

Electronic Supplementary Information

Pyrene fused perylene diimides: synthesis, characterization and applications in organic field-effect transistors and optical limiting with high performance

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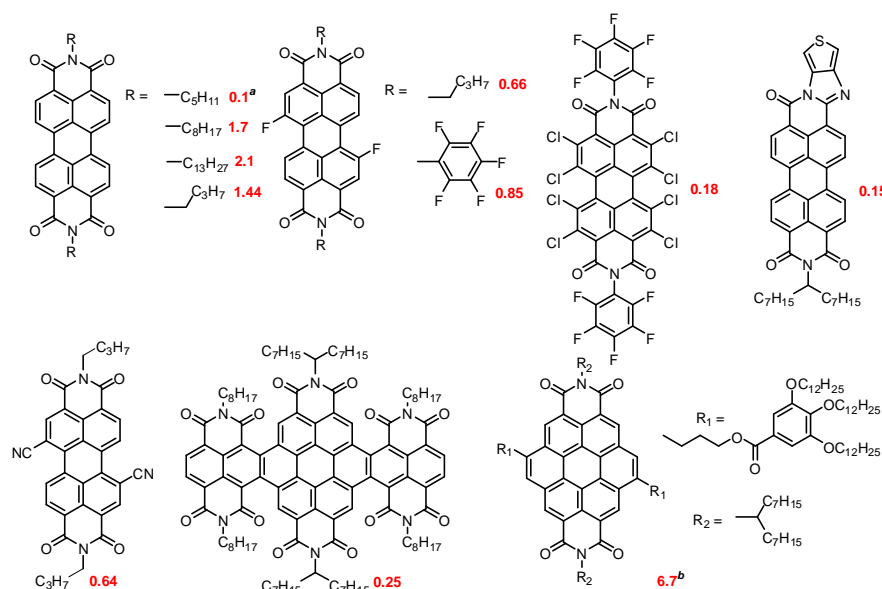


Chart S1. Chemical structure of PDI derivatives used in OFET. (^a All the molecules were n-type, the unit is $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$; ^b Measured using the space-charge limited current)

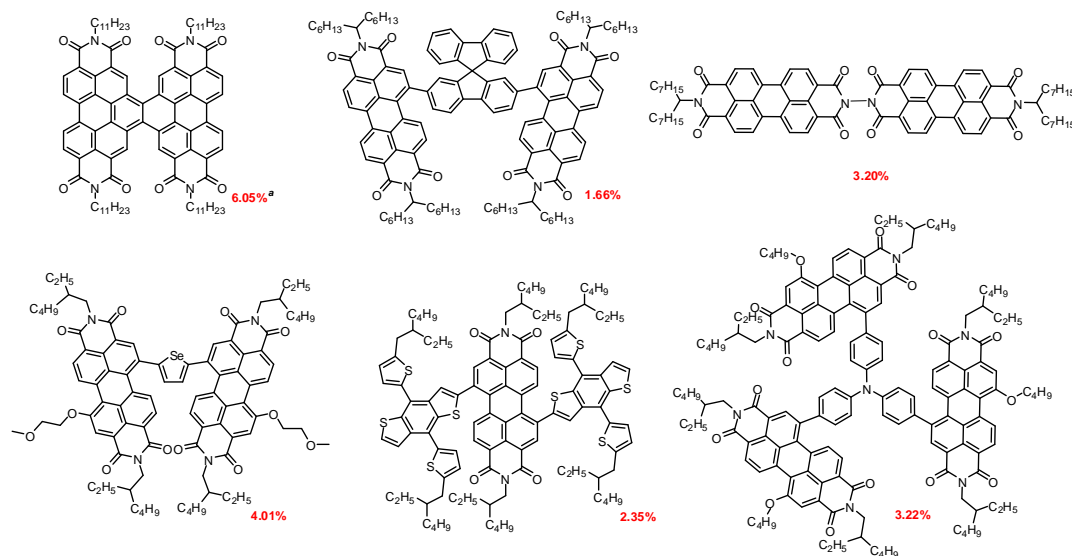


Chart S2. Chemical structure of several representative PDI derivatives used as acceptors in polymer solar cells. (^a PCE value)

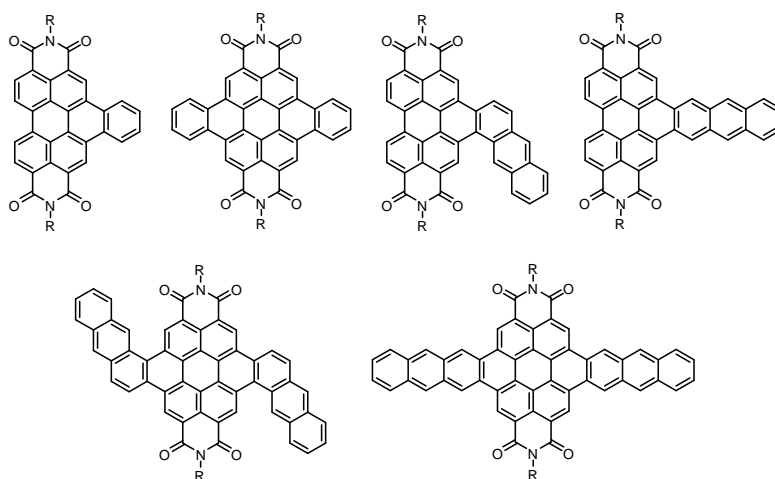


Chart S3. Representative hydrocarbon aromatic rings fused PDI derivatives reported in literatures.



Figure S1. Photographs of the six PDI derivatives. (From left to right: **1**, **2**, **3**, **4**, **5** and **6**; concentration: 10⁻⁴ M in DCM)

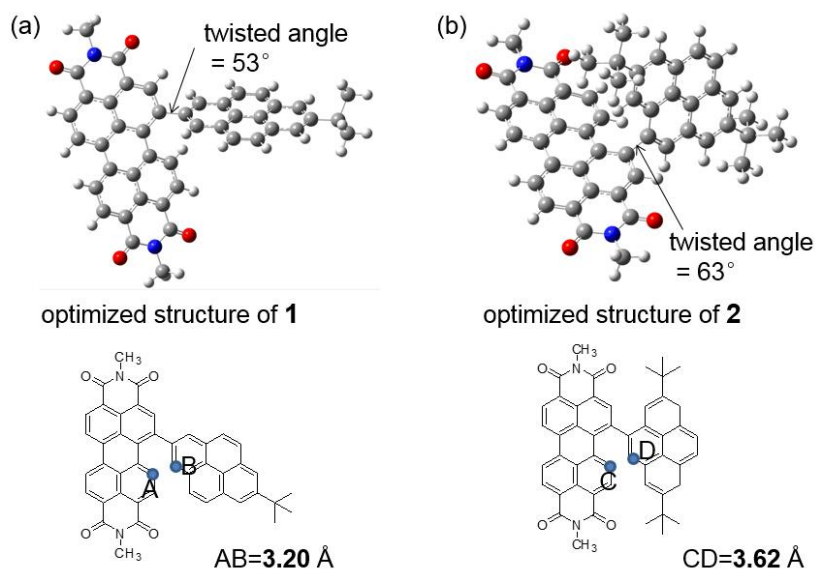


Figure S2. Optimized structures of **1** and **2**. Selected twisted angles and distances in the optimized structures are shown.

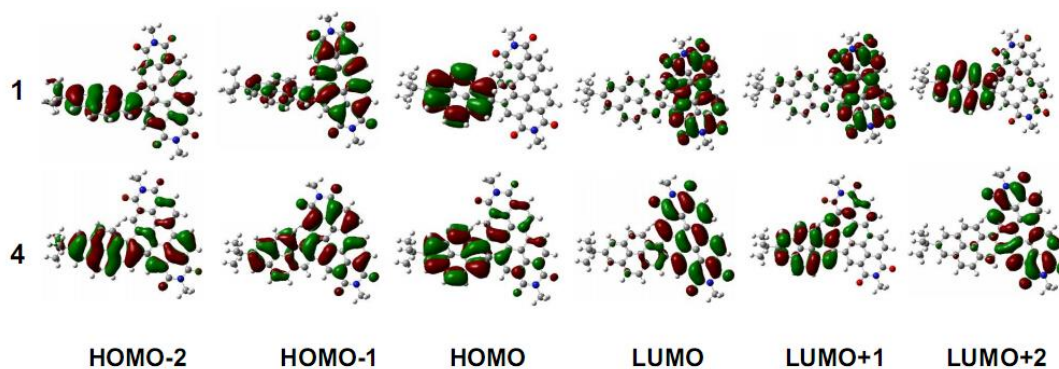


Figure S3. HOMO and LUMO of **1** and **4** calculated by B3LYP/6-31G* level using Gaussian 09 program.

