

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2019

Supporting Information

Design of wide-bandgap polymers with deeper ionization potential enables efficient ternary non-fullerene polymer solar cells with 13% efficiency

Delong Liu, Ying Zhang, Lingling Zhan, Tsz-Ki Lau, Hang Yin, Patrick W.K. Fong, Shu Kong So, Shaoqing Zhang, Xinhui Lu*, Jianhui Hou*, Hongzheng Chen*, Wai-Yeung Wong*, and Gang Li,*

Contents

Experimental Section	
Materials	Page 2
Instruments Measurements	Page 2
Fabrication of polymer solar cells	Page 2
Synthesis	Page 2-6
Experimental data	Page 7-23
References	Page 24

Experimental Section

Materials

5-(bromomethyl)-undecane, 2-bromothiophene-3-carboxylic acid, and dithieno[2,3-d':2',3'-d'']benzo[1,2-b:4,5-b']dithiophene-5,10-dione was synthesized according to the reported literatures.¹ IT-4F were purchased from Solarmer Materials Inc. PBDB-T-SF were supported by Prof. J. H. Hou. All other chemical reagents were used as received.

Instruments Measurements

The number-average molecular weight (M_n) and polydispersity index (PDI) was measured on Aligent PL-GPC220 1,2,4-trichlorobenzene as eluent at 150° with a flow rate of 1.0 mL/min. TGA measurement was performed on mettler toledo TGA/DSC 3+. UV-vis absorption spectroscopy was performed on the Cary 4000 UV-Vis spectrophotometer, Agilent Technologies. Fluorescence emission spectra were measured on the Cary eclipse fluorescence spectrophotometer, Agilent Technologies. Cyclic voltammetry was conducted on electrochemical workstation, Chenhua, Inc., using glassy carbon disk, Pt wire, and Ag/Ag⁺ electrode as working electrode, counter electrode, and reference electrode, respectively, with a scanning rate of 20 mV/s in a 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance III 400 spectrometer. Mass spectra were determined by the Agilent 6540 Accurate-Mass Q-TOF and Bruker ultrafleXtreme MALDI-TOF. Elemental analysis was performed on Elementar Vario EL Cube. GIWAXS measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and Pilatus3R 300K detector. The incidence angle is 0.2°. The current density-voltage (J - V) characteristics were measured in the glove-box with a Keithley 2400 measure unit under 1 sun, AM 1.5G spectra (100 mW/cm²) from a solar simulator (Enli Tech. Co., Ltd., Taiwan). The light intensity was calibrated with a 20 mm×20 mm monocrystalline silicon reference cell with KG5 filter (Enli Tech. Co., Ltd., Taiwan). The EQE was measured by solar cell spectral response measurement system QE-R3-011 (Enli Tech. Co., Ltd., Taiwan). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The molecular modeling calculation was performed with the Gaussian 09 program using the density functional theory with B3LYP/6-31G (d, p) basis set.²

Fabrication of polymer solar cells

Photovoltaic devices were fabricated with the structure of ITO/PEDOT:PSS/active layer/PFN-Br/Al. Specific process is as follows: patterned ITO-coated glass was cleaned in an ultraviolet ozone for 20 min and then a ca. 30 nm thick PEDOT:PSS (Bayer baytron 4083) anode buffer layer was spin-cast onto the ITO substrate. Afterwards, the glass was dried at 150 °C for 15 min. For the binary device, the active layer was deposited on top of the PEDOT:PSS layer by spin-coating from a chlorobenzene solution of polymer and IT-4F (the concentration of polymer is fixed at 10 mg mL⁻¹). The optimal thickness of blend film is ca. 95 nm. For the ternary device, the active layer was deposited on by spin-coating from a chlorobenzene solution of PBDB-SF, IT-4F, and the third component polymer (the concentration of PBDB-SF is fixed at 10 mg mL⁻¹). The active layer was then thermally annealed at 100 °C for 10 minutes to give a ca. 95 nm blend film. 5nm PFN-Br was spin-coated onto the active layer as the cathode buffer layer. Finally, the whole device was completed by vacuum evaporating Ag metal electrodes (100 nm). Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere of nitrogen glove-box.

