Supplementary Information for

Regioisomerically Pure Multiaryl Coronene Derivatives: Highly Efficient Synthesis via Bay-Extended Perylene Tetrabutylester

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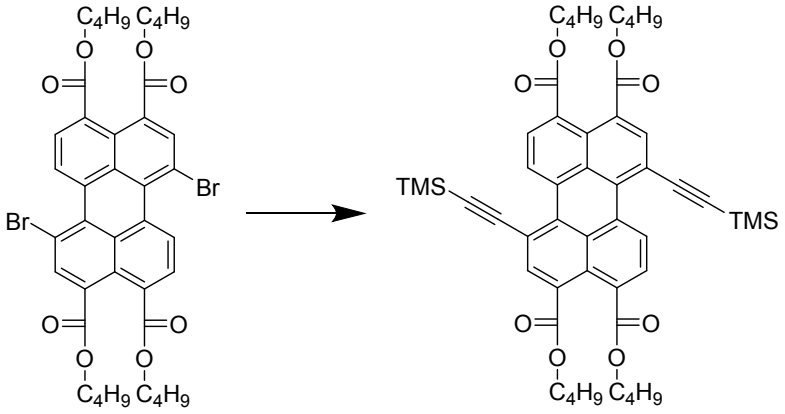
I. Synthesis of all compounds

General methods

Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under argon atmosphere using the standard Schlenk method. Boronic acid and boronate were obtained by the reaction of aryl lithium and triisopropyl borate. All other reagents were of analytical purity and used without further treatment. Solvents used were analytical grade, except those for recrystallization and optical tests, which were purified by distillation. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F254 (MERCK). ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker AM-400 spectrometers with tetramethylsilane (TMS) as an internal reference. $CDCl_3$ was used as solvent. Mass spectra (EI/ESI) were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector. MALDI-TOF mass spectra were recorded on an ABI 4800 Plus MALDI TOF/TOF Analyzer using CHCA as matrix.

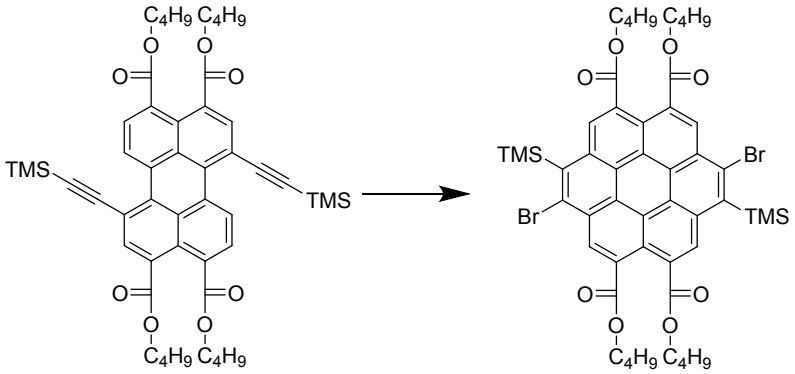


PTE 1 **PTE 2**

Compound **PTE 2**. A Schlenk tube charged with compound **PTE 1** (1.00 g, 1.24 mmol) [S1], CuI (0.15 g, 0.81 mmol), and $PdCl_2(PPh_3)_2$ (0.09 g, 0.13 mmol) was evacuated and backfilled with argon for three times. After a degassed mixture of THF (10mL)/TEA (10 mL) and trimethylsilyl-acetylene (0.96 mL, 6.86 mmol) was added, the tube was sealed under argon atmosphere and heated at 60^{o}C for 12 h. Being cooled to room temperature, the reaction mixture was diluted with dichloromethane and washed with HCl (6 M) and $NaHCO_3$ (aq.) sequentially, before dried over anhydrous Na_2SO_4. The solvents were then removed *in vacuo*. Purification of the crude product with column chromatography over silica gel eluted with petroleum ether/dichloromethane (2/1, v/v) afforded compound **PTE 2** as a red solid (0.95 g, 91%).

Compound **PTE 1**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.91 (s, 1H), 8.89 (s, 1H), 8.28 (s, 2H), 8.08 (s, 1H), 8.06 (s, 1H), 4.34 (t, J = 6.9 Hz, 8H), 1.83 – 1.75 (m, 8H), 1.54 – 1.44 (m, 8H), 1.00 (t, J = 7.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 168.10, 167.14, 136.72, 131.74, 131.64, 131.02, 130.45, 130.27, 128.99, 127.56, 126.44, 118.67, 65.83, 65.61, 30.63, 19.28, 13.92. MALDI TOF MS (HR): Calc'd for $C_{40}H_{42}Br_2O_8$, 808.1246; Found Mass (M^+), 808.0040 (m/z).

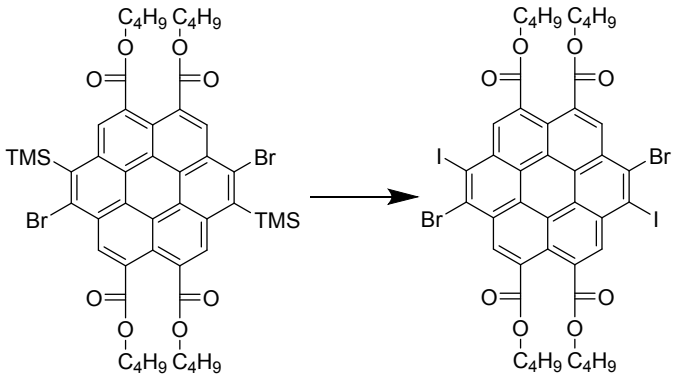
Compound **PTE 2**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.58 (s, 1H), 9.56 (s, 1H), 8.21 (s, 2H), 8.07 (s, 1H), 8.05 (s, 1H), 4.34 (t, J = 6.8 Hz, 8H), 1.78 (dd, J = 14.9, 7.5 Hz, 8H), 1.48 (ddd, J = 14.8, 7.5, 4.1 Hz, 8H), 0.99 (td, J = 7.4, 4.7 Hz, 12H), 0.34 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 168.05, 167.68, 136.01, 133.72, 131.95, 130.44, 129.93, 129.47, 127.06, 126.87, 117.69, 105.79, 102.27, 65.40, 65.23, 30.50, 19.12, 13.67, -0.56. MALDI TOF MS (HR): Calc'd for $C_{50}H_{60}O_8Si_2$, 844.3827; Found Mass (M^+), 844.2615 (m/z).



PTE 2 **CTE 3**

Compound **CTE 3**. To a solution of **PTE 2** (0.95 g, 1.12 mmol) in DCM (200 mL) was added IBr (1.49 g, 6.40 mmol) in DCM (6 mL) at -78 °C for 1h. Then the solution was allowed to be gradually warmed up to room temperature over 1 h and exposed to sun light for additional 24 h. The reaction mixture was washed sequentially with Na_2SO_3 (aq.) and K_2CO_3 (aq.), and then dried over anhydrous Na_2SO_4. Upon removal of solvent *in vacuo*, the residual was purified with column chromatography over silica gel eluted with petroleum ether/dichloromethane (1/1, v/v) to afford **CTE 3** as a yellow solid (0.93 g, 83%).

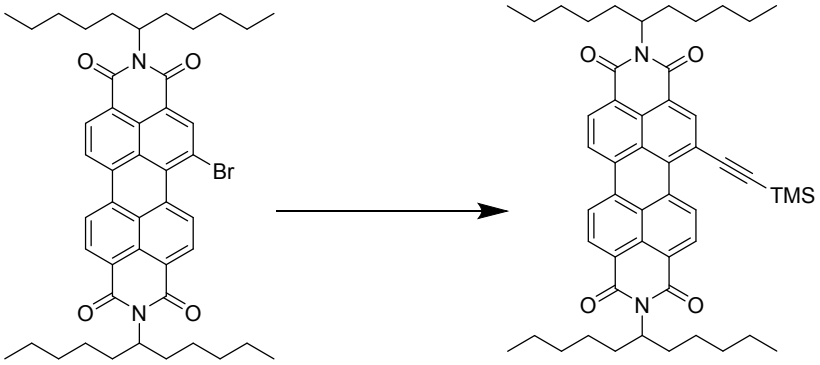
Compound **CTE 3**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 10.03 (d, J = 5.1 Hz, 2H), 9.91 (s, 2H), 4.61 – 4.53 (m, 8H), 1.98 – 1.89 (m, 8H), 1.66 – 1.59 (m, 8H), 1.06 (td, J = 7.4, 5.9 Hz, 12H), 0.98 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 168.76, 168.61, 168.47, 168.29, 167.83, 167.77, 141.67, 141.16, 136.77, 135.87, 134.42, 134.14, 134.06, 133.93, 133.80, 133.13, 132.69, 131.58, 130.96, 130.91, 130.83, 130.31, 130.14, 130.03, 129.26, 129.09, 128.74, 128.27, 128.06, 127.81, 127.66, 127.58, 126.68, 125.98, 125.94, 125.82, 124.76, 123.91, 122.81, 122.54, 65.78, 65.70, 65.61, 65.43, 29.62, 19.35, 19.26, 13.86, 13.79, 4.42, 4.15, -0.42. MALDI TOF MS (HR): Calc'd for $C_{50}H_{58}Br_2O_8Si_2$, 1000.2037; Found Mass (M^+), 1000.1007 (m/z).



CTE 3 **CTE 4**

Compound **CTE 4**. To a solution of Compound **CTE 3** (0.74 g, 0.74 mmol) in DCM (100 mL) was added ICl (0.84 g, 5.19 mmol) in DCM (5 mL) under argon 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 (1/1, v/v) to afford **CTE 4** as a yellow solid (0.74g, 90%).

Compound **CTE 4**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.98 (s, 2H), 9.93 (s, 2H), 4.56 (td, J = 6.8, 4.1 Hz, 8H), 1.95 – 1.88 (m, 8H), 1.64 – 1.56 (m, 8H), 1.04 (td, J = 7.4, 4.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 167.92, 167.81, 137.58, 133.65, 132.51, 131.19, 130.85, 130.74, 128.12, 123.18, 122.95, 122.12, 111.09, 66.11, 30.74, 19.43, 13.96. MALDI TOF MS (HR): Calc'd for $C_{44}H_{40}Br_2I_2O_8$, 1107.9179; Found Mass (M^+), 1107.0532 (m/z).

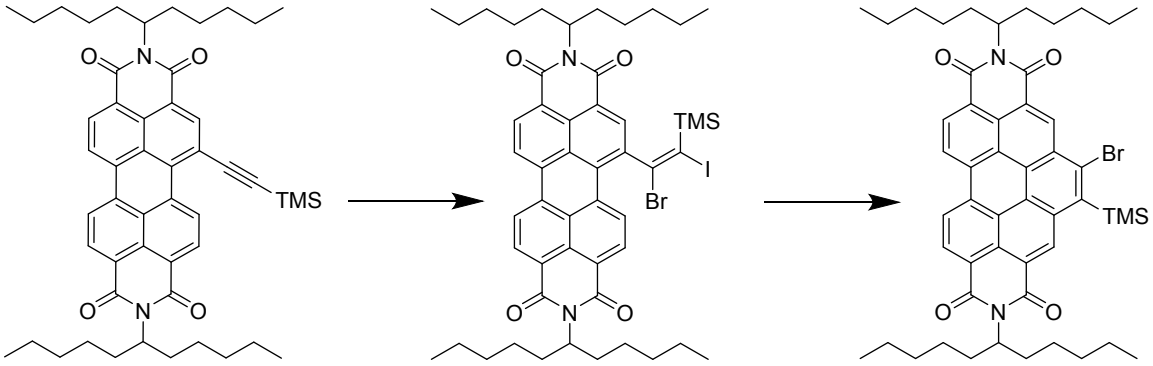


PBI 1 PBI 2

Compound **PBI 2**. A Schlenk tube charged with compound **PBI 1** (1.00 g, 1.29 mmol) [S1], CuI (0.08 g, 0.42 mmol), and $PdCl_2(PPh_3)_2$ (0.05 g, 0.07 mmol) was evacuated and backfilled with argon for three times. After a degassed mixture of THF (10mL)/TEA (10 mL) and trimethylsilyl-acetylene (0.50 mL, 3.57 mmol) was added, the tube was sealed under argon atmosphere and heated at 60°C for 36 h. Being cooled to room temperature, the reaction mixture was diluted with dichloromethane and washed with HCl (6 M) and $NaHCO_3$ (aq.) sequentially, before dried over anhydrous Na_2SO_4. The solvents were then removed *in vacuo*. Purification of the crude product with column chromatography over silica gel eluted with petroleum ether/dichloromethane (3/1, v/v) afforded compound **PBI 2** as a red solid (0.81 g, 79%).

Compound **PBI 1**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.80 (d, J = 11.5 Hz, 1H), 8.94 (t, J = 10.0 Hz, 1H), 8.80 – 8.60 (m, 5H), 5.25 – 5.13 (m, 2H), 2.34 – 2.17 (m, 4H), 1.93 – 1.79 (m, 4H), 1.29 (t, J = 9.0 Hz, 24H), 0.84 (t, J = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 163.39 (C=O), 163.34 (C=O), 133.89, 133.56, 128.92, 128.74, 128.10, 127.10, 123.74, 122.97, 120.94, 54.91, 54.79, 32.32, 32.25, 31.59, 26.59, 22.56, 14.04. ESI TOF MS (HR): Calc'd for $C_{46}H_{54}N_2O_4Br$, 777.3267; Found Mass (M^+), 777.3261 (m/z).

Compound **PBI 2**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.94 (s, 1H), 8.46 (s, 1H), 8.29 (s, 3H), 8.06 (s, 2H), 5.13 (dd, J = 12.5, 7.2 Hz, 2H), 2.29 – 2.16 (m, 4H), 1.96 – 1.82 (m, 4H), 1.31 (d, J = 17.1 Hz, 24H), 0.84 (t, J = 7.0 Hz, 12H), 0.48 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 164.21 (C=O), 163.20 (C=O), 133.84, 133.62, 133.15, 131.01, 128.85, 128.52, 126.71, 126.58, 126.00, 122.96, 122.58, 119.61, 108.76 (C≡C), 106.23 (C≡C), 55.15, 55.07, 32.68, 32.62, 32.21, 27.17, 27.14, 23.02, 14.49, -0.00 (TMS). ESI TOF MS (HR): Calc'd for $C_{51}H_{63}N_2O_4Si$, 795.4557; Found Mass (M^+), 795.4554 (m/z).



PBI 2 PBI 3 BBI 3

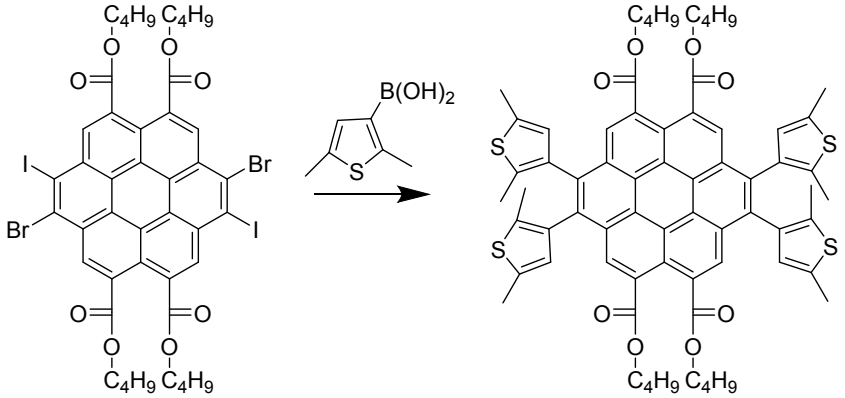
Compound **PBI 3**. To a solution of **PBI 2** (0.81 g, 1.02 mmol) in DCM (200 mL) was added IBr (0.74 g, 3.17 mmol) in DCM (4 mL) at -78 °C for 1h. Then the solution was allowed to be gradually warmed up to room temperature over 3 h under dark conditions. The reaction mixture was washed sequentially with Na_2SO_3 (aq.) and K_2CO_3 (aq.), and then dried over anhydrous Na_2SO_4. Upon removal of solvent *in vacuo*, the residual was purified with column chromatography over silica gel eluted with petroleum ether/dichloromethane (2/1, v/v) to afford **PBI 3** as a red solid (0.87 g, 85%).

Compound **PBI 3**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.90 (d, J = 8.5 Hz, 1H), 8.68 (dd, J = 19.5, 12.3 Hz, 5H), 8.44 (s, 1H), 5.10 (s, 2H), 2.18 (d, J = 9.0 Hz, 4H), 1.76 (d, J = 3.3 Hz, 4H), 1.16 (s, 24H), 0.70 (s, 12H), -0.24 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 164.52 (C=O), 163.43 (C=O), 139.78 (C=C), 138.85 (C=C), 135.33, 134.91, 134.23, 134.02, 133.36, 132.33, 131.63, 131.14, 130.05, 129.46, 129.34, 127.75, 127.70, 127.14, 124.14, 123.60, 118.20, 55.05, 54.94, 32.52, 32.18, 32.00, 29.97, 26.87, 22.96, 22.86, 22.84, 14.32, 1.56, 1.04, -0.00 (TMS). EI TOF MS (HR): [**PBI 3**- (Br and I)] $^{+}$: Calc'd for $C_{51}H_{62}N_2O_4Si$, 794.4479; Found Mass, 794.4484 (m/z).

Compound **BBI 3**. To a solution of **PBI 3** (0.87 g, 0.87 mmol) in DCM (200 mL) exposed to sun light for additional 20 h. Upon removal of solvent *in vacuo*, the residual was purified with column chromatography over silica gel eluted with petroleum ether/dichloromethane (2/1, v/v) to afford **BBI 3** as a yellow solid (0.57 g, 64%).

Compound **BBI 3**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.84 (s, 2H), 9.12 (dd, J = 8.4, 2.6 Hz, 2H), 8.98 (s, 2H), 5.36 – 5.25 (m, 2H), 2.43 – 2.28 (m, 4H), 2.05 – 1.92 (m, 4H), 1.52 – 1.23 (m, 24H), 0.94 (s, 9H), 0.86 (t, J = 7.1 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 164.83 (C=O), 163.86 (C=O), 143.41, 135.61, 134.86, 134.36, 133.78, 133.12, 132.59, 129.16, 127.16, 126.42, 126.24, 124.10, 123.69, 123.07, 122.94, 55.09, 32.44, 31.82, 31.79, 26.79, 22.62, 22.61, 14.08, 4.75. ESI TOF MS (HR): Calc'd for $C_{51}H_{62}BrN_2O_4Si$, 873.3662; Found Mass (M^+), 873.3663 (m/z).

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

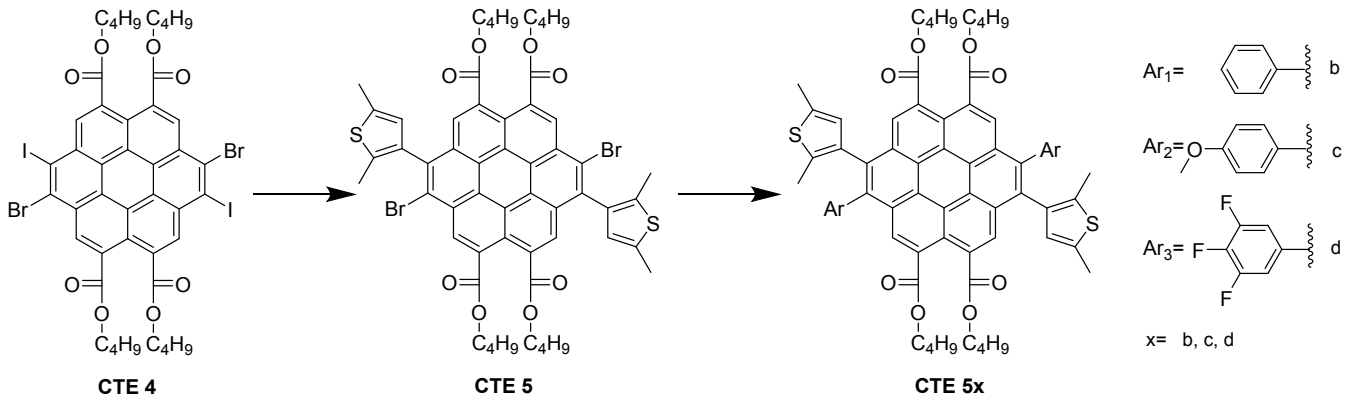


CTE 4 **CTE 5a**

Compound **CTE 5a**. A Schlenk tube containing **CTE 4** (0.11 g, 0.10 mmol), (2,5-dimethyl-3-thiophenyl) boronic acid (0.09 g, 0.60 mmol), and $Pd(PPh_3)_4$ (0.02g, 0.02 mmol) was evacuated and backfilled with argon for three times. After the addition of degassed K_2CO_3 (aq. 2 mL), ethanol (1 ml) and toluene (5 mL), the tube was sealed under argon atmosphere and heated at reflux for 20 h. After being cooled to room temperature, the reaction mixture was diluted with dichloromethane, 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 (1/1, v/v) to afford **CTE 5a** as yellow solids (0.08g, 72%).

Compound **CTE 5a**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.20 (d, J = 2.7 Hz), 9.14 (d, J = 2.2 Hz), 6.72 – 6.62 (m, 4H), 4.47 (t, J = 6.2 Hz, 8H), 2.51 (d, J = 7.8 Hz, 12H), 2.16 – 2.06 (m, 12H), 1.87 – 1.79 (m, 8H), 1.52 (dd, J = 13.0, 6.2 Hz, 8H), 1.02 (t, J = 7.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 168.36, 134.63, 134.45, 134.30, 134.15, 134.03, 133.72, 128.20, 127.93, 127.59, 127.45, 127.02, 126.96, 123.22, 122.17, 121.11, 64.37, 30.86, 29.81, 29.65, 28.63, 28.29, 21.63, 18.30, 14.22, 13.37, 13.31, 13.27, 13.21, 13.06, 12.85, 2.97. MALDI TOF MS (HR): Calc'd for $C_{68}H_{68}O_8S_4$, 1140.3797; Found Mass (M^+), 1140.6627 (m/z).

General procedure for unsymmetrical modifing perylene tetrabutylester



Compound **CTE 5**. A Schlenk tube containing **CTE-B 4** (0.11 g, 0.10 mmol), (2,5-dimethyl-3-thiophenyl) boronic acid (0.033 g, 0.21 mmol), and $Pd(PPh_3)_4$ (0.023 g, 0.02 mmol) was evacuated and backfilled with argon for three times. After the addition of degassed K_2CO_3 (aq. 2 mL), ethanol (1 ml) and toluene (5 mL), the tube was sealed under argon atmosphere and heated at reflux for 12 h. After being cooled to room temperature, the reaction mixture was diluted with dichloromethane, 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 (1/1, v/v) to afford **CTE 5** as a yellow solid (0.10 g, 90%).

Compound **CTE 5**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.99 (s, 2H), 9.08 (s, 2H), 6.88 (d, J = 2.4 Hz, 2H), 4.57 (t, J = 6.7 Hz, 4H), 4.49 (t, J = 6.4 Hz, 4H), 2.65 (s, 6H), 2.22 (s, 6H), 1.95 – 1.91 (m, 4H), 1.86 – 1.81 (m, 4H), 1.64 – 1.60 (m, 4H), 1.55 – 1.49 (m, 4H), 1.03 (t, J = 7.1 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 167.88 (C=O), 167.79 (C=O), 136.33, 135.74, 134.76, 134.66, 134.64, 129.45, 129.42, 128.97, 128.53, 128.44, 126.90, 126.56, 125.48, 123.02, 122.89, 121.85, 121.69, 64.95, 64.61, 30.88, 29.71, 29.61, 28.66, 28.32, 21.65, 18.32, 18.28, 14.41, 13.08, 12.92, 12.85. MALDI TOF MS (HR): Calc'd for $C_{56}H_{54}Br_2O_8S_2$, 1076.1627; Found Mass (M^+), 1076.2879 (m/z).

Compound **CTE 5b-d**. A Schlenk tube containing **CTE-B 5** (0.11 g, 0.10 mmol), phenylboronic acid (0.30 mmol), and $Pd(PPh_3)_4$ (0.01 mmol) was evacuated and backfilled with argon for three times. After the addition of degassed K_2CO_3 (aq. 2 mL), ethanol (1 ml) and toluene (5 mL), the tube was sealed under argon atmosphere and heated at reflux for 20 h. After being cooled to room temperature, the reaction mixture was diluted with dichloromethane, 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 (1/1, v/v) to afford **CTE 5b-d** as yellow solids.

