

New copper porphyrins as functional models of catechol oxidase

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Abstract

In recent years, many research groups, including ours, have focused their attention on the development of synthetic and functional models of biological systems based on copper. In this work, we report the synthetic strategy, characterization and catalytic activity of new copper porphyrins (**CuP2** and **CuP3**) obtained by metallation of the corresponding tetra-ethylenediamine and tetra-*N*-tosylethylenediamine derivatives of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (**H₂P1**). **CuP2** allows the formation of structured and very insoluble solid (**CuP2S**) after metallation with an excess (10 equiv.) of Cu(II) ions, which were explored in oxidative heterogeneous catalysis of 3,5-di-*tert*-butylcatechol and catechol. The catalytic activity of this copper coordination polymer

was compared with their precursor **CuP2** and **CuP3**, not only in heterogeneous phase, but also under homogeneous conditions, using dioxygen or hydrogen peroxide as oxidants. The obtained results show that the new copper porphyrins (**CuP2** and **CuP3**) and the **CuP2S material** are able to efficiently mimic the activity of catecholase, being the last one easily reused and active form more than 3 catalytic cycles.

1. Introduction

Green chemistry approaches to obtain products of commercial interest represent an important challenge for a sustainable development. A well-known pillar of green chemistry is based on the use of catalysts, generally resulting in significant gains to a chemical reaction in terms of overall efficiency [1]. In this area, metalloporphyrins are efficient catalysts for the oxidative insertion of oxygen in hydrocarbons and also in a wide variety of organic compounds with a great efficacy [2-4]. In this context, several studies have already been performed with iron and manganese porphyrins [2, 5, 6] showing the great efficacy of these compounds as models of cytochrome P-450 [5, 7-11]. Besides of that they have been also used for the preparation of oxidized drug metabolites in the context of the pharmaceutical industry.

Although effective in homogeneous systems, particularly for epoxidation and hydroxylation of hydrocarbons, some problems are frequently reported with the use of these complexes in solution, such as deactivation of the catalytic species by secondary reactions which often leads to a low catalytic efficiency or, depending on the structure of the porphyrin ligand, destructive oxidation [11]. To minimize these problems, there has been much effort invested in the synthesis of new porphyrins that do not suffer such effects [12, 13]. Halogenated metalloporphyrin catalysts have been shown to be more robust, and more resistant to degradation by free radical attack than those

substituents containing electron donors. Because of that, porphyrin H₂TPPF₂₀ (**H₂P1**, Scheme 1) is a suitable platform for the synthesis of new robust porphyrins, by simple nucleophilic aromatic substitution of the *para* fluorine atoms of the pentafluorophenyl groups by appropriate nucleophiles.

Metalloporphyrins containing other metals, such as vanadium, nickel, zinc, copper, among others have also been investigated for different purposes over the last few years [REF]. The biological essentiality of copper element is long recognized, however, only in recent decades has been studied by many research groups in the development of synthetic/ functional models of biological systems important for the maintenance of life [14-16]. Proteins containing copper as active center are usually involved as redox catalyst in many biological processes in electron transfer or oxidation of a variety of organic substrates. One of them is the Catechol oxidase (COx), where the active center is a binuclear copper complex, which catalyzes the oxidation of a variety of o-diphenols (catechols), such as caffeic acid and their derivatives to the corresponding o-quinone, in a process known as catecholase. The resulting quinones are highly reactive to auto-polymerization leading to the formation of a brown polyphenolic pigment, i.e. melanin, a process thought to protect the skin cells from UV radiation damage, reducing the risk of skin cancer. against pathogens or insects.

The importance of oxidation of catechol is associated with the respective quinones, since several quinones have great importance in several scientific and technological areas like in materials chemistry. In medicine, they present several biological activities, such as antitumor, anti-inflammatory, anti-oxidant, among others [37].

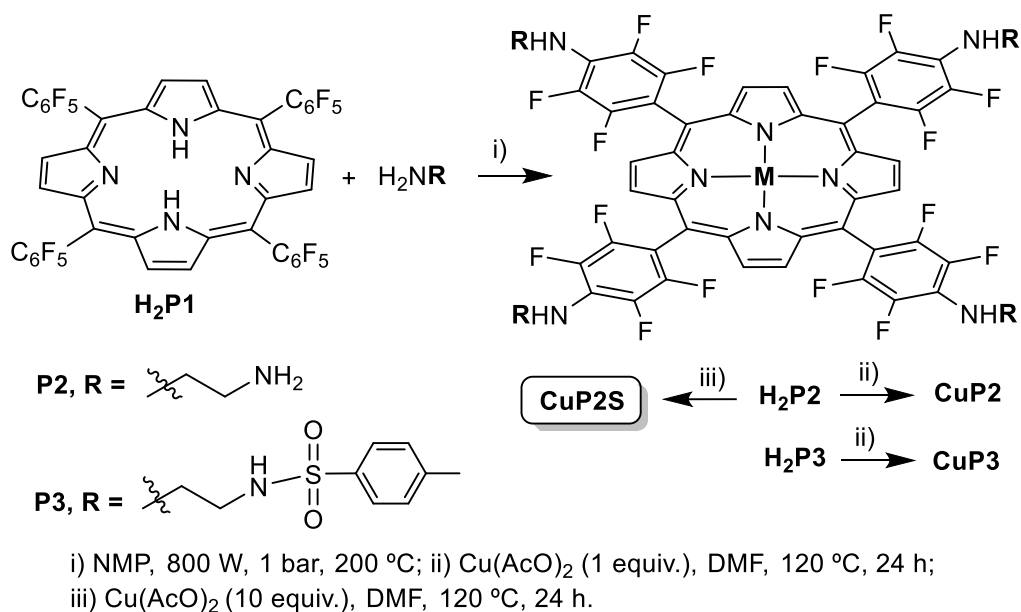
Over the years different functional and structural models, based on mono- and binuclear copper complexes, have been reported, however there are few reports of

copper porphyrins and phthalocyanines as catalysts for oxidation of catechols. Meunier et al. showed that iron phthalocyanines are active in the oxidation of catechol while Cu(II) phthalocyanine are inactive [45]. Some of us [13] reported recently that the copper porphyrins are also able to oxidize catechol very efficiently, in the presence of hydrogen peroxide and under homogeneous or heterogeneous conditions

Also, a new classes of materials, like coordination polymers (CPs), have been recently emerging, as an attractive approach to prepare robust and efficient catalysts [24-27]. In this area, porphyrins with appropriate functional groups on the periphery of the porphyrin ring, can constitute efficient building blocks for the design and synthesis of novel CPs. The connectivity is driven by coordinative chemistry between the functional group of the linker and metal centers, and can extend the structures into one, two or three dimensions [28] [24]. In fact, porphyrin derivatives containing amine, carboxylate, pyridine, phosphonate and sulfonate substituents tend to form CPs [9, 24, 26, 29, 30]. Such behavior is attributed to the affinity of these substituents of the porphyrin ring to metal ions, forming supramolecular insoluble clusters [24].

Based on the efficiency and selectivity of metalloporphyrins and corresponding hybrid materials for oxidation reactions associated with the presence of copper in catechol oxidase, which is the responsible for the catalysis process, we report here the synthetic strategy, characterization and catalytic activity of new copper materials based on the porphyrin $\text{H}_2\text{TPPF}_{20}$ (**H₂P1**, Scheme 1) scaffold. The nucleophilic aromatic substitution of the *para* fluorine atoms of the pentafluorophenyl groups by ethylenediamine and *N*-tosylethylenediamine and subsequent insertion of copper(II), afforded the corresponding CuP2 and CuP3 porphyrins, respectively, and the insoluble solid material **CuP2S**. The two new metalloporphyrins and the hybrid material are able

to mimic the activity of catecholase using hydrogen peroxide or oxygen, from the air, as oxidants.



Scheme 1

2. Experimental

All chemicals used in this study were purchased from Sigma-Aldrich or Merck and were of analytical grade.

HRMS were recorded on an APEXQe FT-ICR mass spectrometer (Bruker Daltonics, Billerica, MA). Electronic spectra (UV-VIS) were obtained on a Shimadzu UV-2501PC spectrophotometer, in the 350-800 nm range. For the solids diffuse reflectance characterization an UV-VIS Jasco V560 spectrophotometer was used. Attenuated total reflectance Transmission Fourier Transform Infrared (ATR-FTIR) spectra were registered on a FT Mattson 7000 galaxy series spectrophotometer in the 400-4000 cm⁻¹ range, the spectra were collected with a resolution of 4 cm⁻¹ and accumulation of 32 scans. For the X-ray diffraction (PXRD) measurements, self-oriented solids were placed on neutral glass sample holders. The measurements were performed in the

reflection mode using X'Pert MPD Philips diffractometer (Cu K α _{1,2} X-radiation, $\lambda_1 = 1.540598$ Å and $\lambda_2 = 1.544426$ Å), equipped with an X'Celerator detector and a flat-plate sample holder in a Bragg–Brentano para-focusing optics configuration (40 kV, 50 mA). Intensity data were collected by the step counting method (step 0.02), in continuous mode. Electron paramagnetic resonance (EPR) spectra of the solid materials were recorded on an EPR Bruker EMX micro X spectrometer operating in the X band (approximately 9.5 GHz) at 77 K using liquid N₂. Dynamic Light Scattering (DLS) measurements were performed in a Zeta Sizer Nano Series (Malvern).

