

Supporting Information for

Direct Synthesis of Large-Scale *ortho*-Iodinated Perylene Diimides: Key Precursors for Functional Dyes

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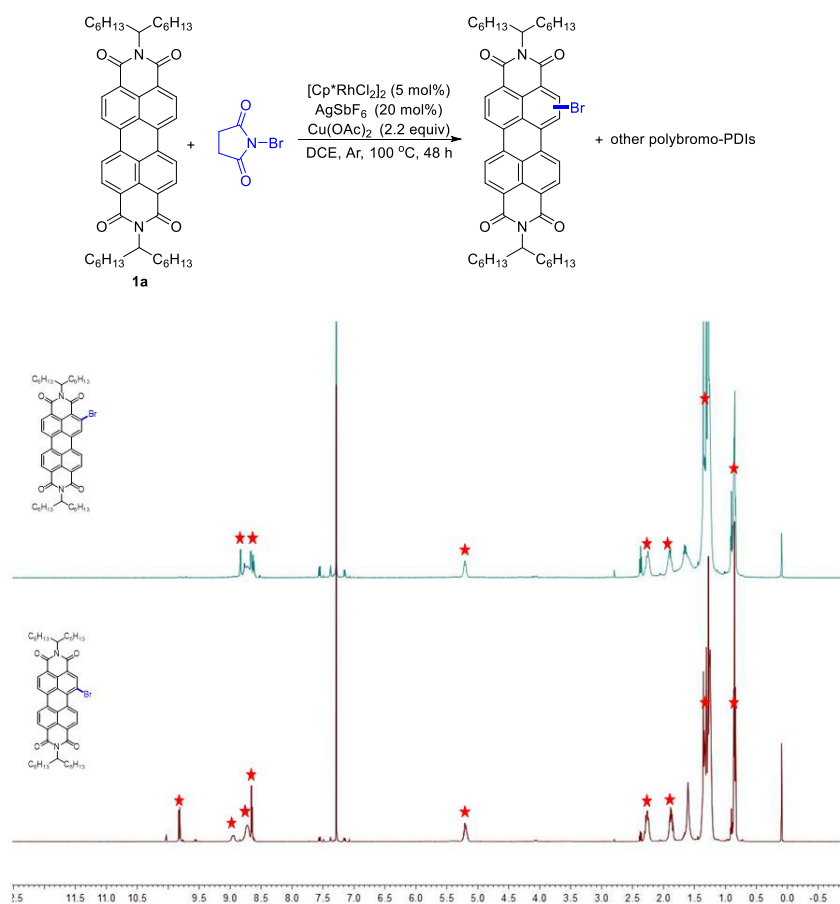
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1) General Information

Deuterated solvents were purchased from Cambridge Isotope Laboratories. The other materials and solvents were commercially available and used without further purification. PDIs **1a** and **1b** were prepared from 3,4,9,10-perylenetetracarboxylic dianhydride according to the literature procedure.^[1] ¹H and ¹³C NMR spectra were recorded at 400 MHz or 500 MHz in CDCl₃ as solvent. Chemical shifts are given in ppm with reference to the residual solvent resonance of the deuterated solvents. High-resolution mass spectra were recorded on a FT-MS instrument using ESI technique or APCI technique. Absorption spectra and Fluorescence spectra were obtained on a Varian Cary 300 UV-Vis spectrophotometer and Hitachi F-4500, respectively. SEM measurements were carried out on Hitachi S-4800. Cyclic voltammetry (CV) measurements were performed on a Bio-Logic-Science Instrument EC-LAB SP-200. Diffuse reflectance UV-Vis absorption spectra were obtained on Varian Cary 5000 UV-Vis spectrophotometer.

2) Reaction Optimization

Bromination



Iodination

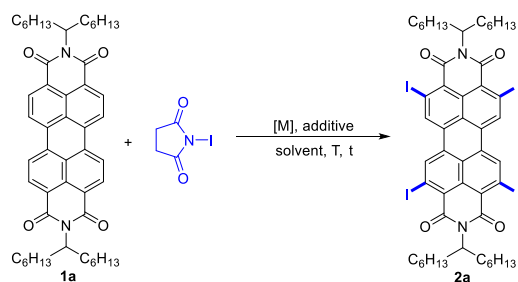


Table S1 Catalyst Screening^a

entry	[M] (mol%)	[Ag] (mol%)	additive (equiv)	<i>t</i> (h)	yield (%) ^b
1	[Cp*RhCl ₂] ₂ (5)	AgSbF ₆ (80)	Cu(OAc) ₂ (4)	48	56
2	-	AgSbF ₆ (80)	Cu(OAc) ₂ (4)	48	NR
3	[Cp*RhCl ₂] ₂ (5)	AgNTf ₂ (60)	Cu(OAc) ₂ (4)	48	49
4	[Cp*RhCl ₂] ₂ (5)	AgOTf (60)	Cu(OAc) ₂ (4)	48	trace
5	Ru ₃ (CO) ₁₂ (10)	-	Cu(OAc) ₂ (4)	36	NR
6	Ru ₃ (CO) ₁₂ (10)	AgOAc (20)	-	36	NR
7	Pd(OAc) ₂ (40)	-	<i>p</i> -TsOH (2)	46	0
8	Rh ₂ (OAc) ₄ (5)	-	Cu(OAc) ₂ (4)	48	NR
9	Cp*Rh(OAc) ₂ (10)	-	Cu(OAc) ₂ (4)	48	NR

^a Reaction conditions: **1a** (0.05 mmol), NIS (0.4 mmol), [M], [Ag], additive, DCE (1 mL), Ar, 80 °C. ^b isolated yield.

Table S2 Solvent Screening^a

entry	AgSbF ₆ (mol%)	solvent (mL)	yield (%) ^b
1	80	HFIP (1)	29 (62) ^c
2	60	DCE (0.8) / <i>t</i> -AmylOH (0.2)	NR
3	60	DCE (0.8) / HFIP (0.2)	33
4	60	DCE (0.2) / HFIP (0.8)	38
5	80	TFA (1)	NR
6	80	CHCl ₃ (1)	NR
7	80	DCE (1.5)	39
8	80	DCE (2)	39

^a Reaction conditions: **1a** (0.05 mmol), NIS (0.4 mmol), [Cp*RhCl₂]₂ (5 mol%), AgSbF₆, Cu(OAc)₂ (0.2 mmol), solvent, Ar, 80

°C. ^b isolated yield. ^c Value in parentheses indicates the yield of corresponding tri-iodinated PDI product.

Table S3 Additive Screening^a

entry	[Ag] (mol%)	additive (equiv)	<i>t</i> (h)	yield (%) ^b
1	AgSbF ₆ (40)	CuBr ₂ (8)	36	0
2	AgSbF ₆ (40)	CuO (8)	28	0
3 ^c	AgSbF ₆ (40)	CuI (8)	28	NR
4	AgSbF ₆ (40)	Cu(OTf) ₂ (4)	30	0
5	AgSbF ₆ (60)	Cu(acac) ₂ (4)	48	NR
6	AgSbF ₆ (80)	-	48	0

7	AgSbF ₆ (20)	Cu(OAc) ₂ (4) / HNTf ₂ (0.6)	48	23
8	AgNTf ₂ (20)	Cu(OAc) ₂ (4) / HNTf ₂ (0.6)	48	19
9	AgSbF ₆ (80)	Cu(OAc) ₂ (4) / <i>t</i> -BuCl (2) ^d	48	NR

^a Reaction conditions: **1a** (0.05 mmol), NIS (0.4 mmol), [Cp*RhCl₂]₂ (5 mol%), [Ag], additive, DCE (1 mL), Ar, 80 °C. ^b isolated yield. ^c 120 °C. ^d *t*-BuCl was added for the generation of a hidden acid catalyst from silver salt.^[2]

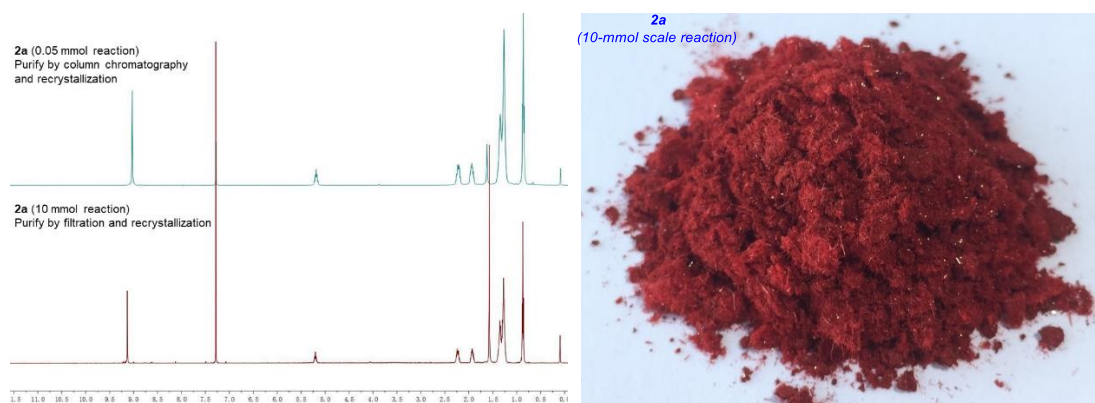
3) Procedures and Characterization Data

General Procedures for the *ortho*-Iodination of PDIs.

Synthesis of **2a**.

0.05 mmol reaction: In a 15-mL Schlenk tube containing a magnetic stirring bar, a mixture of [Cp*RhCl₂]₂ (0.00375 mmol, 2.3 mg) and AgSbF₆ (0.045 mmol, 15.5 mg) in DCE (0.2 mL) was stirred at room temperature for 20 minutes under argon. And then, followed by adding **1a** (0.05 mmol, 37.8 mg), NIS (0.4 mmol, 98.0 mg), Cu(OAc)₂ (0.2 mmol, 36.3 mg), and DCE (0.8 mL) in succession, the tube was sealed and the mixture was stirred at 80 °C for 96 hours under argon. After cooling down to room temperature, the reaction mixture was diluted with CH₂Cl₂ and washed with *sat.* Na₂S₂O₃ solution and brine. The residue was purified by silica gel column chromatography using DCM/PE as eluent. After recrystallization from chloroform/methanol, compound **2a** was obtained in 82% yield (51 mg).

10 mmol reaction: In a 500-mL Schlenk flask containing a magnetic stirring bar, a mixture of [Cp*RhCl₂]₂ (0.5 mmol, 309.1 mg) and AgSbF₆ (8 mmol, 2.75 g) was stirred at room temperature in DCE (20 mL) for 30 minutes under argon. And then, **1a** (10 mmol, 7.55 g), NIS (80 mmol, 19.60 g), Cu(OAc)₂ (10 mmol, 1.82 g), and DCE (180 mL) were added in succession and the flask was sealed with a rubber stopper. The mixture was stirred at 80 °C for 120 hours. After cooling down to ambient temperature, the resulting solution was filtered through a pad of Celite and washed with CH₂Cl₂. The filtrate was concentrated to a small volume under reduced pressure and layered with methanol. Red needle-like crystals (see below) of the product **2a** were isolated and dried under vacuum (10.5 g, 83%). The ¹H NMR spectra of **2a** obtained through two different work-up strategies are shown below.



2a: red solid; ¹H NMR (400 MHz, CDCl₃) δ 9.01 (s, 4H), 5.23 – 5.07 (m, 2H), 2.27 – 2.12 (m, 4H), 1.97 – 1.84 (m, 4H), 1.37 – 1.20 (m, 32H), 0.84 (t, *J* = 6.7 Hz, 12H); ¹³C NMR (126 MHz, CDCl₃) δ 160.86, 138.47, 131.73, 131.29, 125.67, 123.82, 101.16, 56.48,

32.36, 31.92, 29.34, 27.15, 22.75, 14.20; HR-MS (APCI) m/z : $[M+H]^+$ Calcd for $C_{50}H_{59}N_2O_4I_4^+$ 1259.0648; Found 1259.0653.

Synthesis of 2b.

1 mmol reaction: In a 100-mL Schlenk flask containing a magnetic stirring bar, a mixture of $[Cp^*RhCl_2]_2$ (0.075 mmol, 46.4 mg) and $AgSbF_6$ (0.9 mmol, 309.3 mg) in DCE (2 mL) was stirred at room temperature for 30 minutes under argon. Followed by adding **1b** (1 mmol, 530.6 mg), NIS (8 mmol, 1.96 g), $Cu(OAc)_2$ (1 mmol, 181.6 mg), and DCE (18 mL), the flask was sealed with a rubber stopper. The mixture was stirred at 80 °C for 96 hours. After cooling down to room temperature, the reaction mixture was diluted with CH_2Cl_2 and washed with sat. $Na_2S_2O_3$ solution and brine. The residue was purified by silica gel column chromatography using DCM/PE as eluent. After recrystallization from chloroform/methanol, compound **2b** was obtained in 84% yield (868 mg).

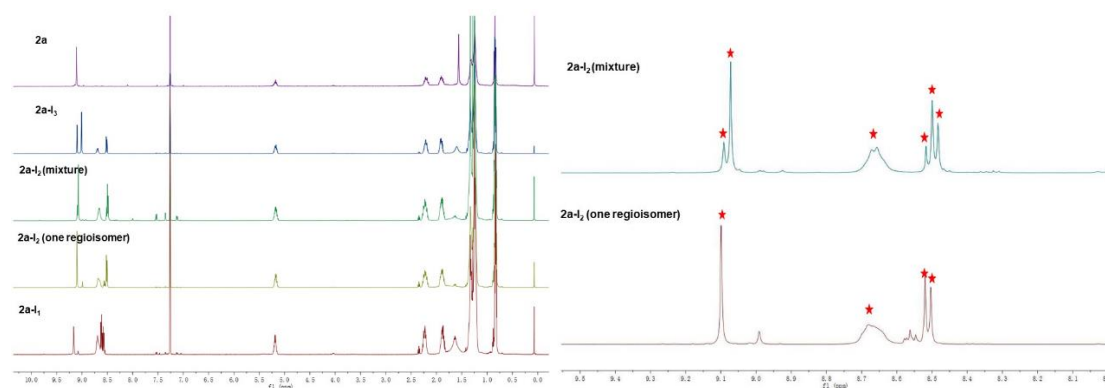
5 mmol reaction: In a 500-mL Schlenk flask containing a magnetic stirring bar, a mixture of $[Cp^*RhCl_2]_2$ (0.25 mmol, 154.5 mg) and $AgSbF_6$ (4 mmol, 1.37 g) was stirred at room temperature in DCE (10 mL) for 30 minutes under argon. And then, **1b** (5 mmol, 2.65 g), NIS (40 mmol, 9.80 g), $Cu(OAc)_2$ (5 mmol, 0.91 g), and DCE (90 mL) were added in succession and the flask was sealed with a rubber stopper. The mixture was stirred at 80 °C for 120 hours. After cooling down to ambient temperature, the resulting solution was filtered through a pad of Celite and washed with CH_2Cl_2 . The filtrate was concentrated to a small volume under reduced pressure and layered with methanol. Red needle-like crystals of the product **2b** were isolated and dried under vacuum with 71% yield (3.7 g).

