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This paper must be cited as:

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., *Adv. Sustainable Syst.* 2019, 3, 1800134. <https://doi.org/10.1002/adsu.201800134>

Sustainable liquid luminescent solar concentrators

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Keywords: luminescent solar concentrators, organic-inorganic hybrids, bundles, sustainable

ABSTRACT

Luminescent solar concentrators (LSCs) appear as photovoltaic (PV) complementary devices to overcome the mismatch between the Si-based PV cells response and the solar spectrum, with the major advantage of permitting PV urban integration. Challenges for the luminescent layer include the use of abundant and sustainable natural organic molecules. Here, LSCs composed of a glass container and based on bundles of cylindrical hollow-core plastic optical fibres (POFs) are presented. The glass container and the fibres' hollow-core were filled with aqueous solutions at different concentrations of R-phycoerythrin (R-PE), which is a phycobiliprotein, extracted from *Gracilaria* sp. algae. The R-PE solutions absorb in the UV/visible spectral range (300-550 nm) and convert this radiation into red-emission (550-700 nm) with a maximum absolute quantum yield of ~ 0.39 . In this work, LSCs with distinct geometries are reported, in which the R-PE emission yields optical conversion efficiency values up to $\sim 6.88\%$ and $\sim 4.74\%$ for a planar device and for a bundle of cylindrical LSCs, respectively, which are the largest values known for liquid-based LSCs using sustainable emitting centres. Moreover, the coupling of the LSCs to commercial Si-based PV devices yielded power conversion efficiency values of to $\sim 0.27\%$ (planar) and $\sim 23.03 \times 10^{-3}\%$, (bundle). These values illustrate the potential of this approach for the development of natural-based LSCs meeting the requirements of reliable, sustainable and competitive energy systems.

1. Introduction

Luminescent solar concentrators (LSCs) appeared in the late 70's with the goal of overcoming the mismatch between the full solar spectrum on Earth and the absorbance of the semiconductor material used in the photovoltaic (PV) cell manufacture.^[1] The first reported examples are planar devices^[2-5] (p-LSCs) containing optical active centres able to complement the absorption of the PV cell and emission in the PV cell absorption spectral range. Given the refractive index contrast between the LSC surface and the air, the emitted radiation is guided in the LSC by total internal reflection to PV cells located at its edges.^[2, 6] Other relevant aspect of the LSC operation is that analogous performance is expected under direct or diffuse light incidence,^[7-9] permitting to prospect the use of PV panels under cloudy conditions, which is a significant advantage for integration of PV cells in urban buildings. An illustrative example of the real-world applicability of these devices, we highlight the implementation of large scale LSC-based panels in a noise barrier configuration as outdoors alongside a roadway in the Netherlands.^[10-12] Other applications are envisaged in PV urban integration, as LSCs are attractive to contribute to zero-energy buildings in which the LSCs are embedded in façades, or windows.^[13-15]

Furthermore, LSCs are candidates to contribute in mobile energy as they may be integrated in wearable fabrics, and outdoor furniture.^[16] In particular, target delivered power values up to 10 W may be feasible with the actual figures of merit for LSCs, allowing to charge low-voltage devices, e.g. mobile phones, sensors and wi-fi routers.^[17] In what concerns mobile energy, cylindrical-based LSCs (c-LSCs) assembled in bundles,^[18] may offer additional advantages arising from the intrinsic properties of the fibres themselves, such as being lightweight, flexible, and may be coupled to other optical fibres for light waveguiding, which may allow remote light harvesting.

Theoretical studies point out a decrease of the optical losses (through reflection) in the case of a bundle structure, when compared to a planar LSC.^[19] Additionally, from an experimental point of view, LSCs based on bundles displayed enhanced performance, when compared with that of planar LSC with analogous surface collection area and light harvesting absorbance, due to the individual waveguiding features of each fibre that contributes to reduce the re-absorption losses.^[20]

Regarding the material selection towards LSC performance optimization, several challenges are still open. Different optically active centres have been tested in LSCs, as reviewed in some works,^[21-23] including organic dyes, quantum dots (QDs), Ln^{3+} ions and, more recently, metal halide clusters.^[24] The best performance single-layer LSC is based on perylimide with optical conversion efficiency values (η_{opt} , defined as the ratio between the output optical power, P_{out} , and the incident optical power, P_{in}) of 18.8%.^[25] Despite the small Stokes-shift of organic dyes, they present high emission quantum yields and large absorption coefficients,^[26] which result in better performance LSC devices, when compared with LSCs based on other optically active centres.

The potential replacement of synthetic organic dyes by luminescent organic molecules extracted from renewable and natural materials could make LSCs cheaper and sustainable, keeping other inherent features such as synthetic versatility, high absorption coefficients and emission quantum yields.^[27, 28] As a matter of fact, previous studies proved the advantages and the possibility of using natural and renewable materials for energy harvesting^[29] and, specifically, for LSCs.^[30] The most common natural dyes used in LSCs are based on phycobilisomes.^[28, 31, 32] These are photosynthetic complexes, mainly composed of phycobiliproteins, with light-harvesting ability over a broad range of the visible spectrum and which concentrate the captured energy at the photosynthetic reaction center.^[31, 33, 34] Nevertheless, studies reporting natural dye molecules for LSCs are scarce. A recent example reports the use of BODIPY emitter covalently linked to

oligofluorene and dispersed in lauryl methacrylate and ethylene glycol dimethacrylate, which when coupled to Si PV cells yielded an external quantum efficiency (EQE) maximum value of $\sim 2.44\%$.^[28] Another p-LSC example is based on phycobilisomes dispersed in acrylamide films^[31, 34] which presented $\eta_{\text{opt}}=12.5\%$.^[31] In this study, the use of phycobilisomes in liquid medium confined in a glass cuvette was also tested, but considered disadvantageous due to the refractive index mismatch between the solution and the cuvette.^[34]

Several LSCs based on optically active centres dispersed in a liquid medium have been proposed in literature,^[8, 31, 34-43] but studies reporting LSCs performance quantification (η_{opt} , EQE or powerconversion efficiency, PCE) figures of merit are not abundant.^[40-42, 44, 45] The maximum η_{opt} values were found for PbS QDs dispersed in toluene ($\eta_{\text{opt}}=12.6\%$, considering collection along the four edges)^[42] and for K₁ organic dye dispersed in a liquid polymer ($\eta_{\text{opt}}=20.2\%$ for direct radiation).^[40] Very recently, an interesting work reporting temperature-responsive LSCs using a liquid crystal as host for a coumarine-derivative/perylene bisimide pair with $\eta_{\text{opt}}=2.4\%$ in the cold state and $\eta_{\text{opt}}=3.2\%$ when warmed was published, stating the potential for LSCs with liquid optically active layers.^[44] Despite the advantages of bio-based dyes in liquid medium, only one report mentions the use of phycobilisomes in liquid medium for LSCs however, without mentioning any performance quantification.^[34]

Among the natural dyes, phycobilisomes are very promising since donor and acceptor molecules are already aggregated in an ideal configuration^[34] and phycobiliproteins can be efficiently extracted, without compromising their conformational structure or chromophore structural integrity through a method already reported by some of us.^[46] Moreover, R-phycoerythrin (R-PE), which is one of the most abundant phycobiliproteins in red macroalgae, has been pointed out as an important macromolecule in the field of

medical diagnosis and biomedical research^[47] due to its high absorption coefficient and emission quantum yield.^[46] Recently, laser effect was observed from R-PE from 602 to 620 nm with pulsed optical excitation in a Fabry-Pérot resonator.^[48]

