

Supporting Information for
Coronenediimides Synthesized via ICI-induced
Cyclization of Diethynyl Perylenediimides

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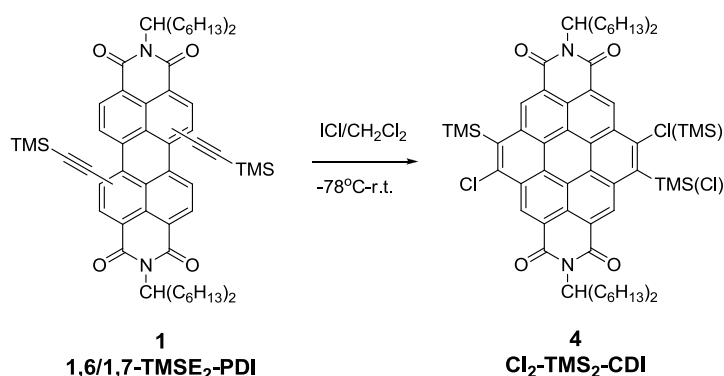
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I. Syntheses and characterizations

General Methods. Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen atmosphere using the standard Schlenk method. Reagent grade tetrahydrofuran (THF) was distilled over sodium and benzophenone. Dichloromethane (DCM) and triethylamine (TEA) were distilled over CaH₂ prior to use. NMR spectra were recorded on a Mercury plus 300 (300 MHz), Bruker-400 (400 MHz) or Bruker-500 (500 MHz) using CDCl₃ as the solvent unless otherwise noted. Chemical shifts in ¹H, ¹³C and ¹⁹F NMR spectra were reported in parts per million (ppm) with referencing to TMS (0 ppm) for ¹H NMR, TMS (0 ppm) or CDCl₃ (77.23 ppm) for ¹³C NMR, CF₃COOH (0 ppm) for ¹⁹F NMR, respectively. High-resolution ESI FT mass spectra were recorded on a Bruker APEX IV mass spectrometer. MALDI-TOF mass spectra were recorded on an ABI 4800 Plus MALDI TOF/TOF Analyzer using CHCA as matrix.^{S1} Elemental analyses were performed using a German Vario EL III elemental analyzer.



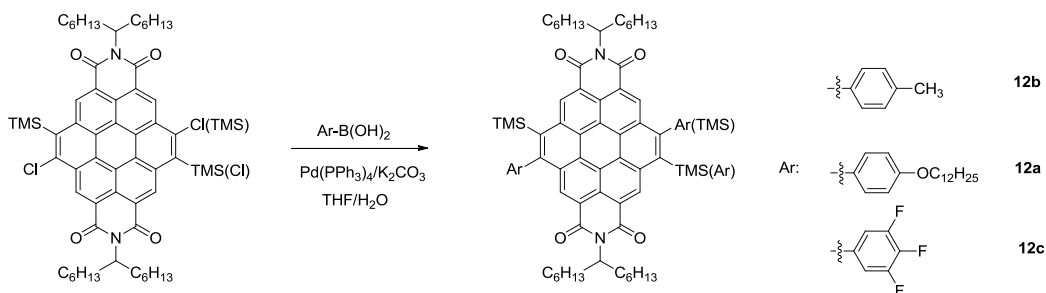
Compound 1. A Schlenk tube charged with 1,6/1,7-dibromoPDI (913 mg, 1.0 mmol), CuI (10 mg, 0.060 mmol), and PdCl₂(PPh₃)₂ (35 mg, 0.05 mmol) was evacuated and backfilled with nitrogen for three times. After a degassed mixture of THF (10

mL)/TEA (10 mL) and trimethylsilylacetylene (0.56 mL, 4.0 mmol) was added, the tube was sealed under nitrogen atmosphere and heated at 40 °C for 48 h. Being cooled to room temperature, the reaction mixture was diluted with chloroform and washed with HCl (6 M) and NaHCO₃ (aq.) sequentially, before dried over anhydrous Na₂SO₄. The solvents were then removed *in vacuo*. Purification of the crude product with column chromatography over silica gel eluted with petroleum ether/dichloromethane (5:1) afforded **1,6/1,7-PDI-TMSE₂ (1)** as a red solid (720 mg, 76%).

1,7-PDI-TMSE₂ (isolated pure isomer) ¹H NMR (300 MHz, CDCl₃, ppm): δ 10.22 (d, 2H, *J* = 8.7 Hz), 8.82-8.85 (m, 2H), 8.66 (m, 2H), 5.17-5.19 (m, 2H), 2.23-2.28 (m, 4H), 1.81-1.87 (m, 4H), 1.23-1.33 (m, 32H), 0.80-0.85 (m, 12H), 0.39 (s, 18H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 164.7 (C=O), 164.4 (C=O), 163.6 (C=O), 163.3 (C=O),^{S2} 138.9, 137.4, 134.4, 134.2, 131.1, 130.6, 128.2, 127.8, 127.7, 124.0, 123.4, 122.8, 122.2, 120.6, 120.0, 106.4 (C≡C), 105.9 (C≡C), 55.1, 55.0, 32.6, 32.0, 29.4, 27.1, 22.8, 14.3, -0.2 (TMS).

Compound **4**. To a solution of **1** (1.0 g, 1.0 mmol) in DCM (1 L) was added ICl (103 mg, 6.0 mmol) in DCM (5 mL) at -78 °C. Then the solution was allowed to be gradually warmed up to room temperature over 6 h and stirred at 30 °C for additional 24 h. The reaction mixture was washed sequentially with Na₂SO₃ (aq.) and K₂CO₃ (aq.), and then dried over anhydrous Na₂SO₄. Upon removal of solvent *in vacuo*, the residual was purified with column chromatography over silica gel eluted with petroleum ether/dichloromethane (6/1, v/v) to afford a mixture of regio-isomers of **4** as a yellow solids (427 mg, 40%; the yield could be improved to 88%, if the reaction

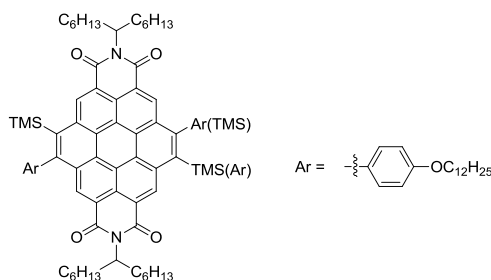
mixture was exposed to sun light after warming up to 30 °C). ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 10.59-10.52 (m, 4H), 5.51-5.42 (m, 2H), 2.48-2.42 (m, 4H), 2.08-2.05 (m, 4H), 1.42-1.38 (m, 16H), 1.26-1.24 (m, 16H), 1.04 (s, 18H), 0.87-0.79 (m, 12H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 164.8-165.4 (C=O), 142.5, 142.3, 140.1, 139.9, 134.8, 134.7, 131.8, 128.3, 128.1, 128.0, 125.3, 125.0, 124.4, 123.3, 122.8, 120.9, 55.8, 33.0, 32.0, 29.5, 27.5, 22.8, 14.2, 4.5. MALDI-TOF MS: Calcd for $\text{C}_{60}\text{H}_{76}\text{Cl}_2\text{N}_2\text{O}_4\text{Si}_2$, 1014.5; Found (M^+), 1014.3 (m/z). Elem. Anal.: Calcd. for $\text{C}_{60}\text{H}_{76}\text{Cl}_2\text{N}_2\text{O}_4\text{Si}_2$: C, 70.91; H, 7.54; N, 2.76. Found: C, 70.46; H, 7.56; N, 2.72.



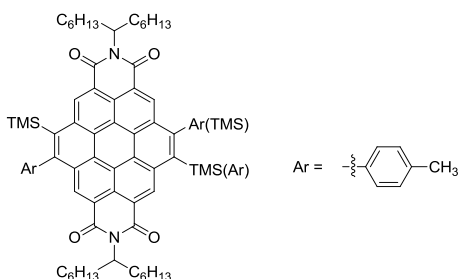
General procedure for Suzuki coupling reactions between aryl halides and phenylboronic acids.

A Schlenk tube containing **4** (0.1 mmol), phenylboronic acid (0.4 mmol), and $\text{Pd(PPh}_3)_4$ (0.006 mmol) was evacuated and backfilled with nitrogen for three times. After the addition of degassed K_2CO_3 (aq. 2 mL) and THF (2 mL), the tube was sealed under nitrogen atmosphere and heated at reflux for 16 h. After being cooled to room temperature, the reaction mixture was diluted with chloroform, washed with water, and dried over anhydrous Na_2SO_4 . Upon removal of solvents *in vacuo*, the residual was purified with column chromatography over silica gel eluted with petroleum ether/dichloromethane (6/1) to afford region-isomer mixture of **12** as

yellow solids.

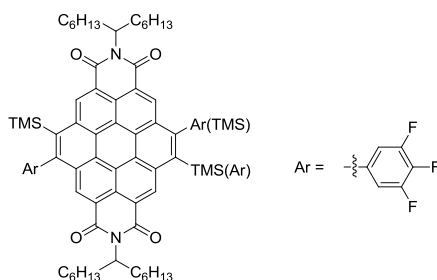


Compound **12a**. Yield: 76%. ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 10.46-10.52 (m, 2H), 9.69-9.71 (m, 2H), 7.61 (d, 4H, $J = 8.1$ Hz), 7.23 (d, 4H, $J = 8.1$ Hz), 5.34-5.45 (m, 2H), 4.19 (t, 4H, $J = 6.3$ Hz), 2.40-2.34 (m, 4H), 1.95-2.03 (m, 8H), 1.56-1.61 (m, 4H), 1.22-1.49 (m, 66H), 0.88-0.90 (m, 6H), 0.78-0.83 (m, 12H), 0.48 (s, 18H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 166.4 (C=O), 165.3 (C=O), 159.9, 149.8, 149.7, 140.5, 134.0, 133.5, 133.5, 133.1, 132.7, 131.9, 130.8, 130.1, 130.0, 127.8, 124.7, 124.6, 124.1, 124.0, 123.0, 122.30, 122.25, 121.6, 121.4, 120.7, 114.9, 114.7, 68.5, 55.5, 55.3, 32.9, 32.8, 32.2, 32.01, 31.97, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 27.4, 26.4, 22.9, 22.8, 14.4, 14.3, 3.5. ESI MS (HR): Calc'd for $\text{C}_{96}\text{H}_{135}\text{N}_2\text{O}_6\text{Si}_2$, 1468.9892 ($\text{M}+\text{H}^+$); Found, 1468.9896. Elem. Anal.: Calc'd. for $\text{C}_{96}\text{H}_{134}\text{N}_2\text{O}_6\text{Si}_2$, C, 78.53; H, 9.20; N, 1.91. Found, 77.53; H, 8.81; N, 1.95.