Synthesis

2-(2-butylloctyl)-3-chlorothiophene (1)

To a solution of 3-chlorothiophene (3.02 g, 25.4 mmol) in THF (30 mL), n-butyllithium (2.4 M, 8.1 mL) was added dropwise at -78°C under protection of argon. The mixture was kept at -78°C for 1 h and then 5-(bromomethyl)-undecane (7.28 g, 29.2 mmol) was added to the solution. The solution was stirred overnight at 70°C and quenched with 50ml of water. The

mixture was extracted with diethyl ether twice, and the organic phase was concentrated by removing of solvent. The coarse product was purified by silica gel chromatography using petroleum ether as eluent to obtain compound 1 as a colorless liquid (5.56 g, 83% yield). ESI-MS (m/z): calculated:286.15, found: 286.31. ¹H NMR (400 MHz, (CD₃)₂CO), δ (ppm): 7.371 (d, 1H, Ar H), 6.926 (d, 1H, Ar H), 2.765 (d, 2H, CH₂), 1.715 (m, 1H, CH), 1.337 (m, 16H, CH₂), 0.886 (d, 6H, CH₃). ¹³C NMR (400 MHz, (CD₃)₂CO), δ (ppm): 205.09, 136.55, 127.19, 123.00, 122.20, 39.40, 33.07, 32.80, 31.73, 31.66, 26.28, 22.75, 22.41, 13.46, 13.44.

4,8-bis(2-(2-butyloctyl)-3-chlorothiophene)-dithieno[2,3-d:2',3'-d']benzo[1,2-b:4,5-b']dithiophene (2)

To a solution of compound 1 (5.40 g, 18.8 mmol) in THF (30 mL), n-butyllithium (2.4 M, 8.6 mL) was added dropwise at -78°C under protection of argon. The mixture was kept at -78°C for 1 h and then dithieno[2,3-d:2',3'-d']benzo[1,2-b:4,5-b']dithiophene-5,10-dione (2.08 g, 6.27 mmol) was added to the solution. The mixture was warmed to 50°C and stirred for 0.5 h. Subsequently, a solution of SnCl₂·2H₂O (9.91 g, 43.9 mmol) in 10% HCl (15 mL) was added, and the reactant was stirred for another 2 h at 50°C. The reaction mixture was poured into 1 M NH₄Cl aqueous solution and extracted by diethyl ether twice. The organic phase was concentrated by removing of solvent. The coarse product was purified by silica gel chromatography using petroleum ether as eluent to obtain compound 2 as a yellow liquid (3.44 g, 63%yield). MALDI-TOF-MS (m/z): calculated: 872.23, found: 870.22. ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.435 (d, 2H, Ar H), 7.266 (d, 2H, Ar H), 7.154 (s, 2H, Ar H), 2.933 (d, 4H, CH₂), 1.862 (m, 2H, CH), 1.448 (m, 32H, CH₂), 0.966 (m, 12H, CH₃). ¹³C-NMR (400 MHz, CDCl₃), δ (ppm): 143.25, 139.71, 139.29, 133.34, 133.27, 130.03, 129.72, 128.82, 122.96, 122.89, 119.91, 39.70, 33.47, 33.16, 32.63, 31.97, 29.79, 28.96, 26.70, 23.15, 22.79, 14.24, 14.20, 14.17.

(4,8-bis(2-(2-butyloctyl)-3-chlorothiophene)-dithieno[2,3-d:2',3'-d']benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane)(3)

To a solution of compound 2 (1.60 g, 1.83 mmol) in THF (20 mL), LDA (2.0 mL, 2.0 M) at -78 °C was slowly added. The mixture was kept at -78 °C for 1h and then trimethyltin chloride solution in THF (2.8 mL, 1.0 M) was added. The solution was stirred at room temperature 2h and quenched with 50ml of 1 M NH₄Cl aqueous solution. The mixture was extracted with diethyl ether twice, and the organic phase was concentrated by removing of solvent. The residue was recrystallized from ethanol to obtain compound 3 as a white solid (1.64 g, 75%yield). MALDI-TOF-MS (m/z): calculated: 1197.84, found: 1198.13. ¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.305 (t, 2H, Ar H), 7.144 (s, 2H, Ar H), 2.935 (d, 4H, CH₂), 1.871 (t, 2H, CH), 1.435 (m, 32H, CH₂), 0.939 (m, 12H, CH₃), 0.321 (t, 18H, CH₃). ¹³C-NMR (400 MHz, CDCl₃), δ (ppm): 144.48, 143.57, 140.90, 139.20, 139.11, 133.57, 129.44, 128.67, 126.92, 123.06, 122.86, 39.49, 33.27, 32.87, 32.30, 31.96, 29.75, 28.75, 26.53, 23.12, 22.71, 14.23, 14.15, -2.09.

