

Dichroic Perylene Bisimide Triad Displaying Energy Transfer in Switchable Luminescent Solar Concentrators

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Supporting Information

Photonic devices such as photovoltaic (PV) cells and luminescent solar concentrators (LSCs) require the controlled molecular organization of chromophores in which energy and charge transport is efficient and directional, similar to that found in biological systems.^{1–5} For example, in an LSC, sunlight is collected, concentrated, and directed to a PV cell. In such a device, a fluorophore embedded in a planar lightguide absorbs sunlight and re-emits light at a longer wavelength that travels to an edge-mounted PV.^{1,2,6,7} The LSC can also be made dynamic for combining light management and solar power generation in urban regions.⁸ In these latter devices, fluorescent dichroic dyes are aligned using liquid crystals (LCs),^{9–11} where the orientation can be controlled by an electric field (Figure 1). Highly ordered switchable systems are critical to achieve high contrast ratios between “on” (transparent) and “off” (dark) states, as the fluorophore predominantly absorbs in a planar alignment.¹²

Recently, several approaches have been reported to improve the sunlight collection and the light incoupling in static LSCs. Dendrimers have been used to broaden and enhance light absorption by light harvesting and employ energy transfer to reduce reabsorption,¹³ one of the key losses in LSCs.¹ Aligned perylene bisimide dyes embedded in an optically transparent polymerizable LC waveguide have been fabricated, leading to highly efficient LSCs with optical quantum efficiencies up to 74%.¹⁴ Improved light coupling in an LSC has also been obtained by combining the absorption of a square-symmetric porphyrin sensitizer with energy transfer to a homeotropically aligned emitter.¹⁵ We now report on a multichromophoric triad combining light harvesting, efficient energy transfer, and excellent alignment that can be applied in a switchable window system.

The design of the triad dye consists of two perylene bisimide donors and one perylene bisimide acceptor, which is substituted at the bay position with two phenoxy units (Figure 1c). Rotational constrained connections are present between the individual chromophores, resulting in orthogonal conformations. The triad has been synthesized according to a reported procedure and the individual monomer donor and acceptor dyes have also been synthesized as references.¹⁶ All dyes have been fully characterized by ¹H NMR, ¹³C NMR, and MALDI-ToF mass analysis. Pure compounds were obtained by recycle GPC and confirmed by GPC analysis.^{16–18}

To confirm energy transfer from donor to acceptor, the triad was dissolved in chloroform and the UV/vis absorption and

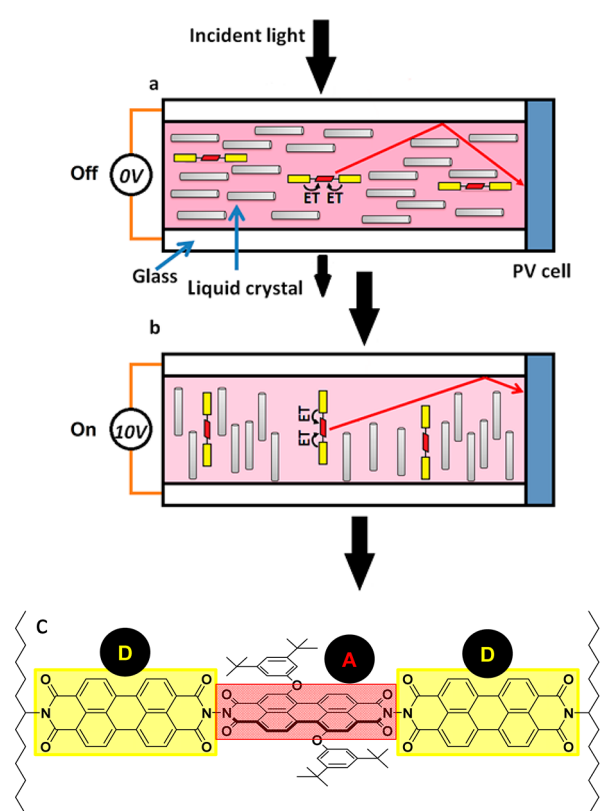


Figure 1. Cartoon of the switchable LSC without (a) and with (b) applied voltage (the “off” and “on” states, respectively). The black arrows depict incident sunlight, and the size of the arrow roughly corresponds to the intensity of the light. Red arrows depict the dye emission. (c) Chemical structure of the triad perylene bisimide dye.

