Supporting information for:

Novel Fluorescent Dyes with Fused Perylene Tetracarboxylic Diimide and BODIPY analog structures

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Contents

1. General Methods

^{1}H NMR spectra were recorded at 300 MHz with the solvent peak as internal standard (in $CDCl_3$). Electronic absorption spectra were recorded in organic solvents at room temperature. Fluorescence spectra and the fluorescence lifetime were measured on a Multifrequency Phase and Modulation Fluorometer with the excitation at 450 nm. The fluorescence lifetimes were measured with multifrequency phase modulation method with a scattering sample as standard. Fluorescence quantum yields are calculated with compound **7** as standard. MALDI-TOF mass spectra were taken on an ultra-high resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. Electrochemical measurements were carried out under nitrogen atmosphere on an electrochemical working station. The cell comprised inlets for a glassy carbon disk working electrode of 2.0 mm in diameter and a silver-wire counter electrode. The reference electrode was Ag/Ag^+, which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode. It was corrected for junction potentials by being referenced internally to the ferrocenium / ferrocene (Fe^+ / Fe) couple [$E_{1/2}$ (Fe^+ / Fe) = 501 mV vs. SCE]. Typically, a 0.1 mol dm^{-3} solution of $[Bu_4N][ClO_4]$ in dichloromethane containing 0.5 mmol dm^{-3} of sample was purged with nitrogen for 10 min, then the voltammograms were recorded at ambient temperature. The scan rate was 20 and 10 mV s^{-1} for CV and DPV, respectively.

2. Synthesis and structure characterizations

*N-n-Butyl-1,6,7,12-tetra(4-tert-butylphenoxy)perylene-3,4:9,10-tetracarboxylic-3,4 -anhydride-9,10-imide (**5**).*

1,6,7,12-Tetra(4-*tert*-butylphenoxy)-perylene-3,4,9,10-tetracarboxylic dianhydride[1] (3.0 g, 3.20 mmol) in toluene (100 mL) was purged with dry nitrogen for 15 min and then was heated to reflux. To this solution *n*-butylamine (0.32 mL, 3.2 mmol) in toluene (10 mL) was slowly added over the course of 30 min. The resulting mixture was refluxed continuously for another 30 min, and then the volatiles were removed under reduced pressure. The product was separated from the residue by column chromatography on silica gel with chloroform as eluent. Repeated chromatography followed by recrystallization from a mixture of $CHCl_3$ and MeOH gave pure product **5** (1.70 g, yield 53.1%): mp. > 300°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 4H), 7.23 (d , J = 8.35 Hz, 8H), 6.82 (d, J = 8.35 Hz, 8H), 4.11 (t, 2H), 1.65 (m, 2H), 1.40(m, 2H), 1.29 (s, 36H), 0.93 (t, 3H); MALDI-TOF MS(*m/z*) 1040.5, Calcd for $C_{68}H_{65}NO_9$ (*m/z*) 1039.5. Anal. Calcd. for $C_{68}H_{65}NO_9$: C, 78.51; H, 6.30; N, 1.35. Found: C, 78.39; H, 6.38; N, 1.36.

*Compound **3**:*

A mixture of **5** (1 g, 0.96 mmol), 2-methylquinoline (2 g, 14 mmol) and fresh dried zinc chloride (0.2 g, 1.5 mmol) by thionyl chloride was heated to 200°C for 3 hours. The reaction cake was extracted several times with dichloromethane. The combined

extract was dried over sodium sulfate for overnight and then was evaporated to dry under reduced pressure. The red solid collected was purified by column chromatography on silica gel using dichloromethane as eluent. Compound **3** was afforded as red powder (0.7 g, 63 %): mp. > 300°C; UV-vis (CH_2Cl_2, ε) 582 nm (6.33×10^4 L mol^{-1} cm^{-1}), 423 nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.64 (d, 1H), 8.34 (s, 2H), 8.26 (d, 1H), 8.21 (s, 2H), 7.80 (d, 2H), 7.73 (t, 1H), 7.51 (t, 1H), 7.22 (m, 4H), 7.21 (d, 4H), 6.89 (br, 4H), 6.81 (d, 4H), 4.12 (t, 2H), 1.66 (m, 2H), 1.40 (m, 2H), 1.31 (s, 36H), 0.94 (t, 3H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 163.1, 155.5, 155.2, 154.9, 153.0, 152.6, 146.4, 146.0, 139.4, 135.5, 132.5, 132.1, 131.6, 129.3, 127.1, 126.0, 125.6, 124.5, 121.9, 121.3, 120.9, 119.4, 119.2, 119.1, 118.9, 118.6, 117.4, 39.8, 33.8, 31.1, 31.0, 29.7, 19.89, 13.29; IR (KBr) ν [cm^{-1}] 2958 (C-H), 2866 (C-H), 1698 (C=O), 1660 (C=O), 1634 (C=O), 1590 (C=C, perylene ring); MALDI-TOF MS (*m/z*) 1165.4, Calcd. For $C_{78}H_{72}N_2O_8$ (*m/z*) 1164.5. Anal. Calcd. For $C_{78}H_{72}N_2O_8$: C, 80.39%; H, 6.23%; N, 2.40%. Found: C, 80.23%; H, 6.32%; N, 2.38%.