2b: red solid; 1H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 4H), 5.13 – 5.00 (m, 2H), 2.28 – 2.16 (m, 4H), 2.04 – 1.94 (m, 4H), 0.94 (t, J = 7.4 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.08, 138.69, 131.97, 131.51, 125.89, 123.69, 101.31, 59.37, 25.07, 11.55; HR-MS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{34}H_{26}N_2O_4I_4Na^+$ 1056.7964; Found 1056.7938.

Synthesis of 2a-I₁. In a 15-mL Schlenk tube, a mixture of $[Cp^*RhCl_2]_2$ (0.0025 mmol, 1.6 mg) and $AgSbF_6$ (0.0175 mmol, 6.0 mg) was stirred at room temperature in DCE (0.2 mL) for 10 minutes under argon. And then, followed by adding **1a** (0.05 mmol, 37.8 mg), NIS (0.06 mmol, 14.7 mg), $Cu(OAc)_2$ (0.025 mmol, 4.5 mg), and DCE (1.3 mL) in succession, the tube was sealed and the mixture was stirred at 80 °C for 12 hours. After cooling down to room temperature, the reaction mixture was diluted with CH_2Cl_2 and washed with sat. $Na_2S_2O_3$ solution and brine. The organic layer was collected, dried with anhydrous Na_2SO_4 , and concentrated. The residue was purified by silica gel column chromatography using DCM/PE as eluent. After recrystallization from dichloromethane/methanol, compound **2a-I₁** was obtained in 50% yield (22 mg).

2a-I₁: red solid; 1H NMR (500 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.67 (d, J = 7.6 Hz, 3H), 8.57 (dd, J = 8.1, 1.7 Hz, 2H), 8.53 (d, J = 8.1 Hz, 1H), 5.23 – 5.13 (m, 2H), 2.29 – 2.16 (m, 4H), 1.93 – 1.83 (m, 4H), 1.34 – 1.20 (m, 32H), 0.83 (td, J = 6.9, 4.5 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.67, 163.22, 138.02, 134.85, 134.28, 133.84, 133.06, 131.82, 130.96, 129.59, 126.45, 126.39, 123.55, 123.34, 123.13, 55.65, 55.05, 32.58, 32.47, 31.91, 29.35, 27.11, 22.73, 14.15; HR-MS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{50}H_{61}N_2O_4INa^+$ 903.3568; Found 903.3548.

Synthesis of 2a-I₂. In a 15-mL Schlenk tube, a mixture of [Cp*RhCl₂]₂ (0.0025 mmol, 1.6 mg) and AgSbF₆ (0.0175 mmol, 6.0 mg) was stirred at room temperature in DCE (0.2 mL) for 10 minutes under argon. And then, followed by adding **1a** (0.05 mmol, 37.8 mg), NIS (0.15 mmol, 36.7 mg), Cu(OAc)₂ (0.025 mmol, 4.5 mg), and DCE (0.8 mL) in succession, the mixture was stirred at 80 °C for 12 hours. After cooling down to room temperature, the reaction mixture was diluted with CH₂Cl₂ and washed with sat. Na₂S₂O₃ solution and brine. The organic layer was collected, dried with anhydrous Na₂SO₄, and concentrated. The residue was purified by silica gel column chromatography using DCM/PE as eluent to give **2a-I₂** with 45% yield (20.5 mg) as a mixture of three regioisomers. One of the three isomers could be isolated through a more careful column chromatography (for ¹H NMR spectra, see below). HR-MS (ESI) m/z: [M+Na]⁺ Calcd for C₅₀H₆₀N₂O₄I₂Na⁺ 1029.2535; Found 1029.2568.



Synthesis of 2a-I₃. In a 15-mL Schlenk tube, a mixture of [Cp*RhCl₂]₂ (0.0025 mmol, 1.6 mg) and AgSbF₆ (0.04 mmol, 13.8 mg) was stirred at room temperature in HFIP (0.2 mL) for 10 minutes under argon. And then, followed by adding **1a** (0.05 mmol, 37.8 mg), NIS (0.4 mmol, 98.0 mg), Cu(OAc)₂ (0.2 mmol, 36.3 mg) and HFIP (0.8 mL) in succession, the tube was sealed and the mixture was stirred at 80 °C for 48 hours. After cooling down to room temperature, the reaction mixture was diluted with CH₂Cl₂, washed with sat. Na₂S₂O₃ solution and brine. The organic layer was collected, dried with anhydrous Na₂SO₄, and concentrated. The residue was purified by silica gel column chromatography with DCM/PE as eluent to afford the product **2a-I₃** in 62% yield (35 mg).

2a-I₃: red solid; ¹H NMR (500 MHz, CDCl₃) δ 9.10 (s, 1H), 9.01 (s, 2H), 8.69 (d, *J* = 7.3 Hz, 1H), 8.51 (d, *J* = 8.2 Hz, 1H), 5.23 – 5.13 (m, 2H), 2.27 – 2.15 (m, 4H), 1.95 – 1.86 (m, 4H), 1.34 – 1.22 (m, 32H), 0.84 (td, *J* = 7.0, 4.5 Hz, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 162.29, 161.03, 138.39, 138.28, 133.27, 132.81, 132.09, 131.80, 131.40, 130.56, 125.94, 125.80, 123.66, 101.36, 56.36, 55.76, 32.40, 32.28, 31.91, 29.83, 29.33, 27.13, 22.74, 14.21; HR-MS (ESI) m/z: [M+Na]⁺ Calcd for C₅₀H₅₉N₂O₄I₃Na⁺ 1155.1501; Found 1155.1479.

Synthesis of 3a. To a 15-mL Schlenk tube, **2a** (0.05 mmol, 62.9 mg) and aniline (2.5 mL) were added under argon. Then, the tube was sealed and the mixture was stirred at 120 °C for 5 hours. After cooling down to ambient temperature, 10 mL of methanol was added. The resulting precipitate was filtered, washed, and dried under vacuum to give product **3a**.

quantitatively.

3a: dark purple solid, (56 mg); ^1H NMR (500 MHz, CDCl_3) δ 11.91 (d, J = 5.5 Hz, 4H), 7.79 (s, 4H), 7.40 – 7.27 (m, 16H), 7.25 – 7.20 (m, 4H), 5.35 – 5.27 (m, 2H), 2.31 – 2.21 (m, 4H), 1.94 – 1.85 (m, 4H), 1.34 – 1.23 (m, 32H), 0.83 (t, J = 6.9 Hz, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.00, 166.69, 151.47, 139.28, 135.22, 135.05, 134.55, 129.82, 125.44, 124.50, 112.91, 106.81, 101.09, 100.56, 54.08, 32.68, 31.94, 29.45, 27.29, 22.75, 14.18; HR-MS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{74}\text{H}_{82}\text{N}_6\text{O}_4\text{Na}^+$ 1141.6290; Found 1141.6245.

Synthesis of 3b and 3c. To a 15-mL Schlenk tube, **2a** (0.05 mmol, 62.9 mg), phenol or thiophenol (0.3 mmol, 6.0 equiv), K_2CO_3 (0.3 mmol, 41.5 mg), and NMP (1.0 mL) were added under argon. Then, the tube was sealed and the mixture was stirred at 120 °C for 5 hours. Subsequently, the reaction mixture was concentrated under vacuum. The residue was purified by column chromatography using DCM/PE as eluent to afford the product **3b** or **3c**.

3b: red solid; yield 64% (36 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.57 (s, 4H), 7.36 (t, J = 7.9 Hz, 8H), 7.22 (t, J = 7.4 Hz, 4H), 7.07 (d, J = 7.8 Hz, 8H), 5.14 – 5.05 (m, 2H), 2.16 – 2.05 (m, 4H), 1.83 – 1.74 (m, 4H), 1.27 – 1.17 (m, 32H), 0.81 (t, J = 6.9 Hz, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ 161.77, 161.02, 155.65, 134.57, 133.70, 130.22, 124.94, 119.68, 118.93, 115.25, 112.16, 54.64, 32.37, 31.90, 29.31, 27.12, 22.68, 14.14; HR-MS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{74}\text{H}_{79}\text{N}_2\text{O}_8^+$ 1123.5831; Found 1123.5795.

3c: dark red solid; yield 95% (56 mg); ^1H NMR (500 MHz, CDCl_3) δ 7.51 – 7.37 (m, 24H), 5.31 – 5.18 (m, 2H), 2.30 – 2.19 (m, 4H), 1.97 – 1.85 (m, 4H), 1.34 – 1.22 (m, 32H), 0.82 (t, J = 7.0 Hz, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ 164.23, 163.59, 151.20, 150.74, 134.52, 132.94, 132.56, 131.13, 130.24, 129.49, 122.16, 121.25, 117.26, 116.73, 55.20, 32.43, 31.90, 29.33, 27.14, 22.71, 14.16; HR-MS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{74}\text{H}_{79}\text{N}_2\text{O}_4\text{S}_4^+$ 1187.4917; Found 1187.4886.

Synthesis of 4. To a 15-mL Schlenk tube, **2a** (0.05 mmol, 62.9 mg), CuCN (0.3 mmol, 26.9 mg), and 1.5 mL of dry DMF were added under argon, and the mixture was stirred at 140 °C overnight. After cooling down to room temperature, the resulting solution was poured into water and extracted with DCM. The organic layer was collected, dried with anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using DCM/PE as eluent to afford the product **4** in 96% yield (41 mg).

4: orange red solid; ^1H NMR (500 MHz, CDCl_3) δ 9.05 (s, 4H), 5.24 – 5.15 (m, 2H), 2.26 – 2.15 (m, 4H), 1.96 – 1.86 (m, 4H), 1.32 – 1.20 (m, 32H), 0.83 (t, J = 6.5 Hz, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ 160.86, 159.70, 132.79, 130.71, 129.55, 128.33, 127.27, 117.32, 116.71, 57.02, 32.17, 31.81, 29.20, 27.10, 22.65, 14.11; HR-MS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{54}\text{H}_{58}\text{N}_6\text{O}_4\text{Na}^+$ 877.4412; Found 877.4392.

Synthesis of 5. In a 15-mL Schlenk tube containing a magnetic stirring bar, **2a** (0.1 mmol, 125.8 mg), alkyne (0.48 mmol, 4.8 equiv), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.02 mmol, 14.1 mg), and CuI (0.02 mmol, 3.8 mg) were dissolved in dry diisopropylamine (4 mL) under argon. The mixture was stirred at room temperature overnight. And then, the diisopropylamine was

evaporated using a rotary evaporator. The residue was purified by silica gel column chromatography using DCM/PE as eluent to afford **5**.

5a: red solid; yield 82% (93 mg); ^1H NMR (500 MHz, CDCl_3) δ 8.60 (s, 4H), 5.20 – 5.09 (m, 2H), 2.26 – 2.17 (m, 4H), 1.93 – 1.83 (m, 4H), 1.36 – 1.22 (m, 32H), 0.85 (t, J = 6.8 Hz, 12H), 0.41 (s, 36H); ^{13}C NMR (126 MHz, CDCl_3) δ 161.92, 132.05, 130.55, 129.80, 127.37, 125.06, 107.46, 104.73, 100.22, 54.97, 32.46, 31.91, 29.38, 27.08, 22.76, 14.19, -0.01; HR-MS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{70}\text{H}_{94}\text{N}_2\text{O}_4\text{Si}_4\text{Na}^+$ 1161.6183; Found 1161.6188.

5b: brown solid; yield 92% (106 mg); ^1H NMR (500 MHz, CDCl_3) δ 8.73 (s, 4H), 7.82 (dd, J = 6.4, 3.0 Hz, 8H), 7.45 (dd, J = 4.9, 1.7 Hz, 12H), 5.29 – 5.20 (m, 2H), 2.35 – 2.24 (m, 4H), 2.00 – 1.90 (m, 4H), 1.39 – 1.21 (m, 32H), 0.83 (t, J = 6.9 Hz, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ 162.32, 132.64, 132.22, 131.04, 129.56, 129.42, 128.67, 128.02, 124.91, 123.26, 100.68, 100.17, 90.54, 55.17, 32.49, 31.95, 29.47, 27.24, 22.79, 14.19; HR-MS (APCI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{82}\text{H}_{79}\text{N}_2\text{O}_4^+$ 1155.6034; Found 1155.6036.

5c: brown solid; yield 76% (96 mg); ^1H NMR (500 MHz, CDCl_3) δ 10.08 (s, 4H), 8.70 (s, 4H), 7.96 (d, J = 1.6 Hz, 16H), 5.27 – 5.19 (m, 2H), 2.35 – 2.22 (m, 4H), 2.01 – 1.90 (m, 4H), 1.37 – 1.23 (m, 32H), 0.82 (t, J = 6.8 Hz, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ 191.42, 136.49, 133.05, 132.24, 130.97, 129.80, 129.38, 129.16, 125.40, 99.27, 93.58, 55.41, 32.45, 31.93, 29.42, 27.22, 22.77, 14.18.