2-butyloctyl 2-bromothiophene-3-carboxylate (4)

To solution of 2-bromothiophene-3-carboxylic acid (4.03 g, 19.4 mmol), dicyclohexylcarbodiimide (DCC) (2.12 g, 10.3 mmol) and 4-dimethylaminopyridine (DMAP) (0.63 g, 5.16 mmol) in 10 mL of dry dichloromethane (CH₂Cl₂) was added 2-butyl-1-octanol alcohol (3.58 g, 19.2 mmol) and the mixture was stirred at room temperature for 48h. The mixture was extracted with CH₂Cl₂ twice, and the organic layer was concentrated by vacuum evaporation. The residue was purified by column chromatography on silica gel to give compound 4 as a colorless liquid (6.57 g, 90% yield). ESI-MS (m/z): calculated: 376.09, found: 374.31. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.583 (d, 1H, Ar H), 7.401 (d, 1H, Ar H), 4.228 (d, 2H, CH₂), 2.055 (m, 1H, CH), 1.468 (m, 16H, CH₂), 0.900 (m, 6H, CH₃). ¹³C NMR (400 MHz, CDCl₃), δ (ppm): 162.1, 131.5, 129.5, 125.7, 119.3, 67.2, 38.8, 30.5, 28.9, 23.9, 22.9, 14.0, 11.0.

2-butyloctyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-3-carboxylate (5)

In a 100 mL double-neck round bottom flask, compound 4 (3.02 g, 8.0 mmol), Pd(dppf)Cl₂ (294.3 mg, 0.4 mmol), bis(pinacolato)diboron (3.05 g, 12.0 mmol) and potassium acetate (3.14 g, 32.0 mmol) were dissolved in 20 mL 1,4-dioxane. After being purged with argon for 20 min. The reaction mixture was stirred at 90°C overnight. The mixture was extracted with ethyl acetate twice, and the organic layer was concentrated by vacuum evaporation. The residue was purified by column chromatography on silica gel to give compound 5 as a colorless liquid (1.35 g, 40% yield). MALDI-TOF-MS (m/z): calculated: 435.29, found: 435.91. ¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.796 (d, 1H, Ar H), 7.716 (d, 1H, Ar H), 4.313 4.15 (d, 2H, CH₂), 1.855 (m, 1H, CH), 1.436 (m, 28H, CH₂, CH₃), 1.27 (m, 6H, CH₂), 0.88 (m, 6H, CH₃). ¹³C NMR (400 MHz, CDCl₃, δ): 162.1, 131.5, 129.5, 125.7, 119.3, 67.2, 38.8, 30.5, 28.9, 23.9, 22.9, 14.0, 11.0.

2,2'-bithiazole (6)

2-bromothiazole (4.0 g, 24.3 mmol), n,n-diisopropylethylamine (DIPEA, 4.28 mL, 24.6 mmol), n-Bu₄NBr (3.96 g, 12.3 mmol), and Pd(OAc)₂ (278.38 mg, 1.24 mmol) were dissolved into toluene (60 mL) under argon. The mixture was heated at reflux overnight, before cooling to room temperature. The mixture was extracted with CH₂Cl₂ twice, and the organic layer was concentrated by vacuum evaporation. The resultant residue was purified by column chromatography to obtain compound 6 as a white solid (1.44 g, 70% yield). ESI-MS (m/z): calculated: 167.98, found: 168.99. ¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.30 (d, 1H, Ar H), 7.15 (d, 1H, Ar H), 4.15 (m, 2H, CH₂), 1.63 (m, 1H, CH), 1.39 (m, 2H, CH₂), 1.27 (m, 6H, CH₂), 0.88 (m, 6H, CH₃). ¹³C NMR (400 MHz, CDCl₃, δ): 162.1, 131.5, 129.5, 125.7, 119.3, 67.2, 38.8, 30.5, 28.9, 23.9, 22.9, 14.0, 11.0.

