

Supplementary Information for

Electron-Transporting PAHs with Dual Perylenediimides: Syntheses and Semiconductive Characterizations

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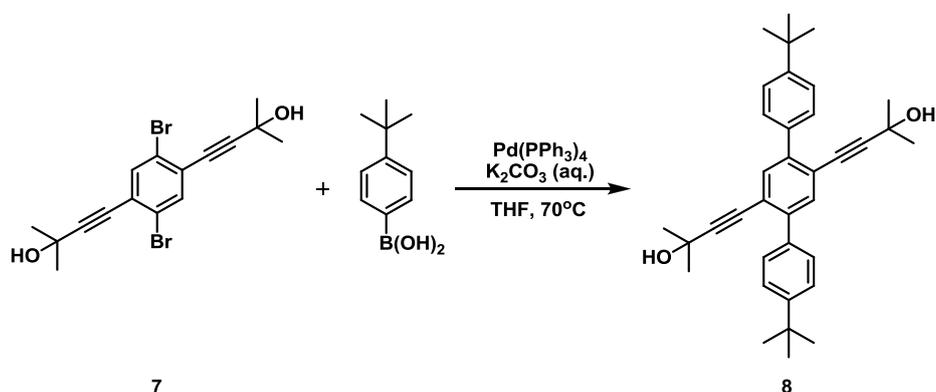
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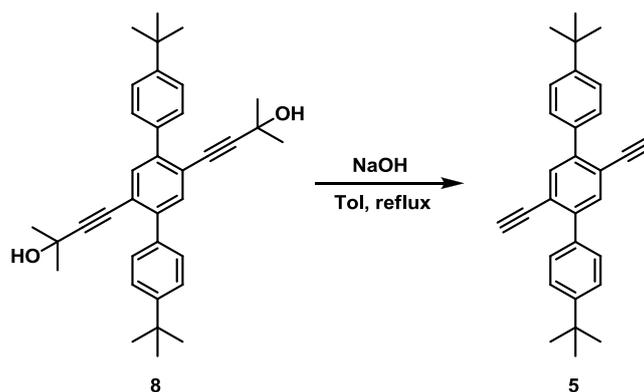
I. Synthetic Procedures and Characterizations

General Methods. Chemicals were used as received unless otherwise noted. All oxygen or moisture sensitive reactions were performed under nitrogen atmosphere using standard Schlenk method. Reagent grade tetrahydrofuran (THF) was distilled over sodium and benzophenone, triethylamine (TEA) was distilled over CaH₂, and toluene was distilled over sodium prior to use. ¹H and ¹³C NMR spectra were recorded on Mercury plus 300 (300 MHz) or Bruker Avance 400 (400 MHz), using CDCl₃ as the solvent unless otherwise mentioned. Chemical shifts were reported in parts per million (ppm) with TMS (0 ppm) and CDCl₃ (77.0 ppm) as standards in ¹H and ¹³C NMR spectra, respectively. ESI mass spectra were recorded on a Bruker APEX IV mass spectrometer. Elemental analyses were performed using a German Vario EL III elemental analyzer. Absorption spectra were recorded on a Hitachi U-4100 UV-vis Spectrometer. Fluorescence emission spectra were recorded in 1-cm quartz cuvette on a Horiba Jobin Yvon FluoroMax-2P spectrofluorometer. Atomic force microscopy studies were performed with a Nanoscope IIIa microscope (Extended Multimode, Digital Instruments, Santa Barbara, CA). The experiments were carried out in tapping mode at ambient temperature.

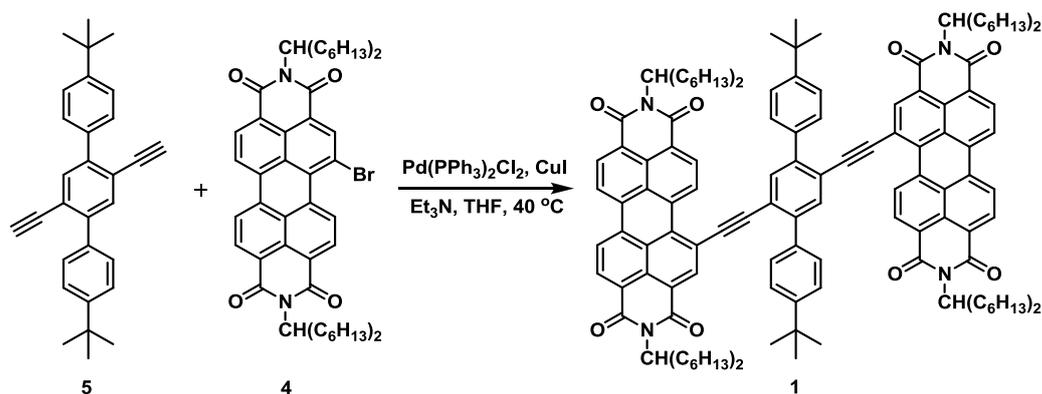
Synthesis procedures



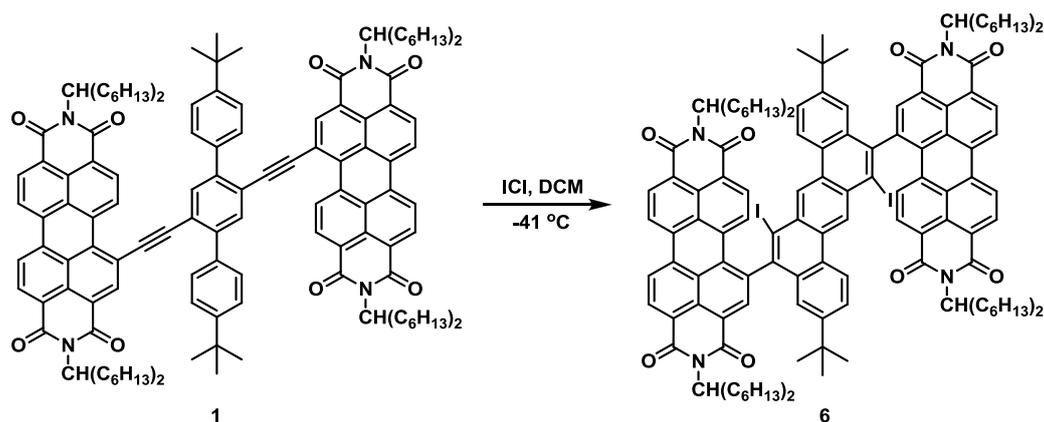
Compound 8. To a Schlenk tube containing 4-*tert*-butylphenylboronic acid (1.50 g, 8.43 mmol), **7** (1.61 g, 4.02 mmol), and Pd(PPh₃)₄ (0.23 g, 0.20 mol) was added degassed aq. K₂CO₃ (2 M, 20 mL) and THF (20 mL). The reaction mixture was heated at 70 °C under nitrogen atmosphere for 30 h. After being cooled to room temperature, the mixture was diluted with ethyl acetate and the aqueous layer was removed. Upon drying over anhydrous Na₂SO₄, the organic layer was condensed under reduced pressure and the residue was purified with column chromatography over silica gel, eluted with petroleum ether/dichloromethan (PE/DCM, 2:1 to 1:1, v/v) to afford **8** as a white solid: 1.48 g (73%). ¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.55 (d, 4H, *J* = 8.4 Hz), 7.54 (s, 2H), 7.44 (d, 4H, *J* = 8.4 Hz), 1.90 (s, 2H), 1.47 (s, 12H), 1.37 (s, 18H). ¹³C NMR (CDCl₃, 300 MHz, ppm): δ 150.7, 142.1, 136.3, 133.6, 128.2, 124.8, 121.1, 97.8, 81.8, 65.6, 34.6, 31.4, 31.0. MS (ESI): Calcd. for C₃₆H₄₂O₂ 506.3. Found: 529.3 (M + Na⁺).



