SUPPORTING INFORMATION

Facile synthesis and characterization of well-defined soluble poly(benzimidazobenzophenanthroline)-Like derivatives

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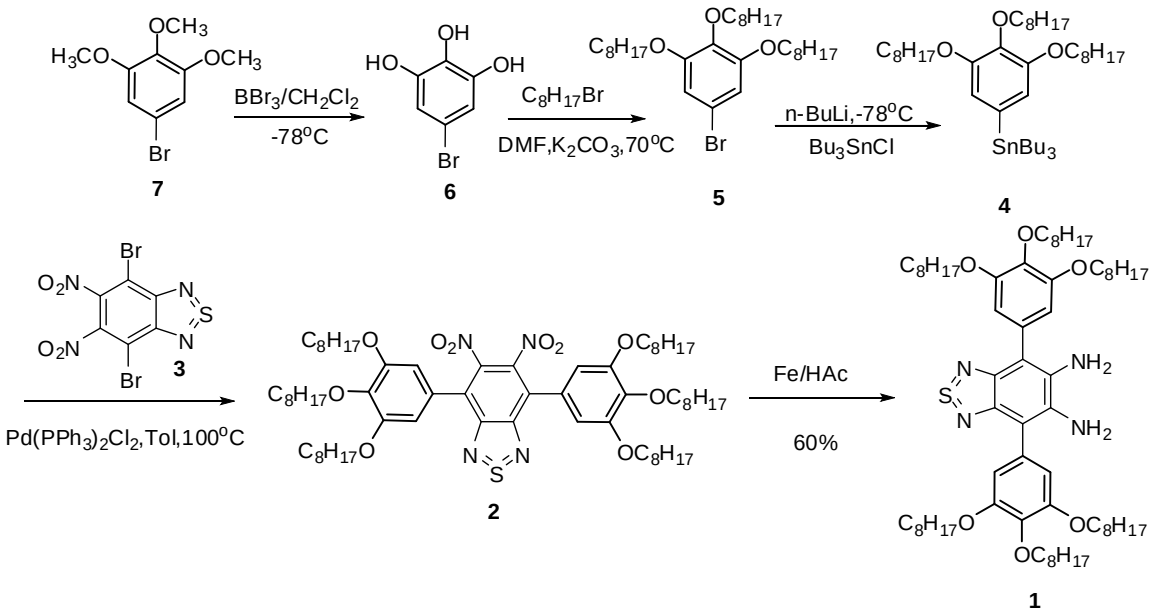
General Method

^{1}H NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer. The high-temperature NMR data were obtained on a Varian Unity 400 MHz spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Elemental analysis was performed on FlashEA1112. The UV-Vis-NIR absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Cyclic voltammetry was performed on a CHI660b electrochemical workstation in dry dichloromethane containing n-Bu_4NPF_6 (0.1 M) with a scan rate of 100 mV/s at room temperature under argon, using a Pt disk (2 mm diameter) as the working electrode, a Pt wire as the counter electrode and a calomel electrode as the reference electrode. Differential scanning calorimetry (DSC) measurements were performed on a TA-DSC Q100 at a heating rate of 10 ℃/min under a continuous nitrogen flow. MALDI-TOF-MS was obtained from Bruker Daltonics Autoflex III TOF/TOF.

Materials

All the chemicals and reagents were used as received from commercial sources without purification. Solvents for chemical synthesis were purified by distillation. All the chemical reactions were carried out under an argon atmosphere. 5-Bromo-1,2,3-trihydroxybenzene, 5-bromo-1,2,3-trioctyloxybenzene, tributyl(3,4,5-trioctyloxyphenyl)stannane, 4,7-dibromo-5,6-dinitro-2,1,3-benzothiadiazole and benzo[1,2-b:6,5-b]dithiophene-4,5-dione were prepared according to literature methods.[1-3]

Scheme S1. Synthetic route to diamine **1**.



Compound 2

Tributyl(3,4,5-trioctyloxyphenyl)stannane **4** (31.6 g, 42.0 mmol) and 4,7-dibromo-5,6-dinitro-2,1,3-benzothiadiazole **3** (7.2 g, 18.7 mmol) and $Pd(PPh_3)_2Cl_2$ (200 mg) were dissolved in 300 mL of toluene and the mixture was heated to 110 ℃ for 20 h. After cooling, the mixture was added into 300 mL saturated aqueous potassium fluoride solution and some flocculent solids were formed. These flocculent solids were removed by filtration and washed with 150 mL toluene. The organic layer of the filtrate were collected and washed with 400 mL brine and then dried over $MgSO_4$. The product was obtained as orange solid (18.6 g, 87%) after column chromatography (silica gel, dichloromethane/petroleum ether = 1/2, V/V).^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 4H), 4.06 (t, *J* = 6.6 Hz, 4H), 3.96 (t, *J* = 6.5 Hz, 8H), 1.84–1.75 (m, 12H), 1.58–1.41 (m, 12H), 1.41–1.20 (m, 48H), 0.94–0.89 (m, 18H).

Compound 1

Compound **2** (6.8 g, 6.0 mmol), iron powder (4.0 g) were charged into a 100-mL round-bottomed flask, followed by addition of 60 mL of acetic acid. The mixture was heated to 80 °C and maintained for 4 h. After cooling, the mixture was diluted with 100 mL dichloromethane and washed with 200 mL brine twice. The separated organic layer was dried over $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography (silica gel, dichloromethane/petroleum ether = 2/1, V/V) and gave a brown oil (3.8 g, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (s, 4H), 4.04 (t, 4H), 3.98 (t, 8H), 3.00 (br, 4H), 1.84–1.77 (m, 12H), 1.55–1.28 (m, 60H), 0.92–0.86 (m, 18H).

Compound N1

1,4,5,8-Naphthalenetetracarboxylic dianhydride (400 mg, 1.5 mmol) and compound **1** (3.3 g, 3.0 mmol) were dissolved in 15 mL of m-cresol. The reaction mixture was heated at 200 °C for 12 h under argon atmosphere. The crude product was precipitated by addition of the cooling reaction mixture to 80 ml of methanol, and collected by filtration and purified by silica gel column chromatography with dichloromethane as the eluent to afford the product as a dark green solid (2.6 g, 80% yield). According to the HNMR spectrum, the product was mixture of two isomers. The ratio of *trans*/*cis* isomers is about 1:1. The peaks at 9.06 and 9.01 were assigned to the *cis* isomer, while the peaks at 9.02, 9.0, 8.67 and 8.66 were assigned to the *trans* one. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.06 (s, 1H), 9.02 (s, 0.5H), 9.00 (s, 0.5H), 8.67 (s, 0.5H), 8.66 (s, 0.5H), 8.62 (s, 1H), 7.55 (d, *J* = 4.0 Hz, 4H), 6.86 (d, *J* = 4.0 Hz, 4H), 4.16–4.12 (m, 16H), 3.98 (t, *J* = 6.5 Hz, 8H), 1.96–1.82 (m, 16H), 1.80–1.76 (m, 8H), 1.64–1.46 (m, 20H), 1.46–1.14 (m, 100H), 0.99–0.76 (m, 36H). ^{13}C NMR (100 MHz, $C_2Cl_4D_2$) δ (ppm) 156.75, 156.59, 154.53, 152.82, 152.56, 145.07, 139.06, 138.24, 138.16, 133.16, 132.12, 132.05, 131.40, 128.72, 128.58, 128.07, 127.20, 126.97, 126.03, 124.30, 123.07, 122.93, 119.85, 111.19, 109.48, 69.37, 32.10, 32.02, 31.97, 30.68, 29.76, 29.65, 29.60, 29.51, 29.48, 29.43, 26.40, 26.32, 22.92, 22.86, 22.82, 14.39, 14.35, 14.32, 14.31. MS (MALDI-TOF): Calcd. 2369.6, Found 2369.6, Elemental analysis: Calcd. for $C_{146}H_{216}N_8O_{14}S_2$ C, 73.94; H, 9.18; N, 4.73; S, 2.70; Found: C, 74.11; H, 9.19; N, 4.56; S, 2.63

Compound N-4NH$_2$

A solution of compound **N1** (2.0 g) in refluxing THF (200 mL) was stirred for 10 h with 10 g Raney nickel catalyst under atmospheric hydrogen. After cooling, the catalyst was removed by filtration. Dark solid was obtained when the solvent was removed from the filtrate and this crude product was purified by column chromatography on silica gel with DCM/EA (50/1,V/V) as eluent to give the final product as dark blue solid (85% yield). According to the HNMR spectrum, the product was also mixture of two isomers. The ratio of *trans*/*cis* isomers is about 1:3. The reduced ratio was caused by the loss of the less spot（*trans* isomer）during the process of speration by chromatography for some by-product were overlapped with the *trans* isomer of N-4NH$_2$. ^{1}H NMR (400 MHz, 298K, $CDCl_3$): δ (ppm) 8.67 (s, 1.5H), 8.65 (s, 0.5H), 8.43 (s, 1.5H), 8.41 (s, 0.5H), 6.84 (s, 4H), 6.56 (s, 4H), 4.17–4.01 (m, 16H), 3.95 (t, *J* = 6.2 Hz, 8H), 1.98–1.69 (m, 24H), 1.64–1.04 (m, 120H), 0.99–0.64 (m, 36H). ^{13}C NMR (101 MHz, 298K, $CDCl_3$) δ (ppm) 157.65, 157.42, 154.31, 154.07, 153.42, 153.18, 137.89, 137.63, 133.06, 131.67, 129.32, 125.74, 119.28, 114.92, 109.27, 108.89, 78.66, 78.25, 77.93, 77.61, 73.53, 73.45, 69.29, 69.16, 32.86, 32.73, 32.70, 31.98, 31.85, 31.82, 31.41, 30.52, 30.47, 30.34, 30.29, 30.20, 30.16, 29.67, 29.65, 29.46, 29.41, 29.32, 29.27, 27.81, 27.06, 26.97, 26.25, 26.22, 26.18, 26.09, 23.63, 23.55, 23.52, 22.75, 22.67, 22.64, 15.02, 14.95, 14.14, 14.07. Elemental analysis: Calcd. for $C_{146}H_{224}N_8O_{14}$ C, 75.74; H, 9.75; N, 4.84; Found: C, 75.63; H, 9.61; N, 4.61.

Compound N2

The reaction was carried out using the same procedure as for compound **N1**, using 460 mg (0.2 mmol) **N-4NH$_2$** and 84 mg (0.4 mmol) phenanthraquinone as the starting materials. The crude product was purified by column chromatography on silica gel with dichloromethane as the eluent to give the final product as dark solid (400 mg, 75 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.17 (br, 4H), 8.54 (br, 6H), 7.75 (br, 4H), 7.65 (br, 4H), 7.52 (br, 4H), 7.02 (br, 4H),4.29–4.09 (m, 24H), 2.21–1.70 (m, 24H), 1.74–1.01 (m, 120H), 1.01–0.66 (m, 36). ^{13}C NMR (100 MHz, $CDCl_3$/CF_3COOD = 2:1) δ (ppm) 157.11, 156.94, 155.78, 155.54, 153.52, 153.46, 153.31, 153.21, 145.22, 137.96, 137.89, 137.14, 137.07, 136.09, 135.03, 134.88, 133.24, 130.52, 130.31, 130.04, 128.84, 128.03, 127.22, 126.84, 126.32, 126.10, 124.97, 124.58, 123.75, 76.00, 70.31, 31.79, 31.67, 31.62, 29.72, 29.62, 29.42, 29.38, 29.24, 29.14, 29.07, 29.01, 28.95, 25.91, 25.82, 25.77, 22.53, 22.41, 22.38, 13.51, 13.46, 13.38, 13.33. MS (MALDI-TOF): Calcd. 2657.77; Found 2657.8. Elemental analysis: Calcd. for $C_{174}H_{232}N_8O_{14}$ C, 78.57; H, 8.79; N, 4.21; Found: C, 78.75; H, 8.83; N, 4.12.

Compound N3

The reaction was carried out using the same procedure as for compound **N1**, using 460 mg (0.2 mmol) **N-4NH$_2$** and 88 mg (0.4 mmol) benzo[1,2-b:6,5-b]dithiophene-4,5-dione as the starting materials. The crude product was purified by column chromatography on silica gel with dichloromethane as the eluent to give the final product as dark solid (348 mg, 65 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (br, 2H), 8.62 (br, 2H), 8.24 (br, 4H), 7.48 (s, 8H), 6.99 (s, 4H), 4.26–4.17 (m, 16H), 4.03 (br, 8H), 1.95 (br, 16H), 1.80 (br, 8H), 1.60–1.26 (m, 120H), 0.94–0.83 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$/CF_3COOD = 2:1) δ (ppm) 157.09, 156.93, 155.78, 155.55, 153.32, 144.87, 137.83, 137.06, 134.83, 134.68, 133.31, 129.66, 128.04, 127.23, 126.89, 126.39, 124.89, 123.80, 122.85, 118.42, 115.60, 112.78, 109.96, 76.06, 70.38, 31.75, 31.64, 31.60, 29.69, 29.37, 29.32, 29.20, 29.13, 29.04, 28.93, 25.87, 25.78, 22.49, 22.37, 13.39, 13.29. MS (MALDI-TOF): Calcd. 2681.6; found 2682.6. Elemental analysis: Calcd. for $C_{166}H_{224}N_8O_{14}S_4$: C, 74.29; H, 8.41; N, 4.18; S, 4.78. Found: C, 74.11; H, 8.49; N, 4.02; S, 4.68.