5,5'-bis(trimethylstannyl)-2,2'-bithiazole (7)

To a solution of compound 6 (1.40 g, 8.32 mmol) in THF (15 mL), LDA (8.7 mL, 2.0 M) at -78 °C was slowly added. The mixture was kept at -78 °C for 1h and then trimethyltin chloride solution in THF (1.3 mL, 1.0 M) was added. The solution was stirred at room temperature 2h and quenched with 30ml of 1 M NH₄Cl aqueous solution. The mixture was extracted with diethyl ether twice, and the organic phase was concentrated by removing of solvent. The residue was recrystallized from n-hexane to obtain compound 7 as a white solid (3.68 g, 90%yield). ESI-MS (m/z): calculated: 493.85, found: 494.91. ¹H-NMR (400 MHz, (CD₃)₂CO), δ, (ppm): 7.885 (t, 2H), 0.463 (m, 18H). ¹³C-NMR (400 MHz, (CD₃)₂CO), δ (ppm): 205.21, 165.80, 150.39, 132.65, -6.95, -7.03, -8.87, -10.71.

bis(2-butyloctyl) 2,2'-([2,2'-bithiazole]-5,5'-diyl)bis(thiophene-3-carboxylate) (8)

In a 100 mL double-neck round bottom flask, compound 7 (1.33 g, 2.69 mmol), compound 4 (3.05g, 8.12 mmol) and Pd(PPh₃)₄ (155.4 mg, 0.13 mmol) were dissolved in 30 mL toluene. After being purged with argon for 20 min. The reaction mixture was stirred at 110°C overnight. The mixture was extracted with diethyl ether twice, and the organic phase was concentrated by removing of solvent. The residue was purified by column chromatography on silica gel to give compound 8 as a yellow solid (1.83, 90%). MALDI-TOF-MS (m/z): calculated: 757.14, found: 757.32. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.547 (d, 2H, Ar H), 7.317 (d, 2H, Ar H), 4.183 (d, 4H, CH₂), 1.696 (s, 2H, CH), 1.277 (d, 32H, CH₂), 0.868 (m, 12H, CH₃). ¹³C NMR (400 MHz, CDCl₃), δ (ppm): 162.87, 162.19, 144.42, 138.08, 131.56, 130.69, 129.88, 125.26, 67.94, 37.34, 31.82, 31.32, 31.00, 29.62, 28.93, 26.70, 22.99, 22.65, 14.10, 14.06.

bis(2-butyloctyl) 2,2'-([2,2'-bithiazole]-5,5'-diyl)bis(5-bromothiophene-3-carboxylate) (9)

In a 100 mL double-neck round bottom flask, compound 8 (1.50 g, 1.98 mmol), N-bromobutanamide (1.41 g, 7.92 mmol) and a spoon of silica gel were dissolved in 10 mL chloroform. The reaction mixture was stirred at 70°C under dark for 48 h. The mixture was extracted with chloroform twice, and the organic layer was concentrated by vacuum evaporation. The residue was purified by column chromatography on silica gel to give compound 9 as a yellow solid (0.81 g, 45%). MALDI-TOF-MS (m/z): calculated: 914.94, found: 915.12. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.072 (s, 2H, Ar H), 7.476 (s, 2H, Ar H),

4.167 (d, 4H, CH₂), 1.682 (s, 2H, CH), 1.271 (d, 32H, CH₂), 0.881 (m, 12H, CH₃). 13C NMR (400 MHz, CDCl₃), δ (ppm): 162.53, 161.71, 144.82, 139.35, 132.88, 130.48, 130.07, 112.26, 68.23, 37.31, 31.82, 31.28, 30.97, 29.60, 28.93, 26.68, 22.97, 22.65, 14.11, 14.06.

5,5'-bithiazole (10)

5-bromothiazole (4.0 g, 24.3 mmol), n,n-diisopropylethylamine (DIPEA, 4.28 mL, 24.6 mmol), n-Bu₄NBr (3.96 g, 12.3 mmol), and Pd(OAc)₂ (278.38 mg, 1.24 mmol) were dissolved into toluene (60 mL) under argon. The mixture was heated at reflux overnight, before cooling to room temperature. The mixture was extracted with CH₂Cl₂ twice, and the organic layer was concentrated by vacuum evaporation. The resultant residue was purified by column chromatography to obtain compound 6 as a white solid (0.83 g, 40% yield). ESI-MS (m/z): calculated: 167.98, found: 168.99. 1H NMR (400 MHz, CDCl₃) δ (ppm): 8.782 (d, 2H, Ar H), 7.998 (d, 2H, Ar H). 13C NMR (400 MHz, CDCl₃), δ (ppm): 152.79, 141.36, 128.19.