fluorescence spectra were recorded (Figure 2). The absorption at 533 nm originates from the two donor moieties, while the absorption at 556 nm is from the acceptor.¹⁶ The absorption spectrum of the triad is similar to the summation of the spectra of the individual compounds, with the acceptor absorbance in the triad being red-shifted relative to that of the free acceptor reference, indicating that some degree of electronic coupling

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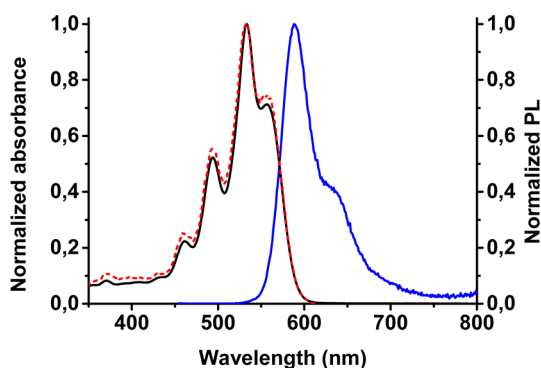


Figure 2. Normalized excitation spectrum of the triad dye in chloroform monitored at 630 nm (dashed red line) and normalized UV-vis absorbance of the triad dye in CHCl_3 solution (black line). Time integrated photoluminescence measured in solution with 450 nm wavelength excitation (blue line). Upon excitation at a wavelength where mostly the donor absorbs,¹⁶ only fluorescence of the acceptor is visible.

may be present^{17,19} between the perylene bisimide chromophores, as reported recently in a series of similar molecules.^{17,20,21} Fluorescence measurements of the individual donor and acceptor reference molecules show emission from the donor located around 540 nm, while the acceptor has a maximum at 588 nm.¹⁶ The fluorescence spectrum of the triad revealed an emission peak at 588 nm, indicating efficient energy transfer as there is no residual fluorescence from the donor detected.¹⁶ By monitoring an excitation spectrum at 630 nm, where the emission of the donor is negligible one achieves a spectrum that is identical in shape to the absorbance spectrum of the linear dye, suggesting energy transfer close to unity (Figure 2).

For the fabrication of switchable LSCs, the triad dye was incorporated in a commercial LC host mixture (MLC-6284-000, Merck licristal) having a nematic phase over a broad temperature range and used to fill an ITO coated alignment cell.²² The polarized absorption spectra showed that the highest absorption is obtained when the light is polarized parallel to the director of the LC host (Figure 3). The order parameter of the dye (S_a) was calculated using

$$S_a = \frac{A(\lambda_{\max\parallel}) - A(\lambda_{\max\perp})}{A(\lambda_{\max\parallel}) + 2A(\lambda_{\max\perp})} \quad (1)$$

where $A(\lambda_{\max})$ is the maximum absorption for light polarized parallel (\parallel) and perpendicular (\perp) to the alignment direction of the LC, respectively (Figure 3, inset). The triad has an order parameter of 0.8 at 536 nm, which is among the highest reported order parameters for a fluorescent dichroic dye in a nematic LC.¹² The edge emission spectrum of the cell only exhibits one maximum at 604 nm, indicating efficient energy transfer (Figure 3). As a control experiment, the edge emission of the reference dye mixture was also measured showing clear emission from both the acceptor and the donor molecules, as evidenced by two peaks, one from the donor at 586 nm and the other from the acceptor at 615 nm.¹⁶ When measuring the emission spectrum from the sides parallel and perpendicular to the alignment of the liquid crystal, a clear difference in intensity was obtained. Coupling individual dyes increased the edge output ratio, defined as edge emission from side 1 divided by edge emission from side 2 (see inset cartoon in Figure 3). For the triad, this ratio is 1.55, among the highest values reported.¹¹