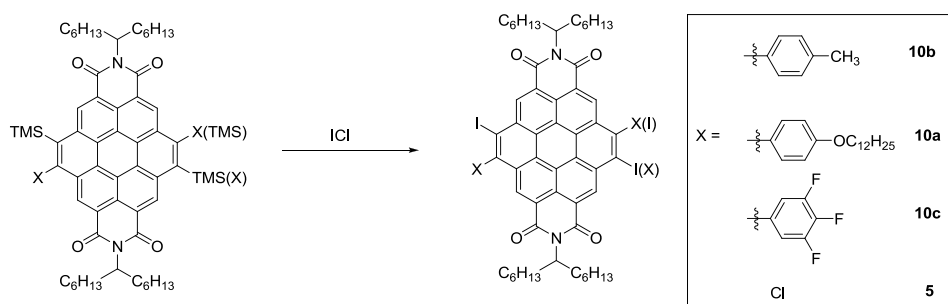


Compound **12b**. Yield: 79%. ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 10.47-10.53 (m,

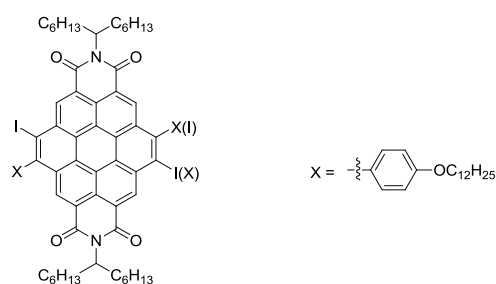
2H), 9.67 (s, 2H), 7.61 (d, 4H, $J = 7.8$ Hz), 7.31 (d, 4H, $J = 7.8$ Hz), 5.43-5.34 (m, 2H), 2.61-2.63 (m, 6H), 2.32-2.41 (m, 4H), 1.80-2.08 (m, 4H), 1.36-1.22 (m, 32H), 0.83-0.74 (m, 12H), 0.47 (s, 18H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 165.3-166.3 (C=O), 150.04, 149.97, 140.3, 138.8, 138.62, 138.58, 132.1, 132.0, 130.0, 129.5, 124.7, 124.2, 123.2, 121.7, 55.5, 33.0, 32.0, 29.9, 29.5, 27.4, 22.8, 21.8, 14.2, 3.5. ESI MS (HR): Calc'd for $\text{C}_{74}\text{H}_{91}\text{N}_2\text{O}_4\text{Si}_2$, 1127.6517 ($\text{M}+\text{H}$) $^+$; Found, 1127.6502. Elem. Anal.: Calc'd. for $\text{C}_{74}\text{H}_{90}\text{N}_2\text{O}_4\text{Si}_2$, C, 78.82; H, 8.04; N, 2.48. Found, C, 77.66; H, 8.00; N, 2.42.



Compound **12c**. Yield: 77%. ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 10.52-10.57 (m, 2H), 9.45-9.49 (m, 2H), 7.38 (t, 4H, $J = 6.6$ Hz), 5.36-5.45 (m, 2H), 2.34-2.40 (m, 4H), 2.00-2.06 (m, 4H), 1.23-1.37 (m, 32H), 0.79-0.83 (m, 12H), 0.56 (s, 18H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 166.0 (C=O), 164.8 (C=O), 152.6-152.8 (C-F), 150.1-150.3 (C-F), 145.9, 141.9, 140.7, 139.4, 137.3, 137.2, 137.1, 134.9, 133.7, 132.9, 132.1, 129.9, 124.6, 124.3, 123.4, 121.4, 116.62, 116.55, 116.47, 116.41, 55.7, 55.5, 32.8, 32.00, 31.97, 27.4, 22.8, 14.2, 3.5. ^{19}F NMR (CDCl_3 , 282 MHz, ppm): δ -54.9, -81.2. ESI MS (HR): Calc'd for $\text{C}_{72}\text{H}_{81}\text{F}_6\text{N}_2\text{O}_4\text{Si}_2$, 1207.5639 ($\text{M}+\text{H}$) $^+$; Found, 1207.5618. Elem. Anal.: Calc'd. for $\text{C}_{72}\text{H}_{80}\text{F}_6\text{N}_2\text{O}_4\text{Si}_2$, C, 71.61; H, 6.68; N, 2.32. Found, C, 71.17; H, 6.94; N, 2.28.



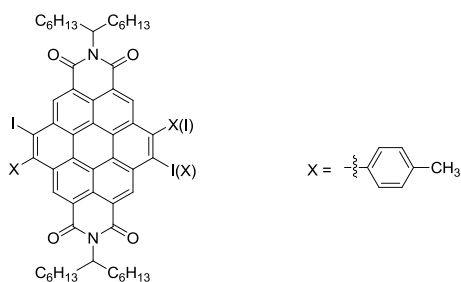
General Procedure for Electrophilic substitution of TMS using ICl. To a solution of the substrate (0.08 mmol) in DCM (40 mL) was added ICl (0.64 mmol) in DCM (5 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 6 h before it was washed with Na_2SO_3 (aq.), and then dried over anhydrous Na_2SO_4 . After removal of solvents *in vacuo*, the residual was purified with column chromatography over silica gel eluted with petroleum ether/dichloromethane (6/1) to afford corresponding products as yellow solids.



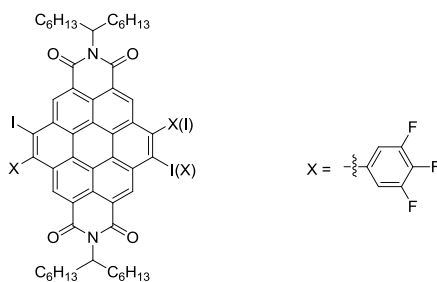
Compound **10a**. Yield: 90%. ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 10.53-10.57 (m, 2H), 9.67-9.69 (m, 2H), 7.53 (d, 4H, $J = 8.4$ Hz), 7.28 (d, 4H, $J = 8.4$ Hz), 5.36-5.47 (m, 2H), 4.21 (t, 4H, $J = 6.3$ Hz), 2.36-2.41 (m, 4H), 1.94-2.01 (m, 8H), 1.59-1.62 (m, 4H), 1.22-1.32 (m, 66H), 0.88-0.92 (m, 6H), 0.79-0.83 (m, 12H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 164-166 (C=O), 160.2, 148.8, 136.4, 132.3, 131.9, 130.8, 124.2, 124.0, 121.4, 115.3, 110.6 (C-I), 68.6, 55.8, 33.0, 32.21, 32.05, 32.02, 31.98, 29.97, 29.93, 29.78, 29.6, 29.54, 29.49, 27.4, 26.5, 22.9, 22.8, 14.3, 14.2. ESI MS (HR):

Calc'd for $C_{90}H_{117}I_2N_2O_6$, 1575.7001 ($M+H$)⁺; Found, 1575.7013. Elem. Anal.:

Calc'd. for $C_{90}H_{116}I_2N_2O_6$, C, 68.60; H, 7.42; N, 1.78. Found, C, 68.29; H, 7.54; N, 1.92.

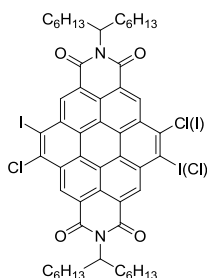


Compound **10b**. Yield: 92%. 1H NMR ($CDCl_3$, 300 MHz, ppm): δ 10.53-10.57 (m, 2H), 9.62-9.65 (m, 2H), 7.59 (d, 4H, $J = 7.6$ Hz), 7.52 (d, 4H, $J = 7.6$ Hz), 5.44 (m, 2H), 2.65 (m, 6H), 2.37-2.51 (m, 4H), 1.96-2.02 (m, 4H), 1.21-1.35 (m, 32H), 0.78-0.82 (m, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 165.7 (C=O), 164.5 (C=O), 148.85, 148.80, 141.2, 139.2, 138.1, 137.4, 137.3, 132.2, 132.1, 130.5, 130.4, 130.0, 124.3, 124.1, 124.0, 123.3, 122.9, 122.2, 121.2, 109.9 (C-I), 55.7, 55.6, 32.90, 32.86, 32.82, 32.03, 31.99, 31.94, 29.9, 29.52, 29.48, 29.44, 27.4, 22.81, 22.78, 22.76, 21.9, 14.25, 14.23. ESI MS (HR): Calc'd for $C_{68}H_{73}I_2N_2O_4$, 1235.3660 ($M+H$)⁺; Found, 1235.3609. Elem. Anal.: Calc'd. for $C_{68}H_{72}I_2N_2O_4$, C, 66.13; H, 5.88; N, 2.27. Found, C, 66.13; H, 6.09; N, 2.33.

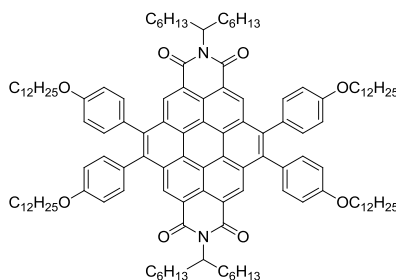


Compound **10c**. Yield: 60%. 1H NMR ($CDCl_3$, 300 MHz, ppm): δ 10.52-10.55 (m,

2H), 9.53-9.57 (m, 2H), 7.28-7.31 (m, 4H), 5.30-5.55 (m, 2H), 2.30-2.52 (m, 4H), 1.93-2.08 (m, 4H), 1.21-1.36 (m, 32H), 0.78-0.82 (m, 12H). ^{19}F NMR (CDCl_3 , 282 MHz, ppm): δ -53.9, -80.5. ESI MS (HR): Calc'd for $\text{C}_{66}\text{H}_{63}\text{I}_2\text{F}_6\text{N}_2\text{O}_4$, 1315.2781 ($\text{M}+\text{H}$) $^+$; Found, 1315.2702. Elem. Anal.: Calc'd. for $\text{C}_{66}\text{H}_{62}\text{I}_2\text{F}_6\text{N}_2\text{O}_4$, C, 60.28; H, 4.75; N, 2.13. Found, C, 61.71; H, 5.32; N, 2.13.

