

# Dichroic perylene bisimide triads displaying energy transfer in switchable luminescent solar concentrators

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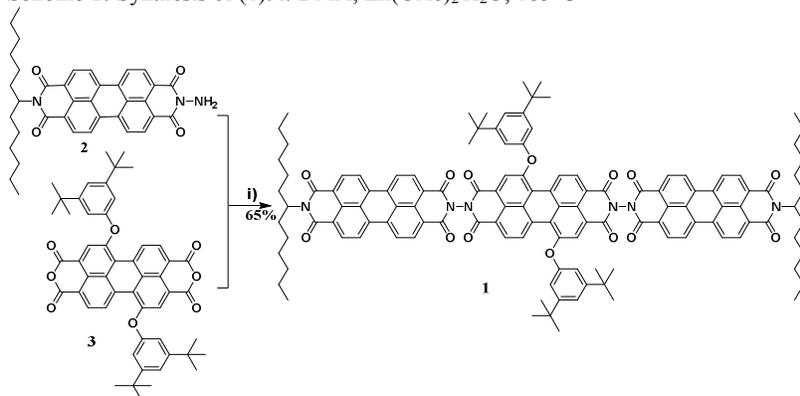
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## 1. Synthesis and characterization

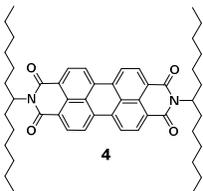
UV-Vis spectroscopy was performed on a Shimadzu UV-3102 PC spectrophotometer. Photoluminescence quantum yields (PLQY) were determined according to the method of Mello et al.<sup>1</sup>, using a PTFE coated integrating sphere (Newport 70682NS) with extra diffusing baffle in front of the exit port. Either frequency doubled output from a Ti:Sapphire oscillator (MaiTai, 100 fs pulse width, 80 MHz repetition rate), or signal output from an OPO (Inspire Auto 100) was attenuated to an average power of 5 mW and used as the excitation source. The photoluminescence was measured with an Ocean Optics USB2000+ spectrometer, connected to the integrating sphere with an optical fiber and was corrected for the spectral response of the sphere, fiber and CCD. In order to account for self-absorption effects, photoluminescence (PL) from dilute solutions (max optical density < 0.1) was scaled to match the tail end of the measured PL spectra and used to calculate the PLQY. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer using CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as internal standard. The matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) mass spectrometry was performed using a Biosystems Voyager-De Pro spectrometer with  $\alpha$ -cyano-4-hydroxycinnamic acid as a matrix. The used dyes are purified on recycle GPC using a Shimadzu LC-10AD VP liquid chromatograph, a Shimadzu SPD-10AV VP UV-Vis detector and two JAIGEL columns (2.5H and 2H) from Japan Analytical Industry with chloroform as solvent. GPC measurements were performed in chloroform with a polystyrene based mixed-D (polymer laboratories) column (200-400.000 Da) equipped with a SPD-M20A photo diode array detector (190-800nm, Shimadzu). All measurements of liquid crystal filled cells are performed in commercial rubbed polyimide cells, coated with indium tin oxide (ITO) (Instec, 20.4  $\mu$ m cell gap). The edge emission spectra of the triad dye are illuminated from the top with light from an AM1.5 solar simulator and subsequent the edge emission is measurement on a SLMS 1050 integrating sphere (Labsphere) equipped with a diode array detector (RPS900, International Light).

