Materials and Measurements

All reactions and operations were carried out under argon (Ar) atmosphere with the use of standard Schlenk techniques. All chemicals, unless otherwise specified, were purchased from Adamas or other commercial resources and used as received. Toluene and dichloromethane were purified by distillation with calcium hydride. N-(2-hexyldecyl)thiophen-3-amine and N-(2-octyldodecyl)thiophen-3-amine were synthesized according to previously reported procedures.[1]

The ^1H and ^{13}C NMR spectra were collected on a Bruker AVANCE III HD 400 spectrometer operating at 400 MHz in deuterated chloroform solution with TMS as reference, respectively. High-resolution mass spectroscopy (HRMS) measurements were performed on a Shimadzu LCMS-IT-TOF and MALDI-TOF experiments were performed using a Bruker Autoflex II. Data collection from single crystals was conducted using a Bruker SMART APEX CCD diffractometer at 173 K. Molecular weights of the polymers were determined using an Agilent Technologies PL-GPC 220 high-temperature chromatograph in 1,2,4-trichlorobenzene at 150 °C using a calibration curve of polystyrene standards. UV-Vis spectra were measured using a PerkinElmer Lambda 365 spectrophotometer. Cyclic voltammetry (CV) of polymer film was conducted using a CHI 660E Electrochemical Analyzer with a standard three-electrode system consisting of ITO working electrode, Ag/AgCl reference electrode and Pt wire counter electrode, calibrated against ferrocene, in acetonitrile with 0.1 M Bu_4NPF_6 at a scan rate of 100 mV s^{-1}. HOMO and LUMO energy levels were calculated from the equations: $E_{LUMO} = -(E_{red} - E_{Fc} + 4.8)$ eV and $E_{HOMO} = -(E_{ox} - E_{Fc} + 4.8)$ eV, where E_{red} and E_{ox} are taken from the onset of reduction and oxidation, respectively, and E_{Fc} is the half-wave potential of ferrocene. The thermogravimetric analysis (TGA) was carried out on a NETZSCH TG209 F1 Thermo Gravimetric Analyzer and the differential scanning calorimetry (DSC) experiments were carried out on a TA Q200 instrument. Both the TGA and DSC was performed under purified nitrogen gas flow with a temperature ramp rate of 10 °C/min. The X-ray diffraction (XRD) pattern was collected using a Rigaku Ultima IV diffractometer with Cu KR radiation. Atomic force microscopy (AFM) image was obtained by using a Smart SPM operated in tapping mode. Photoluminescence (PL) spectra was performed using HORIBA FluoroMax-4. Two-dimensional grazing incidence X-ray diffraction (2D-GIXD) analyses were measured at the XEUSS SAXS/WAXS equipment. The data were obtained with an area Pilatus 100k detector with a resolution of 195 × 487 pixels (0.172 mm × 0.172 mm). The X-ray wavelength was 1.54 Å, and the incidence angle was 0.2°. The samples were spin-coated onto the ZnO/Si substrate.

Fabrication and Characterization of PSCs: The ITO glass substrates were cleaned sequentially under sonication with isopropyl alcohol, detergent, deionized water, and isopropyl alcohol and then dried at 60 °C in a baking oven overnight, followed by an oxygen plasma treatment for 4 min. The ZnO precursor solution was prepared according to literature. It was spin-coated on ITO substrates at 4000 rpm for 30 s. The films (≈30 nm) were annealed at 200 °C in air for 30 min. Then the substrates were transferred into glove box under nitrogen (N_2). The solutions of PBDT-BTP-HD:IT-M (1:1, w/w) and PBDT-BTP-OD:IT-M (1:1.5, w/w) were prepared in chlorobenzene (CB) with the polymer concentration of 8 mg mL^{-1} and stirred on a hot plate at 80 °C overnight. The active layers were spin-coated from the related blend solutions on the substrates to obtain the thicknesses of 100 nm. The film thicknesses were determined with a Dektak 150 stylus surface profiling system (Veeco). The active layer films were then thermal annealed at corresponding temperature for 10 min before the next procedure. Subsequently, the substrates were transferred into the vacuum chamber. At a vacuum level of 1×10^{-6} Torr, a thin layer (10 nm) of MoO_3 was then thermally deposited as the anode interlayer, followed by thermal deposition of 100 nm of Ag as the top electrode through a shadow mask. The active area of all devices was 0.08 cm^2. The current density-voltage (J-V) curves were measured on a computer-controlled Keithley 2400 source meter under 1 sun, the AM 1.5 G spectra was from a class solar simulator (Enlitech, Taiwan), and the light intensity was 100 mW cm^{-2} as calibrated by a China General Certification Center-certified reference monocrystal silicon cell (Enlitech). Before the J-V test, a physical mask with an aperture with precise area of 0.04 cm^2 was used to define the device area. The measurements of J_{sc} and V_{oc} were performed on the above system. The EQE spectra measurements were performed on a commercial EQE measurement system (QE-R3011, Enlitech).

Fabrication and Characterization of Electron-Only and Hole-Only Devices: Devices were fabricated to measure the electron and hole mobilities by using the SCLC method. The electron-only device structure was ITO/Al/active layers/Ca/Al; the hole-only device structure was ITO/PEDOT:PSS/active layers/MoO_3/Ag. The mobility was determined by fitting the dark current to the model of a single-carrier SCLC, which is described by the equation:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu V^2}{8d^3}$$

where J is the current density, μ is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layers, and V is the effective voltage. The effective voltage was obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the series resistance of the whole device except for the active layers from the applied voltage (V_{appl}), $V = V_{appl} - V_{bi} - V_s$. The mobility can be calculated from the slope of the $J^{1/2}$-V curves.

Synthesis of N^1,N^4-bis(2-hexyldecyl)-N^1,N^4-di(thiophen-3-yl)succinamide (DTSA-HD)

To a solution of succinic acid (709 mg, 6.00 mmol) in $CHCl_3$ (30 mL) were added oxalyl chloride (3.65 mL, 42.8 mmol) and 3 drops of DMF. The mixture was stirred for 8 hours at room temperature. The solvent was removed under vacuum to obtain dichloride, which was used in next step without purification. To the solution of N-(2-hexyldecyl)thiophen-3-amine (3.98 g, 12.3 mmol) and triethylamine (2 mL) in dry CH_2Cl_2 (30 mL) at 0 °C was slowly added a solution of dichloride in dry CH_2Cl_2 (20 mL). The mixture was stirred at room temperature overnight. Then, the mixture was poured into water and extracted with CH_2Cl_2 three times. The organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified through a silica gel column with a mixture of petroleum/ethyl acetate (20:1) as eluent to give a brown oil (2.01 g, 46%). ^1H NMR (400 MHz, Chloroform-*d*): δ 7.30 (m, 2H), 7.12 – 7.07 (m, 2H), 6.93 (m, 2H), 3.55 (d, *J* = 7.3 Hz, 4H), 2.38 (s, 4H), 1.44 (s, 2H), 1.23 (m, 48H), 0.94 – 0.82 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 172.3, 141.3, 126.5, 125.7, 121.1, 52.4, 36.1, 31.9, 31.8, 31.1, 30.0, 29.7, 29.7, 29.6, 29.3, 26.3, 26.3, 22.7, 22.6, 14.1, 14.1. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{44}H_{76}N_2O_2S_2$, 751.5240; found, 751.5229.

Synthesis of N^1,N^4-bis(2-octyldodecyl)-N^1,N^4-di(thiophen-3-yl)succinamide (DTSA-OD)

To a solution of succinic acid (1.16 g, 9.86 mmol) in $CHCl_3$ (40 mL) were added oxalyl chloride (4.99 mL, 58.6 mmol) and 3 drops of DMF. The mixture was stirred for 4 hours at room temperature. The solvent was removed under vacuum to obtain dichloride, which was used in next step without purification. To the solution of N-(2-octyldodecyl)thiophen-3-amine (7.85 g, 20.7 mmol) and triethylamine (3 mL) in dry CH_2Cl_2 (30 mL) at 0 °C was slowly added a solution of dichloride in dry CH_2Cl_2 (20 mL). The mixture was stirred at room temperature overnight. Then, the mixture was poured into water and extracted with CH_2Cl_2 three times. The organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified through a silica gel column with a mixture of petroleum/ethyl acetate (20:1) as eluent to give a brown oil (2.47 g, 30%). ^1H NMR (400 MHz, Chloroform-*d*): δ 7.30 (dd, *J* = 5.1, 3.2 Hz, 2H), 7.09 (d, *J* = 2.8 Hz, 2H), 6.93 (d, *J* = 5.0 Hz, 2H), 3.54 (d, *J* = 7.3 Hz, 4H), 2.38 (s, 4H), 1.45 (m, 2H), 1.38 – 1.05 (m, 64H), 0.87 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 172.3, 141.2, 126.5, 125.7, 121.1, 52.4, 36.1, 31.9, 31.9, 31.1, 30.0, 29.7, 29.6, 29.6, 29.6, 29.3, 29.3, 26.3, 22.7, 14.1. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{52}H_{92}N_2O_2S_2$, 863.6492; found, 863.6477.

Synthesis of 4,4'-bis(2-hexyldecyl)-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTP-HD)

Phosphorus oxychloride (0.48 mL, 5.12 mmol) was added dropwise to DMF (5 mL) at 0 °C, and the resulting solution was stirred at room temperature for 30 minutes. A solution of DTSA-HD (747 mg, 1.02 mmol) in DMF (10 mL) was added and the stirred mixture was heated to 95 °C for 90 minutes. After cooling, the mixture was poured into crushed ice and the resulting suspension was treated with excess saturated aqueous solution of NaOAc and stirred for 1 hour at room temperature. Then, the mixture was extracted with CH_2Cl_2 three times and the organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified through a silica gel column with a mixture of petroleum/ethyl acetate (50:1) as eluent to give a yellow oil (714 mg, 93%). ^1H NMR (400 MHz, Chloroform-*d*): δ 8.59 (s, 2H), 7.55 (d, *J* = 5.5 Hz, 2H), 7.03 (d, *J* = 5.5 Hz, 2H), 4.20 (s, 4H), 2.04 (m, 2H), 1.44 – 1.14 (m, 48H), 0.86 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.9, 142.6, 132.5, 122.0, 119.8, 119.7, 119.1, 50.5, 36.9, 31.9, 31.8, 31.5, 30.0, 29.7, 29.6, 29.3, 26.5, 26.5, 22.7, 22.6, 14.1, 14.1. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{46}H_{72}N_2O_2S_2$, 749.5108; found, 749.5108

Synthesis of 4,4'-bis(2-octyldodecyl)-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTP-OD)

Phosphorus oxychloride (1.05 mL, 11.3 mmol) was added dropwise to DMF (10 mL) at 0 °C, and the resulting solution was stirred at room temperature for 30 minutes. A solution of DTSA-OD (1.90 g, 2.25 mmol) in DMF (20 mL) was added and the stirred mixture was heated to 95 °C for 90 minutes. After cooling, the mixture was poured into crushed ice and the resulting suspension was treated with excess saturated aqueous solution of NaOAc and stirred for 1 hour at room temperature. Then, the mixture was extracted with CH_2Cl_2 three times and the organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified through a silica gel column with a mixture of petroleum/ethyl acetate (50:1) as eluent to give a yellow oil (1.87 g, 96%). ^1H NMR (400 MHz, Chloroform-*d*): δ 8.58 (s, 2H), 7.55 (d, *J* = 5.5 Hz, 2H), 7.03 (d, *J* = 5.5 Hz, 2H), 4.20 (s, 4H), 2.03 (m, 2H), 1.44 – 1.14 (m, 64H), 0.86 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.3, 143.3, 133.5, 129.7, 122.3, 118.6, 116.6, 50.5, 37.1, 31.9, 31.9, 31.6, 30.0, 29.6, 29.6, 29.6, 29.3, 29.3, 26.6, 22.7, 22.7, 14.1. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{54}H_{88}N_2O_2S_2$, 861.6360; found, 861.6338.

