Luminescent solar concentrators based on aggregation induced emission

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Abstract

A promising path to cost-effective photovoltaic (PV) systems is sunlight concentration. Over classical non-imaging geometrical concentrators, luminescent solar concentrators (LSCs) possess several advantages: low cost and weight, elevated theoretical concentration factors and aptitude to efficiently working with diffuse light without tracking or cooling equipment. Although considerable progress has been made, current LSC-PV systems attain low power conversion efficiencies due to critical processes that hinder their ability to deliver light to PV cells including fluorescence quenching due to dye aggregation. To overcome this issue, fluorophores with aggregation induced emission (AIEgens) have been proposed thanks to their high Stokes shift and quantum yield in the solid state. In this review, the current state of knowledge concerning the preparation of LSCs based on AIEgens is summarized with special reference on the strategy adopted aimed at increasing the absorption bandwidth while maximizing the solar collection.

1. Introduction

The actual world primary energy demand per time equals to about 15 TW, and it is expected to grow as a result of an increase of industrial activities as well as rise in population.[1] Traditionally, the main primary energy resources consist on fossil and nuclear fuels but a strong input in the use of renewable energies, and in particular solar energy, is nowadays imperative. Solar energy is considered the cleanest available and most abundant renewable energy source being its input reaching about 175,000 TW in the outermost Earth atmosphere, thus exceeding by four orders of magnitude the world primary energy demand.[2] Notwithstanding solar irradiation is free, the equipment required to harvest and convert it into useful forms (heat or electricity) has a cost.[3] Solar energy has the huge defect of being irregular and unpredictable as it depends on the sunshine and the weather. The inability of producing energy on demand has strongly limited the spreading of photovoltaic technologies on the vast scale, however, the possibility of having it implemented in built urban environment, where no other type of ordinary energy production is feasible, makes it an appealing "space-efficient" solution.[4] Still a reduction in costs is necessary for reaching sun energy a good market share. In EU countries, PV module costs around 0.5-2 Euro/Wp (Wp = watt peak capacity), which is still remote from that of ~0.04 Euro/kWh gathered from fossil-fuel technology.[5] The current driving force in solar photovoltaic (PV) technologies is reducing the price per unit of power generated. Sunlight concentration is one of the most promising paths on the way to reduce the price of electrical power from solar cells. This is achieved by reducing the amount of photovoltaic material to convert a given amount of solar irradiance as the price of the moduli has the largest impact on the final energy output cost.[6] Compared to standard concentrators based on passive optical elements such as lenses and mirrors, non-imaging concentration with fluorescent collectors show several advantages: low weight, high theoretical concentration factors, ability to work well with diffuse light and no needs for sun tracking or cooling apparatuses.[7] Luminescent solar concentrators (LSC) basic principles were first conceived more than fifty years ago by Garwin,[8] and their possible application to solar energy conversion discussed during the following years.[9] The limited technology and the young knowledge

of fluorescent systems, as well as the drop in oil prices in during the eighties, limited the activity of researchers in this field. Recent growth in fossil fuels prices as well as new awareness about environmental concerns have regrown interests in LSCs as cheap approach to solar photovoltaics. In their basic design, LSC are made by a slab of a highly transparent material so that the solar light can pass through it without scattering or absorption losses. In the aim of the reduced costs, the slab should be made from inexpensive materials like glass or commodity polymers like poly(methyl methacrylate) (PMMA), polycarbonate (PC), or epoxy resins which still maintain good optical and structural properties. The light that enters the slab is absorbed by a luminescent specie and is re-emitted at longer wavelengths. Being the refractive index of the medium higher (n = 1.5 for glass or PMMA) than the one of the surrounding medium (usually air, n = 1), a fraction of the radiation remains trapped inside the slab by the principles of Total Internal Reflection (TIR), leaving the device at the edges of the plate. PV cells can be therefore placed at the edge to collect the outgoing radiation and to produce electric power (Figure 1).
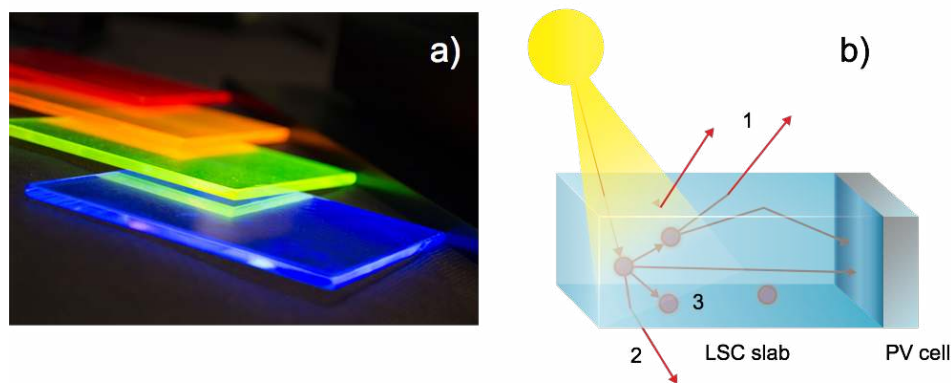
Figure 1. a) Coloured slabs of LSC containing fluorophores with different emission range and b) principle of working of an LSC irradiated by a light source. Most of the emitted radiation by the embedded fluorophore molecules (red spots) are concentrated at the edge and collected by an attached PV cell (in grey). Waveguide losses: 1) reflection and backscattered emission (escape cone loss); 2) transmission; 3) auto-absorption and/or non-radiative energy dissipation.