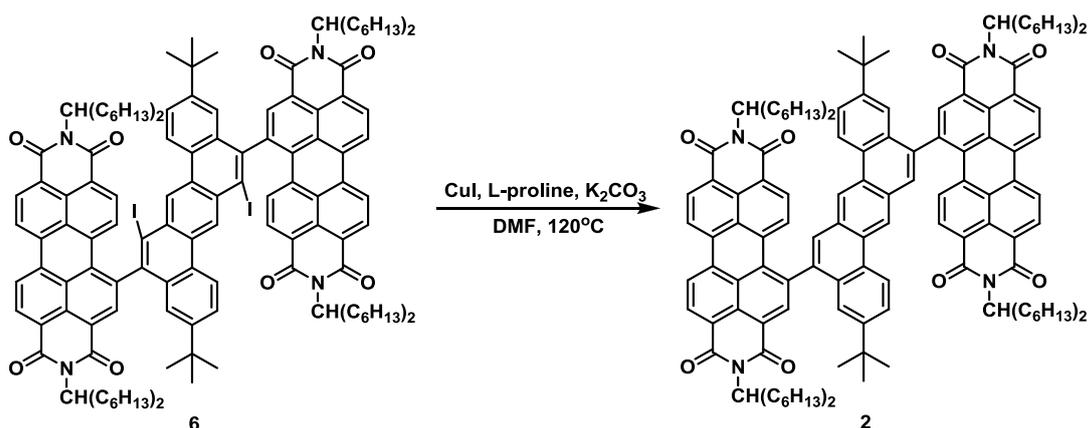
Compound 5. To a flask containing **8** (204 mg, 0.40 mmol) and NaOH (64 mg, 1.6 mmol) was added degassed toluene (30 mL). The reaction mixture was refluxed under nitrogen atmosphere. TLC was taken every 30 min to monitor the reaction until the two protective groups were both removed. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate and washed with saturated NH_4Cl (aq.) and brine sequentially. The organic layer was dried over anhydrous Na_2SO_4 and then condensed under reduced pressure. The residue was purified with flash column chromatography over silica gel, eluted with PE/DCM (10:1, v/v) to afford **5** as a white solid: 147 mg (94%). ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 7.64 (s, 2H), 7.58 (d, 4H, $J = 8.0$ Hz), 7.46 (d, 4H, $J = 8.0$ Hz), 3.15 (s, 2H), 1.37 (s, 18H). ^{13}C NMR (CDCl_3 , 300 MHz, ppm): δ 150.8, 142.4, 135.9, 135.1, 128.7, 125.1, 120.9, 82.8, 81.6, 34.6, 31.4. MS (ESI): Calcd. for $\text{C}_{30}\text{H}_{30}$: 390.2. Found: 391.2 ($\text{M} + \text{H}^+$).



Compound 1. To a schlenk tube containing **5** (222 mg, 0.57 mmol), **4** (1.90 g, 2.28 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (11.8 mg, 0.017 mmol), and CuI (3.2 mg, 0.017 mmol) was added degassed TEA (15 mL) and THF (15 mL). The tube was sealed under nitrogen atmosphere and the reaction mixture was stirred at 40 °C for 24 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure. The condensed mixture was diluted with DCM, washed with saturated NH_4Cl solution and brine sequentially. The organic layer was dried over anhydrous Na_2SO_4 and then condensed under reduced pressure. The residue was purified with column chromatography over silica gel, eluted with PE/DCM (2:1 to 3:2, v/v) to afford **1** as a dark red solid: 880 mg (82%). ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 9.96 (br, 2H), 8.86-8.77 (m, 2H), 8.75-8.63 (m, 8H), 8.24 (br, 2H), 7.94 (s, 2H), 7.84 (d, 4H, $J = 8.0$ Hz), 7.67 (d, 4H, $J = 8.0$ Hz), 5.24-5.14 (m, 4H), 2.34-2.18 (m, 8H), 1.93-1.80 (m, 8H), 1.39-1.18 (m, 82H), 0.87-0.80 (m, 24H). ^{13}C NMR (CDCl_3 , 300 MHz, ppm): δ 165.0, 164.0, 163.8, 163.0, 152.3, 143.9, 139.0, 136.3, 134.7, 134.1, 132.0, 131.6, 131.0, 129.4, 128.9, 127.5, 127.0, 126.7, 126.3, 123.7, 123.1, 122.5, 120.2, 100.8, 95.8, 55.1, 35.1, 32.7, 32.1, 31.6, 30.3, 29.6, 27.3, 23.0, 14.4. MS (ESI): Calcd. for $\text{C}_{130}\text{H}_{150}\text{N}_4\text{O}_8$: 1896.2. Found: 1897.2 ($\text{M} + \text{H}^+$). Elem. Anal.: Calcd. for $\text{C}_{130}\text{H}_{150}\text{N}_4\text{O}_8$: C, 82.33; H, 7.97; N, 2.95. Found: C, 82.00; H, 7.90; N, 2.90.