Synthesis of 2,2'-dibromo-4,4'-bis(2-hexyldecyl)-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTP-HD-diBr)

To a solution of BTP-HD (882 mg, 1.18 mmol) in chloroform (35 mL) was added N-bromosuccinimide (461 mg, 2.59 mmol) and a catalytic amount of acetic acid, and the reaction mixture was stirred for 24 hours at room temperature. Then, the mixture was poured into water and extracted with CH_2Cl_2 three times. The organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified through a silica gel column with a mixture of petroleum/ethyl acetate (30:1) as eluent to give a yellow oil (944 mg, 88%). ^1H NMR (400 MHz, Chloroform-*d*): δ 8.50 (s, 2H), 7.02 (s, 2H), 4.11 (s, 4H), 1.99 (m, 2H), 1.43 – 1.17 (m, 48H), 0.87 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.9, 142.6, 132.5, 122.0, 119.8, 119.7, 119.1, 50.5, 36.9, 31.9, 31.8, 31.5, 30.0, 29.7, 29.6, 29.3, 26.5, 26.5, 22.7, 22.6, 14.1, 14.1. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{46}H_{70}Br_2N_2O_2S_2$, 927.3138; found, 927.3118.

Synthesis of 2,2'-dibromo-4,4'-bis(2-octyldodecyl)-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTP-OD-diBr)

To a solution of BTP-OD (1.75 g, 2.03 mmol) in chloroform (30 mL) was added N-bromosuccinimide (1.08 g, 6.08 mmol) and a catalytic amount of acetic acid, and the reaction mixture was stirred for 12 hours at room temperature. Then, the mixture was poured into water and extracted with CH_2Cl_2 three times. The organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified through a silica gel column with a mixture of petroleum/ethyl acetate (30:1) as eluent to give a yellow oil (1.12 g, 54%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.49 (s, 2H), 7.01 (s, 2H), 4.10 (s, 4H), 1.98 (m, 2H), 1.41 – 1.15 (m, 64H), 0.86 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 160.8, 142.5, 132.5, 121.9, 119.7, 119.7, 119.1, 50.5, 36.9, 31.9, 31.8, 31.4, 30.0, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 26.5, 22.6, 22.6, 14.1. HRMS (ESI, m/z): [M+H]$^+$, calcd. for $C_{54}H_{86}Br_2N_2O_2S_2$, 1017.4570; found, 1017.4551.

Synthesis of 4,4'-bis(2-hexyldecyl)-2,2'-di(thiophen-2-yl)-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTP-T-HD)

A solution of BTP-HD-diBr (944 mg, 1.04 mmol) and 2-(Tributylstannyl)thiophene (970 mg, 2.60 mmol) in dry toluene (30 mL) was degassed for 30 min followed by the addition of $Pd(PPh_3)_4$ (60 mg, 0.052 mmol). The mixture was stirred at 110 °C for 12 h. The reaction mixture was poured into water, extracted with CH_2Cl_2 and then dried over anhydrous Na_2SO_4. After removal of solvent, the crude product was purified by silica gel using a mixture of petroleum/CH_2Cl_2/ethyl acetate (50:50:1) as eluent to afford a red solid (822 mg, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.58 (s, 2H), 7.34 (d, J = 5.0 Hz, 2H), 7.31 (d, J = 3.6 Hz, 2H), 7.08 (d, J = 4.4 Hz, 2H), 7.06 (d, J = 3.4 Hz, 2H), 4.19 (s, 4H), 2.05 (m, 2H), 1.31 (m, 48H), 0.86 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.2, 143.5, 141.0, 136.6, 133.0, 128.2, 126.2, 125.3, 122.0, 117.8, 112.3, 50.3, 37.0, 31.9, 31.9, 31.6, 30.0, 29.7, 29.6, 29.3, 26.7, 26.6, 22.7, 22.6, 14.1, 14.1. MS (MALDI-TOF, m/z): [M+H]$^+$, calcd. for $C_{54}H_{76}N_2O_2S_4$, 913.486; found, 913.415.

Synthesis of 4,4'-bis(2-octyldodecyl)-2,2'-di(thiophen-2-yl)-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTP-T-OD)

A solution of BTP-OD-diBr (1.05 g, 1.03 mmol) and 2-(Tributylstannyl)thiophene (0.82 mL, 2.58 mmol) in dry toluene (30 mL) was degassed for 30 min followed by the addition of $Pd(PPh_3)_4$ (60 mg, 0.052 mmol). The mixture was stirred at 110 °C for 9 hours. The reaction mixture was poured into water, extracted with CH_2Cl_2 and then dried over anhydrous Na_2SO_4. After removal of solvent, the crude product was purified by silica gel using a mixture of petroleum/CH_2Cl_2/ethyl acetate (50:50:1) as eluent to afford a red solid (884 mg, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.58 (s, 2H), 7.33 (dd, J = 5.1, 1.1 Hz, 2H), 7.31 (dd, J = 3.7, 1.1 Hz, 2H), 7.08 (dd, J = 5.1, 3.6 Hz, 2H), 7.06 (s, 2H), 4.19 (s, 4H), 2.05 (m, 2H), 1.46 – 1.17 (m, 64H), 0.86 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.2, 143.5, 141.0, 136.7, 133.0, 128.2, 126.2, 125.3, 122.0, 117.8, 112.3, 50.3, 37.0, 31.9, 31.9, 31.6, 30.0, 29.7, 29.6, 29.6, 29.4, 29.3, 26.7, 22.7, 22.7, 14.1. MS (MALDI-TOF, m/z): [M+H]$^+$, calcd. for $C_{62}H_{92}N_2O_2S_4$, 1025.611; found, 1025.671.

Synthesis of 2,2'-bis(5-bromothiophen-2-yl)-4,4'-bis(2-hexyldecyl)-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTP-T-HD-diBr)

To a solution of BTP-T-HD (822 mg, 0.900 mmol) in chloroform (30 mL) was added N-bromosuccinimide (352 mg, 1.98 mmol), and the reaction mixture was stirred for 12 hours at room temperature. Then, the mixture was poured into water and extracted with CH_2Cl_2 three times. The organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified through a silica gel column with a mixture of petroleum/CH_2Cl_2/ethyl acetate (50:50:1) as eluent to give a red solid (612 mg, 63%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.59 (s, 2H), 7.06 (d, *J* = 3.9 Hz, 2H), 7.04 (d, *J* = 3.9 Hz, 2H), 6.98 (s, 2H), 4.18 (s, 4H), 2.03 (s, 2H), 1.46 – 1.17 (m, 48H), 0.93 – 0.81 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.1, 143.4, 139.8, 138.0, 133.0, 131.0, 125.3, 122.2, 117.9, 113.1, 112.4, 50.3, 37.0, 31.9, 31.9, 31.6, 30.0, 29.7, 29.6, 29.3, 26.6, 26.6, 22.7, 22.7, 14.1.

Synthesis of 2,2'-bis(5-bromothiophen-2-yl)-4,4'-bis(2-octyldodecyl)-[6,6'-bithieno[3,2-b]pyridine]-5,5'(4H,4'H)-dione (BTP-T-OD-diBr)

To a solution of BTP-T-OD (650 mg, 0.634 mmol) in chloroform (30 mL) was added N-bromosuccinimide (248 mg, 1.39 mmol), and the reaction mixture was stirred for 12 hours at room temperature. Then, the mixture was poured into water and extracted with CH_2Cl_2 three times. The organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified through a silica gel column with a mixture of petroleum/CH_2Cl_2/ethyl acetate (50:50:1) as eluent to give a red solid (511 mg, 68%). ^{1}H NMR (400 MHz, Chloroform-*d*): δ 8.58 (s, 2H), 7.05 (d, *J* = 3.9 Hz, 2H), 7.03 (d, *J* = 3.9 Hz, 2H), 6.98 (s, 2H), 4.17 (s, 4H), 2.03 (m, 2H), 1.43 – 1.18 (m, 64H), 0.87 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 161.1, 143.4, 139.8, 138.0, 132.9, 131.0, 125.3, 122.2, 117.9, 113.1, 112.3, 50.3, 37.0, 31.9, 31.9, 31.6, 30.0, 29.7, 29.6, 29.6, 29.4, 29.3, 26.6, 22.7, 14.1. MS (MALDI-TOF, m/z): $[M+H]^+$, calcd. for $C_{62}H_{90}Br_2N_2O_2S_4$, 1181.432; found, 1181.452.

Synthesis of polymer PBDT-BTP- HD

BTP-T-HD-diBr (60 mg, 0.056 mmol) and BDT-diTin (51 mg, 0.056 mmol) were charged in a 25 mL three-neck flask under argon. After adding toluene (4 mL), the mixture was degassed by two freeze/pump/thew cycles to remove O_2. Then $Pd_2(dba)_3$ (1.5 mg, 3 mol%) and $P(o\text{-tol})_3$ (2.1 mg, 12 mol%) were added. The mixture was degassed twice more. Then the mixture was heated at 110 °C for 1 hour. After cooling to room temperature, the mixture was poured into methanol. The precipitate was collected and washed by Soxhlet extraction with acetone, hexane and chloroform sequentially. The polymer was recovered as a solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum, affording a dark red solid (74 mg, 88%). M_n = 7.05 kDa, PDI = 3.33.

Synthesis of polymer PBDT-BTP- OD

The polymerization procedure for BTP-T-OD-diBr (70 mg, 0.059 mmol) and BDT-diTin (54 mg, 0.059 mmol) was the same as that of PBDT-BTP- HD. PBDT-BTP-OD was obtained as a dark red solid (80 mg, 84%). M_n = 7.85 kDa, PDI = 2.93.

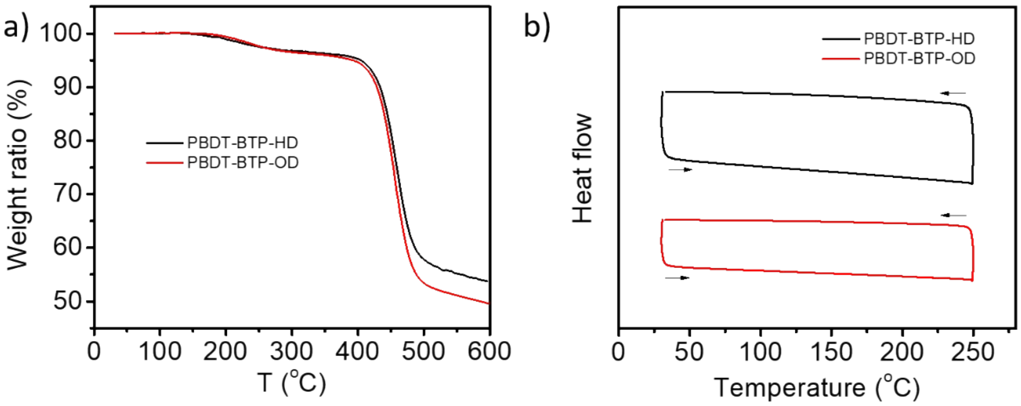


Figure S1. a) TGA curves and b) DSC curves of PBDT-BTP-HD and PBDT-BTP-OD.

Table S1. Molecular weights and thermal properties of PBDT-BTP-HD and PBDT-BTP-OD.

Polymer	M_n (KDa)	M_w (KDa)	PDI	T_d (°C)
PBDT-BTP-HD	7.05	23.5	3.33	404
PBDT-BTP-OD	7.85	23.0	2.93	392

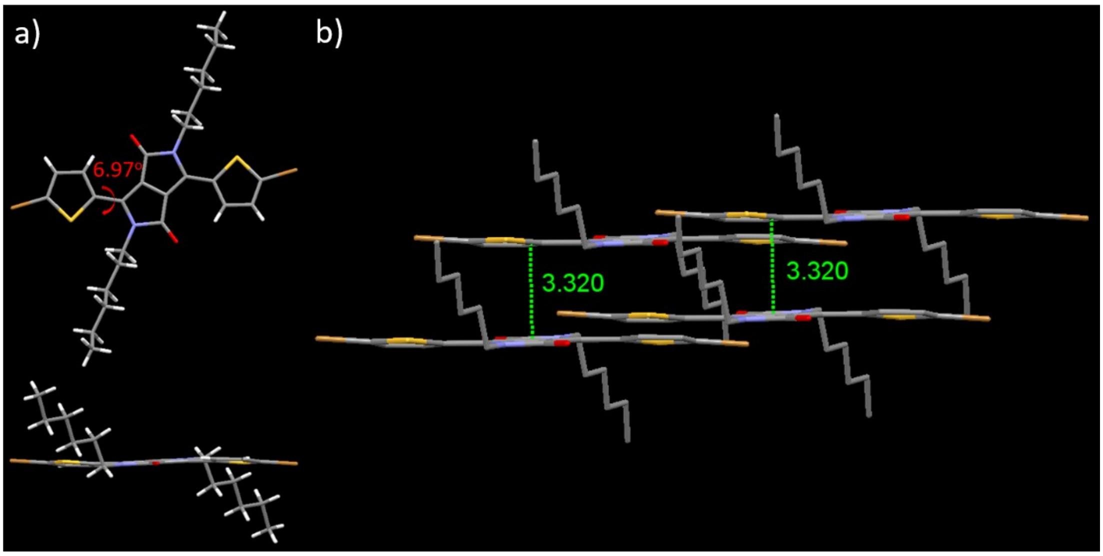


Figure S2. a) Single crystal structure and b) molecular stacking structure of DPP-diBr (CCDC 1020305). C (grey), H (white), O (red), N (blue), S (yellow), Br (brown). π-π distance is marked and the unit is Å.

