Tetrahedron*, **2020**, *76*, 131346.
3. Holmstedt, S.; George, L.; Koivuporras, A.; Valkonen, A.; Candeias, N. R. *Org. Lett.*, **2020**, *22*, 8370.
4. Holmstedt, S.; Efimov, A.; Candeias, N. R.; *Org. Lett.,* **2021**, *23*, 3083.

Chemistry in life sciences

Exploring *N*-1,2,3-triazole-isatin-oxindole hybrids as promising inhibitors against two of the deadliest diseases worldwide

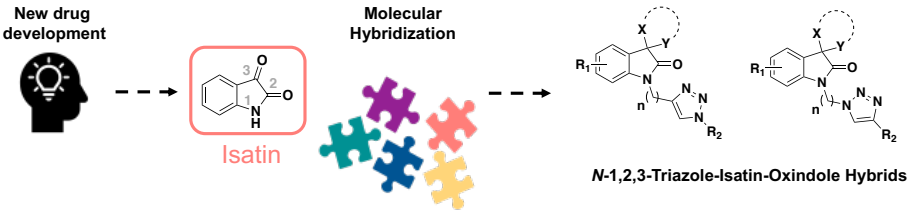
C.S. Marques,[a] A.J. Burke,[a,b]

a) LAQV-REQUIMTE, University of Évora, Institute for Research and Advanced Studies, Rua Romão Ramalho, 59, 7000-671 Évora, Portugal. b) Chemistry Department, School of Science and Technology, University of Évora, Rua Romão Ramalho 59, 7000-671 Évora, Portugal.

Email: carolsmarq@uevora.pt

"In 2019, the top 10 causes of death accounted for 55% of the 55.4 million deaths worldwide… Deaths from noncommunicable diseases are on the rise. Trachea, bronchus and lung cancers deaths have risen from 1.2 million to 1.8 million and are now ranked 6th among leading causes of death… In 2019, Alzheimer's disease and other forms of dementia ranked as the 7th leading cause of death. Women are disproportionately affected. Globally, 65% of deaths from Alzheimer's and other forms of dementia are in women." [1]

With our goal focused on uncurable and chronic diseases (like cancer and neurodegenerative ones), we have targeted the development of new hybrid drugs, a category of molecules with a distinct advantage in improving the therapeutic efficacy, safety and even resistance profiles.
Heterocyclic units are common in many commercial drugs.[2] These structures are quite modular and can be easily manipulated to improve pharmacological, pharmacokinetic, toxicological and other important drug properties. In the last decade our group has been active in the synthesis of new privileged isatin derived heterocyclic scaffolds, focused on the search of promising new compounds with significative bioactivity, taking into account the creation of new efficient atom economical processes that save both time and energy. Special efforts were made for the synthesis of new isatin and oxindole-triazole hybrids (**Scheme 1**).
In this presentation we would like to reveal our latest findings concerning the synthesis of such privileged frameworks, underlining new innovative synthetic methodologies and their potential as cholinesterase inhibitors and also tumour anti-proliferation agents in lymphoma cell lines.



Scheme 1: Molecular hybridization in the synthesis of new isatin and oxindole-triazole hybrids.

Acknowledgements: This work was financed by: National Funds through FCT - Foundation for Science and Technology within the scope of the project UIDB/50006/2020; COST action 15135, Multi-target paradigm for innovative ligand identification in the drug discovery process (MuTaLig).

References:

1. https://www.who.int/en/news-room/fact-sheets/detail/the-top-10-causes-of-death.
2. A. J. Burke, C. S. Marques, N. Turner, G. J. Hermann, *Active Pharmaceutical Ingredients in Synthesis: Catalytic Processes in Research and Development*, 1st Ed., Wiley-VCH, Weinheim, **2018**.

Chemistry in life sciences

Continuous beds: a promising tool for chromatographic purification of plasmid DNA for gene therapy and DNA vaccines

Tomaz CT,[a,b]

a) CICS-UBI – Centro de Investigação em Ciências da Saúde, Universidade da Beira Interior, Av. Infante D. Henrique, 6200-506 Covilhã, Portugal; b) Departamento de Química, Universidade da Beira Interior, R. Marquês d'Ávila e Bolama, 6201-001 Covilhã, Portugal

Email: ctomaz@ubi.pt

The Covid 19 worldwide epidemic has shown the importance of nucleic acid vaccines as a quick and effective way to fight infectious diseases. Also, gene therapy has been used to correct genetic disorders, showing promising results in the treatment of different pathologies, including cancer.[1] Non-viral vectors, like plasmid DNA (pDNA), are being investigated and considered in various current clinical trials due to their safety and high potential for treatment of incurable diseases. Thus, the increasing demand for therapeutic pDNA has put pressure on the biotechnology industry to produce considerable amounts of these bioproducts with purity and quality that accomplish the strict criteria established by regulatory agencies. Nevertheless, the purification of pDNA remains a major challenge due to its low concentration in crude extracts and the presence of impurities, such as genomic DNA, RNA, proteins and endotoxins. Different chromatographic techniques have been applied using conventional particulate supports, however, they exhibit low capacity and high mass transfer resistance for large molecules, such as DNA. To overcome these limitations, in recent years, the development and implementation of continuous beds, such as monoliths and cryogel based systems have emerging as atractive alternatives to solve some of the drawbacks of conventional chromatographic matrices currently used in the pDNA purification. The structural features of these adsorbents allow the purification of biomolecules by convective flow as compared to the diffusional limitation observed in the particle based resins. Thus, the enhanced mass transfer properties, the high binding capacity, and the reduced process time displayed by monoliths and cryogels supports can improve the global purification performance, resulting in the recovery of pDNA with the required stability and biological activity. [2,3]

Acknowledgements: I thank the CICS-UBI by POCI-COMPETE 2020 (Project POCI-01-0145-FEDER-007491) and National Funds by FCT (Project UID/Multi /00709/2019).

References:

1. Lopes A.; Vandermeulen G.; Préat V. *J. Exp. Clin. Cancer Res*. **2019**, *38(1)*,146.
2. Santos, T.; Brito, A.; Boto, R.; Sousa, P.; Almeida, P.; Cruz, C.; Tomaz, C.T. *Sep. Purif. Technol*. **2018**, *206*, 192–198.
3. Bicho, D.; Caramelo-Nunes, C.; Sousa, A.; Sousa, F.; Queiroz, J.A.; Tomaz, C.T. *J Chromatogr B* , **2016**, *1012*, 153-161.

Environment and water

How to reduce analytical interferences in removal studies of micropollutants?

A.R.L. Ribeiro

Laboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal

Email: ritalado@fe.up.pt

The advances on analytical methodologies in the last two decades have triggered the development of environmental occurrence studies of organic micropollutants (MPs) in aquatic compartments. These MPs (*e.g.*, pesticides, pharmaceuticals, hormones, industrial compounds) are continuously introduced into the waterbodies, being typically found at trace concentrations between ng L^{-1} and µg L^{-1}. Most of them are considered pseudo-persistent since they are not completely eliminated by conventional water/wastewater treatments, contributing to the deterioration of water quality and thus, threatening ecosystems, wildlife and human health.[1]
Nowadays, LC coupled to tandem mass spectrometry (LC-MS/MS) using electrospray ionization (ESI) is one of the most used analytical tools for quantification of MPs in environmental samples. In the last years, LC-ESI-MS/MS has been also used to evaluate the removal of MPs by advanced oxidation technologies (AOTs) that are promising alternatives to eliminate them from polluted water/wastewaters.[2] However, the main drawback of the LC-ESI-MS/MS is the matrix effect (**Figure 1**) resulting from the competition between the analytes and the co-eluting interfering species at the ESI source, an effect that is often disregarded in removal studies and that can lead to misinterpretation of results.[3] This presentation aims to give a brief overview on the possible causes of matrix effects in removal studies by AOTs (matrix constituents; reactants needed for the AOT under study; reactants used to quench radicals; and/or sample pretreatment steps).

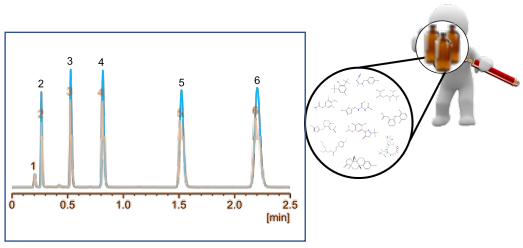


Figure 1: Comparison of two chromatograms of MPs dissolved in ultrapure water (----) and wastewater (----), showing a suppression matrix effect.

Acknowledgements: This work was financially supported by Project POCI-01-0145-FEDER-030521 funded by ERDF funds through COMPETE2020 – POCI and by National Funds (PIDDAC) through FCT/MCTES. ARLR acknowledges FCT funding under DL57/2016 Transitory Norm Programme and the scientific collaboration under Base Funding - UIDP/50020/2020 of the Associate Laboratory LSRE-LCM - funded by national funds through FCT/MCTES (PIDDAC).

References:

1. Barbosa M.O.; Moreira N.F.F.; Ribeiro A.R.; Pereira M.F.R.; Silva A.M.T. *Water Res.* **2016**, *94*, 257.
2. Ribeiro A.R.; Nunes O.C.; Pereira M.F.R.; Silva A.M.T. *Environ. Int.* **2015**, *75*, 33.
3. Gorito A.M.; Barbosa M.O.; Almeida C.M.R.; Pereira M.F.R.; Silva A.M.T., Ribeiro A.R.L. *Sci. Total Environ.*, **2019**, *692*, 995.

Environment and water

CO_2 utilization as a renewable carbon source towards the production of bio-based organic carbonates

A.B. Paninho,[a] M.E. Zakrzewska,[a,b] Y. Borovkov,[a] K.T. Mahmudov,[b] A.J.L. Pombeiro,[b] M.F.C. Guedes da Silva,[b] A.V.M. Nunes[a]

a) LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal; b) Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais 1049–001 Lisbon, Portugal;

Email: ana.nunes@fct.unl.pt

Carbon capture and utilization is a rapidly growing research area. It explores the utilization of carbon dioxide (CO_2) as a C1 building block as alternative to fossil-based resources, bringing carbon back into the value chain and therefore contributing to a circular economy [1]. The topic has recently gained a great attention due to CO_2 increasing atmospheric concentration and consequent environmental impact. As a source of carbon, CO_2 is non-toxic, non-flammable and though less hazard than most of the substances used in the chemical industry. Furthermore, it does not compete with food production and is virtually an inexhaustible source capable of meeting the future growing world demand for chemicals and materials [1].

One of the most reported strategies for CO_2 utilization involves the total incorporation of the CO_2 moiety into an organic substrate for the production of cyclic carbonates, without affecting the oxidation state of the carbon centre. The strategy is highly attractive as a way to introduce CO_2 as a carbon feedstock into large-scale applications. Indeed, cyclic carbonates are versatile compounds that can be used in a wide range of applications, such as, electrolytes, polar aprotic solvents, chemical intermediates and monomers in polymer production [2].

The process although addressing accessible thermodynamic barriers, requires a high-energy substrate, normally highly reactive, volatile and toxic epoxides, obtained from fossil resources. An interesting alternative is the combination of CO_2 with bio-based substrates for the production of fully sustainable organic carbonates. These bio-derived species are generally diols or highly substituted epoxides, which are much more challenging due to their complex structure, with considerably lower reactivities reported [3].

In this work, process intensification strategies exploring biphasic reaction mixtures of ionic liquids and high-pressure CO_2, will be applied for the synthesis of cyclic carbonates derived from CO_2 and bio-based resources. Advantages brought to the process in terms of: i) product separation, ii) catalyst reutilization and iii) chemical equilibrium shift, will be presented and discussed.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support through project PTDC/EQU-EPQ/31926/2017, project UIDB/50006/2020 of the Associate Laboratory for Green Chemistry – LAQV and project UIDB/00100/2020 of Centro de Química Estrutural.

References:

1. Machado, A.S.R.; Nunes, A.V.M.; Nunes da Ponte, M. J. Supercrit. Fluids 2018, 134, 150.
2. Montoya C.A.; Gomez C.F.; Paninho A.B.; Nunes A.V.M.; Mahmudov K.T.; Najdanovic-Visak V.; Martins L.M.D.R.S.; Guedes da Silva M.F.C.; Pombeiro A.J.L.; Nunes da Ponte M.; J.Catal. 2016, 335, 135.
3. Aomchad V.; Cristòfol À.; Della Monica F.; Limburg B.; D'Elia V.; Kleij A.W. Green Chem. 2021,23, 1077.

Environment and water

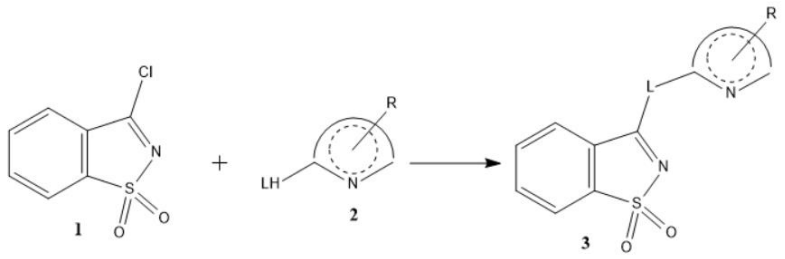
Novel saccharinate-based compounds and their potential for multiple, but selective, applications

J.F. Leal,[a,b] B. Guerreiro,[a,b] P.S.M. Amado,[a,b] A.L. Fernandes,[a,b] L. Barreira,[a,b] J.A. Paixão,[c] M.L.S. Cristiano[a,b]

a) Center of Marine Sciences, CCMAR, Gambelas Campus, University of Algarve, UAlg, 8005-139 Faro, Portugal; b) Department of Chemistry and Pharmacy, Faculty of Sciences and Technology, FCT, Gambelas Campus, University of Algarve, 8005-139 Faro, Portugal; c) CFisUC, Department of Physics, University of Coimbra, 3004-516 Coimbra, Portugal

Email: jfleal@ualg.pt, mcristi@ualg.pt

Saccharin is a water-soluble compound and easily converted in the saccharinate anion, which is able to coordinate with the metal centres in at least four different ways (via nitrogen, oxygen from the carbonyl group, and oxygens from the sulfonic group). These multidentate ligands have been studied by our group, with emphasis on their structure, complexing properties, and potential applications. For example, we demonstrated the effective and selective binding of saccharin-derived ligands to Cu(II).[1] As Cu(II) appears to contribute to the proliferation of cancer cells, its selective chelation may result in antiproliferative activity, and because the saccharyl-based ligands proved safe, but their Cu(II) complexes revealed highly cytotoxic towards various cancer cell lines, we proposed the ligands as pro-drugs for cancer chemotherapy.[2] In addition to medical application, our group has recently designed new compounds/ligands with potential for application in the environmental remediation of water contaminated with metals, namely Cd(II).[3]
These compounds are prepared using a convergent synthetic strategy, whereby the building blocks comprising the partner heterocycles are separately synthesised and then coupled to afford the target conjugates (**Scheme 1**). This approach facilitates the introduction of different spacer-groups and substituents on the unsaturated heterocyclic ring, thereby enabling the optimization of ligands' properties. In this communication we present a set of novel saccharyl-based conjugates and discuss their molecular structure and properties, in view of their potential as selective ligands for environmental remediation.



Scheme 1: Synthesis procedure of saccharinate-based compound. L – linker (-N, -S); R - thiadiazolyl, tetrazolyl.

Acknowledgements: We thank Fundação para a Ciência e Tecnologia for financial support, through projects UIDB/04326/2020 (CCMar) UIDB/04564/2020 (CFisUC) and UIDP/04564/2020 (CFisUC). We also thank the operational programmes CRESC Algarve 2020 and COMPETE 2020 through project EMBRC.PT ALG-01-0145-FEDER-022121. J.F.L. and A.L.F. acknowledge CCMAR for fellowships. P.S.M.A thanks FCT for the doctoral grant SFRH/BD/130407/2017.

References:

1. Ismael A; Henriques M.S.C.; Marques C.; Rodrigues M; Barreira L.; Paixão J. A.; Fausto R.; Cristiano M. L. S. *RSC Adv*. **2016**, *6*, 71628.
2. Cabral L; Brás E; Henriques M; Marques C; Frija L; Barreira L; Paixão J. A; Fausto R; Cristiano M. L. *Chem. Eur. J.* **2018**, *24*, 3251.
3. Leal J. F; Guerreiro B; Amado P. S. M.; Fernandes, A. L.; Barreira L; Paixão J. A.; Cristiano M. L. S. *Molecules* **2021**, *26*, 1501.

Materials chemistry and applications

Silk as a multifaceted source of inspiration for sustainable materials

R.F.P. Pereira

Centre of Chemistry (CQUM), University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

Email: rpereira@quimica.uminho.pt

Nature provides an endless source of inspiration for building new synthetic materials with enhanced performance. The need for solutions to respond to the ever-increasing set of technical, economic, and ecological demands of our society has urged the scientific community to seek more reliable, efficient, recyclable, environmentally friendly, and less energy-consuming materials.

The preparation of advanced materials with formulations including polymers of natural origin has been widely explored in recent years. The development of functional and eco-friendly composites based on the use of natural and renewable resources, which are abundant and readily available, is extremely attractive. Owing to their excellent mechanical and biological characteristics, many biopolymers find application in the area of biomaterials. However, exciting applications in other hot high-tech areas, such as optics, electronics or energy, have been proposed in the last few years.

Silk biopolymer has a long history of use in the textile industry and in the biomedical science. The exceptional intrinsic properties of these fibers (e.g., self-assembly, biocompatibility, non-toxicity, and unique mechanical properties) have attracted considerable interest in a myriad of fields.[1] In this talk, several recent works that demonstrate the tremendous technological potential of silk for the energy and health sectors will be emphasized. We proposed the use of silk-based materials[2a] and silk coocons[2b,c] as separators for lithium ion batteries. A bioinspired strategy was also employed for the synthesis of green silk-based polymer electrolytes.[3] Their potential use in electrochromic devices for smart windows was demonstrated for the first time.[3a] With the same starting material mesoporous SF/silica hybrids with potential application in bone tissue engineering were prepared,[4a] and very recently, we recapitulated, for the first time, the topology of native silk fibers using a radically new materials design-oriented approach to achieve unprecedented porous dermal patches suitable for controlled drug delivery.[4b]

The aforementioned bio-inspired approaches open exciting new avenues in materials research, highlighting the potential of natural proteins in different fields of study.

Acknowledgements: We thank Fundação para a Ciência e Tecnologia (FCT) and, when appropriate, FEDER-COMPETE-QRENEU, for financial support through UID/QUI/00686/2018, UID/QUI/00686/2019, UID/QUI/00686/2020, UID/QUI/50006/2019, UID/QUI/ 00313/2020, PEst-OE/QUI/UI0616/2014, UID/FIS/04650/2013, POCI-01-0145-FEDER-028157, PTDC/CTM-ENE/5387/2014, UID/CTM/50025/2013, PEst-OE/QUI/ UI0616/2014, MAT2016-76039-C4-3-R. ELKARTEK and HAZITEK programs, Deutscher Akademischer Austauschdienst (DAAD)/FCT Transnational Cooperation Project no. 6818 and Pessoa/Hubert Curien 2017/2018 project Ref. 3775/38003ZHR are also acknowledged.

References:

1. Pereira R. F. P.; Silva M. M.; de Zea Bermudez V. *Macromol. Mater. Eng.* **2015**, *300*, 1171.
2. a) Pereira R. F. P.; Brito-Pereira R.; Gonçalves R.; Silva M. P.; Costa C. M.; Silva M. M.; de Zea Bermudez V.; Lanceros-Méndez, S. *ACS Appl. Mater. Interfaces* **2018**, *10*, 5385. b) Pereira R. F. P.; Gonçalves R.; Fernandes M.; Costa C. M.; Silva, M. M.; de Zea Bermudez V.; Lanceros-Mendez S. *Adv. Sustainable Syst.* **2018,** *2*, 1800098. c) Pereira R. F. P.; Gonçalves R.; Gonçalves H.M.R.; Correia D. M.; Costa C. M.; Silva M. M.; Lanceros-Méndez S.; de Zea Bermudez V. *Materials Today Sustainability* **2020,** *9*, 100041.
3. a) Pereira R. F. P.; Sentanin F.; Pawlicka A.; Gonçalves M. C.; Silva M. M.; de Zea Bermudez *ChemElectroChem* **2016**, 3, 1084.; b) Fernandes T. C. D.; Rodrigues H. M. R.; Paz F. A. A.; Sousa J. F. M.; Valente A. J. M.; Silva M. M.; de Zea Bermudez V.; Pereira R. F. P. *J. Electrochem. Soc.* **2020**, *167*, 070551.
4. a) Pereira R. F. P.; Zehbe K.; Günter C.; dos Santos T.; Nunes S. C.; Paz F. A. A.; Silva M. M.; Granja P. L.; Taubert A.; de Zea Bermudez V. *ACS Omega* **2018**, *9*, 10811. b) Qin K.; Pereira R. F.P.; Coradin T.; de Zea Bermudez V.; Fernandes F. *ChemRxiv* **2020**, Preprint.

Materials chemistry and applications

Dendrimers and DNA: a promising marriage

R. Castro,[a] P.L. Granja,[b,c] J. Rodrigues,[a] A.P. Pêgo,[b,c] H.Tomás[a]

a) CQM-Centro de Química da Madeira, MMRG, Universidade da Madeira, Campus Universitário da Penteada, 9020-105 Funchal, Portugal; b) INEB – Instituto de Engenharia Biomédica, Universidade do Porto, Porto, Portugal; c) i3S – Instituto de Investigação e Inovação em Saúde, Universidade do Porto, Porto, Portugal

Email: lenat@staff.uma.pt

Dendrimers are polymers with a peculiar architecture as they possess a central core, from which layers are built, attaining a spherical shape at high generations (high number of layers). Their most important feature is perhaps the exhibited multivalency, that is, they have a high number of end-groups at the surface, which is advantageous having in view their possible biomedical applications. In this regard, a very known example is the ability of cationic dendrimers to interact and compact DNA, thus mimicking the role of histones inside the cell nucleus. Although most of the studies carried out in this area used these interactions for the formation of nanoparticles with application in gene delivery,[1] one cannot rule out the possibility of forming other types of materials with equally important applications.
In the present work, hydrogel films were formed by the self-assembly of poly(amidoamine) (PAMAM) dendrimers with amine termini and double stranded DNA. Films were only achieved in a narrow range of experimental conditions (temperature program, pH, ionic force, amine/phosphate (N/P) ratio and DNA molecular weight), were obtained for G3 to G5 dendrimer generations, and presented a positive surface charge. The presence of dendrimers and DNA in the films was confirmed using rhodamine-labelled dendrimers and ethidium bromide, respectively. These dendrimer/DNA films were left in different media (water, phosphate buffered saline solution, and cell culture medium) for 30 days, at 37ºC, revealing a high stability. The presence of nucleases (foetal bovine serum was used) clearly induced film degradation, being this process dendrimer generation dependent. At pH values higher than 10, dendrimer/DNA films were quickly degraded which showed the important role of dendrimer protonation in the process. Other cationic polymers were assayed for the possibility of obtaining hybrid DNA/polymer films using the same experimental methodology applied with PAMAM dendrimers – namely chitosan and poly(allylamine hydrochloride) (both linear) and polyethylenimine (PEI, branched). However, films were only achieved with branched PEI that resembles dendrimers in terms of molecular architecture. Interestingly, circular dichroism assays showed evidence of the occurrence of gelation-induced supramolecular chirality.[2] Scanning electron microscopy analysis of film surfaces revealed the presence of interconnected globular structures that should be responsible for this chiral response. Possibly, these new dendrimer/DNA films may find application in many different areas, like in the biomedical (e.g., in drug delivery or as platforms for cell-free protein synthesis) and environmental (e.g., for pollutants removal) fields.

Acknowledgements: The authors acknowledge the support of FCT-*Fundação para a Ciência e a Tecnologia* (Base project UIDB/00674/2020; and Programmatic project UIDP/00674/2020, Portuguese Government Funds) and ARDITI-*Agência Regional para o Desenvolvimento da Investigação Tecnologia e Inovação* through the project M1420-01-0145-FEDER-000005-CQM+ (Madeira 14-20 Program). R. Castro also acknowledges FCT for the PhD grant SFRH/BD/87465/2012.

References:

1. a) Martins I.; Tomás H.; Lahoz F.; Rodrigues, J. *Biomacromolecules* **2021**, *22*, 2436. b) Li A.; Fan Y.; Cao X.; Chen L.; Wang L.; Alves C.S.; Mignani S.; Majoral, J.-P.; Tomás H.; Shi, X. *Nanoscale* **2019**,*11*, 17230.
2. Duan P.; Cao H.; Zhang L.; Liu M. *Soft Matter* **2014**,*10*, 5428.

Chemistry in life sciences

2-Arylpurine derivatives as new promising antituberculosis agents

M.A. Carvalho

Centro de Química, Universidade do Minho, Gualtar, 4710-057 Braga, Portugal

Email: mac@quimica.uminho.pt

In 2019, an estimated 10 million people was infected with tuberculosis (TB) worldwide and a total of 1.4 million people died. TB is one of the top 10 causes of death and the leading cause from a single infectious agent, the *Mycobacterium tuberculosis*.[1] TB has treatment however several factors contributed to the emergence of resistance to the treatments and nowadays multidrug-resistant (MDR) strains are infecting a considerable number of patients. European region is not one of the most tuberculosis burden region, however it has the highest rates of MDR-TB, globally. Here, 20% of all new TB patients are affected by MDR-TB.[2] Hence, there is an urgent need for discovery and development of new antituberculosis drugs.

The research community has been deeply involved in the search for new anti-TB drugs and several compounds are in different stages of development.[3] Among others, purine derivatives were identified by our group as active against the *bacillus*.[4]

In this work, we will present the synthesis of new 2-arylpurine derivatives, by reacting functionalized imidazole derivatives with aryl aldehydes. Mechanistic considerations will be presented to support products formation. The biological activity of the purine derivatives against the *Mycobacterium tuberculosis strain* $H_{37}Rv$ will be also presented.

Acknowledgements: The authors acknowledge Universidade do Minho, National NMR Network (PINFRA/22161/2016), the "*Fundação para a Ciência e Tecnologia"* (FCT) for financial support (FEDER-COMPETE, FCT-Portugal, Project UID/QUI/00686/2018, and the PhD grant to C. Correia SFRH/BD/22270/2005) and to US National Institute of Allergy and Infectious Diseases that have performed the antimycobacterial assessment.

References:

1. WHO, https://www.who.int/news-room/fact-sheets/detail/tuberculosis (accessed 11/6/2021)
2. WHO, https://www.euro.who.int/__data/assets/pdf_file/0008/397484/Factsheet_WHO_WTBD_2019.pdf (accessed 11/6/2021)
3. Tiberi S.; Buchanan R.; Caminero J. A.; Centis R.; Arbex M. A.; Salazar M.; Potter J.; Migliori G. B. *Presse Med.* **2017**, 46, e41–e51.
4. Correia C.; Carvalho M. A.; Proença M. F. *Tetrahedron.* **2009**, 65, 6903-6911

Chemistry in life sciences

Synthesis of novel chiral penta- and hexacyclic steroids

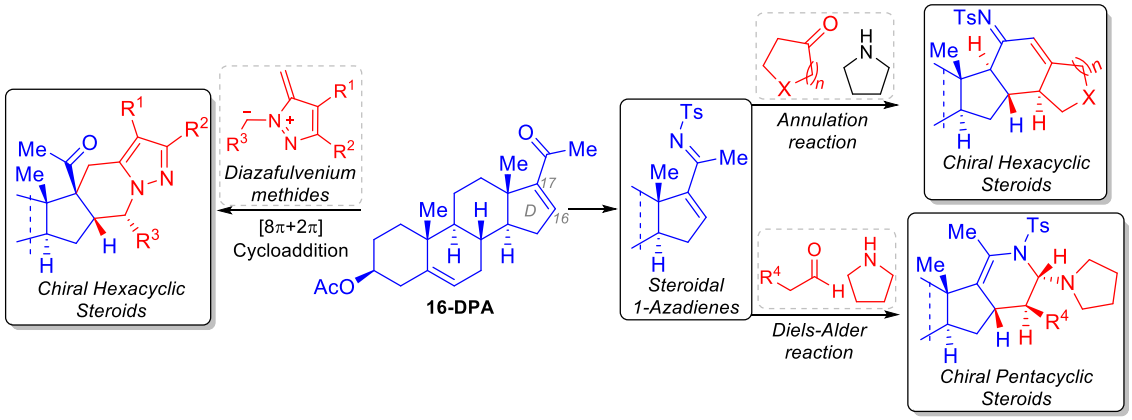
Susana M. M. Lopes

University of Coimbra, Coimbra Chemistry Centre and Department of Chemistry, 3004-535 Coimbra

Email: smlopes@uc.pt

Steroids are an important class of both naturally occurring and synthetic compounds with wide applicability in human physiology and medicine.[1] The structural modification of the steroidal core is an effective strategy to modulate biological properties. 16-Dehydropregnenolone acetate (**16-DPA**) is a commercial and multipurpose building block for the hemisynthesis of different steroidal drugs, such as corticosteroids, anabolic steroid, sex hormones and oral contraceptives, among others. Thus, the versatility of **16-DPA** make it an ideal chiral steroid scaffold for further transformations. One of the most promising synthetic transformations is the introduction of side chains/heterocycles or fused heterocycles at positions 16 and 17 of the D-ring.[2]

In this context, we reported for the first time the [8π+2π] cycloaddition of diazafulvenium methides with **16-DPA** affording a new class of chiral hexacyclic steroids containing a 4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyridine-ring fused to the steroids backbone.[3] Furthermore, **16-DPA** was converted into steroidal 1-azadienes which reacted with carbonyl compounds under enamine catalysis.[4] Interestingly, the reaction with ketones proceeds *via* an annulation mechanism giving chiral hexacyclic steroids, while chiral pentacyclic steroids were obtained *via* Diels-Alder reaction with enamines generated *in situ* from aldehydes. This chemistry was extended to other steroidal scaffolds. Details of these studies as well as on the biological evaluation of the new steroids will be presented.



Scheme 1. Synthesis of novel chiral penta- and hexacyclic steroids.

Acknowledgements: The Coimbra Chemistry Centre (CQC) is supported by the Portuguese Agency for Scientific Research, "Fundação para a Ciência e a Tecnologia" (FCT) through project UIDB/00313/2020 and UIDP/QUI/00313/2020, co-funded by COMPETE2020-UE.

References:

1. a) Gupta, A.; Kumar, B. S.; Negi, A. S. *J. Steroid Biochem. Mol. Biol.* **2013**, *137*, 242. b) Bansal, R.; Singh, R. *Med. Res. Rev.* **2017**, *38*, 1126.
2. Monier, M.; El-Mekabaty, A.; Abdel-Latif, D.; Mert, B. D.; Elattar, K. M. *Steroids* **2020**, *154*, 108548.
3. a) Lopes, S. M. M.; Correia, C. F. O.; Nunes, S. C. C.; Pereira, N. A. M.; Ferreira, A. R. F.; Sousa, E. P.; Gomes, C. S. B.; Salvador, J. A. R.; Pais, A. A. C. C.; Pinho e Melo, T. M. V. D. *Org. Biomol. Chem.* **2015**, *13*, 9127. b) Lopes, S. M. M.; Sousa, E. P.; Marques, C.; Rodrigues, M. J.; Pinho e Melo, T. M. V. D. *Steroids* **2017**, *122*, 16. c) Jorda, R.; Lopes, S. M. M.; Řezníčková, E.; Ajani, H.; Pereira, A. V.; Gomes, C. S.; Pinho e Melo, T. M. V. D. *Eur. J. Med. Chem.* **2019**, *178*, 168.
4. Lopes, S. M. M.; Gomes, C. S. B.; Pinho e Melo, T. M. V. D. *Org. Lett.* **2018**, *20* 4332. b) Lopes, S. M. M.; Santos, J. R. C.; Pinho e Melo, T. M. V. D. *Org. Biomol. Chem.* **2021**, *19*, 1122.

Culture and education

2020: O ano em que a pandemia obrigou a rever o paradigma ensino/aprendizagem

M.F.N.N. Carvalho,[a] T. Coelho[b]

a) *Centro de Química Estrutural e Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal;* b) *Sociedade Portuguesa de Química, A. República,45, 3ºEsq, 1050-187, Lisboa.*

Email: fcarvalho@tecnico.ulisboa.pt

Numa sociedade em rápida mudança, as metodologias de ensino não são exceção. A evolução da ciência e da tecnologia constituem um permanente desafio àqueles cuja função é ensinar: os professores!
A extraordinária velocidade com que tudo acontece torna difícil acompanhar e principalmente motivar os jovens a adquirir conhecimentos em áreas expositivas. A imagem tem que fazer parte da forma de comunicar saberes para conseguir motivar para a aprendizagem.
A pandemia, se por um lado ameaçou e pôs em causa as metodologias convencionais de ensino, acelerou a inevitável introdução no paradigma ensino/aprendizagem de formas de comunicação não presencial, recorrendo a meios digitais. Plataformas como o *Zoom*, o *Teams* e outras, passaram a fazer parte do dia a dia de professores e alunos, tornando a comunicação e o ensino à distância satisfatoriamente próximos, e facilitando a utilização combinada das plataformas de comunicação e das aplicações como o Youtube ou as bibliotecas digitais.
É a 4ª Revolução do Ensino, a par da 4ª Revolução Industrial. A digitalização permite novas formas de comunicação e faz esbater os contornos entre as diferentes ciências, aumentando a interdisciplinaridade entre elas. Tanta mudança, se é uma ameaça aos hábitos, é sobretudo um desafio a inovar a forma de pensar e ensinar. A formação ao longo da vida torna-se assim inevitável e necessária para que os professores possam comunicar ciência de uma forma atualizada e motivadora. Para motivar e despertar curiosidade científica, nos jovens alunos, é preciso estar atualizado e motivado!
Atenta às necessidades de atualização científica, a Sociedade Portuguesa de Química criou em 2018 o Centro de Formação de Professores e desde então tem promovido Ações de formação, tanto presenciais como à distância (Figuras 1), tendo em conta os interesses manifestados pelos professores de química. Até à data participaram nessas ações 764 e foram certificados 689 professores do grupo 510.

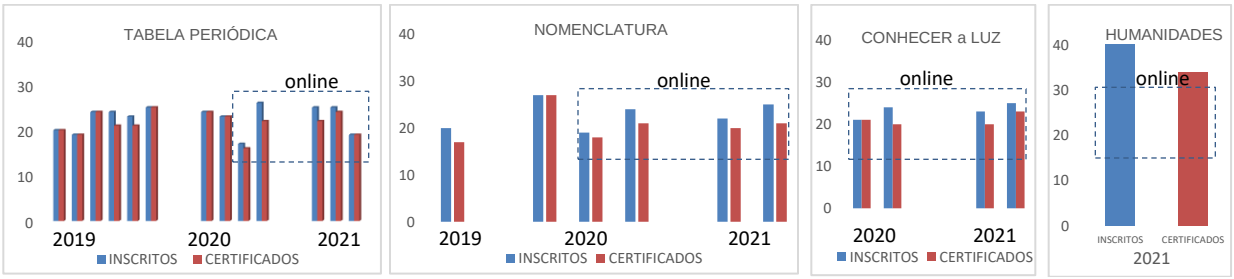


Figure 1: Ações promovidas e número de participantes e professores certificados pelo Centro de Formação da SPQ. Não estão incluídas as Ações associadas a congressos

A adesão aos tópicos e conteúdos das Ações e as opiniões manifestadas no final de cada uma delas, confirmam a necessidade e relevância do tipo de Ações promovidas pela SPQ. A rápida adequação dessas Ações ao ensino *online* (Figura 1) resultante da declaração do Estado de Emergência e confinamento obrigatório, resultantes da pandemia, demonstrou ser essa uma via adequada para promover a formação dos professores, visando a melhoria contínua da qualidade do ensino da Química em Portugal.

Agradecimentos: À Sociedade Portuguesa de Química pela disponibilização de dados. Ao Ministério da Educação pela mobilidade estatutária (ao abrigo do Artigo 68º do ECD, em conjugação com o disposto no n.º 3, do artigo 92.º da LTFP, aprovada pela Lei n.º 35/2014 de 20/06) concedida a professora Tânia Coelho.

Culture and education

"Química para Senhoras": As obras de Marie Meurdrac e Giuseppe Compagnoni

João Paulo André

Departamento/Centro de Química da Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

Email: jandre@quimica.uminho.pt

La chymie charitable et facile en faveur des dames (Paris, 1666) e *La chimica per le donne* (Veneza,1796) são duas obras marcantes da história da química. O primeiro, da autoria da francesa Marie Meurdrac, numa época em que a iatroquímica ganhava terreno na Europa, é considerado o livro inaugural da escrita de química no feminino. O segundo, do italiano Giuseppe Compagnoni, em linha com o ideário iluminista de popularização da ciência, tinha por missão levar a nova química a audiências que ultrapassavam largamente o âmbito que o seu título sugere.

Gravura de *La chymie charitable et facile en faveur des dames* (3ª edição)

Agradecimentos: Este trabalho foi financiado por Fundos Nacionais através da FCT – Fundação para a Ciência e a Tecnologia no âmbito do Financiamento Estratégico UIDB/00686/2020

Oral Communications

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

Materials chemistry and applications

Calorimetry of NBS addition to DMF: unstable or under studied?

Elsa Gonçalves[a], Pedro Serra[a], Filipe Estanislau[a], Nuno Lousa[a]

a) Hovione FarmaCiencia SA, R&D Center, Estrada do Paço do Lumiar, Campus do Lumiar, Edifício R, 1649-038, Lisboa, Portugal

Email: edgoncalves@hovione.com

Scale up of exothermic chemical processes are associated with a variety of hazards and can ultimately lead to thermal runaway and explosion. Given the catastrophic consequences of such scenario, handling and combining chemical reagents, on an industrial scale, requires a detailed risk assessment prior to operation.
At Hovione, the Process Safety team is responsible for understanding and characterizing the thermal hazards associated with a given operation. This is achieved through a systematic screening methodology to predict the thermal behavior of a chemical or a mixture in a case of loss of temperature control (Figure 1). This data is then used to establish adequate safeguards that prevent incidents and reduce operational risk for a safe and successful scale-up.[1]
In this work, reaction calorimetry was used to study the energy released during the preparation of a solution of *N*-Bromosuccinimide (NBS) in dimethylformamide (DMF). The thermal stability of this solution was then characterized from different calorimetric methods and the data obtained was evaluated using model-free kinetics, allowing the determination of important safety metrics such as the self-accelerating decomposition temperature (SADT) and time to maximum rate under adiabatic conditions (TMR_{ad}).

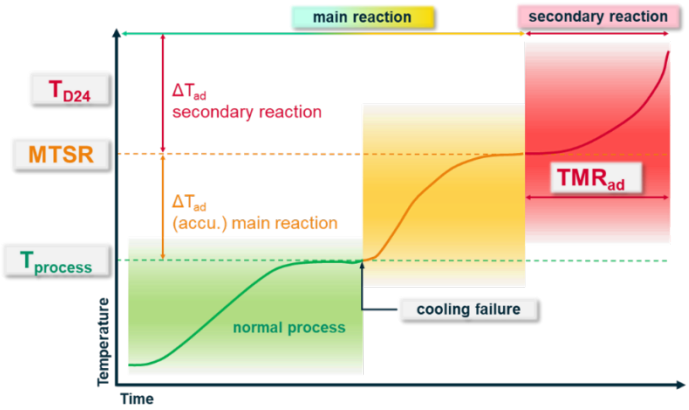


Figure 1: Cooling failure scheme.

References:

1. F. Stoessel, Thermal Safety of Chemical Processes – *Risk Assessment and Process Design*, 2nd ed., **2020**.

Materials chemistry and applications

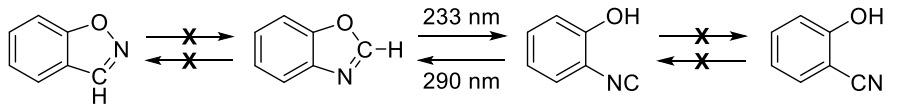
Photochemistry of monomeric benzoxazole and isocyanophenol

Igor Reva,[a] A. J. Lopes Jesus,[b] Cláudio M. Nunes,[c] José P. L. Roque,[c] and Rui Fausto[c]

a) University of Coimbra, CIEPQPF, Department of Chemical Engineering, Rua Sílvio Lima, 3030-790 Coimbra, Portugal
b) University of Coimbra, CQC, Faculty of Pharmacy, Azinhaga de Santa Comba, 3000-548 Coimbra, Portugal
c) University of Coimbra, CQC, Department of Chemistry, Rua Larga, Coimbra 3004-535, Portugal

Email: reva@eq.uc.pt

In this work, we undertook experimental and computational studies to address the mechanisms of photochemistry induced by narrowband UV irradiations of benzoxazole **1** (Scheme 1) isolated in an Ar matrix at 15 K. The monomers of **1** as well as the photoproducts were characterized by infrared spectroscopy. Cleavage of the C−O bond accompanied with H-shift from C to O was found to be the dominant photoprocess upon UV excitation of matrix-isolated **1** at λ = 233 nm, resulting in nearly quantitative generation of isocyanophenol **2**. Subsequent irradiations of the *in situ* produced **2** at λ = 290 nm (where **1** does not absorb) led to photoisomerization of **2** back to **1**.[1] The experimental spectra of authentic matrix-isolated cyanophenol **3** and benzisoxazole **4** (Scheme 1) were characterized, and their photochemistries were also studied. The photochemistries of **3** and especially of **4** were found to be very rich, but never led to **2** or **1**.[2]



Benzisoxazole **4** Benzoxazole **1** Isocyanophenol **2** Cyanophenol **3**

Scheme 1: Photochemical transformations of monomeric benzoxazole and isocyanophenol in a cryogenic argon matrix at 15 K.

The additional observed photoreactions consisted in photodetachment of the H-atom from the OH groups of **2** or **3**, leading to the generation of 2-isocyanophenoxyl or 2-cyanophenoxyl radicals, respectively. The detached H-atoms were found to recombine at the *para*-carbon atom (with respect to the CO group) of the phenyl ring to yield respective oxo tautomers. Further observed photoreactions resulted from elimination of the CN radical and H-atom (which recombined to give HCN or HNC) and formation of fulvenone.[1]
Under the present experimental conditions, we did not find any crossing point that could establish evidence of connection between photochemistries of the [**1**, **2**] pair and the [**3**, **4**] pair. We did not observe any isocyano ↔ cyano isomerization between **2** and **3**. Similarly, we did not observe any photochemically induced permutation of the C and N atoms in the five-membered rings of **1** or **4** that would result in the mutual isomerization of **1** and **4**. All photoproducts were characterized by comparing their observed infrared spectra with those computed at the B3LYP/6-311++G(d,p) level. The mechanistic analysis of the photochemistry occurring in the family of the title compounds will be presented.

Acknowledgements: The Chemical Process Engineering and Forest Products Research Centre (CIEPQPF) is supported by Portuguese Foundation for Science and Technology (FCT) through the projects UIDB/EQU/00102/2020 and UIDP/EQU/00102/2020, co-funded by FEDER/COMPETE 2020-EU. The Coimbra Chemistry Centre (CQC) is supported by the FCT through the projects UIDB/00313/2020 and UIDP/00313/2020. LaserLab-Coimbra (FCT/ROTEIRO/0152/2013) is also acknowledged.

References:

1. Reva, I.; Lopes Jesus, A. J.; Nunes, C. M.; Roque, J. P. L.; Fausto, R. *J. Org. Chem.* **2021**, *86*, 6126-6137.
2. Nunes, C. M.; Pinto, S. M. V.; Reva, I.; Fausto, R. *Eur. J. Org. Chem.* **2016**, *24*, 4152-4158.

Materials chemistry and applications

Highly dispersed noble metal-based carbon nitride as efficient electrocatalytic/photocatalytic hydrogen evolution reaction catalysts

Zhipeng Yu,[a,b] André Torres-Pinto,[a] Maria J. Sampaio,[a] Isilda Amorim,[b,c] Ana Araujo,[a,b] Cláudia G. Silva,[a] Lifeng Liu,[b] Joaquim L. Faria[a]

a) Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal; b) C International Iberian Nanotechnology Laboratory (INL), Avenida Mestre Jose Veiga, 4715-330 Braga, Portugal c) Department of Chemistry, University of Minho, Gualtar Campus, 4715-057 Braga, Portugal

Email: zhipeng.yu@inl.int, lifeng.liu@inl.int and jlfaria@fe.up.pt

Hydrogen (H_2), with a high energy density and environmental friendliness, is considered one of the most promising clean energy carriers. Water splitting to generate H_2 by electrocatalytic/photocatalytic processes is a promising technology for renewable energy and storage. Still, its commercial application requires developing efficient and stable catalysts for hydrogen evolution reaction (HER).[1]

Despite electrocatalytic and photocatalytic HER followed relatively different mechanisms, some main components of electrocatalysts often overlap with many cocatalysts, while for photocatalysts.[2] Hence, advanced catalysts should be highly desired in the combination of electrocatalytic and photocatalytic HER activities. Ruthenium and iridium (Ru, Ir)-based materials have drawn increasing attention for catalyzing the HER, which have been demonstrated both theoretically and experimentally to possess good HER performance.[3] Nevertheless, the utilization efficiency of noble metal seems still not that satisfactory in light of its intrinsic activity, which is restricted by the relatively large particle size, poor size distribution, and high loading amount. Despite their sound performance as electrocatalysts, the use of Ru and Ir in visible-light-driven HER photocatalytic systems have been hindered by the inefficient transfer of electrons from the photosensitive material to the metal. Therefore, graphitic carbon nitride (gCN) has attracted increasing interest owing to its suitable bandgap (2.7 eV), excellent stability, and an abundance of N-group, which can anchor the metal.[4] However, as far as we know, only a few reports on highly dispersed Ru and Ir stabilizing on gCN for photocatalytic hydrogen evolution exist. Also, the mechanistic understanding of the surface proton reduction is still highly desirable for the design of highly efficient photocatalysts.

Hence, we develop efficient noble metal-based gCN (Ir-gCN, Ru-gCN) catalysts by hydrothermal reduction. By aid of the strong metal-support interaction (SMSI) between noble metal and gCN with abundant N-groups, the highly dispersed Ir-gCN and Ru-gCN catalysts were constructed successfully. Impressively, the Ir-gCN and Ru-gCN catalysts with ultra-low loading exhibit superior catalytic activities for both electrocatalytic and photocatalytic HER. This should be attributed to its ultra-small catalyst size and high dispersion of active sites. Significantly, excellent durability was achieved during long-time electrocatalytic and photocatalytic HER benefiting from the SMIS. This study provides a potential strategy for developing high-efficiency, stable and multifunctional catalysts in sustainable energy conversion.

Acknowledgements: Z.P. Yu acknowledges the financial supported offered by the China Scholarship Council (Grant no. 201806150015). This work was partially funded by European Regional Development Fund (ERDF) through COMPETE2020 programme and by National Innovation Agency of Portugal through the Mobilizador Programme (POCI-01-0247-FEDER-046109) as well as Base Funding-UIDB/50020/2020 of the Associate Laboratory LSRE-LCM through FCT/MCTES (PIDDAC).

References:

1. a) Yu Z. P.; Xu J. Y.; Feng S. Q.; Song X. G.; Bondarchuk O.; Faria J. L.; Ding Y. J.; Liu L. F. *New J. Chem.* **2021,** *45*, 5770-5774. b) Da Silva E. S.; Moura N. M. M.; Neves M. G. P. M. S.; Coutinho A.; Prieto M.; Silva C. G.; Faria J. L. *Appl. Catal. B Environ.* **2018,** *221*, 56-69.

2. Yan B. L.; Liu D. P.; Feng X. L.; Shao M. Z.; Zhang Y. *Adv. Funct. Mater.* **2020,** *30*, 2003007.

3. a) Han S. M.; Yun Q. B.; Tu S. Y.; Zhu, L. J.; Cao, W. B.; Lu, Q. P. *J. Mater. Chem. A* **2019,** *7*, 24691-24714; (b) Chen Z. J.; Duan X. G.; Wei W.; Wang S. B.; Ni, B. J. *Nano Energy* **2020,** *78*, 105270.

4. Teixeira I. F.; Barbosa E. C. M.; Tsang S. C. E.; Camargo P. H. C. *Chem. Soc. Rev.* **2018,** *47*, 7783-7817.

Materials chemistry and applications

Ionic liquids and eutectic systems as functional materials for energy

L. C. Branco, H. Cruz, N. Jordão, S. Gago, A. L. Pinto, F. Pina,

LAQV-REQUIMTE, Dept de Química da Faculdade de Ciências e Tecnologia, Univ. NOVA de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal

Email: ***l.branco@fct.unl.pt***

Ionic Liquids and Eutectic systems can be classified as designer and functional materials possessing interesting properties to be explored in materials science and energy applications. Electrochromism is the reversible switch of color resulting from oxidation or reduction of a chemical compound. It is recognized that the suitable electrolyte selection is one of the key parameters for an electrochemical process [1] including for solar cells and electrochromic devices (ECD). Recently, our group have been developed and tested different task-specific Ionic Liquids (ILs) or Deep Eutectic Solvents (DES) as efficient and reversible ECD [2-4]. Deep Eutectic Solvents (DES) have attracted much attention due to the possibility to be used as a possible greener alternative electrolyte [5] as well as functional and efficient multi-colored ECDs [3,4]. Polyoxometalates (POMs) are anionic metal oxides based on early transition metals, with a higher oxidation state, that could be an alternative to the commonly used organic ligands. The preparation of Polyoxometalate-based DES (POM-DES) by combination of POM cluster salts with other HBA or HBD components seems to be very attractive for future application as ECDs. Dye synthetized Solar Cells (DSSCs) show attractive properties associated to their low-cost and simple manufacturing processes together with their advantageous attributes. Herein, we present new electrolytes for DSSCs based on DES composed by the combination between several metal and iodide salts as HBA and ethylene glycol, glycerol and Polyethylene glycol as HBD. Some of these metal-based DES could be used in electroplating/electrodeposition of metals as well as electrolytes for batteries. These new class of ionic materials can open attractive applications for material science and energy devices.

Acknowledgements: This work was performed under the project “SunStorage- Harvesting and storage of solar energy”, with reference POCI- 01-0145-FEDER-016387, H. Cruz and L. C. Branco thanks to financial support of FCT/MCTES (Post-Doc grant SFRH/BPD/102705/2014 and IF/0041/2013/CP1161/CT00). Also, the authors thank to FCT-CAPES (2019-2020) project.

References:

[1] E. L. Smith, A. P. Abbott, K. S. Ryder, *Chem. Rev.* **2014**, 114, 11060.
[2] H. Cruz, N. Jordão, L. C. Branco, *Green Chem.*, 2017, 19, 1653.
[3] H. Cruz, N. Jordão, P. Amorim, M. Dionísio, L. C. Branco, *ACS Sustainable Chem. Eng.* **2018,** *6*, 2240.
[4] N. Jordão, H. Cruz, F. Pina, L. C. Branco, *Electrochimica Acta* 2018, 283, 718.
[5] H. Cruz, A.L. Pinto, J. C. Lima, L.B. Branco, S. Gago Materials Letters: X, **2020**, 6, 100033.

Chemistry in life sciences

Dual-action chimeric peptides and their ionic liquid conjugates as a novel approach to tackle skin infections

A. Gomes,[a] L. Bessa,[a] I. Fernandes,[a] R. Ferraz,[a,b] N. Mateus,[a] P. Gameiro,[a] C. Teixeira,[a] P. Gomes[a]

a) LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo alegre, 4169-007, Portugal b) Ciências Químicas e das Biomoléculas /CISA, Escola Superior de Saúde, Politécnico do Porto, R. Dr. António Bernardino de Almeida, 4200-072, Portugal

Email: anagomes@fc.up.pt

Complicated skin and soft tissue infections (cSSTI), like diabetic foot ulcers, pressure ulcers, or venous leg ulcers, among others, are intimately related to bacterial biofilms. These are extremely difficult to eradicate, as there are shielded against the action of both antibiotics and the immune system. As such, cSSTI delay the healing process which, when combined with other comorbidities like, e.g., being diabetic, bedridden, or having chronic venous insufficiency, result in a very poor prognosis due to a much decreased ability to fight infection and regenerate affected tissues. As such, the most complicated cases culminate in hospitalization where hospital-acquired pathogens (HAI) can exacerbate the infection.[1] Since the efficient options to fight multi-drug resistant bacteria (MDR) associated with HAI are being exhausted, new strategies to fight cSSTI are urgently needed. Moreover, current biomedical approaches should aim at providing protection against MDR bacteria along with a matrix scaffold, e.g., collagen-based, to boost reestablishment of a healthy skin.[2] Having this in mind, we have designed a dual-action chimeric peptide, encompassing an antimicrobial sequence (peptide 3.1) and a collagen-boosting sequence (PP4) covalently linked to each other through different spacers and orientations. The most promising peptide, 3.1-PP4: i) displays potent antimicrobial activity against reference strains of Gram-positive and, especially, against Gram-negative bacteria; ii) is equally potent against gram-negative MDR clinical isolates; iii) hampers the formation of, or disaggregates, biofilms of MDR clinical isolates of *K. pneumoniae*, and iv) retains the collagenesis-inducing behavior of the parent collagen-boosting building block (peptide PP4).[3] Building on this promising peptide lead, 3.1-PP4, we pursued its chemical modification, by conjugation with an imidazole-based ionic liquid via click chemistry, aiming at increasing its enzymatic stability. The resulting conjugate, MeIm-3.1-PP4, retained the parent peptide's antibacterial and antibiofilm activity, while exhibiting much improved stability towards tyrosinase-mediated modification.[4] In conclusion, both the chimeric peptide 3.1-PP4 and its ionic liquid-based conjugate are highly promising leads towards development of innovative topical formulations to tackle cSSTI.

Acknowledgements: We thank to the Fundação para a Ciência e Tecnologia (FCT) for funding our Research Unit LAQV/REQUIMTE (ref. UIDB/50006/2020), and project AntiINFECT (POCI-01-0145-FEDER-031781), and for Doctoral Grant PD/BD/135073/2017 (AG).

References:

1. Leong, H. N.; Kurup, A.; Tan, M. Y.; Kwa, A. L. H.; Liau, K. H.; Wilcox, M. H. *Infection and drug resistance* **2018,** *11*, 1959-1974.
2. a) Gomes, A.; Teixeira, C.; Ferraz, R.; Prudencio, C.; Gomes, P. *Molecules* **2017,** *22* (10). b) Makrantonaki, E.; Wlaschek, M.; Scharffetter-Kochanek, K. *J Dtsch Dermatol Ges* **2017,** *15* (3), 255-275.
3. Gomes, A.; Bessa, L. J.; Fernandes, I.; Ferraz, R.; Mateus, N.; Gameiro, P.; Teixeira, C.; Gomes, P. *Front Microbiol* **2019,** *10* (1915).
4. Gomes, A.; Bessa, L. J.; Correia, P.; Fernandes, I.; Ferraz, R.; Gameiro, P.; Teixeira, C.; Gomes, P. *International Journal of Molecular Sciences* **2020,** *21* (17), 6174.

Chemistry in life sciences

Recent FT-IR trends in protein analysis and Biopharma

E. Monteiro,[a] V. Paixão,[a] S. Schlindwein,[b] M. Luft.[b]

a) Bruker Portugal Unipessoal, Lda; b) Bruker Optik GmbH, Ettlingen, Germany.

Email:eva.monteiro@bruker.com

Biochemical and biopharmaceutical applications utilizing Fourier-Transform Infrared (FT-IR) spectroscopy have been on the rise in recent years. Already a go-to method to elucidate protein structure, stability and concentration, FT-IR is widely applied in research, development, and quality control of protein APIs like monoclonal antibodies. We will discuss the potential of spectral fingerprinting on complex biopharmaceutical formulations of therapeutic proteins and vaccines.

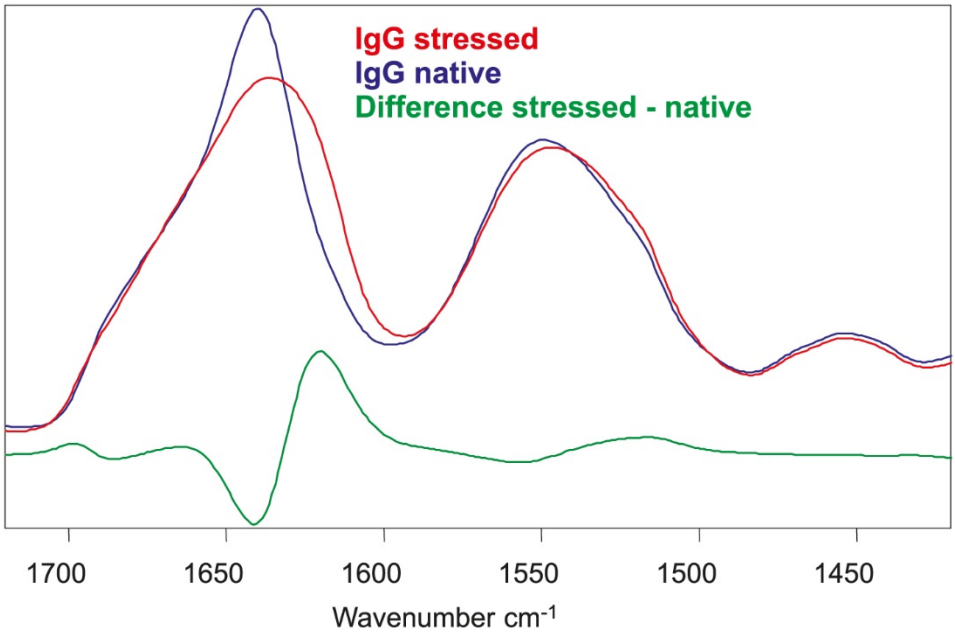


Figure 1: Examination of antibody stability by difference spectroscopy. The difference spectrum (green) of the stressed antibody (red IR spectrum) minus the unstressed antibody (blue IR spectrum) reveals a loss of intramolecular ß-sheets (negative band at 1640 cm^{-1}) and formation of intermolecular ß-sheet (positive band at 1622 cm^{-1}).

Chemistry in life sciences

Light-activated membrane transport of arginine-rich peptides

J.N. Martins,[a] J. Montenegro,[b] J.C. Lima,[a] N. Basílio[a]

[a] *Laboratório Associado para a Química Verde (LAQV), Rede de Química e Tecnologia (REQUIMTE), Departament of Chemistry, NOVA School of Science and Technology (FCT-NOVA), Caparica, Portugal;* [b] *Centro Singular de Investigación en Química Biológica y Materiales Moleculares (CIQUS), Organic Chemistry Department, Santiago de Compostela University, 1578 Santiago de Compostela, Spain.*

Email: jmn.martins@campus.fct.unl.pt

The study of peptides is of great interest, not only due to the variety of functions these molecules present in biological systems (e.g. in signalling, neuromodulation, immune response and metabolism)[1] but also as tools in biotechnology and as pharmacological agents, as is the case of antimicrobial cell-penetrating peptides.[2] Supramolecular receptors have had a rising application in the transport, modulation and sensing of these biomolecules, due to the strong interactions they can establish with affinities up to the nM range.[3] Our work focused on the development of a supramolecular amphiphilic counterion activator, SC6Azo (**Figure 1**), for the light-activated transport of polyarginines across phospholipidic membranes. This transporter is based on a modular amphiphilic system, with p-sulfonatocalix[4]arene as a receptor for cationic targets, monosubstituted in its lower rim with an aliphatic chain of 6 carbons, with a photo-active azobenzene moiety at its end. Not only was it shown that SC6Azo binds to polyarginines with comparable affinities to those of the p-sulfonatocalix[4]arene receptor, up to the nM range, but it was also shown that this molecule presents an efficient light induced isomerization, with quantitative photochemical conversion from trans to cis, when irradiated at 382 nm, and reaching 73% of maximum conversion for the reverse reaction, upon irradiation at 500 nm. This enabled a marked decrease in the EC50 for the peptide transport in phosphatidylcholine liposomes, when irradiating the cis isomer and converting it to the more hydrophobic trans isomer. Furthermore, a marked increase in peptide transport upon cis-trans isomerization was observed in a single dye-displacement assay, yielding a maximum expected increase of release of, approximately, 30%.

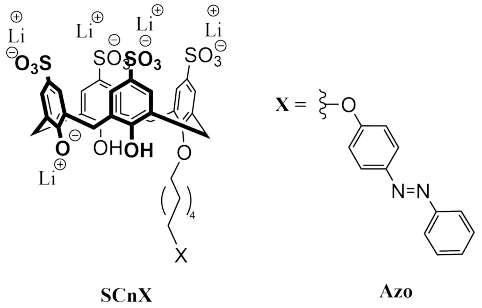


Figure 1: Chemical Structure of the light-controlled counterion activator, SC6Azo.

Acknowledgements: This work was supported by the Associate Laboratory for Green Chemistry - LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/50006/2020). FCT/MCTES is also acknowledged for the grants PTDC/QUI-COL/32351/2017 as well as for the financial support in the "Verão com Ciência" initiative in association with DGES – Direção Geral do Ensino Superior. N.B. also acknowledges the FCT/MCTES for a research contract CEECIND/00466/2017.

References:

1. A. Voigt and H. F. Jelinek, Physiol. Rep., 2016, 4, 1–5.
2. D. I. Chan, E. J. Prenner and H. J. Vogel, Biochim. Biophys. Acta - Biomembr., 2006, 1758, 1184–1202.
3. J. N. Martins, J. C. Lima, N. Basílio, Molecules., 9, 2021, 26(1), 106.

Chemistry in life sciences

Hypoxia-selective triazene prodrugs designed to address glioblastoma microenvironment

Braga C[a,b], Moreira R[a], Bernardes G[b], Fernandes AR[c], Ferreira-Silva M[a,c], Perry MJ[a]

a) Research Institute for Medicines (iMed.ULisboa), Faculdade de Farmácia, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal; b) Instituto de Medicina Molecular, Faculdade de Medicina da Universidade de Lisboa, Av. Prof. Egas Moniz, 1649-028 Lisboa, Portugal; c) Applied Molecular Biosciences Unit (UCIBIO), Departamento de Ciências da Vida, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal.

Email: cbraga@ff.ulisboa.pt

Triazenes (RN=N-NR'R'') display a broad-spectrum chemistry, but are best known for their cytotoxic properties, as exemplified by dacarbazine and temozolomide, well-known anticancer agents. Triazenes exert their chemotherapeutic activity through a unique mechanism of action that involves formation of a reactive alkyl diazonium intermediate capable of alkylating DNA and promoting cell death.[1,2] Herein we report a triazene-based platform, **1**, that can be activated under reducing environments[3] to undergo a self-immolative process that culminates with the release of the cytotoxic triazene. A series of nitroaromatic prodrugs **1** (**Figure 1**) of cytotoxic triazenes was synthesized and NTR-mediated hydrolytic activation was investigated by HPLC and LC-MS, with varying release rates accordingly to the incorporated bioreductive moiety. A549, U87MG and LN-229 human cancer cells were treated with prodrugs **1** under either hypoxic (0.05% O_2) or normoxic (20% O_2) conditions. *In vitro* studies revealed hypoxia selectivity cytotoxicity comparing to non-selective TMZ, used as a reference compound and currently applied in glioblastoma chemotherapy. Overall, this approach intends to deliver a therapeutic payload (DNA-alkylating agent) in an hypoxic-selective manner, bypassing toxic side-effects towards healthy cells.

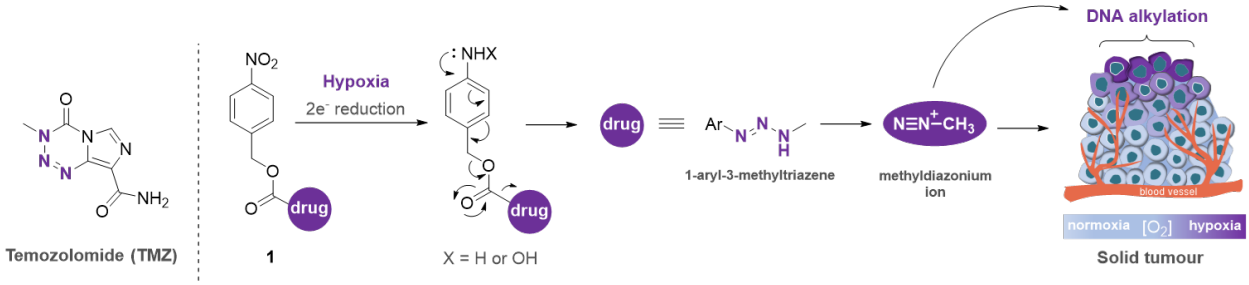


Figure 1: Schematic representation of triazene prodrugs **1** activation under hypoxic conditions.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support through the PhD fellowship awarded (PD/BD/135286/2017) through MedChemTrain PhD Programme and through iMed.ULisboa grant, UID/DTP/04138/2019 from FCT, Portugal.

References:

1. Pinheiro, R; Braga C.; Santos G.; Bronze M.R.; Perry M.J.; Moreira R.; Brites D.; Falcão A.S. *ACS Chem Neurosci.* **2017**, 8, 50-59.
2. Braga, C.; Vaz A.R.; Oliveira M.C.; Marques M.M.; Moreira R.; Brites D.; Perry M.J. *Eur. J. Med. Chem.* **2019**, 172, 16-25.
3. Chevalier, A.; Zhang, Y.; Khdour, O. M.; Kaye, J. B.; Hecht, S. M. *J. Am. Chem. Soc.* **2016**, 138, 12009-12012.

Food and natural products

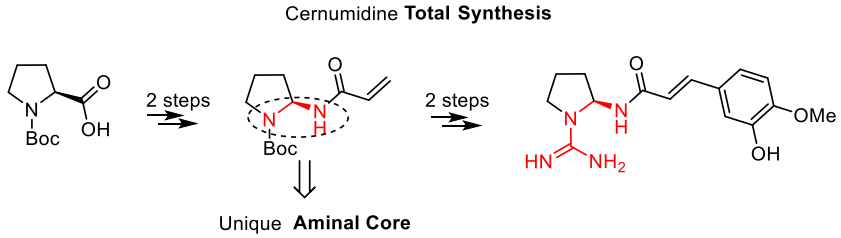
Total synthesis of cernumidine

R Rippel R[a], Leitão F[a], Lourenço A[a], Ferreira L[a], Branco P[a]

a) LAQV-REQUIMTE, NOVA School of Science and Technology, 2829-516 Caparica, Portugal.

Email: r.rippel@campus.fct.unl.pt

Several natural guanidine derivatives present diverse biological activities, which led this functionality to be an important building block in various pharmaceuticals [1]. Cernumidine (Figure 1) is a natural alkaloid present in the leaves of Solanum cernuum Vell. (Solanaceae), a plant originated from Brazil. This compound display inhibition of interleukine-8 production by HT-29 colon carcinoma cells and presents a singular aminoguanidine core [2] not previously reported, involving a proline-based guanidine core ((2-aminopyrrolidin-1-yl)carboxamidine) condensed with an isoferulic (3-hydroxy-4-methoxycinnamic) acid unit. While this interesting structure with five consecutive C-N bonds was already reported by us in a racemic manner [3], an enantioselective approach remains elusive. Although at first glance it might come across as a very simple molecule with only a labile stereogenic center, its unique asymmetric aminal core presents a synthetic major challenge to a synthetic chemist. Here we present the first enantioselective approach to the total synthesis of Cernumidine and analogues, starting from Boc-L-proline. Here we will address the key steps of the envisioned approach and the challenges that we have encountered in each one of them. Additionally, our endeavors to overcome the intricacies of the aminal nucleus synthesis and stability will also be presented.



Scheme 1: Synthetic strategy for the total synthesis of Cernumidine.

Acknowledgements: This work was supported by the Associate Laboratory for Green Chemistry- LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020). The National NMR Facility and the SCXRD facility are supported by Fundação para a Ciência e Tecnologia (RECI/BBB-BQB/0230/2012 and RECI/BBB-BEP/0124/2012, respectively). We acknowledge the Laboratório de Análises REQUIMTE for the technical support and for the mass spectrometry analyses. Rafael Rippel acknowledges the PhD grant SFRH/BD/136692/2018 from Fundação para a Ciência e Tecnologia provide information such as granting agency and other financial support.

References:

[1] Berlinck, R. G. S. et al. The chemistry and biology of organic guanidine derivatives. *Nat. Prod. Rep*. **2010**, 27, 1871.
[2] Lopes L. C.; Roman B; Medeiros M. A.; Mukhopadhyay A.; Utrilla P.; Gálvez J.; Mauriño S. G.; Moltiva V.; Lourenço A.; Feliciano A. S. *Tetrahedron Lett*. **2011**, 52, 6392.
[3] Rippel R, Pinheiro L, Lopes M, Lourenço A, Ferreira LM, Branco PS. Synthetic Approaches to A Challenging and Unusual Structure-An Amino-Pyrrolidine Guanine Core. *Molecules*. **2020**, 25, 797.

Food and natural products

Development of a methodology for the determination of the reactivity of brandies used in wine fortification

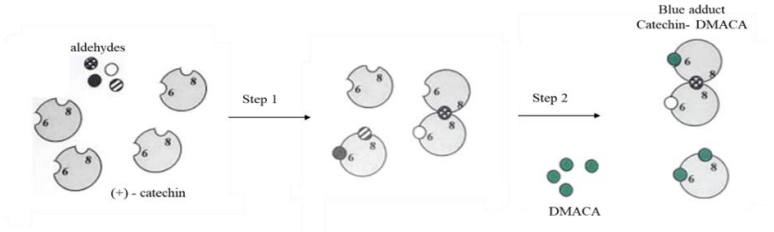
Azevedo J [a, *], Pissarra J [b], Guido L [a], Oliveira J [a], Lopes P [c], Mateus N [a], de Freitas V [a]

a) LAQV – REQUIMTE - Laboratório Associado para a Química Verde- Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal; b) UTAD- Universidade de Trás os Montes e Alto Douro, Quinta de Prados, Vila Real, Departamento de Agronomia, 5001-801 Vila Real, Portugal; c) Amorim Cork S.A. Rua dos Corticeiros 830, 4536-904 Santa Maria de Lamas, Portugal

Email: joana.azevedo@up.pt

During Port wine production, brandies are added to stop the fermentation when about half of the sugar has been converted into ethanol, which represents about 20% of the final volume of these wines[1]. Therefore, brandies chemical composition is an important feature having a strong impact on the final characteristics of Port wines due to the presence of aroma compounds like aldehydes and higher alcohols, and also due to the interaction of some brandies components with other molecules present in wine must. Moreover, the chemical composition of the different commercial brandies varies every year and among producers, which will impact differently on the physical-chemical and sensory characteristics of the final Port wine.

The main purpose of this work is to describe and validate a new methodology for the determination of a brandy reactivity index (BRI) towards flavan-3-ol compounds in wines (catechins and condensed tannins). This new method consists of two main steps: a) the ability of aldehydes to react with C8 and/or C6 positions in the phloroglucinol ring of a catechin present in excess (A ring) [2]; b) further reaction of the remaining free catechin with *p*-dimethylaminocinamaldehyde (DMACA) yielding to the formation of a blue compound that can be quantified by Visible spectroscopy at 640 nm (**Scheme 1**)[1, 3]. The impact of different experimental conditions such as reagent concentrations and reaction time on BRI were also evaluated. The method was validated through the determination of repeatability (intra-day variability) and reproducibility. The repeatability was considered acceptable with a *CV* of 11.87%. The analysis of the reproducibility variance, S^2_R (11.59), the reproducibility limit R (9.5) and the reproducibility coefficient of variation, CV_R (15.25%) postulates BRI methodology to be reliable and robust.



Scheme 1: Scheme of the different steps involved in determining the BRI

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support the scholarships SFRH/BD/139709/2018. This research is supported by AgriFood XXI I&D&I project (NORTE-01-0145-FEDER-000041 cofinanced by European Regional Development Fund (ERDF), through the NORTE 2020 (Programa Operacional Regional do Norte 2014/2020).

References:

1. Pissarra, J.; Lourenço, S.; Machado, J. M.; Mateus, N.; Guimaraens, D.; de Freitas, V., Contribution and importance of wine spirit to the port wine final quality—initial approach. *Journal of the Science of Food and Agriculture* **2005**, 85 (7), 1091-1097.

2. Timberlake, C. F.; Bridle, P., Interactions Between Anthocyanins, Phenolic Compounds, and Acetaldehyde and Their Significance in Red Wines. *American Journal of Enology and Viticulture* **1976**, 27 (3), 97-105.

3. Pissarra, J.; Mateus, N.; Rivas-Gonzalo, J.; Santos Buelga, C.; De Freitas, V., Reaction Between Malvidin 3-Glucoside and (+)-Catechin in Model Solutions Containing Different Aldehydes. *Journal of Food Science* **2003**, 68 (2), 476-481.

Environment and water

Biodegradation potential of paracetamol by marine bacteria consortia

T. Palma,[a,b] J. Valentine, [a,b] M.C. Costa [a,b]

a) Centre of Marine Sciences, University of Algarve, Campus de Gambelas, building 7, 8005-139 Faro, Portugal; b) Faculdade de Ciências e Tecnologias, University of Algarve, Campus de Gambelas, building 8, 8005139 Faro, Portugal

Email: tcpalma@ualg.pt; julia.valentine@imbrsea.eu; mcorada@ualg.pt

Pharmaceutical pollutants are becoming an increasing concern within the scientific community having been detected in many aquatic systems, sewage treatment plant effluents, marine seawaters, and even found in drinking water[1]. Paracetamol, a globally used analgesic and antipyretic is one of the most prescribed drugs during the pandemic time[2] increasing the probability of polluting water resources. This drug is being studied in the project PROBIOMA for its biodegradation potential by bacterial consortia recovered from several marine organisms collected from Queijo Suiço and Catedral marine caves of Algarve coast. For that purpose, bacterial consortia named as 4, 18, and 21 were recovered from *Hymedesmia versicolor* (Porifera), *Didemnum* sp. (Tunicata), and *Filograna implexa* (Annelida) organisms. The bacteria consortia were grown in a mineral salt medium with the targeted pharmaceutical as the sole carbon source at 150 rpm, room temperature and in the dark to avoid photodegradation of the drug. The results show that the marine bacteria of consortia 4, 18 and 21 have the ability to degrade more than half of 86 mg/L of paracetamol in aerobic conditions after 48 h, and 78 ± 14%, 59 ± 8% and 73 ± 6%, respectively after 162 h, using that drug as a sole carbon source (**Figure 1**). From this degradation, the metabolic products 4-aminophenol and hydroquinone were detected. The marine consortia studied were able to remove paracetamol and thus, may display potential to degrade other pharmaceutical compounds with similar structure.
Overall, three and five bacterial isolates were obtained from marine consortia 4 and 21, respectively, which presented the ability to grow in the presence of paracetamol as the sole carbon source.

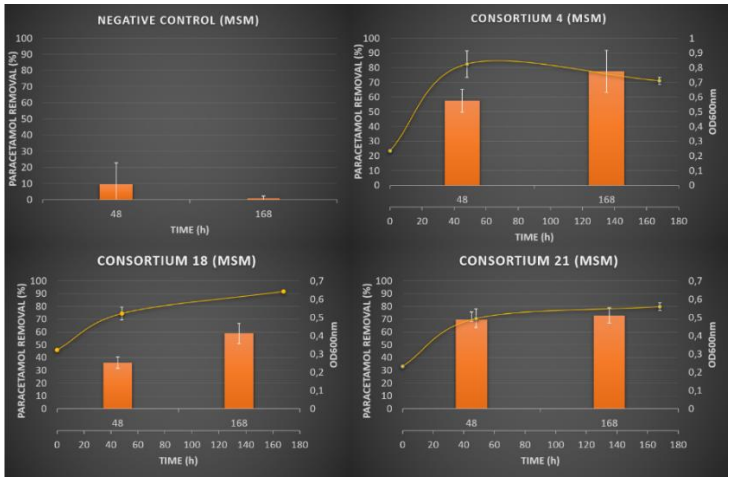


Figure 1: Paracetamol removal (%) and bacterial growth (OD_{600}) of marine bacterial consortia 4, 18 and 21 in MSM liquid cultures in the presence of 86 mg/L of paracetamol, after 48 h and 168 h at room temperature, 150 rpm and in dark conditions (n=3; mean ± standard deviation).

Acknowledgements: Financial support was obtained through project 0483_PROBIOMA_5_E, co-financed by the European Regional Development Fund within the framework of the Interreg V-A Spain-Portugal program (POCTEP) 2014–2020.

References:

1. Togola A.; Budzinski H. *J. Chromatogr.. A* **2008,** 1177(1), 150-158
2. Fusi-Schmidhauser T.; Preston N.J.; Keller N.; Gamondi C. *J. Pain Symptom Manag.* **2020**, 60.

Chemistry in life sciences

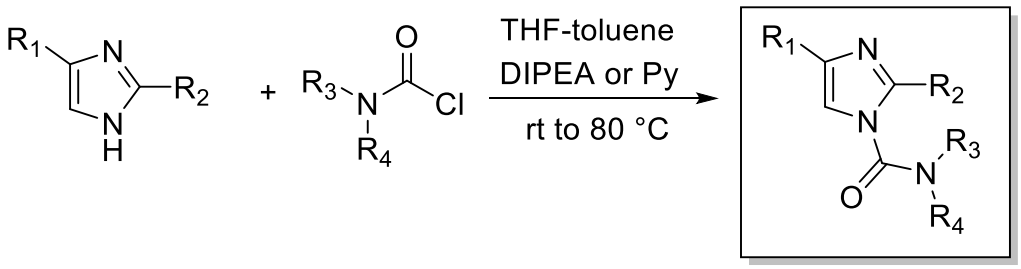
Synthesis of 4-phenylimidazoles in the discovery of potent, long-acting inhibitors of FAAH

Beliaev A.,[a] Kiss L.E.,[a] Soares-da-Silva P.[b]

a) Laboratory of Chemistry, Department of Research & Development, BIAL – Portela & Cª., S.A. À Avenida da Siderurgia Nacional, 4745-457 Coronado (S. Romão e S. Mamede), Portugal b) Laboratory of Pharmacology, Department of Research & Development, BIAL – Portela & Cª., S.A. À Avenida da Siderurgia Nacional, 4745-457 Coronado (S. Romão e S. Mamede), Portugal

Email: alexander.beliaev@bial.com

FAAH is a member of the extensive family of serine hydrolases. It catalyzes the degradation of lipid signalling fatty acid amides including the endogenous cannabinoid anandamide. Modulation of anandamide levels via inhibition of FAAH has potential clinical relevance in a wide range of diseases and pathological conditions.
Here we present the development of a new methodology for the synthesis of 4-phenylimidazoles that allowed SAR exploration in the discovery of potent, long-acting inhibitors of FAAH (**Scheme 1**).



Scheme 1: Preparation of imidazole analogues.

Materials chemistry and applications

Nanohybrids and hybridplexes based on carbon dots and PAMAM dendrimer for bioimaging and gene delivery

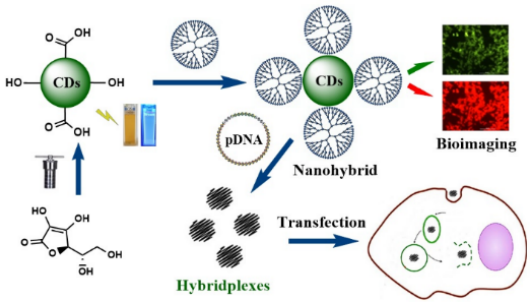
Ivo J. Martins[a], Helena Tomás[a], Fernando Lahoz[b], João Rodrigues[a,c]

[a]CQM - Centro de Química da Madeira, MMRG, Universidade da Madeira, Campus da Penteada, 9020-105 Funchal, Portugal; [b]Departamento de Física, IUdEA, Universidad de La Laguna, 38200 San Cristóbal de La Laguna, Tenerife, Spain; [c]School of Materials Science and Engineering/Center for Nano Energy Materials, Northwestern Polytechnical University, Xi'an 710072, China

Email: joaor@uma.pt

Carbon dots (CDs) and PAMAM dendrimer nanohybrids have been a subject of broad interest in the last few years due to their exciting properties for biomedical applications.[1] CDs are a class of zero-dimensional nanosized particles discovered by Xu *et al.*[2] in 2004, that are photoluminescent, water-soluble, and low cytotoxic. Whereas PAMAM dendrimers are monodispersed polymeric molecules with a branched architecture that possess loading capacity, controlled-molecular weight, surface functionality, and nanomedicine applications.[3] These two nanomaterials, when combined in a hybrid form, can take advantage of their individual properties resulting in versatile nanoplatforms and be more compatible from the biological point of view. In fact, recent developments on CDs/PAMAM nanohybrids led to their application in cancer theranostics, particularly for chemotherapy and gene delivery.[4] In view of bioimaging and gene delivery applications, we combined carbon dots with PAMAM dendrimers (G4, G5, and G6) and obtained nanohybrids that were promising fluorescent nanomaterials and non-viral vectors.

In this study, anionic fluorescent carbon dots were self-assembled with cationic G4-G6 PAMAM-NH_2 dendrimers to form G4-G6 CDs@PAMAM nanohybrids and their potential use for bioimaging and gene delivery was evaluated (**Scheme 1**). CDs were synthesized from ascorbic acid using original reaction conditions and were characterized by UV-Vis, Fluorescence, FT-IR, NMR, TEM, and DLS. Then, CDs and PAMAM dendrimers were combined using a non-covalent approach forming nanohybrids that were photostable, low cytotoxic, and easily internalized by cells, and be detected through fluorescence emission. Furthermore, the G4-G6 CDs@PAMAM nanohybrids showed their ability to compact DNA, forming hybridplexes that transfected cells efficiently. Concluding, we demonstrated their potential for bioimaging and gene delivery, and future use in nanomedicine, particularly for theranostics. All these promising results and future perspectives for CDs and PAMAM dendrimer nanohybrids and hybridplexes will be presented and discussed.



Scheme 1: Fluorescent carbon dots and PAMAM dendrimers nanohybrids for bioimaging and gene delivery.[5]

Acknowledgements: We thank the support of FCT-Fundação para a Ciência e a Tecnologia (Base Fund UIDB/00674/2020 and Programmatic Fund UIDP/00674/2020, Portuguese Government Funds), ARDITI-Agência Regional para o Desenvolvimento da Investigação Tecnologia e Inovação through the project M1420-01-0145-FEDER-000005-CQM+ (Madeira 14-20 Program).

References:

1. Guo, Y.; Shen, M.; Shi, X. *Macromol. Biosci.* **2021**, *2100007*, 1-10.
2. Xu, X.; Ray, R.; Gu, Y.; Ploehn, H. J.; Gearheart, L.; Raker, K.; Scrivens, W. A. *J. Am. Chem. Soc.* **2004**, *126*, 12736-12737.
3. Mignani, S.; Rodrigues, J.; Tomas, H.; Zablocka, M.; Shi, X.; Caminade, A.-M.; Majoral, J.-P. ***Chem. Soc. Rev.*** **2018**, ***47***, 514-532.
4. a) Li, D.; Fan, Y.; Shen, M.; Bányai, I.; Shi, X. *J. Mater. Chem. B* **2019**, *7*, 277-285. b) Ghosh, S.; Ghosal, K.; Mohammad, Sk A.; Sarkar, K. *Chem. Eng. J.* **2019**, *373*, 468–484.
5. Martins, I.; Tomás, H.; Lahoz, F.; Rodrigues, J. *Biomacromolecules* **2021**, Article *ASAP* https://doi.org/10.1021/acs.biomac.1c00232

Materials chemistry and applications

Improved water resistance and large conductivity enhancement of poly(3, 4 -ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) through cross-linking with an oxetane unit

Sara M. Jorge,[a,b] Luís F. Santos,[b] Adelino Galvão,[b] Jorge Morgado,[a,c] and Ana Charas[a]

a) Instituto de Telecomunicações, Instituto Superior Técnico, Av. Rovisco Pais, P-1049-001, Lisboa, Portugal; b) Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av Rovisco Pais, P-1049-001 Lisboa, Portugal; c) Department of Bioengineering, Instituto Superior Técnico, Universidade de Lisboa, Av Rovisco Pais, P-1049-001 Lisboa, Portugal.

Email: sara.jorge@tecnico.ulisboa.pt

Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) (PEDOT:PSS) is a conducting polymer with wide applications in organic electronics and bioelectronics, due to exhibiting remarkable properties, such as high conductivity, high transparency in the visible spectral range, good thermal stability, and easy processing from aqueous dispersions.[1] However, thin films of PEDOT:PSS suffer from poor structural stability in contact with water or very humid environments, this posing impediments to its use in devices interfacing biological/aqueous mediums.[2] Here, we show that the cross-linking of PSS through an oxetane reagent (HMO) (**Figure 1**) can lead to water-resistant films of PEDOT:PSS with greatly enhanced electrical conductivity (increase from 0.2 S/cm to 350 S/cm). The method is new and it brings advantages in comparison with reported ones on conductivity enhancements of PEDOT:PSS. The causes for the improvements are explained on the basis on ^{1}H-NMR, Raman spectroscopy, and Atomic Force Microscopy studies.

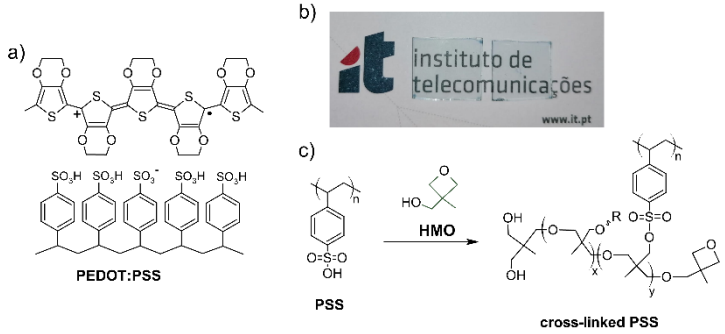


Figure 1: a) Chemical structure of PEDOT:PSS; b) Conducting films PEDOT:PSS deposited on glass substrates; c) general formula and reaction for the cross-linked PSS using HMO.

Acknowledgements: Instituto de Telecomunicações (contract no. UIDB/ 50008/2020) and project SUPRASOL (LISBOA-01-0145-FEDER-028365-PTDC/QUI-QOR/28365/2017), funded by Fundo Europeu de Desenvolvimento Regional (FEDER), through Programa LISBOA2020 and by FCT/Portugal. S. M. Jorge acknowledges FCT/Portugal for a PhD Grant (PD/BD/150593/2020).

References:

1. Fan X., Nie W., Tsai H., Wang N., Huang H., Cheng Y., Wen R., Ma L., Yan F., Xia Y. *Adv. Sci.* **2019**, *6*, 1900813.
2. McQuade J., Vuong L. T. *ACS Omega*. **2018**, 3(4), 3868.

Chemistry in life sciences

Low-field benchtop NMR for solvent swap analysis

M.M. Andrade[a], A.I. Vicente[a], P.Sobral[a,b], P.R. R. Florindo[b], S.D. Lucas[a]

a) R&D, Process Chemistry Development, Hovione FarmaCiência SA, Campus do Lumiar, Building S, 1649-038 Lisboa, Portugal;
b) Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003, Lisboa, Portugal

Email: mandrade@hovione.com

In the commercial manufacturing of Active Pharmaceutical Ingredients (APIs) one of the most used unit operations is solvent swap[1]. Most likely any scalable process has one or more solvent swap steps, being the evident solution to avoid medicinal chemistry procedures such as evaporation to dryness or use of inorganic salts to remove water; these approaches are not feasible at scale.
When executing this unit operation in a chemical process the residual content of solvent removed is usually controlled, due to the impact it may have either on quality or yield of the isolated intermediate or API and, nowadays, process controls heavily rely on gas chromatography as technique by excellence for solvent quantification.
Over the last decade, benchtop NMR spectrometers emerged with numerous companies offering this type of systems. Low-field compact NMR instruments with permanent magnets are easy to use, robust, cryogen-free and inexpensive alternatives offering spectroscopic information without queuing times for analysis of samples in remote laboratories.[2,3]
Benchtop low-field NMR spectrometer (^{1}H-NMR, 43 MHz) was used to quantify solvents in 20 binary systems that are commonly used for swap process under API manufacture processes. The results obtained showed that most solvent systems studied allow the quantification of both solvents.
Monitoring of the chemical shifts revealed several types of interactions between solvents (dipole-dipole, H-bonding, anisotropic, reaction field effect).
A case study showed the application of benchtop low-field ^{1}H-NMR to accurately measure ACN content in solvent swap R&D samples during design space studies. In conclusion, low-field NMR can successfully replace chromatographic methods leading to significant savings on time and resources.

Figure 1: Replacement of chromatographic methods by low-field NMR.

References:
1. Papadakis, E.; Tula, A. K.; Gani, R. Solvent selection methodology for pharmaceutical processes: Solvent swap, *Chem. Eng. Res. Des.* **2016**, *115*, Part B, 443-461.
2. Giberson, J.; Scicluna, J.; Legge, N.; Longstaffe, J. Chapter Three - Developments in benchtop NMR spectroscopy 2015–2020. Annu. Rep. NMR Spectrosc. **2021**, *102*, 153-246.
3. Castaing-Cordier, T.; Bouillaud, D.; Farjon, J.; Giraudeau, P. Recent advances in benchtop NMR spectroscopy and its applications. *Annu. Rep. NMR Spectrosc.* **2021**, DOI: 10.1016/bs.arnmr.2021.02.003.

Chemistry in life sciences

Probing heteroaromatic scaffolds in the melanostatin neuropeptide: A bioisosteric approach using niacin as a pro surrogate

B.L. Pires-Lima[a], S.C. Silva-Reis[a], X.C. Correia[a], H.F. Costa-Almeida[a], X. García-Mera[b], J.E. Rodríguez-Borges[a], I.E. Sampaio-Dias[a,*]

a) LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal; b) Department of Organic Chemistry, Faculty of Pharmacy, University of Santiago de Compostela, E-15782 Santiago de Compostela, Spain.

***Email: idias@fc.up.pt**

Parkinson's disease (PD) is the second most common neurodegenerative disease of the central nervous system, affecting 20 million people around the world.[1] PD symptoms include tremors, bradykinesia, gait alterations, sleeping disorders, fainting, and, at more advanced stages, dementia. PD treatments are mainly focused on dopamine (DA) potentiation through the administration of levodopa (L-DOPA) and inhibitors of the catechol-*O*-methyl transferase (COMT) and monoamine oxidase B (MAO-B) enzymes.[2] Even though L-DOPA regimen controls the progression of PD motor symptoms, long-term therapy causes serious health concerns.[2] In this sense, pharmacological alternatives are mandatory.

Melanostatin (MIF-1, **Figure 1**), formally known as L-prolyl-L-leucylglycinamide, is an endogenous hypothalamic neuropeptide derived from oxytocin hormone that acts as a positive allosteric modulator (PAM) of the D_2 Receptors (D_2R).[3-5] By increasing the D_2R affinity for DA, these receptors are activated at lower DA concentration, being thus clinically relevant. Previous studies developed by our research group have shown that the replacement of L-Proline (Pro) residue by heteroaromatic scaffolds are well tolerated, rendering analogues with PAM activity comparable to the parent neuropeptide. [3-5]

Niacin also known as Vitamin B_3 is an heteroaromatic system that is able to reduce neuroinflammation and oxidative stressand relieve symptoms in PD patients, and potentially slow the disease progression.[6,7]

In this work, Niacin was used as a Pro surrogate and twelve new MIF-1 peptidomimetics have been synthesized and characterized by NMR and mass spectrometry (**Figure 1**). These peptidomimetics are currently being tested for their ability to modulate the activity of D_2Rs by means of pharmacological functional assays measuring the mobilization of cAMP and biological assays through their toxicological profiles in human SH-SY5Y cells. This project is expected to provide useful structure-activity relationship information for the rational design of novel MIF-1 peptidomimetics, paving the way for the development of new anti-Parkinson hits.

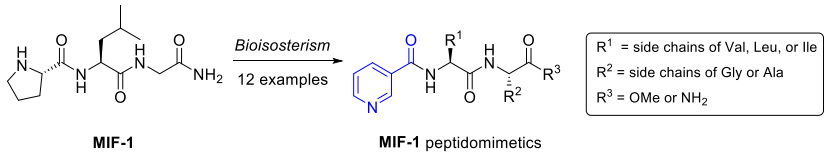


Figure 1: MIF-1 and MIF-1 Peptidomimetics.

Acknowledgements: Thanks are due to Fundação para a Ciência e Tecnologia (FCT, Portugal) for funding our Research Unit (ref. UIDB/50006/2020). IES-D thanks FCT for funding through the Individual Call to Scientific Employment Stimulus (Ref. 2020.02311.CEECIND). XG-M thanks Xunta de Galicia for financial funding with references GPC2017/GI-1597 and REDES2017-REGID. SCS-R thanks FCT for PhD scholarship (Ref. SFRH/BD/147463/2019).

References:

1. Balestrino, R. and A.H.V. Schapira, Eur J Neurol, 2020. **27**(1): p. 27-42
2. Dorszewska, J., et al., Curr Genomics, 2014. **15**(1): p. 11-7
3. Sampaio-Dias, I.E., et al., Journal of Medicinal Chemistry, 2021. **64**(9): p. 6209-6220.
4. Sampaio-Dias, I.E., et al., ACS Chemical Neuroscience, 2021. **12**(1): p. 203-215.
5. Sampaio-Dias, I.E., et al., ACS Chemical Neuroscience, 2019. **10**(8): p. 3690-3702.
6. Ferreira da Costa, J., et al., Eur J Med Chem, 2013. **69**: p. 146-58.
7. Gasperi, V., et al., Int J Mol Sci, 2019. **20**(4).

Environment and water

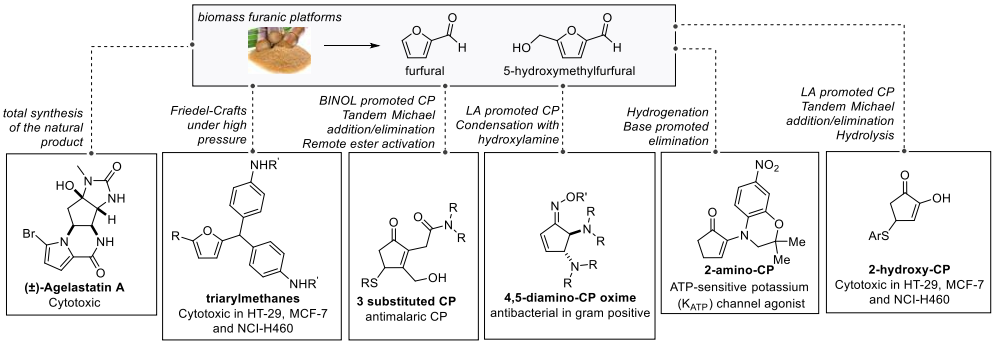
Diversity-oriented synthesis of biomass derived furanic platforms aiming at drug discovery

R.F.A. Gomes,[a] K. Andrade,[a] L. Cavaca,[a] V. Isca,[b] J. Coelho,[a] P. Rijo,[b] C. Afonso[a]

a) iMed.UL, Faculdadade de Farmácia da Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal; b) Universidade Lusófona,CBIOS – Universidade Lusófona's Research Center for Biosciences & Health Technologies, Campo Grande 376, 1749-024 Lisboa, Portugal.

