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## Supporting Information

### Two-dimensional halogenated thiophene side-chain strategy for balancing $V_{oc}$ and $J_{sc}$ and improving efficiency of non-fullerene small molecular acceptors-based organic solar cells

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### Experimental Section

**Materials and Characterization:** All air and water-sensitive reactions were carried out under N<sub>2</sub>. Toluene and THF were dried by Na and then freshly distilled before to use. The other precursors were used as the common commercial level. <sup>1</sup>H and <sup>13</sup>C NMR spectra were carried out on a Bruker Ascend-400 and 700 NMR spectrometer. All chemical shifts were reported in ppm. Chemical shifts in <sup>1</sup>H NMR were referenced to TMS and in <sup>13</sup>C NMR were referenced to CDCl<sub>3</sub>. The peaks positions of <sup>13</sup>C NMR were marked by groups. MALDI-TOF-MS was recorded on a Bruker BIFLEX III mass spectrometer. HR-ESI-MS was recorded on a Bruker Solarix XR mass spectrometer. Thermogravimetric analysis (TGA) was performed using a TA Instrument Q600 analyzer under nitrogen gas flow with a heating rate of 10 °C min<sup>-1</sup>. UV-vis absorption spectra were taken on Hitachi UH5300 UV-vis spectrometer. The electrochemical cyclic voltammetry was carried out on CHI electrochemical workstation with glass carbon disk, Ag/Ag<sup>+</sup> electrode, and Pt wire, as working electrode, reference electrode, and counter electrode, respectively, in a 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) acetonitrile solution. During CV measurements, the films were drop-cast on the glass carbon working electrode from THF solution. For morphological analysis, atomic force microscopy (AFM) images of thin films were obtained on a Nanoscope IIIa AFM (Digital Instruments) in tapping mode and transmission electron microscopy (TEM) was performed on JEOL 2200FS at 80 kV accelerating voltage. Grazing incidence X-ray scattering (GIXD) data were performed at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF).

**BHJ-OSC Fabrication and Characterization:** Non-fullerene organic solar cells were fabricated in a traditional ITO/PEDOT:PSS/active layer/PDINO/Al structure. Prior to

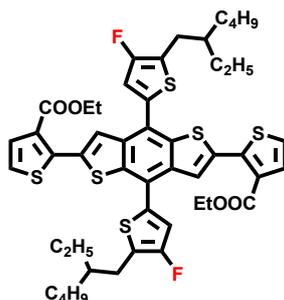
device fabrication, the patterned indium tin oxide (ITO) glass (1.5 cm × 1.5 cm, sheet resistance, 15 Ω<sup>-1</sup>) was subsequently cleaned in an ultrasonic bath with detergent, deionized water, acetone and isopropanol. After being treated in an ultraviolet-ozone chamber for 20 minutes, the cleaned ITO substrates were spin-coated of a poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Baytron P VP AI 4083) layer (~40 nm) and were dried at 150 °C for 20 min. After that, the photoactive blend was spin coated onto the surface of PEDOT:PSS from its chlorobenzene solution to form the active layer, and then a methanol solution (concentration: 1 mg/ml) of PDINO was spin-coated at 3000 rpm for 30 seconds above the active layer. Finally, ~80 nm thick aluminum (Al) were thermally evaporated in a vacuum chamber (10<sup>-4</sup> Pa) to form the electrode. The effective area of each device was 5 mm<sup>2</sup>, defined by a shadow mask. For photovoltaic performance characterization, the J-V curve was recorded by a Precision Source/Measure Unit (B2912A, Agilent Technologies) and an AAA grade solar simulator (XES-70S1, SAN-EI Electric Co. Ltd, 7 × 7 cm<sup>2</sup> beam size) coupled with AM 1.5G solar spectrum filters was taken as the light source. The light power on the surface of the sample was calibrated to be 100 mW cm<sup>-2</sup> in use of a standard monocrystalline silicon reference cell (SRC-1000-TC-QZ, VLSI Standards Inc., 2 × 2 cm<sup>2</sup>). The external quantum efficiency (EQE) was measured by a Solar Cell Spectral Response Measurement System (QE-R3011, Enlitech Co. Ltd) with the light intensity at each wavelength also calibrated by a standard single crystal Si photovoltaic cell.

### **SCLC mobility measurement (SCLC)**

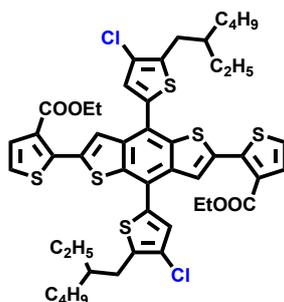
SCLC method was used to determine the hole and electron mobilities in a solar cell device by constructing different single-carrier-transporting device. For example, the hole-only device takes on a configuration of ITO/PEDOT:PSS/active layer/ MnO<sub>3</sub>/Al while the electron-only device taking an Al/active layer/Al configuration. The active layers for the two devices are spin-coated under same condition as that of the real solar cell. The mobilities were determined by fitting the dark current to a SCLC model which is described as:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu_0V^2}{8L^3} \exp\left(0.89\beta \sqrt{\frac{V}{L}}\right)$$

where  $J$  is the current density,  $L$  is the film thickness of the active layer,  $\mu$  is the hole or electron mobility,  $\varepsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-12}$  F m<sup>-1</sup>),  $\varepsilon_r$  is the relative dielectric constant of the transport medium,  $V$  ( $= V_{\text{appl}} - V_{\text{bi}}$ ) is the internal voltage in the device, where  $V_{\text{appl}}$  is the applied voltage and  $V_{\text{bi}}$  is the built-in voltage reflecting the difference of work functions of the two electrodes.

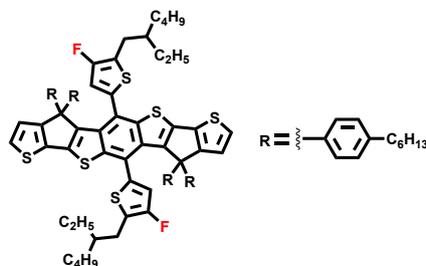


**Compound 2a:** In a 100 mL two-neck round-bottom flask, compound **1a**<sup>S1</sup> (0.96 g, 0.81 mmol), the ethyl 2-bromothiophene-3-carboxylate<sup>S2</sup> (0.76 g, 3.24 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.15 g, 0.10 mmol) was added. The flask was evacuated and back-filled with N<sub>2</sub> three times, and then freshly distilled toluene was injected into the reaction mixture. The resulting mixture was refluxed for 10 h under the N<sub>2</sub> atmosphere. After being cooled to room temperature, the solvents were then removed under reduced pressure. The crude product was purified by silica gel column chromatography, eluting with petroleum ether/dichloromethane (1:1) as the eluent to obtain the product as yellow solid (0.60 g, 81%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.93 (s, 2H, Th-H), 7.53-7.54 (d, *J* = 5.2 Hz, 2H, Th-H), 7.29-7.30 (d, *J* = 5.2 Hz, 2H, Th-H), 7.18 (s, 2H, Th-H), 4.26-4.31 (q, *J* = 7.2 Hz, 4H, CH<sub>2</sub>), 2.77-2.79 (d, *J* = 6.8 Hz, 4H, CH<sub>2</sub>), 1.63-1.69 (m, 2H, CH), 1.31-1.46 (m, 16H, CH<sub>2</sub>), 1.23-1.26 (t, *J* = 7.2 Hz, 6H, CH<sub>3</sub>), 0.88-0.96 (m, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): δ 162.9, (155.6, 153.0, *J*<sub>CF</sub> = 253.0 Hz), 141.8, 139.7, 136.6, 135.9, (133.7, 133.6, *J*<sub>CF</sub> = 9.7 Hz), 130.8, 129.6, 125.4, 124.9, 123.4, (122.5, 122.4, *J*<sub>CF</sub> = 18.2 Hz), (118.2, 117.9, *J*<sub>CF</sub> = 27.0 Hz), 60.9, 40.9, 32.5, 29.1, 28.8, 25.7, 23.0, 14.1, 10.8. HR-ESI-MS (*m/z*): calcd for C<sub>48</sub>H<sub>52</sub>F<sub>2</sub>O<sub>4</sub>S<sub>6</sub>: 922.2158. Found: 940.2503 ([M+NH<sub>4</sub><sup>+</sup>]); 945.2057 ([M+Na<sup>+</sup>]).

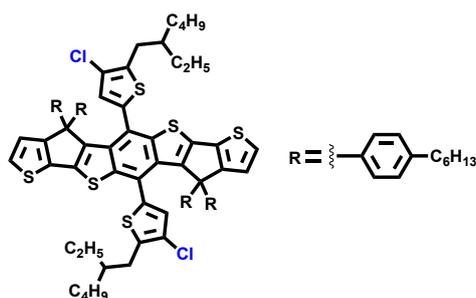


**Compound 2b:** In a 100 mL two-neck round-bottom flask, compound **1b**<sup>S3</sup> (1.57 g, 1.20 mmol), the ethyl 2-bromothiophene-3-carboxylate<sup>S2</sup> (0.90 g, 3.80 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.15 g, 0.10 mmol) was added. The flask was evacuated and back-filled with N<sub>2</sub> three times, and then freshly distilled toluene was injected into the reaction mixture. The resulting mixture was refluxed for 12 h under the N<sub>2</sub> atmosphere. After being cooled to room temperature, the solvents were then removed under reduced pressure. The crude product was purified by silica gel column chromatography, eluting with petroleum ether/dichloromethane (1:1) as the eluent to obtain the product as yellow solid (0.95 g, 78%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.89 (s, 2H, Th-H), 7.53-7.54 (d, *J* = 5.2 Hz, 2H, Th-H), 7.29-7.30 (d, *J* = 5.2 Hz, 2H, Th-H), 7.27 (s, 2H, Th-H),

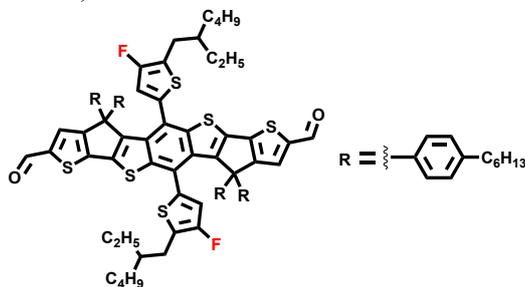
4.26-4.31 (q,  $J = 7.2$  Hz, 4H, CH<sub>2</sub>), 2.82-2.84 (d,  $J = 6.8$  Hz, 4H, CH<sub>2</sub>), 1.69-1.76 (m, 2H, CH), 1.32-1.46 (m, 16H, CH<sub>2</sub>), 1.23-1.26 (t,  $J = 7.2$  Hz, 6H, CH<sub>3</sub>), 0.91-0.96 (m, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 175 MHz, ppm):  $\delta$  162.9, 141.7, 139.8, 138.6, 136.7, 135.9, 135.3, 130.8, 129.7, 128.2, 125.4, 124.8, 123.0, 122.9, 61.0, 40.9, 32.5, 32.0, 28.8, 25.7, 23.0, 14.1, 10.8. HR-ESI-MS ( $m/z$ ): calcd for C<sub>48</sub>H<sub>52</sub>Cl<sub>2</sub>O<sub>4</sub>S<sub>6</sub>: 954.1567. Found: 972.1903 ([M+NH<sub>4</sub><sup>+</sup>]<sup>+</sup>); 977.1463 ([M+Na<sup>+</sup>]).



**FBDT:** 1-bromo-4-hexylbenzene (0.73 g, 3.01 mmol) was dissolved in anhydrous THF (20 mL), *n*-butyllithium in hexane (1.05 mL, 2.51 mmol) was added slowly at -78 °C under N<sub>2</sub> atmosphere. The reaction mixture was stirred at -78 °C for 1 h, and then a solution of compound **2a** (0.24 g, 0.26 mmol) in THF (10 mL) was added dropwise into the reaction mixture. The reaction mixture was then stirred for another 2 h, The reaction mixture was poured into water and extracted with dichloromethane (3 × 50 mL). The organic layer was washed with water, combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the concentrated mixture and p-toluene sulfonic acid was charged into two-neck flask under nitrogen atmosphere. Then freshly distilled toluene was injected into the mixture. The resulting solution was stirred at 80 °C for 1 h. Then the mixture was poured into water, extracted with dichloromethane. Then the organic layers were combined, then washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the crude product was purified by flash column chromatography (silica gel), eluting with dichloromethane/petroleum ether (1:15) to obtain the product as light yellow solid (0.26 g, 67%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  7.05-7.12 (m, 6H, Ph-H, Th-H), 6.84-7.00 (m, 12H, Ph-H), 6.79-6.81 (d,  $J = 4.8$  Hz, 2H, Th-H), 5.76-5.81 (m, 2H, Th-H), 2.62-2.71 (m, 2H, CH<sub>2</sub>), 2.53-2.65 (m, 10H, CH<sub>2</sub>), 1.53-1.59 (m, 10H, CH, CH<sub>2</sub>), 1.31-1.45 (m, 40H, CH<sub>2</sub>), 0.87-0.99 (m, 24H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 175 MHz, ppm):  $\delta$  165.0, (154.2, 154.1, 152.7, 152.6,  $J_{CF} = 257.25$  Hz), 150.1, 149.1, 141.5, 141.3, 141.2, 141.0, 140.9, 136.9, 136.8, 136.3, 136.2, 133.9, (133.2, 133.1,  $J_{CF} = 28.0$  Hz), 130.9, 128.7, 128.6, 128.5, 128.1, 128.0, 127.8, 124.0, 122.5, 122.4, 122.3, 122.2, (120.5, 120.4,  $J_{CF} = 26.25$  Hz), 63.1, 40.8, 35.6, 32.5, 32.4, 31.8, 31.5, 31.4, 29.24, 29.15, 29.0, 28.9, 28.8, 28.7, 25.6, 23.2, 23.1, 22.6, 14.3, 14.1, 10.9, 10.8, 10.7. HR-ESI-MS ( $m/z$ ): calcd for C<sub>92</sub>H<sub>108</sub>F<sub>2</sub>S<sub>6</sub>: 1442.6743. Found: 1443.6828 ([M+H<sup>+</sup>]<sup>+</sup>).