Compound P1

The reaction was carried out using the same procedure as for compound **N1**, using 8.7 g (8 mmol) of compound **1** and 1.6 g (4 mmol) of perylene-3,4,9,10-tetracarboxylic dianhydride as the starting materials. The crude product was purified by column chromatography on silica gel with dichloromethane as the eluent to give the final product as dark solid (7.0 g, 70 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.99–8.97 (m, 2H), 8.71–8.67 (m, 4H), 8.58–8.55 (m, 2H), 7.61 (s, 4H), 6.89 (s, 4H), 4.24–4.08 (m, 16H), 3.99 (t, *J* = 6.5 Hz, 8H), 2.01–1.63 (m, 24H), 1.60–1.57 (m, 20H), 1.57–1.00 (m, 100H), 1.00–0.76 (m, 36H). ^{13}C NMR (100 MHz, $C_2D_2Cl_4$) δ (ppm) 157.34, 154.14, 152.78, 152.45, 145.43, 138.78, 137.96, 133.74, 133.58, 133.25, 132.20, 131.60, 131.53, 129.15, 128.93, 128.40, 127.04, 124.86, 124.52, 123.76, 121.84, 119.52, 111.12, 109.45, 69.30, 32.13, 32.07, 31.98, 30.70, 29.80,

29.69, 29.62, 29.57, 29.47, 26.44, 26.32, 22.94, 22.89, 22.83, 14.41, 14.38, 14.31. MS (MALDI-TOF): Calcd. 2493.6, Found 2493.6. Elemental analysis: Calcd. for $C_{156}H_{220}N_8O_{14}S_2$ C, 75.08; H, 8.89; N, 4.49; S, 2.57. Found: C, 75.45; H, 8.96; N, 4.33; S, 2.55.

Compound P-4NH$_2$

A solution of compound **P1** (2.5 g) in refluxing THF (250 mL) was stirred for 15 h with 12.5 g Raney nickel catalyst under atmospheric hydrogen. After cooling, the catalyst was removed by filtration. Dark solid was obtained when the solvent was removed from the filtrate and this crude product was purified by column chromatography on silica gel with DCM/EA (40/1,V/V) as eluent to give the final product as dark blue solid (1.8 g, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.78–8.76 (m, 2H), 8.53–8.44 (m, 6H), 6.90 (s, 4H), 6.59 (s, 4H), 4.15–4.05 (m, 16H), 3.97 (br, 8H), 1.88–1.74 (m, 24H), 1.62–1.21 (m, 120H), 0.93–0.80 (m, 36H). ^{13}C NMR (100 MHz, $C_2Cl_4D_2$) δ (ppm) 158.11, 153.40, 153.16, 147.30, 137.47, 137.36, 135.65, 135.04, 133.92, 133.79, 131.92, 131.71, 131.34, 131.14, 129.87, 127.87, 126.84, 126.76, 126.33, 126.02, 125.32, 125.22, 125.03, 124.20, 123.58, 122.94, 122.72, 122.32, 122.07, 118.76, 115.40, 109.38, 108.95, 74.32, 74.05, 73.77, 69.36, 69.21, 32.15, 32.13, 32.04, 31.98, 30.68, 30.59, 29.82, 29.78, 29.63, 29.61, 29.58, 29.51, 29.46, 26.42, 26.38, 26.27, 22.94, 22.87, 22.84, 14.41, 14.36, 14.32. Elemental analysis: Calcd. for $C_{156}H_{228}N_8O_{14}$: C, 76.80; H, 9.42; N, 4.59. Found: C, 76.87; H, 9.30; N, 4.30.

Compound P2

The reaction was carried out using the same procedure as for compound **N1**, using 488 mg (0.2 mmol) of **P-4NH$_2$** and 84 mg (0.4 mmol) of phenanthraquinone as the starting materials. The crude product was purified by column chromatography on silica gel with dichloromethane as the eluent and two spots were collected. Both of the two spots were identified as isomers of the target compound, but the assignment of the structures is impossible. The total yield was 65%.

The less polar isomer of P2: ^{1}H NMR (400 MHz, 393K, $C_2Cl_4D_2$) δ (ppm) 9.14 (s, 2H), 9.00 (s, 2H), 8.93 (s, 2H), 8.58–8.42 (m, 10H), 7.65–7.50 (m, 12H), 6.92 (s, 4H), 4.20–4.00 (m, 24H), 1.86–0.73 (m, 110H). ^{13}C NMR (100 MHz, 393K, $C_6D_4Cl_2$) δ (ppm) 156.64, 153.08, 152.97, 152.63, 145.29, 140.81, 140.46, 140.16, 139.78, 138.59, 135.10, 133.56, 133.36, 133.14, 132.77, 132.40, 132.15, 131.16, 130.93, 130.71, 130.40, 130.14, 129.89, 128.89, 127.94, 127.37, 127.12, 126.87, 124.75, 123.31, 123.04, 122.72, 122.60, 122.30, 115.32, 113.60, 73.85, 73.72, 70.55, 32.16, 32.09, 31.99, 31.26, 31.13, 30.56, 30.42, 29.99, 29.86, 29.76, 29.58, 29.45, 26.81, 26.71, 22.78, 22.69, 13.93, 13.86.

The more polar isomer of P2: ^{1}H NMR (400 MHz, 393K, $C_2Cl_4D_2$) δ (ppm) 9.13 (d, J = 7.9 Hz, 2H), 8.98 (d, J = 7.9 Hz, 2H), 8.54 (d, J = 7.9 Hz, 2H), 8.48 (s, 4H), 8.38 (d, J = 7.9 Hz, 2H), 7.64–7.48 (m, 12H), 6.87 (s, 4H), 4.31–4.07 (m, 16H), 3.97 (s, 8H), 1.91–1.88 (m, 16H), 1.77–1.73 (m, 8H), 1.59–1.14 (m, 120H), 0.97–0.53 (m, 36H). ^{13}C NMR (100 MHz, 393K,

$C_6D_4Cl_2$) δ (ppm) 156.70, 152.96, 152.59, 145.21, 140.77, 140.47, 140.17, 139.78, 138.58, 134.79, 134.52, 133.57, 133.14, 132.78, 132.13, 131.28, 130.90, 130.68, 130.40, 130.14, 129.89, 128.84, 128.05, 127.37, 127.12, 126.87, 125.43, 123.02, 122.91, 122.72, 121.64, 115.41, 113.72, 73.85, 73.74, 70.58, 70.53, 32.16, 32.09, 32.00, 31.25, 31.13, 30.57, 30.44, 29.99, 29.86, 29.78, 29.62, 29.58, 29.46, 26.77, 26.72, 22.78, 22.70, 13.94, 13.86. MS (MALDI-TOF): Calcd. 2781.80; Found 2782.8. Elemental analysis: Calcd. for $C_{184}H_{236}N_8O_{14}$ C, 79.38; H, 8.54; N, 4.03; Found: C, 79.04; H, 8.44; N, 3.75.

Compound P3

The reaction was carried out using the same procedure as for compound **N1**, using 488 mg (0.2 mmol) of **P-4NH$_2$** and 88 mg (0.4 mmol) of benzo[1,2-b:6,5-b]dithiophene-4,5-dione as the starting materials. The crude product was purified by column chromatography on silica gel with dichloromethane as the eluent and two spots were collected. Both of the two spots were identified as isomers of the target compound, but the assignment of the structures is impossible. The total yield was 60%.

The less polar isomer of P3 ^{1}H NMR (400 MHz, 393K, $C_2Cl_4D_2$) δ (ppm) 8.89 (d, J = 8.0 Hz, 2H), 8.53 (d, J = 8.0 Hz, 2H), 8.48 (s, 4H), 8.21 (d, J = 5.1 Hz, 2H), 8.04 (d, J = 4.8 Hz, 2H), 7.48 (s, 4H), 7.41 (d, J = 5.1 Hz, 2H), 7.35 (d, J = 4.8 Hz, 2H), 6.87 (s, 4H), 4.33–4.07 (m, 16H), 3.97 (br, 8H), 1.89–1.60 (m, 24H), 1.58–1.02 (m, 120H), 0.97–0.68 (m, 36H). ^{13}C NMR (100 MHz, 393K, $C_6D_4Cl_2$) δ 156.39, 152.88, 152.48, 145.22, 140.37, 139.72, 138.34, 138.25, 137.91, 135.86, 135.69, 135.52, 135.24, 135.00, 134.52, 133.56, 133.14, 131.28, 131.10, 130.65, 128.88, 127.92, 126.31, 125.36, 125.20, 124.79, 124.01, 123.84, 123.26, 122.53, 122.29, 115.33, 113.58, 73.86, 73.68, 70.52, 70.45, 32.19, 32.14, 32.11, 32.00, 31.28, 31.14, 30.57, 30.41, 29.98, 29.89, 29.75, 29.66, 29.60, 29.47, 26.81, 26.74, 26.69, 22.85, 22.79, 22.69, 13.98, 13.94, 13.85.

The more polar isomer of P3: ^{1}H NMR (400 MHz, 393K, $C_2Cl_4D_2$) δ (ppm) 8.87 (s, 2H), 8.50 (s, 6H), 8.20 (s, 2H), 8.04 (s, 2H), 7.48–7.37 (m, 8H), 6.88 (s, 4H), 4.14 (br, 16H), 3.97 (br, 8H),, 2.69–0.21 (m, 136H). ^{13}C NMR (100 MHz, 393K, $C_6D_4Cl_2$) δ (ppm) 156.56, 152.97, 152.88, 152.45, 145.14, 140.47, 140.41, 139.77, 139.72, 138.33, 138.24, 137.90, 135.86, 135.68, 135.51, 135.26, 134.78, 133.57, 133.05, 132.77, 131.28, 130.99, 130.40, 130.14, 129.89, 128.87, 128.07, 127.36, 127.12, 126.87, 126.26, 125.56, 125.28, 124.05, 123.88, 122.90, 121.59, 115.42, 113.73, 73.85, 73.71, 70.58, 70.44, 32.15, 32.10, 32.00, 31.25, 31.14, 30.56, 30.42, 29.98, 29.87, 29.76, 29.59, 29.48, 26.79, 26.69, 22.79, 22.70, 13.94, 13.86. MS (MALDI-TOF): Calcd. 2805.6; Found 2806.7. Elemental analysis: Calcd. for $C_{176}H_{228}N_8O_{14}S_4$: C, 75.28; H, 8.18; N, 3.99; S, 4.57. Found: C, 75.22; H, 8.25; N, 3.86; S, 4.48

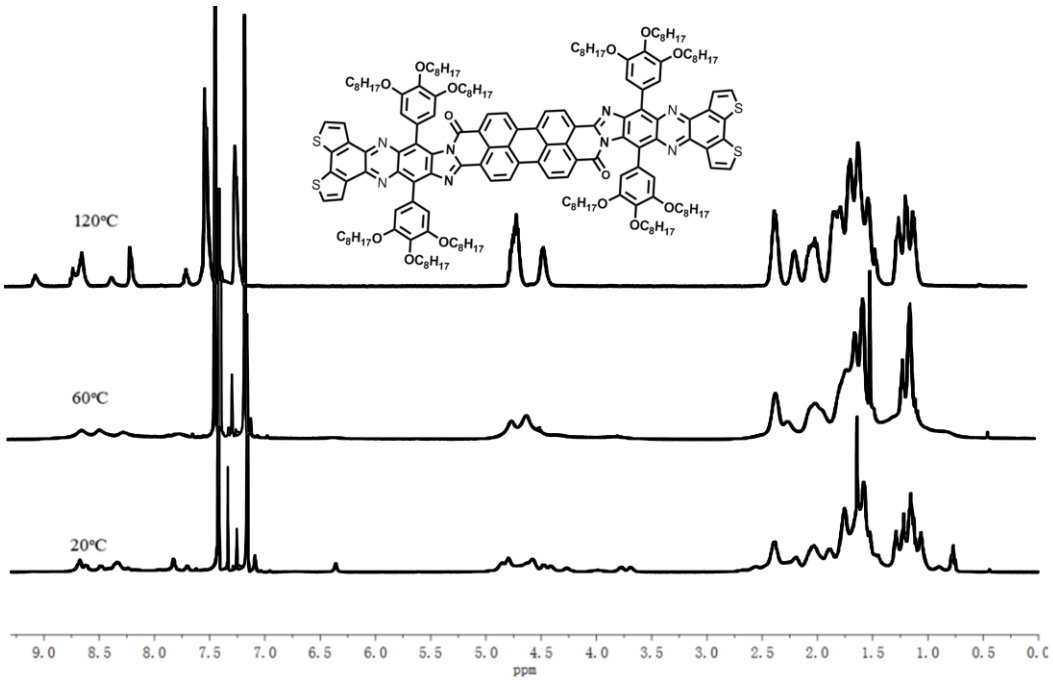


Figure S1. Temperature-dependent ^{1}H NMR spectra of **The less polar isomer of P3** in $C_6D_4Cl_2$ with a concentration of 10 mg/mL.