However, LSCs are plagued by critical processes (waveguide losses) that hinder their ability to deliver light to PV cells (Figure 1b), mostly addressed to fluorophore shortcomings including fluorescence quenching due to aggregation and auto-absorption losses.[7b, 10] Commercially available

fluorophores display a tendency to π-stack, which shortens their emission quantum efficiency. Metal complexes,[11],[12] quantum dots,[13] and phosphors[14] have also been investigated as fluorophores but compatibility issues with host matrices arise that strongly restricts the concentration of the dyes within the LSC active layer. A low dye content is actually associated to a modest capability to harvest sunlight. LSCs based on NIR-emissive dyes with visible-light transparency have been also proposed,[15] but light harvesting efficiency is barely reached.[15c] Nevertheless, maximum power efficiency for LSCs was recorded for PMMA slabs or films coated on glass and embedding perylene-based fluorophores.[16] For example, Lumogen F Red 305 (Basf) is considered the state-of-the-art for LSCs[7b] but cost issues might adversely affect the diffusion of the LSC technology. Therefore, a real breakthrough in fluorophores for LSC technology is needed, and the exclusive features of rotor fluorescent molecular systems show great potential to overcome the issues illustrated above. The concept of aggregation-induced emission (AIE) was first reported by Ben Zhong Tang and co-workers in 2001.[17] AIE molecules (AIEgens) are non-emissive when dissolved in good solvents, but became highly luminescent in poor solvents or in solid state, thus circumventing the issues associated to fluorescence quenching due to dye aggregation also when dispersed in polymers.[18] Prototypical AIEgens are three-dimensional propeller-shaped molecules such as hexaphenylsilole (HPS) and tetraphenylethene (TPE), whose central silole or olefin stators are surrounded by aromatic rotors. Due to steric repulsion between the phenyl rings, these molecules are highly twisted and experience very little π-stacking in the solid state and emit intensely according to the restriction of intra-molecular rotation (RIR) mechanism.[19] Such feature enables such AIEgens to find high-tech applications as biological probes, chemical sensing, solid-state emitters and optoelectronic devices. Notably, AIE ranked 3rd in the Top 100 Research Fronts topics in the field of Chemistry and Materials Science by Thomson Reuters in 2013.[18b]

In this review, the use of AIEgens is described as excellent alternative fluorescent dopants for LSCs. The examples here reported come predominantly from the very recent relevant literature, and they have been selected to illustrate the capacity of the fluorophores with related rotor structures to

effectively harvest sunlight with high concentration factor. Firstly, we discuss the main features of AIEgens for LSC and their performances once embedded in polymer thin films and slabs. Then, the ultimate advancements in AIE technology for increasing LSCs performances are illustrated and eventually, perspectives on the future challenges of AIEgens in solar collectors are examined.

2. Fluorophores features for LSCs

Experimentally, the optical efficiency η_{opt} of a LSC is introduced to define the fraction of incident solar power that reaches the edges of the device and potentially converted into electric power. Light concentration, represented by the factor C, depends on η_{opt} (Equation 1) and the geometry of the device by means of the ratio between the surface exposed to the incoming radiation and the area of the edges where it is collected (G, geometric factor, $G = A_{top}/A_{edge}$):[7b, 10, 20]

$$\eta_{opt} = \frac{C}{G} = \frac{I_{LSC}}{I_{SC} \cdot G} \tag{eq. 1}$$

where I_{LSC} is the short circuit current measured in the case of the cell over the collector edge and I_{SC} is short circuit current of the PV cell when perpendicular to the light source.