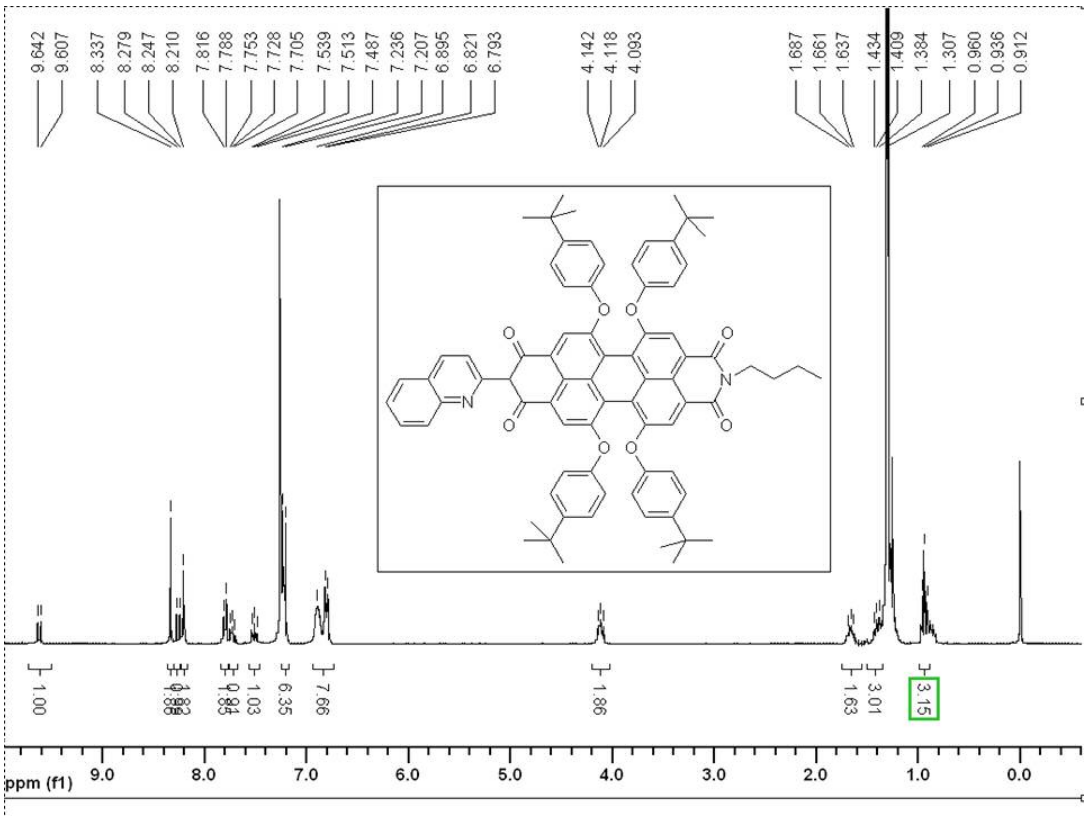

Figure S1. ^{1}H NMR spectrum of **3** in $CDCl_3$

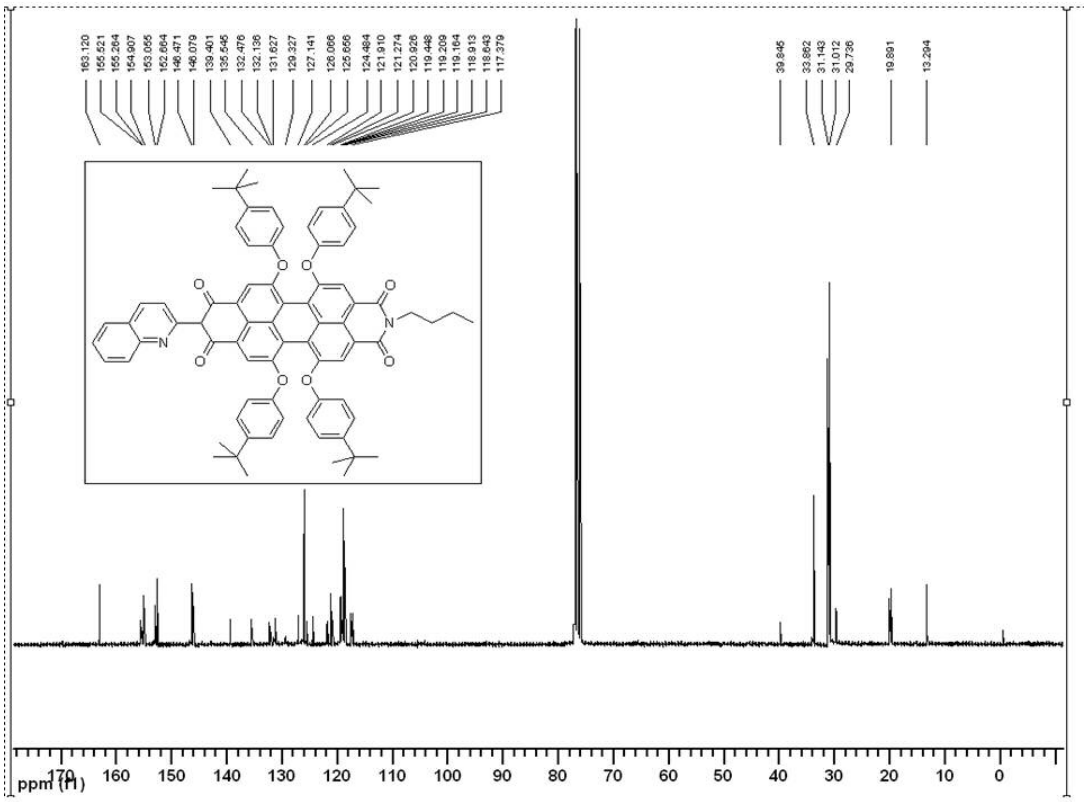

Figure S2. ^{13}C NMR spectrum of **3** in $CDCl_3$

*Compound **4***:*

A mixture of **6** (1 g, 1.02 mmol), 2-methylquinoline (3 g, 21 mmol) and fresh direded zinc chloride (0.4 g, 3.0 mmol) by thionyl chloride was heated to 200 °C for 3 hours. The reaction cake was extracted several times with dichloromethane. The extract was dried over anhydrous sodium sulfate for overnight and was evaporated to dry under reduced pressure to give a red mixture. Which was further purified by column chromatography on silica gel using dichloromethane as eluent to afford compound **4** as red solid **(**0.73 g**,** yield 58%). mp. >300 °C; UV-vis (CH_2Cl_2, ε) 588 nm (8.43 × 10^4 L mol^{-1} cm^{-1}), 423 nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.65 (d, 2H), 8.33 (s, 4H), 8.26 (d, 2H), 7.79 (m, 4H), 7.72 (m, 2H), 7.53 (m, 2H), 7.26 (br, 8H), 6.87(br, 8H), 1.31 (s, 36H); IR (KBr) ν [cm^{-1}] 2959 (C-H), 2866 (C-H), 1632 (C=O), 1571 (C=C, perylene ring); MALDI-TOF MS (*m/z*) 1235.5, Calcd. For $C_{84}H_{70}N_2O_8$ (*m/z*) 1234.5. Anal. Calcd. For $C_{84}H_{70}N_2O_8$: C, 81.66%; H, 5.71%; N, 2.27%. Found: C, 81.58%; H, 5.73%; N, 2.38%.