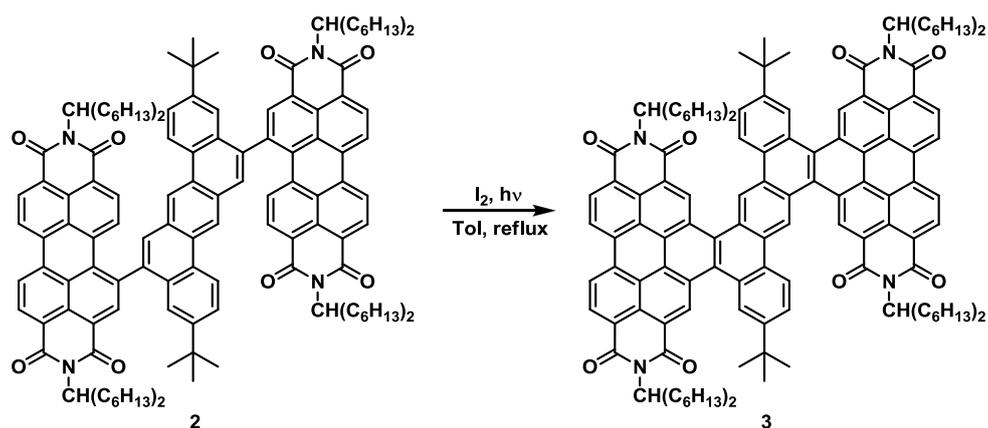


Compound 6. To a solution of compound **1** (735 mg, 0.388 mmol) in degassed CH_2Cl_2 was added dropwise a solution of ICl (138 mg, 0.850 mmol) in degassed CH_2Cl_2 at -41°C . The reaction mixture was stirred at -41°C for 0.5 h. After the reactant was completely consumed, a saturated Na_2SO_3 solution was added to remove the excess ICl, and the mixture was allowed to warm to room temperature gradually. The organic layer was collected, dried over anhydrous Na_2SO_4 , and then condensed under reduced pressure. The residue was purified with column chromatography over silica gel, eluted with PE/DCM (2:1 to 1:2, v/v) to afford **6** as a red solid: 740 mg (88.7%). ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 9.81 (s, 2H), 9.00 (d, 2H, $J = 8.7$ Hz), 8.84 (br, 4H), 8.79-8.72 (m, 4H), 8.54 (br, 2H), 8.14 (d, 2H, $J = 8.4$ Hz), 7.99 (br, 2H), 7.90 (dd, 2H, $J = 9.0$ Hz, 1.5 Hz), 7.54-7.50 (m, 2H), 5.30-5.00 (m, 4H), 2.40-2.05 (m, 8H), 2.00-1.65 (m, 8H), 1.50-1.05 (m, 82H), 0.95-0.75 (m, 24H). ^{13}C NMR (CDCl_3 , 300 MHz, ppm): δ 164.8, 164.3, 163.8, 163.2, 151.8, 147.0, 143.1, 137.2, 136.7, 135.3, 134.3, 133.6, 131.8, 131.5, 131.1, 130.3, 130.0, 129.2, 129.0, 127.7, 127.6, 127.0, 126.9, 123.9, 123.6, 123.3, 123.1, 123.0, 104.7, 54.9, 54.6, 34.8, 32.4, 32.3, 31.8, 31.7, 31.0, 30.7, 29.7, 29.2, 29.1, 27.0, 26.9, 22.6, 22.5, 14.1, 14.0. MS (ESI): Calcd. for $\text{C}_{130}\text{H}_{148}\text{I}_2\text{N}_4\text{O}_8$: 2147.9. Found: 2148.9 ($\text{M} + \text{H}^+$). Elem. Anal.: Calcd. for $\text{C}_{130}\text{H}_{148}\text{I}_2\text{N}_4\text{O}_8$: C, 72.68; H, 6.94; N, 2.61. Found: C, 72.28; H, 6.71; N, 2.54.



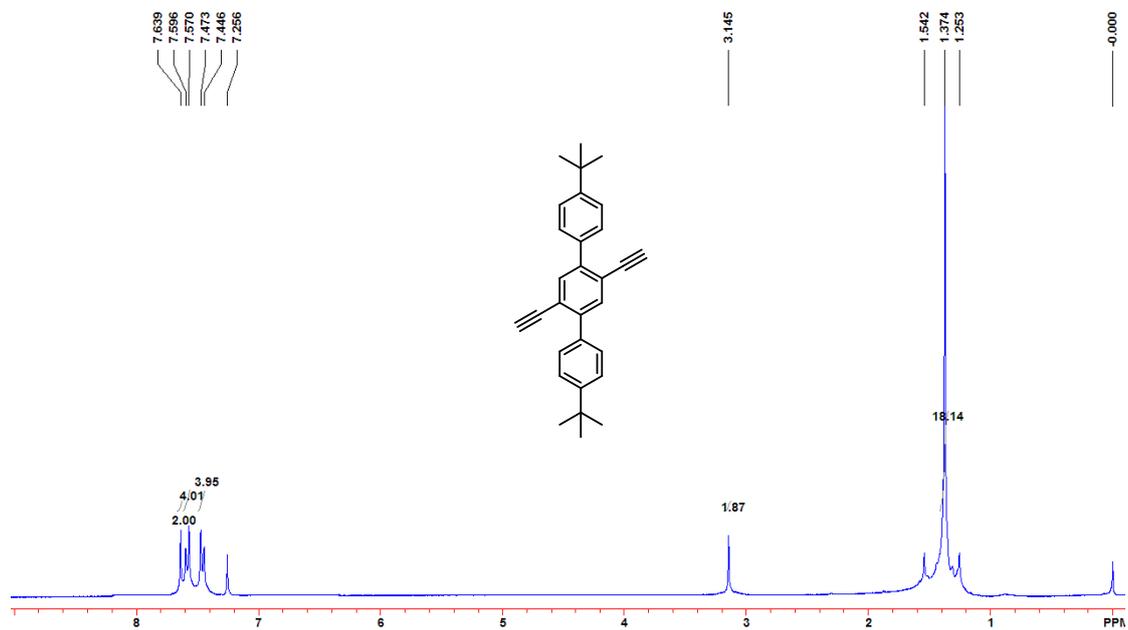
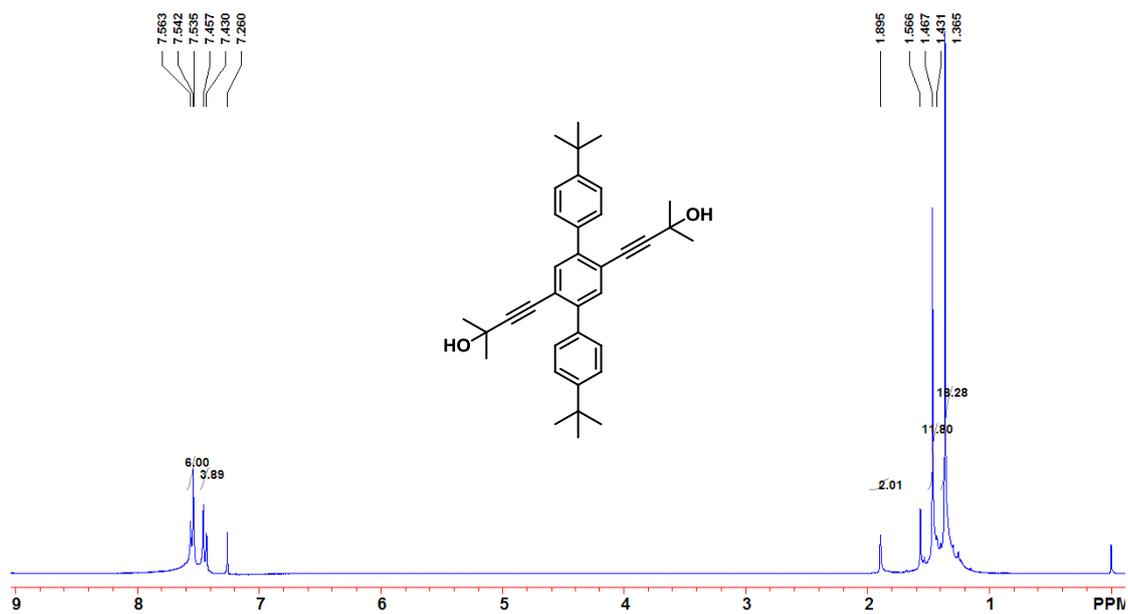
Compound 2. To a schlenk tube containing compound **6** (32 mg, 0.015 mmol), CuI (6 mg, 0.032 mmol), L-proline (5 mg, 0.043 mmol), and K_2CO_3 (10 mg, 0.072 mmol) was added degassed DMF (3 mL). The tube was then sealed under nitrogen atmosphere. The reaction mixture was maintained at 80°C for 10 min until the solution turned dark purple, then heated to 120°C for 3 h. TLC was taken every 30 min to monitor the reaction until completion. After being cooled to room temperature, the mixture was poured into aq. HCl (1 M, 20-30 mL). The precipitated solid was then collected by filtration and washed with CH_3OH (10-15 mL) for 3 times. The crude product (27 mg) was