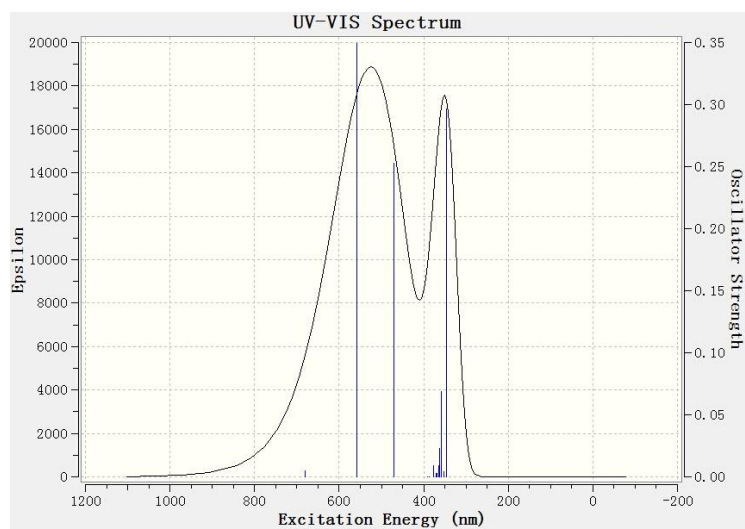


Figure S4. Calculated UV spectrum of compound **1**.

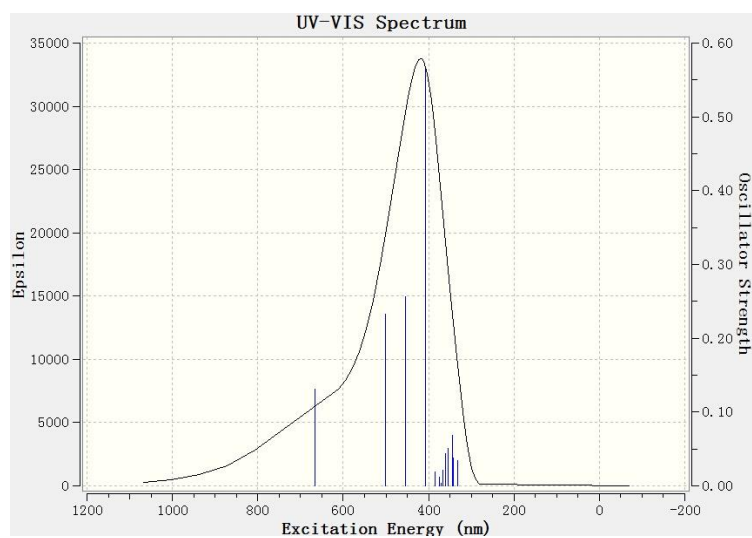


Figure S5. Calculated UV spectrum of compound **4**.

Table S1. Absorption wavelengths and oscillator strength of **1** evaluated by the TD-DFT (B3LYP/6-311G (d, p)) calculation.

Excitation energies	Absorption[nm] (oscillator strength)	Assignments (%)
1.82 eV	679.37 (0.0052)	HOMO→LUMO (98)
2.22 eV	558.00 (0.35)	HOMO-1→LUMO (92)
2.64 eV	469.53 (0.25)	HOMO-2→LUMO (91)
3.58 eV	346.35 (0.30)	HOMO→LUMO+2 (47) HOMO→LUMO+4 (13) HOMO→LUMO+1 (8)

Table S2. Absorption wavelengths and oscillator strength of **4** evaluated by the TD-DFT (B3LYP/6-311G (d, p)) calculation.

Excitation energies	Absorption[nm] (oscillator strength)	Assignments (%)
1.86 eV	666.02 (0.13)	HOMO→LUMO (97)
2.48 eV	500.65 (0.23)	HOMO-1→LUMO (84) HOMO-2→LUMO (8)
2.73 eV	453.63 (0.26)	HOMO-2→LUMO (84)
3.04 eV	407.33 (0.56)	HOMO→LUMO+1 (85) HOMO-1→LUMO (3)

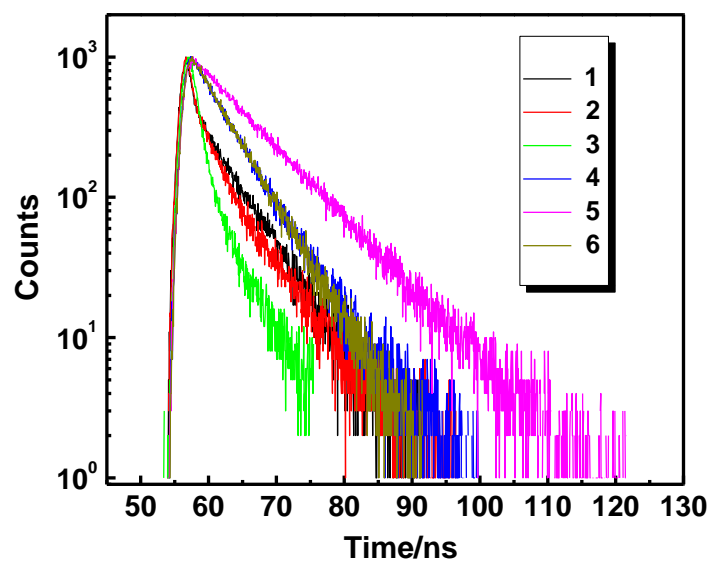


Figure S6. Emission decay of **1-6** in DCM solution at room temperature.

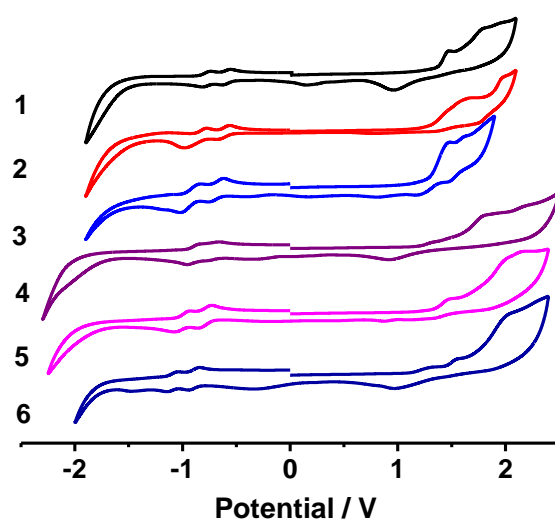


Figure S7. Cyclic voltammograms of compounds **1-6** recorded in dichloromethane.

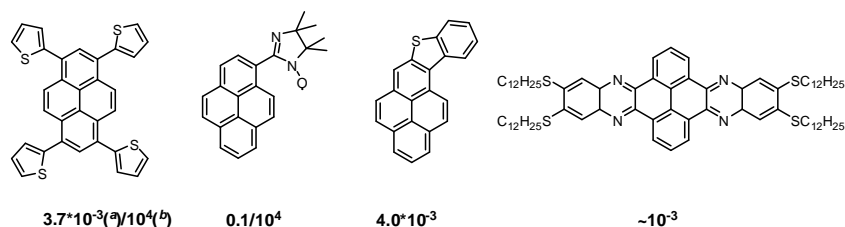
Table S3 Some electrochemical and photophysical data of the PDI derivatives.

no.	HOMO(eV)	LUMO(eV)	E_g (eV)	A_1/A_2^e (%)	τ_1/τ_2^f (ns)	τ^g (ns)	Φ_f^h (%)
1	-5.68 ^a /-5.57 ^b	-3.59 ^c /-3.34 ^b	2.09 ^d /2.23 ^b	88/12	0.30/5.53	0.95	2.89
2	-5.64/-5.47	-3.57/-3.32	2.07/2.15	14/86	2.45/0.15	0.48	0.13
3	-5.59/-5.38	-3.68/-3.21	1.91/2.17	91/9	1.05/4.56	1.37	0.24
4	-5.54/-5.45	-3.68/-3.23	1.86/2.22	19/81	3.19/5.50	5.05	1.12
5	-5.61/-5.58	-3.61/-3.17	2.00/2.41	100/0	8.51/---	8.51	21.1
6	-5.45/-5.32	-3.56/-3.00	1.89/2.32	100/0	5.15/---	5.15	20.2

^aCalculated from the onset oxidation potentials of the compounds. ^bTheoretical calculated value. ^cEstimated using empirical equations $E_{LUMO} = E_{HOMO} + E_g$. ^dBand gap estimated from optical absorption band edge of the solution. ^ePercentage of the corresponding lifetime (τ_1 and τ_2). ^fDifferent lifetime of lived species, fitted by one (**5** and **6**) or two (**1**, **2**, **3** and **4**) exponential. ^gAverage lifetime. ^hDetermined in dichloromethane solution.