Synthesis of 6. A mixture of **2a** (0.05 mmol, 62.9 mg), phenylboronic acid or 2-thienylboronic acid (4.8 equiv), $\text{Pd}(\text{PPh}_3)_4$ (0.01 mmol, 11.6 mg), K_2CO_3 (0.6 mmol, 82.9 mg), and solvent (1 mL, DMF for **6a** and 1,4-dioxane for **6b**) was intensively stirred under argon at 100 °C for 12 hours. Then, the mixture was extracted with DCM, washed with water, dried with anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using DCM/PE as eluent to afford **6**.

6a: red solid; yield 75% (40 mg); ^1H NMR (500 MHz, CDCl_3) δ 8.40 (s, 4H), 7.49 (t, J = 7.5 Hz, 12H), 7.45 (d, J = 7.6 Hz, 8H), 4.97 – 4.87 (m, 2H), 2.13 – 2.01 (m, 4H), 1.63 – 1.58 (m, 4H), 1.29 – 1.21 (m, 32H), 0.85 (t, J = 6.9 Hz, 12H); ^{13}C NMR (101 MHz, CDCl_3) δ 164.01, 163.51, 147.87, 142.32, 132.80, 131.25, 128.59, 128.21, 128.06, 127.43, 125.41, 54.95, 32.21, 32.02, 29.36, 27.06, 22.74, 14.21; HR-MS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{74}\text{H}_{78}\text{N}_2\text{O}_4\text{Na}^+$ 1081.5854; Found 1081.5821.

6b: red solid; yield 85% (46 mg); ^1H NMR (500 MHz, CDCl_3) δ 8.50 (s, 4H), 7.54 (dd, J = 5.1, 1.2 Hz, 4H), 7.26 – 7.12 (m, 8H), 5.04 – 4.93 (m, 2H), 2.22 – 2.11 (m, 4H), 1.71 – 1.62 (m, 4H), 1.31 – 1.21 (m, 32H), 0.84 (t, J = 7.0 Hz, 12H); ^{13}C NMR (126 MHz, CDCl_3) δ 142.86, 132.48, 131.10, 128.30, 127.61, 127.40, 127.07, 125.82, 121.22, 55.34, 32.35, 32.01, 29.38, 27.09, 22.75, 14.22; HR-MS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{66}\text{H}_{70}\text{N}_2\text{O}_4\text{S}_4\text{Na}^+$ 1105.4111; Found 1105.4096.

Synthesis of CMP 7. **2a** (1 mmol, 1.258 g), 1,4-bis(ethynyl)benzene (2 mmol, 0.252 g), $\text{Pd}(\text{PPh}_3)_4$ (10 mol%, 0.115 g) and CuI (10 mol%, 19 mg) were dissolved in dry DMF (50 mL) and the solution was degassed for 5 mins. Then dry Et_3N (50 mL) were added and then the reaction mixture was stirred at 80 °C for 24 h under nitrogen atmosphere.

After the reaction was cooled to room temperature, methanol was added and the precipitated powder was filtered and washed with water. The residue was washed in a Soxhlet-Extractor with methanol and DCM for 12 h respectively. The final product was obtained after drying under reduced pressure overnight to give **CMP 7** as a black solid (1.003 g).

Synthesis of CMP 8. **2a** (0.5 mmol, 0.629 g), 4,4'-diethynybiphenyl (1 mmol, 0.202 g), Pd(PPh₃)₄ (10 mol%, 57.8 mg) and CuI (10 mol%, 9.6 mg) were dissolved in dry DMF (50 mL) and the solution was degassed for 5 mins. Then dry Et₃N (50 mL) were added and then the reaction mixture was stirred at 80 °C for 24 h under nitrogen atmosphere. After the reaction was cooled to room temperature, methanol was added and the precipitated powder was filtered and washed with water. The residue was washed in a Soxhlet-Extractor with methanol and DCM for 12 h respectively. The final product was obtained after drying under reduced pressure overnight to give **CMP 8** as a black solid (0.638 g).

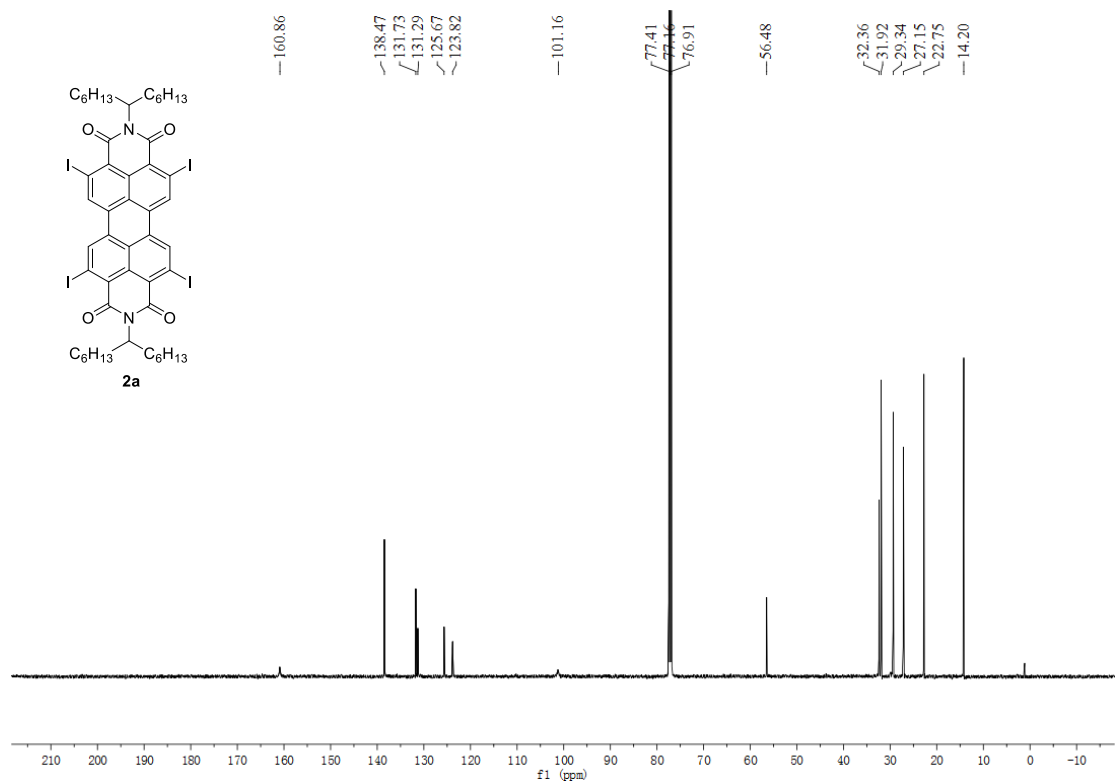
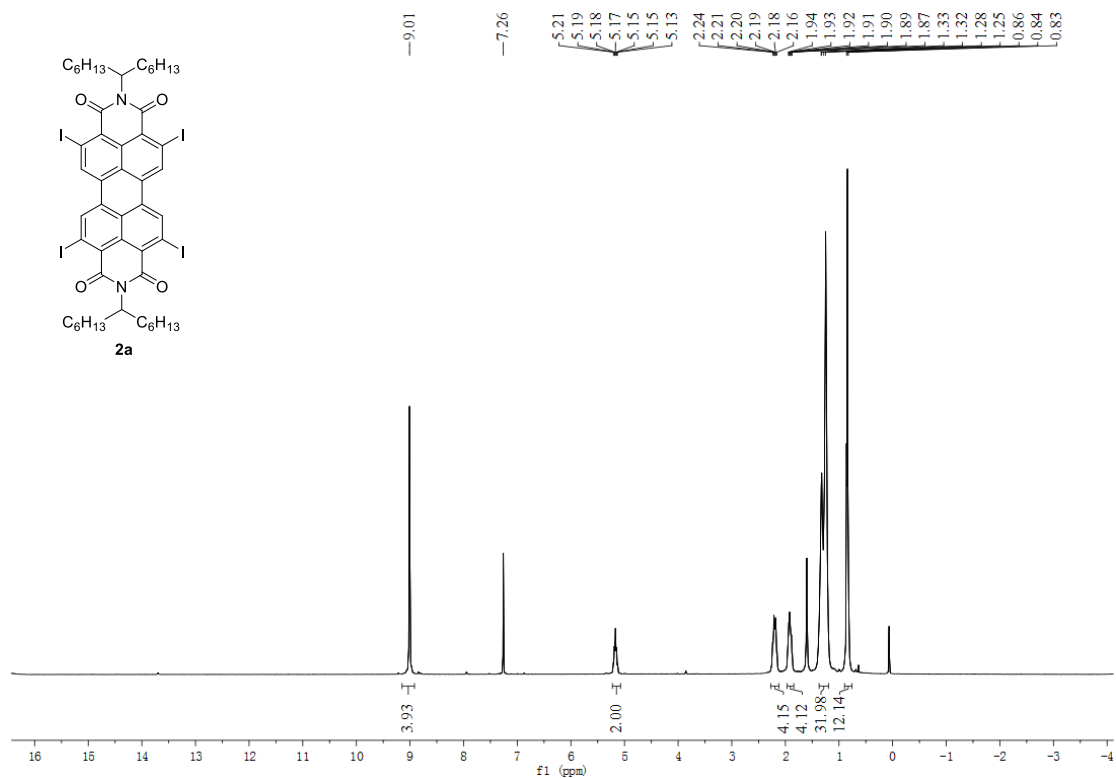
Table S4. Element analysis results for the **CMP 7** and **CMP 8**.

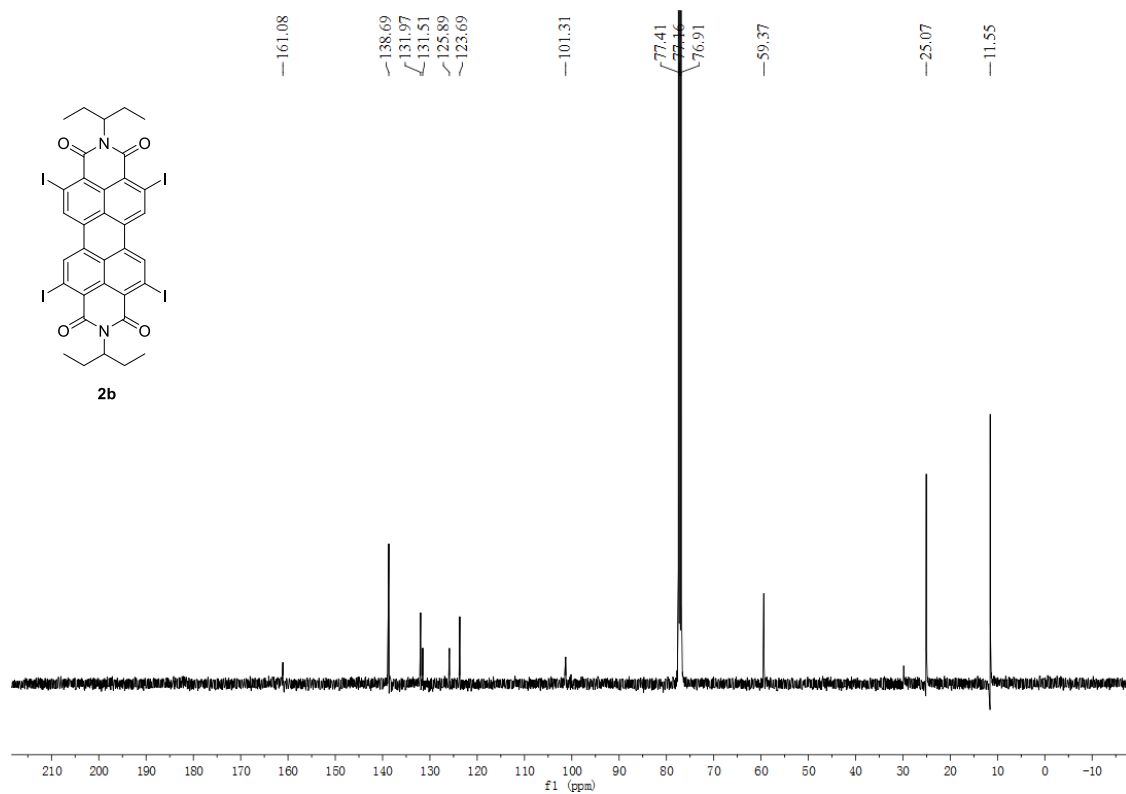
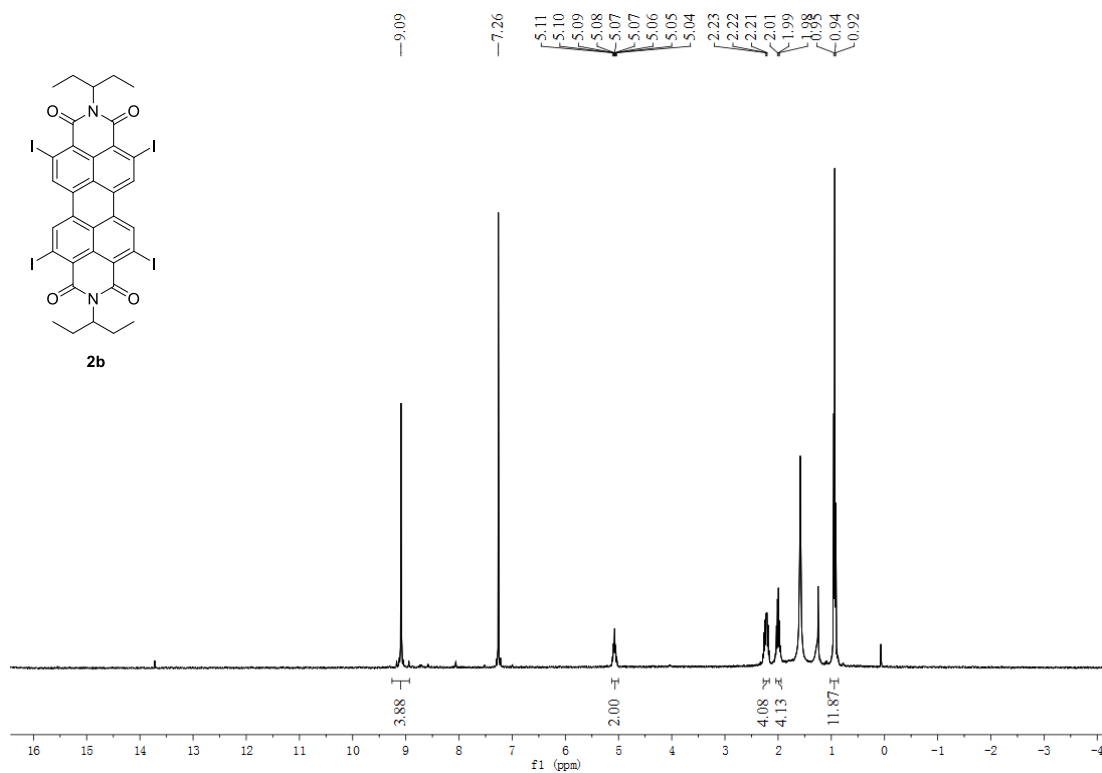
CMP	Theory			Found		
	C	H	N	C	H	N
7	83.80	7.03	2.79	80.43	7.520	3.164
8	85.23	6.80	2.42	81.46	6.897	2.598

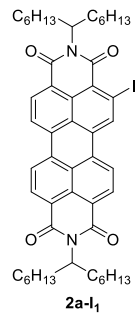
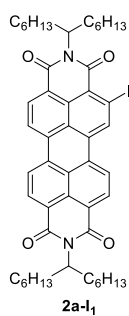
4) References

- [1] (a) Che, Y.; Datar, A.; Balakrishnan, K.; Zang, L. *J. Am. Chem. Soc.* **2007**, *129*, 7234-7235; (b) Huang, Y.; Hu, J.; Kuang, W.; Wei, Z.; Faul, C. F. J. *Chem. Commun.* **2011**, *47*, 5554-5556.
- [2] Dang, T. T.; Boeck, F.; Hintermann, L. *J. Org. Chem.* **2011**, *76*, 9353-9361.

