Supporting Information

High Stokes Shift Perylene dyes for Luminescent Solar Concentrators.

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1. Detailed procedures for the synthesis of all new materials.

General Procedures. ¹H and ¹³C NMR spectra were recorded using a Bruker AMX-500 spectrometer operating at 500 and 125.70 MHz, respectively. Coupling constants are presented in Hz. Absorption spectrometry was performed using a Jasco V570 spectrophotometer. Microwave enhanced reactions were performed in a CEM discover focused oven. All commercially available chemicals and solvents were purchased from Sigma-Aldrich Chemicals. Anhydrous solvents were used without further purification, all other solvents employed were HPLC grade solvents and were used without further purification. Quinoline was dried over KOH overnight and distilled immediately prior to its use. Derivatives **S2**,¹ **S3**,² **S8**³ and **S9**⁴ were prepared according to literature procedures.

Derivative 1 was prepared according to the procedure detained in Scheme S1.



Scheme S1.

Derivative 1. Perylene-3,4,9,10-tetracarboxylic dianhydride (0.500 g, 1.274 mmol), 2,3,4,5,6-Pentafluoroaniline (1.400 g, 7.647 mmol) and anhydrous zinc acetate (0.164 g, 0.892 mmol) are loaded in a 50 mL one-neck round-bottom flask equipped with magnetic stirrer and condenser. The mixture is suspended in freshly distilled quinoline (6 mL) and heated under microwave irradiation (max power 95 W, max temperature 200 °C) for 2 h. A red-magenta reaction environment is obtained which is treated under vigorous stirring with a 3M HCl solution (100 mL), the resulting aqueous suspension is then extracted with CHCl3 (3x150 mL). The organic phase is separated, dried over Na2SO4, and the solvent is removed leading to a reddish solid which is purified by column chromatography (Silica, CH2Cl2 then AcOEt/ETP 6:4) to give the title compound as a bright red powder (0.285 g, 0.394 mmol, 31%).

Characterizations agree with those previously reported in the literature.⁵

Derivative 2 was prepared according to the procedure detailed in Scheme S2.



Scheme S2.

Derivative **S5**. 4-Bromo-1,8-naphthalic anhydride (3.000 g, 10.83 mmol) is loaded in a 500 mL round-bottom flask and dissolved in glacial acetic acid (250 mL) under vigorous stirring at reflux. 2,5-Di-*tert*-butylaniline (4.320 g, 21.00 mmol) is then added and the mixture is heated at reflux temperature for 72 h. The hot solution is poured into ice, a white-beige precipitate is formed which is collected by filtration, washed with distilled water and dried in vacuum at 100 °C overnight. The solid is purified by column chromatography (Silica, CH_2Cl_2) and then crystallized from AcOH:H₂O 90:10 to obtain the pure title compound as a white crystalline powder (3.500 g, 7.54 mmol, 70%).

m.p.: 233 °C. ¹H NMR (500 MHz, Chloroform-*d*) δ [ppm]: 8.72 (dd, 1H, J=7.1, J=0.6), 8.65 (dd, 1H, J=8.5, J=0.6), 8.48 (d, 1H, J=7.8), 8.09 (d, 1H, J=7.8), 7.90 (dd, 1H, J=8.3, J=7.4), 7.58 (d, 1H, J=8.6), 7.46 (dd, 1H, J=8.6, J=2.2), 6.99 (d, 1H, J=2.2), 1.32 (s, 9H), 1.27 (s, 9H); ¹³C NMR (125.7 MHz, Chloroform-*d*) δ [ppm]: 164.72, 164.68, 150.21, 143.84, 133.65, 132.69, 132.57, 131.73, 131.29, 130.99, 130.67, 129.56, 128.88, 128.28, 127.79, 126.43, 123.63, 122.76, 35.60, 34.34, 31.80, 31.32. Anal. Calcd for C₂₆H₂₆BrNO₂: C, 67.24; H, 5.64; N, 3.02. Found: C, 67.31; H, 5.50; N, 3.17.