Table S4 Detailed OFET performance of the PDIs annealed at different temperature.

	Tannealing [°C]					
	RT	80	120	160	200	240
μ [cm ² .V ⁻¹ .s ⁻¹]	1.8E-5 ~7.2E-5	6.0E-5 ~1.34E-4	0.18~0.29	0.84~1.13	0.33~0.64	
lg(I_{on}/I_{off})	3—4	3—4	5—7	7—8	6—7	
$V_{threshold}$ [V]	-25~-26	-23~-44	-4~-10	-9~-10	-15~-24	

**Chart S4.** Pyrene derivatives used in OFET reported in literatures. (^a Hole mobility reported, the unit is cm²V⁻¹s⁻¹; ^b on/off ratio)

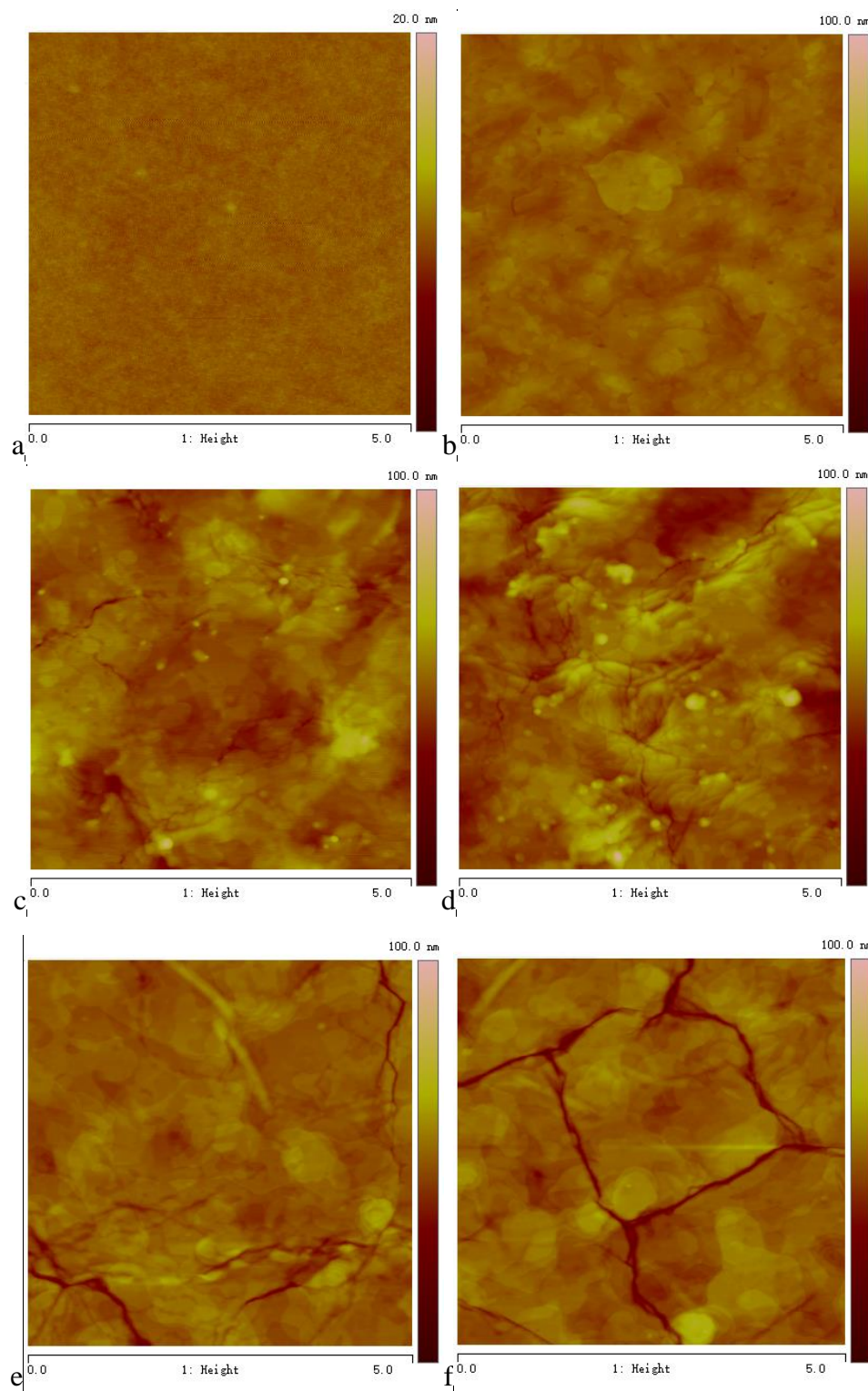


Figure S8. AFM images of thin films of **6** annealed at different temperature: (a) pristine; (b) 80 °C; (c) 120 °C; (d) 160 °C; (e) 200 °C; (f) 240 °C.

Experimental Section

Materials

THF was dried over and distilled from K-Na alloy under atmosphere of argon. All other chemicals and reagents were purchased from commercial suppliers and used without further purification unless otherwise specified. N, N'-bis (2-decyltetradecyl)-perylene-1,4,5,8-tetracarboxylic acid diimide (DT-PDI) and was synthesized according to literature procedures.¹ Pyrene boronic acid esters 2-(7-(*tert*-butyl)pyren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**A1**) and (2,7-di-(*tert*-butyl)pyren-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**A2**) were also synthesized according to literature.²

¹H and ¹³C NMR spectra were measured on a Varian Mercury 300 with TMS as internal standard. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a CARLOERBA-1106 microanalyzer. HRMS spectra were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF (matrix-assisted laser desorption/ionization-time-of-flight) mode with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) as the matrix. UV-vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrometer. Photoluminescence spectra were recorded on a Hitachi F-4500 fluorescence spectrometer. And fluorescence quantum yields were determined by optical dilute method with DT-PDI in DCM as reference ($\Phi_F = 1.0$).³ The emission decay profiles were measured with an HORIBA Temprow fluorescence lifetime spectrometer. Cyclic voltammetry (CV) was carried out on a CHI voltammetric analyzer in a three-electrode cell with a Pt counter electrode, a Ag/AgCl reference electrode, and a glassy carbon working electrode at a scan rate of 100 mVs⁻¹ with 0.1 M tetrabutylammonium perchlorate (purchased from Alfa Aesar) as the supporting electrolyte, in anhydrous dichloromethane solution purged with nitrogen. The potential

values obtained in reference to the Ag/Ag⁺ electrode were converted to values versus the saturated calomel electrode (SCE) by means of an internal ferrocenium/ferrocene (Fc⁺/Fc) standard. The X-ray diffraction (XRD) measurements were carried out using D/max 2500 X-Ray Diffractometer, with scan scale from 2 ° to 30 °, 5 %/min. The atomic force microscope (AFM) measurements were carried out using Veeco Nanoscope IV, tapping mode.

The geometrical and electronic properties were optimized at B3LYP/6-31G* level using Gaussian 09 program. The molecular orbitals were obtain at the same level of theory.