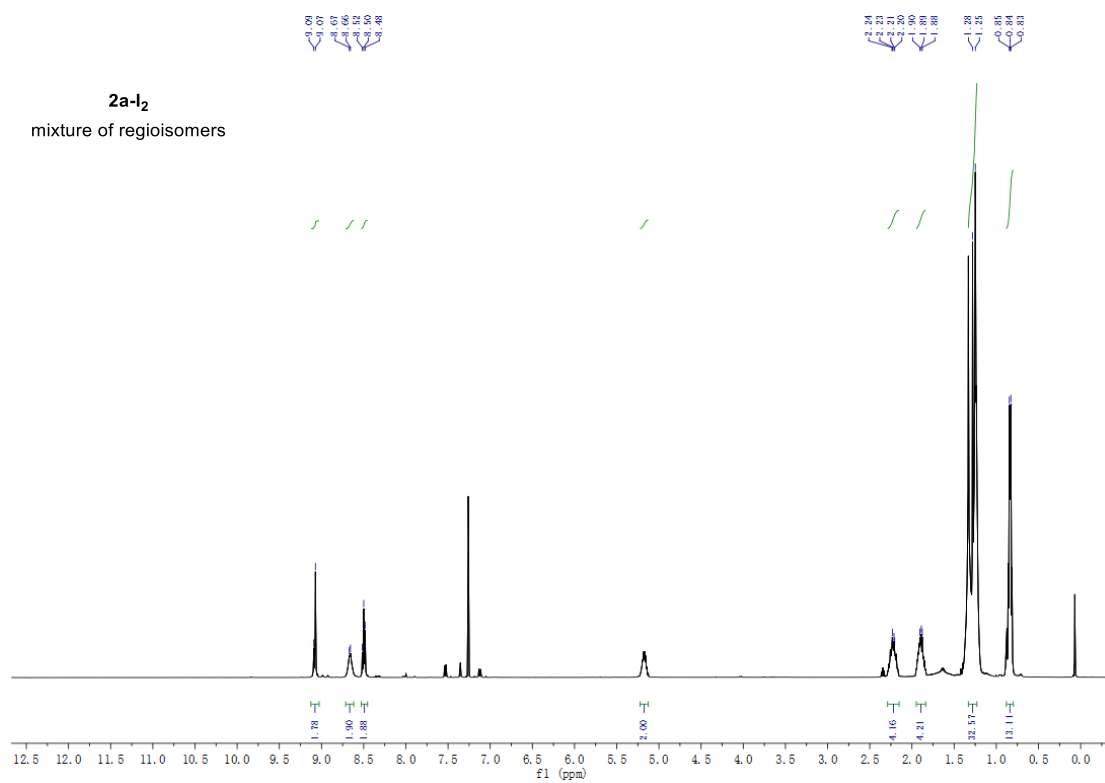
5) ^1H and ^{13}C NMR Spectra

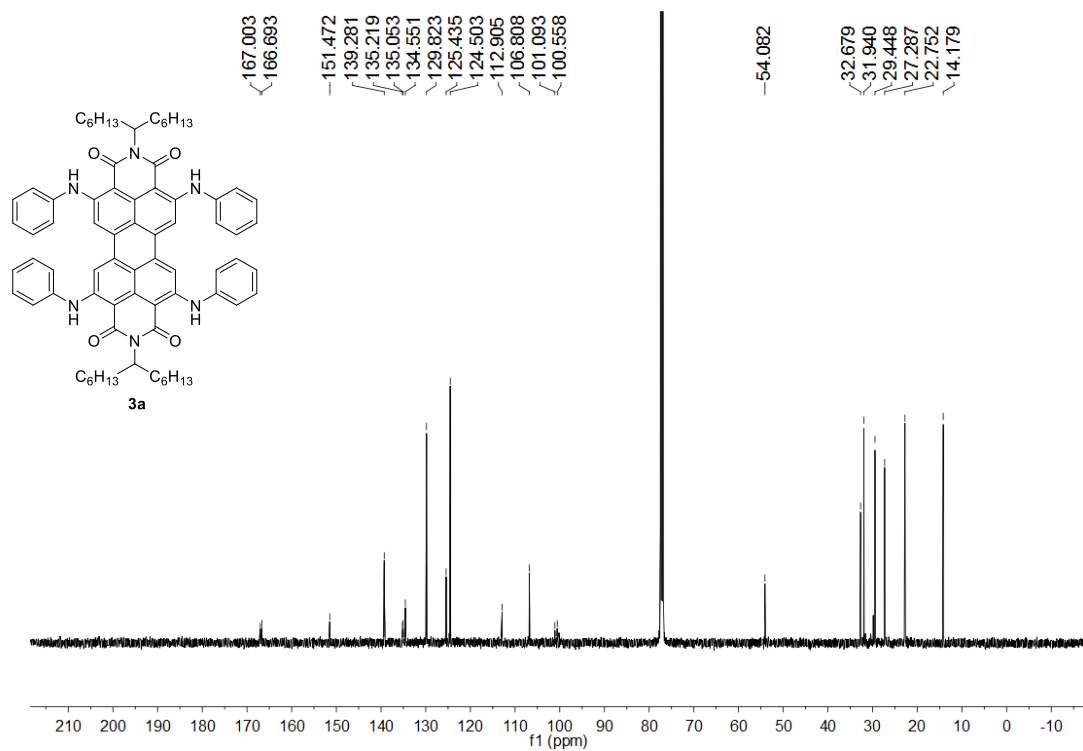
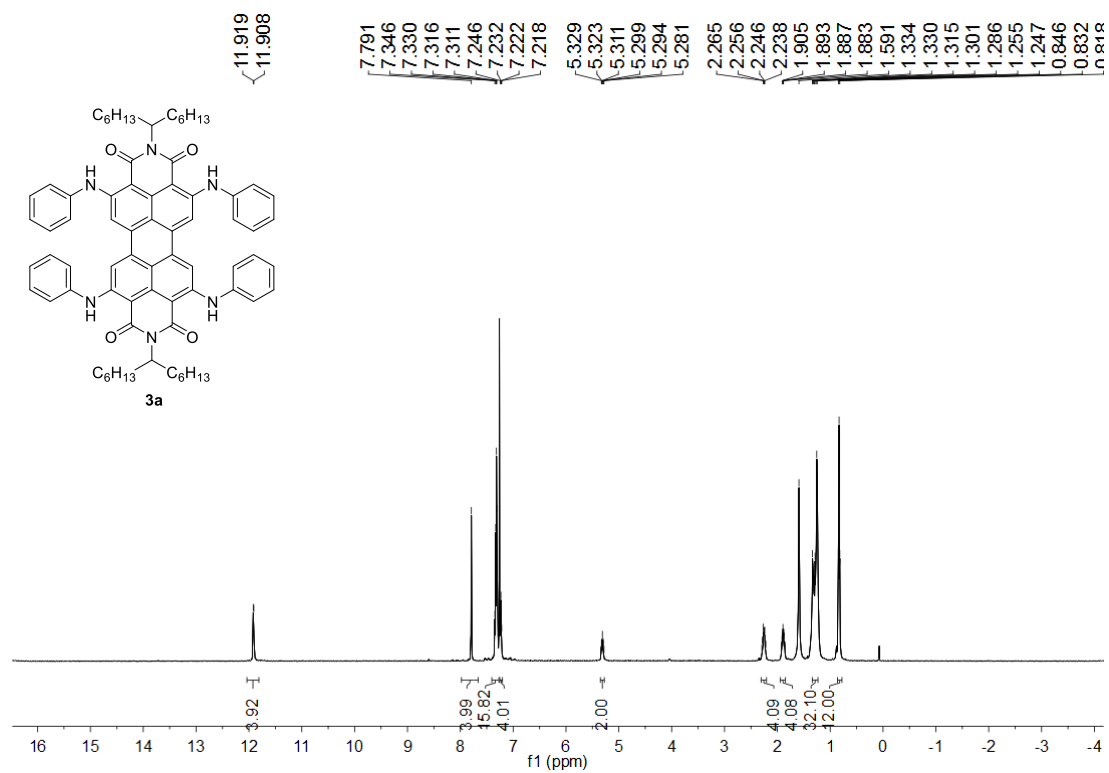


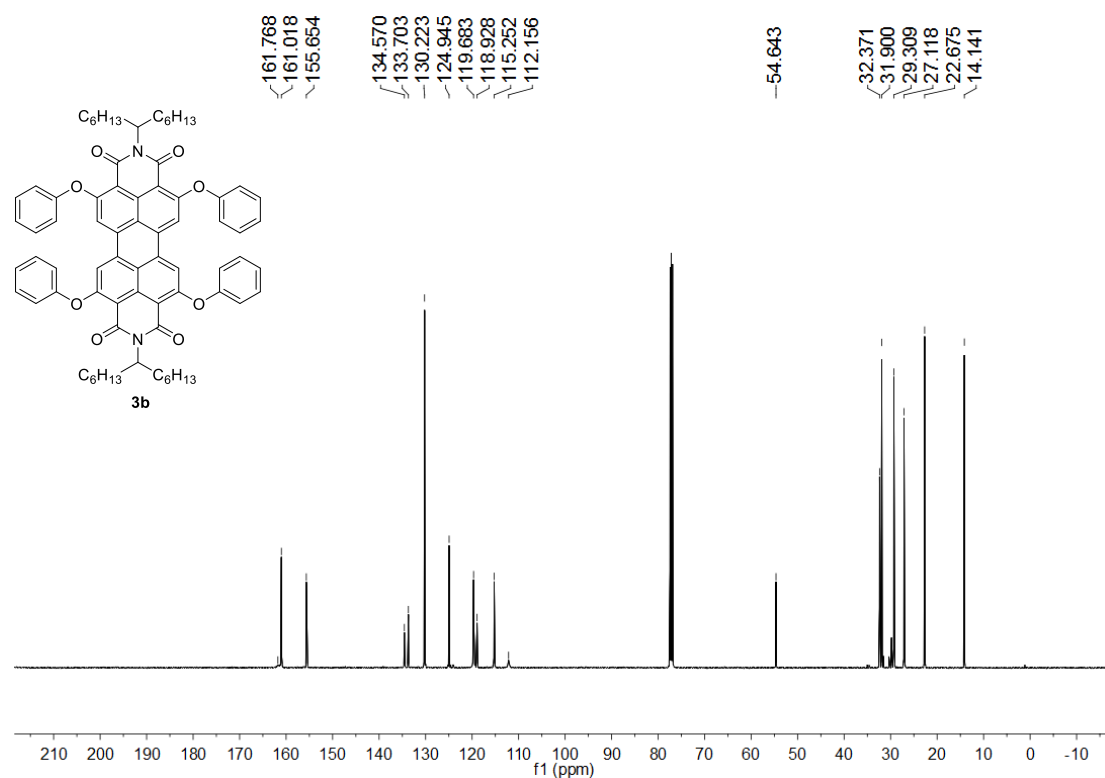
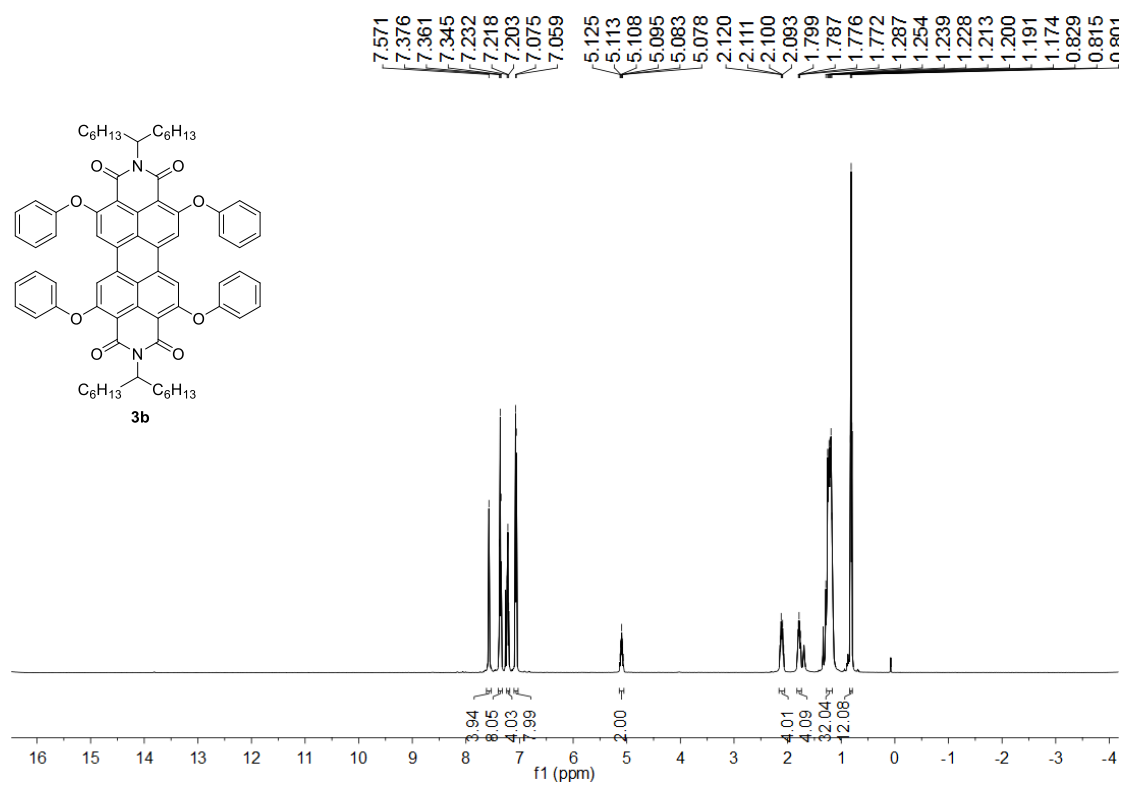