Derivative **S6**. Derivative **S5** (1.370 g, 2.952 mmol), Bis(pinacolato)diboron (0.900 g, 3.543 mmol), $[PdCl_2(dppf)] \cdot CH_2Cl_2$ (0.169 g, 0.207 mmol) and potassium acetate (0.377 g, 3.838 mmol) are dissolved in anhydrous 1,2-dimethoxyethane (210 mL) and heated at 60 °C under argon atmosphere. The reaction mixture gets progressively darker and little black precipitate is formed. After 40 h the solvent is removed in vacuum while keeping the bath temperature below 50 °C, the crude solid is then triturated with *n*-hexane to give the pure title product as a beige solid (1.015 g, 1.985 mmol, 67%). Characterization agree with those previously reported.⁶

¹H NMR (500 MHz, Chloroform-*d*) δ [ppm]: 9.19 (dd, 1H, J=8.4, J=0.8), 8.66 (dd, 1H, J=7.2, J=0.9), 8.62 (d, 1H, J=7.2), 8.34 (d, 1H, J=7.3), 7.82 (dd, 1H, J=8.3, J=7.4), 7.57 (d, 1H, J=8.6), 7.44 (dd, 1H, J=8.5, J=2.2), 7.01 (d, 1H, J=2.2), 1.46 (s, 12H), 1.32 (s, 9H), 1.26 (s, 9H). ¹³C NMR (125.7 MHz, Chloroform-*d*) δ [ppm]: 165.42, 165.38, 150.09, 143.82, 135.91, 135.60, 135.32, 132.98, 131.37, 130.26, 128.79, 128.41, 127.91, 127.25, 126.26, 125.23, 123.11, 84.72, 83.30, 35.57, 34.33, 31.78, 25.13, 25.09, 24.65, 22.76, 14.22. Anal. Calcd for C₃₂H₃₈BNO₄: C, 75.15; H, 7.49; N, 2.74. Found: C, 75.36; H, 7.15; N, 2.84.

Derivative S7. Derivatives S3 (1.000 g, 1.955 mmol) and S6 (0.651 g, 1.303 mmol) are suspended in toluene (120 mL), EtOH (5 mL) and an aqueous 1M K₂CO₃ solution (23.5 mL) are added to the suspension. The mixture is degasated by repeated cycles of vacuum/nitrogen and finally N₂ is bubbled into the biphasic mixture for 30 min. Tetrakis(triphenylphosphine)palladium(0) (0.200 g, 0.156 mmol) is added and N₂ is bubbled again into the mixture for 30 min. The biphasic reaction environment is heated at 80 °C for 20 h under N_2 atmosphere. The dark biphasic mixture is let cool to room temperature and the organic phase is separated, the aqueous phase is extracted with dichloromethane (3x50 mL) and the organic phases are collected together and dried over Na_2SO_4 . The solvent is removed from the dark-brown yellowish organic phase leaving the crude product which is purified by continuous extraction with MeOH. The pure product spontaneously crystallizes in the Soxhlet extractor as a yellow solid (0.400 g, 0.627, 48%).

¹H NMR (500 MHz, Chloroform-*d*) δ[ppm]: 8.82 (dd, 1H, J=7.4, J=3.1), 8.73-8.70 (m, 1H), 8.60 (d, 1H, J=7.1), 8.50 (dd, 1H, J=6.6, J=3.1), 8.30-8.27 (m, 2H), 8.04 (dd, 1H, J=7.9, J=5.8), 7.96-7.92 (m, 2H), 7.83-7.80 (m, 2H), 7.79-7.61 (m, 3H), 7.48 (dd, 1H, J=8.5, J=2.2), 7.06 (dd, 1H, J=4.0, J=2.2), 1.37 (s, 9H), 1.35 (s, 9H). ¹³C NMR (125.7 MHz, Chloroform-*d*) δ[ppm]: 165.29, 165.27, 165.11, 154.21, 153.76, 150.26, 150.21, 143.95, 143.93, 143.78, 143.70, 141.55, 139.38, 139.36, 136.71, 136.69, 132.99, 132.95, 132.69, 132.41, 132.03, 132.01, 131.41, 131.37, 131.06, 131.05, 130.83, 130.63, 129.83, 129.79, 129.74, 129.62, 129.60, 129.57, 129.54, 129.45, 129.03, 128.99, 128.92, 128.88, 128.30, 128.13, 127.88, 127.85, 127.43, 127.41, 126.44, 123.48, 123.47, 123.26, 123.23, 122.57, 122.55, 121.70, 35.68, 34.38, 31.94, 31.89, 31.36. Anal. Calcd for C₄₄H₃₅N₃O₂: C, 82.86; H, 5.53; N, 6.59. Found: C, 82.43; H, 5.77; N, 6.30.