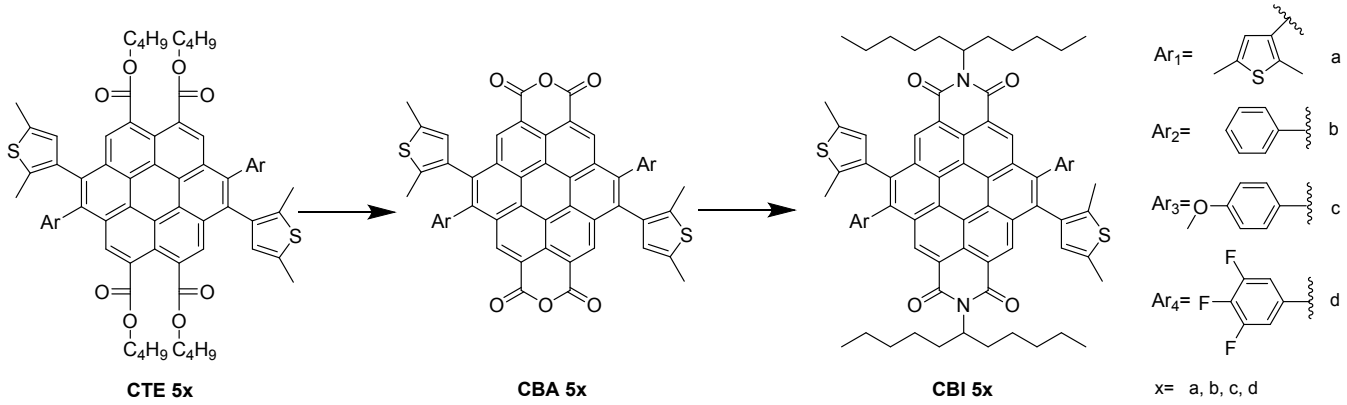
Compound **CTE 5b**. Yield: 81%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.17 (t, J = 2.2 Hz, 4H), 7.56 – 7.44 (m, 10H), 6.70 (d, J = 5.2 Hz, 2H), 4.46 (t, J = 6.4 Hz, 4H), 4.41 (dd, J = 12.6, 6.2 Hz, 4H), 2.47 (s, 6H), 2.04 (d, J = 2.3 Hz, 6H), 1.85 – 1.80 (m, 4H), 1.76 (dd, J = 12.9, 5.8 Hz, 4H), 1.55 – 1.49 (m, 4H), 1.43 – 1.36 (m, 4H), 1.03 – 0.99 (m, 6H), 0.95 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 169.43 (C=O), 169.33 (C=O), 140.52, 138.79, 136.45, 135.68, 135.65, 134.91, 134.89, 134.76, 134.74, 134.70, 134.65, 131.39, 130.79, 130.76, 129.32, 129.26, 129.20, 129.12, 129.00, 128.74, 128.43, 127.94, 127.89, 127.50, 124.20, 123.41, 123.22, 122.26, 122.14, 65.46, 30.81, 30.69, 30.62, 29.73, 26.93, 19.34, 19.28, 15.27, 14.24, 13.92, 13.86. MALDI TOF MS (HR): Calc'd for $C_{68}H_{64}O_8S_2$, 1072.4043; Found Mass (M^+), 1072.1110 (m/z).

Compound **CTE 5c**. Yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.15 – 9.11 (m, 2H), 9.07 (d, J = 2.3 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.37 – 7.31 (m, 2H), 6.96 (tt, J = 7.0, 2.4 Hz, 4H), 6.62 (d, J = 10.8 Hz, 2H), 4.39 (t, J = 6.4 Hz, 4H), 4.34 (ddd, J = 6.5, 4.6, 2.0 Hz, 4H), 3.86 (s, 6H), 2.41 (s, 6H), 1.95 (d, J = 4.4 Hz, 6H), 1.77 – 1.71 (m, 4H), 1.71 – 1.66 (m, 4H), 1.43 (dd, J = 15.1, 7.5 Hz, 4H), 1.34 (dd, J = 8.2, 6.8 Hz, 4H), 0.93 (dd, J = 8.8, 6.0 Hz, 6H), 0.87 (t, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm):

δ 169.45 (C=O), 169.39 (C=O), 158.92, 140.22, 135.69, 135.65, 135.06, 135.04, 134.86, 134.63, 134.50, 132.56, 132.01, 131.01, 129.29, 129.21, 129.19, 129.16, 129.12, 128.94, 128.74, 124.21, 123.44, 123.12, 122.05, 113.50, 113.31, 65.42, 55.30, 30.69, 30.64, 29.72, 19.33, 19.32, 15.33, 14.22, 14.21, 13.93, 13.79. MALDI TOF MS (HR): Calc'd for $C_{70}H_{68}O_{10}S_2$, 1132.4254; Found Mass (M^+), 1132.1115 (m/z).

Compound **CTE 5d**. Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.18 – 9.14 (m, 2H), 9.10 – 9.06 (m, 2H), 7.20 (d, J = 1.0 Hz, 4H), 6.71 (d, J = 5.2 Hz, 2H), 4.49 (d, J = 5.8 Hz, 8H), 2.54 (s, 6H), 2.11 (s, 6H), 1.84 (d, J = 5.7 Hz, 8H), 1.51 (dd, J = 15.2, 7.5 Hz, 8H), 1.03 (dd, J = 7.8, 5.0 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 169.08 (C=O), 168.93 (C=O), 152.08, 149.73, 139.28, 137.19, 136.95, 136.93, 135.32, 135.11, 135.05, 133.94, 129.83, 129.69, 129.32, 128.64, 128.36, 127.70, 124.06, 123.44, 123.36, 122.61, 115.84, 115.67, 115.06, 114.87, 114.08, 65.77, 65.66, 53.53, 33.84, 31.95, 30.66, 30.64, 29.72, 22.71, 19.39, 19.33, 15.29, 14.25, 14.13, 13.89, 13.67. MALDI TOF MS (HR): Calc'd for $C_{68}H_{58}F_6O_8S_2$, 1180.3477; Found Mass (M^+), 1180.2690 (m/z).

General procedure for converting perylene tetrabutylester to perylene bisimides



Compound **CBI 5a-d**. A mixture of compound **CTE 5x** (0.10 mmol) and *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H_2O) (0.09 g, 0.45 mmol), in toluene (3 mL), was stirred for 30 h at 100 °C. After being cooled to room temperature, the reaction mixture was filtered, and the residue was washed with methanol and water several times. Thereafter, the dried precipitate was taken in chloroform (6 mL) and refluxed for a few hours. It was cooled to room temperature and filtered to remove the soluble monoanhydride. The residue was then washed with chloroform and dried to obtain a red solid without further purification, due to its low solubility. Then, a mixture of above red solid and 1-hexylheptylamine (0.07 g, 0.23 mmol), in imidazole (0.22 g, 3.23 mmol), was stirred 3h at 130° C. The reaction mixture was cooled to room temperature, taken up in 4 mL ethanol, treated with 12 mL 2M HCl, and stirred overnight. The dark red precipitate was filtered and rinsed thoroughly with distilled water, and dried *in vacuo* at 60 °C. The residual was purified with column chromatography over silica gel eluted with petroleum ether/dichloromethane (3/1, v/v) to afford **CBI 5a-d** as a red solid.

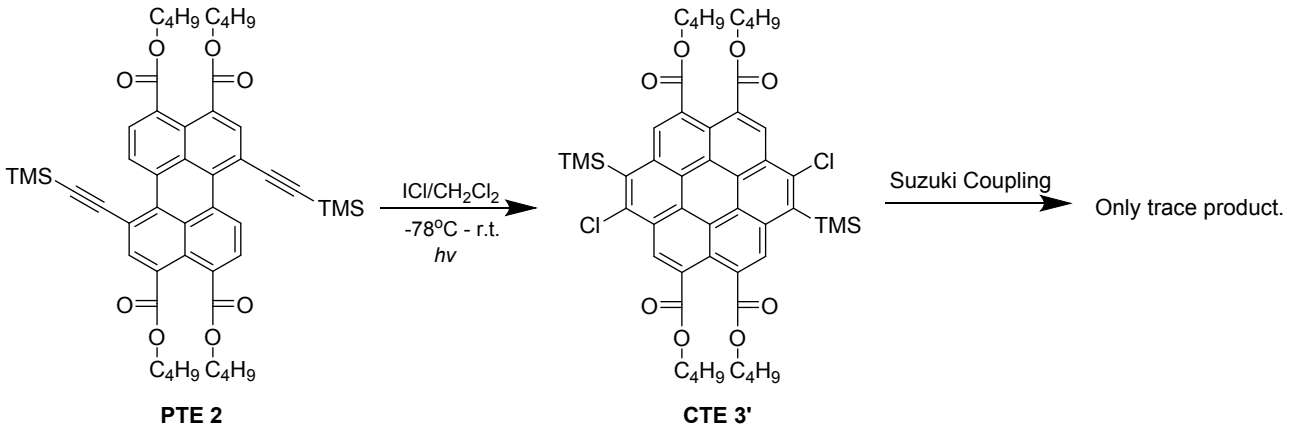
Compound **CBI 5a**. Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.84 (t, J = 16.3 Hz, 4H), 6.72 (d, J = 5.0 Hz, 1H), 6.65 (s, 3H), 5.44 – 5.38 (m, 2H), 2.55 (d, J = 11.3 Hz, 12H), 2.37 (dd, J = 9.4, 4.3 Hz, 4H), 2.20 – 2.14 (m, 9H), 2.11 (d, J = 3.4 Hz, 3H), 2.07 – 2.01 (m, 4H), 1.33 – 1.26 (m, 24H), 0.84 (t, J = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 166.15 (C=O), 165.01 (C=O), 158.81, 141.14, 137.43, 137.25, 136.07, 135.93, 134.75, 134.62, 134.23, 132.68, 130.92, 130.54, 130.32, 130.07, 127.58, 123.57, 123.02, 121.29, 113.80, 55.28, 32.64, 31.82, 29.72, 26.91, 22.59, 15.34, 14.05. EI TOF MS (HR): Calc'd for $C_{74}H_{78}N_2O_4S_4$, 1186.4844; Found Mass (M^+), 1186.4847 (m/z).

Compound **CBI 5b**. Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.76 (s, 2H), 9.72 (s, 2H), 7.46 (d, J = 5.1 Hz, 10H), 6.63 (s, 2H), 5.28 (d, J = 5.0 Hz, 2H), 2.41 (s, 6H), 2.25 (d, J = 6.5 Hz, 4H), 1.99 (d, J = 6.2 Hz, 6H), 1.95 – 1.90 (m, 5H), 1.18 (s, 28H), 0.74 (t, J = 7.1 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$,

ppm): δ 165.85 (C=O), 164.77 (C=O), 158.58, 141.08, 137.19, 137.17, 135.19, 133.92, 133.89, 133.37, 130.21, 128.89, 127.90, 127.15, 126.88, 122.85, 122.65, 122.21, 120.32, 113.82, 113.64, 54.21, 31.61, 30.91, 30.79, 30.57, 28.68, 28.31, 25.87, 24.50, 24.26, 21.64, 21.55, 13.11, 13.02. MALDI TOF MS (HR): Calc'd for $C_{74}H_{74}N_2O_4S_2$, 1118.5090; Found Mass (M^+), 1118.4201 (m/z).

Compound **CBI 5c**. Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.80 (s, 1H), 9.76 (s, 1H), 9.74 (s, 1H), 9.70 (s, 1H), 7.41 (s, 1H), 7.39 (s, 1H), 7.37 (s, 1H), 7.34 (d, J = 2.7 Hz, 1H), 6.99 (dd, J = 10.4, 4.3 Hz, 4H), 6.64 (s, 2H), 5.32 – 5.27 (m, 2H), 3.89 (s, 6H), 2.43 (s, 6H), 2.26 (d, J = 7.6 Hz, 4H), 1.97 (d, J = 6.3 Hz, 6H), 1.91 (d, J = 4.4 Hz, 4H), 0.73 (t, J = 7.1 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 166.16 (C=O), 165.00 (C=O), 159.13, 141.87, 136.56, 136.24, 134.81, 134.56, 132.42, 131.69, 130.38, 130.17, 128.93, 123.74, 123.49, 123.17, 121.37, 113.85, 113.65, 55.34, 55.22, 32.68, 32.64, 31.94, 31.84, 29.72, 29.38, 26.91, 22.71, 22.60, 15.44, 14.28, 14.15, 14.06. MALDI TOF MS (HR): Calc'd for $C_{76}H_{78}N_2O_6S_2$, 1178.5301; Found Mass (M^+), 1178.3100 (m/z).

Compound **CBI 5d**. Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.79 (s, 1H), 9.76 (s, 1H), 9.70 (s, 1H), 9.65 (s, 1H), 7.17 (d, J = 5.3 Hz, 4H), 6.69 (s, 2H), 5.37 (s, 2H), 2.53 (s, 6H), 2.32 (s, 4H), 2.09 (d, J = 4.3 Hz, 6H), 2.00 (s, 4H), 1.26 (d, J = 12.8 Hz, 24H), 0.81 (t, J = 7.0 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 164.71 (C=O), 163.52 (C=O), 151.22, 148.73, 138.26, 137.67, 136.45, 136.03, 134.25, 132.42, 129.00, 128.07, 127.17, 122.75, 122.58, 120.20, 114.68, 114.53, 113.78, 113.57, 113.04, 54.43, 32.80, 31.58, 30.99, 30.75, 28.68, 28.64, 28.34, 25.83, 21.67, 21.54, 14.36, 13.26, 13.09, 12.99. MALDI TOF MS (HR): Calc'd for $C_{74}H_{68}F_6N_2O_8S_2$, 1226.4525; Found Mass (M^+), 1226.2966 (m/z).



Scheme S1. Synthesis of dichlorinated **CTE 3'** and subsequent Suzuki coupling.

II. Features of regioisomerically pure structure and mechanism

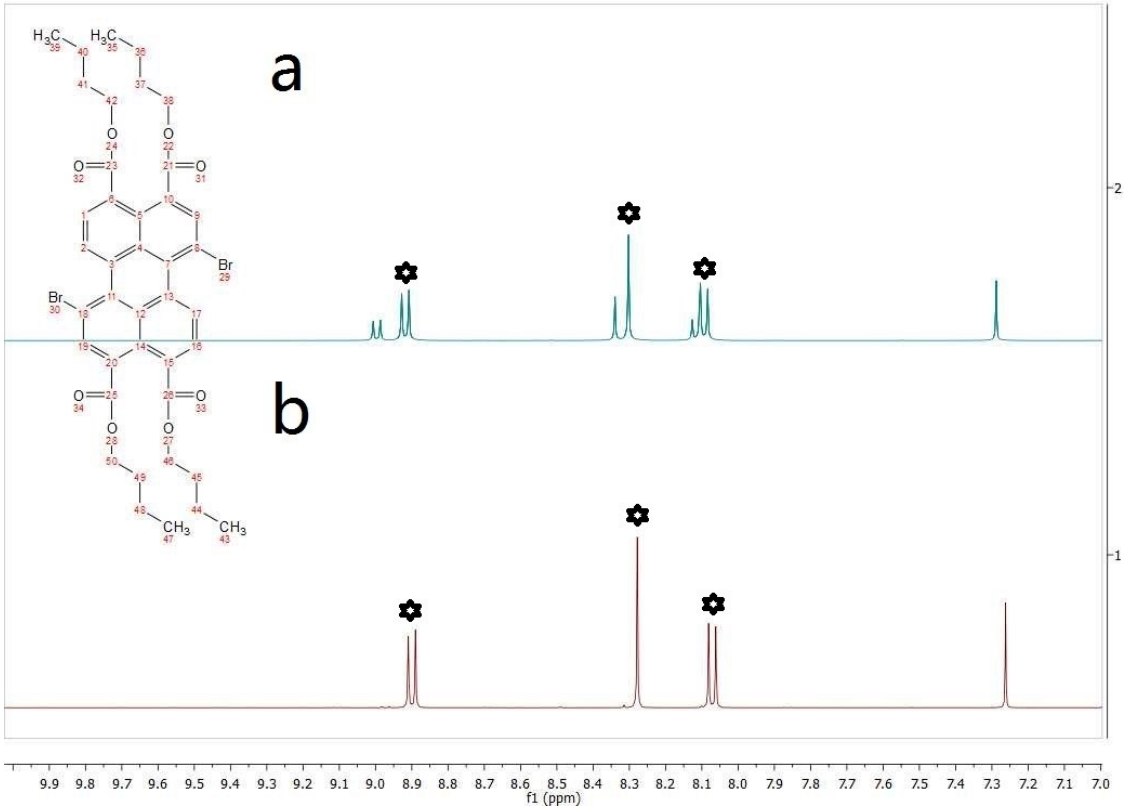


Figure S1. ^{1}H NMR spectrum: (a) 4:1 *regioisomeric* mixture of 1,7- and 1,6- **PTE 1** obtained after the reaction and (b) **PTE 1** after purification by recrystallization. The signals corresponding to the 1,7-regioisomer are marked with asterisks.

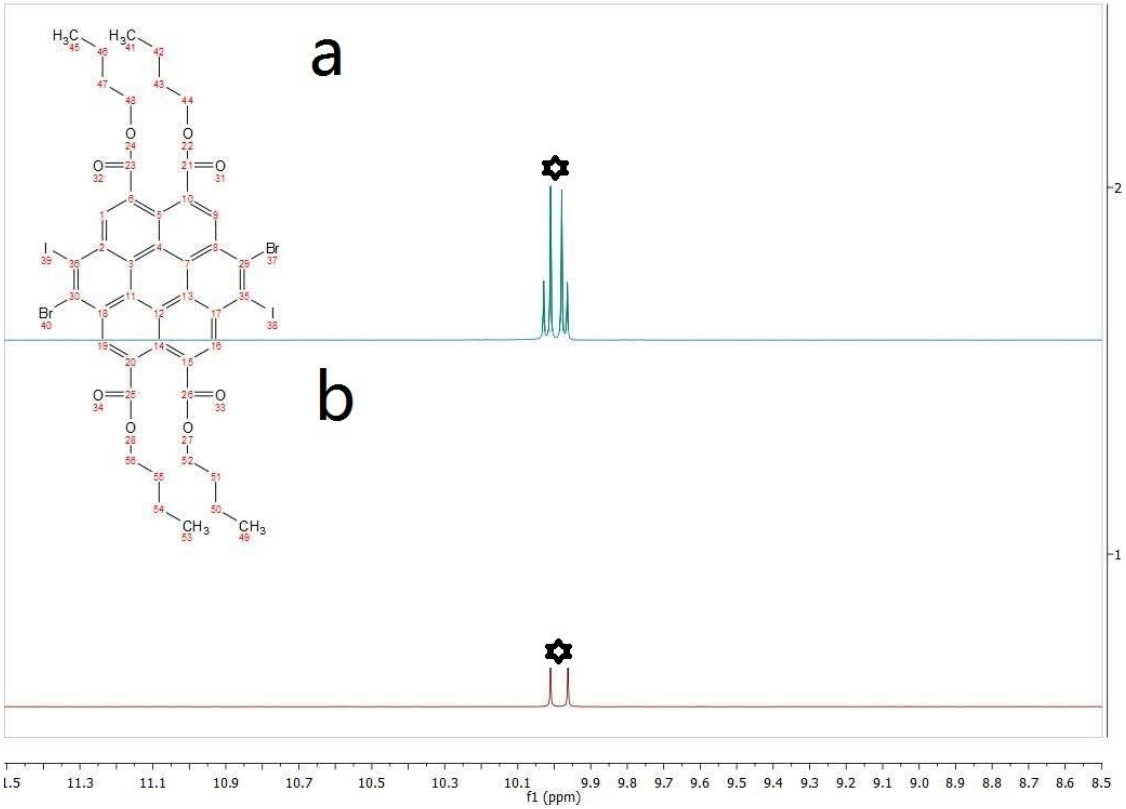


Figure S2. ^{1}H NMR spectrum: (a) 4:1 *regioisomeric* mixture of **CTE 4** obtained after the reaction and (b) *regioisomeric* pure **CTE 4** obtained after the reaction. The signals corresponding to the 1,7-regioisomer are marked with asterisks.

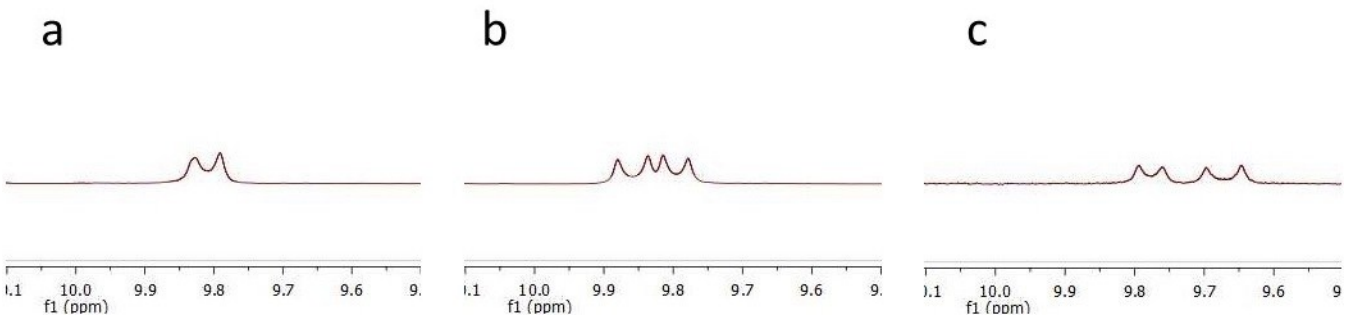


Figure S3. Low-field section of ^{1}H NMR spectrum of: (a) **CBI 5b**, (b) **CBI 5c**, (c) **CBI 5d**.

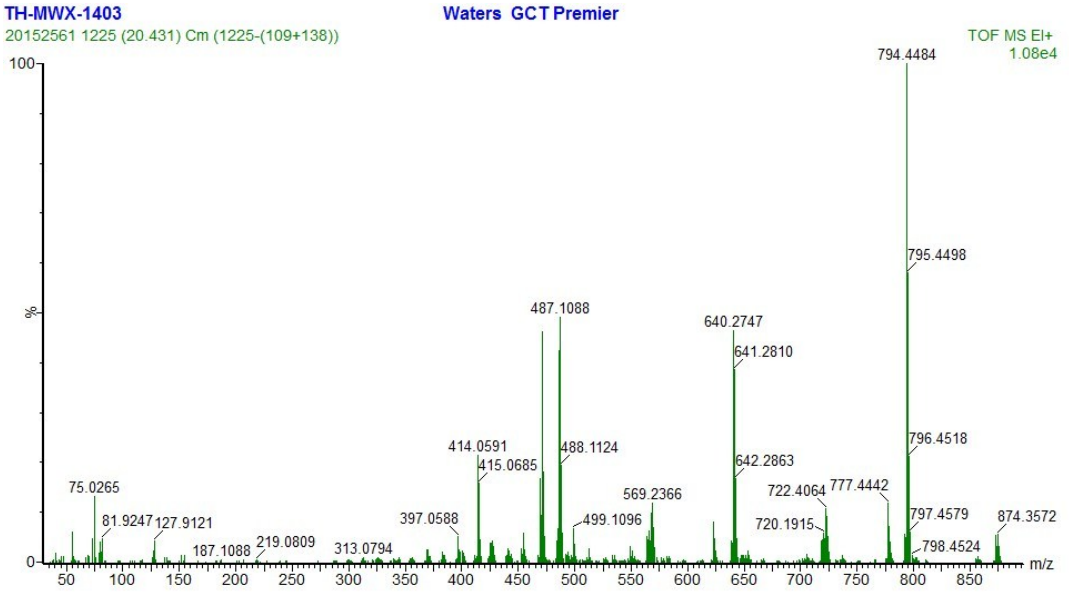


Figure S4. EI-TOF mass spectrum (HR) of **PBI 3**.

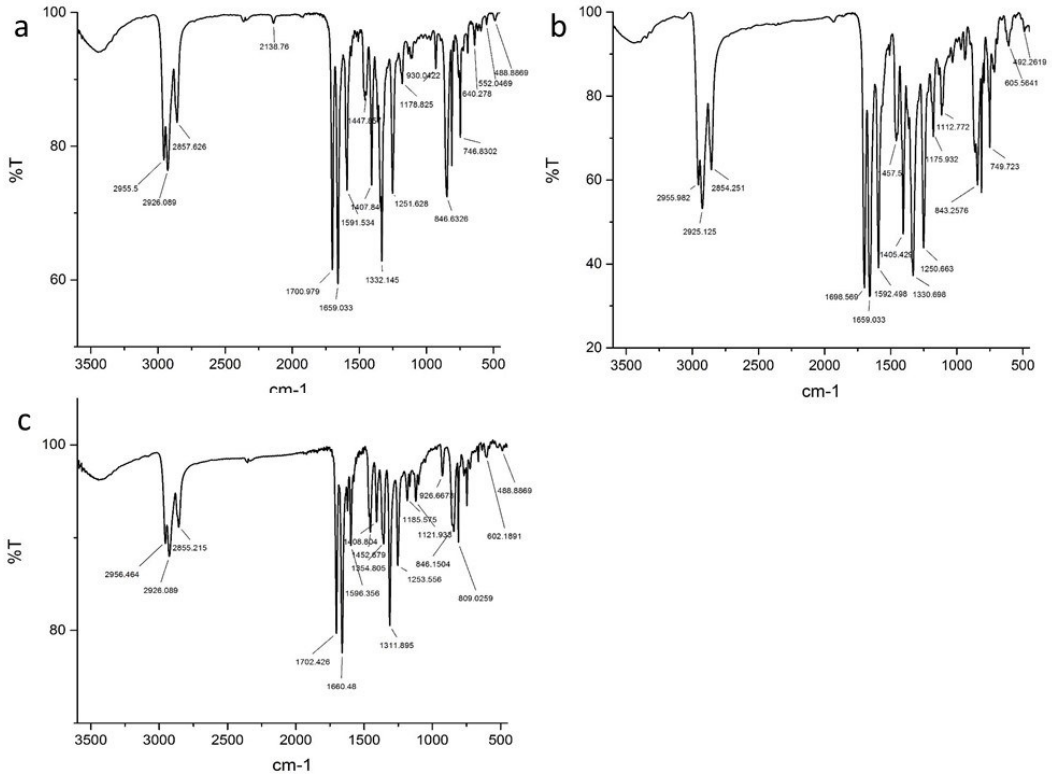


Figure S5. FTIR spectrum: (a) **PBI 2**, (b) **PBI 3**, (c) **BBI 3**.

