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First demonstration of the use of very large Stokes shift Cycloparaphenylenes as promising organic luminophores for Transparent Luminescent Solar Concentrators

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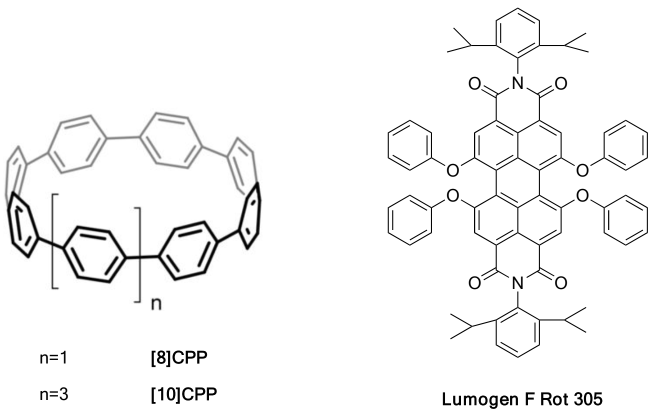
Luminescent Solar Concentrators (LSCs) are rapidly gaining momentum in building integrated photovoltaics. The use of cycloparaphenylenes (CPP) as wide Stokes shift emitters enables the preparation of nearly transparent, large area LSC devices unaffected by reabsorption losses.

LSCs are slabs of transparent, high optical quality materials doped with fluorophores. The fluorophores absorb sunlight and emit inside the slab. Since the refractive index of the slab is higher than that of air, most of emitted light is guided to edges and there collected by small area solar cells. Such a technology was originally introduced in order to cut the cost of conventional photovoltaics.[1] Indeed, progress have been made and various classes of luminophores and devices structures have been tested, leading to optical efficiencies exceeding 7 %.[2] Literature reports essentially two classes of LSCs, full-spectrum and transparent.[2] The first class features luminophores designed to harvest the best possible fraction of the impinging solar light, eventually re emitting it with high efficiency and minimized re-absorption losses. Mostly based on perylene derivatives related to the Lumogen family[3,1,4,5] and other organic fluorophores, [6,7] this field is nowadays also includes colloidal semiconducting nanocrystals of various compositions.[8,9,10] Such strongly absorbing devices may be troublesome for building integration - the main target area for the LSC technology – particularly when emitters with incomplete solar coverage are employed, as this results in LSC devices of well-defined saturated colours. Nevertheless, the use colloidal nanocrystals featuring a broadband absorption spectrum covering the whole visible spectral region and a widely Stokes-shifted luminescence in the near infrared, enables to obtain highly efficient large-area LSCs of neutral coloring (typically referred to as 'colorless' LSCs) with negligible distortion of the transmitted light spectrum.[11]

The second class of LSC emitters is populated by luminophores selectively absorbing in the UV, NIR or both UV and NIR region. On the UV absorption side, lanthanide chelates offer unrivalled separation between absorption and emission. [12] This feature is crucial in cutting reabsorption losses, one of the main parasite processes limiting the efficiency of LSC. Europium chelates are extremely efficient emitters, yet their photon harvesting is very limited.[13] Ytterbium chelates might possess lower optical gaps, unfortunately at the cost of extremely low efficiencies due to vibrational quenching induced by the embedding matrix.[14] High optical gap chalcogenide[15] or perovskite[16] nanocrystals doped with luminescent impurities such as manganese have also been profitably employed as zero reabsorption emitters in low-loss large-area LSCs. On the NIR absorption side, highly conjugated cyanines[17] might offer sufficient spectral coverage - also due to the co-presence of a sizeable UV absorption – but the limited spectral separation between their absorption and emission spectra leads to poor device efficiency.



Scheme 1. Structure of [8]CPP, [10]CPP and commercial dye Lumogen R 305.

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Even though maximum efficiencies are far below those offered by the full spectrum devices, transparent LSC remain a hot topic due to their extremely easy integration into buildings. CycloParaPhenylenes ([n]CPP, See Scheme 1) are conjugated macrocycles consisting of [n] para linked benzene units, which have originally raised much interest as potential seeds for growing uniform single wall carbon nanotubes and as supramolecular hosts for the recognition of fullerenes and pyridinium guests.[18] Beyond these ascertained properties, the [n]CPP show potential applications in photonics[19,20] and optoelectronics. [21]