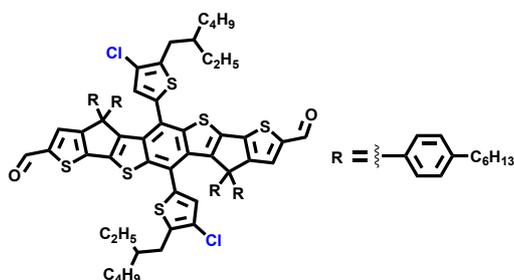


**CIBDT:** 1-bromo-4-hexylbenzene (1.45 g, 6.02 mmol) was dissolved in anhydrous THF (20 mL), *n*-butyllithium in hexane (2.10 mL, 5.02 mmol) was added slowly at -78 °C under N<sub>2</sub> atmosphere. The reaction mixture was stirred at -78 °C for 1 h, and then a solution of compound **2b** (0.48 g, 0.50 mmol) in THF (10 mL) was added dropwise into the reaction mixture. The reaction mixture was then stirred for another 2 h, The reaction mixture was poured into water and extracted with dichloromethane (3 × 50 mL). The organic layer was washed with water, combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the concentrated mixture and *p*-toluene sulfonic acid was charged into two-neck flask under nitrogen atmosphere. Then freshly distilled toluene was injected into the mixture. The resulting solution was stirred at 80 °C for 1 h. Then the mixture was poured into water, extracted with dichloromethane. Then the organic layers were combined, then washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the crude product was purified by flash column chromatography (silica gel), eluting with dichloromethane/petroleum ether (1:15) to obtain the product as light yellow solid (0.45 g, 60%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.06-7.07 (d, *J* = 4.8 Hz, 2H, Th-H), 6.83-7.05 (m, 16H, Ph-H), 6.77-6.79 (m, 2H, Th-H), 5.97-6.01 (m, 2H, Th-H), 2.69-2.79 (m, 2H, CH<sub>2</sub>), 2.52-2.61 (m, 10H, CH<sub>2</sub>), 1.54-1.66 (m, 10H, CH, CH<sub>2</sub>), 1.32-1.34 (m, 40H, CH<sub>2</sub>), 0.87-0.99 (m, 24H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 175 MHz, ppm): δ 165.0, 150.2, 150.1, 149.1, 149.0, 141.4, 141.3, 141.2, 140.9, 140.8, 138.8, 138.5, 136.5, 136.4, 135.2, 135.0, 133.9, 130.8, 130.6, 130.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 123.5, 122.5, 121.6, 121.5, 63.0, 41.0, 40.8, 35.6, 32.5, 32.4, 31.8, 31.7, 31.5, 31.4, 29.2, 29.1, 28.7, 25.7, 25.6, 23.2, 23.1, 22.6, 14.3, 14.1, 10.9, 10.6. HR-ESI-MS (*m/z*): calcd for C<sub>92</sub>H<sub>108</sub>Cl<sub>2</sub>S<sub>6</sub>: 1474.6152. Found: 1475.6231 ([M+H]<sup>+</sup>, 100%).

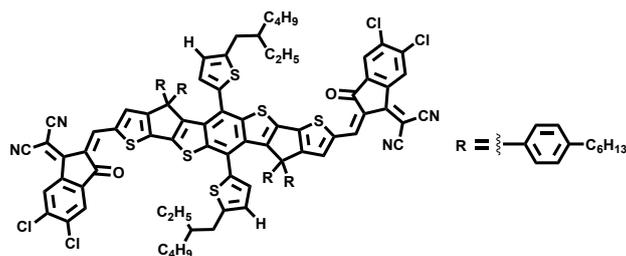


**FBDT-CHO:** To a solution of **FBDT** (0.22 g, 0.15 mmol) in dry 1,2-dichloroethane (80 mL) was added DMF (0.5 mL, 0.30 mmol) and POCl<sub>3</sub> (0.20 mL, 0.24 mmol) dropwise under N<sub>2</sub> atmosphere at 0 °C. After addition, the cooling bath was removed and the reaction mixture was refluxed for 10 h. The mixture was quenched with saturated aqueous solution of sodium acetate and then the mixture was stirred for

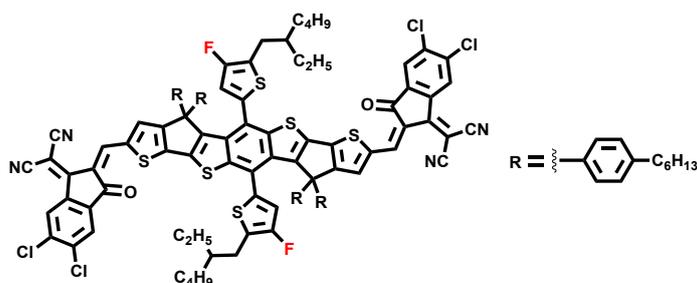
another 2 h, The reaction mixture was then extracted with dichloromethane. The organic layers were combined and washed with saturated brine solution and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the crude product was purified by flash column chromatography (silica gel), eluting with petroleum ether/dichloromethane (1:1) to obtain the product as yellow solid (0.21 g, 94%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  9.67 (s, 2H, CHO), 7.43 (s, 2H, Th-H), 6.97-7.11 (m, 12H, Ph-H), 6.84-6.92 (m, 4H, Ph-H), 5.76-5.81 (m, 2H, Th-H), 2.63-2.72 (m, 2H,  $\text{CH}_2$ ), 2.51-2.57 (m, 10H,  $\text{CH}_2$ ), 1.46-1.60 (m, 10H, CH,  $\text{CH}_2$ ), 1.31-1.45 (m, 40H,  $\text{CH}_2$ ), 0.87-0.99 (m, 24H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 175 MHz, ppm):  $\delta$  182.5, 165.0, (154.2, 154.1, 152.7, 152.6,  $J_{\text{CF}} = 252.0$  Hz), 150.6, 146.1, 143.7, 142.0, 141.7, 141.2, 135.4, 134.9, (132.1, 132.0, 131.9,  $J_{\text{CF}} = 28.0$  Hz), 131.3, 131.2, 130.8, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 125.4, 123.2, 123.1, 123.0, 122.9, (120.8, 120.7, 120.6,  $J_{\text{CF}} = 10.5$  Hz), 63.4, 40.8, 35.6, 35.5, 32.5, 32.4, 31.7, 31.5, 31.4, 29.2, 29.1, 29.0, 28.9, 28.8, 28.7, 25.7, 25.6, 23.2, 23.1, 22.6, 14.3, 14.1, 10.9, 10.7. HR-ESI-MS ( $m/z$ ): calcd for  $\text{C}_{94}\text{H}_{108}\text{F}_2\text{O}_2\text{S}_6$ : 1498.6642. Found: 1498.6652.



**CIBDT-CHO:** To a solution of **CIBDT** (0.24 g, 0.16 mmol) in dry 1,2-dichloroethane (80 mL) was added DMF (0.5 mL, 0.30 mmol) and  $\text{POCl}_3$  (0.20 mL, 0.24 mmol) dropwise under  $\text{N}_2$  atmosphere at 0 °C. After addition, the cooling bath was removed and the reaction mixture was refluxed for 8 h. The mixture was quenched with saturated aqueous solution of sodium acetate and then the mixture was stirred for another 1 h, The reaction mixture was then extracted with dichloromethane. The organic layers were combined and washed with saturated brine solution and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the crude product was purified by flash column chromatography (silica gel), eluting with petroleum ether/dichloromethane (1:1) to obtain the product as yellow solid (0.23 g, 94%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  9.66 (s, 2H, CHO), 7.41-7.42 (d,  $J = 3.2$  Hz, 2H, Th-H), 6.99-7.06 (m, 12H, Ph-H), 6.83-6.91 (m, 4H, Ph-H), 5.97-6.01 (m, 2H, Th-H), 2.70-2.80 (m, 2H,  $\text{CH}_2$ ), 2.54-2.60 (m, 10H,  $\text{CH}_2$ ), 1.54-1.64 (m, 10H, CH,  $\text{CH}_2$ ), 1.30-1.36 (m, 40H,  $\text{CH}_2$ ), 0.87-0.99 (m, 24H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 175 MHz, ppm):  $\delta$  182.5, 165.0, 154.1, 150.6, 150.5, 146.1, 143.6, 142.0, 141.9, 141.6, 141.2, 139.4, 139.1, 135.1, 135.0, 134.1, 133.9, 131.2, 130.9, 130.8, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 125.0, 121.9, 121.8, 63.4, 41.0, 40.8, 35.6, 32.4, 31.8, 31.5, 31.3, 29.2, 29.1, 28.7, 25.7, 23.2, 23.0, 22.6, 14.3, 14.1, 10.9, 10.6. MALDI-TOF MS ( $m/z$ ): calcd for  $\text{C}_{94}\text{H}_{108}\text{Cl}_2\text{O}_2\text{S}_6$ : 1531.6. Found: 1532.2.

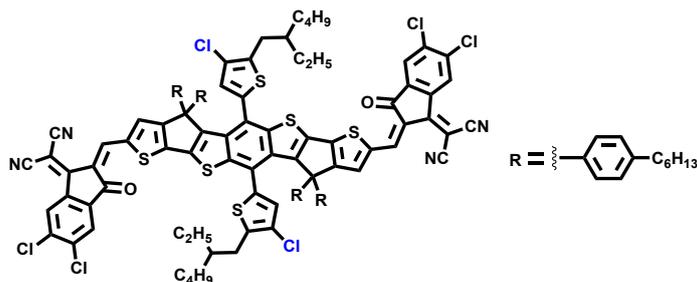


**HBDT-4Cl:** In a 100 mL two-neck round-bottom flask, **IC-2Cl**<sup>S4</sup> (0.14 g, 0.50 mmol) and **HBDT-CHO**<sup>S5-7</sup> (0.15 g, 0.10 mmol) was added. The reaction mixture was evacuated and backfilled with N<sub>2</sub> three times, and then freshly degassed chloroform (30 mL) and pyridine (0.7 mL) were added into the reaction mixture. The reaction mixture was stirred at room temperature for 6 h. Then the solution was poured into methanol and the precipitate was filtered off and washed with methanol. The crude product was purified by silica gel column chromatography, eluting with petroleum ether/dichloromethane (1:1) as the eluent to give the product as black solid (0.16 g, 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 8.71 (s, 4H, CH, Ph-H), 7.87 (s, 2H, Th-H), 7.40 (s, 2H, Ph-H), 6.90-7.00 (m, 16H, Ph-H), 6.41-6.42 (d, *J* = 3.6 Hz, 2H, Th-H), 6.09-6.11 (m, 2H, Th-H), 2.74-2.80 (m, 2H, CH<sub>2</sub>), 2.55-2.69 (m, 10H, CH<sub>2</sub>), 1.55-1.62 (m, 10H, CH, CH<sub>2</sub>), 1.31-1.40 (m, 40H, CH<sub>2</sub>), 0.87-1.02 (m, 24H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 175 MHz, ppm): δ 186.0, 166.1, 158.0, 157.7, 154.8, 152.4, 147.0, 146.9, 142.2, 141.9, 141.6, 141.3, 139.5, 139.2, 138.8, 138.5, 135.9, 135.2, 135.1, 134.8, 134.6, 131.8, 130.4, 128.4, 128.2, 127.1, 126.9, 125.0, 124.6, 120.5, 114.3, 68.9, 63.4, 41.4, 41.2, 35.6, 35.5, 33.8, 32.5, 32.4, 31.8, 31.5, 29.2, 29.1, 28.9, 25.7, 25.4, 23.2, 22.7, 22.6, 14.3, 14.1, 10.9, 10.7. MALDI-TOF MS (*m/z*): calcd for C<sub>118</sub>H<sub>114</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>2</sub>S<sub>6</sub>: 1953.6. Found: 1953.6.

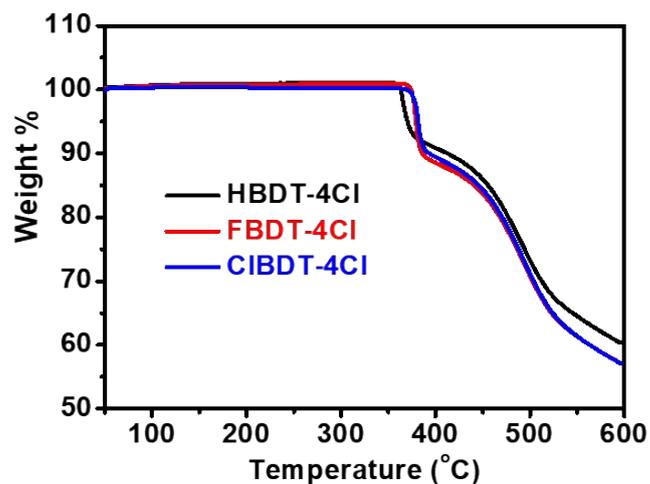


**FBDT-4Cl:** In a 100 mL two-neck round-bottom flask, **FBDT-CHO** (0.14 g, 0.09 mmol), **IC-2Cl**<sup>S4</sup> (0.13 g, 0.50 mmol) was added. The reaction mixture was evacuated and backfilled with N<sub>2</sub> three times, and then freshly degassed chloroform (35 mL) and pyridine (0.8 mL) were added into the reaction mixture. The reaction mixture was stirred at room temperature for 8 h. Then the solution was poured into methanol and the precipitate was filtered off and washed with methanol. The crude product was purified by silica gel column chromatography, eluting with petroleum ether/dichloromethane (1:1) as the eluent to give the product as black solid (0.16 g, 86%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 8.717-8.722 (s, 4H, CH, Ph-H), 7.88 (s, 2H, Th-H), 7.44 (s, 2H, Ph-H), 7.01-7.11 (m, 12H, Ph-H), 6.88-6.95 (m, 4H, Ph-H), 5.80-5.84 (m, 2H, Th-H), 2.69-2.79 (m, 2H, CH<sub>2</sub>), 2.52-2.61 (m, 10H, CH<sub>2</sub>), 1.50-1.62 (m, 10H, CH, CH<sub>2</sub>), 1.32-1.35