Derivative **2**. Potassium *tert*-butoxide (2.055 g, 18.31 mmol) and 1,5-Diazabicyclo[4.3.0]non-5ene (DBN) (1.660 g, 6.280 mmol) are loaded in a screw-capped schlenk flask under N₂, dyglime (4.5 mL) is added and the mixture is stirred vigorously 1 h at 130 °C. **ASB125** (0.200 g, 0.314 mmol) is added to the reaction environment which immediately changes color to deep-blue/purple, the mixture is let react at 130 °C 4 h. After cooling to room temperature, distilled water (50 mL) is added and the mixture is extracted with CH_2Cl_2 (3x100 mL). The organic phase is separated, washed with brine and dried over Na₂SO₄. The organic solvent is removed leaving the crude product as a pink solid which is purified by continuous extraction with MeOH. The pure product is recovered from the Soxhlet thimble as a purple solid (0.100 g, 0.157 mmol, 50%).

m.p. > 400 °C. ¹H NMR (500 MHz, Chloroform-*d*) δ [ppm]: 8.66 (d, 2H, J=7.8), 8.53 (t, 1H, J=8.5), 8.36 (d, 1H, J=7.4), 8.12-8.10 (m, 2H), 7.74-7.71 (m, 2H), 7.62 (d, 1H, J=8.8), 7.48 (dd, 1H, J=8.7, J=2.1), 7.10 (d, 1H, J=2.0), 1.36 (s, 9H), 1.33 (s, 9H); ¹³C NMR (125.7 MHz, Chloroform-*d*) δ [ppm]: 165.43, 154.21, 150.98, 144.69, 141.90, 136.27, 133.76, 133.67, 132.82, 132.59, 131.06, 130.55, 130.44, 129.67, 128.65, 127.83, 127.17, 125.30, 123.82, 123.78, 122.78, 36.43, 35.16, 32.65, 32.14. Anal. Calcd for C₄₄H₃₃N₃O₂: C, 83.13; H, 5.23; N, 6.61. Found: C, 83.24; H, 5.74; N, 7.10.

Derivative **3** was prepared according to the procedure shown in Scheme S3.



Scheme S3.

Derivative 3. Derivative S9 (900 mg, 1.53 mmol), dibenzoazepine (296 mg, 1.53 mmol) and tBuONa (210 mg, 2.18 mmol) were suspended in anhydrous toluene (30 ml). Nitrogen was bubbled in the reaction mixture for 15 minutes. In a different flask, $Pd_2(dba)_3$ (40 mg, 0.04 mmol) and $P(^tBu)_3$ (0.45 ml of a 1 M solution in n-hexane) were suspended in 8 ml of anhydrous toluene. The resulting purple suspension was stirred under nitrogen for 15 minutes and then added under nitrogen stream to the suspension of the other reagents. The resulting dark suspension was heated under microwave irradiation at the constant power of 90 W for 6 h. Solvent was removed and the dark residue was taken up with 100 ml of CH2Cl2 and filtered through a plug of silica gel. The dark purple solution was evaporated to dryness to give a solid residue. Trituration in isopropanol (30 ml) gave the pure title compound as a purple powder (800 mg, 1.14 mmol, 75 % yield). ¹H NMR (500 MHz, Chloroform-d) δ [ppm]: 8.57 (d, 1H, J=8.12), 8.55 (d, 1H, J=8.12), 8.30 (s, 1H), 8.28 (t, 1H, J=3.26), 8.23 (d, 1H, J=8.72), 8.17 (d, 1H, J=8.23), 7.87 (d, 1H, J=8.63), 7.59 (d, 1H, J=8.61), 7.52 (d, 1H, J=8.04), 7.45-7.38 (m, 5H), 7.29 (d, 2H, J=8.29), 7.28 (t, 1H, J=7.20), 7.22 (t, 1H, J=8.46), 7.02 (d, 1H, J=2.20), 7.00 (s, 1H), 1.33 (s, 9H), 1.30 (s, 9H); ¹³C NMR (125.7 MHz, Chloroform-*d*) δ[ppm]: 165.9, 150.8, 147.7, 146.8, 144.6, 139.0, 138.9, 136.2, 134.2, 133.0, 132.6, 132.4, 131.4, 131.0, 130.8, 130.6, 130.0, 129.5, 129.2, 128.7, 128.2, 128.0, 127.3, 127.2, 126.9, 126.2, 125.5, 124.9, 123.8, 121.6, 120.4, 120.3, 119.4, 119.4, 36.4, 35.10, 32.6, 32.1. Anal. Calcd for C₅₀H₄₀N₂O₂: C, 85.68; H, 5.75; N, 4.00. Found: C, 85.64; H, 6.10; N, 3.56.