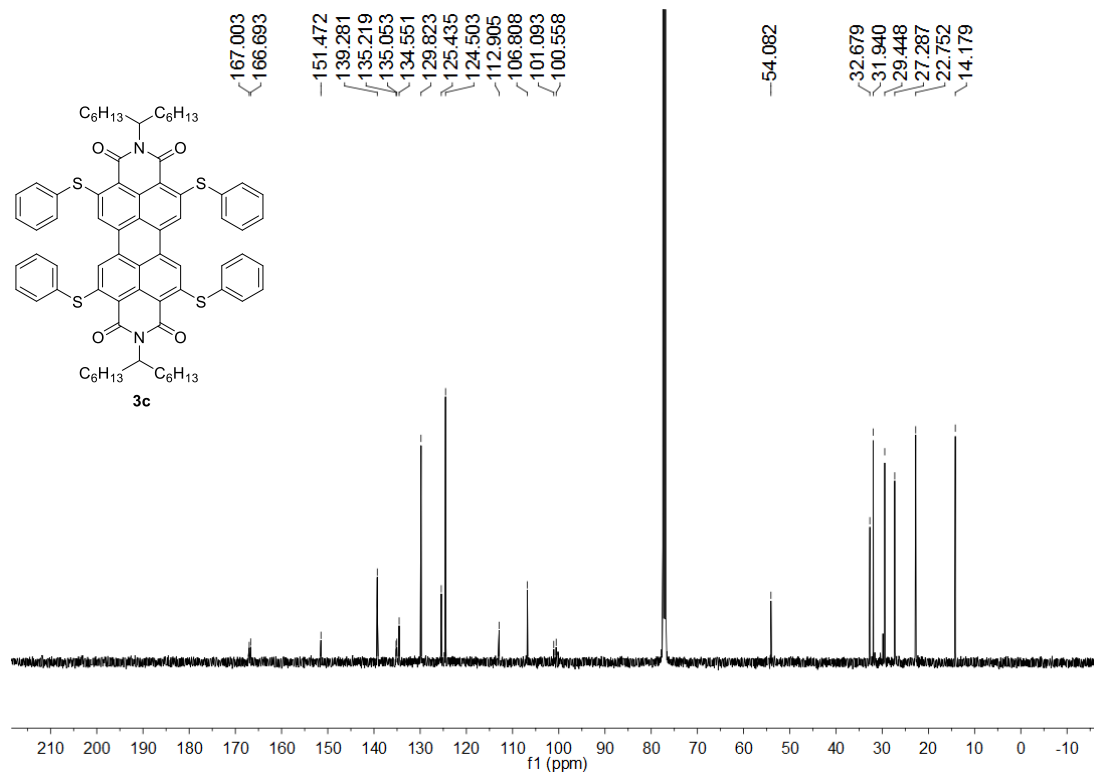
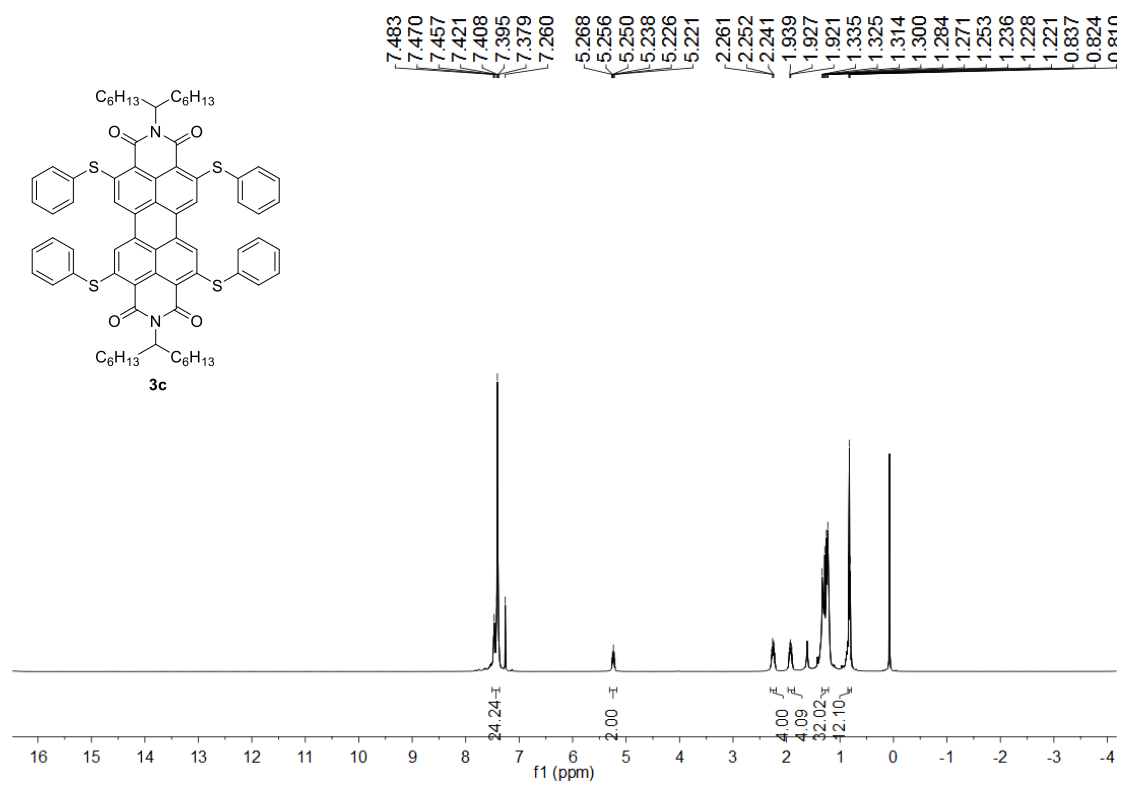


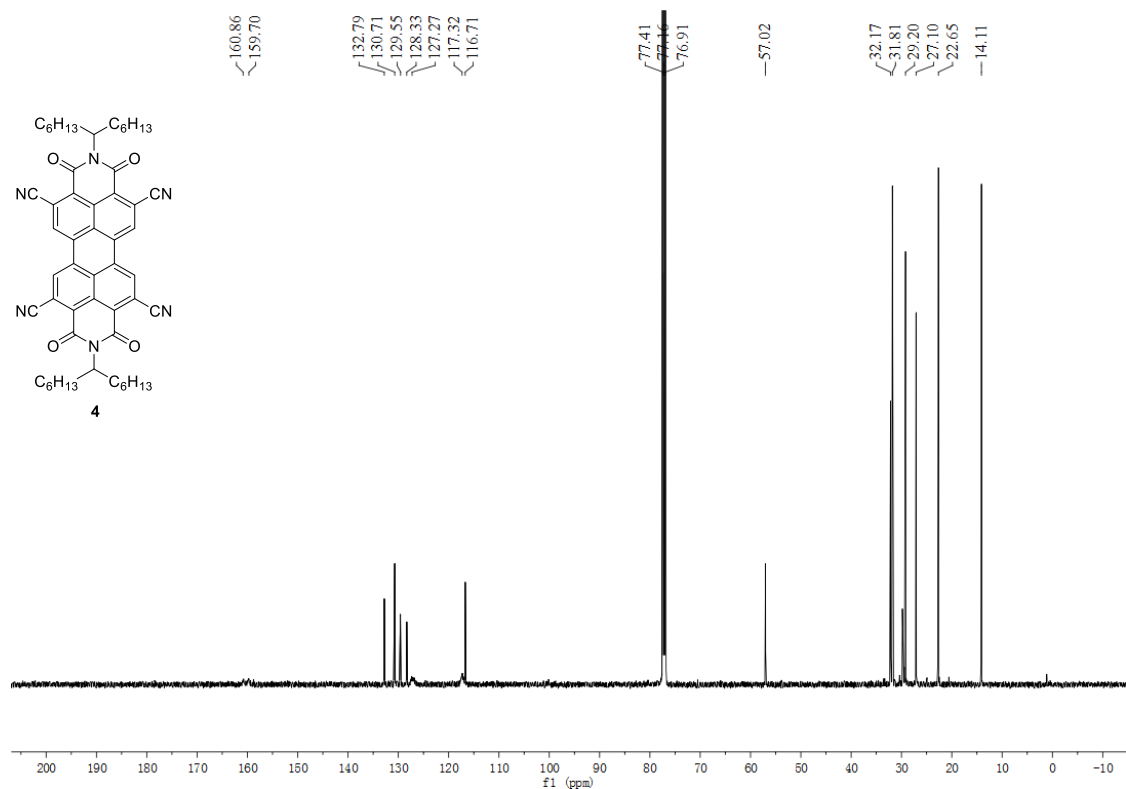
2a-l₂
mixture of regioisomers

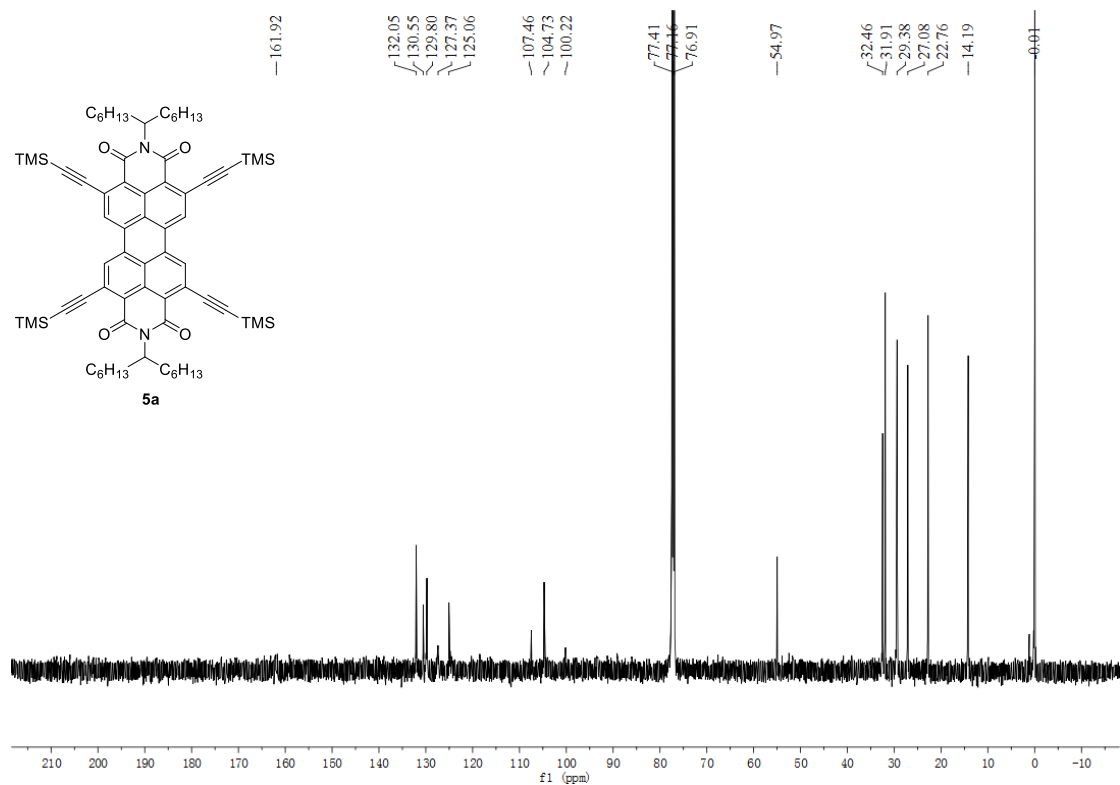
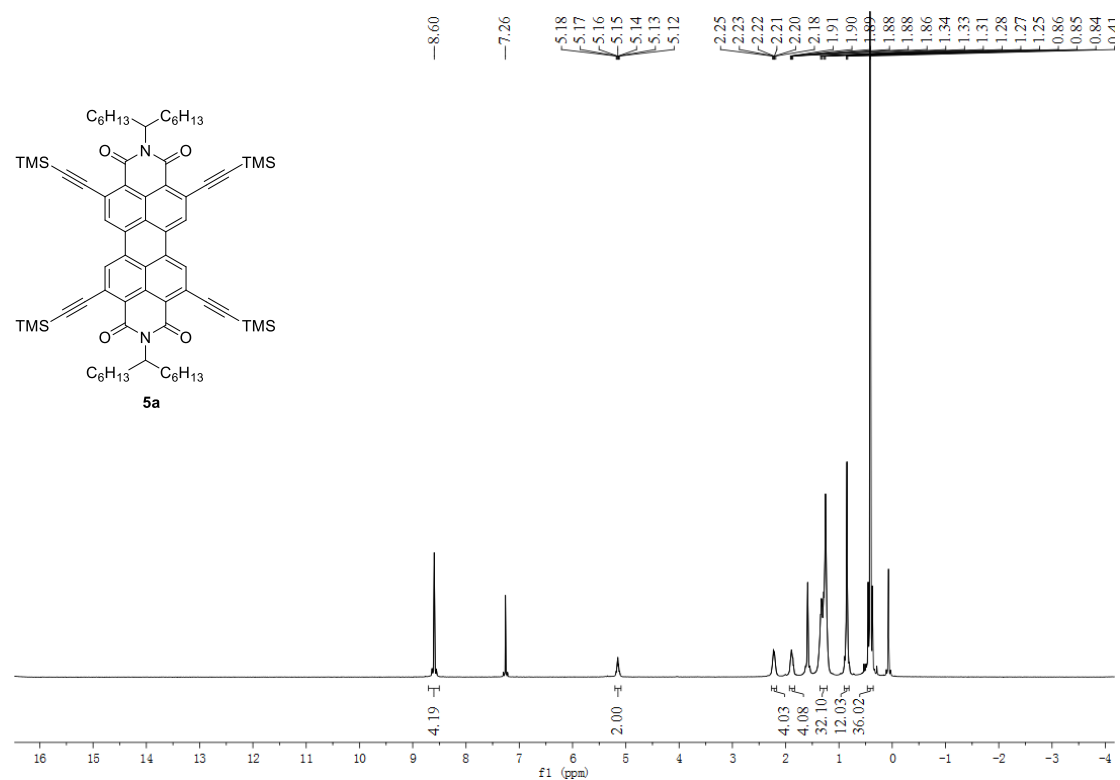