2,2'-dibromo-5,5'-bithiazole (11)

In a 100 mL double-neck round bottom flask, compound 8 (0.70 g, 4.16 mmol), N-bromobutanamide (2.95 g, 16.6 mmol) and a spoon of silica gel were dissolved in 20 mL chloroform. The reaction mixture was stirred at 70°C under dark for 48 h. The mixture was extracted with chloroform twice, and the organic layer was concentrated by vacuum evaporation. The residue was purified by column chromatography on silica gel to give compound 11 as a white solid (0.54 g, 40%). ESI-MS (m/z): calculated: 326.03, found: 326.81. 1H NMR (400 MHz, CDCl₃) δ (ppm): 7.603 (s, 2H, Ar H). 13C NMR (400 MHz, CDCl₃), δ (ppm): 140.55, 136.24, 130.73.

bis(2-butyloctyl) 2,2'-([5,5'-bithiazole]-2,2'-diyl)bis(thiophene-3-carboxylate) (12)

In a 100 mL double-neck round bottom flask, compound 11 (0.30 g, 0.92 mmol), compound 5 (3.05g, 8.12 mmol), 2M potassium carbonate aqueous solution (4.6 mL), ethanol (8 mL) and Pd(PPh₃)₄ (80.9 mg, 0.07 mmol) were dissolved in 30 mL toluene. After being purged with argon for 20 min. The reaction mixture was stirred at 100°C overnight. The mixture was extracted with diethyl ether twice, and the organic phase was concentrated by removing of solvent. The residue was purified by column chromatography on silica gel to give compound 8 as a yellow solid (0.56 g, 82% yield). MALDI-TOF-MS (m/z): calculated: 757.14, found: 756.30. 1H NMR (400 MHz, CDCl₃) δ (ppm): 7.996 (s, 2H, Ar H), 7.515 (d, 2H, Ar H), 7.349 (d, 2H, Ar H), 4.276 (d, 4H, CH₂), 1.796 (m, 2H, CH), 1.380 (m, 32H, CH₂), 0.903 (m, 12H, CH₃). 13C NMR (400 MHz, CDCl₃), δ (ppm): 163.51, 157.96, 144.56, 139.93, 131.20, 130.19, 128.13, 126.83, 68.16, 37.37, 31.79, 31.41, 31.09, 29.61, 28.95, 26.71, 22.99, 22.63, 14.06, 14.03.

bis(2-butyloctyl) 2,2'-([5,5'-bithiazole]-2,2'-diyl)bis(5-bromothiophene-3-carboxylate) (13)

In a 100 mL double-neck round bottom flask, compound 8 (0.50 g, 0.66 mmol), N-bromobutanamide (0.47 g, 2.64 mmol) and a spoon of silica gel were dissolved in 8 mL chloroform. The reaction mixture was stirred at 70°C under dark for 48 h. The mixture was extracted with chloroform twice, and the organic layer was concentrated by vacuum evaporation. The residue was purified by column chromatography on silica gel to give compound 9 as a yellow solid (0.22 g, 38%). MALDI-TOF-MS (m/z): calculated: 914.94, found: 915.13. 1H NMR (400 MHz, CDCl₃) δ (ppm): 7.971 (s, 2H, Ar H), 7.436 (s, 2H, Ar H), 4.266 (d, 4H, CH₂), 1.790 (m, 2H, CH), 1.371 (m, 32H, CH₂), 0.914 (m, 12H, CH₃). 13C NMR (400 MHz, CDCl₃), δ (ppm): 162.51, 156.93, 146.10, 140.28, 132.23, 131.48, 127.97, 115.09, 68.53, 37.32, 31.82, 31.37, 31.05, 29.70, 29.60, 28.96, 26.71, 22.99, 22.66, 14.11, 14.07.

Polymer PDBT(E)BTz-p

In a 50 mL double-neck round bottom flask, compound 3 (0.2 mmol) and compound 9 (0.2 mmol) and 10 mg of Pd(PPh₃)₄ were dissolved in 7 mL toluene. The reaction mixture was purged with argon for 20 min and then stirred at 110°C for 18 h. When the reaction mixture was cooled down to room temperature, the polymer was precipitated by addition of 100 mL

methanol, collected by filtration and then subjected to Soxhlet extraction with methanol, hexane, and chloroform in the end. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum. The yield was 90%. GPC: $M_w = 31.33$ K; $M_n = 58.99$ K; PDI = 1.88. Anal. Calcd for $C_{78}H_{104}N_2O_4S_6$ (%): C, 63.55; H, 6.70; N, 1.72; Found (%): C, 63.25; H, 6.85; N, 1.39.