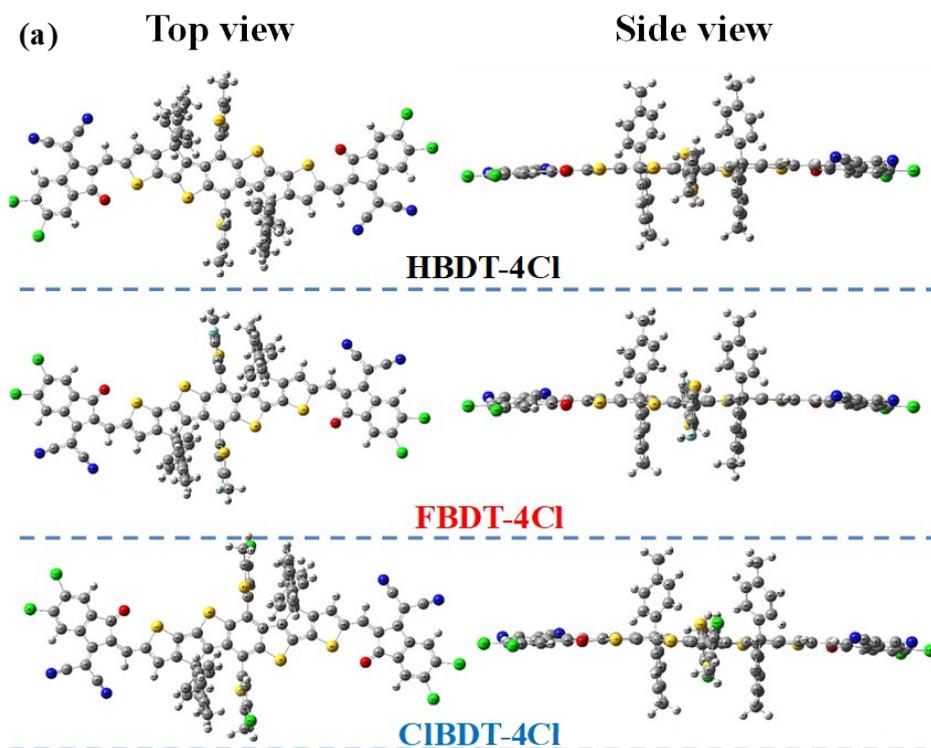
(m, 40H, CH<sub>2</sub>), 0.87-1.03 (m, 24H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 175 MHz, ppm): δ 186.0, 166.0, 157.9, 157.1, (154.3, 154.2, 154.1, 152.8,  $J_{CF}$  = 253.75 Hz), 152.0, 142.4, 142.3, 142.0, 141.4, 139.6, 139.3, 138.8, 138.5, 138.4, 135.9, 134.9, 134.4, 131.7, (131.5, 131.4, 131.3,  $J_{CF}$  = 8.75 Hz), 128.5, 128.4, 128.0, 127.9, 127.8, 126.9, 126.3, 125.1, (123.5, 123.4, 123.3,  $J_{CF}$  = 17.5 Hz), 120.8, 120.7, 114.2, 69.2, 63.4, 40.8, 40.6, 35.6, 35.5, 32.5, 31.7, 31.5, 31.4, 29.2, 29.0, 28.8, 28.7, 28.6, 25.6, 25.5, 23.2, 23.1, 22.6, 14.3, 14.1, 10.8. MALDI-TOF MS ( $m/z$ ): calcd for C<sub>118</sub>H<sub>112</sub>F<sub>2</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>2</sub>S<sub>6</sub>: 1990.4. Found: 1990.0. Elemental Analysis: calcd for C<sub>118</sub>H<sub>112</sub>F<sub>2</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>2</sub>S<sub>6</sub>: C, 71.21; H, 5.67; N, 2.81. Found: C, 71.05; H, 5.70; N, 2.78.

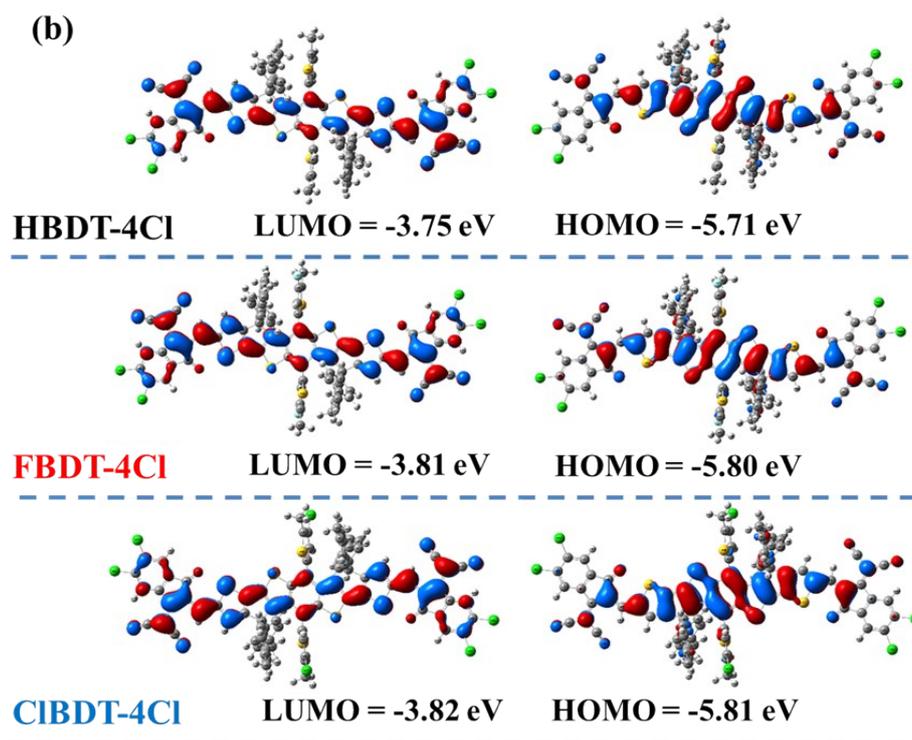


**CIBDT-4Cl**: In a 100 mL two-neck round-bottom flask, **CIBDT-CHO** (0.13 g, 0.09 mmol), **IC-2Cl**<sup>S4</sup> (0.13 g, 0.50 mmol) was added. The reaction mixture was evacuated and backfilled with N<sub>2</sub> three times, and then freshly degassed chloroform (30 mL) and pyridine (0.5 mL) were added into the reaction mixture. The reaction mixture was stirred at room temperature for 8 h. Then the solution was poured into methanol and the precipitate was filtered off and washed with methanol. The crude product was purified by silica gel column chromatography, eluting with petroleum ether/dichloromethane (1:1) as the eluent to give the product as black solid (0.15 g, 88%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 8.72 (s, 4H, CH, Ph-H), 7.89 (s, 2H, Th-H), 7.42 (s, 2H, Ph-H), 6.98-7.06 (m, 12H, Ph-H), 6.86-6.93 (m, 4H, Ph-H), 5.99-6.03 (m, 2H, Th-H), 2.75-2.86 (m, 2H, CH<sub>2</sub>), 2.55-2.64 (m, 10H, CH<sub>2</sub>), 1.54-1.65 (m, 10H, CH, CH<sub>2</sub>), 1.26-1.37 (m, 40H, CH<sub>2</sub>), 0.87-1.01 (m, 24H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 175 MHz, ppm): δ 186.0, 166.1, 158.0, 157.1, 154.0, 152.0, 151.9, 142.4, 142.3, 141.9, 141.4, 139.6, 139.3, 138.8, 138.5, 138.4, 136.1, 134.7, 134.6, 134.5, 133.4, 133.3, 131.6, 131.0, 130.9, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 126.9, 125.9, 125.1, 122.1, 120.9, 114.2, 69.2, 63.3, 40.9, 40.8, 35.6, 32.5, 32.4, 31.8, 31.7, 31.5, 31.4, 31.3, 29.2, 29.1, 28.7, 25.6, 23.2, 23.1, 22.6, 14.3, 14.1, 10.9, 10.7. MALDI-TOF MS ( $m/z$ ): calcd for C<sub>118</sub>H<sub>112</sub>Cl<sub>6</sub>N<sub>4</sub>O<sub>2</sub>S<sub>6</sub>: 2021.5. Found: 2022.5 ([M+H]<sup>+</sup>). Elemental Analysis: calcd for C<sub>118</sub>H<sub>112</sub>Cl<sub>6</sub>N<sub>4</sub>O<sub>2</sub>S<sub>6</sub>: C, 70.05; H, 5.58; N, 2.77. Found: C, 69.96; H, 5.62; N, 2.77.

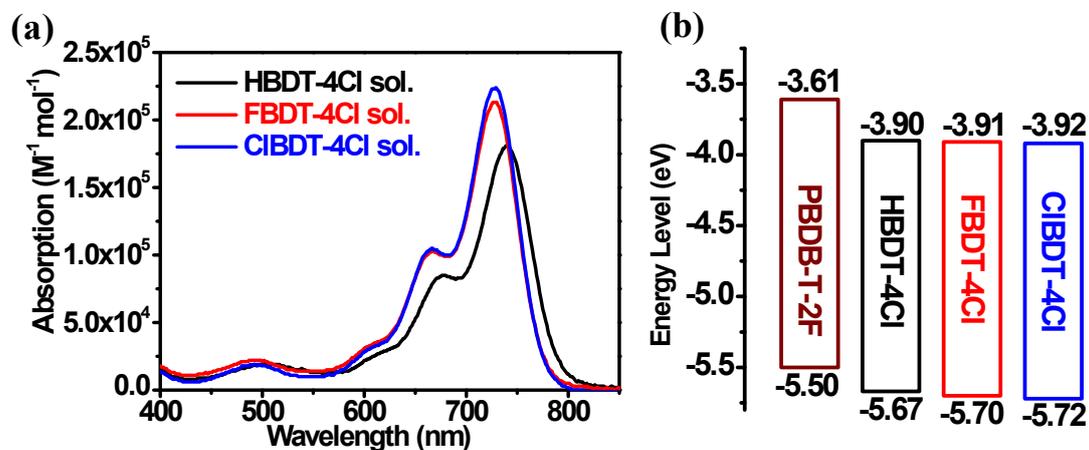


**Figure S1.** Thermal gravity analyse (TGA) of **HBDT-4Cl**, **FBDT-4Cl** and **CIBDT-4Cl** with a heating rate of 10 °C/min under N<sub>2</sub> atmosphere.





**Figure S2.** (a) Molecular geometry of the **HBDT-4Cl**, **FBDT-4Cl** and **CIBDT-4Cl** from the top and side views. (b) Molecular LUMO and HOMO orbital distributions and energy levels calculated by DFT/B3LYP/6-311G.



**Figure S3.** (a) Absorption spectrum of **HBDT-4Cl**, **FBDT-4Cl** and **CIBDT-4Cl** in chloroform solutions ( $2.0 \times 10^{-6}$  M). (b) The energy levels diagram of **PBDB-T-2F**, **HBDT-4Cl**, **FBDT-4Cl** and **CIBDT-4Cl**.

**Table S1.** Photovoltaic parameters of NF-OSCs based on **HBDT-4Cl**:**PBDB-T-2F** blend films coated at different spin speeds.

Spin speed(rpm) <sup>a</sup>	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
1000	0.899	17.92	63.75	10.27[10.06±0.16]

1500	0.898	17.79	64.76	10.35[10.15±0.16]
2000	0.893	16.27	64.78	9.41[9.27±0.10]
2500	0.890	14.86	65.78	8.70[8.55±0.21]

<sup>a</sup>All active layers were as-casted from a chlorobenzene solution of **HBDT-4Cl:PBDB-T-2F** ( $C_{\text{donor}}=10$  mg/ml, blend ratio 1:1).

**Table S2.** Photovoltaic parameters of NF-OSCs based on **HBDT-4Cl:PBDB-T-2F** blend films of different blend ratios.

blend ratio	$V_{\text{oc}}$ (V)	$J_{\text{sc}}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
1:0.5	0.883	17.25	56.84	8.66[8.53±0.11]
1:1	0.898	17.79	64.76	10.35[10.15±0.16]
1:1.5	0.905	15.89	66.11	9.52[9.38±0.11]
1:2	0.904	14.06	67.27	9.36[8.45±0.07]

**Table S3.** Photovoltaic parameters of NF-OSCs based on **FBDT-4Cl:PBDB-T-2F** blend films coated at different spin speeds.

Spin speed(rpm) <sup>a</sup>	$V_{\text{oc}}$ (V)	$J_{\text{sc}}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
1000	0.875	20.13	68.06	11.99[11.82±0.11]
1500	0.888	19.83	70.19	12.36[12.07±0.18]
2000	0.892	17.11	72.09	11.01[10.18±0.07]
2500	0.885	14.70	71.09	9.26[8.99±0.20]

<sup>a</sup>All active layers were as-casted from a chlorobenzene solution of **FBDT-4Cl:PBDB-T-2F** ( $C_{\text{donor}}=10$  mg/ml, blend ratio 1:1).

**Table S4.** Photovoltaic parameters of NF-OSCs based on **FBDT-4Cl:PBDB-T-2F** blend films of different blend ratios.

blend ratio	$V_{\text{oc}}$ (V)	$J_{\text{sc}}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
1:0.5	0.876	17.83	61.40	9.60[9.47±0.14]
1:1	0.888	19.83	70.19	12.36[12.07±0.18]
1:1.5	0.871	19.38	67.09	11.33[11.26±0.07]
1:2	0.885	18.47	67.34	11.01[10.84±0.15]

**Table S5.** Photovoltaic parameters of NF-OSCs based on **CIBDT-4Cl:PBDB-T-2F** blend films coated at different spin speeds.

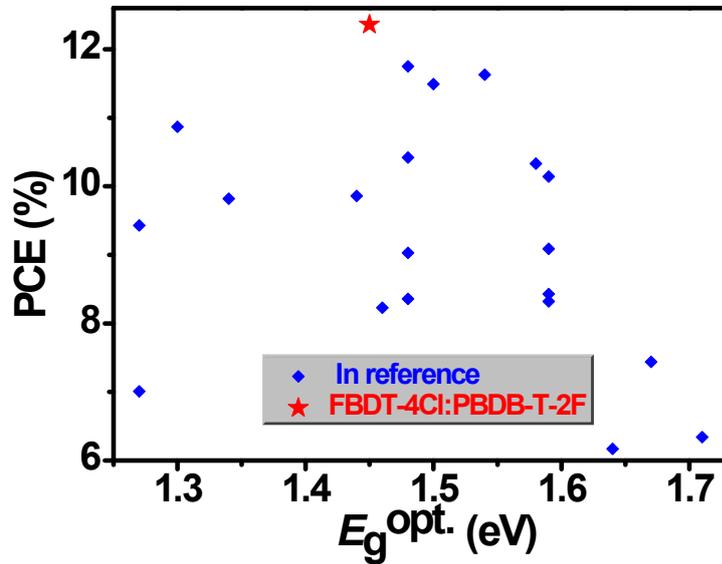
Spin speed(rpm) <sup>a</sup>	$V_{\text{oc}}$ (V)	$J_{\text{sc}}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
1000	0.871	19.85	66.38	11.48[11.14±0.25]
1500	0.879	19.02	69.71	11.65[11.27±0.27]
2000	0.879	16.96	70.28	10.48[10.17±0.23]

2500	0.880	14.75	70.44	9.14[8.56±0.37]
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<sup>a</sup>All active layers were as-casted from a chlorobenzene solution of **CIBDT-4Cl:PBDB-T-2F** ( $C_{\text{donor}}=10$  mg/ml, blend ratio 1:1).