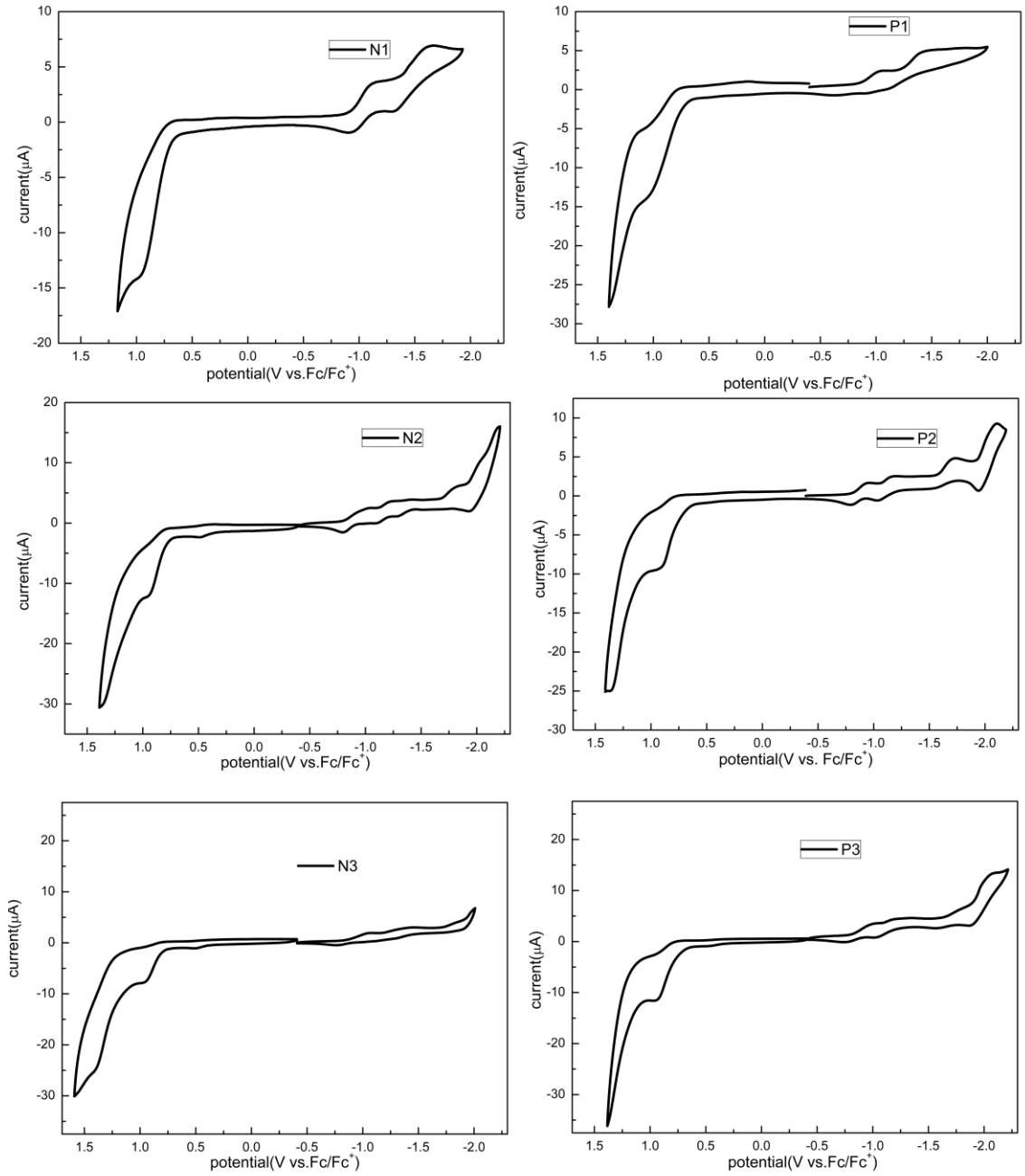


Figure S2: CV of compounds **N1**, **N2**, **N3**, **P1**, the less polar isomers of **P2**, and **P3**.

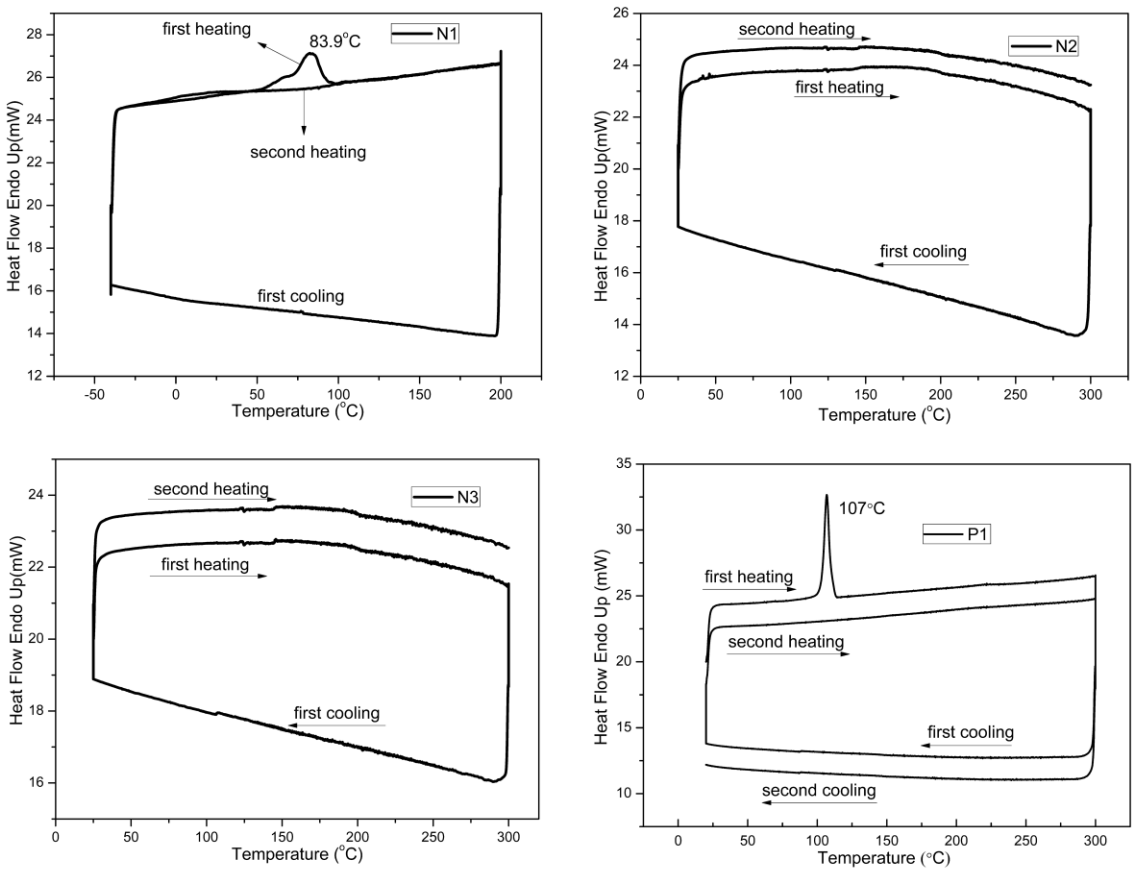


Figure S3: DSC traces of compounds **N1**, **N2**, **N3** and **P1**.

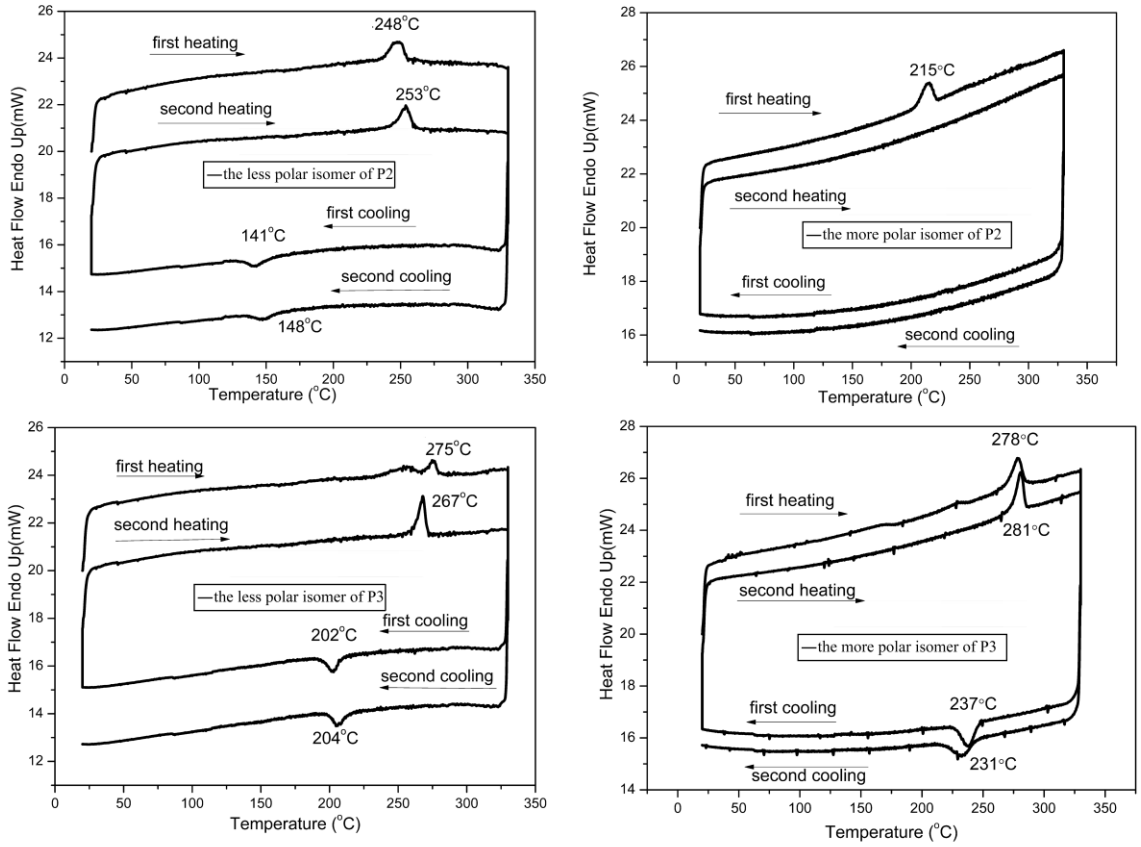


Figure S4: DSC traces of isomers of compounds **P2** and **P3**.

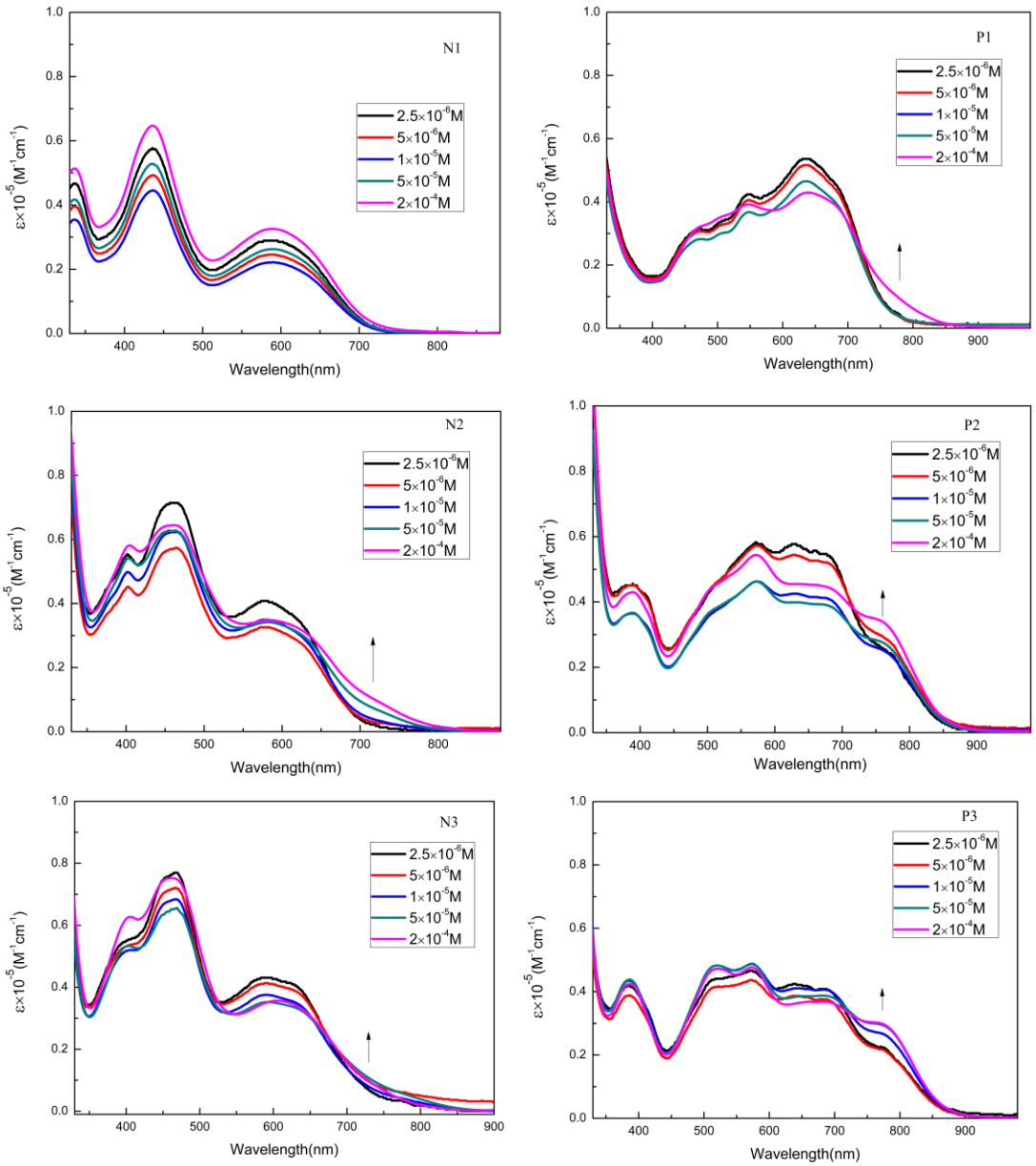


Figure S5: Concentration - dependent absorption spectra of compounds **N1-3** and **P1-3** in toluene.