III. Absorption, emission, and electrochemical characterizations and DFT calculations

Toluene was distilled over molecular sieve prior to use. Absorption and fluorescence spectra were recorded using Varian Cary 500 and Varian Cary Eclipse, respectively. The solid-state absorption and fluorescence spectra were recorded using EvoLution 220 (Thermo Fisher) and Fluorescence Spectrometer LS 55 (Perkin Elmer), respectively. Fluorescence quantum yields were measured by using a commercial spectrometer equipped with an integrating sphere of 3.3 in. in radius (Hamamatsu, C9920-02). The cyclic voltammetry experiments were performed by a Versastat II electrochemical workstation (Princeton applied research) using a conventional three electrode configuration with a glassy carbon working electrode, a Pt wire counter electrode, and a regular calomel reference electrode in saturated KCl solution, 0.1 M Bu_4NPF_6 in dichloromethane solution as the supporting electrolyte with a scan rate of 100 $mV{\cdot}s^{-1}$.

Table S1. Photophysical and electrochemical data of CTEs/CBIs in Toluene and CH_2Cl_2, respectively.

Compound	λ_{abs}/ nm	λ_{em} / nm[a]	Φ_{fl}/ %[b]	V_{red} / V[c]	LUMO / eV[d]	HOMO / eV[e]
CTE 4	437, 465	472	0.3	-1.36	-3.44	-6.05
CTE 5a	435, 463	476	39.2	-1.42	-3.38	-5.97
CTE 5b	434, 461	473	60.9	-1.40	-3.40	-6.09
CTE 5c	437, 465	479	41.7	-1.36	-3.44	-6.11
CTE 5d	432, 459	470	64.1	-1.37	-3.43	-6.13
CBI 5a	431, 517	533	33.3	-1.35	-3.45	-5.76
CBI 5b	430, 513	527	55.4	-1.35	-3.45	-5.87
CBI 5c	432, 521	540	37.6	-1.32	-3.48	-5.86
CBI 5d	427, 507	518	58.5	-1.35	-3.45	-5.83

[a] The excitation wavelengths were 435 nm for these compounds. [b] Fluorescence quantum yields of **CBI 5a-5d** determined at a concentration of c = 1.0×10^{-5}. [c] The first reduction potentials in cyclic voltammogram traces referenced to Fc/Fc^+. [d] Estimated vs vacuum level from LUMO = -4.80 eV - E_{red}. [e] Estimated from HOMO = LUMO - E_g, where E_g = optical gap, calculated from the optical absorption data.

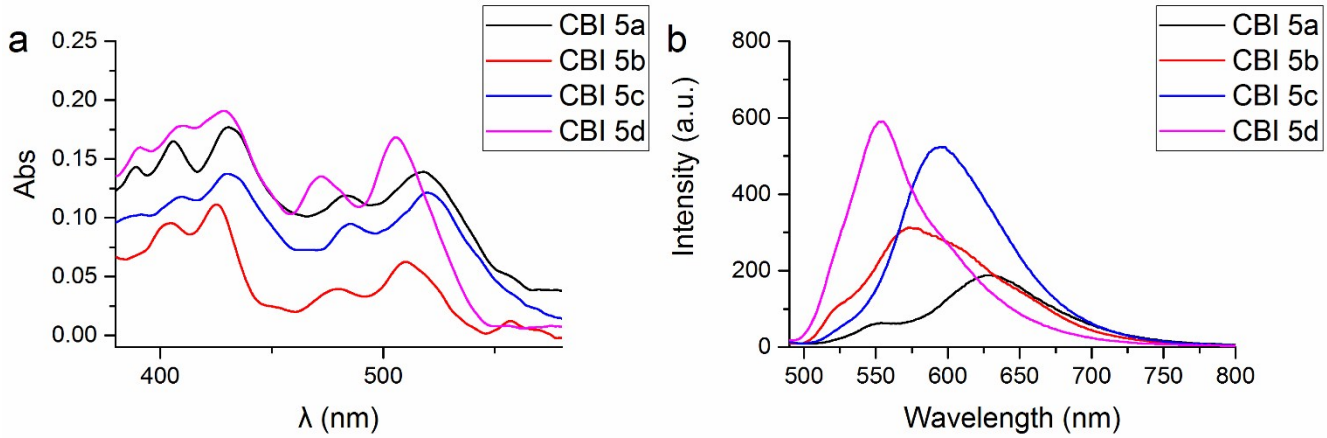


Figure S6. The solid-state absorption spectra (a) and the solid-state fluorescence emission spectra (b) of CBIs, 25 °C.

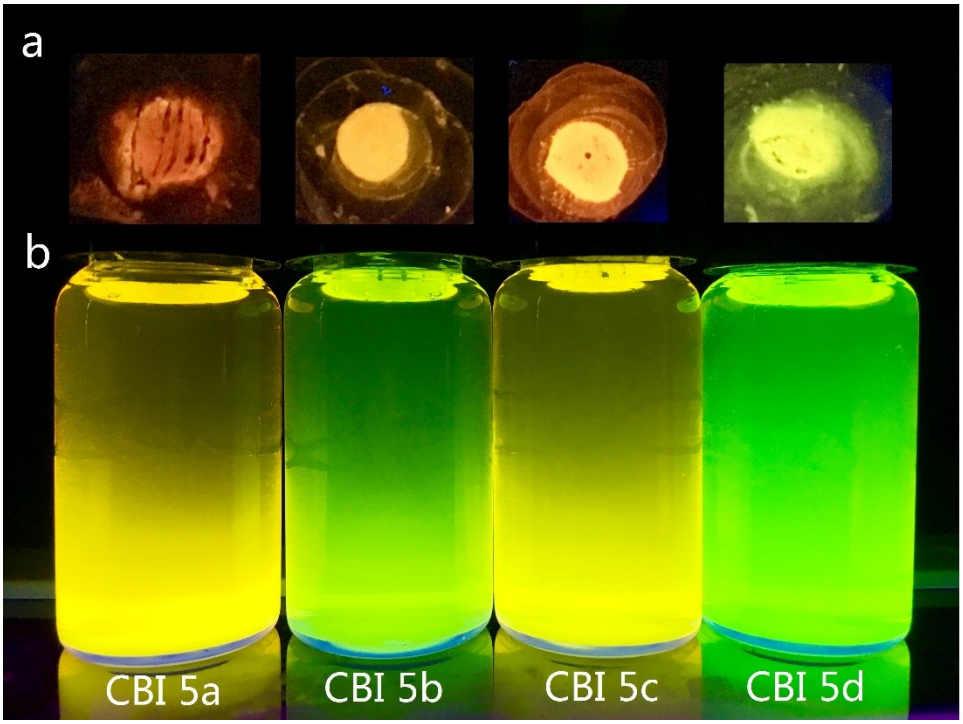


Figure S7. Photograph of visual and fluorescent color of CBIs in solid-state (a) contrast to color in toluene (b), 25 ^{o}C. Excitation was effected at 365 nm.

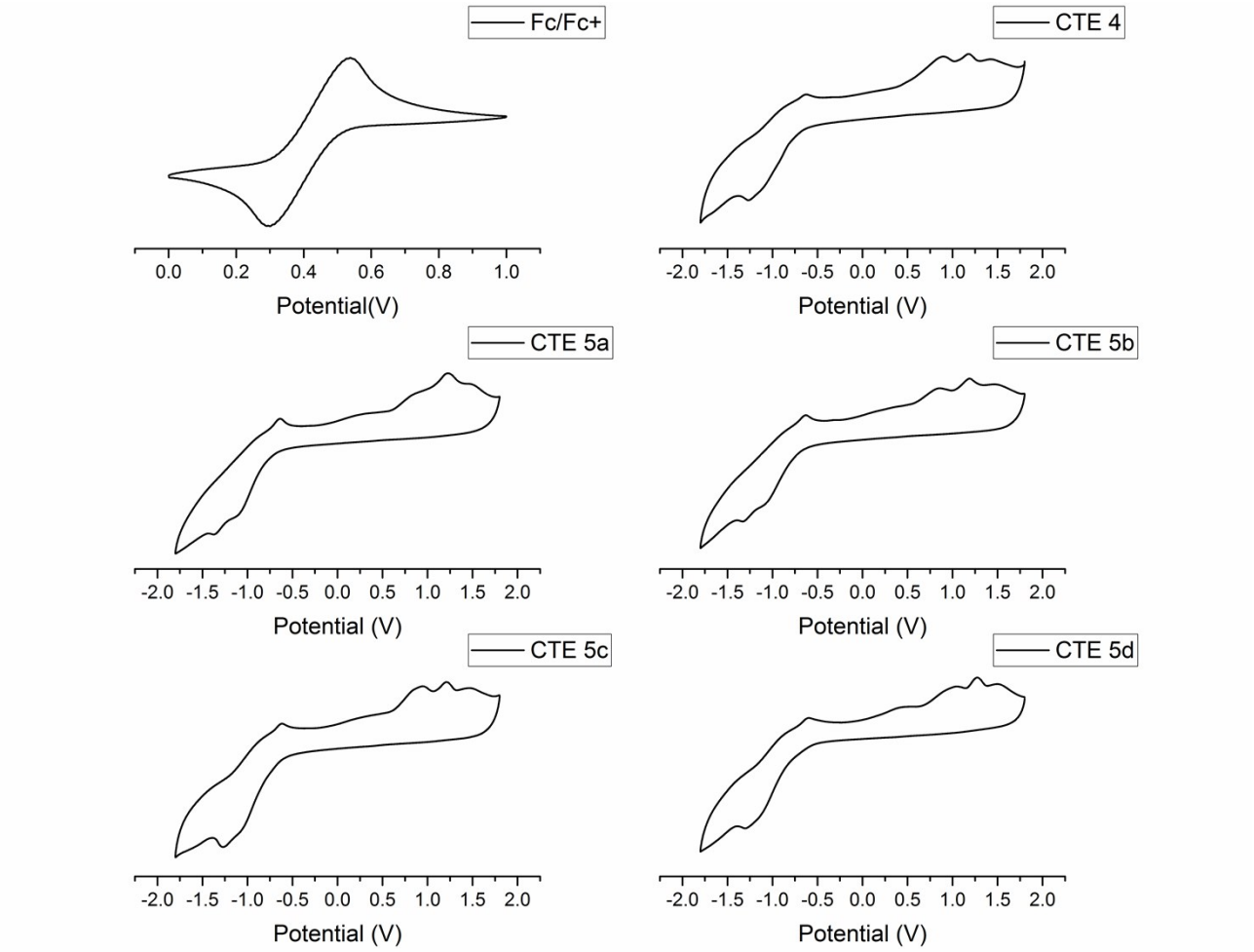


Figure S8. Cyclic voltammograms of ferrocene and **CTE 4** and **5a-5d** in CH_2Cl_2.

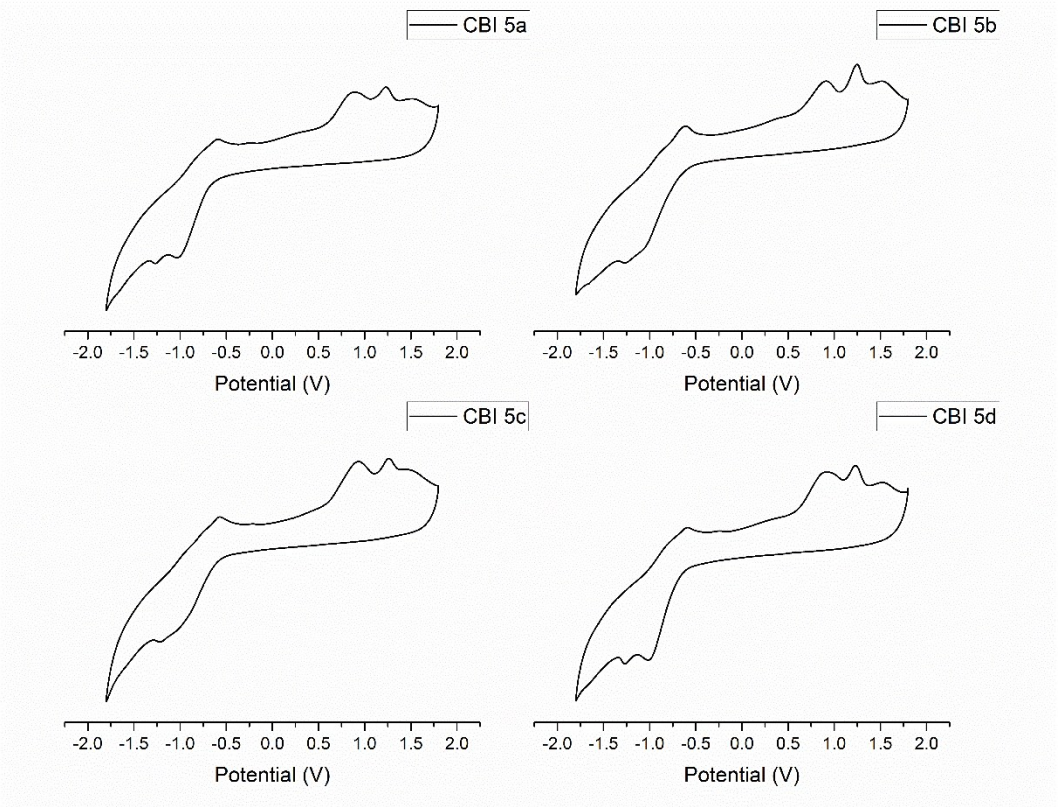


Figure S9. Cyclic voltammograms of **CBI 5a-5d** in CH_2Cl_2.

Computational details

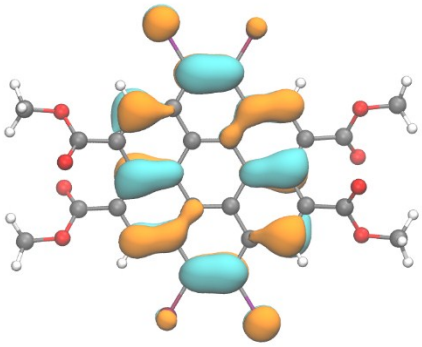
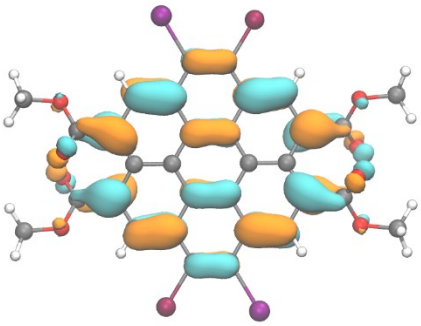
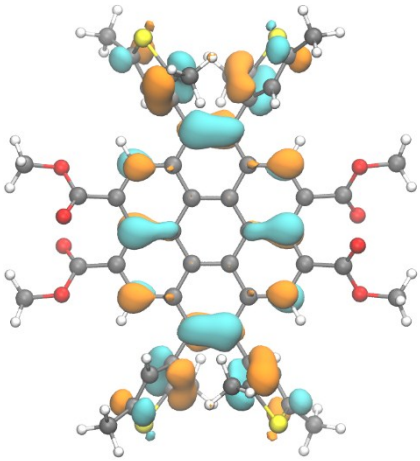
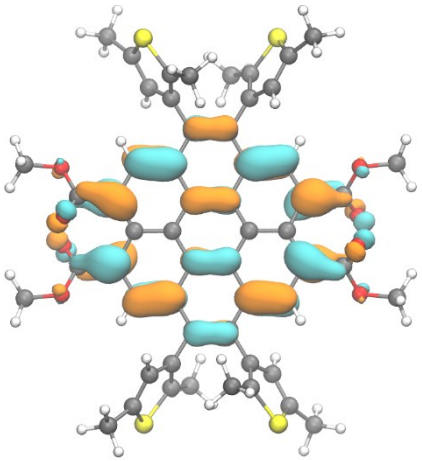
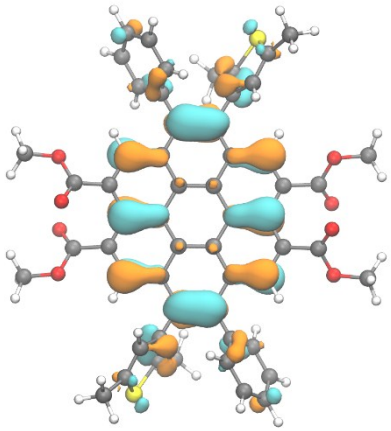
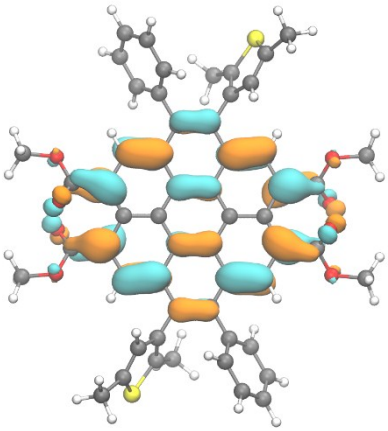
We employed density functional theory (DFT) calculations to optimize the ground state geometries of the molecules, using the hybrid B3LYP functional [S3] and the 6-31G(d) basis set [S4]. For bromine and iodine atoms, the Los Alamos effective core potential basis set (LANL2DZ) was used [S5]. Dispersions were included by the DFT-D3 correction [S6]. To save computational costs, the long alkyl chains were replaced by methyl groups without affecting the validity of the results. All calculations were carried out using the Gaussian09 program package [S7].

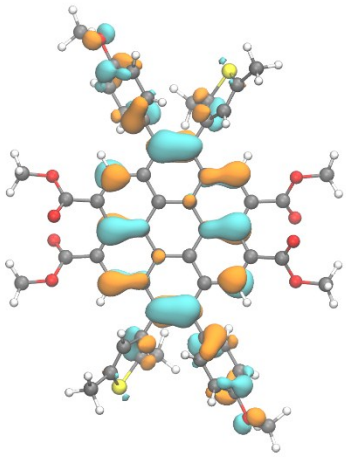
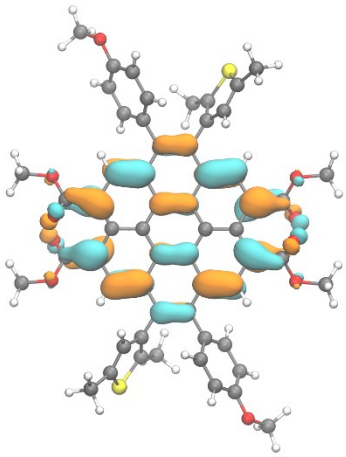
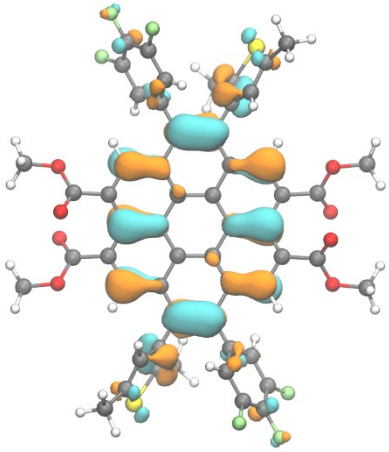
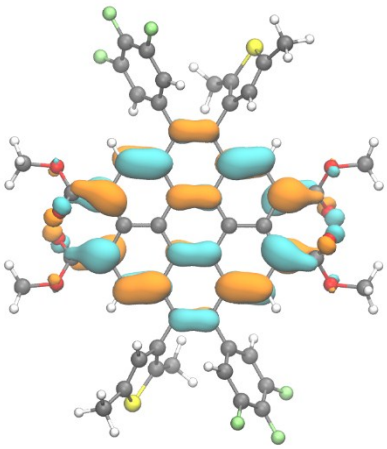
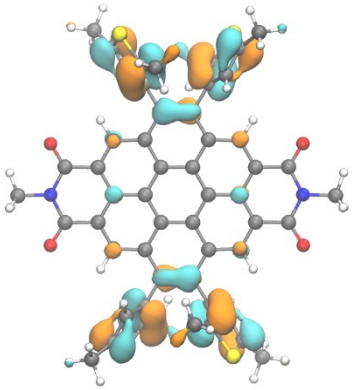
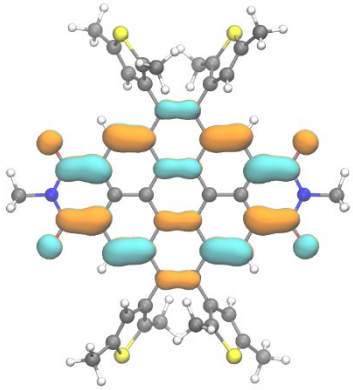
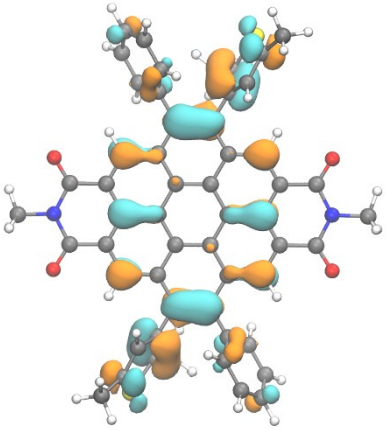
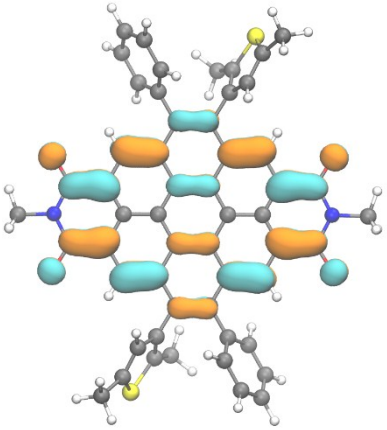
Results

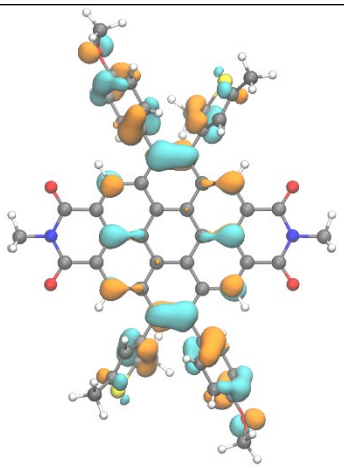
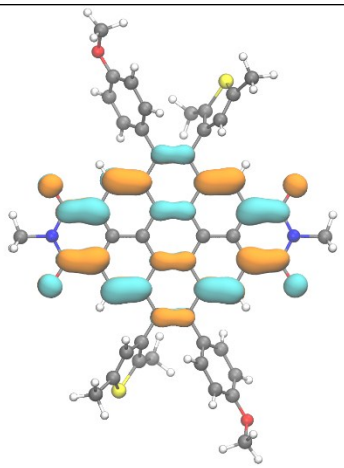
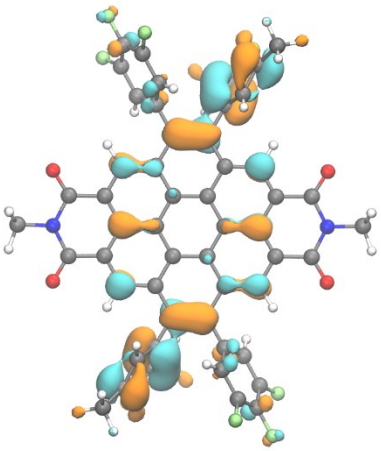
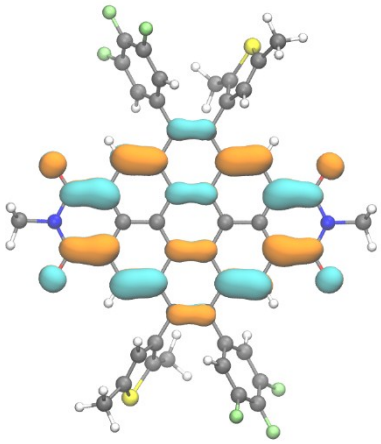
Table S2. Energy levels (in eV) of frontier molecular orbitals.