In this work, we merge two complementary aspects towards enhanced performance sustainable LSCs devices: i) the use of R-PE, extracted from fresh *Gracilaria sp.* red algae and dispersed in an aqueous solution and ii) the exploit of the geometrical factor fabricating c-LSCs based on bundles of cylindrical hollow-core polymethylmethacrylate (PMMA)-optical fibres (POFs) (Figure 1A) and p-LSCs composed of a glass container (Figure 1B). The scalability and economic feasibility of the proposed methodology is granted from both the selection of PMMA and the R-PE. In particular, the substrate is based on PMMA-based optical fibers processed using a semi-industrial facility able to pull meter-length fibers as already reported by some of us.^[49] Moreover, the use of PMMA is a very interesting and practical approach to reduce the price of LSCs because it is one of the most used polymers and thus production methods are quite efficient and cost-effective.^[50, 51] The use of *Gracilaria sp.* algae takes advantage of local resources and markets. The fact of being dispersed in water makes this approach sustainable and without waste nor significant negative impact towards the environment. Moreover, the use of aqueous solutions to extract phycobiliproteins from the fresh biomass can also be easily integrated with further steps of downstream processing by using, for example, conventional liquid-liquid extraction or the alternative aqueous biphasic systems,^[52] which can be easily scaled-up (also to continuous flow). Different concentrations (0.4×10^{-7} to 17×10^{-7} M) of R-PE in aqueous solutions with high molar brightness (B) values (2.2×10^5 to 6.2×10^5 M⁻¹·cm⁻¹) were used to fabricate c-LSCs (Figure 1A) and p-LSCs (Figure 1B). Electrical measurements were performed in coupled c-Si PV devices, yielding maximum η_{opt} values of ~6.88%

(p-LSC) and $\sim 4.74\%$ (c-LSCs bundle), and PCE of $\sim 0.27\%$ (p-LSC) and $\sim 23.03 \times 10^{-3}\%$ (c-LSCs bundle).

2. Results and discussion

2.1. Optical characterization of the R-PE solutions

Figure 2 shows the emission spectra of the R-PE based aqueous solutions, which are formed by a broad band typical of R-PE phosphorescence,^[46] whose relative intensity depends on the dye concentration. For the less concentrated solutions (0.4×10^{-7} M to 3.3×10^{-7} M), the room-temperature emission spectra are dominated by the R-PE characteristic emission with two components centred around 577 nm and 632 nm. The presence of two distinct dye-related components in the emission spectrum points out the formation of dye aggregates.^[53] In fact, by increasing the concentration, the relative intensity of the low-energy component (655 nm) increases and the main peak (577 nm) red-shifts around 6 nm, suggesting the presence of *J*-dimers.^[54]

The excitation spectra (Figure S1A in Supporting Information) are dominated by the excited states of the R-PE in the visible spectral range, revealing also the presence of components in the UV/blue (320-440 nm) attributed to the chromophores' singlet states. The band at 278 nm arises from amino acid residues of the apoprotein.^[55]

The emission properties of the samples were also quantified through the measurement of the absolute emission quantum yield (q , Table 1), as function of the excitation wavelength (310-540 nm). Although a maximum emission quantum yield is observed under excitation in the visible range (498 nm), as the concentration is increased, this value decreases from 0.37 ± 0.04 (0.4×10^{-7} M solution) to 0.16 ± 0.02 (17×10^{-7} M solution). These values are lower than those previously reported on literature of 0.82-

0.85,^[56, 57] found for R-PE in phosphate buffers and for less concentrated samples ($\sim 10^{-15}$ M).^[56]

The light-harvesting ability of all the R-PE aqueous solutions relative to the AM1.5G spectrum (Figure 3A) was studied by absorption spectroscopy. Figure 3B shows the absorption spectra of three selected R-PE aqueous samples (absorption spectra of all samples in Figure S1B in Supporting Information), which resemble the excitation spectra above mentioned, apart from the presence of a component around 590-690 nm, probably ascribed to the presence of other phycobiliproteins, such as phycocyanin and allophycocyanin.^[31] There are no significant spectral changes in the absorption spectra as the concentration is varied, although the absolute absorbance value increases with concentration (Figure 3B and Figure S1B in Supporting Information). The absorbance dependence on the concentration was rationalized by the calculation of the molar extinction coefficient values (ϵ), revealing that with exception of the low-concentrated solution (0.4×10^{-7} M), analogous values within $1.3\text{-}1.9 \times 10^6 \text{ M}^{-1} \cdot \text{cm}^{-1}$ were found, in good agreement with previous studies in literature.^[56, 57] Moreover, in order to quantify the ability of the LSCs to absorb the sunlight available for PV conversion, the overlap integral between the R-PE solutions absorption spectra and the solar irradiation on Earth through was calculated.^[58]

$$O = \int_{\lambda_1}^{\lambda_2} N_{AM1.5G}(\lambda) \times (1 - 10^{-A(\lambda)}) d\lambda \quad (1)$$

where λ_1 and λ_2 are the limits of the spectral overlap between the absorption spectrum of the R-PE solution and the AM1.5G spectrum, $N_{AM1.5G}$ is the photon flux of AM1.5G and A is the absorbance of the R-PE solution. The O values increase with the concentration (Figure 3C and Table 1). The maximum calculated O value indicates that the 17×10^{-7} M

aqueous solution have the potential to absorb $\sim 27\%$ of the solar photon flux on the Earth ($4.3 \times 10^{21} \text{ photons} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$).^[58]

Light emission efficiency and light harvesting ability can be related by the B parameter, given by $B=q \times \epsilon$,^[59] allowing both properties to be compared for distinct samples. The B values were calculated as function of the R-PE concentration (Table 1), and are one order of magnitude larger than those reported for other organic-dye molecules, with light emission in the 530-650 nm range.^[60, 61] We note that the larger B values are found in the R-PE concentration region between $2.1 \times 10^{-7} \text{ M}$ and $5.8 \times 10^{-7} \text{ M}$. At higher concentrations ($7.5 \times 10^{-7} \text{ M}$ and $17 \times 10^{-7} \text{ M}$), B decreases due to the concentration quenching, as suggested by the emission spectra analysis. At lower concentrations ($0.4 \times 10^{-7} \text{ M}$ and $1.7 \times 10^{-7} \text{ M}$), the q values are higher, resulting in larger B values although the absorption coefficient is decreased.

Taking advantage of the ability of the R-PE solutions to harvest the AM1.5G radiation and convert it into visible emission, the solutions were incorporated into hollow core POFs (Figure 4A), permitting the fabrication of c-LSCs based on natural dyes in a liquid medium. The fabrication of these short-length c-LSCs aims at establishing the potential to design large area flexible (Figure 5 and S2 in Supporting Information) and transparent (Figure S3 in Supporting Information) c-LSCs made from the assembling of POFs filled with the R-PE aqueous solution in bundle structures. We notice the transparency of the bundles arising from the high transmittance of the PMMA.^[62] As Figure 6A illustrates, when illuminated by AM1.5G solar radiation, the orange-red emission of the R-PE based solutions is guided to the edges of the device through total internal reflection. Also, as evidenced in Figure 6C, the emission intensity guided in the PMMA cladding is larger (~ 2 times) than that in the hollow-core (further details in Supporting Information).