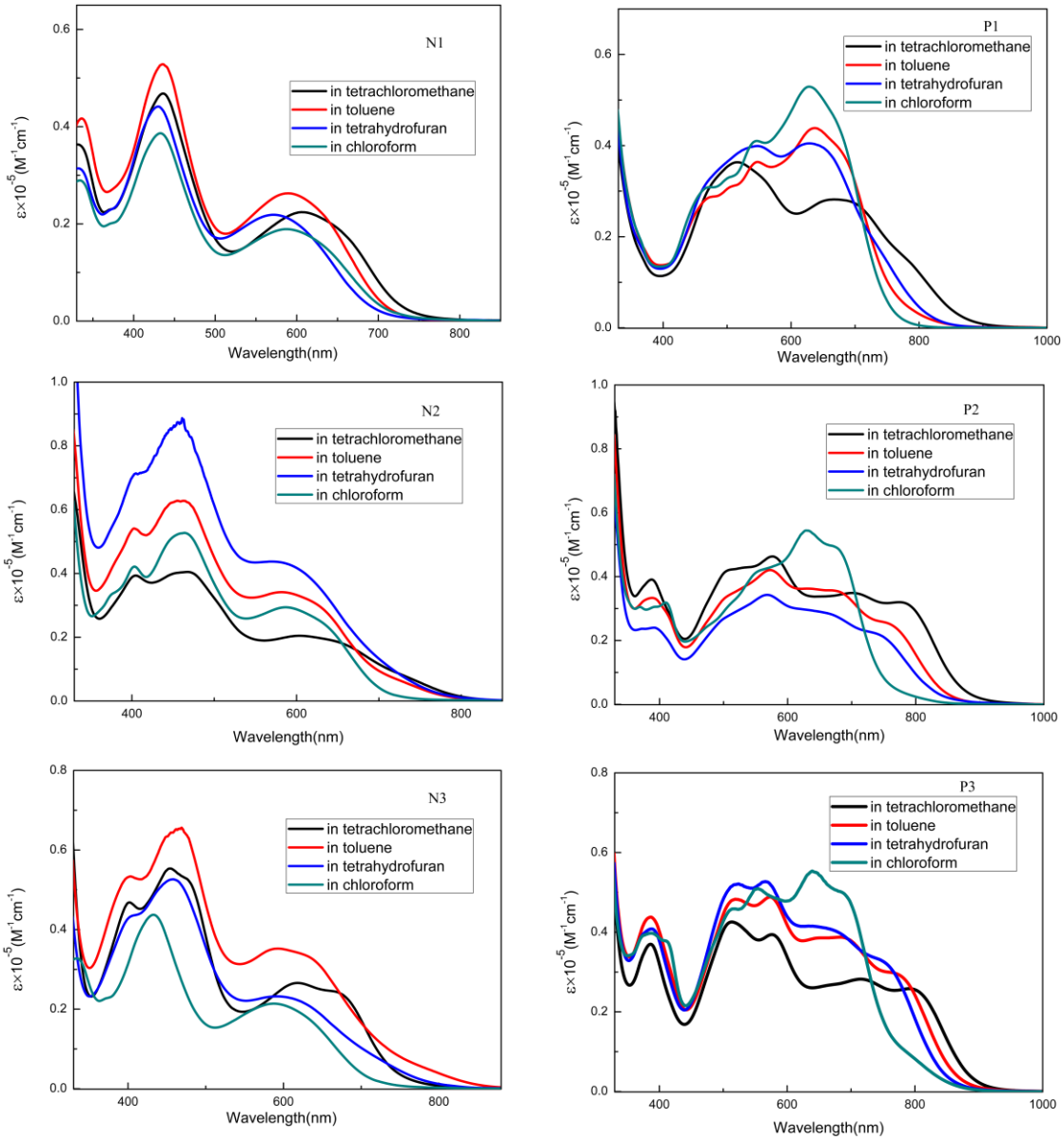


Figure S6: Absorption spectra of compounds **N1-3** and **P1-3** in different solvents at 1×10^{-5} M.

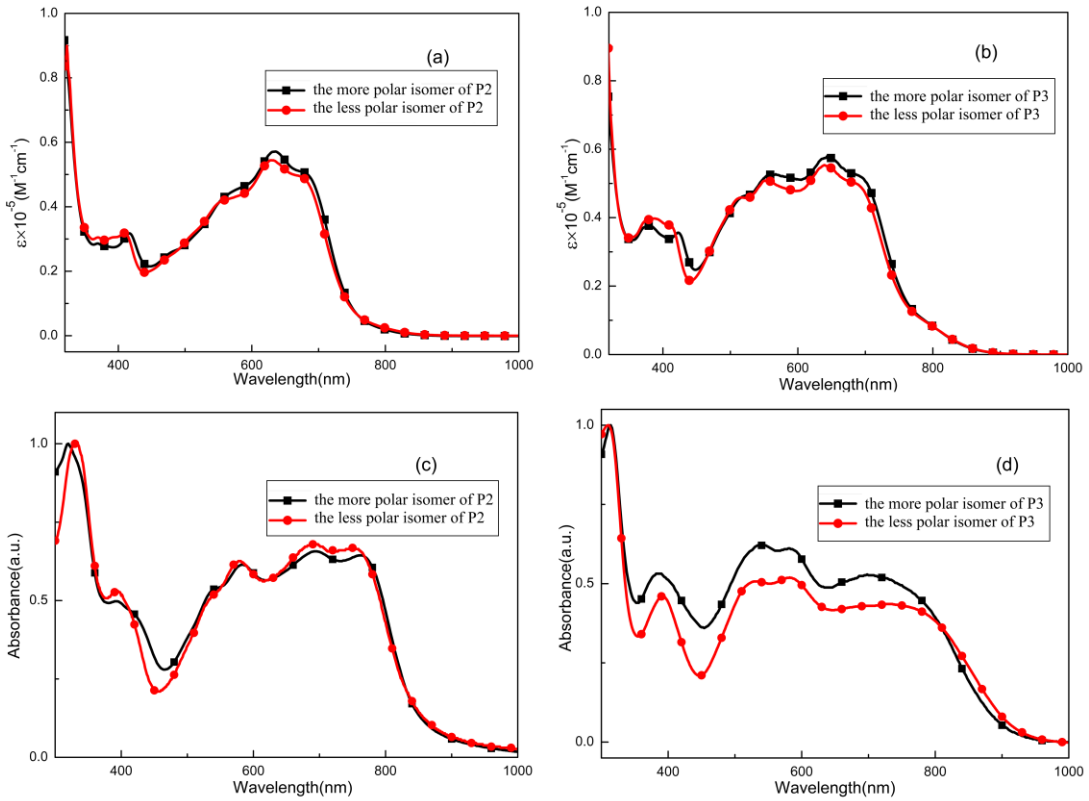


Figure S7: Absorption spectra of two isomers of compounds **P2** and **P3** in chloroform (a, b) and as films (c, d).

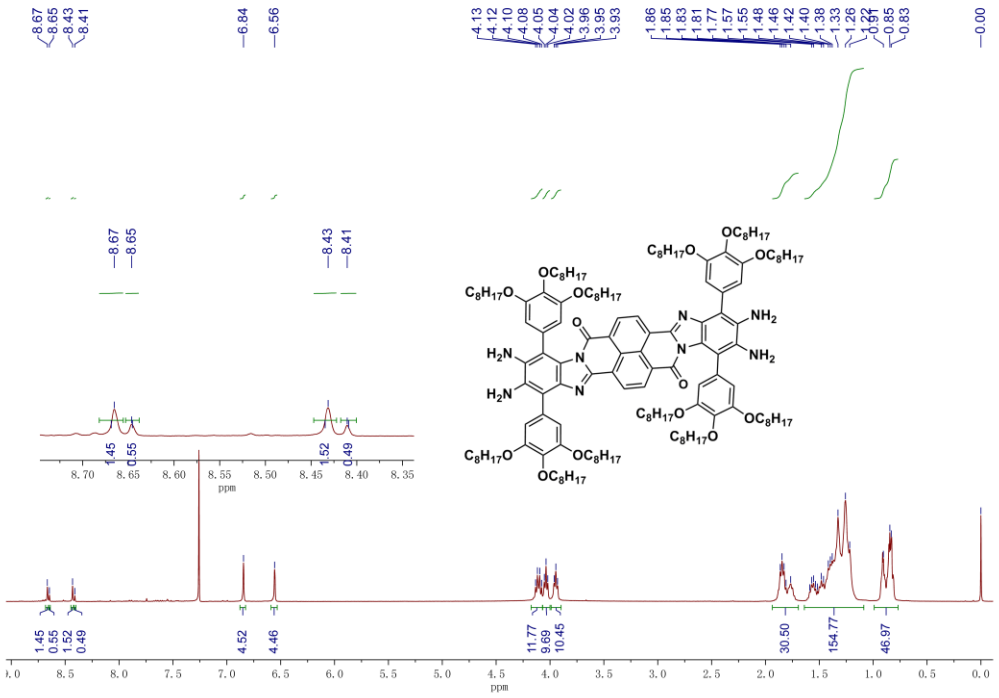


Figure S8: ^{1}H NMR spectrum of compound **N-4NH$_2$** in $CDCl_3$ at room temperature.

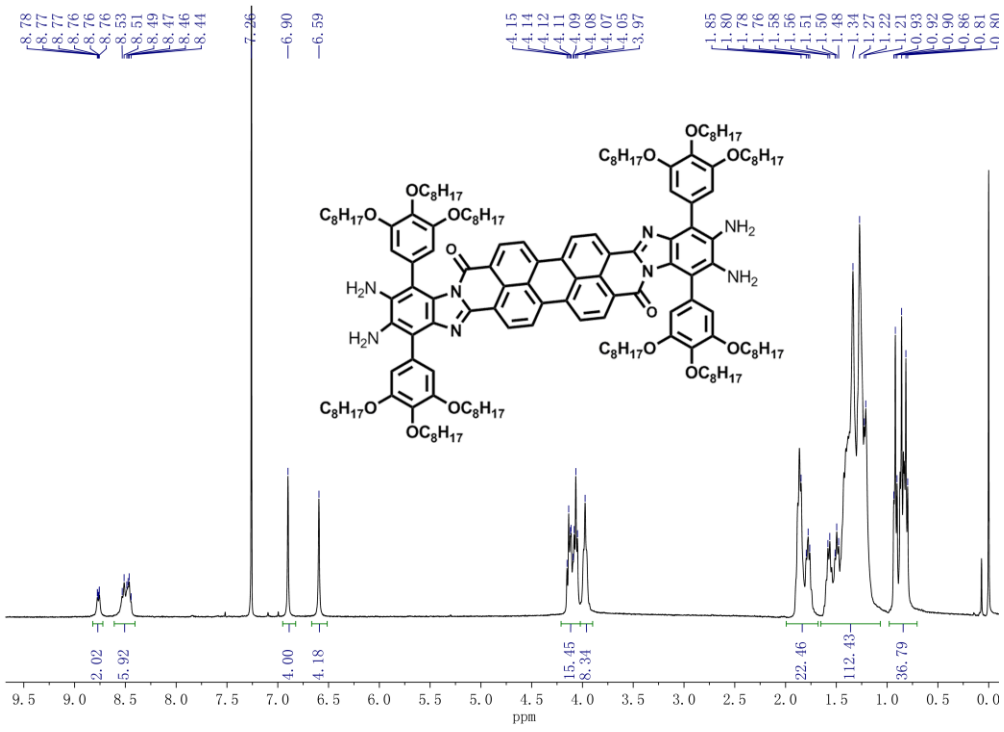


Figure S9: ^{1}H NMR spectrum of compound **P-4NH$_2$** in $CDCl_3$ at room temperature.