Compound	E(HOMO)	E(LUMO)	Gap
CTE 4	-6.24	-2.65	3.59
CTE 5a	-5.47	-2.11	3.36
CTE 5b	-5.51	-2.10	3.41
CTE 5c	-5.34	-2.04	3.30
CTE 5d	-5.83	-2.36	3.49
CBI 5a	-5.67	-2.90	2.77
CBI 5b	-5.79	-2.89	2.90
CBI 5c	-5.57	-2.82	2.75
CBI 5d	-6.10	-3.15	2.95

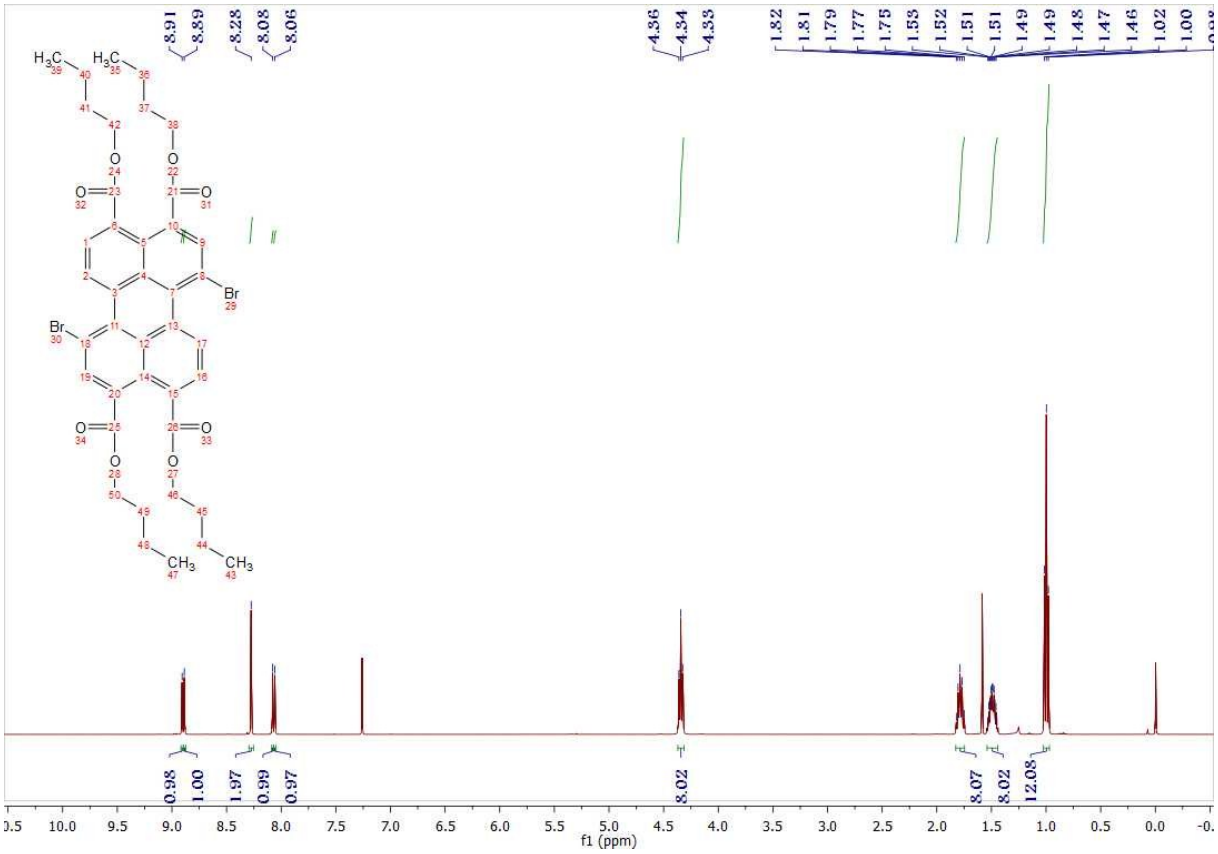
Table S3. Contour plots of frontier molecular orbitals of compounds.