* *Compound **4** failed to give a satisfied ^{13}C NMR spectrum probably because of the bad solubilities in organic solvents. But the structure and the purity of it have been proved by the TLC, HPLC, elemental analysis, and ^{1}H NMR spectra.*

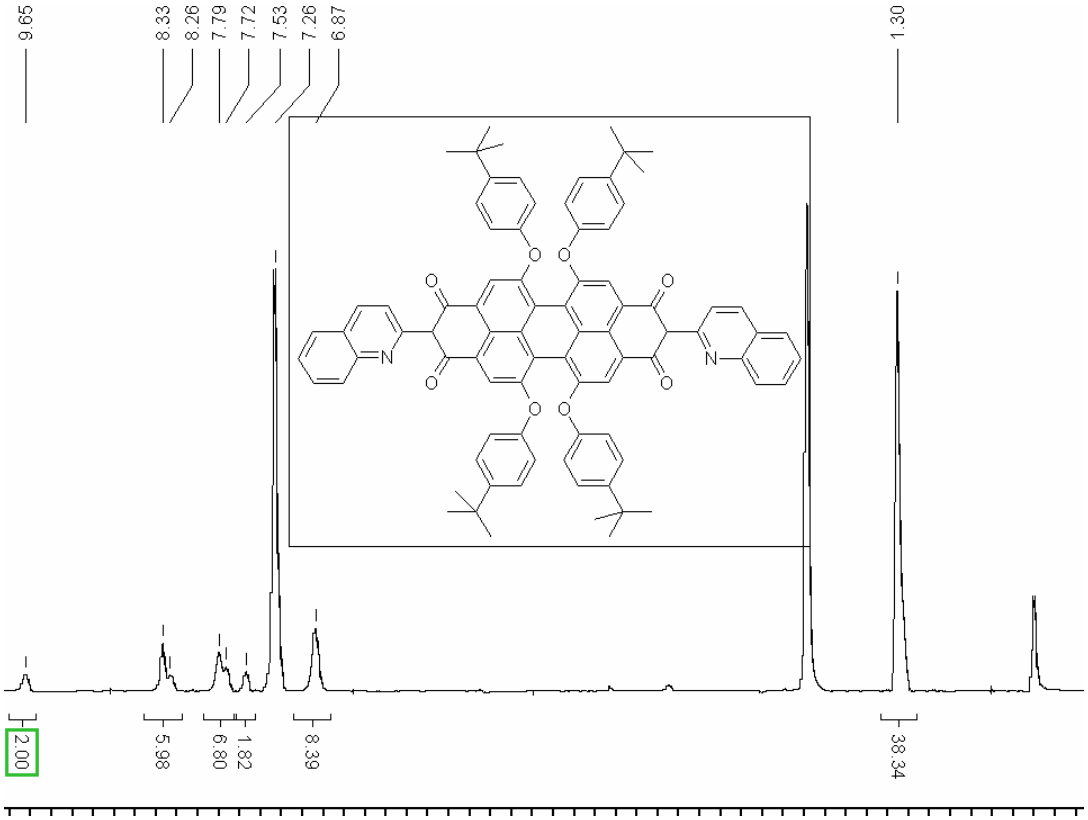

Figure S3. ^{1}H NMR spectrum of **4** in $CDCl_3$

*Compound **1**:*

0.5 ml *N*-Ethyldiisopropylamine and 1 ml $BF_3 \cdot Et_2O$ were added to the solution of 0.2 g compound **3** (0.17 mmol) in 15 ml toluene. The mixture was heated to 60 °C under the protection of nitrogen and stirred at this temperature for 2.5 hours. The reaction mixture was then evaporated to dry under reduced pressure. The residues were purified by column chromatography on silica gel using dichloromethane as eluent. Compound **1** was afforded as red solid (150 mg, yield 72 %). mp. >300°C; UV-vis (CH_2Cl_2, ε): 616 nm (6.37×10^4 L mol^{-1} cm^{-1}), 377 nm; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.50 (d, 1H), 8.78 (d, 1H), 8.46 (s, 1H), 8.43 (d, 1H), 8.37 (s, 1H), 8.22 (s, 1H), 8.19 (s, 1H), 7.89 (d, 1H), 7.85 (t, 1H), 7.64 (m, 1H), 7.25 (m, 8H), 6.91-6.78