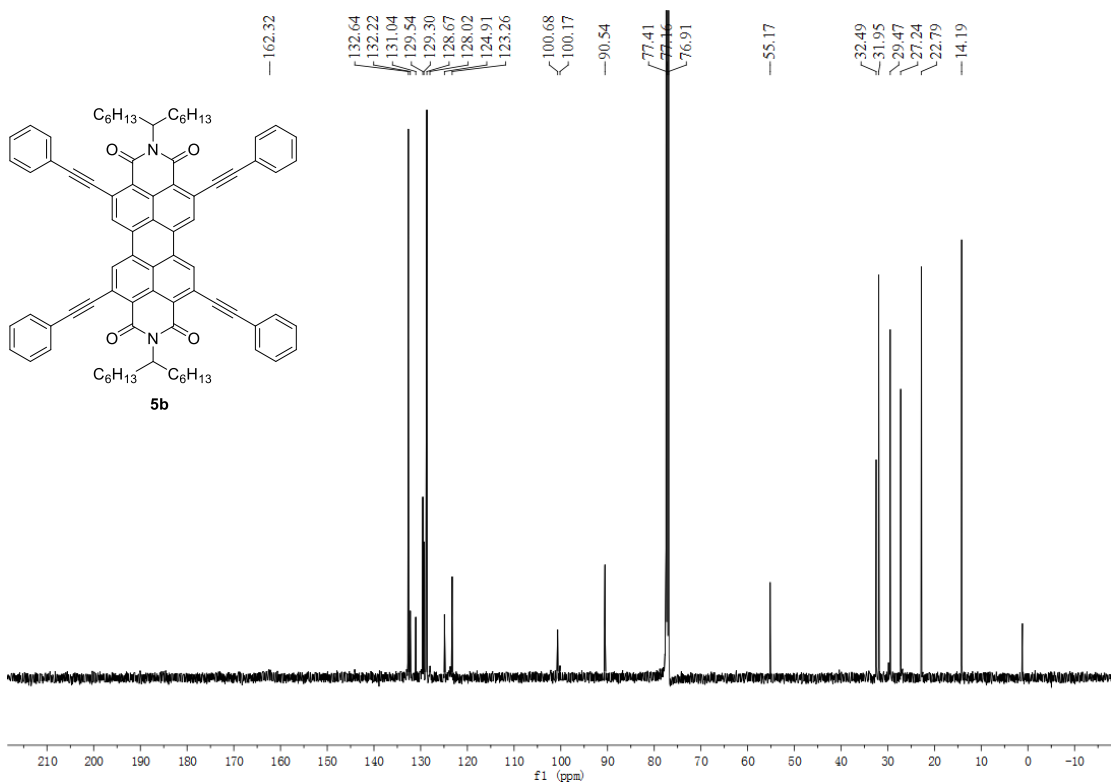


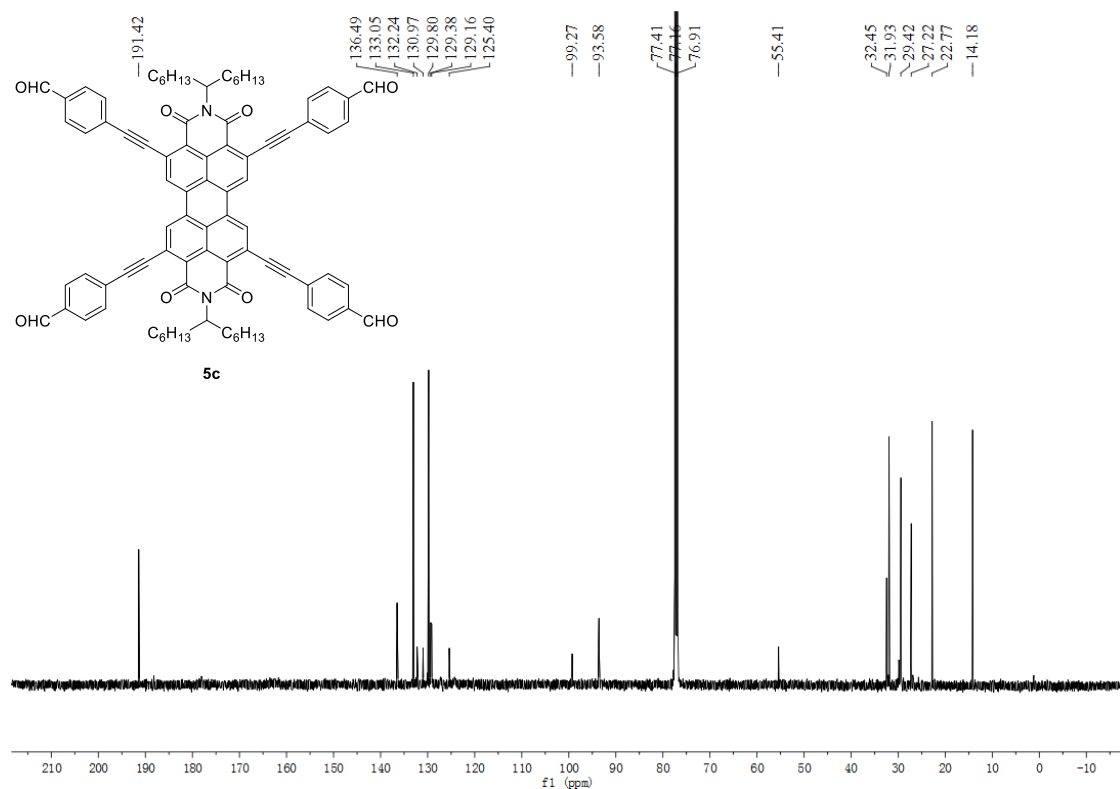
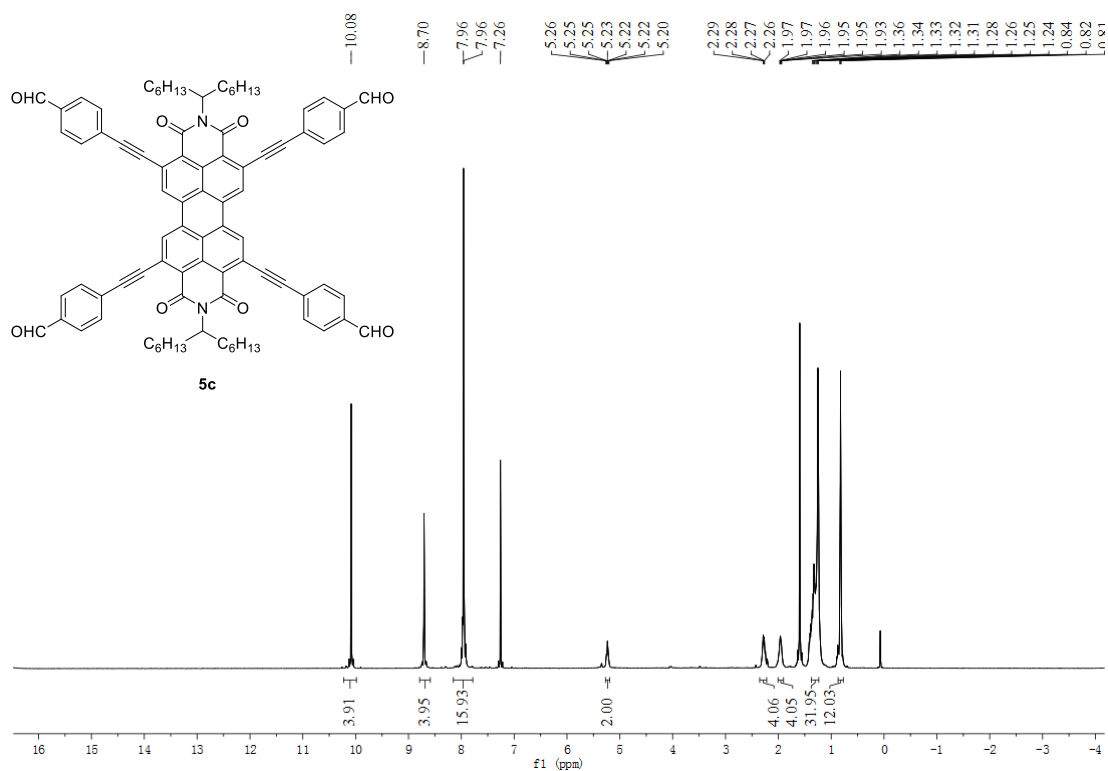


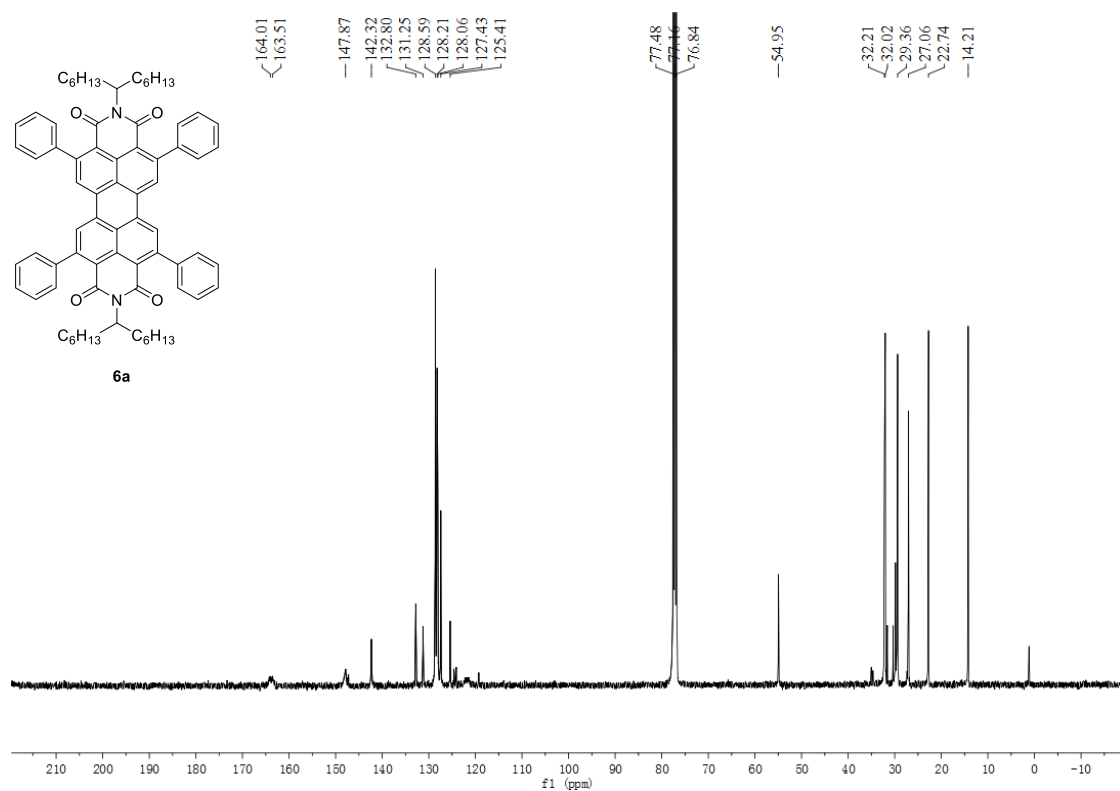
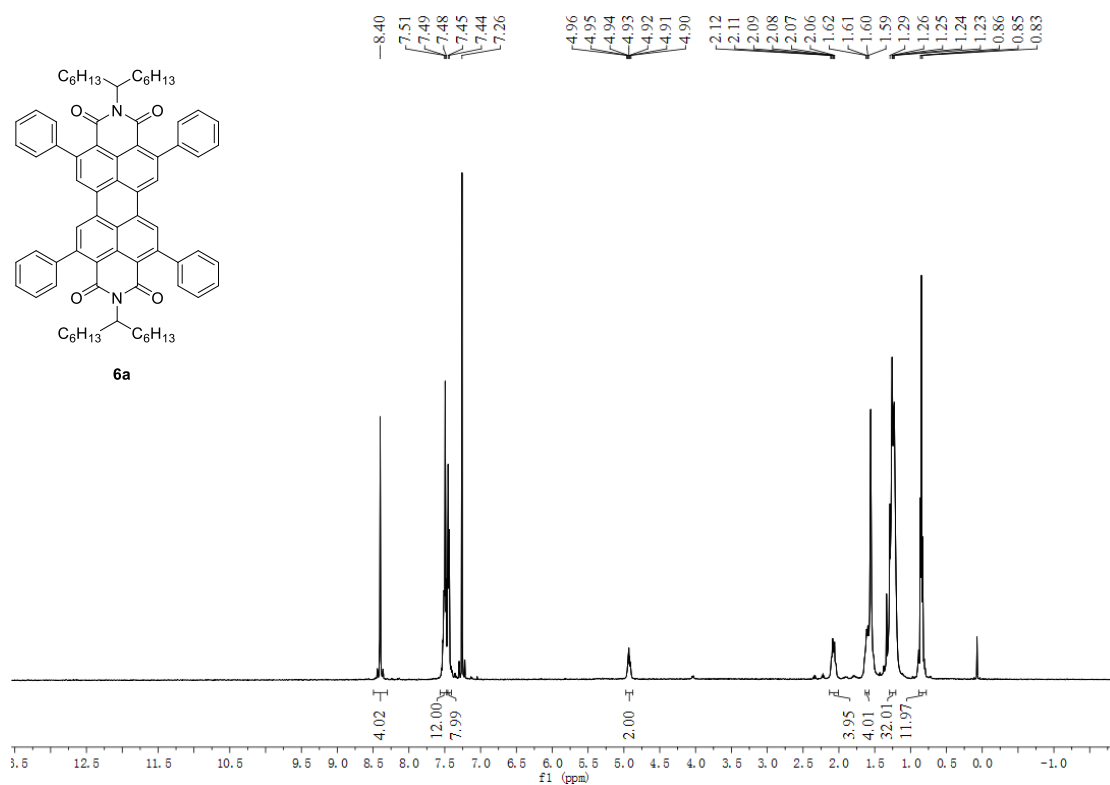