**Scheme 1:** Synthesis of (1). i: DMA, Zn(OAc)<sub>2</sub>·H<sub>2</sub>O, 185°C

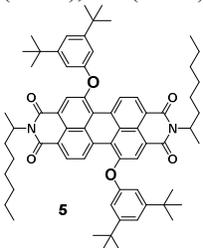


Compound (1) was synthesized according to the procedure reported by Langhals.<sup>2,3</sup> Yield 108 mg (65%) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = (0.83 (t, 12H, CH<sub>3</sub>), 1.25 (m, 32H, CH<sub>2</sub>), 1.34 (s, 36H, t-butyl), 1.89 (m, 4H,  $\beta$ -CH<sub>2</sub>), 2.25 (m, 2H,  $\beta$ -CH<sub>2</sub>), 5.2 (m, 2H, NCH), 7.08 (s, 4H, ortho-H-phenol), 7.36 (s, 2H, para-H-phenol), 8.46 (2H, s, H perylene bisimide), 8.6-8.8 (m, 18H, perylene), 9.77 (d, 2H, perylene bisimide); <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 14.07, 22.61, 27.06, 29.25, 29.71, 31.4, 31.8, 32.39, 35.16, 54.91, 114.55, 119.82, 121.66, 122.34, 122.53, 123.21, 123.39, 125.08, 125.85, 126.28, 129.09, 129.63, 131.08, 132.39, 133.5, 134.12, 135.24, 153.85, 154.14, 156.26, 160.01, 160.12; UV/Vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 461.5 (34200), 494 (79800), 533 (152700), 556 (108800); (MALDI-ToF MS) m/z: calcd for C<sub>126</sub>H<sub>118</sub>N<sub>6</sub>O<sub>14</sub>, 1938.87; found 1938.95([M]).

Compound (4) was synthesized according to procedure reported previously.<sup>4</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.83 (d, 12H, CH<sub>3</sub>), 1.12-1.31 (m, 24H, CH<sub>2</sub>), 1.88 (m, 4H,  $\beta$ -CH<sub>2</sub>), 2.26 (m, 4H,  $\beta$ -CH<sub>2</sub>), 5.19 (m, 2H, NCH), 8.65 (m, 8H, perylene bisimide); UV/Vis (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 459 (16800), 490 (44300), 526.5 (71400); (MALDI-ToF MS) m/z: calcd. for C<sub>20</sub>H<sub>62</sub>N<sub>2</sub>O<sub>4</sub>, 754.47; found 754.48([M]).



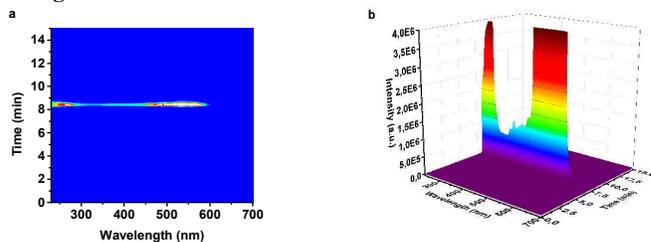
Compound (**5**) was synthesized according to a very similar procedure reported by Langhals.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 0.82 (t, 6H, CH<sub>3</sub>), 1.21 (m, 16H, CH<sub>2</sub>), 1.35 (s, 36H, t-butyl), 1.54 (s, 6H, t-butyl, NCHCH<sub>3</sub>), 1.87 (m, 2H, CH<sub>2</sub>), 2.15 (m, 2H, β-CH<sub>2</sub>), 5.22 (m, 2H, NCH), 7.03 (s, 4H, ortho-H-phenoxy), 7.36 (s, 2H, para-H-phenoxy), 8.35 (s, 2H, perylene bisimide), 8.62 (d, 2H, perylene bisimide), 9.66 (d, 2H, perylene bisimide); UV/Vis (CHCl<sub>3</sub>) λ<sub>max</sub> (ε) = 404 (10800), 513 (33900), 550 (52100); (MALDI-ToF MS) m/z: calcd. for C<sub>68</sub>H<sub>82</sub>N<sub>2</sub>O<sub>6</sub>, 1022.62; found 1022.63([M]<sup>+</sup>).