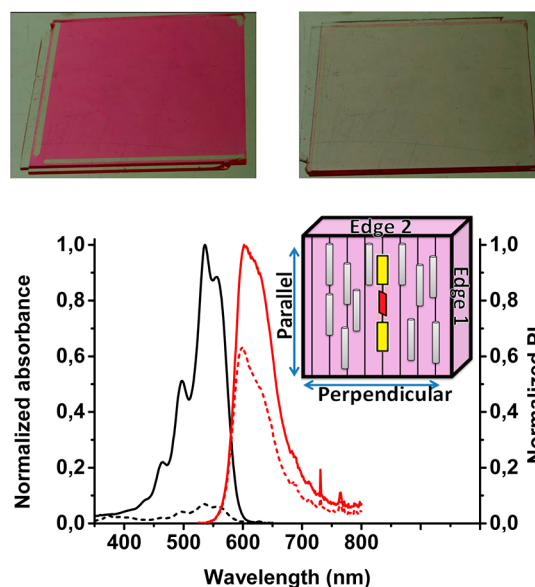


Figure 3. Photographs of cells exposed to light polarized parallel (left-hand side) and perpendicular (right-hand side) to the liquid crystal alignment direction (top panel). The absorption (black) and emission (red) spectra of the triad in liquid crystal (bottom panel). The absorption of the switchable LSC was measured with light polarized parallel (solid) and perpendicular (dashed) to the rubbing direction, indicating high contrast, i.e., high anisotropy. The edge emission is measured for the edge 1 (solid) and edge 2 (dashed), resulting in anisotropic emission. Inset: cartoon defining the emission edges 1 and 2 compared to the rubbing direction.

The switching of the LSC from an absorbing “off” state to a transparent “on” state was achieved by applying 10 V_{p-p} across the cell gap to reorient the molecules in a homeotropic orientation, perpendicular to the cell surface (Figure 1b). The switching behavior of both the triads as the reference mixture was investigated. The polarized absorption spectra are recorded in the “on” (10 V) and “off” (0 V) states (Figure 4). The

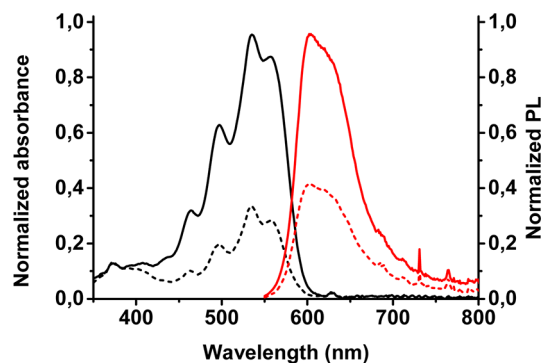


Figure 4. Normalized absorbance in the “off” (black solid) and “on” (black dashed) state, and edge emission from edge 1 in the “off” (red solid) and “on” state (red dashed) of the triad dye in LC.

contrast, C_1 of the switchable LSC is defined as the integrated nonpolarized absorbance from 450 to 600 nm of the LSC in the “off” state divided by the absorbance in the “on” state over the same range, resulting in a contrast for the multichromophoric dye of $C_{1,\text{triad}} = 2.83$, while the reference system has a contrast of $C_{1,\text{ref}} = 1.87$. When using the maximum absorption, a contrast C_2 of $C_{2,\text{triad}} = 2.69$ is reached, while the reference

system has a contrast of $C_{2,\text{ref}} = 1.83$ (Figure 4 and Supporting Information Figure S4b,c). The switching edge output ratio for the triad system, defined as the integrated edge emission from edge I_{0v} divided by edge I_{10v} , is 2.02, while the reference mixture has an output ratio of 1.65,¹⁶ showing the anisotropy in emission direction can be improved upon coupling chromophores as a rigid system.

In conclusion, we have demonstrated that coupling multiple chromophores in a single triad dye results in highly anisotropic and high contrast switchable LSCs. These triads show light harvesting and energy transfer properties, while maintaining contrast in transmission between “on” and “off” states, which has not been possible using individual dye mixtures. Our results are not only relevant for LSCs but are also of importance for achieving efficient control over light distribution in optical devices.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental methods, synthetic procedures, full characterization and optical analysis of the molecules and devices. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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