2.1 Synthesis and characterization

2.1.1 Synthesis of copper porphyrins CuP2 and CuP3

The copper porphyrins **CuP2** and **CuP3** (Scheme 1) were obtained from the respective free-bases **H₂P2** and **H₂P3** already described in the literature [17], using the modified Kobayashi method [18]. The metallation reactions were performed with copper acetate in dimethylformamide (DMF) using stoichiometric ratio of 1:1 (mol:mol) for **CuP2** and an excess for **CuP3**. The reactions were performed at 120 °C for 24 hours under magnetic stirring, and followed by recording the electronic spectra at different reaction times. Then, the solvent was removed under reduced pressure and the desired copper porphyrins **CuP2** and **CuP3** were purified by column chromatography (silica gel) using dichloromethane: methanol as eluent. After isolation, they were characterized by UV-VIS, infrared (ATR-FTIR) and electron paramagnetic resonance (EPR) spectroscopies and HRMS.

CuP2 (C₅₂H₃₆F₁₆N₁₂Cu): UV-VIS (DMF) λ_{max} , nm (log ϵ): 417 (4.54) and 540 (4.03), HRMS-ESI: calcd. for C₅₂H₃₇F₁₆N₁₂Cu [M+H]⁺ 1196.22600 found 1196.22591;

CuP3 ($\text{C}_{80}\text{H}_{60}\text{F}_{16}\text{N}_{12}\text{O}_8\text{S}_4\text{Cu}$) UV-VIS (DMF) λ_{max} , nm (log ϵ): 419 (5.10) and 539 (4.32).
HRMS-ESI: calcd. for $\text{C}_{80}\text{H}_{61}\text{F}_{16}\text{N}_{12}\text{O}_8\text{S}_4\text{Cu}$ $[\text{M}+\text{H}]^+$ 1812.26140 found 1809.51772;
ESI-MS/MS: calcd. for $\text{C}_{80}\text{H}_{61}\text{F}_{16}\text{N}_{12}\text{O}_8\text{S}_4\text{Cu}$ $[\text{M}+\text{H}+\text{Na}]^+$ 1835.25 found 1835.15; (see Figures SI1-4).

2.1.2 Synthesis of the coordination polymer CuP2S

The insoluble **CuP2S** hybrid was prepared by reacting directly **H2P2** with 10 equivalents of copper(II) acetate using the previous conditions. At the end of the reactions, it was observed the precipitation of the desired solid **CuP2S** that was washed with different solvents (chloroform, dichloromethane, DMF, THF, water and acetone) in order to remove/prevent any contamination from free-base porphyrin **H2P2** or copper(II) acetate. Subsequently, the solid was dried in air at room temperature and was characterized using different techniques.

2.1.3 Single-Crystal X-ray Diffraction Studies of CuP3

Purple crystals of porphyrin **CuP3** were obtained by dissolving the porphyrin in a small amount of chloroform and methanol (1:1) and leaving the resulting mixture under slow evaporation at ambient temperature over a period of four days.

2.2 Catalytic Studies

The catalytic activity of the new copper porphyrins was investigated in the oxidation of catechol and 3,5-di-*tert*-butylcatechol (3,5-DTBC) using O_2 or H_2O_2 as oxidants, under homogeneous (**CuP2** or **CuP3**) and heterogeneous (**CuP2S**) conditions.

2.2.1 Oxidation of 3,5-di-tert-butylcatechol under O₂ from the air

In a typical reaction, the solid catalyst and the substrate (3,5-DTBC) were placed in a 10 mL reaction flask, dissolved in 9.0 mL of methanol. Then, 1.0 mL of phosphate buffer (pH = 8.0) was added to the flask. The reaction was carried out in the dark for different reaction times (between 15 min to 2 h) under constant stirring and in a thermostatic bath at 30 °C. The kinetics of the oxidation of 3,5-DTBC was determined by the growing band at 400 nm of the product 3,5 di-tert-butyl-*o*-benzoquinone (3,5-DTBQ), monitored by UV-VIS spectroscopy at different time intervals.

2.2.2 Oxidation of Catechol under H₂O₂ and O₂ from the air

The catalytic activity of **CuP2**, **CuP2S** and **CuP3** was evaluated through the oxidation of the substrate catechol in water. In a typical reaction, the solid catalyst and the substrate (catechol) were placed in a 10 mL volumetric flask. Then, 7.1 mL of phosphate buffer (pH = 8.0) and 30 µL of hydrogen peroxide (30% solution v/v) were added to the flask (CuP_x:H₂O₂:catechol molar ratio = 1:500:100) The reaction was carried out in the dark for different reaction times (between 15 min to 24 h) under constant stirring and in a thermostatic bath (30 °C).

Similar procedure was performed in absence of hydrogen peroxide using oxygen from the air. In this case, the reactions were made in open reaction flask to ensure the presence of oxygen.

The progress of the catalytic reactions were monitored by UV-VIS spectroscopy and quantified using the nitrite method (band at 508 nm, $\epsilon = 13.536 \text{ L mol}^{-1} \text{ cm}^{-1}$) [19]. Nitrite method is based on the fact that catechol (incolor substance), when combined with nitrous acid becomes yellow. The yellow color changes to an intense pink-red in the presence of excess sodium hydroxide (hydrogen ions from the phenolic OH groups

react with nitrite ions from the sodium nitrite, the molecular nitrous acid then forming NO compounds in presence of phenols), being the absorbance intensity directly correlated to the present catechol concentration. The same reactions were also performed using chloroform as solvent (2.0 mL) and phosphate buffer (8.0 mL) in a two phase experiments.

3. Results and Discussion

Synthesis of copper porphyrins CuP2 and CuP3

The new CuP2 and CuP3 metalloporphyrins were prepared from the reaction of the corresponding free-bases **H₂P2** and **H₂P3** derivatives [17] and copper acetate (Scheme 1). After the workup they were isolated, almost in quantitative yields, and fully characterized. The UV-VIS spectra of **CuP2** and **CuP3** present the characteristic Soret band at 418 and 420 nm respectively, with a small red shift in comparison to the Soret band of the free-base porphyrins and two Q-bands at 540 and 616 or 620 nm, resulting from the alteration in the micro symmetry of the porphyrin macrocycle from D_{2h} to D_{4h}, due to the presence of the Cu(II) ion in the porphyrin core (Figures SI1 and SI2).

The FTIR spectra exhibit the typical bands of metalloporphyrins, with bands at 3405 and 3313 cm⁻¹, ascribed to symmetric and asymmetric N-H stretching, and at 2955 and 2812 cm⁻¹, belonging to CH (phenyl) and CH (pyrrole) stretching (Figure SI5). The bands at 1600 cm⁻¹ were attributed to symmetrical angular deformation in the N-H plane of the pyrrole ring; δ N-H (in planarity) and δ N-H (out of planarity) appear at 960 cm⁻¹ and 752 cm⁻¹, among other bands related with skeletal ring vibrations. The bands in **H₂P3** spectrum at 1320 and 1153 cm⁻¹ can be related to the S=O groups [20].

Since EPR analysis is a good tool to investigate copper complexes, providing valuable information with respect to its oxidation state, ligand type and symmetry, we

performed the EPR spectra of **CuP2** and **CuP3** (Figure 1). As expected, they show typical EPR spectra of Cu(II), with a multiple lines pattern in the particular spectrum region, being the expected deployment of each signal in nine lines. This pattern is attributed to a super-hyperfine interaction of the copper ion unpaired electron with the four magnetically equivalent ^{14}N nucleus ($I=1$) [21]. In fact, g_{\parallel} is higher than g_{\perp} for both CuP derivatives, indicating that the unpaired electron of copper is occupying the orbital $d_{x^2-y^2}$, corresponding to the equatorial plane of Cu(II) with elongated tetragonal symmetry [22]. The g_{\parallel} and g_{\perp} values, along with other parameters, are in conformity with a square planar geometry for copper(II) porphyrins (**CuP2** ($g_{\parallel} = 2.20$; $g_{\perp} = 2.06$, $A_{\parallel}/\text{Cu} = 206$ and $A_{\text{N}} = 17.8$) and **CuP3** ($g_{\parallel} = 2.24$; $g_{\perp} = 2.05$, $A_{\parallel}/\text{Cu} = 200$ and $A_{\text{N}} = 17.1$) [23].