Email: rafael.gomes@campus.ul.pt

The modification of simple synthons to structurally complex scaffolds has been a cornerstone of drug discovery and is the foundation of how nature designs biological relevant compounds.[1] This diversity-oriented synthesis (DOS) strategy has emerged on drug discovery programs to increase structural diversity to discover new targets. On the other hand, biomass synthons are looked upon has the solution for sustainability issues that plague the common bulk chemicals derived from oil.[2] Therefore the transformation of biomass synthons to relevant scaffolds is of importance to develop sustainable and cheap drug products. In this work is described a reagent-based DOS strategy, focused on the creation of complex scaffolds from biomass derived furanic platforms. These novel scaffolds exhibit relevant cytotoxic activity, antibacterial activity and antimalarial activity. [3] The versatility of the furanic platforms are showcased by i) the preparation of a cytotoxic natural occurring product, Agelastatin A; ii) preparation of cytotoxic 2-hydroxy-cyclopentenones(CP); iii) hydrogenation followed by elimination led to the preparation of and ATP-sensitive potassium channel agonist; iv) preparation of triarylmethanes under high pressure; v) furan activation with Meldrum's acid yielding complex CP; vi) diamino cyclopentenone and the corresponding oxime ethers exhibit antibacterial activity.



Acknowledgements: We thank the Fundação para a Ciência e a Tecnologia (PD/BD/143127/2019, PTDC/QUI-QOR/32008/2017 and UID/QUI/50006/2019), COMPETE Programme (SAICTPAC/0019/2015). The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 951996.

References:

1. a) Y. Wang, A. Madsen, F. Diness, M. Meldal, Chem. - A Eur. J. **2017**, 23, 13869–13874; b) N. Kato, E. Comer, T. Sakata-kato, A. Sharma, M. Sharma, M. Maetani, J. Bastien, N. M. Brancucci, J. A. Bittker, V. Corey, Nature **2016**, 538, 344–349; c) C. J. O. Connor, S. G. Beckmann, D. R. Spring, C. C. O. Connor, Chem. Soc. Rev. **2012**, 4444–4456.
2. A. Aden, J. Bozell, J. Holladay, P. Northwest, J. F. White, *US Dep. energy* **2004**, *1*.
3. a) R. F. A. Gomes, N. R. Esteves, J. A. S. Coelho, C. A. M. Afonso, *J. Org. Chem.* **2018**, *83*, 7509–7513.; b) R. F. A. Gomes, Y. Mitrev, S. Simeonov, C. A. M. Afonso, *ChemSusChem* **2018**, *11*, 1612–1616; c) R. F. A. Gomes, J. A. S. Coelho, C. A. M. Afonso, *ChemSusChem* **2019**, *12*, 420–425; d) R. F. A. Gomes, J. A. S. Coelho, R. F. M. Frade, A. F. Trindade, C. A. M. Afonso, *J. Org. Chem.* **2015**, *80*, 10404–10411.

Environment and water

Heptakis–aminocyclodextrin nanosponges for imidacloprid removal in aqueous media

G. Utzeri, D. Murtinho, A.J.M. Valente

University of Coimbra, Coimbra Chemistry Centre, Department of Chemistry, 3004–535 Coimbra, Portugal

Email: uc2015276036@student.uc.pt

The pesticide pollution is a serious environmental problem resulting from its massive application in agriculture, household, veterinary and silviculture. Studies shown that ca. 0.1% of agrochemicals reach the targets[1] contributing to soil, water and air pollution as well as high–cost implications. Additionally, indirect hazardous effects on biodiversity and human health must be considered due to pesticide bioaccumulation and bioaugmentation. At this regard, the development of novel technologies for pesticides decontamination and nanopesticide formulations is rising up. Sorbent materials and sorption processes have attracted increasing attention due to ease of application, possible reusability and promising cost-efficiency ratio. As reported in literature, a wide range of materials can be used for environmental remediation processes. Examples are metal oxides, zeolites, clays and activated carbon, which is still the most efficient material thanks to its impressive sorption capability. However, in recent decades, social and scientific concerns associated with nanotechnology application in agriculture have increased due to low stability, persistence in the environment, potential risk to the ecosystem, as well as high costs of the production process[2,3]. In order to overcome these limitations, eco-friendly materials captivated great attention[4]. Herein, β–cyclodextrin–based nanosponges (CD–NSs) were synthesized by microwave–assisted per–functionalization of pristine β–CD with two unconventional linkers, hexane–1,6–diamine (am_6)[5,6] and dodecane–1,12–diamine (am_{12}). More common classes of used linkers are i.e. dicarboxylic acid chlorides, acid anhydrides, diisocyanates, dicarboxylic acids, alkyl dihalides and chlorohydrins[7,8]. The synthesis of CD–am_6–CD and CD–am_{12}–CD has been confirmed by ^{1}H–NMR. Physico–chemical characterization was performed by different techniques such as, gas sorption analysis, dynamic light scattering (DLS) and ζ-potential, scanning electron microscopy (SEM), thermogravimetrical analysis (TGA)and infrared spectroscopy (FTIR). The sorption efficiency and the effect of the chain length of the linkers were assessed for imidacloprid. Sorption tests at solid/liquid ratio of 1 had demonstrated promising pesticide sorption capacities, 25.65 mg g^{-1} and 17.4 mg g^{-1} for CD–am_6–CD and CD–am_{12}–CD, respectively.

Acknowledgements: This work was funded by the Coimbra Chemistry Centre, which is supported by the Fundação para a Ciência e a Tecnologia (FCT) through the programmes UID/QUI/00313/2020 and COMPETE, and by Portuguese funds through FCT in the framework of the BLUEBIO project BIOSHELL-BLUEBIO/0003/2019. Gianluca Utzeri thanks the Ph.D. grant from Fundação Ciência e Tencologia (FCT) (reference: SFRH/BD/146358/2019), Ministro da Ciência, Tencologia e Ensino Superior (MCTES), Fundo Social Europeu (FSE) and União Europeia (UE).

References:

1. Pimentel, D. *J. Agric. Environ. Ethics* **1995**, *8*, 17.
2. Patil, S. S.; Shedbalkar, U. U.; Truskewycz, A.; Chopade, B. A.; Ball, A. S. *Environ. Technol. Innov.* **2016**, *5*, 10.
3. He, X.; Deng, H.; Hwang, H. *J. Food Drug Anal.* **2019**, *27*, 1.
4. Utzeri, G.; Verissimo, L.; Murtinho, D.; Pais, A. A. C. C.; Perrin, F. X.; Ziarelli, F.; Iordache, T.-V.; Sarbu, A.; Valente, A. J. M. *Molecules* **2021**, *26*, 1426.
5. Russo, M.; Saladino, M. L.; Chillura Martino, D.; Lo Meo, P.; Noto, R. *RSC Adv.* **2016**, *6*, 49941.
6. Puglisi, A.; Spencer, J.; Clarke, J.; Milton, J. *J. Incl. Phenom. Macrocycl. Chem.* **2012**, *73*, 475.
7. Sherje, A. P.; Dravyakar, B. R.; Kadam, D.; Jadhav, M. *Carbohydr. Polym.* **2017**, *173*, 37.
8. Pawar, S.; Shende, P.; Trotta, F. *Int. J. Pharm.* **2019**, *565*, 333.

Materials chemistry and applications

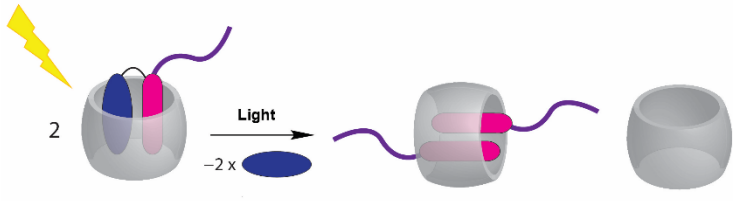
Remotely controlled host-guest assemblies in aqueous solution

Nuno Basílio,[a] A. J. Parola,[a] Uwe Pischel,[b]

a) Laboratório Associado para a Química Verde (LAQV), Rede de Química e Tecnologia (REQUIMTE), Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal; b) CIQSO - Center for Research in Sustainable Chemistry and, Department of Chemistry, University of Huelva, Campus de El Carmen s/n, 21071 Huelva, Spain

Email: nuno.basilio@fct.unl.pt

Supramolecular switches are important components for the realization of complex molecular machines and nanostructured functional materials. Amongst the most common binding pairs, host-guest systems are particularly attractive for the design of supramolecular switches owing to their predictable and controllable recognition properties. During the last years, our group has been interested in the discovery and development of water-soluble photoresponsive host-guest binding pairs foreseeing possible biological applications.[1-7] We focus mainly, but not only, on the use of photocaged and photochromic guests (such as flavylium compounds and dithienylethenes) to develop high-affinity photoresponsive hosts-guest system with water soluble macrocyclic receptors such as cucurbiturils, cyclodextrins and calixarenes. In this communication, I will highlight some of our recent work to illustrate how properly designed guest molecules can be explored to achieve control over the host-guest binding affinities / stoichiometries and how these systems can be explored to control the encapsulation of functional molecules such as drugs, fragrances, peptides, etc.



Scheme 1: Photocontrol over peptide dimerization inside a cucurbituril nanocontainer.[7]

Acknowledgements: This work was supported by the Associate Laboratory for Green Chemistry - LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/50006/2020). FCT/MCTES is also acknowledged for supporting the National Portuguese NMR Network (ROTEIRO/0031/2013-PINFRA/22161/2016, cofinanced by FEDER through COMPETE 2020, POCI, PORL, and FCT through PIDDAC) and for the grants PTDC/QUI-COL/32351/2017and CEECIND/00466/2017.

References:

1. Basílio, N.; Pischel, U. *Chem. - A Eur. J.* **2016**, 22, 15208.
2. Zubillaga, A.; Ferreira, P.; Parola, A. J.; Gago, S.; Basílio, N. *Chem. Commun.* **2018**, *54*, 2743.
3. Romero, M. A.; Fernandes, R. J.; Moro, A. J.; Basílio, N.; Pischel, U. *Chem. Commun.* **2018**, *54*, 13335.
4. Romero, M. A.; Mateus, P.; Matos, B.; Acuña, Á.; García-Río, L.; Arteaga, J. F.; Pischel, U.; Basílio, N. *J. Org. Chem.* **2019**, *84,* 10852.
5. Ferreira P.; Ventura B.; Barbieri A.; Da Silva J. P.; Laia C.; Parola A. J.; Basílio N. *Chem. Eur. J.* **2019**, *25*, 3477.
6. Colaço M.; Máximo P.; Parola A. J.; Basílio N. *Chem. Eur. J.* **2021** DOI:10.1002/chem.202100974
7. Fernandes R.; Remón P.; Moro, A. J.; Seco, A., Ferreira, A. S.; Pischel, U.; Basílio N. *J. Org. Chem.* **2021** (accepted)

Chemistry in life sciences

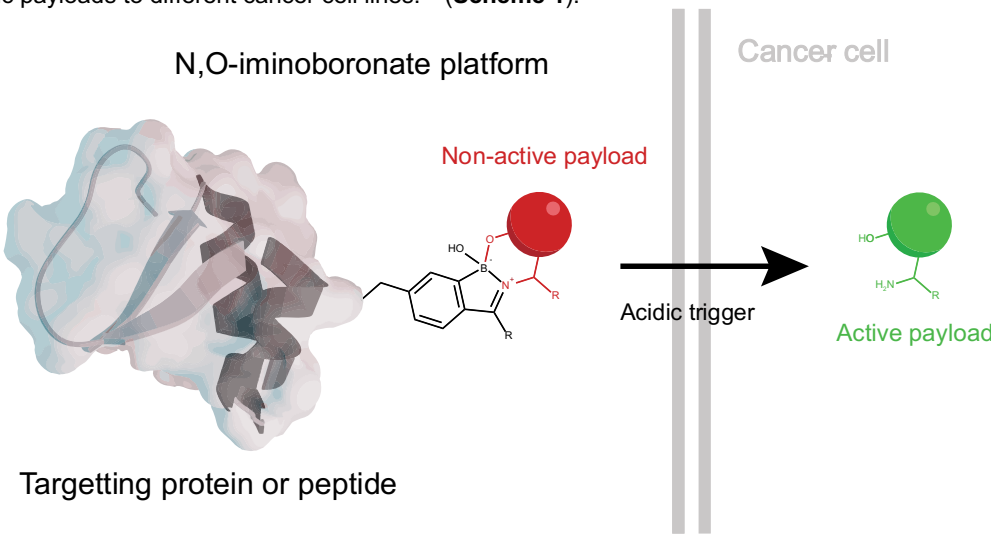
Iminoboronate platforms for the targeted delivery of cytotoxic and fluorogenic payloads into cancer cell lines

R.M.R.M. Lopes,[a] B. Carreira[a], A.E. Ventura,[a,b] L.C. Silva,[a,b] H. Faustino,[a] H. Florindo,[a] P.M.P. Gois[a]

a) Research Institute for Medicines (iMed.ULisboa) Faculty of Pharmacy, Universidade de Lisboa, Lisbon, Portugal; b) Centro de Química-Física Molecular and Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal.

Email: rmr.lopes@campus.fct.unl.pt

Herein we present a new class of iminoboronates[1,2] obtained from 2-acetylbenzene boronic acids and ortho-aminophenols. The N,O-ligand topology enabled the formation of an additional B-O bond that locks the boron centre in a tetrahedral geometry. This molecular arrangement decisively contributes to improve the construct stability in biocompatible conditions, retaining the iminoboronate reversibility in more acidic environments. 2-Acetylbenzene boronic acid was reacted with a fluorescent amino-coumarin to yield a stable and non-fluorescent N,O-iminoboronate. This mechanism was further used to assemble several targeting bioconjugates that selectively delivered fluorogenic and cytotoxic payloads to different cancer cell lines.[3] (**Scheme 1**).



Scheme 1 - N,O-iminoboronate conjugate to selectively deliver active amino-coumarin payloads into cancer cell lines.

Acknowledgements: We acknowledge the financial support of Fundação para a Ciência e a Tecnologia (FCT) Portugal (grants: SFRH/BD/121664/2016, LISBOA-01-0145-FEDER-029967 and PTDC/QUI-QOR/29967/2017

References:

[1] J. P. M. António, R. Russo, C. Carvalho, P. M. S. D. Cal, P. M. P. Gois, *Chem. Soc. Rev.*, **2019**, 48, 3513.
[2] P. M. S. D. Cal, J. B. Vicente, E. Pires, A. V. Coelho, L. F. Veiros, C. Cordeiro, P. M. P. Gois, *J. Am. Chem. Soc.* **2012**, 134, 10299.
[3] R. M. R. M. Lopes, A. E. Ventura, L. C. Silva, H. Faustino, P. M. P. Gois, *Chem. Eur. J.* **2018**, 24, 12495.

Culture and education

“Química ao pé da letra”: o encontro das palavras com o ensino e a divulgação da química

C. Morais [a], J. C. Paiva [a], J. L. Araújo [a], H. Vieira [a], M. Soares [b], L. Moreira [c]

a) CIQUP, UEC, DQB, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal; b) CECH-UC – Coimbra, Faculdade de Letras da Universidade de Coimbra, Largo da Porta Férrea, 3004-530 Coimbra, Portugal; c) CIQUP, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, s/n, 4200-465 Porto, Portugal;

Email: jose.araujo@fc.up.pt

A Química – o seu ensino e a sua divulgação – mantém, ainda, com a palavra uma intrínseca relação. Uma das abordagens que nos permitirá compreender melhor a química é a exploração das raízes das palavras que constituem o seu léxico. A etimologia permite por vezes ancorar os conceitos químicos e, ao mesmo tempo, ampliar o olhar histórico, filosófico, literário, contextual, social e cultural do mundo oferecendo caminhos alternativos para ensinar e comunicar esta ciência. No sentido de se estreitar os laços entre a química e as palavras, foi publicado pela Editora U.PORTO, com o apoio da SPQ e do Centro de Investigação em Química da U.PORTO, o livro “Química ao pé da letra” onde se apresenta a definição química e a exploração etimológica de 118 conceitos – tantos quantos os elementos químicos conhecidos – numa linguagem que conjuga o rigor científico com a simplicidade da comunicação, proporcionando ao leitor as ferramentas para tirar partido da riqueza lexical, que se tece entre as dimensões macroscópica, submicroscópica, representacional e contextual da química. Na obra, os conceitos químicos abordados conduzem o leitor através da história até a consolidação da química enquanto ciência que investiga a estrutura, as propriedades e as transformações da matéria ao nível atómico e molecular. A este propósito, a obra apresenta-nos, como não podia deixar de ser, o termo *Alquimia*, central no léxico histórico da química. Esta palavra deriva do árabe *Al-kimiya*. Na verdade, o termo *kimiya* designava a célebre “pedra filosofal”, tão procurada pelos filósofos árabes medievais do Sul da Europa, a qual teria a propriedade de transformar os metais em ouro. Olhando para a natureza da química, faz também sentido abordarmos a palavra *laboratório*, o local onde esta ciência se faz. O nome deste local de trabalho deriva do latim medieval *laboratorium*. Embora, na prática, labor, fabrico e ação sejam considerados sinónimos, Hannah Arendt, na obra *A Condição Humana* (1958/2001), distingue estes conceitos. Ao labor corresponderiam as funções orgânicas e naturais, como a alimentação diária. Seria da ordem do transitório e do perecível, como a renovação das gerações. Já o fabrico equivaleria à produção de obras, como uma cadeira ou um poema, ou a construção de uma casa. Finalmente, a ação diria respeito à palavra e ao relacionamento humano. Nesta ordem de ideias, o trabalho científico que decorre no laboratório teria o seu quê de provisório, renovando-se constantemente e, apenas pontualmente, dando origem a obras, isto é, as construções articuladas e coerentes sobre a realidade. A etimologia de alguns processos químicos é igualmente sugestiva. Por exemplo, na origem de catálise está o verbo grego *katalyo* e o substantivo cognato *katalysis*, formado pelo prefixo *kata-* (para baixo, contra) e o verbo *lyo* (desligar, soltar, libertar). Por conseguinte, o sentido inerente ao étimo grego é o de dissolver, deitar abaixo, destruir. A adoção da palavra grega (*κatalyo*) para designar o processo de aumento de velocidade de uma reação química implica a comparação do aumento de velocidade da reação química, por exemplo, à destruição de uma cidade e abolição (de um estado de coisas), de pôr um fim a, e, nesse sentido, causar a morte. Recorre-se, assim, a uma imagem analógica para tornar o aumento de velocidade de uma reação química mais compreensível. Com a publicação “Química ao pé da letra”, procurou-se, por um lado, tornar o universo da química mais acessível e relevante e, por outro, promover o debate sempre inacabado sobre a natureza da ciência e a sua relação com a sociedade perfilando-se uma ferramenta interessante para educadores e divulgadores da química. A aproximação ao léxico da química leva-nos ao fascínio de gostar de conceitos que ora estão tão presentes no dia a dia que quase nos passam despercebidos ou tão distantes do dia a dia que se tornam ameaçadores para quem deles pouco ou nada julga conhecer.

Agradecimentos: À Fundação para a Ciência e Tecnologia pelo apoio financeiro no âmbito do projeto UIDB/ 00081/2020 e a L. Moreira (PTDC/CED-EDG/31480/2017).

Flash Communications

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

Materials chemistry and applications

Modeling halogen bonds in molecular dynamics simulations of active pharmaceutical ingredients

Cátia S. D. Lopes, Carlos E. S. Bernardes, Manuel E. Minas da Piedade

CQE, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

Email: csolopes@fc.ul.pt

Many of the active pharmaceutical ingredients (APIs) available on the market today have halogen substituents. These promote non-covalent interactions (e.g., hydrogen and halogen bonds), which can enhance the API properties (e.g., membrane permeability). Hence, a strategy to design new promising APIs is to include halogen atoms within their structure. A cheaper and quicker method to test all the promising APIs during the early stages of drug development is through *in-silico* screenings.[1]

To perform these studies several theoretical methods can be used, such as molecular dynamic (MD) simulations. This methodology relies on molecular force fields that must accurately capture the energetic and structural information of a substance. When applied correctly, this can be used to predict the APIs properties, such as the different solid forms that may arise during the crystallization process of a given molecule (polymorphs). Nevertheless, a prior validation of the force field used needs to be performed. This is based on theoretical predictions of enthalpies of sublimation and unit cell parameters that are compared with experimental results. Structural information can be easily found on the Cambridge Structural Database (CSD) for this validation, however the energetic data that can be correlated to a given crystal phase is rarely found in the literature, particularly for halogenated compounds.[2] In this work, the determination of reference values of enthalpies of sublimation, by Calvet-drop microcalorimetry, for well-characterized single-crystal structures of three halogenated APIs (Figure 1) is described. These results were used to test OPLS-AA based force fields, to determine their ability to accurately describe halogen bonding in solid phases.

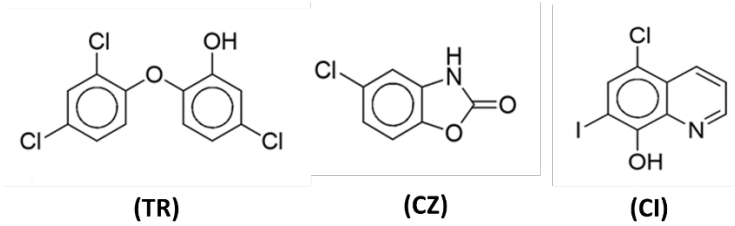


Figure 1: Halogenated APIs investigated in this work: (TR) Triclosan; (CZ) Chlorzoxazone and (CI) Clioquinol.

Acknowledgements: We thank the Fundação para a Ciência e a Tecnologia (FCT) Portugal for financial support (projects PTDC/QUI-OUT/28401/2017, LISBOA-01-0145-FEDER-028401, UIDB/00100/2020, and UIDP/00100/2020). A PhD grant from FCT is also gratefully acknowledged by Cátia S. D. Lopes (SFRH/BD/128794/2017).

References:

1. a) Ford M. C.; Ho P. S. *J. Med. Chem.* **2016**, *59*, 1655. b) Santos L. A.; Prandi I. G.; Ramalho, T. C. E. *Front. Chem.* **2019**, 7: 848.

2. a) Bernardes C. E. S.; Joseph A. *J. Phys. Chem. A* **2015**, *119*, 3023. b) Bernardes C. E. S.; Donato M. T.; Piedade M. F. M.; Diogo Hermínio P.; Lopes J. N. C.; Minas da Piedade M. E. *J. Chem. Thermodynamics* **2019**, *113*, 60.

Materials chemistry and applications

Multi-composition biocompatible catanionic vesicles for the encapsulation and delivery of doxorubicin

Rui L. Machado,[a] Karenina Santos,[a] Isabel S. Oliveira,[a] Andreia C. Gomes,[b] Eduardo F. Marques,[a]

a) CIQUP, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre P-4169-007 Porto, Portugal; b) CBMA – Centro de Biologia Molecular e Ambiental, Departamento de Biologia Universidade do Minho, Campus de Gualtar 4710-057 Braga, Portugal

Email: efmarque@fc.up.pt

Drug delivery is an ever-growing scientific field with a constant demand for new drug carriers with improved stability, cytotoxic profiles and encapsulation efficiencies. Self-assembled colloidal systems have been widely used as nanocarriers due to the varied supramolecular structures that they form (tubules, vesicles, micelles, etc.).[1] Cationic/anionic surfactant mixtures (catanionic mixtures) can spontaneously form vesicles with improved stability, and tunable size and charge controlled by the surfactant mixing ratio, which makes them appealing candidates for drug delivery.[2] In the present work, our aim was to carry out the structural characterization and evaluation of the cytotoxic properties of selected catanionic vesicles, and assess their ability to encapsulate the anti-cancer drug doxorubicin (DOX), **Figure 1**. The catanionic vesicle systems are composed by common commercial surfactants, synthesized gemini and novel amino acid-based surfactants. Generally, it was found by DLS that these multi-composition vesicles exhibit a very diverse mean diameter, high polydispersity and high colloidal stability. By surface tension, the *critical aggregation concentration* values were found to be on the order of 10^{-6} mol·dm^{-3}, indicative of strong interfacial synergism between the surfactants. Cytotoxicity studies were performed on the L929 cell line (mouse fibroblasts) by the lactate dehydrogenase enzyme (LDH) release and resazurin assays in order to determine the IC50 values. In general, the less cytotoxic catanionic mixtures were those consisting of amino acid-derived surfactants. The systems with higher biocompatibility were then selected to test their encapsulation efficiency towards DOX.

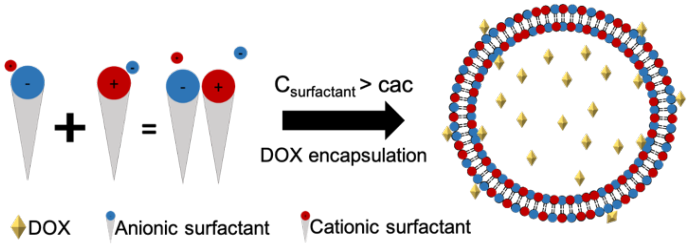


Figure 1: Surfactant interaction in a catanionic mixture, vesicle formation and DOX encapsulation

Acknowledgements: We thank Fundação para a Ciência e Tecnologia, FEDER/COMPETE and P2020|COMPETE for financial support through projects UIDB/00081/2020 and UID/QUI/50006/2019.

References:

1. a) Oliveira, I. S.; Lo, M.; Araújo, M. J.; Marques, E. F., Soft Matter **2019**, 15, 3700. b) Oliveira I. S.; Machado R. L.; Araújo M. J.; Gomes A. C.; Marques E. F., *Chem. Eur. J.* **2021**, *27*, 692. c) Silva, S.; do Vale, M. L.; Marques, E. F., *Chem. Eur. J.* **2015**, *21*, 4092.

2. a) Gonçalves Lopes R. C. F.; Silvestre O. F.; Faria A. R.; Vale M. L. C.; Marques E. F.; Nieder J. B., *Nanoscale* **2019**, *11*, 5932. b) Marques, E. F., Langmuir, **2000**, 16, 4798. c) Dhawan, V. V.; Nagarsenker, M. S., J. Control. Release, **2017**, 266, 331.

Materials chemistry and applications

Supported ionic liquid materials for L-asparaginase bioconjugation

João C. F. Nunes,[a] Mafalda R. Almeida,[a] Valéria C. Santos-Ebinuma,[b] Márcia C. Neves,[a] Mara G. Freire,[a] Ana P. M. Tavares[a]

a) Department of Chemistry, CICECO-Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal; b) School of Pharmaceutical Sciences, Universidade Estadual Paulista-UNESP, Araraquara 14800-903, Brazil

Email: jcfn@ua.pt

Since the average life expectancy is increasing, several fatal diseases usually related to aging, such as cancer, heart and neurological diseases have become predominant. Biopharmaceuticals, namely nucleic-acid-based products, antibodies, recombinant proteins and enzymes are fundamental to overcome these age-related diseases. Actually, the gold standard enzyme for the treatment of acute chronic lymphoblastic leukemia (ALL) is L-asparaginase (ASNase). Hence, the reusability of this high-priced drug enables the cost reduction of treatments, which allows its routinely use by a widespread population.

In this work, functionalized nanomaterials, namely supported ionic liquid materials (SILs) based on silica, formerly described in the literature for the separation of natural compounds from vegetable biomass [1], were studied as a cost-effective support for ASNase immobilization and reuse. Commercial ASNase was used for preliminary tests. Several experimental immobilization conditions, such as pH, contact time, ASNase concentration and SILs recyclability were assessed and optimized, regarding the immobilized ASNase activity, assessed by Nessler reaction, which quantifies the amount of ammonium released after the enzymatic reaction with L-asparagine [2] and immobilization yield. In fact, ASNase immobilization onto the SILs was successfully achieved with an immobilized ASNase activity ranging from 0.6 to 0.9 U of enzyme per mg of SILs under the optimum immobilization conditions. Moreover, all SILs allowed 5 cycles of reaction, while keeping more than 75% of initial ASNase activity. Through the envisioned immobilization strategy, process costs will be considerably reduced, which can lead to a wider use of ASNase in diverse fields of application.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the Fundação para a Ciência e Tecnologia/ Ministério da Educação e Ciência (FCT/MEC) and when appropriate co-financed by Fundo Europeu de Desenvolvimento Regional (FEDER) under the PT2020 Partnership Agreement and project POCI-01-0145-FEDER- 031268 funded by FEDER, through COMPETE2020-Programa Operacional Competitividade e Internacionalização (POCI), and by national funds (OE), through FCT/MCTES. Valéria C. Santos-Ebinuma acknowledges FAPESP (2018/06908-8) for financial support. Márcia C. Neves acknowledges FCT, I.P. for the research contract CEECIND/00383/2017 under the CEEC Individual 2017. Ana P. M. Tavares acknowledges the FCT Investigator Programme and Exploratory Project (IF/01634/2015) with financing from the European Social Fund and the Human Potential Operational Programme. João C. F. Nunes acknowledges Sociedade Portuguesa de Química (SPQ) and FCT for the PhD fellowship (SFRH/BD/150671/2020).

References:

1. Pereira M. M.; Coutinho J. A. P.; Freire M. G. *RSC Green Chemistry.* **2016**, 36, 227-257.
2. Magri A. et al. *Analytical and Bioanalytical Chemistry.* **2018**, 410, 6985-6990.

Materials chemistry and applications

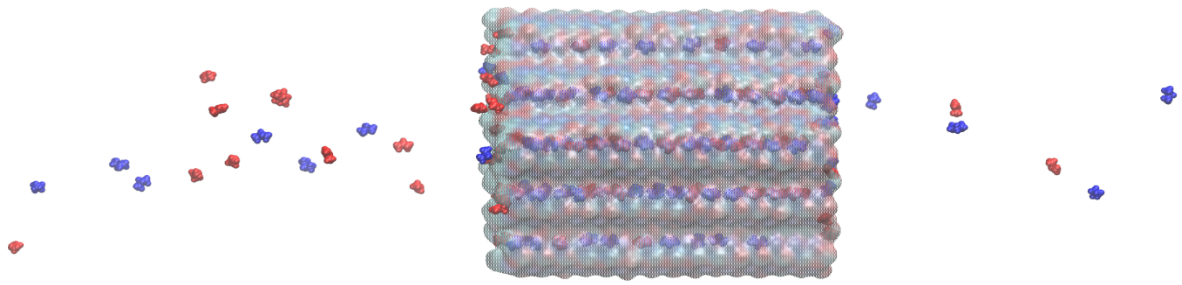
Molecular dynamics studies of dipeptide nano-pores as a membranes for gas storage and separation

K. Biernacki[a], J. Lopes[a], L. Gales[b,c], A.L. Magalhães[a]

a) LAQV/REQUIMTE, Faculdade de Ciências, Universidade do Porto, Porto, PT; b) I3S, Instituto de Investigação e Inovação em Saúde/IBMC, Porto, PT; c) ICBAS, Instituto de Ciências Biomédicas Abel Salazar, Universidade do Porto, PT, Portugal

Email: kbiernacki@fc.up.pt; almagalh@fc.up.pt

Propylene is a very important raw material in the petrochemical industry. A key step in its production is propane/propylene separation, where energy consumption and the degree of propylene recovery achieved due to their similarity have a strong impact on the economy of the process. The separation processes are typically very demanding in terms of energy, due to the physical and chemical similarities of these two gases.[1] Therefore, the separation process of such closely related organic molecules is a big challenge. Propylene is slightly smaller in cross-section than propane, so it is more readily adsorbed into pores of an appropriate size.
For the exposed above, it is not surprising that suitable materials for gas storage and separation are still under investigation. In the present work, the nanopores of dipeptides are investigated. This is a type of material whose crystal structures show well-defined pores at the nanometer scale, suitable for separation purposes, and that are environmentally friendly, thus making them promising materials with potential industrial applications.[2]
Molecular Dynamics (MD) simulations were performed which is a valuable computational tool to complement data gathered by experimental studieson thermodynamics, mechanical and transport properties.[2] In this work, GROMACS 5.1.5 software, employing the General Amber Force Field (GAFF), has been used to perform molecular dynamics simulations. In a first step, the system of 9 nanopores of the self-assembly dipeptides and the mixture of gases were equilibrated separately using molecular dynamics (MD) simulations, and then both systems were merged (Scheme 1.) and studied using non-equilibrium molecular dynamics (NEMD).
The theoretical results compare well with experimental studies and reveal the role of the molecular interactions in the adsorption differentiation. Moreover, the data collected suggest the ability of these porous materials to achieve efficiency in gas separation processes. Moreover, a special emphasis on the geometry of the crystal channels has been started in this project because it was found that gas separation is highly dependent on the diameter of the nanopores.



Scheme 1. Gaseous feed mixture

Acknowledgements: This work was financed by National Funds through FCT/ MCTES within the framework of Project PTDC/QUI-QFI/29914/2017.

References:

1. J. A. D. Dobladez, V. I. Á. Maté, S. Á. Torrellas, M. Larriba, Comput. Chem. Eng. **2020**, 136, 106717.
2. K. Biernacki, S.F. Sousa, L. Gales, M.J. Ramos and A.L. Magalhaes, Chemistryselect, **2018**, 3(20), 5517.

Materials chemistry and applications

Conducting neutral bis(1,2-dithiolene) gold complex [Au(dspdt)$_2$] with a unique crystal structure

Mariana F. G. Velho,[a,b] Rafaela A. L. Silva,[a] Graça Brotas,[a] Elsa B. Lopes,[a,c] Isabel C. Santos,[a,c] Ana Charas,[b] Dulce Belo,[a,c] Manuel Almeida[a,c]

a) Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, E.N. 10, 2695-066 Bobadela LRS, Portugal; b) Instituto de Telecomunicações, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal; c) Departamento de Engenharia e Ciências Nucleares, Instituto Superior Técnico, Universidade de Lisboa, E.N. 10, 2695-066 Bobadela LRS, Portugal

Email: mariana.velho@ctn.tecnico.ulisboa.pt

The first reported Single Component Molecular Metals (SCMM) were the neutral bis(1,2-dithiolene) transition metal complexes [Ni(tmdt)$_2$] (tmdt: trimethylenetetrathiafulvalenedithiolate)[1] and [Au(α-tpdt)$_2$] (α-tpdt: 2,3-thiophenedithiolate)[2] (Figure 1). SCMM are organic based small neutral molecules that display a metallic behaviour, arising from the intermolecular interactions in the solid state. Additionally, these materials offer the possibility of being multifunctional, combining in the same material several physical properties.

Here we present [Au(dspdt)$_2$] (dspdt: 2,3-dihydro-5,6-selenophenedithiolate, Figure 1),[3] a derivative of [Au(α-tpdt)$_2$] that replaces the thiophene ring for a dihydroselenophene moiety, which could improve the solid state interactions and thus the transport properties. [Au(dspdt)$_2$] revealed an unprecedent crystal structure composed by interacting dimer and trimer columns. [Au(dspdt)$_2$] revealed in single crystal a semiconducting behaviour with a relatively high room temperature electrical conductivity of 0.1 S cm^{-1} and low activation energy of 95 meV. The electronic band structure was determined using an extended Hückel approach and showed that the interaction between chains of dimers and trimers leads to a combination of mixed trimer and dimer parallel bands considerably split and partially overlapping, with the Fermi level crossing four central bands. This new mechanism to high electrical conductivity may explain the conducting metallic properties observed in other neutral gold complexes with small organic ligands, such as [Au(α-tpdt)$_2$].

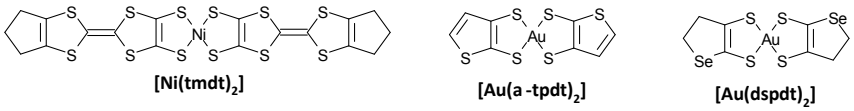


Figure 1: Chemical structures of gold bisdithiolene complexes [Ni(tmdt)$_2$], [Au(α-tpdt)$_2$] and [Au(dspdt)$_2$].

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support through Contracts UIDB/04349/2020, UIDB/50008/2020 and PTDC/ QUI-QIN/29834/2017 and PhD grant PD/BD/135314/2017 to Mariana F. G. Velho.

References:

1. Tanaka H.; Okano Y.; Kobayashi H.; Suzuki W.; Kobayashi A. *Science*, **2001**, *291*, 285.
2. Belo D.; Alves H.; Lopes E. B.; Duarte M. T.; Gama V.; Henriques R. T.; Almeida M.; Pérez-Benítez A.; Rovira C.; Veciana J. *Chem. Eur. J.*, **2001**, *7*, 511.
3. Velho M. F. G.; Silva R. A. L.; Brotas G.; Lopes E. B.; Santos I. C.; Charas A.; Belo D.; Almeida M. *Dalt. Trans.*, **2020**, *49*, 13737.

Materials chemistry and applications

Bio-inspired films based on Buxus sempervirens

André Pinto[a], A.L. Crespi[b], V. de Zea Bermudez[a], M. Fernandes[a]

a) CQ-VR and Chemistry Department, University of Trás-os-Montes e Alto Douro (UTAD), 5000-811 Vila Real, Portugal, b) Herbarium and Botanical Garden, CITAB, Department of Biological and Environmental Engineering, UTAD, 5000-811 Vila Real, Portugal

Email: vbermude@utad.pt

The development of bio-inspired materials and devices with superhydrophobicity and self-cleaning properties is of crucial importance for the coating industry. Many surfaces in Nature, such as plants leaves, are highly hydrophobic and exhibit self-cleaning ability. Green plants are characterized by a diversity of hierarchical surface structures and can be employed as models for the development of biomimetic surfaces [1].
This work is focused on the adaxial (upper) and abaxial (lower) surfaces of the leaflet of the Buxus sempervirens [3] at different growth stages (Figure 1) [2]. The fresh plant material was collected at the Botanical Garden of UTAD. The wettability of the leaf was quantified by means of static contact angle (CA) measurements, using the sessile drop method, performed in different locations of the adaxial and abaxial surfaces. The waxes of the intracuticular and epicuticular wax layers were extracted and quantified. The morphology was analysed by Polarized Optical Microscopy (POM) and Scanning Electronic Microscopy (SEM). To mimic the surface featuring the highest hydrophobic behaviour, a templation approach was adopted using a soft polymer/siloxane replica produced by the sol-gel process [4,5].

Figure 1: Buxus sempervirens at different growth stages (abaxial side on the left, adaxial side on the right).

Acknowledgements: This work was funded by the R&D Project PORPLANTSURF - Superhydrophobic films inspired in the surface of plant leaves and petals from Northern Portugal, POCI-01-0145-FEDER-029785, financed by the European Regional Development Fund (ERDF) through COMPETE 2020 - Operational Program for Competitiveness and Internationalization (POCI) and by the Foundation for Science and Technology (FCT). The author acknowledges CQ-VR for financial support UID/QUI/00616/2013 and UID/QUI/00616/2019. M. Fernandes acknowledges FCT-UTAD for the contract in the scope of Decreto-Lei 57/2016 – Lei 57/2017.

References:

[1] Barthlott W., Mail M., Bhushan B., Koch K, Nano-Micro Lett (2017) 9.

[2]Gou X, Guuo Z, Langmuir 2019, 35, 1047.

[3] https://jb.utad.pt/especie/Buxus_sempervirens

[4] de Zea Bermudez, V., Carlos, L.D., Alcácer, L, Chem. Materi. **1999**, 11, 569.

[5] Rodríguez S. Rocha J., Fernandes M., Ravishankar A. P., Steinbrück N., Cruz R., Bacelar E., Kickelbick G., Anand S., Crespí A. L., Casal S., de Zea Bermudez V., *Langmuir*, 37(6), 2021, 2011-2028.

Materials chemistry and applications

Binary Fe(III) and Mn(III) porphyrin materials with catalase-like activity

Mariana B.M.S. Martins,[a] Craig J. Medforth,[a,b] Susana L.H. Rebelo,[a] Baltazar de Castro[a]

a) LAQV-REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto; b) Department of Chemistry, University of California, One Shields Avenue, Davis, California 95616, USA

Email: marianabmsmartins@gmail.com

Catalase enzymes are crucial antioxidants that regulate the concentration of reactive oxygen species (ROS), therefore preventing oxidative stress in cells and tissues. In this work, we prepared binary structures in water by ionic self-assembly of oppositely charged Fe(III) and Mn(III) porphyrins, and evaluated them as catalase models. The biomimetic materials contained a positively charged porphyrin with 4-pyridinium substituents (THPyP), and a negatively charged porphyrin, tetrakis(4-sulfonatophenyl)porphyrin (TSPP). Significantly better catalytic performance was observed for binary structures in comparison with the individual metalloporphyrins.[1]
The catalytic activity of binary porphyrin materials was assessed in different conditions by measuring the O_2 volume produced in H_2O_2 dismutation reaction. The experiments were performed at different pH values and using binary structures at different stabilization times in the reaction media. The structure MnTHPyP:FeTSPP showed the highest catalase-like activity, whereas for structures with Mn(III) in the negative porphyrin low catalytic activity was observed. For every composite material, catalytic activity was stable from pH 4 to pH 6. We also tested binary structures composed of a metalloporphyrin and a non-metalated porphyrin. The results point out for a bimetallic interaction with mechanistic relevance, as these latter structures barely showed catalase-like activity. Further studies are being performed to fully understand the contribution of each metalloporphyrin to the catalytic mechanism.

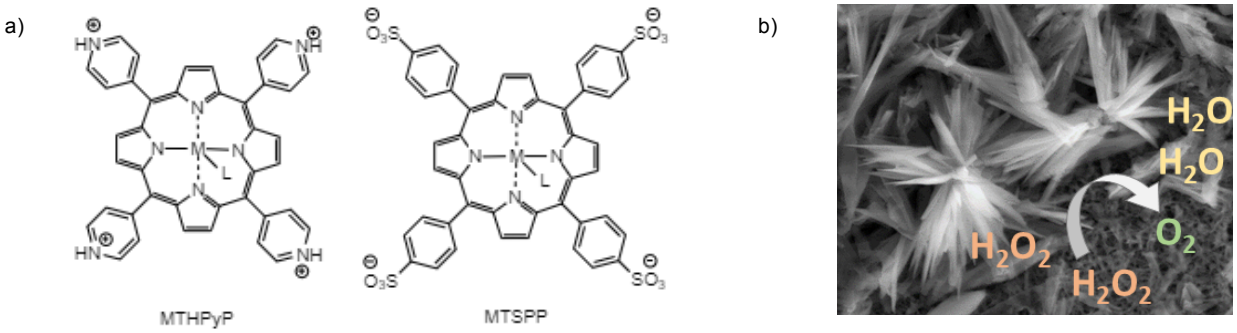


Figure 1: a) Porphyrins used in the preparation of binary structures by ionic self-assembly, where M represents Fe(III) or Mn(III). b) SEM image of the structure FeTHPyP:FeTSPP.

Acknowledgements: We thank FCT/MCTES (Fundação para a Ciência e Tecnologia/Ministério da Ciência, Tecnologia e Ensino Superior) for financial support through the project UIDB/50006/2020 and REQUIMTE/EEC2018/30 (SLHR).

References:

1. Rebelo, S. L. H.; Neves, C. M. B.; de Almeida, M. P.; Pereira, E.; Simoes, M. M. Q.; Neves, M. G. P. M. S.; de Castro, B.; Medforth, C. J., Binary ionic iron(III) porphyrin nanostructured materials with catalase-like activity. *Applied Materials Today* **2020,** *21*, 100830.

Materials chemistry and applications

Sol-gel derived electrolytes for prototype ECDs

Joana Nunes[a], Paulo Nunes[a], Rui F.P. Pereira[b], S.Pereira[c], E. Fortunato[c], M.M. Silva[b], V. de Zea Bermudez,[a] M. Fernandes[a]

a) CQ-VR and Chemistry Department, University of Trás-os-Montes e Alto Douro (UTAD), 5000-811 Vila Real, Portugal, b) Centre of Chemistry, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal; c) Department of Materials Science /CENIMAT, Faculty of Sciences and Technology of the New University of Lisbon, Campus of Caparica, 2829-516 Caparica, Portugal

Email: vbermude@utad.pt

In the last few years it has been demonstrated that electrochromic devices (ECDs) offer great prospects for the future nearly zero-energy performance building, since these windows allow the control of the transmittance of sunlight (visible radiation) and solar heat (near infrared (NIR) radiation) into a building. About 50% of the whole solar energy belongs to the NIR region. Nowadays it is accepted that the control of the vis and NIR regions of the solar spectrum is a key target for the development of advanced ECDs for the next generation of smart windows. The ECDs introduced in this work comprises a multilayer structure, sandwiched between glass plates, and prepared with TCO transparent conducting oxide, e.g., indium zinc oxide, IZO) layers, an active electrode layer (e.g., cathodic tungsten oxide (WO_3), an ion conducting electrolyte/separator, and an ion storage electrode. Aiming the production of NIR emitting ECDs for smart windows of buildings located in cold climate regions, electrolytes doped with erbium salts [1] and an erbium complex [2] were reported. Herein we prepared sol-gel derived transparent and thin di-ureasil [3] electrolyte films. With the goal of further increasing the ionic conductivity, we incorporated, apart from erbium complex, the 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) ionic liquid (ILs). ILs are extremely interesting compounds in the context of energy materials, [Bmim]Cl was chosen because it is practically non-toxic, and has high hydrogen bonding basicity associated with the high tendency of the chloride ion to form hydrogen bonds with other species [4]. The electro-optical performance of the glass/IZO/WO_3/electrolyte/IZO/glass ECDs was studied.

Acknowledgements: This work was funded by the R&D Project “SOLPOWINS – Solar-Powered Smart Windows for Sustainable Buildings”, with reference PTDC/CTM-REF/4304/2020, financed by the Foundation for Science and Technology (FCT).The authors acknowledge CQ-VR (UID/QUI/00616/2013 and UID/QUI/00616/2019) and CQ-UM (Pest-C/QUI/UI0686/2020) for financial support. P. Nunes acknowledges CQ-VR/ FCT for a grant. M. Fernandes acknowledges FCT-UTAD for the contract in the scope of Decreto-Lei 57/2016 – Lei 57/2017.

References:

[1] Nunes S.C., Saraiva S.M., Pereira R.F.P., Pereira S., Silva M.M., Carlos L.D., Fortunato E., Ferreira R.A.S., Rego R., de Zea Bermudez V. *ACS Applied Energy Materials* **2019**.

[2] Fernandes M., Freitas V.T., Pereira S., Leones R., Silva M.M., Carlos L.D., Fortunato E., Ferreira R.A.S., Rego R., de Zea Bermudez V., *Energies*, **2018**.

[3] de Zea Bermudez, V., Carlos, L.D., Alcácer, L, Chem. Materi. **1999**, 11, 569.

[4] Gonçalves M.C., Pereira R.F.P., Alves R., Nunes S.C., Fernandes M., Gonçalves H.M.R., Pereira S., Silva M.M., Fortunato E., Rego R., de Zea Bermudez V., Front. Mater., **2020**, 7, 139.

Materials chemistry and applications

Visible light-driven photocatalytic synthesis of imines assisted by carbon nitride

Joana C. Lopes, Maria J. Sampaio, Joaquim L. Faria, Cláudia G. Silva

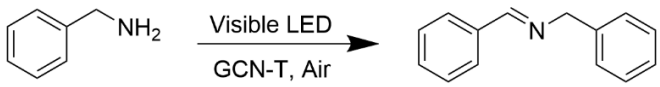
Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal

Email: joanacl@fe.up.pt

Discovering new synthetic routes for chemicals and materials is the basis for human development. Imines and their derivatives lay a significant role in pharmacophores, fragrances and numerous biologically active compounds. Moreover, imines are an active intermediate for synthesising various fine chemicals, biological intermediates, and molecular motors and can participate in several important reactions such as reductions, additions, condensations and cycloadditions. Due to their wide application in many fields, the synthesis of imines has gained attention in recent years.

Multiple strategies have been successfully employed to synthesise imines, namely the condensation of aldehydes and amines, oxidative coupling of alcohols and amines, and direct oxidation of amines. The synthesis of imines generally requires long reaction times, dehydrating agents, Lewis acid catalysts and extremely reactive aldehydes that make handling difficult [1]. The direct oxidation of amines (Scheme 1) has become one of the most attractive routes. However, the traditional reaction for the oxidative coupling of amines is characterised by costly noble metal catalysts and high temperature and O_2 pressure [2]. In this way, photocatalysis appears as a novel alternative for synthesising this family of organic compounds since it is environmentally friendly and straightforward as a reaction strategy, owing to the possibility of operating under mild conditions, being activated by solar light, and generate low amounts of undesirable by-products.

A metal-free carbon nitride catalyst (GCN-T) was used for the photocatalytic selective synthesis of imines in the present work. Different reaction conditions will be explored to understand the photocatalytic pathway of the oxidative coupling of amines to the corresponding imines.



Scheme 1: Photocatalytic synthesis of N-benzylidenebenzylamine via the coupling of benzylamine using GCN-T as the catalyst.

Acknowledgements: This work was financially supported by Base Funding - UIDB/50020/2020 of the Associate Laboratory LSRE-LCM - funded by national funds through FCT/MCTES (PIDDAC) and by projects POCI-01-0145-FEDER-031268 and POCI-01-0145-FEDER-030674, funded by European Regional Development Fund (ERDF) through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. JCL acknowledges the research grant from FCT (Ref. 2020.04651.BD).

References:

1. Largeron, M., Protocols for the Catalytic Oxidation of Primary Amines to Imines. *Eur. J. Org. Chem.* **2013,** *2013* (24), 5225-5235.
2. a) Zhu, B.; Lazar, M.; Trewyn, B. G.; Angelici, R. J., Aerobic oxidation of amines to imines catalyzed by bulk gold powder and by alumina-supported gold. *J. Catal.* **2008,** *260* (1), 1-6. b) Biswas, S.; Dutta, B.; Mullick, K.; Kuo, C.-H.; Poyraz, A. S.; Suib, S. L., Aerobic Oxidation of Amines to Imines by Cesium-Promoted Mesoporous Manganese Oxide. *ACS Catal.* **2015,** *5* (7), 4394-4403.

Materials chemistry and applications

Application of coal fly ash in wastewater treatment

Iwona Kuźniarska-Biernacka[a], Ana Cláudia Santos[b], Alexandra Guedes[b], Bruno Jarrais[a], Andreia F. Peixoto[a], Bruno Valentim[b], Cristina Freire[a]

[a] *REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal*

[b] *Earth Science Institute – Porto pole, Department of Geosciences, Environment and Spatial Plannings, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, 4169– 007 Porto, Portugal*

Email: iwonakb@fc.up.pt

Coal fly ash (CFA) is a solid by-product resulting from coal combustion in thermal power plants that is captured from flue gas by particulate control systems (e.g., cyclones, electrostatic precipitators and baghouse filters). The CFA it is a very complex material whose features (physical and chemical) vary according to the feed coal, the combustion conditions and the location of the collecting systems. However, the main components of CFA are oxides such as SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, Na_2O, TiO_2, and variable amounts of unburned carbon (e.g., char, soot) [1]. Meanwhile, the extensive use of 4-Nitrophenol (4-NPh) in industrial applications makes this compound a common water contaminant [2], which can be removed from wastewater by catalytic reduction with the advantage of producing valuable 4-aminophenol (4-APh). However, to make the process economically desirable the cheap, easily available and facile recyclable material CFA was considered in this study. For that purpose, bulk CFA (bulk), its magnetic and non-magnetic fractions were applied as catalyst for 4-NPh reduction in water solution, at room temperature, in the presence of $NaBH_4$ as H_2 source. Before and after the experiments, the CFA samples were characterized by X-ray fluorescence, Scanning Electron Microscopy with Energy Dispersive Spectroscopy and Raman microspectroscopy. The catalytic reduction of 4-NPh to 4-APh by CFA based catalysts was initiated by addition of $NaBH_4$, and a continuous decrease in the nitrophenolate peak at 400 nm with an increase in a new peak at 300 nm correspondent to 4-APh, was observed (**Figure 1**). The results show that all samples can be successfully used in reduction of 4-NPh to 4-APh without activity lost up to 5 cycles, implying a very good stability of the catalysts. However, the activation of the CFA magnetic sample with particle size <75 μm by washing with $NaBH_4$ or NaOH shortened the time needed to total conversion of 4-NPh from 180 min (not treated sample) to 30 and 5 min for sample activated by washing with $NaBH_4$ and NaOH respectively. It is concluded that the magnetic fractions of CFA are very promising catalysts for the chemical industry regarding organic product synthesis (4-APh) since these materials are effective without the need to add any additional doping by noble metals, are abundant and easy to concentrate via magnetic separation, and are cheap.

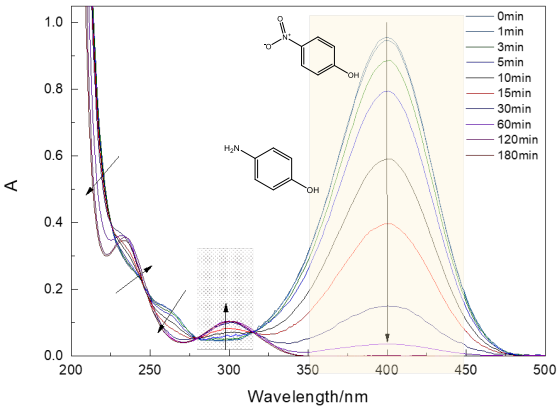


Figure. 1 Change of UV–Vis spectrum of 4-NPh during the reduction to 4-APh

Acknowledgements: The work was supported through the project UIDB/50006/2020, funded by FCT/MCTES through national funds as well as FCT/MEC research project REALM — Reactive Learning Machines (ref. PTDC/QUI-QIN/30649/201), and project CHARPHITE of the 3rd ERA-MIN Program 2015 (FCT ref. ERA-MIN/0005/2015). IK-B thanks FCT for funding through program DL 57/2016 – Norma transitória REQUIMTE/EEC2018/14, and ACS thanks FCT for PhD scholarship Ref: SFRH/BD/131713/2017.

References:

1. Valentim, B.; Białecka, B.; Gonçalves, P. A.; Guedes, A.; Guimarães, R.; Cruceru, M.; Całus-Moszko, J.; Popescu, L. G.; Predeanu, G.; Santos, A.C., Minerals **2018**, *8* (4), 140.

2. Nemanashi, M.; Meijboom, R., *J. Colloid Interf. Sci*., **2013**, *389* (1), 260.

Chemistry in life sciences

Development of novel thiazole-based inhibitors: targeting necroptosis and RIPK1

L. Fidalgo[a], R. Moreira[a], C. Rodrigues[a], A.S. Ressurreição[a]

a) iMed.ULisboa, Faculdade de Farmácia, Universidade de Lisboa. Av. Professor Gama Pinto, 1649-003 Lisboa, Portugal.

Email: lgfidalgo@ff.ulisboa.pt

Necroptosis, a regulated form of necrosis, is the major mechanism of cellular death upon extracellular inflammatory signalling and is crucially dependent on the kinase activity of RIPK1 and its downstream mediators: RIPK3 and pseudokinase MLKL. Consequently, RIPK1 has emerged as a promising therapeutic target for the treatment of a wide range of human neurodegenerative, autoimmune, and inflammatory diseases.[1-3]
To address the lack of chemotypes targeting necroptosis and RIPK1, iMed.ULisboa recently developed a phenotypic high-throughput screening strategy to identify novel necroptosis inhibitors.[4] This collaborative effort led to the discovery of promising new compounds possessing different scaffolds from those reported in the literature (**Figure 1)**.
Taking into account the gathered knowledge, and following Computer-Aided Drug Design (CADD) investigations, we have synthetized a highly diversified library of thiazole-based analogues in order to identify structural features responsible for RIPK1's potency and selectivity.

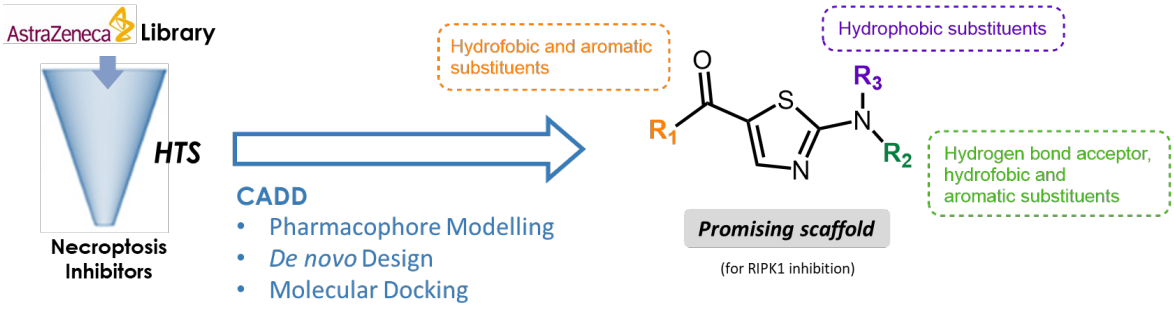


Figure 1. Identification of novel necroptosis inhibitors targeting RIPK1. Probing the chemical space around the thiazole's scaffold.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support through the PhD fellowship grant PD/BD/143157/2019 awarded to Lara Fidalgo.

References:

[1] Yuan, J.; Amin, P.; Ofengeim, D. Necroptosis and RIPK1-Mediated Neuroinflammation in CNS Diseases. Nat. Rev. Neurosci. (2018), 20 (1), 19–33.
[2] Degterev, A.; Ofengeim, D.; Yuan, J. Targeting RIPK1 for the Treatment of Human Diseases. Proc. Natl. Acad. Sci. (2019), 116 (20), 9714-9722.
[3] Harris, P. A.; Marinis, J. M.; Lich, J. D.; Berger, S. B.; Chirala, A.; Cox, J. A.; Eidam, P. M.; Finger, J. N.; Gough, P. J.; Jeong, J. U.; et al. Identification of a RIP1 Kinase Inhibitor Clinical Candidate (GSK3145095) for the Treatment of Pancreatic Cancer. ACS Med. Chem. Lett. (2019), 10 (6), 857–862.
[4] Brito, H.; Marques, V.; Afonso, M. B.; Brown, D. G.; Börjesson, U.; Selmi, N.; Smith, D. M.; Roberts, I. O.; Fitzek, M.; Aniceto, N.; et al. Phenotypic High-Throughput Screening Platform Identifies Novel Chemotypes for Necroptosis Inhibition. Cell Death Discov. (2020), 6 (1).

Chemistry in life sciences

Caffeic acid phenolipids in the protection of cell membranes from oxidative injuries. Interaction with the membrane phospholipid bilayer

R. Lopes[a], M. Costa[a], M. Ferreira[a], P. Gameiro[a], S. Fernandes[a], C. Catarino[b], A. Santos-Silva[b], F. Paiva-Martins[a]

a) REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre 687, Porto, Portugal; b) REQUIMTE/UCIBIO, Department of Biological Sciences, Faculty of Pharmacy, University of Porto, Portugal

Email: mpmartin@fc.up.pt

Caffeic acid (CA) has demonstrated a strong intracellular antioxidant ability by scavenging ROS, contributing to the maintenance of cell membrane structural integrity and to reduce oxidative injuries in other cell components. Nevertheless, caffeic acid has limited usage, due to its hydrophilic character. In this work, the introduction of alkyl chains in the caffeic acid molecule by esterification (methyl - C1, ethyl - C2, butyl - C4, hexyl - C6, octyl - C8 and hexadecyl - C16), significantly increased its lipophilicity. All caffeates tested showed a much higher protective activity than caffeic acid against red blood cells (RBCs) AAPH-induced oxidative stress; this protection was heavily dependent on the length of the alkyl chain of the esters, and on their concentration. At 2.5 and 5 μM, the more lipophilic compounds (C8 and C16) showed a remarkable antioxidant activity, inhibiting haemolysis; probably, their better location within the membrane leads to a better antioxidative protection; however, at 50 μM, the more hydrophilic compounds (C1-C4) showed a better activity against hemolysis than the more lipophilic ones (C8-C16). At this higher concentration, the better interaction of the more lipophilic compounds with the membrane seems to cause changes in RBC membrane fluidity, disturbing membrane integrity. Our data show that the antioxidant activity of these compounds could play an important role for the protection of different tissues and organs, by protecting cell membranes from oxidative injuries.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support (UIDB/QUI/50006/2020).

Chemistry in life sciences

BODIPY-based probe for live-cell imaging of lysosomes in cancer cells

R.C.R. Gonçalves,[a] M.C. Silva,[b] J. Gallo,[b] S.P.G. Costa,[a] M.M.M. Raposo[a]

a) Centre of Chemistry, University of Minho, Campus of Gualtar, 4710-057 Braga, Portugal; b) Nanomedicine Research Group, International Iberian Nanotechnology Laboratory, Av. Mestre José Veiga s/n, 4715-330, Braga, Portugal

Email: raquelrainha10@hotmail.com

Bioimaging is a multi-dimension technique employed in most biomedical research fields for visualization of morphological and biological processes. In particular, fluorescent-based probes able to permeate cell membranes and label a specific biological target represent a powerful tool for noninvasive imaging of living systems in real time with high temporal and spatial resolution.[1]
Among several fluorescent molecules, 3-difluoroborodipyrromethene (BODIPY) derivatives have become a cornerstone for innovative applications such as fluorescent labelling, electroluminescent devices, dye sensitized solar cells (DSSCs), photodynamic therapy (PDT) and optical sensors. BODIPY dyes have received great attention because of their advantageous features: facile synthesis and structural versatility, photochemical stability, sharp absorption/emission with high intensity in visible to NIR region and high fluorescence quantum yields. In fact, a series of fluorescent BODIPY-based probes have been developed for targeting biomolecules, detection of intracellular analytes, mapping cellular environment changes and staining cellular organelles.[2]
In continuation of the investigation developed in our research group concerning BODIPYs for several applications,[3] here we report the synthesis and characterization of a BODIPY derivative functionalized with a benzimidazole group and the *in vitro* evaluation in cells derived from human cervical cancer (HeLa), which showed its bioimaging potential as a selective fluorescent probe for lysosomes (**Figure 1**).

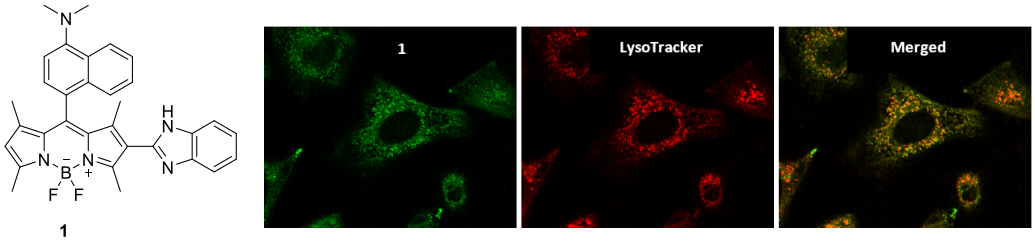


Figure 1: Structure of BODIPY-based probe and confocal fluorescence images of the colocalization study with probe **1** and commercial lysosomes probe (LysoTracker) in HeLa cells.

Acknowledgements: The authors acknowledge Fundação para a Ciência e Tecnologia - FCT (Portugal) for funding through CQUM (UID/QUI/00686/2020) and project PTDC/QUI-COL/28052/2017 and a PhD grant to R. C. R. Gonçalves (SFRH/BD/05278/2020). The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network and was purchased within the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT.

References:

1. a) Alamudi, S. H.; Chang, Y. T. *Chem. Commun*. **2018**, *54*, 13641–13653. b) Yang, X.; Lovell, J. F.; Murthy, N.; Zhang, Y. *Top Med. Chem.* **2020**, *34*, 33–53. c) Terai, T.; Nagano, T. *Pflugers Arch.* **2013**, *465*, 347–359.
2. a) Bañuelos, J. *Chem. Rec*. **2016**, *16*, 335–348. b) Ziessel, R.; Ulrich, G.; Harriman, A. *New J. Chem*. **2007**, *31*, 496–501. c) Loudet, A.; Burgess, K. *Chem. Rev*. **2007**, *107*, 4891–4932. d) Kaur, P.; Singh, K. *J. Mater. Chem. C* **2019**, *7*, 11361–11405.
3. a) Lo Presti, M.; Martínez-Máñez, R.; Ros-Lis, J. V.; Batista, R. M. F.; Costa, S. P. G.; Raposo, M. M.; Sancenón, F. *New J. Chem*. **2018**, *42*, 7863–7868. b) Collado, D.; Casado, J.; González, S. R.; Navarrete, J. T. L.; Suau, R.; Perez-Inestrosa, E.; Pappenfus, T. M.; Raposo, M. M. M. *Chem. Eur. J*. **2011**, *17*, 498-507. c) Gonçalves, R. C. R.; Pinto, S. C. S.; Costa, S. P. G.; Raposo, M. M. M. *Chem. Proc.* **2020**, *3*, 65. d) Gonçalves, R. C. R.; Pinto, S. C. S.; Costa, S. P. G.; Raposo, M. M. M. *Proceedings* **2019**, *41*, 40.

Chemistry in life sciences

Enzymatic production of polydopamine in aqueous biphasic systems

F.F. Magalhães [a], A.F.Pereira [a], A.P. Tavares [a] M.G. Freire [a]

[a]*CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*

Email: flaviamagalhaes@ua.pt

Based on the principles of green chemistry, enzymatic biocatalysis contributes to a more eco-friendly and sustainable industrial chemistry [1]. Therefore, its wide use in industrial and biotechnological processes has increasingly become more evident [1]. Laccase, a multicopper oxidase with high catalytic efficiency and low substrate specificity, has attracted worldwide attention due to its ability to degrade both phenolic and non-phenolic compounds and its involvement in the synthesis of polymers [2].

Polydopamine (PDA), an added-value biopolymer that results from the dopamine polymerization, has been used for many applications, being highlighted the modification and functionalization of surfaces applied in the field of biomedicine [3]. In contrast to the conventional chemical method of dopamine polymerization, which is a time-consuming process and produces PDA films with poor stability, in the presence of laccase the process becomes faster, very efficient and meets the ideals of green chemistry [4]. However, applying a biocatalyst that could be reused and without the loss of its biological properties is an ever-increasing demand for its industrial applications. Thereby, aqueous biphasic systems (ABS), which are mainly composed of water, appear as a promising alternative since they provide a mild and biocompatible environment for proteins [5]. Besides, these systems efficiently allow the separation of the product of interest and the reusability of the enzyme in a unique step [6].

In this study, the polymerization of dopamine using laccase as the biocatalyst was carried out. Several parameters including temperature, pH and initial dopamine concentrations were investigated and optimized on the polymerization of dopamine. To develop an integrated and sustainable platform to produce PDA, that allow the reusability of the enzyme and the separation of this product, different ABS composed of polymers, salts and ionic liquids have been investigated to directly produce and separate polydopamine.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. Ana P.M. Tavares acknowledges the FCT Investigator Programme and Exploratory Project (IF/01634/2015) with financing from the European Social Fund and the Human Potential Operational Programme. Flávia F. Magalhães acknowledges the SPQ/FCT PhD grant (SFRH/BD/150669/2020).

References:

1. Choi JM, Han SS, Kim HS *Biotechnol Adv* **2015** 33:1443–1454.
2. Debnath R, Saha T *Agric Biotechnol* **2020** 26:101645.
3. Ding YH, Floren M, Tan W *Biosurface and Biotribology* **2016** 2:121–136.
4. Milyaeva OY, Bykov AG, Campbell RA, et al. *Colloids Surfaces A Physicochem Eng Asp* **2020** 599:124930.
5. Freire MG, Cláudio AFM, Araújo JMM, et al. *Chem Soc Rev* **2012** 41:4966–4995
6. Ferreira AM, Valente AI, Castro LS, et al. *Biotechnol Bioeng* **2021** 400:0–1

Chemistry in life sciences

Fluorescent-lipid probes: advances towards bioconjugation by flow chemistry

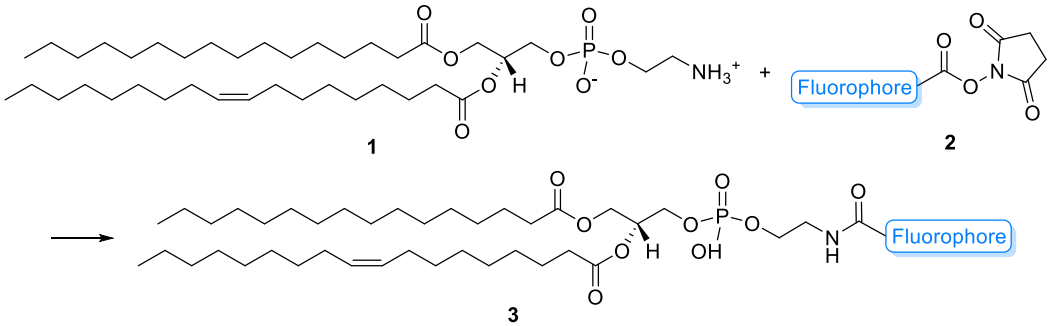
P.A.M.M. Varandas,[a] R.L. Belinha,[a] A.F.M. Cunha,[b] A.J.A. Cobb,[c] M.E. Tiritan,[b,d] M.A. Segundo,[a] E.M.P. Silva[b]

a) LAQV, REQUIMTE, Department of Chemistry Sciences, Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal; b) CESPU, Institute of Research and Advanced Training in Health Sciences and Technologies, Rua Central de Gandra, 1317, 4585-116, Gandra PRD, Portugal; c) Natural and Mathematical Sciences, Department of Chemistry King's College London, 7 Trinity Street, London SE1 1DB; d) Laboratory of Organic and Pharmaceutical Chemistry (LQOF), Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal.

Email: pedrovarandas@hotmail.com

Lipids are a major class of biomolecules responsible for critical biological roles in regulating many vital biological pathways and pathophysiological events. Moreover, lipids act as potent signalling agents since many diseases are associated with disruptions in lipid metabolism and function including neurological disorders, autoimmune diseases, and cancer.[1] A considerable amount of lipid research relies on the use of chemical tools or probes. Regarding live cell experiments, fluorescence-based techniques are the least invasive, allowing the real-time observation of biological membranes and their characteristic physical properties. Therefore, fluorescent labelling is used as the preferred tool for the investigation of biological functions involving lipids, namely for clarifying metabolic pathways and molecular mechanisms of diseases where these molecules are of crucial importance.[2] Additionally, the lack of functionalized lipid probes with the biological and physicochemical properties suitable for this type of studies is still a major limitation concerning this research area. Hence, the development of fluorescent lipid analogues has received increasing interest in recent years.

In this work, we developed a bioconjugation method based on *N*-hydroxysuccinimide (NHS) chemistry to produce fluorescent lipid probes easily. A classic organic synthesis procedure was established concerning the functionalization of phospholipid analogues with fluorescent probes through NHS coupling (**Scheme 1**). The newly synthesised probes were submitted to fluorescence characterization. This method was converted to an automated flow procedure based on multi-syringe flow injection allowing to tailor the most suitable conditions for bioconjugate synthesis.



Scheme 1: Functionalization of phospholipid analogue **1** with the fluorophore succinimidyl ester **2** through NHS coupling.

Acknowledgements: The work was supported through the project UIDB/50006/2020, funded by FCT/MCTES through national funds and CESPU through the projects CHIRALBIOACTIVE-PI-3RL-IINFACTS-2019 and CHIRALSINTE-SE_APSFCT_IINFACTS_2021. Pedro Varandas thanks FCT and ESF through NORTE 2020 - Norte's Regional Operational Programme for his PhD grant ref. SFRH/BD/139714/2018.

References:

1. a) Wymann, M. P.; Schneiter, R. *Nat. Rev. Mol. Cell Biol.* **2008**, 9, 162−176. b) Brown, H. A.; Thomas, P. G.; Lindsley, C. W. *Nat. Rev. Drug Discovery* **2017**, 16, 351−367.
2. Varandas, P. A. M. M.; Cobb, A. J. A.; Segundo, M. A.; Silva, E. M. P. *Bioconjugate Chem.* **2020**, 31, 417−435.

Chemistry in life sciences

A fluorescent probe based on a BODIPY derivative to study cellular ingestion and internalization of solid lipid nanoparticles

S.C.S. Pinto,[a] R.C.R. Gonçalves,[a] M.C. Silva,[b] J. Gallo,[b] S.P.G. Costa,[a] M.M.M. Raposo[a]

a) Centre of Chemistry, University of Minho, Campus of Gualtar, 4710-057 Braga, Portugal; b) Nanomedicine Research Group, International Iberian Nanotechnology Laboratory, Av. Mestre José Veiga s/n, 4715-330, Braga, Portugal

Email: soniapinto4197@gmail.com

Fluorescent probes are a very useful tool for the characterization of biological systems since they allow the visualization of biological structures and phenomena inside living organisms in real-time, and the acquisition of dynamic information of molecules and elucidation of cellular processes. Currently, Solid Lipid Nanoparticles (SLNs) are being applied in the medical and pharmaceutical research field as a drug delivery agent to the target cells/organs. In this sense, fluorescent probes can be used to investigate processes of cellular uptake and *in vivo* distribution of nanoparticles in real-time.[1]

The BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) derivatives have achieved great notoriety in the field of fluorescent imaging due to their excellent photophysical properties, such as large molar extinction coefficients, high quantum fluorescence yields, and good photochemical stability.[2] As an extension of the work developed in our research group,[3] we report the synthesis and characterization of a BODIPY functionalized with a *N*,*N*-dimethyl-1-naphthylamino and a formyl group at the *meso* and 2-position, respectively, and its application as a fluorescent probe to detect internalization of compounds by living cells. As an example, we show the BODIPY derivative **1** imaging capability for the intracellular detection of SLNs internalized by HeLa cells, using a confocal microscope. (**Figure 1**).

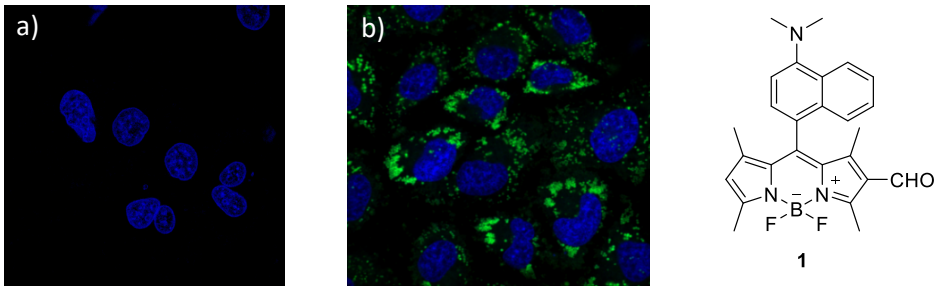


Figure 1: Internalization of SLNs by HeLa cells in the absence (a) and presence (b) of the fluorescent green probe **1** and structure of BODIPY **1**.

Acknowledgements: The authors acknowledge Fundação para a Ciência e Tecnologia - FCT (Portugal) for funding through CQUM (UID/QUI/00686/2020) and project PTDC/QUI-COL/28052/2017 and a PhD grant to R. C. R. Gonçalves (SFRH/BD/05278/2020). The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network and was purchased within the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT.

References:

1. a) Terai, T.; Nagano, T. *Pflugers Arch.* **2013**, *465*, 347–359. b) Kolemen, S.; Akkaya, *E. U. Coord. Chem. Rev.* **2018**, *354*, 121–134. c) Dhiman, N., Awasthi, R., Sharma, B., Kharkwal, H., & Kulkarni, G. T. *Front. Chem.* **2021**, *9*. d) Blasi, P.; Giovagnoli, S.; Schoubben, A.; Ricci, M.; Rossi, C. *Adv. Drug Deliv. Rev.* **2007**, *59*, 454–477
2. Kowada, T.; Maeda, H.; Kikuchi, K. *Chem. Soc. Rev.* **2015**, *44*, 4953–4972.
3. a) Lo Presti, M.; Martínez-Máñez, R.; Ros-Lis, J. V.; Batista, R. M. F.; Costa, S. P. G.; Raposo, M. M.; Sancenón, F. *New J. Chem.* **2018**, *42*, 7863–7868. b) Collado, D.; Casado, J.; González, S. R.; Navarrete, J. T. L.; Suau, R.; Perez-Inestrosa, E.; Pappenfus, T. M.; Raposo, M. M. M. *Chem. Eur. J.* **2011**, *17*, 498-507. c) Pinto, S. C. S., Gonçalves, R. C. R., Costa, S. P. G.; Raposo, M. M. M. *Chem. Proc.* **2021**, *3*(1), 79. d) Gonçalves, R. C. R.; Pinto, S. C. S.; Costa, S. P. G.; Raposo, M. M. M. *Proceedings* **2019**, *41*(1), 40.

Chemistry in life sciences

Cytotoxic activity against HCT-116 colon carcinoma cells of Amaryllydaceae-type alkaloids

Sancha S.[a], Gonçalves J. [a], Rodrigues C.M.P.[a], Ferreira M.J.U.[a]

a) Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal.

Email: shirleysancha@ff.ulisboa.pt

Cancer is one of the main causes of mortality and morbidity worldwide, being multidrug resistance the main challenge in cancer treatment. Despite all efforts in early detection and treatment, the number of cases is expected to increase to 28 million annually by 2040 [1]. Therefore, there is an urgent need of new anticancer compounds. Plants belonging to the Amaryllidaceae family, traditionally used to treat cancer, are recognized for synthesizing diverse and unique bioactive alkaloids. These compounds, named amaryllidaceae alkaloids, are exclusive to the family and are responsible for their strong biological properties, including anticancer activity [2]. Thus, the main goal of this study was to find out new effective anticancer compounds from two species of Amaryllidaceae family, namely *Narcissus bulbocodium* L. subsp *obesus* (Salisb) and *Pancratium maritimum* L.

The phytochemical study of the alkaloid fraction of the methanol extract of the bulbs of *P. maritimum* led to the isolation of several amaryllidaceae-type alkaloids bearing lycorine, tazettine, galanthamine, haemanthamine, and homolycorine scaffolds. In addition, the phytochemical study of the methanol extract of bulbs and flowers of *N. bulbocodium* gave rise to tazetine-type alkaloids, an alkamide and several steroids. The structures of the compounds were assigned based on spectroscopic data (IR, MS, 1D and 2D NMR -COSY, HMQC and HMBC and NOESY experiments).

The cytotoxicity of the compounds was evaluated against HCT-116 colon carcinoma cells by the MTS metabolism assay. Some compounds were found to be cytotoxic, displaying IC_{50} values < 10 μM. Further evaluation for their cytotoxicity in other cancer cell lines and ability to induce apoptosis is planned.

Acknowledgements: This study was financially supported by Fundação para a Ciência e Tecnologia (FCT), Portugal (grant SFRH/BD/130348/2017; projects PTDC/MED-QUI/30591/2017 and SAICTPAC/0019/2015).

References:

1. Sung H., Ferlay J.; Siegel R.L.; Laversanne M., Soerjamatarm I.; Jemal A.; Bray F.*CA Cancer J Clin*. **2021**, 71:209-249.
2. Evidente A.; Kornienko A. *Phytochem Rev.* **2009**, 8, 449–459.

Chemistry in life sciences

ATP binding induces characteristic structural changes in the ABCG2 transport channel

B.M.F. Goncalves [a*], R.J. Ferreira[a,b], M.-J.U. Ferreira[a] , D.J.V.A. dos Santos[c]

[a] *Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal;* [b] *Red Glead Discovery AB, Lund, Sweden;* [c] *LAQV@REQUIMTE/Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal.*

Email: bgoncalves@farm-id.pt

ABCG2 (also known as BCRP) is an ATP-binding-cassette (ABC) protein transporter that uses ATP binding and hydrolysis to export various substrates across cellular membranes, including anticancer drugs. Efficient modulation of the ABCG2 function has been pointed as a powerful therapeutic strategy to overcome multidrug resistance in cancer by improving the pharmacokinetics and efficacy of chemotherapeutic agents [1]. However, the development of effective ABCG2 modulators is dependent on a comprehensive knowledge of the structural and functional mechanism underlying efflux in this efflux pump. For many years after his discovery (1998), the structure and function of ABCG2 remained in the shadows. However, in the last few years a series of exciting findings shed some light on the structure of this transporter[2] and demands new independent assays to get new insights on the BCRP-efflux mechanism.

In this work we aimed to investigate the conformational changes induced by ATP binding and that ultimately result in the transport of substrates. For that, we built a full-length model of human BCRP based on the incomplete structures PDB ID: 5NJ3[3] and PDB ID: 6VXF[4]. The new model was inserted in a membrane bilayer at physiological conditions (ATP, ions), refined, and simulated through molecular dynamics (500 ns production runs) in the presence or absence of ATP. The global motion patterns and binding mode analysis were performed to identify possible structural changes related to the presence/absence of ATP. It was found that ATP induces a clear change in the orientation of motion patterns displayed by ABCG2 compared to the Apo structure. Type of Interactions and binding energies were also evaluated in protein-ATP simulations to identify the residues that play a key role in ATP binding and consequently ATP-induced dimerization.

Acknowledgements: This work was supported by projects PTDC/MED-QUI/30591/2017, SAICTPAC/0019/2015, and UID/DTP/04138/2019 from Fundação para a Ciência e a Tecnologia (FCT), Portugal.

References:

1. Ferreira, R.; Ferreira, M-J.; Santos, D.; *WIREs Comput Mol Sci*, **2015**, 5:27–55.
2. a) Robert E., Ralf A. B., *Br J Pharmacol*. **2020**; 177:1485–1496.
3. Taylor N. M. I; Monalaridis, I.; Jackson, S. M.; Kowal, J.; Stahlberg, H.; and Locher, K. P., *Nature* 546, **2017**, page 504-509
4. Benjamin J. O.; Liao, M; *Nature Communications*, **2020**, volume 11, Article number: 2264

Chemistry in life sciences

Effect of cyclodextrins on the acid-base equilibrium of pyranoanthocyanins

A. Borges[1], P. Araújo[1], N. Basílio[2], V. de Freitas[1], I. Fernandes[1], J. Oliveira[1]

[1] LAQV – REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal [2] LAQV – REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

Email: alexandra.borges@fc.up.pt

Anthocyanins are natural pigments that contribute to the red, purple and blue colours found in plants, especially flowers, fruits, and tubers [1]. These features associated with the many beneficial health effects are the main reasons why anthocyanins can be of great interest for different industries. However, the application of this pigments is still a challenge since in aqueous solutions anthocyanins are very instable and their colour is depending of the pH of the medium. On the other hand, pyranoanthocyanins present a fourth ring that is responsible for the higher chromatic stability of these anthocyanin-derived compounds and can display different colours according to the substitution pattern of the fourth ring. These pigments represent a promising alternative concerning their application in different matrices, although some of these pyranoanthocyanins are known for their low solubility in aqueous solutions [2]. Cyclodextrins (CDs) are oligosaccharides widely applied in different industrial matrices and the formation of molecular inclusion complexes between these molecules and anthocyanins are known to affect important properties of the pigments, namely water solubility and equilibrium and rate constants [3, 4]. Therefore, the formation of inclusion complexes between CDs and pyranoanthocyanins could be a key way of improving its solubility and stability and simplifying its application in food and cosmetic products. In this context, the aim of this work was to study the influence of molecular inclusion complexes of different pyranoanthocyanins with CDs on their acid-base equilibrium and solubility.

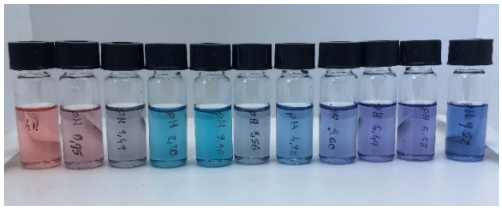


Figure 1: Different colours displayed by a pyranoanthocyanin-cyclodextrin system at different values of pH.

Acknowledgements: This work was supported by the Associated Laboratory for Sustainable Chemistry, Clean Processes and Technologies LAQV through the national funds from UIDB/50006/2020 and UIDP/50006/2020 and by AgriFood XXI I&D&I project (NORTE-01-0145-FEDER-000041) cofi- nanced by European Regional Development Fund (ERDF), through the NORTE 2020 (Programa Operacional Regional do Norte 2014/2020). It was also supported by the project PTDC/QUI-OUT/29013/2017 funded by FCT and FEDER. A.B. and P.A. (SFRH/BD/143309/2019) gratefully acknowledge their doctoral grants from FCT. J.O. and N.B. would like to thank FCT respectively for contract (IF/00225/2015) and CEECIND/00466/2017

References:

1. Khoo, H.E., et al., *Anthocyanidins and anthocyanins: colored pigments as food, pharmaceutical ingredients, and the potential health benefits.* Food & Nutrition Research, 2017. **61**(1): p. 1361779-1361779.
2. Oliveira, J., N. Mateus, and V. Freitas, *Wine-Inspired Chemistry: Anthocyanin Transformations for a Portfolio of Natural Colors.* Synlett, 2017. **28**.
3. Basílio, N., et al., *Effect of β-cyclodextrin on the chemistry of 3',4',7-trihydroxyflavylium.* New J. Chem., 2013. **37**.
4. Dangles, O., et al., *Two very distinct types of anthocyanin complexation: Copigmentation and inclusion.* Tetrahedron Letters, 1992. **33**(36): p. 5227-5230.

Chemistry in life sciences

Exploring the behavior of ruthenium metallodendrimers as anticancer drugs

D. Maciel,[a] Y. Fan,[b] G. Li,[b] X. Shi,[a,b] H. Tomás,[a] J. Rodrigues[a*]

a) CQM - Centro de Química da Madeira, MMRG, Universidade da Madeira, Campus Universitário da Penteada, 9020-105 Funchal, Portugal. b) College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, 201620, China.

Email: joaor@uma.pt

In the last decades, metal complexes have been studied as potential new anticancer therapeutics. Ruthenium complexes, due to their low toxicity, tumor selectivity, different oxidation states, and mechanisms off action[1,2], are considered promising alternatives to the platinum compounds used in the clinic.
As part of our long-term research line on the development of metallodendrimers for biological aplications[3], here we present the preparation of low generation poly(alkylidenamine)-based metallodendrimers (generation 0, 1, and 2) functionalized with the ruthenium moiety $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2]^+$ with the perspective of their use as chemotherapeutics. The prepared ruthenium metallodendrimers were first characterized by NMR, MS, and FTIR techniques. ^{1}H- and ^{31}P-NMR were also used to evaluate their long-term stability at different temperatures (4, 25, and 37°C). The *in vitro* anticancer activity was assessed against several cancer cell lines (MCF-7, A2780, A2780cisR, CAL-72, Caco-2, and U-87MG). These cytotoxicity studies were complemented with transferrin binding and hemolytic activity assays. Cell death mechanisms were investigated using the MCF-7 cell line by assessing reactive oxygen species (ROS), apoptosis/necrosis, and cell cycle arrest. *In vivo* studies were further done to examine the therapeutic efficacy of these metallodendrimers using a mice model where MCF-7 tumors were induced (Figure 1). The *in vitro* cytotoxicity results indicated a generation effect with increased toxicity for higher generations. The metallodendrimers revealed a strong interaction with apo-transferrin, and induced necrosis and late apoptosis in MCF-7 cells, being these important clues for their action. The *in vivo* results showed that the metallodendrimers mainly accumulated at the tumor site and could shrink tumor volume.
Globally, the obtained data, either *in vitro* or *in vivo*, revealed the potential of our metallodendrimers as anticancer agents when comparing with simple metallodrugs, like *cisplatin*, or with other metallodendrimers of higher generation. Clearly, our results confirmed the advantages of using ruthenium complexes as metallodrugs and using this family of low-generation dendrimers as their nanocarriers.

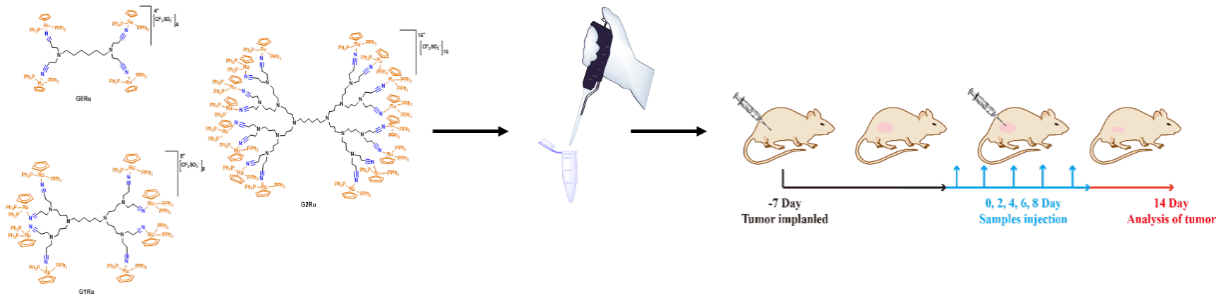


Figure 1: Representation of the metallodendrimers used for the *in vivo* antitumor studies.

Acknowledgments: This research was supported by FCT-Fundação para a Ciência e a Tecnologia through the CQM Strategic Project PEst-OE/QUI/UI0674/2019, CQM Base Fund - UIDB/00674/2020, and Programmatic Fund - UIDP/00674/2020, and by the Ph.D. Grant SFRH/BD/102123/2014 (DM). The authors also acknowledge ARDITI-Agência Regional para o Desenvolvimento da Investigação Tecnologia e Inovação, respectively through the project M1420-01-0145-FEDER-000005 - Centro de Química da Madeira - CQM$^+$ (Madeira 14-20).

References:

1. Liu J.; Lai H.; Xiong Z.; Chen B.; Chen T. *Chem. Commun.* **2019**, 55, 9904; 2. Thangavel P.; Viswanath B.; Kim S. *Int. J. Nanomed.* **2017**, 12, 2749; 3. a) Jardim M.G.; Rissanen K.; Rodrigues J. *Eur. J. Inorg. Chem.* **2010**, 1729; b) Gouveia M.; Figueira J.; Jardim M.G.; Castro R.; Tomás H.; Rissanen K.; Rodrigues J. *Molecules* **2018**, 23, 1471.

Chemistry in life sciences

Targeting necroptosis: discovery and optimization of novel RIPK1 inhibitors

A.F.S. Luz[a], A.C. Vieira[a], V. Marques[a], C. Pinto[a], C.M.P. Rodrigues[a], R.C. Guedes[a], L.C. Gomes-da-Silva[b], R. Moreira[a]

a) iMed.UL, Faculdadade de Farmácia da Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal;
b) Departamento de Química, Universidade de Coimbra, Rua Larga, 3004-535 Coimbra, Portugal

Email: andrefluz@ff.ulisboa.pt

Necroptosis is a regulated form of cell death that is associated with several inflammatory and degenerative diseases. The identification of necroptosis' pathway mediators, such as receptor interacting protein kinase-1 (RIPK1), and the prevalence of this type of cell death in critical human illnesses, led to an intensive, yet unaccomplished, search for high quality necroptosis inhibitors.[1]

To find novel necroptosis inhibitors, a high-throughput cell-based phenotypic screening was performed in the iMed.ULisboa. A new RIPK1 inhibitor (1), with a EC_{50} in the low micromolar range, was identified **(Figure 1A)**. Molecular docking studies revealed that 1 interacts with the kinase-binding pocket of RIPK1.[2]

Aiming to modulate the interaction with the binding pocket, a library of necroptosis inhibitors based on hit 1, was prepared using a multigram synthesis and studied in enzymatic and cell-based assays **(Figure 1B)**. The activity profile of the new family showed to be highly dependent on the rotamer distribution **(Figure 1C)** around the amide bond (R1= C=O), which is determined by the nature of the 5-membered heterocyclic moieties (R2). To further explore the impact of rotamers on activity, NMR and quantum mechanics studies were performed. This research allowed the development of potent RIPK1 and necroptosis inhibitors, and highlights the importance of exploring the stereoelectronic properties to optimize lead compounds and understand the structural requirements for activity.

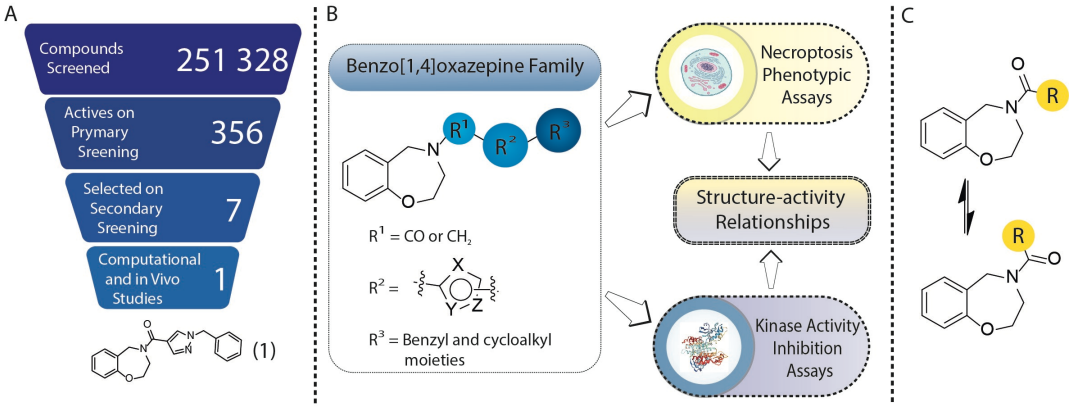


Figure 1: A) Previous high-throughput phenotypic screening and hit compound (1); B) A novel family of synthesised RIPK1 inhibitors were studied in enzymatic and in vitro assays leading to structure-activity relationships; C) Benzo[1,4]oxazepane rotamers interconversion.

Acknowledgements: This research was funded by projects UIDB/04138/2020 and UIDP/04138/2020 (Fundação para a Ciência e Tecnologia (FCT), Portugal). Joint funding from FCT and the COMPETE Program through grant SAICTPAC/0019/2015 is gratefully acknowledged. AFSL also thanks FCT for a PhD fellowship under the MedChemTrain program (PD/BD/143122/2019).

References:

1. Zhuang, C.; Chen, F. J. Med. Chem. 2020, 63, 4, 1490–1510.
2. Brito, H.; Marques, V.; Afonso, M. B.; Brown, D. G.; Börjesson, U.; Selmi, N.; Smith, D. M.; Roberts, I. O.; Fitzek, M.;Aniceto, N.; Guedes, R. C.; Moreira, R.; Rodrigues, C. M. P. Cell Death Discov. 2020, 6 (1).a) González S. D.-; Marion N.; Nolan S. P. *Chem. Rev.* **2009**, *109*, 3621.

Environment and water

Desenvolvimento de um sensor eletroquímico baseado em Pt-GO para quantificação de contaminantes fenólicos

L. Lema,[a,b], A.P. Bettencourt,[b] F. Bento[b]

a) Instituto Superior de Ciências de Educação do Uíge, Rua do Café nº 54 Uíge, Angola; b) Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

Email: id7395@alunos.uminho.pt

O grafeno, tanto na forma de óxido de grafeno (GO) como de óxido de grafeno reduzido (rGO), apresenta características adequadas à utilização como material de elétrodo, sendo utilizado com sucesso na construção de sensores com sensibilidade e limiares analíticos melhorados[1]. Este material é também facilmente combinado com outros materiais, formando materiais nano híbridos, misturado com nanopartículas metálicas ou incorporado em matrizes poliméricas.

Neste trabalho é desenvolvido um sensor eletroquímico para a deteção de contaminantes fenólicos em águas utilizando como material de elétrodo nanopartículas de platina dispersas em grafeno. A constituição deste material foi otimizada de modo a tirar proveito das propriedades eletrocatalíticas da platina e das propriedades elétricas do grafeno. A proporção em que estes constituintes estão presentes e a extensão da redução do GO foi variada. Na **Figura 1** encontram-se apresentadas as respostas voltamétricas registadas em soluções de PBS, na ausência (A) e na presença de hidroquinona, HQ (B), usando um elétrodo de carbono impresso (SPCE) sem modificação e modificado com GO e com o nanohíbrido de grafeno e platina (GO_Pt). As respostas obtidas com o GO_Pt apresentam um aumento da intensidade de corrente de pico, um deslocamento do potencial de pico anódico e uma diminuição da separação dos potenciais de pico anódico e catódico. Estas alterações indicam que o processo de transferência eletrónico é facilitado pelo GO_Pt. Recorrendo a este material foi construído um sensor que permite quantificar compostos fenólicos, com limites de deteção na ordem de 1 µM de HQ e sensibilidade de 2000 µA mM^{-1} cm^{-2}.