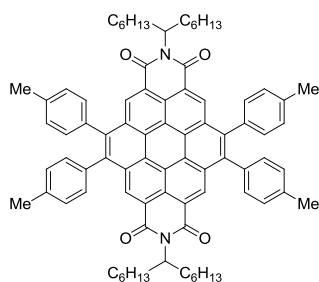


Compound **5**. Yield: 97%. ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 9.60 (m, 2H), 9.39 (m, 2H) 5.34-5.38 (m, 2H), 2.47-2.52 (m, 4H), 2.26-2.30 (m, 4H), 1.40-1.56 (m, 32H), 0.88-0.92 (m, 12H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 163.1 (C=O), 139.6, 136.3, 131.1, 128.7, 128.6, 126.1, 123.2, 122.81, 122.75, 122.4, 121.0, 119.5, 117.9, 107.6 (C-I), 107.4 (C-I), 56.3, 33.0, 32.2, 29.9, 29.7, 27.9, 23.0, 14.3. MALDI-TOF MS: Calcd for $\text{C}_{54}\text{H}_{58}\text{Cl}_2\text{I}_2\text{N}_2\text{O}_4$: 1122.2, Found: 1122.4 (m/z). Elem. Anal.: Calcd. for $\text{C}_{54}\text{H}_{58}\text{Cl}_2\text{I}_2\text{N}_2\text{O}_4$: C, 57.71; H, 5.20; N, 2.49. Found: C, 58.02; H, 5.28; N, 2.51.

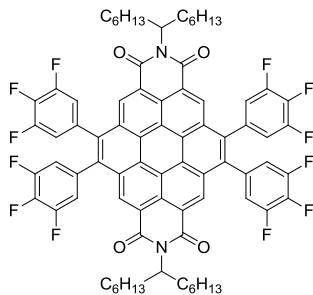


Compound **11a** was obtained from **10a** following the general Suzuki coupling procedure in 87% yield. ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 9.30-9.89 (m, 4H), 9.41

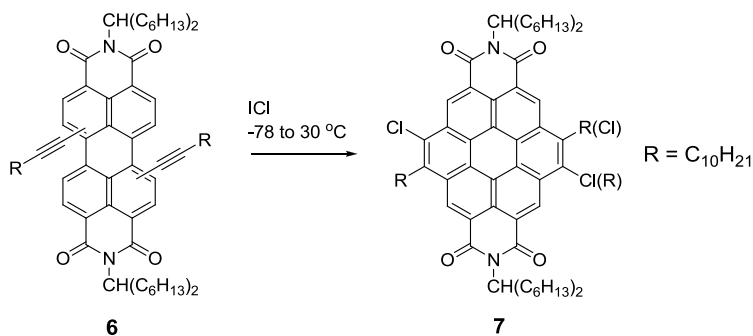
(d, 8H, $J = 8.4$ Hz), 7.03 (d, 8H, $J = 8.4$ Hz), 5.35-5.40 (m, 2H), 4.09 (t, 8H, $J = 6.3$ Hz), 2.33-2.36 (m, 4H), 1.87-1.98 (m, 12H), 1.54-1.63 (m, 8H), 1.21-1.41 (m, 104H), 0.88-0.92 (m, 12H), 0.78-0.83 (m, 12H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm): δ 166.2, 165.0, 141.2, 132.7, 131.0, 130.3, 130.1, 123.5, 122.9, 122.2, 121.4, 121.2, 114.3, 114.2, 68.0, 55.2, 55.1, 32.7, 32.0, 31.8, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 26.2, 22.7, 22.6, 14.2, 14.1. MALDI-TOF MS: Calcd for $\text{C}_{126}\text{H}_{174}\text{N}_2\text{O}_4$: 1844.3, Found: 1843.9 (m/z). Elem. Anal.: Calcd. for $\text{C}_{126}\text{H}_{174}\text{N}_2\text{O}_4$: C, 82.04; H, 9.51; N, 1.52; O, 6.94. Found: C, 81.66; H, 9.38; N, 1.52.



Compound **11b** was obtained from **10b** in 79% yield following the general Suzuki coupling procedure. ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 9.80-9.77 (m, 4H), 7.38 (d, 8H, $J = 7.8$ Hz), 7.28 (d, 8H, $J = 7.8$ Hz), 5.31-5.36 (m, 2H), 2.30-2.36 (m, 4H), 1.90-1.97 (m, 4H), 1.19-1.31 (m, 32H), 0.72-0.81 (m, 12H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 166-165 (broad), 141.3, 137.2, 135.4, 131.5, 130.3, 129.0, 123.7, 123.2, 121.4, 55.3, 32.8, 31.8, 29.3, 27.2, 22.6, 21.4, 14.0. MALDI-TOF MS: Calcd for $\text{C}_{82}\text{H}_{86}\text{N}_2\text{O}_4$: 1162.7, Found: 1163.0 (m/z). Elem. Anal.: Calcd. for $\text{C}_{82}\text{H}_{86}\text{N}_2\text{O}_4$: C, 84.64; H, 7.45; N, 2.41; O, 5.50. Found: C, 84.53; H, 7.35; N, 2.34.



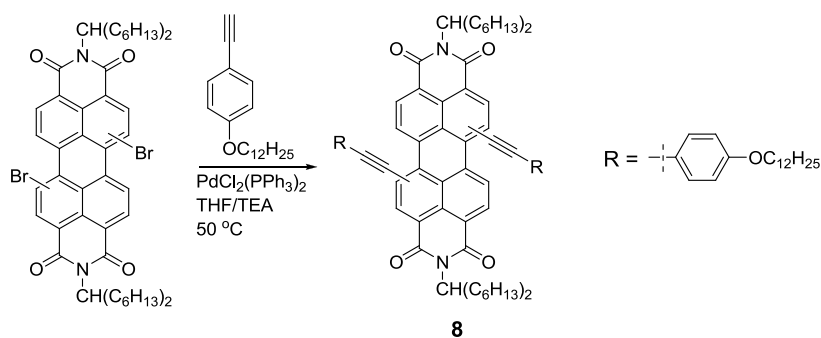
Compound **11c** was obtained from **10c** following the general Suzuki coupling procedure in 92% yield. ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 9.62-9.66 (m, 4H), 7.15-7.19 (t, 8H, $J = 6.6$ Hz), 5.33-5.39 (m, 2H), 2.31-2.38 (m, 4H), 1.94-2.00 (m, 4H), 1.20-1.33 (m, 32H), 0.71-0.82 (m, 12H). ^{19}F NMR (CDCl_3 , 282 MHz, ppm): δ -54.2, -80.8. MALDI-TOF MS: Calcd for $\text{C}_{78}\text{H}_{66}\text{F}_{12}\text{N}_2\text{O}_4$: 1322.5; Found: 1322.9 (m/z). Elem. Anal.: Calcd. for $\text{C}_{78}\text{H}_{66}\text{F}_{12}\text{N}_2\text{O}_4$: C, 70.79; H, 5.03; F, 17.23; N, 2.12; O, 4.84. Found: C, 70.30; H, 5.61; N, 1.98.



Compound **6** was prepared following the reported procedure.^{S3} ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 10.09-10.14 (m, 2H), 8.65-8.75 (m, 4H), 5.17-5.21 (m, 2H), 2.64 (t, 4H, $J = 6.9$ Hz), 2.23-2.31 (m, 4H), 1.71-1.87 (m, 8H), 1.28-1.44 (m, 60H), 0.77-0.86 (m, 18H). ^{13}C NMR (CDCl_3 , 75 MHz, ppm): δ 163-165 (C=O), 138.6, 138.0, 134.0, 133.8, 133.5, 127.5, 127.4, 126.8, 124.5, 121.5, 120.8, 101.8 (C \equiv C, major isomer), 101.6 (C \equiv C, minor isomer), 82.7 (C \equiv C, minor isomer), 82.6 (C \equiv C, major isomer), 54.9,

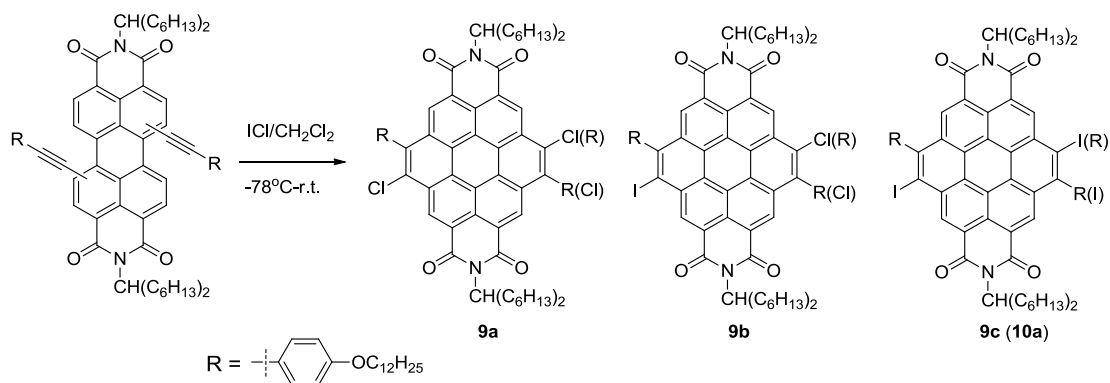
32.5, 32.1, 32.0, 29.8, 29.5, 28.5, 27.2, 22.8, 20.5, 14.2. ESI MS (HR): Calc'd for $C_{74}H_{103}N_2O_4$, 1083.7918 ($M+H$)⁺; Found, 1083.7927. Elem. Anal.: Calc'd. for $C_{74}H_{102}N_2O_4$, C, 82.02; H, 9.49; N, 2.59. Found, C, 81.66; H, 9.46; N, 2.61.

Compound **7** was prepared following the general ICl cyclization protocol in 28% yield. ¹H NMR (CDCl₃, 300 MHz, ppm): δ 10.24 (m, 2H), 9.95 (m, 2H), 5.48 (m, 2H), 3.99 (m, 4H), 2.47 (m, 4H), 2.00-2.13 (m, 8H), 1.73-1.75 (m, 4H), 1.28-1.44 (m, 56H), 0.83-0.90 (m, 18H). ¹³C NMR (CDCl₃, 125 MHz, ppm): δ 165.6 (C=O), 164.5 (C=O), 139.62 (minor isomer), 139.56 (major isomer), 133.34 (major isomer), 133.29 (minor isomer), 129.2, 128.4, 127.8, 122.8, 122.6, 122.5, 121.9, 120.4, 55.72, 55.68, 32.9, 32.15, 32.07, 31.8, 31.0, 30.4, 29.91, 29.87, 29.78, 29.59, 27.54, 27.49, 27.46, 22.92, 22.87, 14.35, 14.29. MALDI-TOF MS: Calcd for $C_{74}H_{100}Cl_2N_2O_4$ (M^+), 1150.7; Found, 1150.6. Elem. Anal.: Calc'd. for $C_{74}H_{100}Cl_2N_2O_4$, C, 77.12; H, 8.75; N, 2.43. Found, C, 77.10; H, 8.71; N, 2.45.