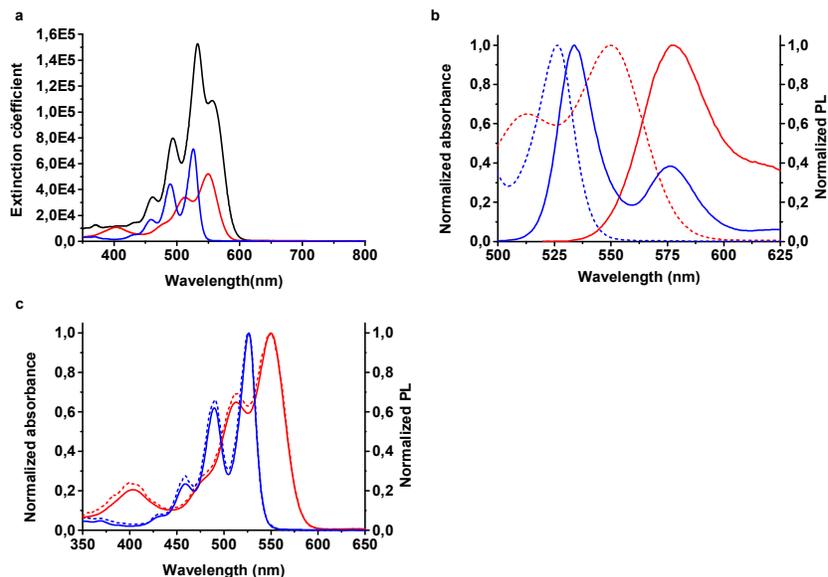
## 2. Sample preparation

Dye (**1**) was mixed in liquid crystalline host materials consisting of respectively E7, MLC-6653 and MLC-6284-000 (Merck Licristal<sup>®</sup>, 0.25 weight% unless otherwise mentioned). The solutions were stirred for ~30 minutes at 135°C to achieve a completely dissolved dye mixture in isotropic “liquid crystal”. Subsequently the mixtures were cooled to room temperature and inspected with optical microscopy to detect any undesired formation of dye crystals. A commercial rubbed polyimide cell coated with indium tin oxide (ITO) (Instec, 20.4 μm space) was heated to 130°C and filled with the liquid crystal mixture in the isotropic state by capillary force and cooled to room temperature. The prepared cells were checked with optical microscopy for crystals and the order parameter measured by UV-Vis. For every sample, a cell is filled with the same liquid crystal as a baseline.

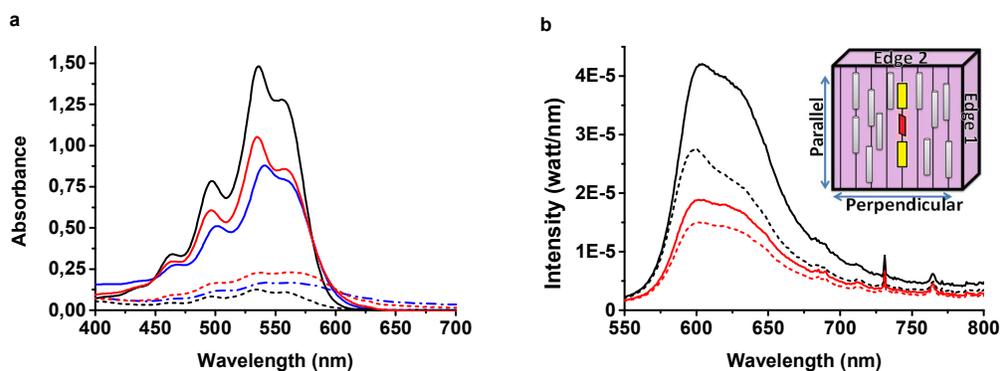
## 3. Figures



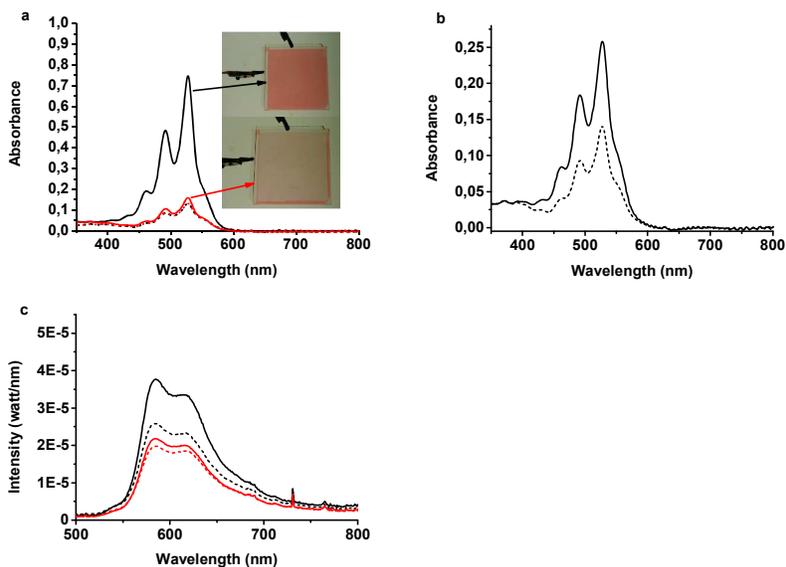
**Figure S1.** (a) Spectrum of (**1**) measured with analytical GPC. The colors indicate intensity; blue is corresponding to a low intensity signal, while red/white indicate high intensities. The difference between the blue and red signal is at least a factor 100. (b) a 3D plot of the GPC measurement, showing the absorption spectrum of the triad dye (**1**). All measurements are performed in chloroform.