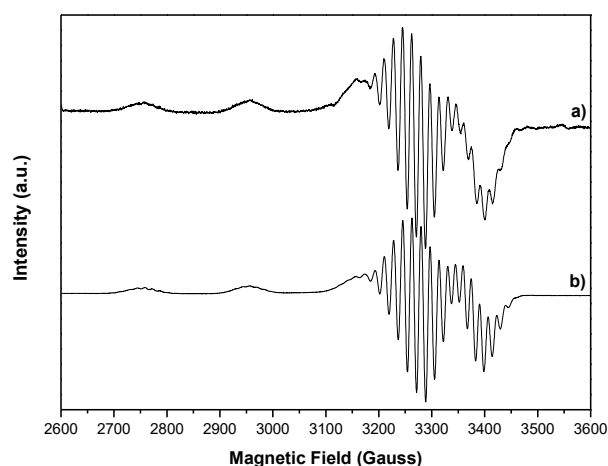


Figure 1. EPR spectra in acetone solution at 77 K: a) **CuP2** and b) **CuP3**.

Synthesis of the solid (CuP2S)

The **CuP2S** was prepared from the reaction of **H2P2** with 10 equivalents of copper acetate in DMF at 120 °C. Under these conditions **CuP2S** precipitated as a dark solid, being insoluble in solvents where **H2P2** and **CuP2** are very soluble or partially soluble (e.g., methanol, chloroform, dichloromethane, acetone, acetonitrile

and dimethylformamide). Here, the fact that solid **CuP2S** emerged during metallation of **H2P2**, by the using of an excess of copper, might be related with the ability of the peripheral amine groups to form solid structures, like CPs, by copper self-assembly mediation. The novel **CuP2S** hybrid solid was characterized by UV-VIS, ATR-FTIR, XRD and EPR techniques.

Diffuse reflectance UV-VIS spectra (DR UV-VIS) for free-base porphyrins and metalloporphyrins are shown in Figure 2. Usually, porphyrins in solid state have an extended Soret band and four bands of lower intensity attributed to the Q bands [31]. In our case, the free-base porphyrins **H2P2** and **H2P3** solids present a characteristic Soret band in the region of 400 nm and a set of four Q bands between 500 and 700 nm.

The UV-VIS spectra of the new complexes **CuP2** and **CuP3** have one maximum in the Soret region (428 nm), showing a hypsochromic shift in comparison to the Soret band of the corresponding free-base porphyrins (**H2P2** at 431 nm and **H2P3** at 435 nm), resulting from the alteration in the micro symmetry of the porphyrin macrocycle due to the presence of the Cu(II) ion in the porphyrin core [13, 33]. The spectrum of the **CuP2S** shows a broad Soret band at 428 nm, the same position observed for **CuP2**, and two Q-band at 552 and 626 nm. The two Q-bands, different from the three and four Q-bands of **CuP2** and **H2P2**, respectively, indicate that **H2P2** was metallated during the self-assembly process and that CuP2S is different from **CuP2**.

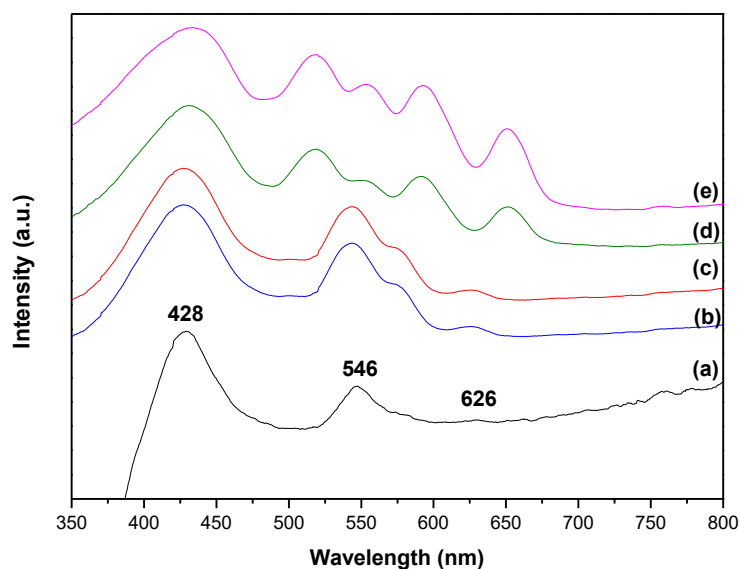


Figure 2. UV-VIS spectra of the solid sample: (a) **CuP2S**, (b) **CuP2**, (c) **CuP3**, (d) **H2P2** and (e) **H2P3**.

The ATR-FTIR spectrum of **CuP2S** (Figure SI5) shows the characteristic bands of porphyrin **CuP2**. The bands at 1544 and 1387 cm^{-1} are assigned to the symmetric and asymmetric vibrations of the C=O group belonging to the cluster acetate [20, 29].

The crystallinity of **CuP2S** was verified by PXRD (Figure 3). The PXRD pattern of **CuP2S** was different from the diffraction pattern of the starting materials (**H2P2** and $\text{Cu}(\text{OAc})_2$, Figure SI6). The PXRD of **CuP2S** showed characteristic feature of nanomaterials, such as high dispersion and disorder of phases; diffraction patterns are characterized by significant broadening of peaks [35].

The particle size, measured from dynamic light scattering (DLS) analyses of **CuP2S** showed an average nanosized diameter of 292.9 nm (Figure SI7).

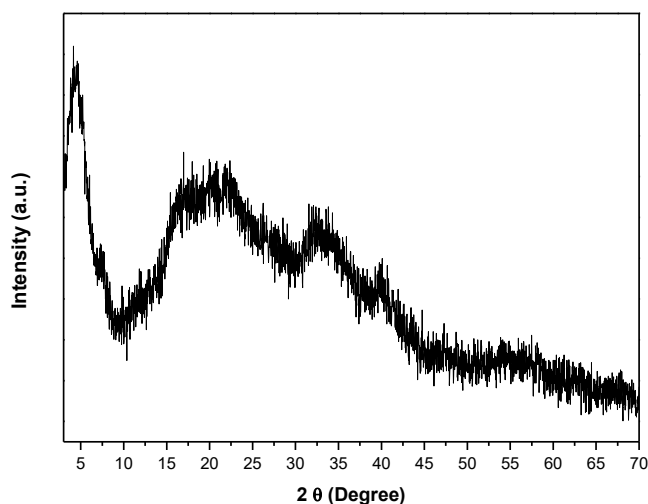


Figure 3. PXRD of the solid material **CuP2S**.

The EPR spectrum of solid **CuP2** presents the characteristic anisotropic signal expected for Cu(II) in axial symmetry, showing the four lines expected for Cu(II) EPR species, with $g_{\parallel} > g_{\perp}$ and with hyperfine splitting ($A_{\parallel} = \sim 210$ G) (Figure SI8) [21]. In case of **CuP2S**, it shows a similar spectrum of those of the **CuP2**, but with appreciable differences in the values for the g_{\parallel} and A_{\parallel} parameters

CuP2S ($g_{\parallel} = 2.227$ and $A_{\parallel} = 192$ G) shows a greater g_{\parallel} and a lower A_{\parallel} than **CuP2** ($g_{\parallel} = 2.191$ and $A_{\parallel} = 210$ G) (Figure 4a and Figure SI8). A greater values of g_{\parallel} and lower values of A_{\parallel} are associated to a larger distortion of the porphyrin macrocycle [21].

Comparing the measured values of g -tensor and A , **CuP2S** has a greater distortion. This difference may indicate the presence of the copper atom as linker in the solid **CuP2S**, since changes in the EPR parameters are observed.

CuP2S stability studies to acidic condition

In general, PCs are not stable in acidic media, since that may occur protonation of the ligands and subsequent metal de-coordination [13]. In order to verify the stability of **CuP2S** to not mild acidic condition it was dissolved in a solution of hydrochloric acid

(4 mol/L) and evaporated to dryness. UV-VIS, ESI-MS and EPR results suggested that **CuP2S** was dissolved in this conditions resulting in **CuP2** in solution that can be isolated by dryness. The EPR spectrum of this acid treated material, dissolved in acetone, displays similar EPR of the free **CuP2** (Figure 4b and 1).