Polymer PDBT(E)BTz-*d*

In a 50 mL double-neck round bottom flask, compound 3 (0.2 mmol) and compound 9 (0.2 mmol) and 10 mg of $Pd(PPh_3)_4$ were dissolved in 7 mL toluene. The reaction mixture was purged with argon for 20 min and then stirred at 110°C for 18 h. When the reaction mixture was cooled down to room temperature, the polymer was precipitated by addition of 100 mL methanol, collected by filtration and then subjected to Soxhlet extraction with methanol, hexane, and chloroform in the end. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum. The yield was 90%. GPC: $M_w = 31.33$ K; $M_n = 58.99$ K; PDI = 1.88. Anal. Calcd for $C_{78}H_{104}N_2O_4S_6$ (%): C, 63.55; H, 6.70; N, 1.72; Found (%): C, 63.52; H, 6.87; N, 1.40.

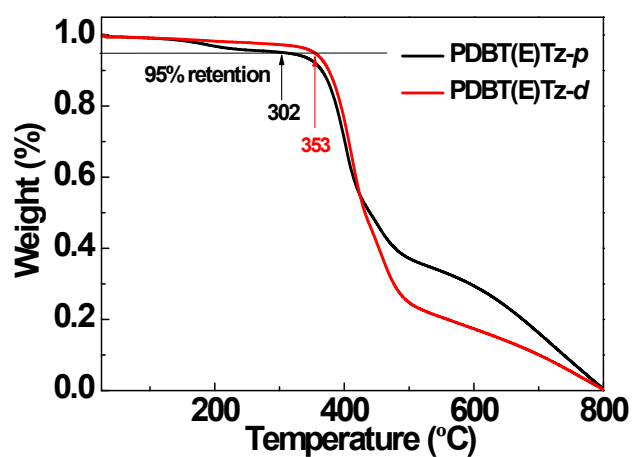


Fig. S1 TGA curves of the polymers with a heating rate of 10 °C/min under N₂ atmosphere.

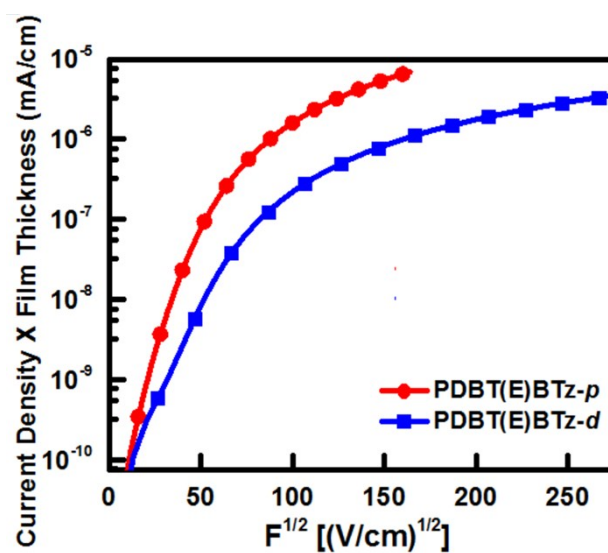


Fig. S2 The current dependence on applied field plots of hole-only transporting devices.

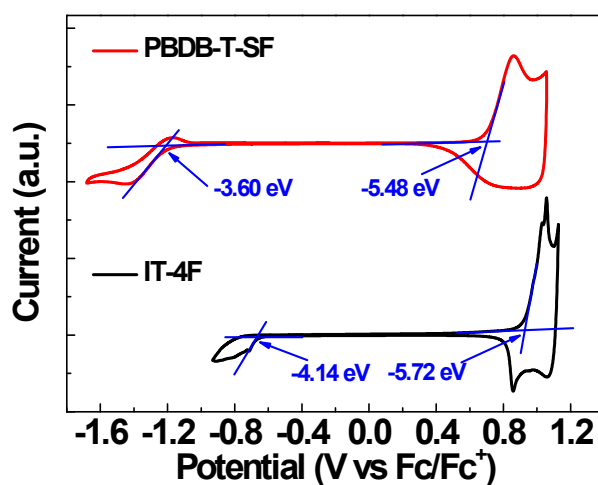


Fig. S3 CV curves of the PBDB-T-SF and IT-4F.