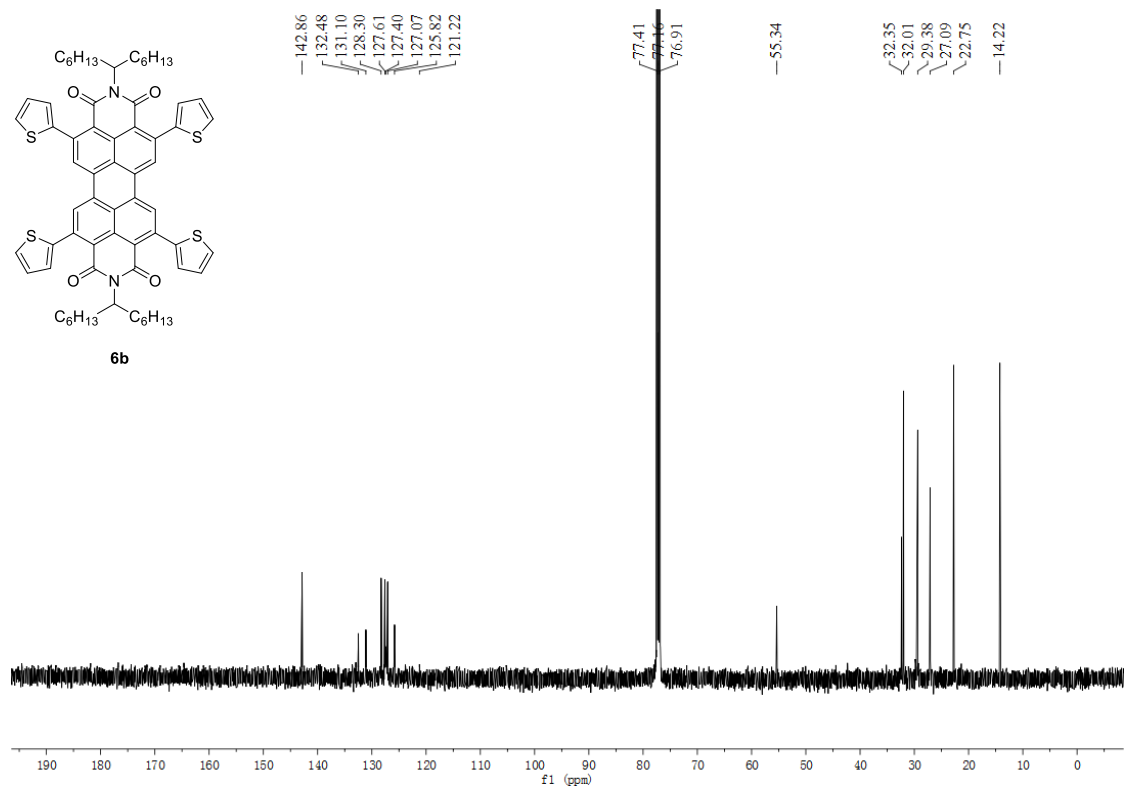
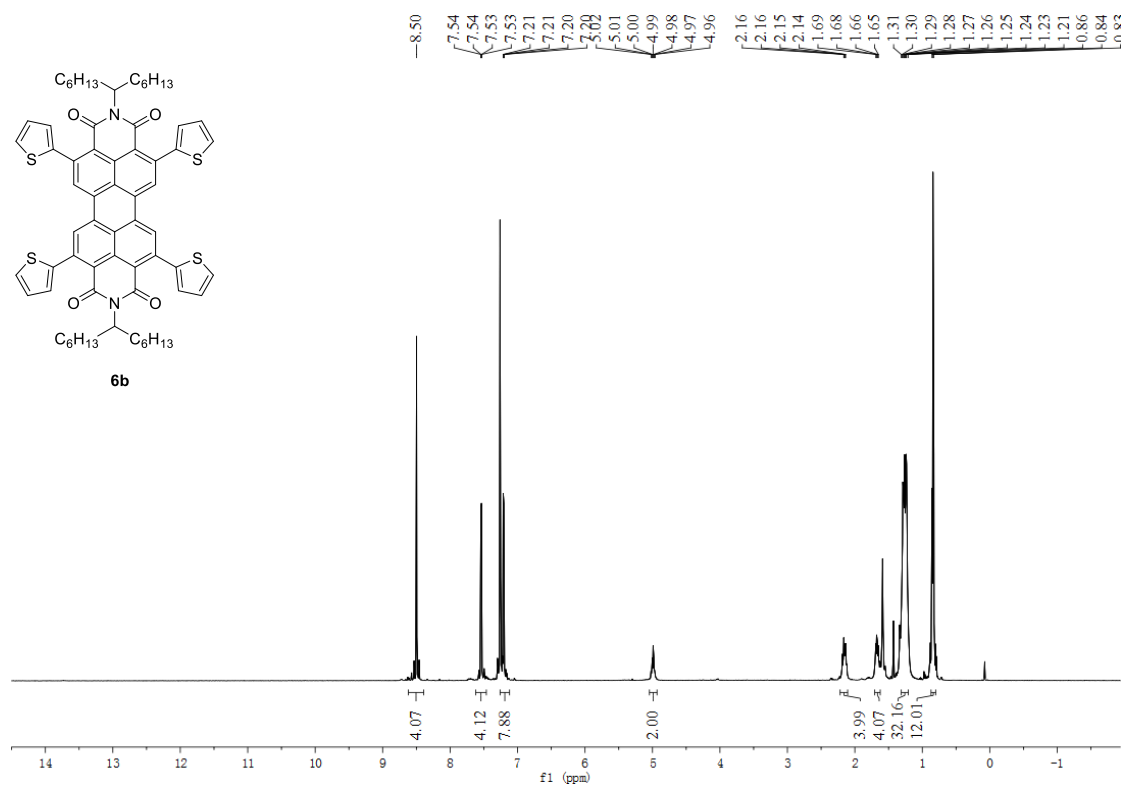












6) X-ray Single-Crystal Structure of 2b

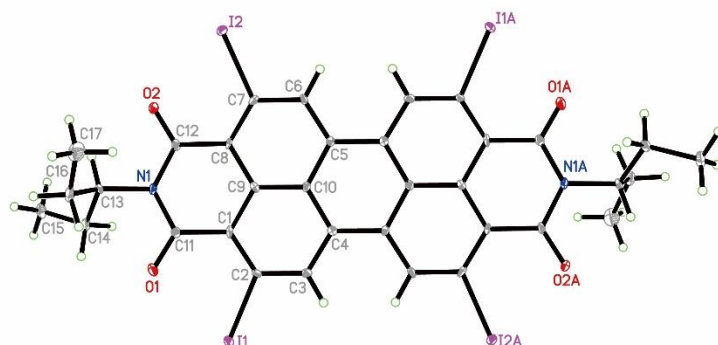


Table S5 Crystal data and structure refinement for **2b**.

Identification code	2b
Empirical formula	C ₃₄ H ₂₆ I ₄ N ₂ O ₄
Formula weight	1034.17
Temperature/K	173
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	18.7978(9)
b/Å	5.0125(2)
c/Å	18.4802(9)
α/°	90
β/°	116.925(6)
γ/°	90
Volume/Å ³	1552.52(14)
Z	2
ρ _{calc} /g/cm ³	2.212
μ/mm ⁻¹	31.875
F(000)	976.0
Crystal size/mm ³	0.1 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	9.58 to 124.21
Index ranges	-20 ≤ h ≤ 21, -5 ≤ k ≤ 5, -21 ≤ l ≤ 17
Reflections collected	7821
Independent reflections	2433 [R _{int} = 0.0567, R _{sigma} = 0.0600]
Data/restraints/parameters	2433/0/201
Goodness-of-fit on F ²	1.037
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0338, wR ₂ = 0.0827
Final R indexes [all data]	R ₁ = 0.0414, wR ₂ = 0.0894
Largest diff. peak/hole / e Å ⁻³	0.92/-1.06

Table S6 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2b**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
I2	7583.4(2)	12090.2(8)	619.2(2)	18.95(15)
I1	6067.0(2)	643.5(9)	3164.8(2)	19.41(16)
O1	7594(3)	3326(10)	3480(3)	24.4(11)
O2	8096(3)	10597(10)	2329(3)	25.3(12)
N1	7829(3)	7051(11)	2935(3)	13.7(11)
C1	6587(4)	4548(13)	2185(4)	12.5(13)
C6	6127(4)	8838(13)	55(4)	13.9(13)
C8	6965(4)	8023(12)	1487(4)	11.0(13)
C7	6816(4)	9337(13)	774(4)	13.2(13)
C10	5708(4)	5521(13)	738(4)	12.1(13)
C4	5162(4)	3556(12)	728(4)	10.8(12)
C5	5567(4)	6996(12)	24(4)	10.0(12)
C3	5331(4)	2203(13)	1439(4)	13.6(13)
C2	6023(4)	2714(12)	2152(4)	12.7(13)
C11	7369(4)	4882(13)	2915(4)	13.8(13)
C12	7667(4)	8692(13)	2271(4)	15.5(14)
C9	6419(4)	6053(12)	1472(4)	10.0(12)
C15	9027(4)	9377(15)	5124(4)	24.8(16)
C13	8578(4)	7625(14)	3694(4)	17.3(14)
C14	8427(4)	7668(14)	4445(4)	18.5(14)
C16	9244(4)	5722(15)	3773(4)	22.0(15)
C17	9493(5)	5943(19)	3097(5)	39(2)

Table S7 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2b**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I2	17.0(3)	25.0(3)	14.5(2)	-0.53(16)	6.73(19)	-8.82(16)
I1	17.2(3)	27.5(3)	10.9(2)	5.09(16)	4.00(18)	-4.29(16)
O1	23(3)	23(3)	15(2)	5(2)	-2(2)	-4(2)
O2	23(3)	24(3)	16(2)	3(2)	-2(2)	-14(2)
N1	10(3)	17(3)	10(3)	-2(2)	1(2)	-3(2)
C1	7(3)	20(4)	8(3)	-5(3)	1(3)	2(2)
C6	9(3)	21(3)	9(3)	4(3)	1(3)	2(2)
C8	5(3)	14(3)	12(3)	-3(2)	1(3)	-1(2)
C7	11(3)	15(3)	15(3)	-6(3)	8(3)	-6(2)
C10	9(3)	16(3)	11(3)	0(3)	4(3)	-1(2)
C4	12(3)	10(3)	11(3)	-1(2)	6(3)	2(2)
C5	10(3)	12(3)	9(3)	-3(2)	5(3)	0(2)

C3	10(3)	18(3)	15(3)	4(3)	8(3)	1(2)
C2	16(3)	10(3)	10(3)	2(2)	4(3)	-2(2)
C11	15(3)	14(3)	12(3)	-1(3)	4(3)	0(3)
C12	17(4)	16(3)	8(3)	-3(3)	1(3)	-2(3)
C9	11(3)	12(3)	8(3)	-1(2)	5(3)	5(2)
C15	21(4)	29(4)	16(3)	-4(3)	0(3)	-1(3)
C13	14(4)	21(4)	9(3)	4(3)	-3(3)	-4(3)
C14	12(3)	26(4)	13(3)	3(3)	2(3)	-1(3)
C16	13(4)	25(4)	20(4)	-3(3)	1(3)	-2(3)
C17	27(5)	54(6)	40(5)	-4(4)	19(4)	0(4)

Table S8 Bond Lengths for **2b**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I2	C7	2.107(6)	C8	C12	1.491(9)
I1	C2	2.109(6)	C8	C9	1.415(9)
O1	C11	1.215(8)	C10	C4	1.415(9)
O2	C12	1.223(8)	C10	C5	1.429(9)
N1	C11	1.379(9)	C10	C9	1.435(9)
N1	C12	1.391(9)	C4	C5 ¹	1.472(9)
N1	C13	1.498(8)	C4	C3	1.382(9)
C1	C2	1.383(9)	C5	C4 ¹	1.472(9)
C1	C11	1.489(9)	C3	C2	1.393(9)
C1	C9	1.424(9)	C15	C14	1.517(10)
C6	C7	1.394(9)	C13	C14	1.537(9)
C6	C5	1.382(9)	C13	C16	1.528(10)
C8	C7	1.384(9)	C16	C17	1.524(11)

Table S9 Bond Angles for **2b**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	N1	C12	124.0(5)	C6	C5	C4 ¹	122.1(6)
C11	N1	C13	119.2(5)	C10	C5	C4 ¹	118.6(6)
C12	N1	C13	116.7(5)	C4	C3	C2	121.5(6)
C2	C1	C11	122.5(6)	C1	C2	I1	124.5(5)
C2	C1	C9	117.9(6)	C1	C2	C3	122.2(6)
C9	C1	C11	119.5(6)	C3	C2	I1	113.2(4)
C5	C6	C7	121.4(6)	O1	C11	N1	120.9(6)
C7	C8	C12	121.9(6)	O1	C11	C1	121.5(6)
C7	C8	C9	118.7(6)	N1	C11	C1	117.5(6)
C9	C8	C12	119.4(6)	O2	C12	N1	120.8(6)
C6	C7	I2	112.7(5)	O2	C12	C8	121.2(6)

C8	C7	I2	125.8(5)	N1	C12	C8	117.9(6)
C8	C7	C6	121.5(6)	C1	C9	C10	119.8(6)
C4	C10	C5	121.2(6)	C8	C9	C1	119.8(6)
C4	C10	C9	120.1(6)	C8	C9	C10	120.4(5)
C5	C10	C9	118.7(6)	N1	C13	C14	111.6(5)
C10	C4	C5 ¹	120.2(6)	N1	C13	C16	110.6(5)
C3	C4	C10	118.4(6)	C16	C13	C14	113.7(6)
C3	C4	C5 ¹	121.4(6)	C15	C14	C13	112.5(6)
C6	C5	C10	119.3(6)	C17	C16	C13	114.8(6)

Table S10 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **2b**.