**Table S6.** Photovoltaic parameters of NF-OSCs based on **CIBDT-4Cl:PBDB-T-2F** blend films of different blend ratios.

blend ratio	$V_{\text{oc}}$ (V)	$J_{\text{sc}}$ ( $\text{mA cm}^{-2}$ )	FF (%)	PCE (%)
1:0.5	0.866	17.27	62.20	9.30[8.49±0.10]
1:1	0.879	19.02	69.71	11.65[11.27±0.27]
1:1.5	0.872	18.82	68.65	11.28[11.21±0.07]
1:2	0.874	17.63	68.87	10.61[10.41±0.19]



**Figure S4.** PCE versus  $E_{\text{g}}^{\text{opt}}$  in our fluorinated central donor core functionalized A-D-A type NF-SMAs in comparison with other fluorinated central donor core functionalized A-D-A type NF-SMAs-based binary organic solar cells (PCE>6%).

**Table S7.** The key parameters of OSCs in fluorinated central donor core functionalized A-D-A type NF-SMAs/polymer donor based binary organic solar cells in comparison with our **FBDT-4Cl/PBDB-T-2F** based devices.

Active layer (D:A)	$V_{\text{oc}}$ [V]	$J_{\text{sc}}$ [ $\text{mA cm}^{-2}$ ]	FF [%]	$\text{PCE}_{\text{max}}^{\text{a}}$ [%]	Ref.
P3HT:DFPCBR	0.80	10.39	64.39	5.34 (5.25)	[S8]
PBDB-T:DF-PCNC	0.86	18.16	72.62	11.63 (11.59)	[S9]
PTQ10:DF-PCIC	1.04	6.51	54.13	3.68 (3.49)	[S10]
PTQ10:HC-PCIC	0.94	15.99	67.96	10.42 (10.23)	[S10]

PBDB-T-2F:HC-PCIC	0.89	18.13	72.06	11.75 (11.66)	[S10]
PBDB-T:DF-PCIC	0.89	15.28	61.87	8.43 (8.42)	[S10]
PBDB-T:FO-PCIC	0.90	15.02	61.12	8.32 (8.29)	[S10]
PBDB-T:HC-PCIC	0.73	17.53	69.08	9.03 (8.52)	[S10]
PBDB-T:DF-PCIC	0.91	15.66	72.0	10.14 (10.12)	[S11]
PBDB-T-2F:HF-PCIC	0.91	17.81	70.77	11.49	[S12]
PBDB-T-2F:HFO-PCIC	0.93	12.62	70.99	8.36	[S12]
PBDB-T-2F:OF-PCIC	0.91	13.76	73.37	9.09	[S12]
PBDB-T:DF-TCIC	0.86	16.39	58.0	8.23 (7.95)	[S13]
PBDB-T:HF-TCIC	0.76	20.04	65.0	9.86 (9.40)	[S13]
PBDB-T:NSTI	0.83	16.47	75.2	10.33	[S14]
PBTA-BO:IFBR	1.06	8.34	43.52	3.85 (3.65)	[S15]
PTB7-Th:T1	0.72	20.95	65.0	9.82 (9.67)	[S16]
PTB7-Th:T2	0.65	24.85	67.0	10.87 (10.65)	[S16]
PTB7-Th:T3	0.61	22.00	70.0	9.43 (9.23)	[S16]
PTB7-Th:T4	0.61	18.57	62.0	7.01 (6.86)	[S16]
PTB7-Th:FpO-ITIC	0.78	12.99	56.7	6.17 (6.10)	[S17]
PBTA-BO:IffBR	1.01	11.77	52.29	6.34 (6.24)	[S18]
PBDB-T:M-0F	0.99	1.88	30.95	0.58	[S19]
PBDB-T:M-1F	0.98	4.62	40.84	1.85	[S19]
PBDB-T:M-2F	0.95	6.25	44.54	2.65	[S19]
PTzBI:IFBR- <i>p</i>	1.00	11.6	62.3	7.44 (7.3)	[S20]
PTzBI:IFBR- <i>d</i>	0.99	9.4	55.9	5.28 (5.2)	[S20]
<b>PBDB-T-2F:FBDT-4Cl</b>	<b>0.888</b>	<b>19.83</b>	<b>70.19</b>	<b>12.36 (12.07)</b>	<b>This work</b>

<sup>a</sup>The values in parentheses are the average PCE values.

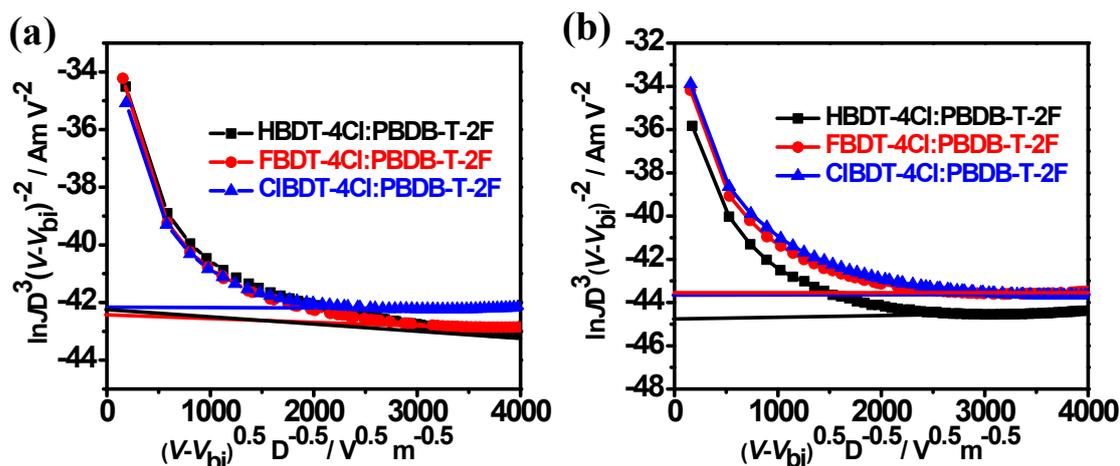


Figure S5. (a) The dark  $J$ - $V$  plots of hole-only devices based on optimal **HBDT-4Cl:PBDB-T-2F**, **FBDT-4Cl:PBDB-T-2F** and **CIBDT-4Cl:PBDB-T-2F** blend films, respectively. (b) The dark  $J$ - $V$  plots of electron-only devices based on optimal **HBDT-4Cl:PBDB-T-2F**, **FBDT-4Cl:PBDB-T-2F** and **CIBDT-4Cl:PBDB-T-2F** blend films.

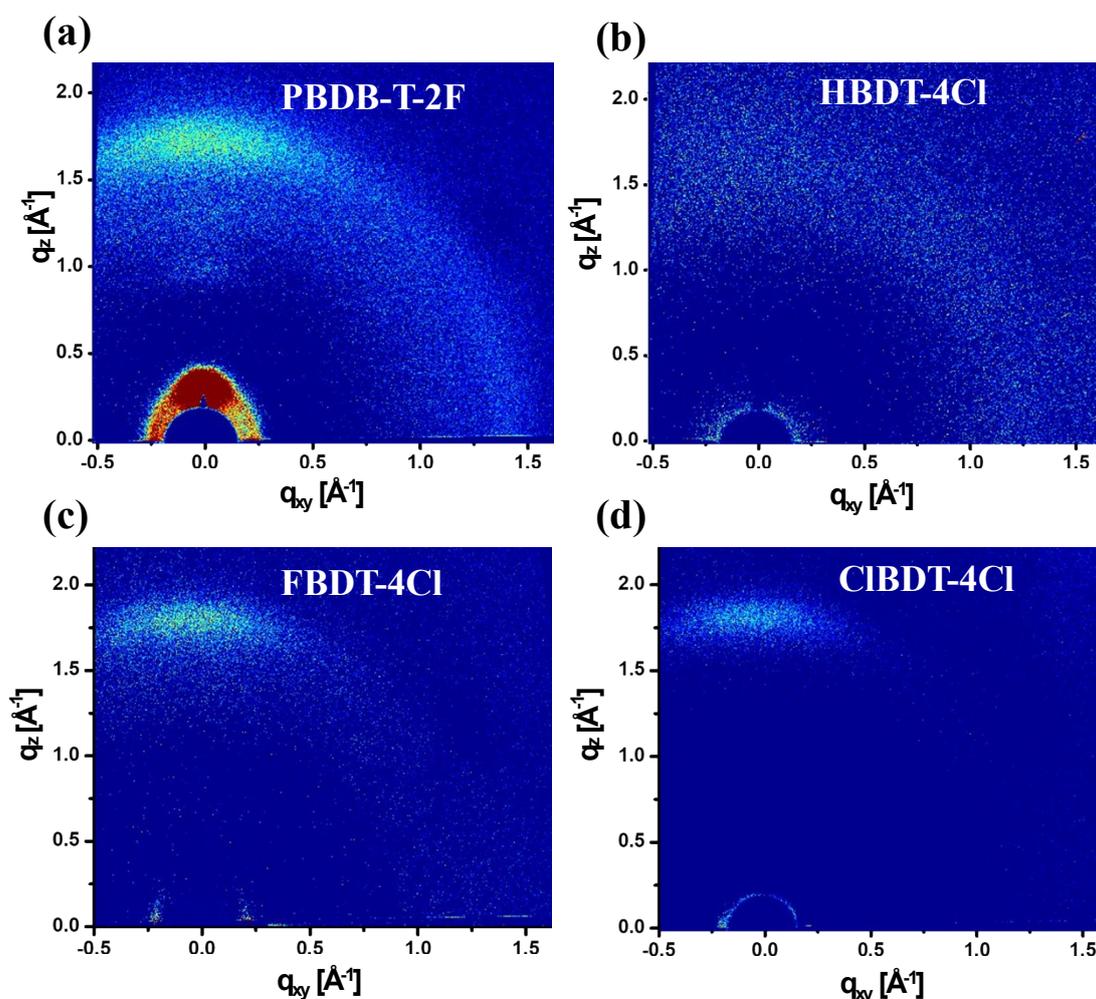
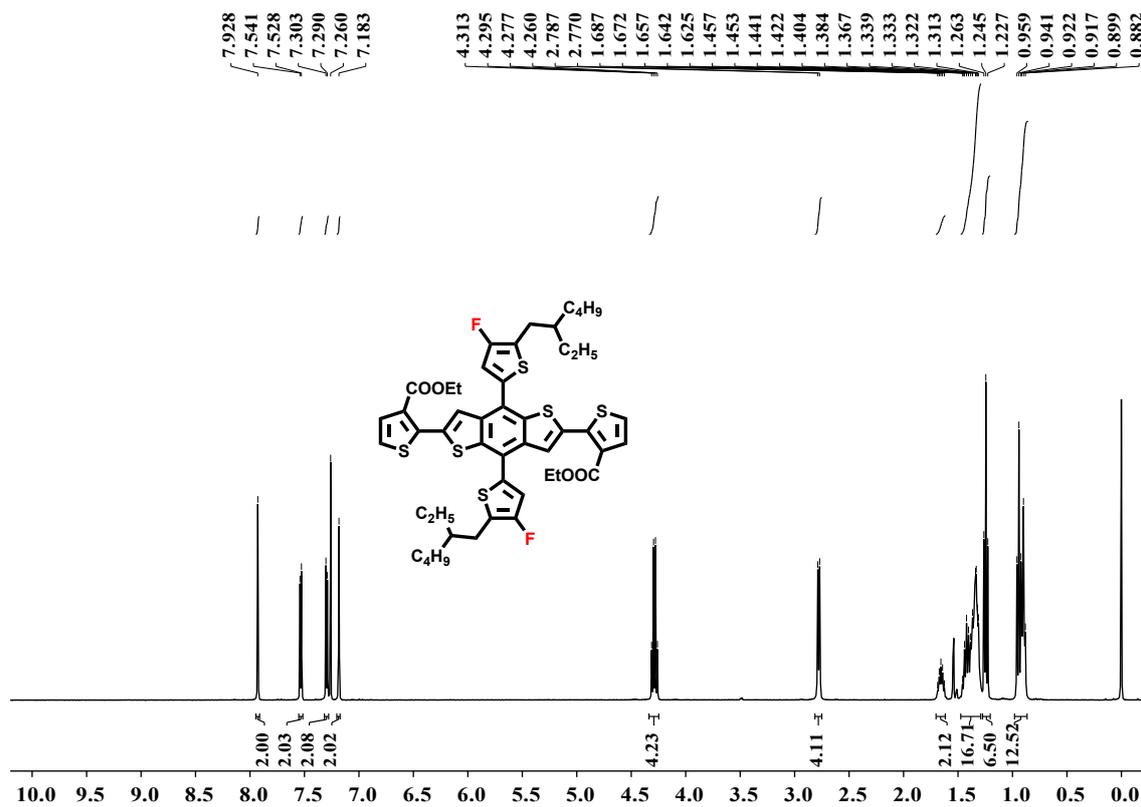


Figure S6. GIXD patterns for neat films (a) **PBDB-T-2F**, (b) **HBDT-4Cl**, (c) **FBDT-4Cl**, (d) **CIBDT-4Cl**.