Table S2. Crystallographic data of BTP-diBr single crystal.

Identification code	BTP-diBr
Empirical formula	$C_{27}H_{34}Br_2N_2O_3S_2$
Formula weight	658.50
Temperature	173(2) K
Wavelength	1.34138 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 13.2762(10) Å α = 90° b = 13.6624(11) Å β = 107.960(2)° c = 16.4580(13) Å γ = 90°
Volume	2839.8(4) Å^3
Z	4
Density (calculated)	1.540 Mg/m^3
Absorption coefficient	3.469 mm^{-1}
F(000)	1344
Crystal size	0.270 × 0.200 × 0.180 mm^3
Theta range for data collection	3.044 to 58.488°.
Index ranges	-16<=h<=16, -17<=k<=17, -20<=l<=20
Reflections collected	42961
Independent reflections	6107 [R(int) = 0.0421]
Completeness to theta = 53.594°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.752 and 0.628
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6107 / 63 / 372
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0455, wR2 = 0.1185
R indices (all data)	R1 = 0.0474, wR2 = 0.1202
Extinction coefficient	n/a
Largest diff. peak and hole	1.908 and -1.081 e.Å^{-3}

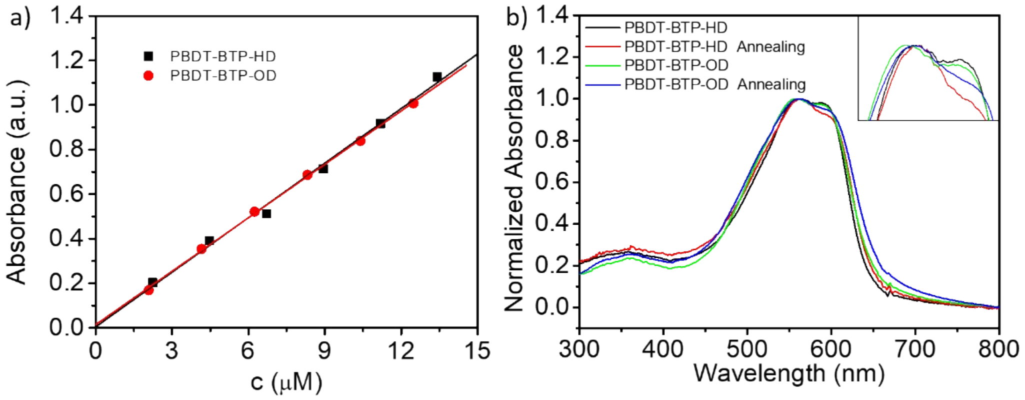


Figure S3. a) The absorbance strength at 583 nm of PBDT-BTP-HD and PBDT-BTP-OD versus concentration; b) UV-vis film absorption spectra of PBDT-BTP-HD and PBDT-BTP-OD before and after annealing.

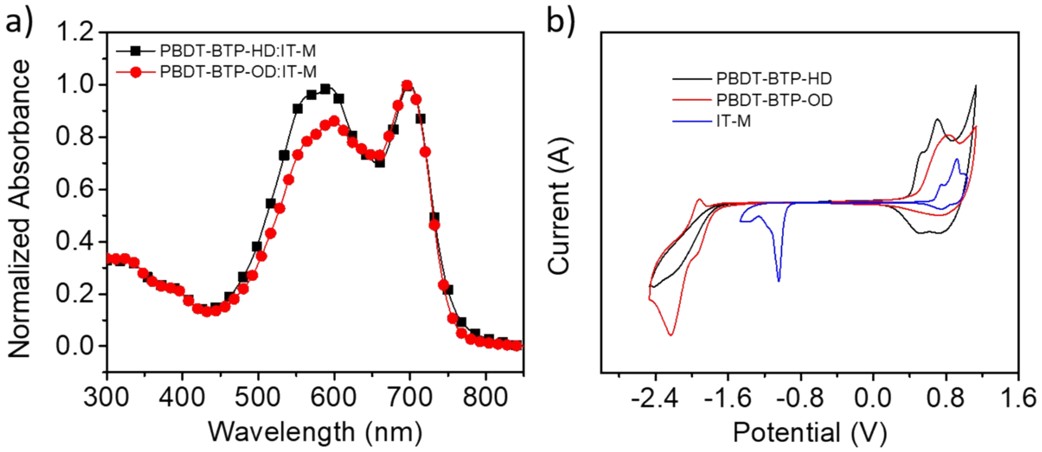


Figure S4. a) UV-vis absorption spectra of the PBDT-BTP-HD:IT-M and PBDT-BTP-OD:IT-M blend films; b) CV curves of PBDT-BTP-HD, PBDT-BTP-OD, IT-M.

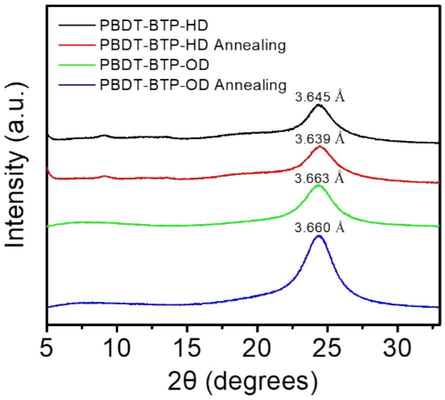


Figure S5. XRD curves of PBDT-BTP-HD and PBDT-BTP-OD before and after annealing.

Table S3. Photovoltaic properties of the PSCs based on PBDT-BTP-HD:IT-M and PBDT-BTP-OD:IT-M with different D/A weight ratios.

Active layer	D/A Ratio (w/w)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE$_{max}$ (PCE$_{ave}$)^a (%)
PBDT-BTP-HD:IT-M	1.5:1	0.92	13.52	67.36	8.39 (8.11)
	1:1	0.92	13.93	68.48	8.76 (8.44)
	1:1.5	0.91	12.98	69.58	8.23 (8.04)
PBDT-BTP-OD:IT-M	1:1	0.91	13.21	66.50	7.98 (7.73)
	1:1.5	0.93	13.30	69.46	8.64 (8.24)
	1:2	0.93	12.54	69.56	8.14 (7.72)

[a] The average PCE was obtained from at least 10 devices.

Table S4. Photovoltaic properties of the PSCs based on PBDT-BTP-HD:IT-M and PBDT-BTP-OD:IT-M with different thermal annealing temperatures.

Active layer	Temperature (^{o}C)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE$_{max}$ (PCE$_{ave}$)^a (%)
PBDT-BTP-HD:IT-M	-	0.92	13.93	68.48	8.76 (8.44)
	100	0.91	13.85	70.84	8.90 (8.69)
	120	0.91	14.29	71.53	9.28 (8.85)
	140	0.90	13.99	71.78	9.03 (8.69)
PBDT-BTP-OD:IT-M	-	0.93	13.30	69.46	8.64 (8.24)
	120	0.92	13.89	71.99	9.21 (8.79)
	140	0.92	13.90	72.91	9.29 (8.94)
	160	0.91	14.10	72.13	9.22 (8.88)

[a] The average PCE was obtained from at least 10 devices.

Table S5. Photovoltaic properties of the PSCs based on PBDT-BTP-HD:IT-M and PBDT-BTP-OD:IT-M with different amount of DIO additives.

Active layer	DIO (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE_{max} (PCE_{ave})[a] (%)
PBDT-BTP-HD:IT-M	0	0.91	14.29	71.53	9.28 (8.85)
	1	0.89	14.82	71.78	9.47 (9.18)
	2	0.86	10.79	67.16	6.26 (5.50)
PBDT-BTP-OD:IT-M	0	0.92	13.90	72.91	9.29 (8.94)
	1	0.91	14.38	72.66	9.54 (9.25)
	2	0.88	12.79	70.77	8.01 (6.89)

[a] The average PCE was obtained from at least 10 devices.

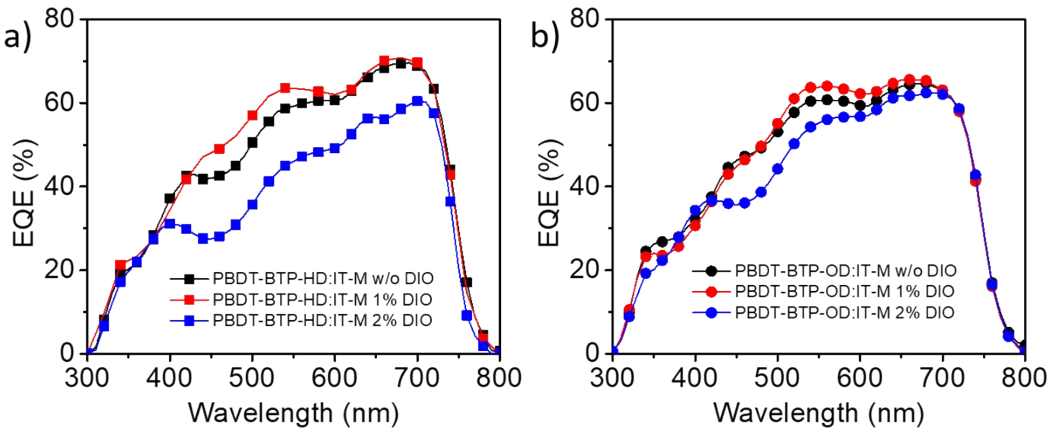


Figure S6. EQE spectra of the PSCs based on a) PBDT-BTP-HD:IT-M and b) PBDT-BTP-OD:IT-M with different amount of DIO additives.

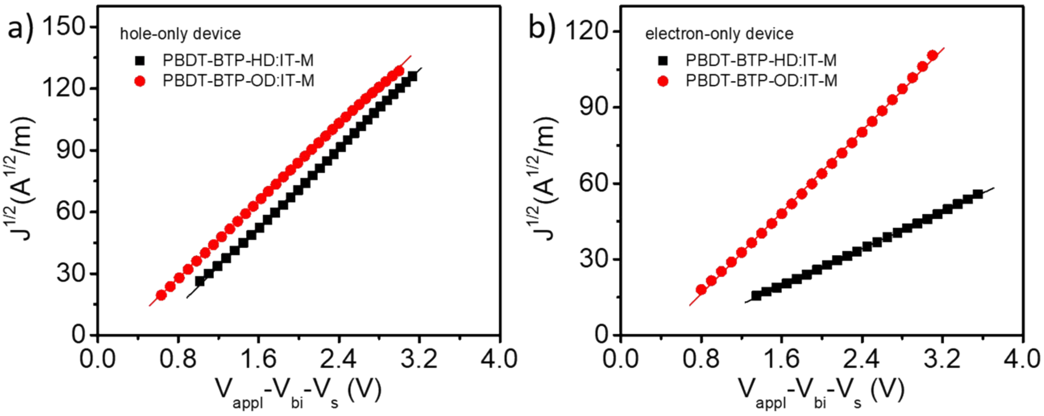


Figure S7. The $J^{1/2}$-V plots of the single charge carrier devices for a) hole-only devices and b) electron-only devices for PBDT-BTP-HD:IT-M and PBDT-BTP-OD:IT-M, respectively. The solid lines represent the best fitting from the SCLC model.