The power conversion efficiency (η_{power}) can be eventually calculated according to equation 2:

$$\eta_{power} = \eta_{opt} \cdot \eta_{PV} \tag{eq. 2}$$

where η_{PV} is the power conversion efficiency of the attached PV cell.[21]

Being LSC works on inherently probabilistic events, the optical efficiency can also be well evaluated by using Monte Carlo simulation.[22] Notably, a Monte Carlo simulation is a numerical analysis based on the generation of random numbers and the use of probabilistic data to determine solutions to both deterministic and non-deterministic problems. A ray-tracing simulation is a type of mathematical model that traces out the photons pathways in a system depending on their physical interaction with the surroundings.

In recent years, the study on PV devices based on the LSC technology has been focused on reaching high optical efficiencies (η_{opt}) by means of fluorophores characterized by a combination of effective characteristics:[23] a) wide absorption spectrum, to maximize the light harvesting efficiency; b) negligible auto-absorption losses caused by spectra overlapping; c) emission spectrum shifted as much as possible to wavelengths higher than 550-600 nm, i.e. where the PV cell efficiency is maximized; d) high fluorescence quantum yield, near to unity; e) high photostability for outdoor environments. Several different fluorophores have been already proposed and reviewed by the recent literature.[7b, 24]

Nevertheless, one of the most important issue on fluorophore design in LSC is maximising solar harvesting by incrementing the chromophore content in the slab, while avoiding the efficiency losses due to the phenomenon of aggregation-caused quenching (ACQ). In this context, a revolutionary class of luminophores demonstrating the fluorescence development with aggregation has drawn great attention since their discovery seventeen years ago by Ben Zhong Tang.[17] The effect called aggregation induced emission (AIE) arises from the restriction of intramolecular motions (RIM) of propeller-like fluorophores (Figure 2). The propeller shape disables the stacking interactions among chromophores thus avoiding the ACQ phenomenon and, in turn, promotes bright luminescence in the aggregate and solid state. By enabling light emission in the practically useful solid state, AIE fluorophores demonstrate to show a striking impact on energy,[25] optoelectronics, life science and environment.[18-19, 26]
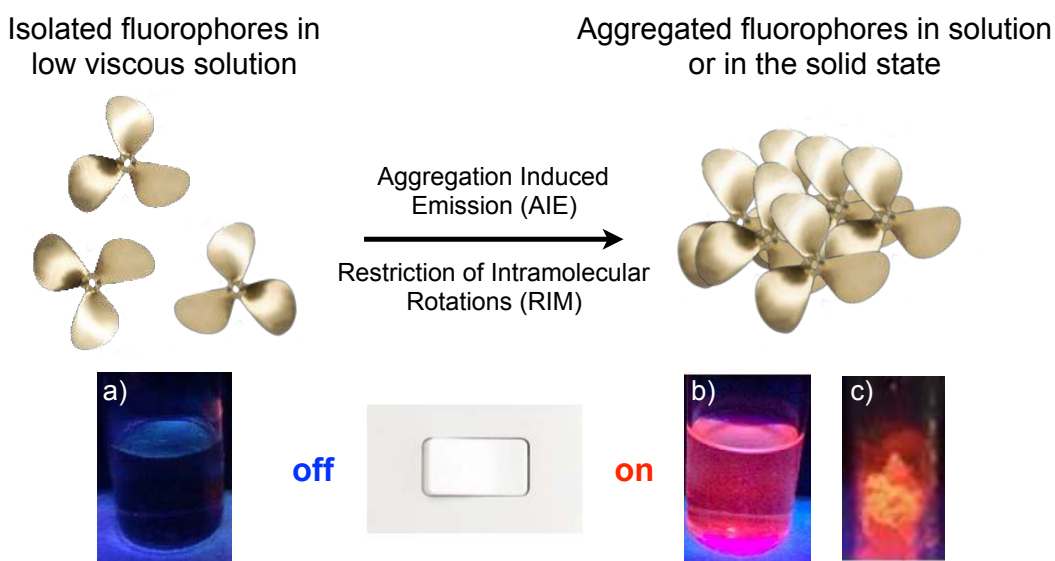
Figure 2. Working principle of the AIE mechanism. Below are photos taken by exciting a red emissive AIE fluorophore respectively in a diluted solution of a good and low viscous solvent (a), in a solvent-non solvent mixture (b) at the same molecule concentration and in the solid state (c)

2. AIE fluorophores for LSCs

Fluorophores with aggregation induced emission features (AIEgens) are the best candidates for the LSC technology since highly emissive polymer slabs are theoretically gathered also at high fluorophore contents, that is useful for maximizing the solar harvesting characteristics.[27] Moreover, the easy design of the AIEgens backbones allows for the utilization of economic and scalable synthetic routes aimed at introducing in the organic core donor-acceptors moieties that favour the downshifting of the emission towards the range of the highest light/electric current conversion by the Si-based PV cell.[18b] Further, AIEgens should be endowed with compatibilizing functional groups in order to help the fluorophore miscibility with the polymer matrix thus avoiding phase segregation from that.[28] Actually, dye segregation while maintaining the high emission of the AIEgen aggregates necessarily caused the formation of scattering points that adversely affect light collection towards the PV cell.