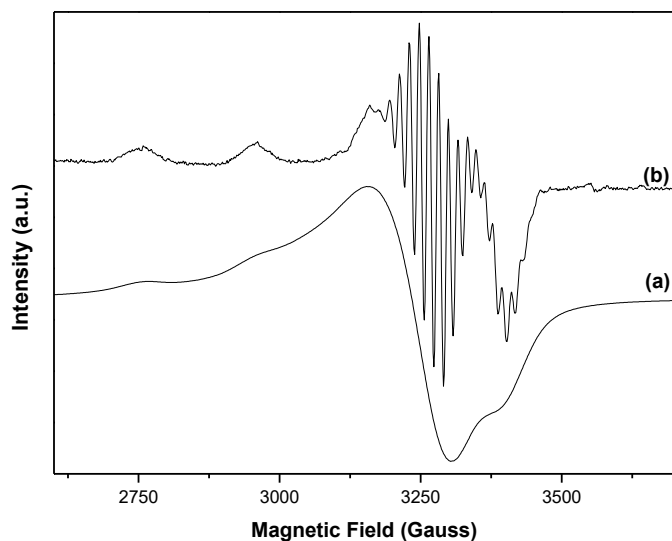


Figure 4. EPR spectra: a) solid sample **CuP2S** at 77 K and b) **CuP2S** dissolved in hydrochloric acid solution, dried, and redissolved in acetone (frozen solution EPR spectrum at 77 K).

From the combined results of all spectroscopic analyses, seems that, most probably, the solid **CuP2S** is a structured solid, like a CP, obtained by self-assembly mediated by the copper ions and the amine groups of **H₂P2**.

Catalytic Studies

The catalytic activity of the prepared copper complexes was investigated in the oxidation of 3,5-DTBC and catechol under homogeneous (**CuP2** and **CuP3**) and heterogeneous (**CuP2S**) conditions, using dioxygen or hydrogen peroxide as oxidants.

Oxidation catalysis of 3,5-Di-tert-butylcatechol (3,5-DTBC) with O₂ from air in methanol and phosphate buffer (pH = 8.0)

As a preliminary experiment, in order to evaluate if the new complexes were catalytic active, 3,5-DTBC was used as model substrate. The choice of this substrate is due to the low redox potential for catechol-quinone in comparison to catechol, which makes it easy to oxidize into quinone [38].

The first oxidation reactions of 3,5-DTBC catalyzed by **CuP2** and **CuP3** under O₂ from the air were done in methanol (homogeneous catalysis). This solvent was chosen because both reactants (3,5-DTBC and catalysts) are fairly soluble in it. **CuP2S** was investigated in heterogeneous conditions since it is insoluble in methanol or in the mixture methanol/substrate.

The reactions were monitored by UV-VIS, the appearance of a band at 400 nm is an indicative of the oxidation of 3,5-DTBC to 3,5-di-tert-butyl-*o*-quinone (3,5-DTBQ). Additionally, the broad band between 500 and 600 nm can also be assigned to the quinone (Figure SI9).

In general, it was observed that the obtained conversions rates of 3,5-DTBQ with **CuP2** and **CuP3** were similar for all studied reaction times (Figure 5), being however slightly higher with **CuP3**. This small and steady, but not negligible, difference can be directly related to the structural differences of both metalloporphyrins. The presence of bulkier substituents on the periphery of the porphyrin macrocycle can affect the ring symmetry and, consequently, influences the formation and stabilization of the catalytic intermediate. The presence of N-tosylethylenediamine bulky groups on **CuP3** can provide additional protection to the effects of oxidative destruction in homogeneous catalysis [39].

For example, Nappa et al. have shown that subtle alterations in the catalyst structure markedly change the selectivity of the reaction products, i.e., the metal catalytic activity can be modulated by the structure of the ligands, which in our case are the porphyrins [40].

Krebs et al., working with the unsymmetrical binuclear compounds containing N_4O as donor ligand, with different coordination surroundings for two copper ions in close proximity, showed that small differences of the binuclear complex structures resulted in different catalytic performances. The authors justified such behavior due of ability coordination sites for substrate binding [41].

Nakagaki et al. showed that it is possible to modulate catalyst selectivity and efficiency by choosing the appropriate porphyrin substituent and metal. Different metalloporphyrins were prepared via structural modification of **H₂P1** with 4-mercaptobenzoic acid. The substituent groups present in the structure of the resulting porphyrins furnished structured solids. The metalloporphyrins, including the structured solids provided good to excellent yields during catalysis of (Z)-cyclooctene, cyclohexane, and heptane oxidation [12].

The conversions observed for **CuP2** and **CuP3** were slightly higher than those observed by He et al. using as catalyst the copper porphyrins *meso*-tetrakis[4-(nicotinoyloxy)phenyl]porphyrinato copper(II) (21.9%) and *meso*-tetrakis[4-(methoxyl)phenyl]porphyrinato copper(II) (23.3%) in the 3,5-DTBC oxidation, using peroxide hydrogen as oxidant [42]. The authors observed similar results for both CuP in homogeneous catalysis and concluded that the catalytic activity was not influenced by nicotinoyl group.

The efficiency of a catalyst can be also analyzed in terms of turnover frequency (TOF). The catalytic rate can be conveniently given in terms of TOF measured in

turnovers per unit time. The turnover rate for **CuP3** (30.3 h^{-1}) is almost two times higher than that observed for **CuP2** (17.7 h^{-1})[13].

Comparing these results with the ones obtained for other copper complexes reported in the literature, it is possible to conclude that the observed catalytic activities of **CuP2** and **CuP3** are comparable to those reported[38, 43].

It was noted that with increasing the reaction time of 1 h to 2 h, the catalytic performance is almost maintained for **CuP2** and **CuP3**. On the other hand, the solid **CuP2S** shows a progressive increase of the product conversion with the increase of the reaction time and after 120 minutes of reaction, it is observed 26% of conversion (Figure 6).

The higher conversion values observed in homogeneous catalysis using **CuP2** (24.2%) and **CuP3** (26.7%) at 90 min, in comparison to the conversion achieved by **CuP2S** (120 min., 26%), clearly show that to achieve similar conversion rate in heterogeneous catalysis an extra time is necessary, which can be directly related with the less access of the substrates to the metal center of the catalytic active species present in the structured solid **CuP2S** in comparison to the complexes in solution. As consequence, longer reaction times are needed to improve the efficiency of **CuP2S**.

The possible presence of channels in the micro- or mesopores of the solid **CuP2S** can improve the catalytic activity, and at the same time provide the benefits of the heterogeneous catalysis with reused capability. Besides of that, effects frequently observed in homogeneous systems are minimized, such as, aggregation and oxidative self-degradation.

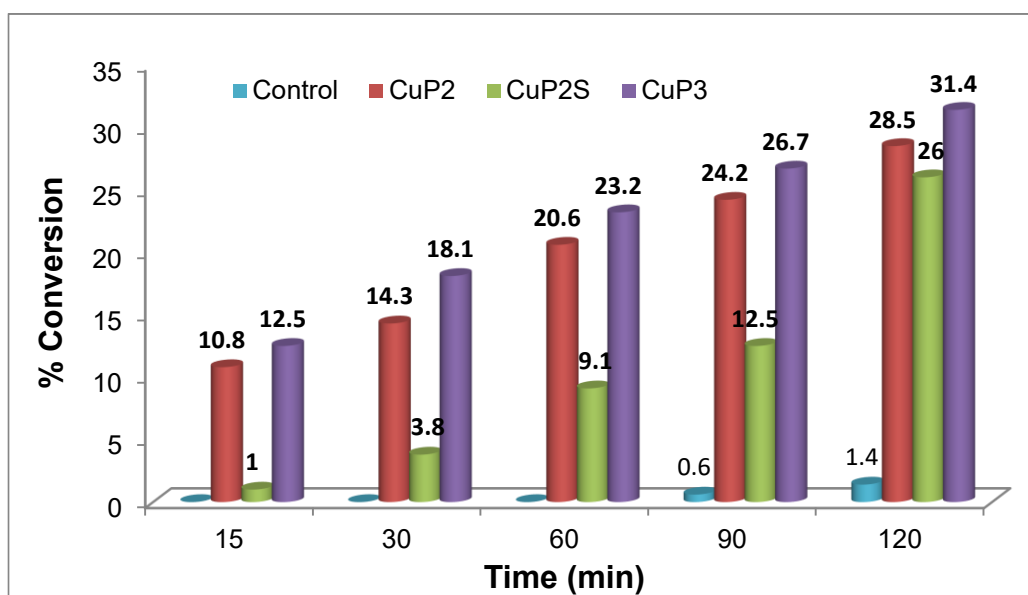


Figure 5. 3,5-DTBC oxidation in presence of O₂ from the air and catalyzed by **CuP2**, **CuP3** and **CuP2S** in methanol with phosphate buffer (pH = 8.0). Conversions were calculated based on the amount of substrate. Results represent reactions performed in duplicate or triplicate. Under these conditions the conversion values were in the range of $\pm 0.7\%$.

Oxidation catalysis of Catechol with O₂ from air in PBF (pH = 8.0)

Considering the capacity of the prepared compounds to catalyse efficiently the conversion of 3,5-DTBC to 3,5-DTBQ (Figure 5), the following studies were focused on their catalytic behaviours when catechol was employed as substrate. However, if compared to 3,5-DTBC, catechol is harder to oxidize [42, 45]. This substrate was used in order to check if the prepared compounds are also catalytic active in this oxidation reaction and if there is some preferential selectivity of each catalyst compounds against different catechols.