Table S6. Hole and electron mobilities

Devices	μ_h 10^{-4} cm^2 V^{-1} s^{-1}	μ_e 10^{-4} cm^2 V^{-1} s^{-1}	μ_h/μ_e
PBDT-BTP-HD:IT-M	7.67	1.12	6.85
PBDT-BTP-OD:IT-M	7.30	5.42	1.35

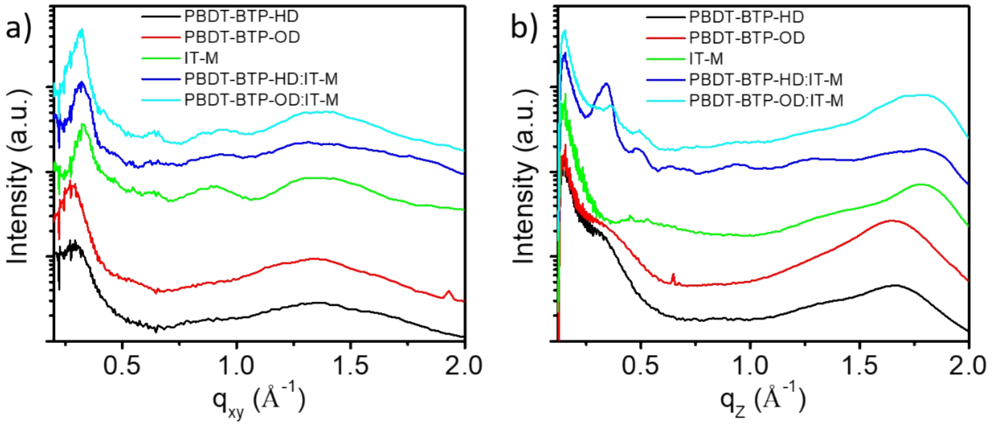
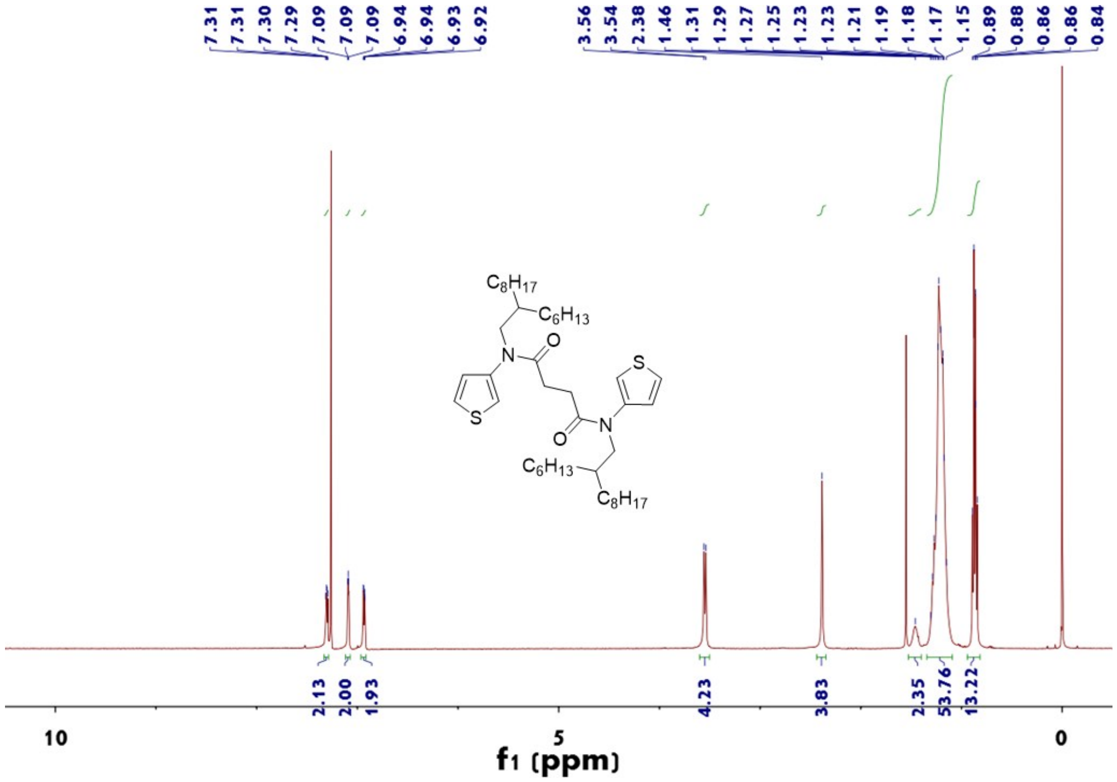


Figure S8. The GIWAXS profiles along the a) in-plane and b) out-of-plane directions.



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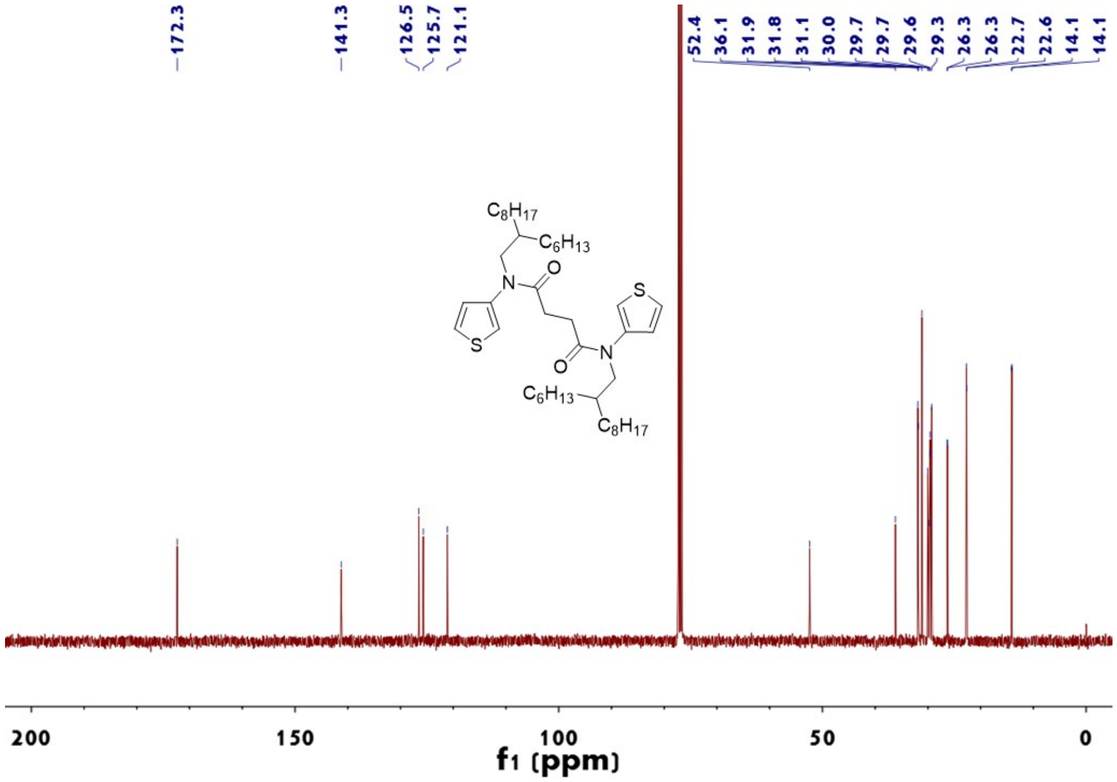

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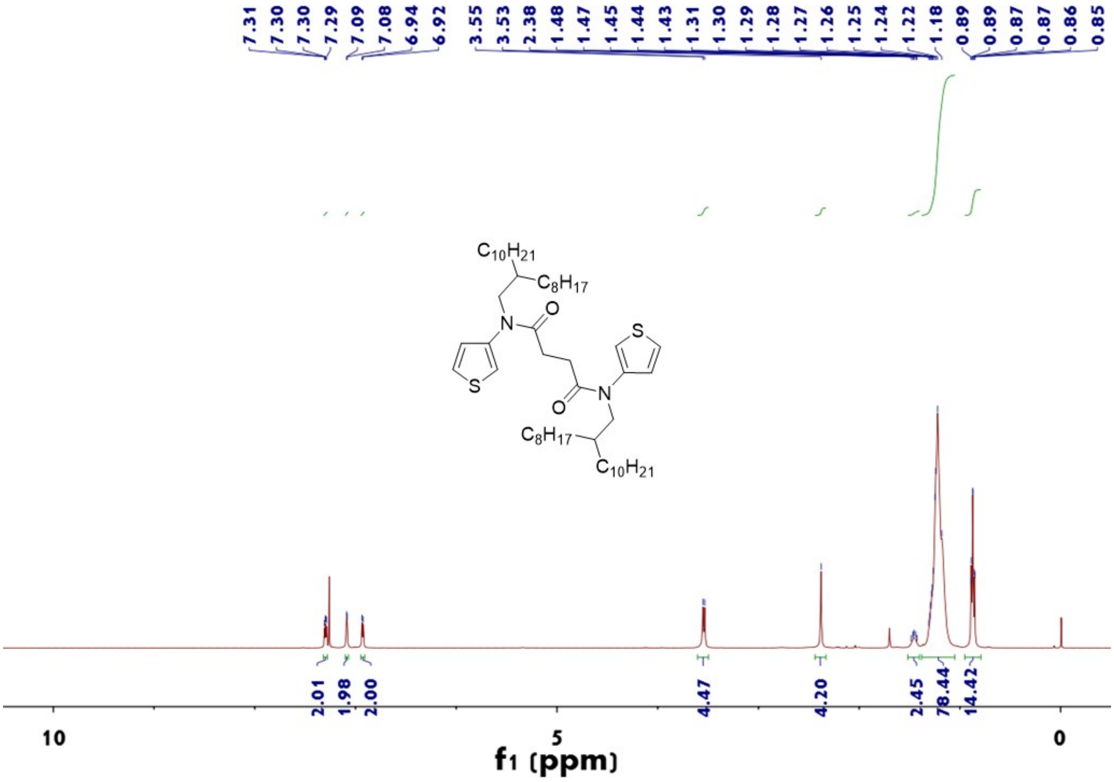

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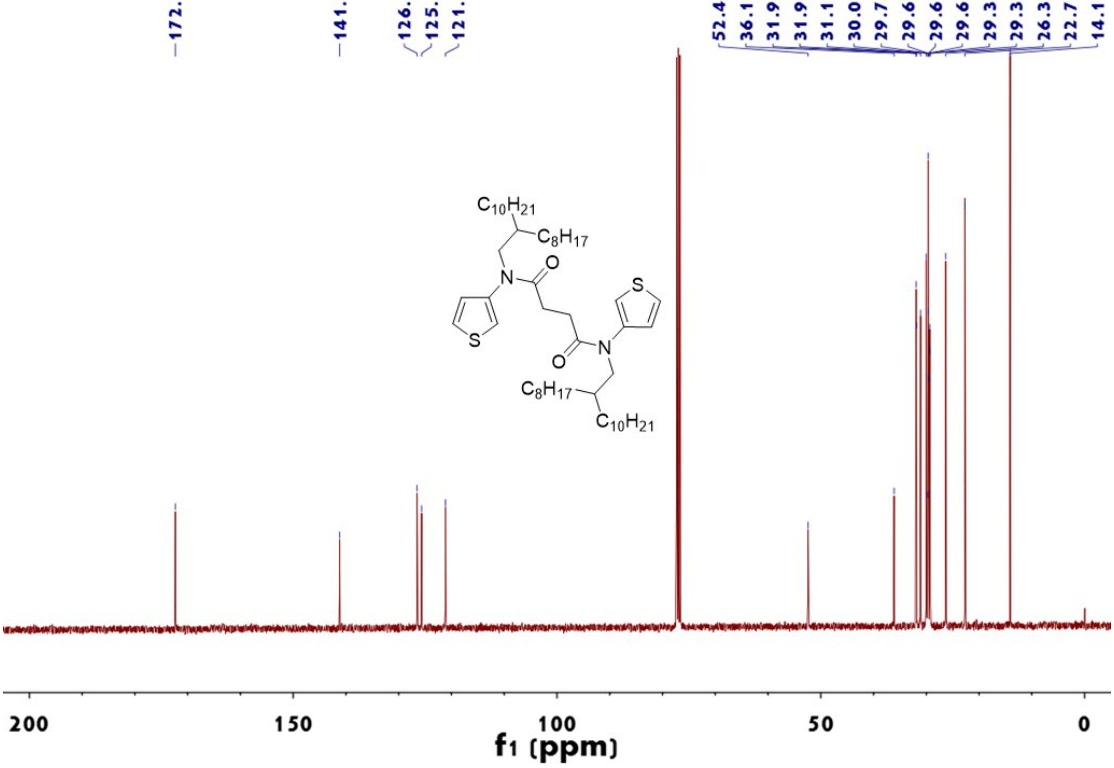