	HOMO	LUMO
CTE 4		
CTE 5a		
CTE 5b		

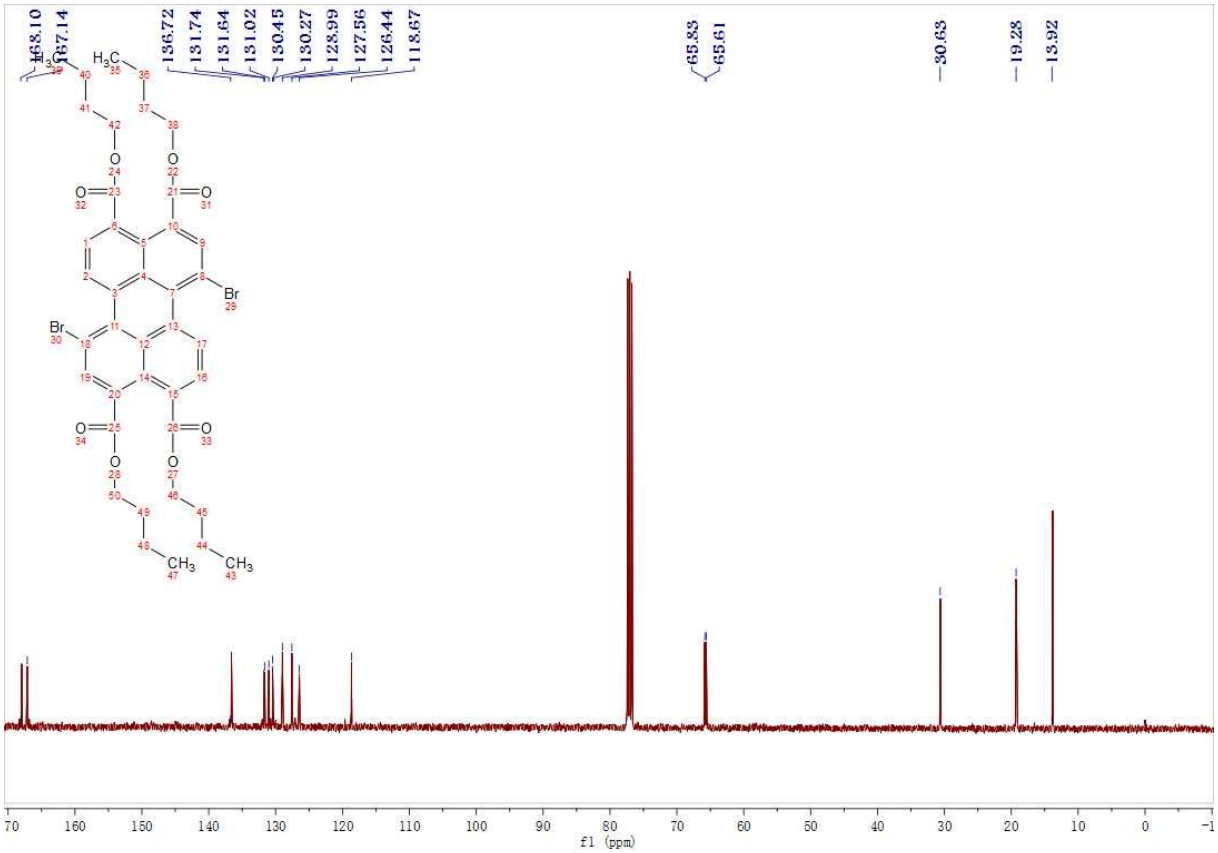
CTE 5c		
CTE 5d		
CBI 5a		
CBI 5b		

CBI 5c		
CBI 5d		

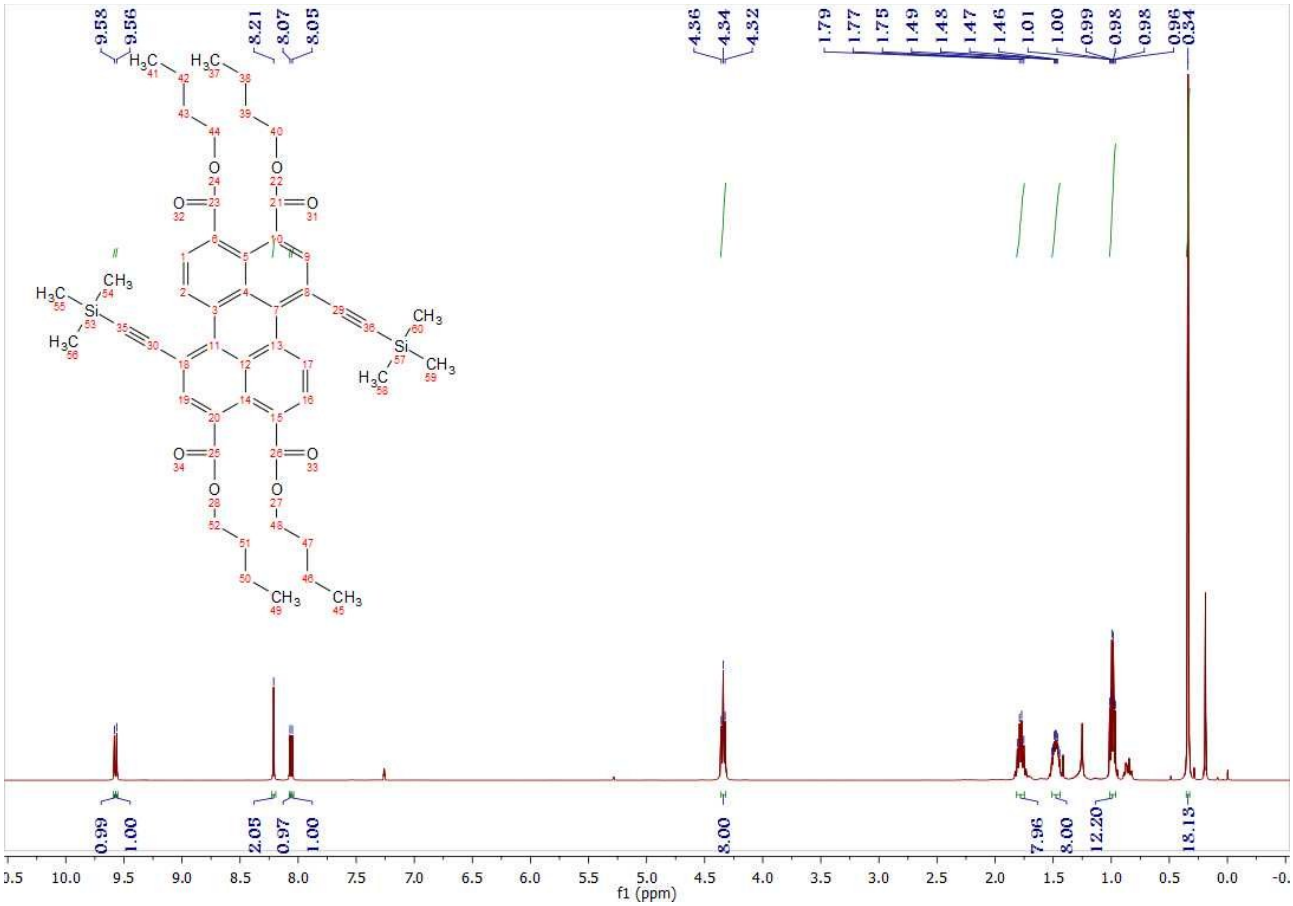
IV. NMR spectra



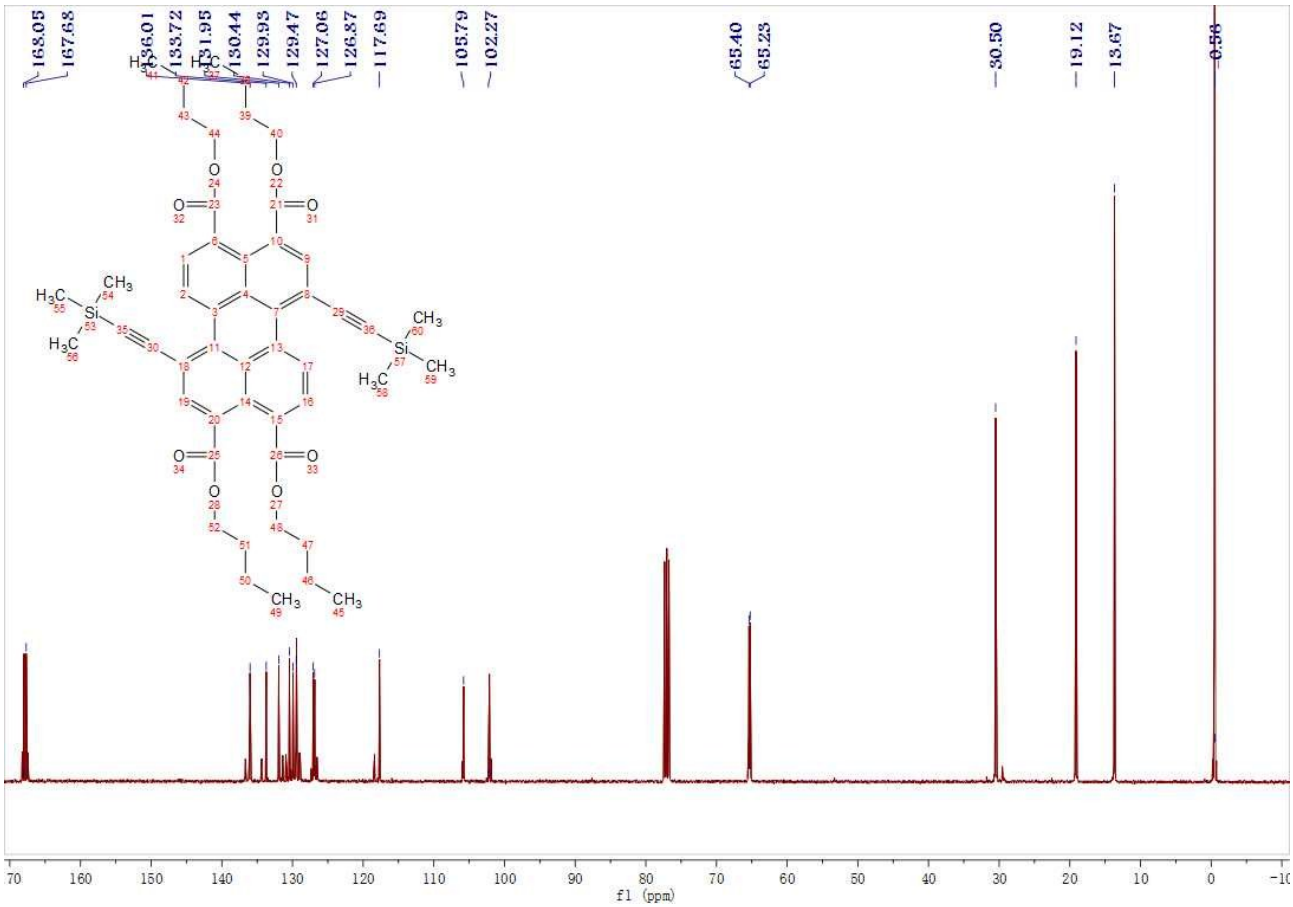
^{1}H NMR spectrum of **PTE 1**



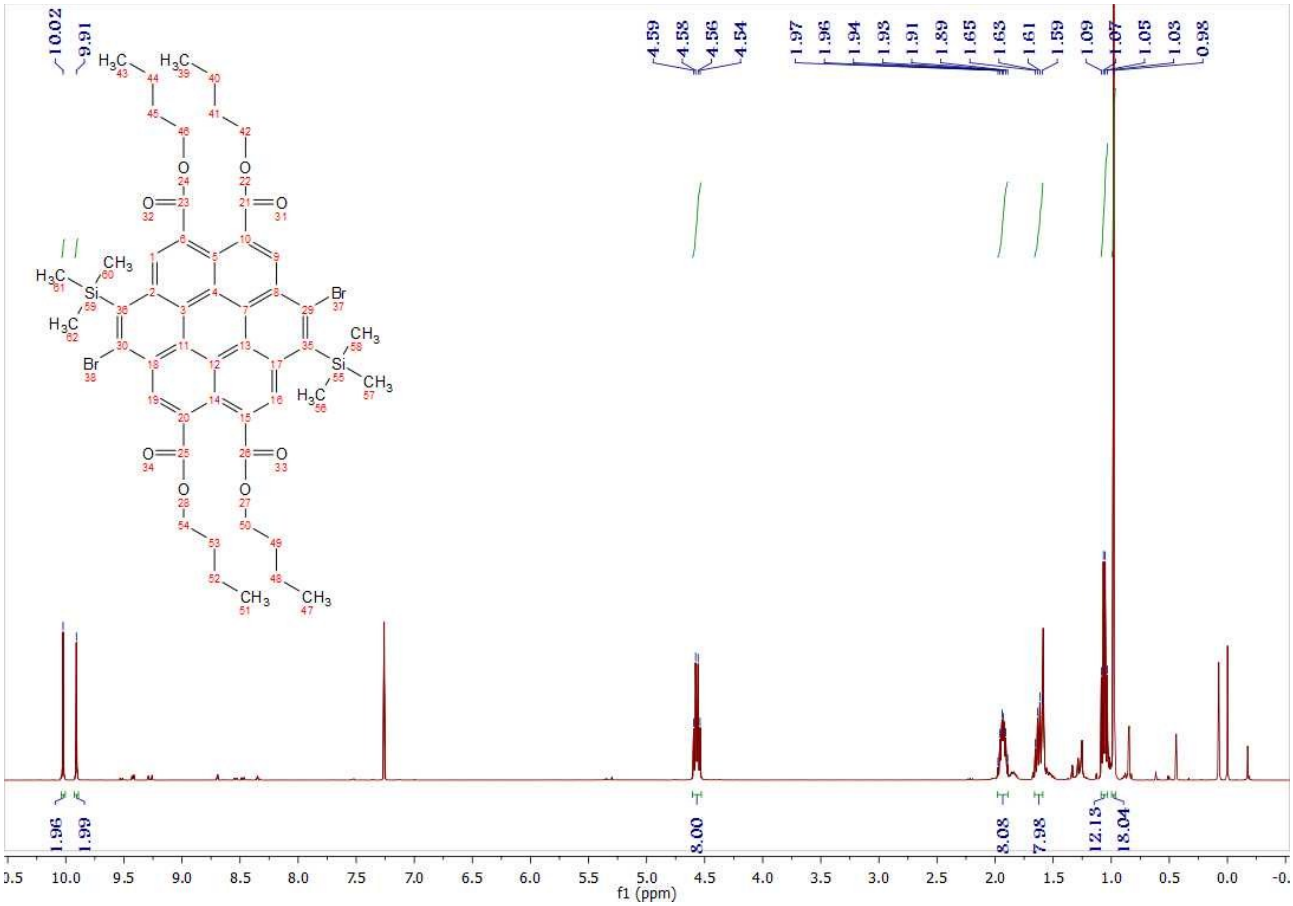
^{13}C NMR spectrum of **PTE 1**



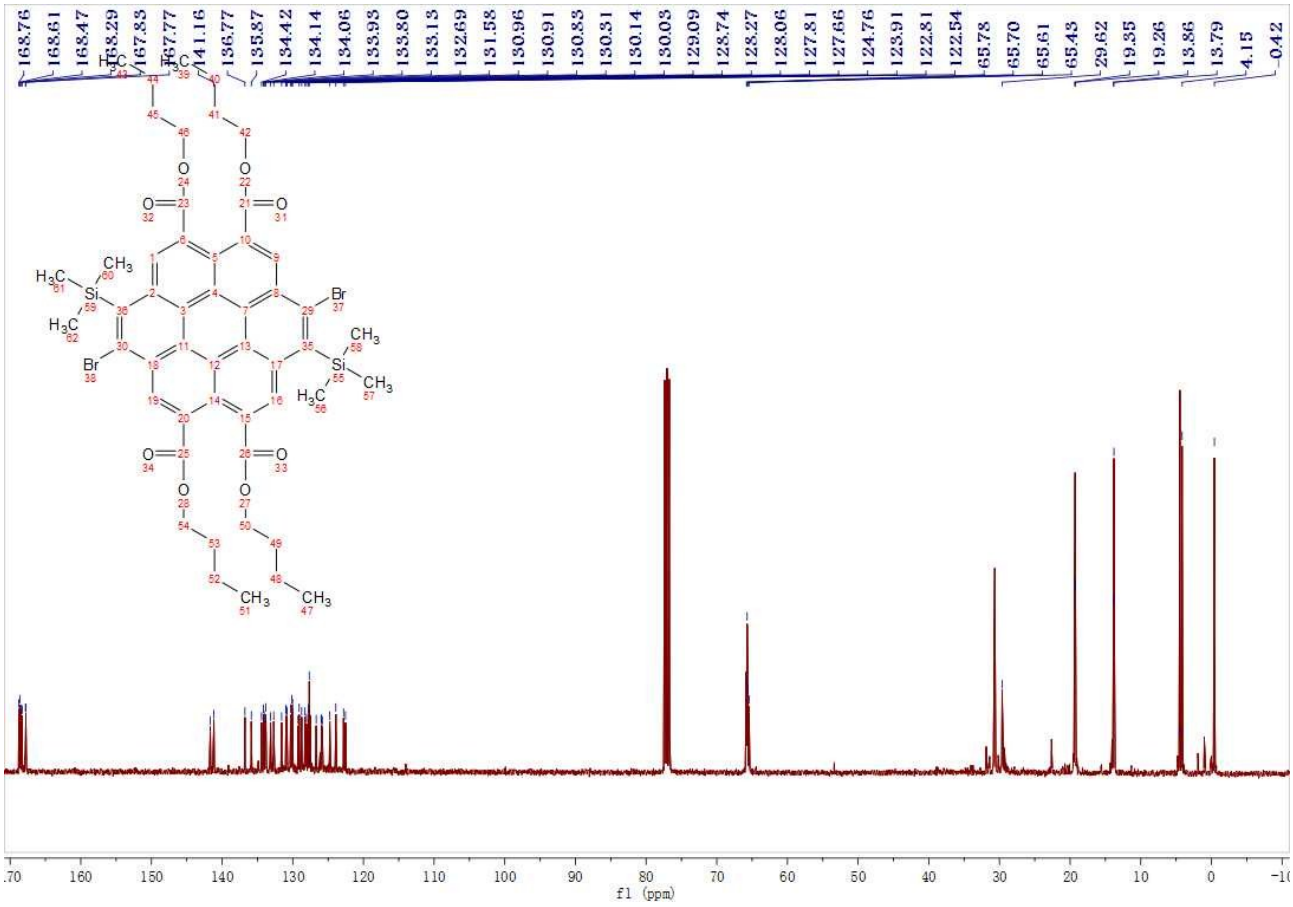
^{1}H NMR spectrum of **PTE 2**



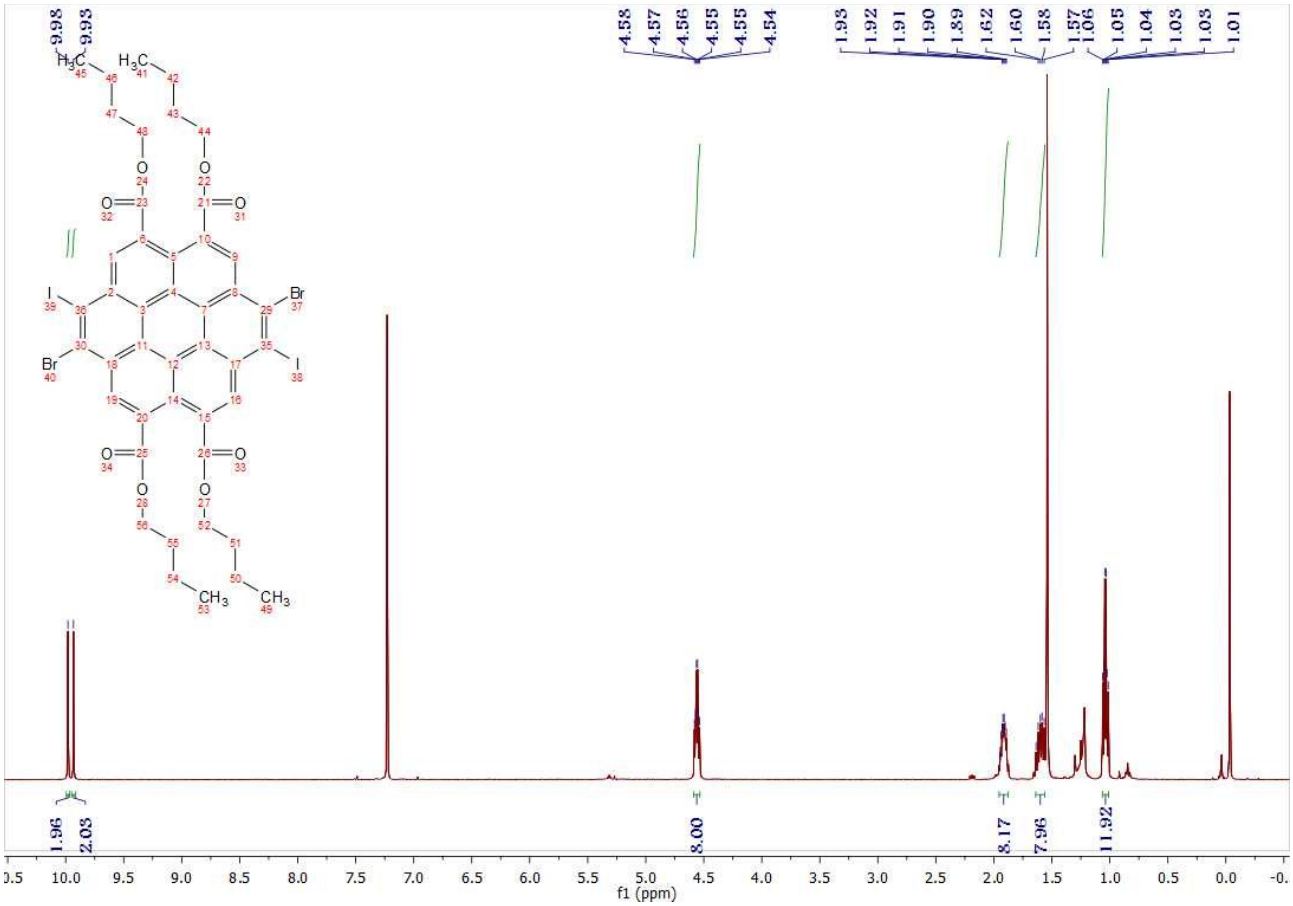
^{13}C NMR spectrum of **PTE 2**



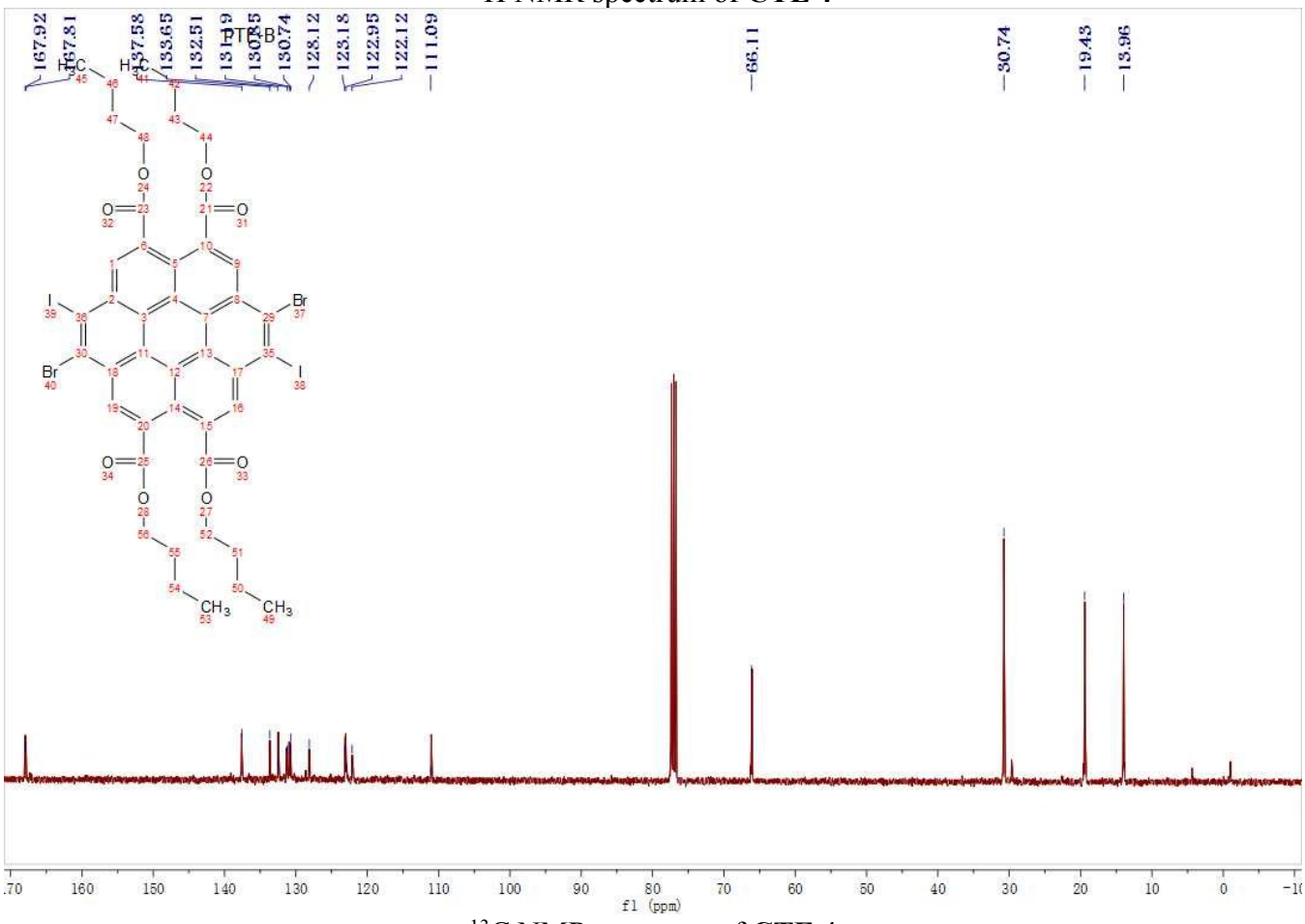
^{1}H NMR spectrum of **CTE 3**



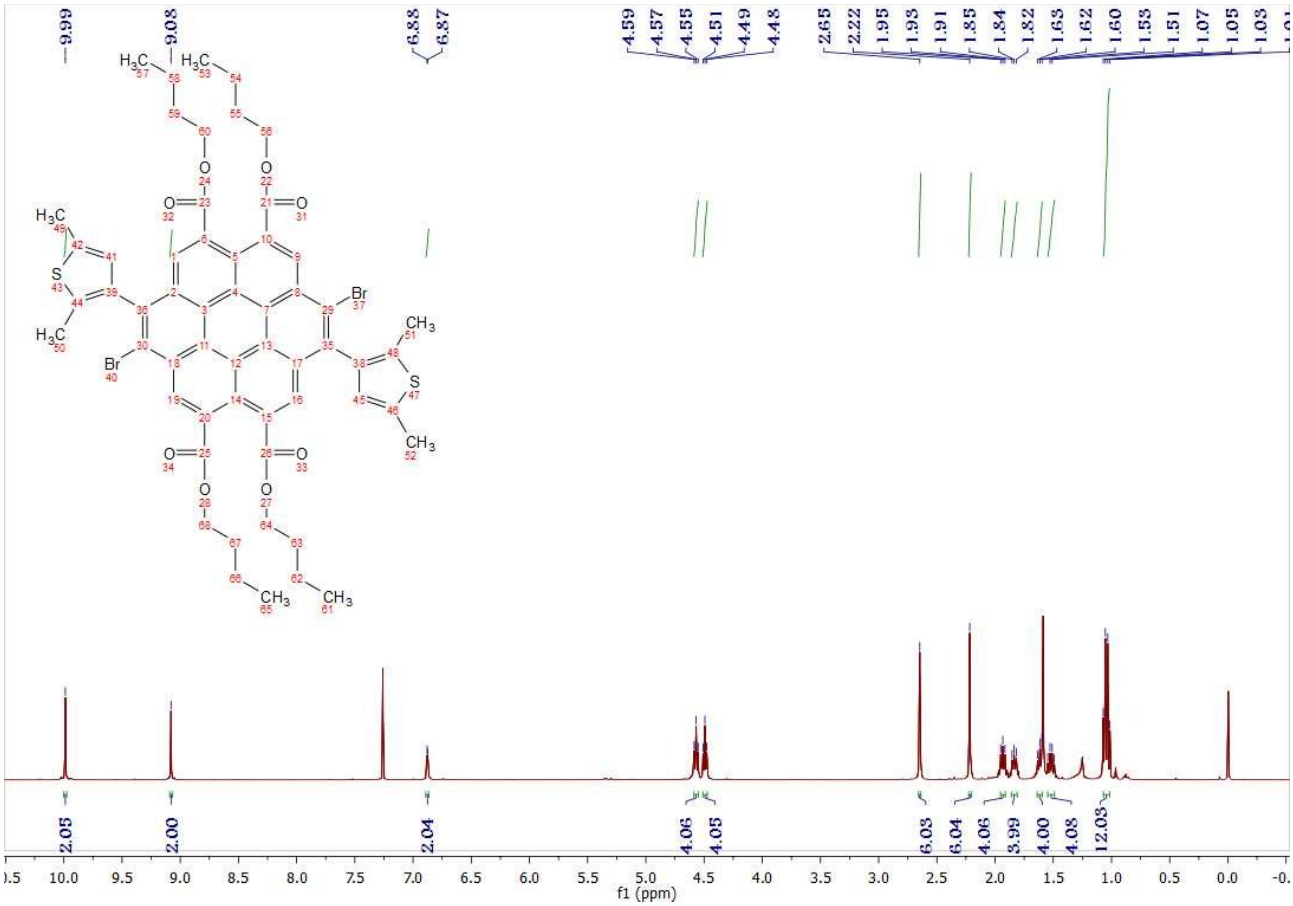
^{13}C NMR spectrum of **CTE 3**



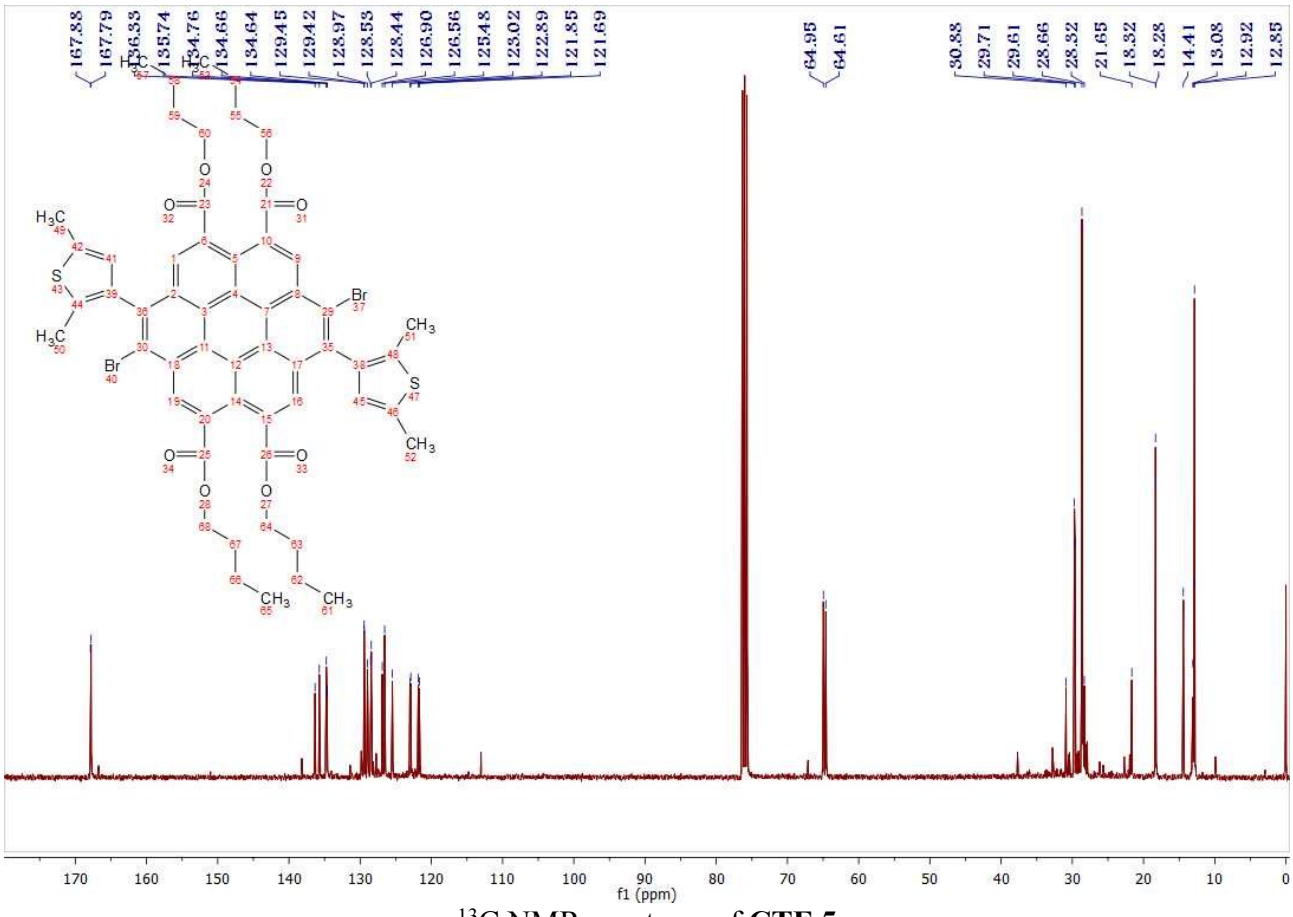