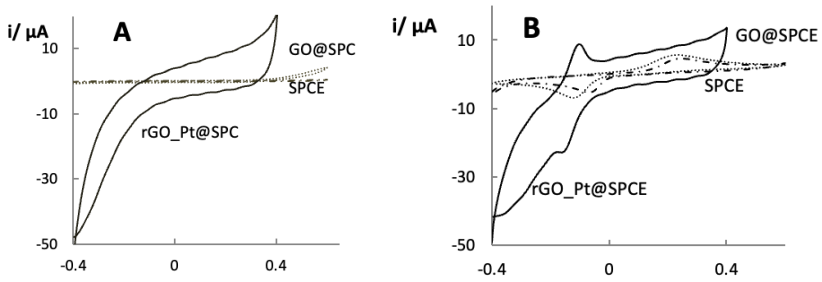


Figura 1: Voltamogramas cíclicos obtidos com SPCE, GO@SPCE e com rGO-Pt em PBS 0,10 M (A) e em solução 100 µM de HQ em PBS 0,10 M (B).

Agradecimentos: L. Lema agradece ao Governo Angolano, MESCT e ISCED do Uíge o financiamento da Bolsa de Doutoramento. Os autores agradecem ao Centro de Química da Universidade do Minho através do projeto UID/QUI/00686/2019 (CQUM) financiado pela FCT, Portugal.

References:

1. Shahdeo D, Roberts A, Abbineni N, Gandhi S. *Comprehensive Analytical Chemistry*. **2020**, *91*,175.

Environment and water

Heterocyclic thiosemicarbazone based on a bithienyl π-conjugated bridge for heavy metal cations detection

R.P.C.L. Sousa,[a] R.B. Figueira,[a,b] S.P.G. Costa,[a] M.M.M. Raposo[a]

a) Centre of Chemistry, University of Minho, Campus of Gualtar, 4710-057 Braga, Portugal; b) Presently at Vasco da Gama CoLAB, Rua Roberto Frias, 4200-465 Porto, Portugal

Email: rui.sousa@quimica.uminho.pt

Aquatic and marine environments are constantly affected by anthropogenic sources and heavy metals are one of the biggest sources of water contamination. For this reason, the detection of these cations is of utter interest and pursued by many. Molecular-based detection systems allows specific analytes' sensing with great sensitivity and selectivity, besides being able to be applied in devices with latest technology to real time sensing of a certain analyte. Specifically, organic optical chemosensors use supramolecular chemistry and molecular recognition mechanisms for recognition of an analyte and transduction of the signal, in a simple and fast detection.[1]

Thiourea derivatives, particularly thiosemicarbazones, are molecules of particular interest in ion sensing due to the conjugation of heteroatoms with electronic properties that can be tuned by the presence of electron donor/withdrawing groups.[2] The combination of this core with π-conjugated bridges can yield selective and sensitive optical chemosensors for different ions. Herein we report a heterocyclic thiosemicarbazone **1**, functionalized with a triphenylamino (TPA) group and a bithiophene π-bridge. Compound **1** was used in preliminary tests with different cations and anions and showed colorimetric/fluorimetric changes in the presence of environmentally important cations, such as Hg^{2+}, Pd^{2+} and Sn^{2+}. Spectrophotometric and spectrofluorimetric titrations were performed to assess the interaction between the chemosensor and the three metal cations.

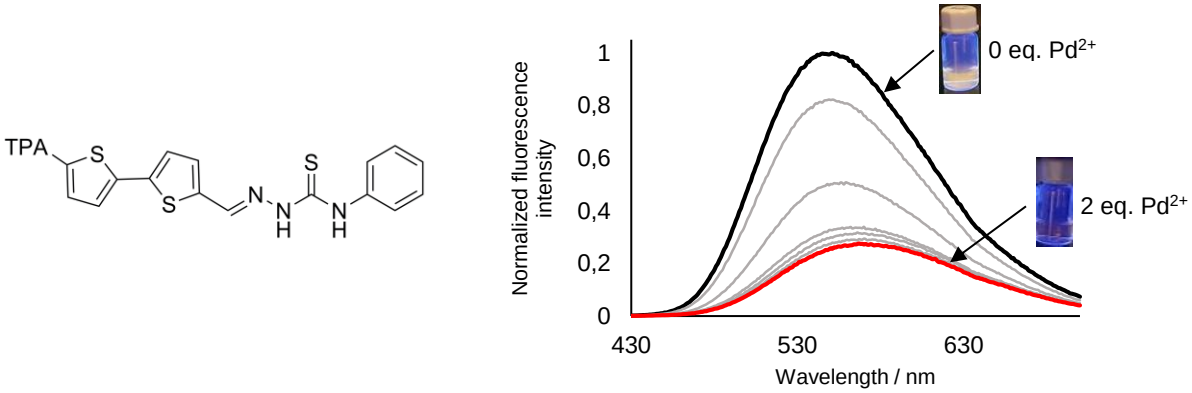


Figure 1: Structure of compound **1** and spectrofluorimetric titration with Pd^{2+}.

Acknowledgments; Thanks are due to Fundação para a Ciência e Tecnologia (FCT) and FEDER (European Fund for Regional Development)-COMPETE-QRENEU for financial support through the Chemistry Research Centre of the University of Minho (Ref. CQ/UM (UIDB/QUI/00686/2019 and UIDB/QUI/00686/2020) and a PhD grant to R. P. C. L. Sousa (SFRH/BD/145639/2019).

References:

1. a) Bordberg, G. F.; Fowler, B. A.; Nordberg, M.; Friberg, L. *Handbook on the Toxicology of Metals*, 3rd ed.; Amsterdam: Elsevier, 2007. b) F. Fu and Q. Wang. *J. Environ. Manage.*, **2011**, *92*, 407-418.
2. a) Raposo, M. M. M.; García-Acosta, B.; Ábalos, T.; Calero; P.; Martínez-Manez, R.; Ros-Lis, J. V.; Soto, J. *J. Org. Chem*. **2010**, *75*, 2922. b) Santos-Figueroa, L. E.; Moragues, M. E.; Raposo, M. M. M., Batista, R. M. F.; Ferreira, R. C. M.; Costa, S. P. G.; Sancenón, F.; Martínez-Máñez, R.; Ros-Lis, J. V.; Soto, J. *Org. Biomol. Chem*. **2012**, *10*, 7418. c) Santos-Figueroa, L. E.; Moragues, M. E.; Raposo, M. M. M., Batista, R. M. F.; Ferreira, R. C. M.; Costa, S. P. G.; Sancenón, F.; Martínez-Máñez, R.; Ros-Lis, J. V.; Soto, J. *Tetrahedron* **2012**, *68*, 7179.

Environment and water

Preparation of aminals under mild conditions and their remarkable applications

J.G. Pereira, R.F.A. Gomes, C.A.M. Afonso

Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003, Lisboa, Portugal

Email: juliana-pereira@edu.ulisboa.pt

Aminals are the condensation product of aldehydes and secondary amines. Structurally similar to acetals, these compounds have been used as intermediates, chiral auxiliaries and protection groups in reactions and in the biology field.[1]

The most common methodology for the formation of aminals involves the condensation of aldehydes with amines in ethanol or toluene under high temperatures using dehydrating agents to remove the water in the reaction, shifting the equilibrium to the product.[2] However, performing the reaction in aqueous media instead of organic solvents is an environmentally competitive process for the preparation of aminals.

This work reports on the formation of aminals, from aromatic aldehydes and furfural derivatives with different secondary amines in water under mild conditions **(Figure 1)**. This is followed by the stability studies of different aminals and their use as protection group for aldehydes. Applying this approach together with the advantages of a continuous flow system allowed us to develop a new, simple and rapid methodology for selective removal of genotoxic aldehydes from APIs (Active Pharmaceutical Ingredient). Our method uses the diamine scavenging resin in a continuous flow system, generating the aminal within the microreactor efficiently **(Figure 2)**.[3]

The described aminal compounds were prepared with a more sustainable methodology allowing the use of these interesting molecules as protection group and presenting a noteworthy role on the removal of genotoxic impurities of the APIs.

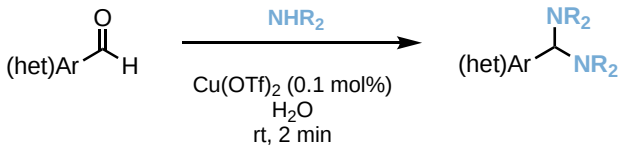
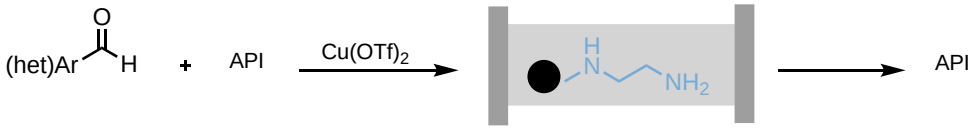


Figure 1. Preparation of aminals from aromatic aldehydes and furfural derivatives with different secondary amines in water under mild conditions.



Aminal formation inside the reactor

Figure 2. A new strategy for selective removal of genotoxic aldehydes from APIs.

Acknowledgments: We thank the Fundação para a Ciência e Tecnologia (PD/BD/128316/2017, PTDC/QUI-QOR/32008/2017, UIDB/04138/2020 and UIDP/04138/2020), COMPETE Programme (SAICTPAC/0019/2015) for financial support. The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 951996.

References

1. Alexakis A.; Lensen N.; Mangeney P. Tetrahedron Letters, **1991**, 109**,** 1171.
2. Ramirez M. A.; Ortiz G.; Levin G.; McCormack; Blanco W. M. M.; Perillo I. A.; Salerno A.; Tetrahedron Letters, **2014,** 55, 4774.
3. Pereira J. G.; António J. P. M.; Mendonça R.; Gomes R. F. A.; Afonso C. A. M. Green Chemistry, **2020**, 22, 7484.

Environment and water

Photocatalytic degradation of tramadol using metal-free carbon nitride

M.A. Barros, M.J. Sampaio, C.G. Silva, J.L. Faria

Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

Email: mabarros@fe.up.pt

Heterogeneous photocatalysis is an attractive alternative to conventional water treatment methods due to its ability to fully degrade organic chemicals such as dyes, pharmaceuticals, pesticides, insecticides, phenols, and others into innocuous end products. Combining nanostructured photocatalysts, such as thermally exfoliated graphitic carbon nitride (GCN-T), with light-emitting diodes (LEDs) is a powerful tool to efficiently degrade organic contaminants in wastewater under mild conditions, resulting in considerable energy savings. Furthermore, GCN-T is a non-toxic and cost-effective catalyst activated by solar radiation having high photocatalytic activity [1]. The present work deals with the photocatalytic degradation of tramadol (TRA), one of the most detected analgesics in aqueous environments. TRA is a centrally acting opioid used to relieve acute and chronic pain, which is extremely difficult to remove and toxic to humans and aquatic fauna. Conventional methods used in water treatment are not efficient in their complete degradation. In addition, oxidation processes such as phototransformation, or the use of ozone, ferrate, and chlorate, are usually related to the formation of more toxic sub-products than the original molecule [2]. Therefore, this work intends to degrade TRA using GCN-T photocatalyst under visible-LEDs. The operation conditions were optimized to maximize the photocatalytic efficiency of the process. An experimental design method was used to assess the effect of the catalyst load, initial concentration of TRA, and initial solution pH. The results (**Figure 1**) revealed 100 % of TRA removal in 30 min of reaction using 0.75 g L^{-1} of GCN-T and starting from an initial concentration of TRA of 5 ppm and a pH of 6.7. The photocatalytic degradation mechanism using GCN-T will be studied using different scavenger agents.

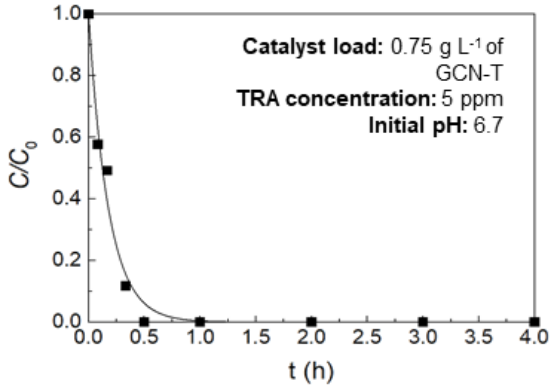


Figure 1: Photocatalytic degradation of TRA using GCN-T photocatalyst with optimal conditions.

Acknowledgments: We would like to thank the scientific collaboration under Base Funding - UIDB/50020/2020 of the Associate Laboratory LSRE-LCM - funded by national funds through FCT/MCTES (PIDDAC), and to the project POCI-01-0145-FEDER-030674 funded by the European Regional Development Fund (ERDF) through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) - and by national funds (PIDDAC) through FCT/MCTES. MAB acknowledges the research grant from FCT (Ref. SFRH/BD/145014/2019).

References:

1. Barros M.A.; Sampaio M.J.; Ribeiro A.R.; Silva C.G.; Silva A.M.T.; Faria J.L. *J. Environ. Chem. Eng.* **2020,** *9*, 104747
2. Bergheim M.; Gminski R.; Spangenberg B., Dębiak M.; Bürkle A.; Mersch-Sundermann V.; Kümmerer K.; Gieré R. *Environ. Chem.* **2014**, *11*, 431.

Environment and water

Contribution of inland sources to microplastics increase in aquatic systems: the Portuguese case

S. Magalhães,[a] L. Alves,[a] B. Medronho,[b] M.G. Rasteiro[a]

a) Department of Chemical Engineering, CIEPQPF, University of Coimbra, Pólo II – R. Silvio Lima, 3030-790 Coimbra, Portugal; b) Faculty of Sciences and Technology (MEDITBIO), University of Algarve, Campus de Gambelas, Ed. 8, 8005-139 Faro, Portugal and FSCN, Surface and Colloid Engineering, Mid Sweden University, SE-851 70 Sundsvall, Sweden

Email: solangemagalhaes@eq.uc.pt

Microplastics (MP) have recently become a central discussion theme around the world mainly due to their potential harmful impact on different ecosystems [1]. Plastics are part of our society and since most of them do not biodegrade in any meaningful way, plastic waste can exist for hundreds of years. Moreover, up to now, only a small percentage of plastic waste is recycled being the rest dumped in landfills, incinerated, or simply not collected. The distribution of MP within the water ecosystem, depends on particle density and environmental characteristics, such as winds, currents, and turbulence [1].
Portugal is a coastal country located in the southwestern part of Europe with 92 212 km^2, 1230 km of Atlantic coast and an exclusive economic zone with 1 727 408 km^2, forming part of the Iberian Peninsula [2]. In the present study, we characterize and identify different effluents (industrial and municipal treatment stations and industrial effluents) to analyse which MP predominate in Continental Portugal and which contribute most to environmental contamination. Overall, this work develops strategies for MP analysis in waste waters, especially in the coastal zone, and maps the types of MP prevalent in Portugal. This data base will allow us to create laboratory models which will be used to test new and green removal processes based either on flocculation by bio-flocculants or via membrane separation.

Acknowledgements: This work was financially supported by the Portuguese Foundation for Science and Technology, FCT, via the PhD grant (2020.07638.BD) and the Strategic Research Centre Projects UIDB00102/2020 and UIDB/05183/2020.

References:

1. Magalhães, S.; Alves, L.; Medronho, B.; Romano, A.; Rasteiro, M.d.G. Microplastics in Ecosystems: From Current Trends to Bio-Based Removal Strategies. Molecules (Basel, Switzerland) 2020, 25, 3954, doi: https://doi.org/10.3390/molecules25173954
2. Antunes, J.; Frias, J.; Sobral, P. Microplastics on the Portuguese coast. Marine Pollution Bulletin 2018, 131, 294-302, doi:https://doi.org/10.1016/j.marpolbul.2018.04.025.

Environment and water

Conversion of plastic waste into value-added compounds using cheap and environmentally friendly catalysts

B.F.S. Nunes, M.C. Oliveira, A.C. Fernandes

Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.

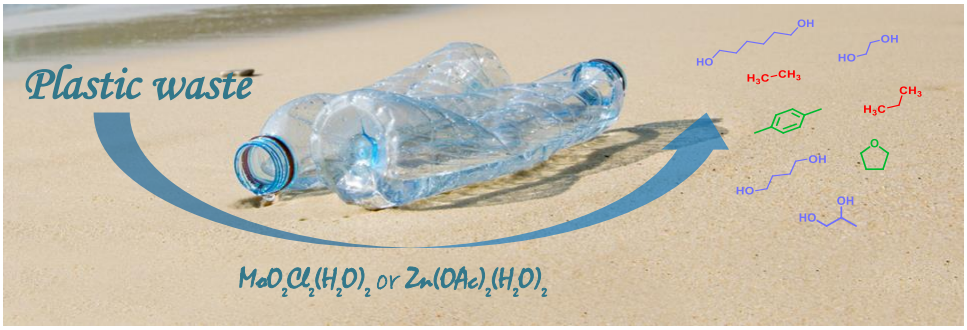
Email: anacristinafernandes@tecnico.ulisboa.pt

Plastics are essential in our lives and will continue to be, so it is urgent to develop cost-efficient methodologies for their recycling, improving the circular economy. In recent years, reductive depolymerization has emerged as an excellent alternative methodology for the valorization of plastic waste and has gained strength as it allows to transform plastic waste into value-added products, which cannot be obtained by other recycling processes. Catalysts can have a fundamental role in this subject.

This communication reports the reductive depolymerization of plastic waste including polycaprolactone (PCL), polylactic acid (PLA), polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) using the cheap and environmentally friendly catalysts $MoO_2Cl_2(H_2O)_2$ and $Zn(OAc)_2.2H_2O$ and a silane as the reducing agent.[1,2]

These catalytic systems proved to be very efficient for the reductive depolymerization of these polyesters into value-added compounds including 1,6-hexanodiol, propane, 1,2-propanediol, *p*-xylene and THF in good yields (Scheme. 1).

This work also demonstrates that it is possible to efficiently recycle plastic waste obtained from domestic waste or generated from different industries including textile or automobile, using eco-friendly, commercially available and inexpensive catalysts, contributing to reduce the large amount of plastic waste that is released into the environment.



Scheme 1 – Reductive depolymerization of plastic waste catalyzed by cheap and environmentally friendly catalysts.

Acknowledgements: This research was supported by Fundação para a Ciência e Tecnologia (FCT) through projects PTDC/QUI-QOR/0490/2020, UIDB/00100/2020 and UIDP/00100/2020. ACF (IF/00849/2012) acknowledges FCT for the “Investigador FCT” Program.

References:

1. Nunes, B. F. S.; Oliveira, M. C.; Fernandes, A. C., *Green Chem.*, **2020**, *22*, 2419.
2. Fernandes, A. C., *ChemSusChem* **2021**, doi:10.1002/cssc.202100130.

Environment and water

Optimization of SPE/HPLC analytical method for 17β-estradiol quantification in wastewater treatment plant (in)effluents using a surface responsive methodology

N.S. Foureaux,[a,b] E.V. Carneiro,[b] A.E. Ribeiro,[a] P. Brito,[a] A. Queiroz[a]

a) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; b) Fundação Mineira de Educação e Cultura (FUMEC), Rua Cobre, nº 200, Cruzeiro, Belo Horizonte – MG, 30310-190, Brasil.

Email: amqueiroz@ipb.pt

The ever-increasing use of endocrine disruptors compounds (EDCs), through pharmaceuticals such as synthetic estrogens, both in humans as well as in animals, are becoming ubiquitous in the environment. In addition to that fact, the poor removal by the conventional biological wastewater treatment plants, becomes a major source of their release into different aquatic matrices. Therefore, the occurrence and, more importantly, the destination of these compounds are matters of utmost importance towards a better public health. The present work is divided in two main experimental steps. First, an SPE/HPLC-UV1 experimental methodology is optimized to detect and quantify 17β-Estradiol (E2) present into aqueous samples. The optimization of HPLC-UV operating conditions consisted of selecting a mobile phase composition that allowed a higher signal of E2, with a lower retention time, after analyzing 10 different compositions, methanol was the chosen one. In Figure 1, it is presented the chromatographic pulses of estradiol using 8 different concentrations (HPLC analysis without SPE extraction) in the 10 combinations of mobile phase tested. The solid phase extraction optimization comprises a three-level Box-Behnken (BBD) experimental design2 with four factors to optimize (sample volume, sample pH, adsorbent drying time and solvent composition in the washing step), combined with a response surface methodology. After the SPE procedure was completed, the samples were analyzed in the HPLC-UV system. The highest responses were obtained with experiments that has pH2, that factor proved to be the one that contributed the most in obtaining a higher recuperation of E2. Figure 2 presents the influence that all 4 parameters, when modified, have in the response (chromatographic area). The validation of the optimized experimental methodology is done by the monitoring of estradiol in wastewater influent and effluent samples from a wastewater treatment plant.

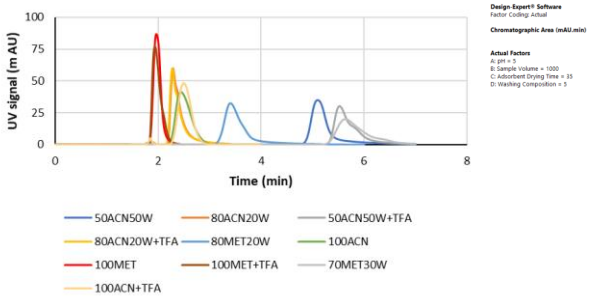


Figure 1. HPLC-UV chromatographic pulses of a E2 standard solution (100 mg/L) injected in 10 different mobile phase combinations.

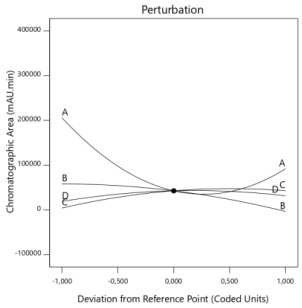


Figure 2. Perturbation graphic relating the influence of each parameter optimized with the response (chromatographic area).

Acknowledgements: The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support by national funds FCT/MCTES to CIMO (UIDB/00690/2020).

References:

1. Fonseca A. P.; Cardoso M.; Esteves V. J Environment Analytic Toxicol 2013, 4(1), 203.
2. Teixeira S.; Delerue-Matos C.; Santos L. Sci Total Environ 2019, 646, 168.

Environment and water

Box-Behnken Design for optimization of Fenton-type reaction for water treatment using heterogeneous catalysts

O. Assila,[a,b] O. Barros O,[c] F. Zerrouq,[b] A. Kherbeche[b] A.M.F. Fonseca,[a,c] P. Parpot,[a,c] T. Tavares,[c] I.C. Neves[a,c]

a) CQUM, Centre of Chemistry, Chemistry Department, University of Minho, Campus de Gualtar, 4710-057, Braga, Portugal; b) Laboratory of Catalysis, Materials and Environment, School of Technology, University Sidi Mohammed Ben Abdellah Fez, Morocco c) CEB - Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal.

Email: ouissal.assila@usmba.ac.ma

Response Surface Methodology (RSM) was widely used in numerous research works for the optimization of different processes for liquid effluents treatment, since water pollution is one of the most serious environmental problem concerning human health and sustainability.[1,2] RSM is a statistical technique applied to reduce the number of experiments, optimize and analyze the experimental independent parameters, that affect a process efficiency, and to generate a mathematical model which describes the process behavior.[1,3] In this work, Box-Behnken design (BBD) was used for optimize the Fenton-type reaction using different bimetallic catalysts based in Rare Earth Elements with iron ion exchanged in zeolite (NaY) or a natural clay from Morocco. The effect of different experimental parameters such as, temperature, concentration of H_2O_2 and the heterogeneous catalysis used, was studied and optimized.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support through Centre of Chemistry (UID/QUI/00686/2013 and UID/QUI/0686/2016) and BioTecNorte (operation NORTE-01-0145-FEDER-000004).

References:

1. Khouni, I. et al., Chem. Eng. J. **2010**, 156, 121–133.
2. a) Assila, O. et al, *J. Chem.* **2020**, 2020, Article ID 6457825, 13; b) Thiam A.et al., *J. Chem.* **2020**, 2020, Article ID 4173152, 14.
3. Shalaby, M.S. et al. *Nano- Structures and Nano-Objects,* **2019**, 100342.

Environment and water

Reusable polymer hybrid membranes for arsenite and arsenate dual-water remediation

H. Salazar,[a, b] P.M. Martins,[c, d] A. Valverde,[e] R. Fernández de Luis,[e] J.L. Vilas,[e] S. Ferdov,[a] S. Lanceros-Mendez.[e, f] G. Botelho[b]

a) Center/Department of Physics, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal; b) Center/Department of Chemistry, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal; c) Centre of Molecular and Environmental Biology, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal; d) IB-S – Institute for Research and Innovation on Bio-Sustainability, University of Minho, 4710-057, Braga, Portugal; e) BCMaterials, Parque Científico y Tecnológico de Bizkaia, 48160 Derio, Spain; f) IKERBASQUE, Basque Foundation for Science, 48009 Bilbao, Spain

Email: hsalazar@fisica.uminho.pt

Water quality is one of the biggest concerns nowadays, since climate change and rapid urbanization/industrialization lead to the overall pollution of the water cycle, and as a final consequence, to the declination and depletion of potable water sources. In this scope, the harmful effects of arsenic (As) are well-known in many geographical areas worldwide affected by As pollution [1].

Currently, different methods have been applied for As removal, and adsorption stands out as one of the most suitable, green, and cheap alternatives due to its high efficiency, simple operation, cost-effectiveness, the potential for reuse and lack side sludges generation [2]. However, the recovery of the nano-sorbents from the aqueous media after their use is not a minor issue since it usually implies time and energy-consuming procedures. Incorporating nano-sorbents into mechanically robust polymeric matrices with the proper macro and mesoporous structure is a suitable approach to overcome the previously mentioned drawbacks [3].

Herein, nanocomposite membranes (NCMs) of poly (vinylidene fluoride-hexafluoropropylene), PVDF-HFP, with different loadings of yttrium carbonate and magnetite were prepared, and their dual adsorption capacity over neutral arsenite (As(III)) and anionic arsenate (As(V)) species was evaluated. The nanoparticles and prepared NCMs were fully characterized in terms of morphology, microstructure, thermal and surface properties. Nanocomposite membranes present a micrometric porous structure with a homogeneous distribution of the active nanoparticles along with the matrix. Chemical, thermal, and water-contact angle characteristics of the NCMs point out that they maintain the chemical and thermal resistant resistance of the parent PVDF-HFP matrix in addition to gain wettability. It was found that As removal was dependent on NPs loading and pH of the media. For instance, efficiencies close to 100% were achieved for arsenate species under acidic conditions whilst adsorption capacity over As(III) was also incremented above 80%. Fe_3O_4/PVDF-HFP nanocomposite showed a dual affinity for the adsorption of As(III) and As(V) species, with maximum adsorption capacities of 92.82 and 137.08 mg/g, respectively. In addition, both NCMs are easily activated and reused without significant efficiency loss. Consequently, PVDF-HFP nanocomposites, especially the iron-based ones, are low-cost, reusable, and efficient water remediation system feasible for the long-term removal of As(III) and As(V) under working conditions mimicking real polluted surface and groundwater worldwide.

Acknowledgements: This work was supported by the European Union and Portuguese Foundation for Science and Technology (FCT): UID/FIS/04650/2020 and UID/QUI/0686/2020. H. Salazar thanks for grant SFRH/BD/122373/2016. The authors thank the financial support from the European Commission Research & Innovation H2020-MSCA-RISE-2017 (Ref.: 778412) INDESMOF project.

References:

1. Ghiorghita, C.A. and M. Mihai, Recent developments in layer-by-layer assembled systems application in water purification. Chemosphere, 2021. 270.
2. Asere, T.G., C.V. Stevens, and G. Du Laing, Use of (modified) natural adsorbents for arsenic remediation: A review. Science of The Total Environment, 2019. 676: p. 706-720.
3. Martins, P.M., et al., Comparative efficiency of TiO2 nanoparticles in suspension vs. immobilization into P(VDF–TrFE) porous membranes. RSC Advances, 2016. 6(15): p. 12708-12716.

Environment and water

Recovery of technology-critical elements from complex aqueous mixtures through live seaweed: optimization by response surface methodology

T. Viana,[a] B. Henriques,[a] N. Ferreira,[a] J. Colónia,[a] J. Pinto,[a] D. Tavares,[a] J. Jacinto,[a] L. Carvalho,[b] J. Pinheiro-Torres,[c] E. Pereira[a]

a) Departament of Chemistry, LAQV-REQUIMTE, University of Aveiro, 3810-193 Aveiro, Portugal; b) LCA – Central Laboratory of Analysis, University of Aveiro, Aveiro, Portugal; c) N9ve – Nature, Ocean, Value, Porto, Portugal

Email: thainara@ua.pt

Electronic waste is one of the most ascending waste streams, whose management has become a priority to avoid environmental impacts, such as water contamination [1]. Nevertheless, e-waste is also a rich source of elements with high economic and technological interest (technology-critical elements – TCE), such as cobalt, europium and platinum, which can be recovered and re-introduced into the production cycle [2]. The use of living macroalgae as biosorbent has been highlighted with potential to recover TCE from contaminated waters [3], yet most studies focus on the removal of an element from simple solutions (synthetic water, containing one element or a small specific group of elements).
The main objective of the present work was to evaluate and optimize the parameters that influence the efficiency of the biosorption/bioaccumulation process performed by *Ulva lactuca* in a complex mixture of contaminants: simulated lamp industry effluent (Y, Eu, La, Ce, Tb, Gd, Hg, Pb, Zn, Cu, Co, Cd, Pt), at different contamination levels (10, 100 and 190 µg/L). Optimization followed the Response Surface Methodology with a Box-Behnken Design (18 trials).
In general, *U. lactuca* presented high removal efficiencies for all elements (central point conditions > 75 %) except for Pt (Figure 1A) and Cd. Results from central point showed a low standard deviation (< 0.99) and a low coefficient of variation (< 1.2 %), which guarantee the reproducibility and feasibility of results. For Eu, which is one of the most valuable TCE, the optimal conditions are 5 g/L of *U. lactuca* (fresh weight) at salinity 15 (Figure 1B), allowing to recover 87 % of the element from the complex solution.

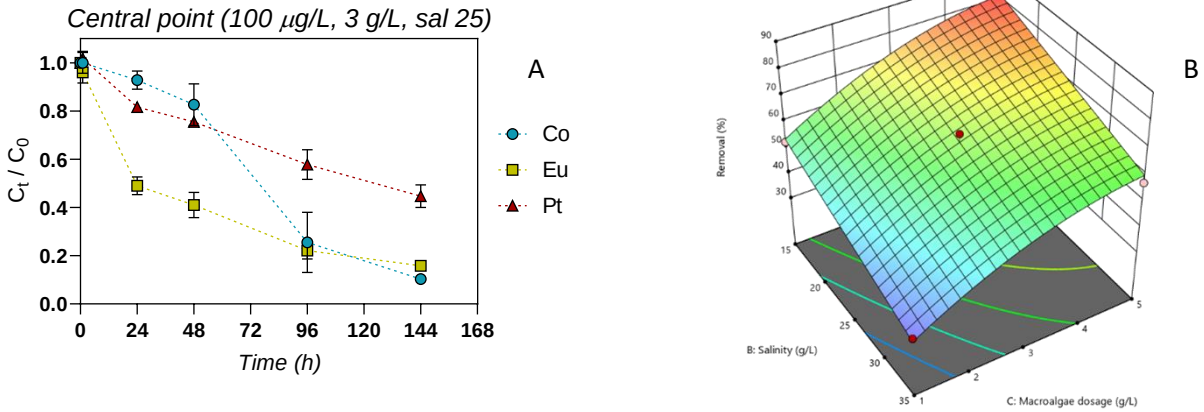


Figure 1: A – Normalized concentrations of Co, Eu and Pt in water; B – 3D-surface response for Eu removal at 48 h of exposure (initial concentration of 100 µg/L).

Acknowledgements: Bruno Henriques benefited from a Research contract (CEECIND/03511/2018) under the CEEC Individual 2018, funded by national funds (OE), through FCT – Fundação para a Ciência e a Tecnologia, I.P. Thanks are also due to University of Aveiro and FCT/MEC for the financial support to REQUIMTE (UIDB/50006/2020) through national funds, and where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement and Compete 2020. This work was supported by the project N°46998_N9ve-REE, co-funded by Portugal 2020 program (PT2020), PO Centro, and European Regional Development Fund.

References:

1. Schweitzer L, Noblet J. Water Contamination and Pollution. In: *Green Chemistry*. Elsevier; 2018:261-290.
2. StEP Initiative. *Annual Report: Five Years of the StEP Initiative*.; 2011.
3. Ferreira N, Ferreira A, Viana T, et al. Assessment of marine macroalgae potential for gadolinium removal from contaminated aquatic systems. *Sci Total Environ*. 2020;749:141488.

Environment and water

Recovery and purification of gold from a chloride multi-metal solution using strong basic anion exchange resins

I.F.F. Neto, M.A.D. Silva, H.M.V.M. Soares

REQUIMTE/LAQV, Departamento de Engenharia química, Faculdade de Engenharia Universidade do Porto, Portugal

Email: up201502999@edu.fe.up.pt

Large quantities of e-waste, such as Printed Circuit Boards (PCB), are produced every year, about 15 to 20 kg per capita in Portugal [1]. Hydrometallurgical methods have proven to be the most efficient when compared to pyrometallurgical methods due to its high selectivity to recovery high value metals. However, this methodology when applied to PCB's results in large volumes of solution with low concentrations of gold (Au), the metal most worth recovering, as well as several other metals, which in turn are in high concentrations. Ion-exchange technology has been recognized as a powerful purification method and provides the possibility of enriching final Au eluate after elution if the resin has high affinity for Au. This method has proved to be interesting from a technological and economical point of view. The low cost, easily handling, and especially being suitable to apply to solutions in which Au is present at trace levels are the main advantages. [2][3][4]

An alternative to existing Au extraction reagents, such as cyanide, is hydrochloric acid. This offers the best commercial expectations, as the chemistry of Au chloride is well studied. Thus, under acid oxidant conditions, the predominant complex ion of the Au (III) species is AuCl4- and basic anion exchange resins, which is the case under study, are positively charged. What differentiates this work from others are the conditions under which they were carried out. The work carried out to date used batch conditions or continuous column tests using mono-element solutions [4]. Thus, these results do not allow us to conclude on the real capacity of these resins to purify Au from multi-metallic solutions, which is of primary importance when considering a real application. In the case of the present work, continuous column assays using multi-metallic solutions were used.

The main objective of this study was to evaluate the performance of two specific anionic-based resins (DOWTM XZ-91419. 00 and PurogoldTM A194) to recover and purify Au contained in a leaching solution with the following metal composition: 4.8x10-5, 5.4x10-5, 1.2x10-3, 3.2x10-3, 2.1x10-3, 2.9x10-4, 8.7x10-5, 5.9x10-4 and 1.1x10-4 mol/L of Au, Ag, Al, Cu, Fe, Ni, Pb, Sn and Zn, respectively. Concentrated (> 3.3 mmol/L) and pure (> 94%) Au eluates were obtained for both resins. The results demonstrated that both resins are interesting options for the purification of Au from multi-metallic chloride solutions containing low grade Au, particularly under the following conditions: (i) the DOWTM XZ-91419.00 resin is suitable for purifying Au from solutions containing Al, Ag, Cu, Fe, Ni, Pb and Zn; (ii) the PurogoldTM A194 resin is suitable for purifying Au from solutions containing Al, Cu, Fe, Ni, Pb and Zn. This is because, although Cu, Fe, Al and Ni were the major metals in the initial multi-metal chloride solution, both resins evidenced high selectivity for Au over these metals. On the other hand, both resins evidenced a poor selectivity for Ag. As a consequence, although Ag was a minor constituent (1.2%) in the initial multi-metal chloride solution, no significant purification occurred for the DOWTM XZ-91419.00 XZ resin and a concentration effect occurred when the PurogoldTM A194 resin was used. Furthermore, for Sn (for both resins) and Pb (for the PurogoldTM A194 resin), lower selectivity of these resins for these metals relative to Au was recorded.

Acknowledgements: This work was financially supported by: Project PTDC/EAMMIN/31041/2017 - POCI-01–0145-FEDER-031041 - funded by FEDER funds through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and with financial support of FCT/MCTES through national funds (PIDDAC).

References:

1. Vanessa Forti, Cornelis Peter Baldé, Ruediger Kuehr, Garam Bel. The Global E-Waste Monitor, 2020.
2. Z. Dong, J. Liu, W. Yuan, L. Zhao. Recovery of Au(III) by radiation synthesized aminomethylpyridine functionalized adsorbents based on cellulose. Chemical Engineering Journal, 283 (2016) 504-513.
3. M. Sethurajan, E.D. van Hullebusch, D. Fontana, A. Akcil, H. Deveci, B. Batinic, J.P. Leal, T. Gasche, M.A. Kücüker, K. Kuchta, I.F.F. Neto, H.M.V.M. Soares, A. Chmielarz. Recent advances on hydrometallurgical recovery of critical and precious elements from end of life electronic wastes - a review. Critical Reviews in Environmental Science and Technology, 49 (2019) 212-275.
4. B.R. Green, M.H. Kotze, J.P. Wyethe. Developments in ion exchange: The Mintek perspective. Jom-Journal of the Minerals Metals & Materials Society. 54 (2002) 37-43.

Materials chemistry and applications

Methanation of CO_2 over Ni-Ce bimetallic oxides supported on SiO_2 aerogel

Daniela R. Ferreira, Joana F. Martinho, Joaquim B. Branco, Ana C. Ferreira

Centro de Química Estrutural, Departamento de Engenharia e Ciências Nucleares, Instituto Superior Técnico, Universidade de Lisboa, Campus Tecnológico e Nuclear, Estrada Nacional 10, ao km 139.7, 2695-066 Bobadela, Portugal

Email: acferreira@ctn.tecnico.ulisboa.pt

The continuous rise of atmospheric CO_2 concentration is the major contributor to climate change.[1] Therefore, adequate measures to capture and valorization are very important to control CO_2 emissions, namely: i) reducing the amount of CO_2 emitted to the atmosphere, ii) increasing the storage of CO_2 and iii) fostering the use of CO_2 as feedstock aiming the production of add value products such as chemicals and fuels [1]. The most promising path is the last one.

Among relevant industrial applications, the methanation of CO_2 is at the core of the Power-to-Gas (PtG) technology for renewable energy storage. [2] The natural gas network is already well established and renewable CH_4 produced via PtG can be fed into the existing grid not only to compensate any fluctuations but, in the future, to completely replace fossil natural gas. [2] Nickel-based catalysts have been at the center of CO_2 methanation numerous studies, normally supported on alumina, zeolites, carbon or silica [3]. In order to avoid the poisoning of the catalyst due to the large amounts of water produced, some studies demonstrated that promising catalysts with bimetallic particles on porous SiO_2 or carbon could solve the problem. [4]

In this work, nanostructured Ni-Ce bimetallic oxide catalysts supported on SiO_2 aerogel were obtained by epoxide addition method (surface area ≈ 550 m^2/g) and prepared by the incipient wetness impregnation technique. The influence of % of metal loading and particle size was evaluated for the CO_2 methanation reaction. The specific activity expressed in liters of $CH_4/g_{Ni}.h$ demonstrated that the best catalyst was 23wt.% ($3NiO.CeO_2$) on SiO_2 aerogel, which corresponds to the smaller nickel oxide crystallite size (≈7 nm), Figure 1.

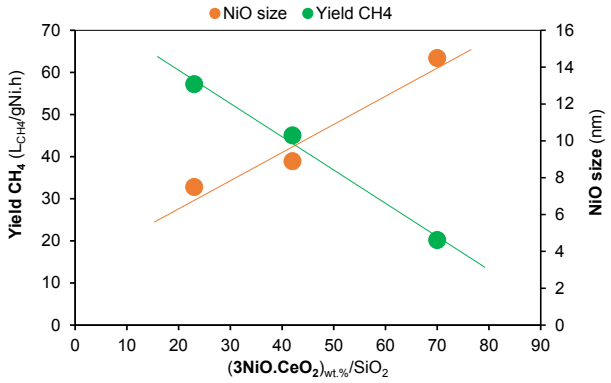


Figure 1: Effect of $NiO.CeO_2$ bimetallic oxide loading on catalytic performance over Ni-Ce supported on SiO_2 aerogel. Reaction conditions: T=350 ºC, H_2/CO_2= 4, GHSV=15000 $mL/g_{cat}.h$

Acknowledgements: Authors gratefully acknowledge the support of the Portuguese "Fundação para a Ciência e a Tecnologia", FCT, through the PTDC/EAM-PEC/28374/2017 and UIDB/00100/2020 project.

References:

1. a) J. Ashok, S. Pati, P. Hongmanorom, Z. Tianxi, C. Junmei, S. Kawi, *Catal. Today* 356, **2020**, 471-489.; b) M. Bowker, *Chemcatchem* 11, **2019**, 4238-4246.
2. a) M. Thema, F. Bauer, M. Sterner, *Renew Sust Energ Rev* 112, **2019**, 775-787. b) M. Gotz, J. Lefebvre, F. Mors, A.M. Koch, F. Graf, S. Bajohr, R. Reimert, T. Kolb, *Renew Energ* 85, **2016**, 1371-1390.
3. M.C. Bacariza, D. Spataru, L. Karam, J.M. Lopes, C. Henriques, *Processes* 8, **2020**.
4. a) Z. A. Qiao, P. Zhang, S. H. Chai, M. Chi, G. M. Veith, N. C. Gallego, M. Kidder, Dai, S., J. the American Chemical Society 136, 2014, 11260-11263. b) Wang, G. H., Hilgert, J.,Richter, F. H., Wang, F., Bonmgard, H. J., Spliethoff, B., Weidenthaler, C., Schüth, F., *Nature Materials* 13, 2014, 293-300.

Materials chemistry and applications

Preparation of photochromic hybrid nanomaterials through different synthetic routes for light-responsive textiles

Marlene Pacheco[a], Tânia V. Pinto[a], Céu M. Sousa[b], Paulo J. Coelho[b], Cristina Freire[a], Clara Pereira[a]

a) REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal; b) Centro de Química - Vila Real, University of Trás-os-Montes e Alto Douro, 5000-801, Vila Real, Portugal

Email: up201811988@fc.up.pt

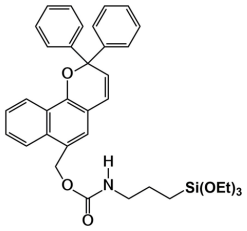


Figure 1. Silylated NPT

The synthesis of light-responsive organic–inorganic hybrid nanomaterials is a promising route to combine multicolor photochromism with a fast response to light stimulus (sunlight/UV light irradiation), high color reversibility and endurance to high temperatures. These materials have ideal characteristics for the production of high-performance photoresponsive textiles for application in anti-counterfeiting, camouflage, NIR reflectance and fashion.[1-3]

In this work, hybrid organic–inorganic nanomaterials were prepared through the functionalization of photochromic inorganic tungsten(VI) oxide (WO_3) with a silylated naphthopyran (NPT), (2,2-diphenyl-2H-benzo[h]chromen-6-yl)methyl (3-(triethoxysilyl)propyl) carbamate, **Figure 1**. After the fabrication of WO_3 by a solvothermal method, the hybrid organic–inorganic nanomaterials were prepared by three strategies (**Figure 2A**): i) covalent *post*-grafting immobilization of the silylated NPT onto WO_3 (WO_3POM_NPTsil_graft); ii) *in situ* immobilization of the silylated NPT during the synthesis of WO_3 (WO_3POM_NPTsil_in situ); and iii) *in situ* immobilization of the non-silylated NPT during the synthesis of WO_3 (WO_3POM_NPT_in situ).The produced photochromic nanomaterials were then incorporated on cotton substrates by screen-printing to develop tailor-made photoresponsive smart textiles. The nanomaterials were characterized by scanning and transmission electron microscopy, X-Ray diffraction, Fourier transform infrared spectroscopy and ^{29}Si and ^{13}C solid-state nuclear magnetic resonance. The photochromic properties of the nanomaterials and screen-printed cotton textiles were studied by diffuse reflectance UV−vis spectroscopy and colorimetry. The colorimetric values were determined by CIE (International Commission on Illumination) Lab color space, in order to calculate the total color difference (ΔE) between the colored (after UV) and uncolored species (before UV). The bleaching constants and half-life times of the nanomaterials and photochromic textiles were determined by UV-Vis spectroscopy.

The three different pathways to immobilize the organic NPT onto WO_3 led to distinct interactions between the organic and inorganic components, resulting in different photochromic properties, namely the initial and final colors of the materials/textiles, the ΔE values and the kinetics of coloration and bleaching (**Figure 2B**). The *in situ* immobilization of the silylated NPT during the fabrication of the photochromic WO_3 led to the hybrid material (WO_3POM_NPTsil_in situ) with the best photochromic response, thus revealing to be the most promising synthetic pathway. The hybrid nanomaterials were successfully applied to textiles by screen-printing maintaining the photochromic characteristics, even after the high temperature required in the process.

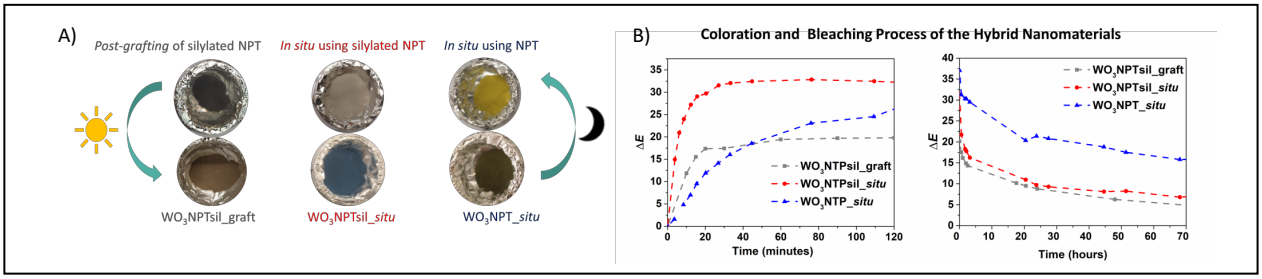


Figure 2.A) Photochromic response of hybrid organic–inorganic materials before and after UV light irradiation. B) ΔE *vs.* time profiles during UV light (λ = 365 nm) irradiation and during bleaching in the dark.

Acknowledgements: Funded by FCT/MCTES through national funds (project UIDB/50006/2020). MP thanks the Doctoral Programme ChemMat and FCT for PhD grant (SFRH/PB/BD/144240/2019). CP thanks FCT for the FCT Investigator contract IF/01080/2015.

1. M. A. Chowdhury *et al.*, *J. Eng. Fibers Fabr.* **2014,** 1, 107-123;
2. D. Sriramulu *et al.*, *Sci. Rep.* **2016**, *6*, 35993;
3. T. V. Pinto *et al.*, *ACS Appl. Mater. Interfaces* **2016**, *8*, 28935-28945.

Materials chemistry and applications

Mononuclear Fe(III) SCO complexes: how do solvates affect the magnetic behaviour?

Rafaela T. Marques,[a*] Liliana P. Ferreira,[a,b] Clara Gomes,[c] Cátia Lopes,[d] Manuel M. Piedade,[d] Paulo N. Martinho[a]

a) BioISI - Biosystems & Integrative Sciences Institute, University of Lisboa, Faculty of Sciences, Campo Grande, C8, 1749-016 Lisboa, Portugal, b) Department of Physics, University of Coimbra, 3004-516 Coimbra, Portugal, c) LAQV-REQUIMTE, University Nova of Lisbon, Faculty of Sciences and Technology, Campus de Caparica, 2829-516, Caparica, Portugal, d) CQE, Centro de Química Estrutural, University of Lisboa, Faculty of Sciences, Campo Grande, C8, 1749-016 Lisboa, Portugal

Email: rafaela.m.1996@gmail.com

With the need to produce materials that store information at the molecular level with increased capacity the spin crossover (SCO) is still a growing field since its relevance ranges from the role of metal ions in biology to magnetic device applications. SCO candidate compounds can be found among a limited group of 3d4–3d7 transition metal ions, such as Fe(III).[1] The effect of the solvent in the lattice of the complex plays an important role in the cooperativity and hysteric transitions due to the intermolecular bonds formed (π-stacking, hydrogen-bonding and van der Waals interactions).[2] The enhancement of the SCO cooperativity mediated by these interactions may also strongly depend on the geometry and electronic structure of the anions and solvent molecules, which should impose appropriate packing favoring significant elastic interactions. The influence of the solvent molecules included in the crystal packing on the SCO properties has already been documented for many different systems, but such changes are rare for mononuclear complexes.[3]

We present the synthesis and characterisation of mononuclear Fe(III) Schiff base complexes that crystallise with different solvates in the crystal lattice. The study of the solvate effect and the influence on the magnetic properties of the compound is also investigated.

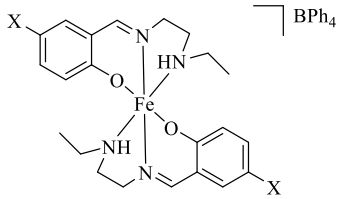


Figure 1: Mononuclear salEen Fe(III) Schiff base complex with BPh_4^- as anion.

Acknowledgements: We thank the Fundação para a Ciência e a Tecnologia, Portugal, for financial support (UIDB/04046/2020 and UIDP/04046/2020) and project PTDC/QEQ-QIN/3414/2014. PNM thanks FTC for the programme CEECIND/00509/2017.

References:

1. Halcrow, M. A., Spin-Crossover Materials: Properties and Applications; John Wiley & Sons Ltd, 2013
2. E. Milin, B. Benaicha, F. El Hajj, V. Patinec, S. Triki, M. Marchivie, C. J. Gómez-García, S. Pillet, J. Am. Chem. Soc. 2014, 90, 12345 Eur. J. Inorg. Chem. 2016, 5305–5314.
3. B. Weber, Coord. Chem. Rev. 2009, 253, 2432–2449.

Materials chemistry and applications

A solid polymer electrolyte based on poly(vinylidene fluoride-co-hexafluoropropylene) combining ionic liquid and zeolite for room temperature lithium-ion battery applications

J. C. Barbosa [a,b], D.M. Correia [a,b], A. Fidalgo-Marijuan [c], R. Gonçalves [d], S. Ferdov [a], C. M. Costa [a,e], V. de Zea Bermudez [b], S. Lanceros-Mendez [c,f]

a) Center of Physics, University of Minho, 4710-058 Braga, Portugal; b) Department of Chemistry and CQ-VR, University of Trás-os-Montes e Alto Douro, 5000-801 Vila Real, Portugal; c) BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain; d) Center of Chemistry, University of Minho, 4710-058 Braga, Portugal; e) Institute of Science and Innovation for Bio-Sustainability (IB-S), University of Minho, 4710-053 Braga, Portugal; f) Ikerbasque, Basque Foundation for Science, 48009 Bilbao, Spain

Email: id8041@alunos.uminho.pt

The growing use of energy storage systems in modern society and the widespread use of lithium-ion technology leads to the need of developing better and safer devices [1]. Solid polymer electrolytes (SPEs) emerged as a suitable option for this purpose, despite their actual performance limitations that are holding back their implementation into devices [2,3]. In this work, a SPE based on a three-component approach (polymer matrix + two fillers) is presented. The effect of the addition of different fillers (1-butyl-3-methylimidazolium thiocyanate ([BMIM][SCN]) and clinoptilolite, a natural zeolite), was studied, as well as the influence of the preparation method on the SPE properties. A stable and uniform SPE (**Figure 1a**) has been obtained with a clear advantage in terms of materials response for battery applications when using the two fillers associated with the poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) matrix, in particular in terms of the thermal and electrochemical properties, with values of ionic conductivity of up to 1.9×10^{-4} S.cm^{-1} at room temperature. The assembled batteries present outstanding performance, with excellent capacity at different discharge rates, and high cycling stability after 50 cycles (**Figure 1b**). The obtained results represent a relevant advance in the field of solid-state electrochemistry.

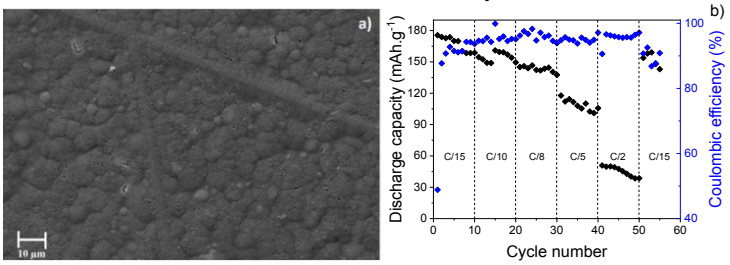


Figure 1: SEM image (a) and battery performance (b) of the PVDF-HFP/[BMIM][SCN]/clinoptilolite SPE.

Acknowledgements: Fundação para a Ciência e Tecnologia: UID/CTM/50025/2021, UID/FIS/04650/2021, UID/EEA/04436/2021, UID/QUI/0686/2021, UID/QUI/00616/2013, UID/QUI/00616/2019, PTDC/FIS-MAC/28157/2017, SFRH/BD/140842/2018 (J.C.B.), SFRH/BPD/121526/2016 (D.M.C), CEECIND/00833/2017 (R.G.), 2020.04028. CEECIND (C.M.C.). Basque Government: ELKARTEK, HAZITEK and PIBA (PIBA-2018-06).

References:

1. Abraham, K.M., Prospects and Limits of Energy Storage in Batteries. The Journal of Physical Chemistry Letters, 2015. 6(5): p. 830-844.
2. Lisbona, D. and T. Snee, A review of hazards associated with primary lithium and lithium-ion batteries. Process Safety and Environmental Protection, 2011. 89(6): p. 434-442.
3. Wu, F., et al., *Polymer electrolytes and interfaces toward solid-state batteries: Recent advances and prospects.* Energy Storage Materials, 2020. **33**: p. 26-54.

Materials chemistry and applications

Enzymatically crosslinked gelatine/alginate hydrogel-based inks applied in 3D printing

Ana C. Lima[a,b], Tamara Calvo-Correas[a], Arantzazu Santamaria-Echart[b], Maria Filomena Barreiro[b], Arantxa Eceiza[a]

a) 'Materials + Technologies' Group, Department of Chemical and Environmental Engineering, Faculty *of* Engineering – Gipuzkoa, *University of the Basque Country, Plaza Europa 1, Donostia-San Sebastian 20018, Gipuzkoa, Spain b) CIMO, Centro de Investigação de Montanha, Instituto Politécnico de Bragança, Campus Santa Apolónia, 5300-253 Bragança, Portugal.*

Email: barreiro@ipb.pt

Hydrogels have attracted interest among all materials applicable in three-dimensional (3D) printing due to their inherent biocompatibility, high degree of flexibility and water holding capacity.[1,2] The 3D structuring enables the use of rapid prototyping techniques, offering flexibility and adaptability, which can be used advantageously from food to pharmaceutical and biomedical applications.[2,3] In this context, hydrogel-based inks' rheological properties must be investigated to fulfil specific requirements, including their processability, print fidelity, and the piece post-printing strength to sustain its structure. To achieve printable mixtures holding suitable physicochemical, rheological, structural and mechanical properties, diverse routes can be adopted, considering hydrogel composite systems, biochemical crosslinking approaches, or reinforced nanocomposites, are among the most promising strategies to provide the needed mechanical properties and/or additional functionalities.[4,5] This versatility is being increasingly directed to sustainable strategies, namely by using biopolymers (e.g., gelatine, alginate), green crosslinkers (e.g., enzymes) or incorporation of natural reinforcements (e.g., cellulose nanocrystals).
Therefore, in this work, gelatine/alginate hydrogel inks were prepared to analyse their viability for direct ink writing 3D printing. Diverse parameters were varied, including the alginate/gelatine ratio (0.5-1%), transglutaminase (TGase) crosslinking enzyme content (10-40%) and cellulose nanocrystals (CNC) incorporation (0-1%). The rheological properties of the gelatine/alginate mixtures, influenced by the total solids content, enzymatic crosslinking with TGase, and cellulose nanocrystals incorporation effects, were analysed, measuring the viscoelastic properties through flow, strain and frequency sweep tests. The mechanical properties of the printed pieces were assessed by compressive tests, and their microstructure was investigated by scanning electron microscopy. In general, all systems showed a shear-thinning behaviour. Except for the 3%Gel-3%Alg system, the inks exhibited a gel-like character in the linear viscoelastic range, indicated by the higher storage modulus (G′>G″). Positive effects were observed with the transglutaminase enzyme addition. A significant viscosity increase was identified at low shear rates for the system with 20% of TGase. Moreover, this system demonstrated the most promising gel behaviour by oscillatory shear stress test.

Acknowledgements: CIMO (UIDB/00690/2020) funded by FCT/MCTES (PIDDAC). National funding by FCT, P.I., through the institutional scientific employment program-contract for A. Santamaria contract. To Erasmus+ (UPV internship). Authors also thank the University of the Basque Country (UPV/EHU) (GIU18/216 Research Group) and the "Macrobehavior-Mesostructure-Nanotechnology" SGIker unit from the UPV/EHU, for their technical support. T. Calvo-Correas thanks the UPV/EHU (ESPDOC19/41).

References:

1. Ma T.; Lv L.; Ouyang C.; Hu X.; Liao X.; Song Y.; Hu X. *Carbohydr. Polym.* **2021**, *253*, 117217.
2. Xu, C.; Dai, G.; Hong, Y. *Acta Biomater.* **2019**, 95, 50.
3. Kuo, C. C.; Qin, H.; Cheng, Y.; Jiang, X.; Shi, X. *Food Hydrocoll.* **2021**, *111*, 106262.
4. Liu, S.; Chen, X.; Zhang, Y. *3D and 4D Printing of Polymer Nanocomposite Materials*. **2020**, 427.
5. Godoi, F. C.; Prakash, S.; Bhandari, B. R. *J. Food Eng.* **2016**, *179*, 44.

Materials chemistry and applications

New 3-ethynylaryl coumarin-based dyes for DSSC applications: synthesis, spectroscopic properties and theoretical calculations

João Sarrato[a], Ana Lucia Pinto[a], Gabriela Malta[a], Eva Röck[b,c], João Pina[b], J. Carlos Lima[a], A. Jorge Parola[a] and Paula S. Branco[a]

a) LAQV-REQUIMTE, Departament of Chemistry, NOVA School of Science and Technology, FCT NOVA, Universidade NOVA de Lisboa, 2829-516, Caparica, Portugal; b) University of Coimbra, Coimbra Chemistry Centre, Department of Chemistry, Rua Larga, 3004-535 Coimbra, Portugal; c)University of Bern, Department of Chemistry, Biochemistry and Pharmaceutical Sciences, Freiestrasse 3, CH-3012 Bern, Switzerland

Email: j.sarrato@campus.fct.unl.pt

A set of 3-ethynylaryl coumarin dyes with mono, bithiophenes and the fused variant, thieno[3,2-*b*]thiophene, as well as an alkylated benzotriazole unit were prepared. For comparison purposes, the variation of the substitution pattern at the coumarin unit was analyzed with the natural product 6,7-dihydroxycoumarin (Esculetin) as well as 5,7-dihydroxycoumarin in the case of the bithiophene dye (**Figure 1**). Crucial steps for extension of the conjugated system involved Sonogashira reactions for introduction of the ethynyl and heterocycle moieties.[1] Photophysical, theoretical (DFT), electrochemical characterization was performed, as well as testing as sensitizers for dye-sensitized solar cells (DSSCs), with a best result of 2% being obtained for the thieno[3,2-*b*]thiophene derivative.

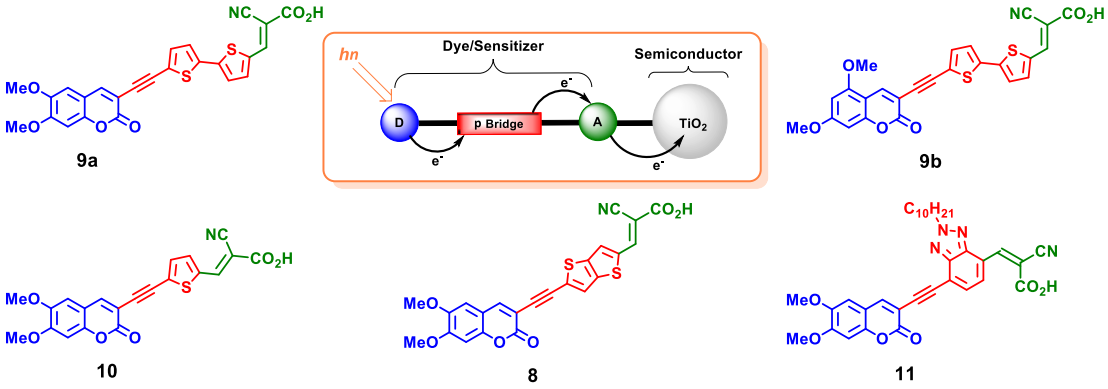


Figure 1: Schematic representation of the D-π-A structure of an organic dye and the respective moieties employed.

Acknowledgements: This work was performed under the projects PTDC/QUI-QOR/7450/2020 "Organic Redox Mediators For Energy Conversion" through FCT – Fundação para a Ciência e a Tecnologia I. P. and POCI-01-0145-FEDER-016387 “SunStorage – Harvesting and storage of solar energy”, funded by European Regional Development Fund (ERDF), through COMPETE 2020 – Operational Programme for Competitiveness and Internationalisation (OPCI). This work was also supported by the Associate Laboratory for Green Chemistry - LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/50006/2020). FCT/MCTES is also acknowledged for the National NMR Facility (RECI/BBB-BQB/0230/2012 and RECI/BBB-BEP/0124/2012,) and PhD grants 2020.09047.BD (J.S.), PD/BD/135087/2017 (A.L.P.) and PD/BD/145324/2019/ (G.M.).

References:

1. Martins, S., et al., Styryl and phenylethynyl based coumarin chromophores for dye sensitized solar cells. *Journal of Photochemistry and Photobiology a-Chemistry,* **2018,** *353,* 564-569.
2. Sarrato, J., et al., 3-Ethynylaryl Coumarin-Based Dyes for DSSC Applications: Synthesis, Spectroscopic Properties, and Theoretical Calculations. *Molecules,* **2021**, *26*, 2934-2950. DOI: 10.3390/molecules26102934.

Materials chemistry and applications

Luminescent aqueous dispersions of lanthanide ions and gum arabic for coatings

Roberto Aguado, Beatriz O. Gomes, Dina Murtinho, Artur J.M. Valente

University of Coimbra, CQC, Department of Chemistry, Rua Larga, 3004-535 Coimbra, Portugal

*Email: rag@uc.pt

The potential of europium(III) and terbium(III) salts for the development of sensors, diodes and other materials with red and green luminescence, respectively, has attracted remarkable interest from researchers and manufacturers.[1] Nonetheless, it is well-known that the f-f transition of lanthanide hydrates is forbidden by the Laporte rule, and thus their luminescence is barely noticeable in solution. Hence, complex formation with an anionic polyelectrolyte and antenna ligands have been sought to enhance (by several orders of magnitude) their light emission under ultraviolet radiation.

This communication reports the use of gum Arabic (GA) to form highly soluble lanthanide-based complexes with RGB properties. GA is a biocompatible and inexpensive branched-chain polysaccharide with the main chain of (1-3)-β-D-galactopyranosyl units and side chains containing L-arabinofuranosyl, L-rhamnopyranosyl, D-galactopyranosyl and D-glucopyranosyl uronic acid units. Metal-ligand interactions take place between lanthanide ions and the carboxyl groups of GA. Interestingly, a water-insoluble antenna can be added to turn the solution into a stable colloidal dispersion that does not precipitate when undisturbed. This is an advantage over other previously used polyelectrolytes, such as the highly hydrophilic poly(sodium acrylate), for which the addition of an organic co-solvent is necessary to avoid phase separation.[2] Such advantage is due to the interfacial activity of GA, given its amphiphilic nature. Figure 1 displays paper strips coated with dispersions of GA, Eu(III) or Tb(III) salts, and a water-insoluble antenna, along with the emission spectra (under UV radiation) of those strips.

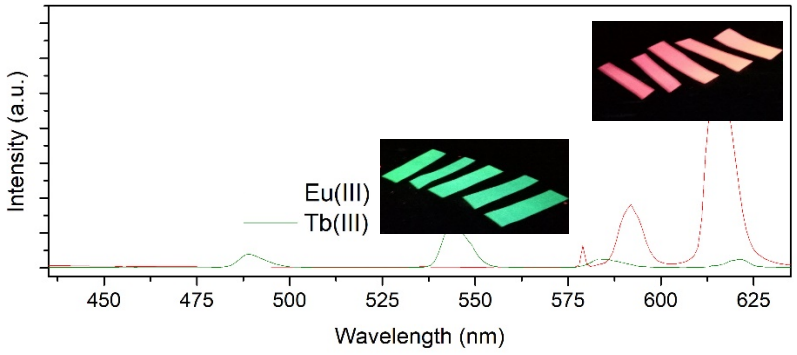


Figure 1: Emission spectra, recorded under radiation at 320 nm, of paper strips coated with Eu(GA)@antenna (upper inset photograph) and Tb(GA)@antenna (bottom inset photograph)..

Acknowledgements: This work was carried out under the Project inpactus – innovative products and technologies from eucalyptus, Project N. º 21874 funded by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of COMPETE 2020 nº246/AXIS II/2017. Financial support from Coimbra Chemistry Centre, which is supported by the FCT through the programmes UID/QUI/00313/2020 and COMPETE, is also gratefully acknowledge.

References:

1. E. Akman, S. Akin, T. Ozturk, B. Gulveren, S. Sonmezoglu, *Solar Ener.,* **2020**, 202, 227.
2. A.F.Y. Matsushita, A.A.C.C. Pais, A.J.M. Valente, *Colloids Surf. A*, **2019**, 569, 93.

Materials chemistry and applications

Determinação cinética de oxitetraciclina usando pontos quânticos de $AgInS_2$ e com recurso a ferramentas quimiométricas

Rafael C. Castro, Ricardo N. M. J. Páscoa, Lúcia M. F. S. Saraiva, João L.M. Santos, David S.M. Ribeiro

LAQV, REQUIMTE, Departamento de Ciências Químicas, Laboratório de Química Aplicada, Faculdade de Farmácia da Universidade do Porto, Rua de Jorge Viterbo Ferreira nº 228, 4050-313 Porto, Portugal

Email: rafael.castro.cl@hotmail.com

A oxitetraciclina (OTC) é um dos antibióticos da família das tetraciclinas e é dos mais comumente usados em veterinária, quer na pecuária, quer na aquacultura. De facto, a OTC é amplamente usada em rações animais como promotor de crescimento, e na prevenção e tratamento de doenças infeciosas, uma vez que possui um amplo espectro atuando contra bactérias gram-positivas e gram-negativas. A utilização abusiva deste antibiótico faz com que seja um poluente do ambiente aquático, o que pode levar a problemas de toxicidade crónica ou de resistência ao fármaco, reduzindo a sua eficácia[1].

Sendo uma ameaça para a saúde pública, diferentes métodos têm sido desenvolvidos para a sua monitorização, tanto em amostras farmacêuticas como em amostras biológicas ou ambientais[2]. No entanto, a maioria destas metodologias necessita de pessoal qualificado para a sua execução, de equipamento sofisticado e procedimentos demorados, e geralmente requer pré-tratamento de amostra. Devido à necessidade de desenvolver metodologias que permitam uma monotorização mais simples, mais rápida e de aplicação no local de amostragem, os métodos baseados em fluorescência têm despertado grande atenção. Assim sendo, o uso de pontos quânticos (QDs) como sondas de deteção fluorescentes pode ser antecipado como uma alternativa valiosa. Nos últimos anos os QDs têm sido amplamente utilizados como sondas fluorescentes, já que exibem propriedades óticas notáveis, como sejam uma fotoluminescência ajustável e dependente do tamanho e/ou composição, elevada foto-estabilidade e elevado rendimento quântico, o que garante simplicidade e versatilidade numa grande variedade de aplicações analíticas[3]. No entanto, até ao momento, o estudo de sondas óticas fluorescentes contemplando o seu perfil cinético tem sido muito pouco explorado, apesar de se mostrar uma alternativa muito promissora. Efetivamente, é expectável que o comportamento cinético da interação entre os QDs e os analitos possa fornecer informações mais úteis para um melhor entendimento dos mecanismos reacionais envolvidos. Para além disso, o uso de ferramentas quimiométricas permite extrair informações adicionais do conjunto de dados, facilitando a perceção das relações entre as amostras e as variáveis analisadas através do recurso a métodos matemáticos e estatísticos que descrevem a relação entre os parâmetros analíticos e os dados obtidos.

Neste trabalho foi explorado o estudo cinético da interação entre a OTC e os QDs ternários de $AgInS_2$ passivados com ácido tiomálico, com o objetivo de realizar a sua quantificação em formulações farmacêuticas. Os resultados obtidos demonstram que, com a adição de concentrações crescentes do antibiótico a intensidade de fluorescência dos QDs é mais inibida ao longo do tempo (**Figura 1**). Os dados recolhidos foram tratados com ferramentas quimiométricas, nomeadamente U-PLS (*unfolded partial least squares*) e os resultados revelaram coeficientes de determinação superiores a 0.95.

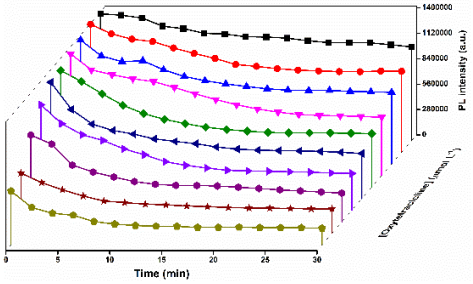


Figure 1: Estudo cinético da interação entre os QDs e concentrações crescentes de OTC.

Agradecimentos: Rafael C. Castro agradece à FCT (Fundação para a Ciência e Tecnologia) a bolsa de doutoramento ref. 2020.08465.BD.

References:

1. Chopra, I.; Roberts, M.; Microbiol Mol Biol Rev **2001**, 65, 232-260
2. Bacanlı, Merve; Başaran, Nurşen; Food Chem Toxicol **2019**, *125*, 462-466.
3. Castro, R.C.; Ribeiro, D.S.M.; Santosm J.L.M.;, Coord. Chem. Rev. **2021**, 429, 213637.

Materials chemistry and applications

Synthesis and characterization of yolk-shell magnetic nanoparticles prepared by a bottom-up approach for biomedical applications

A. Santos Silva[a], T. Sayuri Berberich[a,b], J. L. Diaz de Tuesta[a], S. Delezuk Inglez[b] and H. T. Gomes[a]

a) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; b) Universidade Tecnológica Federal do Paraná, Campus Ponta Grossa, 84017-220 Ponta Grossa – PR, Brasil.

Email: adriano.santossilva@ipb.pt

Magnetic nanoparticles (MNPs) have attracted increasing interest for biomedical applications, due to the possibility of using magnetic fields to drive the nanomaterial to the proper site of administration in drug delivery systems (DDS) [1]. For DDS purposes, MNPs should have biocompatibility to not being harmful to the organism. This limitation can be overcomed by surface modification treatments, increasing biocompatibility of the material, its non-toxicity and dispersibility in water [2]. In this context, in the presented work it was explored the synthesis and characterization of yolk-shell MNPs. The synthesis of yolk-shell MNPs can be classified either as a bottom-up or as a top-down approach, depending if the shell is grown around the core (bottom-up) or if the shell is produced first (top-down). The procedure for the synthesis of the MNPs in this work was done through a bottom-up approach conducted in six steps: I) synthesis of the magnetic core (Fe_3O_4) by solution combustion synthesis, II) coating of the core with formaldehyde-resorcinol resin with tetraethyl orthosilicate, III) annealing in N_2 atmosphere, IV) silica etching with 10 M NaOH, V) surface oxidation with 1 M HNO_3, and VI) functionalization with Pluronic® F-127. Yolk-shell MNPs were analyzed by TGA (air atmosphere) in different steps of the preparation procedure (I-IV), and the core was analyzed by XRD. TGA results (*cf.* Fig. 1(a)) confirm the high purity of the magnetite core (step I), the mass loss reaching around 5% at 900 ºC. The comparison between sample I and IV reveals that the percentage of carbon content in material IV is about 5%, the difference observed between them corresponding to the carbon shell present in material IV. Through DTG (*cf.* Fig. 1(b)), it can be observed the peaks relative to the presence of OH groups of silanols for samples II and III, confirming the presence of silica in the nanomaterials. Moreover, the ash content for samples III and IV indicates the successful leaching of the silica from the MNPs. XRD spectrum in Fig. 1(c) shows characteristic peaks that confirm the presence of magnetite in the material (30.3°, 35.7°, 43.3°, 53.7°, 57.2°, and 62.8°). Thus, the obtained material presents high stability in water, high biocompatibility and can be therefore used for biomedical applications. The main contribution remains on the synthesis of the core by SCS, which can be considered a green method since does not use harmful reactants.

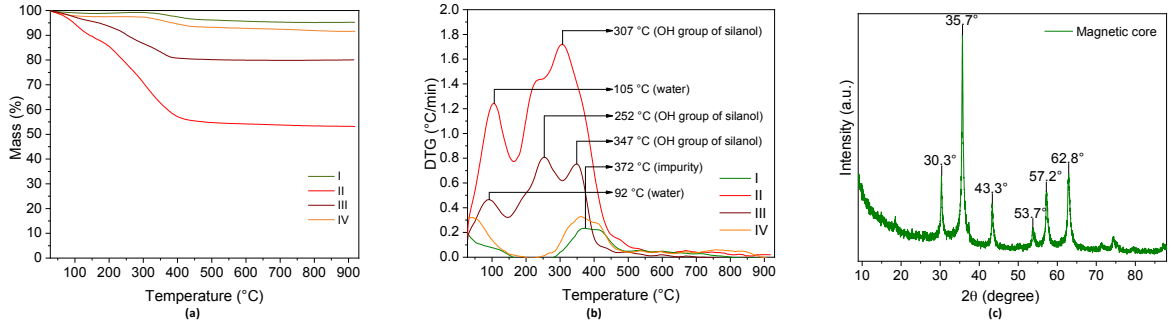


Figure 1: Results for a) TGA, b) DTG for different steps (I-IV) and c) XRD of the core (step I).

Acknowledgements: This work is a result of Project "RTChip4Theranostics - Real time Liver-on-a-chip platform with integrated micro(bio)sensors for preclinical validation of graphene-based magnetic nanocarriers towards cancer theranostics", with the reference NORTE-01-0145-FEDER-029394, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF); and CIMO (UIDB/00690/2020) through FEDER under Program PT2020.

References:

[1] I. Karimzadeh et al., *Adv. Phys. Chem.*, 2017, **2017**.
[2] J. R. P. Oliveira et al., *Jour. of Car. Res.*, 5(1), **2019**.

Materials chemistry and applications

Estudo de diferentes arquiteturas de superfície no âmbito da montagem de um imunosensor piezoeléctrico para determinação de ácido úrico em amostras de urina.

Nelson A. F. Silva[a,b], Magda C. Semedo[a,c], Inês Martins[a], Hugo F. Silva[a,b], Miguel Minhalma[a], Manuel J. Matos[a,d]

a) ADEQ-ISEL/IPL- Área Departamental de Engenharia Química do ISEL/IPL, Rua Conselheiro Emídio Navarro 1, 1959-007, Lisboa; b) CQE - Centro de Química Estrutural, Universidade de Lisboa, FCUL, Campo Grande, 1749-016, Lisboa; c) GeoBioTec – Unidade Geobiociências, Geoengenharias e Geotecnologias, FCT-UNL, Campus da Caparica, 2829-516, Caparica; d) IT – Instituto de Telecomunicações, IST, Av. Rovisco Pais 1, 1049-001, Lisboa

Email: nelson.silva@isel.pt

O presente trabalho visa o desenvolvimento de um biossensor para determinação de ácido úrico em amostras de urina[1]. O dispositivo apresenta uma transdução do tipo piezoeléctrica com utilização de uma microbalança de cristal de quartzo (QCM) cujo sensor consiste num disco de quartzo de 14 mm de diâmetro e 10 MHz de frequência de ressonância nativa, recoberto com um eléctrodo de ouro em ambas as superfícies. O elemento de reconhecimento biológico consiste em anticorpos policlonais contra o ácido úrico, que reconhecerão este antigénio em amostras reais a serem analisadas. O sensor desenvolvido será utilizado na monitorização do teor de ácido úrico na população académica, visando quer o controlo da gota úrica quer o estabelecimento de uma relação com o perfil alimentar desta população alvo. Um dos aspectos mais importantes relacionados com o desenvolvimento e montagem de um biossensor prende-se com a imobilização do elemento de reconhecimento biológico, cujo procedimento se irá refletir na performance analítica global do dispositivo. O presente trabalho versa um estudo comparativo de diversas metodologias de imobilização dos anticorpos contra o ácido úrico na superfície do elétrodo de ouro que recobre o sensor piezoeléctrico[2]. Inicialmente foi testada a utilização de uma monocamada auto-estruturada (SAM) constituída por Ácido 11-Mercapto-Undecanóico (MUA) e ativada com 1-etil-3-(3'-dimetilaminopropil) carbodiimida (EDC) e *N*-Hidroxisuccinimida (NHS). Numa segunda aproximação testou-se a utilização de proteína A recombinante de *Staphylococcus aureus* (SpA) imobilizada diretamente na superfície do sensor piezoeléctrico. Um terceiro estudo versará uma combinação das duas metodologias anteriores, resultando numa biocamada mista, na qual a SpA será ligada à monocamada auto-estruturada de MUA após ativação dos grupos carboxílicos com EDC e NHS. A figura 1 mostra um esquema das diferentes arquiteturas de superfície consideradas no presente estudo.

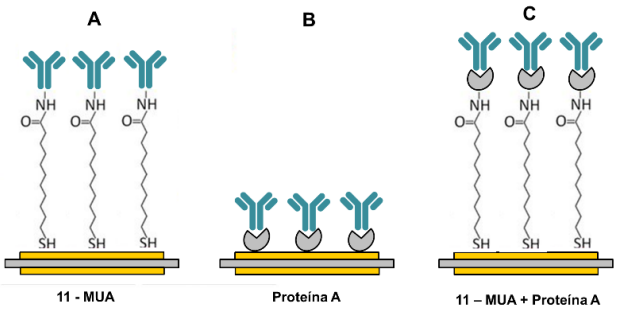


Figura 1: Diferentes arquiteturas de superfície testadas na montagem do biossensor piezoeléctrico.

Agradecimento: Ao Instituto Politécnico de Lisboa pelo financiamento do projeto “BioAURIC” âmbito dos projetos IDI&CA 2020.

Referências:

1. Clebak, k. T.; Morrison, A.; Croad, J. R. *American Family Physician*, **2020**, 1;102(9), 533.
2. Shanehbandi, D.; Majidi, J.; Kazemi, T.; Baradaran, B.; Maleki, L., A.; fathi, F.; Dolatabadi, J.; E.; N. *Advanced Pharmaceutical Bulletin*, **2017**, 7(2), 189

Chemistry in life sciences

Evaluation of a specific OFF-ON fluorescence reporter for Granzyme B activity

C.D.F. Martins,[a] M.C. Silva,[b] J. Gallo,[b] M.M.M. Raposo,[a] S.P.G. Costa,[a]

a) Centre of Chemistry, University of Minho, Campus of Gualtar, 4710-057 Braga, Portugal; b) Nanomedicine Research Group, International Iberian Nanotechnology Laboratory, Av. Mestre José Veiga s/n, 4715-330, Braga, Portugal

Email: catiadf_martins@hotmail.com

Optical imaging with fluorescence probes has been widely used in biochemical assays due to its high sensitivity and fast response.[1] The use of activatable fluorescent probes increases the signal/background ratio in optical imaging, providing reliable tools to monitor protease activity.[2] A promising strategy for the design of these probes is based on an energy transfer between a donor (fluorescent dye) and a complementary acceptor (fluorophore or chromophore) on each end of a peptide. Upon the processing of the peptidic sequence by a specific enzyme, activatable probes switch their fluorescence from an "off" to an "on" state, generating a fluorescent signal proportional to the activity of the enzyme.[1,3] Based on our research interests,[4,5] we have used this principle to synthesize an OFF-ON reporter for Granzyme B (GzmB), a serine protease which plays an important role in target cell apoptosis when released by cytotoxic T lymphocytes (CTL) or natural killer (NK) cells.[6] Therefore, a peptidic sequence specific for GzmB, obtained by microwave-assisted solid-phase peptide synthesis and labelled with a fluorophore (Edans) at the *N*-terminal and a fluorescence quencher (Dabcyl) at the *C*-terminal (**Figure 1**), was used as substrate in activity assays, in order to determine its potential application as a fluorescent substrate for real-time monitoring of GzmB activity in cancer therapy.

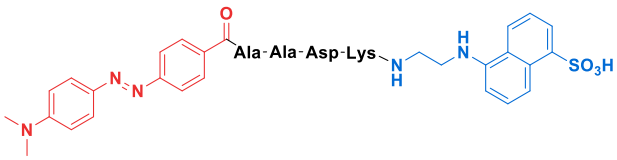


Figure 1: The labelled peptide substrate for Granzyme B.

Acknowledgements: The authors acknowledge Fundação para a Ciência e Tecnologia - FCT (Portugal) for funding through CQUM (UID/QUI/00686/2020) and project PTDC/QUI-COL/28052/2017 and a PhD grant to C. D. F. Martins (SFRH/BD/05277/2020). The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network and was purchased within the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT.

1. Chen, C.; Tian, R.; Zeng, Y.; Chu, C.; Liu, G. *Bioconjugate Chem.* **2020**, *31*, 276-292.
2. Simard, B.; Mironov, G. G.; Tomanek, B.; van Veggel, F. C. J. M.; Abulrob, A. *J. Pept. Sci.* **2016**, *22*, 415–420.
3. Drake, C. R.; Miller, D. C.; Jones, E. F. *Curr. Org. Synth.* **2011**, *8*, 498-520.
4. Martins, C. D. F.; Raposo, M. M. M.; Costa, S. P. G. *Proceedings* **2019**, *41*, 34.
5. Martins, C. D. F.; Raposo, M. M. M.; Costa, S. P. G. *Chem. Proc.* **2021**, *3*, 6.
6. Larimer, B. M.; Wehrenberg-Klee, E.; Dubois, F.; Mehta, A.; Kalomeris, T.; Flaherty, K.; Boland, G.; Mahmood, U. *Cancer Res.* **2017**, *77*, 2318–2327.

Chemistry in life sciences

Synthetic approach for the synthesis of a new family of phosphoglycoglycerols

C.I. Cipriano, F. Santos, P. Máximo, P. S. Branco

LAQV-REQUIMTE: Department of Chemistry, NOVA School of Science and Technology, FCT NOVA, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

Email: ci.cipriano@campus.fct.unl.pt

The isolation of a natural compound with antimicrobial activity containing a D-galactose, a glycerol and a diethanolamine phosphate units led to investigate the synthesis of phosphoglycoglycerols.
As strategy for the synthesis of this new family of phosphoglycoglycerols, an acetyl-protected D-galactose (**1**) was converted into a thiophenol derivative (**2**) that can couple to a diethanolaminephosphoglycerol synthon (**3**) or to a simple glycerol unit (**4**). In the latter case, final reaction with diethanolaminephosphate will provide access to new phosphoglycoglycerols (Figure 1).d
The D-galacto thiophenyl derivative (**2**) was obtained with a global yield of 42% in three steps. [1,2]
The diethanolamine phosphoglycerol (**3**) synthon was obtained as a N-CBz protected derivative starting from 2,2-dimethyl-1,3-dioxolan-4-yl)methanol, $POCl_3$ and N-CBz ethanolamine.
Coupling assays have so far used D-galacto thiophenyl derivative (**2**) and 2,2-dimethyl-1,3-dioxolan-4-yl)methanol (**4**) in the presence of acetone, N-bromosuccinimide and solid $NaHCO_3$, product being obtained in 16% yield.

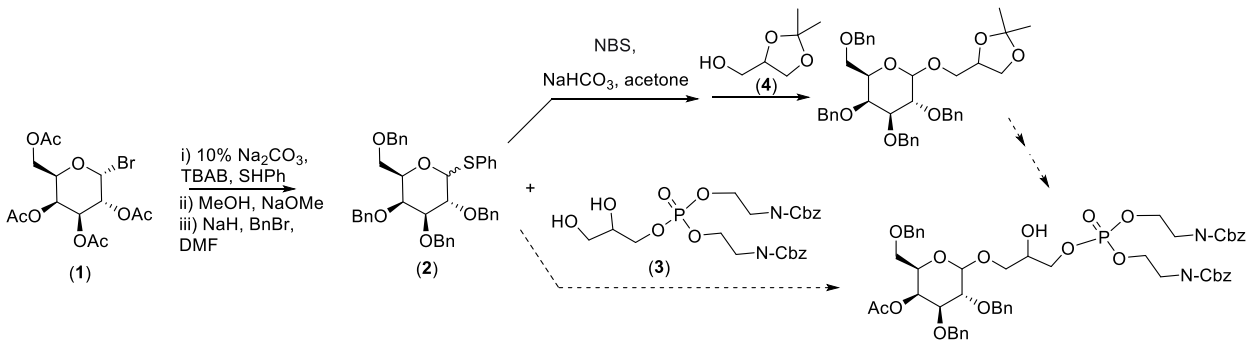


Figure 1: Synthetic pathway outlined for the synthesis of a phosphoglycoglycerols.

Acknowledgements: This work was also supported by the Associate Laboratory for Green Chemistry—LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/50006/2020).

References:

[1] L. Gong et al., Ni-Catalyzed Suzuki-Miyaura Cross-Coupling of α-Oxo-vinylsulfones to Prepare C-Aryl Glycals and Acyclic Vinyl Ethers, **2019**, *J. Am. Chem. Soc.*,141, 7680–7686.
[2] T. Ghosh, A. Santra, and A. K. Misra, Appel-reagent-mediated transformation of glycosyl hemiacetal derivatives into thioglycosides and glycosyl thiols, **2013**, *Beilstein J. Org. Chem*., 9, 974–982.

Chemistry in life sciences

Synthesis of the human neutrophil elastase inhibitor Ala-Ala-Pro-Val using microwave-assisted solid phase

A.F.G. Silva[1], H.P. Felgueiras[2], S.P.G. Costa[1], S.M.M.A. Pereira-Lima[1]

[1] Centre of Chemistry (CQ), University of Minho, Rua da Universidade, 4710-057 Braga, Portugal; [2]Centre for Textile Science and Technology (2C2T), University of Minho, Alameda da Universidade, 4800-058 Guimarães, Portugal

Email: pg40181@alunos.uminho.pt

Some of the most current and frequent diseases in the world population, such as diabetes mellitus and hypertension, can lead to the formation of chronic wounds.[1] These wounds are characterized by a prolonged inflammatory stage that does not evolve throw the subsequent stages of wound healing. This continuous inflammatory stage leads to the continuous activation of inflammatory cells, such as neutrophils, and consequent release of proteases like the human neutrophil elastase (HNE).[2] The released enzymes are related to the wound healing process. However, in chronic wounds HNE activity is uncontrolled and has been implicated in tissue damage. In these cases, endogenous HNE inhibitors are not enough to control the enzyme activity. Consequently, is important to test new potential HNE inhibitors.[3] The tetrapeptide Ala-Ala-Pro-Val (AAPV) (**figure 1**), is known for the ability to inhibit HNE activity.[4] In fact, the incorporation of therapeutic peptides with interesting activities, such as anti-inflammatory and antimicrobial activities, into wound dressings to improve chronic wounds treatment is a raising field.[5]

Here, we have synthesized the peptide AAPV by means of microwave-assisted solid phase peptide synthesis with a CEM Discover SPS microwave. A chlorotritylchloride solid support pre-loaded with valine was used. The α-amino protection was 9-fluorenylmethoxycarbonyl and the coupling reagents pair *N,N'*-diisopropylcarbodiimide/ethyl cyanoglyoxylate-2-oxime. Once synthesized the peptide structure was confirmed by two-dimensional nuclear magnetic resonance spectroscopy and its purity accessed by analytical high performance liquid chromatography. A yield of 65% was obtained. Then we explored the antimicrobial potential of AAPV against bacteria which usually colonize chronic wounds, such as *Staphylococcus aureus*, *Staphylococcus epidermidis* (Gram-positive), *Pseudomonas aeruginosa* and *Escherichia coli* (Gram-negative), by minimum inhibitory concentration evaluations. The peptide only has demonstrated activity at 2mg/mL, which is too high for a cost-effective antimicrobial application.

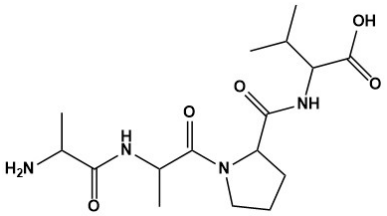


Figure 1- Structure of AAPV peptide

Acknowledgements: Thanks are due to Fundação para a Ciência e Tecnologia (FCT) and FEDER (European Fund for Regional Development)-COMPETE-QRENEU for financial support through the Chemistry Research Centre of the University of Minho (UID/QUI/00686/2020). Thanks are also due to FCT for financial support to the Portuguese NMR network (PTNMR, Bruker Avance III – Univ. Minho).

References:

(1) Sen, C. K. *Adv. Wound Care* **2021**, *10* (5), 281–292.
(2) Menke, N. B.; Ward, K. R.; Witten, T. M.; Bonchev, D. G.; Diegelmann, R. F. *Clin. Dermatol.* **2007**, *25* (1), 19–25.
(3) Vasconcelos, A.; Azoia, N. G.; Carvalho, A. C.; Gomes, A. C.; Güebitz, G.; Cavaco-Paulo, A. *Eur. J. Pharmacol.* **2011**, *666* (1–3), 53–60.
(4) Santos, F. C.; Soares, A. M. S.; Gonçalves, M. S. T.; Costa, S. P. G. *Amino Acids* **2017**, *49* (6), 1077–1088.
(5) Felgueiras, H. P.; Amorim, T. P. In *Research Trends of Microbiology*; MedDocs Publishers LLC, 2019.

Chemistry in life sciences

Expanding the chemical diversity of azaaurones as a new chemical tool in the fight against tuberculosis

A. Campaniço[a]*, S.G. Harjivan[a], E. Freitas[a], M. Serafini[a], A. Jordaan[b], D.F. Warner[b], R. Moreira[a], F. Lopes[a]

a) Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, University of Lisbon, Av. Prof. Gama Pinto, 1649-003 Lisboa (Portugal) b) Institute of Infectious Disease and Molecular Medicine, University of Cape Town, Rondebosch 7701, South Africa; SAMRC/NHLS/UCT Molecular Mycobacteriology Research Unit, Department of Pathology, University of Cape Town, Rondebosch 7701, South Africa; Welcome Centre for Infectious Diseases Research in Africa, University of Cape Town, Rondebosch 7701, South Africa

Email: andrecampanico@campus.ul.pt

Tuberculosis (TB) is a deadly disease caused by a single infectious agent, *Mycobacterium tuberculosis* (M.tb). The complexity and duration of the treatment lead to misuse and low compliance by patients, increasing disease burden and the appearance of multidrug-resistant strains of *M.tb*. Thus, new antibiotics active against drug-resistant *M.tb* and useful for short period therapeutic regimens at lower required doses are urgently needed. [1,2] A family of azaaurone-based derivatives, from a chemical library developed in iMed.ULisboa, revealed to be active against *M.tb*, including multidrug- and extensively drug-resistant tuberculosis from clinical isolates, at a submicromolar level. [3] Despite the promising activities, this new scaffold displayed poor ADME properties. We now report the complete SAR exploration and ADME profiling of newly synthesized derivatives. Along with an enhanced metabolic stability and solubility, rings A and B as well as N-substitutions were extensively explored. (**Figure 1**) The double bond within the scaffold was also reduced to a single bond, generating a new family of saturated azaaurones.

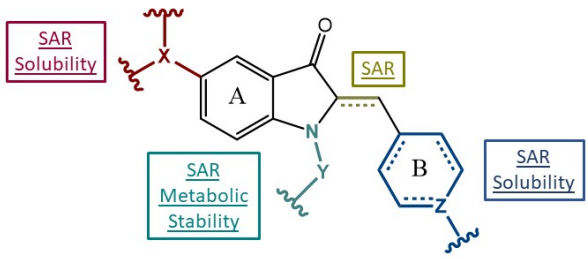


Figure 1: Derivatization of the Azaaurone scaffold, with main objectives per moiety.

Acknowledgements: This research was funded by projects UIDB/04138/2020 and UIDP/04138/2020 (Fundação para a Ciência e Tecnologia (FCT), Portugal) and PTDC/MED-FAR/30266/2017 and LISBOA-01-014-FEDER-030266 (FCT and FEDER). We also acknowledge FCT for fellowship SFRH/BD/131896/2017 (A.C.). This work was also supported by the Strategic Health Innovation Partnerships (SHIP) initiative of the South African Medical Research Council with funds from the National Treasury under its Economic Competitiveness and Support Package (D.F.W.).

References:

1. Campaniço, A., Moreira, R., Lopes, F., Eur J Med Chem., 2018, 150, 525-545.
2. Ehrt S. et al, Cell Microbiol., 2009, 11, 1170-1178.
3. Campaniço A, Carrasco MP, Njoroge M, Seldon R, Chibale K, Perdigão J, Portugal I, Warner DF, Moreira R, Lopes F., ChemMedChem, 2019, 14, 1537-1546.

Chemistry in life sciences

Synthesis and screening of antibacterial activity of 2,4,5-tri(hetero)arylimidazoles based on thieno[3,2-*b*]thiophene

N L.P. Ramos,[a] M. Barros,[a,b] R. Oliveira,[c,d,e] S.P.G. Costa[a] and M.M.M. Raposo[a]

a) Centre of Chemistry, Campus of Gualtar, University of Minho, 4710-057 Braga, Portugal; b) Presently at Instituto Interuniversitario de Investigación de Reconocimiento Molecular y Desarrollo Tecnológico (IDM),Universitat Politècnica de València, Universitat de València, Doctor Moliner 50, Burjassot, 46100 Valencia, Spain; c) Centre of Molecular and Environmental Biology (CBMA), Department of Biology, Campus of Gualtar, University of Minho, 4710-057 Braga, Portugal; d) Centre for the Research and Technology of Agro-Environmental and Biological Sciences (CITAB), Campus of Gualtar, University of Minho, 4710-057 Braga, Portugal; e) Centre of Biological Engineering (CEB), Campus of Gualtar, University of Minho, 4710-057 Braga, Portugal

Email: nuna.ramos15@gmail.com

After the discovery of antibiotics, efforts were made to develop new drugs in order to treat infections caused by a wide range of bacterial strains. With the use of antibiotics for decades, bacteria have adapted, so that resistant strains have emerged. Moreover, the uncontrolled and abusive use of antibiotics has increased, which aggravates the emergence of new resistant strains. The emergence of multidrug resistant (MDR) bacteria has quickly become a worldwide health problem, so new strategies must be developed in order to control MDR bacteria, namely the rational development of new drugs. Imidazole derivatives have several biological activities, including antibacterial activity. In this sense, efforts have been made to develop imidazole-based compounds, because they present higher curative effect than other antibiotics used in clinical practice, lower toxicity and less side effects.[1]
With this in mind, we report the synthesis of two 2,4,5-tri(hetero)arylimidazoles **3a**-**b** based on thieno[3,2-*b*]thiophene heterocyclic spacer (**Figure 1**), through the Radziszewski reaction[2] and their characterization by ^{1}H and ^{13}C NMR, UV-Vis absorption and fluorescence spectroscopies. In addition, a screening for antibacterial activity with the synthetized imidazole derivatives against *Bacillus subtilis* was carried out, using the agar diffusion technique. The results showed the inhibition of *Bacillus subtilis* proliferation, suggesting antibacterial activity. Therefore, these new imidazole derivatives have the potential for the development of new antibacterial drugs.