**Figure S2.** Molecule (1) is depicted in black, (4) in blue and (5) in red. (a) UV-Vis absorption spectra in chloroform of the triad dye (1), reference donor (4) and acceptor (5). (b) UV-Vis absorption (dashed line) and fluorescence (solid line,  $abs < 0.1$ ) measurements of the reference donor (4) and acceptor (5). (c) Normalized absorbance (solid line) and excitation (dashed line,  $abs < 0.1$ ) spectra of the reference donor (4) and acceptor (5) excited at 630 nm. All measurements are performed in  $CHCl_3$ .



**Figure S3.** (a) Triad dye ( $\sim 0.5$  weight%) in the commercial LC's E7 (blue), MLC-6284-000 (black) and MLC-6653 (red) (licristal<sup>®</sup>). The solid lines are the absorbance spectra measured with light parallel to the alignment direction of the host LC, while the dashed lines are with light perpendicular to the alignment direction of the host LC. The highest order parameter is achieved with MLC-6284-000. (b) The edge emission of the triad dye. The black lines indicate the “off” state (0V), while the red lines indicate the “on” state (10V). The solid lines are the edge emission measured on edge 1, while the dashed lines were measured on edge 2.



**Figure S4.** (a) The switchable window in the “off” state (black) and “on” state (red). The solid lines display results with the light polarization parallel to the alignment direction of the host LC, while the dashed lines are with light polarized perpendicular to the LC alignment. (inset) Photographs of the switchable window in the “off” state (top) and “on” state (bottom) with a parallel polarizer. (b) The non-polarized absorbance of the triad dye (0.25 weight%) in MLC-6284-000 in the “off” (0V) and “on” (10V) state. (c) Edge emission spectra of the reference dyes (2:1 donor: acceptor) in MLC-6284-000 for switchable window applications. The black line indicates the “off” state (0V) and the red line indicates the “on” state (10V). The solid lines indicate emission from edge 1 while the dashed lines are the emissions from edge 2.

#### 4. Tables

**Table S1.** Fluorescent quantum yield of various dyes in Chloroform.

| Dye | $\lambda_{\text{ex}}$ (nm) | $\Phi$ |
|-----|----------------------------|--------|
| 1   | 460                        | 0.66   |
|     | 515                        | 0.75   |
|     | 525                        | 0.80   |
| 4*  | 460                        | 0.84   |
|     | 490                        | 0.89   |
| 5   | 475                        | 0.71   |
|     | 510                        | 0.73   |

\* reported as 0.98 in the literature. A lower fluorescent quantum yield was measured.<sup>5,6</sup>

**Table S2:** The order parameters of the triad dye in various liquid crystals, measured in commercial polyimide rubbed cells.

| LC           | Order parameter ( $S_a$ ) |
|--------------|---------------------------|
| E7           | 0.59                      |
| MLC-6284-000 | 0.8                       |
| MLC-6653     | 0.55                      |

**Table S3:** Integrated edge emission (in mW) of the switchable LSC containing 0.25 weight% of (1) in MLC-6284-000 measured from edge 1 and edge 2 in the “off” and “on” state (0 and 10 V applied)

| Cell edge emission | 0 V  | 10 V |
|--------------------|------|------|
| Edge 1             | 3.64 | 1.80 |
| Edge 2             | 2.35 | 1.47 |

#### 5. References

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