^{1}H NMR spectrum of **CTE 4**



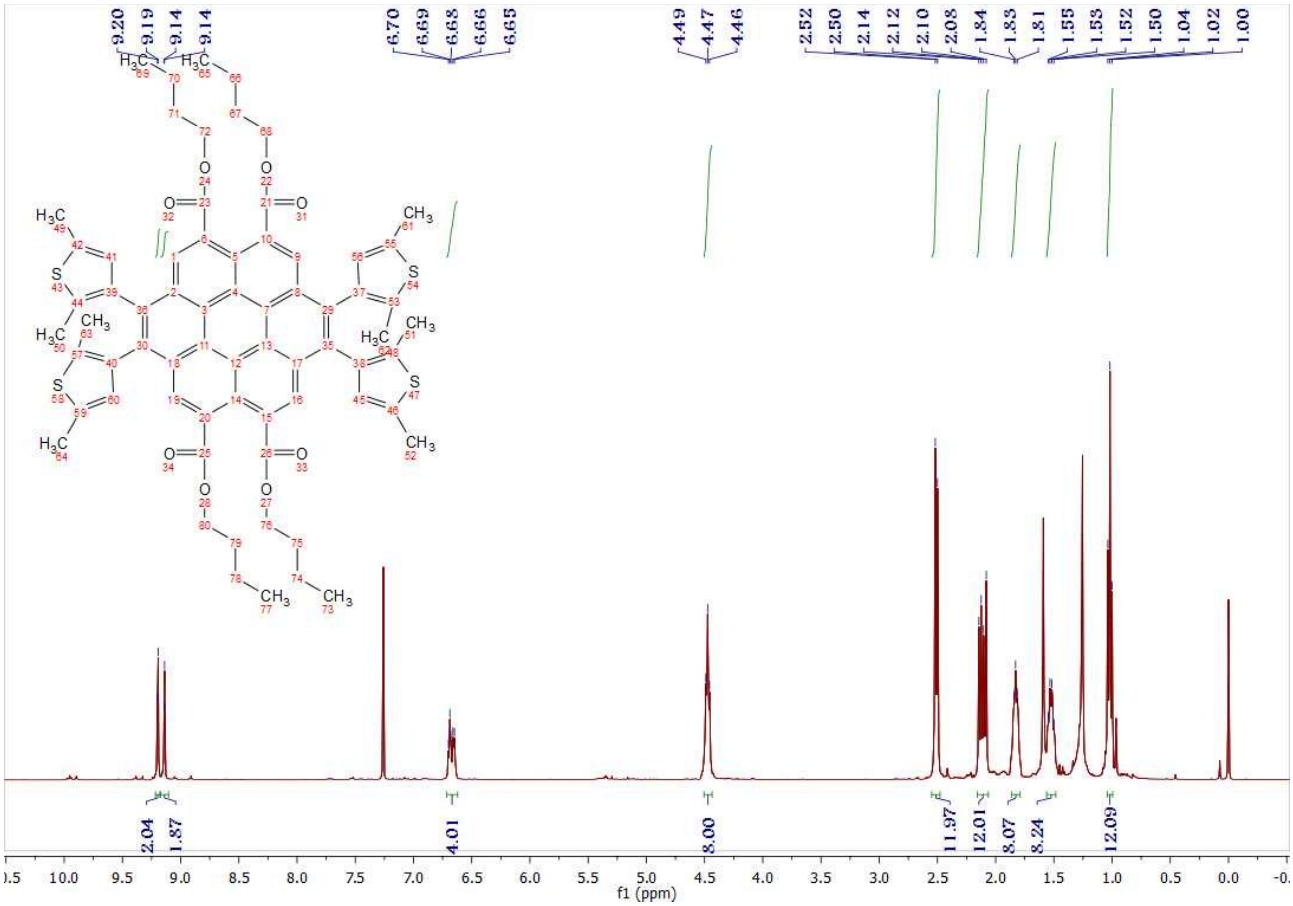
^{13}C NMR spectrum of **CTE 4**



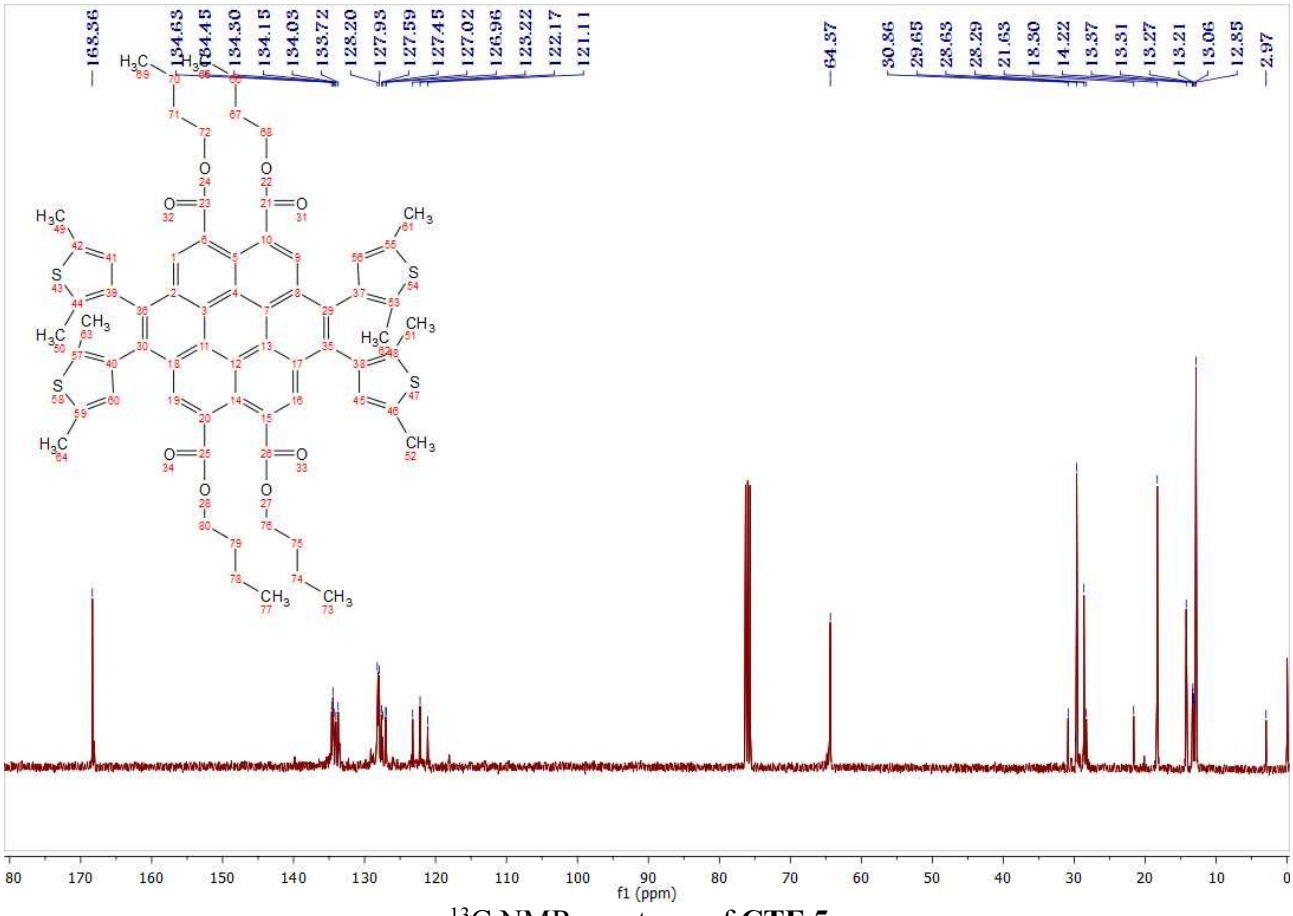
^{1}H NMR spectrum of **CTE 5**



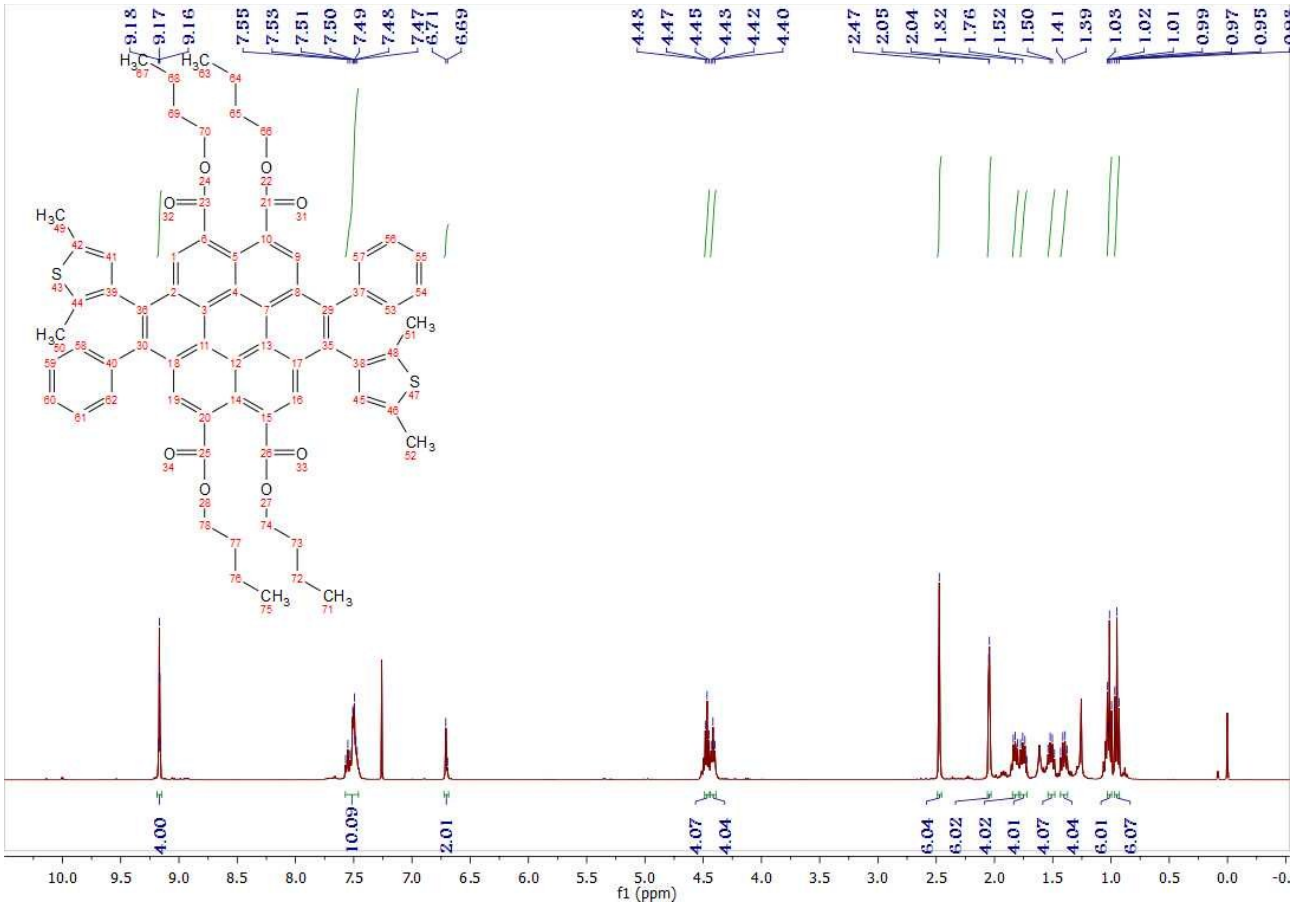
^{13}C NMR spectrum of **CTE 5**



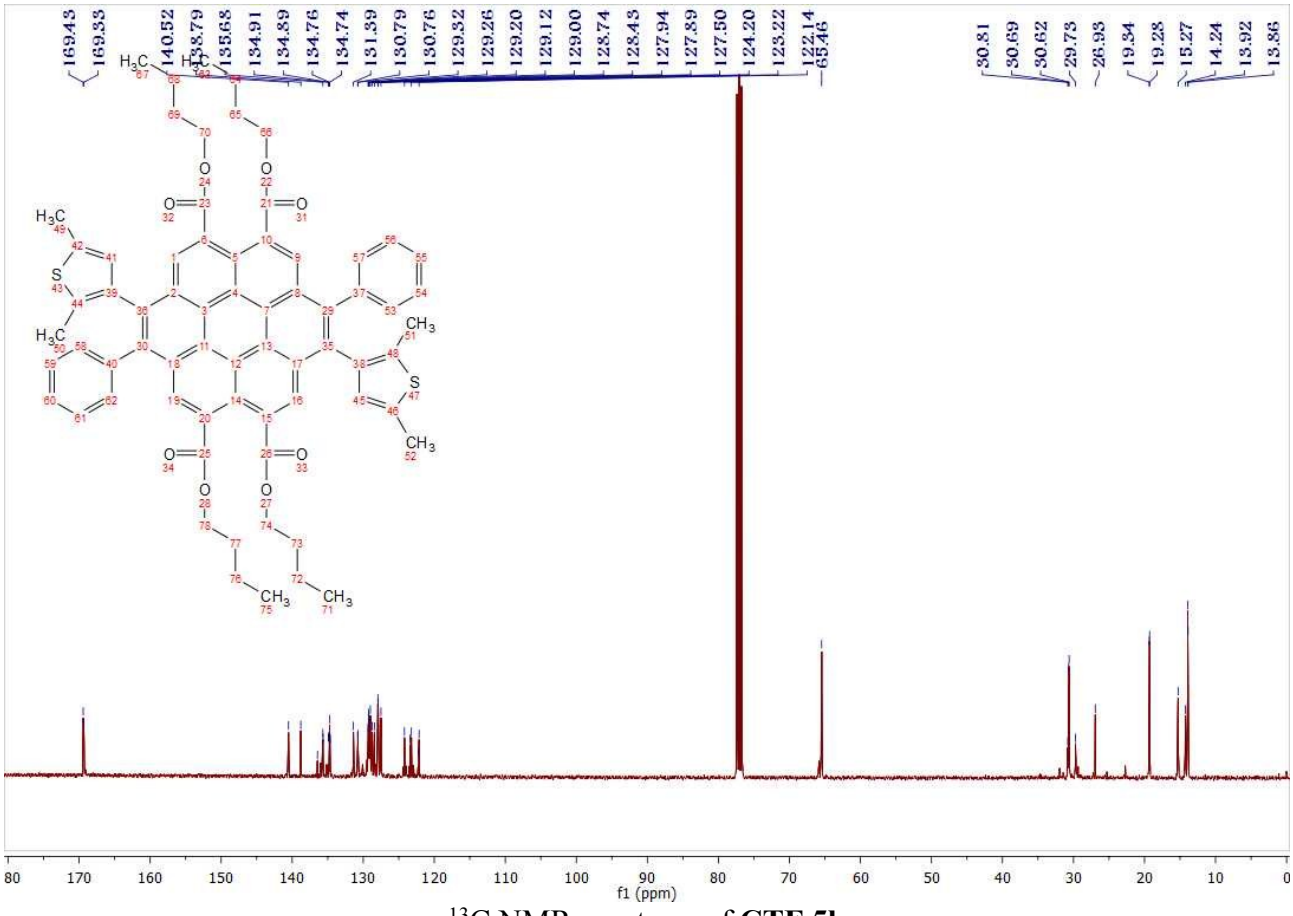
^{1}H NMR spectrum of **CTE 5a**



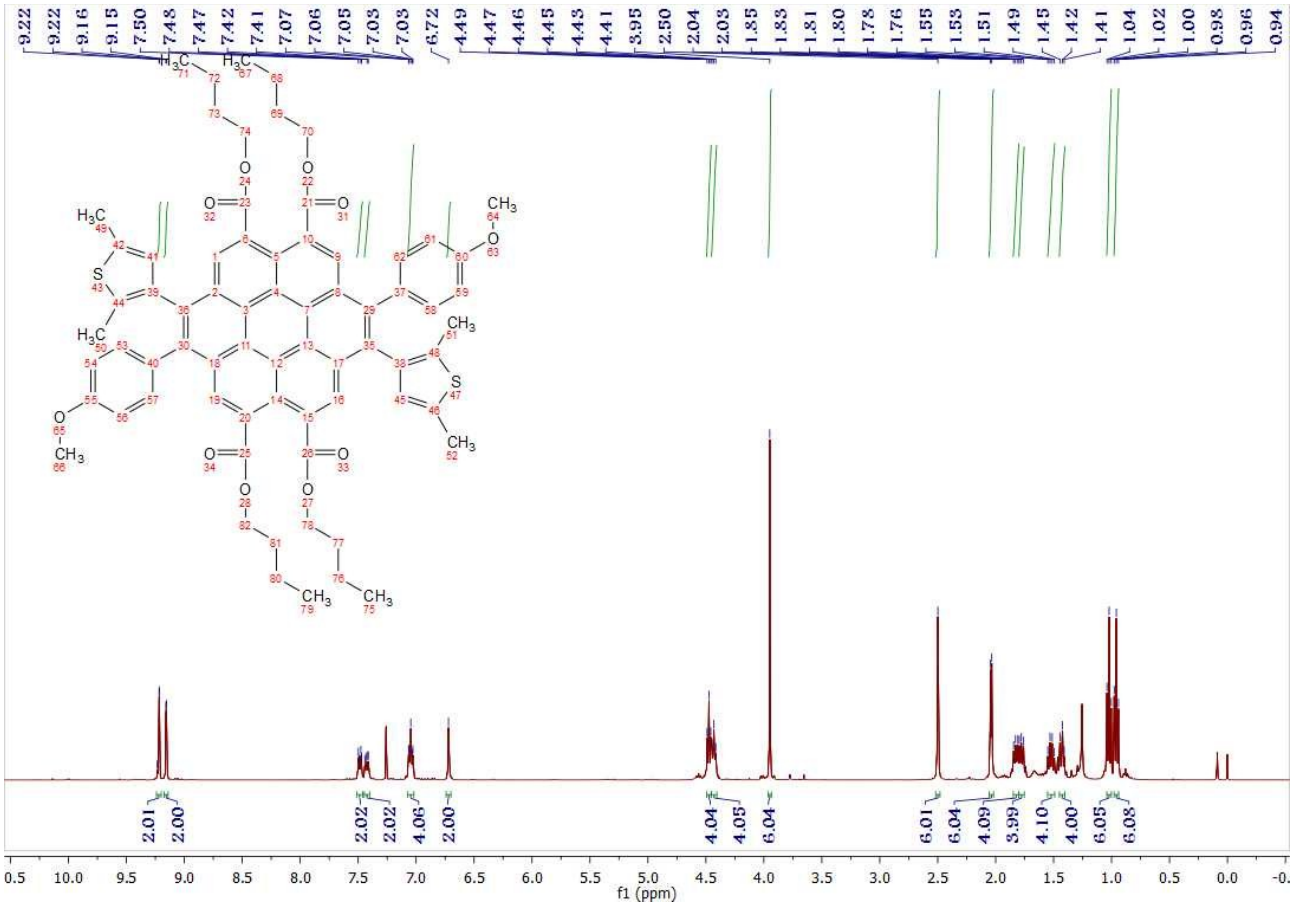
^{13}C NMR spectrum of **CTE 5a**



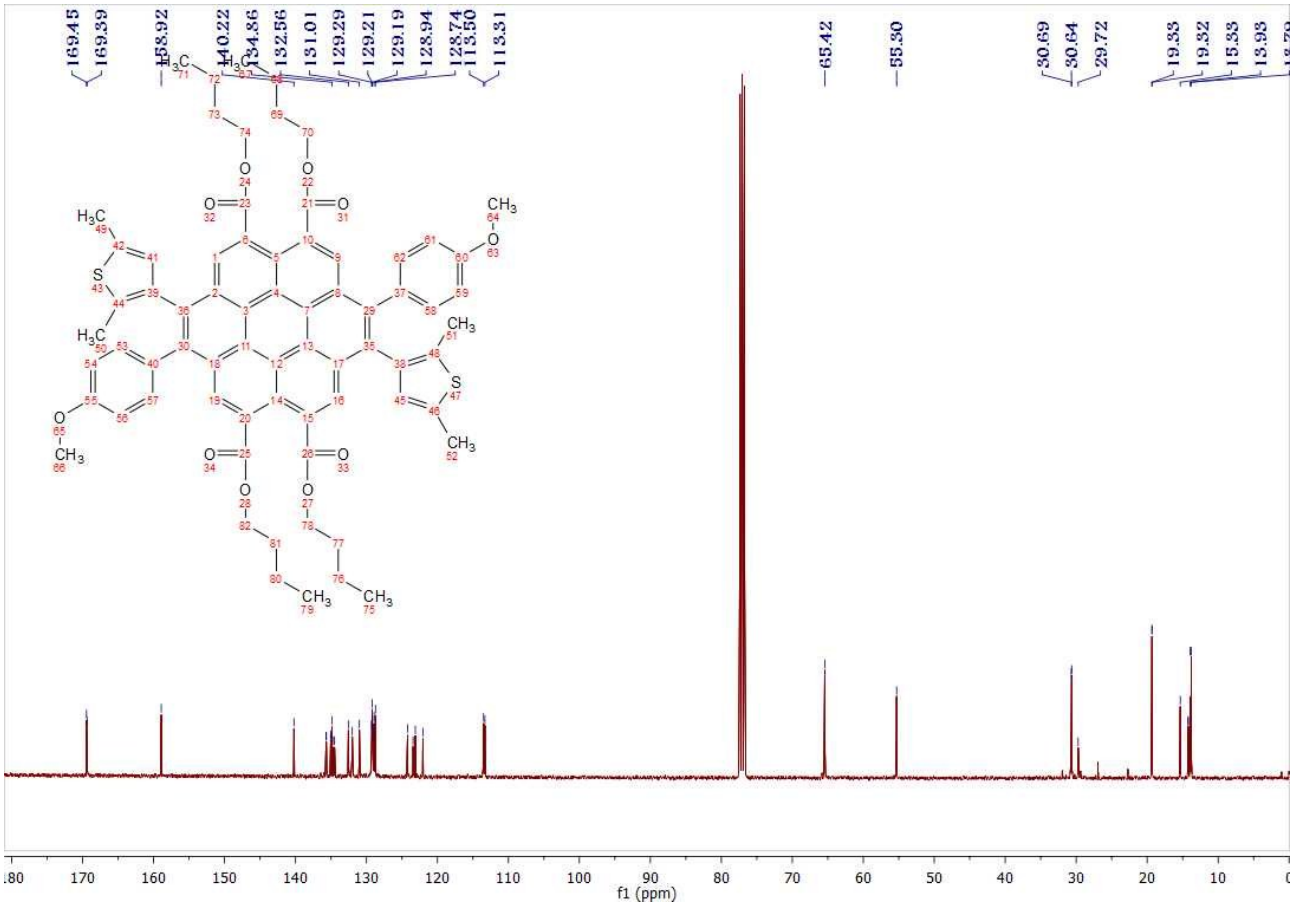
^{1}H NMR spectrum of **CTE 5b**



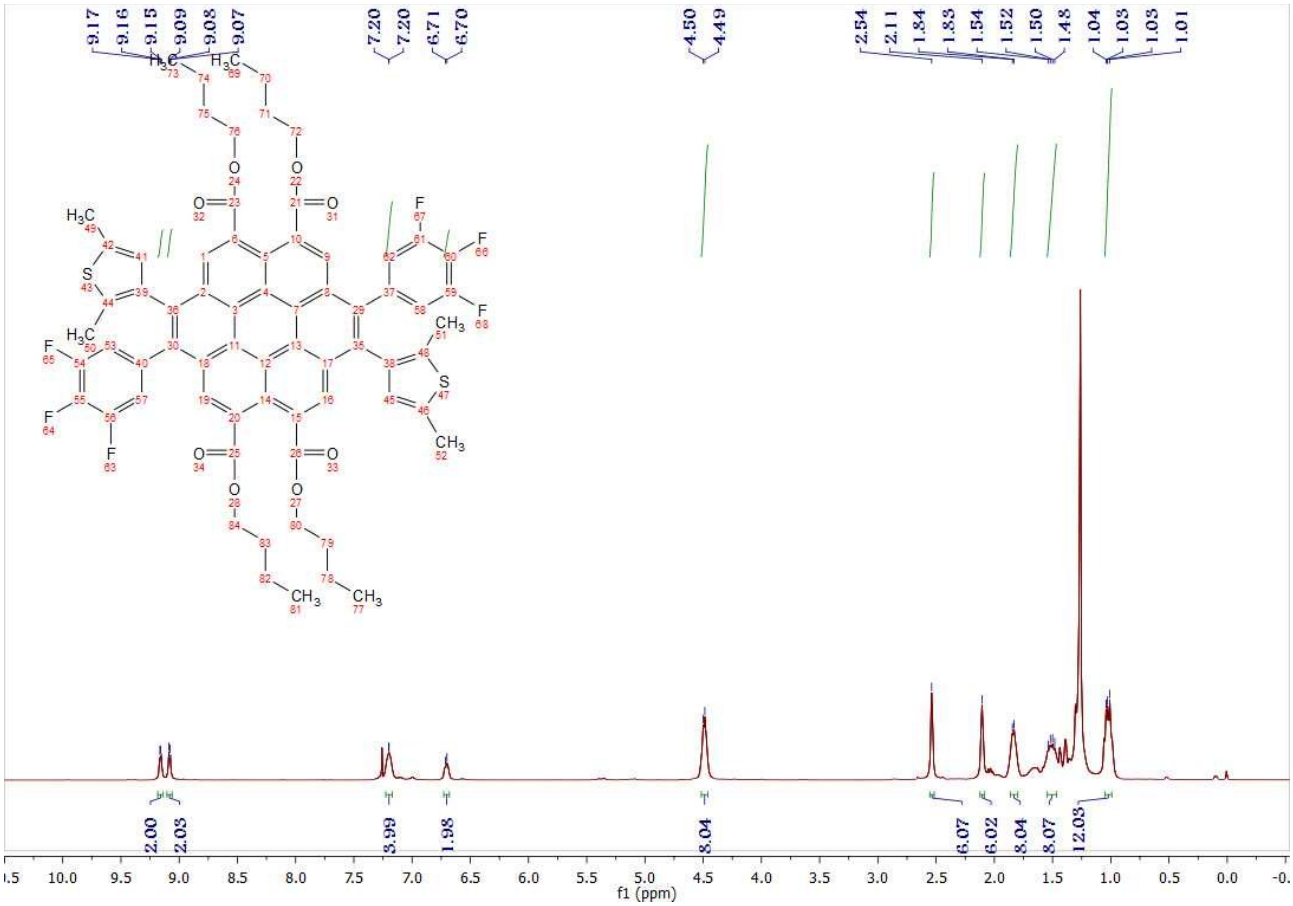
^{13}C NMR spectrum of **CTE 5b**



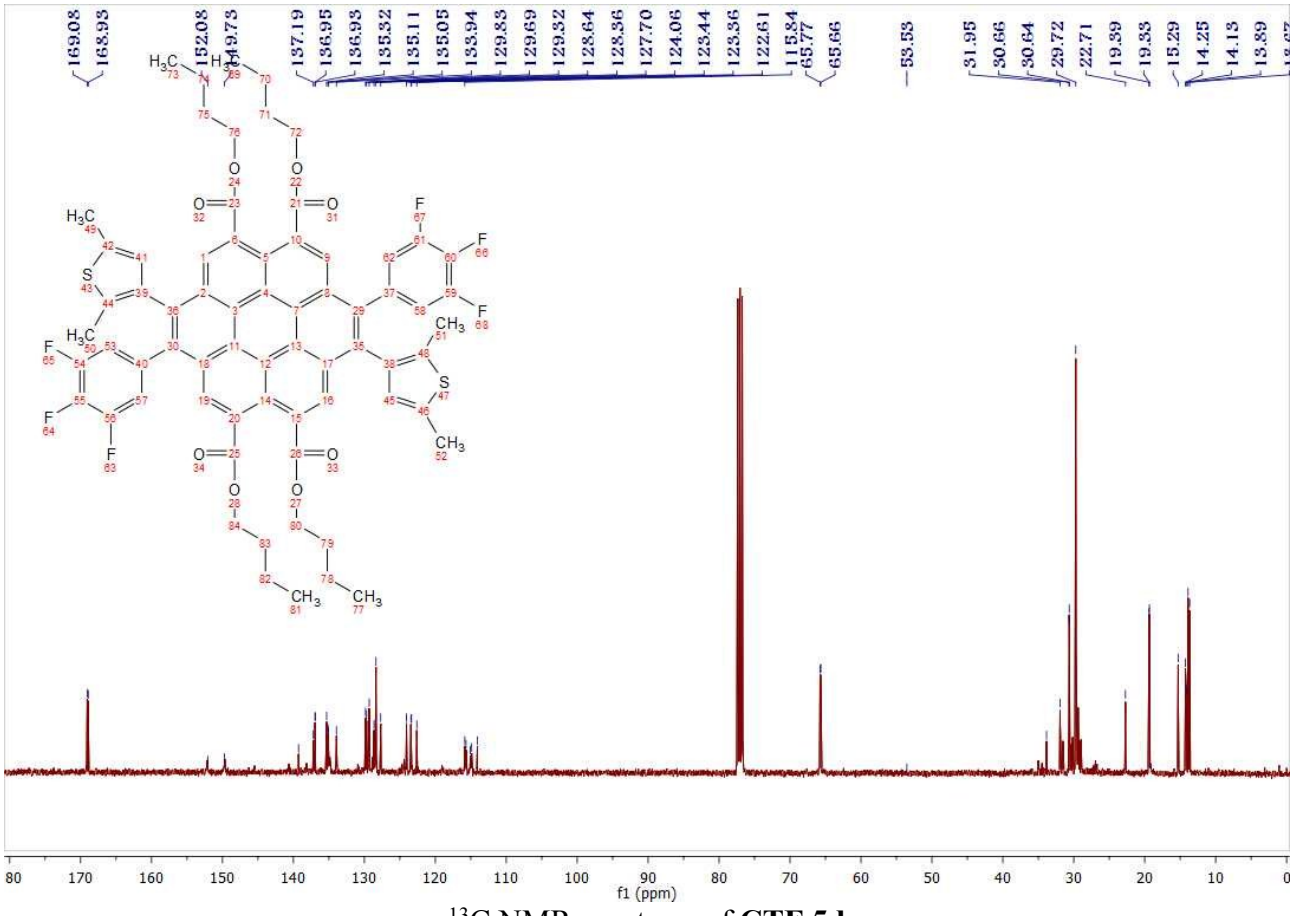
^{1}H NMR spectrum of **CTE 5c**



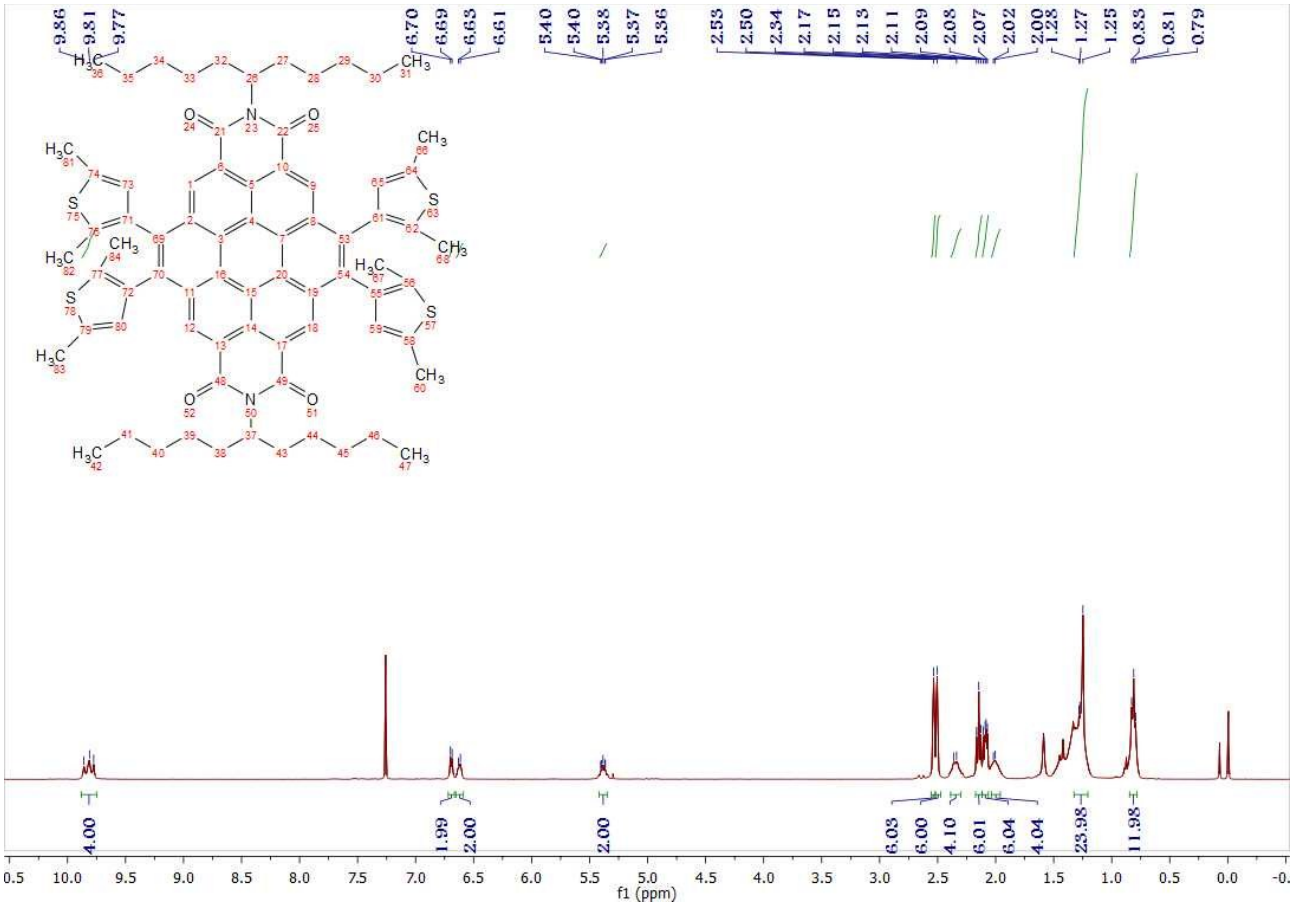