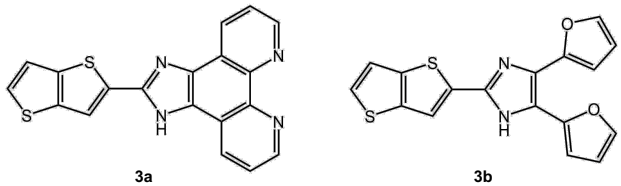


Figure 1: Structures of imidazole derivatives **3a**-**b** based on thieno[3,2-*b*]thiophene.

Acknowledgements: Thanks are due to Fundação para a Ciência e Tecnologia (FCT) and FEDER (European Fund for Regional Development)-COMPETE-QRENEU for financial support through the Chemistry Research Centre of the University of Minho (UID/QUI/00686/2020). This work was also supported by the "Contrato-Programa" UIDB/04050/2020 funded by national funds through the FCT I.P. Thanks are also due to FCT for financial support to the Portuguese NMR network (PTNMR, Bruker Avance III – Univ. Minho).

References:

1. a) Xu Z.; Li H.; Qin X.; Wang T.; Hao J.; Zhao J.; Wang J.; Wang R.; Wang D.; Wei S.; Cai H.; Zhao Y. *AMB Express* **2019**, *9*(1), 101. b) Bulut O.; Oktem H. A.; Yilmaz M. D. *J. Hazard. Mater.* **2020**, *399*, 122902. c) Hossain M.; Nanda A. K. *Scr. Sci. Pharm.* **2018**, *6*(5), 83-94.
2. a) Okda H. E.; Sayed S. E.; Ferreira R. C. M.; Otri, I.; Costa S. P. G.; Raposo M. M. M., Martínez-Máñez R.; Sancenón F. *Dyes Pigments* **2019**, *162*, 303-308. b) Okda H. E.; Sayed S. E.; Ferreira R. C. M.; Costa S. P. G.; Raposo M. M. M., Martínez-Máñez R.; Sancenón F. *Dyes Pigments* **2018**, *159*, 45-48. c) Ferreira R. C. M.; Costa S. P. G.; Gonçalves H.; Belsley M.; Raposo, M. M. M. *New J. Chem.* **2017**, *41*(21), 12866-12878.

Chemistry in life sciences

Camphorimine gold complexes active towards Gram-negative bacteria strains with high selectivity for *Burkholderia contaminans*

M.F.N.N. Carvalho,[a] J.P. Costa,[a] A.M. Galvão,[a] C.F. Soeiro,[b] F. Marques,[c] S.A. Sousa[b] and J.H. Leitão[b]

a) Centro de Química Estrutural e Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal; b) Instituto de Bioengenharia e Biociências, Departamento de Bioengenharia, Instituto Superior Técnico Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal; c) C²TN, Centro de Ciências e Tecnologias Nucleares Instituto Superior Técnico, Departamento de Engenharia e Ciências Nucleares, Universidade de Lisboa, Estrada Nacional 10 (km 139,7), 2695-066 Bobadela LRS, Portugal

Email: fcarvalho@tecnico.ulisboa.pt

The increasing resistance of bacteria to commercially available antibiotics is a threat to human health and represents a significant burden to national health systems. Strategies to face such problem include search for new compounds that act through mechanisms different from those in clinical use. Focused on that, we found that silver camphorimine complexes have good antibacterial and excellent antifungal properties.[1,2] To try to tune and optimize those antibacterial properties, new camphorimine (LY) gold complexes of types $[Au(CN)L_n]$ $[\{Au(CN)\}_2L_n]$ and $K[Au(CN)_2L]$ were synthesized. Since no suitable crystals were obtained for X-ray diffraction analysis, DFT calculations were done to ascertain on the structural arrangement of the complexes. **Figure 1** depicts the structure obtained for $[\{Au(CN)\}_2(LY)]\cdot 2H_2O$ ($Y=C_6H_4CH_3$).The antibacterial activity of the complexes against the Gram-positive *Staphylococcus aureus* and the Gram-negative *Escherichia coli*, *Pseudomonas aeruginosa* and *Burkholderia contaminans* was assessed through the experimental determination of the Minimum Inhibitory Concentration (MIC). Results show that the Au(I) complexes are active towards all the strains under study, having high activity towards *P. aeruginosa* and excellent selectivity towards *B. contaminans* IST408 (**Table 1**). The toxicity of these complexes is still too high aiming at non-topic applications.

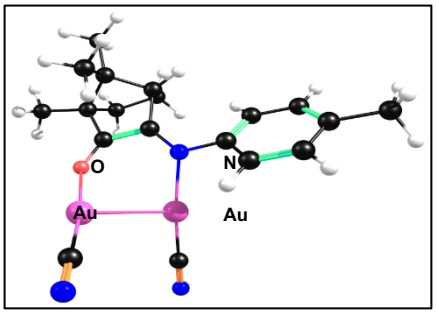
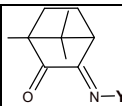


Figure 1 Structural arrangement for $[\{Au(CN)\}_2(LY)]\cdot 2H_2O$ ($Y=C_6H_4CH_3$) found by DFT calculations

Table 1 – Antibacterial activity of camphorimine Au(I) complexes

COMPOUND		MIC (μg/mL)	
		P. aeruginosa 477	*B. contaminans* IST408
$K[Au(CN)_2(LY)]$	**NH_2**	6.9 ± 0.3	3.8 ± 0.2
$Au(CN)(LY)]\cdot CH_3CN$		8.7 ± 1.4	5.4 ± 0.4
$K[Au(CN)_2(LY)]\cdot H_2O$	**$C_6H_4NH_2$**	17.3 ± 2.1	4.6 ± 0.5
$[Au(CN)(LY)_3]\cdot H_2O$		9.1 ± 1.9	8.4 ± 1.2
$[\{Au(CN)\}_2(LY)]\cdot 2H_2O$	**$C_6H_4CH_3$**	17.3 ± 1.3	5.3 ± 0.3
$[Au(CN)(LY)_2]\cdot ½CH_3CN$		25.4 ± 10.9	9.4 ± 1.4
$KAu(CN)_2$	—	13.6 ± 0.7	2.2 ± 0.02

The herein results show that complexes derived from camphorimine ligands with an amine substituent ($Y=NH_2$, $C_6H_4NH_2$) perform better than those with the methyl substituent, pointing out the high relevance of hydrogen interactions in the mechanisms of action of these complexes.

Acknowledgements: We thank financial support by FCT - Fundação para a Ciência e a Tecnologia through projects UIDB/0100/2020, UID/Multi/04349/2019 and UIDB/04565/2020 and a Grant to Joana Costa (BL-CQE/2018-013).

References

1. Cardoso J.M.S; Guerreiro S.I; Lourenço A.; Alves M.M; Montemor M.F.; Mira N.P.; Leitão J.H.; Carvalho M.F.N.N. PLoS ONE, **2017**. *12*(5): e0177355.
2. Costa J.P; Pinheiro M.J.F; Sousa, S.A; Botelho do Rego A.M; Marques F; Oliveira M.C; Leitão J.H; Mira N; Carvalho M.F.N.N. Antibiotics **2019**, *8*, 144.

Chemistry in life sciences

New hydrazone derivatives as promising antimalarial drugs

Teixeira, S.,[a] Meirinho, S.,[b] Ferreira, P.,[b] Carvalho, M.A.[a]

a) CQ, Chemistry Research Centre, University of Minho, Gualtar, 4710-057 Braga, Portugal; b) Life and Health Sciences Research Institute (ICVS), School of Medicine, University of Minho, Braga 4710-057, Portugal; ICVS/3B's-PT Government Associate Laboratory, Braga/Guimarães, Braga, Portugal

Email: id9191@alunos.uminho.pt

Malaria is one of the most devastating and deadliest diseases throughout the world.[1] According to the latest World Malaria Report, in 2019, about half of the world's population was at risk of malaria infections, as well as were estimated 229 million cases of malaria and 409 000 malaria deaths.[1] Malaria is a parasitic disease transmitted by bite of *Anopheles* species mosquitoes and caused by five species of *Plasmodium* protozoans. Among them, *Plasmodium falciparum* and *Plasmodium vivax* causes the most severe infections.[2]

The currently used therapies with antimalarial drugs (chloroquine, artemisinin and its derivatives) are failing due to the development of resistance by *Plasmodium* protozoans against the drugs. Also, the development of resistance against insecticides by the disease vectors (female anopheline mosquitoes) and the inefficacy of chemoprophylaxis constitute a threat to the world society.[3] Thus, new antimalarials are urgently needed. Recently, several heterocycle derivatives (e.g., quinoline, quinolone, pyrimidine derivatives, and hydrazones) with antimalarial activity were discovered by the scientific community.[4]

Among of the new heterocycle derivatives as potent antimalarial agents, the hydrazone derivatives stood out. Thus, in our research group, we designed, synthesized, and evaluated a set of novel hydrazone derivatives against 3D7 and Dd2 strains of *Plasmodium falciparum.* The new compounds showed activity against booth strains. All the results will be presented.

Acknowledgements: The authors acknowledge Universidade do Minho, National NMR Network (PINFRA/22161/2016) and the "*Fundação para a Ciência e Tecnologia"* (FCT) for financial support: FEDER-COMPETE, FCT-Portugal, Project UID/QUI/00686/2018 and FCT funded project PTDC/SAU-PAR/28066/2017.

References:

1. WHO. World malaria report 2019. World Health Organization; **2019**. https://www.who.int/malaria/publications/world_malaria_report/en/. Accessed 11 May 2021.
2. Phillips, M. A.; Burrows, J. N.; Manyando, C.; Van Huijsduijnen, R. H.; Van Voorhis, W. C.; Wells, T. N.C. *Nat. Rev. Dis. Primers* **2017**, *3*, 17050.
3. Bekono B. D.; Ntie-Kang F.; Onguéné P. A.; Lifongo L. L.; Sippl W.; Fester K.; Owono L. C. O. *Malar. J.* **2020**, *19*, 183.
4. Narula A. K.; Azad C. S.; Nainwal L. M. *Eur. J. Med. Chem.* **2019,** *181*, 111353.

Chemistry in life sciences

Quenched activity-based probes as novel biochemical tools to analyze resistance to antibiotics

Félix R.,[a] Mallo-Abreu A,[b,c] Carvalho L. A,[a] Moreira R.[a]

a) iMed.UL, Faculdadade de Farmácia da Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal; b) Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS); c) Departamento de Química Orgánica, Facultade de Farmacia. Universidade de Santiago de Compostela, 15782. Santiago de Compostela, Spain.

Email: ritafelix@ff.ulisboa.pt

Beta-lactamases comprise several serine and metallo-hydrolases that are responsible for the bacterial resistance to beta-lactam antibiotics (BLAs), thus posing a serious threat to the treatment of bacterial infections[1]. The serine-based enzymes are one of the most clinically relevant and challenging medicinal chemistry targets because pathogens have evolved to express previously rare or unknown beta lactamases, highlighting the need for new broad spectrum enzyme inhibitors.[1] There has been an increasing interest in developing methods to profile enzyme activity, identify new therapeutic targets and biomarkers, and understanding their molecular mechanisms.

Quenched activity-based probes (qABP) are compounds that contain a fluorophore (F) and a quencher (Q) part, covalently tagging active enzymes but not their inactive form. In this particular case, qABP only shows fluorescence when it is linked to the enzyme, working as a mechanism-based (suicide) inhibitor (**Figure 1**).[2]

This work started with the development and optimization of the synthetic methodology to obtain several beta-lactam-based qABPs (different linkers, quenchers and fluorophores were used in the new molecules). Fluorescence studies of the compounds were performed to evaluate the quantum fluorescence yield (QY) before and after ring-opening in the presence of nucleophiles and beta-lactamases, obtaining final QY up to 92%. Gel-based proteomic studies measuring the fluorescence and the activity of qABPs against beta-lactamase and detection of beta-lactamase in biological matrices are reported.

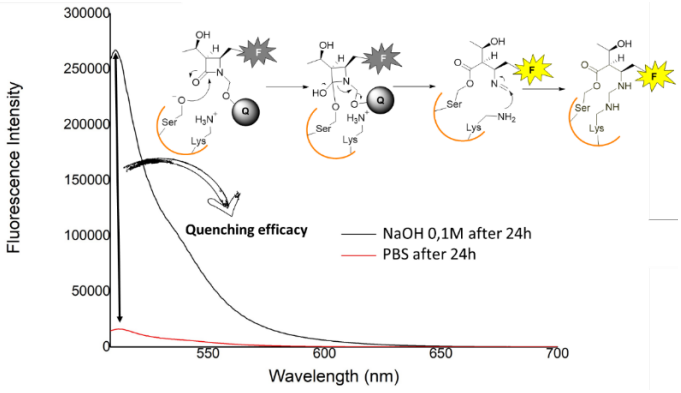


Figure 1 - qABP targeting beta-lactamase mechanism and fluorescence spectrum of qABPs before and after reaction with NaOH.

Acknowledgements: Thanks to FCT through by the funding grants SFRH/BD/137459/2018 and PTDC/BBB-BEP/2463/2014

References:

1. a) Bush, K., *J. Antimicrob. Agents* **2015**, 46, 483. b) Biondi, S; Long S; Panunzio M; Qin WL., *Curr. Med. Chem.* **2011**, 18, 4223.

2. Hu, M., Multicolor, *J. Am. Chem. Soc.*, **2011,** 113, 12009.

Chemistry in life sciences

In silico approach to develop dual inhibitors of MDM2 and MDMX

Lopes EA,[a] Santos MMM,[a] Santos DJVA[a,b]

a) Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy,Universidade de Lisboa, Lisboa, Portugal; b) LAQV@REQUIMTE/Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Porto, Portugal.

Email: ed.lopes@ff.ulisboa.pt / mariasantos@ff.ulisboa.pt

The p53 protein is involved in several biological processes essential to assure the integrity of the human genome. Due to its tumor suppressor function, p53 is considered an attractive therapeutic target for cancer treatment. However, in all types of human cancers, this function is inactivated. In tumors with wild-type p53, p53 downregulation is usually associated with the upregulation of the negative regulators MDM2 and/or MDMX. These two proteins interact with p53 amino acids, Phe19, Leu22, Trp23 and Leu26 in the *N*-terminal domain. Designing small molecules to disrupt the p53-MDM2 and p53-MDMX protein-protein interactions and fully reactivate the p53 tumor suppressor is a promising strategy for the treatment of cancers expressing wild-type p53. However, the conformational differences around the binding site of both negative regulators have made this approach a challenge. For this reason, to date, the development of potent small molecules acting as dual inhibitor of both negative regulators has been unsuccessful[1].
Our research team has been working on the development and optimization of indole-based compounds to obtain dual p53-MDM2/X PPI inhibitors[2]. Previously, we have identified a spiropyrazoline oxindole derivative that induces apoptosis and cell cycle arrest at G0/G1 phase. However, the compound did not bind to MDM2 extensively in a competitive binding assay[2]. Molecular docking simulations revealed that some hydrogen donor/acceptor groups should be introduced in this hit compound to increase interactions with MDM2 and MDMX. In this communication, we report the construction of virtual libraries of spiropyrazoline oxindoles derivatives by adding fragments to the scaffold to obtain dual p53-MDM2/X PPIs inhibitors by structure-based virtual screening of these libraries over the MDM2/X structures (**Figure 1**).

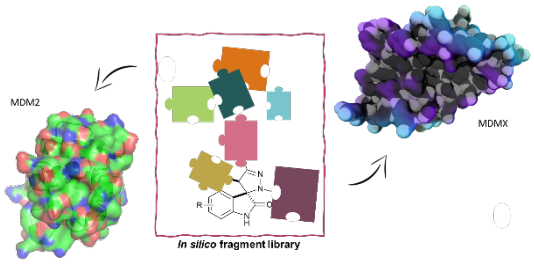


Figure 1: Construction of fragments to obtain dual p53-MDMs PPIs inhibitors.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support through UIDB/04138/2020 (iMed.Ulisboa), project PTDC/QUI-QOR/29664/2017 and PhD fellowship SFRH/BD/137544/2018.

References:

1. a) Espadinha M.; Barcherini V.; Lopes E.A.; Santos M.M.M. *Curr. Top. Med. Chem.* **2018**, *18*, 647. b) Demir Ö.; Barros E.P.; Offutt T.; Rosenfeld M.; Amaro R.E. *Curr. Op. Structural Biology* **2021**, *67*, 187.
2. Nunes R.; Ribeiro C.J.A.; Monteiro Â.; Rodrigues C.M.P.; Amaral J.D.; Santos M.M.M. *Eur. J. Med. Chem.* **2017**, *139*, 168.

Chemistry in life sciences

Chemically comprehensive predictive multivariate models for bioorthogonal metal-free cycloadditions

J.M.J.M. Ravasco,[a] J.A.S. Coelho[a]*

a) iMed.UL, Faculdadade de Farmácia da Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal;

***Email:** jaimeacoelho@campus.ul.pt*

Inverse-electron demand Diels–Alder cycloadditions (IEDDA) have emerged as important bioorthogonal reactions in chemical biology.[1] Among bioorthogonal IEDDA handles, 1,2,4,5-tetrazines are the most used dienes, whereas a variety of structurally diverse linear and cyclic alkynes and alkenes have been used as dienophiles Understanding and predicting reaction rates for bioconjugation reactions is fundamental for evaluating their efficacy in biological systems. Although robust results are often obtained by DFT calculations together with the distortion/interaction model analysis optimization of this transition states geometries are required, which renders this analysis time-consuming.[2]

Here, we present multivariate models generated by a data-driven approach, which are capable of predicting the second order rate constants of bioorthogonal inverse- electron demand Diels−Alder reactions involving 1,2,4,5-tetrazines derivatives and alkene partners. The models are statistically robust and were used to predict/extrapolate the outcome of several reactions as well as to identify mechanistic differences among similar reactants. [3]

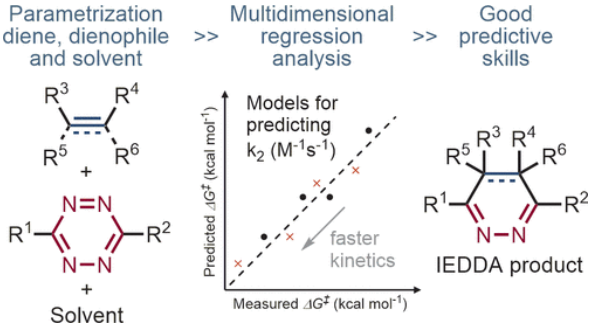


Figure 1: Schematic representation of the workflow to generate the multivariate models

Acknowledgements: Financial support from Fundação para a Ciência e a Tecnologia (PTDC/QEQ QOR/3644/2014, SFRH/BD/120829/2016, and UID/DTP/04138/2019) is gratefully acknowledged.

References:

[1] Oliveira, B. L.; Guo, Z.; Bernardes, G. J. L. Chem. Soc. Rev. **2017**, 46 (16), 4895– 4950,
[2] Liu, F.; Liang, Y.; Houk, K. N. Acc. Chem. Res. **2017**, 50 (9), 2297– 2308
[3] Ravasco, J.M.J.M.; Coelho, J.A.S.C. J. Am. Chem. Soc. **2020**, 142, 9, 4235–4241

Food and natural products

A phenomenological approach to describe and characterize pro- and anti-oxidant activities with useful mechanistic contents

M. Carpena [a], A. Soria-Lopez [a], F. Chamorro [a], A. Silva [a,c], M. Fraga-Corral [a,b], Paz Otero [a], P. Garcia-Perez [a], Hui Cao [a], Jianbo Xiao [a], M.F. Barroso[c], J. Simal-Gandara [a,*] and M. A. Prieto [a,b,*]

a) Nutrition and Bromatology Group, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E32004 Ourense, Spain. b) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal. c) REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr António Bernardino de Almeida 431, 4200-072 Porto, Portugal.

Email: jsimal@uvigo.es; mprieto@uvigo.es

In the last decades, the anti-oxidant activity and in consequence, the pro-oxidant effect, have been assessed on very diverse agents (pure compounds or complex extracts of natural products), applying different quantification methods and treating the results with different calculation procedures. Unfortunately, the studies that have pointed out the impossibility of using most of this information to establish useful comparisons have been equally abundant and have led to classify the current situation as chaotic. Among the main obstacles that make unfeasible to apply useful comparisons between the massive amount of results are the intrinsic factors, which depend on the oxidation mechanism and the surrounding environment, and more heterogeneous accidental factors such as those related with the effects of state or composition variables like temperature, pH, solvents or the appearance of synergistic or antagonistic effects [1]. In this study, a phenomenological approach was developed, considering the real concentrations of all the agents involved in two well-known anti-oxidant methods: β-carotene and Crocin assays. The discoloration of β-carotene is assessed in emulsion with linoleic acid, meanwhile the crocin decomposition is mediated by the rate formation products of 2,2'-Azobis (2-amidinopropane) dihydrochloride (AAPH) in an aqueous medium. Currently, for both methods, their reaction systems are well-known, but poorly used in the evaluation of the anti-oxidant activity. The modifications produced by a heterogeneous set of pro- and anti-oxidant kinetic responses of these reactions are described here by, firstly, solving the rate of equations and mass balances formulated from the corresponding mechanistic processes, and afterwards, by applying a phenomenological global solution that allows including time and the antioxidant and prooxidant concentrations in a multivariate system. When this solution was applied to compare the effects of a diverse range of antioxidants and prooxidants in the two methods that were here used as a case study, it was possible to define a series of regular correspondences between their elements. These correspondences allowed us to use the developed phenomenological models to characterize an antioxidant response in detail and infer its mode of action in terms of the usual classification of antioxidants into primary, secondary and mixed ones.

Acknowledgements: The research leading to these results was supported by MICINN supporting the Ramón y Cajal grant for M.A. Prieto (RYC-2017-22891); by Xunta de Galicia for supporting the program EXCELENCIA-ED431F 2020/12, the post-doctoral grant of M. Fraga-Corral (ED481B-2019/096); by the program BENEFICIOS DO CONSUMO DAS ESPECIES TINTORERA-(CO-0019-2021) that supports the work of F. Chamorro and by University of Vigo for supporting the predoctoral grant of M. Carpena (Uvigo-00VI 131H 6410211). Authors are grateful to Ibero-American Program on Science and Technology (CYTED—AQUA-CIBUS, P317RT0003), to the Bio Based Industries Joint Undertaking (JU) under grant agreement No 888003 UP4HEALTH Project (H2020-BBI-JTI-2019) that supports the work of P. Otero and P. Garcia-Perez. The JU receives support from the European Union's Horizon 2020 research and innovation program and the Bio Based Industries Consortium. The project SYSTEMIC Knowledge hub on Nutrition and Food Security, has received funding from national research funding parties in Belgium (FWO), France (INRA), Germany (BLE), Italy (MIPAAF), Latvia (IZM), Norway (RCN), Portugal (FCT), and Spain (AEI) in a joint action of JPI HDHL, JPI-OCEANS and FACCE-JPI launched in 2019 under the ERA-NET ERA-HDHL (n° 696295). The authors would like to thank the EU and FCT for funding through the project PTDC/OCE-ETA/30240/2017- SilverBrain - From sea to brain: Green neuroprotective extracts for nanoencapsulation and functional food production (POCI-01-0145-FEDER-030240).

References:

1. Frankel, E. N. & Finley, J. W. *J. Agric. Food Chem.* **2008**, 56, 4901–4908.

Food and natural products

Effects of the reactive moiety of phenolipids on their antioxidant efficiency in model emulsified systems

Marlene Costa[a], Sonia Losada-Barreiro[a,b], Júlia Magalhães[c], Luís S. Monteiro[d], Carlos Bravo-Díaz[b], Fátima Paiva-Martins[a]

a) REQUIMTE/LAQV, Dep. of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Campo Alegre 687, 4169-007 Porto, Portugal; b) Department of Physical-Chemistry, Faculty of Chemistry, Universidade de Vigo, 36310 Vigo, Spain; c) REQUIMTE/LAQV, Department of Chemical Engineering, Faculty of Engineering, University of Porto, 4200-465 Porto, Portugal; d) Chemistry Centre, University of Minho, Gualtar, 4710-057 Braga, Portugal

Email: marlene.costa@fc.up.pt

Our previous research was focused on the effects of hydrophobicity on the antioxidant (AO) efficiency of series of homologous antioxidants with the same reactive moieties.[1] In this work we evaluate the antioxidant efficiency of hydrophobic phenolipids in 4:6 olive oil-in-water emulsions, with different phenolic moieties (derived from caffeic, 4-hydroxycinnamic, dihydrocaffeic acids, tyrosol and hydroxytyrosol), with alkyl chains of 8 and 16 carbons, and compare the antioxidant efficiency with that of the parent compounds. All catecholic phenolipids, in particular the C8 derivatives, have proven to be better antioxidants for the oxidative protection of emulsions than their parental compounds with octyl dihydrocafffeate being the most efficient (16-fold increase in relation to the control). To understand the importance of some factors on the antioxidant efficiency of compounds in emulsions, Pearson's correlation analysis was carried out between antioxidant activity and the first anodic potential (E_{pa}), reducing capacity (FRAP value), DPPH radical scavenging activity (EC_{50}) and the concentration of antioxidants in each region of the emulsified system. Results confirm the importance of the effective concentration of AOs in the interfacial region (AO_I) ($\rho = 0.820$) and of the E_{pa} ($\rho = -0.677$) in predicting their antioxidant efficiency in olive oil-in-water emulsions.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support (UIDB/QUI/50006/2020).

References:

1. a) Costa, M.; Losada-Barreiro, S.; Paiva-Martins, F.; Bravo-Díaz, C.; Romsted, L.S. *Food Chem*. **2015**, 175, 233–242. b) Costa, M.; Losada-Barreiro, S.; Bravo-Díaz, C.; Vicente, A.A.; Monteiro, L.S.; Paiva-Martins, F. *Food Chem*. **2020**, 310, 125716.

Food and natural products

Eat your weeds: Nutritional composition of edible atlantic brown seaweeds

J. Echave [a], C. Lourenço-Lopes [a], A. G. Pereira [a,b], A. Soria-Lopez [a], F. Chamorro [a], Paz Otero [a], M. Fraga-Corral [a,b], S. Baamonde [c], F. Fernandez-Saa [c], P. Garcia-Perez [a], J. Simal-Gandara [a,*] M.A. Prieto [a,b,*]

a) Nutrition and Bromatology Group, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E32004 Ourense, Spain. b) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal. c) Centro de Investigación e Innovación Tecnológico en Algas Marinas (CIITAM), Algas Atlanticas Algamar S.L., Polígono de Amoedo, E-36840 - Pazos de Borbén (Pontevedra), Spain

Email: mprieto@uvigo.es, jsimal@uvigo.es

Brown seaweeds (Phaeophyceae) are an intrinsic part of East Asian cuisine and are widely recognized as a healthy diet ingredient due to their content in minerals, proteins, fatty acids, fiber, and bioactive molecules like phlorotannins or pigments [1]. Herein, in this work the nutritional composition of edible brown algae species *Undaria pinnatifida*, *Saccharina latissima*, *Laminaria ochroleuca*, *Hilmanthalia elongata* was analyzed to figure out the total content of lipids, proteins, carbohydrates and organic acids and the profile of fatty acid and minerals. Total lipids were measured gravimetrically as evaporated mass after petroleum-ether Soxhlet extraction of samples. Proteins were quantified following the macro-Kjedahl method. Total organic acids were determined by ultra-filtration liquid-chromatography coupled to an amperometric detector (UFLC-PAD) after an acid extraction. Hydrocarbons were determined as the difference of the rest of components, following AOAC methods. The fatty acid and mineral profile was obtained by gas chromatography coupled to a flame ionization detector (GC-FID) and by inductively coupled plasma atomic emission spectroscopy (ICP-OES), respectively.
Results showed that all studied species were accounted for very low levels of lipids (>1% DW), but levels of the unsaturated fatty acids (UFA), oleic, linoleic and linolenic acids, were present at high concentrations, being *S. latissima* the seaweed with the highest quantities of UFA (>100 mg C18:1 / g extract). *U. pinnatifida* displayed the highest protein content (14.8% DW) and *S. latissima* had the lowest one (8% DW), while *L. ochroleuca* and *H. elongata* shared similar abundance (9% DW). Regarding mineral composition of these algae, the main minerals were K, Cl, Mg and Ca, with *H. elongata* showing the highest Mg content (>800 mg / 100 g DW), whereas *L. ochroleuca* accounted for the highest K levels (1.5 g / 100 g DW). Organic acids were determined to be oxalic, malic and citric acids. These four seaweeds displayed a high content of organic acids on which *L. ochreoleuca* showed the highest content (4.3 % DW). Hitherto, these four seaweed species may be considered a low caloric food, rich in UFA, proteins and organic acids, essential to metabolism.

Acknowledgements: The research leading to these results was supported by MICINN supporting the Ramón y Cajal grant for M.A. Prieto (RYC-2017-22891), by Xunta de Galicia for supporting the program EXCELENCIA-ED431F 2020/12, the post-doctoral grant of M. Fraga-Corral (ED481B-2019/096), the pre-doctoral grant of A.G. Pereira (ED481A-2019/0228), by the program BENEFICIOS DO CONSUMO DAS ESPECIES TINTORERA-(CO-0019-2021) that supports the work of F. Chamorro and the program Grupos de Referencia Competitiva (GRUPO AA1-GRC 2018) that supports the work of J. Echave. Authors are grateful to Ibero-American Program on Science and Technology (CYTED—AQUA-CIBUS, P317RT0003), to the Bio Based Industries Joint Undertaking (JU) under grant agreement No 888003 UP4HEALTH Project (H2020-BBI-JTI-2019) that supports the work of P. Otero, P. Garcia-Perez and C. Lourenço-Lopes and to AlgaMar enterprise (www.algamar.com) for the collaboration and algae material provision. The JU receives support from the European Union's Horizon 2020 research and innovation program and the Bio Based Industries Consortium. The project SYSTEMIC Knowledge hub on Nutrition and Food Security, has received funding from national research funding parties in Belgium (FWO), France (INRA), Germany (BLE), Italy (MIPAAF), Latvia (IZM), Norway (RCN), Portugal (FCT), and Spain (AEI) in a joint action of JPI HDHL, JPI-OCEANS and FACCE-JPI launched in 2019 under the ERA-NET ERA-HDHL (n° 696295).

References:

1. Gomez-Zavaglia, A.; Prieto Lage, M. A.; Jimenez-Lopez, C.; Mejuto, J. C.; Simal-Gandara, J. **2019**. *Antioxidants*, 8.

Food and natural products

Extração de aloeresina B a partir de *Aloe vera* com recurso a solventes alternativos: Otimização do processo e avaliação de bioatividades

Añibarro-Ortega M,[a] Pinela J,[a] Ćirić A,[b] Ferreira O,[a] Molina AK,[a] Lopes E,[c] Soković M,[b] Ferreira ICFR,[a] Barros L[a]

a) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de S.ta Apolónia, 5300-253 Bragança, Portugal; b) Institute for Biological Research "Siniša Stanković" - National Institute of Republic of Serbia, University of Belgrade, Bulevar Despota Stefana 142, 11000 Belgrade, Serbia; c) aCourela do Alentejo, Garro Pinheiro de Baixo CCI3, 7350-422 Varche, Elvas, Portugal

Email: jpinela@ipb.pt

A aloeresina B é uma cromona encontrada em *Aloe* spp. com elevado potencial na industria de cosméticos e alimentos dada a sua capacidade de modular a formação de melanina e os efeitos benéficos nos índices relacionados ao estado pré-diabético, incluindo síndrome metabólico.[1,2] Portanto, dado o valor de mercado da aloeresina B, este estudo foi realizado com o objetivo de otimizar a sua extração a partir da epiderme da folha de *Aloe vera*, camada esta que corresponde a ~31% do peso total da folha e é normalmente descartada como subproduto.[3] Para a otimização do processo de extração, o tempo (10–210 min), a temperatura (25–95 °C) e o solvente (0–100%, *w/w*) foram as variáveis independentes selecionadas e combinadas num desenho de composto central circunscrito de cinco níveis acoplado à metodologia de superfície de resposta. O solvente consistiu em misturas de água com etanol, propano-1,2-diol ou propano-1,2,3-triol (glicerol), dado o potencial para serem usados em diferentes áreas, incluindo alimentar, cosmética e farmacêutica. Os teores de aloeresina B nos 60 extratos foram quantificados por HPLC-DAD e usados como critério de resposta. Os modelos teóricos foram ajustados com sucesso aos dados experimentais, validados estatisticamente com base em valores de R^2 e R^2_{adj} elevados e numa falta de ajuste não significativa e seguidamente usados para "navegar" o desenho experimental e obter as melhores condições de extração. Posteriormente, foi realizada uma análise dose-resposta da razão sólido/líquido nas condições ótimas previamente estabelecidas para cada sistema álcool-água, a qual evidenciou uma melhoria na eficiência de extração com o aumento da razão de 3 para 40 g/L. Esta análise também permitiu validar experimentalmente os três modelos preditivos. Considerando as quatro variáveis envolvidas na extração, foi possível concluir que os maiores teores de aloeresina B foram alcançados com o sistema binário de propano-1,2-diol, enquanto rendimentos de extração consideráveis também foram obtidos com água pura, um solvente preferível em muitas aplicações. Além disso, os extratos obtidos nas condições ótimas apresentaram capacidade de inibir a formação de substâncias reativas ao ácido tiobarbitúrico (TBARS), atividade antimicrobiana contra várias estirpes de bactérias e fungos relacionadas com a pele e alimentos e capacidade de inibir a atividade da enzima tirosinase. Este estudo permitiu obter as condições ótimas para a recuperação de aloeresina B a partir de um subproduto vegetal através de um processo de extração sustentável envolvendo solventes verdes e destacou também o potencial dos extratos para serem usados em formulações cosméticas de aplicação tópica.

Agradecimentos: Os autores agradecem à Fundação para a Ciência e a Tecnologia (FCT) e fundos nacionais FCT/MCTES pelo apoio financeiro ao CIMO (UIDB/00690/2020). M. Añibarro-Ortega e A.K. Molina agradecem as bolsas (2020.06297.BD e 2020.06231.BD, respetivamente) à FCT e J. Pinela (CEECIND/01011/2018) e L. Barros agradecem os contratos no âmbito do contrato-programa de emprego científico. Trabalho financiado pelo Fundo Europeu de Desenvolvimento Regional (FEDER) através do Programa Operacional Competitividade e Internacionalização (POCI) e por fundos nacionais através da FCT, no âmbito do Projeto POCI-01-0145-FEDER-030463: AllNat. Ao programa FEDER-Interreg España-Portugal pelo apoio financeiro através do projeto TRANSCoLAB 0612_TRANS_CO_LAB_2_P. Trabalho apoiado pelo Ministério da Educação, Ciência e Desenvolvimento Tecnológico da República da Sérvia (451-03-68/2020-14/200007). Á empresa "aCourela do Alentejo" pelo material vegetal.

References:

1. Wahedi, H. M. *et al. Phytomedicine* **2017**, *28*, 19.
2. Lynch, B.; Simon, R.; Roberts, A. *Regul. Toxicol. Pharmacol.* **2011**, *61*, 161.
3. Añibarro-Ortega, M. *et al. Antioxidants* **2019**, *8*, 444.

Food and natural products

Detection of species mislabeling in a plant sold as *Nepeta cataria* L.

Mónica Honrado,[a] Andreia Quaresma,[a] Sónia Pedro,[a] M. Alice Pinto,[a] Joana S. Amaral,[a,b,*]

a) CIMO, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; b) LAQV-REQUIMTE, Faculdade de Farmácia da Universidade do Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal

Email: jamaral@ipb.pt

Aromatic plants represent a relevant source of flavoring substances that are used in the food, cosmetic/perfumery, and pharmaceutical industries. *Nepeta cataria*, also known as catnip or catmint due to its irresistible action on cats, or "nêveda" in Portuguese, is an aromatic plant from the Lamiaceae family, native to Asia and Southeastern Europe, that is used in traditional medicine for its carminative, tonic, diaphoretic and antispasmodic properties.[1,2] The essential oil of *N. cataria* has been reported to contain nepetalactones as the major compounds which have shown antibacterial, fungicidal and antiviral activities.[1] Besides being used to prepare infusions, due to its lemony mint flavor its use in culinary has also been reported. As part of a study to assess the chemical composition of the essential oil extracted from different aromatic plants sold in Portuguese herbal stores, a commercial sample of catnip labeled as *Nepeta cataria* L. was submitted to hydrodistillation for 3 hours on a Clevenger system. The obtained essential oil was analyzed by gas chromatography coupled to mass spectrometry (GC-MS). The compounds were identified based on the spectra similarity with the NIST17 database and the calculated linear retention index (LRI). The analysis identified 52 compounds, corresponding to 95.5% of total compounds, with iso-menthone being the major compound (28.8%), followed by 1,8-cineol (17.3%), isopulegone (13.8%), isomenthol (11.9%) and pulegone (4.2%). Considering that nepetalactone isomers are reported as the characteristic and major compounds in this plant, LRI and spectra data for these compounds were searched in the literature. According to Adams (2017), the isomers 4aα,7α,7aα- 4aα,7α,7aβ- and 4aα,7β,7aα-nepetalactone should present a LRI between 1357 and 1391.[3] However, the detailed analysis of the chromatogram in this region did not evidence any peak corresponding to nepetalactones, suggesting a mislabelling of the plant species. Therefore, a molecular analysis based on the ITS2 (internal transcribed spacer 2) plant barcode was carried out for species identification. To that end, DNA was extracted using CTAB and submitted to Sanger sequencing and to Next Generation Sequencing (NGS), in both cases using ITS2 universal primers reported in the literature[2]. The results obtained by Sanger sequencing suggested the presence of a DNA mixture since a large portion of 5´end of the sequence had double peaks. However, a basic logical alignment search tool (BLAST) analysis in GenBank with a partial fragment for which the sequence was clear, did not identified *Nepeta* genus while other genera were suggested. In particular, different *Clinopodium* species presented a high % identity (90.58-91.24%, with a query cover of 99%). NGS results confirmed the presence of mixed DNA in the sample, including 3 different fungi and *Geranium robertianum*, which can possibly be explained by cross-contamination of the commercial sample. While none of the sequence reads was identified as *Nepeta* spp., several reads suggested the presence of *Clinopodium* genus, with *C. pulegium* being identified with 95.49% identity. Curiously, in Portugal, the common name "nêveda" is also attributed to *Clinopodium nepeta*, for which the ITS2 sequence is unavailable in GenBank neither in the ITS2 database of the pipeline used in the NGS analysis, thus explaining the identification with lower % identity. *C. nepeta* essential oil has been reported to contain high amounts of menthone (32%), pulegone (22%), neomenthol (32%) and 1,8-cineol (3%),[4] which is similar to the composition reported herein. Thus, in future works, *C. nepeta* ITS2 will be sequenced and added to the pipeline to for further identity confirmation. Nevertheless, this work strongly suggests the need for an improved quality control of botanicals used in phytotherapy.

Acknowledgements: The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support by national funds FCT/MCTES to CIMO (UIDB/00690/2020).

References:

1. Mohammadi S.; Saharkhiz M. J. *J. Essent. Oil-Bear. Plants* **2011**, *14(4)*, 396.
2. Sickel W.; Ankenbrand M.; Grimmer G.; Holzschuh A.; Härtel S.; Lanzen J.; Steffan-Dewenter I.; Keller A. *BMC Ecol* **2015**, *15:20*.
3. Adams, R.P. Allured Publishing Corporation, Illinois, Ed. 4.1, **2017**.
4. Boudjema K.; Bouanane A.; Gamgani S.; Djeziri M.; Mustapha M.A.; Fazouane F. *Trop. J. Pharm. Res.* **2018**, *17*, 857.

Food and natural products

Interaction between peanut proteins and polyphenols: Impact on protein digestibility and immunogenicity

Rosa Perez-Gregorio,[a] Catarina Bessa, [a] Ricardo Dias, [a] Nuno Mateus, [a] Victor de Freitas [a]

a) LAQV-REQUIMTE Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal.

Email: maria.gregorio@fc.up.pt

Peanut allergy (PA)[1] is one of the primary forms of allergy and may induce severe and life-threatening allergic reactions. The mainstay of treatment is the elimination of peanut proteins from the diet[2]. Growing research have been related the effect of dietary patterns in food allergy[3, 4]. The lack of therapies, the severity of the PA symptoms and the increasing in prevalence promotes the need to establish prophylactic dietary habits, which could stop or control an almost epidemic disease. Indeed, the consumption of dietary polyphenols has been related with a low prevalence of PA[5]. However, there is little information regarding the immunomodulatory mechanisms of polyphenols from ingestion to allergy systemic effects manifestation. This study is focused in analysing the effect of polyphenols in protein digestibility and immunogenicity. The enzymatic modification of proteins during human digestion are closely related with their immunogenicity but the digestion process may be influenced by the way food components interact with each other and with digestive enzymes and ultimately affect human health. Furthermore, the matrix effect were herein assayed. Thus, an onion polyphenol-rich extract was obtained and further fractionated into five fractions with different polyphenol composition. In parallel, peanut proteins was extracted. The whole peanut as well as the protein extract were submited to in vitro human digestion simultaneously with the whole polyphenol extract or the polyphenol fractions. The impact in digestibility was then assayed by characterizing the intact proteins by SDS-PAGE. Likewise, the immunogenic peptides released during digestion were identified by mass spectrometry. Overall, although further studies are needed, the interaction between polyphenols and proteins clearly influences peanut digestion and immunogenicity, thus suggesting that the consumption of dietary polyphenols can significantly affect the degree of PA downstream immune reactions. Furthermore, a strong influence of matrix was highlighted when human digestion was mimicked, claiming for more complex in vitro models to properly analyse the food digestibility.

Acknowledgements: This work was supported by the Associated Laboratory for Sustainable Chemistry, Clean Processes and Technologies Laboratório Associado para Química Verde through the national funds from UIDB/50006/2020. Pérez-Gregorio would like to thank FCT for her contract (SFRH/BPD/85293/2012). This work was financed by FEDER (Fundo Europeu de Desenvolvimento Regional) funds through the COMPETE 2020—Operacional Programme for Competitiveness and Internationalisation (POCI), and by Portuguese funds through FCT—Fundação para a Ciência e a Tecnologia—in the framework of the POCI-01-0247-FEDER-046080—PTDC/SAU-NUT/30448/2017 and PTDC/OCE-ETA/32287/2017 projects. This research was also supported by AgriFood XXI I&D&I project (NORTE-01-0145-FEDER-000041) cofinanced by European Regional Development Fund (ERDF), through the NORTE 2020 (Programa Operacional Regional do Norte 2014/2020)

References:

1.Yu, W., D.M.H. Freeland, and K.C. Nadeau, Food allergy: immune mechanisms, diagnosis and immunotherapy. *Nat Rev Immunol*, **2016**. 16(12): p. 751-765.
2.Linhart, B., et al., Molecular approaches for diagnosis, therapy and prevention of Cow´s milk allergy. *Nutrients*, **2019**. 11(7).
3.Saarinen, K.M. and E. Savilahti, Infant feeding patterns affect the subsequent immunological features in cow's milk allergy. *Clinical and experimental allergy: journal of the British Society for Allergy and Clinical Immunology*, **2000**. 30(3): p. 400-406.
4.Bascuñán Gamboa, K.A., et al., [Association of dietary patterns and food allergy in infants during the first year of life]. *Archivos argentinos de pediatria*, **2012**. 110(5): p. 375-380.
5.Nurmatov, U., G. Devereux, and A. Sheikh, Nutrients and foods for the primary prevention of asthma and allergy: systematic review and meta-analysis. *Journal of Allergy and Clinical Immunology*, **2011**. 127(3): p. 724-733. e30.

Food and natural products

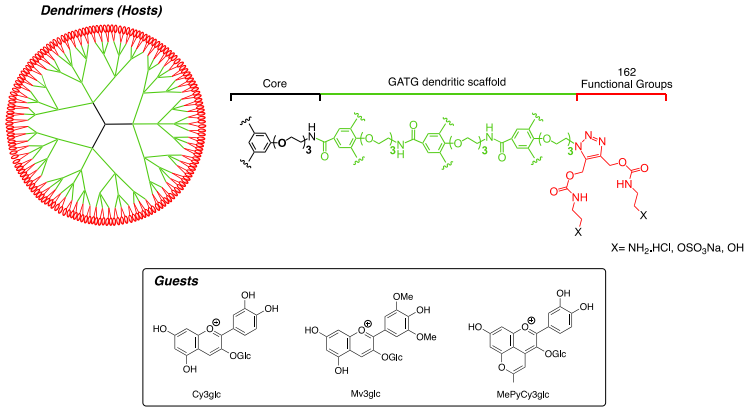
Dendrimer-based polymers as new hosts for color tuning of anthocyanin-type guests

Luís Cruz,[a] Juan Correa,[b] Eduardo Fernandéz-Megia,[b] Victor de Freitas[a]

a) REQUIMTE/LAQV, Chemistry and Biochemistry Department, Faculty of Sciences University of Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal; b) Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela, Jenaro de la Fuente s/n, 15782 Santiago de Compostela, Spain

Email: luis.cruz@fc.up.pt

Anthocyanin-type pigments comprehend a large family of natural pigments responsible for the coloration of many flowers and fruits. In aqueous solution, these compounds display a pH-dependent equilibria network giving rise to a wide portfolio of beautiful colors which as given to them interest from the scientific community to explore different applications as pH-sensors, photosensitizers and photochromic systems for food, textile, cosmetics, energy, and biomedical industries. Over the last years, we have been developing flavylium-based systems for novel cosmetic and food applications which includes the synthesis of pyranoflavylium derivatives, enzymatic acylation with fatty acids, supramolecular host-guest and self-assembled systems (e.g. micelles, macrocyclic structures).[1] In this work, molecular interactions between natural anthocyanin derivatives and a four generation of a gallic acid triethylene glycol-based dendrimer decorated with positive, anionic and neutral functional groups (NH_2.HCl, OSO_3Na and OH, respectively) were studied by means of UV-Vis, stopped-flow and NMR spectroscopy techniques (^1H, T_2, DOSY, NOESY).[2] The results revealed that both dye structure and concentration as well as the dendrimer charge determine the type of interaction mechanisms involved.



Scheme 1:Chemical structures of hosts and guests used.

Acknowledgements: This research was supported by a research project grant (PTDC/OCE-ETA/31250/2017) with financial support from FCT/MCTES through national funds and co-financed by FEDER, under the Partnership Agreement PT2020 (UID/QUI/50006/2020 - POCI/01/0145/FEDER/007265). This research was conducted under the project AgriFood XXI - NORTE-01-0145-FEDER-000041, financed by European Regional Development Fund (FEDER) through North Portugal Regional Operational Programme (Norte 2020). Financial support was also obtained from the Spanish Ministry of Science and Innovation (RTI2018-102212-B-I00), Xunta de Galicia (ED431C 2018/30, and Centro singular de investigación de Galicia accreditation 2019-2022, ED431G 2019/03), Axencia Galega de Innovación (IN845D 2020/09), and the European Union (European Regional Development Fund-ERDF). Luís Cruz gratefully acknowledges the research FCT contract.

References:

1. a) Basílio, N.; Lima, J. C.; Cruz, L.; de Freitas, V.; Pina, F.; Ando, H.; Kimura, Y.; Oyama, K.-I.; Yoshida, K. *European J. Org. Chem*. **2017**, 2017 (37), 5617-5626. b) Gomes, V.; Mateus, N.; de Freitas, V.; Cruz, L. *Dyes Pigm*. **2019**, 167, 60-67. c) Cruz, L.; Basílio, N.; de Freitas, V. *Dyes Pigm*. **2020**, 181, 108592.

2. a) Cruz, L.; Basílio, N.; Mendoza, J.; Mateus, N.; de Freitas, V.; Tawara, M. H.; Correa, J.; Fernandez-Megia, E. *Chem. Eur. J*. **2019**, 25, 11696-11706. b) Cruz, L.; Correa, J.; Mateus, N.; de Freitas, V.; Tawara, M. H.; Fernandez-Megia, E. ACS *Applied Polymer Materials* **2021**, 3 (3), 1457-1464.

Food and natural products

New insights into the oral interactions of different families of phenolic compounds: deepening the astringency mouthfeels

Carlos Guerreiro[a], Elsa Brandão[a], Mónica de Jesus[a], Leonor Gonçalves[a], Rosa Pérez-Gregório[a], Nuno Mateus[a], Victor de Freitas[a], Susana Soares[a]

a) REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 689, Porto, Portugal

Email: susana.soares@fc.up.pt

Astringency is described as a tactile sensation of puckering, tightening and dryness in the oral cavity, commonly induced for by phenolic compounds [1]. One hypothesis for the different phenolic compounds to elicit astringency is the existence of diverse mechanisms inside the oral cavity that could rely on different interactions inside the oral cavity. In this study, the interaction of two mixtures of phenolic compounds, one rich in gallotannins (GT) and another rich in flavonols (FV) with two oral models (one with a tongue cell line, HSC3; another with a buccal mucosa cell line, TR146) was evaluated. These two families of phenolic compounds have been linked to different astringency mouthfeels. The results provided evidence that the GT and the FV studied seem to bind in a different way to the different oral constituents and models used. The overall interaction of GT mixture seems to be driven by salivary proteins while the overall interaction of FV seems to be driven by oral cells. GT mixture seems to bind more to the tongue than to the buccal mucosa cell line, but this difference is overcome by the presence of salivary proteins. On the other hand, for the FV mixture, the presence of salivary proteins seems to restrain the interaction with oral cell lines. Structure-binding activity relationships were evidenced within each mixture: for gallotannins, interactions seem to increase along with the galloylation degree while for flavonol it was observed that increasing number of glucose residues decreases the binding activity.
In the end, the gathered results raise one possible hypothesis to support the different astringency mouthfeels elicited by the studied compounds: the oral interactions driven by salivary proteins could be more related to harsh, dry and puckering sensations while the interactions driven by tongue cell line could be more related to velvety and silky sensations.

Acknowledgements: The authors thank the Science and Technology Foundation (FCT) for financial support the researcher contracts CEECIND/01598/2018, CEECIND/01265/2018 and the scholarships SFRH/BD/148549/2019, UIDB/50006/2020 and UIDBP/50006/2020. This research is supported by AgriFood XXI I&D&I project (NORTE-01-0145-FEDER-000041 cofinanced by European Regional Development Fund (ERDF), through the NORTE 2020 (Programa Operacional Regional do Norte 2014/2020). This research is supported by cLabel+ Project (POCI-01-0247-FEDER-046080) cofinanced by European Regional Development Fund (ERDF), through the COMPETE 2020 - Incentive System to Research and Technological Development, within the Portugal 2020 Competitiveness and Internationalization Operational Program.

References:

1. Fernandes, I.; Pérez-Gregorio, R.; Soares, S.; Mateus, N.; De Freitas, V. *Fermented Foods Heal. Dis. Prev.* **2017**, 593–621.

Food and natural products

Spirulina (*Artrhospira platensis*) protein extract: techno-functional properties and potential application as a natural emulsifier

Samara C. Silva[ab], Thayná Almeida[ac], Giovana Colucci[ab], Arantzazu Santamaria-Echart[a], Yaidelin A. Manrique[b], Madalena M. Dias[b], Lillian Barros[a], Ângela Fernandes[a], Eliane Colla[c], M. Filomena Barreiro[a,*]

a) CIMO, Centro de Investigação de Montanha, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal b) LSRE-LCM, Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal c) DAALM, Departamento Acadêmico de Alimentos – Programa de Pós-graduação em Engenharia de Alimentos (PPGTA), Universidade Tecnológica Federal do Paraná, Câmpus Medianeira, 85884-000 Paraná, Brazil

Email: barreiro@ipb.pt

Microalgae are valuable sources of proteins (20-70%) and have emerged as great alternatives to animal-based proteins (e.g., whey protein, egg yolk)[1]. This work aimed to obtain a microalga protein extract (SpE) from *Artrhospira platensis* (Spirulina) and evaluate its techno-functional properties and emulsion formation capability. The SpE was obtained by ultrasound and conventional mechanical stirring under an alkaline medium (pH 9.0) followed by acid precipitation (pH 3.0)[2]. In addition, the SpE techno-functional (protein solubility; oil and water absorption capacities) and structural properties (FTIR analysis) were investigated. An emulsion (oil/water ratio (30/70); pH 7.0; SpE concentration (3.5%)) was prepared according to two sequential steps: i) high-shear homogenization (UltraTurrax; 11,000 rpm; 3 min) and ii) high-pressure homogenization (100MPa; 6 cycles)[3]. Then, it was analysed by optical microscopy, zeta potential and particle size. The SpE (66.6%±0.31 protein) presented the lowest solubility at pH 3.0 and the highest at pH 8.0. The protein extract showed higher absorption capacity in oil (21.7±0.10 g oil/ g SPE) than in water (10.3±0.50 g water/ g SPE). From the FTIR analysis (**Figure 1a**), the SpE showed two peaks at 1635 cm^{-1} and 1535 cm^{-1} (red circles in **Figure 1a**) attributed to the presence of characteristic protein groups, amide I and amide II, respectively. The oil-in-water emulsion (ESp) presented a light blue-green colour due to the presence of SpE (**Figure 1a**) and remained stable for 30 days (**Figure 1b**). The ESp presented a zeta potential of -47.20 mV and a particle size of 330 nm (D_{50}, volume distribution) on the 30th storage day. Small and spherical droplets were observed, evidencing the particle size and stability over the storage time (**Figure 1c**). Thus, the SpE showed the ability to form emulsions with stability for up to 30 days, being a great alternative to replace animal-based and synthetic emulsifiers.

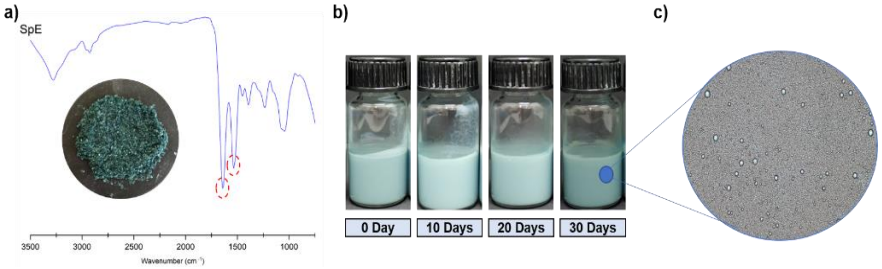


Figure 1: a) FTIR analysis and visual appearance of the SPE; b) Visual inspection of the emulsion over the storage time (30 days); c) optical microscopy (400X) of the emulsion after 30 days of storage.

Acknowledgements: CIMO (UIDB/00690/2020), and LSRE-LCM (UIDB/50020/2020) funded by FCT/MCTES (PIDDAC). National funding by FCT, P.I., through the institutional scientific employment program-contract for L. Barros, A. Fernandes, A. Santamaria, and Y. Manrique contracts. G. Colucci thanks project GreenHealth for her contract. A4F, SA – Algae for Future (www.a4f.pt) for supplying the studied microalga. FCT for the PhD research grant (SFRH/BD/148281/2019) of Samara Cristina da Silva.

References:

1. Bertsch P.; Bocker L.; Mathys A.; Fischer P. *Trends Food Sci Technol.* **2021**, 108, 326-342.
2. Lupatini A.L.; Bispo L.O.; Colla L.M; Costa J.A.V.; Canan C.; Colla, E. *Food Res. Int.* **2017**, 99, 1028-1035.
3. Schreiner T.B.; Santamaria-Echart A.; Ribeiro A.; Peres A.M.; Dias M.M.; Pinho S.P.; Barreiro M.F. *Molecules.* **2020**, 25, 1538.

Food and natural products

Innovative fat-reduced food solutions based on Pickering emulsions

Ghirro, L.C. [a,b], Rezende S.C.[a] , Rodrigues N.[a], Carocho M.[a], Barros L.[a] Pereira, J.A.[a], Santamaria-Echart, A.[a,*], Demczuk Junior, B.[b], Barreiro, M.F.[a]

a) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; b) Post-Graduation Program of Food Technology (PPGTA), Federal University of Technology – Paraná – UTFPR, Campus Campo Mourão, via Rosalina Maria dos Santos, 1233, CEP 87301-899, Campo Mourão, PR, Brazil.

Email: asantamaria@ipb.pt

The increasing trend in the food industry directed to healthy and sustainable products implies the demand for fat-reduced foods while maintaining a sensorial quality similar to traditional products[1]. In this context, Pickering emulsions (PEs), especially the ones using plant-based particles, arises to address these challenges. The PEs consist of systems stabilized by colloidal particles adsorbed at the oil-water interface, providing high resistance to coalescence and Oswald ripening phenomena, besides availing the incorporation of bioactive compounds through their encapsulation in the oil phase or the particles themselves[2,3]. Therefore, this work pursues developing PEs stabilized by curcumin-based particles produced by the solid dispersion technique and evaluate their potential as fat-reduced mayonnaise substitutes. Two particles' formulations (KC1 and KC2) were produced using a natural polymer, k-carrageenan added with curcumin. Then, three Pickering emulsions were developed using different particle concentrations (4.0 and 4.7% w/w) and oil fractions (φ=0.4 and 0.6), namely KC1 φ 0.4 (4.7%), KC2 φ 0.4 (4.7%) and KC2 φ 0.6 (4.0%) (**Figure 1**).
The stability of the emulsions, analysed by optical microscopy and creaming index for 28 days, evidenced the remarkable stability of the formulations KC1 φ 0.4 (4.7%), KC2 φ 0.4 (4.7%), which presented no sign of phase separation and maintained their small-size droplets' morphology. KC2 φ 0.6 (4.0%) showed an increase in the droplet size and a small accumulation of oil on the top after 14 days, indicating a lower stability. The properties of the produced emulsions were analysed and compared with two commercial mayonnaises (traditional and light). The emulsions presented an acid pH and an outstanding enhanced oxidative stability, comparing with the commercial mayonnaise, indicating a longer shelf life. Particularly, KC1 0.4 (4.7%) exhibited similar textural properties and nutritional values relative to the light mayonnaise, pointing out its potential as a natural substitute of this product. Moreover, additional benefits, namely low-fat content and functionalities derived from curcumin and extra virgin olive oil are confer added value to these products.

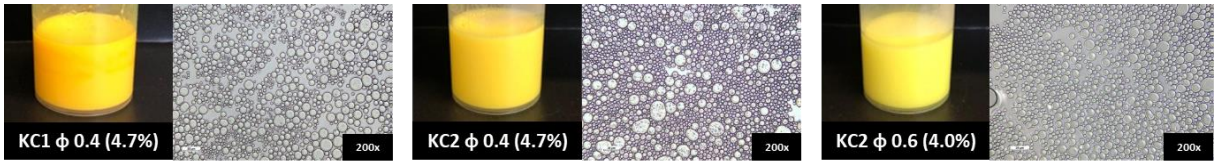


Figure 1. Produced Pickering emulsions: macroscopic and microscopic analysis.

Acknowledgements: CIMO (UIDB/00690/2020) funded by FCT/MCTES (PIDDAC). FCT, P.I., through the institutional scientific employment program-contract for N. Rodrigues, L. Barros, A. Santamaria, M. Carocho (CEECIND/00831/2018) contracts. FCT for the Research grant SFRH/BD/147326/2019 of Stephany Cunha de Rezende and grant "Verão com Ciência" of L. Ghirro.

References:

1. Niroula, A., Gamot, T. D., Ooi, C. W. & Dhital, S. Biomolecule-based pickering food emulsions: Intrinsic components of food matrix, recent trends and prospects. *Food Hydrocoll.* **2021**, *112*, 106303.
2. Sarkar, A. & Dickinson, E. Sustainable food-grade Pickering emulsions stabilized by plant-based particles. *Curr. Opin. Colloid Interface Sci.* **2020**, *49*, 69–81.
3. Mwangi, W. W., Lim, H. P., Low, L. E., Tey, B. T. & Chan, E. S. Food-grade Pickering emulsions for encapsulation and delivery of bioactives. *Trends Food Sci. Technol.* **2020**, *100*, 320–332.

Poster Communications

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

Food and natural products

Polyphenol extraction by deep eutectic solvent for valorisation of portuguese green tea and their impact on chitosan-based films properties

Tiago Filipe P. Alves[a,*], Natércia Teixeira[a], Jorge Vieira[b], António A. Vicente[b], Victor de Freitas[a] and Hiléia K. S. Souza[a]

a) REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal; b) CEB – Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

Email: up201704456@edu.fc.up.pt

The current demand for antioxidant active packaging, that is achieved by introducing antioxidants into food packaging material, is increasing due to both the unquestionable advantages compared to the addition of antioxidants directly to the food and the tendency to consume healthy and fresh products. When developing active packaging materials, research has been focused on natural and biodegradable polymers (such as polysaccharides like chitosan) containing polyphenol compounds (as bio preservative) in their formulation.
Due to their rare solvation properties, the natural deep eutectic solvents (NADES), are considered good solvents to be used as an extraction medium of bioactive products. Moreover, the search for the use of ecological solvents for this field has intensified due to their acceptable toxicity profile and chemical diversity. The use of these inexpensive, non-volatile, and nonaqueous biodegradable solvents, complying with the Green Chemistry principles, could potentially improve the stability of the polyphenolic compounds allowing to retard food spoilage for packaging material,
Catechins (components of green tea (GT)), a polyphenolic group known for its high value-added antioxidant properties, have been associated with health-promoting effects. In this sense, the incorporation of GT components for food application purposes and as active ingredient in packaging materials can be expected to improve food functionality and availability, while performing a dual role (antioxidant and antimicrobial agent) and possibly also having low-cost advantages.
In this work, for the first time, a ternary deep eutectic solvent (ChCl/glycerol/lactic acid) was used as an environmentally friendly media for the extraction of polyphenolic compounds from green tea. The extraction solution was compared with traditional method and used to improve chitosan film properties. The casting method used to produce films with and without GT/NADES plasticizer. Transparent films were obtained and evaluated in terms of mechanical, water resistance, optical and microstructural properties.
The results were compared with those obtained for chitosan films containing binary deep eutectic solvents (ChCl/glycerol and ChCl/lactic acid, with and without GT)) as plasticizers in their formulations.

Acknowledgements: The work was supported through the project UIDB/50006/2020, funded by FCT/MCTES through national funds and by the AgriFood XXI I&D&I project (NORTE-01-0145-FEDER-000041 co-financed by European Regional Development Fund (ERDF), through the NORTE 2020. N Teixeira and Hiléia Souza thanks FCT for CEECIND/00025/2018/CP1545/CT0009 and PTDC/OCE-ETA/31250/2017 project respectively.

Food and natural products

Antioxidant profile of brown algae from the Iberian Peninsula sea

Carla Rodrigues[1], Aurora Silva [1,2],C. Lourenço-Lopes [2], M. Carpena [2], V. F. Domingues [1], M.A. Prieto [2,3], J. Simal-Gandara [2], and M. Fátima Barroso [1*]

1) REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr António Bernardino de Almeida 431, 4200-072 Porto, Portugal; 2)Nutrition and Bromatology Group, Department of Analytical and Food Chemistry, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E32004 Ourense, Spain; 3) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolonia, 5300-253 Bragança, Portugal.

Email: mfb@isep.ipp.pt

Macroalgae are defined as marine macroscopic eukaryotic photosynthetic organisms. They are commonly classified depending on their pigments in three different groups: green algae (Chlorophyta), red algae (Rhodophyta) and brown algae (Ochrophyta) [1]. Macroalgae are an uprising source of bioactive compounds. During the last decades, new compounds have been isolated from these macroalgae, and have been shown to present several biological activities and potential to be used for multiple purposes such as nutritional and medicinal applications [2].
Brown macroalgae were selected due to their increasing potential interest related to their biological activities. Their composition includes polysaccharides, proteins, low lipid content (the main components being sulfated polyunsaturated fatty acids), sterols, carotenoids (fucoxanthin and xanthophylls) and polyphenols, namely phlorotannins [3]. Crude extracts and compounds isolated from brown algae have been demonstrated to present useful properties, namely antibacterial, antihypertensive, antiviral, anticancer and antioxidant activity. Oxidative stress can be defined as the imbalance between the production of reactive oxygen species (ROS) and antioxidant agents. When this imbalance takes place, the increase in ROS causes oxidation and damage to cellular components such as lipids, proteins and DNA. Antioxidants are considered as high value compounds that can delay or prevent oxidation, that is, they will create a defense against free radicals that result from oxidative stress.
In the present work, the antioxidant activity of the extracts from nine species of brown macroalgae (*Ascophyllum nodosum, Himanthalia elongata, Undaria pinnatifida, Pelvetia canaliculate, Saccharina latissimi, Bifurcaria bifurcata, Laminaria ochroleuca, Sargassum muticum* and *Fucus spiralis*) was assessed. Five different solvents (ethanol, chloroform, hexane, acetone and ethyl acetate) were used to evaluate the macroalgae extraction yield. The antioxidant profile of the obtained crude extracts was assessed by different assays: total phenolic content (TPC) and total flavonoid content (TFC), DPPH radical scavenging activity (DPPH-RSA) and ferric reducing antioxidant power (FRAP).

Acknowledgments: The research leading to these results was supported by MICINN supporting the Ramón y Cajal grant for M.A. Prieto (RYC-2017-22891); by Xunta de Galicia for supporting the program EXCELENCIA-ED431F 2020/12 and by University of Vigo for supporting the predoctoral grant of M. Carpena (Uvigo-00VI 131H 6410211). Authors are grateful to Ibero-American Program on Science and Technology (CYTED—AQUA-CIBUS, P317RT0003), to the Bio Based Industries Joint Undertaking (JU) under grant agreement No 888003 UP4HEALTH Project (H2020-BBI-JTI-2019) and to AlgaMar enterprise (www.algamar.com) for the collaboration and algae material provision. The JU receives support from the European Union's Horizon 2020 research and innovation program and the Bio Based Industries Consortium. The project SYSTEMIC Knowledge hub on Nutrition and Food Security, has received funding from national research funding parties in Belgium (FWO), France (INRA), Germany (BLE), Italy (MIPAAF), Latvia (IZM), Norway (RCN), Portugal (FCT), and Spain (AEI) in a joint action of JPI HDHL, JPI-OCEANS and FACCE-JPI launched in 2019 under the ERA-NET ERA-HDHL (n° 696295). The authors would like to thank the EU and FCT for funding through the project PTDC/OCE-ETA/30240/2017-SilverBrain- From sea to brain: Green neuroprotective extracts for nanoencapsulation and functional food production (POCI-01-0145-FEDER-030240).

References:

1. Pereira, L. Guia ilustrado das macroalgas: conhecer e reconhecer algumas espécies da flora portuguesa. Guia Ilus. das macroalgas conhecer e reconhecer algumas espécies da flora Port. **2009**, doi:10.14195/978-989-26-0397-1.
2. Kim, S.K. Handbook of Marine Macroalgae*: Biotechnology and Applied Phycology*; **2011**; ISBN 9780470979181.
3. Silva, A.; Silva, S.A.; Carpena, M.; Garcia-Oliveira, P.; Gullón, P.; Barroso, M.F.; Prieto, M.A.; Simal-Gandara, J. Macroalgae as a source of valuable antimicrobial compounds: Extraction and applications. *Antibiotics* **2020**, 9, 1–41, doi:10.3390/antibiotics9100642.

Food and natural products

Optimization of bioactive compounds with antioxidant activity of *Sargassum muticum* by microwave assisted extraction using the response surface methodology

F. Chamorro [a], L. Cassani [a, b], M. Carpena [a], A. Carreira-Casais [a], J. Echave [a], A. Silva [d, a], M. F. Barroso [d], Paz Otero [a], Hui Cao [a], Jianbo Xiao [a], M.A. Prieto [a, c, *], J. Simal-Gandara [a, *]

a) Nutrition and Bromatology Group, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E32004 Ourense, Spain; b) Research Group of Food Engineering, Faculty of Engineering, National University of Mar del Plata, Argentina; c) Centro de Investigação de Montanha (CIMO-IPB), Campus de Santa Apolónia, Bragança, Portugal; d) REQUIMTE/LAQV, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr António Bernardino de Almeida 431, 4200-072 Porto, Portugal

Email: mprieto@uvigo.es jsimal@uvigo.es

Sargasusum muticum (SM), a brown macroalgae belonging to Phaeophyta class, is a native organism from the Pacific Northwest coast and an invasive species in the Atlantic coasts. In recent years, SM has been used in different functional applications in the pharmaceutical, food and nutraceutical industries [1] due to its innumerable biological properties such as antioxidant, anti-inflammatory, antimicrobial, antiviral, and anti-proliferative capacities, as well as many others health benefits [1,2]. These effects are attributed to the high content of nutrients and secondary metabolites such as phenolic compounds, among others. In this context, the objective of this study is the optimization of the microwave-assisted extraction (MAE) for the recovering of phenolic compounds and flavonoids considering three variables: the concentration of ethanol (0-100%), the extraction time (3-25 minutes) and the pressure (2-20 bar). To determine the total phenolic content (TPC) and the total flavonoid content (TFC), it was performed two biological assays based on 2,2-diphenyl-1-picrylhydrazyl radical scavenging activity (DPPH) and the trolox equivalent antioxidant capacity (TEAC). Finally, it was carried out the optimization by the response surface methodology (RSM) model considering the yield (Y) of each fraction, being 29.2 ± 3.95 % of ethanol, 13.77 ± 0.92 min and 12.86 ± 2.57 bar the optimal variables. Therefore, the RSM was a successful model to establish the optimal MAE conditions, maximizing the content of polyphenols and total flavonoids, as well as the antioxidant capacity and extraction performance of SM.
Keywords: Macroalgae, microwave assisted extraction, Sargasusum muticum

Acknowledgements: The research leading to these results was supported by MICINN supporting the Ramón y Cajal grant for M.A. Prieto (RYC-2017-22891) and the FPU grant for A. Carreira-Casais (FPU2016/06135); by Xunta de Galicia for supporting the program EXCELENCIA-ED431F 2020/12 and the program Grupos de Referencia Competitiva (GRUPO AA1-GRC 2018) that supports the work of J. Echave; by the program BENEFICIOS DO CONSUMO DAS ESPECIES TINTORERA-(CO-0019-2021) that supports the work of F. Chamorro; by University of Vigo for supporting the predoctoral grant of M. Carpena (Uvigo-00VI 131H 6410211). Authors are grateful to Ibero-American Program on Science and Technology (CYTED—AQUA-CIBUS, P317RT0003), to the Bio Based Industries Joint Undertaking (JU) under grant agreement No 888003 UP4HEALTH Project (H2020-BBI-JTI-2019) that supports the work of P. Otero and to AlgaMar enterprise (www.algamar.com) for the collaboration and algae material provision. The JU receives support from the European Union's Horizon 2020 research and innovation program and the Bio Based Industries Consortium. The project SYSTEMIC Knowledge hub on Nutrition and Food Security, has received funding from national research funding parties in Belgium (FWO), France (INRA), Germany (BLE), Italy (MIPAAF), Latvia (IZM), Norway (RCN), Portugal (FCT), and Spain (AEI) in a joint action of JPI HDHL, JPI-OCEANS and FACCE-JPI launched in 2019 under the ERA-NET ERA-HDHL (n° 696295). The authors would like to thank the EU and FCT for funding through the project PTDC/OCE-ETA/30240/2017- SilverBrain - From sea to brain: Green neuroprotective extracts for nanoencapsulation and functional food production (POCI-01-0145-FEDER-030240).

References:

1. Casas, M. P., Conde, E., Domínguez, H. & Moure, A. Process Biochem. 2019 79, 166–173.
2. Puspita, M., Déniel, M., Widowati, I., Radjasa, O., Douzenel, P., Marty , C., Vandanjon , L., Bedoux , G., Bourgougnon , N. J. Appl. Phycol. 2017. 29, 2521–2537

Food and natural products

Antioxidant efficiency of chlorogenic acid in omega-3 enriched emulsified systems and correlation with their distribution

M. Costa,[a] R. Lopes,[a] F.Paiva-Martins,[a] S. Losado-Barreiro,[a,b] C-Bravo-Díaz,[b] Luís S. Monteiro[c]

a) REQUIMTE-LAQV, Faculdade de Ciências, Universidade Do Porto, Porto, Portugal b) Universidade de Vigo, Fac. Química, Dpto Química Física, Vigo, Spain; c) Chemistry Centre, University of Minho, Braga, Portugal

Email: lrafaelaa9@gmail.com

Omega-3 polyunsaturated fatty acids (PUFAs) are highly susceptible to lipid oxidation due to their high degree of unsaturation and frequently they need to be stabilized with antioxidants (AOs). Lipid oxidation is believed to be initiated near the interfacial region, and thus, the antioxidant efficiency in inhibiting lipid oxidation depends, among others, on the concentration of antioxidant in that region.

In this work, we determined the effect of the distribution of chlorogenic acid (CGA) and its derivatives (C1-C16) in food-grade emulsions and nanoemulsions, composed of fish oil, acidic water and Tween 80, on their antioxidant capacity. Auxiliary experiments in binary fish oil-water mixtures in the absence of emulsifier showed that CGA is essentially oil-insoluble, C1-C6 are both oil and water-soluble and C8-C16 are water-insoluble. However, it was interesting to note that the C6 derivative was still quite soluble in water (more than 94%). The distribution of CGA esters in the emulsified systems studied, obtained by using the pseudophase kinetic model[1], that employs a kinetic method based on the reaction between the hydrophobic 4-hexadecylarenediazonium ions and the antioxidant, showed that these esters are at much lower concentration at the interfacial region than the esters of other phenolipids series such hydroxytyrosol or caffeic acid esters[2]. Therefore, no antioxidant activity in the emulsified systems were observed for CGA and CGA esters. Results also showed that the smaller droplet size found in nanoemulsions did not affect partition constants of CGA and its esters.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support (UIDB/QUI/50006/2020).

References:

1. Losada-Barreiro, S., Paz, V. S., Bravi-Diaz, C., & Martins, F. P. (2012). Temperature and Emulsifier Concentration Effects on Gallic Acid Distribution in a Model Food Emulsion. J. Colloid Interface Sci., 370, 73.
2. a) Almeida, J., S. Losada-Barreiro, M. Costa, F. Paiva-Martins, C. Bravo-Díaz, and L.S. Romsted. (2016). “Interfacial Concentrations of Hydroxytyrosol and Its Lipophilic Esters in Intact Olive Oil-in-Water Emulsions: Effects of Antioxidant Hydrophobicity, Surfactant Concentration, and the Oil-to-Water Ratio on the Oxidative Stability of the Emulsions.” Journal of Agricultural and Food Chemistry 64, no. 25, b) Costa, Marlene, Sonia Losada-Barreiro, Fátima Paiva-Martins, Carlos Bravo-Díaz, and Laurence S Romsted. (2015). “A Direct Correlation between the Antioxidant Efficiencies of Caffeic Acid and Its Alkyl Esters and Their Concentrations in the Interfacial Region of Olive Oil Emulsions. The Pseudophase Model Interpretation of the ‘Cut-off’ Effect.” Food Chemistry 175: 233–42.

Food and natural products

Synthesis, insecticidal activity and encapsulation of carvacrol and thymol derivatives

José M. S. G. P. Duarte,[a] Maria José G. Fernandes,[a] David M. Pereira,[b] Renato B. Pereira,[b] A. Gil Fortes,[a] Ana Rita O. Rodrigues,[c] Elisabete M. S. Castanheira,[c] M. Sameiro T. Gonçalves[a]

a) CQUM, Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal; b) REQUIMTE/LAQV, Laboratório de Farmacognosia, Faculdade de Farmácia, Universidade do Porto, R. Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal; c) CFUM, Centro de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

Email: msameiro@quimica.uminho.pt

Essential oils (EOs) have been the target of interest on the part of the scientific community due to their remarkable biological properties and health promoting benefits, including analgesic, anti-inflammatory, antibiotic, antioxidant and antimicrobial activities, as well as potential insecticides.[1]
Carvacrol and thymol are important constituents of several essential oils which are used in several industries such as perfumery, flavouring in the food industry and more recently in the insecticide area, as a green alternative to previously used pesticides.[2] Both carvacrol and thymol have been shown to have insecticidal and repellent activity against some insect species. Various investigations indicated that the structural modification of their chemical constituents promotes the enhancement of the biocidal effect of these substances by increasing their activity.[3] However, the low water solubility, high volatility and rapid oxidation of EOs constituents affect the possibility of biological application, decreasing their real potential. To mitigate these problems, EOs can be incorporated into nanoencapsulation systems.[4]
Considering the relevance of these essential oils, in the present communication new carvacrol and thymol derivatives were synthesised, evaluated against their effect upon the viability of the insect cell line Sf9 (Spodoptera frugiperda) and encapsulation assays in lipid nanosystems were performed, in order to boost their application as alternative insecticides.

Acknowledgements: This work was produced under project nr. PTDC/ASP-AGR/30154/2017 (POCI-01-0145-FEDER-030154) of the COMPETE 2020 program, co-financed by the FEDER and the European Union. The authors acknowledge also to Foundation for Science and Technology (FCT, Portugal), and FEDER-COMPETE-QREN-EU for financial support to the research centres CQ-UM (UID/QUI/00686/2019), CF-UM-UP (UIDB04650/2020) and REQUIMTE (UIDB/50006/2020). The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network and was purchased within the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT.

References:

1. a) Salman M.; Abbas R. Z.; Israr M.; Abbas A.; Mehmood K.; Khan M. K.; Sindhu Z. D.; Hussaind R.; Saleemie M. K.; Shaha S. Vet. *Parasitol*. **2020**, 283, 109178. b) Mishra P. A.; Devkota H. P.; Nigam M.; Adetunji C. O.; Srivastava N.; Saklani S.; Shukla I.; Azmi L.; Shariati M. A.; Coutinho H. D. M.; Khaneghah A. M. *LWT* **2020**, 133, 110116.
2. a) Pavela R. *Ind. Crops Prod*. **2015**, 76, 174. b) Youssefi M. R.; Tabari M. A.; Esfandiari A.; Kazemi S.; Moghadamnia A. A.; Sut S.; Dall'Acqua S.; Benelli G.; Maggi F. *Molecules* **2019**, 24, 1.
3. Novato T.; Gomes G. A.; Zeringóta V.; Franco C. T.; Oliveira D. R.; Melo D.; Carvalho M. G.; Daemon E.; Monteiro C. M. O. *Vet. Parasitol*. **2018**, 260, 1.
4. Lammari N.; Louaer Q.; Meniai A. H.; Elaissari A. *Pharmaceutics* **2020**, 12, 431.

Food and natural products

Eugenol derivatives with potential insecticide activity

José R. A. Coelho,[a] Maria José G. Fernandes,[a] Renato B. Pereira,[b] David M. Pereira,[b] Elisabete M. S. Castanheira,[c] A. Gil Fortes,[a] M. Sameiro T. Gonçalves[a]

a) Centre of Chemistry (CQ/UM), University of Minho, Campus of Gualtar, 4710-057 Braga, Portugal; b) REQUIMTE/LAQV, Laboratory of Pharmacognosy, Department of Chemistry, Faculty of Pharmacy, University of Porto, R. Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal; c) Centre of Physics (CFUM), University of Minho, Campus of Gualtar, 4710-057 Braga, Portugal.

Email: a85799@alunos.uminho.pt

Eugenol, the generic name of 4-allyl-2-methoxyphenol, is the major component of clove's essential oil, and displays antimicrobial, antioxidant and insecticide potential.[1-3] Its structural simplicity, inexpensively and availability makes it a molecule widely used as a starting material in the preparation of derivatives of natural products and their analogs, as well as building block for obtaining complex functionalized bioactive compounds and co-drugs with improved physicochemical properties, macrocycles, heterocycles, and polymers.[4-6] Eugenol is a phenylpropanoid, which has a double bond with capability for further functionalization, namely through epoxidation reaction. As it is well-known, the epoxide is a good and highly reactive synthetic intermediate, because of the associated ring tension, as its opening allows for numerous possibilities, depending on the nucleophiles chosen. Considering all the above facts, in the present work, semisynthetic eugenol derivatives were obtained through epoxidation reaction followed by epoxide opening with nucleophiles, such as sodium azide and sodium cyanide. The optimization of the various reactions was performed using different experimental conditions. The main objective behind obtaining these eugenol derivatives was their evaluation as alternative insecticides, thus the biological activity of all compounds was compared to a commercial synthetic insecticide and tested against *Sf9* (*Spodoptera frugiperda*) insect cell line.

Acknowledgements: We thank the financial support of project PTDC/ASP-AGR/30154/2017 (POCI-01-0145-FEDER-030154) of the COMPETE 2020 program, co-financed by the FEDER and the European Union. The authors acknowledge also to Foundation for Science and Technology (FCT, Portugal), and FEDER-COMPETE-QREN-EU for financial support to the research centres CQ-UM (UID/QUI/00686/2020), CF-UM-UP (UID/FIS/04650/2020) and REQUIMTE (UIDB/50006/2020). The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network and was purchased within the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT.

References:

1. Ju J.; Xie Y.; Yu H.; Guo Y.; Cheng Y.; Qian H.; Yao W. *LWT Food Sci. Technol.* **2020**, *123*, 109128.
2. Sohilait H. J.; Kainama H. *Open Chem.* **2019**, *17*, 422.
3. Raveau R.; Fontaine J.; Sahraoui A. L.-H. *Foods*, **2020**, 9, 365.
4. Kaufman T. S. *J. Braz. Chem. Soc.* **2015**, *26*, 1055.
5. Fernandes M. J. G.; Pereira R. B.; Pereira D. M.; Fortes A. G.; Castanheira E. M. S.; Gonçalves M. S. T. *Int. J. Mol. Sci.* **2020**, *21*, 9257.
6. Potapov V. A.; Ishigeev R. S.; Shkurchenko I. V.; Zinchenko S. V.; Amosova S. V. *Molecules* **2020**, *25*, 376.

Food and natural products

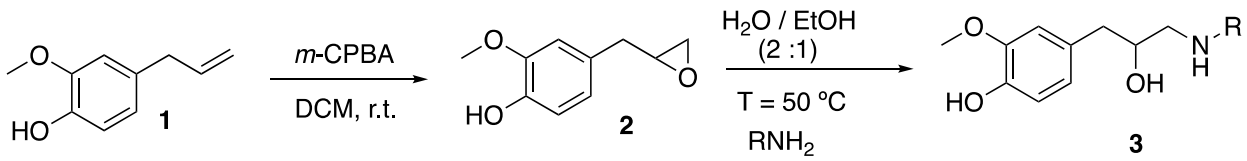
Synthesis of amino alcohols from eugenol and their biological evaluation against AGS cell line

Nuno F. S. Pinto,[a] Cláudia Teixeira,[a,b] David M. Pereira,[b] Renato B. Pereira [b] M. José G. Fernandes,[a] Elisabete M. S. Castanheira,[c] A. Gil Fortes,[a] M. Sameiro T. Gonçalves[a]

a) Centre of Chemistry (CQ/UM), University of Minho, Campus of Gualtar, 4710-057 Braga, Portugal; b) REQUIMTE/LAQV, Laboratory of Pharmacognosy, Department of Chemistry, Faculty of Pharmacy, University of Porto, R. Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal; c) Centre of Physics (CFUM), University of Minho, Campus of Gualtar, 4710-057 Braga, Portugal.

Email: gilf@quimica.uminho.pt

In recent years essential oils became an important natural source of bioactive compounds.[1] Eugenol is a phenylpropanoid and a major constituent of clove essential oil with many applications in pharmaceutical, food, agricultural, and cosmetics industries,[3] showing to be biologically active as antioxidant, antiviral, anti-inflammatory and antimicrobial.[2] Structural changes of eugenol are known to be a useful strategy in order to improve biological activity and to obtain new analogues with reduced side effects.[4]
β-Amino alcohol functionality is found in many biologically active compounds, being an important pharmacophore. *N*-Substituted β-amino alcohols are important building blocks in the preparation of added-value chemicals.[5]
In the present work, a series of amino alcohols were obtained from eugenol epoxide according to **Scheme 1**.The epoxide **2** was prepared from eugenol **1** and was reacted with a series of amine nucleophiles affording the corresponding β-amino alcohols of type **3** in good yields.
The potential of these new compounds will be evaluated against AGS cell line and the results will be presented in this communication.



Scheme 1: Synthesis of amino alcohol **3**.

Acknowledgements: We thank the financial support of project PTDC/ASP-AGR/30154/2017 (POCI-01-0145-FEDER-030154) of the COMPETE 2020 program, co-financed by the FEDER and the European Union. The authors acknowledge also to Foundation for Science and Technology (FCT, Portugal), and FEDER-COMPETE-QREN-EU for financial support to the research centres CQ-UM (UID/QUI/00686/2020), CF-UM-UP (UID/FIS/04650/2020) and REQUIMTE (UIDB/50006/2020). The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network and was purchased within the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT.

References:

1. Silva F. F. M.; Monte F. J. Q.; Lemos T. L. G., Nascimento P. G. G.; Costa A. K. M.; Paiva L. M. M. *Chem. Cent. J*. **2018**, *12*, 34.
2. a) Tripathi A. K.; Upadhyay S.; Bhuiyan M.; Bhattacharya P. R. *J. Pharmacognosy Phytother.* **2009**,*1*, 52. b) Cortés-Rojas D.F.; Souza C. R. F.; Oliveira W. P. *Asian Pacific J. Trop. Biomed.* **2014**, *4*, 90. c) Evambe G.; Canales L.; Banik B.K. *Heterocycl. Lett.* **2011**, *1*, 2231. d) Sun W.-J.; Lv W.-J.; Li L.-N. *New Biotechnol.* **2016**, *33*, 345. e) Fonseca D. V.; Salgado P. R. R.; Neto H. C. A.; Golzio A. M. F. O.; Filho M. R. D. C.; Melo C. G. F.; Leite F. C.; Piuvezam M. R.; Pordeus L. C. M.; Filho J. M. B. *Int. Immunopharmacol.* **2016**, *38*, 402. f) Awasthi P. K.; Dixit S. C.; Dixit N.; Sinha A. K. *Drugs* **2008**, *1*, 215.
3. Cortés-Rojas D. F.; Souza C. R. F.; Oliveira W. P. *Asian Pacific J. Trop. Biomed.* **2014**, *4,* 90.
4. Kodama T.; Ito T.; Dibwe D. F.; Woo, S.-T.; Morita, H. *Bioorg. Med. Chem. Lett*., **2017**, *27*, 2397.
5. Ang W.; Ye W.; Sang Z.; Liu Y.; Yang T.; Deng Y.; Luo Y.; Wei Y. *Bioorg. Med. Chem. Lett.* **2014**, *24*, 1496.

Food and natural products

Avaliação da composição nutricional e atividade antioxidante do caule e folhas de trapoeraba (*Commelina erecta L.)*

Lucas V. Cavichi[a,b*], Ângela Fernandes[a], Ângela Liberal[a], Cristiane Canan[b], Joana S. Amaral [a,c], Lillian Barros[a]

a) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; b) Departamento Académico de Alimentos (DAALM), Universidade Tecnológica Federal do Paraná, Campus Medianeira, 85884-000 Paraná, Brasil; c) LAQV-REQUIMTE, Faculdade de Farmácia da Universidade do Porto, Rua de Jorge Viterbo Ferreira, Porto, Portugal

Email: lucascavichi@hotmail.com

Nos últimos anos tem-se verificado um crescente interesse por plantas silvestres, dada a sua composição rica em nutrientes. Commelina erecta, popularmente conhecida como trapoeraba ou erva de santa-luzia, é oriunda de países tropicais, sendo atualmente descrita como Planta Alimentícia Não Convencional (PANC)[1]. Inúmeros estudos reportaram os seus efeitos benéficos para a saúde, funcionando como antiviral, anti-hemorrágico e antimicrobiano, sendo ainda consumida em saladas e pós cocção[1]. O presente estudo teve por objetivo avaliar a composição nutricional (lípidos, proteína, cinzas, ácidos gordos e ácidos orgânicos) de diferentes partes comestíveis da planta, nomeadamente do caule e folhas de C. erecta, tendo ambos sido colhidos durante e após floração da planta. Procedeu-se ainda à avaliação da atividade antioxidante nos extratos aquosos medindo a inibição da peroxidação lipídica usando o ensaio de substâncias reativas ao ácido tiobarbitúrico (TBARS). A composição proximal foi avaliada segundo os procedimentos oficiais da AOAC. Os ácidos orgânicos foram determinados por cromatografia líquida de alta eficiência acoplada a um detector de fotodíodos (HPLC-DAD) e os ácidos gordos por cromatografia gasosa e deteção de ionização de chama (GC-FID). Em ambos os períodos de colheita, verificou-se um teor de proteína significativamente superior nas folhas comparativamente aos caules. No pós-floração, observou-se um aumento de 8x e 15x do teor de lípidos do caule e folhas, respetivamente. Os ácidos gordos (AG) polinsaturados foram o grupo predominante em todas as amostras (44.8-62.8%), sendo o ácido α-linolénico o maioritário nas folhas e o linoleico nos caules. Após a floração, verificou-se um aumento de AG saturados e decréscimo de monoinsaturados nos caules, ocorrendo o oposto nas folhas. A amostra que apresentou um perfil de AG mais adequado do ponto de vista nutricional foram as folhas colhidas após floração. No que respeita os ácidos orgânicos, em todas as amostras o shikímico foi o maioritário, seguido pelo ascórbico, oxálico e málico. No que respeita a avaliação da atividade antioxidante, foram observadas diferenças significativas entre as amostras avaliadas, sendo amostra de caule pós floração apresentou a melhor atividade com um valor de EC50 de 43 ± 1 µg/mL. De uma maneira geral, os resultados obtidos indicam que os caule e folhas de C. erecta podem ser uma fonte vegetal relevante de nutrientes e compostos antioxidantes, confirmando o interesse da sua inclusão na dieta como PANC.

Agradecimentos: Os autores agradecem à Fundação para a Ciência e Tecnologia (FCT, Portugal) pelo apoio financeiro dos fundos nacionais FCT / MCTES ao CIMO (UIDB / 00690/2020) e ao projeto UTFPR / IPB 01 / 2019-2020-85 “Avaliação da composição química e atividade biológica de plantas alimentícias não convencionais (PANCs) com vista à sua valorização”. L. Barros e A. Fernandes agradecem ainda o financiamento nacional da FCT, P.I. através do contrato-programa de emprego científico institucional.

References:

1. Bezerra J.A.; Corrêa R.F.: Salomé K. et al. Phytochemical Study and Antioxidant Evaluation of Commelina erecta (Commelinaceae) Stems. *Rev Virtual Quim.* **2019**,11, 255. doi:10.21577/1984-6835.20190018

Food and natural products

Evaluation of the phenolic composition and bioactivities of plants from Asteraceae family

Marta Barral-Martinez [a], Paula Garcia-Oliveira [a,b], Tiane C. Finimundy [b], Ricardo Calhelha [b], Tânia C. S. P. Pires [b], Marija Nenadic [c], Marina Sokovic [c], Bernabe Nuñez-Estevez [a,b], Pascual Garcia-Perez [a], Jesus Simal-Gandara [a], Lillian Barros [b,*] and Miguel A. Prieto [a,b,*]

Nutrition and Bromatology Group, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E32004 Ourense, Spain. b) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.c) Institute for Biological Research "Siniša Stanković"- National Institute of Republic of Serbia, University of Belgrade.

Email: mprieto@uvigo.es, lillian@ipb.pt

Plants have been widely employed in traditional medicine, known as medicinal plants, and, currently, they play an important role in the design of modern drugs and healthy foods. Numerous studies have reported that the health-enhancing properties of medicinal plants (*e.g.*, antioxidant, antimicrobial, antitumor, etc.) are a consequence of the biosynthesis of bioactive compounds, especially phenolic compounds. Nowadays, most medicinal plants are employed in shelf-care, usually consumed as herbal products, but their consumption is decreasing dramatically [1]. The aim of this work was to evaluate the phenolic profile and the biological activities of two plants from Asteraceae family, *Arnica montana* and *Taraxacum officinale*, to valorize their use as a source of bioactive compounds for further industrial applications.

Heat-assisted extraction was employed to obtain extracts rich in bioactive compounds, leading to the determination of phenolic profile and the evaluation of their associated *in vitro* bioactivities, including antioxidant, antimicrobial, anti-inflammatory and cytotoxic activities. The results showed that *A. montana* extracts present a higher content of phenolic compounds compared to *T. officinale*, with values of 119 and 18 mg/mL of extract (MetOH/H_2O), respectively. The results for the antioxidant activity of these extracts were similar for both species, according to ABTS, β-carotene-bleaching and TBARS assays. Moreover, *A. montana* showed the highest antibacterial and antifungal effects, with minimal bactericidal and fungicidal concentrations ranging between 0.25-0.5 mg/mL and 0.5-1 mg/mL, respectively. Finally, both plants displayed similar anti-inflammatory properties (106 and 111 µg/mL, respectively), while *A. montana* exerted cytotoxic effects against a wider range of tumor cell lines.

These results suggest the possibility of obtaining new extracts with exceptional biological activities that may be of interest for the development of new products for the nutraceutical, cosmetic or pharmaceutical industries.

Acknowledgements: The research leading to these results was supported by MICINN supporting the Ramón y Cajal grant for M.A. Prieto (RYC-2017-22891); by Xunta de Galicia for supporting the program EXCELENCIA-ED431F 2020/12, the pre-doctoral grant of P. Garcia-Oliveira (ED481A-2019/295), and the program Grupos de Referencia Competitiva (GRUPO AA1-GRC 2018) that supports the work of M. Barral-Martínez; and by EcoChestnut Project (Erasmus+ KA202) that supports the work of B. Nuñez-Estevez. Authors are grateful to Ibero-American Program on Science and Technology (CYTED—AQUA-CIBUS, P317RT0003), to the Bio Based Industries Joint Undertaking (JU) under grant agreement No 888003 UP4HEALTH Project (H2020-BBI-JTI-2019) that supports the work of P. Garcia-Perez. The JU receives support from the European Union's Horizon 2020 research and innovation program and the Bio Based Industries Consortium. The project SYSTEMIC Knowledge hub on Nutrition and Food Security, has received funding from national research funding parties in Belgium (FWO), France (INRA), Germany (BLE), Italy (MIPAAF), Latvia (IZM), Norway (RCN), Portugal (FCT), and Spain (AEI) in a joint action of JPI HDHL, JPI-OCEANS and FACCE-JPI launched in 2019 under the ERA-NET ERA-HDHL (n° 696295). Foundation for Science and Technology (FCT, Portugal) for financial support through national funds FCT/MCTES to the CIMO (UIDB/00690/2020). L. Barros and R. Calhelha thank the national funding by FCT, P.I., through the institutional and individual scientific employment program-contract for their contracts, respectively.

References:

1. Garcia-Oliveira, P.; Fraga-Corral, M.; Pereira, A.G.; Lourenço-Lopes, C.; Jimenez-Lopez, C.; Prieto, M.A. *Food Chem.* **2020**, *330*, 127197.