The relative performance of the c-LSCs based on a single POF was quantified by the calculation of the η_{opt} and PCE. The quantification of η_{opt} from the experimental data is

attained in different ways in the literature. In this work, we used the definition given by:^[25]

$$\eta_{\text{opt}} = \frac{P_{\text{out}}}{P_{\text{in}}} = \frac{I_{\text{SC}}^L V_0^L A_e \eta_{\text{solar}}}{I_{\text{SC}} V_0 A_s \eta_{\text{PV}}} \quad (2)$$

where I_{SC}^L and V_0^L represent the short-circuit current and the open voltage when the PV device is coupled to the LSC (I_{sc} and V_0 are the corresponding values of the PV device exposed directly to the solar radiation), η_{solar} is the efficiency of the PV device relatively to the total solar spectrum and η_{PV} is the efficiency of the PV device at the LSC emission wavelengths (experimental details can be found in Supporting Information). The maximum η_{opt} values ($0.16 \pm 0.02\%$ using Eq. (2), for $G \sim 7$) were found for concentration solutions within 2.5×10^{-7} M to 5.8×10^{-7} M, (Table S1 in Supporting Information). To enable a comparison with the literature, an alternative definition will be also considered:^[41]

$$\eta_{\text{opt}} = \frac{I_{\text{SC}}^L A_e}{I_{\text{SC}} A_s} \quad (3)$$

The PCE was calculated as follows:

$$\text{PCE} = \frac{P_{\text{out}}^{\text{el}}}{P_{\text{in}}} = \frac{I_{\text{SC}}^L V_0^L \text{FF}}{A_s \int_{\lambda_1}^{\lambda_2} I_{\text{AM1.5G}}(\lambda) d\lambda} \quad (4)$$

where $P_{\text{out}}^{\text{el}}$ and $\text{FF}=0.75$ are the PV device output electrical power and fill factor, respectively. The effective contribution of this c-LSC on a PV device yielded a PCE value of $(3.2 \pm 0.1) \times 10^{-3}\%$. We should note that losses of the guided light due to the bending of the fibres can be neglected, as negligible leakage losses are reported for POFs with a bending angle of 180° and a curvature radius higher than 30×10^{-3} m,^[63] which was already considered valid for a POF-based LSC.^[49]

The performance was also evaluated by measuring I_{SC}^L as function of the incident wavelength and calculating the EQE of the PV devices coupled to the c-LSCs. The EQE was calculated as follows:

$$EQE(\lambda) = \frac{I_{SC} \cdot h \cdot c}{P_{in} \cdot e \cdot \lambda} \quad (5)$$

where e is the charge of the electron, h is the Planck's constant, c is the speed of light and λ is the wavelength (Supporting Information for details). For all the c-LSCs tested, the maximum EQE values for the PV device are well correlated with the peaks found in the absorption spectra of the active layer (Figure 7 and Figure S4, S5 and S6 in Supporting Information), with the larger EQE variation between 500 and 600 nm. The maximum value of $EQE = 0.1647 \pm (0.0002)\%$ was found for the c-LSC with G~7 filled with the 4.2×10^{-7} M solution.

2.2. Bundle of c-LSCs and a p-LSC

The previous results point out that POFs filled with R-PE solutions can be used to fabricate c-LSCs and that the use of optically active centres dispersed in a liquid medium in LSCs presents some advantages when compared to the case of a solid matrix LSC. For instance, the concentration of the solutions can be easily varied,^[8, 36, 38, 43] liquids are easily moulded to the container geometry, the performance of the solar cells at the edges of the LSC is fixed and constant, removing the variability when comparing different fluorophores and concentrations,^[43] and liquid solutions can be easily replaced when compared with materials that undergo a phase exchange to solid.^[41]

To demonstrate the potential of these two approaches, it is necessary to enlarge A_s and, consequently, PCE values which will permit to envisage the application in PV cell to supply low-power consumption devices. Therefore, to enhance the PV cell performance in the presence of an LSC, A_s was increased following two methods: i) the assembling of c-LSCs into a bundle structure (Figure 4B and Figure S7 in Supporting Information) and ii) p-LSC based on a glass container (Figure 4C).

The solutions with concentration values within 3.3×10^{-7} M to 4.2×10^{-7} M combine larger emission quantum yield, brightness and integral overlap, and, therefore, they were used to fabricate a bundle of c-LSCs and a p-LSC. When coupled to a Si-based PV device maximum η_{opt} values of $2.71 \pm 0.07\%$ and $5.6 \pm 0.2\%$ ($4.74 \pm 0.01\%$ and $6.88 \pm 0.01\%$ when using Eq. (3)) respectively, were found. These values are larger than those reported for c-LSCs formed by a single POF. Also, the PCE values found for the p-LSC and c-LSCs bundle were $0.27 \pm 0.01\%$ and $(23.03 \pm 0.02) \times 10^{-3}\%$, respectively. EQE measurements were performed showing good correlation with the absorption spectra, yielding maximum values of $2.7134 \pm (0.0002)\%$, for the p-LSC (Figure S8 and S9 in Supporting Information). It is worth noting that, considering LSCs based on natural organic dyes, the η_{opt} value of the p-LSC here reported is higher than the recently reported p-LSC based on chlorophyll with $\eta_{opt} = 3.70\%$.^[17] The η_{opt} and PCE values of the two types of LSCs fabricate in this work cannot be directly compared as the absorption dependence of A_s was not considered (a calculus lying beyond the scope of this work).

As far as we know, only p-LSCs in which the optically active centres are dispersed in liquid medium were reported. Moreover, all the studies refer to the use of synthetic dyes or QDs in organic solvents, rather than natural dyes in water. Nevertheless, the η_{opt} values calculated in the present work are among the highest values in literature (Table 2). Higher values were only reported for LSC based on synthetic dyes (Rhodamine B,^[41] Red F,^[41, 45] KI, Sulphorhodamine 101, BASF-402 and BASF-241 dyes),^[40] and PbS QDs.^[42] Concerning PCE, care should be taken for comparison purposes, as it is dependent on the optical properties of the semiconductor used to fabricate the PV cell. For LSCs characterized with similar c-Si PV cells, the values here reported are lower than those reported for other LSCs with optically active centres dispersed in liquid medium (Table 2).

3. Modelling

Simulations of the performance (η_{opt}) of the p-LSC were carried out using a Monte Carlo ray-tracing approach, in which the photon propagation follows geometrical optical laws.^[64-66] The thickness of the active layer ($\sim 10^{-2}$ m) is much larger than that of the light coherent length ($\sim 10^{-7}$ m), thus, interference effects were neglected. The stochastic nature of the model is assured by the use of a variable seed in the random function used to describe the photons interactions and is also reflected in the fact that the propagated rays cannot split when reaching an interface but rather either transmitted or reflected, as predicted by Fresnel laws. We also note that light polarization is not taken into account. By modelling the path of each propagated ray, it is possible to know whether the photons are trapped inside the LSC, absorbed by the luminescent species, lost due to the escape cone and if they were collected at the edges of the LSC.

The input of the Monte Carlo ray-tracing simulation consists in photons following the solar spectrum probability density function AM1.5G (280-1600 nm, photons with angle of incidence between -45° and 45°), the absorption and emission spectra, the absolute emission quantum yield and refractive index of the R-PE aqueous solutions ($n \sim 1.3335$) and the dispersion curve of the cuvette glass (Figure S10 in Supporting Information). Furthermore, we consider a thin layer of air underneath the LSC.