The first example of AIEgens designed for LSC was proposed by Ghiggino et al.[29] to answer some concerns that have arisen regarding first-generation LSC dyes such as emission reabsorption and solid-state quenching. The first experiment involved the dispersion the 10 wt.% of

tetraphenylethylene (TPE, 1 in figure 3) in PMMA thin films which showed promising quantum yield of about 41%. Ray-tracing calculations and fluorescence experiments evidenced that very low reabsorption losses were gathered even doping PMMA with high concentration of TPE and at practical geometric factor (G) higher than 100. Light concentration losses occurred only due to the formation of organic microcrystals that adversely affected LSC performances due to the increased light scattering. Nevertheless, even if this result was considered promising in harvesting light in the near-UV range, contorted highly conjugated AIEgens 2-5 were also tested to extend the chromophore absorption towards the visible range (Figure 3).
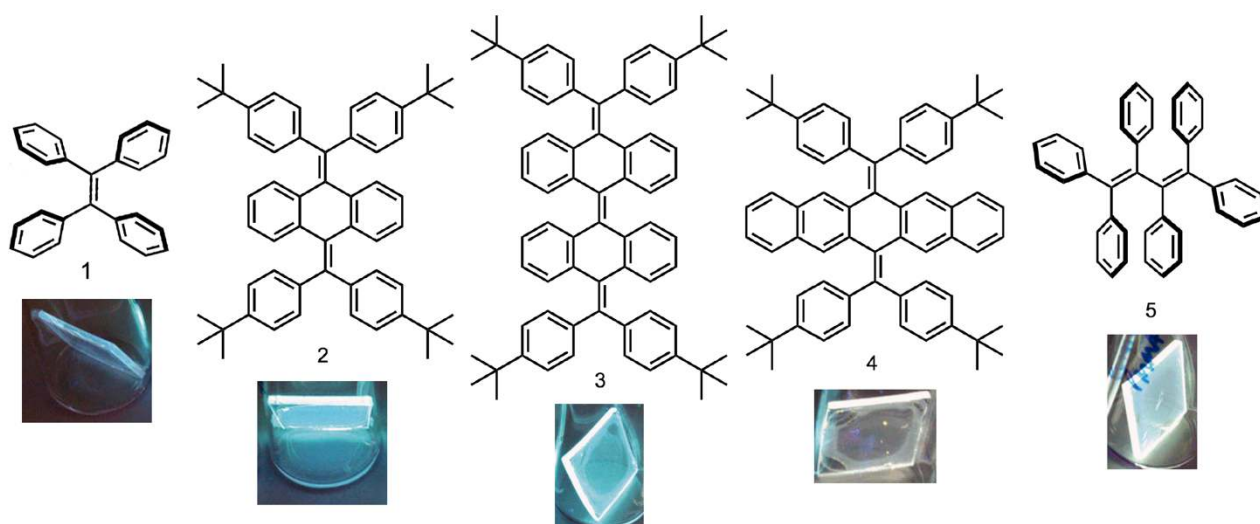

Figure 3. First fluorophores with AIE characteristics studied in LSC slabs. Adapted with permission from J. L. Banal, B. Zhang, D. J. Jones, K. P. Ghiggino, W. W. H. Wong, *Acc. Chem. Res.* **2017**, *50*, 49-57. Copyright (2017) American Chemical Society

The emission quantum yields of the fluorophores embedded in PMMA films were however found to decrease with increasing number of the polyaromatic rings in 2, 3 and 4 from about 10% to 4%, respectively, notwithstanding their non-planar structures and negligible π-π interactions. This behaviour was addressed to the increased number of voids in the crystal lattice for AIEgens 2-4, which would possibly promote more mobility of the phenyl rings, thus favouring dissipative disexcitation pathways. For this reason the authors also tested molecule 5 in which a fully substituted butadiene was chosen to extend the spectral absorption of TPE instead of the polyaromatic strategy. LSC based on 10 wt.% 5/PMMA dispersions showed a quantum yield of 31% that was still lower

than 1 even though both AIEgens have Stokes shift of about 1 eV. Moreover, ray-tracing simulation performed on the same LSC evidenced concentration efficiencies that decrease with increasing the geometric ratio compared to 1 possibly due to the significant absorption tail of 5 that broaden into the emission band.