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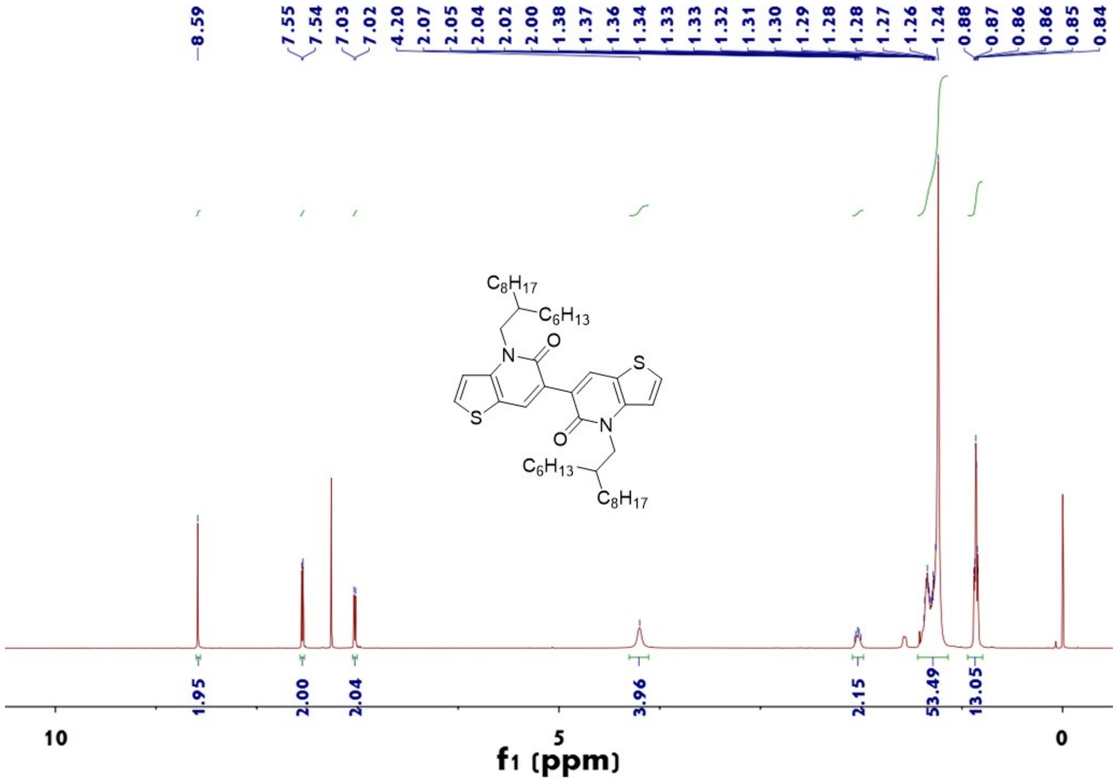

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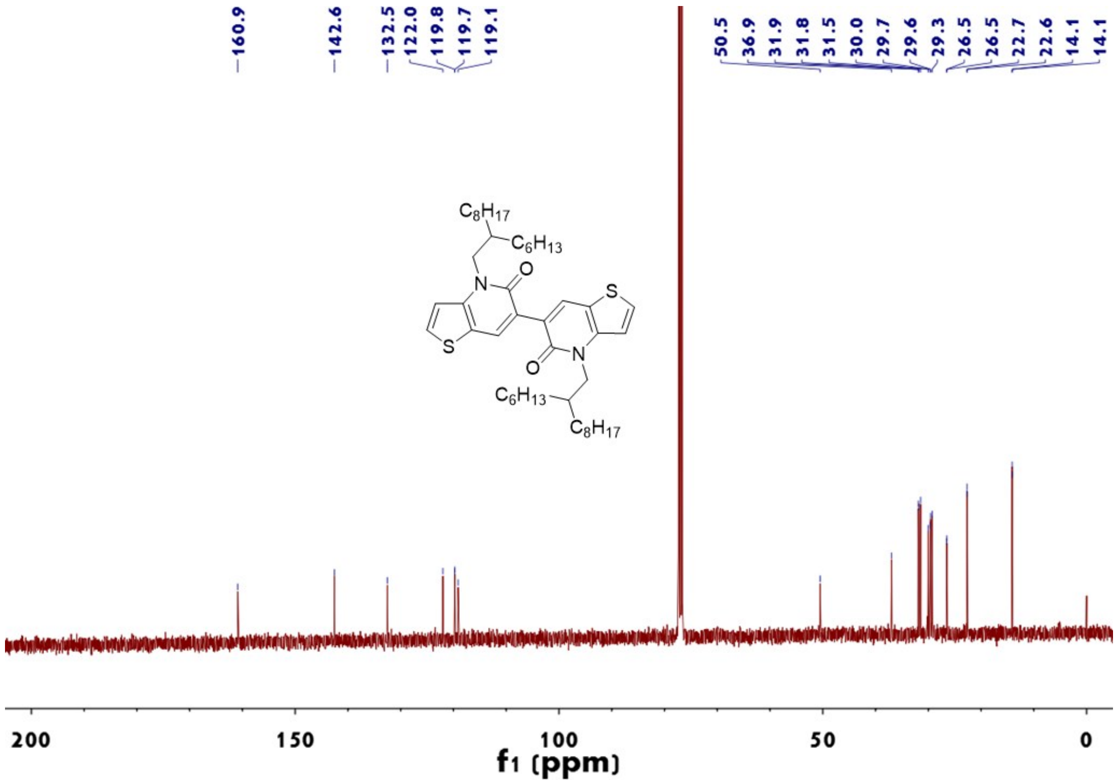

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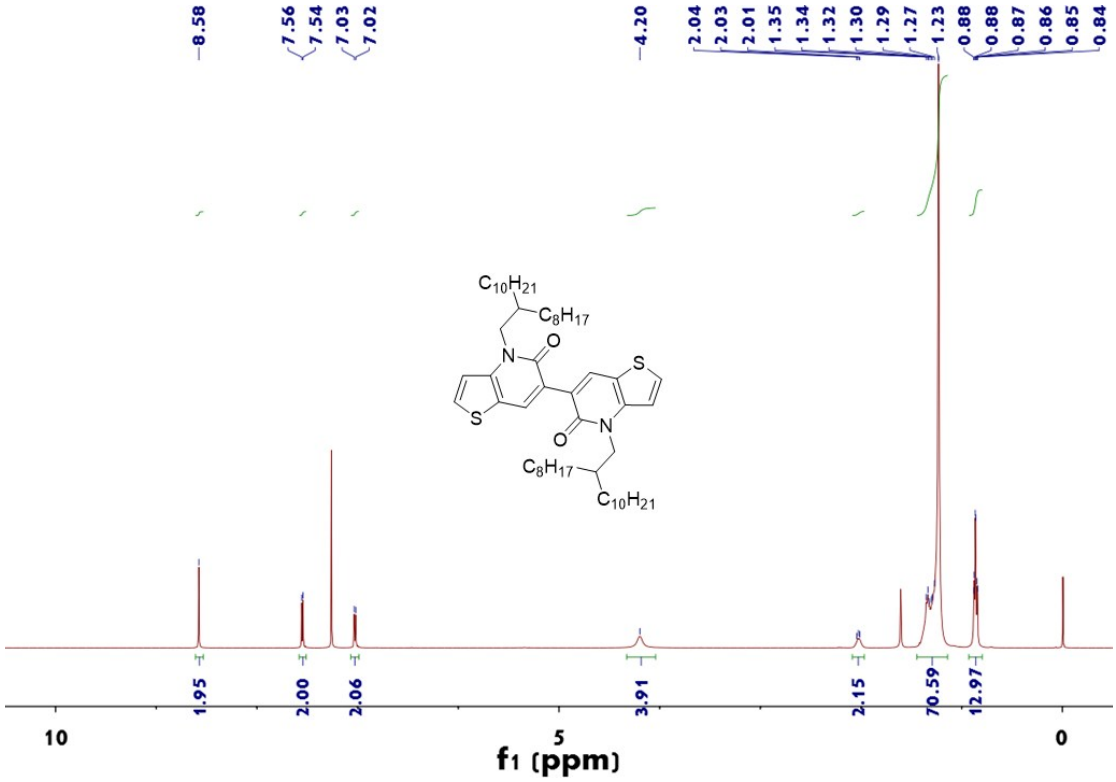

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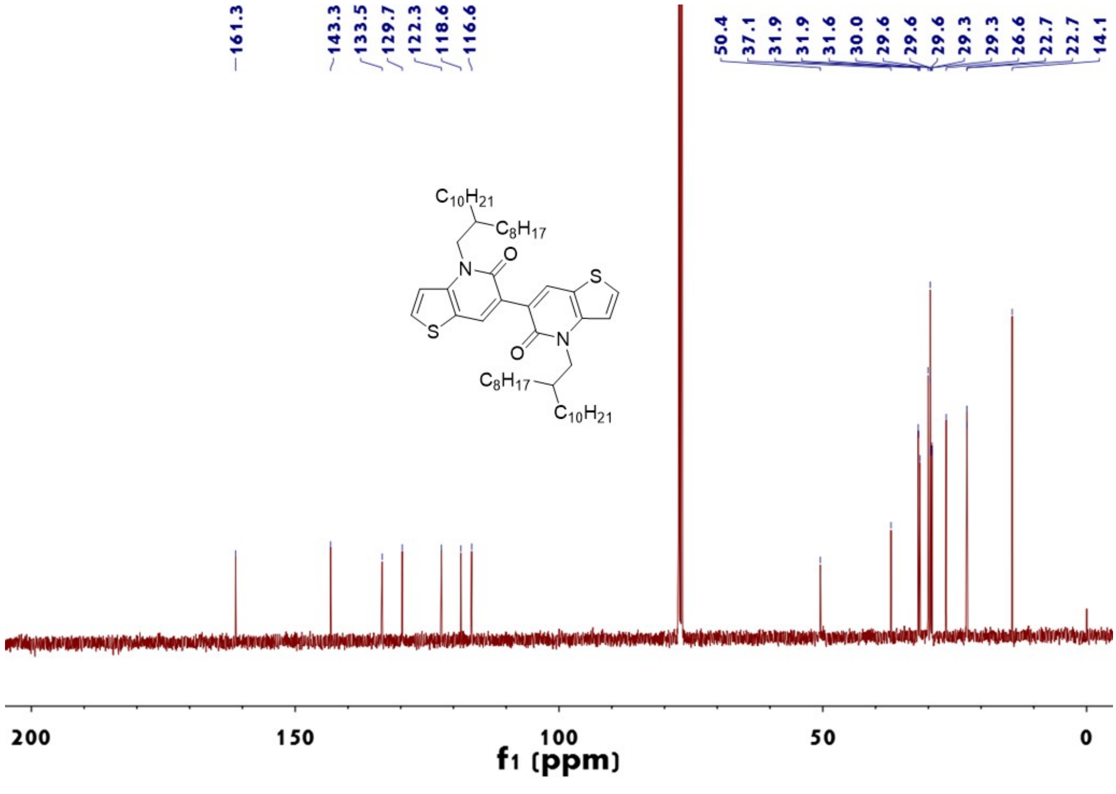

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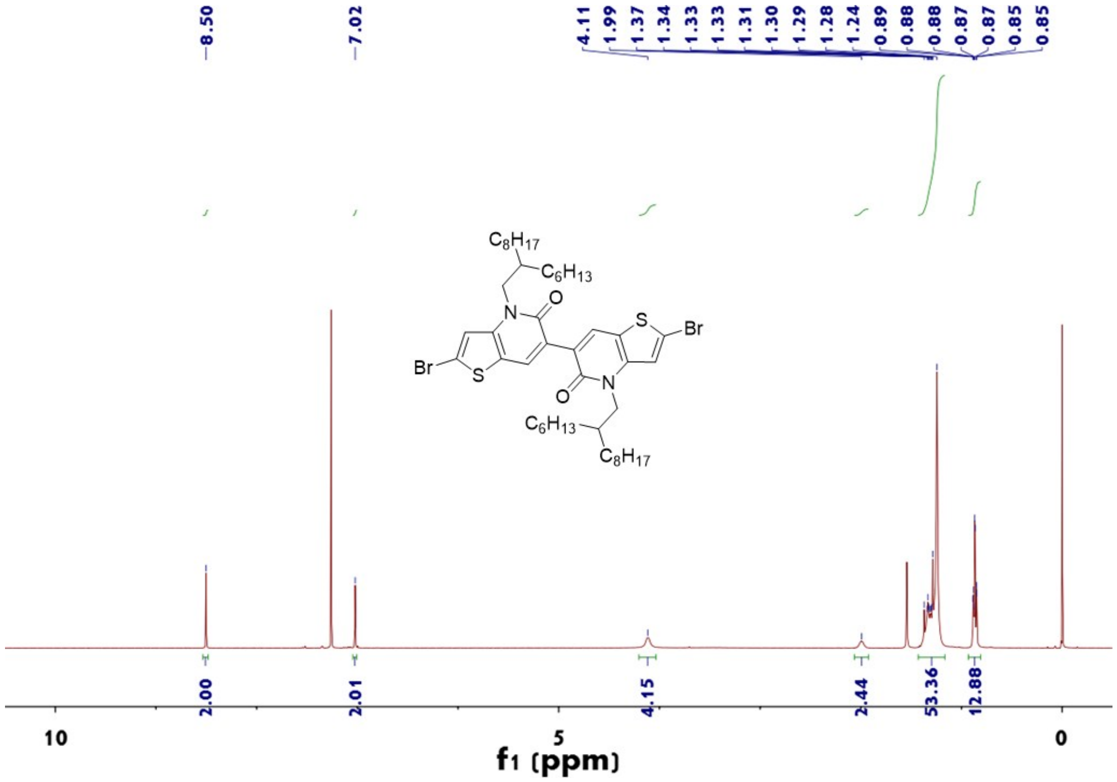