Compound **8**. A schlenk tube containing 1,6/1,7-dibromoPDI (277 mg, 0.30 mmol), (4-dodecoxyphenyl)ethyne (261 mg, 0.90 mmol), PdCl₂(PPh₃)₂ (2 mg, 0.003 mmol), and CuI (trace) was evacuated and backfilled with nitrogen for three times. After the addition of degassed THF (3 mL)/TEA (3 mL), the tube was sealed under nitrogen atmosphere and heated at 50 °C for 48 h. After being cooled to room temperature, the

reaction mixture was diluted with PE, and washed with NH_4Cl (aq.) and then dried over anhydrous Na_2SO_4 . Upon removal of solvents *in vacuo*, the residual was purified with column chromatography over silica gel eluted with petroleum ether/dichloromethane (3/1) to pure dichloromethane to afford regio-isomer mixture of **8** as a purple solid (362 mg, 90%). ^1H NMR (CDCl_3 , 500 MHz, ppm): δ 10.09-10.11 (m, 2H), 8.78 (m, 2H), 8.66 (m, 2H), 7.55-7.57 (m, 4H), 6.95-6.70 (m, 4H), 5.20-5.23 (m, 2H), 4.03 (t, 4H, $J = 6.5$ Hz), 2.28-2.33 (m, 4H), 1.81-1.92 (m, 8H), 1.47-1.52 (m, 4H), 1.26-1.38 (m, 68H), 0.83-0.90 (m, 18H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm): δ 164.7 (C=O), 164.6 (C=O), 164.4 (C=O), 163.8 (C=O), 163.7 (C=O), 163.3 (C=O), 160.6 (C-OC₁₂H₂₅), 138.1, 137.4, 134.2, 134.0, 133.8, 133.3, 130.8, 130.1, 128.7, 128.2, 127.8, 127.7, 127.4, 127.2, 126.84, 126.75, 123.7, 122.9, 122.8, 121.4, 120.6, 115.2, 114.22, 114.17, 99.7 (major isomer), 99.4 (minor isomer), 90.4, 68.4, 55.1, 55.0, 54.9, 32.7, 32.6, 32.5, 32.1, 32.0, 29.89, 29.86, 29.83, 29.81, 29.63, 29.56, 29.48, 29.39, 27.2, 26.3, 22.9, 22.8, 14.32, 14.26. ESI MS (HR): Calc'd for $\text{C}_{90}\text{H}_{119}\text{N}_2\text{O}_6$, 1323.9068 ($\text{M}+\text{H}$)⁺; Found, 1323.9066. Elem. Anal.: Calc'd. for $\text{C}_{90}\text{H}_{118}\text{N}_2\text{O}_6$, C, 81.65; H, 8.98; N, 2.12. Found, C, 81.44; H, 8.93; N, 2.15.



Compound **9** was prepared following the general protocol of ICl induced cyclization reaction with about 60% yield (under sun-light irradiation). As suggested by the ^1H NMR spectrum and mass spectroscopy, three different CDI derivatives were produced, which could not be separated by flash column chromatography. MALDI-TOF mass spectrum showed six peaks in the high m/z region, corresponding to chemical formula of **9c/10a** $^+$ (Calc'd for $\text{C}_{90}\text{H}_{116}\text{I}_2\text{N}_2\text{O}_6$, 1574.7; Found, 1574.6), **9b** $^+$ (Calc'd for $\text{C}_{90}\text{H}_{116}\text{IClN}_2\text{O}_6$, 1482.8; Found, 1482.7), [**9b-Cl/9c-I**] $^+$ (Calc'd for $\text{C}_{90}\text{H}_{116}\text{IN}_2\text{O}_6$, 1447.8; Found, 1447.7), **9a** $^+$ (Calc'd for $\text{C}_{90}\text{H}_{116}\text{Cl}_2\text{N}_2\text{O}_6$, 1390.8; Found, 1390.8), [**9a-Cl/9b-I**] $^+$ (Calc'd for $\text{C}_{90}\text{H}_{116}\text{ClN}_2\text{O}_6$, 1355.6; Found, 1355.8), and [**9a-2Cl/9b-I-Cl/9c-2I+H**] $^+$ (Calc'd for $\text{C}_{90}\text{H}_{116}\text{N}_2\text{O}_6$, 1320.9; Found, 1321.8), respectively (Figure S1). ^1H NMR spectrum of **9** showed two sets of doublets at 7.53 and 7.62 ppm with an integrals ratio of ca. 1:3. The doublets with a chemical shift of 7.53 ppm agreed with that observed in **10a** (Figure S2). Elemental Analysis of **9** gave an elemental composition of C, 71.35; H, 8.04; N, 1.77, roughly also matching a mixture with Cl/I ratio of 1:3 (Calc'd, C, 70.65; H, 7.64; N, 1.83). These results combined indicated that **9** was a mixture of three compounds, **9a**, **9b**, and **9c/10a** with a Cl/I mole ratio of approximately 1:3.

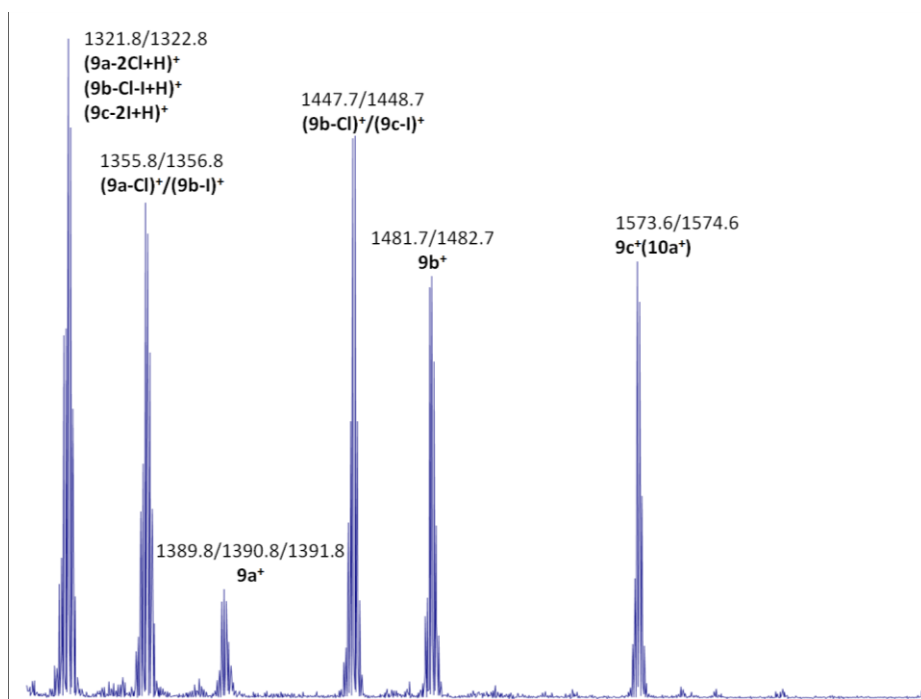


Figure S1. MALDI-TOF mass spectrum of **9** (m/z values of two or three highest peaks are noted for each species).