Also, the search for efficient catalysts for the catechol oxidation that are functional in water is a major challenge [44]. For this purpose the oxidation of this substrate was investigated in phosphate buffer (PBF) and organic solvent using O₂

from the air as oxidant. Under these conditions, **CuP2** and **CuP3** are sparingly soluble and **CuP2S** is insoluble. The reaction rates were followed using the absorbance decrease at 508 nm, the characteristic band of the presence of catechol by nitrite method (Figure SI10,).

For both CuP, an increase of quinone yield was observed compared to 3,5-DTBQ at the same reaction time (**CuP2**: 21.7% vs 30.6 and **CuP3**: 34.5 vs 40.4%). Although 3,5-DTBC is more susceptible to oxidation, steric hindrance promoted by the bulky groups on the substrate affects the catalytic efficiency of both CuP, resulting in a slower kinetics.

The quinone conversion yield was slightly lower for **CuP2** than for **CuP3**. These results suggesting again that the difference of substituents present on the copper porphyrins affects the catalytic activity. These results can be related to the macrocycle distortions, caused by the nature of the substituents present on the porphyrin ring. For example, the structure of [Cu(OETPP)] is highly distorted in comparison to [Cu(TPP)] due to the steric crowding of the multiple peripheral substituents [46].

CuP3 has greater steric hindrance provided by substituents compared to **CuP2** as discussed before. This fact may prevent the formation of inactive species and the porphyrin ring auto-oxidative destruction [47]. The best result for **CuP3** can also be partly explained by the different solubility compared to **CuP2**.

By monitoring the, a dependence of the conversion *versus* time was observed for both CuP. The catalytic conversion values *versus* reaction time show that **CuP2** has a slower kinetic (Figure 7). After 24 h of the reaction time (**CuP2**: 57.5% and **CuP3**: 62.2%), the difference in catalytic performance observed is lower compared to 1 h of reaction (**CuP2**: 30.6% and **CuP3**: 40.4%). This study confirms the importance of the proper choice of substituents in the periphery of the macrocycle.

The results obtained here (Figure 7) using **CuP2** and **CuP3** are very promising in comparison to previous reports and, particularly, for using oxygen from air as the oxidant, showing that the solids are catalytically active under mild conditions. For example, Constantino et. al reported that catechol conversion obtained for FePcTs in homogeneous conditions is 21%, being by lower than that obtained for both CuP [48].

CuP2S also showed better catalytic activity for the catechol (22.9%) compared to 3,5-DTBC (9.1%) at the same reaction time (1 h). To understand if under heterogeneous reaction conditions the access of the reactants to the catalyst metal center may be limited, longer reaction times could be used [49]. In general, this improves the efficiency of the hetero-catalytic system. In fact, conversion values increase considerably with the increase of the reaction time for **CuP2S**, being at 24 h even better than the ones obtained with **CuP2** and **CuP3**. The best result observed for **CuP2S** can be justified by the structure of this solid compound, that can minimize the deactivation effects, sometimes observed in homogeneous catalysis, as the oxidative destruction of the catalyst during the catalytic reactions, with consequently diminish of the catalytic performance.

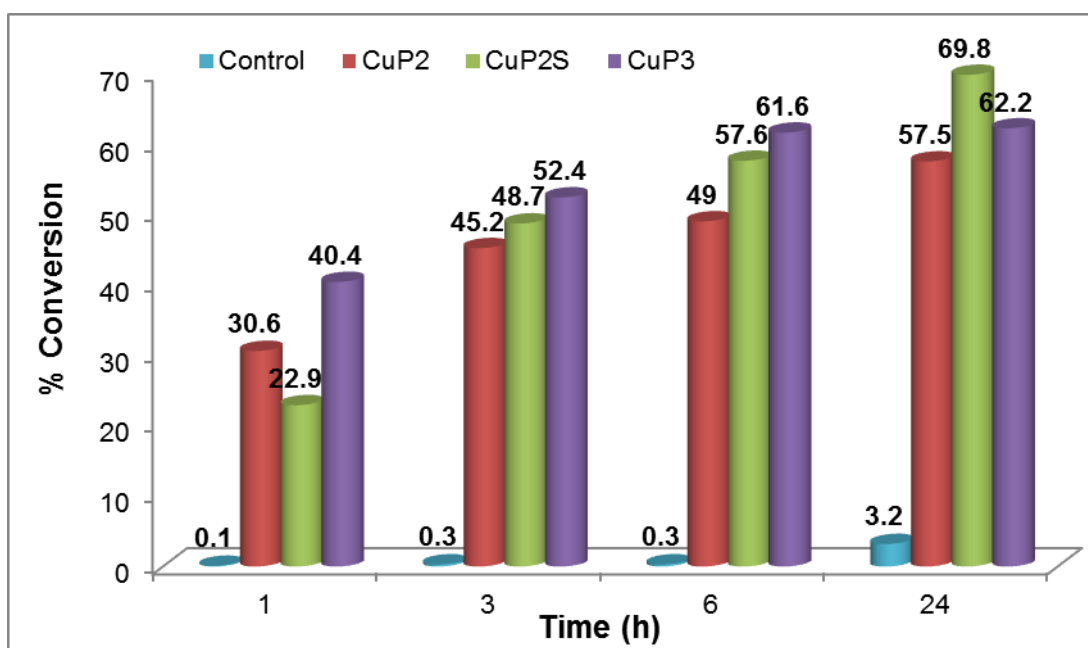


Figure 6. Catechol oxidation in presence of O₂ from the air catalysed by **CuP2**, **CuP3** and **CuP2S** using water and phosphate buffer (pH = 8.0). Conversions were calculated based on the amount of substrate remaining. Results represent reactions performed in duplicate or triplicate. Under these conditions the conversion values were in the range of $\pm 2.0\%$.

Oxidation catalysis of Catechol with O₂ from air in a biphasic system

In order to verify the influence of the solvent in the reactions, the oxidation reactions were performed using biphasic system. The biphasic system could be applied to the oxidation of organic substrates, wherein the catalyst is fully soluble in one phase while the substrates and/or products are soluble in the other phase. In order to ensure solubility of the catalysts was used chloroform as solvent. Catechol is poorly soluble in this solvent, to ensure its solubility it was used water and phosphate buffer, making the reaction medium a biphasic system.

The reaction at interface depends on the reactants meeting at the interface boundary, the diffusion rate across the bulk of the phase. Diffusion across in the interface is more important for reaction proceeded in one of the phases.

Catechol oxidation by **CuP2** and **CuP3** in presence of oxygen probably occurs at the interface phase. This assumption is based on the catalytic results obtained (Figure 7). Catalysis processed in a biphasic system, in general, has a slower kinetics, since diffusion processes are crucial for the reaction. Diffusion across the interface is more difficult than the diffusion across. If the reaction takes place in aqueous phase it is expected conversion values similar those obtained in aqueous system but with larger reaction time. On the other hand if the reaction occurs at the interface, lower conversion results are expected in the same time reaction. In fact, the conversions

values observed for **CuP2** and **CuP3** in biphasic system were lower than those observed for aqueous system in the same time reaction (**CuP2**: 18.3% vs 30.6% and **CuP3**: 23.5% vs 40.4%) suggesting that the reaction probably occurs at the interface.

In spite of the CuP catalyst are not completely soluble in this biphasic systems (it is not a true homogeneous catalytic system), the advantage of using biphasic system is that the catalyst can be easily separable, and when stable can be reused. In fact, at the end of the reaction the catalyst was easily separated by decanting and liquid-liquid extraction process.

The same trend catalytic from for 3,5-DTBC was observed for both CuP, the metalloporphyrins in solution (in fact biphasic system) showed differences in the catalytic performance.

As observed for the oxidation of 3,5-DTBC (Figure 6), the conversion results obtained using **CuP2** and **CuP3** as catalyst ("homogeneous catalysis") varied between 18.3% to 35.8% depending on the reaction time. For this substrate, again the compound **CuP3** presented best catalytic results than **CuP2** confirming that the structure influence the catalytic activity.

For both CuP, after about 3 h the catalytic reaction seems to reached a plateau and no significative catalyst conversion modification (21.6% and 35.6%) was observed for the catechol oxidation by **CuP2** and **CuP3**, respectively (Figure 8). This behaviour can be explained by diffusion across of the reactants from one phase to another which can be affected by the concentration of relation to saturation of solution. Such behaviour was not observed 3,5-DTBC oxidation.

Gamez et. al [44] investigated the catecholase activity in biphasic system water/toluene solvent mixture in the presence of dioxygen atmosphere and good conversion results were obtained in the oxidation of 3,5-DTBC.