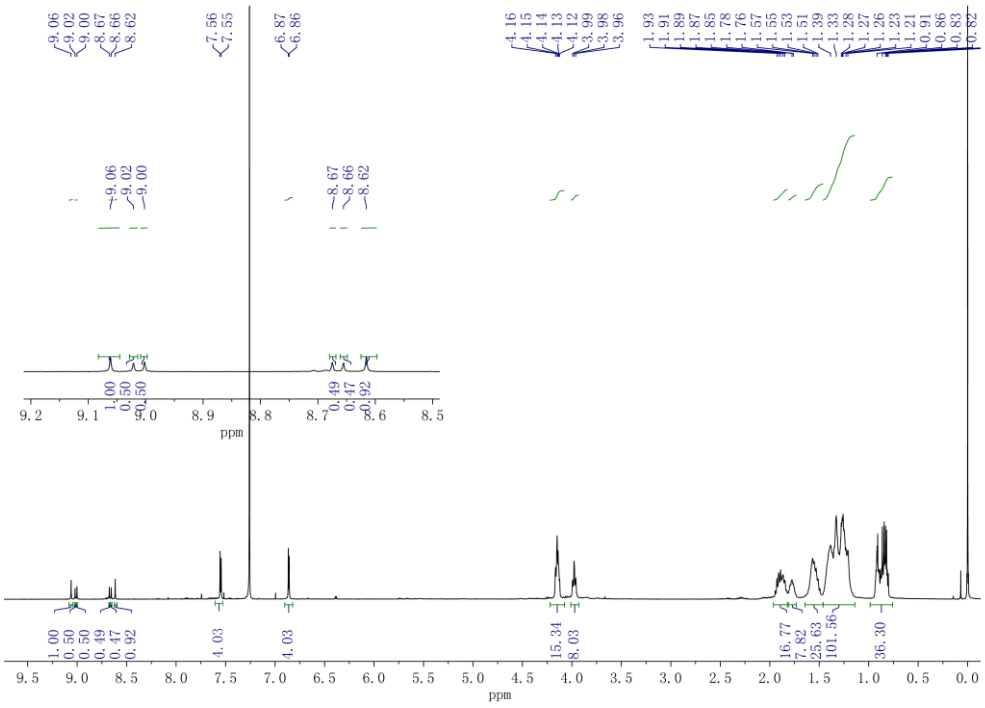


Figure S10: ^{1}H NMR spectrum of compound **N1** in $CDCl_3$ at room temperature.

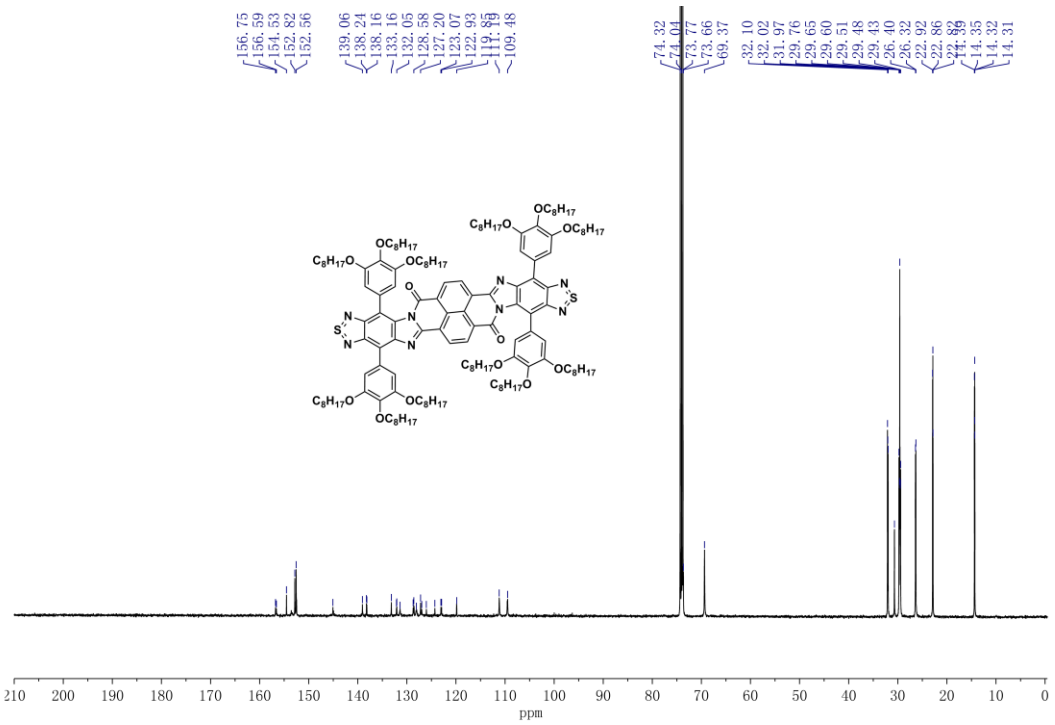


Figure S11: ^{13}C NMR spectrum of compound **N1** in $C_2D_2Cl_4$ at room temperature.

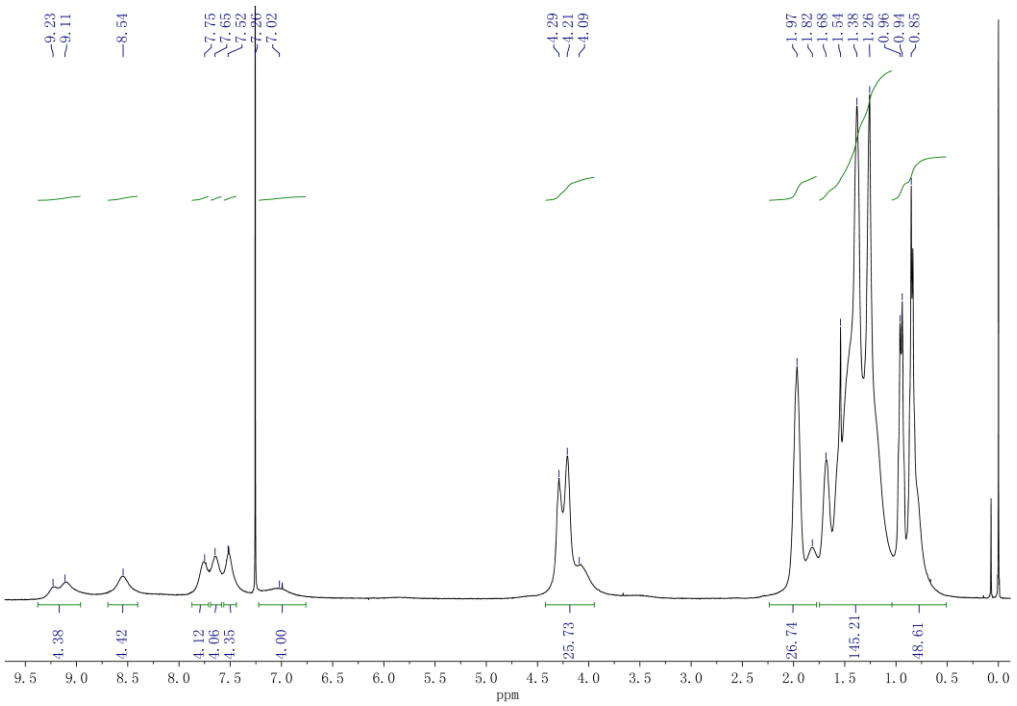


Figure S12: ^{1}H NMR spectrum of compound **N2** in $CDCl_3$ at room temperature.

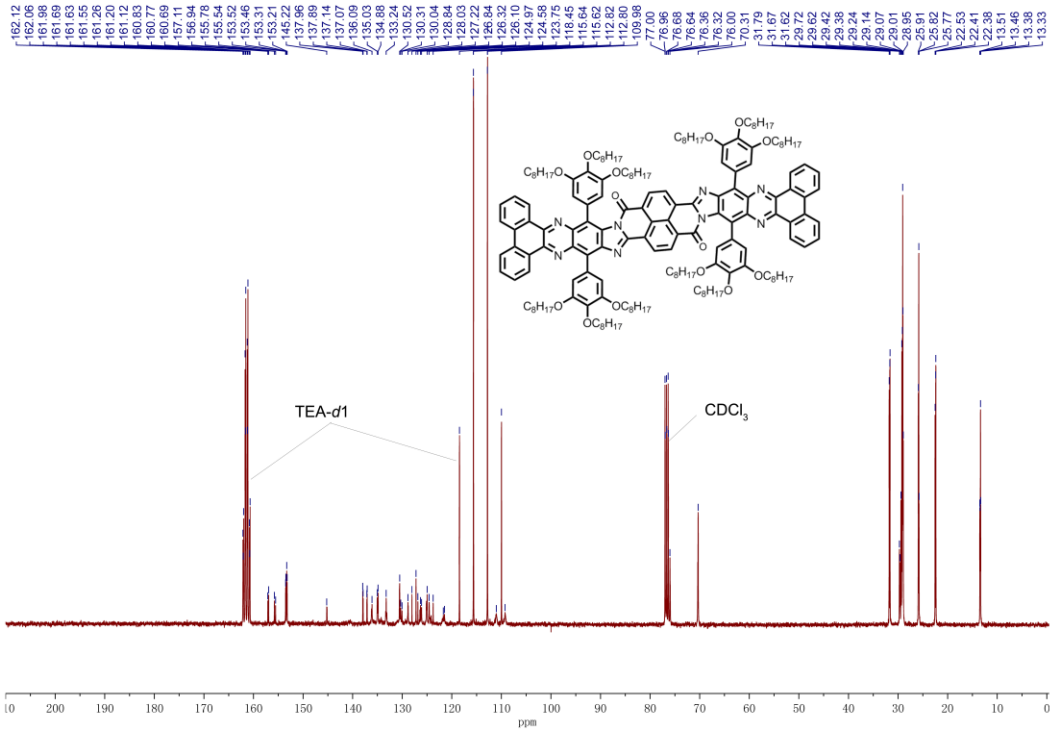


Figure S13: ^{13}C NMR spectrum of compound **N2** in $CDCl_3$ and TFA-*d*1 at room temperature.

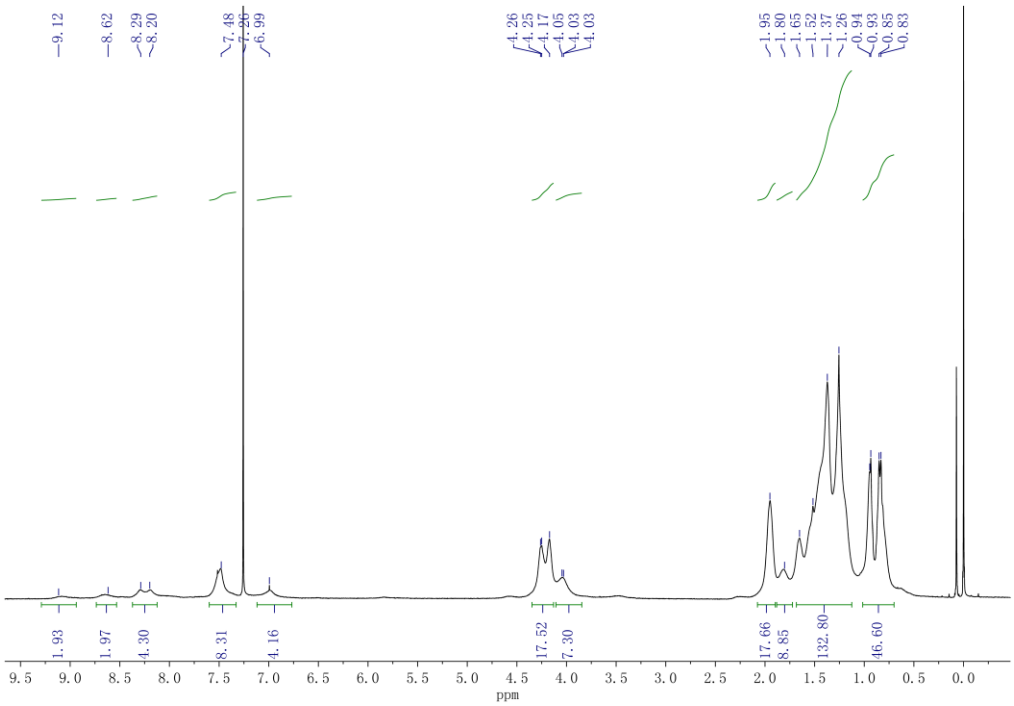


Figure S14: ^{1}H NMR spectrum of compound **N3** in $CDCl_3$ at room temperature.

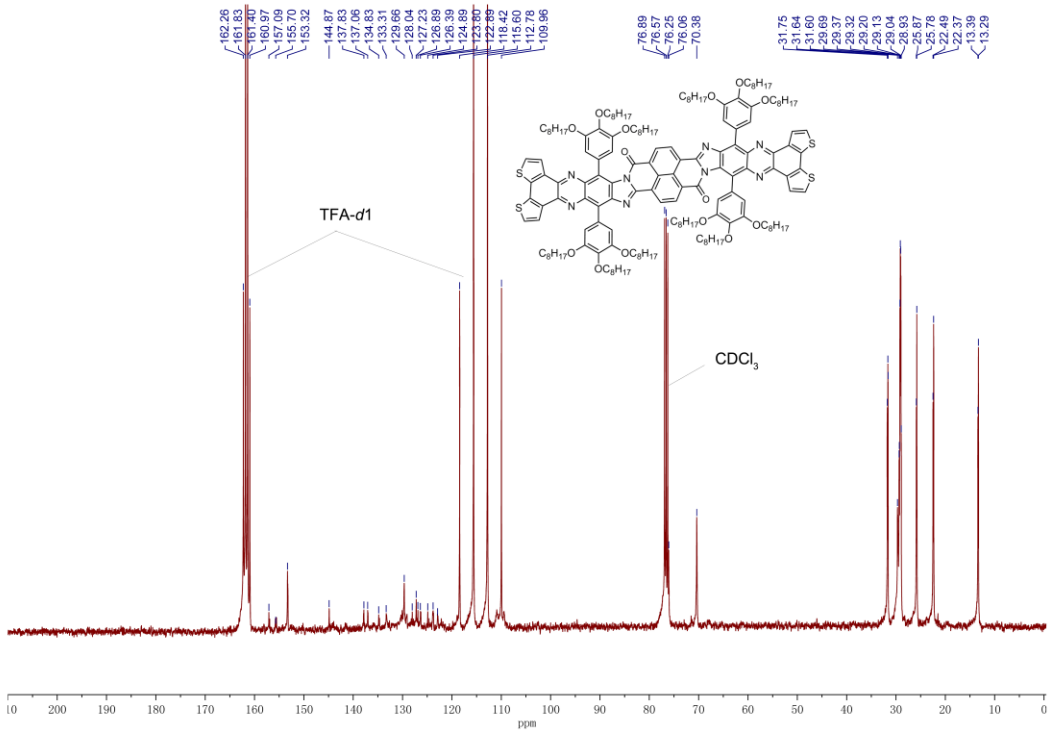


Figure S15: ^{13}C NMR spectrum of compound **N3** in $CDCl_3$ and TFA-*d*1 at room temperature.