Food and natural products

Study of phenolic composition and biological properties of traditionally used plants *Achillea millefolium, Calendula officinalis* and *Chaemelum nobile*

Paula Garcia-Oliveira[a,b], Marta Barral-Martinez[a], Tiane C. Finimundy[b], Ricardo Calhelha[b], Tânia C. S. P. Pires[b], Marija Nenadić[c], Marina Soković[c], Maria Carpena[a], Paz Otero[a], Pascual Garcia-Perez[a], Jesus Simal-Gandara[a], Lillian Barros[b*], Miguel A. Prieto[a,b*]

a) Nutrition and Bromatology Group, Faculty of Food Science and Technology, University of Vigo, Ourense Campus, E32004 Ourense, Spain; b) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; c) Institute for Biological Research "Siniša Stanković"- National Institute of Republic of Serbia, University of Belgrade.

Email: *mprieto@uvigo.es; lillian@ipb.pt

Nowadays, numerous studies have evaluated “traditional plants”, plant species that have been employed in traditional medicine, due to their beneficial effects on health. These studies have linked diverse biological properties of these plants (e.g., antioxidant, antimicrobial, antitumor, among others) to the presence of different bioactive compounds, including phenolic compounds [1]. However, the use of traditional plants like Achillea millefolium, Calendula officinalis and Chaemelum nobile is decreasing, being relegated as herbal products [2]. Thus, the main aim of this study was to determine the phenolic composition and also biological properties of these plants, with the aim of re-valorizing their use in nutraceutical, cosmetic or pharmaceutical industries. Dried samples of the selected species were extracted by heat-assisted extraction to obtain extracts rich in bioactive compounds. Then, the phenolic composition of such extracts was determined, together with the determination of their antioxidant (ABTS, β-carotene-bleaching and TBARS assays), antimicrobial (both against bacterial and fungi), anti-inflammatory (inhibition of inflammation on RAW264.7 murine macrophages) and cytotoxic activities (performed on four tumor cell lines: MCF-7, CaCo, AGS and NCI-H460). The results of total phenolic compounds ranged between 100 and 14 mg/mL of extract for C. nobile and C. officinalis, respectively, while A. millefolium showed a phenolic content of 81 mg/mL of extract. The results for antioxidant activity reported variable effects, highlighting the effectiveness of A. millefolium extracts in β-carotene-bleaching and TBARS assays. In antimicrobial tests, C. officinalis showed the best antibacterial and antifungal activities (minimal bactericidal and antifungal concentrations between 0.25-0.5 mg/mL of extract). Finally, C. nobile displayed the highest anti-inflammatory effects (IC50=15.2 µg/mL) and cytotoxic effects against different tumor cell lines (GI50 values ranging between 54 and 10.3 µg/mL). The present results indicate that these plants may be interesting to obtain bioactive compounds-enriched extracts with biological properties associated for the development of new applications.

Acknowledgements: The research leading to these results was supported by MICINN supporting the Ramón y Cajal grant for M.A. Prieto (RYC-2017-22891), by Xunta de Galicia for supporting the program EXCELENCIA-ED431F 2020/12, the pre-doctoral grant of P. Garcia-Oliveira (ED481A-2019/295) and the program Grupos de Referencia Competitiva (GRUPO AA1-GRC 2018) that supports the work of M. Barral-Martínez; by University of Vigo for supporting the predoctoral grant of M. Carpena (Uvigo-00VI 131H 6410211). Authors are grateful to Ibero-American Program on Science and Technology (CYTED—AQUA-CIBUS, P317RT0003), to the Bio Based Industries Joint Undertaking (JU) under grant agreement No 888003 UP4HEALTH Project (H2020-BBI-JTI-2019) that supports the work of P. Otero and P. Garcia-Perez. The JU receives support from the European Union’s Horizon 2020 research and innovation program and the Bio Based Industries Consortium. The project SYSTEMIC Knowledge hub on Nutrition and Food Security, has received funding from national research funding parties in Belgium (FWO), France (INRA), Germany (BLE), Italy (MIPAAF), Latvia (IZM), Norway (RCN), Portugal (FCT), and Spain (AEI) in a joint action of JPI HDHL, JPI-OCEANS and FACCE-JPI launched in 2019 under the ERA-NET ERA-HDHL (n° 696295). Authors are also grateful to Foundation for Science and Technology (FCT, Portugal) for financial support through national funds FCT/MCTES to the CIMO (UIDB/00690/2020). L. Barros and R. Calhelha thank the national funding by FCT, P.I., through the institutional and individual scientific employment program-contract for their contracts, respectively.

References:

1. Garcia-Oliveira P.; Fraga-Corral M.; Pereira A.G.; Lourenço-Lopes C.; Jimenez-Lopez C.; Prieto M.A., Simal Gandara J. *Food Chem*. **2020**, *330*, 127197.
2. Garcia-Oliveira P., Barral M., Carpena M., Gullón P., Fraga-Corral M., Otero, P., Prieto M.A, Simal-Gandara J. *Food & Function.* **2021***, 12*(7), 2850-2873.

Food and natural products

Polyphenols-rich functional foods in the prevention and management of type 2 Diabetes Mellitus

Filipa Campos,[a] Ana Fernandes,[a] Iva Fernandes,[a] Nuno Mateus,[a] Victor de Freitas[a]

a) Requimte-LAQV: Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto - Rua do Campo Alegre, s/n, 4169-007 Porto

Email: ana.fernandes@fc.up.pt ; iva.fernandes@fc.up.pt

Diabetes Mellitus is a relevant public health problem that is defined by high blood sugar levels and it can be accompanied by metabolic abnormalities of proteins, lipids, electrolytes or minerals salts.[1-3] The most frequent type is type 2 diabetes.[4] The available therapeutic options include, in addition to insulin, several oral antidiabetic agents. However, many of them have seriously adverse effects.[5] Thus, new antidiabetic agents with therapeutic efficacy are needed.[6]

Recently, the association between bioactive compounds in food stuff and health benefits has gained a attention.[7] In our daily life, foods rich in bioactive compounds, which includes, for example, phenols, flavonoids, polysaccharides, xanthones and alkaloids can be consumed.[8] The interest in the health effects of phenolic compounds has grown exponentially in the past few years and one of its biological effects that is studied most intensively is their antidiabetic effect.[9-10]

Beside extractable phenolic compounds, a considerable quantity of non-extractable phenolic compounds that still remains bounded to cell-wall matrix can be present in the residues that are disregarded in the aqueous organic extractions.[11] This way, extracts rich in polyphenols and polyphenols-polysaccharides conjugates may be an alternative therapeutic strategy to the ones typically applied.

In this word, it is intended to extract free polyphenols and polyphenols-polysaccharides conjugates from agro-food by-products and to study the impact of these extracts on digestive enzymes, such as pancreatic α-amylase and on modulation of glucose transepithelial transport using in vitro intestinal cell models (Caco-2).

Funding: This work was financially supported by UIDB/50006/2020 with funding from FCT/MCTES through national funds.

Acknowledgements: The authors thank the support by AgriFood XXI I&D&I project (NORTE-01-0145-FEDER-000041) cofinanced by European Regional Development Fund (ERDF), through the NORTE 2020 (Programa Operacional Regional do Norte 2014/2020. A.F and I.F. would like to thank the FCT for their research contracts (CEECIND/00029/2018/CP1545/CT0010 and SFRH/BPD/86173/2012, respectively).

References:

1. Bekele, H et al. 2020. J Diabetes Res 2020:7948712.
2. Artasensi, A., et al. 2020. J Physiol Biochem 25(8):1987.
3. Les, F., et al., J Physiol Biochem 2020. 77(1):109-131.
4. Olokoba, A.B. et al. 2012. Oman Med J 27(4): 269.
5. Jung, M., et al. 2006. Curr Med Chem 13(10):1203-1218.
6. Prabhakar, P.K. and Doble, M. 2009. Phytomedicine 16(12):1119-1126.
7. de Araújo, F.F., et al., 2021. Food Chem 338:127535.
8. Oliveira, H., et al., 2020. Molecules 25(17):3813.
9. Potì, F., et al. 2019. Int J Mol Sci 20(2):351.
10. Pandey, K.B. and Rizvi S.I. 2014. Integr Med Res 3(3):119-125.
11. Saura-Calixto, F. 2012. J Agric Food Chem 60(45):11195-200.

Food and natural products

Anthocyanins-Polysaccharides nanocomplexes for food application

Inês Pereira,[a] Ana Fernandes,[a] Nuno Mateus,[a] Victor de Freitas[a]

a) Requimte-LAQV: Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto - Rua do Campo Alegre, s/n, 4169-007 Porto

Email: ana.fernandes@fc.up.pt

In the last years, consumers demands have been oriented towards natural, safe and healthy foodstuffs, which has promoted the development of new food systems. Anthocyanins are polyphenolic pigments responsible for a large diversity of colors in plants. They present a great potential as natural colorants and as functional ingredients, due to their distinct beneficial effects for human health. Thus, their application in foodstuffs is currently encouraged to fulfill this request [1,2]. However, their color stability, processability and biological activity are highly affected after their extraction and transformation procedures. The formation of polyelectrolyte complexes with charged polysaccharides is a possible aproach to stabilize anthocyanins [3].
The aim of this work is to develop nano/microcomplexes of anthocyanins, using polysaccharides extracted from algae, namely carrageenans, as building blocks. Furthermore, it is intended to understand anthocyanins-polysaccharides binding mechanisms and to perform a characterization of the complexes.
Interaction was studied by UV-Vis and ITC at different pH values, ratios and concentrations, while incorporation yield and efficiency were determined by HPLC. Size, zeta potential and morphology were studied by DLS and CRYO-SEM. The results showed the formation of soluble and insoluble complexes, whose stability against temperature and pH, along with their chromatic and antioxidant properties were assessed. Complexes' bioavailability was evaluated based on their stability on in vitro digestions and their ability to cross intestinal barriers [4-6].
With this approach, it will be tempted to develop innovative strategies to produce nanostructured anthocyanins with polysaccharides in food products, with proper sensorial and health properties.

Funding: This work was financially supported by UIDB/50006/2020 with funding from FCT/MCTES through national funds.

Acknowledgements: The authors thank the support by AgriFood XXI I&D&I project (NORTE-01-0145-FEDER-000041) cofinanced by European Regional Development Fund (ERDF), through the NORTE 2020 (Programa Operacional Regional do Norte 2014/2020. A.F would like to thank the FCT for the research contract (CEECIND/00029/2018/CP1545/CT0010).

References:

1. Scalbert, A. & Williamson, G. 2000. J Nutr 130: 2073.
2. Manach, C. et al. 2005. Am J Clin Nutr 81: 230.
3. Luo, Y. et al. 2020. J Agr Food Chem 68: 12993.
4. Azevedo, J. et al. 2010. Food Chem 119: 518.
5. Klimaviciute, R. et al. 2015. Carbohyd Polym 129: 70.
6. Navikaite, V. et al. 2016. Carbohyd Polym 148: 36.

Food and natural products

Changes in the secondary structure of lysozyme by interactions with gallic acid

Daiana Leithardt,[a,b] Cândida Tomaz ,[a,b] António Mendonça[a,b]

a) CICS-UBI – Centro de Investigação em Ciências da Saúde, Universidade da Beira Interior, Av. Infante D. Henrique, 6200-506 Covilhã, Portugal; b) Departamento de Química, Universidade da Beira Interior, R. Marquês d'Ávila e Bolama, 6201-001 Covilhã, Portugal

Email: daiana.leithardt@ubi.pt

Egg (Gallus spp.) is an important food from the nutritional point of view with proteins of high biological value. Lysozyme (LYS, EC 3.2.1.17) is a globular, ubiquitous and thermolabile protein, with high enzymatic and bacteriostatic activity. Chicken egg white is a natural source of LYS that makes up about 3 to 4% of its total protein.[1] The interactions between phenolic compounds and proteins, can modify the native structure of proteins, changing their functional properties. Gallic acid (GA) is a natural antioxidant widely present in plants and beverages such as wine or tea. In this work, the circular dichroism spectra (CD) of LYS in the absence and presence of AG were recorded in the range of 190-260 nm in a 0.1 cm quartz cell under a nitrogen atmosphere (1 bar) with a flow of 2 L/min. The molar ratio between LYS (2 μM) and GA were 1:1; 1:5; 1:10, respectively. The samples were incubated for 10 min, at 310K, in 50mM phosphate buffer pH 7.40.[2]
The CD spectra (Figure 1 - A) and the data from the CDSSTR analysis program[3] (Table 1) show that there was a decrease in α-helix content of lysozyme in agreement with the formation of the complexes LYS-GA.[4] In addition, molecular docking (software) (Figure 1 - B) of GA with LYS also indicates interactions. Therefore, the interactions of LYS with GA, promote changes at the secondary structure of the protein that may have consequence on its conformational structure and the functional properties.

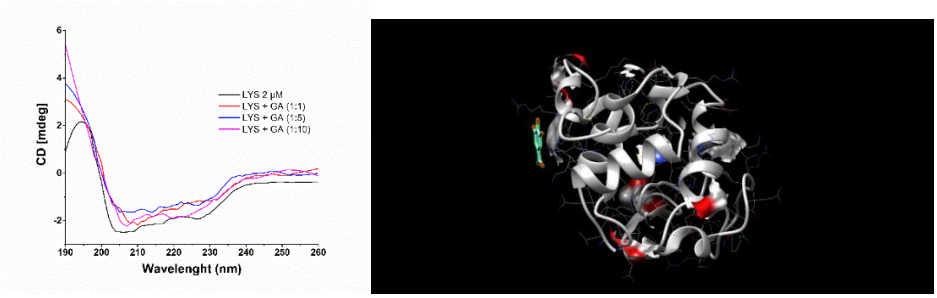


Figure 1: A - CD spectra of LYS (2μM) with gallic acid solutions and B - Molecular docking.

Table 1 - Secondary structural analysis of LYS in the absence and presence of different concentrations of GA.

Sample	GA (μM)	α-helix (%)	β-sheet (%)	β-turns (%)	Unordered (%)
LYS 2 μM	0	0.44	0.25	0.10	0.21
LYS 2 μM + GA	2	0.41	0.29	0.10	0.20
	10	0.25	0.31	0.14	0.30
	20	0.11	0.35	0.20	0.34

Acknowledgements: CICS-UBI - Health Sciences Research Center. Daiana Leithardt acknowledges the Ph.D. Incentive Grant Banco Santander-Totta/UBI and the Faculty of Sciences.

References:

1. Tiantian W.; Qingqing J.; Dan W.; Yaqin H.; Shiguo C.; Tian D.; Xingqian Y.; Donghong L.; Jianchu C. *Food Chemistry*. **2019**, 274, 698-709.
2. Su C.; Xin G.; Hongwei T., Yang L.; Lan H.; Jin O. *Talanta*. **2020**, 211, 120762.
3. Lee W.; Bonnie A. W. *Biopolymers*. **2008**, 89, 392-400.
4. Sourav D.; Somdev P.; Sharat S.; Mostofa A. R.; Debojit P.; Madhurima J.: Atanu S. R. *Phys. Chem. Chem. Phys*. **2019**, 21, 12649–12666.

Food and natural products

Understanding of the effect of successive exposure in astringency: oral interactions of a green tea flavanol extract

Mónica Jesus, [a] Elsa Brandão, [a] Carlos Guerreiro, [a] Nuno Mateus, [a] Victor de Freitas, [a] Susana Soares [a]

a) REQUIMTE, LAQV, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal

Email: monica.g.jesus@hotmail.com

Astringency is reported as a tactile sensation (dryness, tightening and puckering), mainly to the sensation of lubrication reduction of the oral cavity.[1] It is known that astringency is linked to salivary proteins (SP) precipitation by phenolic compounds (PC), however it is not the only mechanism behind this complex organoleptic sensation. Some astringent compounds do not precipitate SP and the interaction of PC with other oral constituents has already been demonstrated.[2] For a realistic approach to the development of astringency in the oral cavity, more complex and realistic new cell-based models have been developed which include mucin, oral epithelial cells and mucosal pellicle.[3] The consumption of (astringent) foods and beverages is performed through repeated sips, so the astringency perceived is relative to a sequence of stimuli. Consequently, the perception of the second stimulus may be influenced by the changes caused by the previous one. Thus, this work is focused in deepen the knowledge about the effect of two repeated exposures on oral interactions between a green tea extract, rich in flavanols, and a cell-based oral model. To attend this goal, we focused on: a) study how phenolic compounds bound in successive exposures, b) analyze possible differences between exposures, c) study the behaviour of different flavanols, d) research how saliva stimulation can affect the interaction between PC and oral constituents.

The results suggested that there is a greater interaction of PC in the model with all oral constituents considered (mucin, epithelial cells, mucosal pellicle and SP). There seems to be a tendency for the 2nd exposure stimulated salivary flow to have a higher PC connection than for the 1st exposure or 2nd exposure non-stimulated salivary flow. Furthermore, the chemical structure of the flavanols seems to influence the linkage with the different oral constituents. And it also shows that different families of SP may be involved in different stages of the development of astringency.

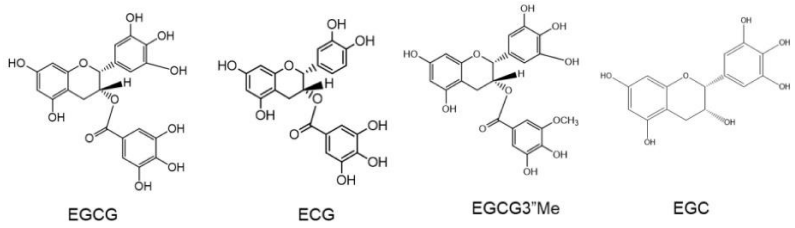


Figure 1: Flavanols more abundant in green tea extract: Epigallocatechin (EGCG), epicatechin gallate (ECG), epigallocatechin-3-O-(3-O-methyl) gallate (EGCG3"Me) and epigallocatechin (EGC).

Acknowledgements: The authors would like to thank FCT (PTDC/AGR-TEC/6547/2014, SFRH/BD/148549/2019, LAQV research unit (UIDB/50006/2020, POCI/01/0145/FEDER/007265) and FEDER-Interreg España-Portugal Programme (0377_IBERPHENOL_6_E) for the financial support. This work was financially supported by AgriFood XXI I&D&I project (NORTE-01-0145-FEDER-000041) co-financed by European Regional Development Fund (ERDF), through the NORTE 2020 (Programa Operacional Regional do Norte 2014/2020).

References:

1. Huang, R.; Xu, C. *Compr. Rev. Food Sci. Food Saf*. **2021**, 20 (1), 1036-1074.
2. a) Soares, S.; Soares, S.; Brandão, E.; Guerreiro, C.; Mateus, N.; de Freitas, V. Sci. Rep. 2020, 10 (1), 1-16. b) Canon, F.; Neiers, F.; Guichard, E. *J. Agric. Food Chem*. **2018**, 66 (30), 7873-7879.
3. Soares, S. n.; Brandão, E.; Guerreiro, C.; Mateus, N.; de Freitas, V.; Soares, S. *J. Agric. Food Chem*. **2019**, 67 (46), 12833-12843.

Food and natural products

Chemical composition and antimicrobial activity of the essential oil of winter savory (*Satureja montana* L.)

Lina Cancela,[a] Joana S. Amaral,[a,b,*]

a) CIMO, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; b) LAQV-REQUIMTE, Faculdade de Farmácia da Universidade do Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal

Email: jamaral@ipb.pt

Since ancient times, aromatic plants, which are frequently used in gastronomy for their aromatic and flavoring properties, have been playing a fundamental role in traditional medicine due to their therapeutic properties. Those are frequently associated to the essential oils present in these plants, whose antimicrobial and antioxidant activities have been described in numerous studies.[1] These properties have gained prominence in recent decades since an increasing number of consumers are seeking for products that include natural preservatives in substitution of synthetic additives. Therefore, different studies have been conducted on the evaluation of the antimicrobial activity of several natural products, including plant's essential oils. Winter savory (*Satureja montana* L.), botanically included in the Lamiaceae family, is an aromatic plant often used in culinary of different regions in the globe, as well as in traditional medicine for its anti-inflammatory, analgesic, anti-diabetic and anti-hypercholesterolemic properties.[2] This work aims at evaluating the chemical composition and antimicrobial activity of two samples of *S. montana* essential oil (EO), one commercial and other obtained by hydrodistillation from fried leaves of *S. montana*. The volatile composition was determined by gas chromatography coupled to mass detection (GC-MS) and the antimicrobial activity against 3 Gram-positive, 6 Gram-negative bacteria and 1 yeast was screened by using the disk diffusion assay, and the minimum inhibitory (MIC) and minimum bactericidal (MBC) concentrations were determined by using the Clinical and Laboratory Standards Institute (CLSI) broth macrodilution assay, with minor modifications.[3]

A total of 58 compounds were identified in the two samples. In the hydrodistilled EO, 52 compounds were identified corresponding to 96.6% of total compounds, while the commercial EO evidenced a much smaller diversity of compounds, namely 24 identified compounds corresponding to 96.0% of total compounds. Despite presenting qualitative and quantitative differences, in both EOs the major group was oxygenated monoterpenes, followed by monoterpenes. However, the hydrodistilled EO showed a significantly higher amount of sesquiterpenes (7.2%) when compared to the commercial EO (0.7%). The compounds with highest relative abundance in the hydrodistilled EO were carvacrol (50.4%), *p*-cymene (14.8%), β-caryophyllene (3.4%) and γ-terpinene (3.1%) while in the commercial EO were thymol (28.2%), *p*-cymene (18.9%), linalool (10.2%) and limonene (9.3%). In general, the hydrodistilled EO showed much better antimicrobial activity (inhibition halos of 14-35 mm) compared to the commercial EO (12-16 mm). With the exception of *P. aeruginosa* (2.5%) the hydrodistilled EO showed MIC values ranging between 0.08% and 0.31% (v/v) while the commercial oil had MIC of 2.5% for most tested microorganisms, with the exception of *Bacillus subtilis*, *Klebsiella pneumoniae* and *Candida albicans* (1.25% v/v). The different activity of the oils is most probably related to the different content in compounds with antimicrobial activity, such as phenols or aldehydes, namely due to the high carvacrol content (50.4%) compared to the sum of the isomers thymol+carvacrol (32.2%) in the commercial oil. In addition, the larger diversity of compounds in the hydrodistilled oil should also be considered as minor compounds can play a role in possible synergic effects. Overall, the results of this work highlight the promising antimicrobial properties of *S. montana* hydrodistilled EO and evidences the impact of differences in composition on the activity of EOs.

Acknowledgements: The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support by national funds FCT/MCTES to CIMO (UIDB/00690/2020).

References:

1. Burt S. *Int. J. Food Microbiol.* **2004**, *94*, 223.
2. Momtaz S.; Abdollahi M. *Int. J. Pharmacol.* **2010**, *6*, 454.
3. Falcão S.; Bacém I.; Igrejas G.; Rodrigues P. J.; Vilas-Boas M.; Amaral J. S. *Ind. Crops Prod.* **2018**, 124, 878.

Food and natural products

Phenolic compounds of propolis: optimization of extraction by response surface methodology recovery

Amar Otmani[a,b], Salim Ouchemoukh[a], Maria Eduarda Araújo [b]

a) Laboratoire de Biochimie appliquée, Faculté des Sciences de la Nature et de la Vie, Université de Bejaia, 06000 Bejaia, Algeria;
b) Centro de Química Estrutural and Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa.

Email: otmaniamar2015@hotmail.com

Propolis, a resinous material produced by bees from beewax and exudates of several trees can be used as a therapeutic agent against several ailments. Extracts obtained from some organic solvents are usually more active than the raw material. The extraction process must eliminate the inert materials and preserve the bioactive compounds (polyphenols) that are known for their preventive and curative effects of many diseases due to their antibacterial, anticancer, anti-inflammatory and immunostimulating activities among others).
This work aimed to optimize the extraction conditions of phenolic compounds (Y_1) and the antioxidant potential using the DPPH free radical scavenging activity (Y_2) of propolis produced by Apis mellifera bees.
This study was performed using a factorial design and analyzed by the response surface method to reveal the main factors influencing the extraction, such as ethanol concentration (X_1), time (X_2) and temperature (X_3). The results of the optimization aproach using the Box-Behnken method showed the significant linear influence of the tested parameters (X_1, X_2 and X_3) on both responses (phenolic compounds content and DPPH inhibition). However, the quadratic effects of factors (X_1^2, X_2^2 and X_3^2) were not statistically significant. No significant interactions of the parameters ($X_1 \times X_2, X_1 \times X_3$ and $X_2 \times X_3$) were observed on the phenolic compounds content. The fitted linear models for phenolic compounds content and DPPH inhibition considering the significant terms are given in Equations 1 and 2, respectively.

$$Phenolic\ compounds\ (mg\ GAE\ g^{-1}) = 5.32 + 1.15X_1 + 0.53X_2 + 0.95X_3\ (1)$$

$$DPPH\ (\%) = 60.75 + 10.59X_1 + 4.94X_2 + 8.92X_3\ (2)$$

The optimal conditions for extraction of phenolic compounds from propolis were: ethanol 80%, (v/v), T= 70 °C and t=180 min. With these conditions values of 8.28 mg GAE g^{-1} for total phenolic content and 86.41% free radical scavenging activity (DPPH) were obtained (Figure 1)

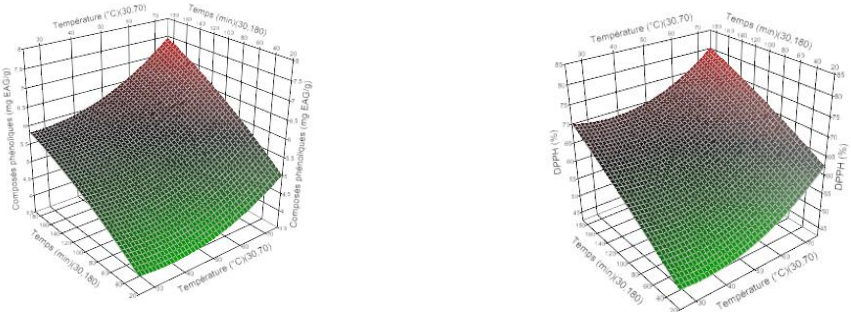


Figure 1: Surface graphic showing the influence of the studied parameters on the phenolic content and DPPH inhibition of propolis.

Acknowledgements: Amar Otmani acknowledge the Algerian Ministry of High Education and Scientific Research for sponsoring this work and Maria Eduarda Araújo acknowledge FCT financial support through the project UID/00100/2020

Food and natural products

Saponin-rich extracts as new natural emulsifiers

Tatiana B. Schreiner,[a,b] Giovana Colucci,[a] Arantzazu Santamaria-Echart,[a] Isabel P. Fernandes,[a] Madalena M. Dias, [b] Simão P. Pinho,[a,*] Maria Filomena Barreiro[a,*]

a) Centro de Investigação de Montanha(CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; b) Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials(LSRE-LCM), Department of Chemical Engineering, Faculty of Engineering University of Porto, Rua Dr. Roberto Frias, S/N, 4200-465 Porto, Portugal

Email: spinho@ipb.pt and barreiro@ipb.pt

Most emulsifiers used at the industrial level are of synthetic origin, and their replacement by natural alternatives is gaining increased interest[1]. Saponins are molecules with amphipathic character, combining hydrophilic moieties (sugars) with hydrophobic ones (steroidal or triterpene aglycones). They can be found in abundance in nature from a vast range of vegetal matrices[2]. Given this background, three saponin-rich extracts (Tribulus terrestris -TT-, Trigonella foenum-graecum -FG-, and Ruscus aculeatus -RA-), with saponin contents of 93.1, 50.3, and 20.3 wt%, respectively, were studied concerning their emulsifying capacity (EC), emulsion stability (ES), foaming capacity (FC) and stability (FS). For comparison proposes, Pure Quillaja Bark Saponin (PS), the most studied saponin form, was selected. Additionally, pseudo ternary diagrams were constructed to map the composition range to form emulsions.

Figure 1 (a) shows the emulsifying capacity of the saponin-rich extracts and PS as a function of pH, which strongly impacts emulsion formation by influencing the electrostatic repulsion among droplets. It can be seen that, in general, the higher the amount of saponin is, the more efficient the extract is as an emulsifier. However, for other pHs, this behaviour was not observed. At pH 9, the EC of the four samples becomes similar. Also, the performance of RA was slightly superior to FG for pH 7 and 9. The ES of samples also presented satisfactory outcomes, with extracts reaching values up to 53%. Regarding FC and FS, the values for PS showed to be considerably higher (up to 390%) than the ones of the extracts, which were similar among them (112 - 130%). This outcome can be advantageous for cases where it is not interesting for the final product to present a high foam amount. **Figure 1 (b)** represents the ternary diagram of TT, which was the extract with the best performance. A wide single-phase area (red points), located at the top of the diagram, was observed; and high viscous emulsions, named gel-like samples (blue points), which comprise water and emulsifier contents of 20% and ≤40%, respectively, were also obtained. Overall, the saponin-rich extracts can be positioned as potential emulsifiers, offering advantages over saponin pure forms, holding similar or even additional functional properties while avoiding complex extraction and purification treatments.

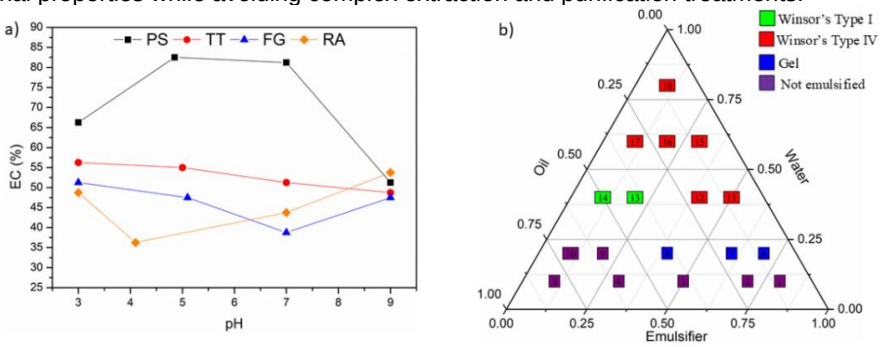


Figure 1: a) Emulsifying capacity of PS and extracts (TT, FG, RA) with pH variation, and b) Ternary Diagram of TT extract.

Acknowledgments: CIMO (UIDB/00690/2020), and AL LSRE-LCM (UIDB/50020/2020) funded by FCT/MCTES (PIDDAC). National funding by FCT, P.I., through the institutional scientific employment program-contract for I.P Fernandes and A. Santamaria-Echart, and the individual research Grant 2020.05564.BD of Tatiana Schreiner. Project AIProcMat@N2020–NORTE-01-0145-FEDER 000006 supported by NORTE2020 under the Portugal 2020 Partnership Agreement, through ERDF.

References:

1. McClements D.J.; Bai L.; Chung C.; *Annu. Rev. Food Sci. Technol.* **2017**, *8*, 205–236.
2. Schreiner T. B.; Colucci G.; Santamaria-echart A.; Fernandes I. P.; Dias M. M.; Pinho S. P.; Barreiro M. F.; *Colloids Surf. A Physicochem. Eng. Asp*. **2021**, 6*23*, 126748.

Food and natural products

High-value biomolecules from *Tetraselmis chuii* and *Chlorella vulgaris*: Production and extraction strategies

Hussen, S.[a*], Semedo, M.C. [a,b], Martins, S.[a,b], Barata, P.D.[a,c], Silva, J.L. [d]

a) Área Departamental de Engenharia Química, ISEL-IPL, R. Conselheiro Emídio Navarro 1, 1959-007 Lisboa, Portugal; b) Unidade de Geobiociências, Geoengenharias e Geotecnologias (GeoBioTec), FCT-UNL, Monte de Caparica, 2829-516 Caparica, Portugal; c) Centro de Química-Vila Real, UTAD, Quinta de Prados, 5001-801, Vila Real, Portugal; d) Allmicroalgae – Nactural Products,S.A., Av. Eng. Duarte Pacheco 19, 9º piso, 1070-100, Lisboa, Portugal

Email: a43003@alunos.isel.pt

Microalgae are a promising resource for a highly sustainable production of high-value biomolecules, such as proteins, phenolic compounds, lipids, polysaccharides, pigments, and vitamins. Bioactive compounds from microalgae have attracted increasing attention in different sectors of animal feed, food, cosmetic, biopharmaceutical and nutraceutical industries.[1,2] Polysaccharides, including sulfated polysaccharides and *β*-glucans, can be considered as the main groups of compounds that are responsible for a great range of health effects.[3]

This communication presents results concerning the production of bioactive compounds by the species *Tetraselmis chuii* and *Chlorella vulgaris* under autotrophic conditions and in three different growth phases (lag, exponential and stationary). Various extraction methods were evaluated: multistep extraction (ME), conventional Soxhlet extraction (SE) and microwave-assisted extraction (MAE). The detection and quantification of total polysaccharides, sulfated polysaccharides, *β*-glucans, carotenoids, chlorophylls, total protein, B-phycoerythrin, phenolic compounds and flavonoids were performed following well-established methods. The antioxidant activities were also analysed by *in vitro* assays.[4,5]

The biomass collected in the stationary phase, showed a higher content of total polysaccharides and sulfated polysaccharides, especially in the acidic fraction (FHCl) and boiled water fraction (FW2) from ME. Ethanol and KOH extracts from MAE also exhibited high amounts of these biomolecules. However, the SE appeared to be the most efficient for the extraction of sulfated polysaccharides.

For the optimization of the MAE conditions, a systematic study was carried out regarding several parameters such as solvent, irradiation time and temperature. The screening experiment was arranged in 2^3 statistical factorial design, with a total of eight experiments, replicated twice. The variables selected were the nature of the solvent (KOH and ethanol), as categorical variable and irradiation time (15 and 30 min) and extraction temperature (120 and 150 ºC), as numeric variables. The response was measured in terms of the total content of polysaccharides, sulfated polysaccharides, *β*-glucans and phenolic compounds. The optimal MAE conditions for extraction of value-added biocompounds with high yields were 0.1M KOH at 150 ºC for 30 min.

Therefore, the biochemical properties presented by the extracts under study suggest their potential incorporation in the formulation of new functional foods or nutraceutical preparations.

Acknowledgements: We thank the Instituto Politécnico de Lisboa for financial support (PoliMAlga/IPL/IDI&CA-2019).

References:

1. Khan, M.I.; Shin, J.H.; Kim, J.D. *Microb. Cell Fact.* **2018**, *17*, 1.
2. Bhalamurugan, G.L.; Valerie, O.; Mark, L. *Environ. Eng. Res.* **2018**, *23*, 229.
3. Raposo, M.; Morais, R.; Morais, A. *Life Sci*. **2013**, *93*, 479.
4. Semedo M. C.; Karmali A.; Fonseca L. *J. Microbiol. Methods* **2015**, *109*, 140.
5. Gallego, R.; Martínez, M.; Cifuentes, A.; Ibáñez, E.; Herrero, M. *Molecules* **2019**, *24*, 1564.

Food and natural products

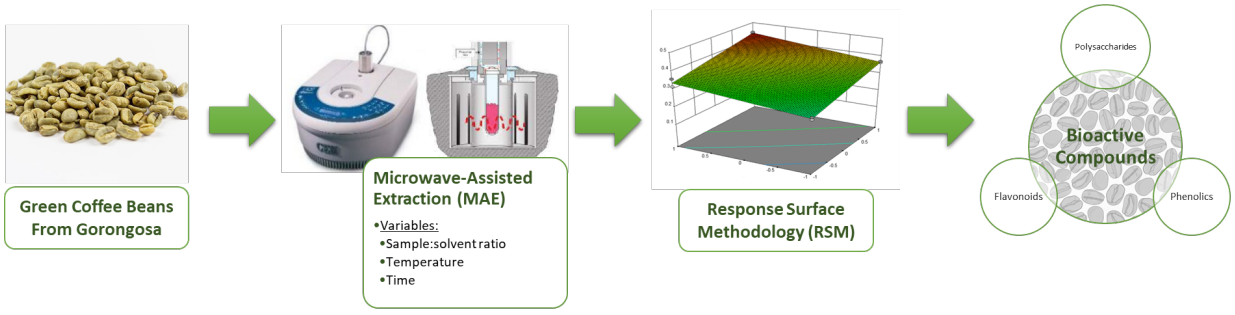
Optimization of microwave-assisted extraction of bioactive compounds from coffee beans produced in Gorongosa, Mozambique

Fernandes, J. M.[a*], Martins, S.[a,b], Semedo, M.C. [a,b], Barata, P.D.[a,c], Ferreira-Pinto, M.[d], Ramalho, J.C. [b,d], Ribeiro-Barros, A.I. [b,d]

a) Área Departamental de Engenharia Química, ISEL-IPL, R. Conselheiro Emídio Navarro 1, 1959-007 Lisboa, Portugal; b) Unidade de Geobiociências, Geoengenharias e Geotecnologias (GeoBioTec), FCT-UNL, Monte de Caparica, 2829-516 Caparica, Portugal; c) Centro de Química-Vila Real, UTAD, Quinta de Prados, 5001-801, Vila Real, Portugal; d) PlantStress & Biodiversity Lab, Centro de Estudos Florestais (CEF), ISA-UL, Tapada da Ajuda, 1349-017 Lisboa e 2784-505 Oeiras, Portugal.

Email: a43723@alunos.isel.pt

Bioactive compounds, such as proteins, polysaccharides and polyphenols, isolated from natural sources frequently exhibit proven activities in several fields, namely in nutraceutics, cosmetics, pharmaceutics and medicine [1]. Although different extraction methods do exist, some raise environmental concerns, have long extraction times and high costs [2]. The present work aimed to efficiently extract bioactive compounds from green beans of *Coffea arabica* L. produced in a sustainable agroforestry system in the Gorongosa National Park (Mozambique). In addition, we intended to study the impact of cropping conditions associated with altitude on the accumulation of those compounds in coffee beans. For these purposes and based on the previous results achieved for different extraction methods, microwave-assisted extraction (MAE) was used. Factorial design was employed to evaluate the effects of MAE conditions on the yield of total polysaccharides, β-glucans, phenolics, flavonoids and antioxidant activities recovered from coffee beans. Several operational parameters were investigated: sample/solvent ratio, temperature, and irradiation time. In order to identify the optimal conditions in MAE, an experimental planning comprising a 2^3 factorial design was developed, with a total of 8 experiments, replicated twice (**Scheme 1**). The obtained results revealed that MAE constitutes an alternative approach to conventional techniques, since it allows a high recovery of bioactive compounds from beans of *C. arabica* L. and thus contributing to quality assessment and commercial valorization of Gorongosa coffee.



Scheme 1: The Experimental Flowchart.

Acknowledgements: This work received funding support from Camões - Instituto da Cooperação e da Língua, I.P., through the project Gorongosa Coffee, and from Fundação para a Ciência e a Tecnologia, I.P. (FCT), through the research units UIDB/00239/2020 (CEF), and UIDP/04035/2020 (GeoBioTec).

References:

1. Semedo M. C.; Karmali A.; Fonseca L. J. Microbiol. Methods 2015, 109, 140.
2. Lopes G. R.; Passos C. P.; Rodrigues C.; Teixeira J. A.; Coimbra M. A. Food Res. Int. 2020, 129, 108864.

Environment and water

Biodegradation studies in seawater of a new polyphenolic antifouling agent

C. Vilas-Boas,[a,b] A. Neves,[a,b] V. Gonçalves,[c] E. Sousa,[a,b] M. Tiritan,[a,c] M. Correia-da-Silva,[a,b]

a) Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal; b) CIIMAR – Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR), Universidade do Porto, Avenida General Norton de Matos, S/N, 4450-208 Matosinhos,Portugal; c) CESPU, Instituto de Investigação e Formação Avançada em Ciências e Tecnologias da Saúde, Rua Central de Gandra, 1317, 4585-116 Gandra PRD, Portugal.

Email: m_correiadasilva@ff.up.pt

The attachment of marine organisms to anthropogenic underwater surfaces, such as ship hulls, buoys, and harbors, brings many economic repercussions to the marine industry. To combat marine biofouling, most coatings in use contain toxic, bioaccumulative, and pseudo-persistent biocides, and are causing severe consequences on marine ecosystems [1]. However, the ban of these hazardous agents has been delayed due to the lack of safer alternatives with acceptable ecological characteristics. In our research group, some nature-inspired compounds were synthesized, and interesting antifouling (AF) properties were revealed on the settlement of Mytilus galloprovincialis larvae, with no toxicity observed against various non-target organisms [2-5]. In this work, the seawater biodegradation of the most promising compound, an aminated polyphenolic compound, AGNH3Br+, was evaluated according to Environmental Protection Agency (EPA) and American Society for Testing and Materials (ASTM) protocols, after the development and validation of a suitable method according to International Council on Harmonisation (ICH) Guidance for Industry Q2 (R1) through various parameters, namely specificity/selectivity, linearity, precision, accuracy, range, limits of detection (LOD), and quantification (LOQ) [6]. The assay was found to be precise, sensitive, and the calibration curves were linear within the studied concentration range, allowing the quantification of this amphoteric compound in seawater. After 7 days at 50 °C in four different natural seawater conditions (sterile, non-sterile, and in the presence and absence of light), total degradation of AGNH3Br+ was observed as early as 24 h in all conditions. Adding to the previously obtained results regarding high water solubility (greater than 100 mg/mL), low bioaccumulation potential (Log P of -0.79), and successful incorporation into marine coating formulations, this work strengthens the inherent marketability of AGNH3Br+ as a future biodegradable and eco-friendly additive for coating formulations.

Acknowledgements: This research was supported by national funds through FCT - Foundation for Science and Technology within the scope of UIDB/04423/2020 and UIDP/04423/2020 (CIIMAR) and under the project PTDC/AAG-TEC/0739/2014 (reference POCI-01-0145-FEDER-016793 (Project 9471-RIDTI)) co-financed by COMPETE 2020, Portugal 2020 and the European Union through the ERDF, and by FCT through national funds; This work was also funded by the structured program of R&D&I ATLANTIDA - Platform for the monitoring of the North Atlantic Ocean and tools for the sustainable exploitation of the marine resources (reference NORTE-01-0145-FEDER-000040), supported by the North Portugal Regional Operational Programme (NORTE2020), through the European Regional Development Fund (ERDF). CVB and ARN also acknowledges FCT for the PhD scholarship (grant number SFRH/BD/136147/2018 and SFRH/BD/114856/2016, respectively).

References:

1. Hernández-Moreno, D., et al., Acute hazard of biocides for the aquatic environmental compartment from a life-cycle perspective. Science of The Total Environment, 2019. 658: p. 416-423.https://doi.org/10.1016/j.scitotenv.2018.12.186.
2. Neves, A.R., et al., Overcoming environmental problems of biocides: Synthetic bile acid derivatives as a sustainable alternative. Ecotoxicology and environmental safety, 2020. 187: p. 109812.10.1016/j.ecoenv.2019.109812.
3. Almeida, J.R., et al., Structure-Antifouling Activity Relationship and Molecular Targets of Bio-Inspired(thio)xanthones. Biomolecules, 2020. 10(8): p. 1126.
4. Vilas-Boas, C., et al., One Step Forward towards the Development of Eco-Friendly Antifouling Coatings: Immobilization of a Sulfated Marine-Inspired Compound. Mar Drugs, 2020. 18(10).10.3390/md18100489.
5. Almeida, J.R., et al., Antifouling potential of nature-inspired sulfated compounds. Scientific Reports, 2017. 7: p. 42424.10.1038/srep42424https://www.nature.com/articles/srep42424#supplementary-information
6. ICH, Validation of Analytical Procedures: Text and Methodology, in Geneva, Q2(R1), 17 p. 2005.

Environment and water

Synthesis of carbon dots composite materials and their use for the photodegradation of water contaminants

G.S. Catalão,[a,b] O.C. Monteiro,[b] J.V. Prata,[a,c]

a) Departamento de Engenharia Química, ISEL – Instituto Politécnico de Lisboa, Portugal; b) CQE-FCUL, Faculdade de Ciências, Universidade de Lisboa, Portugal; c) Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, Vila Real, Portugal

Email: a37085@alunos.isel.pt

Currently, the global concern about contamination of water systems by pharmaceutical and personal care products is raising. A commonly researched methodology for remediation of this issue is the photodegradation of these pollutants with the assistance of catalysts.

In this work several environmentally friendly photocatalytic composite materials of carbon dots (C-dots) and harmless solid supports (e.g., silica and alumina) were synthesized. After characterization, the catalysts were tested in the photodegradation of caffeine, a well-known model pollutant.[1] The photocatalytic samples were made by hydrothermal treatment using olive mill waste waters as C-dots green precursor,[2] and in the presence of silica or alumina, using ethylenediamine as an additive. Alternatively, a different set of samples were prepared by simple mixing of C-dots with the supports, in aqueous media.

The samples were characterized from a structural, morphological, and optical point of view and their use as a photocatalyst for caffeine degradation was tested under UV-vis radiation conditions.

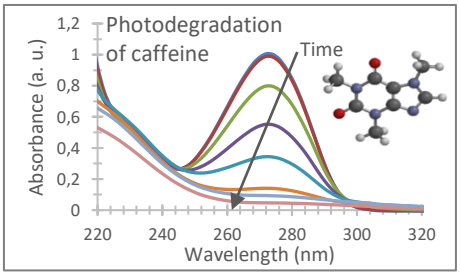


Figure 1 – Absorbance spectra of a caffeine solution during irradiation.

It was found that a C-dots/silica composite, where the solid support was added during the C-dots synthesis, was the best photocatalyst with the complete caffeine photocatalytic degradation being achieved within 1 hour of irradiation (Figure 1). Considering that photolysis was not able to completely degrade caffeine until 2 hours of light irradiation, a remarkable improvement on the degradation of such pollutant was achieved by these catalytic systems.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support under the projects UIDB/00100/2021, UIDB/00616/2021 and UIDP/00616/2021.

References:

1. Barrocas B.T.; Conceição Oliveira M.; Nogueira H.I.S.; Fateixa S.; Monteiro O.C. *ACS Appl. Nano Mater*. **2019**, *2*, 1341.
2. Sousa D.A.; Costa A.I.; Alexandre M.R.; Prata J.V *Science of the Total Environment* **2019**, *647*, 1097.

Environment and water

Volatility and thermodynamic stability of Clopyralid

A.R.R.P. Almeida, M.A. Ferreira, M.J.S. Monte

Centro de Investigação em Química (CIQUP), Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto. Rua do Campo Alegre, P-4169-007 Porto, Portugal

Email: ana.figueira@fc.up.pt

Organochlorines (OC) are a group of chlorinated compounds, widely used as pesticides, that belong to the class of persistent organic pollutants (POPs). These chemicals are identified by their great toxicity, slow degradation, and bioaccumulation.[1] The effects on humans and the environment of pesticide exposure are a constant worry and so the knowledge of properties with important applications in predicting the environmental mobility of these compounds (and its metabolites) is of great importance. Thus, a thermodynamic study of the phase transitions of the selective organochlorine herbicide Clopyralid (3,6-dichloropicolinic acid, Figure 1) was performed. This compound is used to kill unwanted annual and perennial broadleaf plants in lawn and turf, pasture, range, rights-of-ways, and some agricultural crops such as wheat, barley, oats, sugar beets, and mint.[2] It is a synthetic plant growth hormone that has some structural similarities to natural hormones called auxins, being more persistent than these in plant tissue. This pesticide binds to molecules that are commonly used as receptors for natural growth hormones, interrupting the plant's normal growth and leading to its death.[3] The vapor pressures of the crystalline phase of Clopyralid were measured using the Knudsen effusion technique[4] over the temperature range T = (338.1 – 362.6) K. The standard molar enthalpy, entropy, and Gibbs energy of sublimation ($\Delta_{cr}^{g}H_{m}^{o}$, $\Delta_{cr}^{g}S_{m}^{o}$ and $\Delta_{cr}^{g}G_{m}^{o}$, respectively) of the compound studied, at T = 298.15 K, were derived from the experimental results. Additionally, the thermodynamic tendency of the herbicide to decompose into its constituent elements, under standard-state conditions, was evaluated considering the related value of $\Delta_{f}G_{m}^{o}(298.15\ \mathrm{K}, \mathrm{cr})$. The temperature and molar enthalpy of fusion of Clopyralid were also determined using differential scanning calorimetry.

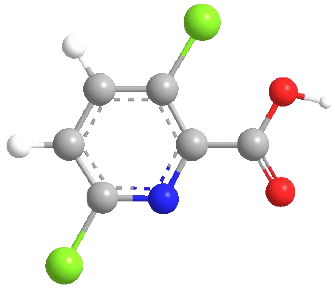


Figure 1: Structural formula of Clopyralid.

Acknowledgements: Thanks are due to the project UIDB/00081/2020 awarded to CIQUP, financed by FCT (Portugal) with national funds of MEC. ARRPA acknowledges financial support through the FCT - I.P., in the framework of the execution of the program contract provided in paragraphs 4, 5 and 6 of art. 23 of Law no. 57/2016 of 29 August, as amended by Law no. 57/2017 of 19 July.

References:

1. Jayaraj R., Megha P., Sreedev P. *Interdiscip Toxicol*. **2016**, *9*, 90.
2. Cox C. *J. Pest. Ref*. **1998**, *18*, 15.
3. Persistent Herbicides Risk Management Program, Research report and recommendations. Department of Environment and Conservation (NSW) by the Recycled Organics Unit, University of New South Wales. **2004**.
4. Ribeiro da Silva M. A. V.; Monte M. J. S.; Santos L. M. N. B. F. *J. Chem. Thermodyn*. **2006**, *38*, 778.

Environment and water

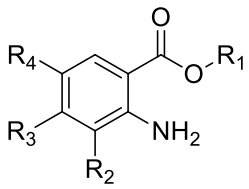
Gas-phase standard molar enthalpies of formation of some anthranilate derivatives

C.A.O. Silva, V.L.S. Freitas, M.D.M.C. Ribeiro da Silva

Centro de investigação em Química (CIQ-UP), Department of Chemistry and Biochemistry, Faculty of Sciences – University of Porto
Rua do Campo Alegre, S/N, P-4169-007 Porto, Portugal

Email: carlos.silva@fc.up.pt

Fragranced goods are sought and consumed every day due to their appealing aroma. The main disposal pathway for these products are the urban wastewaters plants. However, it has been noticed that most of the fragrance compounds are not removed with conventional wastewater treatment technologies. The continued release of these chemicals to wastewater effluents will cause long-term hazards due to its persistence and ability of bioaccumulation, with unknown consequences for aquatic life and the food chain. Consequently, fragrances have been acknowledged as emerging pollutants in aquatic systems.[1]
We have been devoted to the molecular thermodynamic studies, and some of our goals are the determination and estimation of thermodynamic properties of organic compounds, with the consequent establishment of relationships between energetics and molecular structure of homocyclic and heterocyclic compounds, as well as the evaluation of their thermodynamic stability/reactivity in gaseous and crystalline phases to provide reliable data for their environmental risk assessment.[2]
The present work reports experimental and computational results for seven anthranilate derivatives (**Figure 1**) to evaluate and discuss their energetic properties.
The gas-phase standard molar enthalpy of formation at *T*=298.15 K was derived from the enthalpy of formation in the condensed phase obtained from static-bomb combustion calorimetry, and the phase transition enthalpy using Calvet microcalorimetry and/or Knudsen mass-effusion method techniques. The gas properties of the compounds were also estimated through computational studies using the G3(MP2)//B3LYP composite method.
Structural changes and the inherent energetic effects are analysed by comparison of the several molecules results.



Methyl anthranilate: $R_1 = CH_3$; $R_2 = R_3 = R_4 = H$
Ethyl anthranilate: $R_1 = C_2H_5$; $R_2 = R_3 = R_4 = H$
Butyl anthranilate: $R_1 = C_4H_9$; $R_2 = R_3 = R_4 = H$
Methyl 3-methylanthranilate: $R_1 = CH_3$; $R_2 = CH_3$; $R_3 = R_4 = H$
Methyl 5-methylanthranilate: $R_1 = CH_3$; $R_2 = R_3 = H$; $R_4 = CH_3$
Methyl 5-hydroxyanthranilate: $R_1 = CH_3$; $R_2 = R_3 = H$; $R_4 = OH$
Methyl 4,5-dimethoxyanthranilate: $R_1 = CH_3$; $R_2 = H$; $R_3 = R_4 = OHCH_3$

Figure 1: Molecular structures for anthranilate derivatives.

Acknowledgements: This work had the financial support of national funds, through Fundação da Ciência e Tecnologia (FCT), within the scope of the R&D project reference UIDB/00081/2020. C.A.O.S. thanks FCT for the doctoral grant SFRH/BD/137672/2018. V.L.S.F. thanks FCT and FCUP for the Program Contract established under the transition rule of Decree Law 57/2016, amended by Law 57/2017.

References:

1. Vecchiato M.; Barbaro E.; Spolaor A.; Burgay F.; Barbante C.; Piazza R.; Gambaro A. *Environ. Pollut.* **2018**, *242*, 1740.
2. Freitas V.L.S.; Silva C.A.O.; Ribeiro da Silva, M.D.M.C. *J. Chem. Thermodyn.* **2021**, 158, 106441.

Environment and water

Development of innovative materials for antibiotics removal

A. Saraiva,[a,b] M.C. Neves,[a] M.R. Pastorinho,[b] A.C.A. Sousa,[a,d] M.G. Freire[a]

a) CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro, Portugal; b) Department of Chemistry, University of Évora, Évora, Portugal; c) Department of Medical Sciences and Comprehensive Health Research Centre (CHRC), University of Évora, Évora, Portugal; d) Department of Biology, University of Évora, Évora, Portugal

Email: m44803@alunos.uevora.pt

Currently, about 100,000 tons of antibiotics are consumed each year worldwide, and its excessive and indiscriminate use has been causing serious environmental and public health issues, including the increase in antimicrobial resistance (AMR). According to the World Health Organization, AMR is one of the most important public health problems in the XXI century. Therefore, it has become imperative to develop new strategies for the efficient removal of these compounds before they enter the ecosystem. In this sense, this study aims to synthesize and characterize several materials functionalized with ionic liquids (SILs), which have shown to be a promising and low-cost technology. Their ability to adsorb different antibiotics from aqueous solutions and synthetic urine was evaluated, in order to mitigate their environmental impact. The adsorption of tetracycline, a frequently used antibiotic, was evaluated and the synthesized SILs proved to be promising materials for its removal, with removal efficiencies higher than 30%.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the Fundação para a Ciência e Tecnologia/ Ministério da Educação e Ciência (FCT/MEC) and when appropriate co-financed by Fundo Europeu de Desenvolvimento Regional (FEDER) under the PT2020 Partnership Agreement. This work was financially supported by the project IonCytDevice (POCI-01-0145-FEDER-031106, PTCD/BTA-BTA/31106/2017) funded by FEDER, through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI), and by national funds (OE), through FCT/MCTE). The NMR spectrometers used in this work are part of the National NMR Network (PTNMR) and are partially supported by Infrastructure Project Nº 022161 (co-financed by FEDER through COMPETE 2020, POCI and PORL and FCT through PIDDAC. Márcia C. Neves acknowledges FCT, I.P. for the research contract CEECIND/00383/2017 under the CEEC Individual 2017.

References:

[1] Ahmed, M. B., Zhou, J. L., Ngo, H. H., & Guo, W. (2015). Adsorptive removal of antibiotics from water and wastewater: Progress and challenges. *Science of the Total Environment*, *532*, 112–126. https://doi.org/10.1016/j.scitotenv.2015.05.130

[2] Alnajrani, M. N., & Alsager, O. A. (2020). Removal of Antibiotics from Water by Polymer of Intrinsic Microporosity: Isotherms, Kinetics, Thermodynamics, and Adsorption Mechanism. *Scientific Reports*, *10*(1), 1–14. https://doi.org/10.1038/s41598-020-57616-4

[3] Eniola, J. O., Kumar, R., & Barakat, M. A. (2019). Adsorptive removal of antibiotics from water over natural and modified adsorbents. *Environmental Science and Pollution Research*, *26*(34), 34775–34788. https://doi.org/10.1007/s11356-019-06641-6

Environment and water

New strategies for the removal of cytostatics from urine

R. Francisco,[a] A.C.A. Santos,[a] M.C. Neves,[a] A.C.A. Sousaa,[b] M.G. Freire[a]

a) CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro, Portugal; b) Department of Biology, University of Évora, Évora, Portugal.

Email: rafaelfrancisco@ua.pt

Cytostatics drugs such as Mycophenolate Mofetil (MMF), Mycophenolic acid (MPA) and Capecitabine (CAP) are used in the treatment of cancer and also to prevent organ rejection after hepatic, renal, and cardiac transplants. However, cytostatic drugs are highly toxic and thus their handling and disposal is a matter of great concern.

Supported ionic liquids (SILs) are promising materials to remove target compounds from aqueous solutions, since they can be designed and tailored in order to remove specific compounds.

In this work, several SILs were synthetized and their ability to remove the target cytostatic drugs from artificial urine wsa evaluated by completing a series of kinetics and isotherm studies. In parallel, the experiments were performed using active carbon (AC) as control.

Some of the synthetized SILs showed higher adsorption rates when compared to AC, especially at shorter times of contact, namely [Si][N3888]Cl for the three cytostatics. Such promising results open the possibility to use these SILs as a filters to remove cytostatics from urine, avoiding they entrance into the environment.

Acknowledgements: This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the Fundação para a Ciência e Tecnologia/ Ministério da Educação e Ciência (FCT/MEC) and when appropriate co-financed by Fundo Europeu de Desenvolvimento Regional (FEDER) under the PT2020 Partnership Agreement. This work was financially supported by the project IonCytDevice (POCI-01-0145-FEDER-031106, PTCD/BTA-BTA/31106/2017) funded by FEDER, through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI), and by national funds (OE), through FCT/MCTE). The NMR spectrometers used in this work are part of the National NMR Network (PTNMR) and are partially supported by Infrastructure Project Nº 022161 (co-financed by FEDER through COMPETE 2020, POCI and PORL and FCT through PIDDAC. Márcia C. Neves acknowledges FCT, I.P. for the research contract CEECIND/00383/2017 under the CEEC Individual 2017.

References:

1. Berheim, E.H., Jenks, J.A., Lundgren, J.G. et al. Effects of Neonicotinoid Insecticides on Physiology and Reproductive Characteristics of Captive Female and Fawn White-tailed Deer. Sci Rep 9, 4534 (2019).

Environment and water

Determination of sertraline antidepressant drug in aqueous effluents by SPE/HPLC-DAD

V. Machado, A. Queiroz, P. Brito, A.E. Ribeiro

Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de S^{ta} Apolónia, 5300-253 Bragança, Portugal;

Email: aribeiro@ipb.pt

The presence of pharmaceutical drugs, their metabolites and degradation products in the environment requires research and monitoring studies to assess the potential risks to human health and to the ecosystem. This type of compounds is present in the environment in very low concentrations, in the order of magnitude of μg.L^{-1} and ng.L^{-1}, which requires an optimization of the removal processes, so that they are simpler, faster, cheaper and more environmentally friendly than traditional techniques.[1] There are several possible sources and routes for drugs to reach the environment, but wastewater treatment plants (WWTP) have been identified as one of the main sources. After the treatment carried out at the WWTP, the treated effluents are discharged into rivers, and the sludge produced is disposed of or reused in agriculture as a fertilizer. As a consequence of the incomplete elimination of drugs and metabolites in the WWTP, these compounds end up reaching almost all the environmental matrices.[2] For this study, sertraline (See Fig. 1) was chosen because it is one of the most prescribed antidepressants in recent years in Portugal. Therefore, it is not surprising that it is regularly detected in wastewater, surface water and sediments and in WWTP.[3] The main objective of this study is to experimentally implement an expeditious method of solid phase extraction followed by quantification using high performance liquid chromatography with diode array detector (SPE/HPLC-DAD) to monitor sertraline concentration levels in aqueous matrices (see Fig. 2).

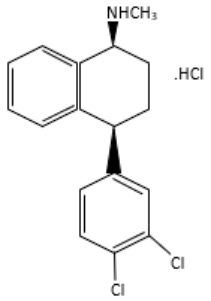


Figure 1. Sertraline chemical structure.

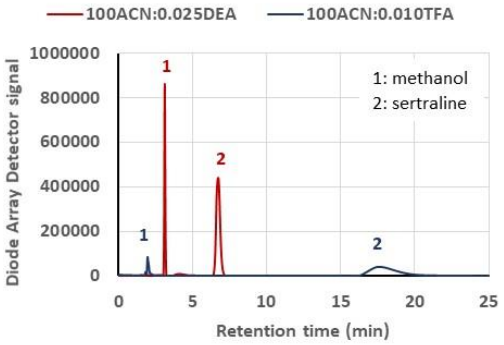


Figure 2. HPLC-DAD pulses of sertraline standard using two different mobile phase compositions. (Effect of mobile phase composition on retention and dispersion).

Acknowledgements: The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support by national funds FCT/MCTES to CIMO (UIDB/00690/2020).

References:

1. Fernandes M.; Paíga P.; Silva A.; Llaguno, C.; Carvalho M.; Vázquez F; Delerue-Matos C. *Chemosphere* **2020**, *239*, 124729.
2. Nikolaou A.; Meric S.; Fatta D. *Analytical and Bioanalytical Chemistry* **2007**, *387(4)*, 1225.
3. Zhou M.; Foley J. *Journal of Chromatography A* **2004**, *1052(1-2)*, 13.

Environment and water

Effect of zeolite nanomaterials in methanogenic communities

J.F. Faria,[a] A.C.S. Rocha,[a] M.S. Duarte,[b] C.S.N. Braga,[b] A.M. Fonseca,[a,b] I.C. Neves,[a,b] M.M. Alves[b]

a) CQUM, Centre of Chemistry, Chemistry Department, University of Minho, Campus de Gualtar, 4710-057, Braga, Portugal; b) CEB - Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal;

Email: a87550@alunos.uminho.pt

Recently, the application of zeolite structures in methanogenic communities has attracted significant attention, since they may enhance the anaerobic digestion process, by affecting specifically the methanogenic activity of the sludges[1]. Zeolites are solid inorganic crystalline materials comprised of silicon, aluminum and oxygen in the three-dimensional structure. The building blocks become arranged in a periodic way to form channels and cages on a nano- and subnanometer scale of strictly regular dimensions, named micropores. The presence of the aluminum in the zeolite framework create a negative charge in the lattice, which can be balanced by the exchangeable cations, as sodium or metal ions.[2] In this study, commercial zeolite structures (ZSM5, USY, NaX and NaY) with different particle sizes and different exchangeable cations (Co, Cu, Zn, Fe) were used in order to investigate their effect towards the specific methanogenic activity, both acetoclastic and hydrogenotrophic, of anaerobic sludge. In the acetoclastic methanogenic activity, NaY modified with Cobalt (CoY) decreased the activity in comparison with the control (without zeolite). The remaining zeolites (ZSM5, USY, NaX and NaY), even when modified with metal ions (Zn, Fe, Cu), seems to have no effect on this methanogenic pathway. On the other hand, the hydrogenotrophic methanogenesis was improved by the presence of NaY (109 %), which did not happen in the presence of ZSM5 and USY zeolites. Additionally, the effect of different zeolite concentration was accessed. Overall, the increase of zeolite concentration from 1 g/L to 5 g/L resulted in a higher inhibition towards the methanogenic activity. In addition, the application of these nanomaterials can be evaluated in pure cultures of methanogens, in order to understand and fine-tune the best zeolite nanomaterial concentration that may improve the specific methanogenic activity.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia (FCT) for financial support through Centre of Chemistry (UID/QUI/00686/2013 and UID/QUI/0686/2016) and BioTecNorte (operation NORTE-01-0145-FEDER-000004), and through Centre of Biological -engineering (UIDB/04469/2020 unit). Cátia S. N. Braga holds a grant SFRH/BD/132003/2017 funded by FCT and European Union (EU), through the Portuguese State Budget and the European Social Fund under the scope of Programa Operacional Regional do Norte.

References:

1. Milán, Z. et al., Journal of Environmental Science and Health Part A, **2010**, 45:11, 1307-1314.
2. Ferreira, L. et al., *Colloids and Surfaces B: Biointerfaces*, **2016**, 142, 141.

Environment and water

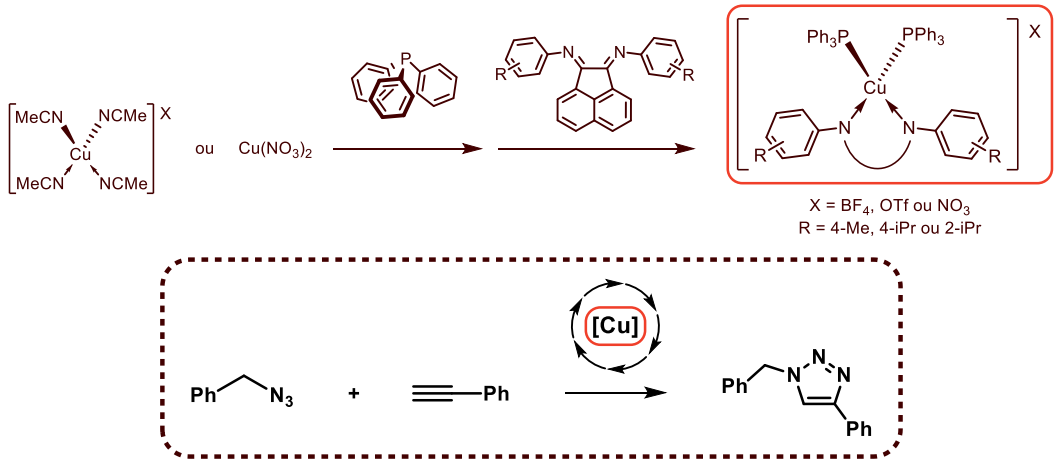
Complexos heterolépticos de cobre (I) como catalisadores da CuAAC

M.S. Viana, C.S.B. Gomes, V. Rosa

LAQV-REQUIMTE, Departamento de Química, NOVA School of Science and Technology (FCT NOVA), 2829-516 Caparica, Portugal

Email: ms.viana@campus.fct.unl.pt

A CuAAC (cicloadição azida-alcino catalisada por cobre), um exemplo de *click chemistry*,[1] é uma ferramenta sintética muito poderosa aplicada industrialmente na produção de diversos compostos, como materiais poliméricos por exemplo.[2] Devido à maior consciencialização ambiental da indústria química, a catálise é uma das abordagens mais utilizadas para melhorar eficiência dos processos, tornando-os mais sustentáveis. É portanto fundamental a procura de novos catalisadores mais eficazes que tornem o uso deste tipo de reações mais viável. Com este propósito, foi sintetizada uma família de nove complexos heterolépticos do tipo [Cu(BIAN)(PPh_3)$_2$]X, em que BIAN = bis(aril)acenaftenodiimina, PPh_3 = trifenilfosfina e X = tetrafluoroborato (BF_4), triflato (OTf) ou nitrato (NO_3). Todos os complexos foram caracterizados por espectroscopia 1D- e 2D-RMN mono e heteronuclear, IV, UV-Vis, AE, LC/MS e difração de raios-X, apresentando uma geometria tetraédrica ligeiramente distorcida. Foi testada a eficiência destes como catalisadores na reação de CuAAC utilizando diversas condições, e benzilazida e fenilacetileno como substratos (**Esquema 1**). Obteve-se 1-benzil-4-fenil-1,2,3-triazol com altas percentagens de conversão sem ser necessária a presença de aditivos, e foi isolado com bons rendimentos. O [Cu(4-iPr-BIAN)(PPh_3)$_2$]NO_3, que obteve melhores resultados, foi ainda testado com diferentes azidas e alcinos.



Esquema 1: Síntese e aplicação dos complexos como catalisadores na CuAAC.

Agradecimentos: Este trabalho foi financiado pelo Laboratório Associado para a Química Verde - LAQV financiado por fundos nacionais através da FCT/MCTES (UIDB/50006/2020 e UIDP/50006/2020).

References:

1. Kolb, H. C.; Finn, M. G.; Sharpless, K.B. *Angew. Chem. Int. Ed.* **2001**, 40, 2004-2021.
2. Neumann, S.; Biewend, M.; Rana, S.; Binder, W.H. *Macromol. Rapid Commun.* **2020**, 41, 1900359.

Environment and water

Heterogeneous photocatalysis and photo-Fenton as integrated water treatment

A. Torres-Pinto, M.J. Sampaio, C.G. Silva, J.L. Faria, A.M.T. Silva

Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, s/n 4200-465, Porto, Portugal

Email: andretp@fe.up.pt

A significant cause of water pollution is the inadequate release of organic contaminants to the environment. Water treatment is thus crucial to achieve sustainable development worldwide.[1] However, some phenolic compounds are recalcitrant to conventional treatments. Advanced oxidation technologies (AOTs), such as heterogeneous photocatalysis, represent a possible solution as a polishing step for removing refractory organic compounds in water treatment. We demonstrated that a graphitic carbon nitride photocatalyst could produce hydrogen peroxide (H_2O_2) during the degradation of phenolic compounds using energy-efficient visible-light emitting diodes.[2] In specific conditions, the H_2O_2 produced can be continuously photo-activated and transformed into oxy-radical species. The screening of dissolved oxygen content, ferrous ion concentration and pH was thus performed to investigate the formation and usage of H_2O_2 produced during the photocatalytic treatment. Mineralisation of the four target phenolic compounds (phenol, resorcinol, gallic acid and benzoic acid) in a synthetic mixture was achieved at natural pH by the combination of a graphitic carbon nitride photocatalyst and dissolved iron, as shown in **Figure 1**.[3] This treatment system could mitigate environmental burdens in comparison with more conventional heterogeneous photocatalysis and Fenton processes, by using economic light sources, eliminating the need of pH adjustment and reducing the need of transportation/storage of H_2O_2 (since it is produced *in situ*).

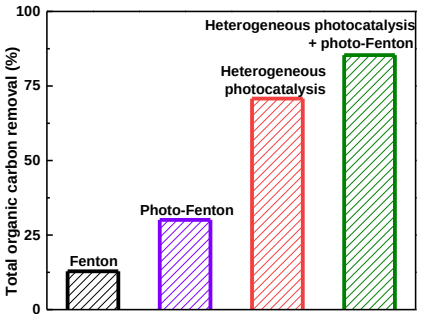


Figure 1: Total organic carbon removal by classical Fenton and different photoactivated treatment processes.

Acknowledgements: Funding from projects NORTE-01-0145 FEDER-031049 (InSpeCt PTDC/EAM AMB/31049/2017) and Base Funding - UIDB/50020/2020 of the Associate Laboratory LSRE-LCM through FCT/MCTES (PIDDAC) are acknowledged. A.T-P. and M.J.S. acknowledge SFRH/BD/143487/2019 and POCI-01-0145-FEDER-030674 (MicroPhotOGen), respectively.

References:

1. "Transforming our world: the 2030 Agenda for Sustainable Development", United Nations, **2015**.
2. Torres-Pinto A.; Sampaio M. J.; Silva C. G.; Faria J. L.; Silva A. M. T. *Appl. Catal. B-Environ.* **2019**, *252*, 128.
3. Torres-Pinto A.; Sampaio M. J.; Teixo J.; Silva C. G.; Faria J. L.; Silva A. M. T. *J. Water Process Eng.* **2020**, *37*, 101467.

Environment and water

Evaluation of a triphenylamine-derived thiosemicarbazone as an optical chemosensor for anions

A.B.M.P. Leite, N. Ramos, M.M.M. Raposo, S.P.G. Costa

Centre of Chemistry, University of Minho, Campus of Gualtar, 4710-057 Braga, Portugal

Email: angelavscbeatriz@gmail.com

Thiosemicarbazones exhibit diverse biological activity (anticancer, antileukemic, analgesic, antimicrobial, anti-inflammatory, antimalarial, antihypertensive, anti-tuberculosis, antioxidant, anticoagulant, vasodilator, analgesic, insecticide, etc.).[1] In addition, derivatives of thiosemicarbazones also exhibit very interesting optical, electronic and redox properties and may therefore be used as selective optical sensors of anions with medicinal, biological and environmental relevance.[2-4]
Considering our previous work on thiosemicarbazones substituted with various (hetero)aryl groups,[2-4] in this communication we report the synthesis of a new thiosemicarbazone bearing a triphenylamino group, using a simple synthetic methodology (Figure 1). The new compound was characterized by the usual spectroscopic techniques and a detailed photophysical study was undertaken. The evaluation of the thiosemicarbazone as an optical chemosensor (colorimetric and fluorimetric) was carried out in acetonitrile in the presence of selected anions with biological and environmental relevance.

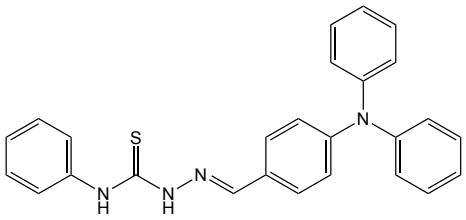


Figure 1: Structure of the synthesized thiosemicarbazone

Acknowledgements: The authors acknowledge Fundação para a Ciência e Tecnologia - FCT (Portugal) for funding through CQUM (UID/QUI/00686/2020). The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network and was purchased within the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT.

References:

1. Shim, J.; Jyothi, N. R.; Farook, N. A. M. *Asian J. Chem*. **2013**, *25*, 5838.
2. Raposo, M. M. M.; García-Acosta, B.; Ábalos, T.; Calero; P.; Martínez-Manez, R.; Ros-Lis, J. V.; Soto, J. *J. Org. Chem*. **2010**, *75*, 2922.
3. Santos-Figueroa, L. E.; Moragues, M. E.; Raposo, M. M. M., Batista, R. M. F.; Ferreira, R. C. M.; Costa, S. P. G.; Sancenón, F.; Martínez-Máñez, R.; Ros-Lis, J. V.; Soto, J. *Org. Biomol. Chem*. **2012**, *10*, 7418.
4. Santos-Figueroa, L. E.; Moragues, M. E.; Raposo, M. M. M., Batista, R. M. F.; Ferreira, R. C. M.; Costa, S. P. G.; Sancenón, F.; Martínez-Máñez, R.; Ros-Lis, J. V.; Soto, J. *Tetrahedron* **2012**, *68*, 7179.

Environment and water

Biodegradation potential of microplastics by bacteria recovered from the marine environment

N. Fernández de Villalobos,[a], I. Marín-Beltrán,[a] M.C. Costa,[a,b]

a) Centro de Ciências do Mar do Algarve, Universidade do Algarve, Campus de Gambelas, building 7, 8005-139 Faro, Portugal; b) Faculdade de Ciências e Tecnologia, Universidade do Algarve, Campus de Gambelas, building 8, 8005-139 Faro, Portugal.

Email: nuria.fernandezdevillalobos@imbrsea.eu

Microplastics (< 5 mm)1 can nowadays be found in every corner of the world. For this reason, and the risk they pose to aquatic life, they are becoming a huge concern to scientists, policymakers, and the general public. Low density polyethylene (LDPE) and polyethylene terephthalate (PET) are two of the most produced plastics worldwide. Although several studies have identified different microbial strains capable of colonizing and bio-deteriorating LDPE(2,3), its complete biodegradation has not been proved so far. Biodegradable plastics seem to be a partial solution to the problem, however, the conditions at which they may degrade remains understudied. In this study, we assessed the potential of a consortium of marine bacteria to biodegradade microplastics (films of around 2 mm2) from a plastic bag made of LDPE or a PET plastic bag labelled as “biodegradable”. The experiment consisted on five different treatments, LDPE and PET microplastics inoculated with bacteria, negative controls (both types of microplastics without inoculum) and the inoculum, used as positive control. All treatments were performed in triplicates. Sampling was carried out periodically, during 45 days, to analyse bacterial growth by means of optical density, pH, and the chemical oxygen demand (COD). We also looked for changes in the functional groups of each polymer by Attenuated Total Reflectance-Fourier Infrared spectroscopy (ATR-FTIR). At the end of the experiment, particles of each treatment were subjected to scanning electron microscopy (SEM). Optical density and pH showed high and moderate differences, respectively, between the samples inoculated with bacteria and the controls. COD analysis indicated certain signs of biodegradation of the particles treated with marine bacteria, as lower oxygen demand was determined in these samples compared to the controls. ATR-FTIR analysis of both types of microplastics showed moderate changes in the absorbance spectrum after 45 days of exposure to marine bacteria (see Figure 1). SEM analysis showed changes in the surface features of both plastic polymers treated with bacterial communities in comparison with the controls, such as the presence of fractures and the formation of a bacterial biofilm.

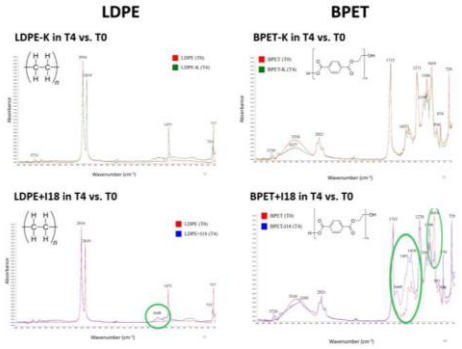


Figure 1. Results and comparison of FTIR analysis of both polymers in T0 (initial time) and T4 (final time, after 45 days) of both the control and the samples inoculated with the bacterial community (referred as I18). The figures on the left correspond to LDPE spectra and the “biodegradable” PET (BPET) spectra are shown on the right.

Acknowledgements: Financial support was obtained through project UID/04326/2020, funded by the Fundação para a Ciência e Tecnologia (FCT), and project 0483_PROBIOMA_5_E, co-financed by the European Regional Development Fund within the framework of the Interreg V-A Spain-Portugal program (POCTEP) 2014–2020. I. Marín-Beltrán also thanks the FCT for Individual Support through its programme of Stimulus of Scientific Employment (CEECIND/03072/2017).

References:

1. Arthur, C., Baker, J. & Bamford, H., 2009. Proceedings of the International Research Workshop on the Occurrence, Effects, and Fate of Microplastic Marine Debris. NOAA Technical Memorandum NOS-OR&R-30.
2. Auta, H. S., Emenike, C. U., & Fauziah, S. H. (2017). Screening of Bacillus strains isolated from mangrove ecosystems in Peninsular Malaysia for microplastic degradation. Environmental Pollution, 231, 1552-1559.
3. Skariyachan, S., Patil, A. A., Shankar, A., Manjunath, M., Bachappanavar, N., & Kiran, S. (2018). Enhanced polymer degradation of polyethylene and polypropylene by novel thermophilic consortia of Brevibacillus sps. and Aneurinibacillus sp. screened from waste management landfills and sewage treatment plants. Polymer Degradation and Stability, 149, 52-68.

Environment and water

Optimization of SPME/GC-MS analytical method using Response Surface Methodology for pesticides monitoring in aqueous matrices

F. Cáceres,[a,b] R. Pepino,[b] P. Brito,[a] A.E. Ribeiro,[a] A. Queiroz[a]

a) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; b) Universidad Tecnológica Nacional - Facultad Regional Córdoba, Maestro M. López esquina. Cruz Roja Argentina, Ciudad Universitaria, 5016 Córdoba, Argentina

Email: amqueiroz@ipb.pt

Emerging pollutants are a type of contaminants that can occur in water sources. They can be defined as any synthetic or naturally occurring chemical or microorganism that is not usually monitored or regulated in the environment and have the potential to cause detrimental ecological and human health impacts. These compounds can be found in the environment in very low concentrations, at scales ranging from nanograms to micrograms per liter.[1] Pesticides are an important group of emerging pollutants due to the continuous increase in their use in agricultural production process to control diseases, pests and weeds.[2]

In this work, it will be presented the optimization of solid phase microextraction (SPME), using a response surface methodology (RSM) based on an experimental planification defined using a Box-Behnken Design (BBD). After optimization of the complete analytical methodology (SPME/GC-MS), the method validation is done by monitoring six of the most used pesticides in northeast of Portugal (acetochlor, alachlor, dimethoate, heptachlor, metolachlor and terbuthylazine). The molecular structures of the compounds under study are presented in **Figure 1**. The method is validated through its application using real samples of aqueous matrices collected from different rivers of the region.

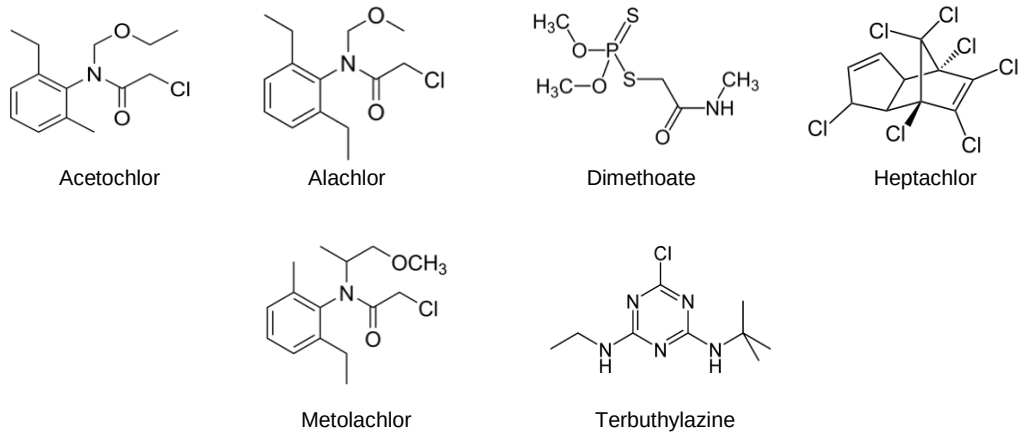


Figure 1: Chemical structures of the studied pesticides.

.

Acknowledgements: The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support by national funds FCT/MCTES to CIMO (UIDB/00690/2020).

References:

1. Calvo-Flores, F. G.; Isac-García, J.; Dobado, J. A. *Emerging pollutants: origin, structure, and properties*. Wiley-VCH **2018**, 6-9.
2. Stefanakis A. I.; Becker J. A. *A review of emerging contaminants in water: classification, sources, and potential risks*. *Impact of Water Pollution on Human Health and Environmental Sustainability* (McKeown A. E., Bugyi G., eds.) **2016**, 55-80.

Environment and water

Atmospheric deposition of microplastics in Southern Portugal

I. Marín-Beltrán,[a,b] M.C. Costa[a,b]

a) Centro de Ciências do Mar do Algarve, Universidade do Algarve, Campus de Gambelas, building 7, 8005-139 Faro, Portugal; b) Faculdade de Ciências e Tecnologia, Universidade do Algarve, Campus de Gambelas, building 8, 8005-139 Faro, Portugal.

Email: imbeltran@ual.pt

Plastics have been with us for barely 70 years. However, plastics, and more precisely microplastics (plastics ≤ 5 mm)[1], are already found everywhere, from the deep ocean[2] to high mountains[3]. Because of their lightweight, microplastics can be transported by the wind through long distances, reaching even the most remote environments. In this study, we analyzed microplastics from atmospheric fallout in the coastal area of the city of Faro (Southern Portugal), in the Ria Formosa Natural Park, during 1 year. Samples were taken monthly from passive collectors that consisted on borosilicate glass bottles with a funnel on top. Every sampling date, funnels would be rinsed thoroughly with distilled water, collecting the particles within the glass bottles. Samples were subsequently filtered through 25 µm pore-size cellulose filters (Whatman™). These filters were digested by the addition of H_2O_2 (15%), and kept at 50 ºC for 2h. The solution was then filtered through a 5 µm pore-size silicon membrane (MakroPor). These transparent filters allow for the quick identification of microplastics under a micro-FTIR (Fourier Transform Infrared), working in transmission mode. Figure 1 shows the overall protocol followed for collection and analysis of airborne microplastics. Atmospheric deposition of microplastics in the city of Faro ranged from 0 to 670 particles m^{-2} day^{-1}, the upper limit being higher than values reported thus far for microplastics from air samples in different parts of the world[3-5]. This could be explained by differences in the methodology followed, which, in the present study, allowed for the identification of microplastics as small as 10 µm. Polystyrenes and polyamides were the more abundant polymers found in our samples, which are plastics commonly used for packaging and clothing, respectively.

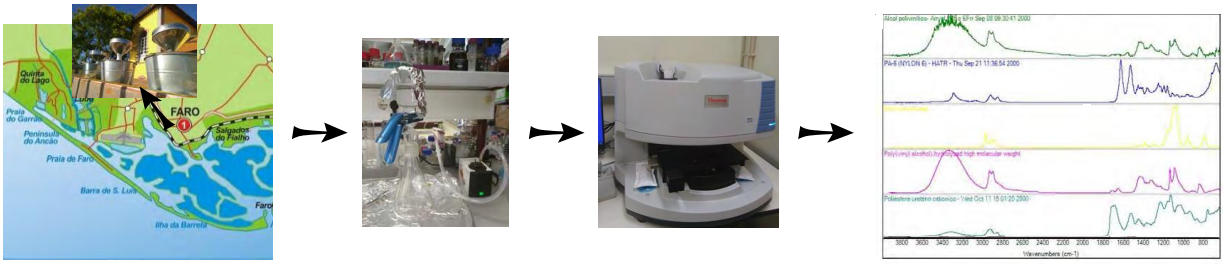


Figure 1: Collection and chemical analysis of airborne microplastics by means of micro-FTIR.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support through project UID/04326/2020 and the Stimulus of Scientific Employment, Individual Support 2017 Call (CEECIND/03072/2017).

References:

1. Arthur, C., Baker, J. & Bamford, H., 2009. Proceedings of the International Research Workshop on the Occurrence, Effects, and Fate of Microplastic Marine Debris. NOAA Technical Memorandum NOS-OR&R-30.
2. Peng, X. et al., 2018. Microplastics contaminate the deepest part of the world's ocean. Geochem. Perspect. Lett. 9, 1–5.
3. Allen, S., Allen, D., Phoenix, V.R., Le Roux, G., Durántez Jiménez, P., Simonneau, A., Binet, S., Galop, D., 2019. Atmospheric transport and deposition of microplastics in a remote mountain catchment. Nat. Geosci. 12, 339–344. https://doi.org/10.1038/s41561-019-0335-5
4. Dris, R., Gasperi, J., Saad, M., Mirande, C., Tassin, B., 2016. Synthetic fibers in atmospheric fallout: A source of microplastics in the environment? Mar. Pollut. Bull. 104, 290–293. https://doi.org/10.1016/j.marpolbul.2016.01.006
5. Cai, L., Wang, J., Peng, J., Tan, Z., Zhan, Z., Tan, X., Chen, Q., 2017. Characteristic of microplastics in the atmospheric fallout from Dongguan city, China: preliminary research and first evidence. Environ. Sci. Pollut. Res. 24, 24928–24935. https://doi.org/10.1007/s11356-017-0116-x

Environment and water

Recovery of strategic metals from extreme acid mine drainage by combining solvent extraction methods and biological strategies

A. Nobahar,[a,b] A.B. Melka,[a,b] J.D. Carlier,[a] J.P. Lourenço,[b] M.C. Costa[a,b]

a) CCMAR, Centre of Marine Sciences, University of Algarve, Gambelas Campus, 8005-139 Faro, Portugal; b) FCT, Faculty of Sciences and Technology, University of Algarve, Gambelas Campus, 8005 139 Faro, Portugal

Email: mcorada@ualg.pt

Most of strategic metals are obtained through mining of finite primary sources which are rapidly decreasing, and according to estimations of supply risk some industries will struggle to maintain supplies in the next twenty to thirty years. Therefore, there has been an increasing interest in exploring the potential of metals' recycling from secondary sources.

In the scope of MetalChemBio project several experiments combining Solvent Extraction (SX) methods and conventional pH precipitation and/or addition of plant extracts or biogenic sulphide were performed to separate and recover copper and zinc from an extremely acidic and concentrated Acid Mine Drainage (AMD): pH 1.2; ~142 g/L SO_4^{2-}; ~56 g/L Fe^{3+}; 7.8 g/L Fe^{2+}; ~6.5 g/L Al^{3+}; ~5.3 g/L Cu^{2+} and ~1.9 g/L Zn^{2+}.

Promising results were obtained in a three-stage strategy: (1) a first SX method allows to produce 2M sulfuric acid solutions with copper concentrations (~46 g/L Cu^{2+}) suitable for electrowinning, or for a biogenic sulphide based-process leading to the production of pure covellite nanoparticles; (2) a second SX method is used to remove ~ 92% of ferric iron from the copper-free AMD, preventing its simultaneous precipitation with zinc in the next stage; (3) biogenic sulphide is added to the copper-free and low-iron AMD at a controlled pH to produce pure aggregates of zinc sulphide (Wurtzite and Sphalerite) nanoparticles.

Acknowledgements: We thank (1) the national funds from the Portuguese Foundation for Science and Technology (FCT) co-financed by the Algarve´s Regional Operational Program (CRESC Algarve 2020) through Portugal 2020 and European Regional Development Fund (FEDER), under the project METALCHEMBIO (no. 29251) and (2) FCT funds through the project UIDB/04326/2020.

Environment and Water

Impact of interfering compounds on arsenic removal from water through polymer nanocomposite membranes

R. Abreu,[a] H. Salazar,[a, b] P.M. Martins,[c, d] S. Lanceros-Mendez,[e, f] G. Botelho[a]

a) Center/Department of Chemistry, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal; b) Center/Department of Physics, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal; c) Centre of Molecular and Environmental Biology, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal; d) IB-S – Institute for Research and Innovation on Bio-Sustainability, University of Minho, 4710-057, Braga, Portugal); e) BCMaterials, Parque Científico y Tecnológico de Bizkaia, 48160 Derio, Spain; f) IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Spain

Email: a89296@alunos.uminho.pt

Water quality is one of the biggest environmental concerns nowadays, mainly caused by uncontrolled water sources contamination. Rapid industrialization and population growth result in the release of various contaminants in aquatic ecosystems. In this scope, one of the major environmental concerns is the presence of heavy metals in water. Inorganic arsenic (As) is one of the twenty most abundant species in water, and it is considered one of the most potential carcinogens. Long term arsenic exposure may cause several disorders, including skin lesions, different types of cancer, cardiovascular diseases, pulmonary problems, neurological deficiencies, and reproductive toxicity [1].

The currently available technologies for the remediation of this pollutant are not fully effective, so it is necessary to develop new technologies that are more efficient. Adsorption by using nanomaterials is one of the most promising alternatives for solving this problem. However, many of the studies in this area use suspended materials, which prevents reuse or requires additional procedures, which can be time-consuming or expensive. To overcome this drawback, the combination of adsorption with membrane filtration can be very advantageous. Membrane processes are considered a promising technology for As removal from water and, therefore, the development of water remediation systems based on polymer membranes has received increasing consideration. Membranes based on poly (vinylidene fluoride), PVDF, and its co-polymers have attracted large interest for water remediation applications, mainly due to its outstanding properties such as thermal and chemical stability, and mechanical resistance [2].

One of the main challenges in As-contaminated water remediation is the selective removal of this contaminant, in the presence of high concentrations of background competing pollutants such as other heavy metals, inorganic ions, and organic compounds. Selective removal is a key parameter for any As removal technology as this not only increases the removal efficiency but also the capacity and lifetime of units while lowering the process cost [3].

In this study, PVDF nanocomposite membranes with immobilized active materials (Fe_2O_3 and $Y_2(CO_3)_3$) have been prepared and characterized, and their arsenic adsorption capacity in water evaluated in an up-scaling reactor. The interference of co-existing contaminants on adsorption behavior, including hexavalent chromium, nitrate, and diclofenac, were assessed, in order to understand the selectivity of nanocomposite filter on As adsorption.

Acknowledgements: This work was supported by the European Union and Portuguese Foundation for Science and Technology (FCT): UID/FIS/04650/2020 and UID/QUI/0686/2020. H. Salazar thanks for grant SFRH/BD/122373/2016. The authors thank the financial support from the European Commission Research & Innovation H2020-MSCA-RISE-2017 (Ref.: 778412) INDESMOF project.

References:

1. A. Basu,D. Saha, R. Saha, T. Ghosh and B. Saha, A review on sources, toxicity and remediation technologies for removing arsenic from drinking water. Research on Chemical Intermediates, 2014. 40(2): p. 447-485.2. Nair V.; Menon R. S.; Biju A. T.; Sinu C.R.; Paul R. R.; Jose A.; Sreekumar V. *Chem. Soc. Rev.* **2011**, *40*, 5336.
2. H. Salazar, J. Nunes-Pereira, D. M. Correia, V. F. Cardoso, R. Gonçalves, P. M. Martins and S. Lanceros-Méndez, Poly(vinylidene fluoride-hexafluoropropylene)/bayerite composite membranes for efficient arsenic removal from water. Materials Chemistry and Physics, 2016. 183: p. 430-438.
3. Weerasundara, L., Y.-S. Ok, and J. Bundschuh, Selective removal of arsenic in water: A critical review. Environmental Pollution, 2021. 268: p. 115668.

Environment and Water

Natural polymer membranes for removal of volatile organic compounds

J.L. Teixeira,[a,b,c] P.M. Martins,[c,d] R.F. de Luiz,[e,f] G. Botelho,[b] S. Lanceros-Mendez[f,g]

a) Centro de Física das Universidades do Minho e Porto, Universidade do Minho, 4710-057 Braga, Portugal; b) Centro de Química da Universidade do Minho, 4710-057 Braga, Portugal; c) IB-S, Institute of Science and Innovation for Bio-Sustainability, Universidade do Minho, 4710-057 Braga, Portugal; d) Centro de Biologia Molecular e Ambiental, Departamento de Biologia da Universidade do Minho, 4710-057 Braga, Portugal; e) Departamento de Mineralogía y Petrología, Facultad de Ciencia y Tecnología, Universidad del País Vasco, UPV/EHU, Apdo. 644, E-48080 Bilbao, Spain; f) BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain; g) IKERBASQUE, Basque Foundation for Science, 48009 Bilbao, Spain

Email: id8042@alunos.uminho.pt

Outdoor and indoor pollutants have been identified as the cause for deaths rising by cardiovascular and respiratory diseases, with 98% of the low to medium income cities over 100000 habitants failing to meet air quality standards, according to the World Health Organization. [1]

Volatile organic compounds (VOC's) are considered as one of the main pollutants contributors for smog, ozone layer depletion and global warming [2, 3]. VOCs like methane, benzene, toluene and propane have an ubiquitous presence, being in car and wall paints, private homes, personal care products and other man-made sources [4]. With an astounding 3.3 million deaths per year related to low air quality, VOC control became one of the main problems to be addressed by new research and technologies.

Currently, mitigation of this problem is being led by High Efficiency Particulate Air filters (HEPA), active carbon filters, ionic generators and ultraviolet purifiers.

In this work, porous polymeric membranes based in natural polymers like alginate and carrageenan were processed via freeze dry method under varying processing conditions to optimize pore size and overall porosity. The physical and chemical properties of the produced membranes were evaluated to access their suitability to be applied as a filter in the removal of different VOC. Further, active materials with various affinities for each tested VOC, such as metal organic frameworks (MOFs) (e.g. MIL-125, UiO-66-NH_2), photocatalytic nanoparticles (e.g. $AgTiO_2$) or zeolites (e.g. NaY), were incorporated into these membranes, showing promising results in their adsorption and/or degradation.

Acknowledgements: Portuguese Foundation for Science and Technology (FCT): UID/QUI/0686/2020, UID/FIS/04650/2020, PTDC/CTM-ENE/5387/2014, SFRH/BD/141642/2018, and 2020.02802.CEECIND. Basque Government Industry Department: ELKARTEK program.

References:

1. Hoek, G., et al., *Long-term air pollution exposure and cardio- respiratory mortality: a review.* Environmental Health, 2013. **12**(1): p. 43.
2. Fuzzi, S., et al., *Particulate matter, air quality and climate: lessons learned and future needs.* Atmos. Chem. Phys., 2015. **15**(14): p. 8217-8299.
3. Pöschl, U. and M. Shiraiwa, *Multiphase Chemistry at the Atmosphere–Biosphere Interface Influencing Climate and Public Health in the Anthropocene.* Chemical Reviews, 2015. **115**(10): p. 4440-4475.
4. Gallego, E., et al., *Determining indoor air quality and identifying the origin of odour episodes in indoor environments.* Journal of Environmental Sciences, 2009. **21**(3): p. 333-339.