(m, 8H), 4.11 (t, 2H), 1.65 (m, 2H), 1.40 (m, 2H), 1.31 (s, 36H), 0.94 (t, 3H); ^{13}C NMR (100 Hz, CDCl3) δ 181.2, 167.2, 163.4, 156.4, 156.2, 156.0, 155.4, 153.4, 153.2, 152.9, 152.7, 152.3, 147.4, 147.3, 147.0, 146.9, 142.1, 139.8, 132.8, 132.3, 131.7, 128.5, 128.2, 127.6, 127.5, 126.7, 126.6, 126.5, 124.0, 123.9, 123.8, 122.7, 122.6, 121.7, 121.5, 120.8, 120.5, 120.3, 119.8, 119.7, 119.5, 119.4, 119.3, 119.2, 119.1, 118.7, 107.7, 40.4, 34.4, 31.5, 30.2, 20.4, 13.8; IR (KBr) ν [cm^{-1}] 2959 (C-H), 2867 (C-H), 1701 (C=O), 1662 (C=O), 1575 (C=C, perylene ring), 1148 (B-F); MALDI-TOF MS (*m/z*) 1212.1, Calcd. For $C_{78}H_{71}BF_2N_2O_8$ (*m/z*) 1212.5.

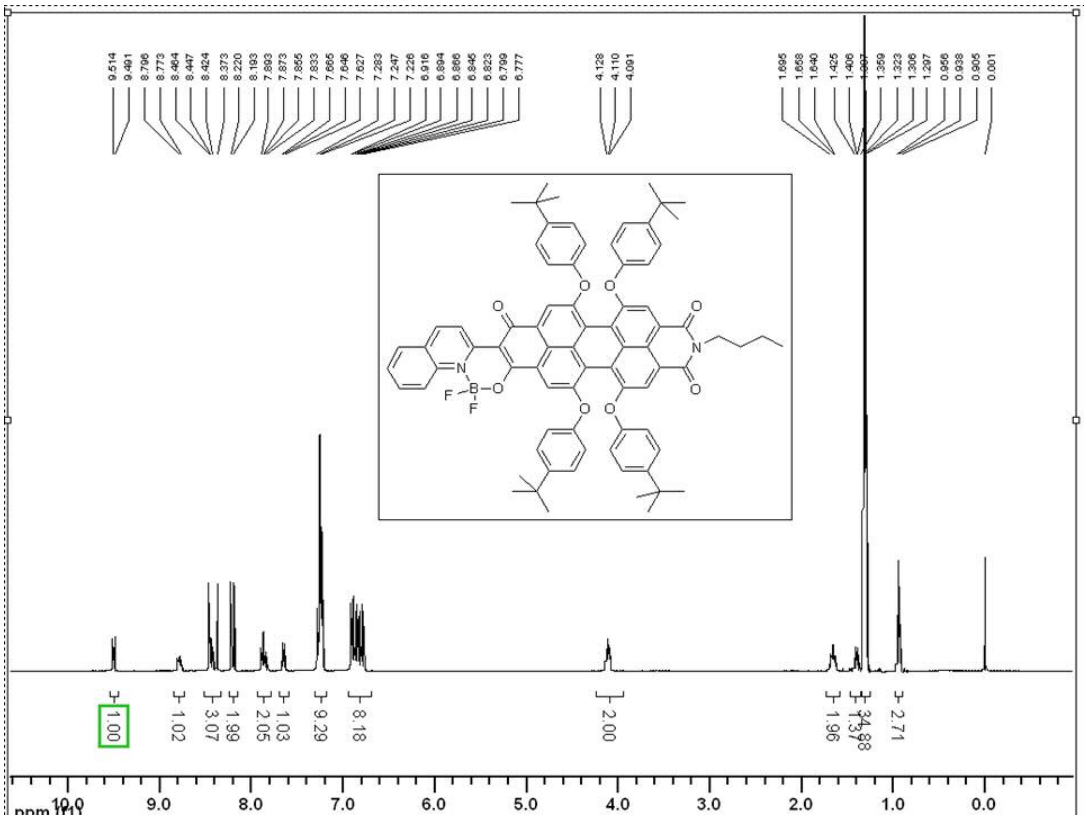

Figure S4. ^{1}H NMR spectrum of **1** in $CDCl_3$

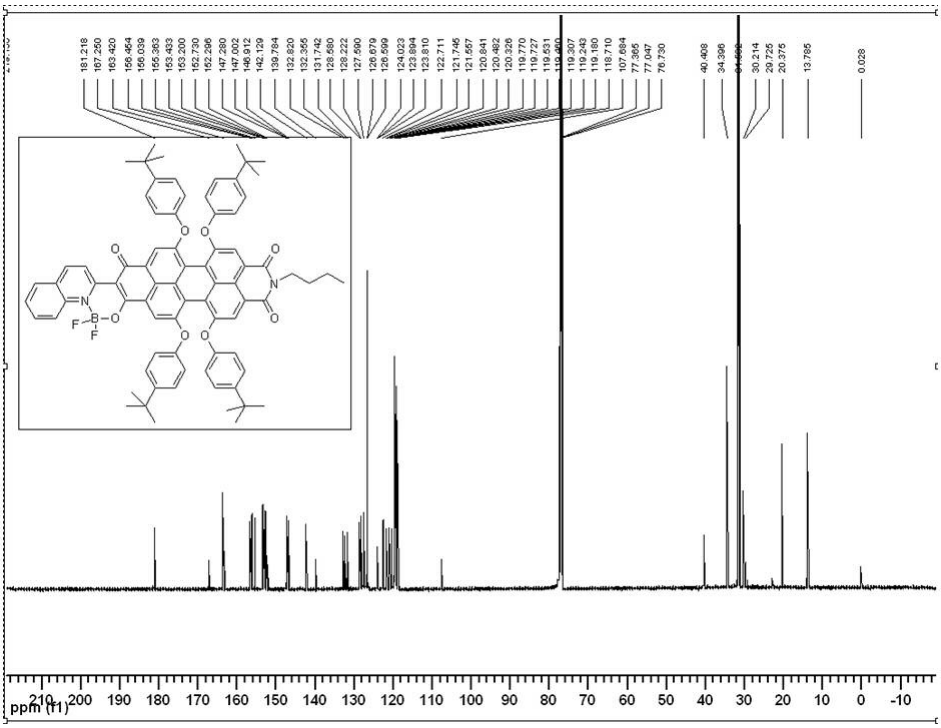

Figure S5. ^{13}C NMR spectrum of **1** in $CDCl_3$

*Compound **2**:*

1 ml N-Ethyldiisopropylamine and 2 ml $BF_3 \cdot Et_2O$ were added to the solution of 0.2 g compound 4 (0.16 mmol) in 15 ml toluene. The mixture was heated and stirred at 60 °C under nitrogen for 2.5 hours. The reaction mixture was evaporated to dry under reduced pressure and the residues were purified by column chromatography on silica gel using dichloromethane as eluent. Compound 1 was collected as red solid (147 mg, yield 68 %). mp. >300°C; UV-vis (CH_2Cl_2, ε) 650 nm (8.21×10^4 L mol^{-1} cm^{-1}), 382 nm; ^1H NMR (300 MHz, $CDCl_3$) δ 9.49 (d, 2H), 8.78 (d, 2H), 8.45 (s, 2H), 8.43 (s, 2H), 8.34 (d, 2H), 7.89-7.84 (m, 4H), 7.64 (m, 2H), 7.28 (m, 8H), 6.87 (m, 8H), 1.33 (s, 36H); δ 181.3, 167.3, 156.6, 156.3, 155.8, 155.6, 153.4, 153.3, 153.2, 153.0, 152.3, 147.1, 147.0, 146.9, 142.1, 139.8, 132.4, 131.7, 128.8, 128.7, 128.3, 127.6, 127.5, 126.7, 126.6, 126.5, 124.3, 124.2, 123.9, 121.7, 121.6, 121.5,

120.9, 120.7, 119.7, 119.5, 119.4, 119.1, 119.0, 118.9, 118.8, 107.7, 34.4, 31.5; IR (KBr) ν [cm^{-1}] 2959 (C-H), 2867 (C-H), 1633 (C=O), 1573 (C=C, perylene ring), 1144 (B-F); MALDI-TOF MS (*m/z*) 1330.0, Calcd. For $C_{84}H_{68}B_2F_4N_2O_8$ (*m/z*) 1330.5.