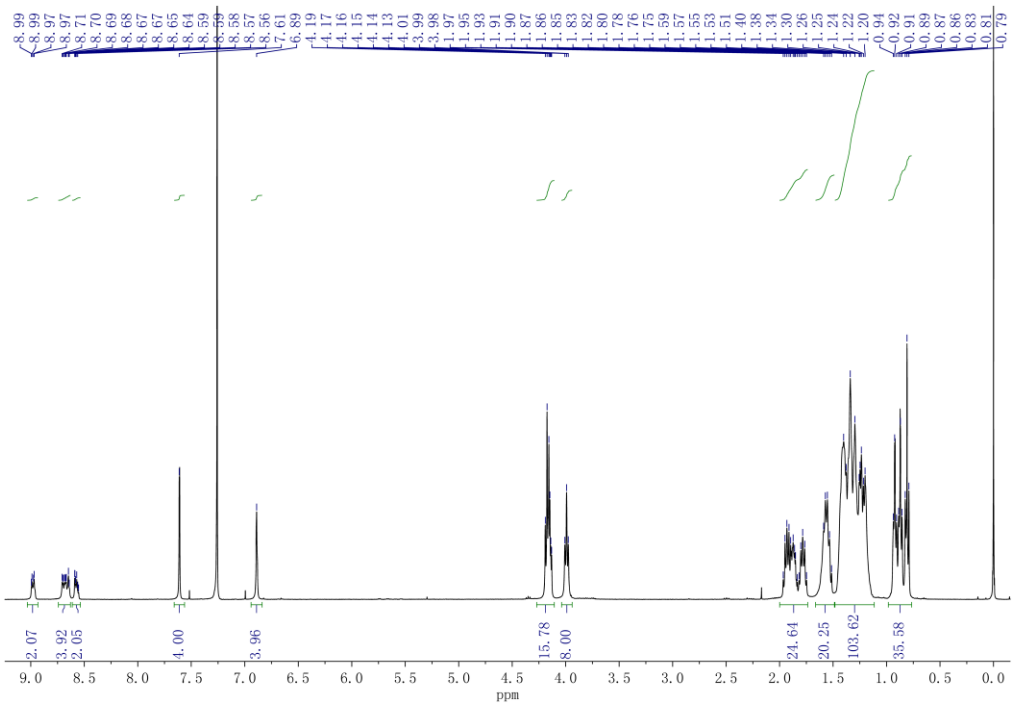


Figure S16: ^{1}H NMR spectrum of compound **P1** in $CDCl_3$ at room temperature.

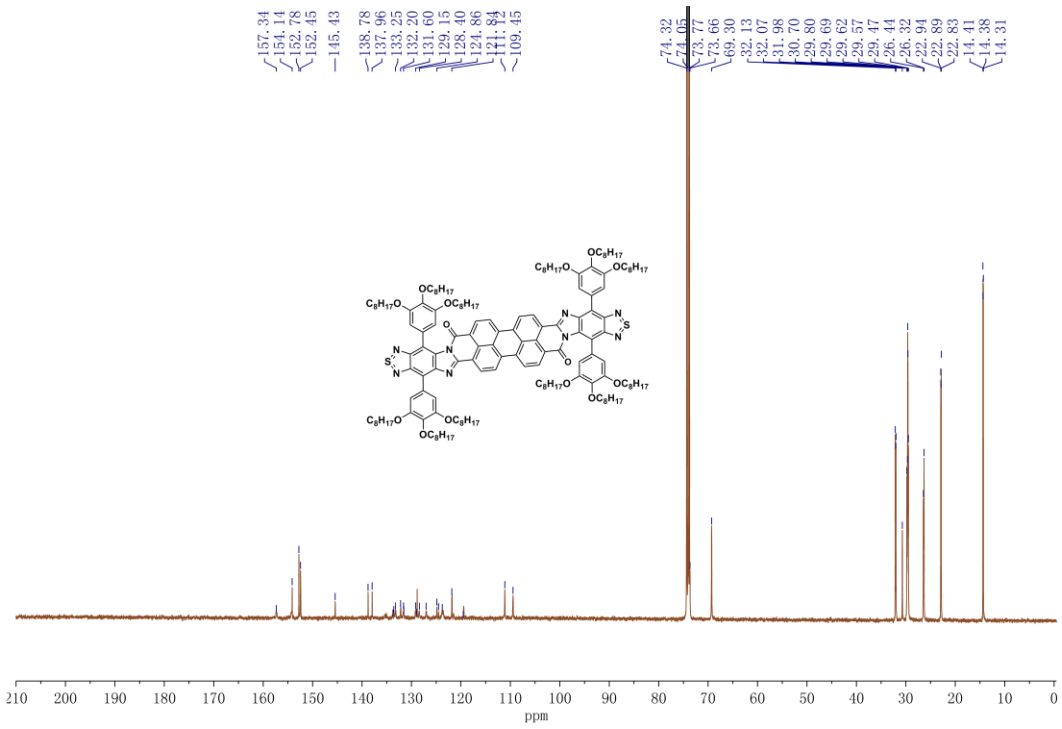


Figure S17: ^{13}C NMR spectrum of compound **P1** in $C_2D_2Cl_4$ at room temperature.

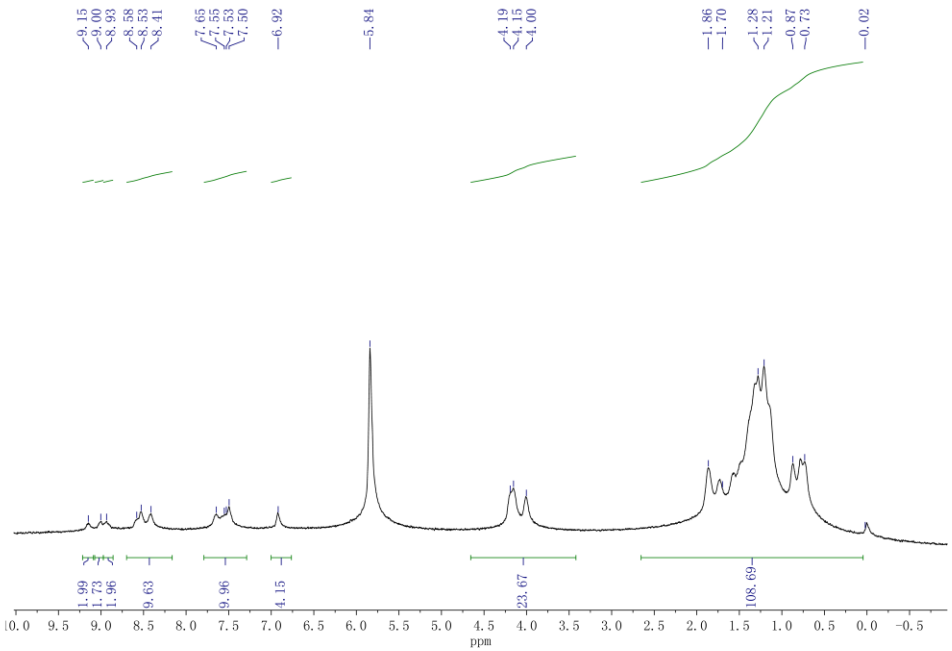


Figure S18: ^{1}H NMR spectrum of the less polar isomer of **P2** in $C_2D_2Cl_4$ at 393K.

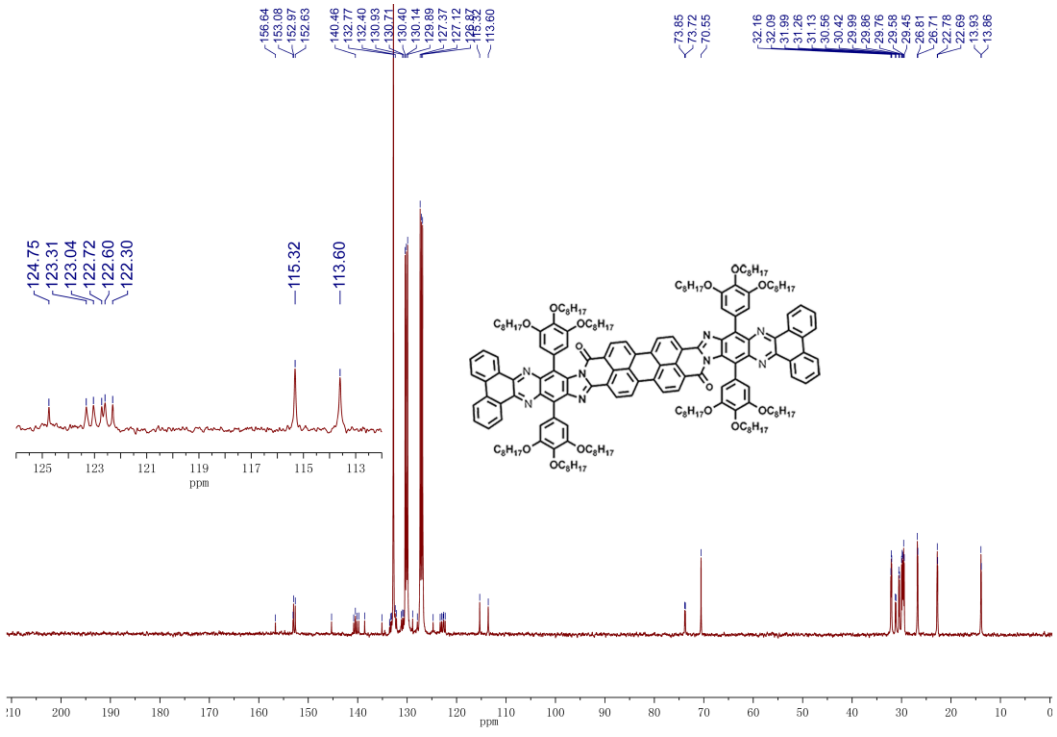


Figure S19: ^{13}C NMR spectrum of the less polar isomer of **P2** in $C_6D_4Cl_2$ at 393K

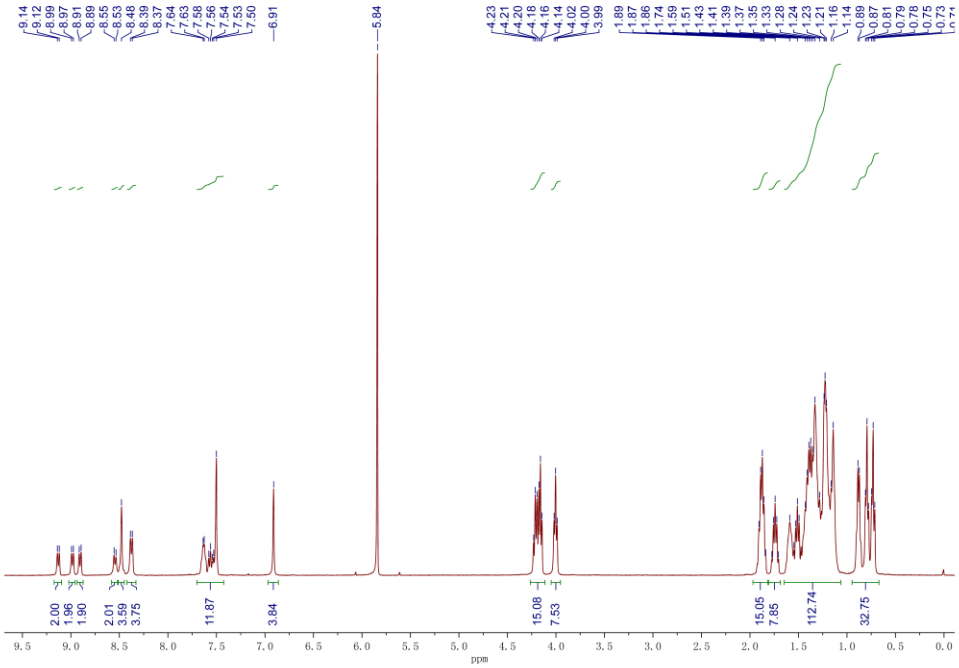


Figure S20: ^{1}H NMR spectrum of the more polar isomer of **P2** in $C_2D_2Cl_4$ at 393K.