Being red-emitting LSCs generally preferred for their best matching with the Si-based PV cells band gap, Pucci et al.[30] studied a TPE derivative (TPE-AC, Figure 4) efficiently decorated with the electron donor dimethylamine and malononitrile as the electron acceptor. These features confer to the AIEgen intense emission in the aggregated state of solvent mixtures close to the near infrared portion of the solar spectrum and a good photostability.[31]
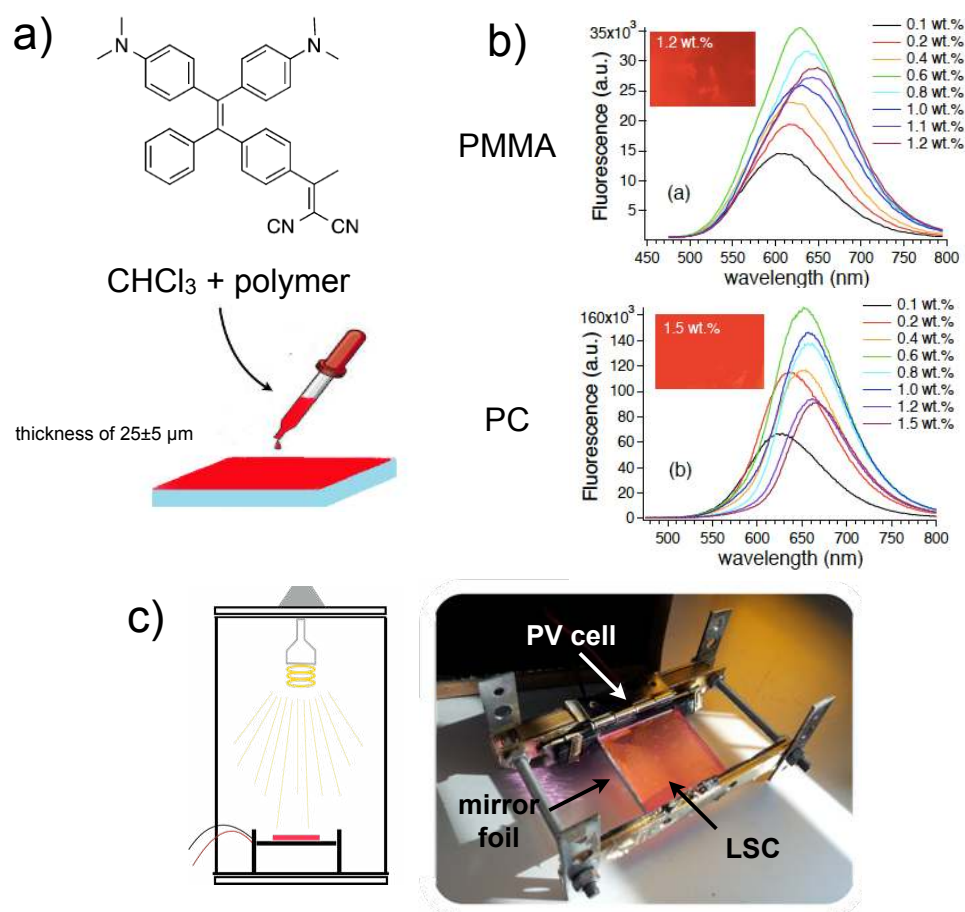
Figure 4. a) Chemical structure of TPE-AC and preparation of thin polymer blend films by solution casting; b) Fluorescence spectra, of TPE-AC/PMMA and TPE-AC/PC films as a function of fluorophore concentration (wt.%). In the insets, pictures of the same films with the highest TPE-AC content were taken under illumination with a near-UV lamp at 366 nm; c) setup used for measuring the optical efficiency. Reproduced from Ref. 28 with permission from the Royal Society of Chemistry

TPE-AC was dispersed at 0.1–1.5 wt.% contents in transparent and amorphous polymers, like PMMA and polycarbonate (PC) to obtain highly homogeneous thin films with absorption between 400 and 550 nm and fluorescence peaked at 600–620 nm with promising Stokes shift larger than 100 nm. The quantum yield was found to reach maximum values of around 50% for the lowest TPE-AC content in both polymer films, whereas a decline occurred to reach values around 30% for the highest TPE-AC. The authors was found that this behavior happened more gently for PC films and it was addressed to a more compatibility between the AIEgen and this polymer matrix and to less pronounced auto-absorption issues due to inner-filter effects. The effective combination of red emission and quantum yield in the solid state allowed the preparation of thin film LSCs with optical efficiencies calculated between 4.8% and 6.7% with a geometrical factor G of about 16. These features were reported to be comparable and even far greater than that obtained from LSCs with the same G factors and doped by similar contents of red-emitting organic fluorophores. The authors also suggested that future strategies aimed at fostering concentration efficiency should be focused on increasing AIEgens compatibility in the polymer matrices while limiting the auto-absorption phenomena to definitely lessen fluorescence quenching.