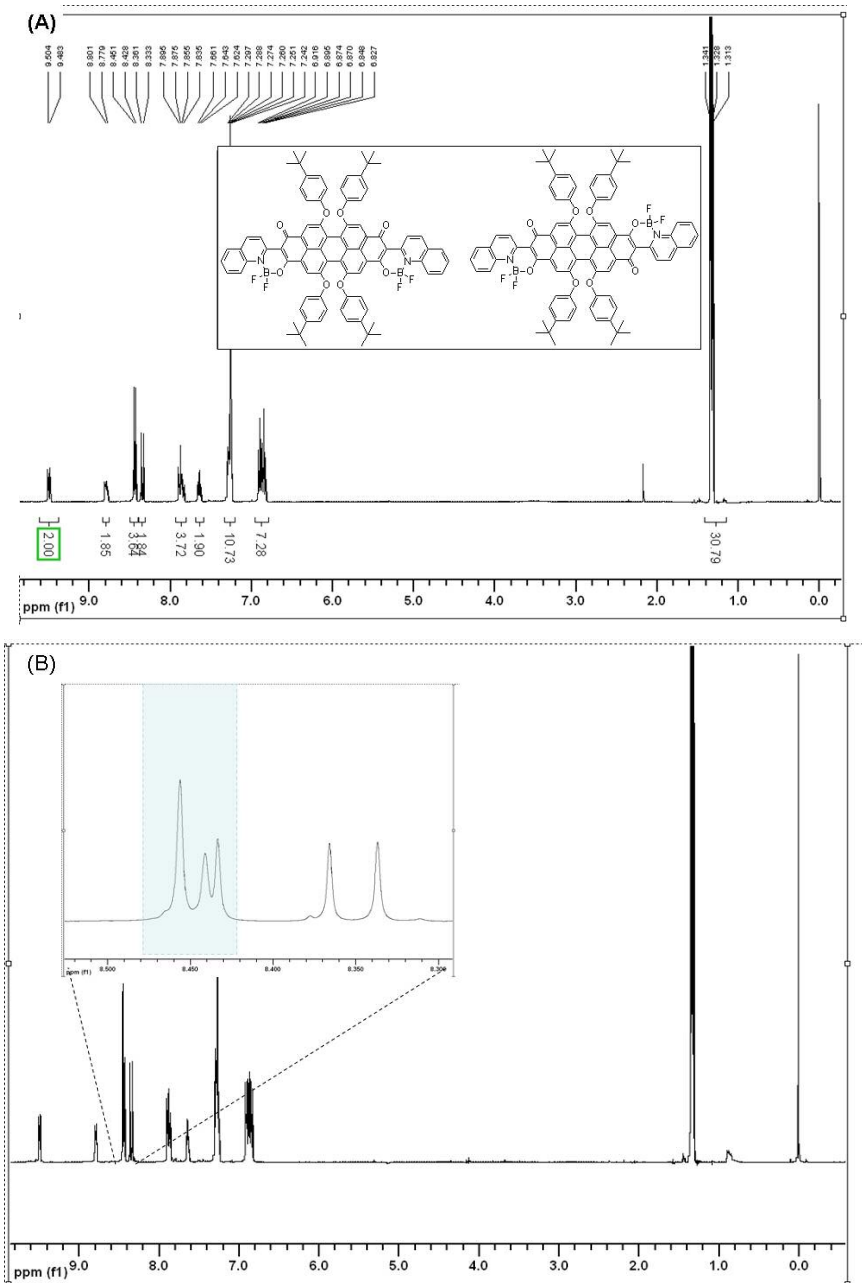

Figure S6. ^{1}H NMR spectrum of **2** in chloroform-d_1 recorded (A) on a 300 MHz instrument, (B) on a 600 MHz instrument (inset shows the splitting signals at 8.46 ppm of the protons on perylene ring because of the presence of *cis* and *trans* isomers).

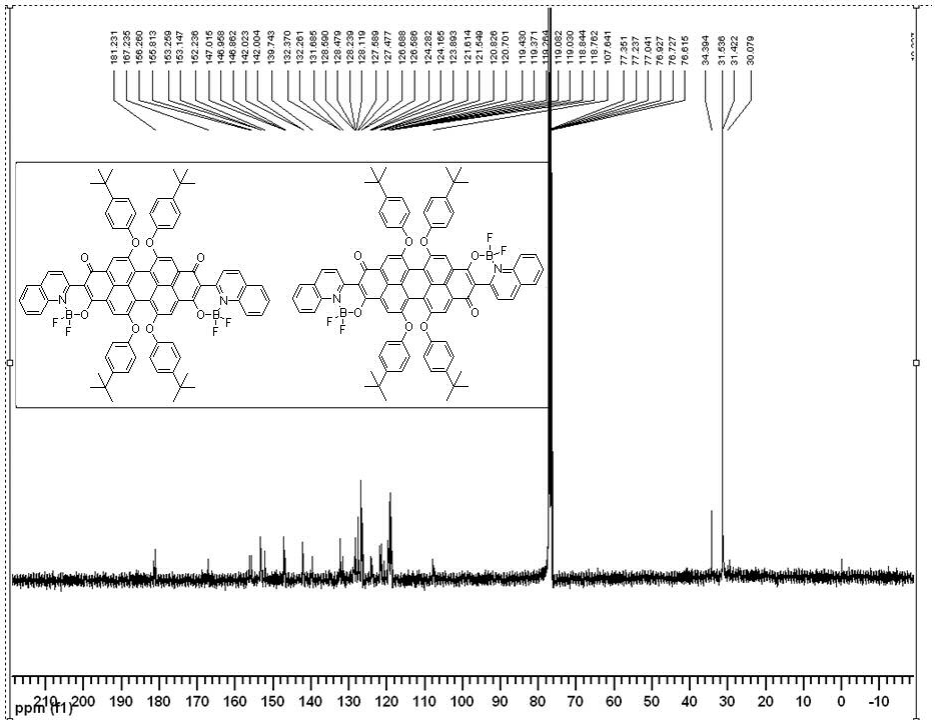