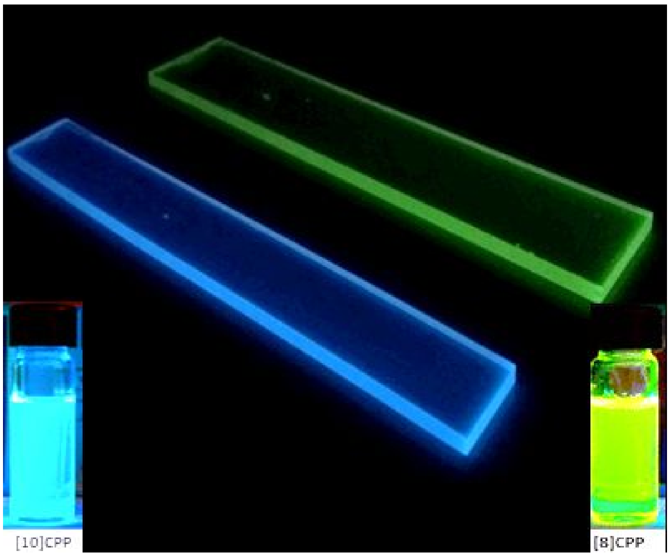

Figure 1. $CHCl_3$ solutions and PMMA slabs containing [8]CPP and [10]CPP under UV light irradiation (365 nm). The characteristic colour of the emission is retained upon embedding in PMMA.

[n]CPPs offer a unique feature amongst other organic fluorophores: their absorption spectrum shows very little dependency upon the macrocycle dimension [n] and is typically fully localized within the UV region (λ_{max} around 340 nm). Conversely, the corresponding emission maxima span the 450-590 nm interval on going from the largest ([n]=13) to the smallest ([n]=7) documented [n]CPPs. As a result, the Stokes shift of [n]CPP increases enormously with decreasing ring size.

Two CPP derivatives are particularly good candidates for LSC applications, [8]CPP and [10]CPP. The former features a huge Stokes shift of 1.4 eV, at the cost of a 10 % luminescence quantum yield. The latter shows a relatively narrower, but still remakable Stokes Shift (still as wide as 1.07 eV) and also presents a high 65 % luminescent quantum yield.

In this communication we show how it is possible to use such compounds for the fabrication of poly methyl methacrylate (PMMA) LSCs using thermally or photochemically driven cell cast polymerization method. We show that both molecules preserve their spectral properties upon embedding in PMMA and, more importantly, the luminescence efficiency of both molecules is enhanced in the polymer waveguides with respect to liquid solution. Crucially, as a result of the favourable Stokes shift, LSCs based on either [n]CPP derivative show nearly negligible reabsorption losses, especially when compared to identical slabs containing Lumogen R 305 (Scheme 1), one of the reference emitters for organic LSCs.

We prepared CPP[8] and CPP[10] according to literature procedures (see Supporting Information for details) and selected PMMA as the embedding matrix both for its favourable optical and structural properties and to ensure direct comparison with most of available literature data. Indeed, PMMA can be polymerized directly in a mould having the required shape and polished at optical-grade quality. Building upon our previous experience, we first tested a thermal polymerization according to the cell cast method.[22-24] Working under conditions analogous to those suited for both perylene dyes and lanthanide chelates, we obtained slabs having an absorption profile undistinguished from the solution one. Close examination of the emission profile shows, however, the formation of an unexpected high-energy emission contribution possibly due by-products of parasitic radical reactions affecting the [n]CPP systems at high temperature. Indeed, [n]CPP derivatives suffer from a ring tension effect increasing reactivity at decreasing ring dimensions.[18] The presence of such a high energy emission shoulder reduces the spectral separation between the absorption and emission profiles resulting in lowered LSC efficiency (details are given in the ESI).

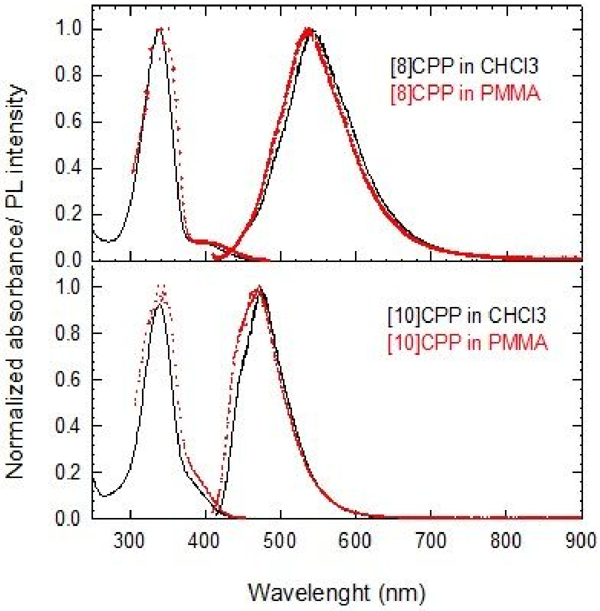

Figure 2. Absorption and emission spectra of [8]CPP (top panel) and [10]CPP (bottom panel) in $CHCl_3$ solution (black lines) and embedded in photo-polymerized PMMA slabs (red lines).