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2. Copy of the ¹H and ¹³C spectra for all new materials.

2.1 Derivative S5.











2.2 Derivative S7.











2.3 Derivative 2.













2.4 Derivative 3.









3. Experimental procedures for Electrochemical characterization.

For the electrochemical characterization perylene derivatives were dissolved (concentration about 10^{-4} M) in the supporting electrolyte that was a 0.1 M solution of tetrabutylammonium *p*-toluenesulfonate (Fluka, electrochemical grade, $\geq 99.0\%$) in anhydrous acetonitrile (Aldrich, 99.8%). Cyclic Voltammetries at scan rate of 100 mV/s were carried out using a PARSTA2273 potentiostat in a single chamber three electrodes electrochemical cell in a glove box filled with Argon ([O₂] ≤ 1 ppm). The working, counter and pseudo-reference electrodes were a Glassy Carbon (GC) disc, a Pt flag, and a Ag/AgCl wire, respectively. The GC disc was well polished with alumina 0.1 µm suspension, sonicated for 15 min. in deionized water and washed with 2-propanol before using. The Ag/AgCl pseudo-reference electrode was calibrated before and after each measurement using a 1 mM ferrocene solution in the electrolyte, no more than 5 mV in difference was observed between two successive calibrations.





Figure S1.

5. Experimental procedure for the PMMA slab polymerization.

Preparation of the PMMA slab. In a typical procedure for the preparation of a 0.1 % slab, 100 mg of AIBN were dissolved in 100 ml of freshly distilled MMA. The solution was placed in a beaker and slowly heated on a hot plate until the temperature of 80 °C was reached. This temperature was maintained for 2 minutes, during which time viscosity increased substantially. The solution was immediately transferred in an ice bath and cooled at 20°C. A solution of the appropriate perylen dye in freshly distilled MMA (60 ml) was added along with 150 mg of lauryl peroxide. The viscous syrup thus obtained was poured in a mould of 7 mm thickness and 100 cm² area and heated in a water bath at 56°C for 48 h. At the end of this thermal treatment the syrup turns into a solid slab that is further cured at 95°C for 24 h. After cooling, the slab can be easily separated by the glass mould and polished for optical measurements.

6. Photo bleaching experiment on derivatives 1 and 3 based LSCs.

General procedure. A cylindrical bulk polymerized PMMA sample containing a 0.1 % by weight perylene dye (either derivative 1 or 3) was irradiated in the dye maximum of absorption at the constant power of 0.45 mW (as measured directly at the sample position) in ambient atmosphere and at 25 °C. The corresponding fluorescence intensity was recorded as a function of the irradiation time. Figure S2 shows the fluorescence versus time trend for derivative 1 containing PMMA. Figure S3 shows the fluorescence versus time trend for derivative 3 containing PMMA.



Figure S2. Fluorescence intensity @ 535 nm as a function of the irradiation (@ 528 nm, 0.45 mW) time for a PMMA sample loaded with derivative 1.



Figure S3. Fluorescence intensity @ 674 nm as a function of the irradiation (@ 577 nm, 0.45 mW) time for a PMMA sample loaded with derivative **3**.



7. Pictures of derivative 1, 2 and derivative 3 containing PMMA slabs.

Figure S4. Bulk polymerized PMMA slab containing a 0.01 % by weight of derivative 1.



Figure S5. Bulk polymerized PMMA slab containing a 0.01 % by weight of derivative 2.



Figure S6. Bulk polymerized PMMA slab containing a 0.01 % by weight of derivative 3.

8. Absolute quantum yield measurements.

Absolute quantum yield measurements were conducted following the well-known procedure described by de Mello et al.,⁷ using a 405 nm (3.06 eV) pulsed diode laser with a repetition rate of 2 MHz (Edinburgh EPL405) and a Labsphere Spectraflect integrating sphere connected to a Hamamatsu mini-spectrometer through an optical fiber with a 600 nm core. The spectral response of the system (integrating sphere, optic fiber and spectrometer) was corrected by a calibrated tungsten halogen lamp (Ocean Optics LS-1-CAL).

9. References for the Supporting Information.

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