Figure S7. ^{13}C NMR spectrum of **2** in chloroform-d_1

Reference

1. Würthner, F.; Thalacker, C.; Diele, S.; Tschierske, C. *Chem. Eur. J.* **2001**, *7*, 2245-2253.

3. Simulated absorption spectra of 3 and 4

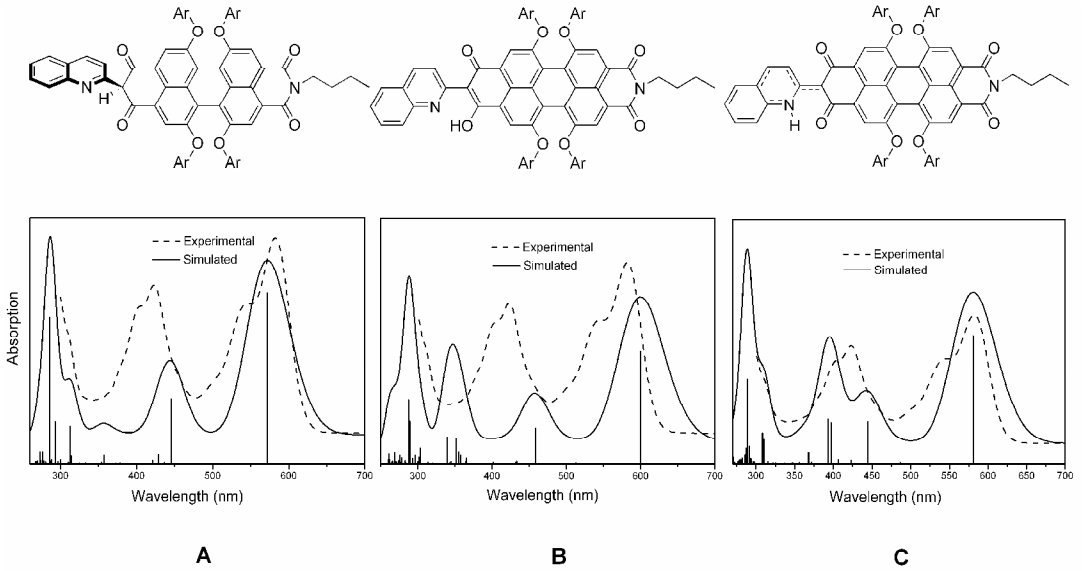

Figure S8. Simulated absorption spectra of **3** with different structures based on TD-DFT calculation.