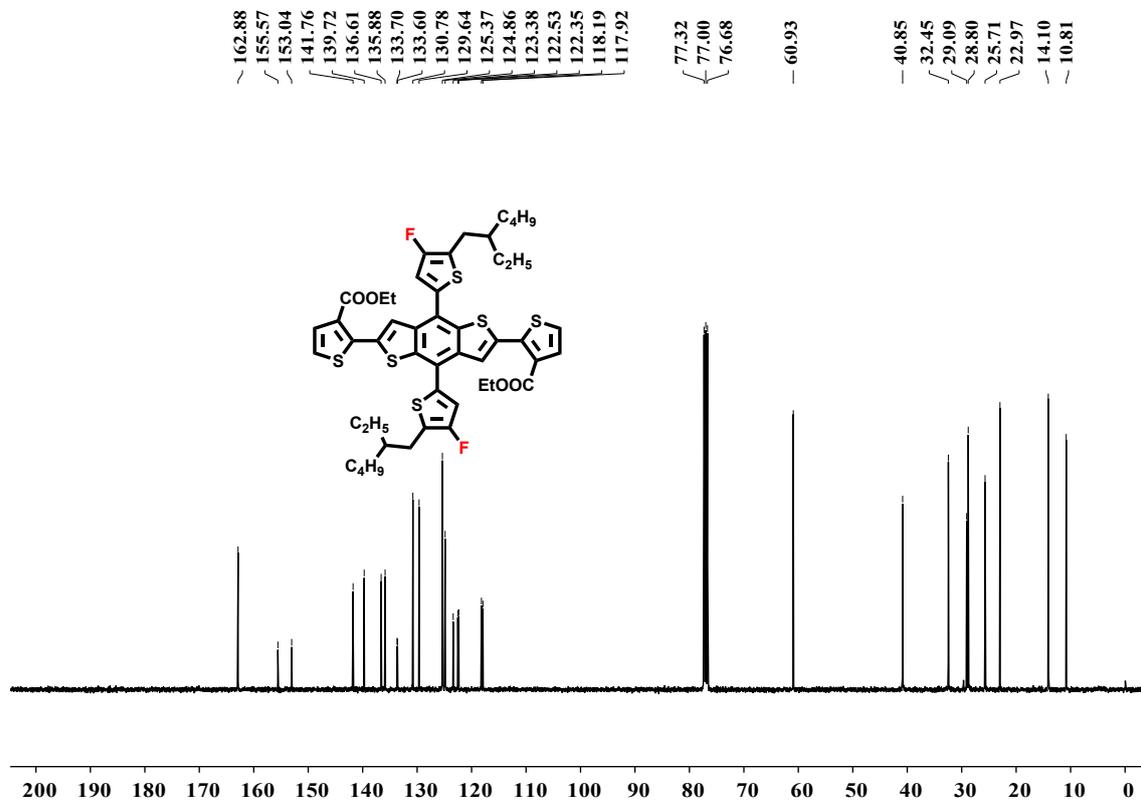
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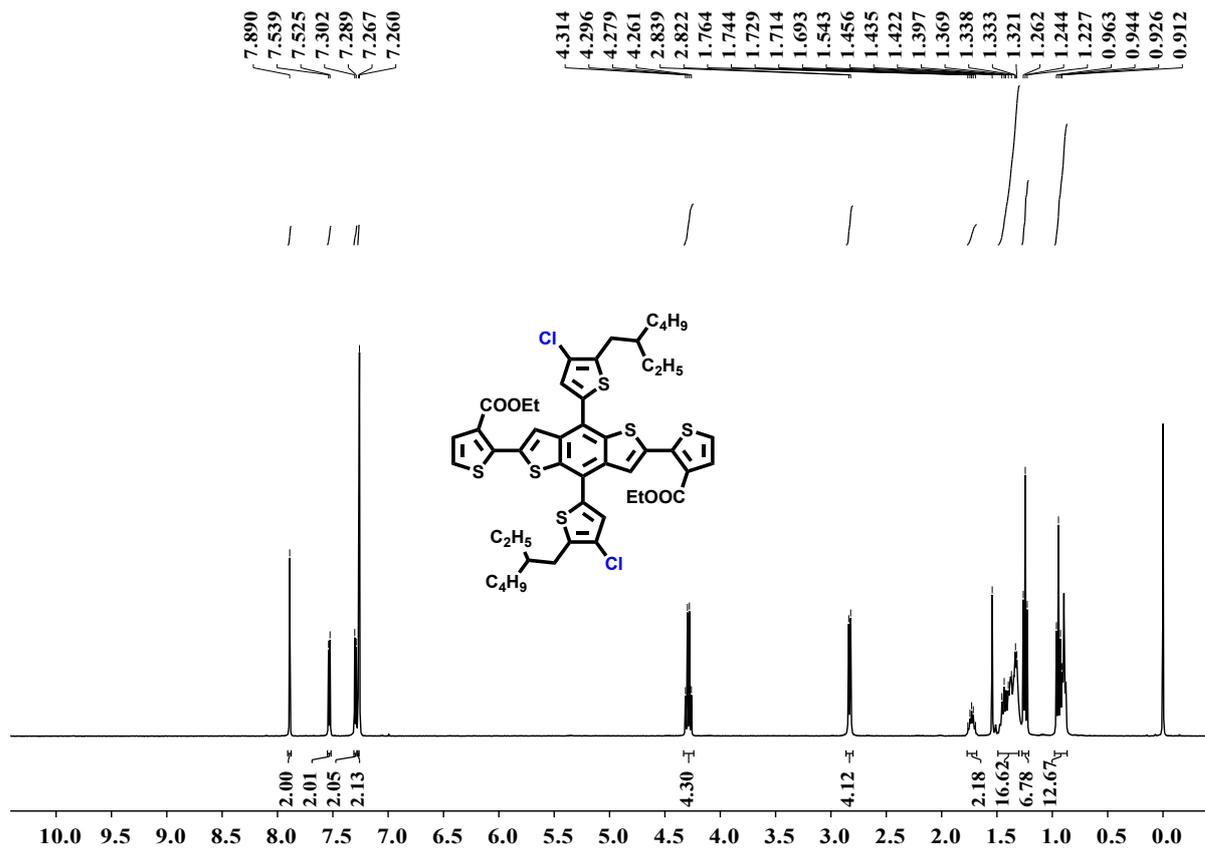
# Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR, and MALDI-TOF MS Spectra



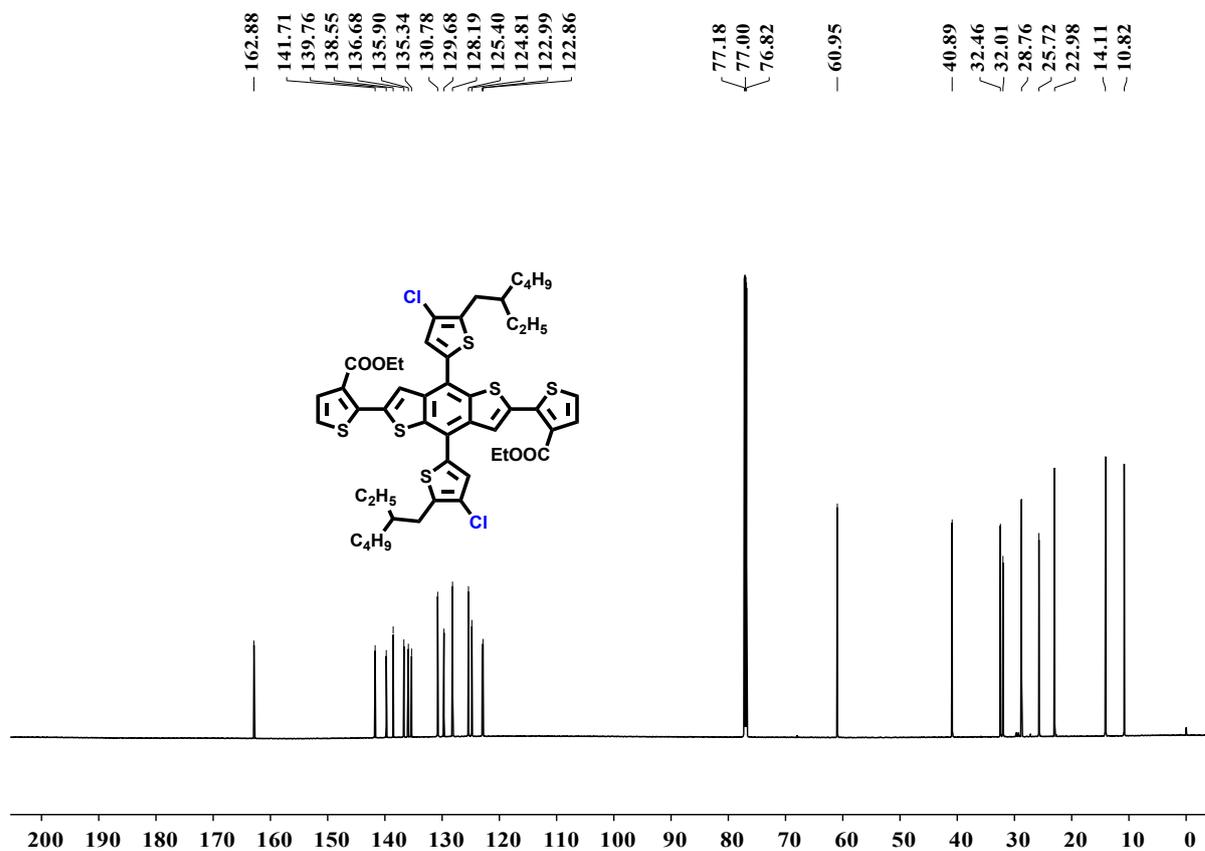
$^1\text{H}$  NMR spectrum for compound **2a**