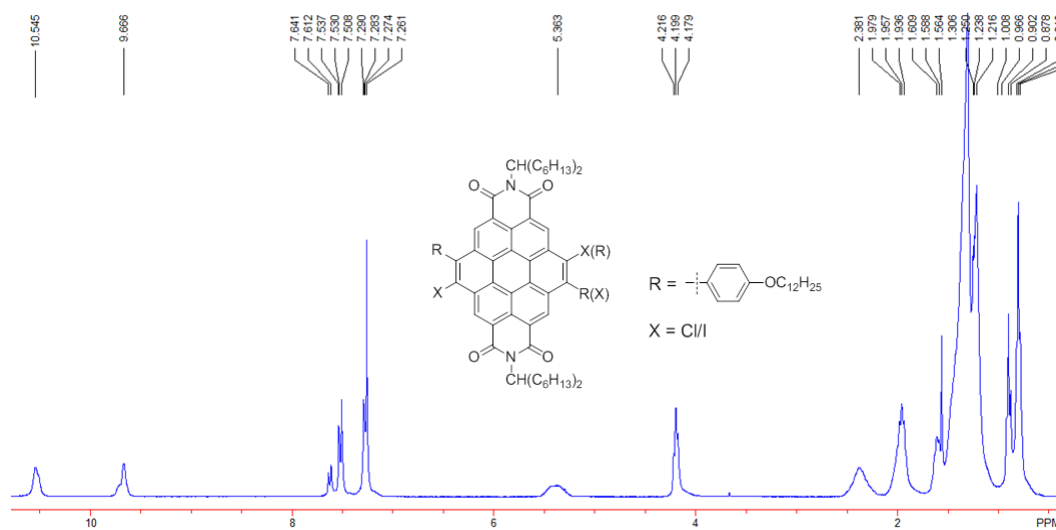
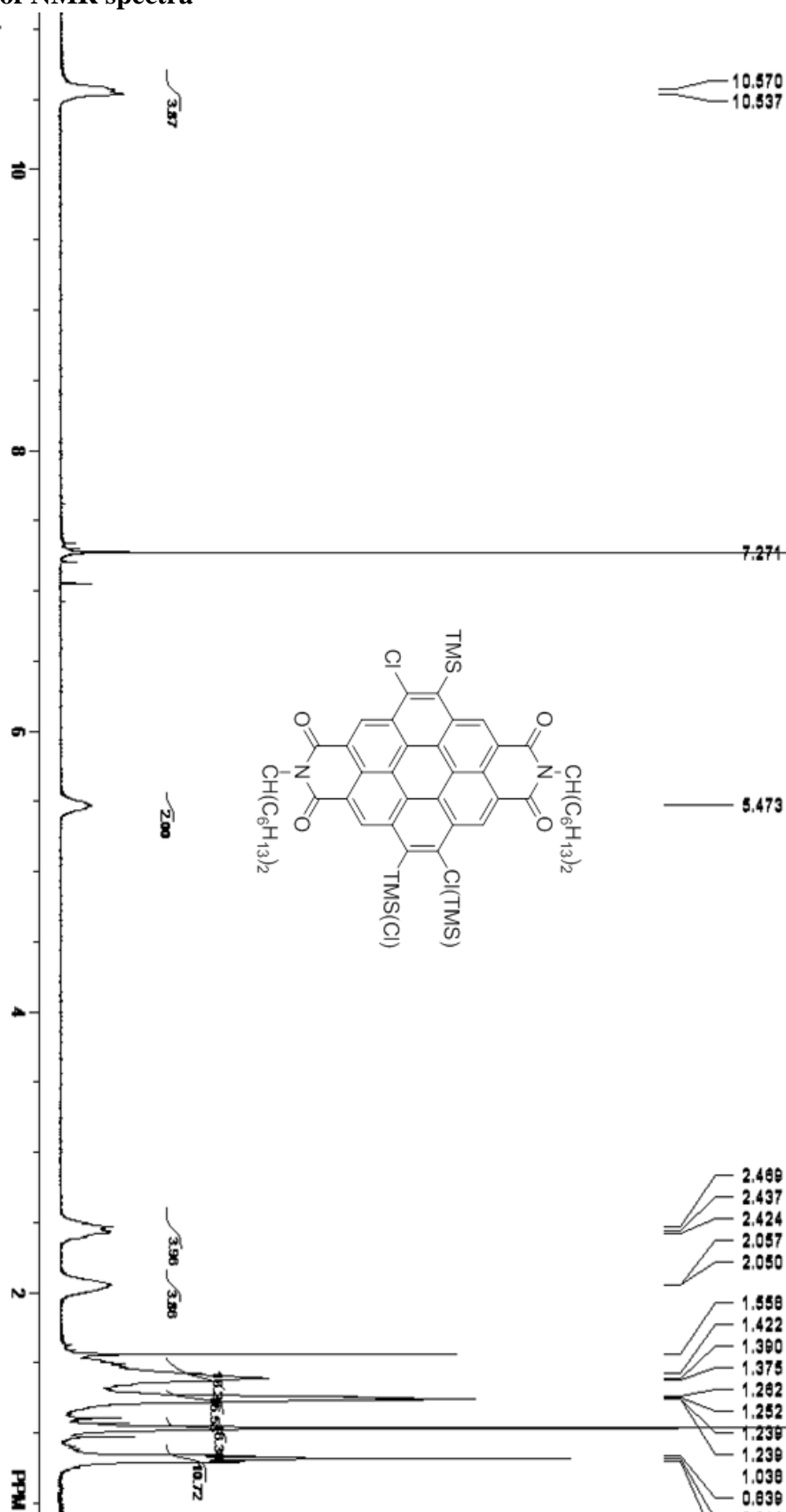
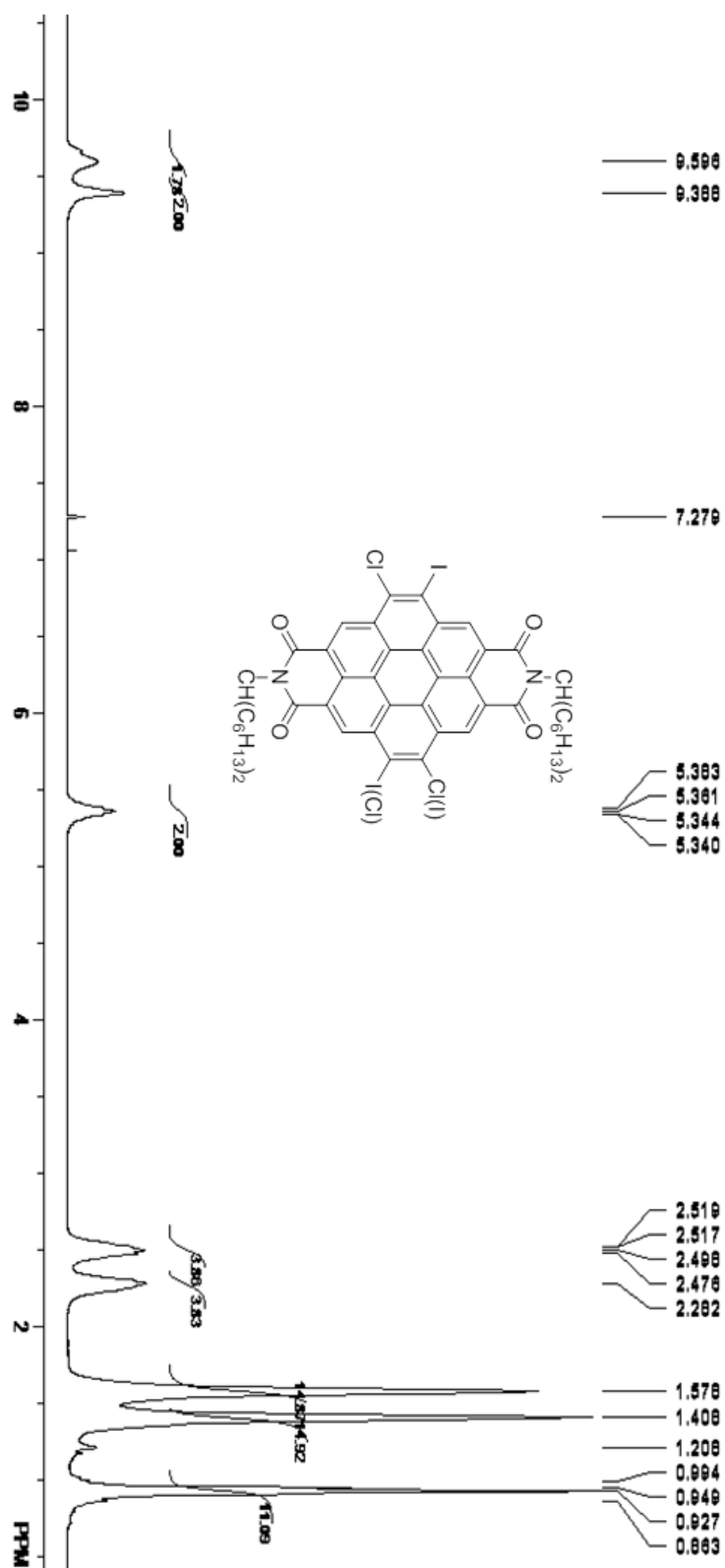


Figure S2. ¹H NMR spectrum (300 MHz, CDCl₃) of **9**.