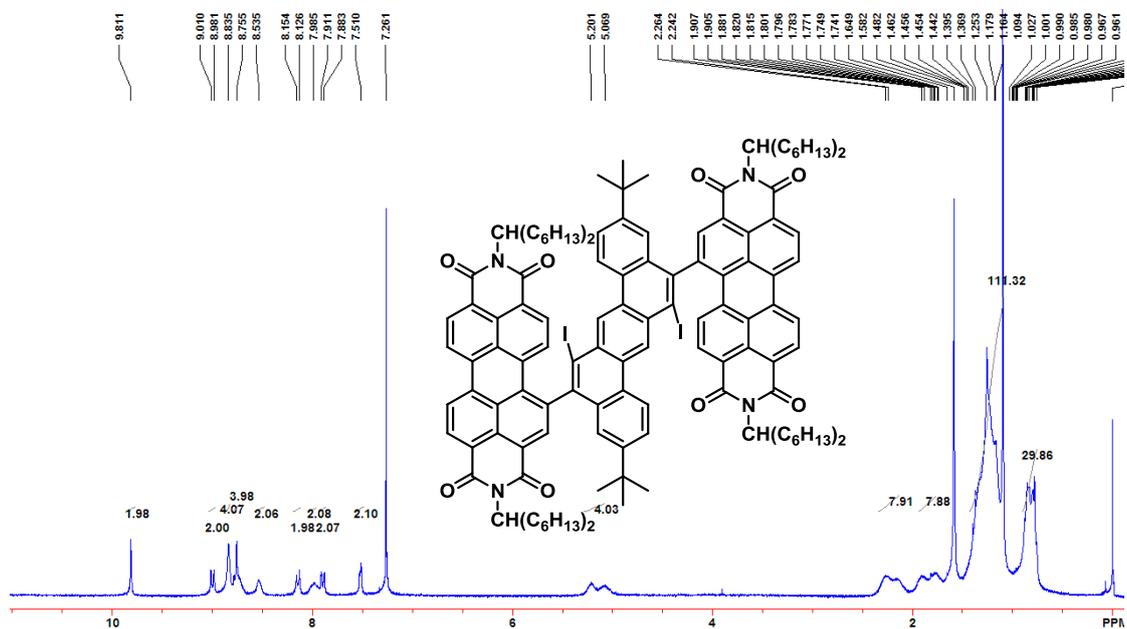
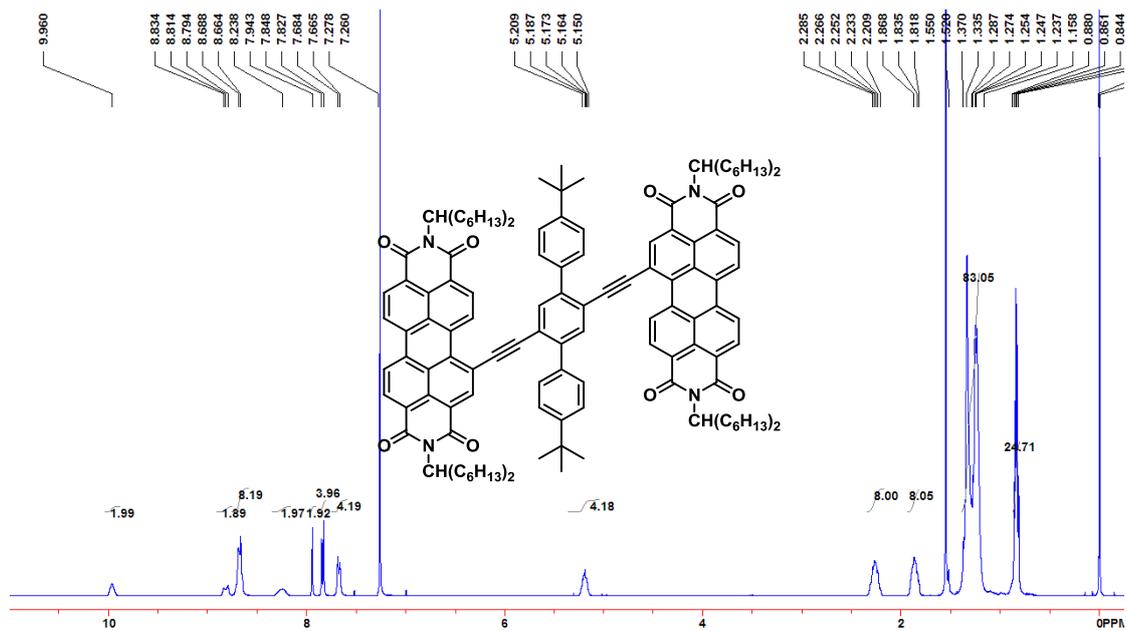
used in the next step without further purification: **2a** ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 9.28 (s, 2H), 8.95-8.65 (m, 12H), 8.35 (s, 2H), 8.06 (d, 2H, $J = 8.4$ Hz), 7.85 (br, 2H), 7.73 (d, 2H, $J = 7.5$ Hz), 7.57 (s, 2H), 5.32-5.00 (m, 4H), 2.40-2.05 (m, 8H), 2.00-1.70 (m, 8H), 1.45-1.10 (m, 82H), 0.90-0.50 (m, 24H). ^{13}C NMR (CDCl_3 , 300 MHz, ppm): δ 165.0, 150.4, 140.0, 139.2, 135.7, 134.9, 134.5, 134.2, 133.7, 131.2, 129.4, 129.3, 129.0, 128.9, 128.7, 127.7, 127.0, 125.9, 123.6, 122.9, 121.8, 121.7, 115.7, 54.6, 34.6, 32.4, 31.8, 30.8, 29.7, 29.3, 29.1, 27.0, 26.8, 22.6, 22.5, 14.1, 14.0. MS (ESI): Calcd. for $\text{C}_{130}\text{H}_{150}\text{N}_4\text{O}_8$: 1896.2. Found: 1897.1 ($\text{M} + \text{H}^+$). Elem. Anal.: Calcd. for $\text{C}_{130}\text{H}_{150}\text{N}_4\text{O}_8$: C, 82.33; H, 7.97; N, 2.95. Found: C, 82.11; H, 8.26; N, 2.87. **2b** ^1H -NMR (CDCl_3 , 300 MHz, ppm): δ 9.27 (s, 2H), 8.95-8.65 (m, 12H), 8.32 (s, 2H), 8.06 (d, 2H, $J = 8.4$ Hz), 7.80 (br, 2H), 7.73 (d, 2H, $J = 8.4$ Hz), 7.60 (s, 2H), 5.32-5.00 (m, 4H), 2.40-2.05 (m, 8H), 2.00-1.70 (m, 8H), 1.45-1.10 (m, 82H), 0.90-0.50 (m, 24H).