Devices Fabrication

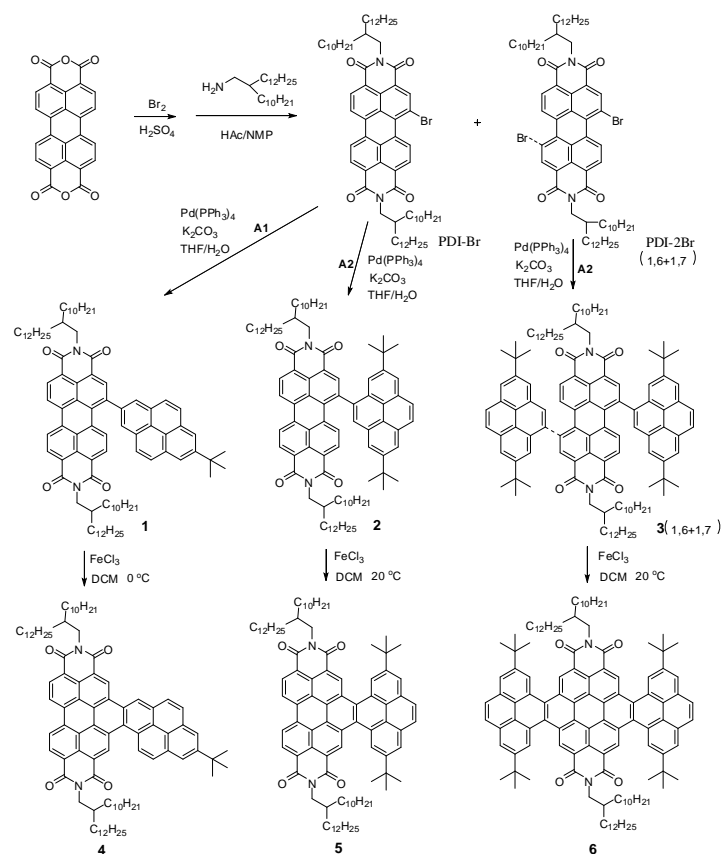
OTFT devices were fabricated in a bottom-contact configuration. Before the deposition of organic semiconductors, source and drain electrodes made of gold were pre-prepared on the SiO₂/Si substrates. The octyltrichlorosilane (OTS) treatment was performed on the gate dielectrics which were placed in a vacuum oven with OTS at a temperature of 120 °C to form an OTS self-assembled monolayer. Then the thin film were spin-coated on the OTS modified SiO₂/Si substrates from the chloroform solutions. The OTFTs characteristics of the devices were determined at room temperature in air by using a Keithley 4200 SCS. The mobility of the devices was calculated in the saturation regime. The equation is listed as follows:

$$I_{DS} = (W / 2L) C_i \mu (V_{GS} - V_{th})^2$$

where W/L is the channel width / length, C_i is the insulator capacitance per unit area, and V_{GS} and V_{th} are the gate voltage and threshold voltage, respectively. The channel length of the interdigital gold electrode is 30 μm, and the channel width is 1400 μm. In addition, the thickness of gold electrode and SiO₂ layer are ~50 nm and 300 nm, respectively.

The Z-scan was performed by using a Q-switched Nd:YAG laser of 5 ns pulse length at 532 nm with a repetition of 10 Hz.

Synthesis



Scheme S1. Synthesis of the pyrene substituted PDI and their cyclization

PDI-Br and PDI-2Br:

A mixture of perylene-3,4,9,10-tetracarboxylic acid bisanhydride (10.0 g, 25.50 mmol) and 40 mL 98 wt% H_2SO_4 was stirred at room temperature for 12 h. I_2 (260 mg, 1.02 mmol) was then added, the mixture was heated to $85\text{ }^\circ\text{C}$ with vigorous stirring for 30 min. Then bromine (4.08 g, 25.50 mmol) was added dropwise over a time period of 3 h and the reaction mixture was stirred for 16 h at $85\text{ }^\circ\text{C}$. After being cooled to room

temperature, the mixture was poured into 100 g of ice. The precipitate was filtered, washed with 100 mL 50% sulfuric acid and then a large amount of H₂O until neutral. The residue was dried to give 11.3 g of red powder. The crude product was used for the next step directly.

A suspension of brominated perylene bisanhydrides (5.00 g) obtained in the above reaction, 2-decyl-1-tetradecylamine (10.40 g, 29.5 mmol), and acetic acid (3.0 mL) in 125 mL of N-methyl-2-pyrrolidinone was stirred at 85 °C under N₂ for 12 h. After the mixture was cooled to room temperature, the precipitate was separated by filtration, washed with 250 mL of MeOH, and dried in a vacuum. The crude product was purified by silica gel column chromatography. The first fraction was collected to afford **PDI-2Br**(**1,6-PDI-2Br** and **1,7-PDI-2Br**) as a solid. The second fraction afforded **PDI-Br** as a black solid (a small fraction of substitution byproduct also exist, but can be separated in the following steps). The **1,6-PDI-2Br** and **1,7-PDI-2Br** could not be separated by column chromatography.

PDI-Br:

¹H NMR (300 MHz, CDCl₃) δ (ppm): 9.81 (d, J=8.1 Hz, 1H), 8.93 (s, 1H), 8.72 (m, 3H), 8.62 (d, J=9.0 Hz, 2H), 4.14 (m, 4H), 2.00 (m, 2H), 1.21 (m, 80H), 0.85 (m, 12H). ¹³C NMR (400 MHz, CDCl₃) δ (ppm): 163.4, 163.1, 163.0, 162.2, 139.1, 133.1, 132.7, 132.4, 131.2, 130.6, 130.3, 128.5, 128.0, 127.6, 126.3, 123.5, 123.1, 122.5, 121.1, 45.1, 37.1, 32.4, 32.1, 30.6, 30.2, 29.8, 26.9, 24.2, 23.1, 14.5.

HRMS (MALDI-TOF, m/z): 1141.7379 ([M⁺], calcd for C₇₂H₁₀₅BrN₂O₄, 1140.7258).

Anal. Calcd for C₇₂H₁₀₅BrN₂O₄: C, 75.69; H, 9.26; N, 2.45. Found: C, 75.65; H, 9.37; N, 2.73.

1: A mixture of **PDI-Br** (400 mg, 0.35 mmol), **A1** (202 mg, 0.53 mmol), Pd(PPh₃)₄ (30 mg) and potassium carbonate (483 mg, 3.5 mmol) in THF (10 mL) and distilled

water (1.7 mL) was refluxed for 24 h under nitrogen in a 100 mL Schlenk tube. The mixture was extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na₂SO₄ and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum ether as eluent to afford the product as black solid in the yield of 83%.

¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.77 (s, 1H), 8.71 (t, J=7.5 Hz, 1H), 8.66 (m, 3H), 8.29 (s, 2H), 8.25 (s, 2H), 8.13 (d, J=9.0 Hz, 2H), 8.00 (d, J=9.0 Hz, 2H), 7.79 (d, J=8.1 Hz, 1H), 7.72 (d, J=8.1 Hz, 1H), 4.17 (d, J=7.2 Hz, 2H), 4.04 (d, J=6.9 Hz, 2H), 2.02 (m, 1H), 1.93 (m, 1H), 1.62 (s, 9H), 1.19 (m, 80H), 0.85 (m, 12H).

¹³C NMR (400 MHz, CDCl₃) δ (ppm): 163.4, 163.2, 163.1, 163.0, 149.7, 141.6, 139.1, 136.5, 134.1, 133.7, 132.4, 132.0, 131.0, 130.4, 129.8, 129.7, 128.4, 127.6, 127.4, 126.9, 126.8, 124.0, 123.8, 123.0, 122.9, 122.7, 122.4, 122.2, 121.9, 121.7, 44.6, 44.4, 36.6, 36.5, 35.3, 31.8, 31.7, 31.6, 30.0, 29.9, 29.8, 29.6, 29.3, 26.5, 26.4, 22.6, 14.0.

HRMS (MALDI-TOF, m/z): 1319.9460 ([M⁺], calcd for C₉₂H₁₂₂N₂O₄, 1318.9405).

Anal. Calcd for C₉₂H₁₂₂N₂O₄: C, 83.71; H, 9.32; N, 2.12. Found: C, 83.53; H, 9.51; N, 2.37.

2: A mixture of **PDI-Br** (300 mg, 0.26 mmol), **A2** (174 mg, 0.39 mmol), Pd(PPh₃)₄ (30 mg) and potassium carbonate (362 mg, 2.6 mmol) in THF (8 mL) and distilled water (1.3 mL) was refluxed for 24 h under nitrogen in a 100 mL Schlenk tube. The mixture was extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na₂SO₄ and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum ether as eluent to afford the product as black solid in the yield of 78%.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 8.88 (s, 1H), 8.83 (d, $J=7.5$ Hz, 1H), 8.77 (d, $J=8.1$ Hz, 1H), 8.71 (s, 1H), 8.32 (m, 3H), 8.15 (m, 3H), 8.08 (t, $J=8.4$ Hz, 1H), 7.86 (s, 1H), 7.65 (d, $J=8.7$ Hz, 1H), 4.19 (d, $J=6.3$ Hz, 2H), 4.02 (d, $J=6.6$ Hz, 2H), 2.05 (m, 1H), 1.89 (m, 1H), 1.61 (s, 9H), 1.19 (m, 80H), 0.84 (m, 12H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 163.7, 163.4, 163.1, 149.3, 148.6, 139.5, 137.5, 134.6, 134.4, 134.0, 133.5, 131.4, 130.9, 130.7, 130.6, 130.4, 129.0, 128.7, 128.5, 128.4, 127.8, 127.5, 126.6, 126.4, 123.5, 123.3, 123.2, 122.9, 122.8, 122.7, 122.5, 122.0, 119.7, 44.7, 44.5, 36.7, 36.4, 35.2, 34.8, 31.9, 31.8, 31.6, 31.2, 30.0, 29.9, 29.6, 29.2, 26.5, 26.4, 22.6, 14.0, 13.9.