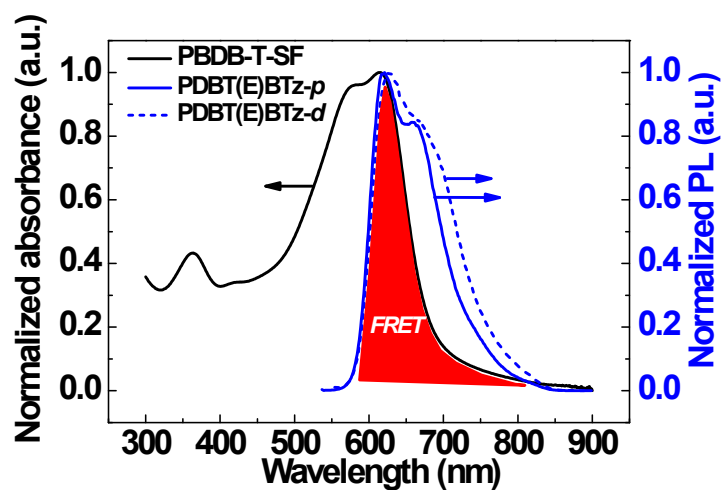


Fig. S4 Normalized absorbance of PBDB-T-SF and PL of PDBT(E)Tz-*p* and PDBT(E)Tz-*d*.

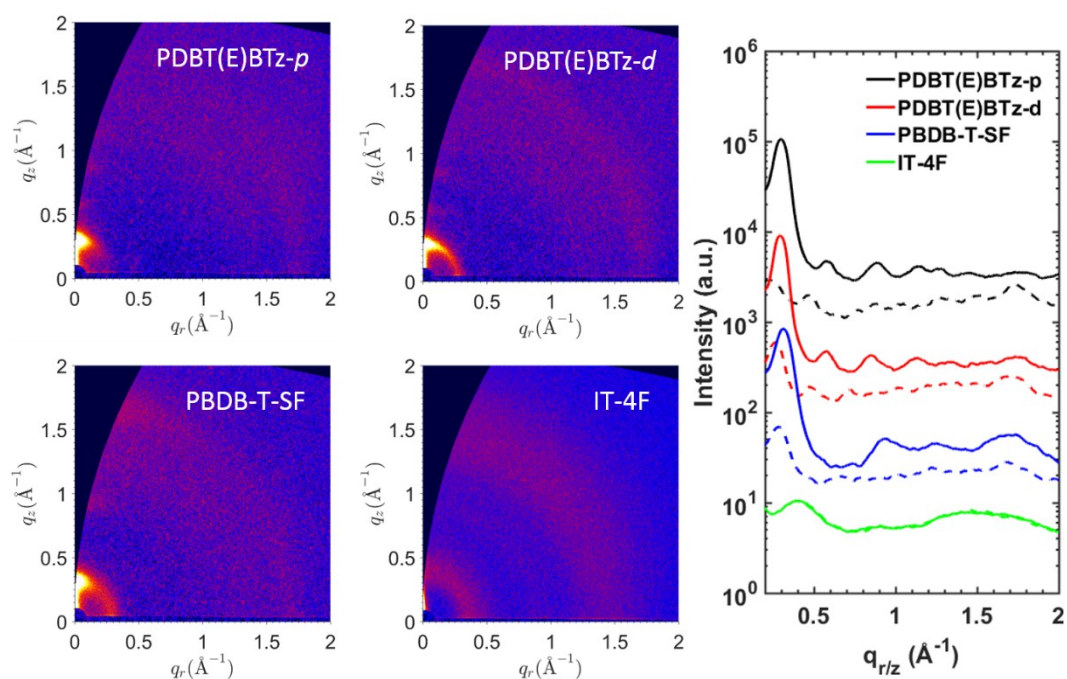


Fig. S5 Two-dimensional GIWAXS patterns of the pure films and the corresponding intensity profiles along the out-of-plane (solid lines) and in-plane (dashed lines) directions.