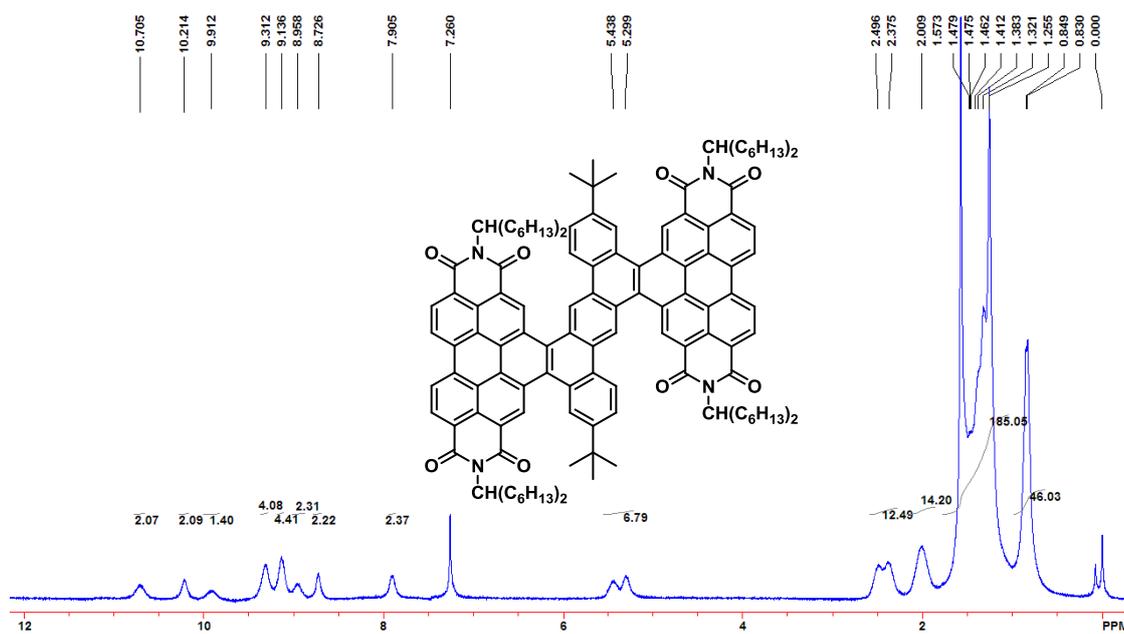
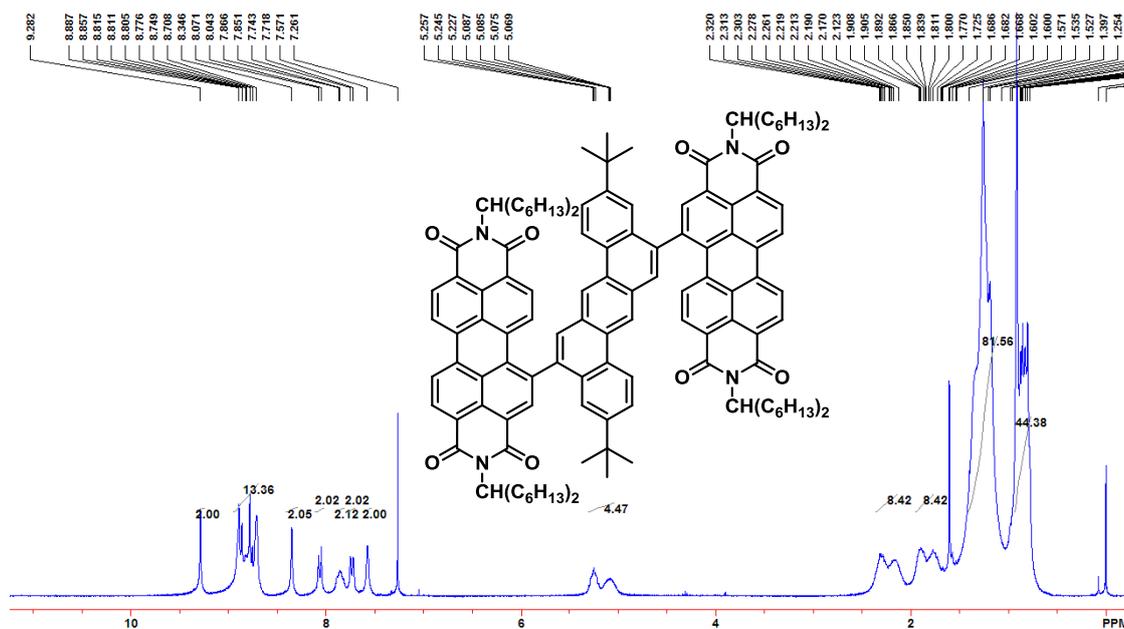


Compound 3. To a photoreaction tube containing crude compound **2** (27 mg) was added degassed iodine (18.9 mg, 0.074 mmol) solution in toluene (10 mL). The tube was sealed under nitrogen atmosphere. The reaction mixture was irradiated with the UV lamp at 120 °C with strong stirring for 8 h. After being cooled to room temperature, the mixture was dilute with PE, washed with saturated Na_2SO_3 (aq.) and brine sequentially. The organic layer was collected and the solvent was removed under reduced pressure. The residue was purified with column chromatography over silica gel, eluted with PE/DCM (3:2, v/v) to afford **3** as a red solid: 19 mg (67.5% for 2 steps). ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 10.71 (br, 2H), 10.21 (br, 2H), 9.91 (br, 2H), 9.31 (br, 4H), 9.14 (br, 4H), 8.96 (br, 2H), 8.73 (br, 2H), 7.91 (br, 2H), 5.45-5.23 (m, 4H), 2.60-2.30 (m, 8H), 2.10-1.90 (m, 8H), 1.50-1.10 (m, 82H), 0.95-0.70 (m, 24H). ^{13}C NMR (CDCl_3 , 300 MHz, ppm): δ 165.4, 164.9, 164.1, 151.2, 133.5, 132.9, 132.7, 130.3, 129.3, 128.4, 128.1, 127.1, 127.0, 126.6, 126.3, 125.6, 124.6, 124.4, 123.6, 123.2, 122.9, 122.0, 55.3, 55.2, 35.1, 32.0, 31.8, 31.5, 29.7, 29.3, 22.7, 14.1. MS (ESI): Calcd. for $\text{C}_{130}\text{H}_{146}\text{N}_4\text{O}_8$: 1892.1. Found: 1893.1 ($\text{M} + \text{H}^+$). Elem. Anal.: Calcd. for $\text{C}_{130}\text{H}_{146}\text{N}_4\text{O}_8$: C, 82.50; H, 7.78; N, 2.96. Found: C, 82.31; H, 8.00; N, 2.96