$^{13}\text{C}$  NMR spectrum for compound **2a**

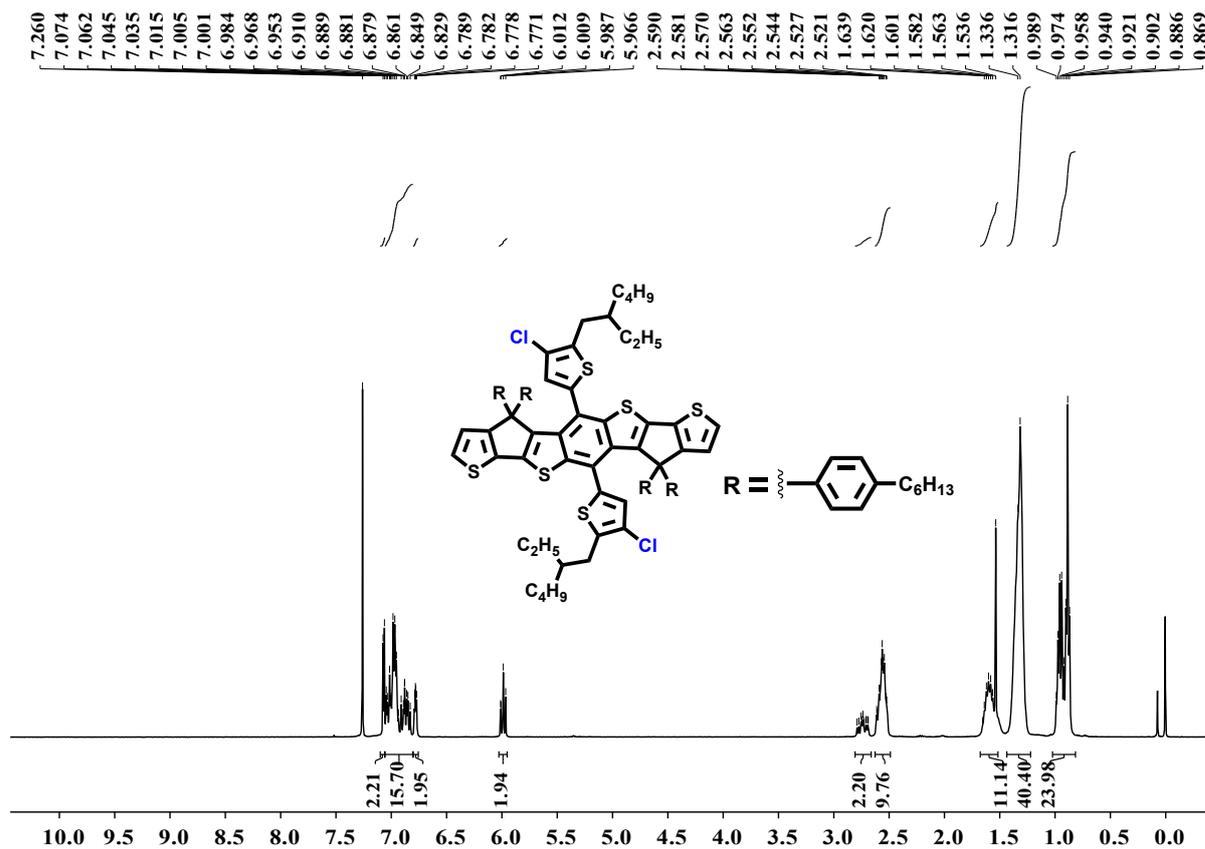


$^1\text{H}$  NMR spectrum for compound 2b

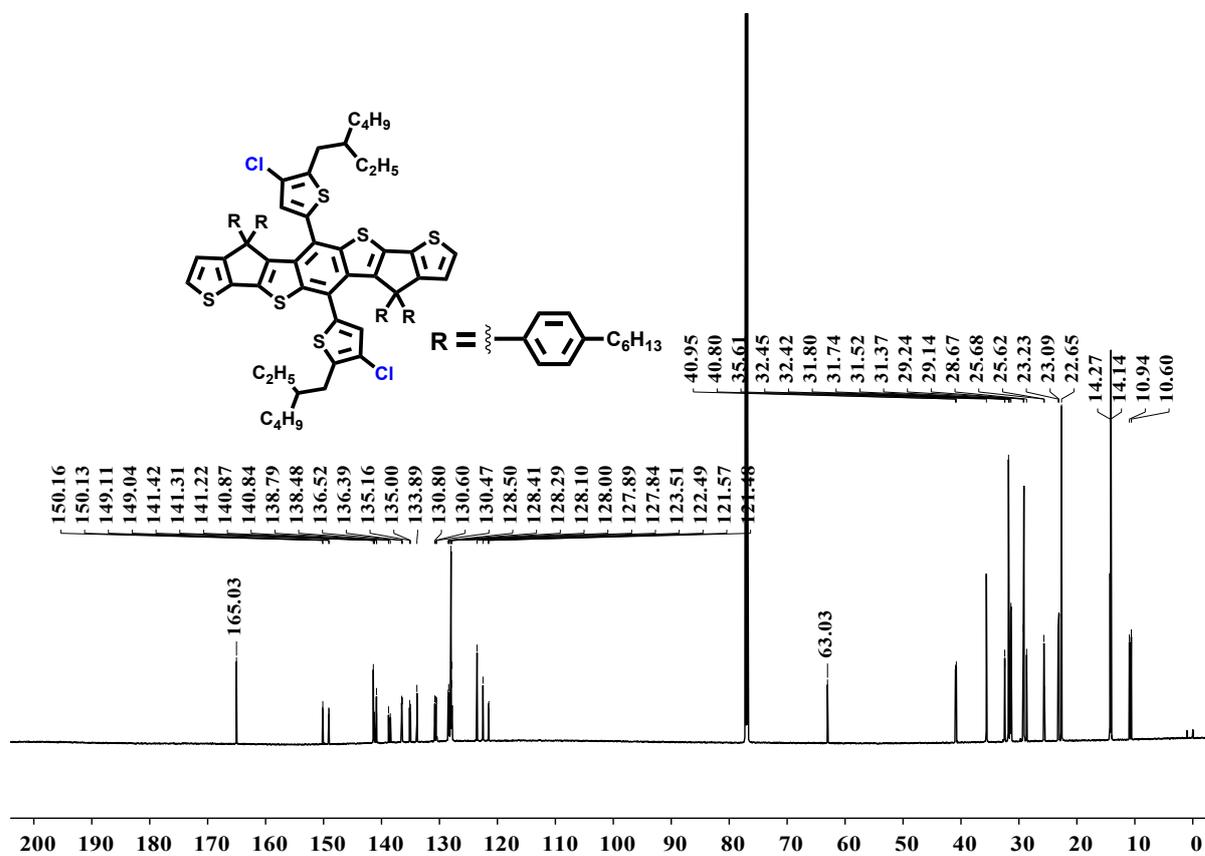


$^{13}\text{C}$  NMR spectrum for compound 2b

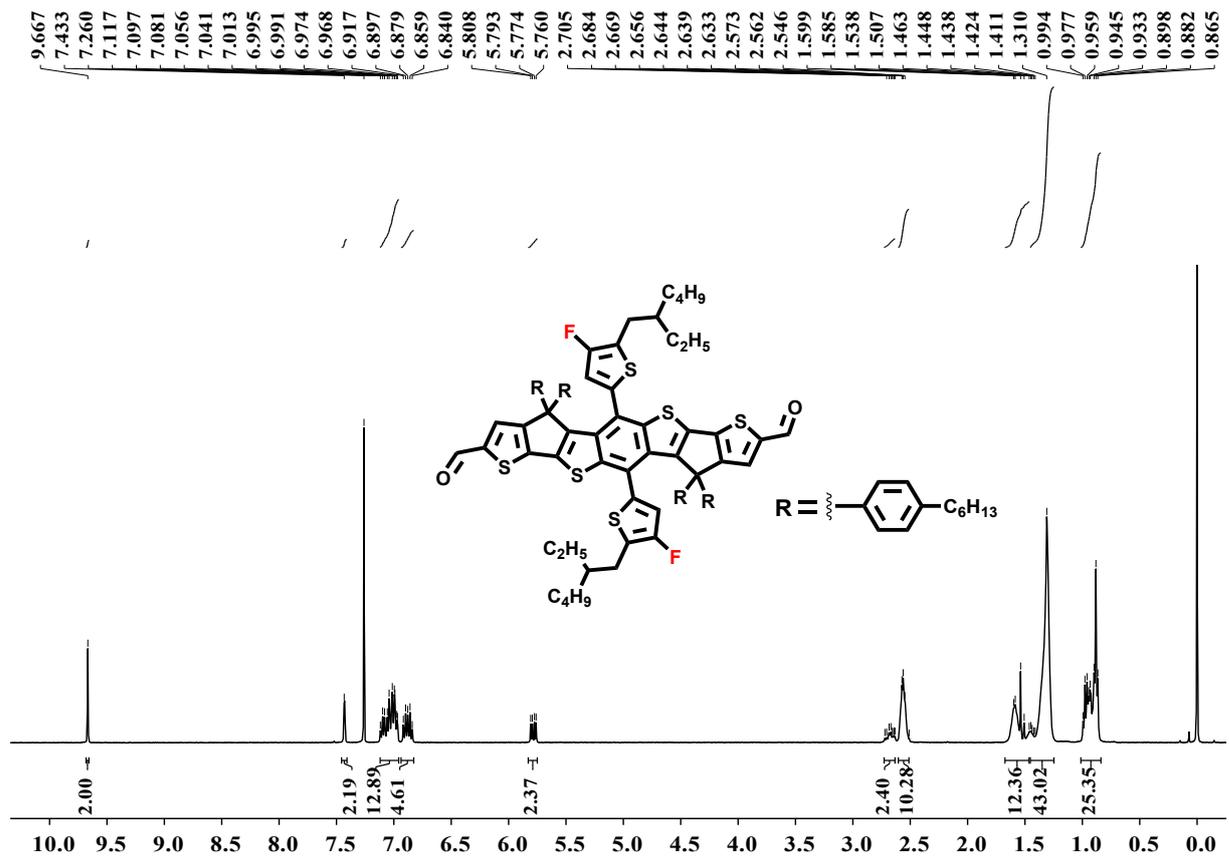




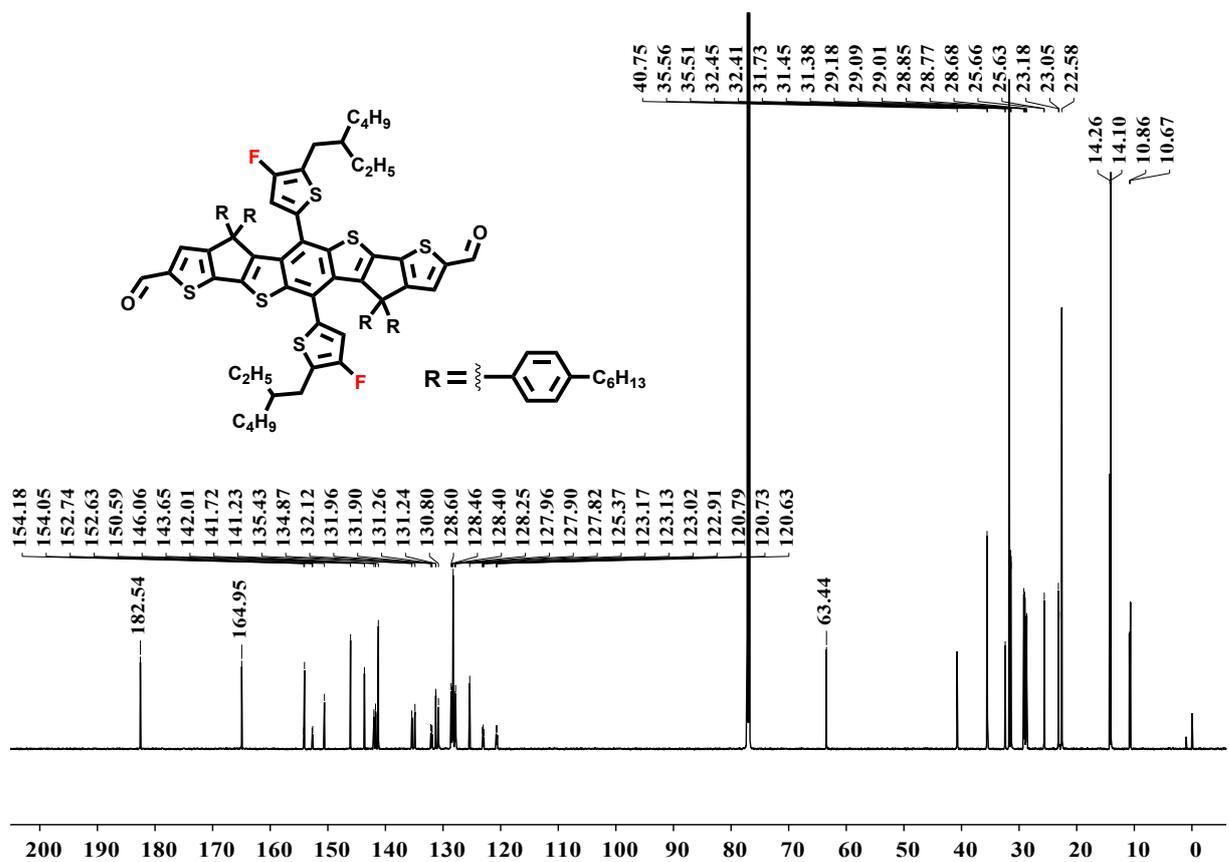
<sup>1</sup>H NMR spectrum for CIBDT



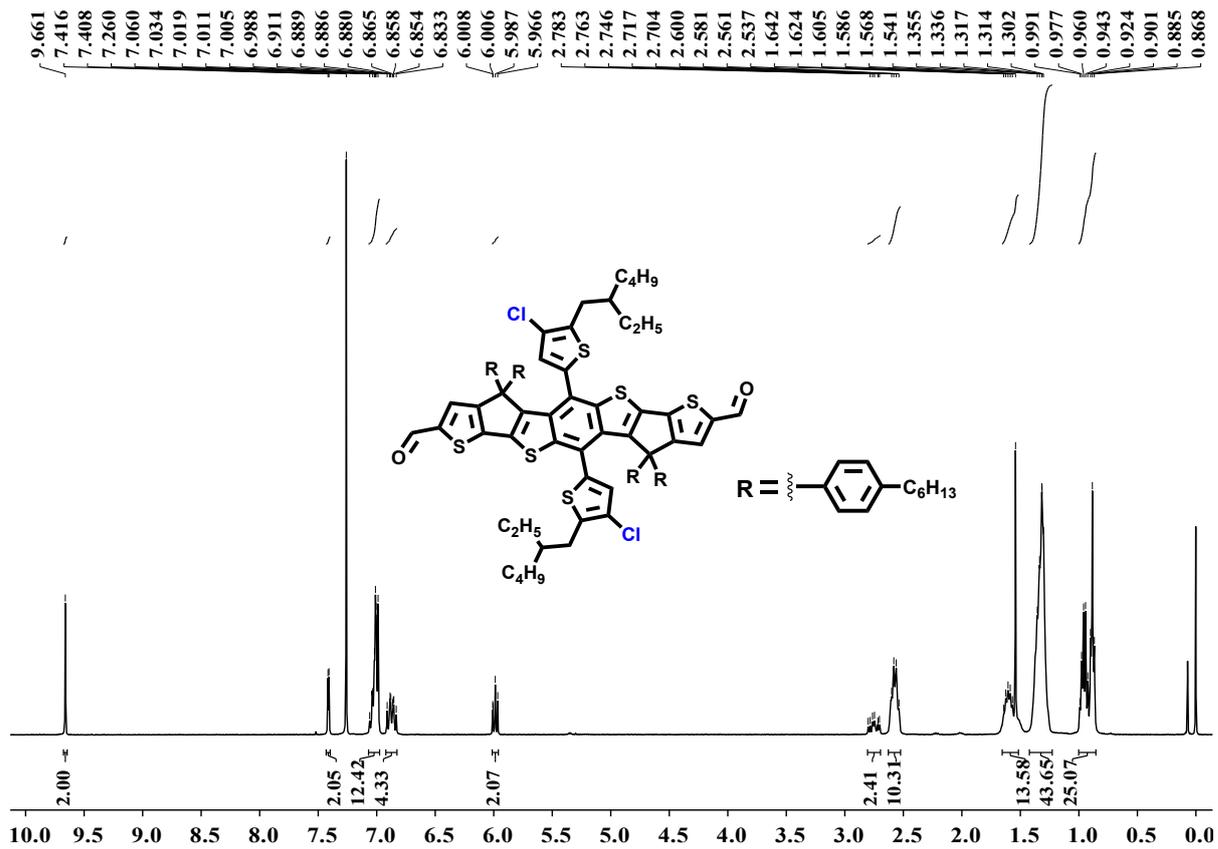