^{13}C NMR spectrum of **CTE 5c**



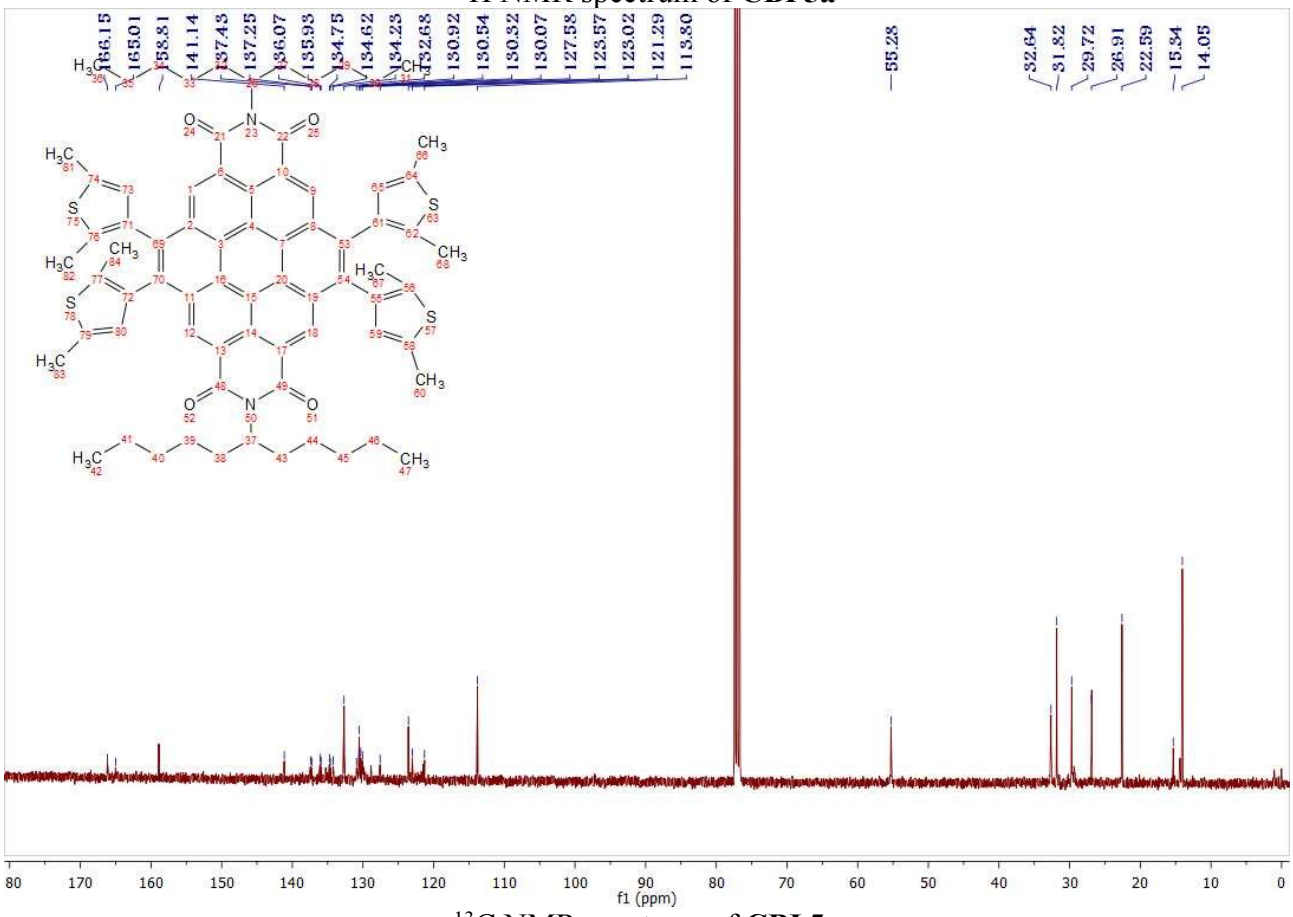
^{1}H NMR spectrum of **CTE 5d**



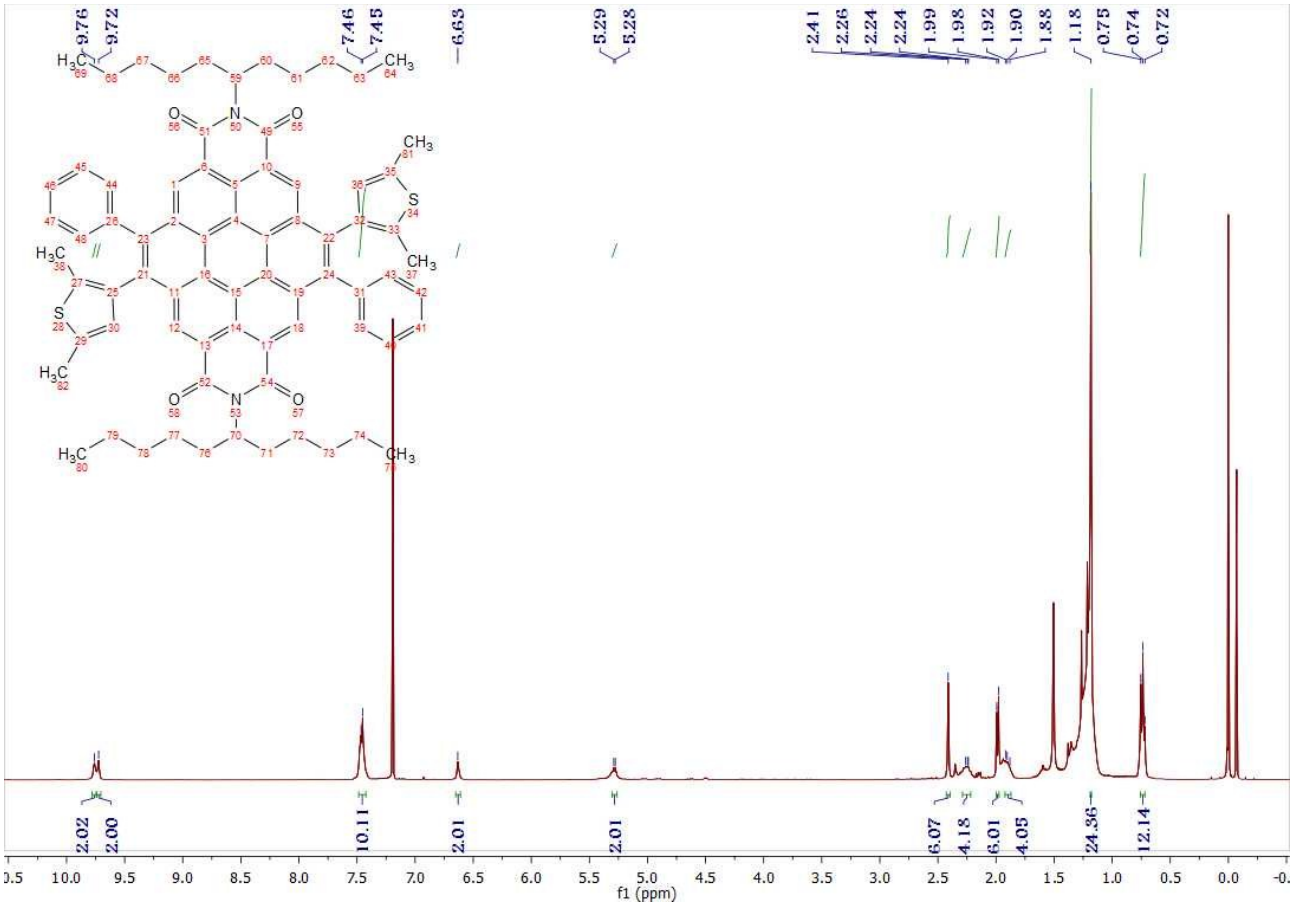
^{13}C NMR spectrum of **CTE 5d**



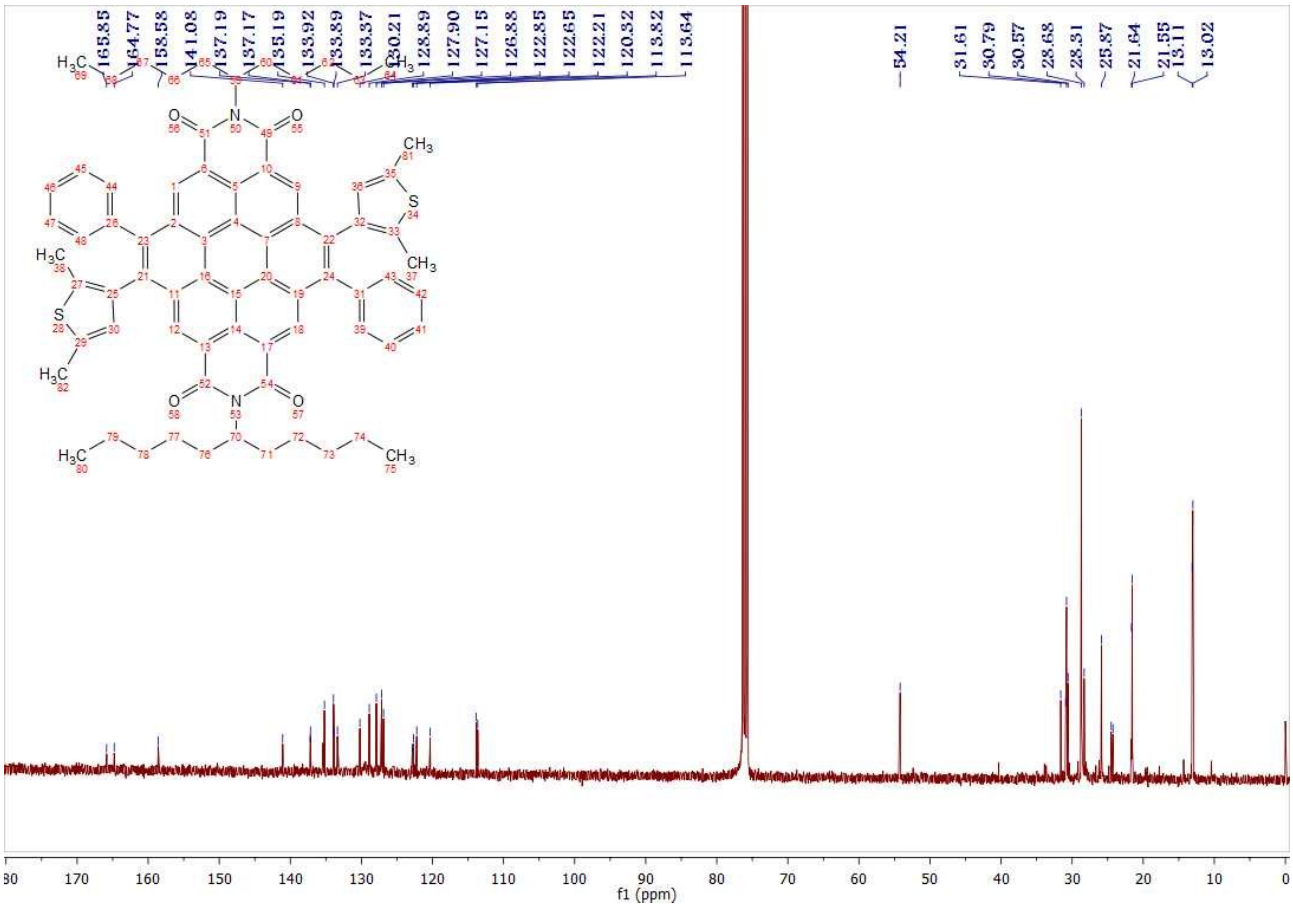
^{1}H NMR spectrum of **CBI 5a**



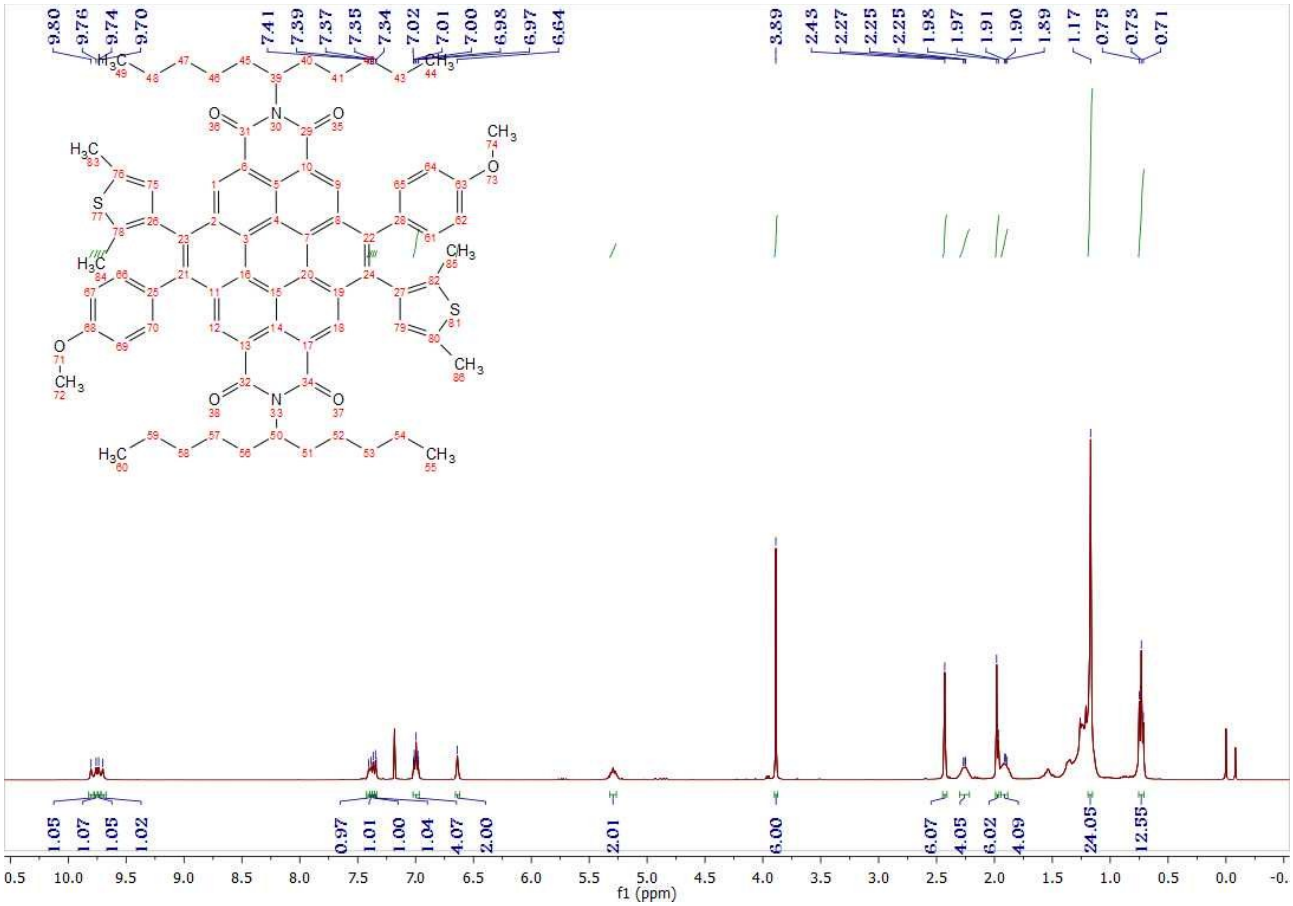
^{13}C NMR spectrum of **CBI 5a**



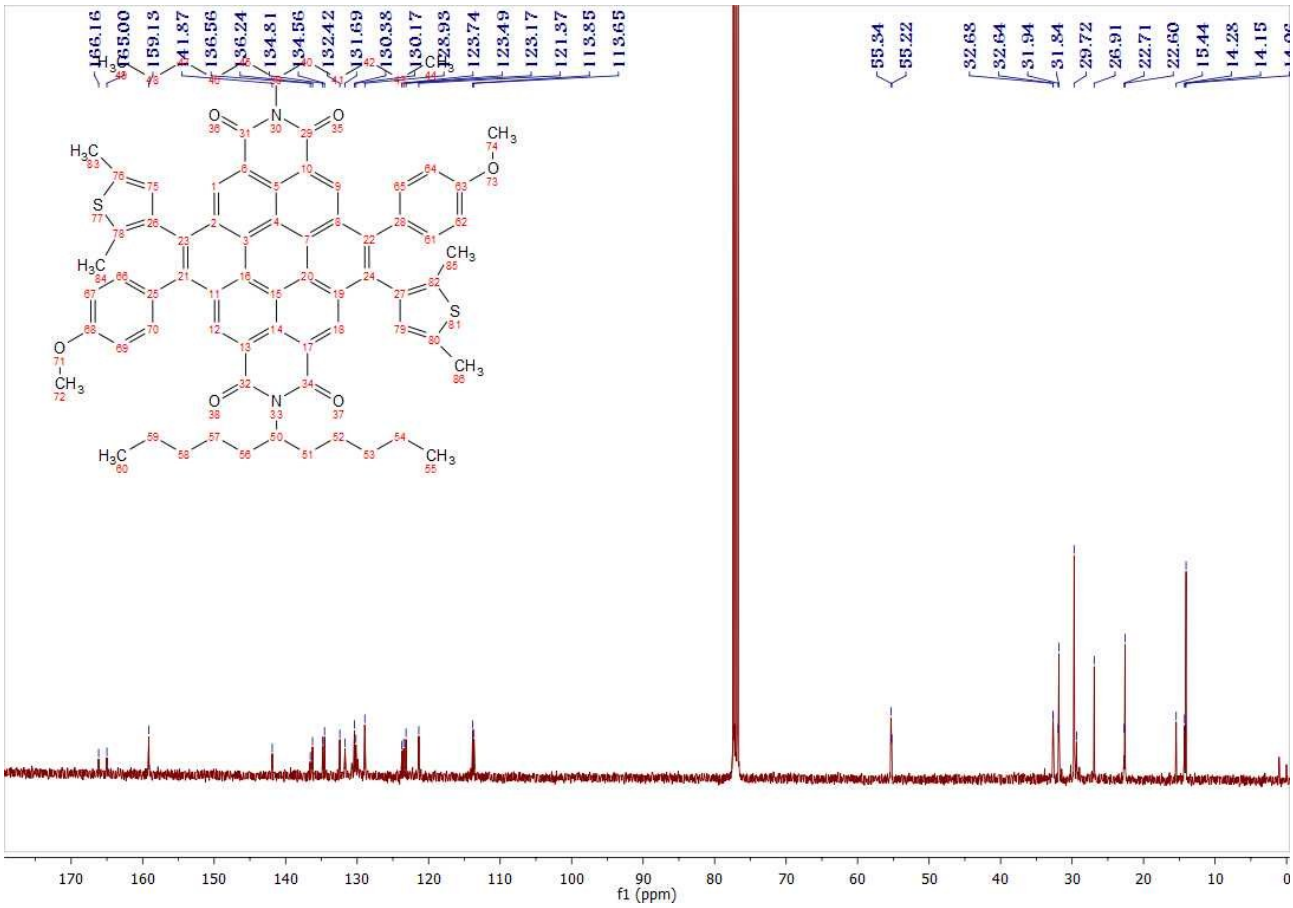
^{1}H NMR spectrum of **CBI 5b**



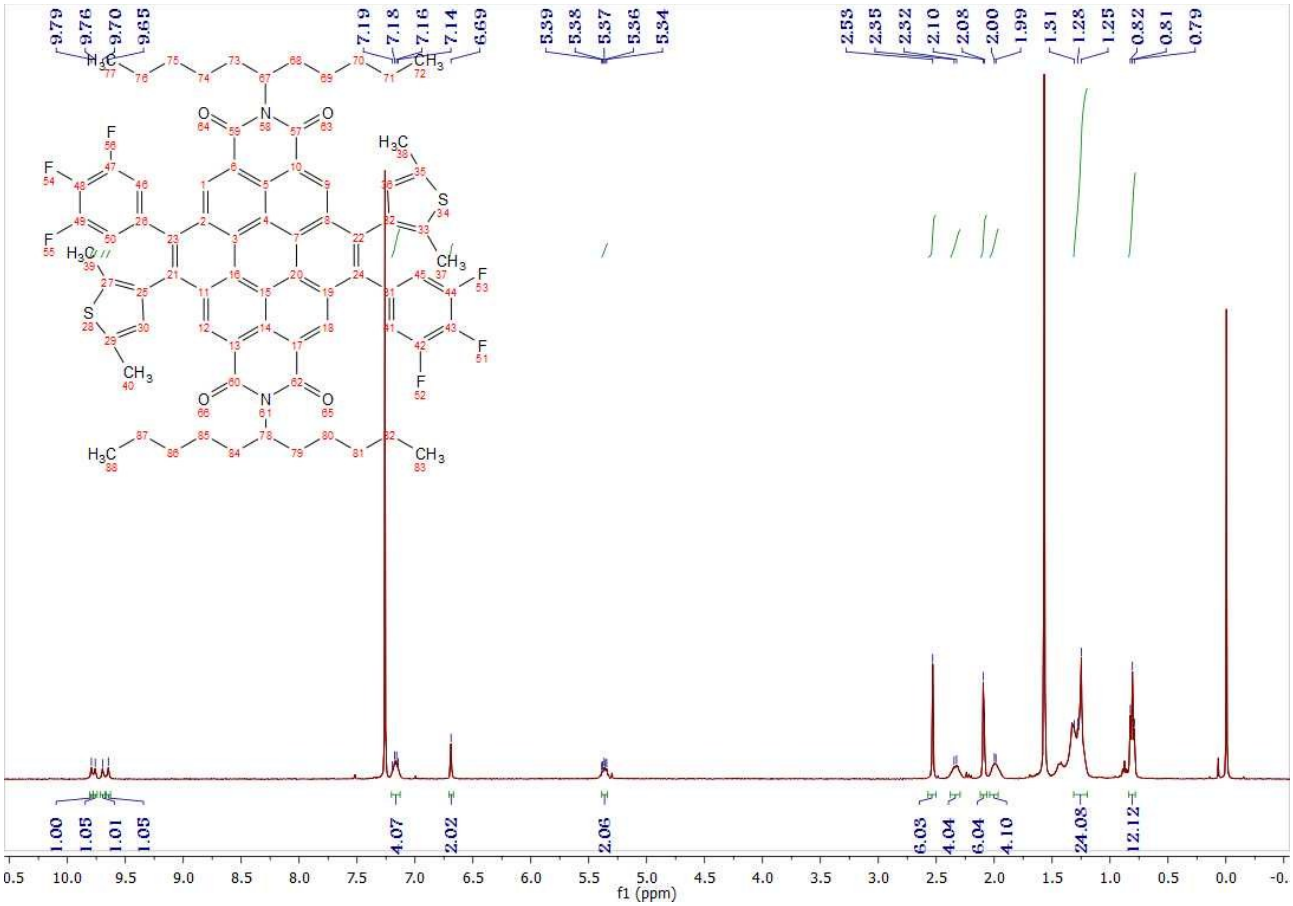
^{13}C NMR spectrum of **CBI 5b**



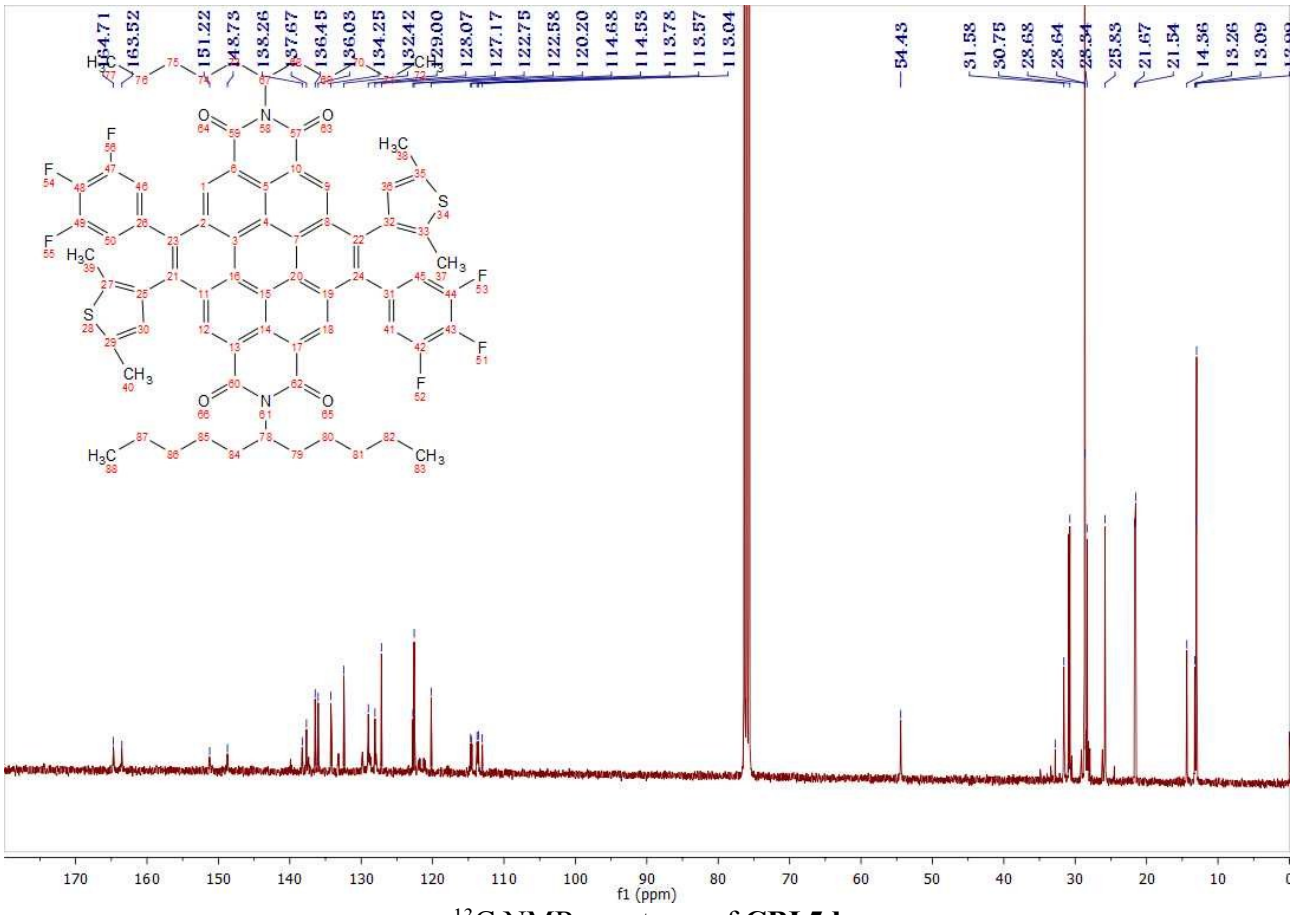
^{1}H NMR spectrum of **CBI 5c**



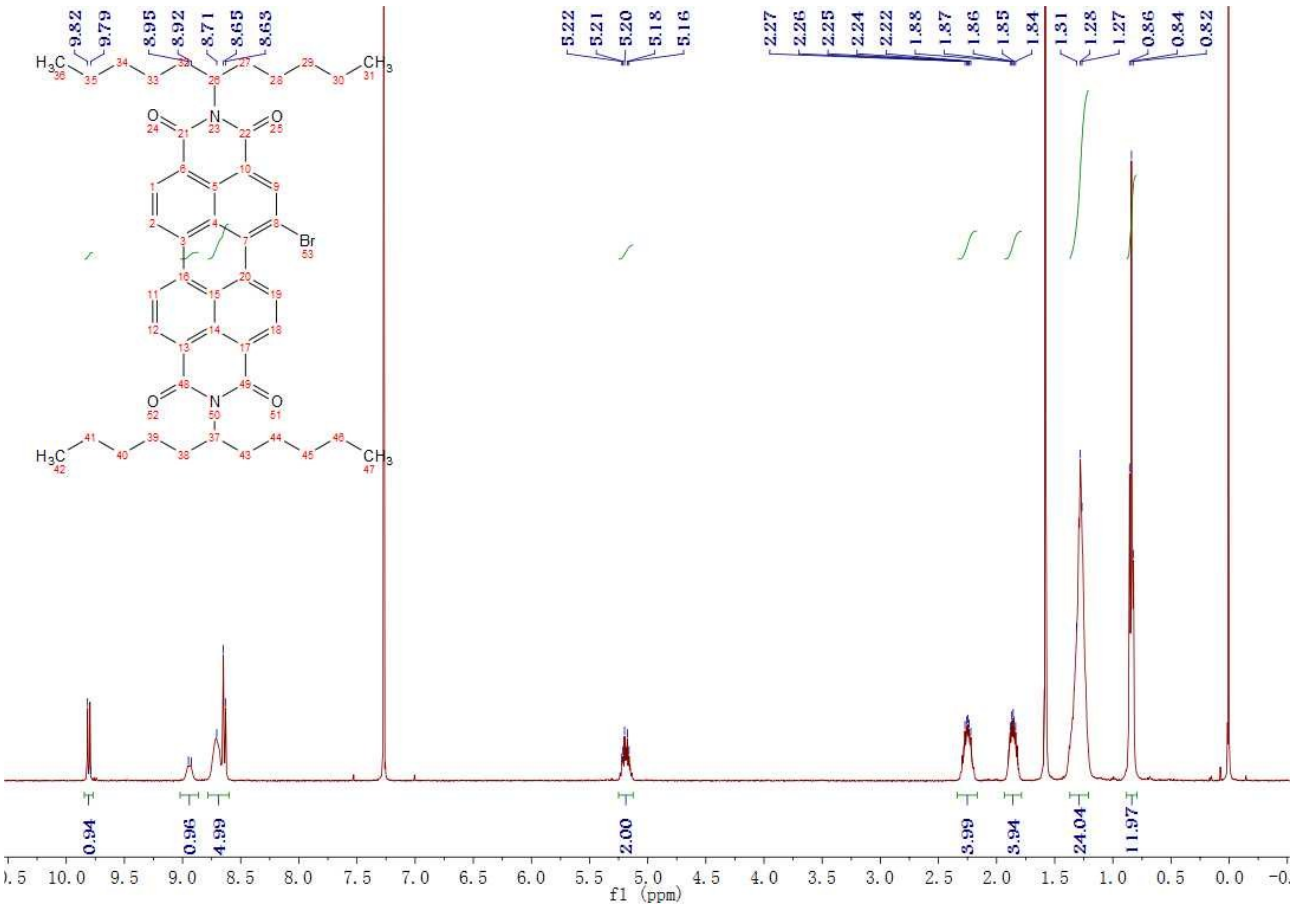
^{13}C NMR spectrum of **CBI 5c**