This model does not include individual molecules or optically active centres but applies statistical averaging of the absorption. First, the absorption probability is calculated by $p_{abs} = 1 - 10^{-\alpha d}$, where α is the attenuation coefficient (in cm^{-1}) and d is the photon desired step size (0.02 cm) in each iteration, as function of the wavelength and compared with a random generated number between 0 and 1 for each launched photon. If p_{abs} proves to be higher than the random number, the photon is absorbed, otherwise

the photon continues to propagate according to its direction vector. Once a photon is absorbed, the subsequent fate of the excitation (that is, emission or non-radiative relaxation) is again determined by the Monte Carlo sampling according to the emission quantum yield. The direction of the emission is randomly distributed and the emission wavelength is sampled randomly from the normalized emission spectrum. The fate of each photon is either loss due to non-radiative recombination or escape from the LSC from the incident light interface. When a photon hits the PV interface, it counts as a PV absorption and the wavelength of the photon and its position on the PV interface is recorded.

The η_{opt} for simulation purposes is defined by the energy emitted (*per* unit of time) from the edge of the LSC divided by the solar energy falling on the p-LSC (*per* unit of time), as stated in Eq. (2). The simulations (10^6 photons) were performed for a p-LSC with dimensions of $2.00 \times 2.00 \times 1.00 \text{ cm}^3$ and as function of the concentration of the R-PE solution. The optical conversion efficiency was predicted for solutions of R-PE with all the concentrations tested considering all the photons reaching the edge and considering only the converted photons (Table S2 in Supporting Information).

Takin into consideration the integral overlap (O , Table 1) and simulation results (Table S2 in Supporting Information), the $3.3 \times 10^{-7} \text{ M}$ solution displays the better optical performance at lower dye concentration and that was the rationale behind the selection of this solution for the fabrication of the p-LSC. In this case, we highlight that the simulated η_{opt} values for the $3.3 \times 10^{-7} \text{ M}$ solution (6.28%) are slightly larger than those experimentally determined ($5.6 \pm 0.2 \%$), pointing out that the device may be further optimised, particularly the PV cell coupling.^[64, 67]

4. Conclusions

In this work, natural-based LSCs made of R-phycoerythrin (R-PE) aqueous solutions were studied. These optically active centres display large overlap with the solar irradiance on Earth (absorption at 300-700 nm) and emission spectra centred around 580 nm. Moreover, these aqueous solutions present the highest molar brightness values reported so far for organic dye molecules emitting in the 530-650 nm range, and thus LSCs based on R-PE aqueous solutions with distinct concentrations (4.2×10^{-8} to 1.7×10^{-6} M) were tested. The best performance (η_{opt} and PCE values) was found for c-LSCs ($G \sim 7$) filled with the aqueous solutions with R-PE concentration of 4.2×10^{-7} M. Also, the POF-based c-LSCs were assembled in a bundle structure, yielding η_{opt} and PCE values of $\sim 4.74\%$ and $\sim 23.03 \times 10^{-3}\%$, respectively. Nevertheless, the top performance device reported in this work was a p-LSC based on a glass cuvette, with η_{opt} and PCE values of $\sim 6.88\%$ and $\sim 0.27\%$, respectively. These values are a starting point for the use of natural dyes as optical active centres for sustainable LSCs, demonstrating the potential of nature-inspired LSCs as a relevant step towards cheap and sustainable PV energy conversion.

5. Experimental section

Materials. The red macroalgae *Gracilaria sp.* was grown in a land-based integrated aquaculture system at ALGApplus - Produção e Comercialização de Algas e seus Derivados, a company specialized in the production of macroalgae, located in Ílhavo, Portugal. The ammonium sulphate (99.5%) used in phycobiliproteins precipitation was purchased at Merck. A commercial standard of R-phycoerythrin ($\geq 10.0 \text{ mg.mL}^{-1}$) was purchased at Sigma- Aldrich.

Solid-liquid extraction. The solid-liquid extraction procedure used in this work was adapted from the methodology already proposed by Martins *et al.*^[46] Briefly, after the harvesting of the macroalgae, the samples were cleaned and washed with fresh and

distilled water at least 3 times to eliminate small particles and residues from the cultivation. The biomass was then stored at $-20\text{ }^{\circ}\text{C}$. When needed, the macroalgae samples were frozen in liquid nitrogen and grounded to increase the contact surface, thus enhancing the extraction. The biomass was homogenized in distilled water at a solid-liquid ratio of 0.5 (weight of biomass *per* volume of solvent). Then, the solid-liquid extraction was performed with water at 250 rpm in an incubator (IKA KS 4000 ic control) protected from light exposure, during 20 minutes at room temperature. At the end of this step, a pinkish solution was obtained, filtered and centrifuged in a Thermo Scientific Heraeus Megafuge 16 R centrifuge at 5000 rpm for 30 minutes at $4\text{ }^{\circ}\text{C}$. The resultant pellet was discarded while the phycobiliprotein-based pinkish supernatant was collected. An ammonium sulphate aqueous solution at 30% was used to pre-treat the crude extract rich in phycobiliproteins obtained from the solid-liquid extraction performed. This step was realized aiming at the elimination of some of the contaminant proteins extracted simultaneously with the phycobiliproteins. With this stage, it was also possible to identify the potential effect of the purity level of the phycobiliproteins-rich extract as optically active centres in LSCs. After the pre-treatment, the salt was dissolved and the solution was left at $4\text{ }^{\circ}\text{C}$ for 4 hours, being then centrifuged at 5000 rpm for 30 minutes at $4\text{ }^{\circ}\text{C}$. After the precipitation of the target proteins, the pellet was resuspended in distilled water at different concentrations. The phycobiliproteins concentration of each extract was calculated using a UV-Vis microplate reader (Synergy HT micro-plate reader - BioTek) at 565 nm and a calibration curve previously established for the commercial standard R-PE.

LSCs fabrication. The c-LSCs were based on hollow-core POFs with distinct diameter values (Figure 1A), resulting in different geometrical gain factors (G), which is given by the ratio between the exposed (A_s) and edge (A_e) areas. The POFs were fabricated using a semi-industrial optical fibre manufacturing facility^[49] and cut into segments with

length $l \sim 5 \times 10^{-2}$ m. The hollow-core was filled with the R-PE solutions with a syringe. The edge coupled to the PV device was sealed with the polymeric resin NOA68[®], while the opposite one was kept open. The individual POFs were, then, assembled into bundles (Figure 1A). The p-LSCs were fabricated using an optical glass cuvette (CM Scientific) with dimensions tailored to fit the PV cell surface, as illustrated in Figure 1B. A total number of 39 and 4 c-LSCs and p-LSCs, respectively, were fabricated.

UV/Visible Absorption. UV/visible absorption spectra of the R-PE solutions were measured using a Lambda 950 dual-beam spectrometer (Perkin-Elmer). All measurements were performed using a 1 cm square quartz cell. Using the Beer–Lambert law, the molar extinction coefficient (ϵ , $\text{M}^{-1}\text{cm}^{-1}$) was calculated from the linear dependence (slope) found for absorbance *versus* concentration.

Photoluminescence Spectroscopy. The photoluminescence spectra were recorded at room temperature with a modular double-grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Horiba Scientific) coupled to a R928 Hamamatsu photomultiplier.

Absolute Emission Quantum Yield. The absolute emission quantum yield values (q) were measured at room temperature using a C9920-02 Hamamatsu system.^[68] The method is accurate within 10%. The reference measurement was performed with an empty 1 cm square quartz cell, as the interest was the emission quantum yield value of the aqueous solution, rather than of the R-PE emitting centres alone.

Refractive index. The refractive index values of the R-PE solutions were measured using an Abbemat 200, Anton Paar refractometer. Refractive index results are relative to 589 nm, a temperature of 22 °C and accurate to $\pm 10^{-4}$.