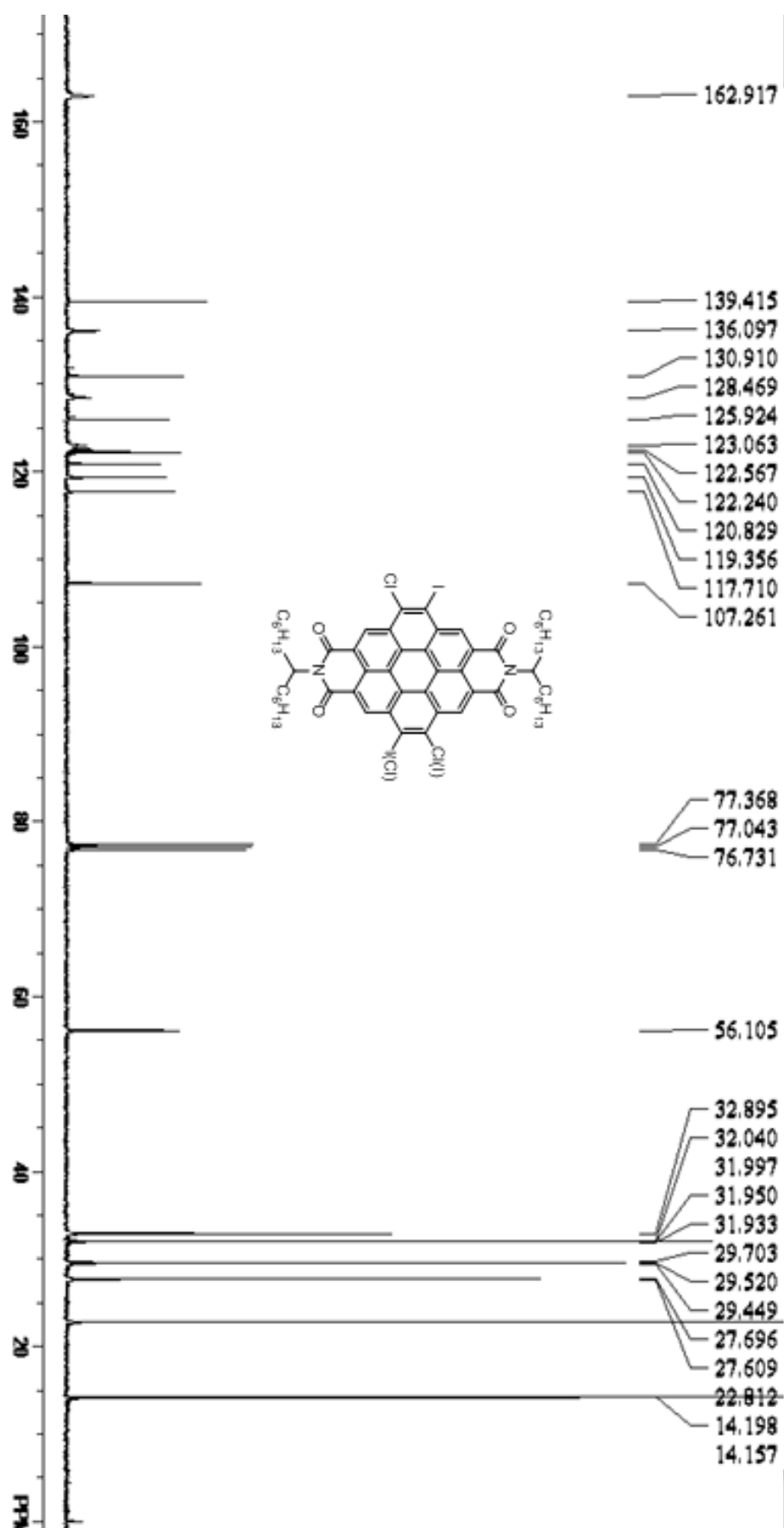
Copies of NMR spectra



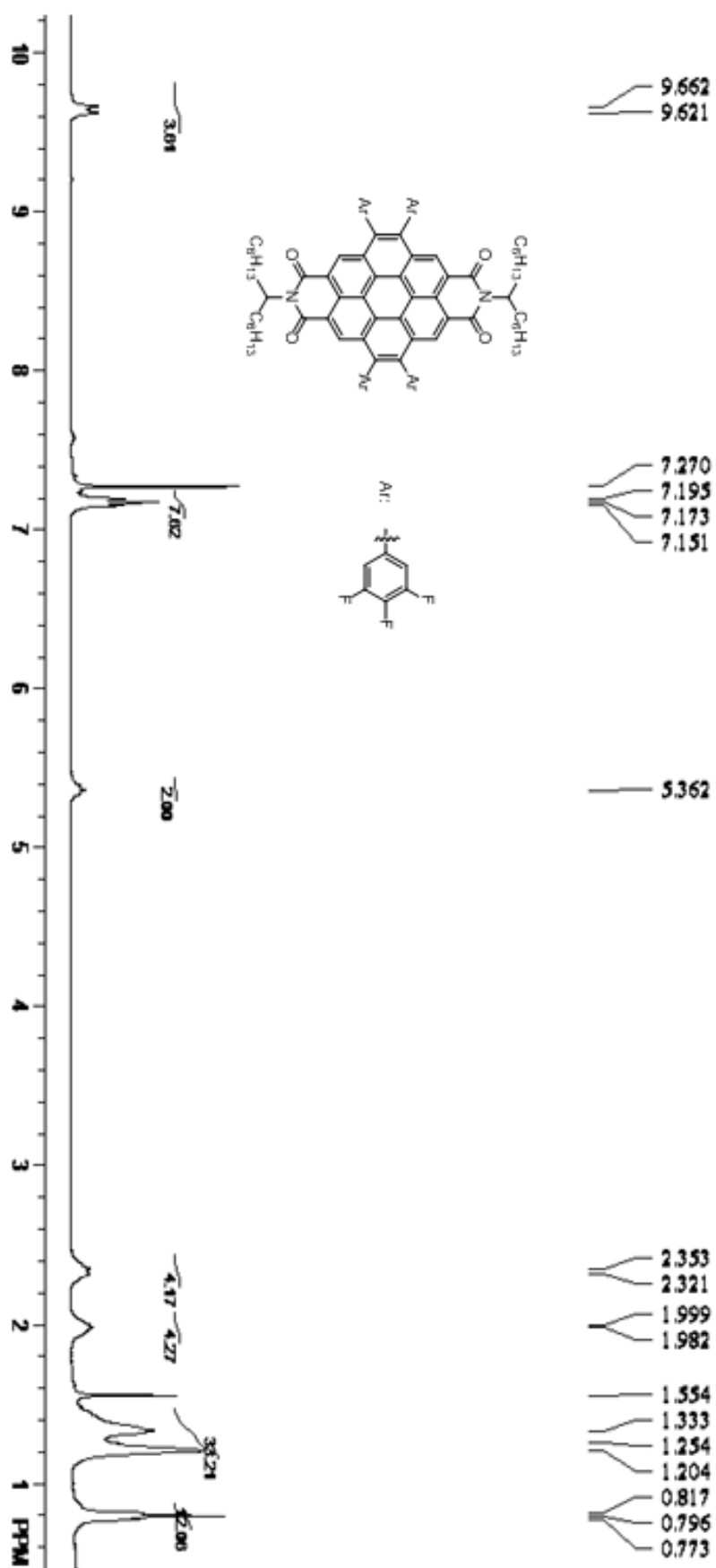
^1H NMR spectrum of **4**



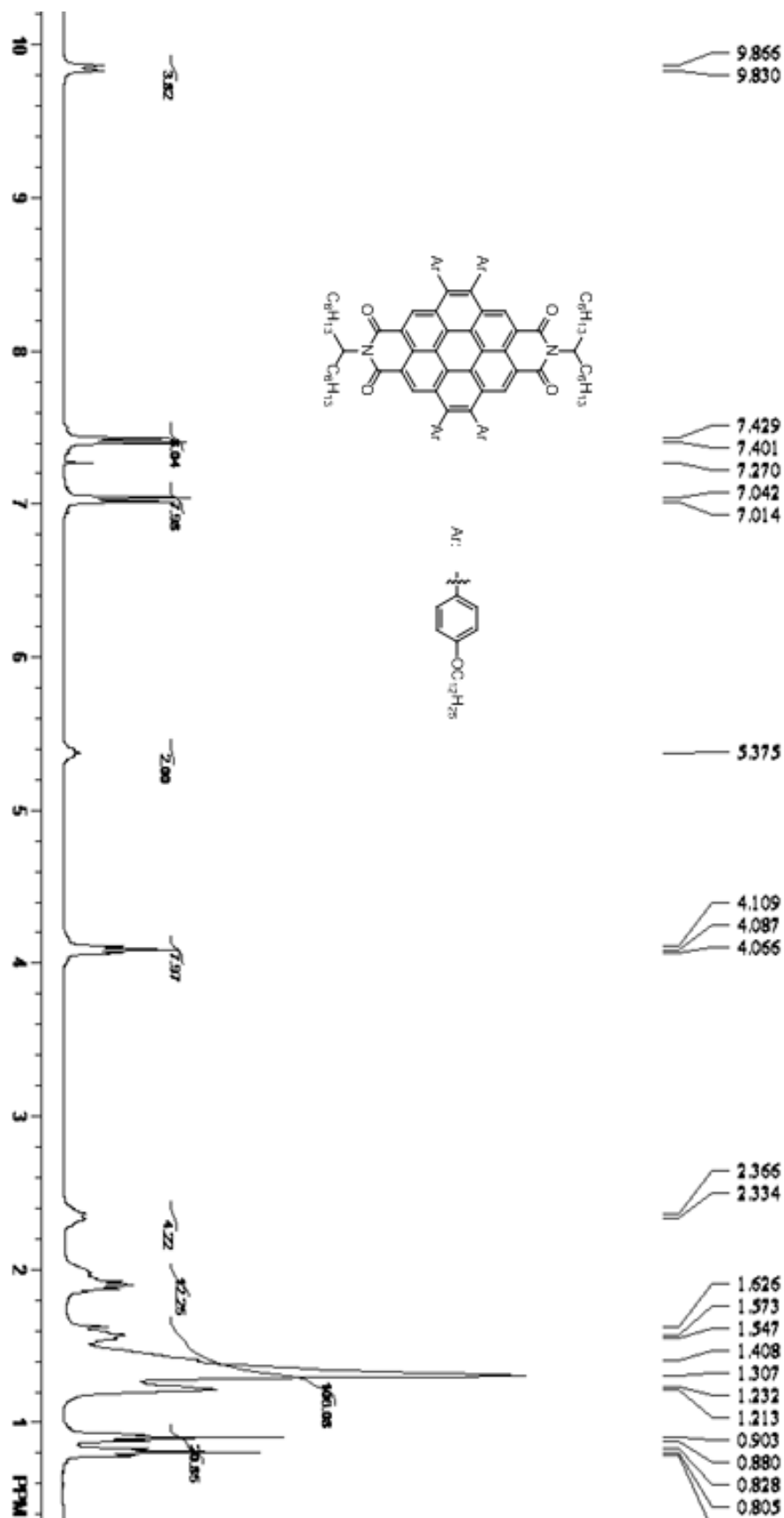
^1H NMR spectrum of **5**



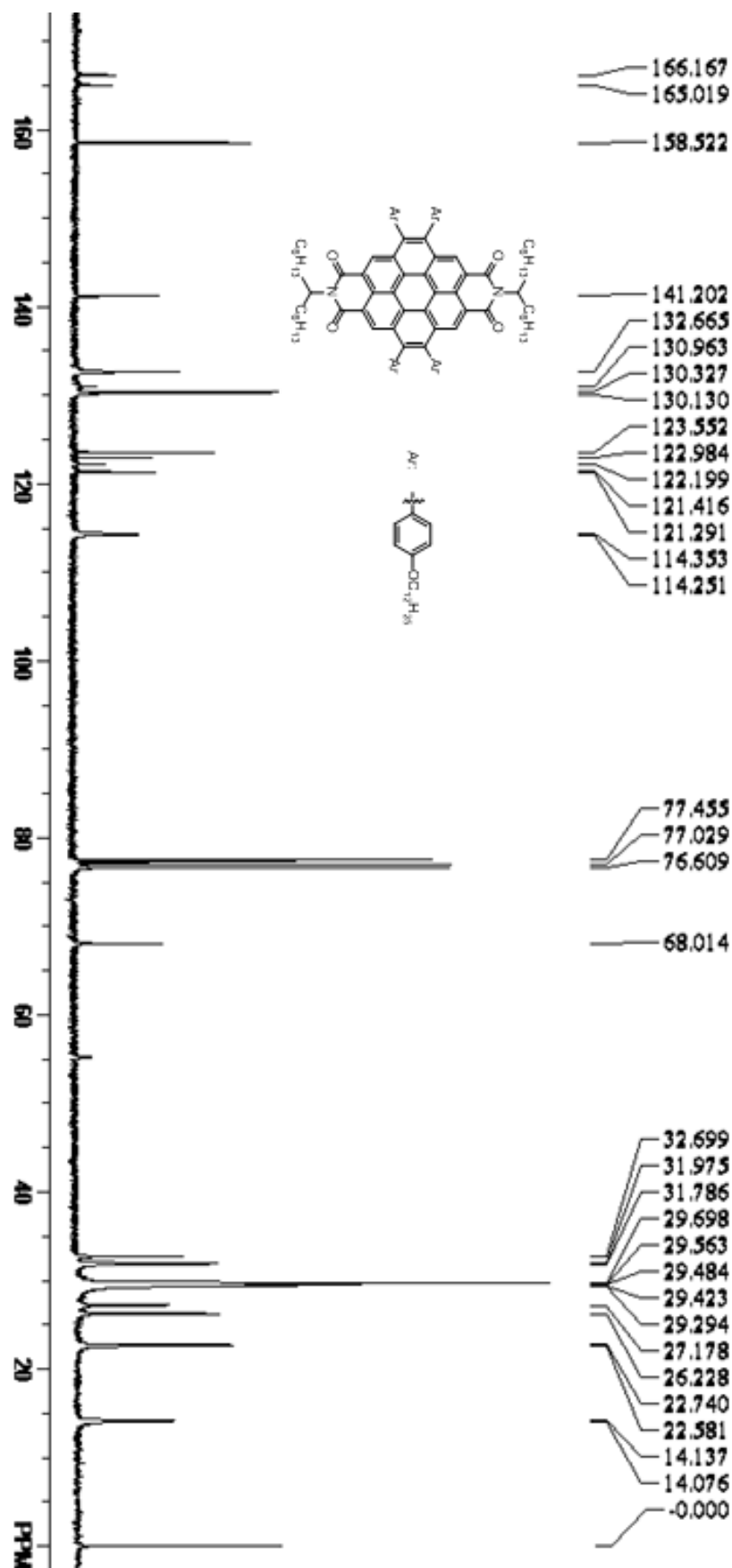
¹³C NMR spectrum of **5**



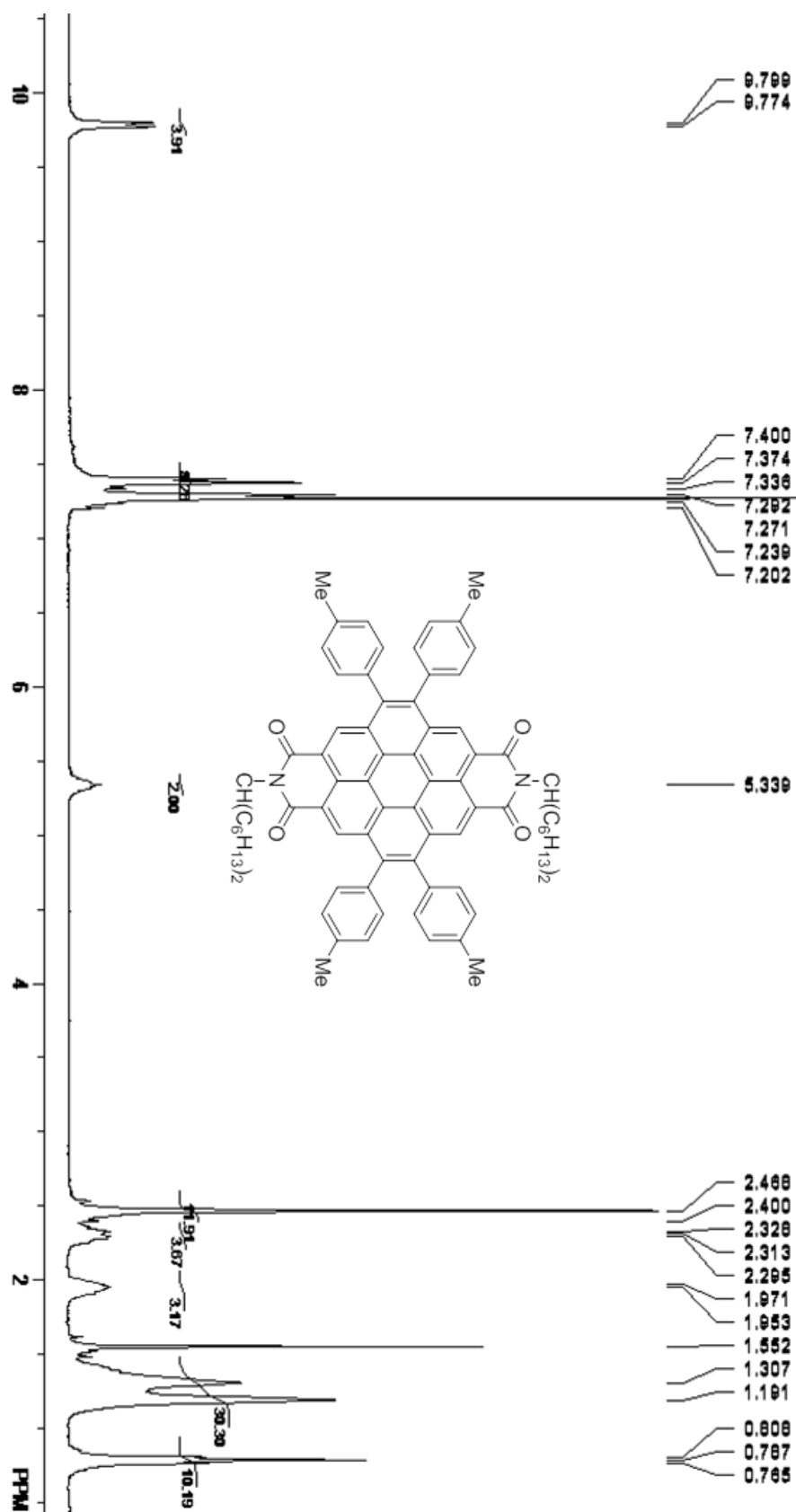
1H NMR spectrum of **11c**



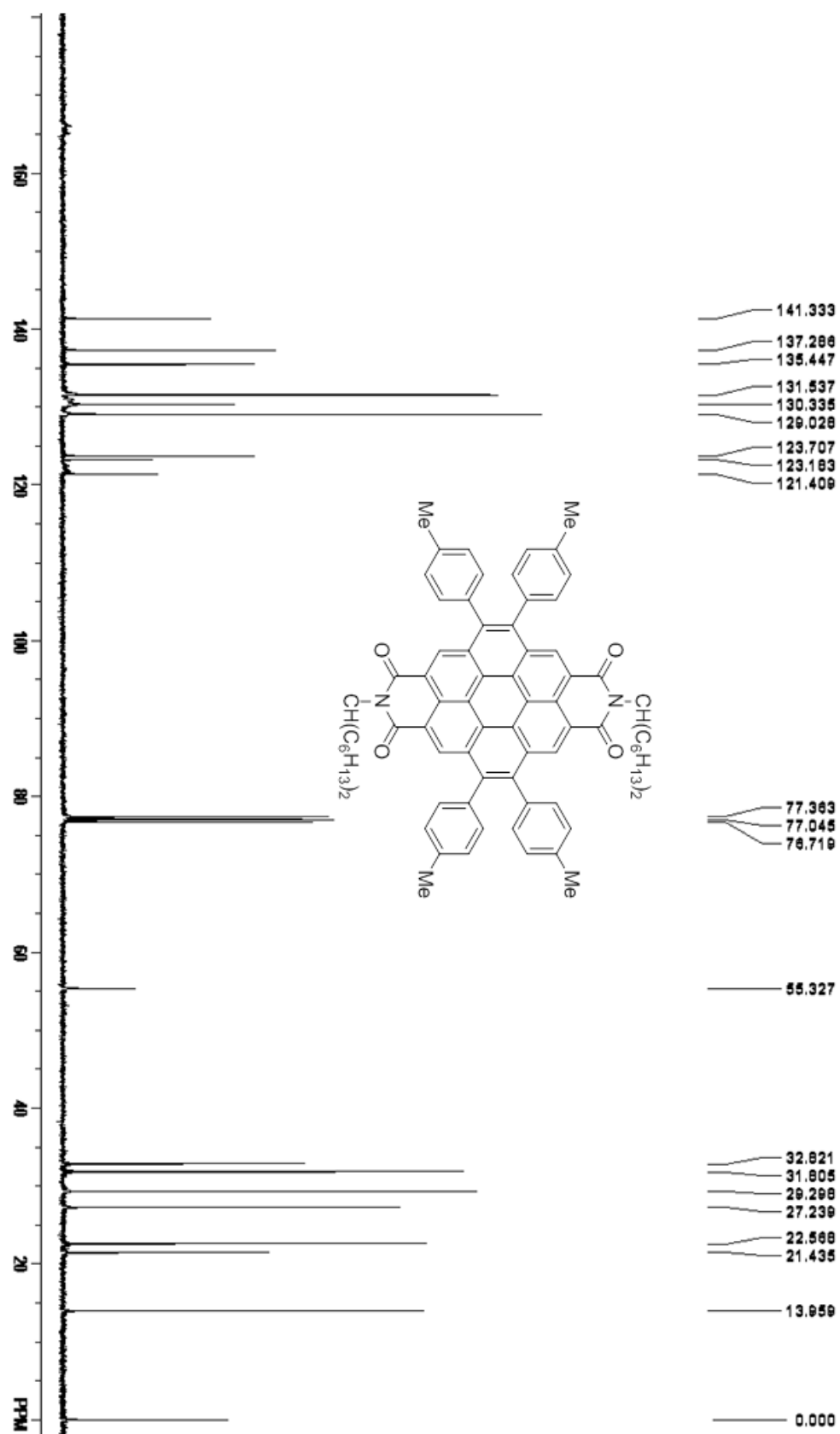
^1H NMR spectrum of **11a**



¹³C NMR spectrum of **11a**



^1H NMR spectrum of **11b**



^{13}C NMR spectrum of **11b**

II. Absorption, emission, and electrochemical characterizations

Dichloromethane was distilled over CaH₂ prior to use. UV-Vis absorption spectra were recorded on a Hitachi U-4100 spectrophotometer using the absorption mode in a 1-cm quartz cell. Fluorescence emission spectra were recorded in 1-cm quartz cuvette on a Horiba Jobin Yvon FluoroMax-4P spectrofluorometer. *N,N'*-bis(1-hexylheptyl)perylene-diimides ($\Phi_{\text{fl}} = 1.00$ in CH₂Cl₂) was used as the fluorescence quantum yield standard. Cyclic voltammetry was performed on a BASI Epsilon workstation with three electrodes configuration, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. Samples were dissolved in CH₂Cl₂ with 0.1 M Bu₄NPF₆ as the supporting electrolyte for cyclic voltammetry measurements.