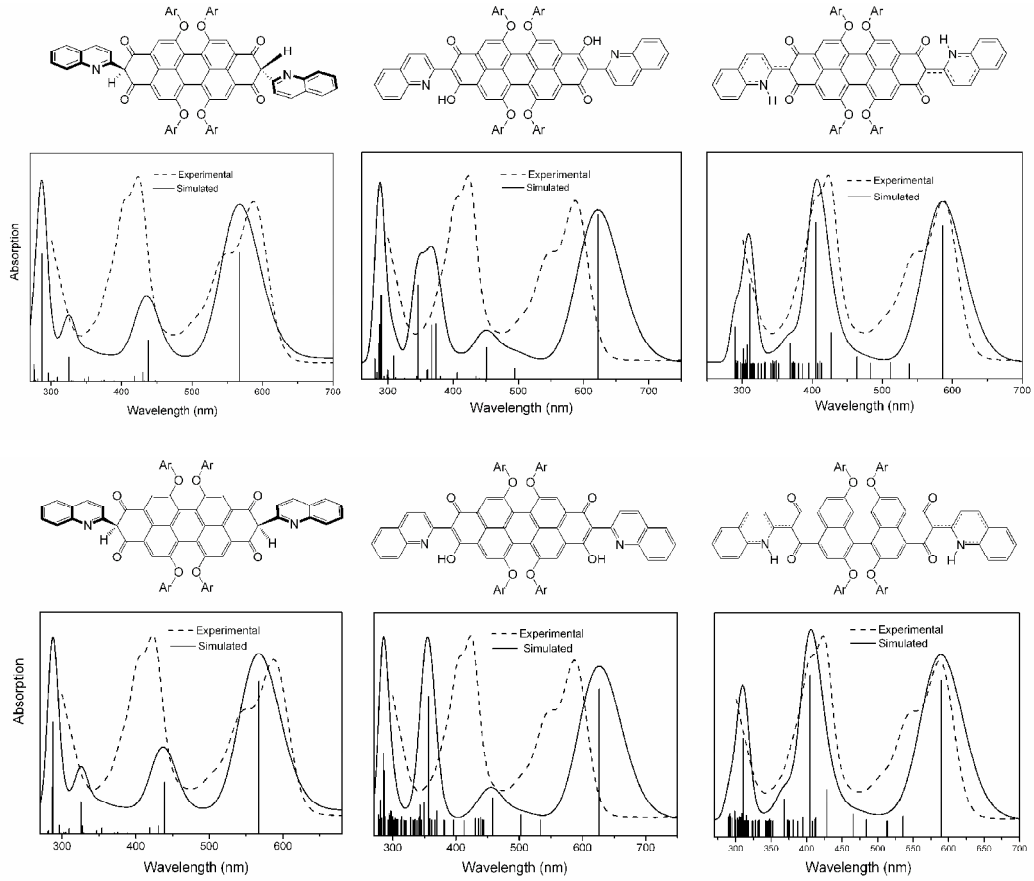

Figure S9. Simulated absorption spectra of **4** with different structures based on TD-DFT calculation.

4. Simulated absorption spectra of 1 and 2.

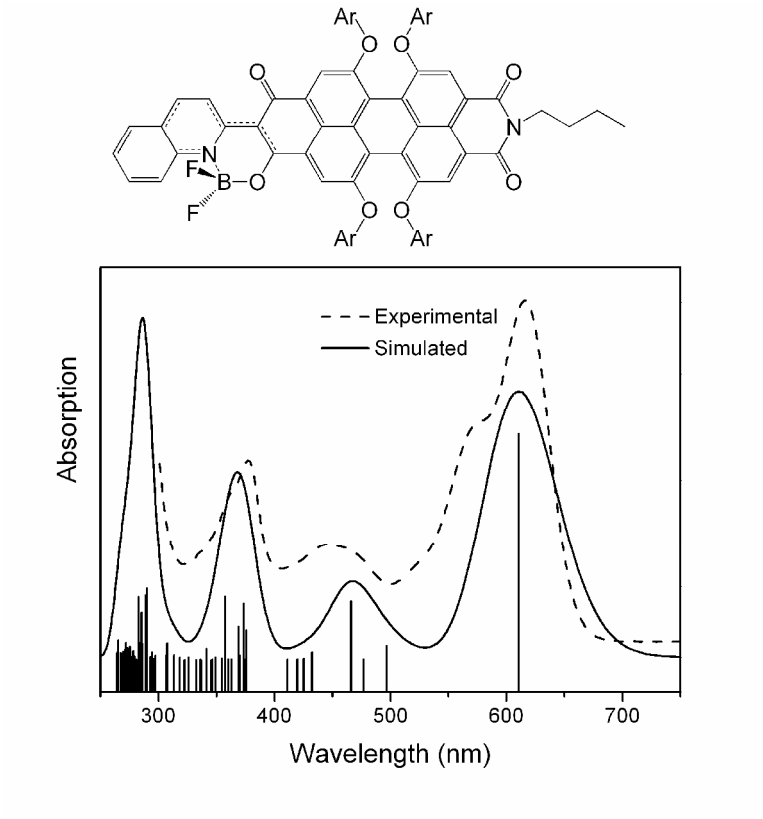

Figure S10. Simulated absorption spectrum of **1** (solid) compared with the experimental recorded spectrum (dash).