II. Copies of ^1H NMR Spectra of Synthesized Compounds







III. UV-vis Absorption and Electrochemical Characterizations

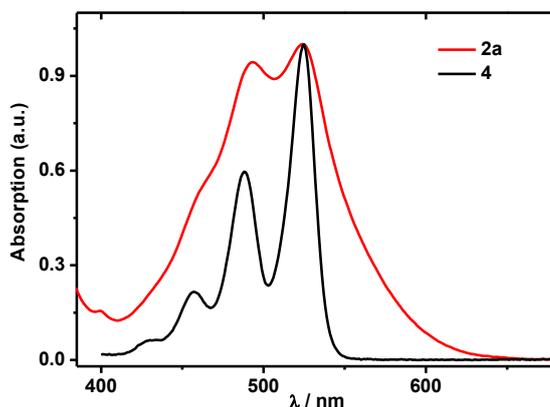


Figure S1 Normalized UV-vis absorption spectra of compounds **2a** and **4**

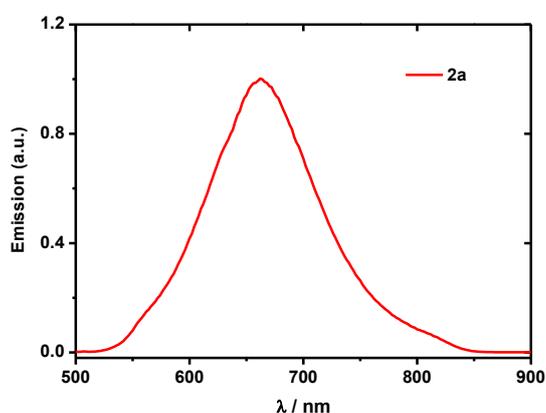


Figure S2 Emission spectrum of compound **2a**

Cyclic voltammograms (CVs) were recorded on a BASI Epsilon workstation using glassy carbon discs as the working electrode and Pt plate as the counter electrode. Ag/AgCl electrode as the reference electrode, and ferrocene/ferrocenium was the internal reference. The scan speed was 100 mV s^{-1} . The measurement was carried out with CH_2Cl_2 solutions using tetrabutylammonium hexafluorophosphate (TBAPF_6 , 0.1 M) as the supporting electrolyte. The energy level of Fc/Fc^+ is assumed to be -4.8 eV below the vacuum level. The LUMO level of compound **1** and **4** were estimated from the half-wave potentials of the first reduction peaks.

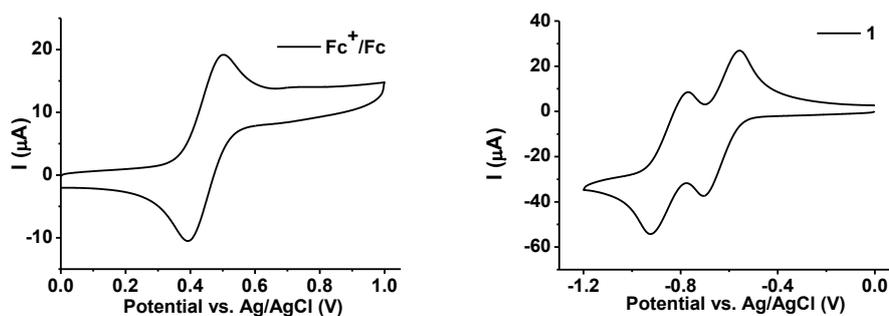


Figure S3 Cyclic voltammograms of ferrocene and **1** in CH_2Cl_2

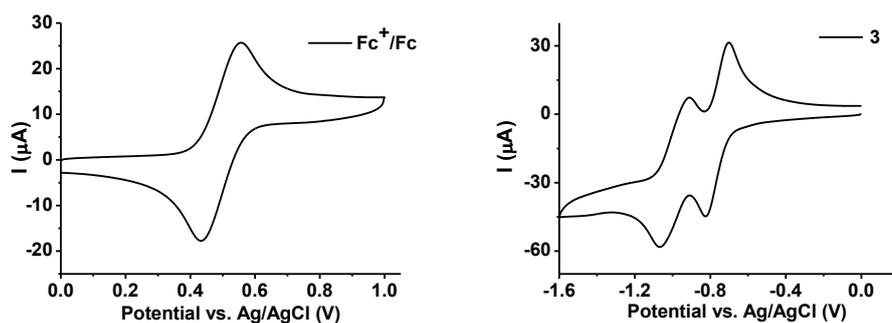


Figure S4 Cyclic voltammograms of ferrocene and **3** in CH₂Cl₂

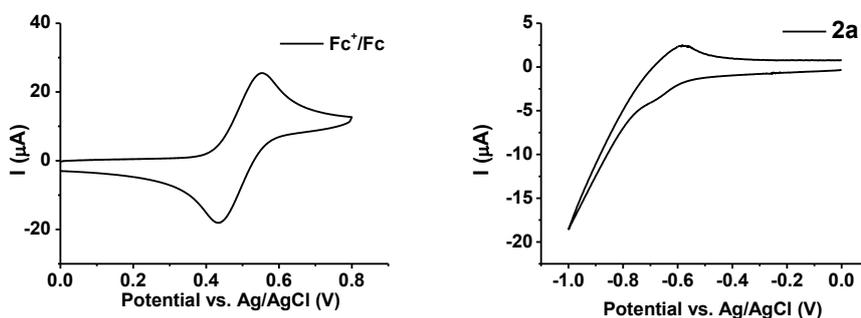


Figure S5 Cyclic voltammograms of ferrocene and **2a** in CH₂Cl₂

V. Computations

The geometry was optimized with Density Functional Theory (DFT) using B3LYP hybrid functional with a basis set limited to 6-31g**. All *N*-hexylheptyl substituents were replaced with methyl groups in calculations, and hydrogen atoms were omitted for clarity.