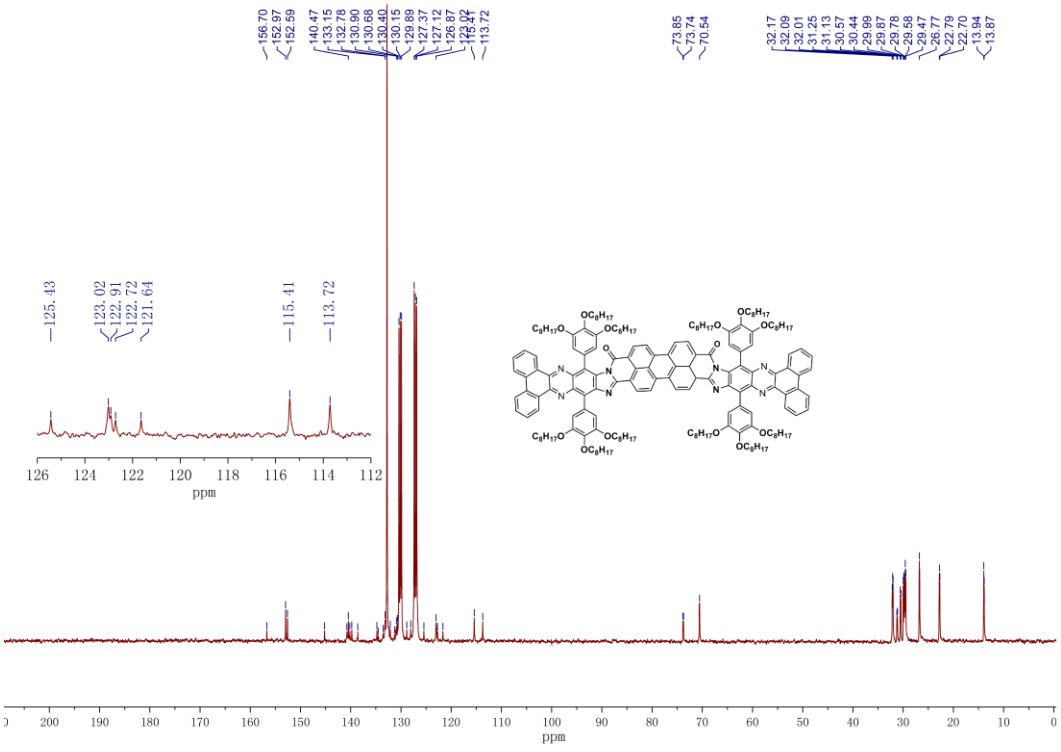


Figure S21: ^{13}C NMR spectrum of the more polar isomer of **P2** in $C_6D_4Cl_2$ at 393K

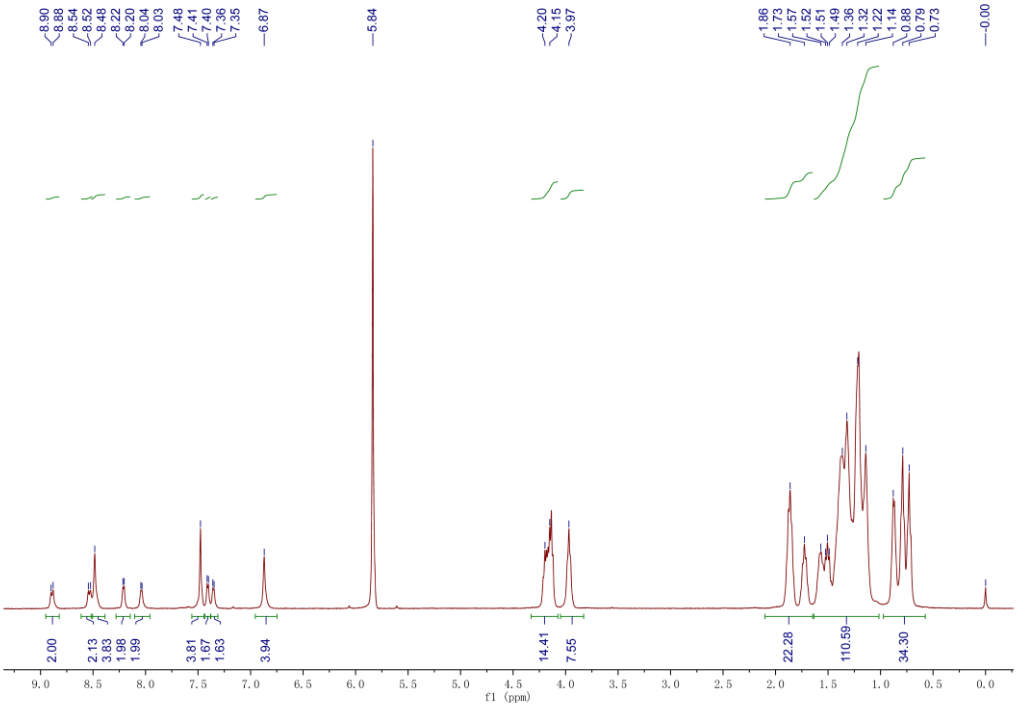


Figure S22: ^{1}H NMR spectrum of the less polar isomer of **P3** in $C_2D_2Cl_4$ at 393K.

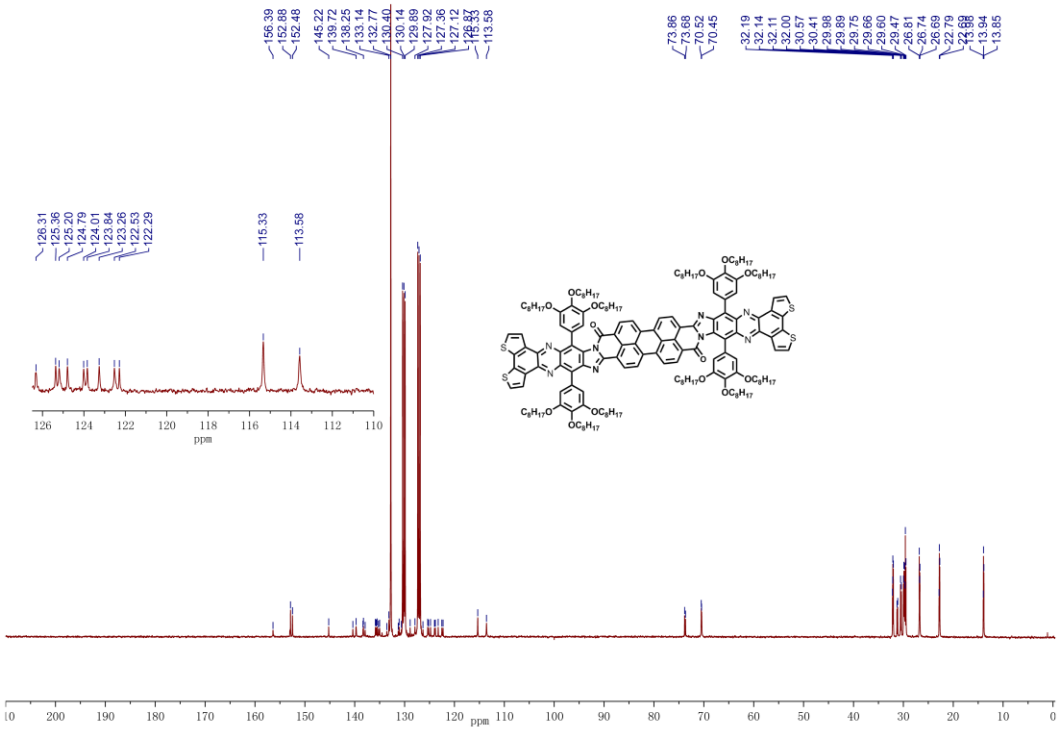


Figure S23: ^{13}C NMR spectrum of the less polar isomer of **P3** in $C_6D_4Cl_2$ at 393K.

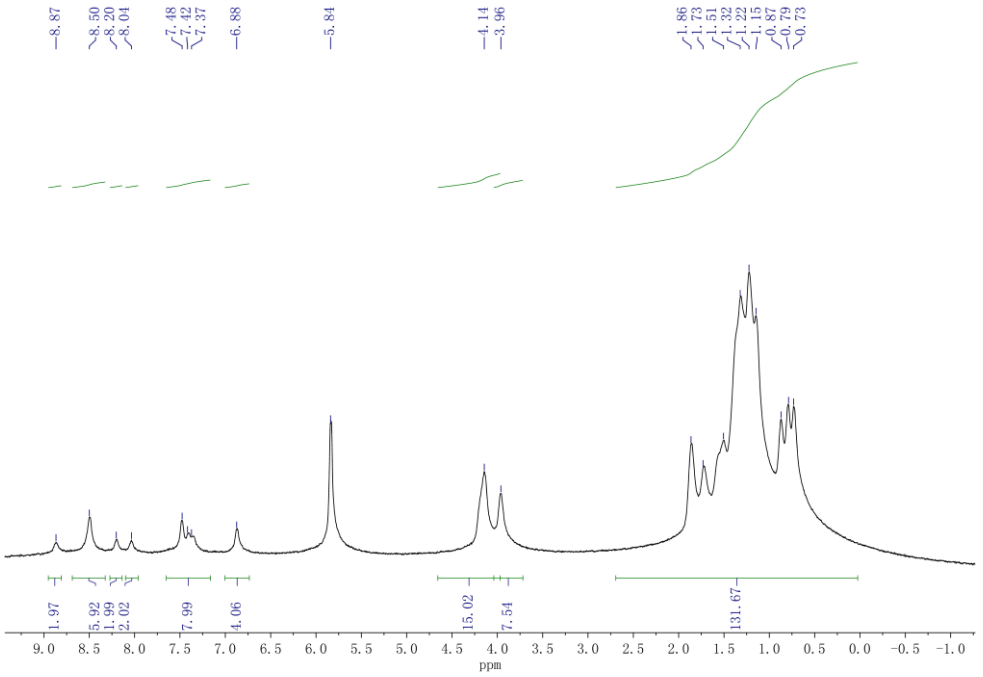


Figure S24: ^{1}H NMR spectrum of the more polar isomer of **P3** in $C_2D_2Cl_4$ at 393K.

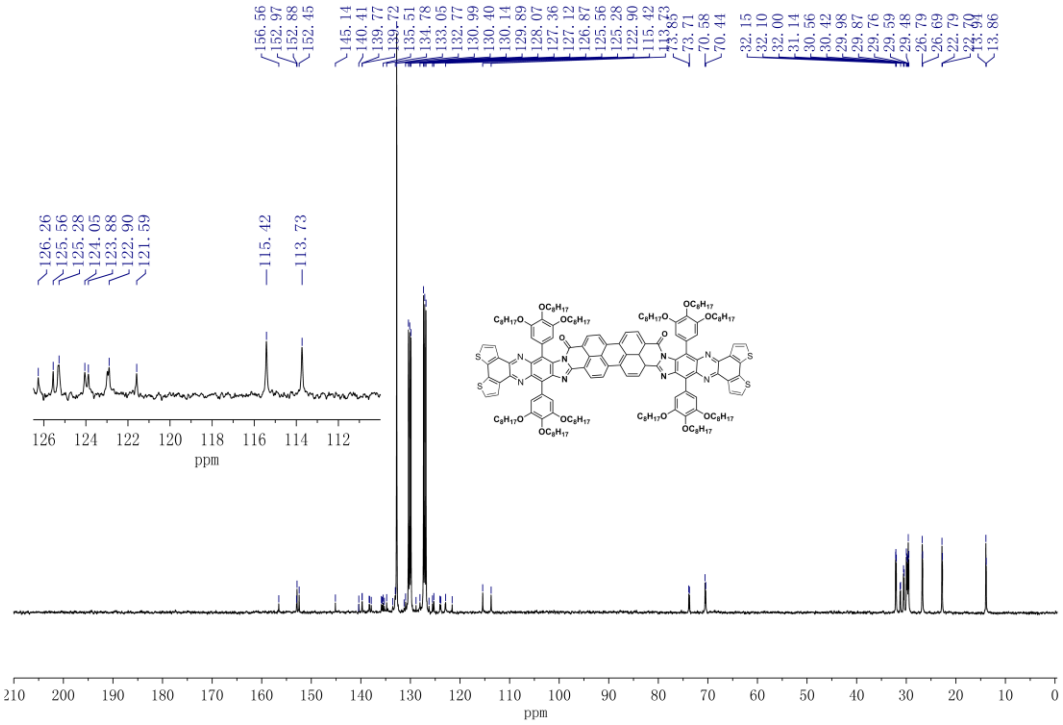


Figure S25: ^{13}C NMR spectrum of the more polar isomer of **P3** in $C_6D_4Cl_2$ at 393K.