In order to circumvent this issue, we reverted to a photo-polymerization approach recently employed for the preparation of LSCs based on nanocrystal-polymer nanocomposites. [16] Briefly, [n]CPP is dispersed in a small volume of MMA monomer for 3 hours in order to ensure fine dispersion. The monomer-[n[CPP mixture is then added to a large volume of MMA and a radical photo-initiator (IRGACURE 651; 1% w/w). After stirring the mixture for 20 minutes and

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sonication for 10 minutes, the homogeneous mixture is poured into a mould made of two low-roughness pieces of tempered glass linked by a PVC gasket, and irradiated with 365 nm light from a UV lamp for 15 minutes, in order to trigger radical polymerization. The polymerization is then completed by keeping samples in dark for 40 minutes while leaving them in the mould in order to avoid creation of cracks. After the completion of the procedure, the slabs are removed from the mould, laser cut in pieces of desired sizes, and polished.

Figure 1 shows a photograph of PMMA slabs containing [8]CPP or [10]CPP under 365 nm UV illumination, compared to digital pictures of the corresponding $CHCl_3$ solutions. The preservation of the characteristic emission colour and the effective wave-guiding of the luminescence towards the slab edges are clearly observed.

The preservation of the spectral properties of both [8]CPP and [10]CPP molecules is confirmed by looking at the absorption and photoluminescence (PL) spectra in $ChCl_3$ solution and embedded into the PMMA slabs (Figure 2), showing identical profiles in the two conditions.

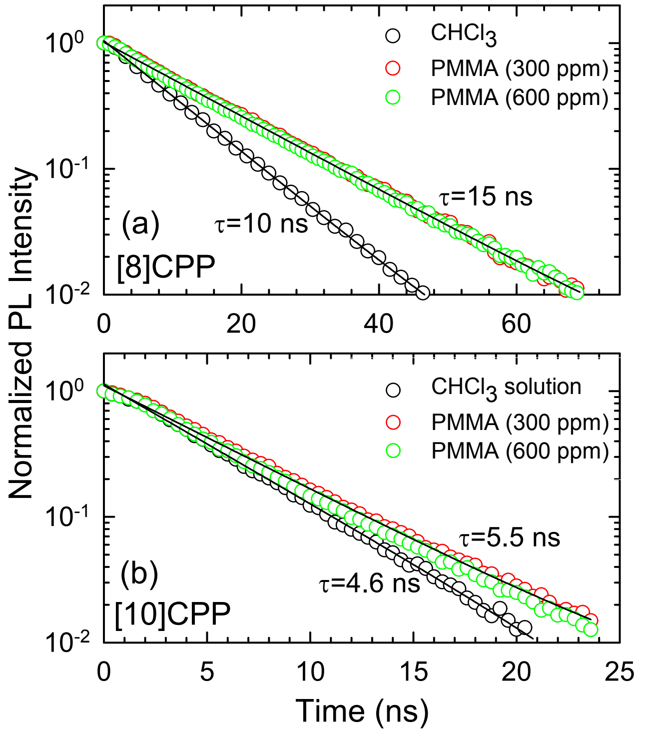

Figure 3. Time decay curves of $CHCl_3$ solution (black circles) and a photopolymerized PMMA slabs containing 300 ppm (red circles) or 600 ppm (gree circles) of (a) CPP[8] and (b) CPP[10]. The black lines are the single exponential fits yielding the indicated lifetimes. Given the nearly perfect overlap between the decay traces in PMMA, only one fitting curve is shown for clarity.

Notably, the incorporation in PMMA is found to benefit the PL efficiency of both systems. This is highlighted in Figure 3, where we show the PL decay traces for PMMA slabs and $CHCl_3$ solutions of the two systems. In both cases we also investigated the effect of concentration within the slab by comparing the results obtained with 300 ppm and 600 ppm of [n]CPP over starting MMA monomer. All PL decay follow a single exponential kinetics suggesting fine dispersion of the luminophores in PMMA with no effects of aggregation due to phase separation. For both [n]CPP, the decay time of the slab samples is longer than the corresponding solution. Very interestingly, the effect is particularly strong for the [8]CPP derivative, whose solution luminescence quantum yield is rather poor. The increase in the lifetime from the 10 ns measured in solution to the 14 ns of the PMMA slab at any concentration translates into an increase in the luminescence efficiency from 10 to 14 %. In the case of [10]CPP, showing high luminescence efficiency already in solution, the effect is less pronounced. Specifically, the emission lifetime goes from 5 to 6 ns, corresponding to an increase in the emission quantum yield from 65% to a remarkable 78 %.