Overall, Ghiggino and Pucci demonstrated the potentiality offered by the utilization of AIEgens as effective dopants for solar harvesting in LSC technology but also pointed the attention on useful improvements on the AIEgen desing required to produce practical LSCs with optical efficiencies higher than those of the state-of-the-art.

3. Latest advancements of AIEgens for LSCs

The modern solutions proposed in the literature for increasing LSCs performances above the state-of-the-art suggest the design of AIE systems even more efficient and performing. Actually, one of the major issues in LSC is the partial coverage of the light visible spectra during sun irradiation. Recently, the research on LSC-PV systems has been focusing on high power conversion efficiencies (η_{power}) by enhancing the spectral absorption window of the

LSC, therefore increasing the number of available photons. For example, Slooff described a device based on stacked slabs doped with different dyes that use different portions of the solar spectrum and characterized by a η_{power} of 7.1%, which is the highest value ever reported for LSC-PV.[32] Another accessible solution has been that of mixing different fluorophores in the same slab aimed at combining their absorption features, while maintaining the high quantum yield via efficient energy cascade mechanisms such as the fluorescence resonance energy transfer (FRET).[12, 33]

In this regard, Wong, in collaboration with Ghiggino and Tang based their very recent experiments[34] on the fact that an strong emitting AIEgen at significantly high concentration within the LSC polymer film is able to transfer its energy non-radiatively via FRET to an acceptor fluorophore at a comparatively lower concentration in the same film (Figure 5). As designed, the acceptor can then emit light at a wavelength well red-shifted compared to the incident light and with an efficiency that depends on the optimization of fluorophores content in the film. This approach has been recently demonstrated to mitigate the dissipative auto-absorption phenomena of the acceptor fluorophore while preserving its solar harvesting features.[29b] The AIEgen 2-(4-(diphenylamino)phenyl)-3,3-diphenylacrylonitrile (DPATPAN) was selected as the donor fluorophore in combination with the high quantum yield acceptor 4-(dicyanomethylene)-2-tert-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4Hpyran (DCJTB). Nevertheless, even if the system worked, the laser dye DCJTB experienced strong photobleaching and ACQ phenomena that prevent practical applications of the LSC technology.[29b] In their recent work, the authors substitute the acceptor fluorophore with the benzothiadiazole-based emissive aggregate, PITBT-TPE, which showed emission peaked at about 650 nm and quantum yields in PMMA of 45% even at 225 mM. The authors identified the best doping content of the donor-acceptor couple to be 250 mM and 22.5 mM for DPATPAN and PITBT-TPE, respectively. At these concentrations, the emission of DPATPAN was fully quenched and the quantum yield of the mixture resulted higher than

PITBT-TPE alone, with a FRET efficiency close to unity. The Monte Carlo ray tracing simulation were again utilized to determine the solar harvesting performances of the prepared LSCs.
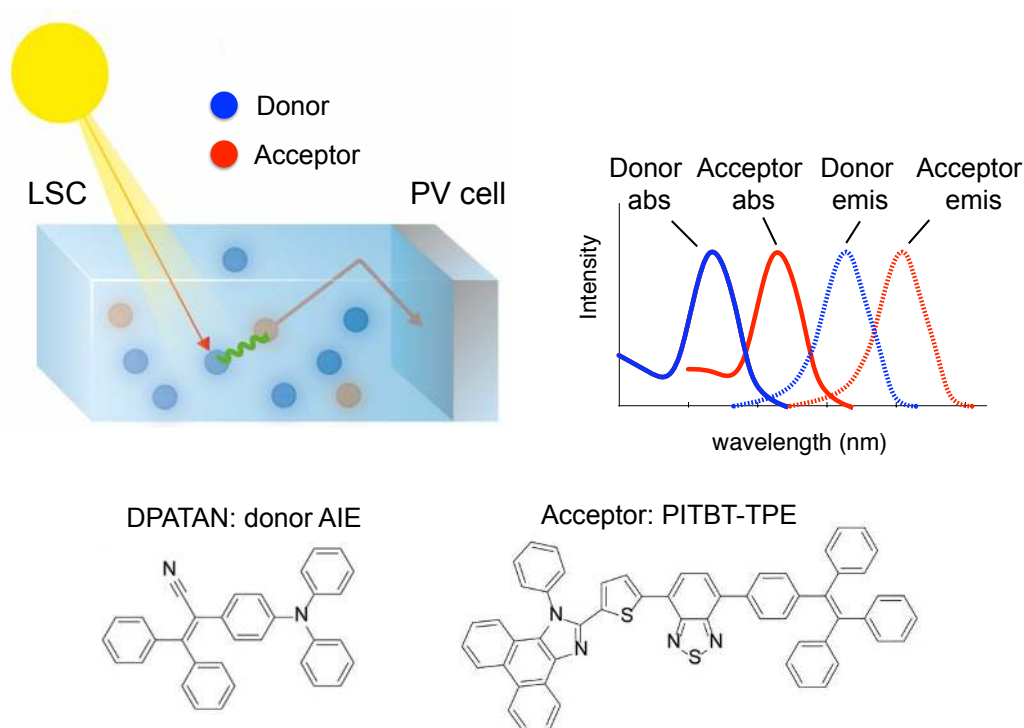