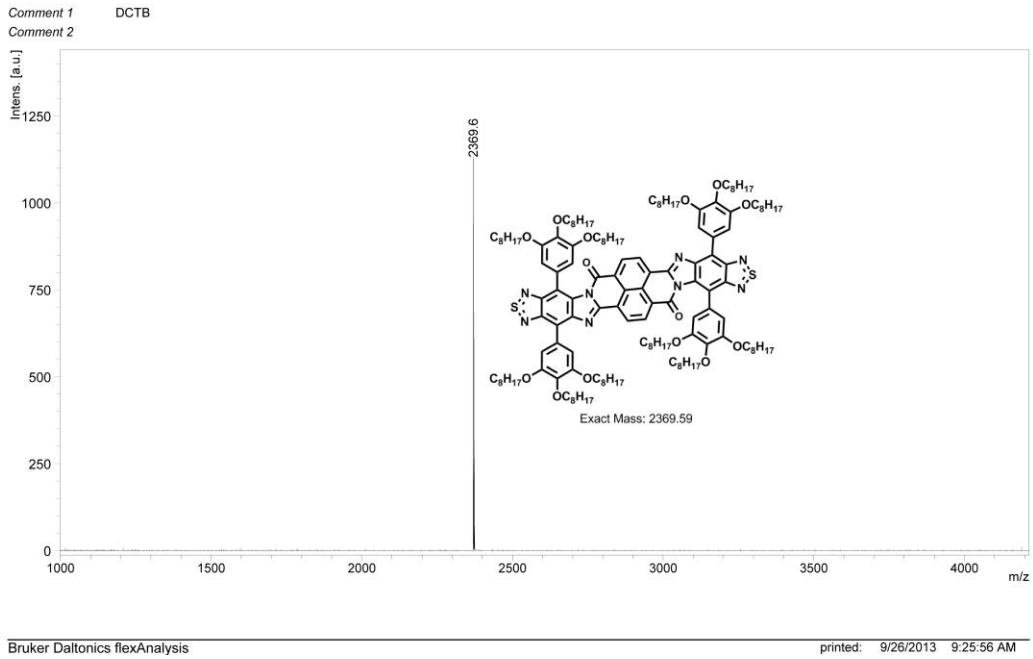


Figure S26: MS (MALDI-TOF) spectrum of compound **N1**.

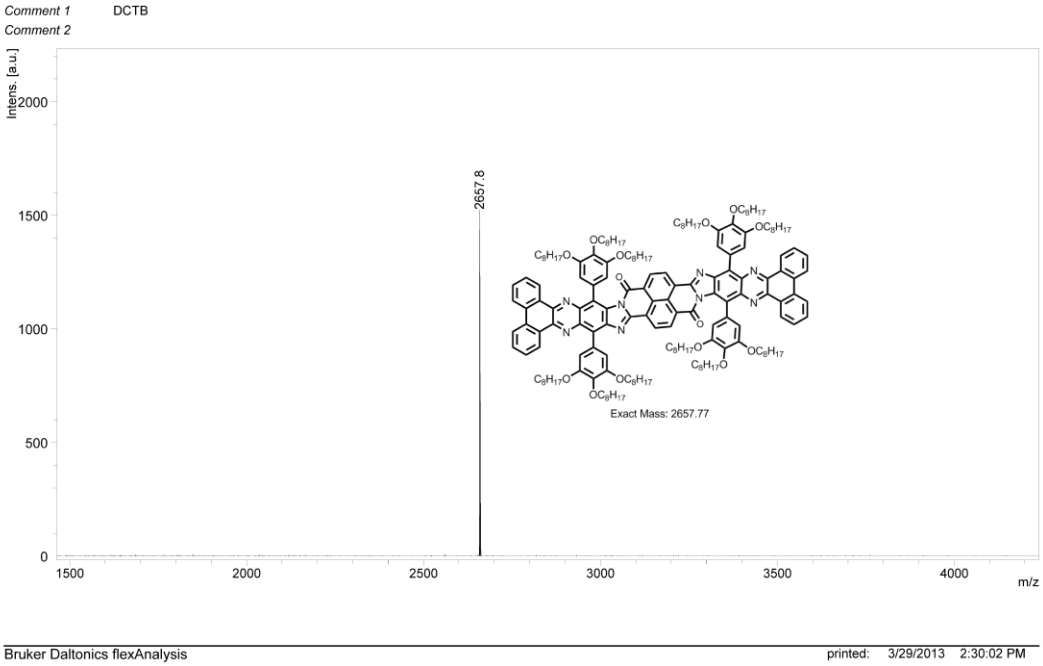


Figure S27: MS (MALDI-TOF) spectrum of compound **N2**.

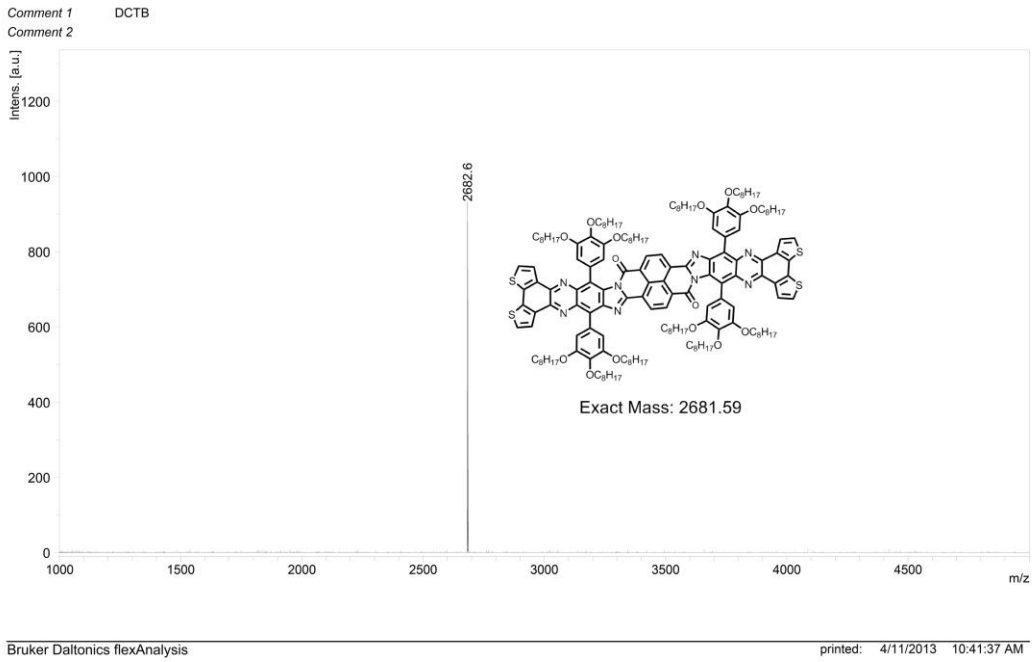


Figure S28: MS (MALDI-TOF) spectrum of compound **N3**.

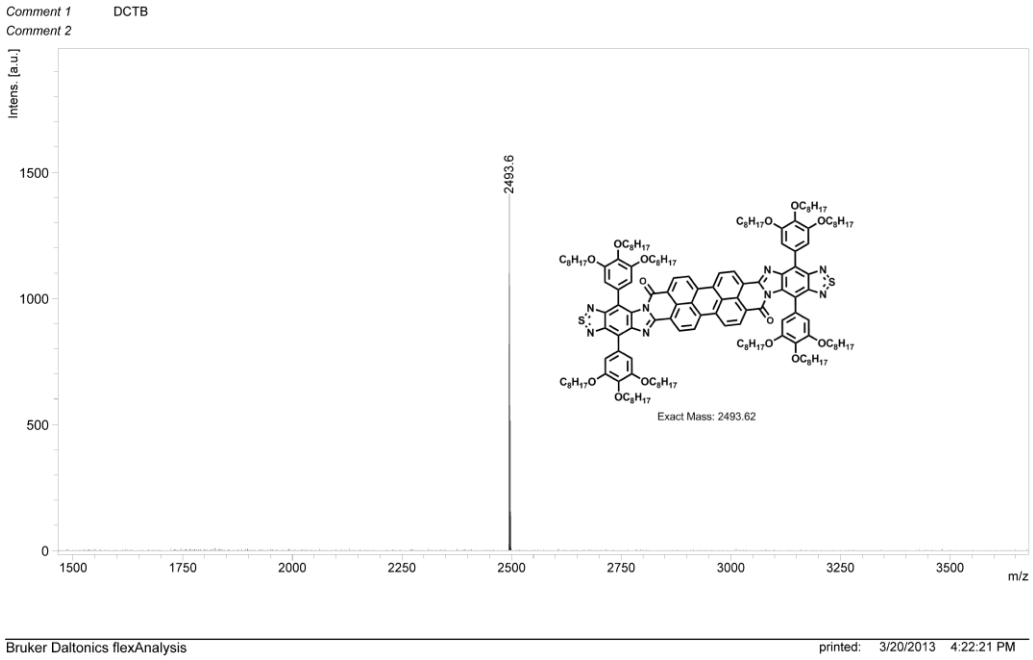


Figure S29: MS (MALDI-TOF) spectrum of compound **P1**.

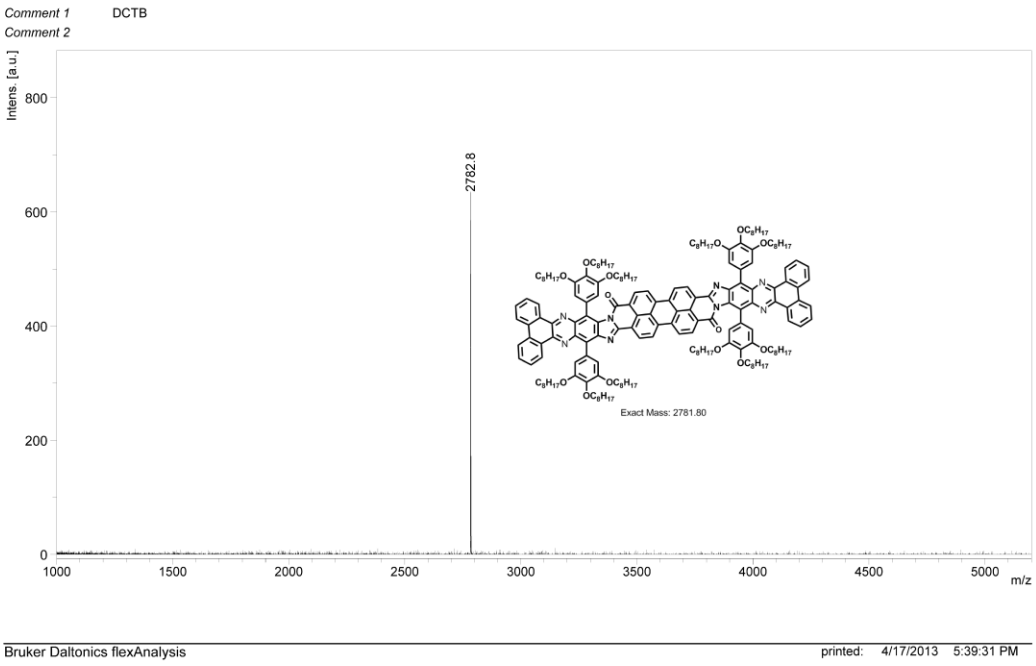


Figure S30: MS (MALDI-TOF) spectrum of compound **P2**.

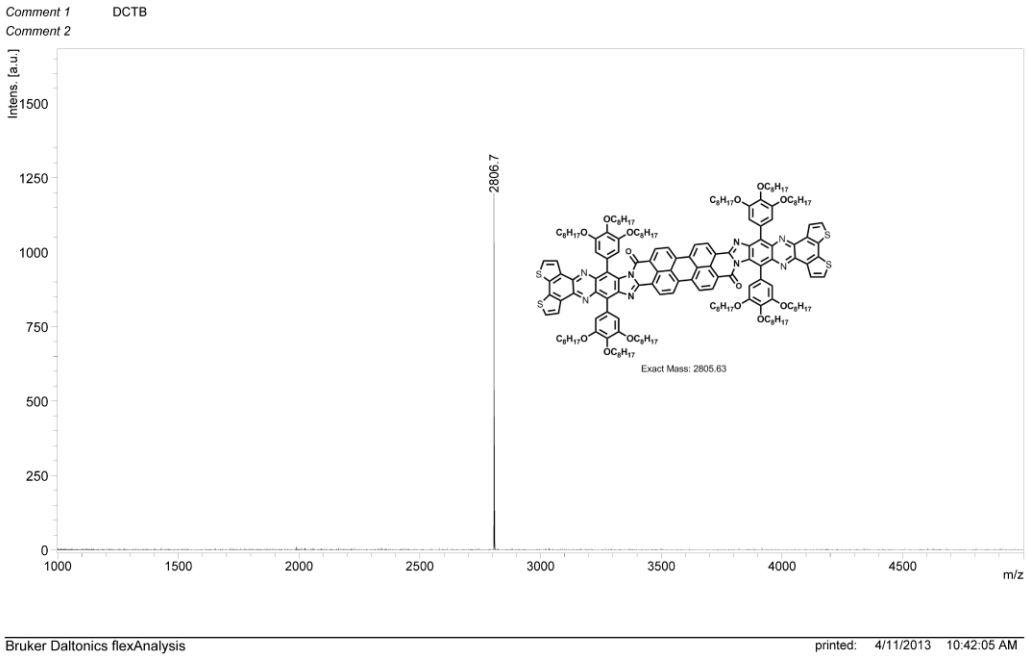


Figure S31: MS (MALDI-TOF) spectrum of compound **P3**.

References

(1) Maeda, H.; Haketa, Y.; Nakanishi, T. *J. Am. Chem. Soc.***2007**, *129*, 13661.
(2) Arroyave, F. A.; Richard, C. A.; Reynolds, J. R. *Org. Lett.* **2012**, *14*, 6138.
(3) Wang, E.; Hou, L.; Wang, Z.; Hellström, S.; Mammo, W.; Zhang, F.; Inganäs, O.; Andersson, M. R. *Org. Lett.* **2010**, *12*, 4470.