HRMS (MALDI-TOF, m/z): 1376.1708 ($[\text{M}^+]$, calcd for $\text{C}_{96}\text{H}_{132}\text{N}_2\text{O}_4$, 1377.0187).

Anal. Calcd for $\text{C}_{96}\text{H}_{132}\text{N}_2\text{O}_4$: C, 83.67; H, 9.65; N, 2.03. Found: C, 83.42; H, 9.71; N, 2.12.

3: A mixture of **PDI-2Br** (195 mg, 0.16 mmol), **A2** (210 mg, 0.48 mmol), $\text{Pd}(\text{PPh}_3)_4$ (30 mg) and potassium carbonate (440 mg, 3.2 mmol) in THF (10 mL) and distilled water (1.6 mL) was refluxed for 24 h under nitrogen in a 100 mL Schlenk tube. The mixture was extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using dichloromethane/petroleum ether as eluent to afford the product as black solid in the yield of 75%. The mixture of **1,6-PDI-Pyrene** and **1,7-PDI-Pyrene** could not be separated and was used as a mixture in the next step.

4: A solution of compound **1** in DCM was degassed for 20 min in ice bath. The solution was bubbled through N_2 in the whole experiment. Then anhydrous FeCl_3 in CH_3NO_2 was slowly added by syringe. After being stirred for 30 min at 0 °C, the

reaction was quenched by adding methanol. The solvents was removed by rotary evaporation and the residue was purified by column chromatography on silica gel to give compound **4** as a black solid in the yield of 78%.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 9.75 (s, 1H), 9.17 (s, 1H), 8.68 (m, 4H), 8.52 (d, $J=8.7$ Hz, 2H), 8.28 (s, 2H), 8.18 (d, $J=9.0$ Hz, 1H), 7.84 (d, $J=8.7$ Hz, 1H), 7.63 (d, $J=8.1$ Hz, 1H), 4.13 (d, $J=6.3$ Hz, 2H), 3.83 (d, $J=6.9$ Hz, 2H), 1.98 (m, 2H), 1.77 (s, 9H), 1.26 (m, 80H), 0.79 (m, 12H).

^{13}C NMR (400 MHz, CDCl_3) δ (ppm): 163.1, 162.9, 150.2, 132.2, 131.5, 130.8, 130.1, 129.8, 129.1, 128.3, 128.2, 128.0, 126.8, 126.5, 125.9, 125.4, 125.3, 125.0, 124.8, 124.0, 123.5, 122.4, 122.2, 121.9, 121.8, 121.7, 121.4, 121.0, 120.8, 120.2, 117.0, 42.9, 42.2, 36.9, 36.6, 35.3, 32.0, 31.8, 31.6, 31.5, 31.2, 29.7, 29.4, 29.3, 29.2, 29.1, 26.6, 26.3, 22.6, 14.1, 14.0.

HRMS (MALDI-TOF, m/z): 1316.9269 ($[\text{M}^+]$, calcd for $\text{C}_{92}\text{H}_{120}\text{N}_2\text{O}_4$, 1316.9248).

Anal. Calcd for $\text{C}_{92}\text{H}_{120}\text{N}_2\text{O}_4$: C, 83.84; H, 9.18; N, 2.13. Found: C, 83.87; H, 9.25; N, 2.12.

5: A solution of compound **2** in DCM was degassed for 20 min in ice bath. The solution was bubbled through N_2 in the whole experiment. Then anhydrous FeCl_3 in CH_3NO_2 was slowly added by syringe. After being stirred for 30 min at 0°C , the reaction was stirred for 30 min at room temperature. Quenched by adding methanol, the solvents was removed by rotary evaporation and the residue was purified by column chromatography on silica gel to give compound **5** as a red solid in the yield of 73%.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 10.5 (s, 2H), 9.24 (d, $J=4.8$ Hz, 2H), 9.10 (s, 2H), 9.03 (d, $J=8.1$ Hz, 2H), 8.42 (s, 2H), 8.22 (s, 2H), 4.24 (d, $J=6.3$ Hz, 4H), 2.08 (m, 2H), 1.70 (s, 9H), 1.26 (m, 80H), 0.84 (m, 12H).

^{13}C NMR (400 MHz, CDCl_3) δ (ppm): 163.5, 149.3, 133.9, 132.3, 132.2, 131.0, 129.3, 127.9, 127.8, 127.7, 127.2, 126.9, 126.6, 126.1, 126.0, 123.8, 123.4, 123.2, 122.0, 121.9, 121.6, 121.0, 44.3, 36.6, 35.5, 31.8, 31.7, 30.1, 29.6, 29.3, 29.2, 26.4, 22.6, 14.0.

HRMS (MALDI-TOF, m/z): 1373.9950 ($[\text{M}^+]$, calcd for $\text{C}_{96}\text{H}_{130}\text{N}_2\text{O}_4$, 1375.0031).
Anal. Calcd for $\text{C}_{96}\text{H}_{130}\text{N}_2\text{O}_4$: C, 83.79; H, 9.52; N, 2.04. Found: C, 83.56; H, 9.71; N, 1.98.

6: A solution of compound **3** in DCM was degassed for 20 min in ice bath. The solution was bubbled through N_2 in the whole experiment. Then anhydrous FeCl_3 in CH_3NO_2 was slowly added by syringe. After being stirred for 30 min at $0\text{ }^\circ\text{C}$, the reaction was stirred for 1 h at room temperature. Quenched by adding methanol, the solvents was removed by rotary evaporation and the residue was purified by column chromatography on silica gel to give compound **6** as a red solid in the yield of 58%.

^1H NMR (300 MHz, CDCl_3) δ (ppm): 11.1 (s, 4H), 9.49 (s, 4H), 8.48 (s, 4H), 8.27 (s, 4H), 4.50 (d, $J=7.2\text{ Hz}$, 4H), 2.23 (m, 2H), 1.76 (s, 9H), 1.26 (m, 80H), 0.81 (m, 12H).

^{13}C NMR (400 MHz, CDCl_3) δ (ppm): 165.0, 149.2, 131.0, 130.9, 129.0, 127.5, 127.0, 126.5, 123.8, 123.5, 123.1, 122.2, 121.0, 44.8, 36.7, 35.5, 31.8, 31.7, 30.0, 29.6, 29.5, 29.4, 29.2, 29.1, 26.6, 22.5, 14.0, 13.9.

HRMS (MALDI-TOF, m/z): 1684.2430 ($[\text{M}^+]$, calcd for $\text{C}_{120}\text{H}_{154}\text{N}_2\text{O}_4$, 1687.1909).
Anal. Calcd for $\text{C}_{120}\text{H}_{154}\text{N}_2\text{O}_4$: C, 85.36; H, 9.19; N, 1.66. Found: C, 85.21; H, 9.34; N, 1.67.

Additional References:

1. W. Jiang, Y. Li, W. Yue, Y. Zhen, J. Qu and Z. Wang, *Org. Lett.*, 2010, **12**, 228.
2. A. C. Bédard, A. Vlassova, A. C. H-Perez, A. Bessette, G. S. Hanan, M. A. Heuft and S. K. Collins, *Chem. Eur. J.*, 2013, **19**, 16295.
3. Y. Li, L. Xu, T. Liu, Y. Yu, H. Liu, Y. Li and D. Zhu, *Org. Lett.*, 2011, **13**, 5692.