Environment and water

Efficient and rapid delamination of waste printed circuit boards using microwave-assisted organic swelling

P.M.S. Sousa,[a] L.M. Martelo,[a] B. Monteiro,[a] M.M.S.M. Bastos,[b] H.M.V.M. Soares[a]

a) REQUIMTE/LAQV, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, rua Dr. Roberto Frias, 4200-465 Porto, Portugal; b) LEPABE, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, rua Dr. Roberto Frias, 4200-465 Porto, Portugal

Email: paulosousa@fe.up.pt

Every year, a large amount of waste printed circuit boards (WPCBs) are generated, being considered as valuable secondary source of precious and base metals [1]. PCBs are a core part of supporting and connecting of electrical and electronic components and are constituted by a multi-layer structure of glass fibers and copper, reinforced by a brominated epoxy resin (BER), which is very difficult to separate into the metallic and non-metallic components [2,3]. So, the main aim of this work was to evaluate the efficiency of microwave for assisting in the delamination of WPCBs by organic swelling of the BER and compare the performance with other techniques (thermostatic and ultrasonic baths). Eight solvents, [dimethyl formamide (DMF), dimethyl acetamide (DMAc), dimethyl sulfoxide (DMSO), N-methylpyrrolidone (NMP), cyclohexanone (CH), γ-butyrolactone (GBL), tetrahydrofurfuryl alcohol (TFA) and dimethyl malonate (DM)], previously selected from a list of 91 solvents based on the Hansen´s solubility calculation and other exclusion parameters (e.g.: toxicity, price, etc.), were tested using the three techniques (Figure 1A) [2]. Microwave demonstrated to be the most efficient approach and subsequent optimization of key parameters (dimensions of WPCBs (Figure 1B) and reaction time (Figure 1C) were obtained: dimensions of 225 mm^2 using NMP (S/L ratio of 300 g/L) at 200°C with 2 cycles of 10 min. In conclusion, microwave-assisted swelling revealed to be more efficient and faster process to delaminate WPCBs into metallic and non-metallic components, which are important advantages when envisaging a future industrial implementation.

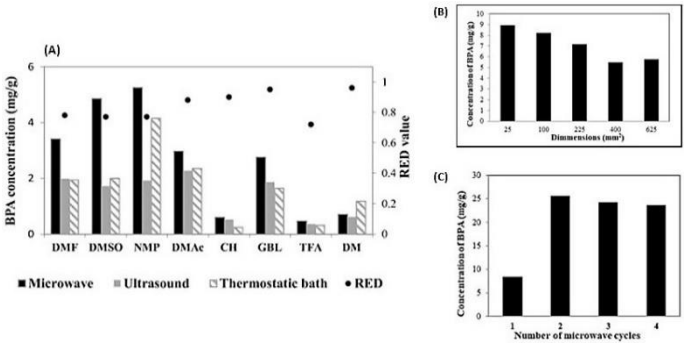


Figure 1: **(A)** Efficiency of various solvents on the dissolution of BER from WPCBs (dimensions of 25 mm^2), expressed in Bisphenol-A (BPA) (mg)/residue(g) and according to their relative energy difference (RED) value, using microwave at 200°C for 10 min, ultrasound bath at 60°C for 25 h and thermostatic bath at 153°C for 10 min. Influence of the dimensions of the WPCBs **(B)** and reaction time **(C)** on the dissolution of BER by NMP using microwave.

Acknowledgements: We thank FCT for financial support by Project PTDC/EAM-MIN/31041/2017 - POCI-01–0145-FEDER-031041 FCT/MCTES through national funds (PIDDAC). Base Funding: UIDB/00511/2020 and FCT/MCTES (PIDDAC) of (LEPABE UIDB/50006/2020 and FCT/MCTES (PIDDAC) of LAQV-REQUIMTE.

References:

1. A. Hubau et al. 2019, “Recycling-oriented methodology to sample and characterize the metal composition of waste Printed Circuit Boards “Waste Manag., 91 (2019), pp. 62-71, 10.1016/j.wasman.2019.04.041;
2. B. Monteiro et al. 2020, “Microwave-assisted organic swelling promotes fast and efficient delamination of waste printed circuit boards”, Waste Management Volume 126, 1 May 2021, Pages 231-238, 10.1016/j.wasman.2021.03.012;
3. Dangtungee, R., Somchua, S. & Siengchin, S. Recycling Glass Fiber/Epoxy Resin of Waste Printed Circuit Boards: Morphology and Mechanical properties. Mech Compos Mater 48, 325–330 (2012), 10.1007/s11029-012-9279-1.

Environment and water

THIS ABSTRACT WAS WITHDRAWN BY THE AUTHORS

Environment and water

Sensing microplastics in aqueous suspensions using pyrene fluorescent probe

C.Q.V. Costa, I.I. Afonso, J.P. da Silva

Center of Marine Science (CCMAR), University of Algarve, Gambelas campus, 8005-194, Faro, Portugal

Email: camilaqvdacosta@gmail.com

Plastics are environmental persistent materials of great public concern. Their persistence, together with an increasing production and poor waste management, has led to severe pollution problems worldwide. These materials can break down into smaller size particles, micro/nanoplastics (size ≤ 5 mm), facilitating their incorporation in marine organisms and environments[1,2]. Reliable and quick analytical methods are therefore required for risk assessment and control[3]. Fluorescence methods involving Nile Red and Pyrene fluorescent probes have been developed and proposed to sense microplastic particles in different matrices[4]. Our objective is to explore the use of Pyrene fluorescent probe to sense microplastic particles in aqueous suspensions. Polystyrene and polyethylene particles were used as example[5] **(Figure 1A).** Polystyrene showed intrinsic fluorescence properties, allowing for its direct detection while no fluorescence was detected from polyethylene. Both polymers can be detected with pyrene fluorescent probe using the ratio I1/I3 of its vibronic bands **(Figure 1B).**

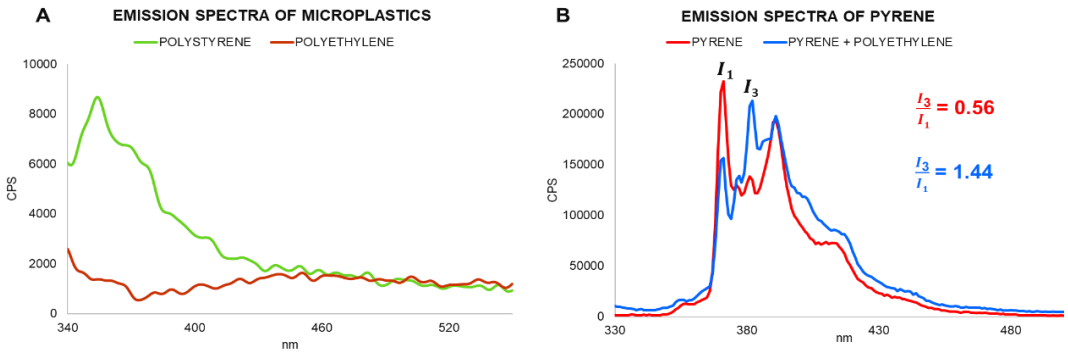


Figure 1: **(A)** Fluorescence emission spectra of Polystyrene (— PS) and Polyethylene (— PE) in Milli-Q Water. Excitation wavelength: 330 nm. **(B)** Fluorescence emission spectra of Pyrene without (— red) and with polyethylene particles (— blue**)** in aqueous suspensions. Excitation wavelength: 318 nm.

Acknowledgements: We thank Fundação Azul for funding, grant "Size Matters— Looking for invisible plastics," reference FA_05_2017_024. This study received Portuguese national funds from FCT—Foundation for Science and Technology through project UIDB/04326/2020, and from the operational programmes CRESC Algarve 2020 and COMPETE 2020 through project EMBRC.PT ALG-01-0145-FEDER-022121.

References:

1. Koelmans AA, Besseling E, Shim WJ (2015) Nanoplastics in the aquatic environment critical review. In: Bergmann M, Gutow L, Klages M (eds) Marine anthropogenic litter. Springer, Cham. https://doi.org/10.1007/978-3-319-16510 -3_12
2. Padervand, M., Lichtfouse, E., Robert, D., & Wang, C. (2020). Removal of microplastics from the environment. A review. Environmental Chemistry Letters, 1-22.
3. Gallo, F., Fossi, C., Weber, R., Santillo, D., Sousa, J., Ingram, I., Romano, D. (2018). Marine litter plastics and microplastics and their toxic chemicals components: the need for urgent preventive measures. Environmental Sciences Europe, 30(1), 13.
4. Costa, C. Q. V., Cruz, J · Martins, J. Teodósio A. M.A., Jockusch, S., Ramamurthy, V., Da Silva, J.P. (2020). Fluorescence sensing of microplastics on surfaces. Environmental Chemistry Letters. https://doi.org/10.1007/s10311-020-01136-0.
5. Shahul Hamid, F., Bhatti, M. S., Anuar, N., Anuar, N., Mohan, P., & Periathamby, A. (2018). Worldwide distribution and abundance of microplastic: how dire is the situation?. Waste Management & Research, 36(10), 873-897.a) González S. D.-; Marion N.; Nolan S. P. *Chem. Rev.* **2009**, *109*, 3621. b) Hahn F. E. *Angew. Chem. Int. Ed.* **2006**, *45*, 1348.

Environment and water

Marine pollutants: identifying microplastics through volatile and non-volatile degradation products obtained after a heat treatment

I.I. Afonso, C.Q.V. Costa, J.P. da Silva

Centre of Marine Sciences (CCMAR), University of Algarve, Gambelas Campus, 8005-139 Faro, Portugal

Email: inesiafonso13@gmail.com

The production of plastic materials has been continuously rising in the last decades. According to The United Nations World Water Development Report 2017, 80% of wastewater, mostly untreated and containing plastic materials, ends up in rivers, lakes and oceans, damaging ecosystems and the human health.[1] Plastic particles showing less than 5 mm (microplastics), can be found almost everywhere in nature.[2] Currently, the analysis of microplastics is still challenging and time-consuming, particularly for particles with sizes below 10 µm. Volatile compounds formed after pyrolysis have been used as fingerprint for identification.[3] The aim of this work is to evaluate the identification of microplastic particles based on the distributions of volatile and non-volatile compounds resulting from heat treatment. Formed products were obtained at different temperatures and analyzed by µ-FTIR, GC-MS and LC-MS. Main detected compounds are fragments of plastic polymer chains (**Figure 1**) containing different monomer units, which can be used for particle identification.

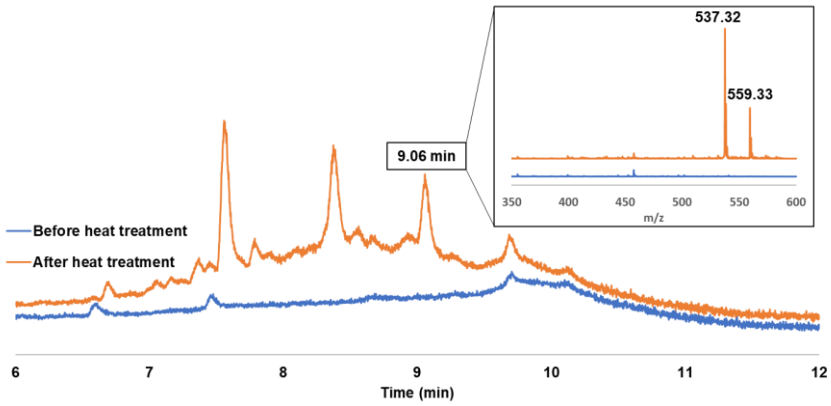


Figure 1: LC-MS traces of polystyrene before and after the heat treatment. Insert: mass spectrum at 9.06 min

Acknowledgements: We thank Fundação Azul for funding, grant “Size Matters — Looking for invisible plastics,” reference FA_05_2017_024. This study received Portuguese national funds from FCT — Foundation for Science and Technology through project UIDB/04326/2020, and from the operational programmes CRESC Algarve 2020 and COMPETE 2020 through project EMBRC.PT ALG-01-0145-FEDER-022121”

References:

1. WWAP (United Nations World Water Assessment Programme), **2017**, The United Nations World Water Development Report 2017, Wastewater: The Untapped Resource, Paris, UNESCO, Water Science and Technology, p 2.
2. Ter Halle, A.; Jeanneau, L.; Martignac, M.; Jarde, E.; Pedrono, B.; Brach, L.; Gigault, J. **2017**, Nanoplastic in the North Atlantic Subtropical Gyre, Environ Sci Technol 51(23):13689–13697
3. Picó, Y.; Barceló, D. **2020**, Pyrolysis gas chromatography-mass spectrometry in environmental analysis: focus on organic matter and microplastics. Trends in analytical chemistry.

Environment and water

Fenton-type heterogeneous catalysts based in zeolites for water treatment

B.L.C. Santos,[a,b] A.M. Fonseca,[a,c] I.C. Neves[a,c]

a) CQUM-Center of Chemistry, Chemistry Department, University of Minho, 4710-057 Braga, Portugal; b) Departamento de Química, Faculdade de Ciências, Universidade Agostinho Neto, Av. 4 de Fevereiro, 71, 815 Luanda, Angola; b) CEB – Center of Biological Engineering, University of Minho, 4710-057 Braga, Portugal

Email: id7175@alunos.uminho.pt

Water pollution is one of the most important environmental problems in the world. Large amounts of synthetic organic contaminants are released daily into different types of wastewaters and ultimately enter into natural water bodies. It is well known the vast majority of these compounds are persistent organic pollutants, owing to their high stability to sunlight irradiation and resistance to microbial attack. Advanced oxidation processes (AOPs) have been demonstrated to achieve good results for the elimination of organic pollutants from wastewater with very short treatment times. Fenton-type heterogeneous processes have received much attention for their low cost, high efficiency, and moderate conditions among these AOPs.[1] In heterogeneous Fenton-type catalysis, iron (or other transition metals) is stabilized on/in the catalyst's structure and thus can reduce hydroxide precipitation over a wider pH range.[2] This work report the preparation of bimetallic heterogeneous catalysts based in NaY zeolite with Fe, Cu and Mn by ion-exchange method using different routes (Figure 1). Different characterization techniques show that the metals are cationic and show higher oxidation efficiency against the azo dyes, tartrazine and procion yellow, and the order of metal ion exchanging are important to improve their catalytic activity. The prepared bimetallic catalysts can be used at least three times without a significant loss of catalytic activity, proving to have a very high stability.

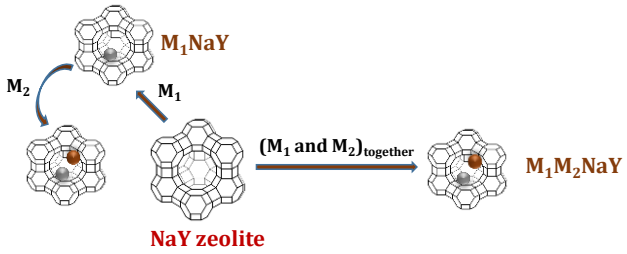


Figure 1: Different routes for preparing the heterogeneous Fenton-type catalysts by ion exchange

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support through Centre of Chemistry (UID/QUI/00686/2013 and UID/QUI/0686/2016) and BioTecNorte (operation NORTE-01-0145-FEDER-000004), and the INAGBE (Instituto Nacional de Gestão de Bolsas de Estudo, Angola) for the PhD grant of BLCS.

References:

1. a) Kalra, A.; Gupta, A.R., *Review. Mater. Today Proc.* **2021**, 36, 689; b) González S.D. et al., *Chem. Rev.* **2009**, 109, 3621.
2. a) Santos, B.L.C. et al, *Catalysts*, **2021**, 11, 32; b) Rache, M.L et al., *Appl. Catal. B Environ.* **2014**, 146, 192.

Environment and water

THIS ABSTRACT WAS WITHDRAWN BY THE AUTHORS

Environment and water

Synthesis of α-enaminones from biomass – sustainable continuous flow hydrogenation of furfural-derived *trans*-diamino cyclopentenones

L.A.S. Cavaca,[a] R.F.A. Gomes,[a] S.D. Lucas,[b] R.M.S. Loureiro,[b] C.A.M. Afonso[a]

a) iMed.UL, Faculdadade de Farmácia da Universidade de Lisboa, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal; b) Hovione FarmaCiencia SA, Sete Casas, 2674-506 Loures, Portugal

Email: l.cavaca@campus.fct.unl.pt

The search for novel methods to prepare value added compounds from bio-based synthons such as furfural is of great importance.[1] In line with our interest for the transformation of furfural into valuable enone systems,[2] we explored the creation of a more sustainable chemical process for the synthesis of α-enaminones. α-Enaminones are versatile synthons due to their dual enamine/enone character, being important intermediates for the construction of heterocyclic compounds.[3] These compounds are known to act as ATP-sensitive potassium (KATP) channel agonists, and their core is also present in key precursors of indole compounds for inhibition of acetylcholinesterase and monoamine oxidase.[4] Over the years, different approaches have been developed for the synthesis of α-enaminones.[5] Despite all the progress, these elegant methods have some limitations, as they require pre-functionalized amination reagents, use of additives and/or oxidants or can be limited to the use of aromatic amines. We described a sustainable continuous flow synthesis of functionalized cyclopentanones and α-enaminones, involving a tunable selective hydrogenation of furfural-derived trans-diamino cyclopentenones under mild conditions. The method allowed the synthesis of a described K_{ATP} channel agonist (**Figure 1**).

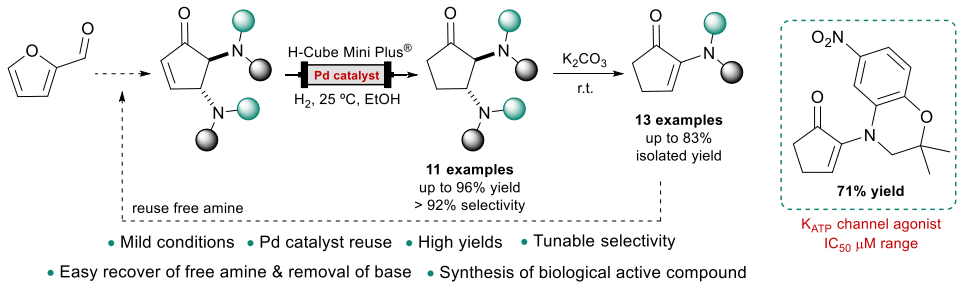


Figure 1: Tunable selective continuous flow hydrogenation of trans-diamino cyclopentenones into bifunctionalized cyclopentanones and α-enaminones; synthesis of ATP sensitive potassium (KATP) channel agonist using the described method.

Acknowledgements: The authors acknowledge Fundação para a Ciência e Tecnologia (FCT) for financial support (PD/BD/143127/2019, PTDC/QUI-QOR/32008/2017 and UID/QUI/50006/2019), COMPETE Programme (SAICTPAC/0019/2015). The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 951996).

References:

1. G. Shen, B. Andrioletti, Y. Queneau, Curr. Opin. Green Sustain. Chem., (2020) 100384.
2. R. F. Gomes, N. R. Esteves, J. A. Coelho, C. A. M. Afonso, J. Org. Chem., 83 (2018) 7509
3. D. Lankri, G. Albarghoutu, M. Mahameed, D. Tsvelikhousky, J. Org. Chem., 82 (2017) 7101.
4. P. Masiello et. al., J. Med. Chem., 56 (2013) 4718; J. O'Malley et. al., Bioorg. Med. Chem. Lett., 6 (1996) 625.
5. J. P. Nunes, C. A. M. Afonso, S. J. R. A. Caddick, RSC Advances, 3 (2013) 14975.

Environment and water

Influence of DNA in pulp water absorption capacity

A.J.M. Valente[a], D. Murtinho[a], A.M.S. Carta[b], R. Bértolo[b], A.C.S. Ferreira[a]

a) University of Coimbra, CQC and Department of Chemistry, Rua Larga, 3004-535 Coimbra, Portugal; b) RAIZ - Forest and Paper Research Institute, Quinta de S. Francisco, Apartado 15, 3801-501 Aveiro, Portugal

Email: ana.ferreira@uc.pt

The aim of this work is to improve the water absorption ability of eucalyptus kraft pulp using salmon DNA as additive. Therefore, water absorption studies were carried out using mixtures of pulp with different percentages of DNA.
Natural polymers, obtained from renewable resources, can be used as substituents of synthetic polymers in a wide variety of applications, including biomedical and biochemical[1]. Biopolymers are biodegradable materials, thus contributing to environmental preservation, a major concern nowadays. DNA and cellulose are amphiphilic macromolecules and the resulting blends are water insoluble, which is the main condition to be used as a water absorbent[2,3].
In this study, the water uptake of pulp samples containing 1%, 5% and 10% of single stranded DNA (ssDNA) and double stranded DNA (dsDNA) was evaluated. DNA was previous solubilized in water, before adding cellulose. Then, the solutions were stirred at room temperature, for 24 hours, poured into plastic vessels and dried at 60ºC in an oven. The water uptake results for pulp/dsDNA and pulp/ssDNA mixtures are presented in Figure 1. Pulp with 10% of dsDNA shows an increase in the water uptake of 40%, when compared with pulp alone. The study has been complemented by the measurement of papermaking properties.

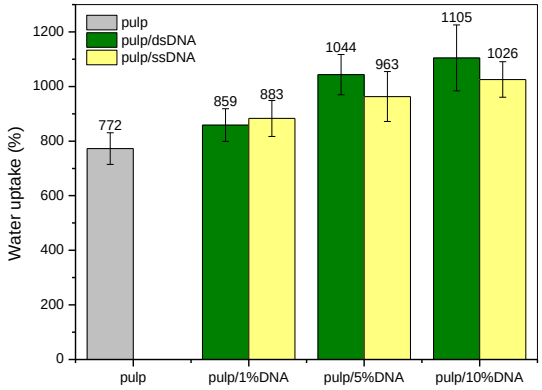


Figure 1. Water uptake results for pulp/dsDNA (green column) and pulp/ssDNA (yellow column).

Acknowledgements: This work was carried out under the Project inpactus – innovative products and technologies from eucalyptus, Project N.º 21874 funded by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of COMPETE 2020 nº246/AXIS II/2017. Financial support from Coimbra Chemistry Centre, which is supported by the Fundação para a Ciência e a Tecnologia (FCT) through the programmes UID/QUI/00313/2020 and COMPETE, is also acknowledge.

References:

1. K. Aoi, A. Takasu and M. Okada, *Polymer*, **2000**, 41, 2847–2853.
2. T. Y. Lee, H. J. Kim, J. O. Moon and Y. B. Shim, *Electroanalysis*, **2004**, 16, 821–826.
3. N. Orakdogen, P. Karacan and O. Okay, *React. Funct. Polym.*, **2011**, 71, 782–790.

Chemistry in life sciences

Synthesis of DSPE-PEG2000-NH_2-*D*-amino acids conjugates to overcome the biofilm formation caused by *Staphylococcus aureus*

D.R.P. Loureiro,[a,b,c*] J.X. Soares,[c] C. Nunes,[c] C.M.M. Afonso,[a,b] S. Reis[c]

a) Department of Chemical Sciences, Laboratory of Organic and Pharmaceutical Chemistry, Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal; b) Interdisciplinary Center of Marine and Environmental Investigation (CIIMAR/CIMAR), Edifício do Terminal de Cruzeiros do Porto de Leixões, Av. General Norton de Matos s/n, 4050-208 Matosinhos, Porto, Portugal; c) LAQV-REQUIMTE, Department of Chemical Sciences, Laboratory of Applied Chemistry, Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal.

Email: dloureiro@ff.up.pt

Biofilms are bacterial communities adhered to a surface which constitutes a defense mechanism from environmental stresses, such as antimicrobial drugs. The biofilm assembles due to the self-secretion of the extracellular polymeric substance (EPS), a matrix composed by proteins, exopolysaccharides, and often DNA.[1] *D*-Amino acids play an important role in the biofilm disassembly as they prompt the release of the matrix protein component, in special, with Gram-positive bacterium *Staphylococcus aureus*.[2] The combination of *D*-amino acids with an antimicrobial have shown a synergic effect on the anti-biofilm activity.[3] However, the combination of the biofilm disruptive effect with the superior antimicrobial loading capacity of liposomes could be a solution to overcome the problems associated with antimicrobial resistance biofilms. This strategy requires the coupling between a *D*-amino acid and the liposome lipid. Traditionally, the coupling is achieved by *N*-hydroxysuccinimide (NHS) and dicyclohexylcarbodiimide (DCC) chemistry.[4] However, NHS/DCC strategy requires long reaction times and the desired conjugated are obtained low yields and purity.

In this work, we present a new and more efficient synthetic route for the coupling of DSPE-PEG-2000-NH_2 (1,2-distearoyl-*sn*-glycero-3-phosphoethanolamine-N-[amino(polyethylene glycol)-2000]), the lipid used to assemble liposomes, with *D*-amino acids. The new route comprises three steps: i) *N*-protection of *D*-amino acid, ii) coupling synthesis between lipid and *D*-amino acid using COMU as coupling reagent, and iii) deprotection of protecting group. The new synthetic route was applied for the functionalization of DSPE-PEG-2000-NH_2 with four amino acids (*D*-phenylalanine, *D*-aspartic acid, *D*-glutamic acid, and *D*-proline) which were elucidated by ^{1}HNMR, FTIR and MALDI-TOF. When compared with the standard NHS/DCC, our method allowed the synthesis of DSPE-PEG-2000-NH_2-*D*-amino acid in fewer steps, with high yields and purity. The synthetized conjugates will be used to produce a nano delivery system targeted to disturb the biofilm formation caused by *Staphylococcus aureus*.

Acknowledgements: This research was partially supported by FCT/MCTES - Foundation for Science and Technology from the Minister of Science, Technology and Higher Education and European Regional Development Fund (ERDF) under the projects, co-financed by COMPETE 2020, Portugal 2020, PTDC/SAU-PUB/28736/2017 (POCI-01-0145-FEDER-028736), and PTDC/NANMAT/31444/2017 and within the scope of UIDB/04423/2020, UID/QUI/5000612019, and UIDP/04423/2020 (Group of Natural Products and Medicinal Chemistry). DRPL thanks FCT for her PhD grant (SFRH/BD/140844/2018). JXS thanks for the FCT PhD Programmes, specifically by the BiotechHealth Programme (PD/00016/2012), and for the grants (SFRH/BD/98105/2013 and SFRH/BD/116167/2016).

References:

1. Koo, H.; Allan, R. N.; Howlin, R. P.; Stoodley, P.; Hall-Stoodley, L., *Nat. Rev. Microbiol.* **2017,** *15* (12), 740-755.
2. Hochbaum, A. I.; Kolodkin-Gal, I.; Foulston, L.; Kolter, R.; Aizenberg, J.; Losick, R., *J. Bacteriol.* **2011,** *193* (20), 5616-5622.
3. Warraich, A. A.; Mohammed, A. R.; Perrie, Y.; Hussain, M.; Gibson, H.; Rahman, A., *Sci. Rep.* **2020,** *10* (1), 9021.
4. Lopes-de-Araújo, J.; Neves, A. R.; Gouveia, V. M.; Moura, C. C.; Nunes, C.; Reis, S., *Pharm Res* **2016,** *33* (2), 301-14.

Chemistry in life sciences

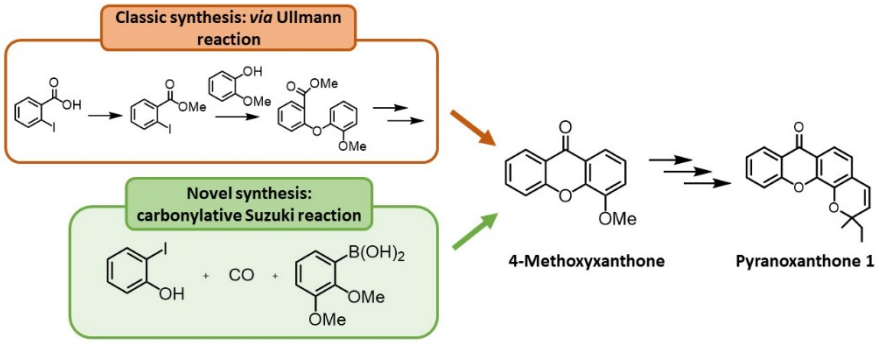
A novel palladium-catalyzed synthetic route to obtain a key xanthonic chemical precursor of potential antitumor pyranoxanthones

A. Dias[a], D.R.P. Loureiro[a,b,c], J.X. Soares[c], M.M.M. Pinto[a,b], C.M.M. Afonso[a,b]

a) Department of Chemical Sciences, Laboratory of Organic and Pharmaceutical Chemistry, Faculty of Pharmacy, University of Porto, Porto, Portugal; b) Interdisciplinary Centre of Marine and Environmental Research (CIIMAR /CIMAR), Porto, Portugal; c) LAQV-REQUIMTE, Department of Chemical Sciences, Laboratory of Applied Chemistry, Faculty of Pharmacy, University of Porto, Porto, Portugal.

Email: cafonso@ff.up.pt

Pyranoxanthones are compounds presenting a pyran ring fused to the xanthone dibenzo-γ-pyrone scaffold.[1] Firstly found in Nature as secondary metabolites, natural and synthetic pyranoxanthones have been associated with important biological activities. For example, the synthetic pyranoxanthone 1 (**Scheme 1**) has demonstrated a promising antitumor activity.[2] 4-Methoxyxanthone is the key chemical precursor for this pyranoxanthone.[2,3]
In this work, we describe a classical synthetic pathway to 4-methoxyxanthone, based on the Ullmann coupling (**Scheme 1**). This classical pathway uses harsh experimental conditions and provides low yields of the target compound. Consequently, an alternative synthetic method was explored and optimized based on a palladium-catalyzed carbonylative Suzuki coupling (**Scheme 1**). The optimization involved the evaluation of the categorical reaction parameters, namely the boronic acid, CO surrogate, base, and solvent. Then, with the aid of machine learning, a multivariable optimization was performed to determine the best relative amounts of each reaction parameters.[4] This novel synthetic route allowed a more environmentally-friendly synthesis of 4-methoxyxanthone, in a single step and better yields. This method has a good potential to be explored and applied to the synthesis of other pyranoxanthone derivatives.



Scheme 1 – Synthetic pathways to 4-methoxyxanthone, a key chemical precursor for antitumor pyranoxanthone 1.

Acknowledgements: This research was partially supported by FCT/MCTES - Foundation for Science and Technology from the Minister of Science, Technology and Higher Education and European Regional Development Fund (ERDF) under the projects, co-financed by COMPETE 2020, Portugal 2020, PTDC/SAU-PUB/28736/2017 (POCI-01-0145-FEDER-028736), and within the scope of UIDB/04423/2020, UID/QUI/5000612019, and UIDP/04423/2020 (Group of Natural Products and Medicinal Chemistry). DRPL thanks FCT for her PhD grant (SFRH/BD/140844/2018). JXS thanks for the FCT PhD Programmes, specifically by the BiotechHealth Programme (PD/00016/2012), and for the grants (SFRH/BD/98105/2013 and SFRH/BD/116167/2016).

References:

1. Pinto, M. M. M.; Palmeira, A.; Fernandes, C.; Resende, D. I. S. P.; Sousa, E.; Cidade, H.; Tiritan, M. E.; Correia-da-Silva, M.; Cravo, S. *Molecules* **2021,** *26,* 431.
2. França, F.; Silva, P. M. A.; Soares, J. X.; Henriques, A. C.; Loureiro, D. R. P.; Azevedo, C. M. G.; Afonso, C. M. M.; Bousbaa, H. *Molecules* **2020,** *25,* 5845.
3. Loureiro, D. R. P.; Soares, J. X.; Maia, A.; Silva, A. M. N.; Rangel, M.; Azevedo, C. M. G.; Hansen, S. V.; Ulven, T.; Pinto, M. M. M.; Reis, S.; Afonso, C. M. M. *ChemistrySelect* **2021,** *6,* 4511.
4. Reker, D.; Hoyt, E. A.; Bernardes, G. J. L.; Rodrigues, T. *Cell Rep. Phys. Sci.* **2020,** *1,* 100247.

Chemistry in life sciences

Targeting chitinase 3-like 1 in pancreatic cancer: *in silico* identification of inhibitors from a DrugBank database and confirmation of growth inhibition effect in cell lines

C.P.R. Xavier[a,b,#], S. Sousa[c,d,#], H. Branco[a,b], L.L. Santos[e,f], A. Palmeira[c,d,*], M.H. Vasconcelos[a,b,g,*]

a) i3S - Instituto de Investigação e Inovação em Saúde, Universidade do Porto, Rua Alfredo Allen 208, 4200-135 Porto, Portugal; b) Cancer Drug Resistance Group, IPATIMUP - Institute of Molecular Pathology and Immunology, University of Porto, Rua Júlio Amaral de Carvalho 45, 4200-135 Porto, Portugal; c) Laboratory of Organic and Pharmaceutical Chemistry/ Department of Chemical Sciences, FFUP - Faculty of Pharmacy, University of Porto, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal; d) Medicinal chemistry: drug discovery and drug design, CIIMAR – Interdisciplinary Centre of Marine and Environmental Research, 4450-208 Matosinhos, Portugal; e) Experimental Pathology and Therapeutics Group, IPO - Instituto Português de Oncologia, R. Dr. António Bernardino de Almeida 865, 4200-072 Porto, Portugal; f) ICBAS - Biomedical Sciences Institute Abel Salazar, Universidade do Porto, R. Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal; g) Department of Biological Sciences, FFUP -Faculdade de Farmácia da Universidade do Porto, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal

# These authors equally contributed to this work; * Corresponding authors
***Email: apalmeira@ff.up.pt; hvasconcelos@ipatimup.pt**

Pancreatic ductal adenocarcinoma (PDAC) is one of the most aggressive cancers worldwide, being the 4th leading cause of cancer-related deaths. This is one of the most challenging cancers to treat, due to drug resistance and lack of alternative treatment [1,2]. The tumor microenvironment, which comprises multiple stromal cells including tumor-associated macrophages, is known to influence PDAC therapy response [3]. Previous work by some of us identified, by proteomic analysis, chitinase 3-like 1 (CHI3L1) as one of the most abundant proteins present in the cargo of extracellular vesicles released by human macrophages, and responsible for PDAC cellular resistance to gemcitabine (GEM) [4]. Therefore, our data suggested CHI3L1 as a putative therapeutic target for PDAC treatment.
The aim of the present work was to: i) confirm that CHI3L1 is a molecular target for PDAC treatment; ii) identify *in silico* inhibitors of CHI3L1 from a DrugBank database; and iii) screen promising identified CHI3L1 inhibitors for growth inhibition effect in PDAC cell lines.
Using human recombinant protein (rh), we confirmed that CHI3L1 induced PDAC cellular resistance to GEM[4] and to the combination treatment of GEM plus paclitaxel, in BxPC3 and PANC1 cell lines. A docking study (AutoDock Vina) using 11,741 molecules from DrugBank database was carried out on CHI3L1 protein (PDB code 1NWU) . This structure-based virtual screening revealed that 568 molecules presented higher affinity towards CHI3L1 than the well-known ligand chitotetraose. Thus, several potential CHI3L1 ligands from known therapeutic classes (such as antibiotics or antivirals) were identified, including pentoxyfilline. We had previously demonstrated that pentoxyfilline, an antifibrotic drug known to inhibit CHI3L1, increased PDAC cellular sensitivity to GEM[4]. Other top ranked known compounds were selected from the molecular docking and tested in several PDAC cell lines. Interestingly, we found a drug previously approved for other diseases which inhibited the growth of BxPC3 and PANC1 cell lines with GI_{50} concentrations of 26 μM and 13.6 μM, respectively
This work highlights the relevance of CHI3L1 as a therapeutic target for PDAC treatment, and the possibility of repurposing pentoxyfilline and other drugs (as off-target inhibitors of CHI3L1) for PDAC treatment. Future work will confirm the PDAC cell growth inhibition effect of other drugs identified in the *in silico* screening.

Acknowledgements: Cristina P. R. Xavier is supported by the Fundação para a Ciência e Tecnologia (FCT) and Fundo Social Europeu (FSE), Portugal, through the post-doc grant SFRH/BPD/122871/2016. This work was funded (in part) by Programa Operacional Regional do Norte and co-funded by European Regional Development Fund under the project "The Porto Comprehensive Cancer Center" with the reference NORTE-01-0145-FEDER-072678 - Consórcio PORTO.CCC – Porto.Comprehensive Cancer Center.

References:
1. Siegel RL, Miller KD, Jemal A. CA Cancer J Clin, **2020**, 70(1), 7-30.
2. Zeng, S., *et al*. Int J Mol Sci **2019**, *20* (18), 4504.
3. Valkenburg, K. C.; de Groot, A. E.; Pienta, K. J. Nat Rev Clin Oncol **2018**, *15* (6), 366-381.
4. Xavier CPR, *et al*. Cancer Letters **2021**, 501, 210-223.

Chemistry in life sciences

Click chemistry approach for the synthesis of new flavonoid derivatives with potential biological activities

D.Pereira[a,b], B.T. Martins[a], M. Pinto[a,b], M. Correia-da-Silva[a,b], H. Cidade[a,b*]

a) Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua de Jorge Viterbo Ferreira nº 228, 4050-313, Porto, Portugal; b) Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR), Universidade do Porto, Terminal de Cruzeiros do Porto de Leixões, Av. General Norton de Matos s/n 4450-208 Matosinhos, Portugal

***Email: hcidade@ff.up.pt**

Natural flavonoids, namely chalcones and flavones, have been extensively reported over the last years for their large diversity of pharmacological activities, being considered as a privileged scaffold for Medicinal Chemistry.[1] In order to obtain analogues with improved potency and/or pharmacokinetic profile, several synthetic strategies have been developed, namely hybridization of flavonoids with 1,2,3-triazole giving rise to new bioactive compounds with a wide range of biological activities.[2] Copper-Catalysed Azide-Alkyne Cycloaddition (CuAAC) between terminal alkynes and azides, commonly referred to as "click chemistry" is one of the most useful reaction for the synthesis of 1,2,3-triazoles.[3] Considering this, a series of chalcone- and flavone-1,2,3-triazole hybrids were obtained through this methodology. The synthesis of chalcones was firstly accomplished by Claisen-Schmidt condensation using appropriate substituted acetophenone and benzaldehydes as building blocks. Flavones were synthesized by Mentzer Pyrone synthesis, in the presence of phloroglucinol and β-ketoesters.[4] Then, flavonoid-1,2,3-triazole hybrids were obtained by click chemistry between propargylated flavonoids and different substituted azides, giving rise to twelve new hybrids with moderate yields. The structure of all synthesized compounds was confirmed by NMR (^{1}H, ^{13}C NMR, HSQC and HMBC) techniques. Biological activities described for triazole-derived compounds, namely antimicrobial and antifungal activities[2] will be explored in the near future.

Acknowledgements: This research was supported by national funds through the FCT—Foundation for Science and Technology under the strategic funding UIDB/04423/2020 and UIDP/04423/2020 (Group of Natural Products and Medicinal Chemistry—CIIMAR) and PTDC/SAU-PUB/28736/2017 (reference POCI-01-0145-FEDER-028736), co-financed by FCT, PORTUGAL2020 COMPETE 2020, through the European Regional Development Fund (ERDF); by the structured program of R&D&I ATLANTIDA (reference NORTE-01-0145-FEDER-000040), supported by the North Portugal Regional Operational Programme (NORTE2020), through the ERDF; and by IINFACTS, grant number CHIRALBIOACTIVE-PI-3RL-IINFACTS-2019 and CHIRALSINTE-SE_APSFCT_IINFACTS_2021. Daniela Pereira acknowledges for her grant (SFRH/BD/147207/2019).

References:

1. Jucá, M.; Filho, F.; Almeida, J.; Mesquita, D.; Barriga, J; Dias, K.; Barbosa, T.; Vasconcelos, L.; Leal, L.; Ribeiro, J.; Vasconcelos, S. *Nat. Prod. Res.*, **2020**, *34*, 692-705.
2. Tome, S.M.; Tome, A.C.; Soengas, R.G.; Silva, A.M.S. *Curr. Org. Chem.*, **2018**, *22*, 1307-1325.
3. Rani, A.; Singh, G.; Singh, A.; Maqbool, U.; Kaur, G.; Singh, J. *RSC Adv.*, **2020**, *10*, 5610.
4. Seijas, J.A.; Vázquez-Tato, M.P.; Carballido-Reboredo, R. *J. Org. Chem.*, **2005**, *70*, 2855-2858.

Chemistry in life sciences

Oligonucleotide-modified AuNPs for the development of rapid tests for detecting single nucleotide polymorphisms

B. Ferreira[a], M.P. Almeida[a], M. Enea[b], A. Dias[b], R. Jurado[b], C. Bernardes[c], O. Flores[c], R. Franco[b], E. Pereira[a]

a) LAQV, REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal; b) UCIBIO, REQUIMTE, Departamento de Química, NOVA School of Science and Technology, 2829-516 Caparica, Portugal; c) STABVIDA, Investigação e Serviços em Ciências Biológicas, Lda., Madan Parque, 2825-182 Caparica, Portugal

Email: up201909165@up.pt

Gold nanoparticles (AuNPs) have distinct chemical, physical and optical properties that make them attractive for biomedical applications, such as biosensing[1]. Localized surface plasmonic resonance (LSPR) is one of the most prominent properties, with AuNPs presenting an absorption peak in the visible region of the electromagnetic spectrum, depending on characteristics such size and shape[2]. Furthermore, AuNPs are easily modified and functionalized with various ligands, without compromising their properties[3].

Nanoprobes for rapid colorimetric detection of single nucleotide polymorphisms (SNP) can be obtained by modifying AuNPs with specific thiolated oligonucleotides. The detection is based on the induced aggregation of nanoprobes with salt, which results in a shift of the LSPR band, changing the color of the nanoprobes solution from red to purple/blue, detectable by the naked eye. The nanoprobes are exposed to target DNA, obtaining different results based on the complementarity between the target DNA and the oligonucleotides on the surface of the AuNPs. In samples without SNP, the target DNA is complementary to the oligonucleotide, protecting the nanoprobes from aggregation, maintaining a red color. In samples with SNP, the complementarity between the target DNA and the oligonucleotide sequence is not complete, leading to a partial aggregation of the nanoprobes, turning into a purple solution (**Figure 1**).

To develop a detection method with high sensitivity and specificity, techniques such as ultraviolet-visible spectrophotometry (UV-Vis), dynamic light scattering (DLS), electrophoretic light scattering (ELS) and nanoparticle tracking analysis (NTA) were used. This last technique has the advantage of detecting aggregation at extremely low concentrations (~10^{-12} M), which can significantly improve the sensitivity of the test.

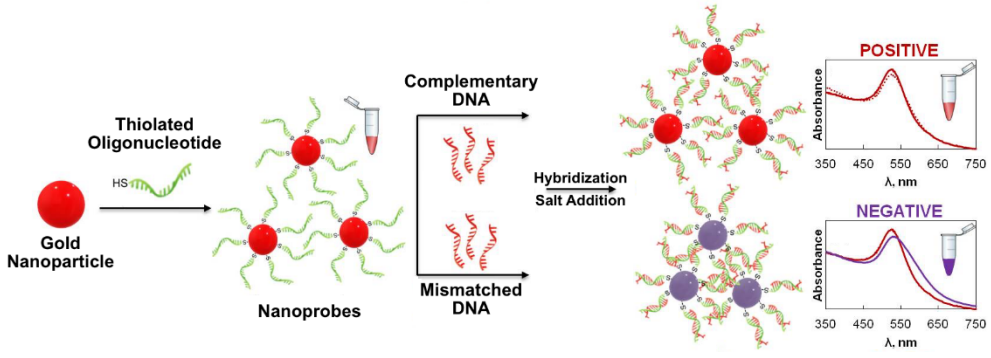


Figure 1: Development of rapid tests for the detection of SNPs with AuNPs modified with thiolated oligonucleotides.

Acknowledgements: This work received financial support from Portuguese national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) and European Union (FEDER funds through COMPETE), through projects UIDB/50006/2020 (LAQV), UIDB/04378/2020 (UCIBIO) and PTDC/NAN-MAT/30589/2017 (NANOMODE).

References:

1. Hwu S.; Garzuel M.; Forró C.; Ihle S.J.; Reichmuth AM; Kurdzesau F, et al. *Colloids Surfaces B Biointerfaces*. **2020**,187, 110650.
2. a) Chen Y.; Xianyu Y.; Jiang X. *Acc Chem Res*. **2017**, *50*, 310–319. b) Zhou W.; Gao X.; Liu D.; Chen X. *Chemical Reviews. American Chemical Society*. **2015**, *115*, 10575–636.
3. Alkilany A.M.; Lohse S.E.; Murphy C.J. *Acc Chem Res*. **2013**, *46*, 650–61.

Chemistry in life sciences

Detection of immunoglobulins by nanoparticle tracking analysis

C. Machado, E. Pereira, M.P. Almeida

LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal

Email: up201805412@up.pt

Currently, the world is living a new reality because of COVID-19. In the future, similar outbreaks can happen. Early diagnosis of people infected is paramount to stop the spread of the virus. For this reason, new efficient, quick and cheap tests are important to mitigate outbreaks like this.[1] Gold nanoparticles are an interesting tool to develop new detection methods, due to their unique physical, chemical, and optical properties.[2]
This work developed model nanobioconjugates (NBCs) between spherical gold nanoparticles, functionalized with 11-mercaptoundecanoic acid (11-MUA) or 4-mercaptobenzoic acid (4-MBA), to bind Protein L. These NBCs were then used to capture IgG immunoglobulins in the media (**Figure 1**). The detection is performed using primarily nanoparticle tracking analysis (NTA), through the increase of hydrodynamic diameter upon binding. NTA is a recent tool for detecting and quantify nanoparticles at very low concentrations (within picomolar range), which revealed to be an advantage for our work. All the results from NTA show there is efficient binding between nanobioconjugates and IgG, which allows its detection.
In the future, this method will be also optimized for the detection of immunoglobulin M (IgM), that will also enable the relative quantification of these two types of immunoglobulins.

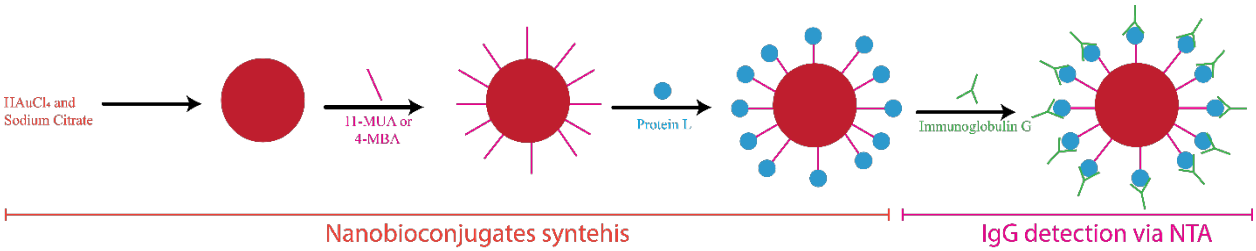


Figure 1: Schematic representation of the synthesis of the nanobioconjugates and respective detection via NTA.

Acknowledgements: This work received financial support from Portuguese national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) and European Union (FEDER funds through COMPETE), through projects UIDB/50006/2020 and PTDC/NAN-MAT/30589/2017 (NANOMODE).

References:

1. Ciotti M, Angeletti S, Minieri M, et al.; *Chemotherapy*. **2020**, *64*, 215-223.
2. a) Khlebtsov NG.; *Anal Chem*. **2008**, *80*, 6620-6625. b) Oliveira MJ, de Almeida MP, Nunes D, et al.; *Nanomaterials*, **2019**, *9*.

Chemistry in life sciences

Antimicrobial studies of a library of diarylpentanoids and their potential in the reversal of antibacterial resistance

F. Durães[a, b, #], J. Moreira [a, b, #], J. Freitas-Silva [b, c], N. Szemerédi [d], P. Martins-da-Costa [b, c], M. Pinto [a, b], E. Pinto [b, e], G. Spengler [d], H. Cidade [a, b], E. Sousa [a, b]

a) Laboratory of Organic and Pharmaceutical Chemistry, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto; b) CIIMAR-Interdisciplinary Centre of Marine and Environmental Research, University of Porto; c) ICBAS – Institute of Biomedical Sciences Abel Salazar, Universidade do Porto; d) Department of Medical Microbiology, Albert Szent-Györgyi Health Center and Faculty of Medicine, University of Szeged; e) Laboratory of Microbiology, Department of Biological Sciences, Faculty of Pharmacy, University of Porto

 # authors contributed equally for this work
Email: esousa@ff.up.pt

The burden of antimicrobial resistance is one of the heaviest of our current society. This arises from the remarkable capability of microorganisms to adapt and develop mechanisms in order to protect themselves from xenobiotics [1]. One of the most notable resistance mechanisms is the overexpression of efflux pumps, which has consequences not only in the decrease of the intracellular concentration of antimicrobials, but also favors the production of biofilm through quorum-sensing, contributing to increased virulence [2]. It is, therefore, imperious that new compounds with ability to revert these resistance mechanisms are discovered.
Diarylpentanoids are a class of compounds structurally related to chalcones, and considered monocarbonyl analogues of curcumin [3]. Considering the previously described potential of chalcones as efflux pump inhibitors [4], a library of forty-five diarylpentanoids was synthesized, in order to investigate their potential as antimicrobial agents and as reversers of antimicrobial resistance.
The compounds were investigated for their antimicrobial activity in susceptible and resistant bacterial and fungal strains. Their potential as resistance inhibitors was accessed through the synergy with antimicrobials and inhibition of efflux pumps in resistant Gram-positive and Gram-negative bacterial strains from the ESKAPE bacteria. The compounds that displayed promising results were also evaluated for their activity in efflux pump-related virulence mechanisms, such as biofilm formation and quorum-sensing, respectively. Finally, the compounds were also tested for their cytotoxicity in a mammalian cell line. The results obtained show the potential of these new compounds as antimicrobial adjuvants, as they were successful in the circumvention of resistance mechanisms.

Acknowledgements: This research was supported by national funds through FCT (Foundation for Science and Technology) within the scope of UIDB/04423/2020, UIDP/04423/2020 (Group of Natural Products and Medicinal Chemistry - CIIMAR), and under the project PTDC/SAU-PUB/28736/2017 (reference POCI-01–0145-FEDER-028736), co-financed by COMPETE 2020, Portugal 2020 and the European Union through the ERDF and by FCT through national funds and structured program of R&D&I ATLANTIDA (NORTE-01-0145-FEDER-000040), supported by NORTE2020, through ERDF, and CHIRALBIO ACTIVE-PI-3RL-IINFACTS-2019. FD and JM thank FCT for their PhD grant (SFRH/BD/114681/2019 and SFRH/BD/135852/2018, respectively).

References:

1. Prestinaci, F.; Pezzotti, P.; Pantosti, A. *Pathog. Glob. Health* **2015**, *109*, 309-318.
2. a) Alav, I.; Sutton, J.M.; Rahman, K.M. *J. Antimicrob. Chemother.* **2018**, *73*, 2003-2020. b) Durães, F.; Resende, D.I.S.P.; Palmeira, A.; Szemerédi, N.; Pinto, M.M.M.; Spengler, G.; Sousa, E. *Antibiotics* **2021**, *10*, 600.
3. Moreira, J.; Saraiva, L.; Pinto, M.M.; Cidade, H. *Eur. J. Med. Chem.* **2020**, *192*, 112177.
4. Durães, F.; Pinto, M.; Sousa, E.. *Curr. Med. Chem.* **2018**, *25*, 6030-6069.

Chemistry in life sciences

Preliminary virtual screening studies to explore the potential of chemical-diverse *in house* families of compounds as inhibitors of SARS-CoV-2

F. Carvalhal,[a,b] A. Palmeira,[a,b] M.H. Vasconcelos,[c,d,e] E. Sousa,[a,b] M. Correia-da-Silva[a,b*]

a) Laboratory of Organic and Pharmaceutical Chemistry/ Department of Chemical Sciences, FFUP - Faculty of Pharmacy, University of Porto, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal; b) Medicinal chemistry: drug discovery and drug design, CIIMAR – Interdisciplinary Centre of Marine and Environmental Research, Terminal de Cruzeiros do Porto de Leixões, Matosinhos, Portugal; c) Cancer Drug Resistance Group, i3S – Instituto de Investigação e Inovação em Saúde, Universidade do Porto, Rua Alfredo Allen 208, 4200-135 Porto, Portugal; d) IPATIMUP - Institute of Molecular Pathology and Immunology of the University of Porto, Rua Júlio Amaral de Carvalho 45, 4200-135 Porto, Portugal; e)Department of Biological Sciences, FFUP - Faculty of Pharmacy of the University of Porto, Rua Jorge de Viterbo Ferreira 228, 4050-313 Porto, Portugal;

***Email: m_correiadasilva@ff.up.pt**

During viral recognition, viruses form a complex with receptors displayed at the surface of host cells, triggering subsequent steps necessary for cellular attachment, infection and viral replication.[1] Therefore, targeting viral recognition and attachment to its cellular receptor is a therapeutic strategy to develop affordable antivirals with broad-spectrum activity. This is particularly relevant given the current viral epidemics and pandemics, such as the Covid-19 caused by the severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2). The cell-surface glucose-regulated protein 78 (GRP78) was identified as an important host target which facilitates the attachment and entry of different viruses into host cells[2]. Recent virtual studies hypothesized that inhibiting the interaction between SARS-CoV-2 Spike protein and cell surface GRP78 could possibly decrease the rate of viral infection, suggesting this host protein as a putative good molecular target to fight SARS-CoV-2 infection.[2]
In our group, several small molecules have been obtained in the last decade and promising hits were discovered particularly with anticoagulant[3], antiviral[4], and antifouling[5] activities. In this work, a docking study of an in-house library of about 300 bioactive compounds synthesized by Grupo de Produtos Naturais e Química Medicinal (CIIMAR/FFUP) was carried out on GRP78 protein (PDB code 5E84), using AutoDock Vina. Virtual screening revealed interaction of approximately 30 compounds with the GRP78 binding pockets. These promising compounds are mainly xanthones and steroids that present bulky, aminated or carboxylated functional groups. Molecular structure and function are the most important considerations to have concerning library diversity. Therefore, this new series of compounds deserves further exploration as potential inhibitors of SARS-CoV-2 infection.

Acknowledgements: This research was supported by national funds through FCT - Foundation for Science and Technology within the scope of UIDB/04423/2020 and UIDP/04423/2020 (CIIMAR). Francisca Carvalhal acknowledges FCT for her PhD grant (Ref. 2020.07873.BD).

References:

1. Aquino R.S. and Park P.W. Front. Biosci. **2016**, 21, 1260-1277.
2. Palmeira, A. et al. Pharmaceuticals **2020**, 13.
3. a) Correia-da-Silva, M., et al. J. Med. Chem. **2011**, 54(1), 95-106. b) Correia-da-Silva, M., et al., J. Med. Chem. **2011**, 54(15), 5373-84. c) Correia-da-Silva, M., et al. Eur. J. Med. Chem. **2011**, 46(6), 2347-58.
4. Lima, R.T., et al. Chem. Biol. Drug Des. **2013**, 81(5), 631-44.
5. a) Almeida, J.R., et al. Sci. Rep. **2017**, 7, 42424. b) Neves, A.R., et al. Ecotoxicology and Environmental Safety. **2020**, 187, 109812.

Chemistry in life sciences

A new diarylpentanoid as potential disruptor of p53-MDM2/MDMX interactions

J. Moreira [a, b], J. Almeida [c], M. Pinto [a, b], L. Saraiva [c], H. Cidade [a, b] *

a) Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Portugal; b) Centro Interdisciplinar de Investigação Marinha e Ambiental (CIIMAR), Universidade do Porto, Portugal; c) LAQV/REQUIMTE, Laboratório de Microbiologia, Departamento de Ciências Biológicas, Faculdade de Farmácia, Universidade do Porto, Portugal

***Email: hcidade@ff.up.pt**

The p53 protein is one of the most important tumor suppressors. In about half of human cancers retaining wild-type (wt) p53, its pathway is inactivated due to the overexpression of endogenous negative regulators, namely murine double minute 2 (MDM2) and X (MDMX). Therefore, the disruption of p53-MDM2/X interactions represent an efficient and selective therapeutic strategy against wt p53-expressing tumors.[1]

Diarylpentanoids are chalcone analogues with two aromatic rings connected by a five carbon bridge. These compounds are described as having several pharmacological properties, being antitumor activity one of the most broadly studied.[2] Although the underlying molecular mechanism by which these compounds suppress cancer cell growth is still unclear, the interference with the p53 pathway has been described.[3, 4] However, the interference with p53-MDM2/X interactions was never explored.

In order to obtain new dual antagonists of p53-MDM2/X interaction, *in silico* studies of a library of diarylpentanoids led us to the identification of potential new MDM2/X ligands. The diarylpentanoids with the best docking scores obeying the druglikeness and ADMET prediction properties were subsequently synthesized and evaluated for their antiproliferative activity on colon cancer HCT116 and fibroblasts HFF-1 cells, being the most potent and selective compounds to HCT116 cells further studied to explore their effect as inhibitors of p53–MDM2/X interactions in yeast-based screening assays. Diarylpentanoid **BP-C4** was identified as potential dual inhibitor. Additionally, in absence of p53 and in breast adenocarcinoma MDA-MB-231 cells expressing a mutant p53 form the growth inhibitory effect was significantly reduced. Furthermore, the growth inhibitory effect of **BP-C4** was associated with induction of cell cycle arrest and apoptosis. Computational docking studies were performed in order to predict docking poses and residues involved in the inhibition of p53-MDM2/X interactions.

Acknowledgments: This research was partially supported by the Strategic Funding UIDB/04423/2020 and UIDP/04423/2020 (Group of Natural Products and Medicinal Chemistry, CIIMAR) and UIDB/50006/2020 (LAQV/REQUIMTE), through national funds provided by the FCT and ERDF, within the framework of the program PT2020 and the project PTDC/SAUPUB/28736/2017. This research was also supported by IINFACTS, grant number CHIRALBIOACTIVE-PI-3RL-IINFACTS-2019 and CHIRALSINTESE_APSFCT_IINFACTS_2021. Joana Moreira and Joana Almeida acknowledges their grants (SFRH/BD/135852/2018 and 2020.05026.BD, respectively).

References:

1. Lemos, A.; Leao, M.; Soares, J.; Palmeira, A.; Pinto, M.; Saraiva, L.; Sousa, M. E. *Med. res. rev.* **2016**, 36, (5), 789-844.

2. Moreira, J.; Saraiva, L.; Pinto,M.M.; Cidade, H. *Eur. J. Med. Chem.*, 2020, 112177.

3. Selvendiran, K.; Tong, L.; Vishwanath, S.; Bratasz, A.; Trigg, N. J.; Kutala, V. K.; Hideg, K.; Kuppusamy, P. *J. Biol. Chem.* **2007,** 282, (39), 28609-28618.

4. Modzelewska, A.; Pettit, C.; Achanta, G.; Davidson, N. E.; Huang, P.; Khan, S. R.. *Bioorg. Med. Chem.* **2006**, 14, (10), 3491-3495.

Chemistry in life sciences

Synthesis of chitosan conjugates with potential as inhibitors of growth of human tumor cell lines

R. Lima [a], M.E. Tiritan [a,b,c], M.M.M. Pinto [a,b], C. Fernandes [a,b*]

a) Laboratório de Química Orgânica e Farmacêutica, Departamento de Ciências Químicas, Faculdade de Farmácia, Universidade do Porto, Rua Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal; b) Centro Interdisciplinar de Investigação Marinho e Ambiental (CIIMAR), Edifício do Terminal de Cruzeiros do Porto de Leixões, Av. General Norton de Matos s/n, 4050-208 Matosinhos, Portugal c) CESPU, Instituto de Investigação e Formação Avançada em Ciências e Tecnologias da Saúde (IINFACTS), Rua Central de Gandra, 1317, 4585-116 Gandra PRD, Portugal

***Email: cfernandes@ff.up.pt**

Polysaccharides have aroused great interest due to their structures, giving them unique properties, such as biocompatibility, biodegradability, and non-toxicity[1]. One example of a polysaccharide with great interest is chitosan, which can be obtained from marine sources. Chitosan proved to have a diversity of applications and biological activities, including antitumor[2,3]. The functional groups present in this molecule allow a wide variety of chemical modifications. In addition, chitosan is also able to undergoing conjugation with other interesting bioactive compounds[3]. Both chemical modifications and conjugation are responsible for improvements in the properties of these compounds, for example in solubility, or in the biological activities, enlarging their applications[3]. Moreover, chitosan oligosaccharides proved to have better solubility and lower viscosity under physiological conditions, compared to polysaccharides, because of shorter chain lengths and free amino groups in D-glucosamine units[1].
In this work, new chitosan conjugates were obtained by reaction between chitosan oligosaccharides and promising small molecules (xanthones), through a Schiff base (**Figure 1**). The total synthesis of xanthone derivatives was also performed. The structure elucidation was established by spectroscopic methods (NMR, and IR). The inhibition of growth of human tumor cell lines of all synthesized chitosan conjugates is being investigated.

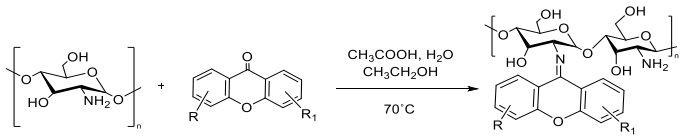


Figure 1. General scheme of synthesis of chitosan conjugates through a Schiff base.

Acknowledgements: This research was supported by national funds by FCT through the projects UIDB/04423/2020 and UIDP/04423/2020 (Group of Natural Products and Medicinal Chemistry - CIIMAR) and ERDF, through the COMPETE-POFC program in the framework of the program PT2020; The Project No. POCI-01-0145-FEDER-028736, co-financed by COMPETE 2020, under the PORTUGAL 2020 Partnership Agreement, through the ERDF; CHIRALBIOACTIVE-PI-3RL-IINFACTS-2019 and CHIRALSINTESE-APSFCT-IINFACTS_2021.

References:

1. Rinaudo, M., Chitin and chitosan: properties and applications. *Progress in polymer science* **2006,** *31* (7), 603-632.
2. Park, J. K.; Chung, M. J.; Choi, H. N.; Park, Y. I. J. I. j. o. m. s., Effects of the molecular weight and the degree of deacetylation of chitosan oligosaccharides on antitumor activity. **2011,** *12* (1), 266-277.
3. Qin, Y.; Li, P., Antimicrobial Chitosan Conjugates: Current Synthetic Strategies and Potential Applications. *International Journal of Molecular Sciences* **2020,** *21* (2), 499.

Chemistry in life sciences

Bis-(thio)barbiturates as promising xanthine oxidase inhibitors for gout treatment

J. L. Serrano[a], D. Lopes[a], P. Almeida[a], S. Silvestre[a,b]

a) CICS-UBI – Health Sciences Research Center University of Beira Interior, Av. Infante D. Henrique, 6200-506 Covilhã, Portugal;
b) CNC – Center for Neuroscience and Cell Biology, University of Coimbra, Rua Larga, 3400-517 Coimbra, Portugal.

Email: joao.serrano@ubi.pt

Overproduction and/or underexcretion of uric acid can lead to hyperuricemia and subsequently to gout. Xanthine Oxidase (XO), a molybdoflavoprotein that catalyses the oxidative hydroxylation of hypoxanthine and xanthine to produce uric acid, is the main target to its treatment. The main drugs used to treat gout are allopurinol and febuxostat; however, these drugs have several adverse effects.[1] Barbituric and thiobarbituric acid derivatives have called the attention of the scientific community due to their wide range of biological activities, in addition to the well-known sedative-hypnotic activities. Recently it was evidenced their interesting anticancer, antiviral, antifungal, antimicrobial and antihyperuricemic effects.[2] Thus, looking for new, alternative, and more potent XO inhibitors with fewer side effects, a series of thirty bis-thiobarbiturates (**Figure 1**) was synthesized in moderate to excellent yields, and their capacity as xanthine oxidase inhibitors was evaluated. After two initial screenings at 30 and 5 μM, the half-maximal inhibitory concentrations were determined for the most potent molecules, which were below of 1 μM. Interestingly, the tested *bis*-thiobarbiturates are near ten times most active than the commercial drug allopurinol. Kinetic studies to identify the XO inhibitory mechanism of these *bis*-thiobarbiturates are now in evaluation in our laboratory.

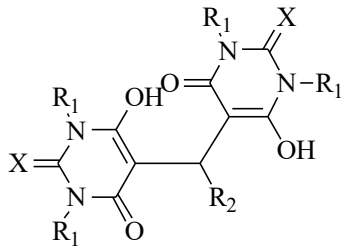


Figure 1: General structure of bis-(thio)barbiturates inhibitors of XO. X is O or S; R_1 is H or ethyl; R_2 is alkenyl, aryl or heteroaryl.

Acknowledgements: This work is supported by funds from the Health Sciences Research Center (CICS-UBI) (UID/Multi/00709/2019) through National Funds by Fundação para a Ciência e Tecnologia (FCT). FEDER funds also support this work through the POCI-COMPETE 2020-Operational Programme Competitiveness and Internationalization in Axis I–Strengthening research, technological development and innovation [Programa Operacional Competitividade e Internacionalização (COMPETE 2020), project No. 007491)]. It is also acknowledged founding from C4- Cloud Computing Competences Center project (CENTRO-01-0145-FEDER-000019). J. L. Serrano acknowledges a doctoral fellowship grant from FCT (SFRH/BD/148028/2019).

References:

1. Serrano, J.L.; Figueiredo, J.; Almeida, P.; Silvestre, S. *Evid. Based Complement Alternat. Med.* **2020**, *2020*, 9531725.
2. Figueiredo, J.; Serrano, J.L.; Cavalheiro, E.; Keurulainen, L.; Yli-Kauhaluoma, J.; Moreira, V.M.; Ferreira, S.; Domingues, F.C.; Silvestre, S.; Almeida, P. *Euro. J. Med. Chem.* **2018**, *143*, 829.

Chemistry in life sciences

Synthesis of novel 1,2,3-triazole *epi*cinchona compounds: applications from organocatalysis to biological activities

A.C. Amorim[a], P. Barrulas[b], E.P. Carreiro[b], P. Rosental[c], O. Lopez[d], A. Puerta[e], J.M. Padrón[e], A.J. Burke[a,b,f]

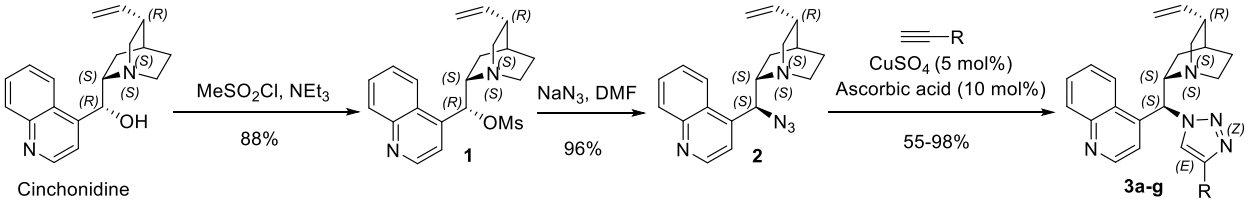
a) Chiratecnics, LDA, PO Box,59, Rossio, Évora,7006-802, Portugal and Polo da Mitra, University of Évora, 7006-554 Évora, Portugal; b) LAQV-REQUIMTE, Institute for Research and Advanced Studies, Universidade de Évora, Rua Romão Ramalho 59, 7000-671 Évora, Portugal; c) *Department of Medicine, University of California, San Francisco, CA 94143, USA;* d) *Departamento de Química Orgánica, Facultad de Química, Universidad de Sevilla, Apartado 1203, E-41071, Seville, Spain;* e) *BioLab, Instituto Universitario de Bio-Orgánica Antonio González (IUBO-AG), Universidad de la Laguna, Apartado 456, E-38200, Spain;* f) *Departamento de química, School of Science and Technology, Universidade de Évora, Rua Romão Ramalho 59, 7000-671 Évora, Portugal.*

Email: anacatarina.amorim@hotmail.com; ajb@uevora.pt

Knowing the large scope of applications that Cinchona alkaloids have in medicine[1] and asymmetric synthesis[2], we prepared a small family of *epi*cinchona-1,2,3-triazole compounds with very good overall yields (49-87%) (**Scheme 1**) via a linear synthesis from commercial cinchonidine.[3]

One of the main goals of this work was to test these compounds as organocatalysts in some benchmark reactions, namely ketamine hydrosilylation, Michael-addition and Biginelli reaction, and understand their catalytic role through catalytic screening and preliminary Density Functional Theory (DFT) mechanistic studies.[3]

Also, since Cinchona alkaloids are known for their multiple biological activities[4], these new compounds were tested against *Plasmodium falciparum* (W2 strain) (antimalarial activity), against *ee*AChE and *eq*BuChE (anticholinesterase activity, Alzheimer's disease) and against six well-known tumor cell lines (anti-proliferative activities, showing a lowest GI_{50} of 11μM). In this last study we observed that none of the compounds were cytotoxic against healthy cell lines (BJ-hTERT). In general, these compounds showed very good predicted pharmacological properties, making this system a good candidate for further exploration.



Scheme 1: Synthetic pathway leading to the new *epi*-cinchonidine-(9)-1,2,3-triazoles.

These results will be discussed in this communication.

Acknowledgements: We thank FCT for funding to LAQV-REQUIMTE through project UIDB/50006/2020.

References:

1. Kurek J. *Alkaloids-Their Importance in Neture and Human life. Intechopen. Ed* **2019**. b) Iftikhar F.; Ali H.; Musharraf S. *RSC Adv.,* **2019**, 9, 17551. c) Thawabteh A.; Juma S.; Sacrano L.; Karaman R. *Toxins* **2019**, 11, 656.
2. Boratyński PJ Zielińska-Błajet M, Skarżewski J. *Cinchona Alkaloids-Derivatives and Applications. Alkaloids Chem Biol.* **2019**, 82:29-145.
3. Barrulas P.; Carreiro E.; Veiros L.; Amorim A.; Gut G.; Rosental P.; Lopez Ó.; Puerta A.; Padrón J.; Fernández-Bolaños J.; Burke A. *Novel 1,2,3-triazole epiCinchonas: Transitioning from OrganoCatalysis to Biological Activities*. Manuscript in revision by Synthetic Communications.
4. Cushnie T.; Cushnie B.; Lamb A. *Int J Antimicrob Agents*. **2014**, 44(5):377-86.

Chemistry in life sciences

Synthesis and biological evaluation of novel quinoline analogues against *T. brucei* and *L. infantum* parasites

A. Lopes,[a] N. Santarém,[b] A.C. Silva,[b,c] M.A. Carvalho[a]

a) Departamento de Química, Centro de Química da Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal; b) Parasite Disease Group, Instituto de Investigação e Inovação na Saúde (I3S), 4200-135 Porto, Portugal; c) Departamento de Ciências Biológicas, Faculdade de Farmácia da Universidade do Porto

Email: pg33722@alunos.uminho.pt

Leishmaniasis and Trypanosomiasis have become a huge threat to health in third world countries. They are considered by the WHO (World Health Organization) as neglected tropical diseases caused by vector borne protozoa.[1] Considering that no vaccine exists the control of these diseases relies on chemotherapy. The available treatment options can be associated with diminished efficacy, serious side effects, and may require hospitalization. Furthermore, treatment failure associated to drug resistance is a growing concern.[2] Therefore, nowadays, the search for new treatment options has become a priority. Quinoline based compounds have been described as new promising compounds with activity against *Leishmania* [3] and *Trypanosoma* [4] parasites.

In our research group we synthesized a set of new quinoline analogues and evaluated their activity against *T. brucei* bloodstream and the promastigote form of *L. infantum.* We also evaluated their cytotoxicity against THP1 cell-line derived macrophages. The new compounds showed hight activity against *T. brucei*, low activity against *L. infantum* promastigotes and low toxicity against THP1 derived macrophages. These new compounds may represent new promising scaffolds for drug development in African Trypanosomiasis, more commonly known as sleeping sickness.

All the results will be presented.

Acknowledgements: The author acknowledges Universidade do Minho and I3S, as well as the National NMR Network (PINFRA/22161/2016) and the "*Fundação para a Ciência e Tecnologia"* (FCT) for financial support: Project n°F-COMP-01-0124-FEDER-022716 (ref. FCT PEst-/QUI/UI0686/2011) FEDER-COMPETE, FCT-Portugal; Project UID/QUI/00686/2018 and PTDC/SAU-PAR/31013/2017-031013

References:

1. a) https://www.who.int/leishmaniasis/burden/en/, (accessed 11/05/2021). b) https://www.who.int/news-room/fact-sheets/detail/trypanosomiasis-human-african-(sleeping-sickness), (accessed 11/05/2021).
2. a) R. Balaña-Fouce, R. Álvarez-Velilla, C. Fernández-Prada, C. García-Estrada, R. M. Reguera, Int. J. *Parasitology: Drugs and Drug Resistance* 4, **2014**, 326–337. b) J. Williamson, *Review of chemotherapeutic and chemoprophylactic agents: The African trypanosomiasis*, **1970**, 125-221. c) S.L. Croft, P. Olliaro, *Clin. Microbiol. Infect*. 17, **2011**, 1478–1483.
3. P. M. Loiseau, S. Gupta, A. Verma, S. Srivastava, S. K. Puri, F. Sliman, M. Normand-Bayle and D. Desmaele, *Antimicrob. Agents Chemother.*, **2011**, 55, 1777–1780.
4. B. Singh, J. A. Bernatchez, L. I. McCall, C. M. Calvet, J. Ackermann, J. M. Souza, D. Thomas, E. M. Silva, K. A. Bachovchin, D. M. Klug, H. B. Jalani, M. J. Buskes, S. E. Leed, N. E. Roncal, E. C. Penn, J. Erath, A. Rodriguez, R. J. Sciotti, R. F. Campbell, J. McKerrow, J. L. Siqueira-Neto, L. Ferrins, and M. P. Pollastri, *ACS Med. Chem. Lett.*, **2020**.

Chemistry in life sciences

Rational design of novel selective PI3K inhibitors for cancer therapy

Lobo V. [a], Castro T.G.[b], Carvalho M.A. [a]

a) Departamento de Química, Centro de Química da Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal;
b) Centro de Engenharia Biológica, Universidade do Minho, Campus de Gualtar, 4710-057, Braga, Portugal.

Email: pg40189@alunos.uminho.pt

Cancer is currently one of the leading causes of death in the world, where the cancer burden is gradually rising[1]. Estimates for 2020 pointed to 19.3 million new cases of cancer and 10.0 million cancer deaths worldwide, and it is predicted that by 2040, the number of new cancer cases per year will likely rise to 29.5 million and the number of cancer-related deaths to 16.4 million[1,2]. Chemotherapy is the most used treatment for the majority of cancer types, being also commonly combined with other treatments, but usually present hight toxicity due to lack of selectivity[3]. Thus, there is a tremendous need for new and effective therapeutic solutions.

A rational approach to develop new anticancer drugs is based in the identification of a biological target involved in the disease. In the literature it is reported that one of the most common events in human cancer is the activation of the PI3K/AKT/mTOR signalling pathway, generally described as a consequence of genetic alterations of pathway members, such as point mutations of PI3K genes or inactivation of PTEN, having a critical role in driving tumour initiation and progression[4,5]. Hence, inhibiting PI3K is an attractive strategy for cancer therapy. Additionally, there is evidence that selective inhibitors for the class I PI3K isoforms lead to toxicity decrease[4].

In the literature there are examples of compounds with selective activity towards the PI3K isoforms having a scaffold similar with that presented in **figure 1**. This scaffold was used as template for the design of new potential selective inhibitors of class I PI3K isoforms. In silico approaches, as molecular docking and molecular dynamics simulations, were applied to allow the identification of the derivatives with the higher affinity towards the biological targets. All the results will be presented.

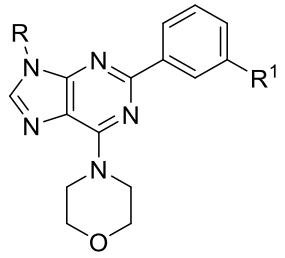


Figure 1: General scaffold of PI3K inhibitors

Acknowledgements: We acknowledge the financial support from University of Minho, Fundação para a Ciênciae a Tecnologia (FCT) and FEDER COMPETE for financial support through Centro de Química (UID/QUI/0686/2016 and UID/QUI/00686/2018.).

References:

1. Gco.iarc.fr. Cancer today. (2021). Available at: https://gco.iarc.fr/today/online-analysis-pie. (Accessed: 23rd January 2021)
2. National Cancer Institute. Cancer Statistics. (2021). Available at: https://www.cancer.gov/about-cancer/understanding/statistics. (Accessed: 23rd January 2021)
3. National Cancer Institute. Cancer Treatment. (2021). Available at: https://www.cancer.gov/about-cancer/treatment. (Accessed: 8th February 2021)
4. Elmenier, F. M., Lasheen, D. S. & Abouzid, K. A. M. Phosphatidylinositol 3 kinase (PI3K) inhibitors as new weapon to combat cancer. Eur. J. Med. Chem. 183, 111718 (2019).
5. Lien, E. C., Dibble, C. C. & Toker, A. PI3K signaling in cancer: beyond AKT. Curr. Opin. Cell Biol. 45, 62–71 (2017).
6. Lobo, V; Castro, T. G.; Carvalho, M.A. Unpublished results.

Chemistry in life sciences

Novel halochromic and antimicrobial azopyrimidine dyes: synthesis, colorimetric studies and biological assays

D. Dantas,[a] A. I. Ribeiro,[b] L. F. Carvalho,[a] E. Pinto,[c,d] F. Cerqueira,[d,e,f] A. Zille,[b] A. Dias[a]

a) Centre of Chemistry of University of Minho (CQ-UM), Departamento de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal; b) Centre for Textile Science and Technology (2C2T), Departamento de Engenharia Têxtil, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal; c) Laboratory of Microbiology, Biological Sciences Department, Faculty of Pharmacy of University of Porto, 4200-135 Porto, Portugal; d) Interdisciplinary Centre of Marine and Environmental Research (CIIMAR/CIMAR), University of Porto, 4450-208 Matosinhos, Portugal; e) FP-ENAS Research Unit, UFP Energy, Environment and Health Research Unit, CEBIMED, Biomedical Research Centre, Fernando Pessoa University, Praça 9 de Abril, 349, 4249-004 Porto, Portugal, and Faculty of Health Sciences, Fernando Pessoa University, Rua Carlos da Maia, 296, 4200-150 Porto, Portugal; f) Molecular Oncology and Viral Pathology GRP - IC, Portuguese Institute of Oncology of Porto (IPO Porto), Rua Dr. António Bernardino de Almeida, 4200-072 PORTO, Porto, Portugal.

Email: ad@quimica.uminho.pt

Halochromism is the occurrence of a color change induced by a pH alteration. The main commercial classes of halochromic dyes are phthalides, triarylmethanes and fluorans, but other minor classes exist including styryl, merocyanines, indophenols and azobenzenes.[1a] The success of azobenzene dyes is due to their structural diversity, high molar extinction coefficient, and fastness properties in relation to light and washing fastness.[1b] Replacing one or both aryls with a heteroaryl offers broader structural diversity.[1c] In addition, the presence of basic sites, as well as H-bonding interactions, further affects the azo chromophore, leading to very different spectral properties. The synthesis of azopyrimidines and azopurines has long been known, and similarity to DNA nucleobases makes them promising candidates for applications in photopharmacology and biocompatible real-time information transmission.

In a recent work, a novel method for the synthesis of a new class of azo-pyrimidines with both halochromic and antimicrobial properties has been developed to obtain compounds with an unusual pattern of substituents in the heteroaryl unity. The new synthetic approach starts from imidazole derivatives that are easily obtained from accessible commercial reagents.[2] Preliminary results had suggested that these imidazole precursors easily evolve in the presence of oxygen leading to the *in situ* formation of highly colored products. These results motivated us to study the reactions of imidazole-based precursors in the presence of oxidants such as silver and copper salts. A very fast reaction occurred leading to azo imidazole intermediates that promptly reacted with secondary amines through a novel and unexpected rearrangement. Deep colored products were obtained, which were identified as azo-pyrimidines on the basis of NMR spectroscopy (including ^{1}H RMN, D_2O shake, ^{13}C RMN, HMQC, HMBC and NOE techniques), mass spectroscopy, ATR-FTIR, melting point and elemental analysis data. Colorimetric studies have been performed by UV-Vis spectroscopy at variable pH values and in different solvents, revealing interesting halochromic properties. The antimicrobial activity of these new azopyrimidine dyes has been also evaluated and highly promising results were obtained. All the results will be presented and discussed.

Acknowledgements: We thank Fundação para a Ciência e a Tecnologia (FCT) for financial support through the Chemistry Research Centre of the University of Minho (UID/QUI/00686/2020) and CIIMAR (UIBD/04423/2020). This work was also supported under the projects MEDCOR (PTDC/CTM-TEX/1213/2020) and UID/CTM/00264/2019, and the PhD grant SFRH/BD/137668/2018.

References:

1. a) Bamfield M. H. *Chromic Phenomena*. RSC Publishing: 2018. 2. Gawale Y.; b) Jadhav A.; Sekar N. *Fibers and Polymers* **2018,** *19* (8), 1678-1686. c) Crespi S.; Simeth N. A.; König B. *Nature Reviews Chemistry* **2019,** *3* (3), 133-146.
2. Ribeiro A. I.; Gabriel C.; Cerqueira F.; Maia M.; Pinto E.; Sousa J. C.; Medeiros R.; Proença M. F.; Dias A. M. *Bioorganic & Medicinal Chemistry Letters* **2014,** *24* (19), 4699-4702.

Chemistry in life sciences

Synthesis and antimicrobial activity of a new class of azoimidazoles

D. Dantas,[a] A.I. Ribeiro,[b] R. Rodrigues,[a] L.F. Carvalho, [a] E. Pinto,[c,d] F. Cerqueira,[d,e,f] D. Geraldo,[a] A. Zille, [b] A. Dias[a]

a) Centre of Chemistry of University of Minho (CQ-UM), Departamento de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal; b) Centre for Textile Science and Technology (2C2T), Departamento de Engenharia Têxtil, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal; c) Laboratory of Microbiology, Biological Sciences Department, Faculty of Pharmacy of University of Porto, 4200-135 Porto, Portugal; d) Interdisciplinary Centre of Marine and Environmental Research (CIIMAR/CIMAR), University of Porto, 4450-208 Matosinhos, Portugal; e) FP-ENAS Research Unit, UFP Energy, Environment and Health Research Unit, CEBIMED, Biomedical Research Centre, Fernando Pessoa University, Praça 9 de Abril, 349, 4249-004 Porto, Portugal .an Faculty of Health Sciences, Fernando Pessoa University, Rua Carlos da Maia, 296, 4200-150 Porto, Portugal; f) Molecular Oncology and Viral Pathology GRP - IC, Portuguese Institute of Oncology of Porto (IPO Porto), Rua Dr. António Bernardino de Almeida, 4200-072 PORTO, Porto, Portugal.

Email: ad@quimica.uminho.pt

The emergence of infectious diseases caused by new pathogens or multidrug-resistant (MDR) strains has been a global health threat over the last decades.[1] These infections are among the most severe healthcare problems and have been associated to several deaths and heavy economic burden per year.[2,3]
The imidazole ring is present in several natural and synthetic molecules with biological activity namely on effective antimicrobial agents, which make it a vital anchor for the development of new therapeutic molecules in this field.[4]
Furthermore, amidrazones are known for their high reactivity thus being useful intermediates for the synthesis of compounds with a wide range of biological activities including antimicrobial. The amidrazone derivatives have been applied in different subjects of chemistry, specifically in the synthesis of azo molecules.[5]
In a previous work, novel imidazole-based 5-aminoimidazole-4-carboxamidrazones were prepared and exhibited potent antimicrobial activity against *C. krusei* and *C. albicans*.[6] Further biological studies to elucidate the action mechanism revealed an interesting relationship between the antimicrobial activity and total intracellular ROS production by the yeasts.[7] As these carboxamidrazones had previously evidenced a particular susceptibility to the presence of oxygen, all of these results combined prompted us to study the reactivity of 5-aminoimidazole-4-carboxamidrazones in the presence of different oxidant and antioxidant agents. Here, we present results of the electrochemical characterization by cyclic voltammetry to elucidate the oxidation mechanism of these compounds, and the results of the attempts performed to oxidize amidrazones in order to obtain the corresponding azoimidazoles. These products were fully characterized by NMR spectroscopy (including 1H RMN, D_2O shake, ^{13}C RMN, HMQC, HMBC and NOE techniques), mass spectroscopy, ATR-FTIR, melting point and elemental analysis.
The antimicrobial activity of these new products has been also evaluated and highly promising results were obtained. All the results will be presented and discussed.

Acknowledgements: We thank Fundação para a Ciência e a Tecnologia (FCT) for financial support through the Chemistry Research Centre of the University of Minho (UID/QUI/00686/2020) and CIIMAR (UIBD/04423/2020). This work was also supported under the projects MEDCOR (PTDC/CTM-TEX/1213/2020) and UID/CTM/00264/2019, and the PhD grant SFRH/BD/137668/2018.

References:

1. Morsy M. A.; Ali E. M.; Kandeel M.; Venugopala K. N.; Nair A. B.; Greish K.; El-Daly M. *Antibiotics* **2020,** *9* (5).
2. van Oosterhout C.; Hall N.; Ly H.; Tyler K. M.. *Virulence* **2021,** *12* (1), 507-508.
3. Pietsch F.; O'Neill A. J.; Ivask A.; Jenssen H.; Inkinen J.; Kahru A.; Ahonen M.; Schreiber F. *Journal of Hospital Infection* **2020,** *106* (1), 115-125.
4. Chopra P. N.; Sahu J. K. *Current Drug Discovery Technologies* **2020,** *17* (5), 574-584.
5. Mazur L.; Sączewski J.; Jarzembska K. N.; Szwarc-Karabyka K.; Paprocka R.; Modzelewska-Banachiewicz B. *Cryst Eng Comm* **2018,** *20* (29), 4179-4193.
6. Ribeiro A. I.; Gabriel C.; Cerqueira F.; Maia M.; Pinto E.; Sousa J. C.; Medeiros R.; Proença M. F.; Dias A. M. *Bioorganic & Medicinal Chemistry Letters* **2014,** *24* (19), 4699-4702.
7. Cerqueira F.; Maia M.; Gabriel C.; Medeiros R.; Cravo S.; Ribeiro A. I.; Dantas D.; Dias A. M.; Saraiva L.; Raimundo L.; Pinto E. *Antibiotics* **2021,** *10* (2).

Chemistry in life sciences

New highly fluorescent nucleobase analogues as biological tools: photophysical studies

S. Pêra,[a] E.M.S. Castanheira,[b] P.J.G. Coutinho,[b] A. Dias[a]

a) Centre of Chemistry of University of Minho (CQ-UM), Departamento de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal; b) Centre of Physics of Minho and Porto Universities (CF-UM-UP), Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

Email: ad@quimica.uminho.pt

Fluorescence DNA-based diagnostic technologies are currently empowering personalized medicine and have been crucial in SARS-Cov-2 detection.[1] As the native nucleobases are non-fluorescent, many fluorescent nucleobase analogues (FNA) have been synthesized in the past two decades and notable examples emerged.[2] Nevertheless, the development of brighter fluorescent purine analogues emitting at long wavelengths (beyond the blue and green spectral regions) is still needed. As the design strategy has mostly involved increasing conjugation, the major challenge is still enhancing fluorescence, while keeping size small to avoid perturbation of DNA structure.

The highly fluorescent adenine analogue 2-aminopurine (2AP), discovered in 1969, is still the most used FNA due to its high brightness, small size and affinity.[3] However, its excitation in the UV region demands for high energy sources endangering living cells, and lack of synthesis efficiency is responsible for its high cost. Despite great advantages, till date, 2AP analogues with optimized and useful photophysical properties are very scarce within the few hundreds of newly synthesized FNA.

In a previous work, highly fluorescent 2AP derivatives were synthesized using novel, simpler, but very efficient synthesis methods.[4] Recently, photophysical measurements and *ab-initio* calculations of quantum chemistry and molecular/ semi-empirical methods have been carried out to understand at a molecular level the photophysical behavior of these purine derivatives. We found that these analogues may be excited with light of $\lambda > 400$ nm and exhibit fluorescence in the blue region with high fluorescence quantum yields and large Stokes' shifts. Fluorescence emission and quantum yields have also shown significant sensitivity to the environment.

These preliminary results demonstrated advantageous photophysical properties over 2AP, making these compounds excellent candidates for the development of new biological and pharmacological tools. The smaller size of our recently synthesized compounds, combined with canonical base pairing and potential binding with enzymes, receptors and transporters, ensures their putative use in biological assays.

Acknowledgements: We thank Fundação para a Ciência e a Tecnologia (FCT) for financial support through the Chemistry Research Centre of the University of Minho (UID/QUI/00686/2020) and CF-UM-UP (UIDB/04650/2020).

References:

1. a) Tsongalis G. J.; Coleman W. B. *Clin. Chim. Acta* **2006**;*363*; 127–37. b) Corman V. M.; Landt O.; Kaiser M.; Molenkamp R.; Meijer A.; Chu D. K. W; et al. Eurosurveillance **2020**; *25*; 1–8.
2. Xu W.; Chan K. M.; Kool E.T. *Nat. Chem*. **2017**; *9*; 1043–55.
3. Wilhelmsson L.M. *Q. Rev. Biophys* **2010**; *43*; 159–83.
4. Senhorães N. and Dias A. *Results not yet published*.

Chemistry in life sciences

Boosting antimicrobial activity of ionic fluoroquinolones by functionalization of mesoporous silica nanoparticles

L. Filipe[a], B. de Mora[a], A. Forte[a], M. M. Santos[a], C. Alves[b], M. R. Carrott[c], L. C. Branco[a], S. Gago[a]

[a]LAQV-REQUIMTE, Dept de Química da Faculdade de Ciências e Tecnologia, Univ. NOVA de Lisboa, Campus da Caparica, 2829-516 Caparica, Portugal; [b]MARE—Marine and Environmental Sciences Centre, Politécnico de Leiria, Avenida Porto de Pesca, 2520-630 Peniche, Portugal; [c]Centro de Química de Évora, LAQV-REQUIMTE, Dept de Química, Escola de Ciências e Tecnologia, Colégio Luís António Verney, Univ. Évora, 7000-671 Évora, Portugal

Email: lm.filipe@campus.fct.unl.pt

The combination of ILs and APIs have been recently reported [1]. This novel API-ILs can improve the original drug performance in terms of its stability, solubility, permeability and delivery [1]. Mesoporous silica nanoparticles (MSNs) offer several advantages to drug formulations, as they can function as antimicrobial agents, while also increasing therapeutic effects, targeted delivery to the site of infection, controlled release that lowers adverse side effects by minimizing non-specific interactions and decreasing the required treatment dose [2]. The development of novel silica nanomaterials based on ionic microbial systems appears as an innovative route for the development of new and more efficient drug delivery systems. Herein, we report the preparation of ionic nanomaterials based on the immobilization of fluoroquinolones such as ciprofloxacin and moxifloxacin in mesoporous silica nanoparticles, either as the counter-ion of the choline derivative cation (MSN-[Ch][Cip]) or via anchoring on the surface of amino-group modified MSNs via an amide bond (MSN-Cip) [3]. All (ionic) nanomaterials have been characterized by TEM, FTIR and solution 1H NMR spectroscopies, elemental analysis, XRD and N2 adsorption at 77 K in order to elucidate the desired structures. The antimicrobial activity of the nanomaterials was determined against Gram-positive (Staphylococcus aureus and Bacillus subtilis) and Gram-negative (Klebsiella pneumoniae) bacteria and the results were promising against S. aureus. In the case of K. pneumonia, they exhibited higher activity than neutral ciprofloxacin. No cytotoxicity from the prepared mesoporous nanoparticles on 3T3 murine fibroblasts was observed.

Figure 1: The most promissory mesoporous silica NPs based Ciprofloxacin

Acknowledgements: The authors also thank Fundação para a Ciência e Tecnologia for the projects PTDC/QUI-QOR/32406/2017, PEst-C/LA0006/2013, RECI/BBBBQB/0230/2012 as well as MAR2020 (MAR-02.01.01-FEAMP-0042–INOVA4AQUA). The NMR spectrometers are part of the National NMR Network (PTNMR) and are partially supported by Infrastructure Project N◦ 022161 (co-financed by FEDER through COMPETE 2020, POCI and PORL and FCT through PIDDAC).

References:

1. a) Marrucho, I.M.; Branco, L.C.; Rebelo, L.P.N. *Annu. Rev. Chem. Biomol. Eng,* **2014**, 5, 527-546. b) Santos, M.M., Alves, C., Silva, J., Florindo, C., Costa, A., Petrovski, Z., Marrucho, I.M., Pedrosa, R., Branco, L.C., *Pharmaceutics* **2020**, 12(8), 694.
2. Zhou, Y.; Quan, G.; Wu, Q.; Zhang, X.; Niu, B.; Wu, B.; Huang, Y.; Pan, X.; Wu, C. *Acta Pharm. Sin. B.* **2018**, 8, 165–177.
3. de Juan Mora, B.; Filipe, L.; Forte, A.; Santos, M.M.; Alves, C.; Teodoro, F.; Pedrosa, R.; Ribeiro Carrott, M.; Branco, L.C.; Gago, S. *Pharmaceutics* **2021**, 13, 218.

Chemistry in life sciences

Evaluation of the potential application of a barbiturate squaraine dye as a fluorescent probe for HSA detection

V.S.D. Gomes,[a,b] R.E.F. Boto,[c] P. Almeida,[c] P.J.G. Coutinho,[d] M.R. Pereira,[d] M.S.T. Gonçalves,[b] L.V. Reis[a]

a) Centre of Chemistry-Vila Real (CQ-VR, Department of Chemistry, University of Trás-os-Montes and Alto Douro, Quinta de Prados, 5001-801, Vila Real, Portugal; b) Centre of Chemistry (CQ-UM), Department of Chemistry, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal; c) Health Sciences Research Centre (CICS-UBI), University of Beira Interior, Av. Infante D. Henrique, 6201-506 Covilhã, Portugal; d) Centre of Physics (CF-UM-UP) / Department of Physics, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal.

Email: v.s.d.gomes@gmail.com

Since its synthesis, first reported in 1965 by Triebs and Jacob, squaraine dyes have been the subject of increasing interest due to their appealing photophysical properties. Features like high molar extinction coefficient, good photochemical stability and good photoconductivity, make this class of compounds a strong candidate in both technological and biological applications[1]. Some published works have demonstrated that squaraine dyes can be used as fluorescent probe in the detection of biomacromolecules, being the search for new compounds for this purpose an emerging area[2].

This work presents the synthesis of an indolenine-derived squaraine dye containing a fraction of dimethylthiobarbituric acid linked to the central four-membered ring (**Figure 1**). After carrying out the respective characterization by the usual techniques, the ability of the dye to be used as a fluorescent probe for the detection of HSA was evaluated. The results demonstrated a strong interaction between HSA and the synthesized dye, and through molecular docking tests it was possible understand the interactions that occur between the dye and the protein under study.