In order to evaluate the impact of reabsorption of the guided luminescence over the maximum useful dimension of a LSC, we measured the intensity of the luminescence emerging from the short side of both CPP[8] and CPP[10] LSCs upon varying the distance, *d*, between the excitation spot and the slab edge (Figure 4, see ESI for a sketch of the optical setup). We then compared the results with identical LSCs containing Lumogen R 305.

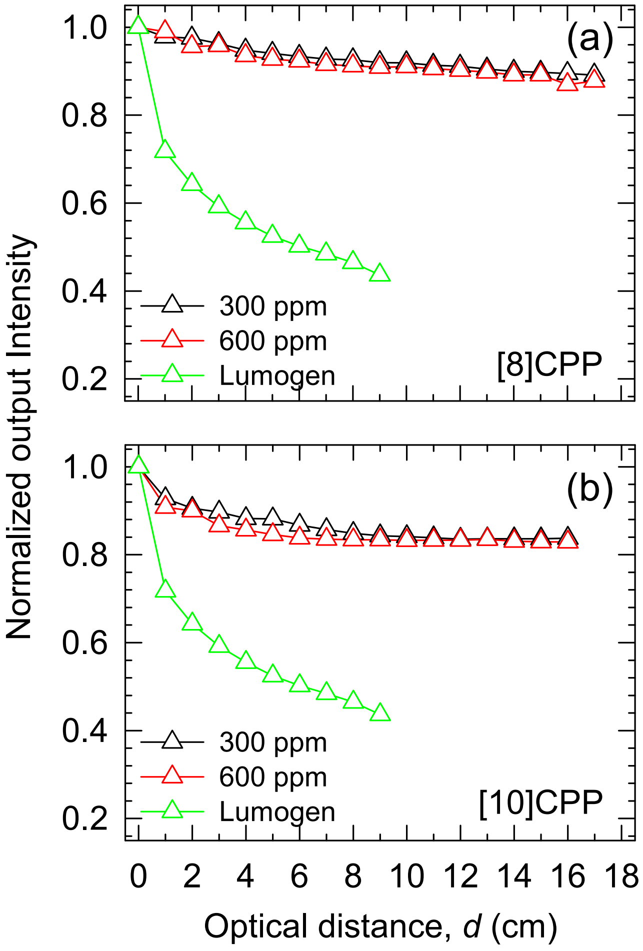

Figure 4. Integrated PL output as a function of the optical distance, *d*, from the excitation spot for LSCs based on a) CPP[8] and b) CPP[10].

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In the Lumogen-based LSC, the emission intensity is attenuated by ca. 40 % for d=3 cm due to the significant overlap between the sharp absorption edge and the high-energy portion of the luminescence spectrum. As previously discussed,[2] for longer optical distances (d>8-10 cm or so), the output intensity levels off as the residual luminescence propagates unaffected by reabsorption. More importantly for our study, LSCs based on [8]CPP and [10]CPP show very minor attenuation (~10%) for optical distances as long as d=18 cm. The optical power efficiency expressed as the ratio between the incident solar power provided by a solar simulator (1.5 AMG) and the optical power measured by a calibrated photodiode index-matched to the narrow edge of the LSC slabs is 0.25% and 0.40% for [8]CPP and [10]CPP respectively and is mostly determined by the spectral coverage that is limited to the UV-blue spectral region. Accordingly, reabsorption losses of such compounds is so low that a fairer comparison should be made with LSCs based on Europium chelates having similar absorption features as our CPP derivatives. [25] We further highlight that the very low attenuation of the guided luminescence in our CPP-based LSCs indicates that optical losses by light scattering are also essentially negligible, also in agreement with the absence of phase-segregation effects indicated by the photoluminescence decay curves in Figure 3.

In conclusion, we prepared the first examples of PMMA LSCs using CPP derivatives as emitters. The very large Stokes shift of such systems enables the preparation of LSC devices essentially unaffected by reabsorption losses. As a result, their waveguiding performance matches closely that of LSCs based on lanthanide chelates, that are to date unrivalled for applications in transparent LSC. Further exploitation of such very promising luminophores, including evaluation of the substituent effect in the light harvesting, emission efficiency trade-off is underway.

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Conflicts of interest

There are no conflicts to declare.

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