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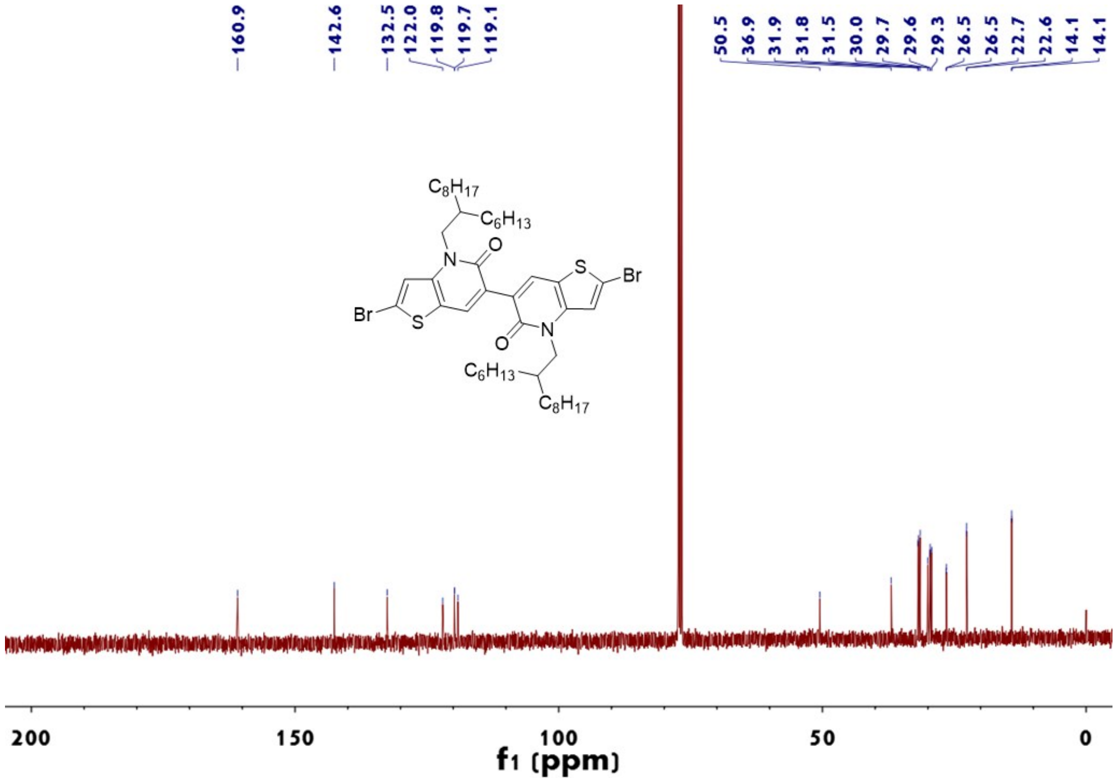

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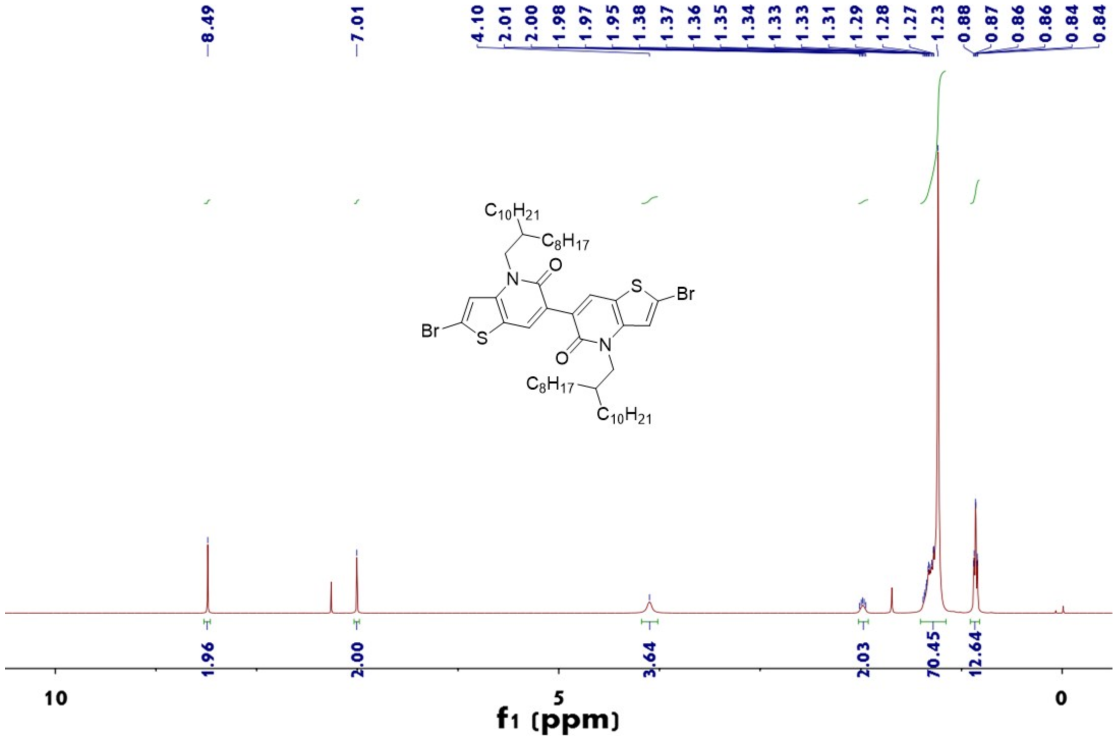

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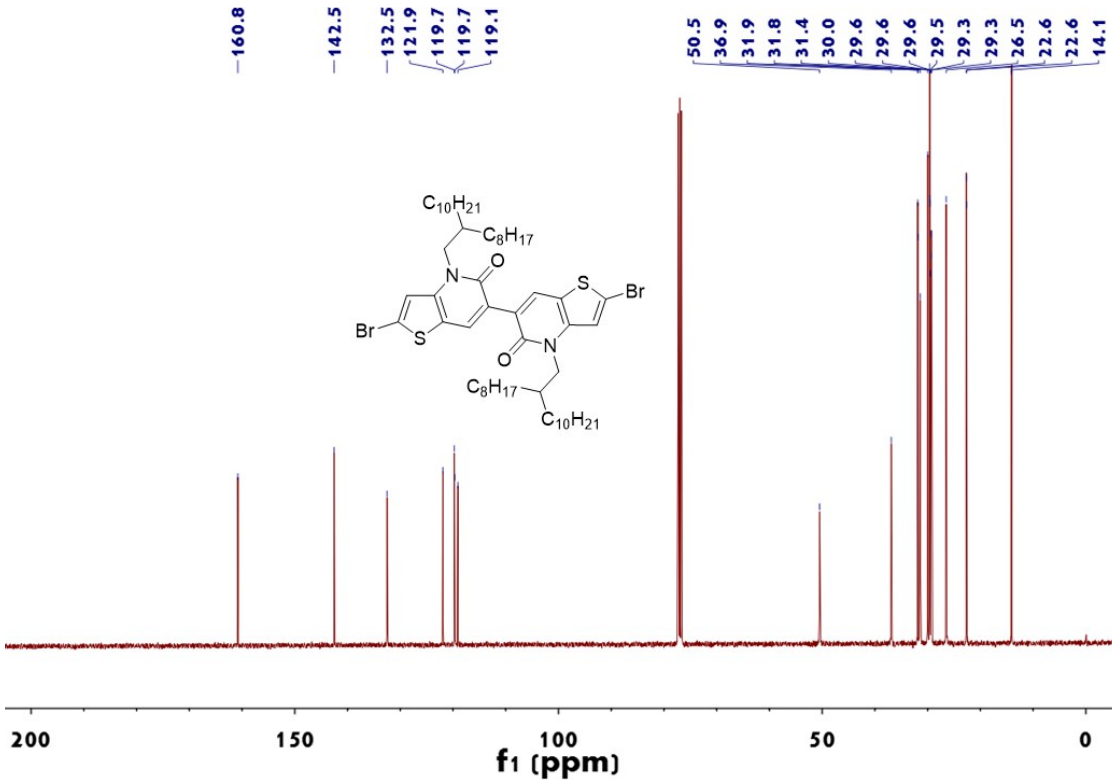

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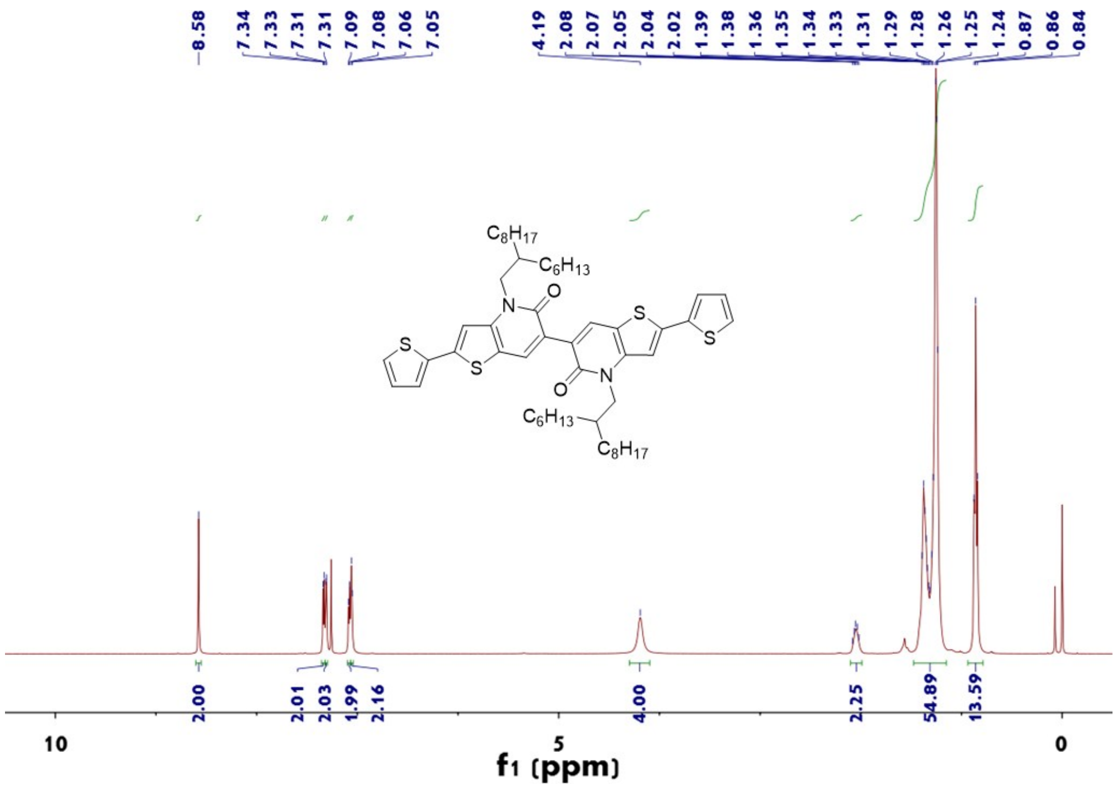