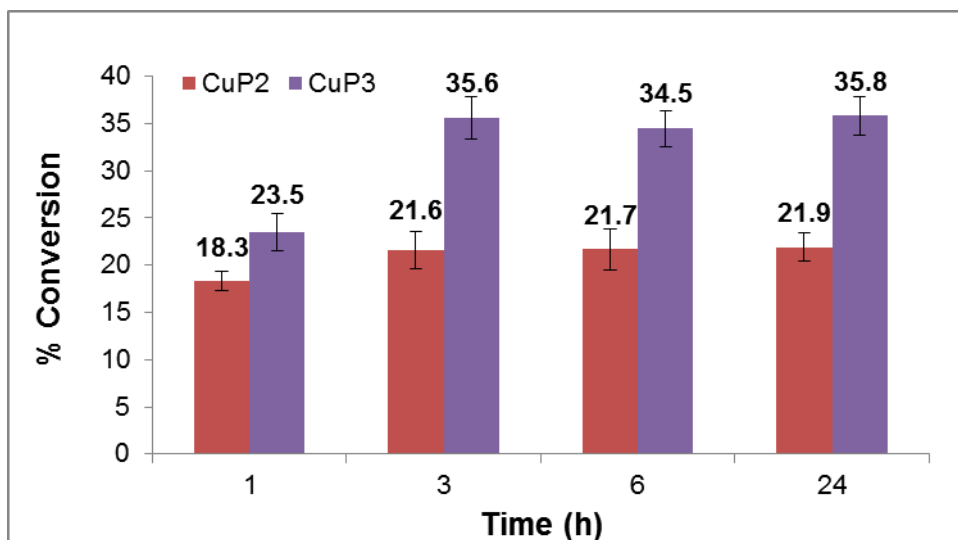


Figure 7. Catechol oxidation in presence of O₂ from the air catalyzed by **CuP2** and **CuP3** using a biphasic system. Conversions were calculated based on the amount of substrate remaining. Results represent reactions performed in duplicate or triplicate.

For both CuP, better results were obtained in aqueous system (Figure 7). The explanation for these results is due to the fact the catalyst and substrate are in the same phase, since the conditions the access of the reactants to the metal center is more easy, although CuP are slightly soluble in the reaction medium, the small amount of CuP is able to catalyze the oxidation of catechol. Oxidation rates of catechol were dependent on the reaction time. In general, longer contact time between the catalyst and the substrate can facilitate access of both species promoting catalysis.

Oxidation catalysis of Catechol with H₂O₂ in PBF (pH = 8.0)

In order to investigate the influence of oxidant in the catechol oxidation reaction, the same reactions were also performed in the presence of hydrogen peroxide. Under

these conditions, **CuP2** and **CuP3** show similar results (Figure 8). However, comparing these results, in the presence of hydrogen peroxide to the ones under O₂ similar results are achieved but with less reaction times. In both cases after about 6 h the catalytic reaction seems to reached a plateau. The plateau in the absence of peroxide was achieved using 6 h of reaction time to **CuP3** and 24 h for **CuP2** in the presence of oxygen of the air and without using H₂O₂ (Figure 7).

Meunier et. al [45] studied the oxidation of catechol using a series of MPcs as catalysts with different oxygen donor compounds. In this study it was found an oxidizing dependence for the oxidation of catechol. Depending on the oxygen compound, pH and reaction time it was observed complete conversion of the catechol using iron(III) Pcs. In the presence of peroxide hydrogen, the conversions values observed for iron(III) Pcs varies between 15% and 40% at 1 h.

Comparing the results obtained here for the CuP investigated with those reported by Meunier [45] for iron(III) Pcs at the same reaction time, it is noted that **CuP2** showed a similar result (37.9%) and **CuP3** (58.3%) a better catalytic performance.

Beside of that, CuP2 and CuP3 show a better catalytic performance than the parent CuP1 (63.4% and 60.9% vs 41.5%) suggesting that both catalysts are more stable than CuP1. However, **CuP2S** was more effective than **CuP2** and **CuP3** under the similar reaction conditions. **CuP2** shows a conversion rate of 63.7% after 24 hours of reaction, while the solid **CuP2S** give complete conversion in the same time of reaction. **CuP3** shows a conversion rate of 63%.

Good linear plots of $\ln A/A_0$ vs time were obtained under the pseudo-first order conditions, for a constant H₂O₂ concentration. The rates of the non-catalyzed reactions ($k_{\text{obs}} = 6.85 \times 10^{-4} \text{ min}^{-1}$) were smaller than those observed for the catalyzed reactions

(**CuP2** $k_{\text{obs}} = 1.78 \times 10^{-2} \text{ min}^{-1}$, **CuP3** $k_{\text{obs}} = 1.77 \times 10^{-2} \text{ min}^{-1}$ and **CuP2S** $k_{\text{obs}} = 1.00 \times 10^{-2} \text{ min}^{-1}$). The k_{obs} for **CuP2S** is about fifteen times greater than those observed for non-catalyzed reaction and similar to observed for **CuP2** and **CuP3**. The k_{obs} observed for all the catalyzed reactions were similar to that observed by us for the material **Cu₄CuP3S** using a lower concentration of hydrogen peroxide and higher than observed for meso-tetra(2,6-dichloro-3-sulfonatophenyl)porphyrinate of iron(III) chloride ($k_{\text{obs}} = 3.95 \times 10^{-4} \text{ min}^{-1}$) [50].

Iron Pcs immobilized in LDH (HT-FePcTs) have been used as catalysts in the oxidation of catechol; the conversion observed for this solid catalyst varied between 63% and 88% after 2 h using hydrogen peroxide [48]. This study showed higher conversions for this material than those observed for the free FePc complex in solution (21%).

For **CuP2S** solid catalyst lower result was observed in comparison to HT-FePcTs. However, as shown by Meunier [45], the increase in pH increases the conversion. The lower result observed can be justified by the difference in pH. Furthermore, total conversion was attained for **CuP2S** by increasing the reaction time.

Structured solids, such as coordination polymers associate the catalytic process heterogeneous with the benefits of homogeneous catalysis; in this case, each part of the solid catalyst contains the metalloporphyrin. This situation does not occur for the solids prepared by immobilization of metalloporphyrins in supports as the example cited using LDH as support [48]. One of the great advantage of using **CuP2S** as heterogeneous catalyst is the possibility of easy reuse. For this purpose, the stability of the solid **CuP2S** after reaction was evaluated by powder XRD and UV-VIS.

The great advantage of the solid catalyst **CuP2S** is its insolubility in the reaction media. Because of that it acting as a solid catalyst for heterogeneous processes and

the reuse capacity was improved after each reaction since no evidences of soluble metalloporphyrin was observed by the monitoring the reaction solution using UV-Vis spectroscopy.

In both catalyzed reactions a large enhancement in the conversion percentages was observed for the catalyzed reactions when compared to the control reaction.

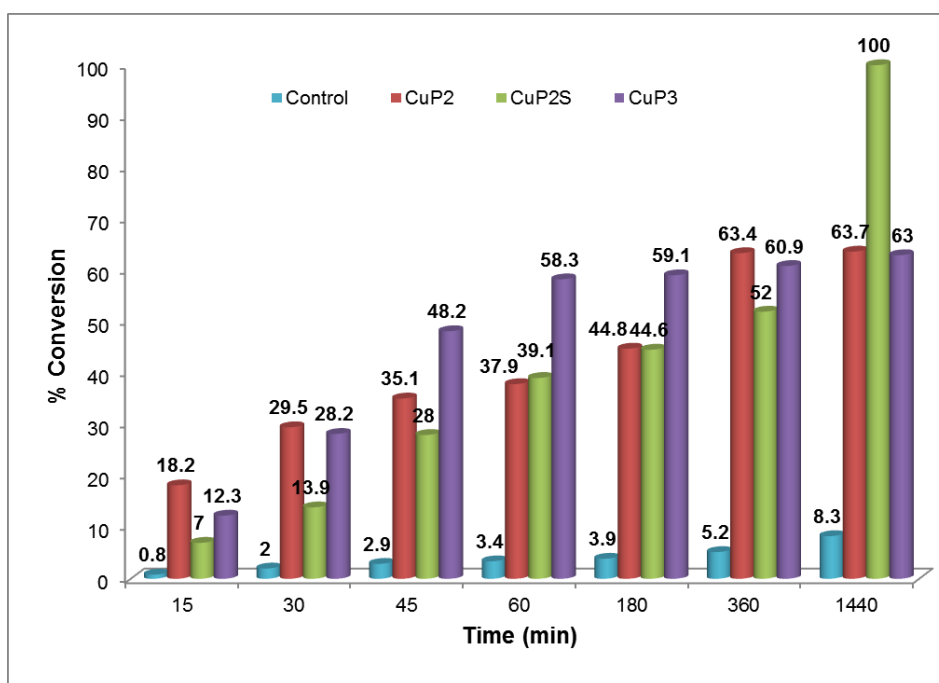


Figure 8. Catechol oxidation in presence of H_2O_2 (30%) catalyzed by **CuP2**, **CuP3** and **CuP2S** using phosphate buffer ($\text{pH} = 8.0$) as solvent. Conversions were calculated based on the amount of substrate remaining. Results represent reactions performed in duplicate or triplicate. Under these conditions the conversion values were in the range of $\pm 1.2\%$.