Characterization data

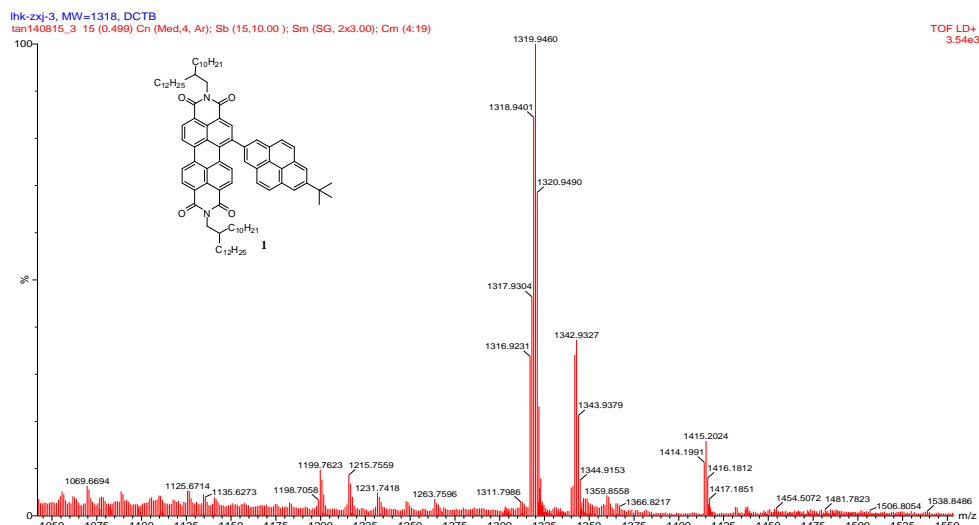


Figure S9. HRMS (MALDI-TOF) spectrum of the PDI derivative **1**.

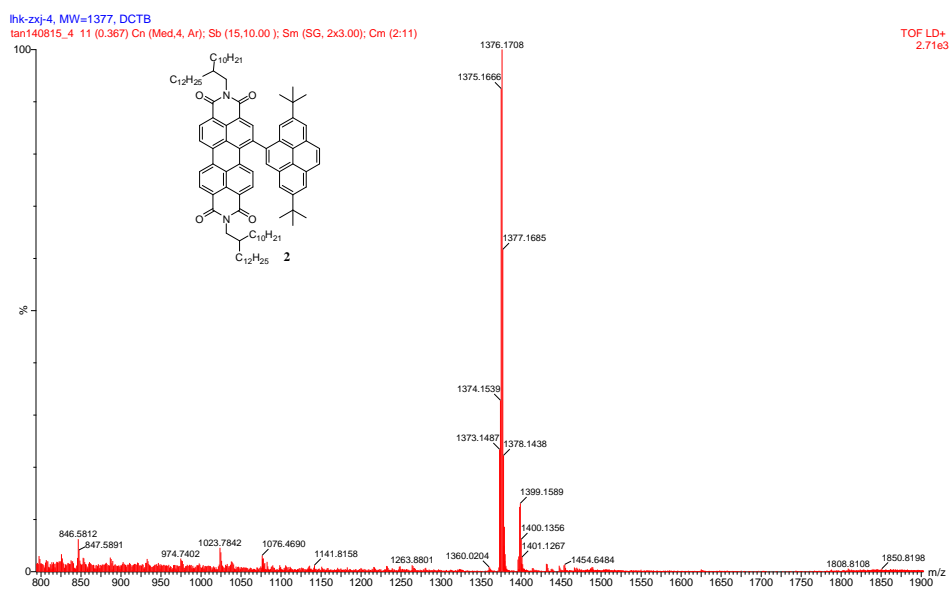


Figure S10. HRMS (MALDI-TOF) spectrum of the PDI derivative **2**.

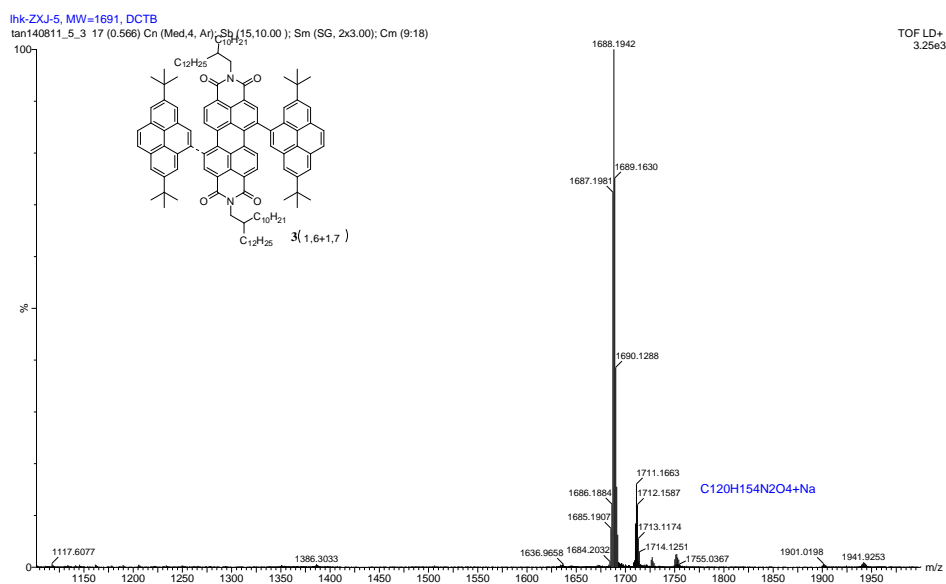


Figure S11. HRMS (MALDI-TOF) spectrum of the PDI derivative **3**.

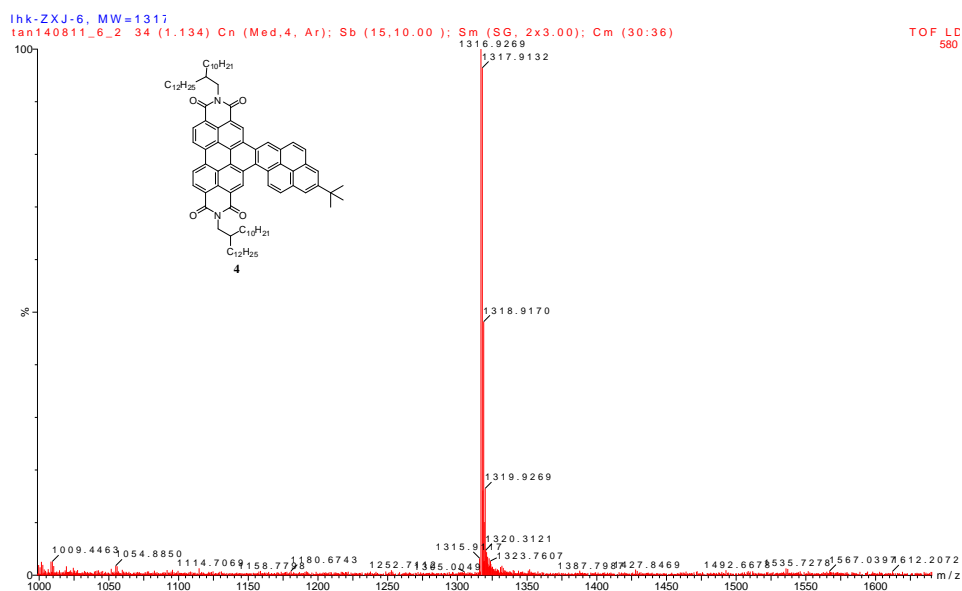


Figure S12. HRMS (MALDI-TOF) spectrum of the PDI derivative **4**.

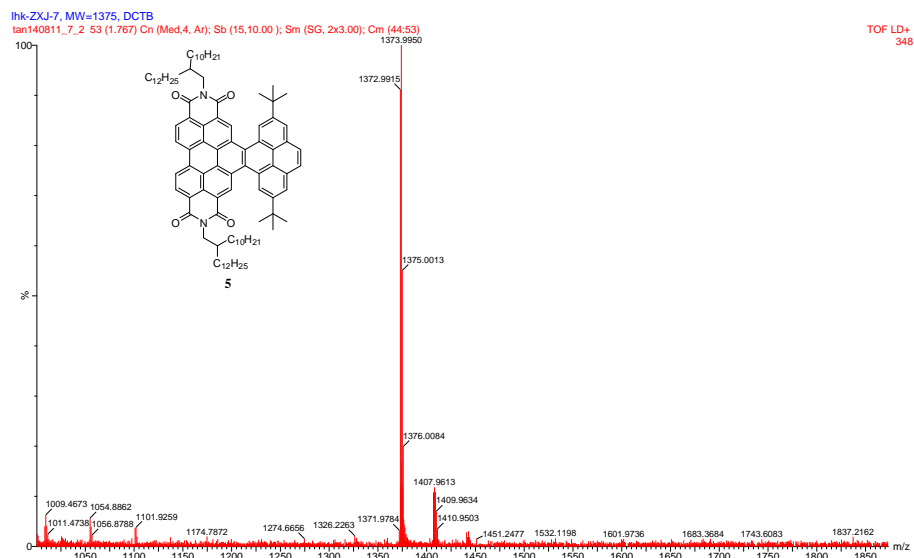


Figure S13. HRMS (MALDI-TOF) spectrum of the PDI derivative **5**.