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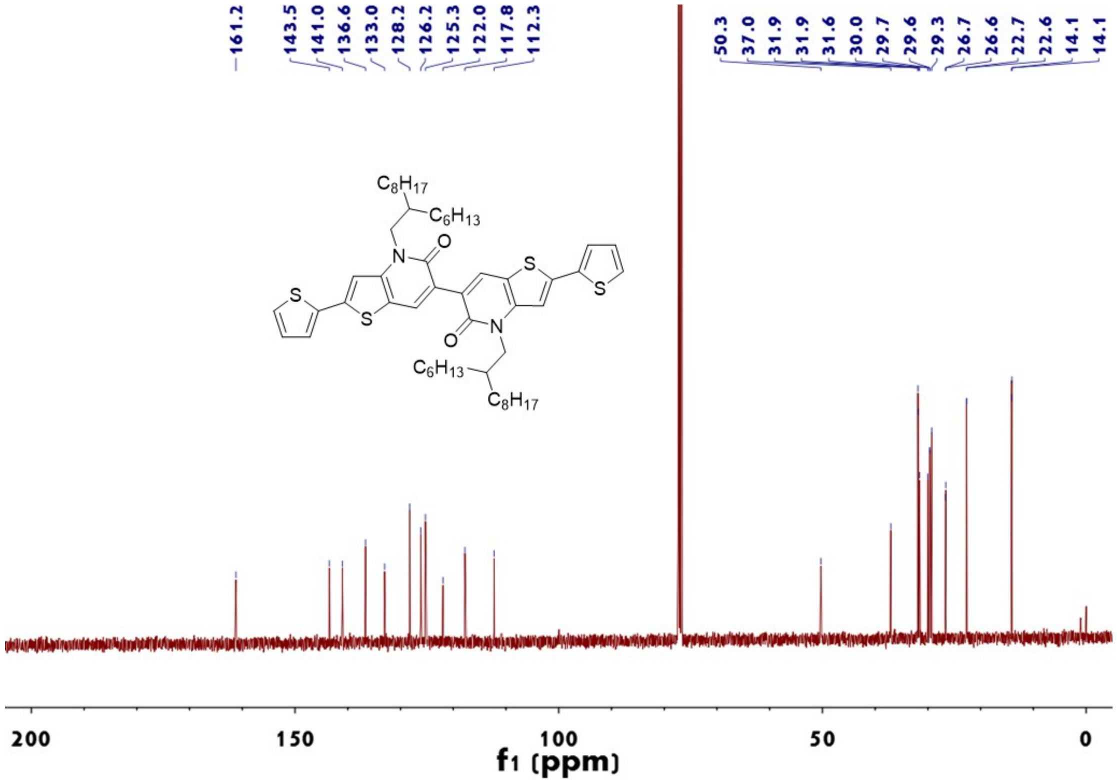

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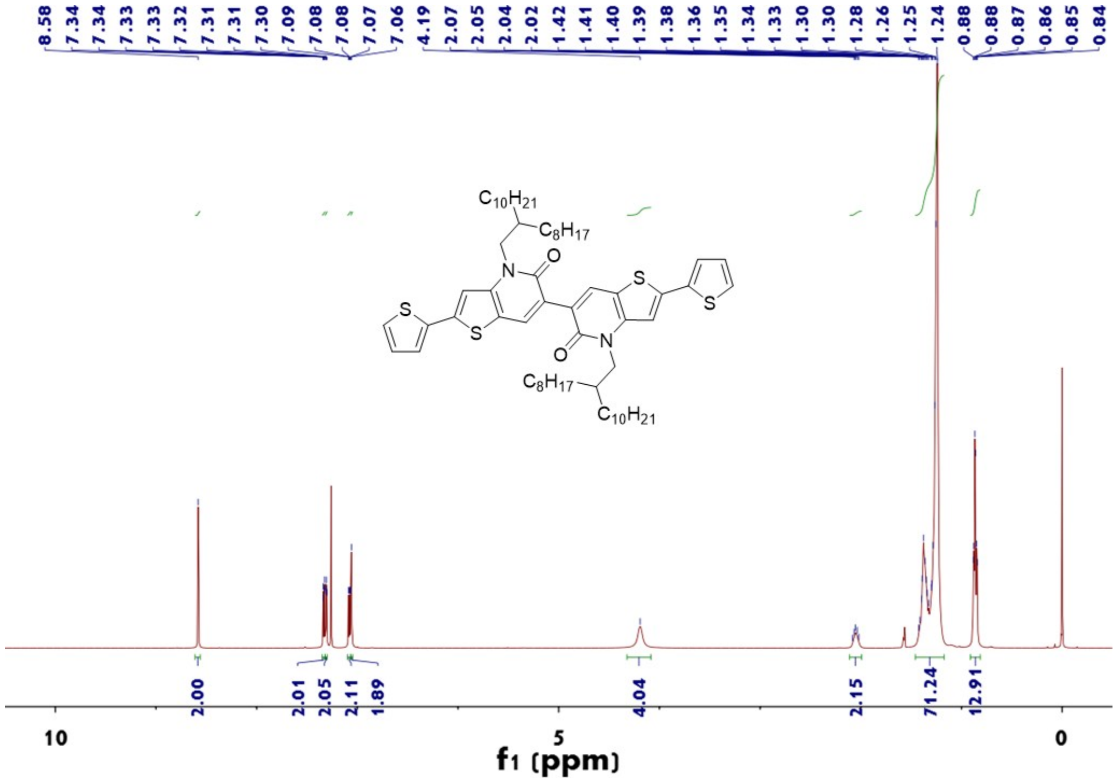

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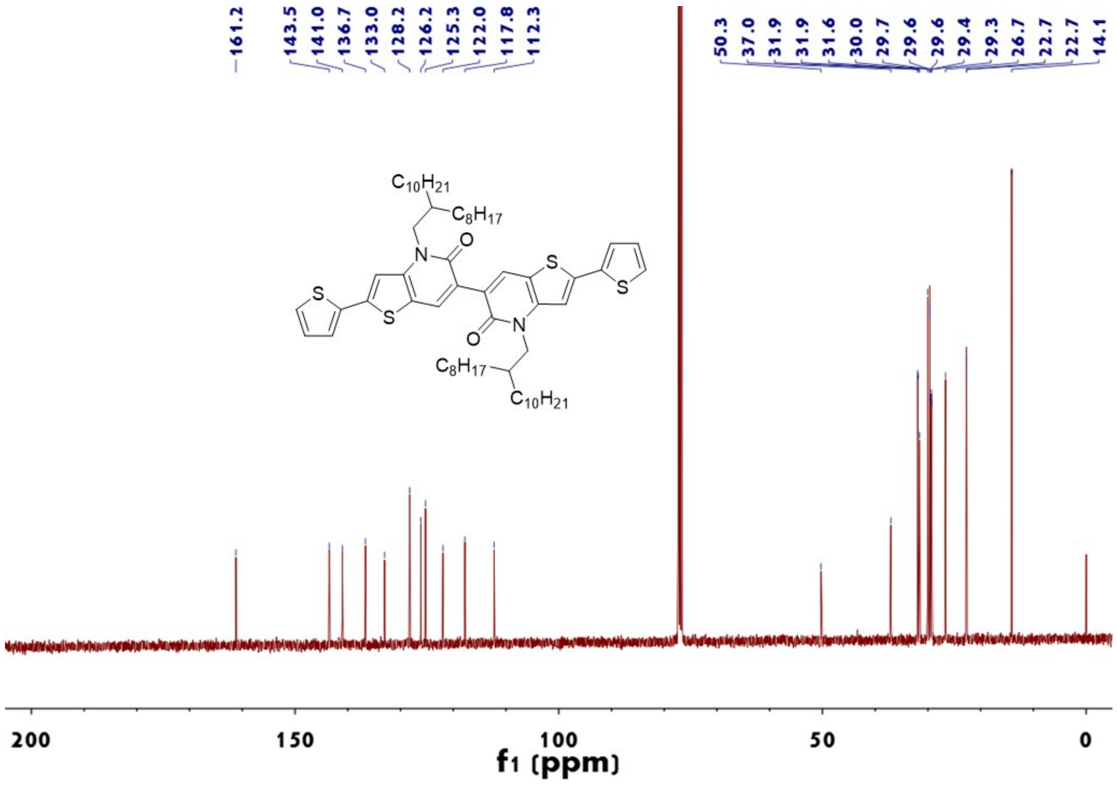

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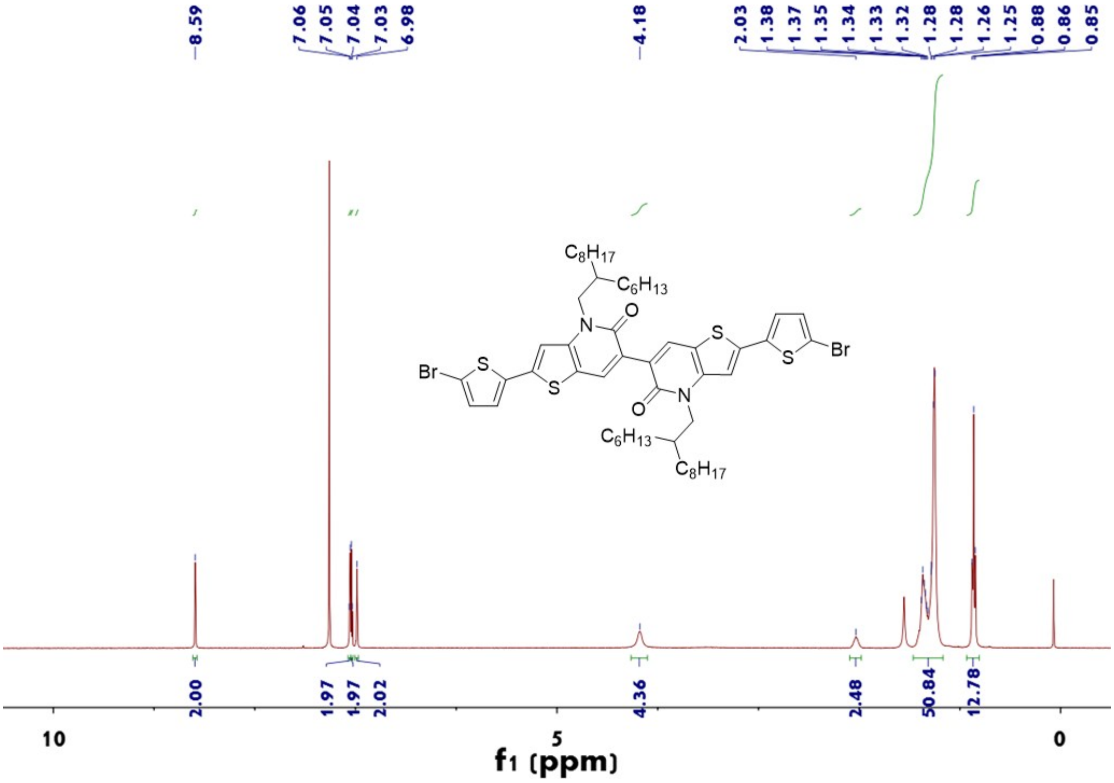

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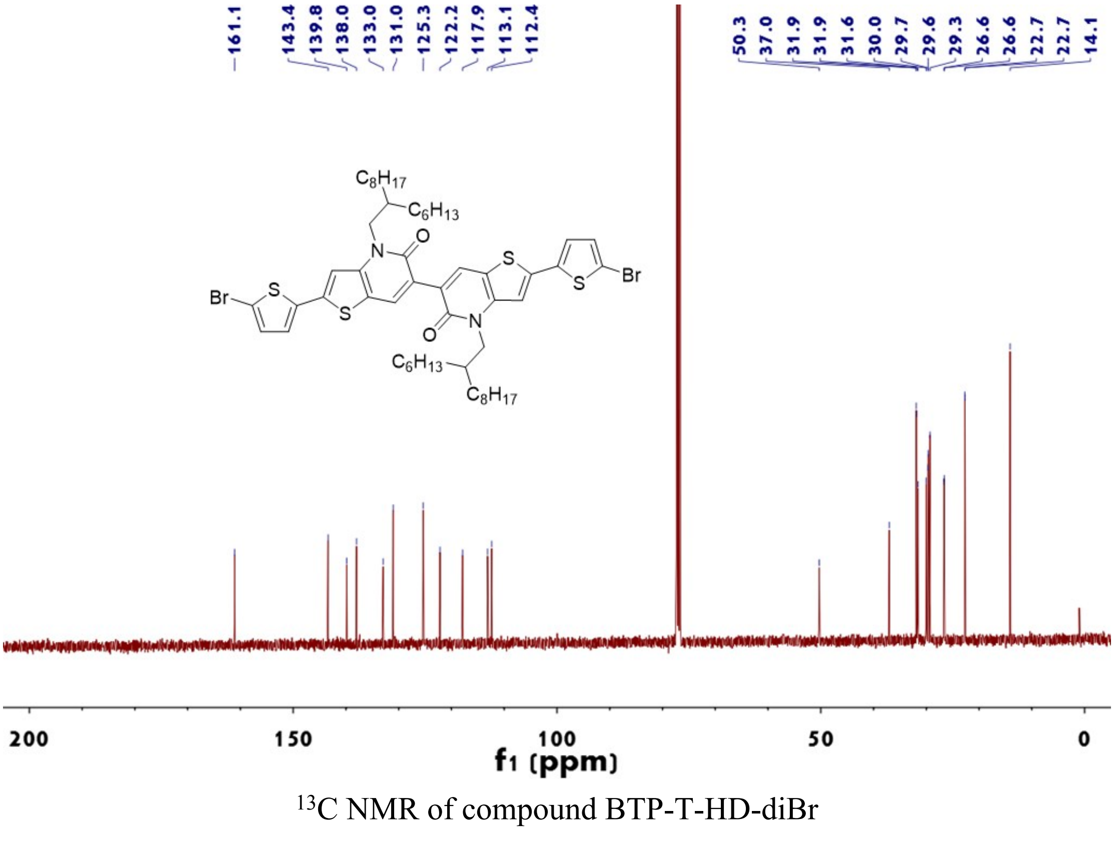

