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Enhancing optical efficiency of thin-film luminescent solar concentrators by combining energy transfer and stacked design

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ABSTRACT

We report on a new approach aimed at enhancing the optical efficiency of luminescent solar concentrators (LSCs) based on poly(methyl methacrylate) (PMMA) thin-films doped with highly emissive fluorophores. In detail, a series of high-energy absorbing fluorophores (HEF) and perylene bisimides (PBI) red-emitting dyes were utilized in order to favor the collection of a large number of incident photons by the thin-film LSCs. The use of two fluorescent PMMA layers coated on the opposite surfaces of a glass slab was found to effectively increase the light concentration. The worthwhile combination of the appropriate HEF and PBI fluorophores within the secondary (bottom) PMMA layer assured optically efficiencies 10–14% greater than the maximum value of single-dye LSCs.

1. Introduction

Luminescent solar concentrators (LSCs) have been widely studied as a viable alternative to decrease the price of photovoltaic energy [1]. LSCs show advantages like the ability to work with diffuse light [2,3], light weight, reduced costs, and transparency, which makes them available to be implemented in architectural solutions [4]. LSCs consist in a slab of transparent material doped with a fluorophore able to absorb the solar spectrum [4–6]. The higher refractive index of the host compared to the environment makes it possible to trap a fraction of the emitted photons by means of total internal reflection [7]. Photons are then collected at the edges of the device to produce electric power by means of photovoltaic (PV) cells. In recent years, the research on PV devices based on LSC technology has been focusing on obtaining high power conversion efficiencies [3,8–17]. Still, for prototype single-dye LSCs coupled to commercial Si cells efficiencies higher than 3–4% are rarely met [4]. This is due to the many losses of such devices, both related to the physics of the phenomena involved and to a not-yet-optimized fluorescent system [18]. A simple approach to obtain higher concentrations is to enhance the spectral window of absorption of the LSC. For example, multiple dyes have been proposed to cope for the narrow absorption characteristic of organic dyes as well as new design solutions [2,13,19,20]. Noble metals nanoparticles [21,22] and quantum dots have also been investigated for their broad absorption features although compatibility problems with host matrices seldom arise [9,23–25]. Among the proposed designs, the stacking of two or more differently dyed slabs and the mixing of multiple fluorophores in the same bulk are the more often encountered in the literature. In the stacked geometry [15–18,26], slabs doped with different dyes that use different portions of the solar spectrum are piled up on top of the other and are connected to different PV cells. Sloff et al. [17] described a stacked device with a power conversion efficiency of 7.1%, which is, at best of our knowledge, the highest efficiency ever reported for LSC-PV systems. Conversely, a dye mixture in a single slab offers the possibility of cascading of emission via non-radiative processes such as the fluorescence resonance energy transfer (FRET) [2,27].

In striving to contribute towards improved LSC outcomes, we report on the preparation of LSCs based on fluorophore-doped poly(methyl methacrylate) (PMMA) thin-films coated onto high optical quality glass slab. A series of high-energy absorbing fluorophores (HEF), such as 2,5-bis(5-tert-butyl-benzoxazol-2-yl)thiophene (BTBBT), perylene (Per), and two different perylene bisimide (PBI) red-emitting dyes such as N,N′-bis-(1′-phenylethyl)-perylene-3,4,9,10-tetracarboxydiimide (PE-Pery) [28] and Lumogen F 350 (LR) were utilized (Fig. 1).

The LSCs were prepared taking inspiration from the previously mentioned geometries for bulk-dyed LSCs, namely a stacked geometry that was also flanked with a cascading of emission via FRET.

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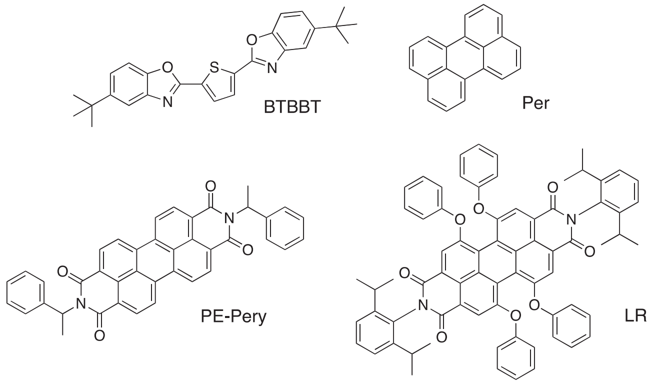
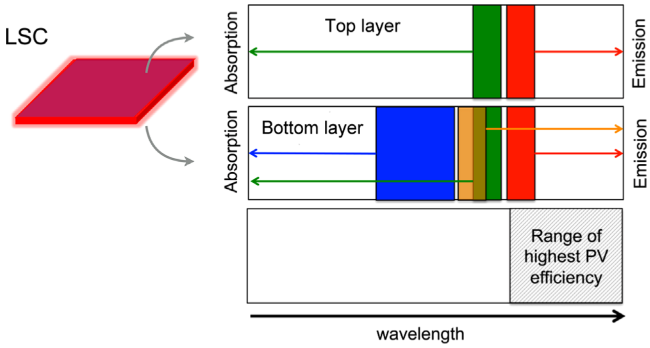


Fig. 1. Chemical structures of the investigated fluorophores.