Optical Conversion Efficiency (η_{opt}) and Power Conversion Efficiency (PCE) The η_{opt} and PCE values here reported were measured at least three times (including for R-PE solutions prepared at different times) and the results were reproducible with a standard

deviation of $\pm 4\%$. All η_{opt} and PCE values reported in this manuscript presents an absolute error inferred through Eq. S8 and Eq. S9 in Supporting Information. All performance measurements were done under standard simulated AM1.5G radiation.

External Quantum Efficiency (EQE). The solar simulator was coupled to a monochromator (Triax 180, Horiba Scientific). The I_{sc} and P_{in} values were measured using a sourcemeter (2400 SourceMeter SMU Instruments, Keithley) and a c-Si calibrated photodiode (FDS1010, Thorlabs), respectively. The reported EQE values present an absolute error inferred through Eq. S12 in Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Portuguese funding was provided by Fundação para a Ciência e a Tecnologia (FCT), EU/FEDER COMPETE and Mais Centro-PORC, under contracts PEST-OE/EEI/LA0008/2013 and CENTRO-07-ST24-FEDER-002032. This work was developed within the scope of the projects CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID/CTM/50011/2013), SusPhotoSolutions - Soluções Fotovoltaicas Sustentáveis, CENTRO-01-0145-FEDER-000005, Solar-Flex, CENTRO-01-0145-FEDER-030186, and Instituto de Telecomunicações (FCT Ref. UID/EEA/50008/2013), financed by funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement. Solar-Flex is a bilateral FCT/Fundação de Amparo à Pesquisa do Estado de São Paulo, Brazil, project (2018/07727-7). The authors acknowledge ALGAPlus - Produção e Comercialização de Algas e seus Derivados for seaweed samples and ARF and MM thank FCT for the PhD grants (PD/BD/114454/2016 and SFRH/BD/122220/2016, respectively). SFHC and SPMV thank SusPhotoSolutions for the post-doctoral grant and FCT for the IF (IF/00402/2015) contract, respectively.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

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Figures and Tables

A

B

Figure. 1. Scheme of the (A) fibre c-LSCs bundle structure and (B) p-LSC.

Figure 2. Emission spectra of the R-PE solutions excited at 498 nm.

Figure 3. (A) Solar photon flux on Earth at AM1.5G, (B) absolute absorbance of 1.7×10^{-7} M (blue line), 3.3×10^{-7} M (red line) and 17×10^{-7} M (green line) and (C) integral overlap between the solar photon flux and the absolute absorbance.

Figure 4. Photographs of (A) a c-LSC based on the 17×10^{-7} M solution, (B) a bundle structure of c-LSCs based on 4.2×10^{-7} M solution and (C) a p-LSC (with reflective tape) based on 3.3×10^{-7} M solution and under AM1.5G illumination (scale bars: 1×10^{-2} m).

Figure 5. Photos of the bundle being bended showing the flexibility of the POFs.

Figure 6. (A) Cross-section optical microscopy images of a c-LSC under UV irradiation at 365 nm (scale bar: 3×10^{-4} m), (B) hyperspectral image of a selected area and (C) corresponding emission spectra measured in the core and PMMA regions.

Figure 7. Cross correlation between the EQE of the photodiode coupled to the c-LSCs (G~9) and the absorption spectrum of the correspondent R-PE solution for the illustrative examples of (A) 4.2×10^{-7} M, (B) 5.8×10^{-7} M, (C) 7.5×10^{-7} M and (D) 17×10^{-7} M solutions. We note that increasing concentration the correlation is more evident. The colour-scale intensity is a measure of the correlation.

Table 1. Integral overlap (O , photons $\cdot$ s $^{-1}\cdot$ m $^{-2}$), molar extinction coefficient (ϵ , M $^{-1}\cdot$ cm $^{-1}$), absolute emission quantum yield (q) and brightness (B , M $^{-1}\cdot$ cm $^{-1}$) as function of the R-PE concentration ($[I]$, M). The ϵ , q and B values refer to 498 nm.

$[I]$ ($\times 10^{-7}$)	O ($\times 10^{20}$)	ϵ ($\times 10^6$)	q	B ($\times 10^6$)
0.4	0.9	1.7	0.37 $\pm$ 0.04	6.2
1.7	2.1	1.0	0.39 $\pm$ 0.04	3.9
2.1	3.0	1.3	0.34 $\pm$ 0.03	4.2
2.5	3.8	1.4	0.32 $\pm$ 0.03	4.5
3.3	4.8	1.4	0.30 $\pm$ 0.03	4.0
4.2	5.5	1.4	0.28 $\pm$ 0.03	3.7
5.8	6.9	1.5	0.25 $\pm$ 0.03	3.8
7.5	8.0	1.6	0.24 $\pm$ 0.02	3.2
17	10.4	1.5	0.16 $\pm$ 0.02	2.2

Table 2. η_{opt} (%) and PCE (%) values of the LSCs prepared here, the former values were calculated through Eq. (2). For p-LSCs literature values of active centres dispersed in distinct liquid media are also listed for comparison. The concentration ($[\]$, M) of the active centres on the liquid media and the LSC surface area A_s ($l \times w$, cm^2) are also presented.

	Medium	Active centre	$[\]$	A_s	η_{opt}	PCE	Ref.
c-LSCs	Water	R-PE	4.2×10^{-7}	3.5×1.4	4.74	0.02 (Si)	<i>This work</i>
	Water	R-PE	3.3×10^{-7}	2.0×2.0	6.88	0.27 (Si)	
p-LSC	Rhodamine B				15.3		
	PPC/EG	LDS698	-		3.6		
		LDS821	$\sim 10^{-4}$		2.9		
	Cl-benzene	MDMO-PPV	$\sim 10^{-3}$	2.5×7.6	5.9	-	[1]
		MEH-DOO-PPV	-		5.0		
		Red F	8×10^{-6}		19.8		
	toluene	CdSe/ZnS	3×10^{-6}		1.6		
	K_1				20.2		
	TX-100	Sulphorhodamine 101			18.2		
		BASF-402	-	5×10	19.7	-	[2]
		BASF-241			13.9		
	toluene	CdSe/ZnS	3×10^{-6}	4.5×1.2	0.5	1.2 (Si)	[3]
		PbS	1.93×10^{-4}		12.6	3.2 (Si)	
	LC E7	Coumarine/ perylene	8×10^{-3}	5×5	3.2*	-	[4]
	toluene	Lumogen F Red 300	4×10^{-3}	2×2	12.0	-	[5]
	toluene	Lumogen Red 305	1.23×10^{-7}	10×3.5	-	2.3 (Si)	[6]

Liquid crystal Nematic=LC E7, TX-100=polymer Triton X-100, PPC=Propylene carbonate, EG=ethylene glycol, Cl-bez=Chlorobenzene; $\ast\eta_{\text{opt}}$ is simply defined as $\eta_{\text{opt}} = P_{\text{out}}/P_{\text{in}}$, without mentioning the definition behind it.

Luminescent solar concentrators (LSCs) appear as a solution to cope with the mismatch between solar cells absorption and the solar spectrum. The use of R-phycoerythrin (R-PE) protein as optically active centres dispersed in aqueous solutions, is a sustainable strategy for light harvesting with no significant negative effects on the environment.