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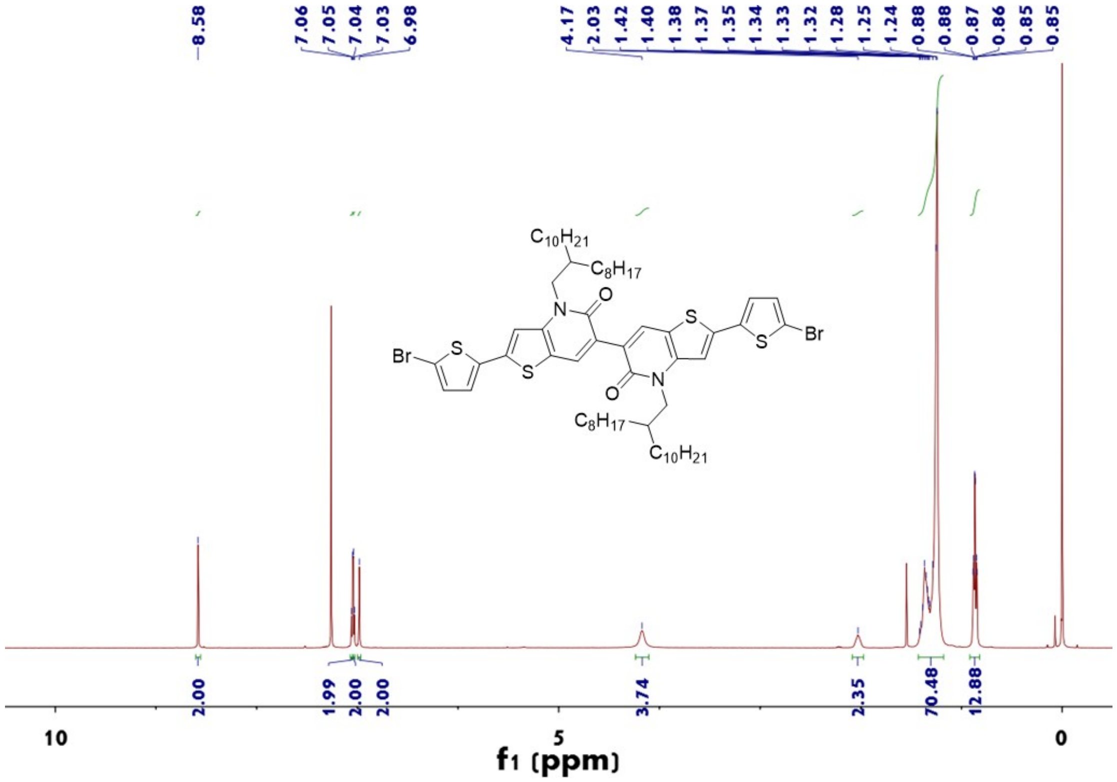

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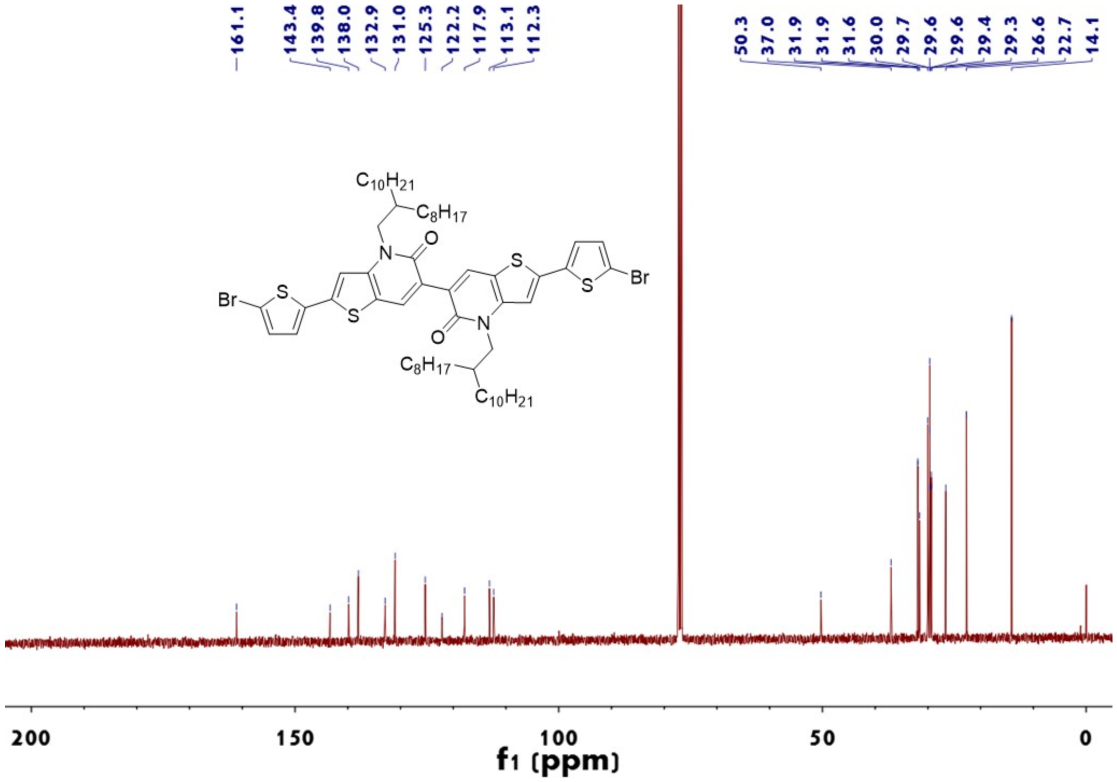

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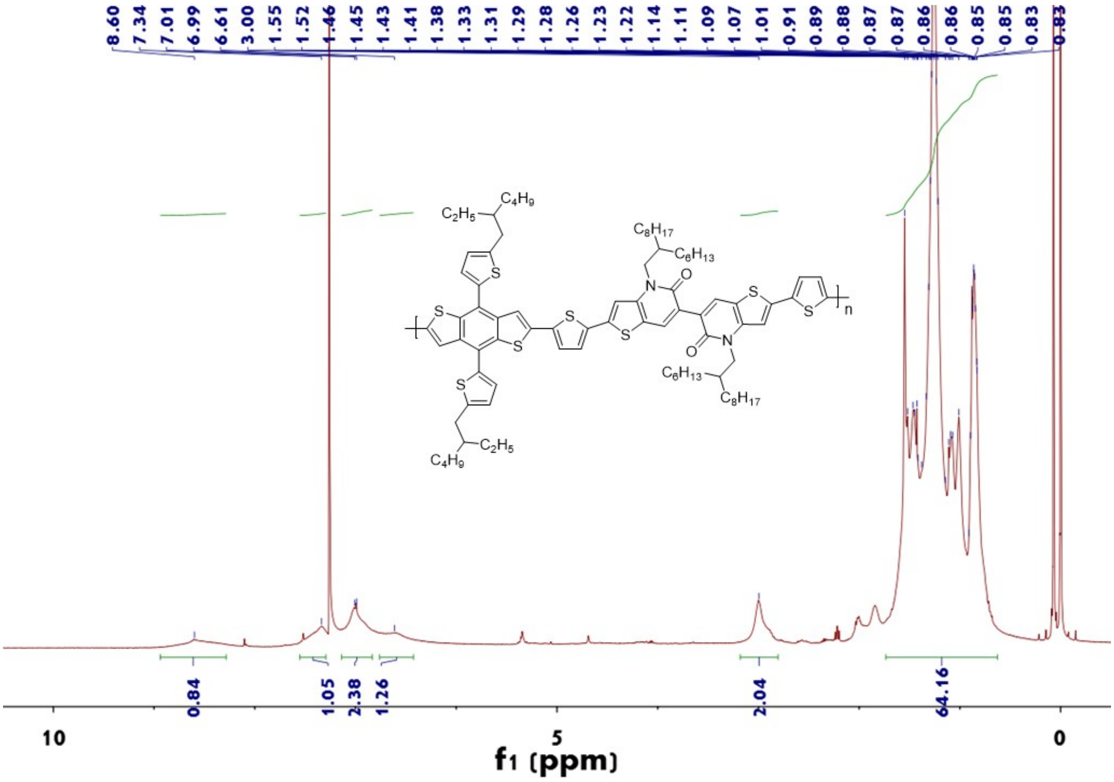

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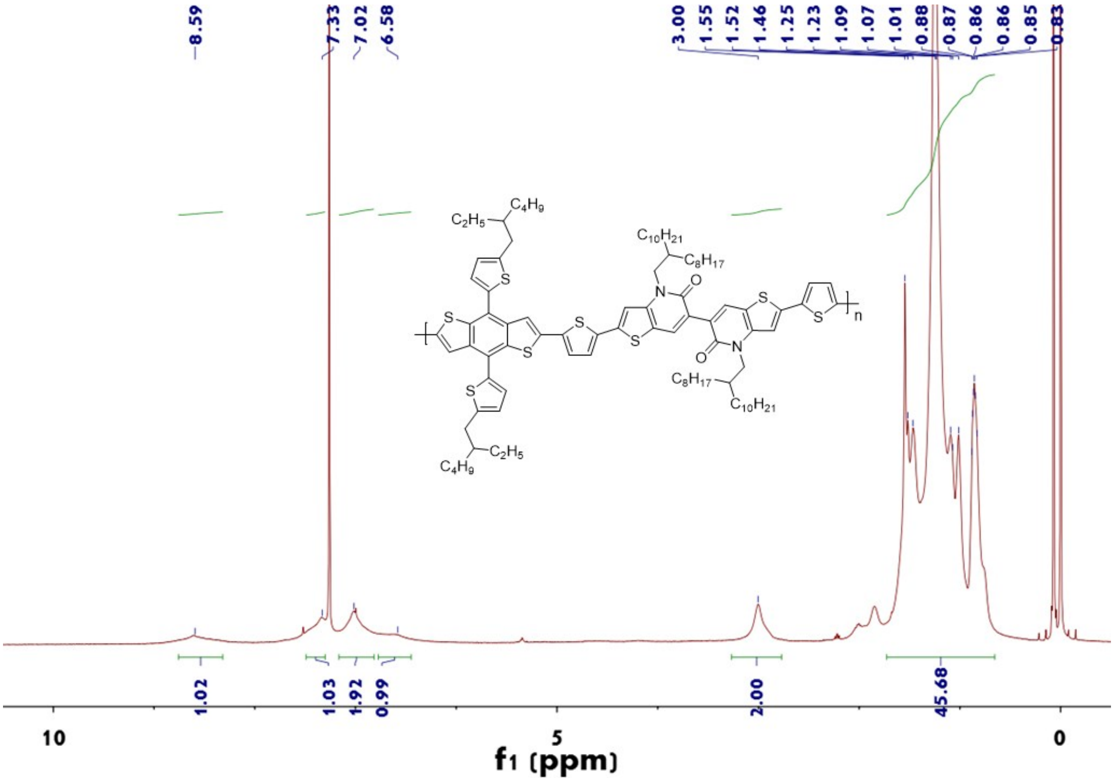

^{1}H NMR of compound PBDT-BTP-OD

1. M. S. Chen, J. R. Niskala, D. A. Unruh, C. K. Chu, O. P. Lee and J. M. J. Fréchet, *Chem. Mater.*, 2013, **25**, 4088-4096.