Figure 5. Working principle of an LSC with the typical cascade mechanism via FRET by donor and acceptor fluorophores and chemical structures of the DPATAN and PITBT-TPE used by Wong et al.

Notably, 1 mm thick LSCs based on the DPATPAN/PITBT-TPE mixture in thin film PMMA showed optical efficiencies that were higher than that including only the AIEgen donor in the range of simulated G factors, i.e. with improvements of 8% at G = 25 (Figure 6) thanks to the reduced re-absorption losses. It is worth noting that the concentration efficiency of the LSC devices proposed by authors was found to be comparable to those of the state-of-the-art LSCs with similar G factors.[12]
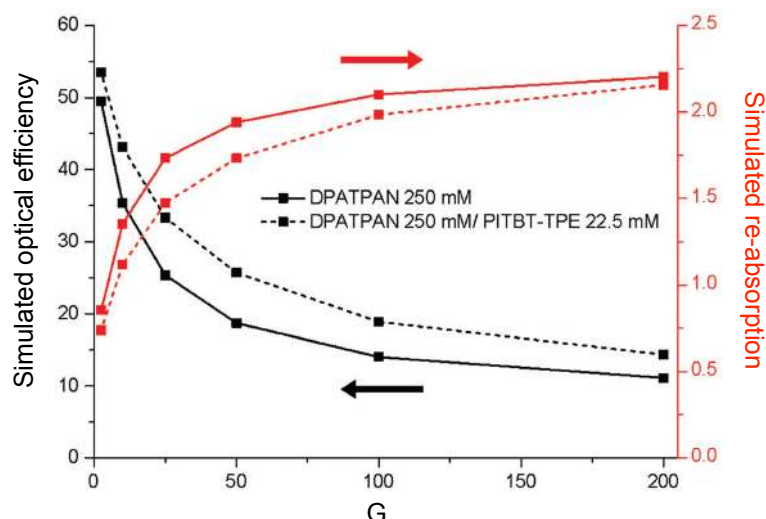
Figure 6. Simulated optical efficiencies (black lines) and re-absorption (red lines) of the LSCs as a function of the geometric factor G. LSCs were based on PMMA thin-films containing 250 mM DPATPAN with (dashed lines) or without (solid lines) PITBT-TPE. Reproduced from Ref. 32 with permission from the Royal Society of Chemistry.