Scheme 1. Scheme of a LSCwith the *sandwich* design with ideal absorption and emission ranges of fluorophores embedded in the top and bottom polymer layers coated on glass.

In this last design, named "*sandwich*", two distinct polymer layers containing different dyes were coated on the opposite faces of the glass slab. The top (primary) layer of the glass, i.e. that exposed to the light source, was coated by the polymer film containing the PBI dyes, that are responsible of the highest LSC optical efficiency. Conversely, the bottom (secondary) layer of the glass was coated by the polymer film containing a selected mixture of the HEF and PBI (Scheme 1).

Moreover, compared to the ordinary stacked design, the *sandwich* LSC does not possess any air gap between the slabs. To the best of our knowledge, no study is reported on the proposed design for thin-layer LSCs.

2. Experimental

2.1. Materials

Poly(methyl methacrylate) (PMMA, Aldrich, Mw = 350,000 g/mol), Lumogen Red F350 (LR, BASF), 2,5-bis(5-tert-butyl-benzoxazol-2-yl)thiophene (BTBBT, Aldrich) and perylene (Per, Aldrich) were used as received. N,N′-Bis-(1′-phenylethyl)-perylene-3,4,9,10-tetracarboxidiimide (PE-Pery) was synthetized according to the literature [28,29].

2.2. Preparation of polymer films for optical studies

Dye/PMMA thin films were prepared by drop casting, i.e. pouring 0.8 mL chloroform solution containing 30 mg of the polymer and the proper amount of dye to obtain concentrations in the range 0.05–2 wt% over a 76 × 25 × 0.8 mm^3 microscope slide. The glass slides were previously cleaned with chloroform and immerged in 6 M HCl for at least 12 h, then they were rinsed with water, acetone and isopropanol and dried for 8 h at 120 °C. Solvent evaporation was performed on a warm hot plate (about 30 °C) and in a closed environment. The thickness of the films was measured to be 25 ± 5 μm.

2.3. Preparation of LSC samples for concentration efficiency measurements

Dye/PMMA thin films were prepared by drop casting, i.e. pouring 0.9 mL chloroform solution containing 40 mg of the polymer and a proper quantity of dye to obtain concentrations in the range 0.05–2 wt% over a 50 × 50 × 3 mm optically pure glass substrate (Edmund Optics Ltd. BOROFLOAT window 50 × 50 TS). Solvent evaporation was performed on a warm hot plate (about 30 °C) and in a closed environment. Prior deposition the glass slides were cleaned as described before. The films thickness was measured to be 25 ± 5 μm. "*Sandwich*" samples were prepared by successive depositions on the opposite faces of the glass substrates.

2.4. Apparatus and methods

Absorption spectra were recorded at r.t. on a Perkin-Elmer Lambda 650 spectrometer. Fluorescence spectra were measured at r.t. on a Horiba Jobin-Yvon Fluorolog®-3 spectrofluorometer and equipped with a 450 W xenon arc lamp, double-grating excitation and single-grating emission monochromators. The thickness of the films was measured with a Starrett micrometer.

2.5. Photocurrent measurements [30]

A proper apparatus was build and composed by a plywood wooden box 15 × 15 × 30 cm with walls 1.5 cm thick. During the measurement a solar lamp TRUE-LIGHT® ESl E27 20 W was used. The spectrum of the lamp is reported in Fig. S1. Two 50 × 3 mm slits were carved out at 5 cm from the bottom of the box to exactly fit the LSC systems. On the outer side of the slit, a set of three 1 × 1 cm photodiodes (THORLABS FDS1010 Si photodiode, with an active area of 9.7 × 9.7 mm and high responsivity (A/W) in the spectral range of 400–1100 nm (Fig. S2)) connected in parallel fashion was placed and coupled to a multimeter (KEITHLEY Mod. 2700).

2.6. Efficiency measurement using a PV-cell

A different set of LSC samples was prepared to measure the concentration efficiency attaching a Si-PV cell (IXYS SLMD121H08L mono solar cell 86 × 14 mm, with a solar cell efficiency of 14.7% and a fill factor $>70\%$, Fig. S3) to one edge of the sample using silicone grease, while the remaining edges were covered with an aluminum tape. These devices where then placed over a white poly(ethylene terephthalate) scattering sheet (Microcellular® MCPET reflective sheet, ERGA TAPES Srl) and placed about 20 cm under a solar lamp (TRUELIGHT® ESL E27 20 W, with a correlated color temperature of 5500 K).

3. Results and discussion

BTBBT and Per were selected as high-energy absorbing fluorophores (HEF), whereas PE-Pery and LR were tested as highly fluorescent red-emitting dyes (Fig. 1).

BTBBT displays blue fluorescence and shows excellent heat stability. It has found several optical applications such as optical brightener in many polymers and textiles and as scintillation dye [31,32]. Per emits blue light as well, and it is used as a dopant