<sup>13</sup>C NMR spectrum for CIBDT



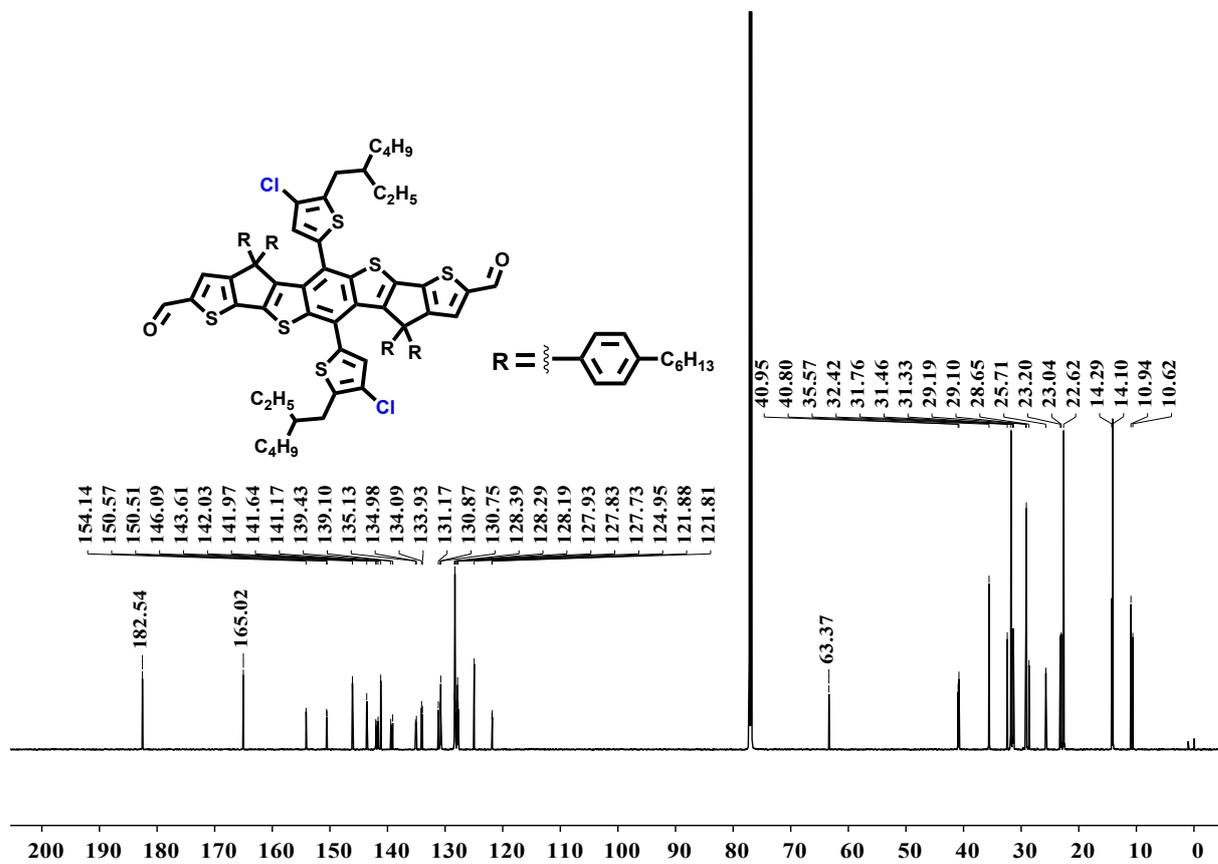
<sup>1</sup>H NMR spectrum for FBDT-CHO



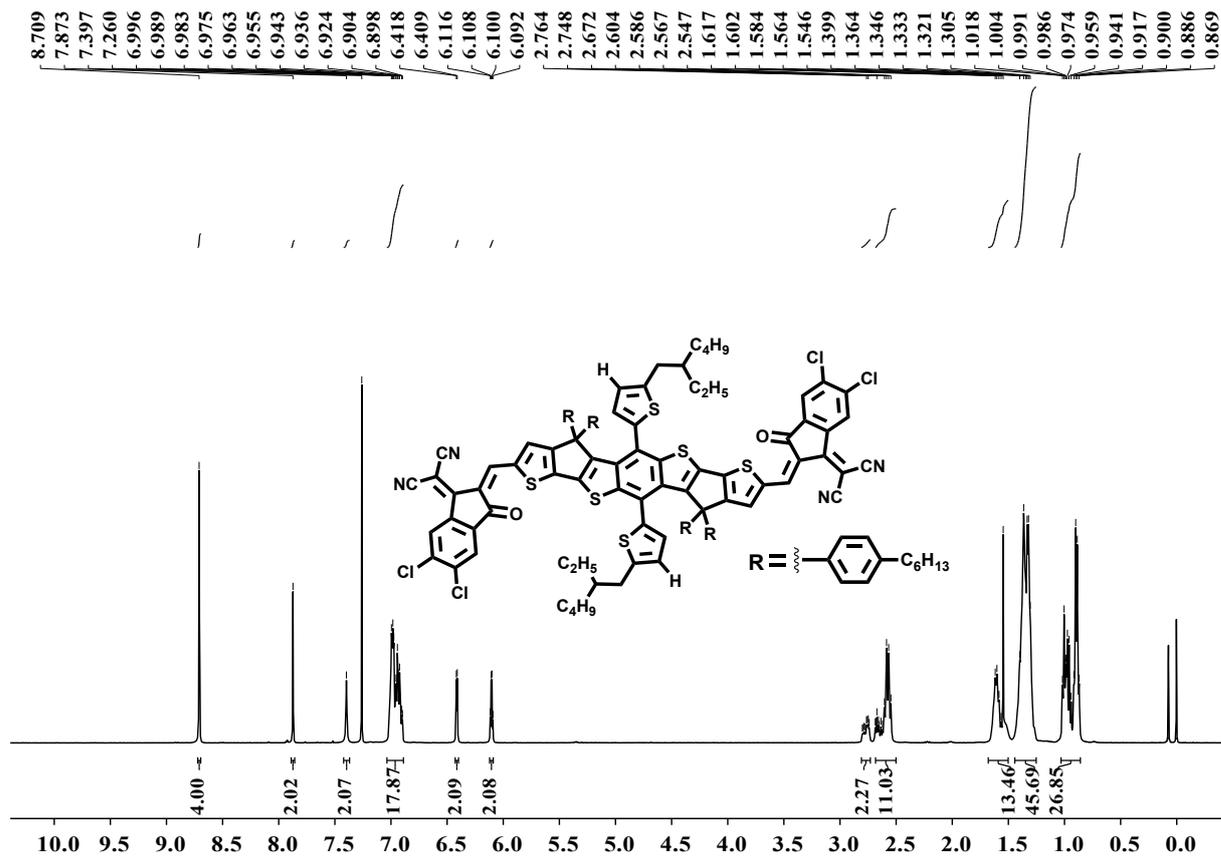
<sup>13</sup>C NMR spectrum for FBDT-CHO



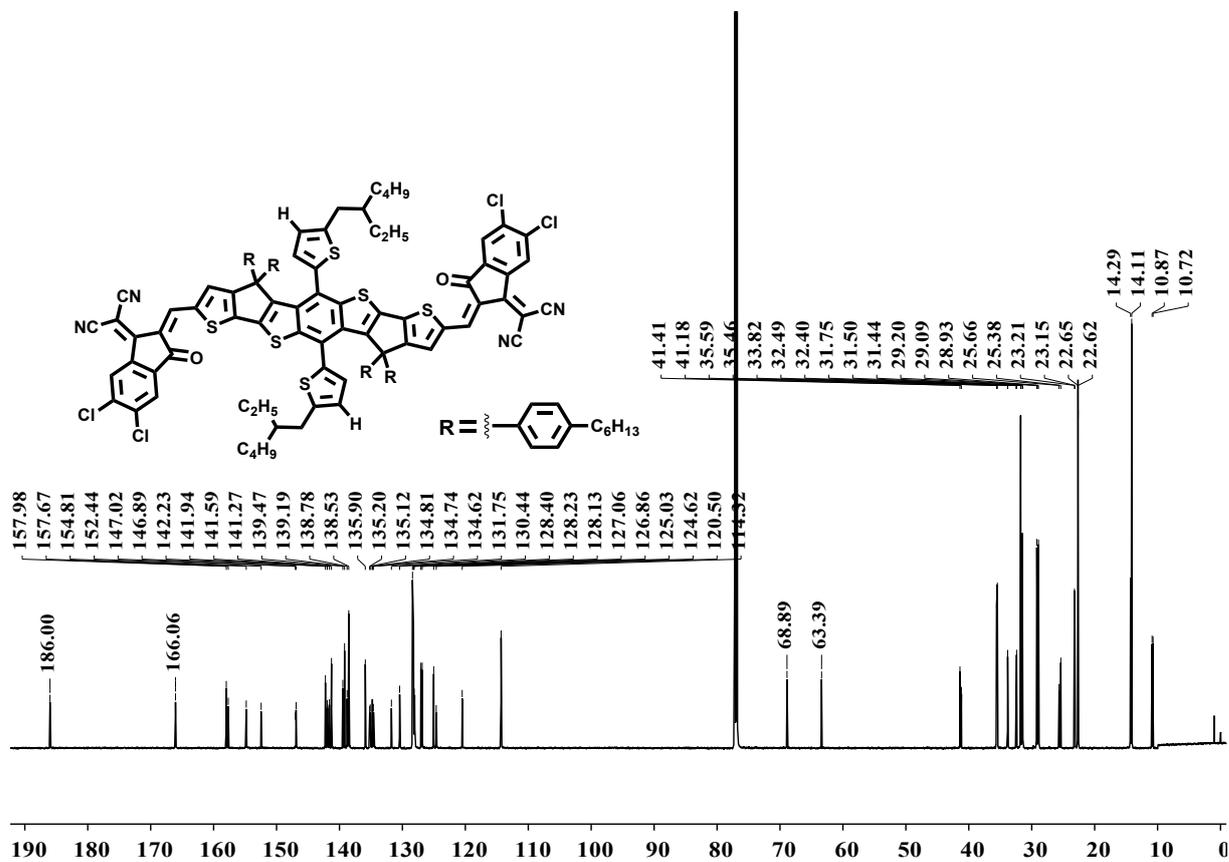
**<sup>1</sup>H NMR spectrum for CIBDT-CHO**



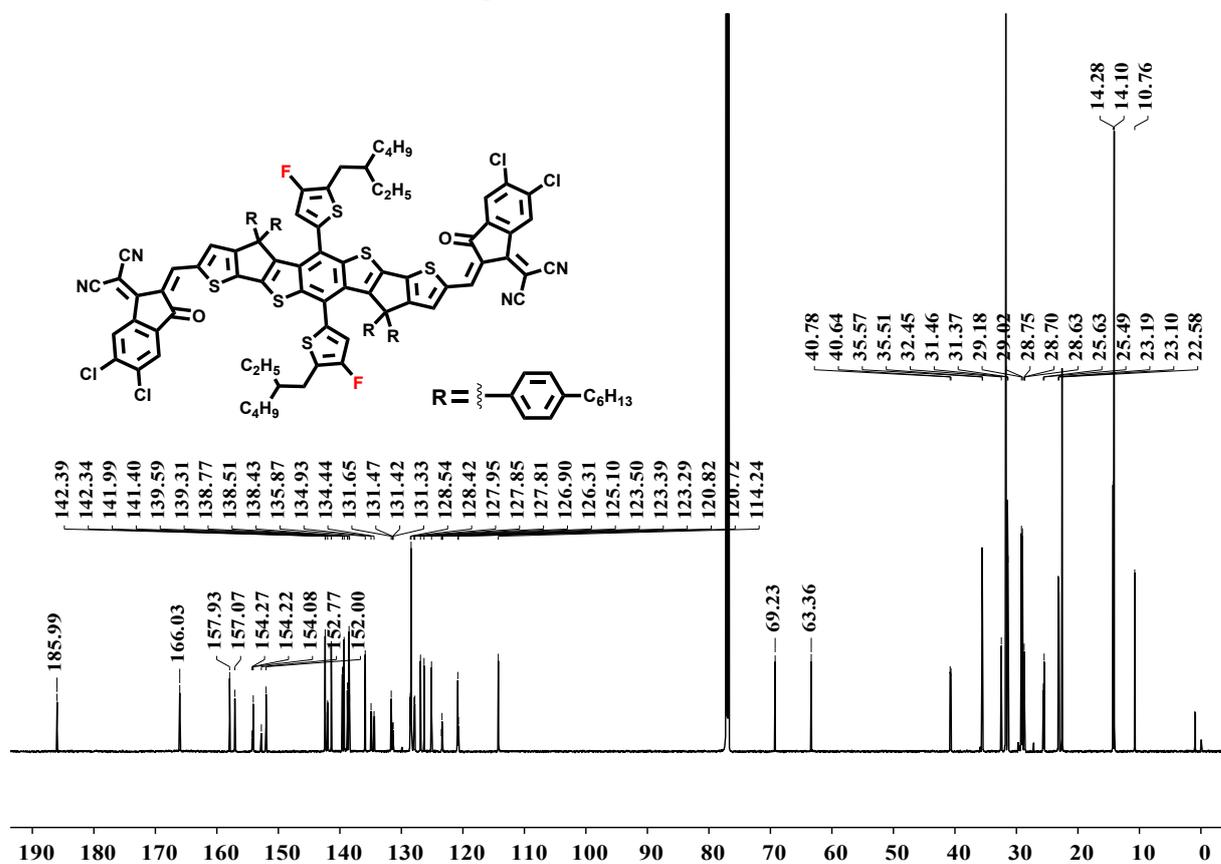
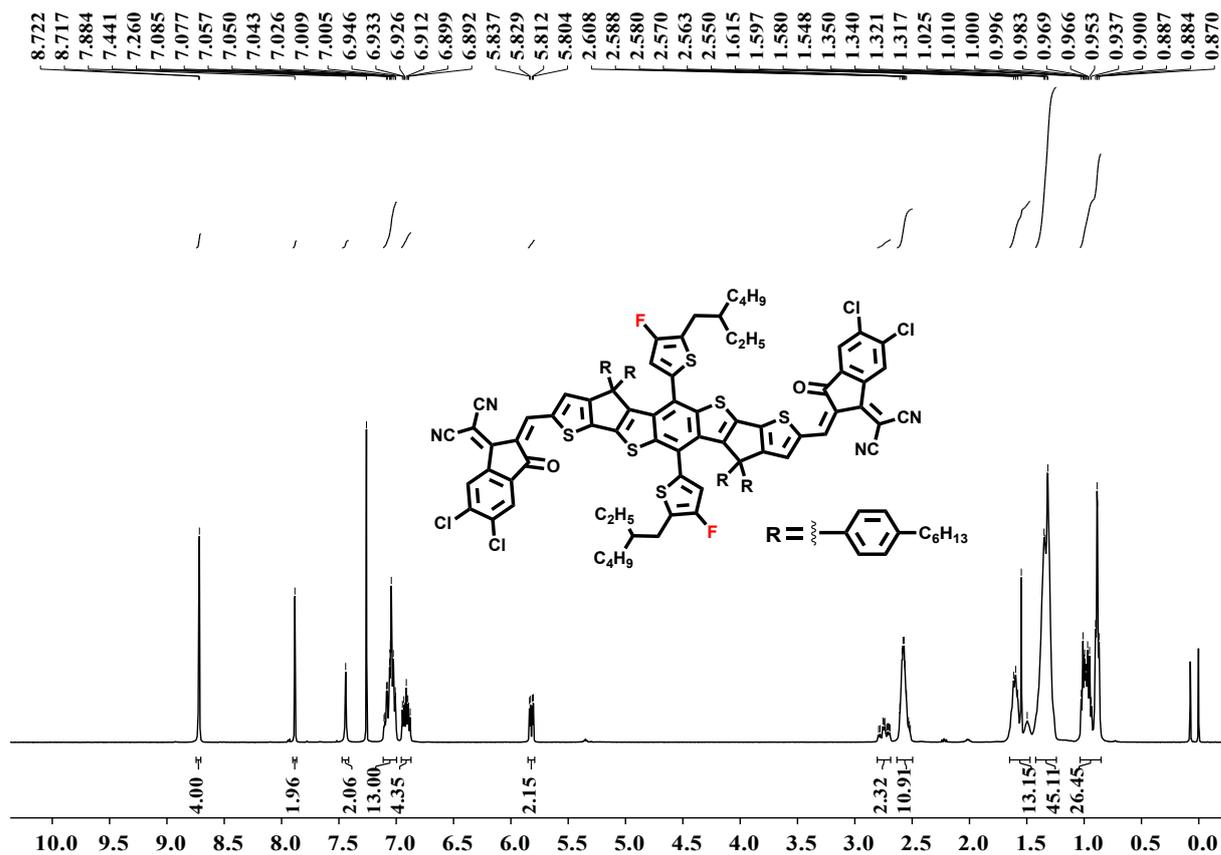
**<sup>13</sup>C NMR spectrum for CIBDT-CHO**