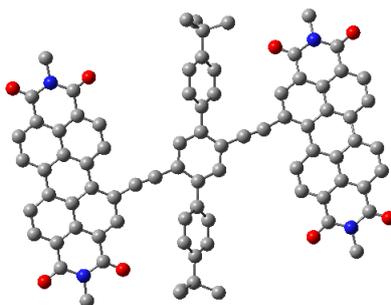


Figure S6 DFT calculated conformation of compound **1**

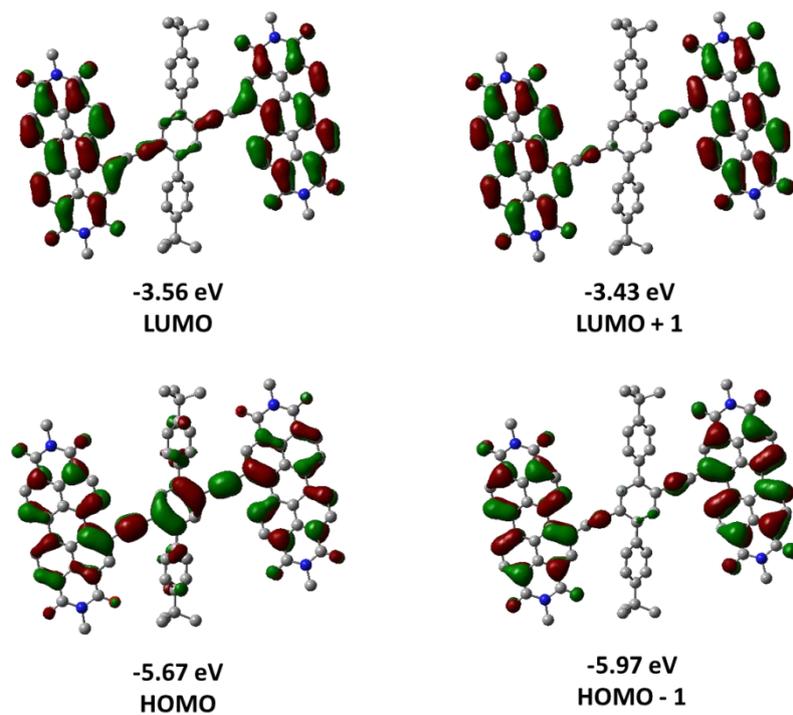


Figure S7 DFT calculated frontier molecular orbitals (FMOs) of compound **1**

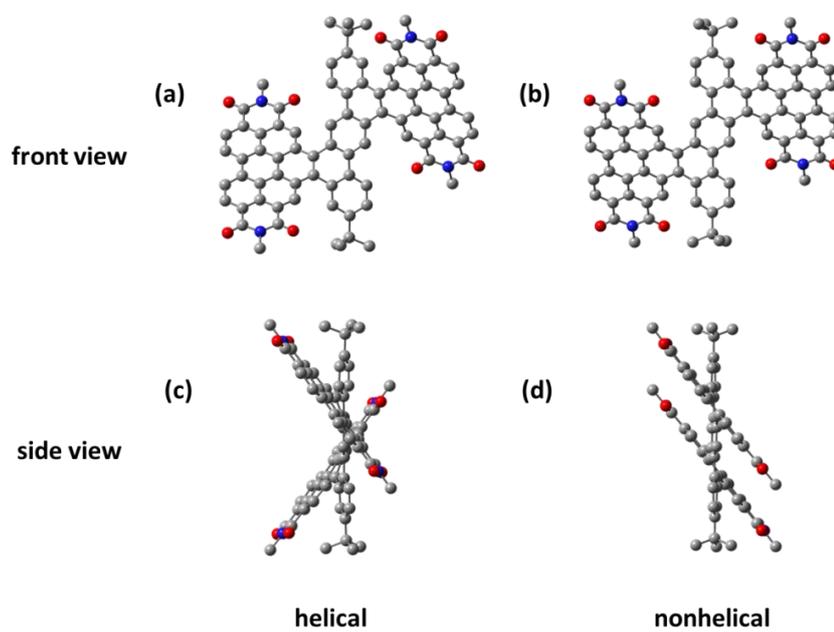


Figure S8 DFT calculated conformations of compound **3**

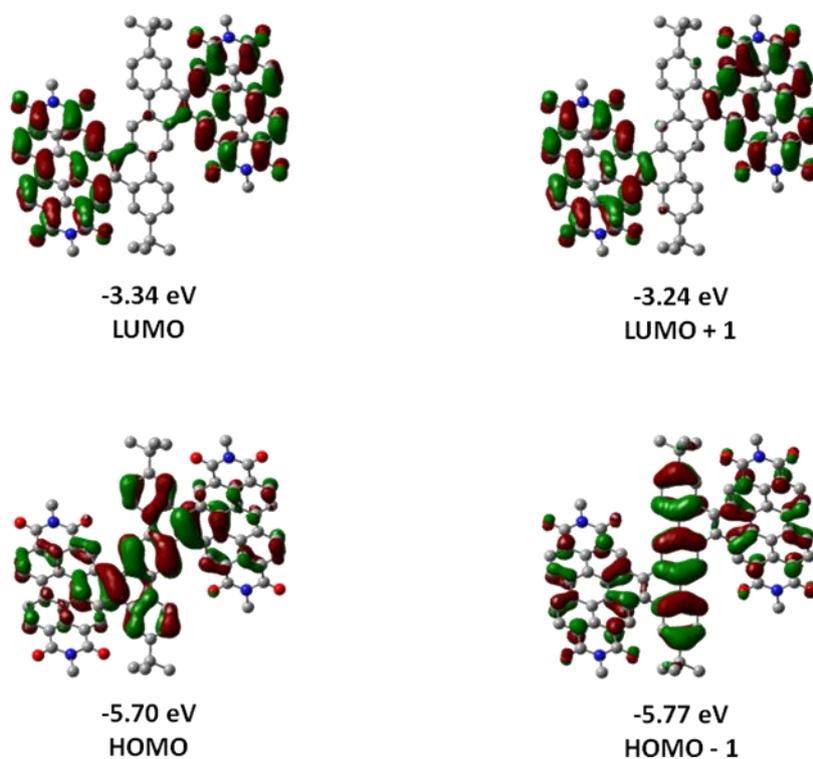


Figure S9 Optimized helical conformation and FMOs of compound **3**

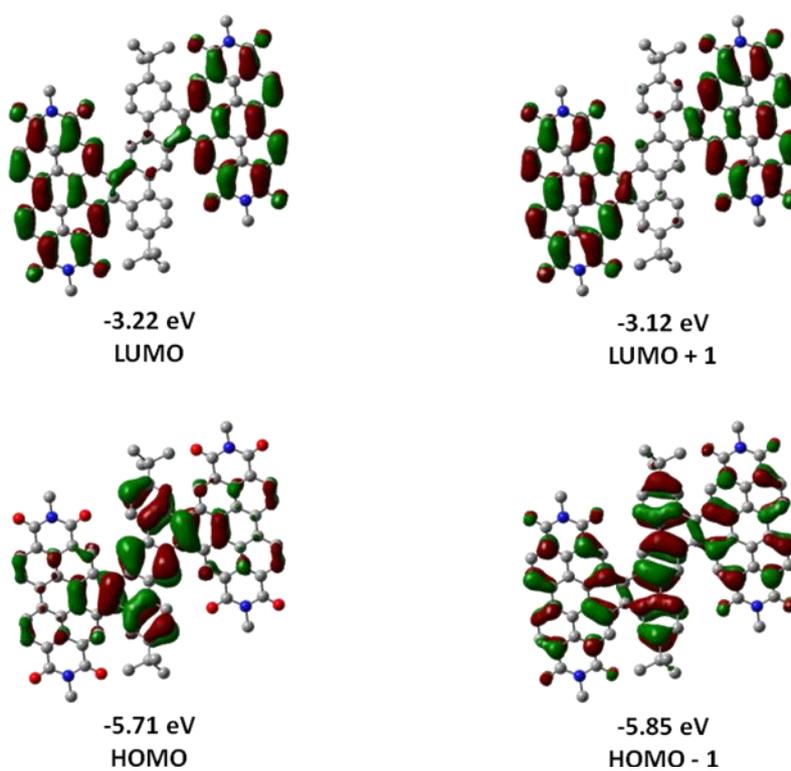


Figure S10 Optimized nonhelical conformation and FMOs of compound **3**

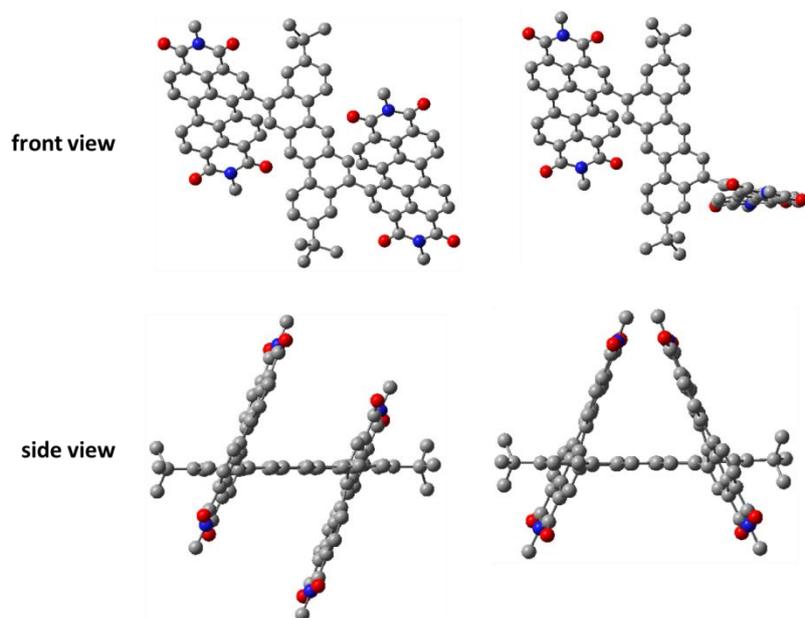


Figure S11 DFT calculated two possible conformations of compound **2**

VI. TGA and DSC Analyses

Thermal gravity analyses (TGA) traces of compounds **1**, **2a** and **3** were recorded on a TA Instrument Q600 analyzer, and the measured decomposition temperatures under nitrogen atmosphere were ca. 334, 355 and 356 °C, respectively.