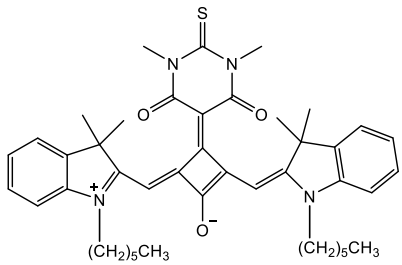


Figure 1: Structural formula of the synthesized and tested squaraine dye.

Acknowledgements: We thank to Portuguese Foundation for Science and Technology and FEDER (European Fund for Regional Development)-COMPETEQREN-EU for financial support to the research centres CQ/UM (UIDB/00686/2020), CQ/VR (UID/QUI/UI0616/2019) and CICSUBI (POCI-01-0145-FEDER-007491), as well as PhD grants to V. S. D. G. (UMINHO/BD/43/2016).

References:

1. a) Treibs A.; Jacob K. *Angew Chem. Int. Ed.* **1965**, *4*, 694. b) Saikiran M.; Sato D.; Pandey S. S.; Kato T. *J. Phys.* **2016**, *704*, 1.
2. a) Martins T. D.; Pacheco M. L.; Boto R. E.; Almeida P.; Farinha J. P. S.; Reis L. V. *Dyes Pigm.* **2017**, *147*, 120. b) Barbero N., Butnarasu C., Visentin S., Barolo C. *Chem Asian J.* **2019**; *14*, 896.

Chemistry in life sciences

Biocompatible excipients to enhance the stability of avian immunoglobulin Y (IgY) antibodies, envisaging their use as biopharmaceuticals

Almeida, C.A.S. [a]; Silva, L.C.V. [a]; Silva, M.C. [a]; Neves, M.C. [a]; Freire, M.G. [a]

a) CICECO- Aveiro Institute of Materials, Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal

Email: ac.almeida@ua.pt

Immunoglobulins, also termed antibodies, are glycoproteins produced by jawed vertebrates, providing them immunity against bacteria, viruses, and other foreign agents[1]. Within the known numerous immunoglobulins classes, avian immunoglobulin Y (IgY), that can be found in the serum of chickens and other egg laying animals and also in egg yolk, is a promising antibody[2].

In contrast to its mammalian analogous immunoglobulin G (IgG), IgY exhibits several advantages, among them high immunogenicity and binding avidity, and the capacity to be recovered by a non-invasive method from egg yolk at high yields[3-5]. The amount of IgY antibodies obtained from an egg is equal to that from 200-300 mL of mammalians blood, being possible for a hen to lay approximately 300 eggs *per* year and to produce 17 to 35 g of total IgY[3,6]. Furthermore, IgY is a polyclonal antibody, being capable to recognize more epitopes on an antigen[4]. As such, IgY is a promising candidate to be engaged in various applications, such as in research, diagnosis, and in the treatment and prophylaxis of several diseases, for instance bacterial infections[3,4]. However, by being proteins present in a complex media such as egg yolk, the use of IgY antibodies as biopharmaceuticals is restricted by their recovery at high yields and high purity, together with their preservation[2].

IgY antibodies were isolated from the yolk of commercial chicken eggs and then purified by two precipitation steps. The purity degree and recovery yields of the obtained IgY antibodies were evaluated by Size Exclusion- High Performance Liquid Chromatography (SEC-HPLC) and dodecyl sulphate polyacrylamide gel electrophoresis (SDS-PAGE), being > 98% and > 85%, respectively. Several carbohydrates and polyols were studied as alternative stabilizers of IgY antibodies. The stability of IgY was evaluated in different storage time, temperature, and pH conditions by several techniques, among them SEC-HPLC and Circular Dichroism Spectroscopy (CD).

Novel bio-based compounds have been identified as promising stabilizers to improve the stability of avian immunoglobulin Y antibodies, paving the way for their usage as excipients in IgY therapeutic formulations.

Acknowledgements:
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the Fundação para a Ciência e Tecnologia/ Ministério da Educação e Ciência (FCT/MEC) and when appropriate co-financed by Fundo Europeu de Desenvolvimento Regional (FEDER) under the PT2020 Partnership Agreement. M.G. Freire acknowledges the European Research Council (ERC) for the Grant ERC-2020-PoC-899921. Márcia C. Neves acknowledges FCT, I.P. for the research contract CEECIND/00383/2017 under the CEEC Individual 2017.

References:

1. Sun, Yi, Zhancai Liu, Liming Ren, Zhiguo Wei, Ping Wang, Ning Li, and Yaofeng Zhao. Journal of Animal Science and Biotechnology. **2012**, 3, 1-5.
2. Kovacs-Nolan, Jennifer, and Yoshinori Mine. Avian and Poultry Biology Reviews. **2004**, 15, 25–46.
3. Pereira, E. P.V., M. F. van Tilburg, E. O.P.T. Florean, and M. I.F. Guedes. International Immunopharmacology**. 2019**, 73, 293–303.
4. Kovacs-Nolan, Jennifer, and Yoshinori Mine. Annual Review of Food Science and Technology. **2012**, 3, 163–82.
5. Zhang, Wei Wei. Drug Discovery Today. **2003**, 8, 364–71.
6. Larsson, Anders, Ros-mari Balow, Tomas L Lindahl, and Per-Olof Forsberg. Poultry Science. **1993**, 72, 1807–12.

Chemistry in life sciences

Surface active ionic liquids based on antimalarial drugs

A.T. Silva,[a] I.S. Oliveira,[b] D.Fontinha,[c] I. Morais,[d] F. Nogueira,[d] M. Prudêncio,[c] C. Teixeira,[a] E.F. Marques,[b] R. Ferraz,[a,e] P. Gomes

a) LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo alegre, 4169-007, Portugal; b) CIQ-UP, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, P-4169-007 Porto, Portugal; c) IMM - Instituto de Medicinal Molecular João Lobo Antunes, Faculdade de Medicina, Universidade de Lisboa, Av. Prof. Egas Moniz, P-1649-028 Lisboa, Portugal; d) GHTM - Global Health and Tropical Medicine, Instituto de Higiene e Medicina Tropical, Universidade Nova de Lisboa, Rua da Junqueira, P-1349-008 Lisboa, Portugal72, Portugal; e) Ciências Químicas e das Biomoléculas / CISA, Escola Superior de Saúde, Politécnico do Porto, Rua Dr. António Bernardino de Almeida, P-4200-072 Porto, Portugal

Email: up201303026@edu.fc.up.pt

Ionic liquids (ILs) derived from classical antimalarials are emerging as a new approach towards the cost-effective rescuing of those drugs. Acid-base combination of basic antimalarial aminoquinolines like primaquine or chloroquine with cinnamic acids was first pursued.[1] This afforded a collection of room-temperature ILs (RTILs) that were active *in vitro* against the liver, blood, and gametocyte stages of *Plasmodium* parasites. Such straightforward re-formulation of primaquine in the form of cinnamate salts, instead of the standard commercial biphosphate, produced new RTILs as triple-stage antimalarial hits that may offer advantageous physico-chemical properties such as improved solubility and. Relevantly, the RTILs had stronger antimalarial activity *in vitro* than their covalent (amide bond *versus* ammonium carboxylate ion pair) analogues and parent drugs.

Encouraged by the above findings, we next produced RTILs based on combination of natural fatty acids with the basic antimalarial drugs primaquine and chloroquine.[2] In most cases, these new compounds exhibited *in vitro* antimalarial activity greater than those of the reference drugs. Moreover, this second generation of antimalarial RTILs showed significant surface activity, hence being classifiable as surface-active ionic liquids (SAILs). We are now working towards a deeper understanding of their interfacial and self-assembling properties, and preliminary results are quite interesting and will be timely communicated.

Overall, these findings can lead to new approaches regarding both antimalarial chemotherapy and therapeutic use of SAILs derived from active pharmaceutical ingredients (APIs). In view of this and on the panoply of recent literature reports on API-derived ILs, these will likely give a significant contribution towards the low-cost recycling of classical drugs that are either shelved or in decline, and not limited to antimalarial agents.

Acknowledgements: We thank to the Fundação para a Ciência e Tecnologia (FCT) for funding our Research Unit LAQV/REQUIMTE (ref. UIDB/50006/2020), and project grant PTDC/BTM-SAL/29786/2017. Thanks are due to FCT for doctoral grants to I.S.O. (SFRH/BD/108629/2015) and to A.T.S. (SFRH/BD/150649/2020).

References:

1. Ferraz R. *et al.*, Rsc Adv. **2016**, 6, 56134. 2. a) Silva A. T. *et al.*, Int. J. Mol. Sci. **2020**, 21, 5334. b) Silva, A. T. *et al.*, Drug-derived surface-active ionic liquids: a cost-effective way to expressively increase blood-stage antimalarial activity of primaquine. – Submmitted.

Chemistry in life sciences

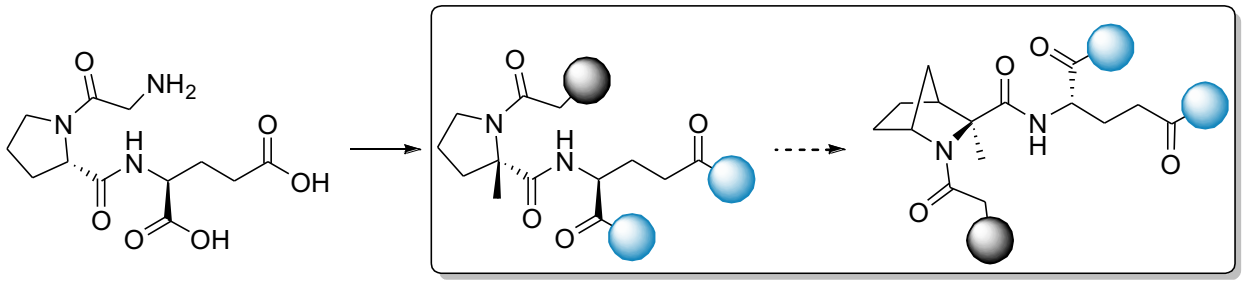
The design of new Trofinetide® conjugates using constrained prolines

S.C. Silva-Reis,[a] I.E. Sampaio-Dias,[a] V.M. Costa,[b] B.L. Pires-Lima,[a] X.C. Correia,[a] H.F. Costa-Almeida,[a] X. García-Mera,[c] J.E. Rodríguez-Borges[a]

a) LAQV/REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Porto, Portugal;
b) UCIBIO, REQUIMTE, Laboratory of Toxicology, Faculty of Pharmacy, University of Porto, Porto, Portugal;
c) Department of Organic Chemistry, Faculty of Pharmacy, University of Santiago de Compostela, Santiago de Compostela, Spain

Email: sarac.silva-reis@hotmail.com

Neurodegenerative diseases (NDs), such as Alzheimer (AD) and Parkinson (PD) diseases, affect millions of people worldwide and consist in the gradual degeneration of the Central Nervous System (CNS) neurons. Since age constitutes a major factor for the onset of these NDs, the continuous rising of life expectancy will increase substantially the impact of these neurological conditions in future societies.[1] In this sense, the scarcity of neuroprotective drugs constitutes a serious problem to fight these NDs.
Therefore, it becomes urgent the development of new neuroprotective therapies to contribute with the strengthening of the clinical response. Glypromate® (Figure 1) is a tripeptide developed by Neuren Pharmaceuticals with the capacity of stimulating the release of acetylcholine and dopamine, however the clinical trials failed due to the low oral absorption and few evidences of its neuroprotective potential in phase III.[2]
Trofinetide®, developed also by Neuren Pharmaceuticals, is a constrained derivative of Glypromate® and promising neuroprotective agent that is currently undergoing clinical trials for Rett and Fragile X syndrome.[3]
This project aims the design, synthesis and biological evaluation of Trofinetide® analogues and conjugates with active pharmaceutical ingredients (APIs). The design of a more constrained Trofinetide® analogues by replacing α-methylproline by a bicyclic system and the conjugation with APIs allows to the development of new neuroprotective hits (Figure 1) with higher metabolic resistance[3] exploring the synergism effect.
All the conjugates will be biologically evaluated to assess their neuroprotection using *in vitro* models of AD and PD.
More information about this project can be found at @NeuroPro_SR twitter account.



Glypromate® **Trofinetide® analogues/conjugates**

Figure 1: Chemical structure of Glypromate® and global structure of Trofinetide® analogues/conjugates.

Acknowledgements: We thank the to Fundação para a Ciência e Tecnologia (FCT, Portugal) for funding our Research Unit (ref. UIDB/50006/2020). SCS-R and IES-D thank FCT for the PhD grant SFRH/BD/147463/2019 and funding through the Individual Call to Scientific Employment Stimulus (Ref. 2020.02311.CEECIND), respectively. VMC acknowledges FCT for her grant (SFRH/BPD/110001/2015 through FCT, I.P:, under the Norma Transitória – DL57/2016/CP1334/CT0006. XG-M thanks Xunta de Galicia for financial funding with references GPC2017/GI-1597 and REDES2017-REGID.

References:

1. WHO, Dementia, **2019**.
2. Alonso De Diego, S. A. et al., Bioorg Med Chem Lett, **2006**, *16*(13), 3396-3400.
3. M. J. Bickerdike et al., J. Neurol. Sci., **2009**, *278*(1), 85-90.

Chemistry in life sciences

Indole alkaloid derivatives as P-glycoprotein inhibitors

Cardoso D.S.P,[a] Spengler G.[b] Mulhovo S,[c] dos Santos J.V.A.D,[a,d] Ferreira M.J.U[a]

a) Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Portugal; b) Department of Medical Microbiology and Immunobiology, Faculty of Medicine, University of Szeged, Hungary. c) Centro de Estudos Moçambicanos e de Etnociências (CEMEC), Faculdade de Ciências Naturais e Matemática, Universidade Pedagógica, Moçambique d) LAQV@REQUIMTE/Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal.

Email: davidpcardoso@ff.ulisboa.pt

Multidrug resistance (MDR) has been considered one of the major hurdles for successful chemotherapy in cancer. It is characterized by the development of resistance by cancer cells to drugs that are structurally unrelated and with distinct targets. The most significant mechanism of MDR is due to the overexpression of transmembrane transporter proteins of the ATP-binding cassette (ABC) superfamily, which act as efflux pumps for chemotherapeutic agents, decreasing their intracellular concentration. One of the most implicated ABC transporter proteins is P-glycoprotein (P-gp), which plays a key role on MDR.

Aiming at optimizing monoterpene indole alkaloids for their MDR reversing activity in cancer[1], two major alkaloids, isolated from Tabernaemontana elegans, were derivatized by alkylation of the indole nitrogen. Twenty-six new derivatives were prepared. Their MDR reversal ability was assessed, using as models resistant human colon adenocarcinoma and human ABCB1-gene transfected L5178Y mouse lymphoma cells, overexpressing ABCB1. A noteworthy increase of activity was found for most of the derivatives, being the strongest ABCB1 inhibitors those having *N*-phenethyl moieties, exhibiting strong inhibitory activity concomitant with weak cytotoxicity. Furthermore, in combination assays, most of the compounds have shown strong synergistic interactions with doxorubicin, substantiating their potential as MDR reversers.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support (PTDC/MED-QUI/30591/2017, FCT/NKFIH, and PhD grant PD/BD/135291/2017).

References:

1. Paterna A.; Kincses A.; Spengler G.; Mulhovo S.; Molnár J.; Ferreira M.J.U. *Eur. J. Med. Chem*. 2017, **128**, 247–257.
2. Cardoso D.S.P.; Kincses A.; Nové M.; Spengler G.; Mulhovo S.; Aires-de-Sousa J.; dos Santos DJVA; Ferreira M.J.U. *Eur. J. Med. Chem*. **2020**, *210*, 112985.

Chemistry in life sciences

The boron hot-spot methodology: peptide functionalization

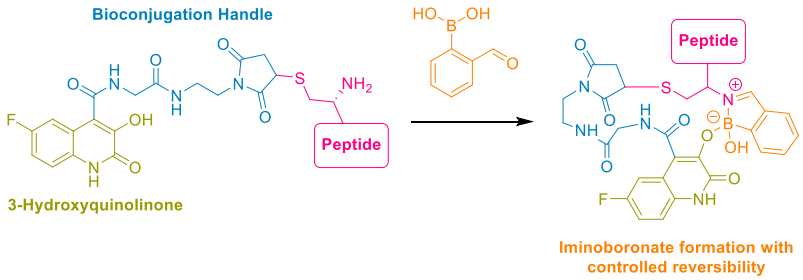
R. Padanha[a], R. Russo[a], P.M.P. Gois[a]

a) Research Institute for Medicines (iMed.ULisboa), Faculty of Pharmacy, Universidade de Lisboa, Lisbon, Portugal

Email: ritapadanha@gmail.com

Bioconjugation strategies allow the combination of biomolecules and a variety of payloads with different properties. Recently, several bioconjugates reached the market as therapeutics with high-specific targeting capacity. [1] While most of these strategies relies on the formation of stable constructs under complex physiological conditions, stimuli-responsive constructs are being developed to be applied in drug delivery and live-cell imaging. [1,2] Boronic acids (BA) can be explored as a molecular construction tool due to their ability to establish reversible covalent bonds with vicinal/nitrogen nucleophiles. [1,3]

Here, we developed a "boron hot-spot" (BHS) with the ability to be installed specifically on *N*-terminal cysteines (Cys) of peptides chains. The BHS is composed by a bioconjugation handle and a 3-hydroxyquinolinone heterocicle (3HQ) that stabilizes the formation of iminoboronates in the presence of the boronic acid. **(Scheme 1).** The incubation of the BHS-Cys with 2-formylbenzeneboronic acid (2-FBBA) in ammonium acetate solution (20 mM, pH 7.0) afforded the desired imine within 2h at 37 °C. Electrospray ionization mass spectrometry (ESI-MS) studies were performed, showing the compatibility of the BHS with different amino acid side chains and competing functionalities. Installed in more complex peptides (c-Ovalbumin and RGD), the BHS favors the N-terminal iminoboronate over the formation of in-chain iminoboronates. Exhibiting an *N*-terminal and an in-chain Cys residue, RGD was used to install two BHS, but only the *N*-terminal modification promoted the assembly with 2-FBBA. The resulting iminoboronates showed to be stable in ammonium acetate solution at pH 7 and 4.5 or in the presence of bovin serum albumin (BSA), although in the presence of glutathione they showed to be reversible.



Scheme 1. BHS Methodology

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support (UID/QUI/00100/2013 and PTDC/QEQ-QOR/1434/2014).

References:

[1] António, J. P. M.; Russo, R.; Carvalho, C. P.; Cal, P. M. S. D., Chem. Soc. Rev., 2019, 48, 3513.
[2] Koniev, O.; Wagner, A. Chem. Soc. Rev. 2015, 44 (15), 5495–5551.
[3] Boutureira, O.; Bernardes, G. J. L. Chem. Rev. 2015, 115 (5), 2174–2195

Chemistry in life sciences

Metal ion-zeolite nanomaterials for chemodynamic therapy

Ferreira SDC[a], Carvalho VMC[a], Bertão AR[a,b,c], Rodrigues FC[a,d], Oliveira RD[d], Fonseca AM[a,e], Almeida-Aguiar C[d,e,f,g], Baltazar F[b,c], Neves IC[a,e]

a) CQUM, Centre of Chemistry, Chemistry Department, University of Minho, Campus de Gualtar, 4710-057, Braga, Portugal; b) Life and Health Sciences Research Institute (ICVS), School of Medicine, University of Minho, 4710-057 Braga, Portugal; c) ICVS/3B's - PT Government Associate Laboratory, Braga/Guimarães, Portugal; d) Department of Biology, University of Minho, Campus de Gualtar, 4710-057, Braga Portugal; e) CEB - Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal; f) CITAB, Centre for the Research and Technology of Agro-Environmental and Biological Sciences, University of Minho, Campus de Gualtar, 4710-057, Braga, Portugal; g) CBMA - Centre of Molecular and Environmental Biology, University of Minho, Campus de Gualtar, 4710-057, Braga, Portugal;

Email: a87548@alunos.uminho.pt

A new therapeutic approach called chemodynamic therapy (CDT), which can be defined as specific $^{\bullet}OH$ generation in cancer cells via Fenton reactions, was recently proposed.[1] The advantages of CDT can be ascribed to the higher specificity, no external field penetration depth restriction, lower side effects in normal tissues, higher-level ROS generation, lack of equipment restrictions, and non-multidrug resistance, showing the promising future of CDT for clinical translation.[1] The varied and highly controlled structural along with the chemical properties of inorganic nanomaterials, like zeolites, make them suitable for this type of CDT. Zeolites already proved to be interesting candidates for medical and healthcare applications,[2] and also as Fenton heterogeneous catalysts for organic degradation.[3] The aim of this study was to assess the dual activity (antibacterial and anticancer) of metal ion-zeolite nanomaterials. The prepared metal ion-zeolite nanomaterials were tested *in vitro* using a human skin cancer cell line, A375, and the anti-bacterial activity was evaluated against *Escherichia coli*, *Staphylococcus aureus* and MRSA. Results obtained so far suggest that metal ion-zeolite nanomaterials could be explored as antibacterial and/or anticancer agents.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support through Centre of Chemistry (UID/QUI/00686/2013 and UID/QUI/0686/2016) and BioTecNorte (operation NORTE-01-0145-FEDER-000004).

References:

1. Tang, Z. et al, *Chem. Rev.*, **2021,** 121, 1981.
2. a) Vilaça, N. et al., *Materials Science & Engineering C*, **2021**, 120, 111. b) Ferreira, L. et al., *Colloids and Surfaces B: Biointerfaces*, **2016**, 142, 141.
3. Santos, B.L.C. et al., *Catalysts*, **2021**, 11, 32, 1.

Chemistry in life sciences

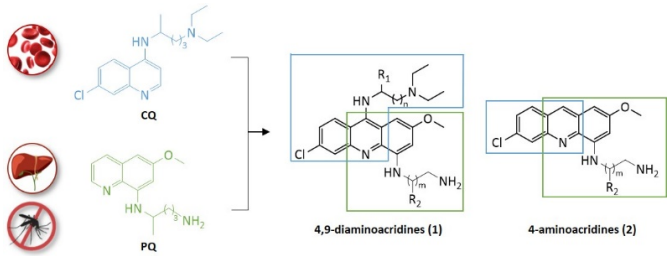
4,9-Diaminoacridines and 4-aminoacridines as dual-stage antiplasmodial hits

M. Fonte[a,*], N. Tassi[a,*], D. Fontinha[b], I. Bouzón[c], R. Ferraz[a,d], M.J. Araújo[a], X. Fernàndez-Busquets[c,e,f], M. Prudêncio[b], P. Gomes[a], C.Teixeira[a]

a) LAQV-REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Portugal; b) Instituto de Medicina Molecular, Faculdade de Medicina, Universidade de Lisboa, Portugal; c) Nanomalaria Group, Institute for Bioengineering of Catalonia (IBEC), The Barcelona Institute of Science and Technology, Spain; d) Ciências Químicas e das Biomoléculas, Escola Superior de Saúde, Politécnico do Porto, Portugal; e) Barcelona Institute for Global Health (ISGlobal), Barcelona Center for International Health Research (CRESIB), Hospital Clínic-Universitat de Barcelona, Spain; f) Nanoscience and Nanotechnology Institute (IN2UB), University of Barcelona, Spain. * The authors contributed equally to this work.

Email: up201305020@edu.fc.up.pt

The eradication of malaria remains to be achieved, partly due to the emergence of parasite resistance to all antimalarial drugs used in clinic over the years. Multi-stage drugs have been prioritized in antimalarial drug discovery, since by targeting more than one process in the *Plasmodium* life cycle may increase efficiency, while decreasing the chances of emergence of resistance by the parasite. Quinacrine (QN) was the first synthetic blood schizonticide antimalarial drug, but its serious adverse effects led to its quickly replacement by chloroquine (CQ), whose efficiency, bioavailability, and safety were much superior. Interestingly, "dissection" of the QN structure reveals its acridine moiety as a "fusion" between CQ and the heterocycle core of primaquine (PQ), another well-known antimalarial drug active against all liver forms of the parasite, and gametocytes. One cost effective strategy to accelerate development of new antimalarials is to recycle classical pharmacophores.[1] In this context, we report the chemical synthesis and *in vitro* assessment of two new families (**Scheme 1**) which correspond to the fusion of (i) CQ and PQ (**4,9-diaminoacridines (1)**), and (ii) CQ and the heterocycle core of PQ (**4-aminoacridines (2)**). All the synthesized compounds were evaluated *in vitro* for their a) activity against erythrocytic forms of *P. falciparum* (CQ-sensitive 3D7, and CQ-resistant W2 strains), b) activity against liver-stages of *P. berghei*, and c) cytotoxicity towards human hepatocellular carcinoma (Huh7) cells. The results obtained were very promising, since the derivatives were able to retain the antimalarial activity of the parent compounds, i.e., active against the blood-stage, as in CQ and QN, as well as against liver forms, similarly to PQ.[2, 3]



Scheme 1: Chemical structure of the two families developed in this work: **4,9-diaminoacriidnes (1)** and **4-aminoacridines (2)**, which are the fusion of the two emblematic antimalarial drugs primaquine **(PQ)** and chloroquine (**CQ)**.

Acknowledgements: This work was developed within the scope of projects UIDB/50006/2020, PTDC/BTM-SAL/29786/2017 and PTDC/SAU-INF/29550/2017, financed by national funds through the Fundação para a Ciência e Tecnologia (FCT). MF thanks the FCT for the doctoral grant SFRH/BD/147345/2019.

References:

1. Teixeira, C. *et al. Chem Rev.* **2014**, *114*, 11164-11220. 2. Fonte, M. *et al. Tetrahedron Lett.*, **2019**, *60*, 1166-1169. 3. Fonte, M. *et al. ChemMedChem*, **2021**, *16*, 788.

Chemistry in life sciences

First insights into the ability of silver camphorimine complexes to functionalize PCL coatings with anti-*Candida* activity

J.P. Costa[a], M.J.F. Pinheiro[b], M.M. Alves[a], N.P. Mira[b], M.F.N.N. Carvalho[a]

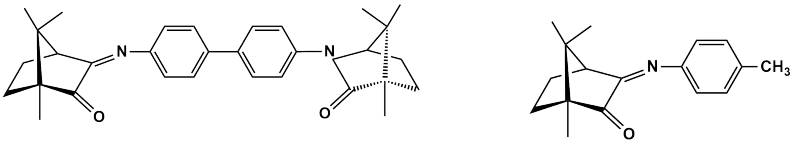
[a]CQE Instituto Superior Técnico, Departamento de Engenharia Química, Universidade de Lisboa, Portugal; [b]iBB, Instituto de Bioengenharia e Biociências, Instituto Superior Técnico, Departamento de Bioengenharia, Universidade de Lisboa, Portugal

Email: joanavcosta@tecnico.ulisboa.pt

The fungi belonging to the *Candida* genus are commensals of the human microbiome, however, when the immune system of the host is compromise these yeasts can overgrow causing severe infections which are difficult to treat specially because some *Candida* spp (such as C. glabrata, C. auris or C. krusei) can rapidly acquire resistance to the antifungals in use. Therefore, new molecules with antifungal activity, in particular acting through mechanisms different from the antifungals in clinical use, are needed to counteract the emergence of resistant *Candida* stains. Complexes are feasible alternatives due to the specific characteristics of the metal that may prompt mechanisms of action different from those of the currently used organic molecules.

In order to search for their antimicrobial activity, several silver camphorimine complexes of general formula $[Ag(NO)_3L]$ were synthesized and assessed for anti-*Candida* activity. Several complexes showed outstanding activity towards *C. glabrata*, *C. parapsilosis* and *C. tropicalis* (MIC values as low as 2 μg/mL)[1] while they had no activity towards *C. albicans*. Such drawback was overcome through the redesign of the complexes keeping the camphorimine skeleton and modifying the anionic co-ligand. The new complexes [Ag(OH)L] and $[(AgL)_2(\mu\text{-}O)]$ showed high activity against *C. albicans* while preserving or even enhancing the activity towards *C. glabrata*.[2,3]

A step forward is now reported concerning the ability of the silver camphorimine complexes to functionalize polymer coatings with antifungal and antibiofilm activities. First results show that complexes $[Ag(NO)_3L]$ ($L=OC_{10}H_{14}N(C_6H_4)_2C_{10}H_{14}O$, P) and $[(AgL)_2(\mu\text{-}O)]$ ($L= OC_{10}H_{14}NC_6H_4CH_3$-4, Q, **Figure 1**) efficiently embedded in a PCL coating, prevent colonization by *C. albicans* and inhibit microfilm formation.



$L=OC_{10}H_{14}N(C_6H_4)_2C_{10}H_{14}O$, $L= OC_{10}H_{14}NC_6H_4CH_3$-4

Figure 1 Camphor imine ligands used in the design of complexes P (left) and Q (right)

Such results encourage further studies to design materials that combine the properties of prosthesis and surgical instruments with new antimicrobial properties to overcome the increasing microbial resistance.

Acknowledgements We acknowledge Financial support by FCT -Fundação para a Ciência e a Tecnologia through projects UIDB/0100/2020 and UID/BIO/04565/2020 and Grant to Joana Costa (BL-CQE/2018-013).

References

1 Cardoso J.M.S; Guerreiro S.I; Lourenço A.; Alves M.M; Montemor M.F.; Mira N.P.; Leitão J.H.; Carvalho M.F.N.N. PLoS ONE, **2017**. *12*(5): e0177355.

2 Costa J.P; Pinheiro M.J.F; Sousa, S.A; Botelho do Rego A.M; Marques F; Oliveira M.C; Leitão J.H; Mira N; Carvalho M.F.N.N. Antibiotics **2019**, *8*, 144.

3 Leitão, J.H.; Sousa, S. A.; Leite, S.A.; Carvalho, M.F.N.N. Antibiotics, 2018, 7, 65-76.

Chemistry in life sciences

Electrochemical cyanation of quinolizidine alkaloids

R.M. Durão[1], J.A.S. Coelho[2], S.P. Simeonov[1], C.A.M. Afonso[1]

[1]*Instituto de Investigação do Medicamento (iMed.ULisboa), Faculty of Pharmacy, University of Lisbon, Av. Prof. Gama Pinto, 1649-003 Lisboa, Portugal;* [2]*Centro de Química Estrutural, Faculty of Sciences, University of Lisbon, Campo Grande, 1749-016 Lisboa, Portugal*

Email: raquel-durao@campus.ul.pt

Quinolizidine alkaloids (QAs) are largely abundant in the *Leguminosae* family[1], especially in the genera *Lupinus*, namely in the *Lupinus albus L* species.[2] In our team we developed a process for the preparation of lupanine and sparteine by extraction from *Lupinus albus* seeds wastewater.[3] These natural products are known for their pharmacological activities, which includes antimicrobial, antihypertensive, antimuscarinic and antidiabetic, as hyperglycemia agents, effects on the central nervous system and uses in asymmetric organic synthesis.[4] Based on the potential added value of QA derivatives, we explored the selective functionalization of QAs using electrochemistry. This modern electrochemical process offers an efficient and greener alternative to conventional oxidation/reduction procedures.[5] Herein we present an electrochemical cyanation methodology for the selective C-H activation of QAs such as lupanine (**Figure 1**), including reaction conditions optimization and solutions for issues found during development.

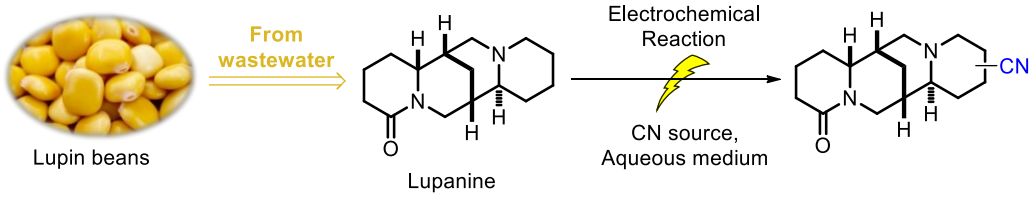


Figure 1: Electrochemical cyanation methodology.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support (Ref. 2020.06352.BD, UIDB/04138/2020 and UIDP/04138/2020) and COMPETE Programme (SAICTPAC/0019/2015). The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 951996.

References

1. Kolanoś, R., Wysocka, W. & Brukwicki, T. A comparative study of NMR chemical shifts of sparteine thiolactams and lactams. *Tetrahedron* **59,** 5531–5537 (2003).
2. Bunsupa, S., Yamazaki, M. & Saito, K. Quinolizidine alkaloid biosynthesis: Recent advances and future prospects. *Front. Plant Sci.* **3,** 1–7 (2012).
3. N. Maulide, B. Peng, C. A. M. Afonso, R. F. M. Frade. Process for converting lupanine into sparteine, EP2808326A1; WO2014191261A1; 3-12-2013.
4. (a) Pothier, J., Cheav, S. L., Galand, N., Dormeau, C. & Viel, C. A comparative study of the effects of sparteine, lupanine and lupin extract on the central nervous system of the mouse. *J. Pharm. Pharmacol.* **50,** 949–954 (1998). (b) Romeo, F. V. *et al.* Characterization and antimicrobial activity of alkaloid extracts from seeds of different genotypes of Lupinus spp. *Sustain.* **10,** 6–10 (2018). (c) Wiedemann, M. *et al.* Lupanine improves glucose homeostasis by influencing KATP channels and insulin gene expression. *Molecules* **20,** 19085–19100 (2015). (d) Carmalia, S., Alves, V. D., Coelhoso, I. M., Ferreira, L. M. & Lourenço, A. M. Recovery of lupanine from Lupinus albus L. leaching waters. *Sep. Purif. Technol.* **74,** 38–43 (2010).
5. Folgueiras-Amador, A. A., Philipps, K., Guilbaud, S., Poelakker, J. & Wirth, T. An Easy-to-Machine Electrochemical Flow Microreactor: Efficient Synthesis of Isoindolinone and Flow Functionalization. *Angew. Chemie - Int. Ed.* **56,** 15446–15450 (2017).

Materials chemistry and applications

Phase transition studies of 5-methyl-1*H*-benzotriazole

A.C.M.O. Lima, A.L.R. Silva, M.D.M.C. Ribeiro da Silva

Centro de Investigação em Química, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, P-4169-007, Porto, Portugal

E-mail: ana.lima@fc.up.pt

Benzotriazole and its derivatives are commonly used in industrial applications due to their corrosion inhibiting capability on metals.[1,2] Also, these compounds present versatile biological properties, such as antimicrobial, antiparasitic, and even antitumor agents,[3] in which the knowledge of the corresponding stability is relevant for further studies.

The thermodynamic properties of these compounds are not well established and we are involved in a project aiming the determination of thermochemical and thermophysical properties of benzotriazoles.

In this context, the present work reports an energetic study of 5-methyl-1*H*-benzotriazole (**Figure 1**), involving the measurement of the sublimation enthalpy of this compound by high temperature Calvet microcalorimetry and Knudsen effusion method. The fusion enthalpy has been also determined from differential scanning calorimetry.

The results obtained in this work will be analysed comparing their consistency, as well as by comparison with other data available in the literature.[4]

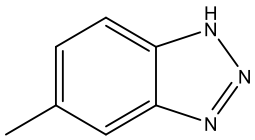


Figure 1 - Molecular structure of 5-methyl -1*H*-benzotriazole.

Acknowledgements: Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Porto, Portugal for the financial support to Project UIDB/00081/2020. Ana C.M.O. Lima thanks FCT for the doctoral grant 2020.08577.BD. Ana L.R. Silva thanks FCT/MCTES for her contract under Stimulus of Scientific Employment 2017 (CEECIND/01161/2017)

References:

1. Yan-fei BIAN, Wen-jie ZHAI, Bao-quan ZHU, *Trans. Nonferrous Met. Soc. China* **2013**, 23, 2431−2438
2. Jinwei Liu, Liang Jiang, Hanqiang Wu, Ting Zhao, Linmao Qian, *J. Electrochem. Soc.* **2020**, 167, 13
3. I. Briguglio, S. Piras, P. Corona, E. Gavini, M. Nieddu, G. Boatto, A. Carta, Eur. J. Med. Chem. **2015**, 97, 612-648
4. P. Jimenez, M.V. Roux, C. Turrion, *J. Chem. Thermodyn.* **1989**, 21, 759-764

Materials chemistry and applications

Hybrid sol-gel materials doped with AgY and NaY Zeolites

B.R. Gomes,[a] R.F.P. Pereira,[a] S.C. Nunes,[b] A.M. Fonseca,[a,d] I.C. Neves,[a,d] R.B. Figueira[a,c]

a) CQUM, Centre of Chemistry, Chemistry Department, University of Minho, Campus de Gualtar, 4710-057, Braga, Portugal; b) FibEnTech - Fiber Materials and Environmental Technologies, University of Beira Interior, Covilhã, Portugal; c) Presently at Vasco da Gama CoLAB, Rua Roberto Frias, 4200-465 Porto, Portugal; d) CEB - Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

E-mail: rita.figueira@vgcolab.com

The sol-gel process is a chemical synthesis often considered as a green technology due to mild conditions preparation since is waste-free and the processing temperature is generally low (*e.g.*, close to room temperature). Also, uses compounds that do not introduce impurities into the end material and excludes the washing stage. Compared to other chemical routes, sol-gel method has several advantages in the design and synthesis of organic-inorganic hybrid (OIH) materials.[1] This method allows the control of several experimental conditions leading to a simple sequence, which may be tuned to the nature, final shape, and according to a desired function. This route allows to obtain end products with high specific porosity and surface area which favours the introduction of material's complementary functionalities, such as UV protection, anti-fouling, anti-reflection, moisture resistance, corrosion and adhesion protection. Moreover, the low synthesis temperatures minimize the thermal volatilization and degradation of the entrapped species. Therefore, the introduction of supplementary functionalities together with the enhancement of the mechanical, thermal, and optical properties, opens a wide range of applications in numerous fields of science.

This work reports the synthesis of OIH sol-gel matrices, which were obtained using a functionalized siloxane, 3-glycidoxypropyltrimethoxysilane, by reaction with an oligopolymer named Jeffamine®THF 170.[2] The OIH matrices were doped with different contents of AgY or NaY zeolites (*i.e.*, 1, 3 and 5 wt%). The doped and undoped OIH matrices were characterized by different techniques namely Fourier-transform infrared spectroscopy, electrochemical impedance spectroscopy analysis, X-ray diffraction spectroscopy and scanning electron microscopy. Results obtained so far suggest that the introduction of AY or NaY enhance the stability of the hybrid sol-gel materials and could be explored as sensors.

Acknowledgements: This research was funded by Operational Program Competitiveness and Internationalization (COMPETE 2020), the Lisbon Regional Operational Program (in its FEDER component), and by Foundation for Science and Technology (FCT), grant reference POCI-01-0145-FEDER-031220. The support of Centro de Química-UM through FCT project UID/QUI/00686/2019 is also acknowledged and BioTecNorte (operation NORTE-01-0145-FEDER-000004).

References:

1. Figueira R.B., Silva, C. J. R., in *Hybrid Organic-Inorganic Interfaces*, John Wiley & Sons, Ltd, **2017**, pp. 355–412.
2. Gomes, B.R., Figueira, R.B., Costa, S.P.G., Raposo, M.M.M., Silva, C.J.R., *Polymers*, **2020**, 12, 2671.

Materials chemistry and applications

Pyranoflavylium salt incorporated in cellulose acetate films with glycerol as colorimetric pH-sensors for food packaging applications

V. Gomes, A.S. Pires, N. Mateus, V. de Freitas, L. Cruz

REQUIMTE/LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua Do Campo Alegre, 687, 4169-007, Porto, Portugal

Email: luis.cruz@fc.up.pt

Anthocyanins are natural pigments found in many fruits and vegetables that have been widely studied for application in smart food packaging as a color sensor due to their ability to change color by pH. This property is very suitable for monitoring the freshness of perishable food products (e.g., meat, fish) in real time, and consequently, increasing the shelf-life of these products as well as the food safety for the consumer.[1] However, these natural pigments have a complex multi-state equilibrium that leads to color fading over time[2], which is a limitation for their application as pH-indicators. In this work, a bio-inspired anthocyanin-type pigment, namely a pyranoflavylium salt represented in figure 1a, was synthesized and its color properties with pH variation were studied.[3] The pigment (0.1 – 0.2% (w/w)) was immobilized in cellulose acetate films (8% (w/w) in acetone) with incorporation of different percentages of glycerol (0 – 40% (w/w)) as a plasticizer. The films were prepared by the casting method and their characterization, namely, the thickness, thermogravimetric analysis (TGA), scanning electron microscope (SEM), water vapor permeability (WVP) is ongoing. The functional properties of the films were tested in solutions at different pH values (between 4 to 8) (figure 1b). The results showed that the films without glycerol do not change their color when exposed at different pH environments. On the other hand, the incorporation of glycerol above 20 % (w/w) demonstrated an effective pH-responsiveness after 30 min of immersion (figure 1b shows a noteworthy response for 30 % (w/w) of glycerol). The glycerol-based films showed relevant and remarkable color change at the pH range of food spoilage indicating a great potential for application as food freshness sensor.

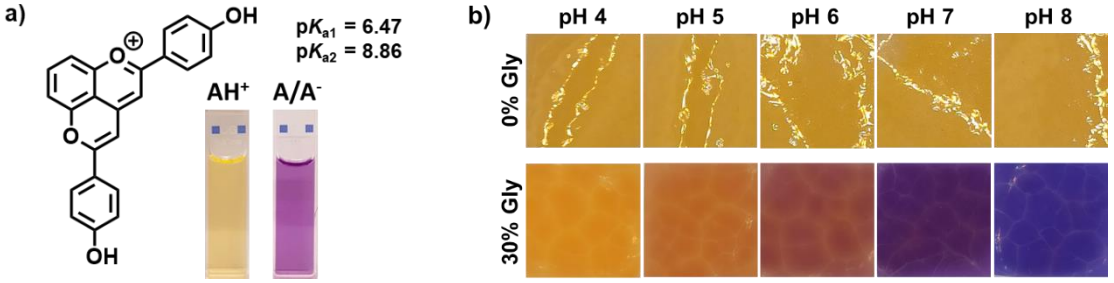


Figure 1: a) Pyranoflavylium salt developed as pH-sensor.[3] b) Colorimetric response of cellulose acetate films incorporated with pyranoflavylium salt (0.2 % (w/w)) without glycerol (0 % Gly) and with 30 % (w/w) of glycerol (30% Gly) immersed in buffer solutions at different pH values after 30 min.

Acknowledgements: This work was supported by the Associate Laboratory for Sustainable Chemistry, Clean Processes, and Technologies LAQV. The latter is financed by national funds from UIDB/50006/2020. This work was also supported by the project PTDC/OCE-ETA/31250/2017 funded by FCT and FEDER. Luís Cruz acknowledges the FCT research contract, and Vânia Gomes acknowledges the Ph.D. grant from FCT (SFRH/BD/136556/2018).

References:

1. R. Becerrila, C. Nerína, F. Silva, *Trends Food Sci. Technol.* **2021**, 111, 495.
2. J.L.C. Sousa, V. Gomes, N. Mateus, F. Pina, V. de Freitas, L. Cruz, *Tetrahedron* **2017**, 73, 6021.
3. V. Gomes, A. S. Pires, I. Fernandes, N. Mateus, V. de Freitas., L. Cruz, *J. Photoch. Photobio. A* **2021**, 415, 113313.

Materials chemistry and applications

Solid polymer electrolytes based on HPMC and $Tm(CF_3SO_3)_3$

T. Pontes, M.M. Silva

Center/Department of Química, University of Minho, Campus de Gualtar, 4710 - 057 Braga, Portugal

Email: nini@quimica.uminho.pt

Polymer electrolytes (PEs) are currently the focus of much attention as potential electrolytes in electrochemical devices such as batteries, display devices and sensors[1,2]. Generically, solid polymer electrolytes (SPEs) are mixtures of salts with soft polar polymers such as poly(ethylene oxide) (PEO). SPEs have many advantages including high energy density, no risk of leakage, no issues relate to the presence of solvent, wide electrochemical stability windows, simplified processability and light weight. With the goal of developing a new family of environmentally friendly multifunctional biohybrid materials displaying simultaneously high ionic conductivity and high electrochemical we have produced. In the present work a electrolyte systems based on a cellulose derivative (hydroxypropyl)methyl cellulose (HPMC) doped with thulium triflate ($Tm(CF_3SO_3)_3$) have been synthesized by the solvent casting process. The resulting biohybrid films exhibit high transparency as exemplified on Figure 1 and were studied in terms of thermal behaviour and ionic conductivity.

Figure 1. *Representative photo of the biohybdrid film doped with thulium triflate.*

Acknowledgements: This work was funded by the R&D Project "SOLPOWINS – Solar-Powered Smart Windows for Sustainable Buildings", with reference PTDC/CTM-REF/4304/2020, financed by the Foundation for Science and Technology (FCT). The authors thankfully acknowledge the funding from the Chemistry Centre at Minho University (Pest-C/QUI/UI0686/2020).

References:

1. F.M. Gray, in Solid Polymer Electrolytes: Fundamentals and Technological Applications, VCH Publishers, Inc. (1991).
2. J.R. MacCallum, C.A. Vincent, Polymer Electrolyte Reviews, vol. 1, Elsevier, London, 1987.

Materials chemistry and applications

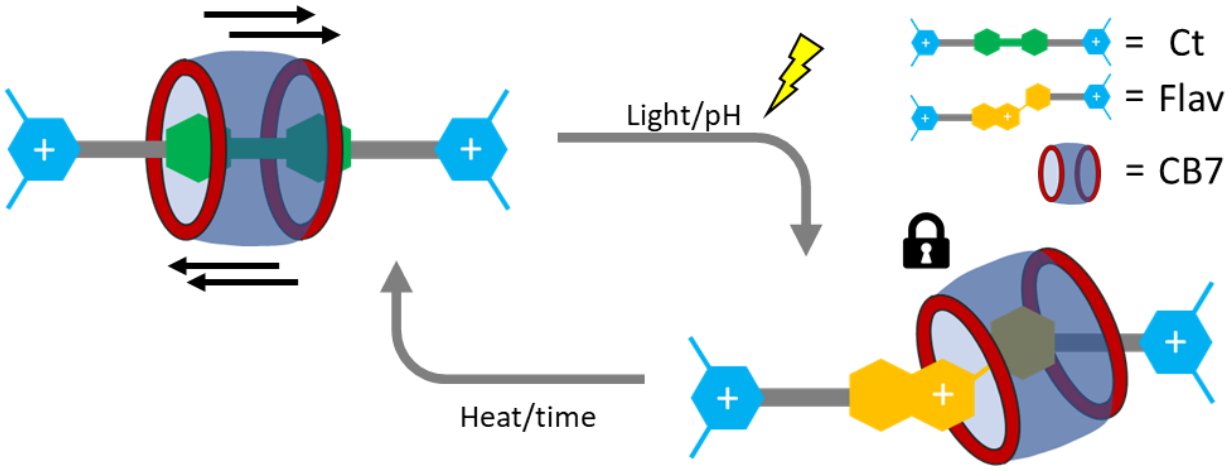
Flavylium compounds meet cucurbiturils: a light responsive pseudo-rotaxane

A. Seco,[a] N. Mcclenaghan,[b] A.J. Parola,[a] N. Basílio[a]

a) Associated Laboratory for Green Chemistry - LAQV, REQUIMTE, Chemistry Department - NOVA School of Science and Technology, 2829-516 Monte de Caparica, Portugal. b) CNRS/Univ. Bordeaux, Institut des Sciences Moléculaires, Talence, France.

Email: am.seco@campus.fct.unl.pt

Over the last five years the field of molecular machines has received widespread attention following the 2016 chemistry Nobel prize. A well-known type of molecular machine is called rotaxane and it is constituted by two molecules, one serving as wheel and one serving as axle, almost like the wheel of a motorcycle around the drive shaft[1].
In this work it will be presented a pseudo-rotaxane that can, using light or pH stimuli, lock the macrocycle in a specific position of the axle as opposed to it being oscillating along the guest molecule.
This is possible due to the well-known capability of controlled interconversion between flavylium cations and 2-hydroxychalcones. Both these species belong to the vast multistate of anthocyanins and their synthetic analogues can be tailored to exhibit more photoswitch-like properties, making them ideal candidates for application in building molecular machines[2]. **Scheme 1**, bellow depicts a scheme of the operation of this pseudo-rotaxane when prompted with pH and/or light stimuli.



Scheme 1: Scheme of the molecular device in the two conformations with indication of the stimuli that can trigger a structure rearrangement leading to CB7 being locked in a strict position or unlocked to go back and forth along the axle (enclosed abbreviations: **Ct** = *trans*-Chalcone; **Flav** = Flavylium cation and **CB7** = Cucurbit[7]uril).

Acknowledgements: This work was supported by the Associated Laboratory for Sustainable Chemistry, Clean Processes and Technologies LAQV through national funds from FCT/MCTES under project UIDB/50006/2020. A.S. acknowledges FCT for his doctoral grant (2020.07313.BD).

References:

1. J. F. Stoddart, Angew.Chem.Int. Ed., 56, (2017), 11094 –11125;
2. A. Seco, A.M. Diniz, J. Sarrato, H. Mourão, H. Cruz, A.J. Parola and N. Basílio, Pure Appl. Chem. 92, (2019), 301-313.

Materials chemistry and applications

Development of hierarchical 1D/2D nanocomposites as electrocatalysts for the oxygen reactions in fuel cells

M. Rocha,[a,b] B. Abreu,[a,b] M. Nunes,[b] C. Freire[b], E.F. Marques[a]

a) Centro de Investigação em Química - CIQUP, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, 4169-007 Porto, Portugal b) LAQV@REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, 4169-007 Porto, Portugal.

Email: efmarque@fc.up.pt

The development of hybrid hierarchical nanomaterials is an emerging area in nanotechnology. These materials are generally made up of two or more component materials with different properties and/or dimensionalities (e.g. 1D and 2D), often also including organic and inorganic compounds.[1] Suitable combinations of building blocks may yield synergistic effects, resulting in enhanced or innovative properties.[2] Among myriad applications is the development of novel efficient electrocatalysts for the oxygen reactions related to fuel cells and batteries.[2,3]
In this work, various methodologies were explored to prepare 2D nanocomposites of transition metal dicalcogenides and graphene (TMD@GnPs) and hybrid nanocomposites of the 2D composites with multiwalled carbon nanotubes (TMD@GnPs)@MWNT via electrostatic self-assembly. Non-covalent functionalization of the materials by adsorption of surfactants and polymers allowed the hierarchical assembly of the composites.[3,4] Furthermore, Scanning Electron Microscopy (SEM) structural characterization was performed for all fabricated nanocomposites. Lastly, the materials were evaluated for their electrocatalytic activity, for the oxygen reduction and evolution reactions (ORR and OER, respectively). Electrochemical studies provided information on the reaction kinetics and structure-activity relationship between the nanocomposites and electrocatalytic parameters. The results allowed us to select the most promising materials, in terms of assembly simplicity, structuration and performance.

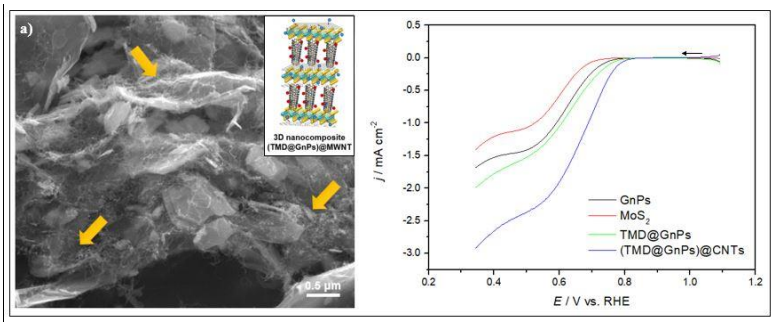


Figure 1: a) SEM micrograph of a (TMD@GnPs)@MWNT composite (arrows indicates dense MWNT networks); b) Illustration of linear sweep voltammograms (O_2-saturated 0.1mol·dm^{-3} KOH, v = 0.005 V·s^{-1}, 1600 rpm) for the starting materials, TMD@GnPs and (TMD@GnPs)@MWNT nanocomposites.

Acknowledgements: This work received support from Fundação para a Ciência e Tecnologia (UID/QUI/50006/2013-POCI/01/0145/FEDER/007265); UniRCell project (Ref[a]. POCI-01-0145- FEDER-016422); Fundação para a Ciência e Tecnologia for financial support through PhD grant PD/BD/128129/2016 and PEst-C/QUI/UI0081/2013, and to FEDER and FCT/MES through NORTE-01-0145-FEDER-000028.

References:

1. Huang, J.; Her, S.-C.; Yang, X.; Zhi, M., Nanomaterials **2018**, 8, 786.
2. Araújo, M. P.; Nunes, M.; Rocha, I. M.; Pereira, M. F. R.; Freire, C., ChemistrySelect **2018**, 3, 10064.
3. Ferreira, P.; Abreu, B.; Freire, C.; Fernandes, D. M.; Marques, E. F., Materials **2021**, 14, 896.
4. Abreu, B.; Montero, J.; Buzaglo, M.; Regev, O.; Marques, E. F., J. Mol. Liq. **2021**, 333, 116002.

Materials chemistry and applications

Thermotropic ionic liquid crystal phase behavior of double-tailed lysine-based surfactants

I.S. Oliveira,[a] R.F. Fernandes,[a] M.J. Araújo,[b] E.F. Marques[a]

a) CIQUP, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal b) LAQV-REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal

Email: isabel.oliveira@fc.up.pt

Thermotropic liquid crystals (TLCs) are structures that possess an intermediate degree of order between the crystalline solid and the isotropic liquid phases. Often they can respond to external stimuli such as mechanical stress or electrical fields, thus changing their optical properties (e.g. birefringence and color).[1] Beyond their fundamental interest, e.g. assessment of structure-behavior-performance relationships, TLCs find a wide variety of applications in electric-optical devices, sensors, liquid crystals displays, and medical applications.[1b)] In the last two decades, ionic liquid crystals which are liquid crystalline phases containing cations and anions have also been subject to intense research, due to the combination of properties of conventional uncharged TLCs and those of ionic liquids.[2] In this context, the thermotropic phase behavior of amino acid-based surfactants were addressed in the past, and it was observed that these compounds typically form smectic phases for C12 chain lengths.[3] In this work, we present the systematic study of the thermal phase behavior of lysine-based amphiphiles (sodium salts) with two asymmetric tails lengths, generally designated as *m*Lys*n*, where *n* and *m* = 8, 10, 12, 14 and 16, represent the number of carbon atoms in alkyl chains. The experimental toolbox include DSC, TGA, polarized light microscopy and XRD. As will be shown, structural isomerism (*m*/*n* vs. *n*/*m*) and total chain length (*n* + *m*) have a significant impact on the TLCs formed and their optical properties. All the compounds show several thermotropic phase transitions denoting a complex melting process. Results show that when the charge is located on the same side of the longer chain, Figure 1a), the phase behavior of the surfactants is much more complex than for the respective isomers. Furthermore, the lysine surfactants phase behavior is dominated by high temperature smectic phases, characterized by focal conics textures (Figure 1).

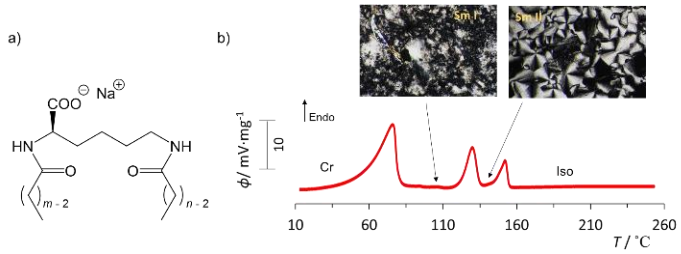


Figure 1: Molecular structure of the *m*Lys*n* lysine-based surfactants (a). DSC thermogram of the surfactant 16Lys10 and micrographs of the birefringent smectic phase textures (Sm I and Sm II) obtained by polarized light microscopy (b).

Acknowledgements: FCT is gratefully acknowledged for financial support through Ph.D grant SFRH/BD/108629/2015. CIQUP acknowledges financial support from FEDER/COMPETE and FCT through grants UID/QUI/0081/2020, POCI-01-0145-FEDER-006980 and NORTE-01-0145-FEDER-000028.

References:

1. a) O'Neill M.; Kelly S. M. *Adv. Mater.* **2003**, *15*, 1135. b) Lagerwall J. P. F.; Scalia, G. *Curr. Appl. Phys.* **2012**, *12*, 1387.
2. a) Goossens K.; Lava K.; Bielawski C. W.; Binnemans K. *Chem. Rev.* **2016**, *116*, 4643. b) Fernandes R. F.; Wang Y.; Tavares P.; Nunes S.; Pais, A.; Marques E. F. *J. Phys. Chem. B* **2017**, *121*, 10583.
3. Brito R.; Marques E. F.; Gomes P.; Araújo M. J.; Pons R. *J. Phys. Chem. B* **2008**, *112*, 14877.

Materials chemistry and applications

Supramolecular photochemical control of fluid rheology

P. Máximo, C. Laia, N. Basílio, A.J. Parola, A. Camuenho

LAQV-REQUIMTE, FCT - Universidade NOVA de Lisboa, 2829-516 Monte de Caparica, Portugal.

Email: a.camuenho@campus.fct.unl.pt

Modifying the viscosity of a fluid with light defines the area of fluid photorheology. Most of the photorheological fluids developed so far use photoisomerization reactions that through molecular level structural changes lead to macroscopic variations in the rheological properties.[1] Based on previous results,[2,3] the selected receptors able to form homoternary complexes with those units is the cucurbit[8]uril. In order to take advantage of the affinity of the cucurbit[8]uril rim towards positively charged ligands, was synthesized of chalcones units through poliethyleneglycol bridges that by irradiation or pH jump is converted into a flavylium cation , Figure 1.

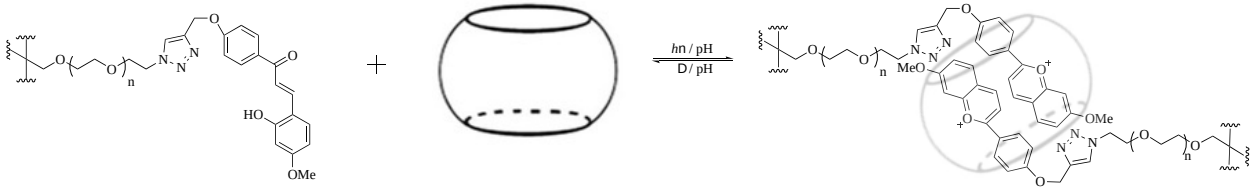
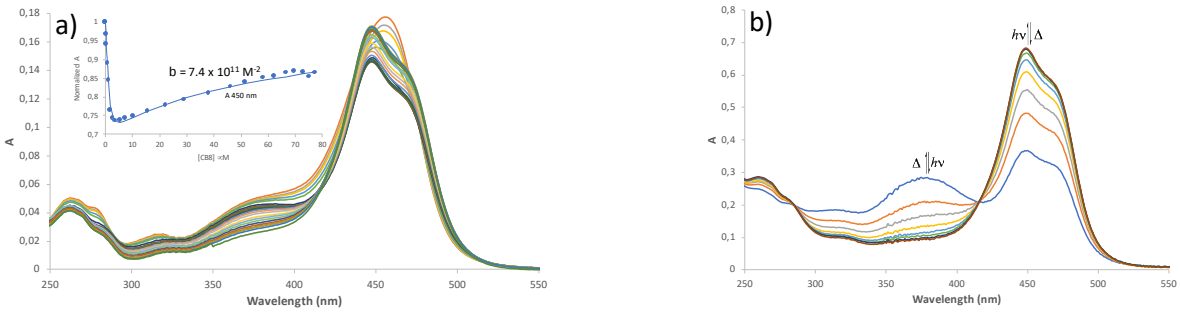


Figure 1: General complexation scheme between the 4–arm PEG-CT (n=55) with Cucurbit[8]uril.

Structural elucidation of the synthesized compound was done by 1H. The studies in solution were follow by UV-Vis spectroscopy and spectrofluorimetry, that allowed to determine, quantum yields, association constant, stoichiometries of the complex and the formation of hydrogel by the irradiation.



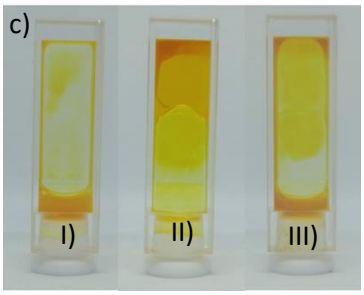


Figure 2: characterization of compound 4-arm PEG-CT in aqueous solution with CB8: **a)** Titration of 4–arm PEG-CT (1.8E-6 M) with CB8 (0-7.7E-5 M) at pH 1 followed by absorption uv-vis. **b)** Photochemistry of compound 4 – arm PEG-CT (1.83E-6 M, pH 4.8) irradiation at 365 nm between 0 - 365 seconds. **c)** transformation of 4 - arm PEG-CT/CB[8] (4%wt) into hydrogel by irradiation at 365 nm, fractions of solute 1:2 at pH 4.8; **I)** Non-irradiated; **II)** After 1h30 of irradiation; **III)** After 1 day in the dark.

Acknowledgments: This work was supported by the Associate Laboratory for Green Chemistry- LAQV which is financed by national funds from FCT/MCTES (UID/QUI/50006/2013) and co-financed by the ERDF under the PT2020 Partnership Agreement (POCI-01-0145-FEDER – 00726).

Reference:

1. Zou L.; Webber M. J.; *Chem. Commun.* ***2019****, 55,* 9931.
2. Ferreira P.; Ventura B.; Barbieri A.; Da Silva P. J.; Laia C. A. T.; Parola A. J.; Basílio N. *Chem. - A Eur. J.* ***2019****. 25*, 3477.
3. M. A. Romero, R. J. Fernandes, A. J. Moro, N. Basílio, and U. Pischel; *Chem. Commun.* ***2018****, 54,*13335.

Materials chemistry and applications

Characterization of coal fly ash applied in wastewater treatment

A.C. Santos,[a] I. Kuźniarska-Biernacka,[b] C. Freire.[b] A. Guedes,[a] B. Jarrais,[b] A.F. Peixoto,[b] B. Valentim[a]

a) Earth Science Institute – Porto pole, Department of Geosciences, Environment and Spatial Plannings, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, 4169– 007 Porto, Portugal; b) REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal

Email: anasantos@fc.up.pt

Every year approximately 750 million tons of coal fly ash (CFA) are produced, and a significant part is landfilled[1]. Initially, this material raised concern regarding environment and human health and stressed the need on research to find applications for this material, which was found mainly in concrete production. Nowadays, CFA has been pointed out as a material with huge potential for many applications, including heterogeneous catalyst to 4-nitrophenol (4-NPh), which is a toxic compound commonly found in wastewater that can be easily removed via catalytic reduction. The abundance and low price of the CFA could allow the process to be economically viable on an industrial scale. Nevertheless, this requires a detailed knowledge of the materials and assessment of the changes imposed during its utilization in 4-NPh reduction process.

The CFA sample used in this study was provided by PEGOP pulverized coal-fired power plant (Abrantes, Portugal), and was collected in first row of the electrostatic precipitator which retain approx. 80 % of the particles carried by the flue gas. The CFA sample was beneficiated via a sequence of sieving and magnetic separation with a ferrite magnet to obtain sized and magnetic fractions (MF)[2], and the MF <75 μm was washed with NaOH and $NaBH_4$. The characterization of the raw samples was made before and after experiments via X-ray fluorescence, Scanning Electron Microscopy with Energy Dispersive Spectroscopy and Raman microspectroscopy.

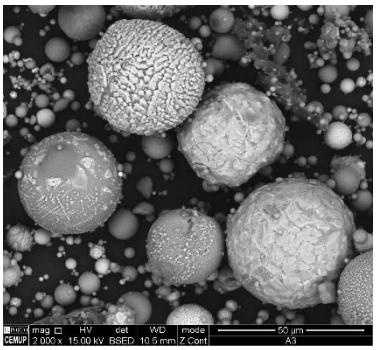


Figure 1 - Micrograph of coal fly ash magnetic fraction (SEM-EDS, BSE mode): Fe-rich morphotypes.

The MF show lower concentrations of SiO_2, Al_2O_3, K_2O, TiO_2 than the respective size fractions, but contain nearly ten times more Fe_2O_3 (up to 68 wt. %). The SEM-EDS experiments showed that the MF are mainly composed by Fe-rich morphotypes (**Figure 1**) while glassy aluminosilicate spheres prevail in the tailings. Raman microspectroscopy analysis confirmed the presence of magnetite (Fe_3O_4), hematite (α-Fe_2O_3) and Maghemite (γ-Fe_2O_3). After NaOH and $NaBH_4$ washing, the MF <75 μm exhibits a slight decrease in the concentration of SiO_2, Al_2O_3 and CaO while the MgO and Fe_2O_3 content increased, and SEM via secondary electrons detector mode experiments revealed that particles surface was etched. Meanwhile, a lack of Raman features pertaining to Fe-oxides in several Fe-rich morphotypes indicates a conversion into elemental iron[3] and explains the better performance as catalyst of the MF <75 μm sample washed with $NaBH_4$.

Acknowledgements: The work was supported through the project UIDB/50006/2020, funded by FCT/MCTES through national funds as well as FCT/MEC research project REALM — Reactive Learning Machines (ref. PTDC/QUI-QIN/30649/201), and project CHARPHITE of the 3rd ERA-MIN Program 2015 (FCT ref. ERA-MIN/0005/2015). IK-B thanks FCT for funding through program DL 57/2016 – Norma transitória REQUIMTE/EEC2018/14, and ACS thanks FCT for PhD scholarship Ref: SFRH/BD/131713/2017.

References:

1. Blissett, R. S.; Rowson, N. A., A review of the multi-component utilisation of coal fly ash. Fuel 2012, 97, 1-23.
2. Badenhorst, C. S., C.; Lázaro-Martínez, J.; Białecka, B.; Cruceru, M.; Guedes, A.; Guimarães, R.; Moreira, K.; Predeanu, G.; Suárez-Ruíz, I.; Cameán, I.; Valentim, B.; Wagner, N., Assessment of Graphitized Coal Ash Char Concentrates as a Potential Synthetic Graphite Source. Minerals Engineering 2020, 10 (11), 986.
3. Wang, L.; Lu, X.; Han, C.; Lu, R.; Yang, S.; Song, X., Electrospun hollow cage-like α-Fe2O3 microspheres: synthesis, formation mechanism, and morphology-preserved conversion to Fe nanostructures. CrystEngComm 2014, 16 (46), 10618-10623.

Materials chemistry and applications

Water-in-oil nanoemulsions as delivery systems of hydrophilic natural extracts: a stability and functionality study

G. Colucci.[a] M.L. Cruz,[a] I.P. Fernandes,[a] V.V. Pinto,[b] M.J. Ferreira,[b] J. Duarte,[c] M.F. Barreiro[a]

a) Mountain Research Centre (CIMO), Polytechnic Institute of Bragança, Campus Santa Apolonia - 5300-253 Bragança, Portugal,
b) Centro Tecnológico do Calçado de Portugal (CTCP), Rua de Fundões - Devesa Velha, 3700-121 S. João da Madeira, Portugal
c) Curtumes Aveneda, R. Aveneda, S. Vicente Pereira, Ovar, Portugal

Email: barreiro@ipb.pt

Nanoemulsions are biphasic systems characterized by droplets in the nanometric range, feature that increases the bio-efficacy of the incorporated functionalities[1]. One challenging point of emulsified systems for commercial applications is their stability under storage. In particular, the impact of incorporating bioactive ingredients may contribute to instability[2]. Therefore, this work aimed to develop water-in-oil (W/O) nanoemulsions, using sweet almond oil and natural extracts, and study their stability under storage, targeting a stable fatliquoring product to be used in leather applications. For this purpose, nanoemulsions with different concentrations of green tea (*Camellia sinensis*) aqueous extract as a model extract and a base nanoemulsion (without extract) were prepared. The system composition corresponded to a 40/60 W/O ratio using Span 80/Tween 80 mixture (54/46 ratio, v/v) as emulsifier at a concentration of 6% (total emulsion-basis). The extracts were added to the aqueous phase at concentrations of 3.75% and 5% (w/v). Firstly, a coarse emulsion was prepared by using a mechanical homogenizer (11000 rpm, 5 min). Then, the droplet size was reduced using a high-pressure homogenizer (HPH) during 12 cycles of homogenization. Thereafter the prepared emulsions were stored at 4°C. The formulations' stability was analyzed along a storage time of 5 months, through periodic microscopic and visual analyses, accompanied by a photographic register. In addition, accelerated stability tests, namely centrifugation and thermal stress were performed to foresee the stability under future application. Furthermore, the antimicrobial activity of formulations was tested by the agar diffusion test with the microorganism *Staphylococcus aureus* ATCC 29213 to check functionality maintenance. As results, the nanoemulsions presented macroscopic and microscopic stability; no instability phenomena were detected after 5 months at the tested storage temperature, regardless the extract concentration. For the thermal stress, instability was detected for the 3.75% and 5% green tea nanoemulsions at 60 ºC and 40 ºC, respectively, whereas the base was stable until 80 ºC (higher tested temperature). For the centrifugation tests, extract sedimentation was noticed after just one centrifugation cycle, increasing in the next cycles (**Figure 1a**). The antimicrobial activity of 3.75% and 5% green tea nanoemulsions showed a prolonged effect against *S. aureus* bacteria, maintaining the same inhibition zone (10 and 12 mm, respectively) after 5 months, revealing the formulation ability to preserve and deliver bioactive ingredients (**Figure 1b**). In conclusion, this study allowed the development of stable and functional nanoemulsions with high potential to be explored as technological solutions for the leather industry, such as fatliquoring products for leather treatment.

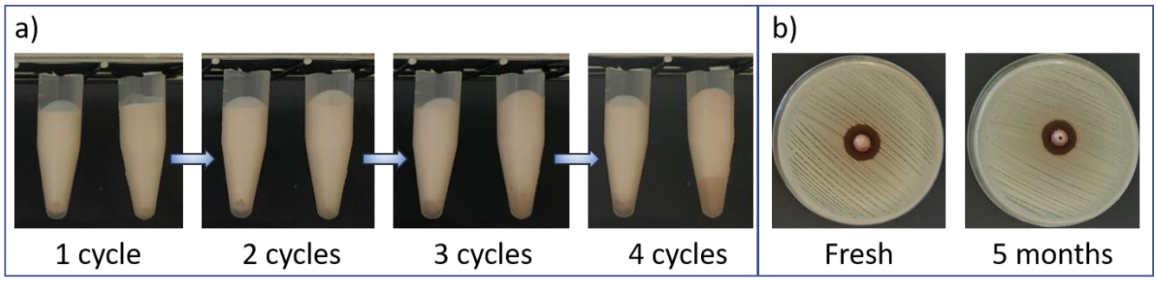


Figure 1: a) Centrifugation assay of 3.75% and 5% formulations (left and right, respectively) after cycles of 3000 rpm, 30 minutes. b) Antimicrobial assay for 5% green tea nanoemulsion.

Acknowledgements: FCT/MCTES (PIDDAC) - CIMO (UIDB/00690/2020). FCT - Institutional scientific employment program (I.P Fernandes) and project FAMEST (Norte-01-0247-FEDER24529) through FEDER under Program PT2020.

References:

1. McClements, D. J. *Prog. Lipid Res.* **2021**, *81*, 101081.
2. Karthik, P.; Ezhilarasi, P. N.; Anandharamakrishnan, C. *Crit. Rev. Food Sci. Nutr.* **2017**, 57, 1435-1450.

Materials chemistry and applications

Modified nanostructured cobalt foams as electrocatalysts for the oxygen evolution reaction

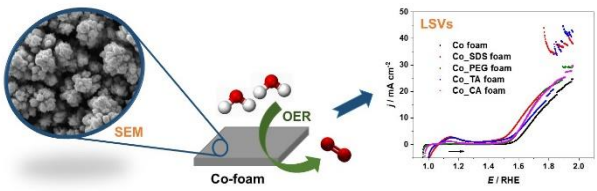
M. Nunes,[a] C. Alves,[b] H.C. Novais,[a] D.M. Fernandes,[a] A. Adán-Más,[b] F. Montemor,[b] C. Freire[a]

a) LAQV@REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, 4169-007 Porto, Portugal. b) Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico,1049-001 Lisboa, Portugal.

Email: marta.nunes@fc.up.pt; diana.fernandes@fc.up.pt

The oxygen evolution reaction (OER), the half reaction of the water-splitting process, is crucial for the real implementation of promising energy storage and conversion systems, such as regenerative batteries and electrolyzer systems. In order to replace the high-cost and scarce ruthenium and iridium oxides electrocatalysts (ECs), known by their excellent electrocatalytic OER performances, important efforts have been performed to find alternative ECs with high surface area and chemical stability, good catalytic activity and lower cost.[1,2] Nanostructured metallic foams are 3D structures of interconnected pores with nano-ramified walls that combine good electric conductivity with high surface area and low density.[3] Such structures can be produced by electrodeposition in the hydrogen evolution regime and the optimization of the electrodeposition parameters makes possible to design nano-ramified foam structures with properly tailored architectures to enhance mass and charge transfer processes.

In this work, cobalt foams prepared by dynamic hydrogen bubbling templated electrodeposition (DHBT-ED)[4] in the presence of several chemical additives (e.g., citric acid (CA), tartaric acid (TA), polyethylene glycol (PEG), sodium dodecyl sulfate (SDS)) were tested as ECs for the OER. The effect of the selected chemical additives was correlated with the foams morphology (evaluated by Scanning Electron Microscopy, SEM) and with their electrocatalytic activity for OER (evaluated by Linear Sweep Voltammetry, LSV) (Scheme 1). Several parameters, such as overpotential values and Tafel slopes, were calculated to evaluate the OER performance of these electrodes alongside their long-term electrochemical stability. All prepared Co-foams showed interesting OER electrocatalytic activity. The chemical additive employed revealed a main role in the morphology that ultimately influences the electrocatalytic activity of the obtained foams. The Co-foam prepared with SDS as chemical additive showed the best electrocatalytic activity with an overpotential of η_{10} = 0.39 V.



Scheme 1: Application of Co-foams as OER electrocatalysts (LSVs at 1600 rpm and 5 mV s^{-1} in N_2-saturated 0.1 mol dm^{-3} KOH).

Acknowledgements: We thank Fundação para a Ciência e Tecnologia by the support (UID/QUI/50006/2013-POCI/01/0145/FEDER/007265). This work was financially supported by FOAM4ENER project (PTDC/QUI-ELT/28299/2017).

References:

1. Araújo M.P.; Nunes M.; Rocha I.M; Pereira M.F.R; Freire C. *ChemistrySelect* **2018**, *3*, 10064.
2. Abdelkader-Fernández V.K.; Fernandes D.M.; Balula S.; Cunha-Silva L.; Pérez-Mendoza M.J.; López-Gárzon F.J.; Pereira M.F.R.; Freire C. *ACS Appl. En. Mater.* **2019**, *2*, 1854.
3. Cardoso D.S.P; Eugénio S.; Silva T.M.; Santos D.M.F.; Sequeira C.A.C; Montemor M.F. *RSC Adv.* **2015**, *5*, 43456.
4. Arévalo-Cid P.; Adán-Más A.; Silva T.M; Rodrigues J.A.; Maçôas E.; Vaz M.F.; Montemor M.F. *Mater. Charact.* **2020**, *169*, 110598.

Materials chemistry and applications

CuAl-LDH/g-C_3N_4 Nanohybrids for photocatalytic H_2 and O_2 generation via water splitting

H. Boumeriame,[a,b,c] E.S. Da Silva,[a] D.H. Apaydin,[c] D. Eder,[c] T. Chafik,[b] A.S. Cherevan,[c] J.L. Faria[a]

a) Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias s/n 4200-465 Porto, Portugal; b) Laboratory of Chemical Engineering and Valorization of Resources (LGCVR-UAE/L01FST), Faculty of Sciences and Techniques, University Abdelmalek Essaadi, Tangier, Morocco; c) Institute of Materials Chemistry, Technical University of Vienna, Getreidemarkt 9, Vienna, 1060, Austria

Email: hanane@fe.up.pt

Graphitic carbon nitride (g-C_3N_4, abbreviated as GCN), a visible-light responsive metal-free optical semiconductor, has recently attracted interest in photocatalytic water splitting owing to its excellent properties such as bandgap of 2.7 eV, thermal and chemical stability, and easy synthesis from inexpensive precursors such as cyanamide, thiourea, dicyandiamide, or melamine. Nevertheless, this bandgap, the transport gap, still allows rapid recombination of electron-hole pairs and presents small surface area.[1] Among the several strategies proposed to overcome these limitations, building two-dimensional (2D) heterostructured nanohybrids has shown to be an effective approach for enhancing photocatalytic performance.[2] These 2D/2D nanohybrids can offer a short migration distance and boost the separation of photoinduced carriers, thus improving light conversion efficiency.

Therefore, this work aims to design and fabricate 2D/2D materials by combining thermally exfoliated GCN (GCNN) with another 2D material, CuAl layered double hydroxide (LDH),[2] *via* an electrostatic co-assembly method. The materials were irradiated at 445 nm and tested towards H_2 and O_2 generation, without addition of cocatalyst. According to the photocatalytic results, the nanohybrids enhanced the visible-light photocatalytic H_2 generation by 32- and 47-fold, as compared to bare GCNN and CuAl-LDH, respectively. Concerning the O_2 evolution, results showed that the nanohybrids displayed 1.5 times higher photocatalytic activity than pristine GCNN. However, pristine CuAl-LDH also presents interesting values of O_2 generation (120 μmol g^{-1} h^{-1}). Consequently, the enhanced photocatalytic performance was attributed to i) hindered electron-hole separation at the intimate heterojunction interface (according to steady-state and time-resolved photoluminescence), ii) improved visible light absorption and narrower bandgap (as shown by diffuse reflectance spectroscopy), and iii) higher specific surface area. These results will hopefully offer new insights on the construction of innovative GCNN-LDH nanomaterials for photocatalytic applications.

Acknowledgements: This work This work was financially supported by: Base Funding - UIDB/50020/2020 of the Associate Laboratory LSRE-LCM - funded by national funds through FCT/MCTES (PIDDAC) and project 2DMAT4FUEL (POCI-01-0145-FEDER-029600-COMPETE2020-FCT/MCTES-PIDDAC, Portugal). H.B. acknowledges OeaD-Ernst Mach Grant worldwide (Vienna, Austria) and A.C. acknowledges the Austrian Science Fund (FWF) project number P32801.

References:

1. Da Silva E. S.; Moura N. M. M.; Coutinho A.; Dražić G.; Teixeira B. M. S.; Sobolev N. A.; Silva C. G.; Neves M. G. P. M. S.; Prieto M.; Faria J. L. *ChemSusChem.* **2018**, *11*, 2694.
2. Boumeriame H.; Da Silva E. S.; Cherevan A. S.; Chafik T.; Faria J. L.; Eder D. *J. Energy Chem.* **2021**, https://doi.org/10.1016/j.jechem.2021.04.050.

Materials chemistry and applications

Amphiphilic carbon nanotubes for catalytic wet peroxide oxidation of 4-nitrophenol

F.F. Roman,[a,b] F.K.K. Sanches,[a,c] J.L. Diaz de Tuesta,[a] P. Marin,[c] B.F. Machado,[d] P. Serp,[d] A.M.T. Silva,[b] J.L. Faria,[b] H.T. Gomes[a]

a) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; b) Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal; c) Universidade Tecnológica Federal do Paraná, Campus Londrina, 86036-370 Londrina, Brasil; d) Laboratoire de Chimie de Coordination, ENSIACET, Université de Toulouse, France.

Email: roman@ipb.pt

Carbon nanotubes (CNTs) were synthesized via chemical vapor deposition (CVD) over an $AlCoFeO_4$ catalyst by a sequential feed of ethylene (E, as carbon source) and acetonitrile (A, as nitrogen source). The resulting samples were noted E20 (hydrophobic), E10A10 (amphiphilic), and A20 (hydrophilic), the number referring to the feed time (minutes) of each precursor, as reported elsewhere[1]. These materials were tested in the catalytic wet peroxide oxidation (CWPO) of 4-nitrophenol (4-NP). The reaction was monitored by HPLC (to determine the concentration of 4-NP and respective intermediates), TOC analyzer, and UV-vis spectrophotometry (to quantify H_2O_2) (Figure 1). After 8 h of reaction, A20 led to the highest consumption of H_2O_2 (90%), followed by E10A10 (61%) and E20 (52%). On the other hand, the highest degradation of 4-NP was observed with the amphiphilic E10A10 material (98%) followed by E20 (95%), whereas A20 only led to a removal of 69%. Similar behavior was found when analyzing the formation of reaction intermediates (data not shown), i.e., while A20 resulted in the accumulation of 4-nitrocatechol (4-NTC) and hydroquinone (HQ) E10A10 and E20 led to the total conversion of formed 4-NTC and HQ. This resulted in a lower TOC removal for A20 (37%) than to E10A10 and E20 (53%). Therefore, the amphiphilic E10A10 material is a promising catalyst for the CWPO of 4-NP.

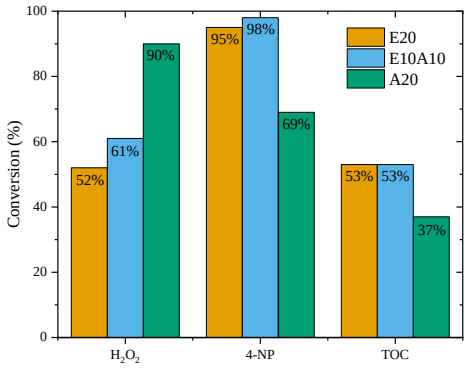


Figure 1: CWPO of 4-NP (operating conditions: $[4\text{-NP}]_0 = 1$ g L^{-1}, $[H_2O_2]_0 = 3.6$ g L^{-1}, [catalyst] = 2.5 g L^{-1}, 80 °C, pH 3.5, 8 h).

Acknowledgements: This work was financially supported by project "PLASTIC_TO_FUEL&MAT – Upcycling Waste Plastics into Fuel and Carbon Nanomaterials" (PTDC/EQU-EQU/31439/2017), Base Funding - UIDB/50020/2020 of the Associate Laboratory LSRE-LCM - funded by national funds through FCT/MCTES (PIDDAC), and CIMO (UIDB/00690/2020) through FEDER under Program PT2020. Fernanda F. Roman acknowledges the funding by FCT, Foundation for Science and Technology, and FSE, European Social Fund, through the individual research grant SFRH/BD/143224/2019.

References:

1. Diaz de Tuesta, J. L .; Machado, B. F.; Serp, P.; Silva, A. M. T.; Faria, J. L.; Gomes, H. T. *Catal. Today* **2020**, *356*, 205.

Materials chemistry and applications

Rhododendron ponticum as a possible candidate for the creation of biomimetic films inspired by plant leaves

R. Rua,[a] A.L. Crespi,[b] M. Fernandes,[a] V. de Zea Bermudez[a]

a) CQ-VR and Chemistry Department, University of Trás-os-Montes e Alto Douro (UTAD), 5000-811 Vila Real, Portugal, b) Herbarium and Botanical Garden, CITAB, Department of Biological and Environmental Engineering, UTAD, 5000-811 Vila Real, Portugal

Email: vbermude@utad.pt

In the last years some research effort has been inspired by Nature. Examples of advanced functional material have been developed by precisely mimicking the chemical components, surface structures and exceptional properties presented in natural systems [1]. Green plants are characterized by a diversity of hierarchical surface structures [2] and can be employed as models for the development of biomimetic surfaces. The main goal of the current work has been to study in depth the surface of Rhododendron ponticum's [3] adaxial (upper) and abaxial (lower) surfaces. The fresh plant material was collected at the Botanical Garden of UTAD. This Ericaceae, a monocotyledon belonging to the order Ericales, is originated in the Iberian Peninsula. It is very common across the world, and even considered an invasive species in some countries. The wettability of the leaf was determined by means of static contact angle (CA) measurements, using the sessile drop method, performed in different locations of the adaxial and abaxial surfaces. The morphology was analysed by Polarized Optical Microscopy (POM) and Scanning Electronic Microscopy (SEM). The sample's waxes were extracted using chloroform by solvent extraction (total waxes) and by freeze embedding [4] (epicuticular waxes). Using Rhododendron ponticum leaves as templates for the biomimetic fabrication of artificial films, negative replicae of the leaves surfaces were produced using sol-gel derived polymer/silica hybrids [5].

Figure 1: Rhododendron ponticum's leaves (abaxial and adaxial side)

Acknowledgements: This work was funded by the R&D Project PORPLANTSURF - Superhydrophobic films inspired in the surface of plant leaves and petals from Northern Portugal, POCI-01-0145-FEDER-029785, financed by the European Regional Development Fund (ERDF) through COMPETE 2020 - Operational Program for Competitiveness and Internationalization (POCI) and by the Foundation for Science and Technology (FCT). The author acknowledges CQ-VR for financial support UID/QUI/00616/2013 and UID/QUI/00616/2019. M. Fernandes acknowledges FCT-UTAD for the contract in the scope of Decreto-Lei 57/2016 – Lei 57/2017.

References:

1. Xia F.,Jiang L., *Adv. Mater,* **2008**, 20 2842.
2. Barthlott W., Mail M., Bhushan B., Koch K., *Nano-Micro Letters* **2017**, 9.
3. https://jb.utad.pt/especie/Rhododendron_ponticum_subesp_baeticum
4. Ensikat H.J., Neinhuis C., Barthlott W., *Int. J. Plant Sci.* **2000**, 161(1) 143.
5. Rodríguez S. Rocha J., Fernandes M., Ravishankar A. P., Steinbrück N., Cruz R., Bacelar E., Kickelbick G., Anand S., Crespí A. L., Casal S., de Zea Bermudez V., Langmuir, 37(6), **2021**, 2011-2028.

Materials chemistry and applications

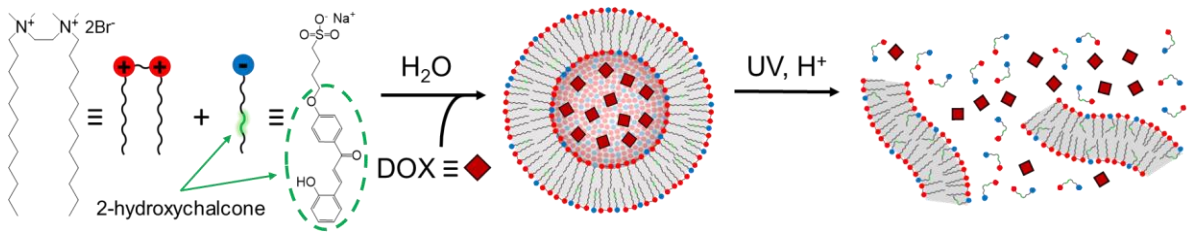
Photoswitchable and pH-gated self-assembled nanostructures for controlled delivery of an antineoplastic agent

D.X. Moreira,[a] O. Regev,[b] N. Basílio,[c] E.F. Marques[a]

a) CIQUP, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre P-4169-007 Porto, Portugal; b) Department of Chemical Engineering and Ilse Katz Institute for Nanotechnology, Ben-Gurion University of the Negev, 84105 Beer-Sheva, Israel; c) LAQV—REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

Email: efmarque@fc.up.pt

Over the last decades, stimuli-responsive delivery systems have been intensively investigated owing to their ability to provide activation-mediated drug release and hence potential increase in therapeutic efficacy. The stimuli can be either physiological, like pH or redox changes, or exogenous, such as light irradiation.[1] Among the myriad nanocarriers studied, mixed cationic/anionic surfactant vesicles display interesting physicochemical features, such as facile assembly, long-term stability and composition tunability.[2] Herein, we present recent work on the design and development of catanionic vesicles sensitive to UV irradiation and acidification, and on their ability to effectively entrap and release a model anticancer drug, doxorubicin (DOX) (**Scheme 1**). The catanionic vesicles are composed of an anionic amphiphile based on a 2-hydroxychalcone as the photosensitive unit, which presents an intricate chemical network combining the dynamics of other common photoswitches (e.g. spyropirans and azobenzenes),[3] and a cationic gemini surfactant. Upon irradiation in acidic media, a vesicle-to-bilayer transition is triggered and a 4-fold increase in release of incorporated DOX is observed compared to the non-irradiated system. The developed vesicles are a proof-of concept for a smart colloidal nanocarrier where the pH can be envisioned as a “lock mechanism”, and light as the trigger. The combination of stimuli works as an “AND” logic gate, conferring higher sensitivity on the drug release.



Scheme 1: Catanionic vesicle formation and co-encapsulation of DOX with its consequent release *via* stimuli application.

Acknowledgements: We thank Fundação para a Ciência e Tecnologia, FEDER/COMPETE and P2020|COMPETE for financial support through projects POCI-01-0145-FEDER-032351 (PhotoSAN), UID/QUI/0081/2020, POCI-01- 0145- FEDER-006980, NORTE-01-0145-FEDER-000028, UID/QUI/50006/2013 and UID/QUI/50006/2019.

References:

1. a) Alvarez-Lorenzo C.; Concheiro A. *Chem. Commun.* **2014**, *50*, 7743. b) Oliveira I. S.; Machado R. L.; Araújo M. J.; Gomes A. C.; Marques E. F. *Chem. – Eur. J.* **2021**, *27*, 692.
2. Gonçalves Lopes R. C. F.; Silvestre O. F.; Faria A. R.; do Vale M. L. C.; Marques E. F.; Nieder J. B. *Nanoscale* **2019**, *11*, 5932.
3. a) Basílio N.; Pischel U. *Chem. – Eur. J.* **2016**, *22*, 15208. b) Basílio N.; García-Río L. *Curr. Opin. Colloid In*. **2017**, *32*, 29.

Materials chemistry and applications

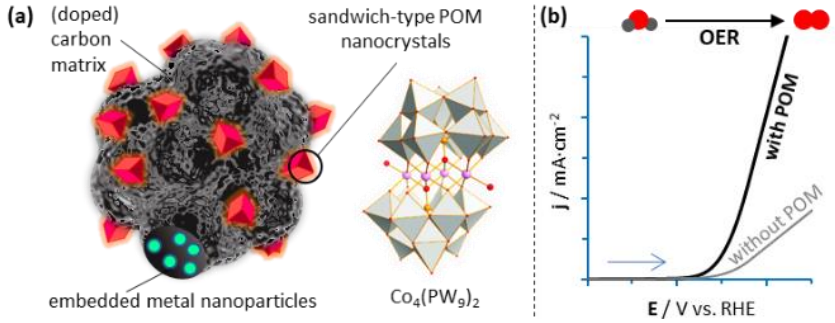
$Co_4(PW_9)_2$ POM "Bulk"-deposition on MOF-74 derived nanocarbons to the synthesis of ternary OER electrocatalysts

V.K. Abdelkader-Fernández,[a] D.M. Fernandes,[b] L. Cunha-Silva,[b] C. Freire[b]

a) Dpt. de Q. Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071, Granada, Spain; b) REQUIMTE/LAQV, Dto. Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal

Email: diana.fernandes@fc.up.pt

An efficient oxygen production from water —Oxygen Evolution Reaction (OER)— is strategic for the real implementation of fuel cell/electrolyzer systems. This fact has encouraged the development of new nanostructured OER electrocatalysts to replace the high-cost benchmark RuO_2 and IrO_2. For this purpose, previously, we carbonized selected metal-organic framework precursors involving different active metals and heteroatoms: Co-MOF-74, Co/Ni-MOF-74, Co-MOF-74[N,S] and Co/Ni-MOF-74[N,S] —achieving significant OER performances.[1] Now, taking advantage of the excellent electrocatalytic properties of polyoxometalates (POMs) and the low solubility of its potassium salts in the reaction medium, we have bulk-deposited nanocrystals of a Co-rich sandwich-type phosphotungstate —$Co_4(PW_9)_2$— on the surface of the previously obtained metal nanoparticles (NP)-containing MOF-74 derived nanocarbons (**Scheme 1a**). The composition/structure/morphology of the as-prepared ternary $Co_4(PW_9)_2$@NP@C nanocomposites have been characterized by XPS, ATR-IR, PXRD, Raman and TEM/EDS. Then, cyclic (CV) and linear sweep voltammetry (LSV) curves were acquired to assess the effect of the POM decoration on their electrochemically active surface areas (ECSAs) and OER performances. Besides, 12h-chronoamperometry was carried out to evaluate the electrocatalysts stabilities. Interestingly, although all the $Co_4(PW_9)_2$@X-Y@C combinations (with X = dual doped N,S or undoped, and Y = Co or Co/Ni) results in OER nominal activity improvements (**Scheme 1b**), the magnitude of these increments strongly depends on the carbon doping: while the overpotential of Co@C is ~210 mV-decreased when is POM-coated, the analogue doped N/S-Co@C only undergoes an overpotential decrease lower than 10 mV.



Scheme or Figure 1: (a) Ideal structure of ternary $Co_4(PW_9)_2$@NP@C electrocatalysts, and (b) comparison of OER LSV curves for a material with and without POM decoration.

Acknowledgements: The work was funded by Fundação para a Ciência e a Tecnologia de Portugal (FCT)/MEC under FEDER under Program PT2020 - project UIDB/50006/2020 | UIDP/50006/2020 and project "UniRCell" (ref.: POCI-01-0145-FEDER-016422). V. K. Abdelkader Fernández thanks Junta de Andalucía (Regional government of Spain) for his Postdoctoral research contract within the framework of "Programa de Contratación de Jóvenes Doctores 2020".

References:

1. Abdelkader-Fernández V. K.; Fernandes D. M.; Balula S. S.; Cunha-Silva L.; Pérez-Mendoza M. J.; López-Garzón F. J.; Pereira M. F.; Freire C; *ACS Appl. Energy Mate*r. **2019**, *2*, 1854.

Materials chemistry and applications

Biodiesel production from residual edible oils catalyzed by ionic liquid hydrogen sulfate 1-butyl-3-methylimidazolium, [BMIM][HSO_4]

F. M. Almeida, A. Queiroz, A.E. Ribeiro, P. Brito

Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 - Bragança, Portugal

Email: fretson2@gmail.com

Due to the countless environmental and energy problems related to the burning of fuels from fossil resources, that is, non-renewable fuels such as oil, natural gas, or coal, leading to a significant decrease in reserves and to an increase in concern about the global warming problem, has led the scientific community to look for sustainable and renewable alternatives. Thus, biofuels have emerged as a promising way to replace non-renewable fuels, including biodiesel.[1]
Biodiesel is defined as a mixture of monoalkyl esters of long chains of fatty acids (FAME), which can be obtained by converting vegetable oils or animal fats through transesterification or esterification reactions. Due to its numerous advantages, such as biodegradability, low viscosity, high flash point and low environmental impacts, it has the potential to be used directly in diesel engines, without any modification.[2]
The objective of the present work is to evaluate the potential of the use of the ionic liquid [BMIM] [HSO4] in the catalysis of the reactions of production of biodiesel from a simulated oil, composed of used cooking oil incorporated with oleic acid, and methanol.
The operation parameters: reaction time (2, 4 and 6h), catalyst dosage (5, 10 and 15%), molar ratio of oil/methanol (1: 5, 1:10 and 1:15 mol/mol) and incorporation of oleic acid (20, 40 and 60%) were studied applying a Response Surface Methodology (RSM), from an experimental Box-Behnken planning of a 3^4 factorial. The FAME content and the acidity reduction in the biodiesel produced were selected as the studied responses. The methodology establishes a set of 27 runs for the quantification of the influence of each factor on the responses. The methodology estimates that 27 runs are adequate to understand the influence of each factor on the response. A reaction temperature of 65ºC is maintained for all experiments.
After the synthesis, the biodiesel acidity, and the reaction conversion in terms of acidity decrease were determined by volumetric titration of the light biodiesel organic phase with potassium hydroxide (KOH) solution. Also, the FAME (fatty acid methyl esters) content of the biodiesel sample was quantified by gas chromatography (GC-FID). Table 1 shows for 6 selected runs, the correspondent experimental conditions and the obtained values in terms of decrease in acidity of biodiesel and conversion of FAME.