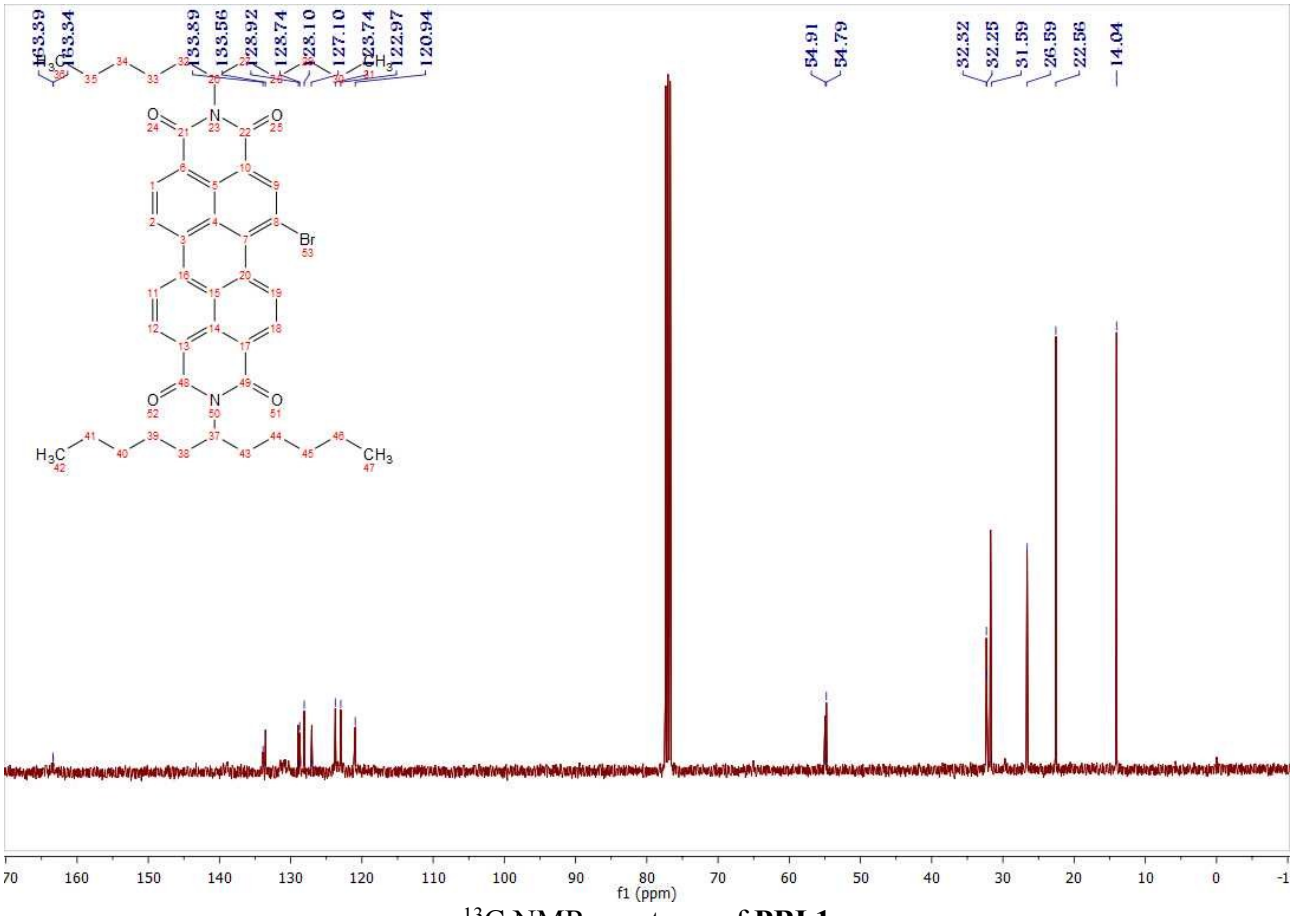
^{1}H NMR spectrum of **CBI 5d**



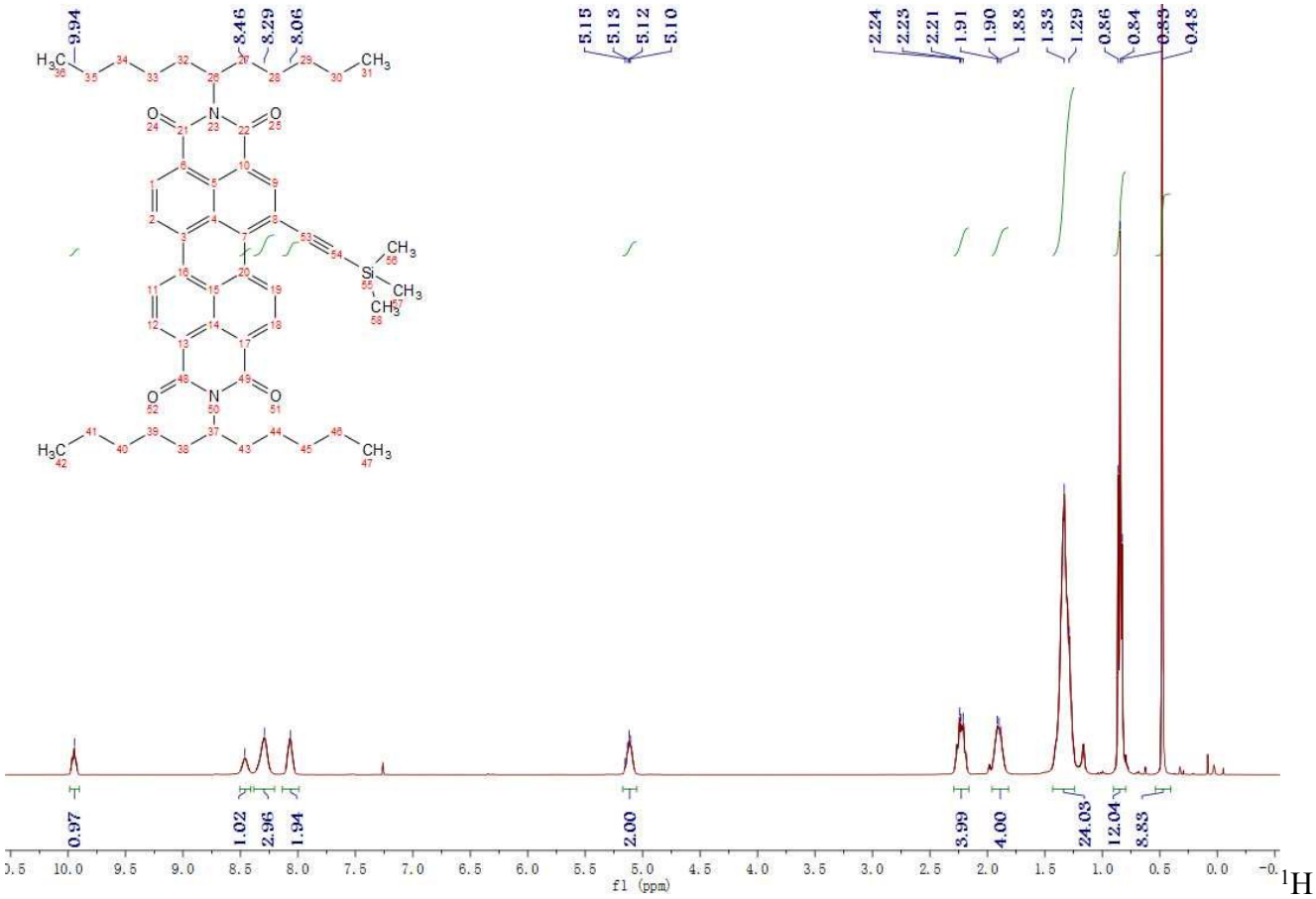
^{13}C NMR spectrum of **CBI 5d**



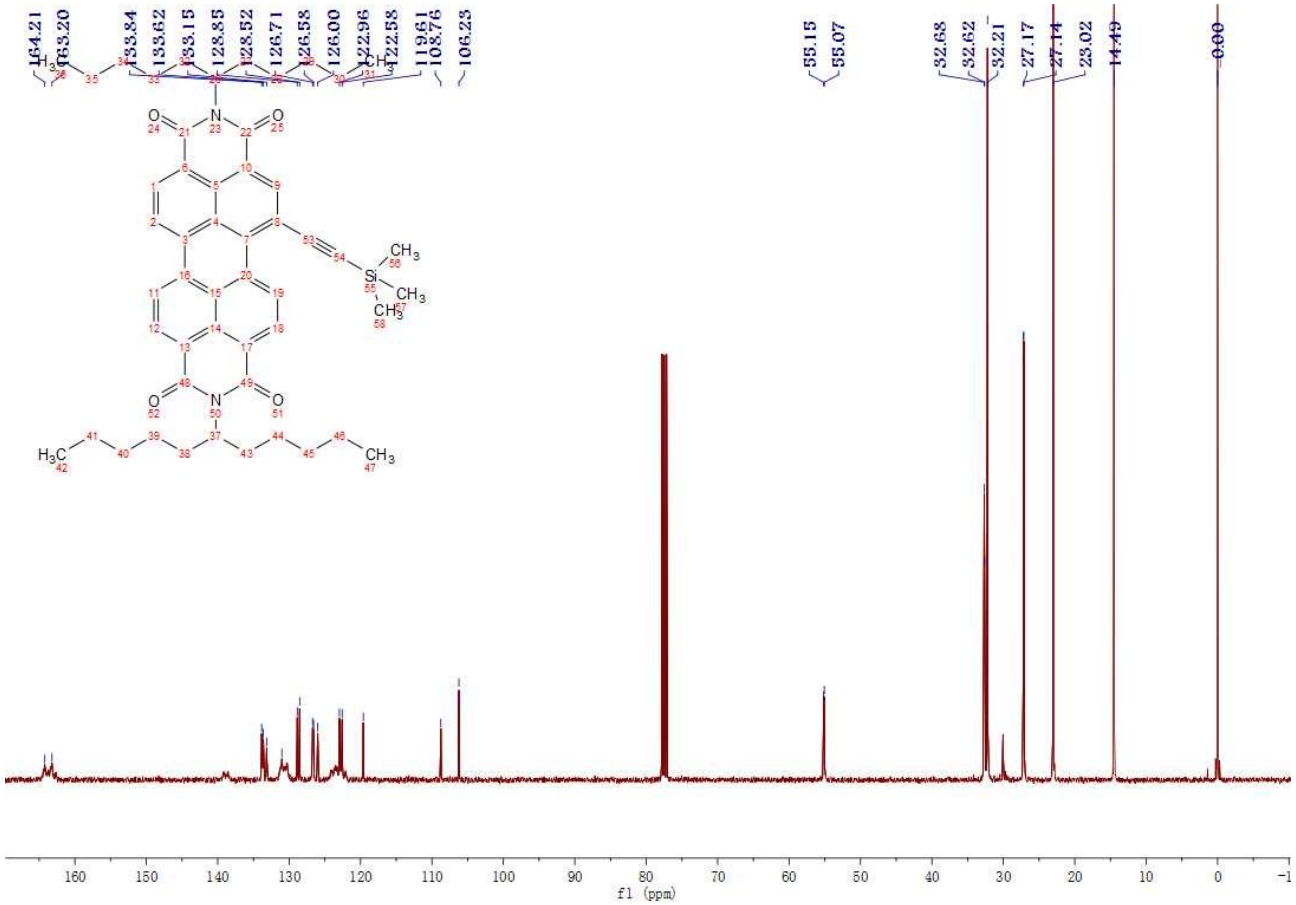
^{1}H NMR spectrum of **PBI 1**



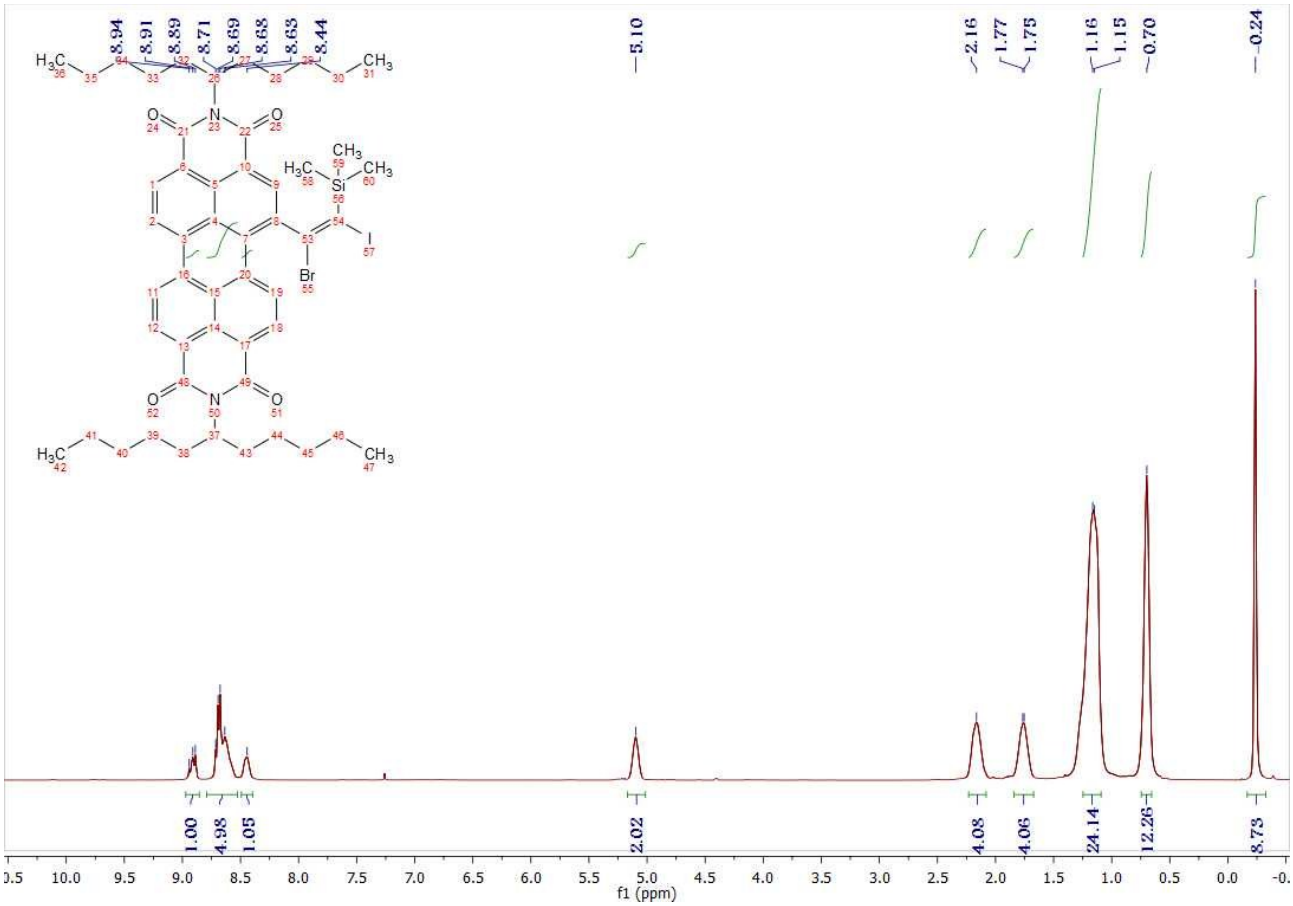
^{13}C NMR spectrum of **PBI 1**



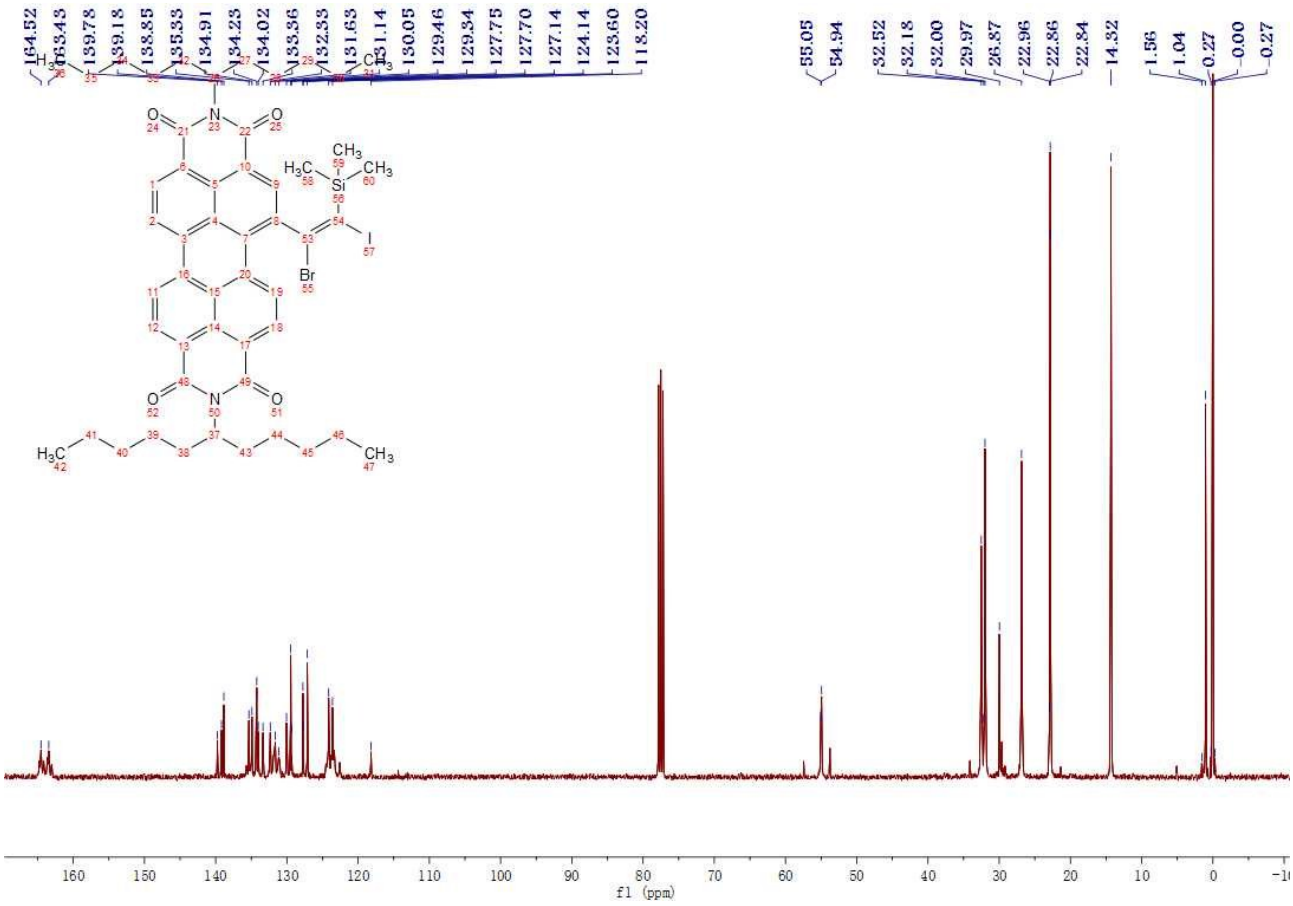
^{1}H NMR spectrum of **PBI 2**



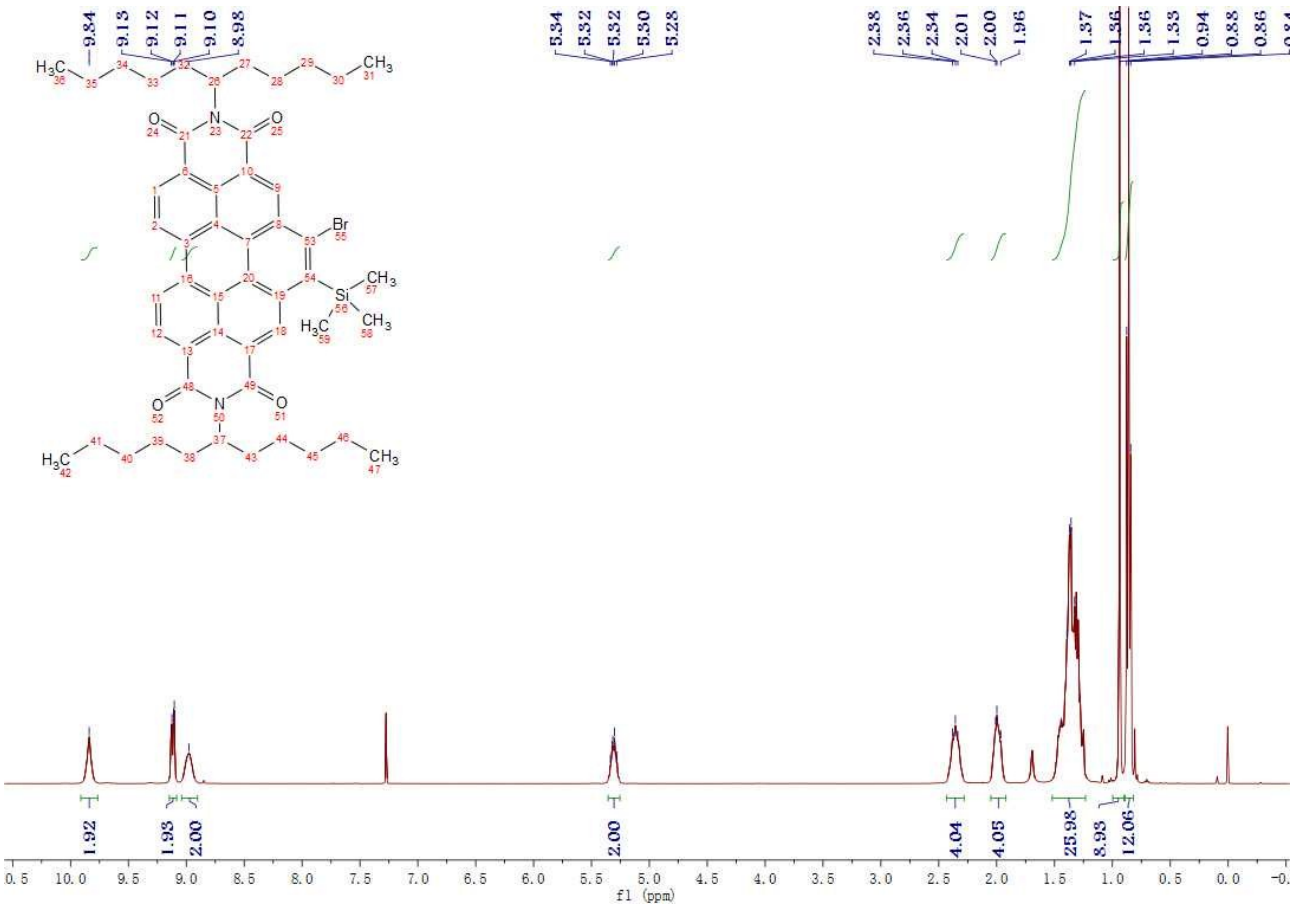
^{13}C NMR spectrum of **PBI 2**



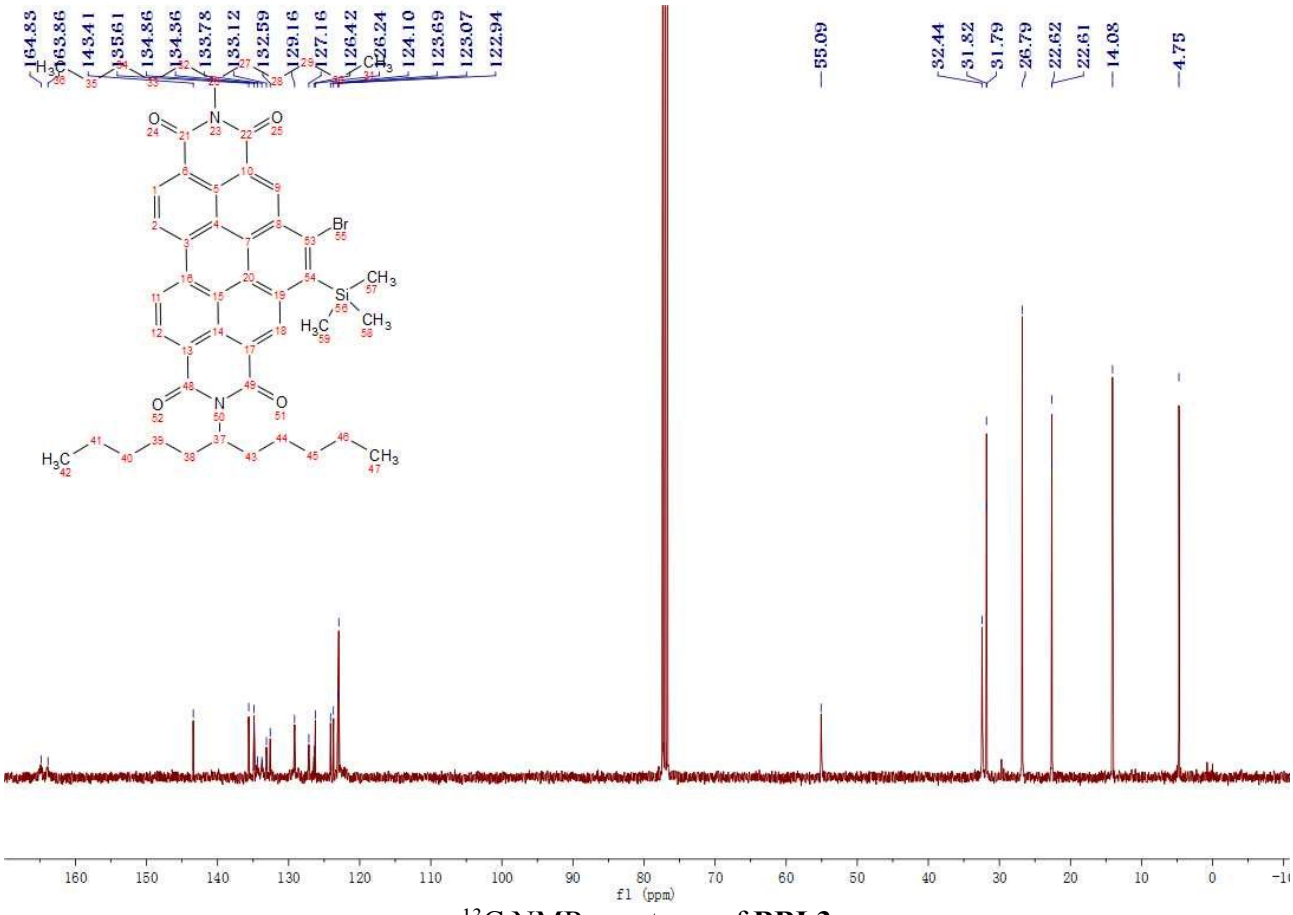
^{1}H NMR spectrum of **PBI 3**



^{13}C NMR spectrum of **PBI 3**



^{1}H NMR spectrum of **BBI 3**



^{13}C NMR spectrum of **BBI 3**

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