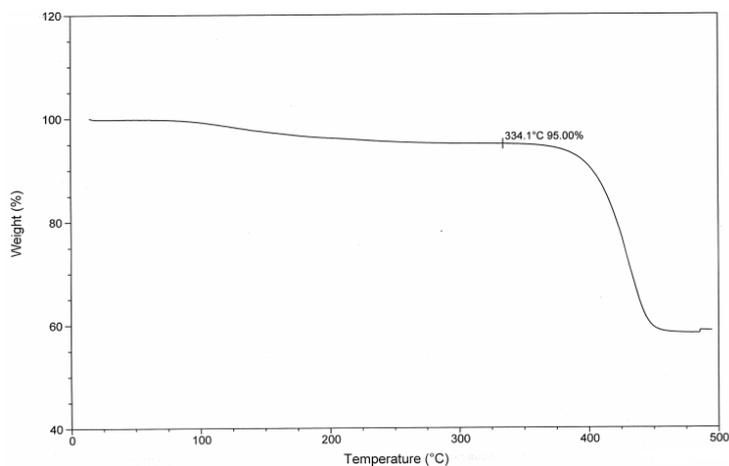


Fig S12 TGA trace of compound **1**

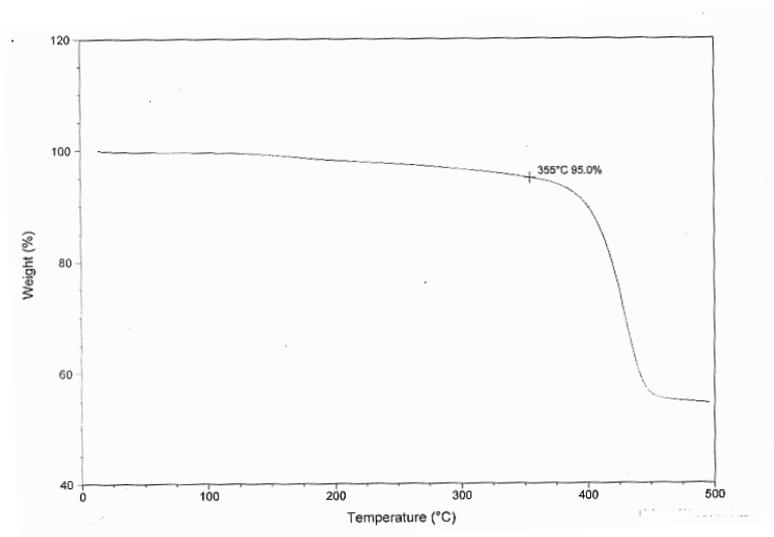


Fig S13 TGA trace of compound **2a**

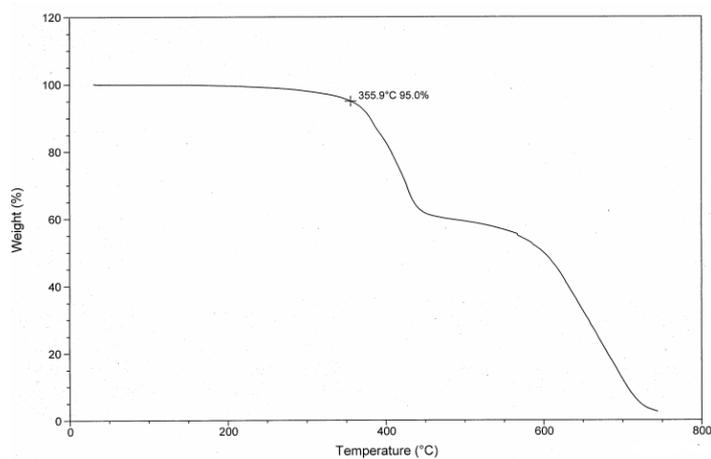


Figure S14 TGA trace of compound **3**

Differential scanning calorimetry analyses (DSC) were performed on a METTLER TOLEDO Instrument DSC822 calorimeter. The DSC traces were measured under nitrogen atmosphere with a scan rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

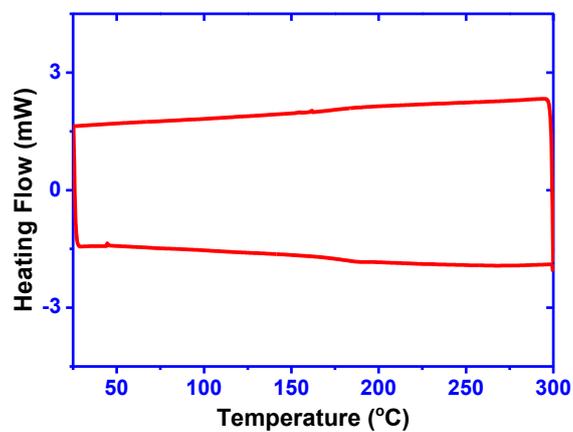


Figure S15 DSC trace of compound **1**

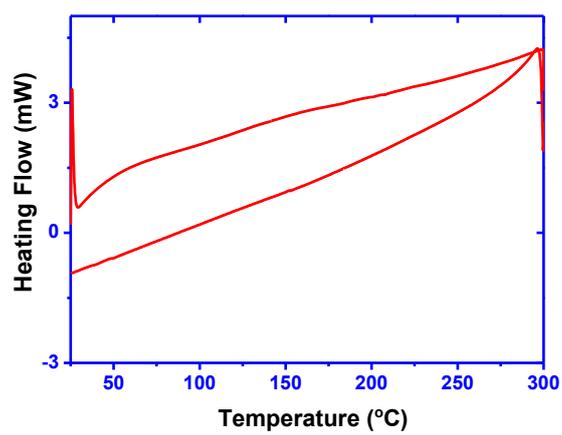


Figure S16 DSC trace of compound **2a**

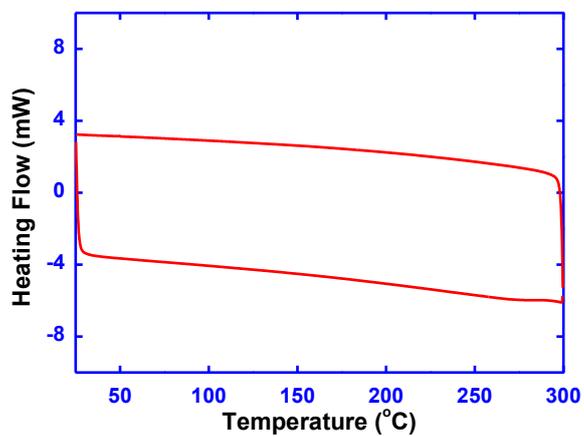


Figure S17 DSC trace of compound **3**