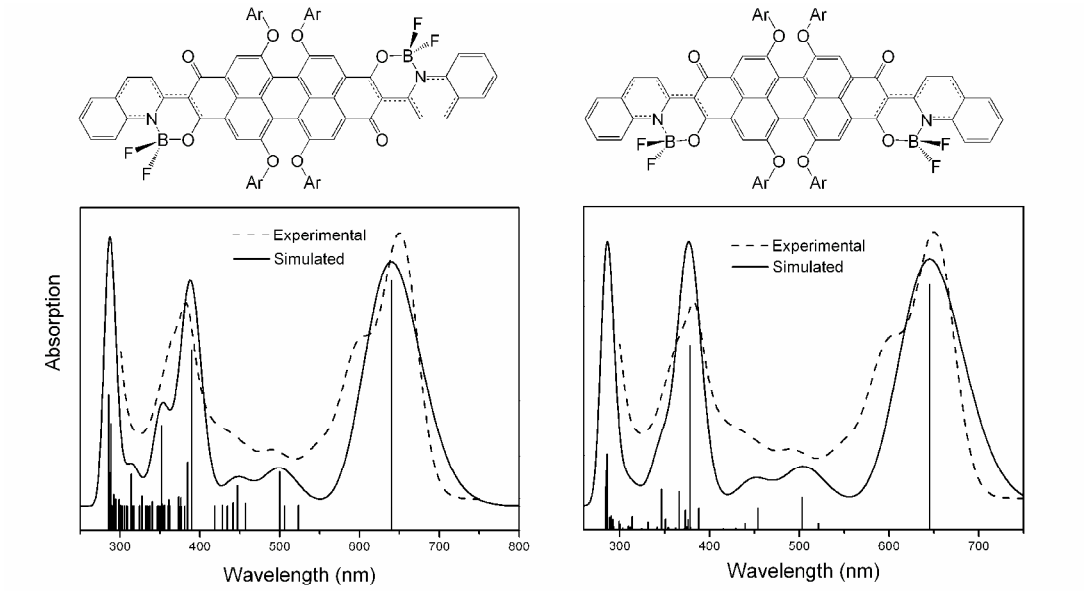

Figure S11. Simulated absorption spectra of **2** (*cis* and *trans* isomer) (solid) compared with the experimental recorded spectra (dash).

5. Calculated energy levels and the orbital maps of 1 and 2.

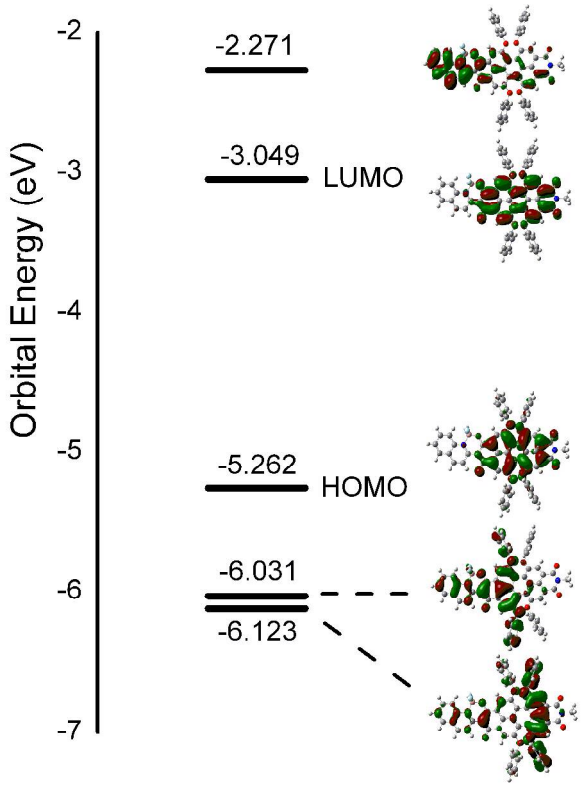

Figure S12. The frontier orbital energy levels and orbital maps of **1**.

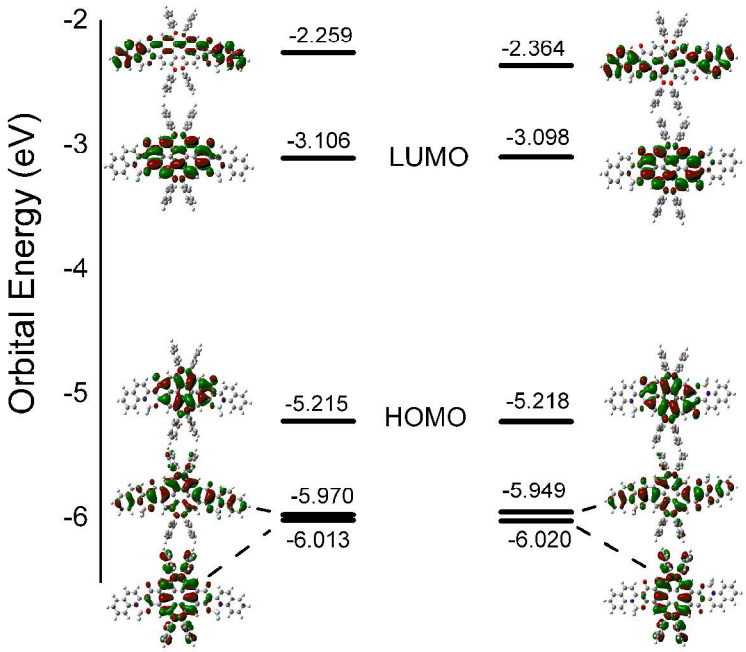

Figure S13. The frontier orbital energy levels and orbital maps of *cis* (left) and *trans* (right) isomer of **2**.