Keywords: luminescent solar concentrators, organic-inorganic hybrids, bundles, sustainable

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Sustainable liquid luminescent solar concentrators

Supporting Information

Sustainable liquid luminescent solar concentrators

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Excitation and absorption spectra of R-PE aqueous solutions

Figure S1. (A) Excitation monitored at 580 nm and (B) absorption spectra of the R-PE solutions.

Flexibility test

Figure S2. Photos of the bundle being bended showing the flexibility of the POFs.

Transmittance of plastic optical fibres

Figure S3. Transmittance spectrum of the plastic optical fibres assembled in bundle.

Figure S4. (A) Measured output voltage (V_{PD} , absolute error of ± 0.001 V) values for calibrated photodiode and (B) calculated incident optical power (P_{in}); (C,E) measured short-circuit current values (I_{sc} , absolute error of $\pm 10^{-10}$ A) and (D,F) calculated EQE for c-LSCs with (C,D) G~7 and (E,F) G~9, according to the concentration (0.4 to 17×10^{-7} M). The colour code for (D), (E) and (F) is the same as in (C).

Figure S5. Cross correlation between the photodiode EQE and the absorption spectrum of the coupled LSC based on (A) 0.4×10^{-7} M, (B) 1.7×10^{-7} M, (C) 2.1×10^{-7} M, (D) 2.5×10^{-7} M, (E) 3.3×10^{-7} M, (F) 4.2×10^{-7} M, (G) 5.8×10^{-7} M, (H) 7.5×10^{-7} M and (I) 17×10^{-7} M solutions, for c-LSCs with $G \sim 7$.

Figure S6. Cross correlation between the photodiode EQE and the absorption spectrum of the coupled LSC based on the (A) 0.4×10^{-7} M, (B) 1.7×10^{-7} M, (C) 2.1×10^{-7} M, (D) 2.5×10^{-7} M, (E) 3.3×10^{-7} M, (F) 4.2×10^{-7} M, (G) 5.8×10^{-7} M, (H) 7.5×10^{-7} M and (I) 17×10^{-7} M solutions, for c-LSCs with G~9.

Bundle structure of c-LSCs

Figure S7. Video showing the effect of coupling a bundle structure of c- LSCs to a PV cell under simulated solar radiation. The full video is found as Electronic Supplementary Information. Please note that as explained in the manuscript, during the measurements the PV cell was used with a black mask with dimensions matching A_e .

Figure S8. (A) Measured output voltage (V_{PD} , absolute error of ± 0.001 V) values for calibrated photodiode and (B) calculated incident optical power (P_{in}); (C) measured short-circuit current values (I_{sc} , absolute error of $\pm 10^{-8}$ A) and (D) calculated EQE for the p-LSCs based on the 3.3×10^{-7} M solution.

Figure S9. Cross correlation between the PV cell EQE and the absorption spectrum of the coupled p-LSC.

Glass cuvette refractive index

Figure S10. (A) Ellipsometric parameters I_s (open circles) and I_c (open triangles) measured for the glass cuvette. The solid lines represent the data best fit; (B) dispersion curve of the cuvette glass considered for the Monte-Carlo simulation of the p-LSC.

Optical conversion efficiency (η_{opt})

The η_{opt} can be described by weighting all the losses in the LSC, given by the product of several terms:^[7]

$$\eta_{opt} = (1 - R)\eta_{abs}\eta_{SA}\eta_{yield}\eta_{Stokes}\eta_{trap}\eta_{mat} \quad (S1)$$

in which:

- $R=(1-n_i)^2/(1+n_i)^2$ **Erro! Dígito esperado.** is the Fresnel reflection coefficient for perpendicular incidence, in which n_i represents the refractive index of the emitting medium at the incident wavelength (λ_i).
- $\eta_{abs}=1-10^{-A}$ is the ratio of photons absorbed by the emitting layer to the number of photons falling on it, with A representing the absorbance value at λ_i .
- η_{SA} is the self-absorption efficiency, arising from self-absorption of the emitting centres, as detailed elsewhere.^[6]
- η_{yield} is the emission quantum yield of the optically active centre at λ_i .
- $\eta_{Stokes}=\lambda_i/\lambda_p$, is the Stokes efficiency calculated by the energetic ratio between the average energy of the emitted photons and the incident energy.
- η_{tr} takes into account the transport losses due to matrix absorption and scattering, frequently it is considered that $\eta_{tr}=1$, as the transport and scattering losses are neglected.
- η_t is the trapping efficiency. The emission intensity guided in the polymethylmethacrylate (PMMA) cladding is larger (~ 2 times) than that in the hollow-core. These later results may be further rationalized using a simple analytic expression that, for a uniform distribution of emitting centers and isotropic emission over a solid angle, depends on the difference between the refractive index values (at the emission wavelength range) of the optically active layer at the core (n_{core}) and at the PMMA (n_{clad})^[8],

$$\eta_t = 1 - (n_{clad}/n_{core})^2 \quad (S2)$$

In the case of LSCs based on R-PE solutions, the larger refractive index of the cladding ($n_{clad} \sim 1.49$) compared with that of the core ($n_{core} \sim 1.3335$) yields to a dominant light guidance in the PMMA, as illustrated in [Figure 6](#) of the manuscript.

Another parameter that contributes to η_t is the distance r from the fibre center at which the emission occurs which, for a POF with external radius R , is given by:^[9]

$$\eta_t = 1 - \frac{1}{\pi} \int_0^\pi \frac{\sqrt{\left((n_{PMMA})^{-2} - \left(\frac{r}{R}\right)^2 \sin^2 \beta\right)}}{1 - \left(\frac{r}{R}\right)^2 \sin^2 \beta} d\beta \quad (S3)$$

with a maximum value near the surface, that decreases as radius of the inner core r approaches the center of the POF ([Figure S11](#) in Supporting Information). We note that for the geometry here proposed, for both cases of $G \sim 7$ and $G \sim 9$, average η_t values of 0.37 were estimated ([Figure S11](#) in Supporting Information).

The experimental η_{opt} values were determined by illuminating the top surface of the LSCs with simulated AM1.5G illumination. For p-LSCs and the c-LSCs bundle structure the optical power at the LSC output was estimated using a c-Si PV cell (KXOB22-12X1L, IXYS coated by the manufacturer with an EVA film with a maximum EQE around 80%, [Figure S12](#) in Supporting Information). The I_{sc} and V_0 values were measured using a sourcemeter device (2400 SourceMeter SMU Instruments, Keithley). Whereas no reflective devices were used on the c-LSC bundle structure, for the case of p-LSCs, a reflective tape (reflectance curve in [Figure S13](#) in Supporting Information) was used on all the edges of the cuvette, in the backside and in the area which is not illuminated by uniform solar simulator radiation. All measurements were performed under AM1.5G illumination ($1000 \text{ W} \cdot \text{m}^{-2}$) using a 150 W xenon arc lamp, class A, solar simulator (Model 10500, Abet Technologies). The mismatch in the UV spectral region between the AM1.5G solar irradiance and that of the Xe lamp in the solar simulator was taken

into consideration following a methodology reported in detail elsewhere,^[10] revealing that it does not affect the calculation of the η_{opt} values for the particular case of R-PE solution-based LSCs.

We note that for the single-based c-LSCs the lack of commercial PV-cell with analogous circular geometry and dimensions prevents an accurate estimation of P_{out} . In this case, to enable a relative comparison between the distinct c-LSCs and study the effect of the RPE concentrations and G factor, the optical power at the LSC output was estimated using a commercial photodiode (IF D91, Industrial Fiber Optics, Inc.) with a wall-plug efficiency of 4% to the AM1.5G solar spectrum distribution (maximum EQE around 80%, Figure S14 in Supporting Information). The photodiode was coupled to one edge of the LSC while kept inside a black cap to prevent the influence of direct illumination from the solar simulator (Figure S15 in Supporting Information). These experimental limitations yield to underestimated η_{opt} values, as no correction between the LSC and photodiode dimensions' mismatch was performed.

