## **Supporting Information**

# Superior alignment of multi-chromophoric perylenebisimides in nematic liquid crystals and their application in switchable, optical waveguides

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#### **Materials and Methods**

#### Methods

<sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded at room temperature on a Varian 300 or Varian Mercury 400. Chemical shifts are given in ppm (d) relative to tetramethylsilane. Abbreviations used are s = singlet, d = doublet, dd = doublet doublet, t = triplet and m = multiplet. MALDI-TOF MS spectra were measured on a Perspective DE Voyager spectrometer utilizing a-cyano-4-hydroxycinnamic acid matrix.

#### Materials

All solvents, purchased from Acros Chimica or Sigma-Aldrich-Fluka, were of p.a. quality. **E7** was obtained from Merck. Deuterated solvents were from Cambridge Isotope Laboratories. All other chemicals were commercially available and were used without purification.

*Synthesis and characterization of 1-3.* Compounds 1-3 were synthesized and characterized by following the literature procedures described by Langhals et al.<sup>S1</sup>

Synthesis and characterization of **4**: N-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-imide (0.116 g, 0.194 mmol), 1,2,4,5-Tetramethylbenzene (0.016 g, 0.097mmol), imdazole (2 g) and catalytic zinc acetate (0.02 g) were heated to 160 °C and stirred under argon atmosphere. After 6 h, TLC analysis was performed which showed no anhydride was present anymore, and the reaction mixture was cooled to room temperature. The reaction mixture was dissolved in CHCl<sub>3</sub> and washed with 2 N HCl and distilled water. The solution was dried on anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, subsequently concentrated on rotary evaporation and dried in vacuo. The product was purified by column chromatography (silica gel, CHCl<sub>3</sub> with 1 % Ethanol) which yielded a red solid (0.035 g, 14 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 8.81-8.63 (M, 16H), 5.22-5.14 (m, 2H), 2.29-2.20 (m, 4H), 2.15 (s, 6H), 2.05 (s, 3H), 1.97 (s,

3H), 1.91-1.83 (m, 4H), 1.33-1.23 (m, 32H), 0.84-0.80 (t, 12H). MALDI-TOF-MS calculated for (C84H82N4O8) 1274.61  $[M^+]^+$  and observed 1275.13  $[M + H]^+$ .

Synthesis and characterization of 5: N-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic-3,4-anhydride-9,10-imide (0.122 g, 0.199 mmol), 1,7-diaminoheptane (0.013g, 0.099mmol), imidazole (2 g), and catalytic zinc acetate (0.020 g) were heated to 160 °C and stirred under argon atmosphere. After 6 h no more anhydride was detected by TLC analysis, and the reaction mixture was cooled to room temperature. The crude reaction mixture was dissolved in CHCl<sub>3</sub> and washed with 2 N HCl and brine. The solution was dried on anhydrous Na<sub>2</sub>SO<sub>4</sub>, subsequently filtered, concentrated on rotary evaporation and dried in vacuo. The product was purified by column chromatography (silica gel, CHCl<sub>3</sub> with 1 % ethanol) afforded a red solid (0.086 g, 40 %).<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 8.45 (bm, 8H), 8.31 (m, 8H), 5.15 (m, 2H), 4.16 (t, 4H), 2.25(m, 4H), 1.89(m, 4H), 1.78 (m, 4H), 1.50 (bs, 6H), 1.35-1.25 (m, 32H), 0.84 (t, 12H); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>): 162.83, 133.81, 133.52, 130.70,m 129.06, 128.80, 125.65, 125.60, 122.82, 122.46, 122.36, 54.85, 40.56, 32.34, 31.79, 29.26, 28.07, 27.02, 26.77, 22.63, 14.08. MALDI-TOF-MS calculated for (C81H84N4O8) 1240.62 [M<sup>+</sup>]<sup>+</sup> and observed 1241.34 [M + H]<sup>+</sup>.

#### Preparation of the dye/liquid crystalline mixtures

Each of the dyes were dissolved at 0.5 % by weight in the liquid crystal blend E7 (Merck). Custom made 5 x 5 cm<sup>2</sup> ITO coated glass cells with a 20  $\mu$ m spacing (LCTec) were filled with the dye solutions via capillary action. The polarized absorbance of the filled cells was measured on a UV-3102 spectrophotometer (Shimadzu) and determined by exposing the cells to light polarized both parallel and perpendicular to the alignment direction of the polyimide within the cells, with the absorbance of a cell filled with the liquid crystal E7 alone as a reference. For homeotropic measurements, the cells had 10 V<sub>p-p</sub> applied across the gap; the homeotropic state was confirmed by placing the waveguide between crossed polarizers and observing the transmission. Reflectance of the cells was corrected for from the spectra taken of a cell filled with E7 in reflectance mode.

#### Determination of the edge emission output

Edge emission was determined by placing the samples on a platform  $\sim 15$  cm from the emission aperture of a 300 W solar simulator (LOT Oriel) equipped with an AM 1.5 filter, and producing 1688 mW (350 -1000 nm) over the sample surface with one end of the waveguide placed so as the emission enters an integrating sphere equipped with a SLMS LED 1050 light detection array (Labsphere).

### Calculation of S value of absorption

The polarized absorption of each sample was measured, and the order parameter of absorption,  $S_a$ , was derived using the equation

$$S_a = \frac{A_{par} - A_{per}}{A_{par} + 2A_{per}}$$

where  $A_{par}$  and  $A_{per}$  are the absorbance of the sample with the rubbing direction of the alignment layer oriented parallel and perpendicular to the polarization direction of the incident light, respectively.

Scheme







Scheme S1. Chemical composition (weight %) of E7.

Figures



Figure S1. Peak absorbance of 1 (light gray), 2 (dark gray) and 3 (black) with light polarized parallel to the alignment direction of the host liquid crystal E7 (all dyes were at 0.5 % by weight in E7).



**Figure S2.** Measured absorption of **5** with light polarized parallel (blue) and perpendicular (red) to the alignment direction of the host liquid crystals E7 (0.5 weight % in **E7**).

## **References:**

S1 H. Langhals, W. Jona, Angew. Chem. Int. Ed., 1998, 37, 952.