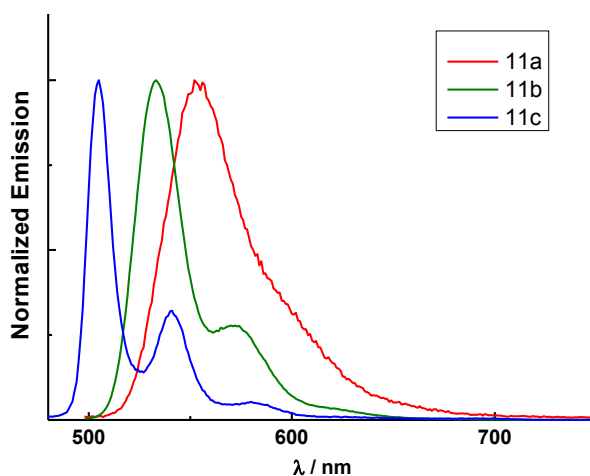


Figure S3. Normalized fluorescence emission spectra of **11a-c** in CH₂Cl₂

Table S1. Photophysical and electrochemical data of **11a-c** in CH₂Cl₂

compd	$\lambda_{\text{abs}}/\text{nm}$ (lg ϵ)	$\lambda_{\text{em}}/\text{nm}$	Φ_{fl}^a	V_{red}/V^b
11a	524 (4.2), 433 (4.6)	554	0.48	-1.4
11b	518 (4.4), 431 (4.8)	533	0.40	-1.1
11c	500 (4.3), 424 (4.7)	505	0.58	-1.2

^a Fluorescence quantum yields were measured in CH₂Cl₂, with *N,N'*-bis(1-hexylheptyl) perylene-diimides ($\Phi_{\text{fl}} = 1.00$) as the reference; the excitation wavelengths were 488 nm for **11a** and 475 nm for **11b** and **11c**, respectively. ^b the first reduction potentials in cyclic voltammogram traces referenced to Fc⁺/Fc.

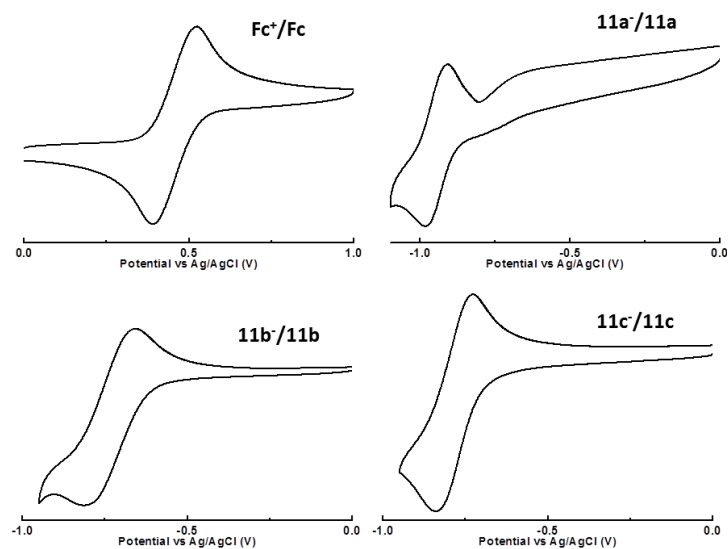


Figure S4. Cyclic voltammograms of ferrocene and **11a-c** in CH₂Cl₂

III. DFT calculations

The geometry was optimized with Density Functional Theory (DFT) using B3LYP hybrid functional with a basis set limited to 6-31g**. TD-DFT calculations were performed at optimized geometries using the same theory level. Quantum-chemical calculation was performed with the Gaussian03^{S4} package and the orbital pictures were prepared using Gaussview.^{S5} All alkyl substituents were replaced with methyl groups in calculations.