Still very recently, Pucci et al. attempted to answer to the compatibility issues that caused performances losses of LSCs based on the TPE-AC AIEgen (Figure 4). In their contribution,[35] the authors synthesized a novel AIEgen (TPE_RED, Figure 7) and utilized it as the initiator to prepare red-emitting PMMA polymers (PMMA_TPE_RED) via atom transfer radical polymerization (ATRP). In particular, ATRP was utilized for the first time to control the introduction of the AIEgen on the macromolecular backbone to provide the desired phase stability between the fluorophore and the polymer matrix, that is an essential feature for maximizing LSC performances.
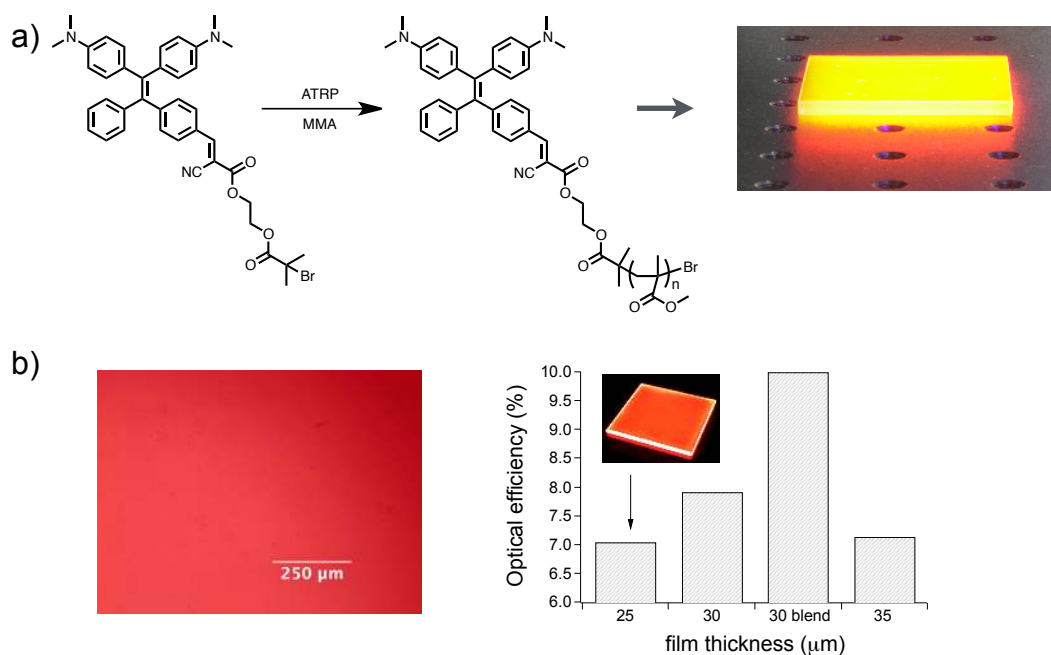
Figure 7. a) Chemical structure of TPE_RED initiator and the derived PMMA-based polymer (PMMA_TPE_RED) and image of the LSC obtained by casting a solution of the polymer over a glass slab of G = 16.6 and illuminated by a solar simulator; b) optical microscopy image of the most performing LSC and the optical efficiencies as calculated experimentally. Reproduced from Ref. 33 with permission from the Royal Society of Chemistry

PMMA_TPE_RED films containing the 0.98–3.05 wt% of the TPE_RED AIEgen showed emission in the range of 610–650 nm with a maximum quantum yield of 26.5% that was however affected by auto-absorption phenomena and the formation of less emissive micro-sized clusters of fluorophores. Regardless of that, the authors found that smooth and uniform films were obtained by blending PMMA_TPE_RED polymers with 50 wt.% of commercially available PMMA. This procedure positively affected phase dispersion (Figure 7b) as well as the overall emission intensity, thus providing 30 μm thick blend films with max optical efficiencies of 10% that was the highest ever registered with the same setup, G factor (16.6) and using benchmark fluorophores such as Lumogen Red. Notably, PMMA_TPE_RED was also found photostable to continuous light excitation at the absorption peak, and therefore consistent for uses in LSC technology.

4. Conclusions and outlook

Since their discovery, conspicuous advance has been made on fluorophores with aggregation induced emission features. Notwithstanding the few number of papers regarding the use of AIEgens in luminescent solar concentrators, the results here reported appear extremely promising in addressing all the issues of benchmark fluorophores such as emission quenching due to aggregation. AIEgens effectively contribute in producing thin film LSCs containing a relatively high dye content without adversely affecting the solar harvesting characteristics of the device. In this regard, AIEgens provide some key advantages: a) minimising the re-absorption losses thanks to the effective molecular design that promotes large Stokes shift and down-shifting collectors suitable for different available PV cells; b) the abolished π-stacking thanks to the propeller-like shape maximizes fluorescence quantum yield in aggregated form and enables high doping rate to amplify solar harvesting; c) the tuneable features of the AIE core allows the synthesis of AIEgens with optical features that cover the entire spectrum of visible light thus allowing the preparation of dye mixtures with broad absorption bandwidth while maintaining the high quantum yield via efficient energy cascade mechanisms.

Even if a lot of progress has been made during the last few years in the field of AIEgens for LSC devices, various new and intriguing challenges are still open. For example, the design of fluorophores with AIE characteristics in the near-infrared (NIR) portion of light aimed at extending the solar collection window and also enabling the use of modern and effective PV-cell based on elements and compounds different from Silicon.[13c, 15d, 36] Moreover, the design and the preparation of photostable AIEgens is nowadays mandatory for the diffusion of commercially-viable LSCs in the building-integrated PV technology. Notably, LSCs based on PMMA_TPE_RED films have recently demonstrated to retain the 97% of their emission after three hours of continuous excitation with a 450 W Xe arc lamp under aerobic conditions. This excellent photostability, could be furhter enhanced by endowing the fluorophore with triplet state quenchers by a covalently attached protective agent[37] profiting on the versatile chemistry of AIEgens. This last feature can surely take advantages of the enormous research focused on the development of AIEgen even more performing in all the fields of science.

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