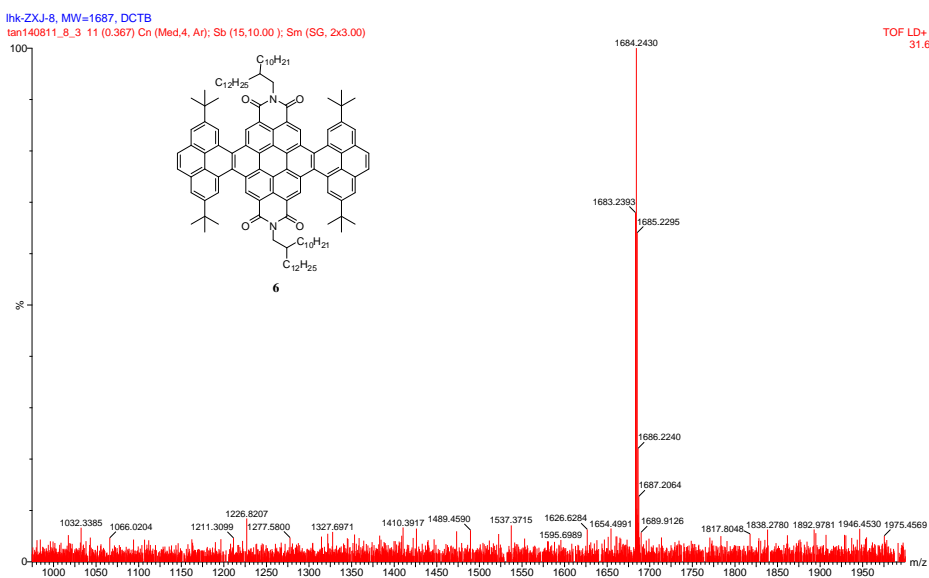


Figure S14. HRMS (MALDI-TOF) spectrum of the PDI derivative **6**.

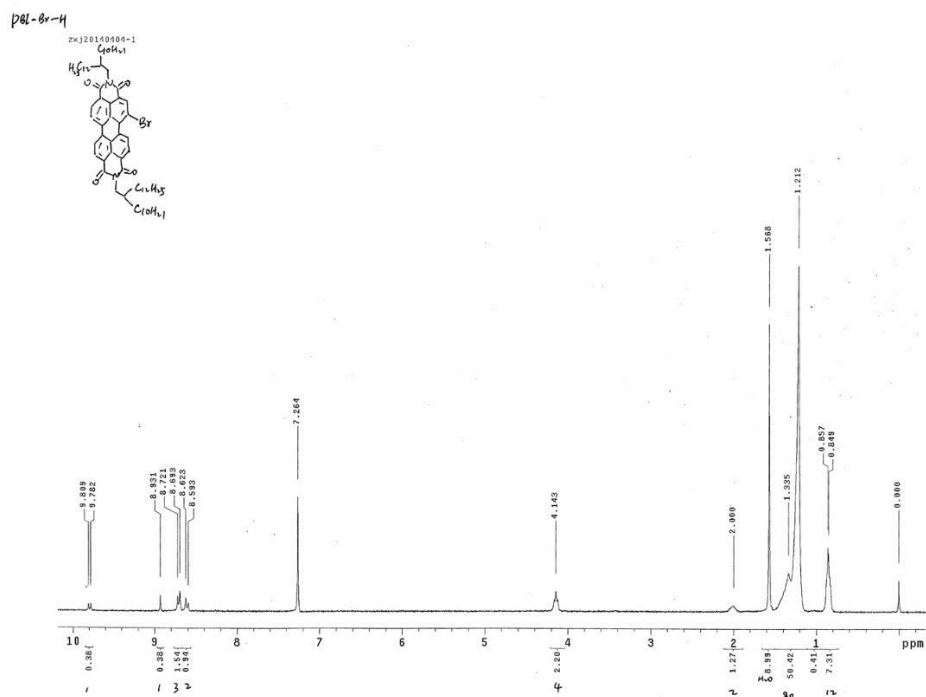


Figure S15. ¹H NMR spectrum of the **PDI-Br** in CDCl₃.

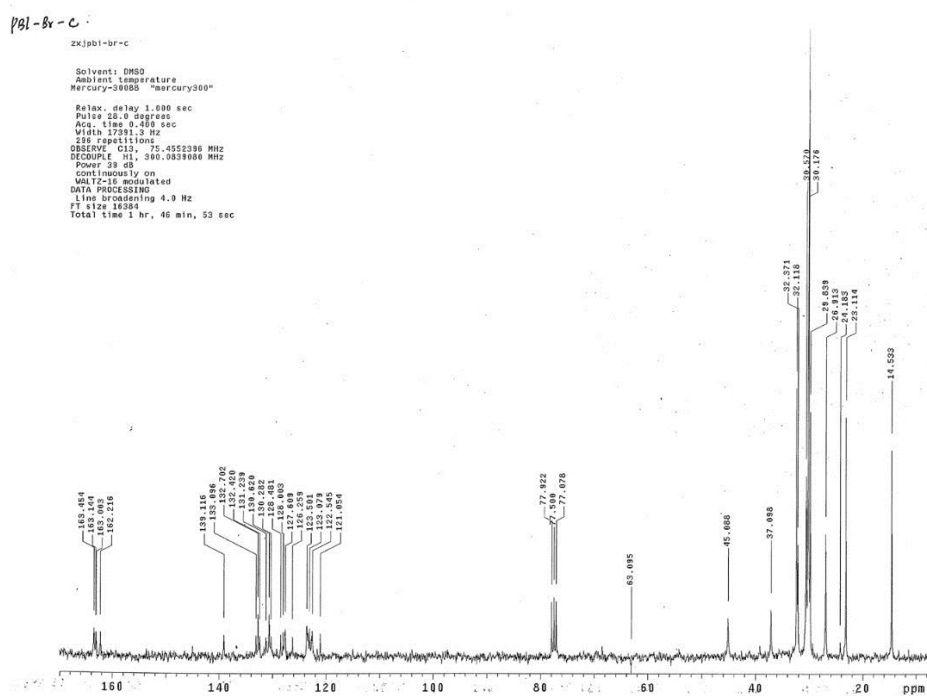


Figure S16. ¹³C NMR spectrum of the **PDI-Br** in CDCl₃.

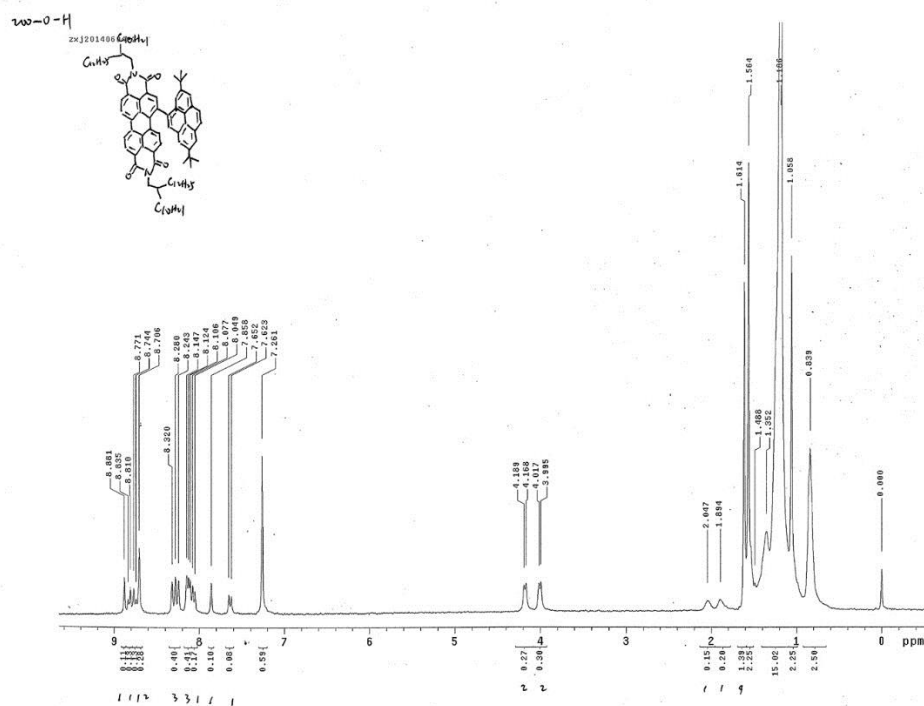


Figure S19. ¹H NMR spectrum of the **2** in CDCl₃.