Reused studies of CuP2S in catechol oxidation with H_2O_2 in PBS ($\text{pH} = 8$)

In order to investigate the recyclability capability of **CuP2S**, reuse tests were performed using hydrogen peroxide as oxidant. After recovery and reuse of the solid catalyst **CuP2S**, the catechol conversion remains similar to the first use (Figure 9). It

was observed that after the first use, the kinetics is only slightly slower. Therefore, it was possible to efficiently recycle this catalyst, at least three times, without loss of catalytic efficiency.

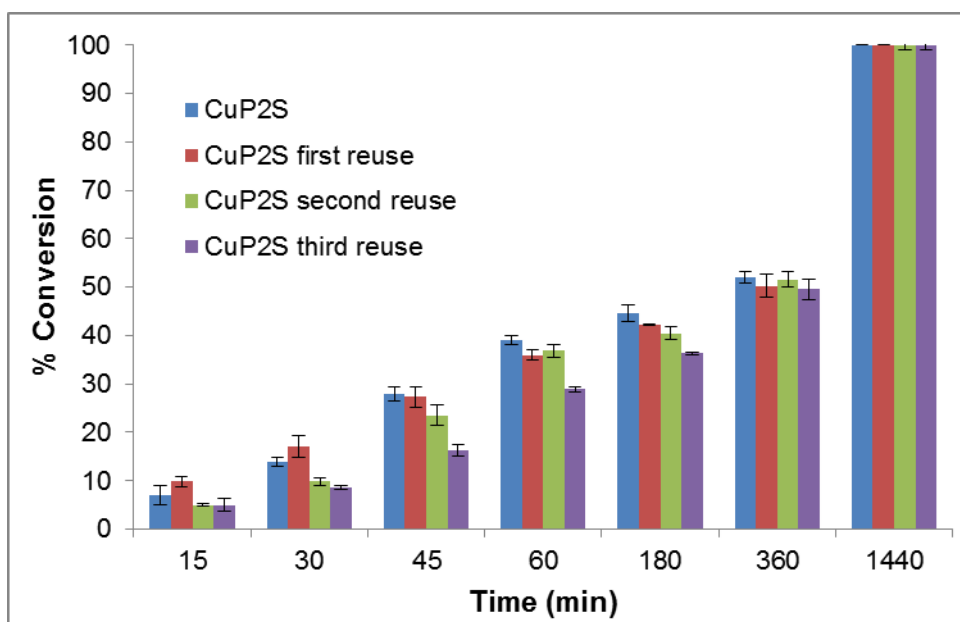


Figure 9. Catechol oxidation conversion results in presence of H_2O_2 (30%) catalyzed by **CuP2S** at different times under reuse conditions. Conversions were calculated based on the amount of substrate remaining. Results represent reactions performed in duplicate.

4. Conclusion

The new synthesized metalloporphyrins **CuP2**, **CuP3** and the insoluble solid **CuP2S** were prepared, characterized and evaluated as catalysts in oxidation reactions. The obtained results show that they are able to mimic the catalytic activity of catecholase, affording good conversions of catechol and 3,5-di-tert-butylcatechol to the correspond quinone derivatives.

In this study it was verified that appropriate substituents at the *p*-positions of the *meso*-aryl groups of a porphyrin macrocycle can fine-tune the catalytic efficiency of the resulted compounds/materials. For example, it was observed better results using **CuP3**, that presents appropriate number of bulky groups on the parent H₂TPPF₂₀(**H₂P1**), when compared to **CuP2**.

The steric effect of the substrate 3,5-DTBC used in the catalytic reaction was also important for the best catalytic performance of the compounds used as catalyst. It was observed that when 3,5-DTBC was used instead catechol, the catalytic results for both CuP were lower for the same time reaction.

The influence of the solvent and the oxygen donor agent was also studied in the oxidation reactions of catechol. The catalytic results for both catalysts are promising, since those are active under mild conditions. The conversions obtained using both CuP suggested that introduction of appropriate bulky groups into the structure of **H₂P1**, created a suitable environment to obtain more efficient biomimetic catalysts.

In the presence of the solid catalyst **CuP2S** a full conversion of catechol was observed after 24 hours of reaction. The high insolubility of this solid in the reaction medium can be considered a great advantage since it can be reused. **CuP2S** showed the ability to be reused in the catechol oxidation for at least three cycles without loss of catalytic efficiency, proving to be indeed a strong and efficient reusable catalyst.

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References

- [1] P.T. Anastas, M.M. Kirchhoff, T.C. Williamson, Catalysis as a foundational pillar of green chemistry, *Applied Catalysis A: General*, 221 (2001) 3-13.
- [2] B. Meunier, Metalloporphyrins as versatile catalysts for oxidation reactions and oxidative DNA cleavage, *Chemical Reviews*, 92 (1992) 1411-1456.
- [3] W. Liu, J.T. Groves, Manganese Catalyzed C–H Halogenation, *Accounts of Chemical Research*, 48 (2015) 1727-1735.
- [4] G. Pratviel, Porphyrins in complex with DNA: Modes of interaction and oxidation reactions, *Coordination Chemistry Reviews*, (2015).
- [5] W.J. Song, M.S. Seo, S.D. George, T. Ohta, R. Song, M.-J. Kang, T. Tosha, T. Kitagawa, E.I. Solomon, W. Nam, Synthesis, Characterization, and Reactivities of Manganese(V)-Oxo Porphyrin Complexes, *Journal of the American Chemical Society*, 129 (2007) 1268-1277.
- [6] J.T. Groves, T.E. Nemo, EPOXIDATION REACTIONS CATALYZED BY IRON PORPHYRINS. OXYGEN TRANSFER FROM IODOSYLBENZENE, *Journal of the American Chemical Society*, 105 (1983) 5786-5791.
- [7] S. Banfi, F. Legramandi, F. Montanari, G. Pozzi, S. Quici, Biomimetic models of cytochrome P-450. A doubly tailed manganese(III)-tetraaryl porphyrin; an extremely efficient catalyst for hydrocarbon oxygenations promoted by 30% H₂O₂, *Journal of the Chemical Society, Chemical Communications*, (1991) 1285-1287.
- [8] J.P. Collman, T. Kodadek, S.A. Raybuck, B. Meunier, Oxygenation of Hydrocarbons by Cytochrome-P-450 Model Compounds - Modification of Reactivity by Axial Ligands, *P Natl Acad Sci USA*, 80 (1983) 7039-7041.
- [9] S. Nakagaki, G. Ferreira, G. Ucoski, K. Dias de Freitas Castro, Chemical Reactions Catalyzed by Metalloporphyrin-Based Metal-Organic Frameworks, *Molecules*, 18 (2013) 7279.
- [10] P.R. Ortiz de Montellano, Hydrocarbon Hydroxylation by Cytochrome P450 Enzymes, *Chemical Reviews*, 110 (2010) 932-948.
- [11] A.A. Guedes, J.R.L. Smith, O.R. Nascimento, D.F.C. Guedes, M.D. Assis, Catalytic activity of halogenated iron porphyrins in alkene and alkane oxidations by iodosylbenzene and hydrogen peroxide, *J Brazil Chem Soc*, 16 (2005) 835-843.
- [12] K.A.D.D. Castro, M.M.Q. Simoes, M.D.P.M.S. Neves, J.A.S. Cavaleiro, R.R. Ribeiro, F. Wypych, S. Nakagaki, Synthesis of new metalloporphyrin derivatives from [5,10,15,20-tetrakis (pentafluorophenyl)porphyrin] and 4-mercaptobenzoic acid for homogeneous and heterogeneous catalysis, *Appl Catal a-Gen*, 503 (2015) 9-19.
- [13] K.A.D.F. Castro, S. Silva, P.M.R. Pereira, M.M.Q. Simoes, M.D.P.M.S. Neves, J.A.S. Cavaleiro, F. Wypych, J.P.C. Tome, S. Nakagaki, Galactodendritic Porphyrinic Conjugates as New Biomimetic Catalysts for Oxidation Reactions, *Inorg Chem*, 54 (2015) 4382-4393.
- [14] F. Zippel, F. Ahlers, R. Werner, W. Haase, H.F. Nolting, B. Krebs, Structural and functional models for the dinuclear copper active site in catechol oxidases: Syntheses,

X-ray crystal structures, magnetic and spectral properties, and X-ray absorption spectroscopic studies in solid state and in solution, *Inorg Chem*, 35 (1996) 3409-3419.

[15] A.M.D. Ferreira, M.L.P. Dos Santos, E.M. Pereira, M.O. Damasceno, W.A. Alves, Mimics of copper proteins: Structural and functional aspects, *An Acad Bras Cienc*, 72 (2000) 51-57.