Trapping efficiency

Figure S11. Trapping efficiency (η_t) as function of the ratio r/R (Eq. S3).

c-Si PV cell EQE curve

Figure S12. (A) Measured output voltage (V_{PD} , absolute error of ± 0.001 V) values for calibrated photodiode and (B) calculated incident optical power (P_{in}); (C) measured short-circuit current values (I_{sc} , absolute error of $\pm 10^{-8}$ A) and (D) calculated EQE for the used c-Si PV cell.

Reflective tape

Figure S13. Reflectance curve of the reflective tape used on the p-LSC.

c-Si photodiode EQE curve

Figure S14. (A) Measured output voltage (V_{PD} , absolute error of ± 0.001 V) values for calibrated photodiode and (B) calculated incident optical power (P_{in}); (C) measured short-circuit current values (I_{sc} , absolute error of $\pm 10^{-8}$ A) and (D) calculated EQE for the used c-Si photodiode.

Coupling of PV devices to LSCs

Figure S15. Diagram of the photodiode coupling to the LSC. The scale refers to the device dimensions.

Power conversion efficiency and PV cell responsivity

To experimentally evaluate the power conversion efficiency (PCE) of the PV cell coupled to the bundle structure of c-LSCs, to cope with the larger surface area of the PV cell compared with the bundle edges, the PV cell was used with a black mask with dimensions matching A_e . In this case, a direct comparison between the PCE values calculated in the presence of the p-LSC and of the bundle-based LSCs cannot be made due to induced differences in the PV cell responsivity (Figure S16 in Supporting Information).

Figure S16. Electrical power output P_{out}^{el} as function of the incident optical power P_{in} for the PV cell as used for the p-LSC and for the bundle structure of the c-LSCs (with mask matching A_e), for 580 nm incident radiation. The solid lines represent the best data fit ($r^2 > 0.99$). All data present a relative error $< 1\%$.

External quantum efficiency (EQE)

The PV devices' EQE was calculated through:

$$EQE = \frac{\#electrons}{\#photons} = \frac{I_{SC} \cdot E_v}{P_{in} \cdot e} = \frac{I_{SC}}{e} \frac{hc}{P_{in} \lambda} = \frac{I_{SC}}{e} \frac{hc}{\lambda} \frac{R_{PD} R_L}{V_{PD}} \frac{A_{PD}}{A_{PV}} \quad (S4)$$

where I_{sc} is the PV device generated short-circuit current, e is the charge of the electron, E_v is the energy of the incident photons, P_{in} is the incident optical power, h is the Planck's constant, c is the speed of light in vacuum, λ is the wavelength of the incident photons, R_{PD} , V_{PD} , R_L and A_{PD} are the responsivity, the output voltage, the coupled load resistor (10 k Ω) and the active area of the reference calibrated photodiode, respectively, and A_{PV} is the area of the PV device.

When the PV device was coupled to a LSC, the PV devices' EQE was calculated using the following approximation:

$$S_{LSC} = P_{in} \frac{A_s}{A_e} \quad (S5)$$

$$P_{LSC} = S_{LSC} A_{PV} = P_{in} \frac{A_s}{A_e} A_{PV} \quad (S6)$$

$$EQE = \frac{I_{SC}}{e} \frac{hc}{\lambda} \frac{A_e}{A_s \times A_{PV}} \frac{R_{PD} R_L A_{PD}}{V_{PD}} \quad (S7)$$

where S_{LSC} and P_{LSC} are the optical power density and the optical power from the LSC reaching the PV cell.

Calculus of the optical conversion efficiency error ($\Delta\eta_{opt}$)

The η_{opt} values were calculated through Eq. (2) in the manuscript. The associated error ($\Delta\eta_{opt}$) is given by:

$$\begin{aligned}
(\Delta\eta_{opt})^2 &= \left(\frac{\delta\eta_{opt}}{\delta I_{SC}^L} \Delta I_{SC}^L\right)^2 + \left(\frac{\delta\eta_{opt}}{\delta V_0^L} \Delta V_0^L\right)^2 + \left(\frac{\delta\eta_{opt}}{\delta A_e} \Delta A_e\right)^2 + \left(\frac{\delta\eta_{opt}}{\delta \eta_{solar}} \Delta \eta_{solar}\right)^2 \\
&\quad + \left(\frac{\delta\eta_{opt}}{\delta I_{SC}} \Delta I_{SC}\right)^2 + \left(\frac{\delta\eta_{opt}}{\delta V_0} \Delta V_0\right)^2 + \left(\frac{\delta\eta_{opt}}{\delta A_s} \Delta A_s\right)^2 \\
&\quad + \left(\frac{\delta\eta_{opt}}{\delta \eta_{LSC}} \Delta \eta_{LSC}\right)^2 \\
&= \left(\frac{V_0^L A_e \eta_{solar}}{I_{SC} V_0 A_s \eta_{LSC}} \Delta I_{SC}^L\right)^2 + \left(\frac{I_{SC}^L A_e \eta_{solar}}{I_{SC} V_0 A_s \eta_{LSC}} \Delta V_0^L\right)^2 \\
&\quad + \left(\frac{I_{SC}^L V_0^L \eta_{solar}}{I_{SC} V_0 A_s \eta_{LSC}} \Delta A_e\right)^2 + \left(\frac{I_{SC}^L V_0^L A_e}{I_{SC} V_0 A_s \eta_{LSC}} \Delta \eta_{solar}\right)^2 \\
&\quad + \left(-\frac{I_{SC}^L V_0^L A_e \eta_{solar}}{(I_{SC})^2 V_0 A_s \eta_{LSC}} \Delta I_{SC}\right)^2 + \left(-\frac{I_{SC}^L V_0^L A_e \eta_{solar}}{I_{SC} (V_0)^2 A_s \eta_{LSC}} \Delta V_0\right)^2 \\
&\quad + \left(-\frac{I_{SC}^L V_0^L A_e \eta_{solar}}{I_{SC} V_0 (A_s)^2 \eta_{LSC}} \Delta A_s\right)^2 + \left(-\frac{I_{SC}^L V_0^L A_e \eta_{solar}}{I_{SC} V_0 A_s (\eta_{LSC})^2} \Delta \eta_{LSC}\right)^2
\end{aligned} \tag{S8}$$

where I_{SC}^L and V_0^L represent the short-circuit current and the open voltage when the PV device is coupled to the LSC, (I_{sc} and V_0 are the corresponding values of the PV device exposed directly to the solar radiation), A_s and A_e are the exposed and edge area respectively, η_{solar} is the efficiency of the PV device relatively to the total solar spectrum and η_{PV} is the efficiency of the PV device at the LSC emission wavelengths. The errors associated with each variable were considered as follows: $\Delta I_{SC}^L = \Delta I_{SC} = 10^{-10}$ A is the current experimental uncertainty, $\Delta V_0^L = \Delta V_0 = 10^{-3}$ V is the voltage experimental uncertainty, $\Delta A_e = \Delta A_s = 10^{-7}$ m² is the experimental uncertainty associated with the areas and $\Delta \eta_{solar} = \Delta \eta_{LSC} = 10^{-2}$ is the photodiode experimental uncertainty.