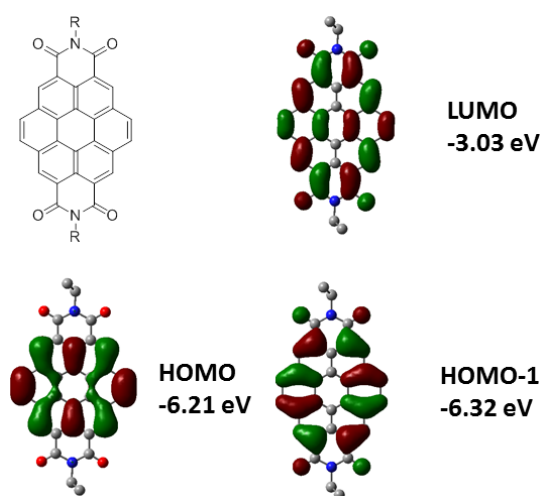


Figure S5. Molecular structure and FMO of CDI

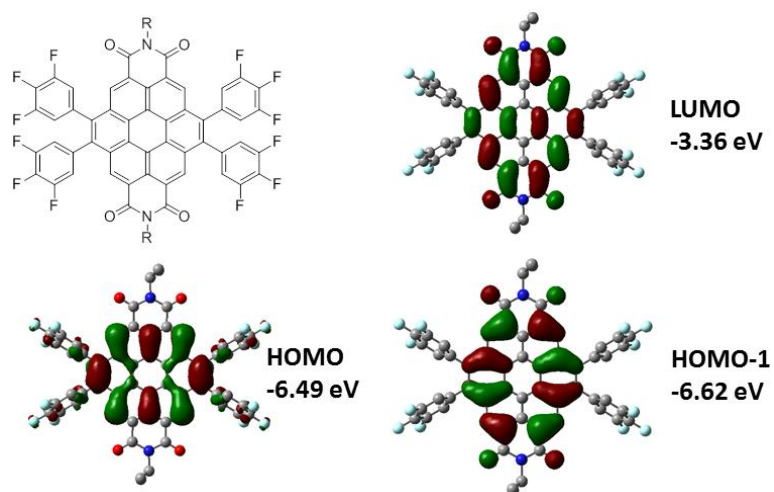


Figure S6. Molecular structure and FMO of 11c

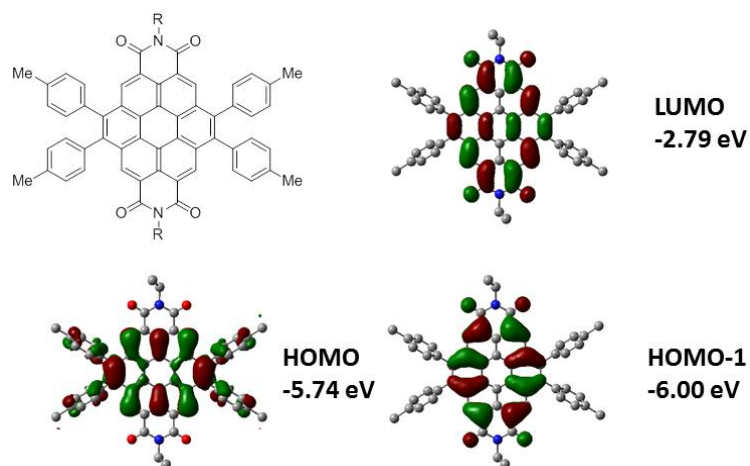


Figure S7. Molecular structure and FMO of 11b

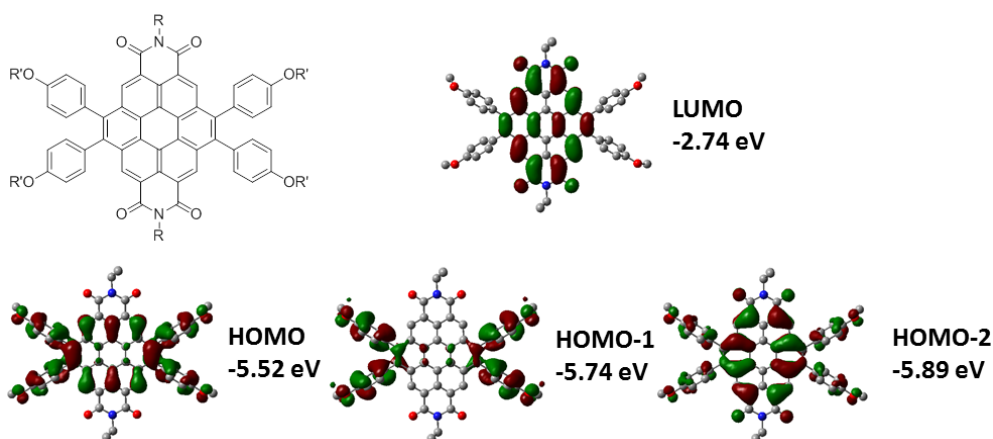


Figure S8. Molecular structure and FMO of 11a

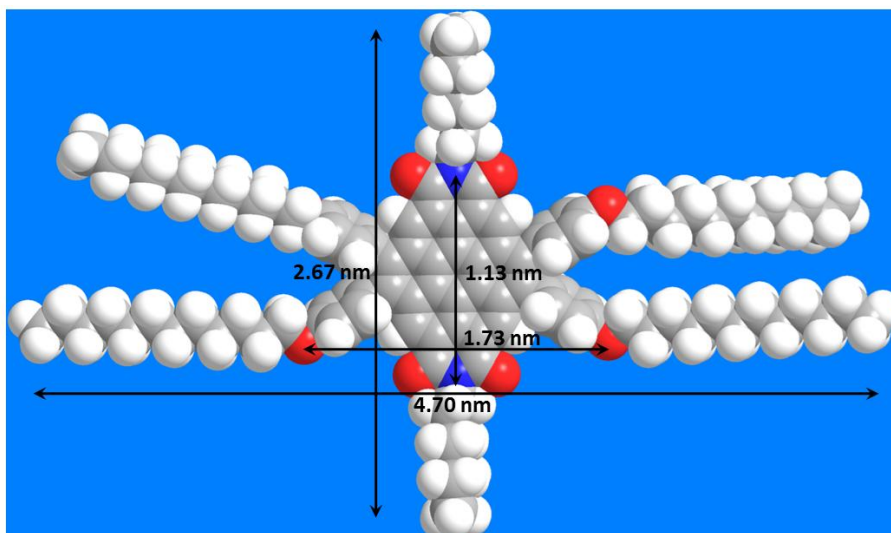


Figure S9. Molecular dimensions of **11a** (alkyl substituents were attached after geometry optimization)

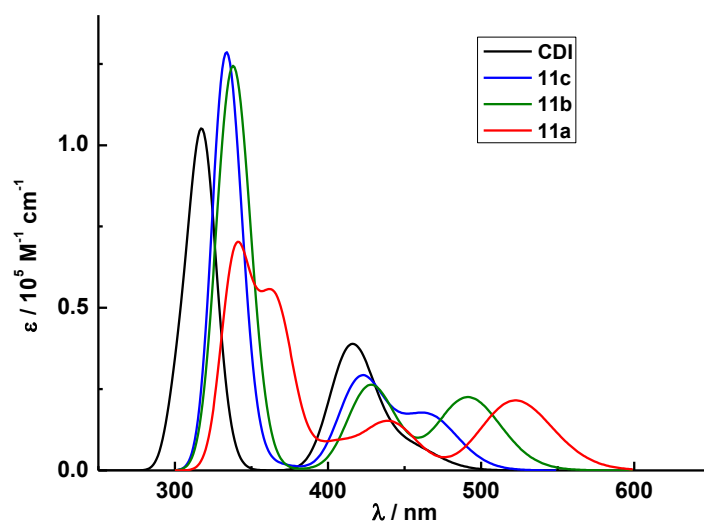


Figure S10. TD-DFT simulated UV-vis absorption spectra of CDI and tetraaryl CDIs. (FWHM was set to be 1000 cm^{-1})

Table S2. DFT calculated FMO level and electronic transition of CDI and tetraaryl-CDIs

		11c	11b	11a	CDI
LUMO / eV		-3.36	-2.79	-2.74	-3.03
HOMO / eV		-6.49	-5.74	-5.52	-6.21
HOMO-1 / eV		-6.62	-6.00	--	-6.32
HOMO-2 / eV		--	--	-5.89	--
S ₀ -S ₁	λ /nm	466	492	522	454
	transition	3.89	4.65	4.69	2.47
	dipole/Debye				
	assignments	H \rightarrow L (86%) ^a	H \rightarrow L (91%)	H \rightarrow L (96%)	H \rightarrow L (84%)
S ₀ -S ₂	λ /nm	422	428	441	416
	transition	4.87	4.69	3.48	5.60
	dipole/Debye				
	assignments	H-1 \rightarrow L (84%)	H-1 \rightarrow L (84%)	H-2 \rightarrow L (86%)	H-1 \rightarrow L (85%)
H: HOMO; L: LUMO; ^a only major contributor shown					

References

- S1. High-resolution ESI or MALDI FT mass spectroscopy was performed for all new molecules reported herein, however certain molecules did not ionize well with these methods. MALDI-TOF was the only ionization-analysis technique that could generate signals with sufficient signal/noise for these molecules, but the MALDI-TOF intrinsically provides limited analysis resolution. The observed masses all matched well with the theoretical values within the limit of instrumentation.
- S2. The high rotational energy barrier of the N-C bond connecting the alkyl group with the imide functionality caused multiple C=O signals in the ^{13}C NMR spectra of all relevant compounds, see: Rajasingh, P.; Cohen, R.; Shhirman, E.; Shimon, L. J. W.; Rybtchinski, B. *J. Org. Chem.* **2007**, 72, 5973.
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- S5. Dennington, R., II; Keith, T.; Millam, J.; Eppinnett, K.; Hovell, W. L.; Gilliland, R. *GaussView*, Version 3.09; Semichem, Inc.: Shawnee Mission, KS, 2003.