[16] Isidoros Iakovidis, Ioannis Delimaris, S.M. Piperakis, Copper and Its Complexes in Medicine: A Biochemical Approach, *Molecular Biology International*, 2011 (2011) 1-13.

[17] J.M.M. Rodrigues, A.S.F. Farinha, P.V. Muteto, S.M. Woranovicz-Barreira, F.A.A. Paz, M.G.P.M.S. Neves, J.A.S. Cavaleiro, A.C. Tome, M.T.S.R. Gomes, J.L. Sessler, J.P.C. Tome, New porphyrin derivatives for phosphate anion sensing in both organic and aqueous media, *Chem Commun*, 50 (2014) 1359-1361.

[18] H. Kobayashi, T. Higuchi, Y. Kaizu, H. Osada, M. Aoki, Electronic-Spectra of Tetraphenylporphyrinatoiron(II) Methoxide, *B Chem Soc Jpn*, 48 (1975) 3137-3141.

[19] B.V. Rao, J.V. Bhat, A Colorimetric Method for Determination of Pyrocatechol in Microbial Cultures Containing Other Phenolics, *Anal Biochem*, 27 (1969) 366-&.

[20] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds parts A and B*, 5th ed., Wiley Interscience Publication

[21] Y. Nonomura, N. Yoshioka, H. Inoue, ESR Studies on Distortion in the Macrocyclic Ring of Copper(II) Chlorophylls, *Inorg Chim Acta*, 224 (1994) 181-184.

[22] M. Valente, C. Freire, B. de Castro, Comparative analysis of the electronic and EPR spectra of copper(II) and nickel(I) complexes; insights into nickel(I) electronic structure, *J Chem Soc Dalton*, (1998) 1557-1562.

[23] A.C. Mot, S.A. Syrbu, S.V. Makarov, G. Damian, R. Silaghi-Dumitrescu, Axial ligation in water-soluble copper porphyrinates: contrasts between EPR and UV-vis, *Inorg Chem Commun*, 18 (2012) 1-3.

[24] Q.Z. Zha, X. Rui, T.T. Wei, Y.S. Xie, Recent advances in the design strategies for porphyrin-based coordination polymers, *Crystengcomm*, 16 (2014) 7371-7384.

[25] M. Shmilovits, M. Vinodu, I. Goldberg, Coordination polymers of tetra(4-carboxyphenyl)porphyrins sustained by tetrahedral zinc ion linkers, *Cryst Growth Des*, 4 (2004) 633-638.

[26] K.S. Suslick, P. Bhyrappa, J.H. Chou, M.E. Kosal, S. Nakagaki, D.W. Smithenry, S.R. Wilson, Microporous porphyrin solids, *Accounts of Chemical Research*, 38 (2005) 283-291.

[27] J. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, Metal-organic framework materials as catalysts, *Chemical Society Reviews*, 38 (2009) 1450-1459.

[28] S. Kitagawa, R. Kitaura, S. Noro, Functional porous coordination polymers, *Angew Chem Int Edit*, 43 (2004) 2334-2375.

[29] T. Ohmura, A. Usuki, K. Fukumori, T. Ohta, M. Ito, K. Tatsumi, New Porphyrin-Based Metal-Organic Framework with High Porosity: 2-D Infinite 22.2-Å Square-Grid Coordination Network, *Inorg Chem*, 45 (2006) 7988-7990.

[30] K. Biradha, M. Sarkar, L. Rajput, Crystal engineering of coordination polymers using 4,4'-bipyridine as a bond between transition metal atoms, *Chem Commun*, (2006) 4169-4179.

[31] R.L. Musselman, R.W. Larsen, B.M. Hoffman, Electronic spectra of porphyrins in the solid state: Newly observed transitions, collective and structural effects, and protein-mimicking environments, *Coordination Chemistry Reviews*, 257 (2013) 369-380.

- [32] M. Makarska, S. Radzki, J. Legendziewicz, Spectroscopic characterization of the water-soluble cationic porphyrins and their complexes with Cu(II) in various solvents, *J Alloy Compd*, 341 (2002) 233-238.
- [33] M. Gouterman, Spectra of Porphyrins, *J Mol Spectrosc*, 6 (1961) 138-&.
- [34] B.A. Gregg, M.A. Fox, A.J. Bard, Effects of Order on the Photophysical Properties of the Liquid-Crystal Zinc Octakis(Beta-Octoxyethyl)Porphyrin, *J Phys Chem-Us*, 93 (1989) 4227-4234.
- [35] E.M. Moroz, X-Ray diffraction structure diagnostics of nanomaterials, *Russ Chem Rev+*, 80 (2011) 293-312.
- [36] N. Schweigert, A.J.B. Zehnder, R.I.L. Eggen, Chemical properties of catechols and their molecular modes of toxic action in cells, from microorganisms to mammals, *Environ Microbiol*, 3 (2001) 81-91.
- [37] J. Madeo, A. Zubair, F. Marianne, A review on the role of quinones in renal disorders, *Springerplus*, 2 (2013).
- [38] D. Dey, S. Das, H.R. Yadav, A. Ranjani, L. Gyathri, S. Roy, P.S. Guin, D. Dhanasekaran, A.R. Choudhury, M.A. Akbarsha, B. Biswas, Design of a mononuclear copper(II)-phenanthroline complex: Catechol oxidation, DNA cleavage and antitumor properties, *Polyhedron*, 106 (2016) 106-114.
- [39] D. Dolphin, T.G. Traylor, L.Y. Xie, Polyhaloporphyrins: Unusual ligands for metals and metal-catalyzed oxidations, *Accounts of Chemical Research*, 30 (1997) 251-259.
- [40] M.J. Nappa, C.A. Tolman, Steric and Electronic Control of Iron Porphyrin Catalyzed Hydrocarbon Oxidations, *Inorg Chem*, 24 (1985) 4711-4719.
- [41] M. Merkel, N. Moller, M. Piacenza, S. Grimme, A. Rompel, B. Krebs, Less symmetrical dicopper(II) complexes as catechol oxidase models - An adjacent thioether group increases catecholase activity, *Chem-Eur J*, 11 (2005) 1201-1209.
- [42] C. Li, W. Qiu, W. Long, F. Deng, G. Bai, G. Zhang, X. Zi, H. He, Synthesis of porphyrin@MOFs type catalysts through "one-pot" self-assembly, *Journal of Molecular Catalysis A: Chemical*, 393 (2014) 166-170.
- [43] D. Kim, B.J. Kim, T.H. Noh, O.S. Jung, New topological 3D copper(II) coordination networks: catechol oxidation catalysis and solvent adsorption via porous properties, *Crystengcomm*, 17 (2015) 2583-2590.
- [44] P. Gamez, P. de Hoog, M. Lutz, A.L. Spek, J. Reedijk, Coordination compounds from 1,3,5-triazine-derived multidirectional ligands: application in oxidation catalysis, *Inorg Chim Acta*, 351 (2003) 319-325.
- [45] A. Sorokin, L. Fraisse, A. Rabion, B. Meunier, Metallophthalocyanine-catalyzed oxidation of catechols by H₂O₂ and its surrogates, *J Mol Catal a-Chem*, 117 (1997) 103-114.
- [46] M. Inamo, K. Aoki, N. Ono, H.D. Takagi, Electron transfer reaction of Cu(II) porphyrin complex: Effect of structural deformation on the electron self-exchange rate, *Inorg Chem Commun*, 8 (2005) 979-982.
- [47] K.A.D.F. Castro, M.M.Q. Simoes, M.G.P.M.S. Neves, J.A.S. Cavaleiro, F. Wypych, S. Nakagaki, Glycol metalloporphyrin derivatives in solution or immobilized on LDH and silica: synthesis, characterization and catalytic features in oxidation reactions, *Catal Sci Technol*, 4 (2014) 129-141.
- [48] C.A.S. Barbosa, P.M. Dias, A.M.D. Ferreira, V.R.L. Constantino, Mg-Al hydrotalcite-like compounds containing iron-phthalocyanine complex: effect of aluminum substitution on the complex adsorption features and catalytic activity, *Appl Clay Sci*, 28 (2005) 147-158.
- [49] K.A.D.F. Castro, S.M.G. Pires, M.A. Ribeiro, M.M.Q. Simoes, M.G.P.M.S. Neves, W.H. Schreiner, F. Wypych, J.A.S. Cavaleiro, S. Nakagaki, Manganese chlorins

immobilized on silica as oxidation reaction catalysts, *J Colloid Interf Sci*, 450 (2015) 339-352.

[50] D. Smejkalova, A. Piccolo, Rates of oxidative coupling of humic phenolic monomers catalyzed by a biomimetic iron-porphyrin, *Environ Sci Technol*, 40 (2006) 1644-1649.