Calculus of the power conversion efficiency error (ΔPCE)

The PCE values were calculated through Eq. (4) in the manuscript. The associated error (ΔPCE) is given by:

$$\begin{aligned}
 (\Delta PCE)^2 &= \left(\frac{\delta PCE}{\delta I_{SC}^L} \Delta I_{SC}^L \right)^2 + \left(\frac{\delta PCE}{\delta V_0^L} \Delta V_0^L \right)^2 \\
 &+ \left(\frac{\delta PCE}{\delta \int_{\lambda_1}^{\lambda_2} I_{AM1.5G}(\lambda) d\lambda} \Delta \int_{\lambda_1}^{\lambda_2} I_{AM1.5G}(\lambda) d\lambda \right)^2 + \left(\frac{\delta PCE}{\delta A_s} \Delta A_s \right)^2 \\
 &= \left(\frac{V_0^L FF}{A_s \int_{\lambda_1}^{\lambda_2} I_{AM1.5G}(\lambda) d\lambda} \Delta I_{SC}^L \right)^2 + \left(\frac{I_{SC}^L FF}{A_s \int_{\lambda_1}^{\lambda_2} I_{AM1.5G}(\lambda) d\lambda} \Delta V_0^L \right)^2 \quad (S9) \\
 &+ \left(\frac{I_{SC}^L V_0^L FF}{A_s \left(\int_{\lambda_1}^{\lambda_2} I_{AM1.5G}(\lambda) d\lambda \right)^2} \Delta \int_{\lambda_1}^{\lambda_2} I_{AM1.5G}(\lambda) d\lambda \right)^2 \\
 &+ \left(\frac{I_{SC}^L V_0^L FF}{\int_{\lambda_1}^{\lambda_2} I_{AM1.5G}(\lambda) d\lambda (A_s)^2} \Delta A_s \right)^2
 \end{aligned}$$

where FF=0.75 is the fill factor of the PV device. The errors associated with each variable were considered as follows: $\Delta I_{SC}^L = 10^{-10}$ A is the current experimental uncertainty, $\Delta V_0^L = 10^{-3}$ V is the voltage experimental uncertainty and $\Delta \int_{\lambda_1}^{\lambda_2} I_{AM1.5G}(\lambda) d\lambda = 0.01$.

Calculus of the external quantum efficiency error (ΔEQE)

The EQE values were calculated through Eq. (4) in the manuscript. The associated error (ΔEQE) is given by:

$$\begin{aligned}
 (\Delta EQE)^2 &= \left(\frac{\delta EQE}{\delta I_{SC}} \Delta I_{SC} \right)^2 + \left(\frac{\delta EQE}{\delta V_{PD}} \Delta V_{PD} \right)^2 \\
 &= \left(\frac{hc R_{PD} R_L A_{PD}}{e \lambda V_{PD} A_{PV}} \Delta I_{SC} \right)^2 + \left(\frac{I_{SC} hc R_{PD} R_L A_{PD}}{e \lambda A_{PV}} \Delta V_{PD} \right)^2
 \end{aligned}
 \tag{S10}$$

The errors associated with each variable were considered as follows: $\Delta I_{SC}^L = 10^{-10}$ A is the current experimental uncertainty, $\Delta V_0^L = 10^{-3}$ V is the voltage experimental uncertainty. All the remain parameters are constants (h , c , e) or given by the device manufacturer (R_L , R_{PD} , A_{PD} , A_{PV}).

Spectroscopic ellipsometry

The spectroscopic ellipsometry measurements were made using an AutoSE ellipsometer (HORIBA Scientific) with a total of 250 points in the wavelength interval 450-850 nm, an incidence angle (θ_0) of 70 ° and a signal quality of 30. A measurement spot area of 250×250 μm^2 was used. Three measurements were performed in each sample. The refractive index values of the films were estimated using the direct inversion methodology.

Table S1. Optical conversion efficiency (η_{opt} , %) values of R-PE based c-LSCs made of a single POF.

[R-PE] ($\times 10^{-7}$ M)	G~7	G~9
0.4	0.137 $\pm$ 0.004	0.073 $\pm$ 0.003
1.7	0.153 $\pm$ 0.005	0.093 $\pm$ 0.003
2.1	0.105 $\pm$ 0.003	0.091 $\pm$ 0.003
2.5	0.193 $\pm$ 0.006	0.089 $\pm$ 0.003
3.3	0.162 $\pm$ 0.005	0.065 $\pm$ 0.002
4.2	0.164 $\pm$ 0.005	0.077 $\pm$ 0.003
5.8	0.151 $\pm$ 0.005	0.058 $\pm$ 0.002
7.5	0.101 $\pm$ 0.003	0.085 $\pm$ 0.003
17	0.134 $\pm$ 0.004	0.102 $\pm$ 0.004

The dependence of η_{opt} with the concentration is more evident for the c-LSCs with lower geometrical gain G (given by the ratio between A_s and A_e), varying from $\sim 0.101\%$ to $\sim 0.193\%$, comparing to a variation between $\sim 0.058\%$ and $\sim 0.102\%$ for POFs with higher G , demonstrating that as the concentration increases from 0.4×10^{-7} M to 5.8×10^{-7} M, the photon flux at the LSC ends is enhanced due to the increase in the absolute number of optically active centres that compensates the self-absorption losses, after the saturation is reached, as previously demonstrated.^[6] The larger η_{opt} values found for the c-LSCs with lower G values may be rationalised as follows. Among the several physical mechanisms that control the η_{opt} (see Supporting Information for details), the absorption efficiency (η_{abs}) and the trapping efficiency (η_t) are certainly dependent on geometrical aspects (G). Whereas the η_{abs} is larger for c-LSCs with G~7 (0.9%) compared with that for G~9 (0.7%), the η_t is analogous (37%, Figure S1 in Supporting Information). These results suggest that the larger optical conversion efficiency is assigned to the larger optical absorption path found in the c-LSCs with G~7 compared with those with G~9.

Table S2. Simulated optical conversion efficiency values considering all the photons reaching the edge (η_{opt} , %) and only the converted photons (η'_{opt} , %) for p-LSCs using R-PE solution with different concentrations. All data present an absolute error of $\pm 0.005\%$.

[R-PE] ($\times 10^{-7}$ M)	η_{opt} (%)	η'_{opt} (%)
0.4	5.787	0.000
1.7	6.013	0.236
2.1	6.423	0.906
2.5	6.350	0.980
3.3	6.284	1.171
4.2	6.168	1.234
5.8	5.870	1.250
7.5	5.321	0.978
17	3.448	0.418

In what concerns η_{opt} , the values are nearly independent of the concentration except for the more concentrated solutions (7.5×10^{-7} M and 17×10^{-7} M) for which a decrease is noticed. This decrease may be rationalised based on the quantum yield decrease, induced by the formation of dye-aggregates at higher concentrations. If only the converted photons are taken into consideration, η'_{opt} is nearly constant only in the concentration range of 2.1×10^{-7} M to 5.8×10^{-7} M solutions. Whereas the lower η_{opt} and η'_{opt} values found for low concentrated solutions (0.4×10^{-7} M and 1.7×10^{-7} M) arise from lower ε (despite the higher q), those of the higher concentrated ones (7.5×10^{-7} M and 17×10^{-7} M) are mainly caused by the decrease in q (despite the higher ε).

We note that only the η_{opt} values are directly comparable with the experimental ones, as it is not possible to experimentally neglect the contribution of non-converted AM1.5 guided photons (even if no direct radiation is incident on the PV cell).

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