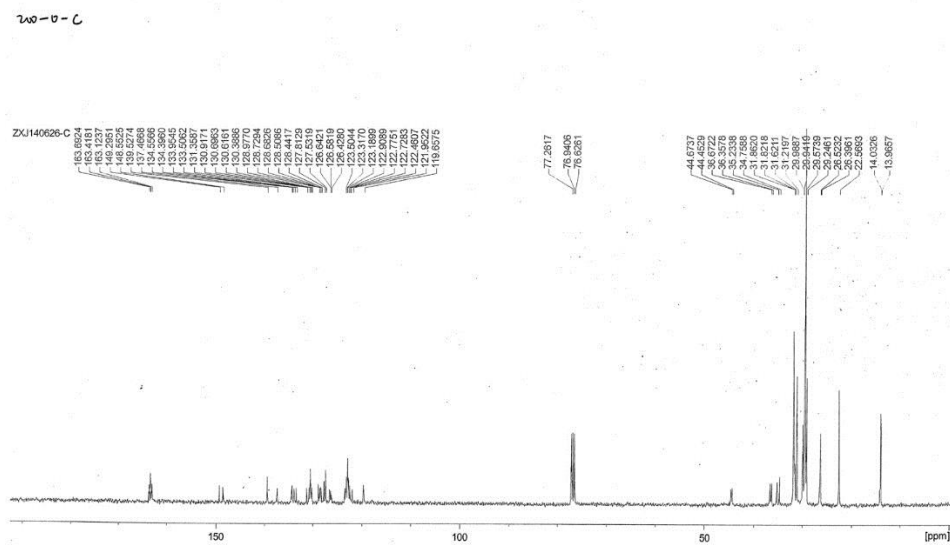


Figure S20. ¹³C NMR spectrum of the **2** in CDCl₃.



17-1-C

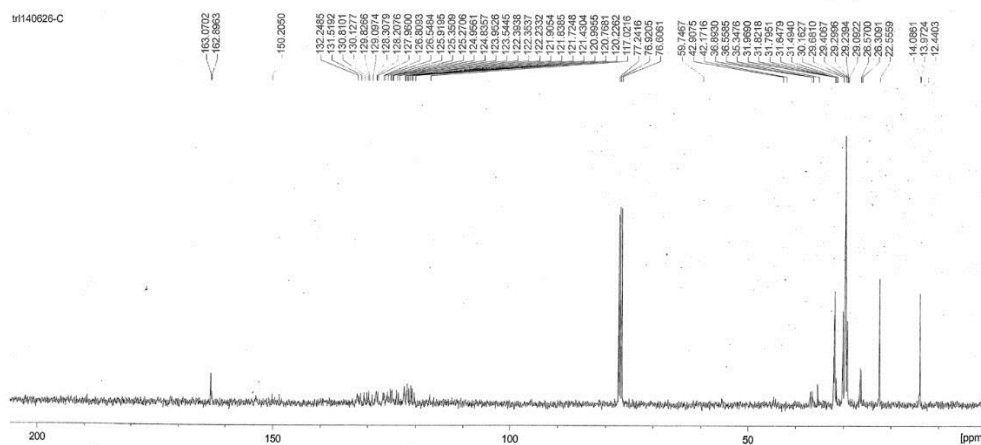


Figure S23. ^{13}C NMR spectrum of the **4** in CDCl_3 .

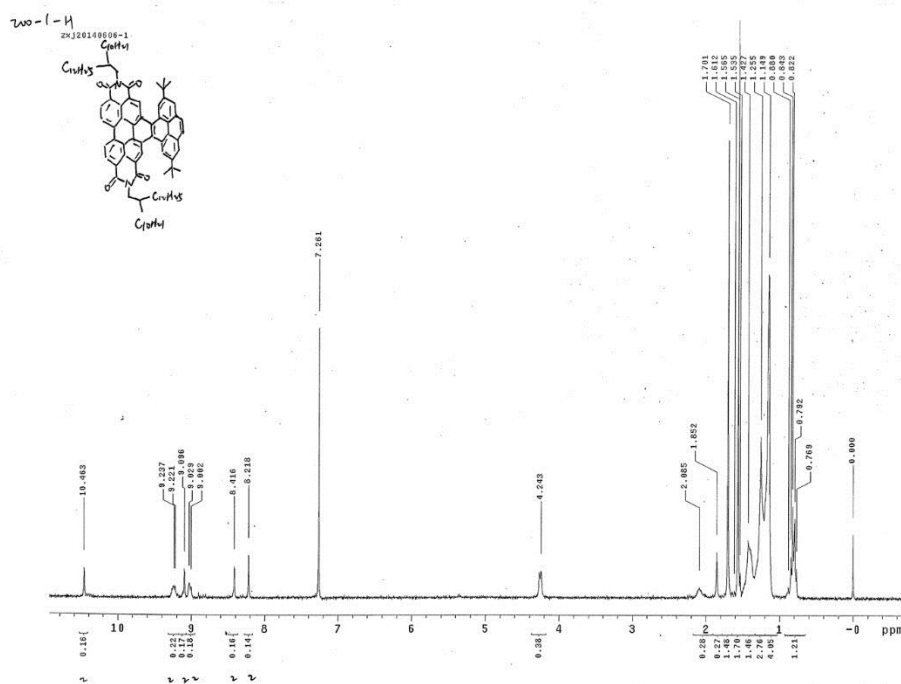


Figure S24. ^1H NMR spectrum of the **5** in CDCl_3 .

13C NMR spectrum of compound 14. The spectrum shows peaks at the following chemical shifts (ppm): 163.4804, 149.3437, 133.8019, 133.7855, 132.2105, 131.0221, 129.8231, 127.8649, 127.8433, 127.6810, 126.8736, 126.6974, 126.5735, 126.3532, 126.3188, 123.2210, 121.9861, 121.8314, 121.8514, 121.0046, 86.2027, 77.2539, 77.0014, 76.6188, 44.2769, 38.6392, 35.4261, 31.8087, 31.6785, 29.6371, 29.2871, 29.1633, 26.4437, 22.5724, and 13.9585.

201-11

ZKJ00140620-1

Chemical structure of a substituted phthalocyanine derivative is shown, featuring a central macrocyclic core with four phenyl groups and two ethyl groups attached to the nitrogen atoms.

¹H NMR spectrum (CDCl₃) of the compound. The spectrum displays peaks corresponding to the structure, with chemical shifts (ppm) and integrations (area) labeled:

Chemical Shift (ppm)	Integration (Area)
11.114	0.52
9.486	0.56
8.403	0.57
8.274	0.54
7.261	
6.804	
4.489	0.51
4.475	
2.235	
1.687	
1.760	
1.614	
1.567	
1.554	
1.515	
1.499	
1.255	
0.890	
0.853	
0.800	
0.714	
0.705	
0.695	
0.000	

Figure S26. ^1H NMR spectrum of the **6** in CDCl_3 .

201-1-C

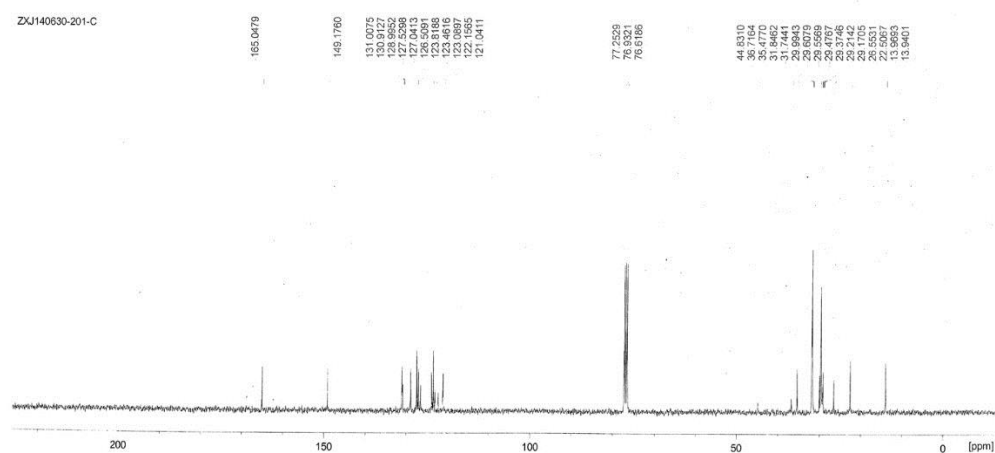


Figure S27. ^{13}C NMR spectrum of the **6** in CDCl_3 .