Atom	x	y	z	U(eq)
H6	6041	9784	-423	17
H3	4967	893	1442	16
H15A	8966	11244	4949	37
H15B	9569	8772	5259	37
H15C	8935	9219	5604	37
H13	8752	9462	3634	21
H14A	7883	8362	4287	22
H14B	8452	5821	4645	22
H16A	9717	6066	4298	26
H16B	9068	3870	3786	26
H17A	9048	5398	2581	59
H17B	9953	4780	3219	59
H17C	9639	7794	3055	59

7) Optical and Redox properties of PDIs 1-6

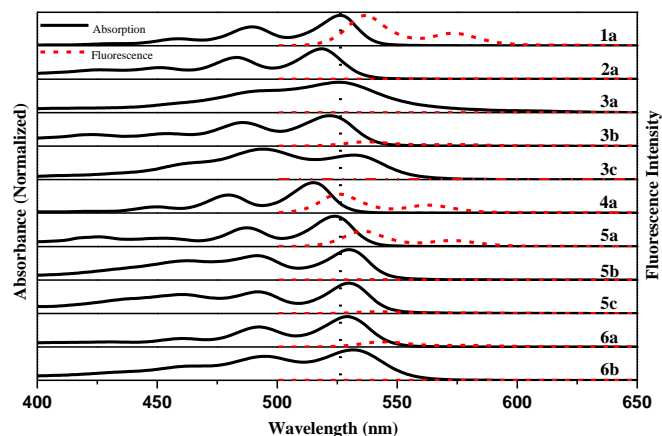


Fig. S1. UV-visible absorption spectra and fluorescence spectra ($\lambda_{\text{exc}} = 490 \text{ nm}$) of PDI **1-6** in DCM (10 μM).

The electronic absorption spectra of compounds **1-6** were recorded in DCM (**Fig. S1**). Distinct from most of those known *bay*-substituted PDIs which exhibit substantial bathochromic shifts due to the twisting of the perylene core, the *ortho*-substituents have little influence on the absorption maximum of PDIs **2-6**. Also, the drop of their maximal absorption intensities were observed. Compared with PDI **1a**, hypsochromic shift (7 nm, 10 nm) of absorption maxima is observed for PDIs **2a** and **4a** probably because of the involvement of electron-withdrawing iodo and cyano substituents. For PDI **3a**, the broadening of the absorption line and the loss of the detailed vibronic structure were observed which may be attributed to the enhanced participation of the side groups in the conjugation with PDI core caused by intramolecular hydrogen bonding between carbonyl and NH groups (12.0 ppm of for NH in the ^1H NMR spectra). For PDIs **5b-6**, the conjugation of the PDI core with alkynyl and (hetero)aryl substituents gave rise to small bathochromic shifts of the main absorption band to about 530 nm.

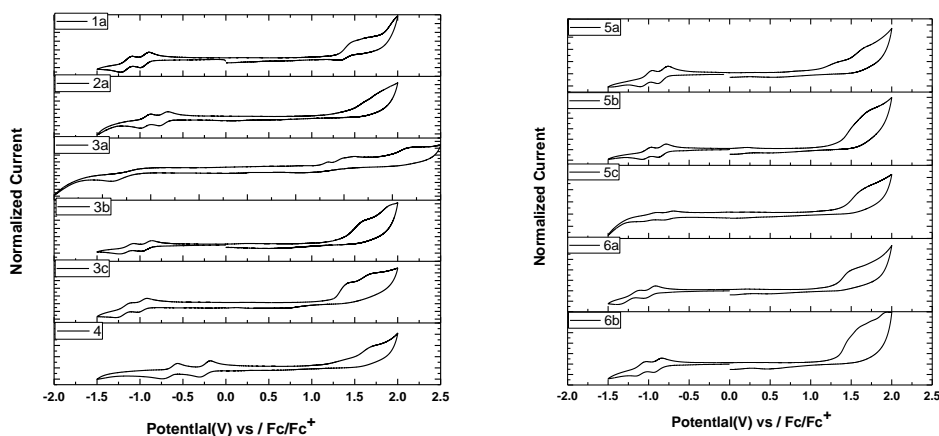


Fig. S2. Cyclic voltammograms of PDI **1-6** in 0.1 M Bu₄NPF₆ CH₂Cl₂ solution. Potentials are reported vs the Fc/Fc⁺ redox couple as an internal standard; Counter electrode: Pt, Reference electrode: Ag/ AgNO₃, scan rate = 100 mV/s.

Table S11 Optical and Redox properties of PDIs **1-6**

PDIs	λ_{abs} nm	ϵ_{max} (M ⁻¹ cm ⁻¹)	λ_{em} nm	ϕ_f^a	E_{red1} V	E_{red2} V	E_g eV	LUMO ^b eV	HOMO ^c eV
1a	526	71600	538	0.89	-1.03	-1.18	2.29	-3.77	-6.06
2a	519	55600	—	—	-0.82	-0.97	2.32	-3.98	-6.30
3a	528	54400	—	—	-1.31	—	2.23	-3.49	-5.72
3b	522	43000	540	0.16	-0.99	-1.03	2.30	-3.81	-6.11
3c	494	46600	—	—	-1.06	-1.22	2.24	-3.74	-5.98
4	516	57000	528	0.95	-0.33	-0.71	2.33	-4.47	-6.80
5a	524	65900	534	0.51	-0.92	-1.02	2.29	-3.88	-6.17
5b	530	53000	—	—	-0.90	-0.99	2.27	-3.90	-6.17
5c	530	45100	—	—	-0.82	-0.98	2.26	-3.98	-6.24
6a	530	54200	540	0.19	-1.05	-1.22	2.27	-3.75	-6.02
6b	532	43300	—	—	-0.94	-1.06	2.23	-3.86	-6.09

^aAbsolute quantum yield determined by a calibrated integrating sphere system in DCM solution. ^bLUMO was estimated vs vacuum level from LUMO = 4.80 eV - E_{red1} , ^cHOMO was calculated from HOMO = LUMO - E_g

The fluorescence quantum yields of these PDI derivatives except PDI **4a** (ϕ_f : 95%) were strongly decreased (ϕ_f : **3b** (16%), **5a** (51%), **6a** (19%), other derivatives showed a complete quenching, Table S11). For PDI **2a**, the fluorescence quenching might be ascribed to the heavy atom effect. For PDIs **3**, **5** and **6**, higher degree of electronic interaction between the electron-rich substituents and the planar electron-deficient PDI core compared with *bay*-substituted PDIs is responsible for the decrease of fluorescence quantum yields.

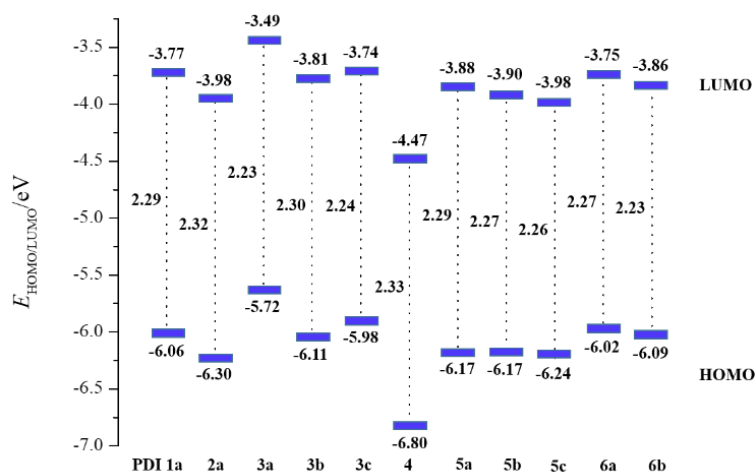


Fig. S3. Energy level diagram of PDIs **1-6**

8) FTIR spectra, FESEM images and Diffuse reflectance UV-vis absorption spectra of CMP 7-8

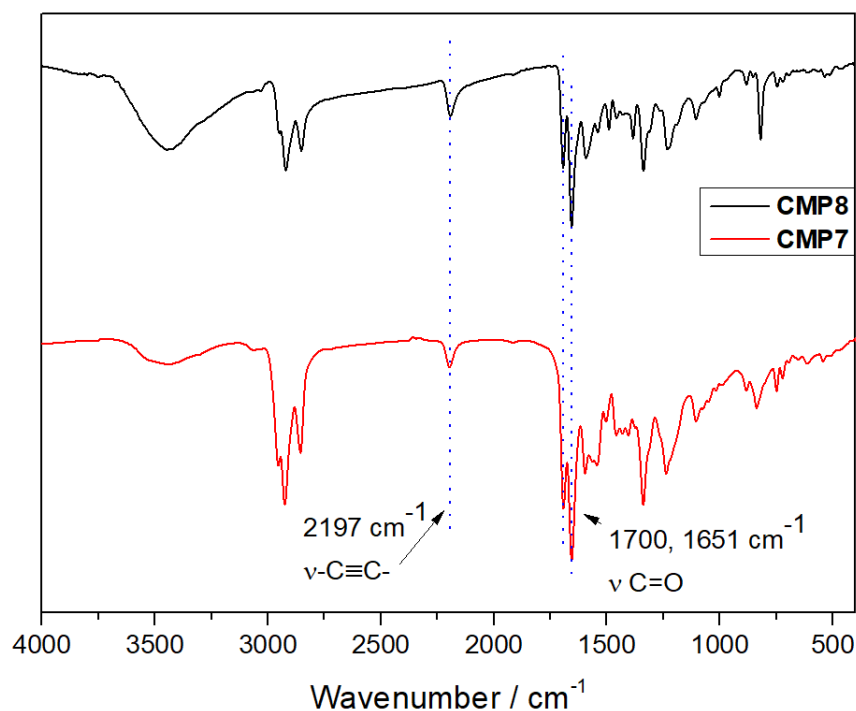


Fig. S4. FTIR spectra of the prepared CMPs.

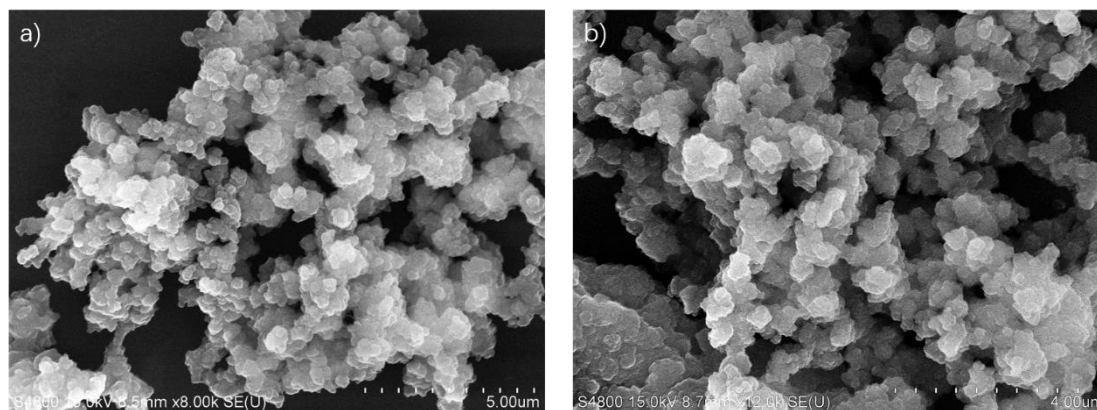


Fig. S5. SEM images of the prepared a) **CMP 7** and b) **CMP 8**. (SEM samples were prepared by ultrasonic dispersion in ethonal and then drop-casting solutions on freshly cleaved Silicon dioxide sheet and dried at room temperature for 12 hours.

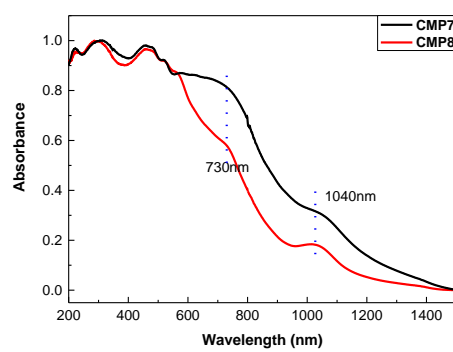


Figure S6. Diffuse reflectance UV-vis absorption spectra of **CMP 7** and **CMP 8**