Table 1. Experimental conditions and correspondent values obtained in terms of acidity decrease (%) and FAME (%).

Run	A: Time (h)	B: Catalyst dosage (% wt)	C: Molar ratio oil:methanol	D: Incorporation of Oleic Acid (% wt)	Conversion, acidity reduction (%)	Conversion, FAME (%)
1	2	10	1:15	40	48	28
2	2	10	1:10	60	47	29
3	2	5	1:10	40	30	16
4	2	10	1:5	40	30	14
5	2	10	1:10	20	23	8
6	2	15	1:10	40	34	12

Acknowledgements: The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support by national funds FCT/MCTES to CIMO (UIDB/00690/2020).

References:

1. Troter D. Z.; Todorović Z. B.; Đokić-Stojanović D. R.; Stamenković O. S.; Veljković V. B. *Renew. Sust. Energ. Rev.* **2016**, *61*, 473.
2. Yaakob O.; Mohammad M.; Alherbawi M.; Alam Z. *Renew. Sust. Energ. Rev.* **2013**, *18*, 184.

Materials chemistry and applications

Silk-based polymer electrolytes incorporating glycerol, DMSO and LiTFSI

S.D.F. Silva,[a] P. Nunes,[b] M. Fernandes,[b] V. de Zea Bermudez,[b] M.M. Silva,[a] R.F.P. Pereira[a]

a) Centre of Chemistry (CQUM), University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal; b) CQ-VR and Chemistry Department, University of Trás-os-Montes e Alto Douro (UTAD), 5000-811 Vila Real, Portugal

Email: rpereira@quimica.uminho.pt

Polymer electrolytes (PEs) are a class of materials essentially composed of a host polymer bearing electron-donor atoms and a guest ionic salt. These systems offer several attractive features, in particular good electrochemical properties, low cost, high safety, reduction of problems associated with environmental issues, elimination of electrolyte leakage problems, and good flexibility. They find application in many current and future technologies, including energy storage, energy conversion, electrochromic devices, sensors and actuators, separations or water desalination/purification.[1]

In the last decades, and due to the environmental challenged faced by all the humanity, it got clear the need to find cleaner, safer, cheaper, and more efficient energy materials and devices. With these concerns in mind, a part of the community of PEs turned its attention to natural polymers.[2]

Silk has a long history of use in the textile industry and in the biomedical science.[3] The exceptional intrinsic properties of these fibers, such as self-assembly, biocompatibility and non-toxicity, among others, offer a wide range of application opportunities.[3] A significant number of new challenging applications for the two proteins of silk fibers (the core silk fibroin (SF) and the external silk sericin (SC)) are arising in large potential areas, such as optics, electronics, energy and smart windows. Silk-based materials have been incorporated in advanced batteries, offering significant advantages with respect to traditional materials, including enhanced eco-friendly approach, reliability and improved safety.[4]

Seeking the preparation of improved SF based electrolytes with boosted properties, we decided to re-think the previous proposed formulations,[2] and synthesize a green, conductive, transparent and flexible electrolyte films composed of a *Bombyx mori* SF host biopolymer doped with glycerol, dimethyl sulfoxide and lithium bis(trifluoromethanesulfonyl)imide. This bio-inspired work paves the way toward the fabrication of environmentally friendlier PEs for the next-generation sustainable and safer devices.

Acknowledgements: We thank Fundação para a Ciência e Tecnologia (FCT) and, when appropriate, FEDER (European Fund for Regional Development)-COMPETE-QRENEU for financial support through CQUM (UID/QUI/00686/2020), CQ-VR (UID/QUI/00616/2019 and UID/QUI/00616/2020). P.Nunes acknowledges CQ-VR/ FCT for a grant. M. Fernandes and R.F.P. Pereira acknowledges FCT-UTAD and FCT-UM, respectively, for the contract in the scope of Decreto-Lei 57/2016 – Lei 57/2017.

References:

1. Bocharova, V.; Sokolov, A. P. *Macromolecules* **2020**, 53, 4141.
2. a) Pereira, R. F. P.; Sentanin, F.; Pawlicka, A.; Gonçalves, M. C.; Silva, M. M.; de Zea Bermudez, *ChemElectroChem* **2016**, 3, 1084.; b) Fernandes, T. C. D.; Rodrigues, H. M. R.; Paz, F. A. A.; Sousa, J. F. M.; Valente, A. J. M.; Silva, M. M.; de Zea Bermudez, V.; Pereira, R. F. P. *J. Electrochem. Soc.* **2020**, 167, 070551.
3. Pereira, R. F. P.; Silva, M. M.; de Zea Bermudez, V. Bombyx mori silk fibers: an outstanding family of materials. *Macromol. Mater. Eng.* **2015**, 300, 1171.
4. Pereira, R. F. P.; Brito-Pereira, R.; Gonçalves, R.; Silva, M. P.; Costa, C. M.; Silva, M. M.; de Zea Bermudez, V.; Lanceros-Méndez, S., *ACS Appl. Mater. Interfaces* **2018,** 10, 5385.

Materials chemistry and applications

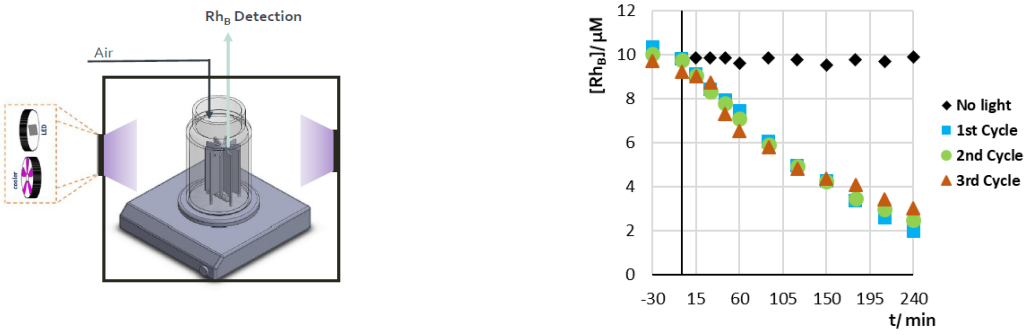
Additive manufacturing applied to the design of photocatalytic reactors

I.S.O. Barbosa,[a] Y.A. Manrique,[a] D. Paiva,[b] J.L. Faria,[a] R.J. Santos RJ,[a] C.G. Silva,[a]

a) Laboratory of Separation and Reaction Engineering-Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal; b) Laboratory for Process Engineering, Environment, Biotechnology and Energy (LEPABE), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

Email: isob@fe.up.pt

Additive Manufacturing (AM) technologies are a valuable tool for developing and building highly tailored photoreactors. In photocatalytic systems, some parameters must be considered, like radiation field, the interaction of the material of the reactor with the photocatalyst, and the optimization of photochemical reactions. Using AM technologies presents a particular disadvantage, which is the limited range of available materials.
In this work, a material composed of a commercial resin and a benchmark catalyst (TiO_2) is proposed and demonstrated to fabricate photoreactors using AM. A 3D structure was designed so that light reached all the system plates and was placed inside a cylindrical batch reactor and printed using the stereolithography (SLA) technique. A hybrid material composed of a commercial photoreactive resin (Formlabs Clear V4) and the benchmark photocatalyst TiO_2 P25 Evonik was prepared and characterized by scanning electron microscopy (SEM) and rheological tests of fluids (resins) and solids. The photocatalytic activity of the materials was experimentally benchmarked using the degradation of Rhodamine B (Rh_B) as a model molecule. These experiments were carried out using the 3D printed structure, and its performance was assessed by monitoring the concentration at specific times using UV-Vis spectrophotometry.
Figure 1a shows a schematic diagram of the experimental setup used to perform degradation of Rh_B by photocatalysis in a batch system, and **Figure 1b** presents the results of the photocatalytic activity of the developed material. When the reactor was irradiated by 370 nm LEDs, an 80% decrease in RhB concentration after 240 min was observed. Moreover, the photo-stability of the 3D structure was confirmed for at least 3 cycles of utilization. This simple, cost-effective, and fast technique to immobilize catalysts used in photocatalytic applications is effectively demonstrated.



(a) (b)

Figure 1: (a) Experimental setup of photocatalytic degradation of Rh_B. (b) Photocatalytic degradation of Rh_B over 3 consecutive cycles.

Acknowledgments: This work was financially supported by Base Funding - UIDB/50020/2020 of the Associate Laboratory LSRE-LCM - funded by national funds through FCT/MCTES (PIDDAC) and projects POCI-01-0145-FEDER-030674 and POCI-01-0145-FEDER-031398, funded by European Regional Development Fund (ERDF) through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT. This work was also financially supported by Base Funding - UIDB/00511/2020 of the Laboratory for Process Engineering, Environment, Biotechnology, and Energy – LEPABE - funded by national funds through the FCT/MCTES (PIDDAC). I.S.O. Barbosa acknowledges her FCT scholarship UI/BD/151092/2021.

Materials chemistry and applications

Valorization of used cooking oils through ionic liquid catalyzed biodiesel conversion processes

F. Monteiro, A. Queiroz, A.E. Ribeiro, P. Brito

Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

Email: f.monteiro1997@gmail.com

Population growth has been increasing dramatically in recent decades, with approximately 8 billion inhabitants worldwide. The industrialization and urbanization increasing leads to high energy demand and to an increasing need for clean air, both mandatory factors concerning the socio-economic development of society. To date, fossil fuels predominate as the primary source of energy, with high consumption in transport and industries, which makes them a major problem for our Planet, due to the weak environmental sustainability, as the case of its high greenhouse gas emissions to the atmosphere and also because there are limited reserves. To overcome these high percentages of fossil fuels, several alternatives must be found to avoid serious consequences for our ecosystem.[1]

In this context, biodiesel emerges as a biofuel, that is biodegradable and less toxic when compared to fossil diesel, and since it is environmentally sustainable is already commercialized in several countries in a pure or mixed form with diesel. Biodiesel, can de chemically defined as a mixture of fatty acid alkyl esters (usually fatty acid methyl esters – FAME), produced through transesterification reactions of a raw material, normally vegetable oils or animal fat, with an alcohol, typically methanol, in the presence of homogeneous basic or acid catalysts, which are highly corrosive and difficult to recover.[2]

The objective of this work is to study the production of biodiesel applying 1-methylimidazolium hydrogen sulfate ([HMIM][HSO_4]) ionic liquid as a catalyst in esterification/transesterification reactions with methanol in artificially acidified waste cooking oil conditions.

In order to estimate the optimal operating conditions, Design Expert 11 software was used for the construction of a Box-Behnken Design (BBD) for a Response Surface Methodology (RSM) analysis. An experimental design was used to generate a matrix with four factors with three levels and two extra central points. The chosen factors were: percentage of incorporated oleic acid (20, 40 and 60% wt.), oil/methanol molar ratio (1:5, 1:10 and 1:15), catalyst dosage (5, 10 and 15% wt.) and reaction time (2, 4 and 6 h). Through this methodology a set of 27 runs was established to quantify the influence of each factor on the two responses, acidity reduction and fatty acid methyl ester (FAME) conversion. A reaction temperature of 65ºC was maintained during all runs.

After the biodiesel synthesis, the reaction conversion in terms of acidity decrease was determined by volumetric titration of the organic phase with potassium hydroxide standard solution and the FAME content of the biodiesel samples was quantified by gas chromatography (GC-FID). Table 1 shows the experimental values for both types of conversion for 3 selected run using different reaction conditions.

Table 1: Conversions in terms of acidity reduction and FAME's.

Run	Time (h)	Catalyst dosage (% wt)	Molar ratio oil:methanol	Incorporation of Oleic Acid (% wt)	Conversion in terms of acidity reduction (%)	Conversion in FAME's (%)
1	2	10	1:15	40	57.35	29.28
2	2	10	1:10	60	32.25	19.68
3	2	10	1:5	40	22.12	15.61

Acknowledgements: The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support by national funds FCT/MCTES to CIMO (UIDB/00690/2020).

References

1. Mahlia T.; Syazmi Z.; Mofijur M.; Abas A.; Bilad M.; Ong H.; Silitonga A. *Renew. Sust. Energ. Rev.* **2020**, *118C*, 109526.
2. Wu Q.; Chen H.; Han M.; Wang D.; Wang J. *Ind. Eng. Chem Res.* **2007**, *46*, *24*, 7955

Materials chemistry and applications

Light and pH-responsive cucurbit[8]uril-dithienylethene host-guest complexes

M. Colaço, P. Máximo, A.J. Parola, N. Basílio

a) Laboratório Associado para a Química Verde (LAQV), Rede de Química e Tecnologia (REQUIMTE), Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal

Email: mr.colaco@campus.fct.unl.pt

The development of molecular machines, nanotechnological devices and advanced materials based on supramolecular interactions strongly depends on the binding selectivity and affinity displayed by the interacting building blocks. Multi-stimuli responsive host-guest binding pairs are extremely valuable in this context, allowing tighter control over binding affinity/selectivity whereby amplifying the range and complexity of functions and applications.
In this communication, a host-guest pair with high-affinity in water is presented. It is based on a 1:1 complex between a cucurbit[8]uril (CB8) host[1] and a photochromic dithienylethene (DTE) guest[2] comprising a zwitterionic arm. At acidic pH values, the DTE can be protonated leading to the formation of two pyridinium cations, as is the case of the DTE previously reported.[3,4] It was demonstrated that the affinities of the deprotonated compounds are lower by just over an order of magnitude. Furthermore, the colored ring-closed isomers are both thermically[3] and kinetically[4] more stable at about two orders of magnitude than the fluorescent open forms, that can be obtained by means of the bio-penetrating near infrared light (NIR). Thus, this DTE allows the development of stimuli-responsive host-guest assembly controlled according to an AND molecular logic gate operation through light and pH stimuli, showing affinities that range from micro (open deprotonated) to nanomolar binding (closed protonated), depending on the applied conditions (**Figure 1**).

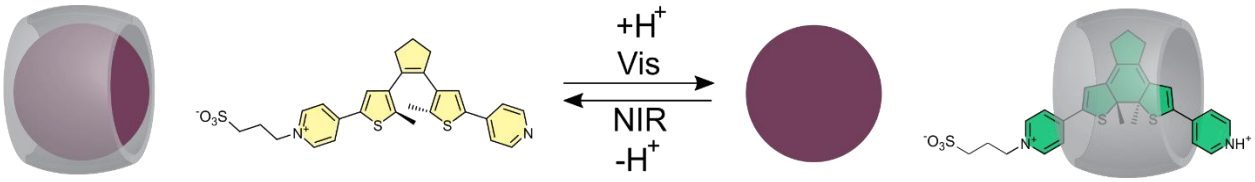


Figure 1: Light and pH-responsive competitive host-guest system formed by CB8 (grey ring), the DTE guest that contains a zwitterionic arm (the open deprotonated isomer in yellow and the closed protonated isomer in green) and a competitor guest (purple sphere).

Acknowledgements: This work was supported by the Associate Laboratory for Green Chemistry - LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/50006/2020). FCT/MCTES is also acknowledged for supporting the National Portuguese NMR Network (ROTEIRO/0031/2013-PINFRA/22161/2016, co-financed by FEDER through COMPETE 2020, POCI, PORL, and FCT through PIDDAC) and for the grants PTDC/QUI-COL/32351/2017, PTDC/QUI-QFI/30951/2017 and CEECIND/00466/2017.

References:

1. Barrow S. J.; Kasera S.; Rowland M. J.; Barrio J.; Scherman O. A. *Chem. Rev.* **2015**, *115*, 12320.
2. Irie M.; Fukaminato T.; Matsuda K.; Kobatake S. *Chem. Rev.* **2014**, *114*, 12174.
3. Ferreira P.; Ventura B.; Barbieri A.; Da Silva J. P.; Laia C.; Parola A. J.; Basílio N. *Chem. Eur. J.* **2019**, *25*, 3477.
4. Colaço M.; Máximo P.; Parola A. J.; Basílio N. *Chem. Eur. J.* 10.1002/chem.202100974 (accepted).

Materials chemistry and applications

A different kind of aminal: challenges and insights

F. Leitão, R. Rippel, L. Ferreira, P. Branco

LAQV-REQUIMTE, Departamento de Química, NOVA School of Science and Technology, 2829-516 Caparica, Portugal

Email: fl.leitao@campus.fct.unl.pt

Aminals are commonly referred to as *N,N* analogs of *O,O*-Acetals and are usually prepared by the condensation of amines (or diamines) and an aldehyde[1] with the outcome of symmetric structures (Figure 1). This chemical scaffold can be found in several molecules, ranging from biologically active ones to organic catalysts, which make them a valuable core to be synthetized. Chemically, there are also relevant features observed in aminals, such as the fact that they mostly present themselves in endocyclic systems and their stability will depend on the conformational energy of the ring system, making them particularly unstable in acidic conditions.[2]
Cernumidine (Figure 1) is a peculiar molecule with a unique aminal core. When compared with other molecules with this functionality, the aminal core of Cernumidine does not have both nitrogen atoms in an endocyclic system. In our efforts to synthesize this molecule, we have encountered problems related to the synthesis and stability of the aminal core, previous to the guanilation step. Although this asymmetry on the aminal structure may seem a small difference, it will play a major role in the aminal stability.
The insights about the stability of this uncommon aminal core, and how we overcome the intricacies found along the way, will be here presented.

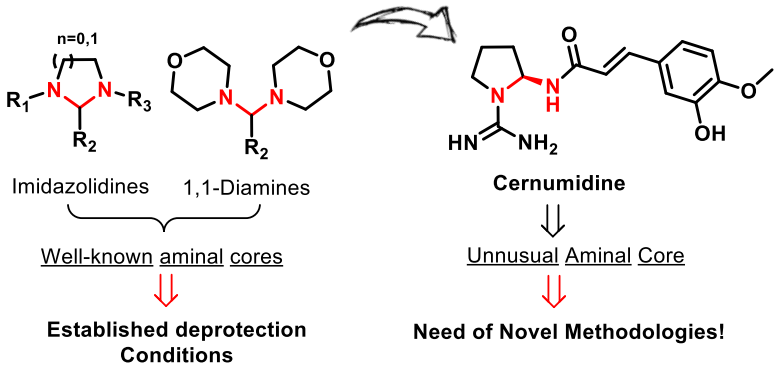


Figure 1: General structure of Imidazolidines and other aminal molecules (at the left) and Cernumidine (at the right), a molecule known to cause the inhibition of IL-8 production by HT-29 cells of colon carcinoma with an unusual aminal core.[1–3]

Acknowledgements: This work was also supported by the Associate Laboratory for Green Chemistry—LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 and UIDP/50006/2020). Rafael Rippel acknowledges the PhD grant SFRH/BD/136692/2018 from Fundação para a Ciência e Tecnologia provide information such as granting agency and other financial support.

References:

1 J. G. Pereira, J. P. M. António, R. Mendonça, R. F. A. Gomes and C. A. M. Afonso, *Green Chem.*, **2020**, 22, 7484–7490.
2 E. Sawatzky, A. Drakopoulos, M. Rölz, C. Sotriffer, B. Engels and M. Decker, *Beilstein J. Org. Chem.*, **2016**, 12, 2280–2292.
3 L. C. Lopes, B. Roman, M. A. Medeiros, A. Mukhopadhyay, P. Utrilla, J. Gálvez, S. G. Mauriño, V. Moltiva, A. Lourenço and A. S. Feliciano, *Tetrahedron Lett.*, **2011**, 52, 6392–6395.

Materials chemistry and applications

Solid biopolymer electrolytes applied to diverse electrochemical systems

S.C. Barros,[a] P.P. Alday,[c] M. Fernandes,[b] R. Rego,[b] V. de Zea Bermudez,[b] N. Harudin,[d] Z. Osman,[d] J.P. Esquivel,[c], M.M. Silva,[a]

a) Center/Department of Química, University of Minho, Campus de Gualtar, 4710 - 057 Braga, Portugal; b) Department of Chemistry and CQ-VR, University of Trás-os-Montes e Alto Douro, 5001-801 Vila Real, Portugal; c) Institute of Microelectronic of Barcelona IMB-CNM (CSIC), Campus Universitat Autònoma de Barcelona (UAB), 08193 Bellaterra, Barcelona, Spain; d) Center for Ionics and Physics Department, University of Malaya, 50603 Kuala Lumpur.

Email: xana@quimica.uminho.pt

Currently there is an emerging demand to develop sustainable materials in all areas of materials science. Thus, in energy storage systems the perspective is no different and there is been a huge effort to gradually replace the conventional synthetic components by environmentally friendly materials. In this particular case, the focal point is the solid polymer electrolyte (SPE) and in this perspective, we proposed the replacement of the standard synthetic base polymer by natural polymers (e.g., cellulose derivatives and chitosan). In order to attain a full eco-friendly SPE, the polymeric formulation was admixed with greener additives (e.g., plasticizers and/or specific ionic liquids) to boost the conductive performance of the resulting electrolyte. In this sense, we report the development of green solid biopolymer electrolytes (SBEs), based on the blend composed by two polysaccharides: chitosan (CH) and the cellulose derivative (hydroxypropyl)methyl cellulose (HPMC).[1,2] To the HPMC:CH blend (prepared in different ratios) a polyol (Gly, glycerol) and/or an ionic liquid (IL, cholinium chloride ($[N_{111}(2OH)]Cl$)) were added, with the goal of enhancing the total ionic conductivity of the polymeric system. The resulting materials are completely transparent, colourless, flexible, adhering and present an appropriate ionic conductivity for electrochromic and battery applications ($1.82x10^{-4}$ and $1.39x10^{-2}$ $S.cm^{-1}$ at 25 ºC, for the HPMC:CH blends doped with Gly and IL, respectively. The aforementioned materials were characterised in terms of total ionic conductivity (complex impedance spectroscopy), thermal (DSC and TGA), structural (FTIR-ATR) and morphological (POM) properties. Moreover, these materials were assembled and evaluated in an electrochromic device, in magnesium batteries and in biotically degradable batteries.[3]

Acknowledgements: The authors thankfully acknowledge the funding from the Chemistry Centre at Minho University (Pest-C/QUI/UI0686/2020)

References:

1. Barros S. C., da Silva A. A., Costa D. B., Cesarino I., Costa C. M., Lanceros-Méndez S., Pawlicka A., Silva M. M. *Cellulose* **2014,** *21 (6)*, 4531-4544.
2. Barros S. C., da Silva A. A., Costa D. B., Costa C. M., Lanceros-Méndez S., Maciavello M. N. T., Ribelles J. L. G., Sentanin F., Pawlicka A., Silva M. M. *Cellulose* **2015,** *22 (3)*, 1911-1929.
3. Alday P.P., Cerqueira Barros S., Alves R., Esperança J. M. S. S., Navarro-Segarra M., Sabaté N., Silva M.M., Esquivel J.P. *Adv. Sustainable Syst.* **2019**, *4(2)*, 1900110.

Materials chemistry and applications

Development and characterization of polysulfone dialysis membranes doped with human elastase inhibitors pilot study

R. Rebelo,[a] K. Morgošová,[b] M.J. Valente,[c] C. Amorim,[d] A. Araújo,[d] R. Moreira,[e] A.S. Silva,[c] M.C.B.S. Montenegro,[d] Susana Rocha[d]

a)Faculty of Sciences, University of Porto, Porto, Portugal; b)Faculty of Pharmacy, Hradec Králové University, Czech Republic; c)UCIBIO/REQUIMTE, Biochemistry Laboratory, Department of Biological Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal; d)LAQV/REQUIMTE, Applied Chemistry Laboratory, Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Porto, Portugal; e)iMed.ULisboa, Faculty of Pharmacy University of Lisbon, Lisbon, Portugal

Emails: rutesarabrandao@gmail.com; srocha@ff.up.pt

Human neutrophil elastase (HNE) is increased in End Stage Kidney Disease patients undergoing hemodialysis treatment, due to the recurrent contact of blood with the artificial dialysis membranes used, that may trigger neutrophil activation. This inflammatory response seems to contribute to an increased morbidity and mortality in these patients. Based on the experience of our group in the manufacture of flat-sheet polysulfone (PSF) membranes by spin-coating using phase-inversion method [1] and in the synthesis of HNE inhibitors (HNEIs), namely 4-oxo-β-lactam based compounds [2], the present work aimed to dope PSF membranes with HNEIs and assess their bioactivity and biocompatibility, which may contribute to the development of a bioactive membrane that with the potential of improving the life quality of these patients.

Sivelestat (SIV), from Abcam, and an *in house* synthesized compound, D4L-2, were used as HNEIs and were immobilized into the PSF membranes by adsorption. In 3 independent assays, triplicates of PSF membrane circles (Ø = 0.6 cm) were incubated with HNEIs vehicle (2.5% DMSO) or with 10 - 2000 nM SIV or D4L-2 during 3 h at 25 ºC for adsorption of the inhibitors. The bioactivity of the modified PSF membranes with each HNEI was evaluated through a HNE activity assay [2]. For biocompatibility evaluation (n=3), PSF membrane circles (Ø = 2 cm) were also incubated with HNEIs vehicle (2.5% DMSO) or with 10 - 2000 nM SIV or D4L-2 (3 h at 25ºC, in duplicates), followed by incubation with 1.0 mL of whole-blood for 3.5 h at 37 ºC. Afterwards, plasma hemoglobin (Hb) concentration and platelet activation were determined [1].

The bioactivity of the PSF membranes doped with HNEIs increased in a concentration-dependent manner and the highest HNE inhibition capacity was consistently presented by D4L-2 (approximately 3-fold higher, on average). For all SIV-PSF membranes, the Hb concentration in plasma was lower in comparison to the vehicle; however, the platelet activation was higher. Compared to the vehicle, D4L-2 doped membranes presented similar plasma Hb values and lower platelet activation.

In conclusion, the immobilization of HNEIs into the PSF membranes by adsorption was successful and these biomaterials bioactivity was directly dependent on the concentration of HNEI solution used. The 4-oxo-β-lactam derivate D4L-2 modified membranes showed higher inhibitory capacity of HNE than the SIV-PSF biomaterials. These results are in accordance with the assumption that the 4-oxo-β-lactam-based inhibitors are more stable molecules and present higher specificity for HNE. Concerning biocompatibility, all SIV-PSF and D4L-2-PSF membranes were non-hemolytic. However, only D4L-2-PSF membranes presented no platelet activation.

Acknowledgements: This work received financial support through PT national funds from FCT/MCTES (UIDB/50006/2020 | UIDP/50006/2020 and UIDP/04378/2020 | UIDB/04378/2020) and support from the European Union (FEDER funds through COMPETE POCI-01-0145-FEDER-031322) and National Funds (FCT, Fundação para a Ciência e Tecnologia) through project PTDC/MEC-CAR/31322/2017.

References:

[1] J. Mater. Sci. 2020, 55, 1292–1307; DOI: 10.1007/s10853-019-04123-1
[2] J. Med. Chem. 2010, 53, 241–253; DOI: 10.1021/jm901082k

Materials chemistry and applications

Time-dependent self-assembly of copper(II) coordination polymers and tetranuclear rings: new catalysts for oxidative functionalization of saturated hydrocarbons

I.F.M. Costa, M.V. Kirillova, V. André, T.A. Fernandes, A.M. Kirillov

Centro de Química Estrutural and Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001, Lisboa, Portugal

Email: inesfmcosta@tecnico.ulisboa.pt

The present study describes a time-dependent self-assembly generation of new copper(II) coordination compounds from an aqueous-medium reaction mixture composed by copper(II) nitrate, H_3bes biobuffer (*N*,*N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid), ammonium hydroxide and benzenecarboxylic acid, namely 4-methoxybenzoic (Hfmba) or 4-chlorobenzoic (Hfcba) acid. Two products were isolated from each reaction, namely 1D coordination polymers $[Cu_3(\mu_3\text{-}OH)_2(\mu fmba)_2(fmba)_2(H_2O)_2]_n$ (**1**) or $[Cu_2(\mu\text{-}OH)_2(\mu\text{-}fcba)_2]_n$ (**2**) and discrete tetracopper(II) rings $[Cu_4(\mu Hbes)_3(\mu\text{-}H_2bes)(\mu\text{-}fmba)]\cdot 2H_2O$ (**3**) or $[Cu_4(\mu\text{-}Hbes)_3(\mu\text{-}H_2bes)(\mu\text{-}fcba)]\cdot 4H_2O$ (**4**), respectively. The compounds were obtained as microcrystalline air-stable solids and characterized by standard methods, including the single-crystal X-ray diffraction.[1] The structures of **1** and **2** feature distinct types of metal-organic chains driven by the μ_3- or μ-OH^- ligands along with the μ-benzenecarboxylate linkers. The structures of **3** and **4** disclose the chair-like Cu_4 rings assembled from four μ-bridging and chelating aminoalcoholate ligands along with μ-benzenecarboxylate moieties. Catalytic activity of **1**−**4** was investigated in two model reactions, namely (a) the mild oxidation of saturated hydrocarbons with hydrogen peroxide to form alcohols and ketones, and (b) the mild carboxylation of alkanes with carbon monoxide, water and peroxodisulfate to generate carboxylic acids. Effects of different parameters were investigated, including an effect of acid co-catalyst and various selectivity parameters. Apart from notable catalytic activity, this study showcases a novel time-dependent synthetic strategy for the self-assembly of two different Cu(II) compounds from the same reaction mixture.

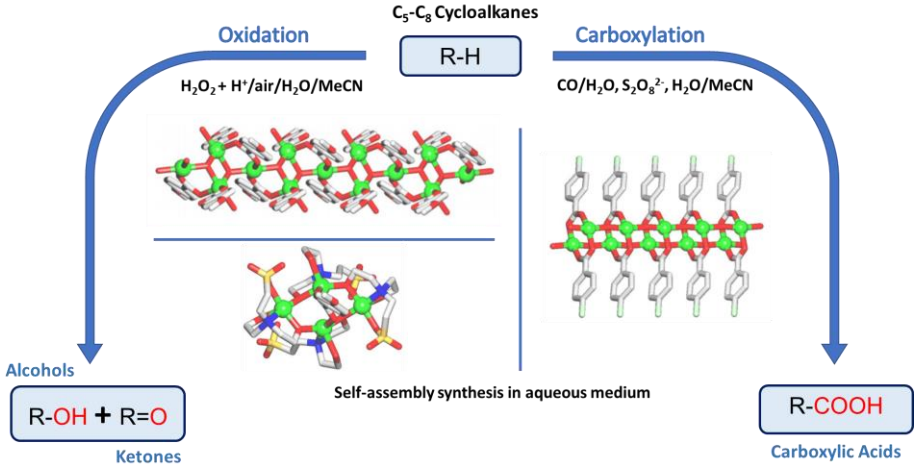


Figure 1: Model Cu-catalyzed hydrocarbon oxidation and carboxylation reactions.

Acknowledgements: This work has been supported by the Foundation for Science and Technology (FCT) (grant PD/BD/150418/2019 and projects UIDB/00100/2020, PTDC/QUI-QIN/3898/2020, CEECIND/03708/2017, LISBOA-01-0145-FEDER-029697, UIDP/00100/2020, and REM2013).

References:

1. Costa, I.F.M.; Kirillova, M.V.; André, V.; Fernandes, T.A.; Kirillov, A.M.; Time-dependent Self-Assembly of Copper(II) Coordination Polymers and Tetranuclear Rings: New Catalysts for Oxidative Functionalization of Saturated Hydrocarbons, *Inorg. Chem.* 2021 (submitted).

Materials chemistry and applications

Valorization of waste cooking oils through conversion processes catalyzed by choline hydroxide

Y. Gué, A. Queiroz, A.E. Ribeiro, P. Brito

Centro de Investigação de Montanha, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, wwPortugal

Email: araygue@hotmail.com

The world is facing great challenges due to the reduction of unrecoverable fossil fuels, the dependence on its industry, the increase in energy consumption and the increase in environmental pollution. A large amount of energy needs across the world is met by fossil fuels (petrochemical, coal, and natural gas).[1,2]
The development of renewable energy resources is necessary to create the need for other alternatives to fossil fuels.[3] Biodiesel, as a renewable energy resource, is used as an alternative fuel in diesel engines.[2] Biodiesel can be defined as mono-alkyl esters of long-chain fatty acids produced from vegetable or animal oils and alcohol with or without a catalyst. It can be produced by esterification of fatty acids or transesterification of triglycerides with short chain alcohols, such as methanol and ethanol. Methanol is used mainly due to its lower cost compared with other alcohols, so biodiesel most commonly refers to fatty acid methyl esters (FAME).[1,3]
The raw material is obtained from edible and non-edible oil sources including palm oil, jatropha oil, mustard oil, beauty leaf oil, microalgae oil, rubber seed oil, mahua oil, animal fats, waste cooking oil, can be used for biodiesel synthesis.[2,3]
The effective way to sustain biodiesel productivity is to reduce dependence on edible raw materials and oil. This current study focused on the use of waste cooking oil (WCO) to produce biodiesel. The processing of WCO waste facilitates a consistent supply of raw material compared to competition with edible raw materials, which are more valuable as part of consumable food items. Thus, the use of WCO as a low-grade raw material for the synthesis of renewable fuel ensures price stability and process sustainability.[4]
Ionic liquids were initially introduced as alternative green reaction media due to their unique physicochemical properties such as non-volatility, non-flammability, thermal stability, and controlled miscibility. At present, these are extensively used in controlling the reaction as catalysts. Synthesis of biodiesel using ILs as a catalyst is a promising pathway to an eco-friendly production.[1]
The objective of this work is to study Choline Hydroxide as a catalyst in esterification/transesterification reaction with methanol to produce biodiesel from waste cooking oil samples.
A numerical optimization method was devised using the Design-Expert 11 software, by the generation of a Box-Benhken Design (BBD), applied for a Response Surface Methodology (RSM) analysis. Hence, a matrix with four factors at three levels (-1 0 1) was constructed. The selected factors were the percentage of catalyst (2wt%, 4wt% and 6wt%), the oil/methanol molar ratio (1:5,1:10 and 1:15), the reaction temperature (55ºC, 60ºC and 65ºC) and the incorporation of oleic acid (0wt%, 1wt% and 2wt%) for an artificial control of the raw material acidity. Through this strategy, 27 runs were established in order to quantify statistically the influence of each factor in the response: the FAME content of the produced biodiesel. A constant reaction time of 30 minutes was maintained during all runs.

Acknowledgements: The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support by national funds FCT/MCTES to CIMO (UIDB/00690/2020).

References:

1. Ong H.C.; Tiong Y.W.; Goh B.H.H.; Gan Y.Y.; Mofijur M.; Rizwanul Fattah I.M.; Chong C.T., Alam A.; Lee H.V.; Silitonga A.S.; Mahlia T.M.I., *Energy Conversion and Management* **2020**, *228*, 113647.
2. Mohadesi M.; Gouran A.; Dehnavi A.D. Energy **2021**, *219*, 119671.
3. Deive F.J.; Rodríguez A.; Ionic liquids for enzyme-catalyzed production of biodiesel, in *Green Sustainable Process for Chemical and Environmental Engineering and Science*, Ionic Liquids as Green Solvents (Inamuddin A.M.A; Suvardhan K., eds.) **2020**, 31.
4. Yusuff A.S.; Gbadamosi A.O.; Popoola L.T. *Jornal of Environmental Chemical Engineering* **2021**, *9(2)*, 104955.

Materials chemistry and applications

Natural materials based polymer blends for photoluminescent applications

B.D.D. Cruz,[a] D.M. Correia,[b,c] V. de Zea-Bermudez,[c] G. Botelho,[a] S. Lanceros-Méndez[d, e]

a) Centro de Química, Universidade do Minho, 4710-057 Braga, Portugal; b) Centro de Física, Universidade do Minho, 4710-057 Braga, Portugal; c) CQ-VR, Universidade de Trás-os-Montes e Alto Douro, 5000-801 Vila Real, Portugal d) BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain; e) Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain

Email: barbara.cruz5@hotmail.com

Natural polymers are being explored for an increasing number of applications as smart materials due to their interesting properties and abundance in nature. Sodium alginate is a linear polysaccharide derivative of alginic acid comprised of 1,4-β-d-mannuronic (M) and α-l-guluronic (G) acids.[1] The combination of sodium alginate with photoluminescent compounds allows the development of smart materials able to convert incident electromagnetic radiation of specific wavelengths (ultraviolet, UV, in the present case) into emitted electromagnetic radiation of different regions of the spectra (visible or infrared).[2] Those materials find applications in areas such as sensors and actuators.[3]
In the present work, photoluminescent materials based on sodium alginate and different amounts (5, 10 and 20% wt.) of the luminescent compound sodium tetra(2-thenoyltrifluoroacetonate) europate (III) (Na [Eu(tta)$_4$])[4] were developed by solvent casting. The morphology, physical-chemical and thermal properties were evaluated, and their luminescence properties accessed after UV irradiation. Independently of the Na [Eu(tta)$_4$] concentration, a non-porous surface is obtained. The physical-chemical properties were evaluated from FTIR-ATR and DSC analysis showing that no relevant changes occur in the alginate properties. The thermal stability of the materials reveals a small increase of the composites with respect to neat sodium alginate. The photoluminescence properties were evaluated under different light excitation wavelengths, being observed a colour change from opaque yellow to a red (sodium alginate/Na [Eu(tta)$_4$]) colour (**Figure 1**).

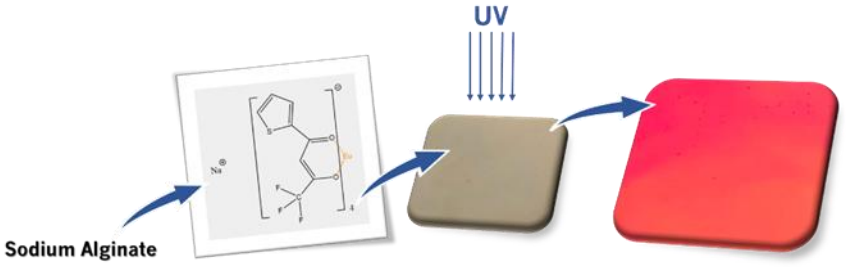


Figure 1. Sodium alginate/Na [Eu(tta)$_4$] films before and after the exposure of UV light of 365 nm.

Acknowledgements: Portuguese Foundation for Science and Technology (FCT): UID/FIS/04650/2020, UID/QUI/0686/2020, UIDB/50006/2020, UIDP/50006/2020, PTDC/FIS-MAC/28157/2017 and SFRH/BPD/121526/2016 (D.M.C). Spanish State Research Agency (AEI) and European Regional Development Fund (ERFD): PID2019-106099RB-C43 / AEI / 10.13039/501100011033. Basque Government Industry and Education Departments: ELKARTEK, HAZITEK and PIBA (PIBA-2018-06) programs.

References:

1. Kakita, H.; Kamishima, H. *Journal of Applied Phycology*. **2008**, *20*, 543-549.
2. Wang, F.; Liu, X-K; Gao, F. Micro and Nano Technologies, 2019, 1-35
3. Correia, D. M.; Fernandes, L. C.; Martins, P. M.; García-Astrain, C.; Costa, C. M.; Reguera, J.; Lanceros-Méndez, S. *Adv. Funct. Mater*. **2020**, *30*, 1909736.
4. Cardoso, M. A.; Correia, S. F. H.; Frias, A. R.; Gonçalves, H. M. R.; Pereira, R. F. P.; Nunes, S. C.; Armand, M.; André, P. S.; de Zea Bermudez, V.; Ferreira, R. A. S. *Journal of Rare Earths*. **2020**, *38*, 531-538.

Materials chemistry and applications

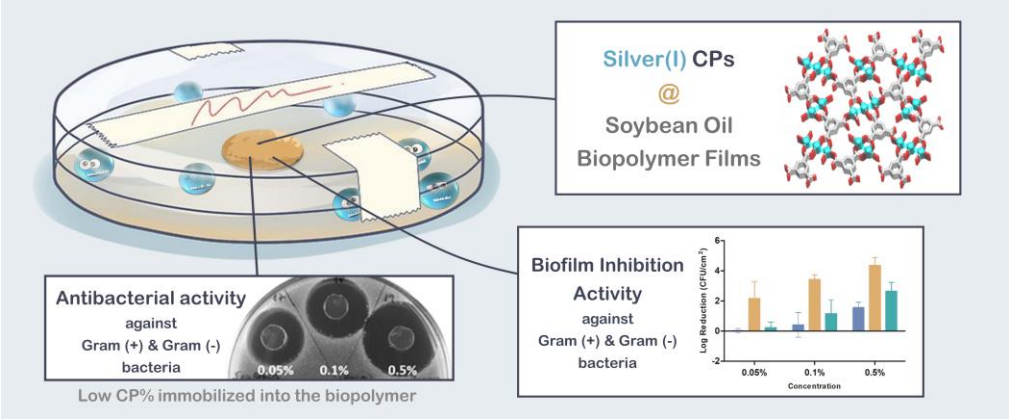
Biopolymer films doped with silver(I) coordination polymers against bacterial biofilms

T.A. Fernandes,[a] I.F.M. Costa,[a] P. Jorge,[b] A.C. Sousa,[a,c] V. André,[a] N. Cerca,[b] A.M. Kirillov[a]

a) Centro de Química Estrutural and Departamento de Engenharia Química, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001, Lisboa; b) Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga; c) Área Departamental de Engenharia Química, ISEL - Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro, 1, 1959-007 Lisboa

Email: tiago.a.fernandes@tecnico.ulisboa.pt

This report describes a template-mediated self-assembly synthesis, full characterization, and structural features of two new silver-based bioactive coordination polymers (CPs) as well their immobilization into acrylated epoxidized soybean oil (ESOA) biopolymer films for antimicrobial applications. The 3D silver(I) CPs $[Ag_4(\mu_8\text{-}H_2pma)_2]_n \cdot 4nH_2O$ (**1**) and $[Ag_5(\mu_6\text{-}H_{0.5}tma)_2(H_2O)_4]_n \cdot 2nH_2O$ (**2**) were generated from $AgNO_3$ and pyromellitic (H_4pma) or trimesic (H_3tma) acid, also using *N*,*N*′-dimethylethanolamine (Hdmea) as a template. Both **1** and **2** feature the intricate 3D layer-pillared structures driven by distinct polycarboxylate blocks. Topological analysis revealed binodal nets with the **flu** and **tcj**/hc topology in **1** and **2**, respectively. These CPs were used to create new hybrid materials, namely by doping the $[ESOA]_n$ biopolymer films with very low amounts of **1** and **2** (0.05, 0.1, and 0.5%). Their antimicrobial activity and ability to inhibit bacterial biofilm formation was investigated in detail against both Gram-positive (*Staphylococcus epidermidis* and *Staphylococcus aureus*) and Gram-negative (*Pseudomonas aeruginosa* and *Escherichia coli*) bacteria. Both silver(I) coordination polymers and derived biopolymer films showed activity against all the tested bacteria in a concentration dependent manner. Compound **1** was far more active, especially in preventing biofilm formation, with mean bacterial load reductions ranging from 3.7 to 4.3 log against the four bacteria (99.99% bacterial eradication). Thus, the present study expands the antibiofilm applications of CP-doped biopolymers, offering new perspectives and promising results for the design of functional biomaterials (**Scheme 1**).[1]



Scheme 1

Acknowledgements: This work was supported by the Foundation for Science and Technology (FCT) and Portugal 2020 (projects PTDC/QUI-QIN/29697/2017, LISBOA-01-0145-FEDER-029697, UIDB/00100/2020, UIDP/00100/2020, IPL/2020/HyBioPol and REM2013), contracts CEECIND/02725/2018 and CEECIND/00194/2020.

References:

1. Fernandes, T.A.; Costa, I.F.M.; Jorge, P.; Sousa, A.C.; André, V.; Cerca, N.; Kirillov, A.M.; *ACS Appl. Mater. Interfaces*, **2021**, *13*, 12836–12844.

Materials chemistry and applications

Nanostructured biomimetic catalysts for solar light-assisted redox reactions

M.P. Loureiro, S.L.H. Rebelo, I. Kuźniarska-Biernacka, C. Freire

LAQV/REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal

Email: up201709309@edu.fc.up.pt

Metalloporphyrins and their analogues are compounds with a central role in several fundamental biological processes, such as oxygen transport, oxidative metabolism or photosynthesis. The mode of action of these macromolecules has been a source of inspiration for biomimetic processes of great relevance in the current eco-energy context, namely the use of sunlight to remove pollutants, the conversion of CO_2 or the development eco-sustainable syntheses [1].
In this context, the use of nanostructured metalloporphyrins is of great interest since it allows to obtain structural organization and high surface areas that are determining factors for the efficiency of catalysis.
In the present study, nanostructures based on metalloporphyrins with (photo)catalytic properties have been prepared, using ionic self-assembly processes [2]. The materials have been characterized and tested in photo-redox reactions under visible light irradiation.
The catalytic activity of the materials has been tested in degradation of the pollutant 4-nitrophenol and, in the presence of solar light, it was significantly higher than the reaction performed in the dark.

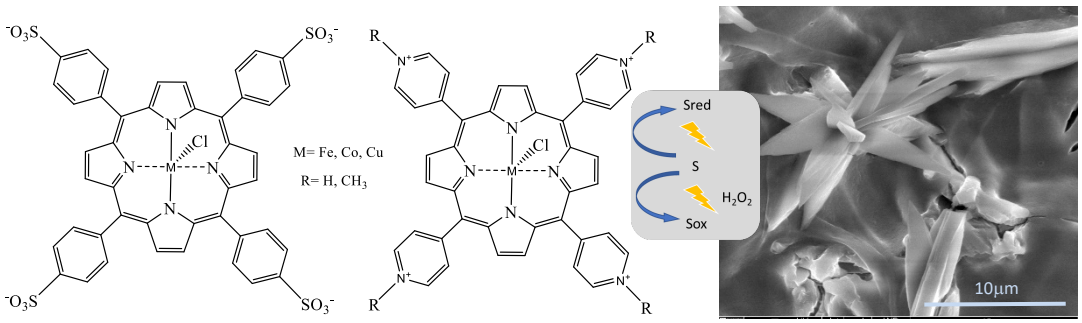


Figure 1: Preparation of binary metalloporphyrin structures

Acknowledgements: We thank the FCT/MCTES for financial support through the projects UIDB/50006/2020, REQUIMTE/EEC2018/30(SLHR) and REQUINTE/EEC2018/14(IKB).

References:

1. Khalil, M.; Gunlazuardi, J.; Ivandini, T. A.; Umar, A., Photocatalytic conversion of CO2 using earth-abundant catalysts: A review on mechanism and catalytic performance. *Renew Sust Energ Rev* **2019,** *113*.
2. Frigerio, C.; Santos, J. P. G.; Quaresma, P.; Rebelo, S. L. H.; Gomes, A.; Eaton, P.; Pereira, E.; Carvalho, P. A.; Shelnutt, J. A.; Jiang, L.; Wang, H.; Medforth, C. J., Ionic self-assembly reactions of a porphyrin octacation. *Tetrahedron* **2016,** *72* (44), 6988-6995.

Materials chemistry and applications

Poliuretanos microcelulares com propriedades de regulação térmica para calçado de segurança com propriedades de conforto incrementadas

H.M. Rafael,[a] I.P. Fernandes,[a] V.V. Pinto,[b] M.J. Ferreira.[b] M.F. Barreiro[a]

a) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; b) Centro Tecnológico do Calçado de Portugal (CTCP), Rua de Fundões - Devesa Velha, 3700-121 S. João da Madeira, Portugal

Email: ipmf@ipb.pt

Atualmente, os consumidores de calçado de segurança procuram produtos que garantam a proteção do pé associados a propriedades incrementadas como o conforto e o bem-estar. Os materiais de base poliuretano (PUs), nomeadamente os microcelulares, são tipicamente aplicados na construção de calçado devido às suas boas propriedades de conforto. Apesar da seleção criteriosa destes materiais, as condições de temperatura e humidade geradas no interior do calçado ao longo do período de utilização, podem resultar na diminuição do conforto térmico do pé. Esta condição verifica-se quando a temperatura no interior do calçado varia entre 28 e 32°C, sendo importante garantir a regulação térmica de forma a minimizar variações fora deste intervalo. Assim, o presente trabalho visa o desenvolvimento de poliuretanos microcelulares (PU) com propriedades de regulação térmica, destinados à incorporação em calçado de segurança com conforto térmico incrementado. Estes materiais foram produzidos utilizando uma formulação e um sistema químico de base poliéster tipicamente empregues na produção de entressolas para calçado. Os PUs com capacidade de regulação térmica foram produzidos por aditivação da formulação de base com 5 e 10% (m/m) de um material de transição de fase (PCM), encapsulados numa matriz de acrílico (designado microA). Os PUs foram posteriormente caracterizados relativamente às propriedades mecânicas através da avaliação da resistência à flexão de Ross (Norma BS 5131: 1991), resistência ao rasgamento (ISO 20875:2018) e à abrasão (ISO 20344:2011). Avaliou-se também a capacidade de termorregulação por Calorimetria de Varrimento Diferencial (DSC), tendo sido determinada a retenção e libertação de energia quando as amostras foram sujeitas a um ciclo de aquecimento seguido de arrefecimento. A análise dos resultados obtidos nos testes mecânicos (Tabela 1) permitiu verificar que as propriedades dos PUs aditivados são semelhantes às do material base, cumprindo as especificações das normas de teste. Estes resultados apontam para a viabilidade da utilização dos materiais desenvolvidos na construção de calçado de segurança. Relativamente à análise da capacidade termorreguladora, os resultados obtidos ao longo da etapa de aquecimento mostram que os PUs aditivados apresentam uma capacidade de absorção e retenção de calor numa gama de temperaturas compreendida entre 29 e 30ºC, correspondendo a uma energia retida de 236 e 242 J/g_{microA} respetivamente para o PU5microA e o PU10microA. Por outro lado, durante o arrefecimento ocorre a libertação da energia retida nos PCM numa gama de temperaturas de 25 a 27ºC, libertando uma energia de 233 J/g_{microA} no caso do PU5microA e 239 J/g_{microA} no caso do PU10microA. Os resultados deste teste apontam para a viabilidade da utilização do aditivo baseado em PCM para regular a temperatura no interior do calçado, promovendo o conforto térmico do pé.

Tabela 1. Resultados dos testes de resistência à flexão, rasgamento e abrasão do PU base e PU aditivado com 5 e 10% de microA.

Amostra	Flexão Ross (23 ºC) (mm/Kc)	Rasgamento (N/mm)	Abrasão (mm^3)
PUBase	0.00	4.90	43/47/39
PU5microA	0.00	4.50	78/75/76
PU10microA	0.00	3.60	79/92/88
Especificação Normas	<0.10	>1.70	<250

Agradecimentos: FCT/MCTES (PIDDAC) - CIMO (UIDB/00690/2020). FCT – Programa de emprego científico institucional (I.P Fernandes), e SHOE@FUTURE – Soluções tecnológicas para calçado profissional (projeto SI I&DT - Projetos em Co-Promoção Nº 33835) cofinanciado pelo FEDER, através do COMPETE 2020.

Materials chemistry and applications

Direct ink writing of poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) as polymer binder for printed cathodes for energy storage system

J.C. Barbosa,[a,b] R. Pinto,[a,c] J. Serra,[a] L. Hilliou,[d] C.M. Costa,[a,c] M.M. Silva,[e] R. Gonçalves,[e] S. Lanceros-Méndez[f,g]

a) Centre of Physics, University of Minho, 4710-057 Braga, Portugal; b) Department of Chemistry and CQ-VR, University of Trás-os-Montes e Alto Douro, 5000-801, Vila Real, Portugal; c) Institute of Science and Innovation for Bio-Sustainability (IB-S), University of Minho, Portugal; d) IPC/i3N - Institute for Polymers and Composites, University of Minho, Campus de Azurem, 4800-058 Guimarães, Portugal; e) Centre of Chemistry, University of Minho, 4710-057 Braga, Portugal; f) BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain; g) IKERBASQUE, Basque Foundation for Science, 48009 Bilbao, Spain

Email: r.goncalves@quimica.uminho.pt

The growing number of portable electronic devices with increasing energy demanding and sustainability features lead to the necessity of developing smaller and adjustable batteries. Lithium-ion batteries (LIBs) are well established in the energy storage field, due to its high energy and power densities, as well as long life cycles [1]. Frequently the battery must be tailored to be confined in a small space in the device, meaning that the size, weight and flexibility of the battery are essential characteristics to consider.[2]

In this work, a novel P(VDF-TrFE-CFE) terpolymer was used and tested as a binder for Direct Ink Writing (DIW) printed cathodes in $LiFePO_4$ based lithium-ion batteries (**Figure 1a**). The rheology of the cathode slurry was studied to screen their printability and the obtained cathodes were fabricated and characterized. The results proved that the printing lines distance influences cathode performance and, when compared with conventional doctor blade electrodes, leads to a higher discharge capacity of around 120 vs. 70 $mAh.g^{-1}$ at 1C-rate (**Figure 1b**).

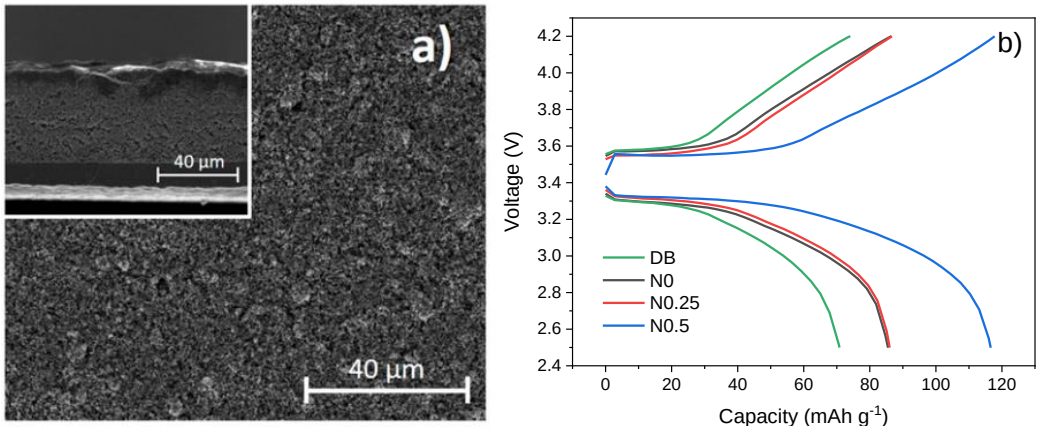


Figure 1: a) Representative SEM image of the prepared cathodes and b) electrochemical performance of the cathodes with the different samples performed by doctor blade (DB) and printed by different lines distances (0, 0.25 and 0.5 mm).

Acknowledgements: Fundação para a Ciência e Tecnologia: UID/CTM/50025/2021, UID/FIS/04650/2021, UID/EEA/04436/2021, UID/QUI/0686/2021, PTDC/FIS-MAC/28157/2017, SFRH/BD/140842/2018 (J.C.B.), IF/00606/2014 (LH), 2020.04028.CEECIND (C.M.C.) and CEECIND/00833/ 2017 (R.G.). Basque Government: ELKARTEK, HAZITEK and PIBA (PIBA-2018-06).

References:

1. Costa, C. M.; Gonçalves, R.; Lanceros-Méndez, S. Energy Storage Materials **2020**, 28, 216-234.
2. Gür, T. M. Energy & Environmental Science **2018**, 11 (10), 2696-2767

Materials chemistry and applications

Development of superparamagnetic yolk-shell nanoparticles as nanocarriers of antineoplastic drugs

S. Moretto,[a,b] A.S. Silva,[a] J.L. Diaz de Tuesta,[a] R. Cortesi,[c] A.R. Bertão,[d] M. Bañobre-López,[d] H.T. Gomes[a]

a) CIMO, Centro de Investigação de Montanha, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal; b) Dipartimento di Scienze della Vita e Biotecnologie, Università degli Studi di Ferrara, 44121, Ferrara, Italia; c) Dipartimento di Scienze Chimiche, Farmaceutiche ed Agrarie, Università degli Studi di Ferrara, 44121, Ferrara, Italia; d) Advanced (Magnetic) Theranostic Nanostructures Lab, International Iberian Nanotechnology Laboratory, Av. Mestre José Veiga s/n, 4715-330 Braga, Portugal

Email: htgomes@ipb.pt

The main feature of magnetic yolk-shell nanoparticles (MYSNP) is the void between the inner magnetic core and the surrounding shell. In medicine, MYSNPs have aroused interest as nanocarriers of anticancer agents since they can load the drug inside the cavity and be driven to the area of interest using an external magnetic field.[1] To achieve this aim, MYSNPs must be designed to be biocompatible and to show a superparamagnetic behaviour.[2] Given this background, the purpose of this work is to synthesize MYSNPs for biomedical application as nanocarriers of antineoplastic agents. MYSNPs were prepared following this pathway: (1) synthesis of nickel ferrite core by sol/gel, (2) coating the core with a polymer of tetraethyl orthosilicate, resorcinol and formaldehyde ($NiFe_2O_4$@polymer) (3) etching of the silica with 10 M NaOH solution, (4) surface oxidation and functionalization with Pluronic® F-127 ($NiFe_2O_4$@C-F127) to promote the biocompatibility. The process of synthesis was monitored by FT-IR spectroscopy and the magnetic properties were investigated by SQUID magnetometer analysis. Figure 1 shows the FT-IR results of the $NiFe_2O_4$@polymer and $NiFe_2O_4$@C-F127 MYSNPs. The formation of a $NiFe_2O_4$ spinel structure is confirmed by the bands at 488, 600 and 809 cm^{-1}, visible in both spectrums. In the $NiFe_2O_4$@polymer MYSNPs, the presence of polymer is detected by the bands at 471, 796, 960, 1092 and 1235 cm^{-1}, assigned to different vibrations of the Si-O, Si-O-Si and Si-C bonds. These bands disappear after silica etching, whereas the signal related to the vibration of C-O bonds and the alkyl chain emerge at 1110 and 2858 cm^{-1} in the $NiFe_2O_4$@C-F127 MYSNPs spectrum as a result of the surface treatment with Pluronic® F-127. In Figure 2, the results of the magnetic analysis of $NiFe_2O_4$@C-F127 MYSNPs are described as the relationship between mass-relative magnetization (M) and magnetic field (H). The high saturation magnetization of 42.7 kOe and the absence of an appreciable magnetic hysteresis, demonstrate the superparamagnetic-like behaviour of the $NiFe_2O_4$@C-F127 MYSNPs. FT-IR results confirm the composition at different stages during the synthesis of the MYSNPs: nickel ferrite core, the core coated with the polymer layer and the silica etching, as well as the surface functionalization with Pluronic® F-127 (results not shown). The final MYSNPs product manifests a superparamagnetic-like behaviour as proven by the absence of magnetic hysteresis.

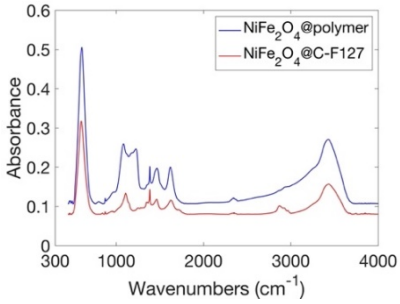


Figure 1: FT-IR spectra of the $NiFe_2O_4$@polymer (blue) and $NiFe_2O_4$@C-F127 MYSNPs (red).

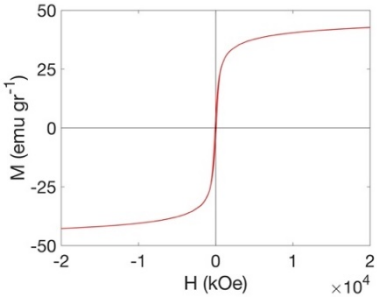


Figure 2: Magnetometry analysis of the $NiFe_2O_4$@C-F127 MYSNPs (red).

Acknowledgements: This work is a result of Project "RTChip4Theranostics - Real time Liver-on-a-chip platform with integrated micro(bio)sensors for preclinical validation of graphene-based magnetic nanocarriers towards cancer theranostics", with the reference NORTE-01-0145-FEDER-029394, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF); and CIMO (UIDB/00690/2020) through FEDER under Program PT2020.

References:

1. Rodrigues R. O.; Baldi G.; Doumett S.; Garcia-Hevia L.; Gallo J.; Bañobre-López M.; Dražić G.; Calhelha R. C.; Ferreira I. C. F. R.; Lima R.; Gomes H. T.; Silva A. M. T. *Mater. Sci. Eng. C* **2018**, 93, 206.
2. Prince P. M.; Waleed M. E.; Al-Ghamdi A. A.; Bronstein L. M. *Front. Chem*. **2018**, 6, 619.

Materials chemistry and applications

Cobalt-lanthanide bimetallic oxide nanofibers as catalysts for the selective hydrogenation of CO_2

J.F. Martinho, J.B. Branco, A.C. Ferreira

Centro de Química Estrutural, Departamento de Engenharia e Ciências nucleares, Instituto Superior Técnico, Universidade de Lisboa, Campus Tecnológico e Nuclear, Estrada Nacional 10, ao km 139.7, 2695-066 Bobadela, Portugal.

Email: *joana.martinho@ctn.tecnico.ulisboa.pt

The "greenhouse effect", the increase of the global temperature and climate change have been triggered by the increase of CO_2 concentration in the atmosphere linked to the intensive use of fossil fuels. [1] The use of CO_2 as feedstock in important and viable catalytic processes, aiming the production of valuable chemicals and fuels, could be a major contribution to avoid such negative effects. [2,3]

The selective hydrogenation of CO_2 to CH_4, the *Sabatier* reaction, associates the reaction of carbon dioxide with hydrogen ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O, \Delta H^0_{298} = -164.9\ \mathrm{kJ/mol}$) usually over supported metals (e.g. noble metals, Ni, Co) at atmospheric pressure. [4] Cobalt-based catalysts are active and selective to methane. However, the use of additives, namely f-block element oxides, is essential to improve their catalytic behaviour. [5]

The purpose of this work was the preparation of cobalt- lanthanide bimetallic oxide nanofibers using two different approaches: electrospinning and the incipient wetness impregnation technique:

1) Preparation of Co+Ln precursor solution (nitrates, molar ratio 1:1) → electrospinning (1 mL/h, 16 kV, 10cm)→ calcination (air, 500 ºC, 1 ºC/min, 2 hours) → Co-Ln bimetallic oxides [e.g. $Co_3O_4.3CeO_2$; $2Co_3O_4.3Ln_2O_3$ (Ln=La, Dy, Yb)]
2) Preparation of Ln precursor solution (nitrates) → electrospinning → calcination → Lanthanide oxides nanofibers (La_2O_3, CeO_2, Dy_2O_3 and Yb_2O_3) → incipient wetness impregnation of cobalt (nitrate) → calcination → Cobalt oxide supported on lanthanide oxide nanofibers (20 wt%)

Their catalytic behaviour was evaluated for the hydrogenation of CO_2 aiming the production of methane. As an example, Figure 1 show SEM images obtained after the two types of preparation techniques and Figure 2 illustrates the enhancement of catalytic performance over CeO_2 nanofibers impregnated with cobalt compared with $Co_3O_4.3CeO_2$ obtained by the electrospinning technique that clearly favours the first one.

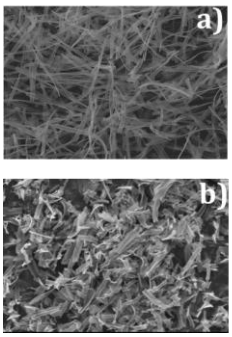


Figure 2- SEM images obtained after the two types of preparation techniques: a) electrospinning, b) incipient wetness impregnation.

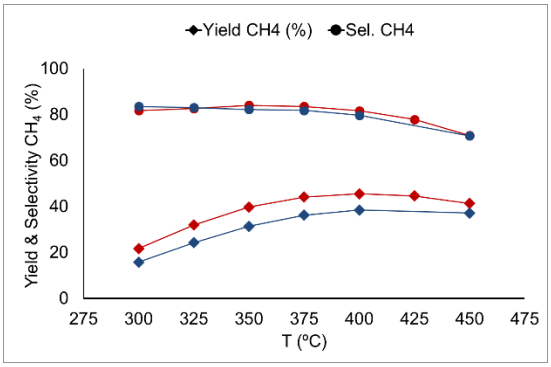


Figure 1 – CH_4 yield and selectivity over the two types of catalysts: blue, electrospinning; red, incipient wetness impregnation.

Acknowledgements: Authors gratefully acknowledge the support of the Portuguese "Fundação para a Ciência e a Tecnologia", FCT, through the PTDC/EAM-PEC/28374/2017 and UIDB/00100/2020 projects.

References

[1] Zhou Y., Jiang Y., Qin Z., et al., *Chinese Journal of Chemical Engineering*, 2018, **26** 768-774.
[2] Zhou G., Liu H., Xing Y., et al., *Journal of CO_2 Utilization,* 2018, **26** 221-229.
[3] Porosoff M. D., Yan B., Chen J. G., *Energy and Environmental Science,* 2016, **9** 62-73.
[4] Ferreira A. C., Branco J. B., *International Journal of Hydrogen Energy*, 2019, **44** 6505-6513.
[5] Alcade-Santiago V., Davó-Quinonero A., Lozano-Castello D., et al., *ChemCatChem*, 2019, **11** 810-819

Materials chemistry and applications

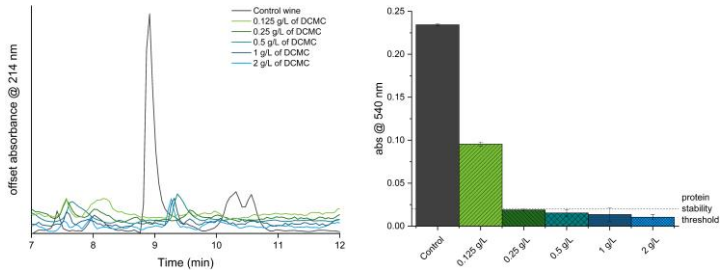
Evaluation of dicarboxymethyl cellulose efficiency in white wine protein stabilization

D. Gago,[a] R. Chagas,[b] L.M. Ferreira[a]

a) LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Portugal;
b) Food4Sustainability - Associação para a inovação no alimento sustentável, Centro Empresarial de Idanha-a-Nova, Portugal

Email: dx.gago@campus.fct.unl.pt

Wine clarity is an important characteristic to most consumers. Protein aggregation plays a significant role in wine stability and haze formation, which can impart a significant impact on wine clarity. Proteins, namely thaumatin-like proteins and chitinases, promote protein haze and should be removed from wines prior to bottling. Bentonite is the most commonly used processing aid in the winemaking industry for protein removal. However, this clay has major drawbacks, such as handling and disposal.[1] In the search for sustainable alternatives to bentonite fining emerges dicarboxymethyl cellulose (DCMC). DCMC is a cellulose derivative is able to perform cation exchange at low pH, making it suitable for wine stabilization.[2]
Wine fining trials were performed over white wine with different dosages of DCMC. Protein content in the wine samples was analyzed by high-performance liquid chromatography (HPLC). An HPLC method was optimized and validated for protein quantification. Following protein quantification, the samples underwent heat stress tests to evaluate wine turbidity.[3] The results show that the addition of DCMC successfully reduces the protein content in wine. Increasing the dosage of the fining agent consecutively reduces protein content and wine turbidity **(Figure 1)**. DCMC treatment originated heat-stable wines with dosages above 0.25 g/L. Heat stress results corroborate the HPLC analysis, supporting this quantification method. DCMC has the commercial potential for wine protein removal, while reducing the environmental impact of bentonite application.



a) b)

Figure 1: White wine treated with dicarboxymethyl cellulose: (a) HPLC chromatogram and (b) heat stress results.

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support through the PhD grant DFA/BD/5529/2020 and Associate Laboratory for Green Chemistry - LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020).

References:

1. Sommer, S.; Tondini, F. Sustainability 2021, 13.
2. Gago, D.; Chagas, R.; Ferreira, L.M.; Velizarov, S.; Coelhoso, I. Membranes 2020, 10.
3. Marangon, M.; Van Sluyter, S.C.; Haynes, P.A.; Waters, E.J. J. Agric. Food Chem. 2009, 57, 4415-4425.

Materials chemistry and applications

Sambucus nigra L. colour stabilization through microencapsulation studies

L.G. Teixeira,[a,b] V. Klimša,[a] A. Santamaria-Echart,[b] M.F. Barreiro.[b], F. Štěpánek,[a] G. Ruphuy[a]

a) University of Chemistry and Technology, 166 28, Prague, Czech Republic; b) Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança Campus de Santa Apolonia - 5300-253 Bragança, Portugal

Email: barreiro@ipb.pt

Elderberry (*Sambucus nigra* L.) is an important source of bioactive compounds, namely anthocyanins, water-soluble pigments. They constitute one of the main flavonoid groups in nature allowed to be used as food additives (E163).[1] However, their application is limited due to their vulnerability to light, pH medium, and temperature factors causing oxidative breakdowns. For this reason, the application of microencapsulation technologies is a relevant strategy to protect the anthocyanins from these weaknesses. In this context, this study aimed to evaluate two encapsulation procedures for the protection of elderberry anthocyanins. The first method comprised two steps, emulsion preparation followed by spray drying. The second one explored the encapsulation of the elderberry emulsion in alginate microbeads, followed by freeze-drying. The emulsions were prepared in two steps. The primary emulsion (W_1/O) includes elderberry juice (W_1), corn oil (O) and PGPR as the stabilizer. Double emulsions with varying (W_1/O)/W_2 ratios were prepared using water and Tween 80/Gum Arabic (GA) as stabilizer (W_2). Creaming index analysis was made to evaluate emulsion's stability. The emulsions were spray dried using a two-fluid-nozzle and the morphology examined by SEM. The colour stability of the dry emulsions was evaluated against buffers of different pH (pH 4, 6 and 8). The double emulsions containing 40 wt.% GA were successfully spray dried for all (W_1/O)/W_2 ratios and, when added to the buffers of different pH, the samples prepared with 35/65 and 40/60 (W_1/O)/W_2 ratios were the most stable in terms of colour variation. Simple emulsions drying was also tested using a three-fluid-nozzle, where the simple emulsion was the core and a 40 wt.% GA phase the shell. Overall, the spray drying of simple emulsions using the three-fluid-nozzle was successfully achieved; nevertheless, after testing the powders in the pH e buffers, no colour was observed.
The most stable simple emulsion from the previously described experiments was selected to be tested for encapsulation in alginate microbeads using a BUCHI B-395 Pro encapsulator. The simple emulsion served as a core, while cross-linked alginate coated the particles, acting as a physical barrier preventing emulsion's colour instability. For comparison purposes, pure elderberry juice was dispersed in an alginate solution and subsequently encapsulated to form homogenous matrix-particles. The prepared particles were observed by optical microscopy being possible to perceive the diffusion of the colorant from the particles to the surrounding medium. The produced microbeads were freeze-dried, and their colour stability evaluated at different pHs. The obtained core-shell particles showed the best results, since their colour has not changed within the tested broad pH range.

Acknowledgements: CIMO (UIDB/00690/2020) funded by FCT/MCTES (PIDDAC). National funding by FCT, P.I., through the institutional scientific employment program-contract for A. Santamaria contract. Erasmus+ program (University of Chemistry and Technology internship). FCT, research grant 2020.08803.BD of Liandra Gracher Teixeira.

References:

1. Yang, W.; Kaimainen, M.; Järvenpää, E.; Sandell, M.; Huopalahti, R.; Yang, B.; Laaksonen, O. Red Beet (Beta Vulgaris) Betalains and Grape (Vitis Vinifera) Anthocyanins as Colorants in White Currant Juice – Effect of Storage on Degradation Kinetics, Color Stability and Sensory Properties. *Food Chem.* **2021**, *348*. https://doi.org/10.1016/j.foodchem.2020.128995.
2. Toledo-Madrid, K.; Gallardo-Velázquez, T.; Osorio-Revilla, G. Microencapsulation of Purple Cactus Pear Fruit (Opuntia Ficus Indica) Extract by the Combined Method W/O/W Double Emulsion-Spray Drying and Conventional Spray Drying: A Comparative Study. *Processes* **2018**, *6* (10), 1–18. https://doi.org/10.3390/pr6100189.

Materials chemistry and applications

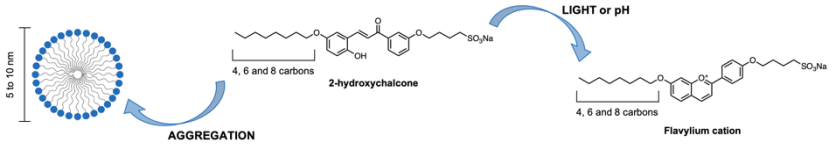
Self-assembly of 2-hydroxychalcones amphiphilic derivatives: A new approach for a drug-delivery system

R. Anastácio,[a] A. Seco,[a] P. Mateus,[a] E.F. Marques,[b] N. Basílio[a]

a) Associated Laboratory for Sustainable Chemistry-Clean Processes and Technologies (LAQV), Network of Chemistry and Technology (REQUIMTE), NOVA School of Sciences and Technology, 2829-516 Caparica, Portugal; b) CIQUP, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal.

Email: r.anastacio@campus.fct.unl.pt

In the last few decades, it has been one of the major goals of the scientific community to develop new mechanisms for drug delivery systems. The encapsulation of a drug and its controlled release as a response to an external stimulus is an approach that increases the bioavailability of the drug and simplifies its targeted delivery.[1] It is well established that amphiphilic compounds can self-assemble, giving rise to supramolecular aggregates that may encapsulate hydrophobic drugs.[2] Adding a component that has a response to external stimuli, such as light, temperature or pH, is the key to control the aggregation.[2] In this work, we synthesized new amphiphilic compounds, that are light- and pH-sensitive, due to the presence of a 2-hydroxychalcone moiety, in order to build new soft materials with potential applications in drug delivery systems.[1,3] The critical aggregation concentration (CAC) was determined for all the compounds through tensiometry and ^{1}H NMR measurements, showing an increase in the CAC with the decrease of the hydrophobic chain length.[4] DOSY studies allowed us to calculate the size of the aggregates, concluding that its diameter is within the range of 5 to 10 nm, suggesting the presence of micellar structures. These results indicate that we successfully achieved aggregation in the 2-hydroxychalcone form. Additionally, photochemical studies and pH jumps were done for the monomers, confirming the responsiveness to external stimuli. The next steps of this investigation include the study of the aggregates' ability to encapsulate and release hydrophobic drugs as well as their behavior in biological medium.



Scheme 1: Schematic representation of the aggregation of the 2-hydroxychalcone form into micellar structures and its conversion to the flavylium cation by a light or pH stimulus.

Acknowledgements: This work was supported by the Associated Laboratory for Sustainable Chemistry-Clean Processes and Technologies-LAQV which is financed by national funds from FCT/MCTES (UIDB/50006/2020 e UIDP/50006/2020). We are also grateful for the direct support of FCT/MCTES through the project PTDC/QUI-COL/32351/2017 and the contract CEECIND/00466/2017 (N.B.). Finally, we want to acknowledge the funding from FCT, in collaboration with DGES, within the scope of the special support "Verão com Ciência".

References:

1. Hu X.; Jia K.; Cao Y.; Li Y.; Qin S.; Zhou F.; Lin C.; *Chem. Eur. J.* **2014**, 20, 1.
2. a) Yu J.; Cao Z.; Zhang Q.; Yang S.; Qu D.; Tian H. *Chem. Commun.* **2016**, 52, 12056. b) Djiken D.; Chen J.; Stuart M.; Hou L.; Feringa B.; *J. Am. Chem. Soc.* **2016**, 138, 660.
3. a) Basílio N.; Pina F.; *Molecules* **2016**, 21, 1502. b) Pina, F; *J. Agric. Food. Chem.* **2014**, 62, 6885.
4. Perinelli D.; Cespi M.; Lorusso N.; Palmieri G.; Bonacucina G; Blasim P. *Langmuir* **2020**, 36, 5745.

Materials chemistry and applications

Synthesis of nanoparticles for controlled delivery of anticancer compound

T.I. de Menezes, T. Andreani, C.M.M. Pereira

FCUP, Faculdade de Ciências da Universidade do Porto, Departamento de Química e Bioquímica, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal.

Email: up201811986@edu.fc.up.pt

Dithiocarbazates that emerged as chelating agents for transition metal complexes in the late 19th century, have been widely synthesized and characterized in recent times, but there are few previous studies that report their physicochemical properties or even their medical and pharmaceutical applications.[1] A recent study has demonstrated that 3-methyl-5-phenyl-pyrazoline-1- (S-benzildithiocarbazate) (DTC - Figure 1) possess significant potential for Chagas disease treatment.[2] However, the lipophilic character of DTC limits its administration leading to a low oral bioavailability, a problem that can be overcome with the encapsulation of DTC in nanoparticles (NP), such as mesoporous silica nanoparticles (MSiNP) synthesized by the Stöber method which allows to control the pore walls and surfaces, facilitating the entry into NP of complex organic groups, such as DTC.[3] In this sense, the present work aims at contributing to the understanding of several physicochemical characteristics related to the mean particle size (Z-Ave), polydispersity index (PdI), zeta potential (ZP), internal structure (Fourier-transform infra-red), drug load capacity (DL) and encapsulation efficiency (EE) of MSiNP proposed as a nanocarrier for DTC delivery. MSiNP were synthesized according to the methodology described by Paula et al., obtaining MCM41 (Mobil Composition of Matter No. 41). The results show that Z-Ave of unloaded MCM41 was (168.43 ± 3.93 nm) while for MCM41-DTC the Z-Ave was (175.67 ± 0.97 nm) which corroborated that the immobilization of the DTC did not drastically change the particle size of MSiNPs. The obtained PdI values for MCM41 (0.286± 0.020) and MCM41-DTC (0.381 ± 0.041) indicate the formation of monodisperse suspensions. The ZP values changed from positive MCM41 values (+14.57 ± 0.45 mV) to negative values (- 21.90 ± 0.33 mV), suggesting the modification of the NP surface with DTC. The FTIR of DTC showed two intense bands in 1574 and 1031 cm^{-1}, which can be attributed to the ν(C=N) and ν(N-N) modes, respectively. Special attention must be paid to these bands, since a possible shift in their frequencies can be an indication of DTC entrapment in the silica matrix. From MCM41-DTC spectrum, the appearance of new bands was no observed. However, the main DTC bands reported above suffered displacement by increasing the intensity of the bands regarding to MCM41 in 1627 cm^{-1} (vibration bands ν(C=N)). The percentage of the total amount of DTC loaded into MCM41 matrices was %DL (9.94 ± 0.0001%) and %EE (99.36 ± 0.002%). Therefore, these findings demonstrate that due to their physicochemical properties, MSiNP can be an excellent candidate for DTC incorporation.

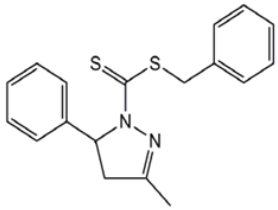


Figure 1: Structures of the 3-methyl-5-phenyl-pyrazoline-1- (S -benzyldithiocarbazate) (DTC).

Acknowledgements: T.I. Menezes thanks the NORTE2020 through project Norte-08-5369-FSE-000050 for financial support of a PhD grant. This work was partially supported by the FCT under Research Grant UIDB/00081/2020 – CIQUP.

References:

1. Manan, M. A. F. A.; Tahir, M. I. M.; Crouse, K. a.; How, F. N.-F.; Watkin, D. J.J. Chem. Crystallogr. **2011**, 42 (2), 173–179.
2. a) Costa, A. R.; de Menezes, T. I.; Nascimento, R. R.; dos Anjos, P. N. M.; Viana, R. B.; de Araujo Fernandes, A. G.; Santos, R. L. S. R. J. Therm. Anal. Calorim. 2019, 138,1683–1696. b) de Menezes, T. I.; de Oliveira Costa, R.; Sanches, R. N. F.; de Oliveira Silva, D.; Santos, R. L. S. R. Colloid Polym. Sci. 2019, 297 (11–12), 1465–1475.
3. Paula, A. J.; Martinez, D. S. T.; Júnior, R. T. A.; Filho, A. G. S.; Alves, O. L. *J. Braz. Chem. Soc.* **2012**, *23* (10), 1807–1814.

Materials chemistry and applications

Coffee grounds as a valuable source for production of fluorescent carbon nanomaterials for nitroanilines detection

B. Moraes,[a] A.I. Costa,[a,b] P.D. Barata,[a,b] J.V. Prata[a,b*]

a) Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro, 1, 1959-007, Lisboa, Portugal; b) Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801, Vila Real, Portugal.

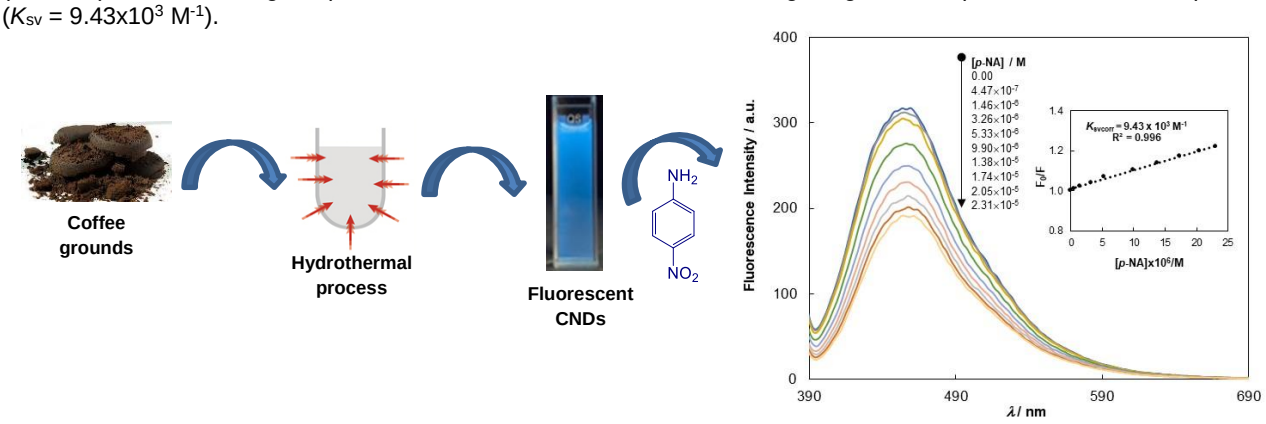
Email: acosta@deq.isel.ipl.pt

Carbon nanomaterials, so-called carbon nanodots (CNDs) are a very recent class of spherical-shaped nanosized carbon materials (< 10 nm) that are nowadays considered to be superior materials for application in bioimaging and nanomedicine, chemo/biosensing, photocatalysis and optoelectronics, owing to their highly luminescence, outstanding photostability and biocompatibility.[1-4]

Recently, our group had shown that fluorescent CNDs can be obtained directly from olive mill and cork industry wastewaters[3,4] in excellent yields following expedite and sustainable hydrothermal processes. The as-synthesized CNDs showed a remarkable high sensitivity and selectivity towards hemeproteins and nitroanilines (NAs) detection.[3,4,5]

Coffee is widely consumed worldwide and generates large amounts of lees, a residue with relevant content of organic matter (e.g. caffeine, phenols, tannins) of low biodegradability.[6,7]

With a goal to achieve the coffee grounds valorization, this communication aims to report the synthesis of fluorescent CNDs using this residue. The synthesis processes were based on Green Chemistry Principles, carried out by conventional heating treatment or microwave irradiation and their behaviour as chemical sensors for NAs assessed by steady-state fluorescence titration experiments (**Scheme 1**). The synthesized CNDs present a moderate quantum yield (*ca*. 0.17) and exhibit a good performance for NAs detection, even though a greater response was found for *p*-NA (K_{sv} = 9.43x10^3 M^{-1}).



Scheme 1. Fluorescent CNDs synthesis by hydrothermal process and emission spectra of CNDs upon varying the amounts of *p*-NA (inset: Stern-Volmer plot); [CNDs] = 0.01 mg/mL; λ_{exc} = 380 nm.

Acknowledgements: We are grateful to Fundação para a Ciência e a Tecnologia/Ministério da Ciência, Tecnologia e Ensino Superior (FCT/MCTES) for financial support (UIDB/00616/2021 and UIDP/00616/2021) and IPL (Projecto DotCoffee/IDI&CA/2020).

References:

1. Das, R., Bandyopadhyay, R., Pramanik, P. *Mater. Today Chem.* **2018**, 8, 96.
2. Sharma, V., Tiwari, P., Mobin, S. M. *J. Mater. Chem. B* **2017**, 5, 8904.
3. Sousa, D. A., Costa, A. I., Alexandre, M. R., Prata, J. V. *Sci. Total Environ.* **2019**, *647*, 1097.
4. Alexandre, M. R., Costa, A. I., Santos, M. N. B., Prata, J. V. *Molecules* **2020**, 25 2320.
5. Costa, A. I., Martelo, L.C., Sousa D. A., Berberan-Santos, M. N., Prata, J. V. 6th Nano Today Conference, 2019, Lisbon, Portugal.
6. Tokimoto, T., Kawasaki, N., Nakamura, T., Akutagawa, J., Tanada, S. *J. Colloid Interface Sci.* **2005**, 281, 56.
7. Mussatto, S. I.; Machado, E. M. S.; Martins, S.; Teixeira, J. A. *Food Bioprocess Technol.* **2011**, *4*, 661.

Materials chemistry and applications

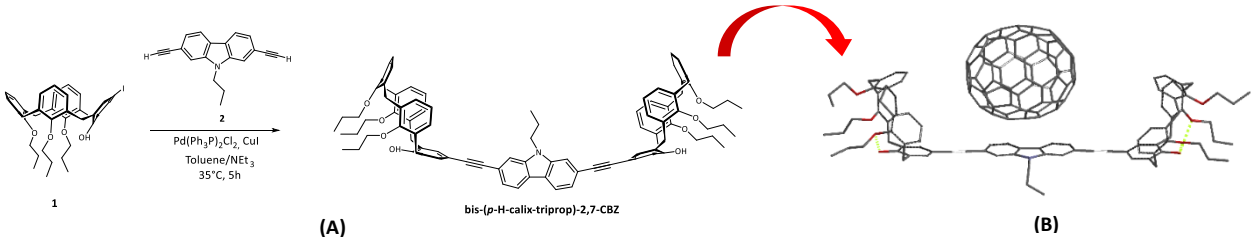
A novel calixarene-carbazole capsule for fullerene complexation

S. Costa,[a] P.D. Barata,[a,b] A.I. Costa,[a,b] J.V. Prata[a,b]

a) Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro, 1, 1959-007, Lisboa, Portugal; b) Centro de Química-Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801, Vila Real, Portugal.

Email: pbarata@deq.isel.ipl.pt

The creativity of supramolecular chemistry is often inspired by nature, in particular by the different types of interactions that replicates biological systems. The base of supramolecular chemistry is the use of non-covalent interactions (e.g. hydrogen bonding, metal coordination, π-π stacking) to create self-assembled structures.[1]
In last decades, several macrocyclic architectures, such as calixarenes, have been developed as supramolecular synthetic hosts. Calixarenes are one of the most valuable classes of molecular receptor in host-guest chemistry because of their rigid structures and well-defined π-electron-rich cavity, which make them perfect candidates for complexation studies with ions and neutral molecules through the formation of inclusion complexes.[2] In this scope, several calixarene structures, standing alone as a sole entity or incorporated into a polymeric systems, were reported by us as highly sensitive and selective chemosensors for detection of explosives (e.g. NACs), pollutants (e.g. nitroaromatic amines), proteins and metals.[3]
Recently, our group has designed a new bis-calixarene-3,6-carbazole host having an enlarged intramolecular cavity that revealed a remarkable affinity for fullerene-C_{60} and C_{70}.[4] In this communication, we will explore the influence of the carbazole linkage in the fullerene complexation event using a new fluorescent calixarene-2,7-carbazole architecture with more available space among the binding sites of calixarene units. The **bis-(*p*-H-calix-triprop)-2,7-CBZ** dimer was obtained by a Sonogashira cross-coupling reaction with catalytic amounts of $PdCl_2(PPh_3)_2$/CuI in toluene/NEt_3 (**Scheme 1**). The compound was characterized by FT-IR and $^1H/^{13}C$ NMR and its photophysical properties studied by UV-Vis and fluorescence spectroscopy. The results concerning the complexation ability and selectivity of both bis-(*p*-H-calix-triprop)-CBZs dimers toward fullerene-C_{60} and C_{70} will be presented.



Scheme 1: (**A**) Cross-coupling of calix[4]arene-tripropyl-mono-iodo (**1**) and 2,7-diethynyl-9-propyl-9*H*-carbazole derivatives (**2**); (**B**) Best conformers of C_{60} complex with **bis-(*p*-H-calix-triprop)-2,7-CBZ**, after Monte Carlo/MMFF94 molecular mechanics calculations.

Acknowledgements: We are grateful to Fundação para a Ciência e a Tecnologia/Ministério da Ciência, Tecnologia e Ensino Superior (FCT/MCTES) for financial support (UIDB/00616/2021 and UIDP/00616/2021).

References:

1. Ma, X.; Zhao, Y. *Chem. Rev.* **2015**, *115*, 7794.
2. Calixarenes 2001; Asfari, Z.; Böhmer, V.; Harrowfield, J.; Vicens, J., Eds.; Kluwer Academic: Dordrecht, Netherlands, 2001.
3. a) Barata, P. D.; Prata, J. V. *Chemosensors* **2020**, *8*, 128; b) Prata, J. V.; Costa, A. I.; Teixeira, C. M. *J. Fluoresc*. **2020**, *30*, 41; c) Prata, J. V.; Barata, P. D. *RSC Adv.* **2016**, *6*, 1659; d) Costa, A. I.; Barata, P. D.; Fialho, C. B.; Prata, J. V. *Molecules* **2020**, *25*, 2456.
4. Costa, S.; Barata, P. D.; Costa, A. I.; Prata, J. V. *Chem. Proc.* **2021**, *3*, 95.

Materials chemistry and applications

Antimicrobial activity of fruit packages coated with nanomaterials based in metal-ions zeolites

F.C. Rodrigues,[a,b] S. Barbosa,[c] A.J. Pontes,[c] A.M.F. Fonseca,[a,d] C. Almeida-Aguiar,[b,d,e,f] I.C. Neves[a,d]

a) CQUM, Centre of Chemistry, Chemistry Department, University of Minho, Campus de Gualtar, 4710-057, Braga, Portugal; b) Department of Biology, University of Minho, Campus de Gualtar, 4710-057, Braga Portugal; c) IPC-Institute of Polymers and Composites, Department of Polymer Engineering, University of Minho, Campus de Azurém, 4800-058, Guimarães, Portugal; d) CEB - Centre of Biological Engineering, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal; e) CITAB, Centre for the Research and Technology of Agro-Environmental and Biological Sciences, University of Minho, Campus de Gualtar, 4710-057, Braga, Portugal; f) CBMA - Centre of Molecular and Environmental Biology, University of Minho, Campus de Gualtar, 4710-057, Braga, Portugal.

Email: a84465@alunos.uminho.pt

The transport and storage of fruits is frequently compromised by microbial contaminations, especially during the delivery of these perishable foods to the public. The development of smart packages against microbial contaminations is an alternative of great interest to help controlling post-harvest diseases. The incorporation of nanomaterials, such as metal-ions zeolites with antimicrobial properties[1], in the semi-rigid alveolar structure for fruits transport/storage could allow the preservation of fruit with safety and quality, by inhibiting/reducing the growth of microrganisms[2,3].
In this work, metal-ions zeolite nanomaterials were incorporated on the packaging material and the antibacterial activity was tested against *Escherichia coli* and *Staphylococcus aureus*. The package material exhibited good antimicrobial activity against the two bacteria (Figure 1), which are promising results for industrial application.

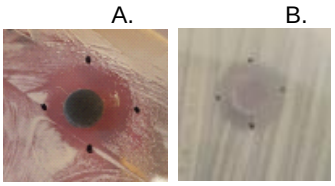


Figure 1: Antimicrobial effects of packaging discs with the incorporated metal-ions zeolites against *E.coli* (A) and *S. aureus* (B).

Acknowledgements: We thank the Fundação para a Ciência e Tecnologia for financial support through Centre of Chemistry (UID/QUI/00686/2013 and UID/QUI/0686/2016) and BioTecNorte (operation NORTE-01-0145-FEDER-000004).

References:

1. Ferreira, L.et al. *Colloids and Surfaces B: Biointerfaces,* **2016**, 142, 141-147.
2. Akbar, A.; Anal, A.K. *Food Control* **2014**, 38, 88-95.
3. Azlin-Hasim, S. *et al. Innov. Food Sci. Emerg. Technol.* **2015**, 27, 136-143.

Materials chemistry and applications

Production of sustainable polymers from the valorization of sugars and derivatives obtained by catalytic depolymerization of lignocellulosic materials

A.P. Rauter,[a] R. Galhano dos Santos,[b] J.C. Bordado,[b] P. Pinto,[c N.M.] Xavier,[a] L.B. Silva[a,b]

a) CQE - Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, Campo Grande; b) CERENA - Centro de Recursos Naturais e Ambiente, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portuga; c) RAIZ- Forest and Paper Research Institute,Quinta de S. Francisco, Apartado 15, 3801-501 EIXO, Portugal.

Email: lbsilva@fc.ul.pt

The depolymerization process of lignocellulosic biomass can be a very useful tool for the access to various types of chemical products, namely sugars and derivatives [1]. Biomass of lignocellulosic origin has been preferentially used for the production of bio-oil by liquefaction due to its abundance and easy access [2,3], to obtain green chemical products and / or for the conversion into sustainable energy sources [4]. Through the liquefaction process, hemicellulose and cellulose lead to the formation of sugars which composition has not yet been investigated in depth [5]. In this context, the study of the lignification process of lignocellulosic biomass is of great relevance since the chemical reactions that occur during this process, as well as the mechanisms that lead to the formation of sugars, have not yet been properly elucidated, constituting an innovation in view of the state of the art [6]. The main objective of this work is to investigate the valorization of sugars and their derivatives, present as major components in the aqueous fraction resulting from the liquefaction processes of the wood biomass, aiming at its use in the production of sustainable and biodegradable polymers, which can be applied to industrial or agro-industrial processes. Therefore, the importance of product valorization from the aqueous extract of wood liquefaction is demonstrated, aiming at a greater sustainability of the process, as well as the use of these sugars, their derivatives and analogues for the production of sustainable polymers, which are of commercial and industrial interest.

Acknowledgements: This work was carried out under the Project Inpactus – innovative products and technologies from eucalyptus, Project N.º 21874 funded by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of COMPETE 2020 nº246/AXIS II/2017.

References:

1. Isikgor F. H.; Becer C. R. *Polym Chem*. **2015**, 6, 4497–4559.
2. Galhano dos Santos R.; Bordado J. C.; Mateus M. M. J *Clean Prod*. **2016**, 137, 195-199.
3. Fernandes F.; Matos S.; Gaspar D.; et al. *Sustainability*. **2021**, 13, 3717.
4. Hertzog J.; Carre V.; Le Brech Y.; at al. *Energy & Fuels*. **2016**, 30, 5729-5739.
5. Galhano dos Santos R.; Ventura P.; Bordado J. C.; Mateus M. M. *Environ Chem Lett*. **2017**, 15, 453-458.
6. Hu Y. L.; Feng S. H.; Bassi A.; et al. *Energy Conversion and Management*. **2018**, 171, 618-625.

Author Index

XXVII ENCONTRO NACIONAL
Sociedade Portuguesa de Química

A

B

C

D

E

F

G

H

I

J

K

L

M

N

O

P

Q

R

S