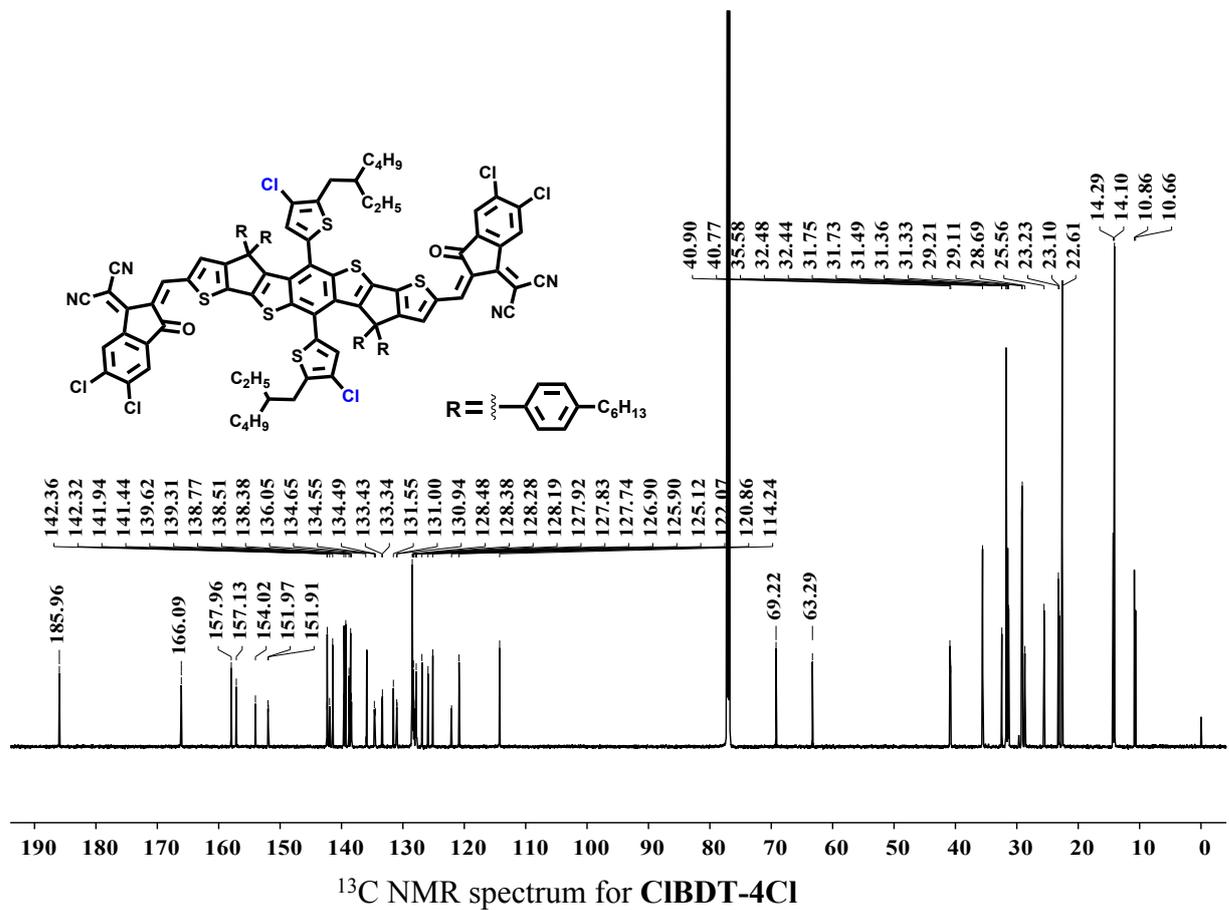
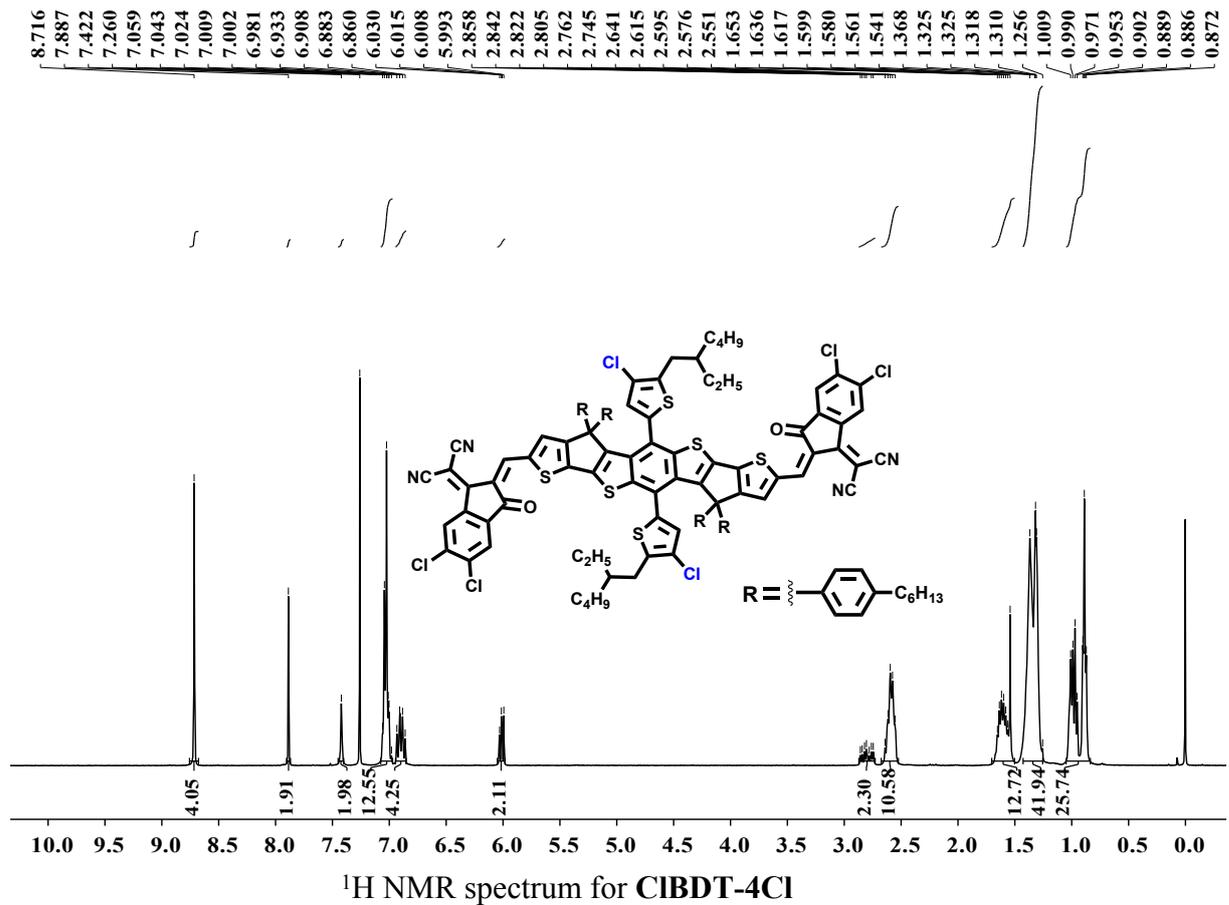


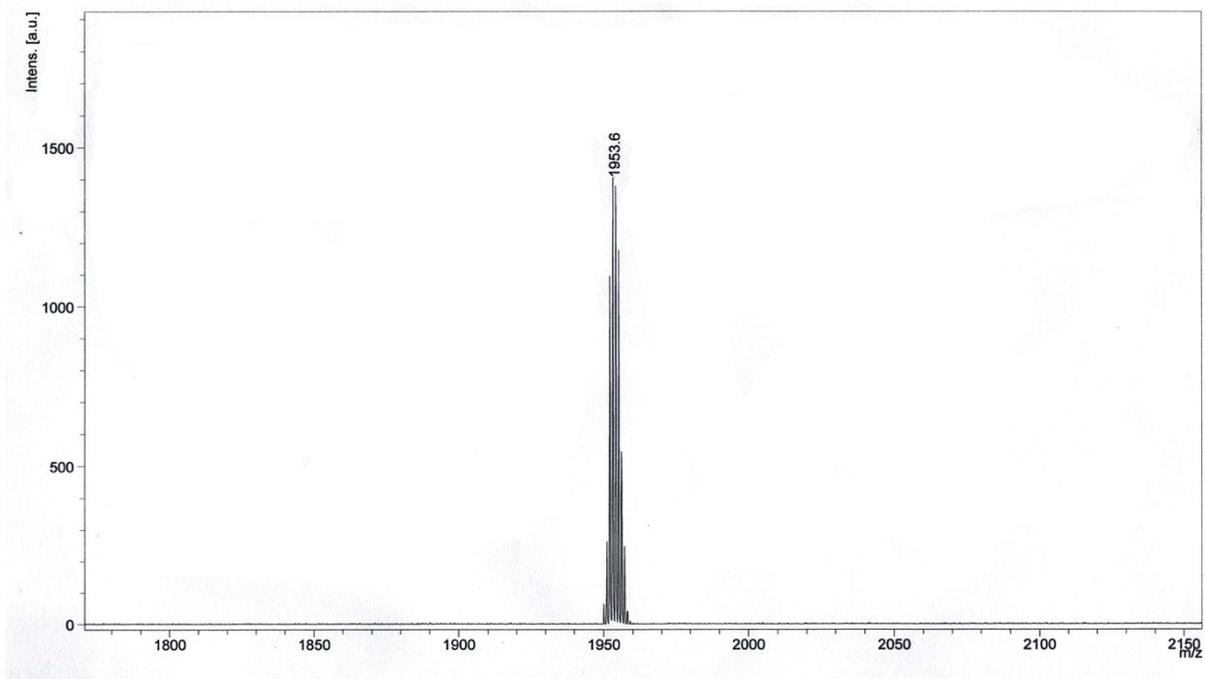
<sup>1</sup>H NMR spectrum for HBDT-4Cl



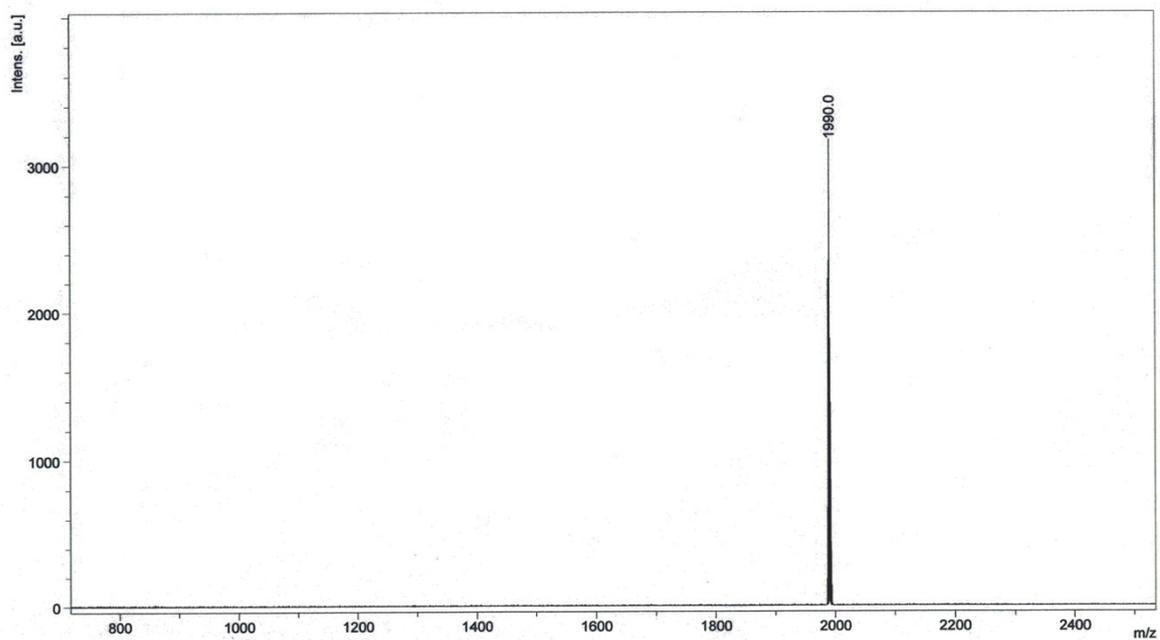
<sup>13</sup>C NMR spectrum for HBDT-4Cl



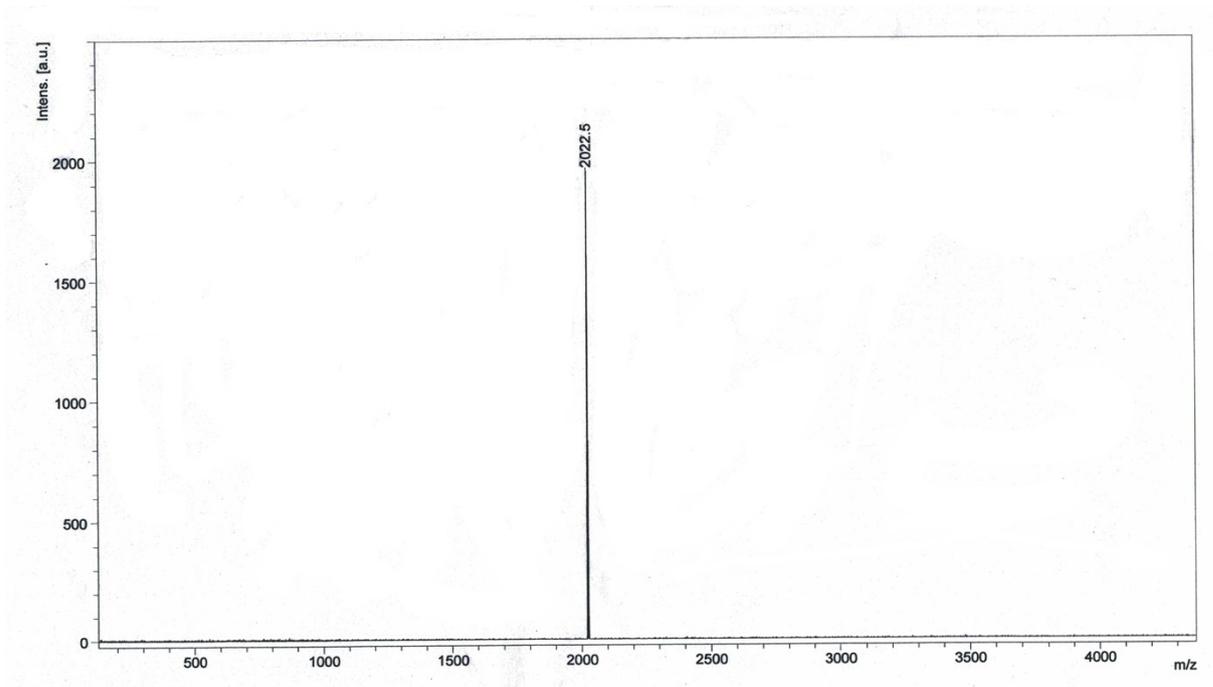




MALDI-TOF mass spectrum of **HBDT-4Cl**



MALDI-TOF mass spectrum of **FBDT-4Cl**



MALDI-TOF mass spectrum of **CIBDT-4Cl**