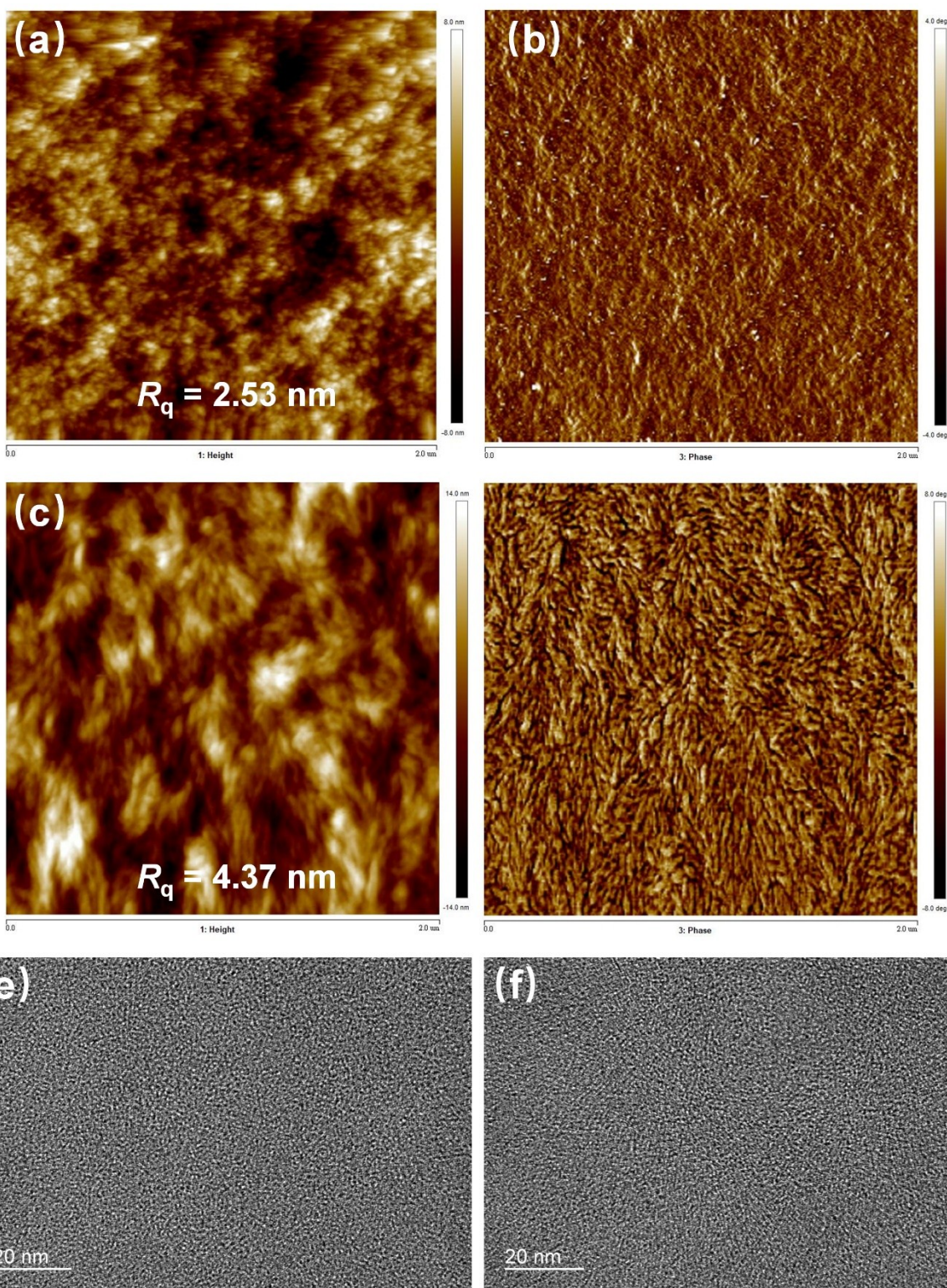


Fig. S6 The topography and TEM images of PDBT(E)Tz-*p*:IT-4F (a, c) and PDBT(E)Tz-*d*:IT-4F (b, d).

Table S1. Photovoltaic parameters of the ternary devices with different ratio of the third component and PBDB-T-SF.

Active Layer	V_{oc} (V)	J_{sc} ($J_{calc.}^a$) (mA/cm ²)	FF (%)	PCE (%)
PDBT(E)BTz- <i>p</i> /PBDB-T-SF/IT-4F (0.1/1/1.1)	0.87	18.21	75.6	12.0
PDBT(E)BTz- <i>p</i> /PBDB-T-SF/IT-4F (0.2/1/1.2)	0.87	17.06	72.1	10.7
PDBT(E)BTz- <i>d</i> /PBDB-T-SF/IT-4F (0.1/1/1.1)	0.87	18.56	77.0	12.4
PDBT(E)BTz- <i>d</i> /PBDB-T-SF/IT-4F (0.2/1/1.2)	0.87	17.36	76.4	11.4

NMR

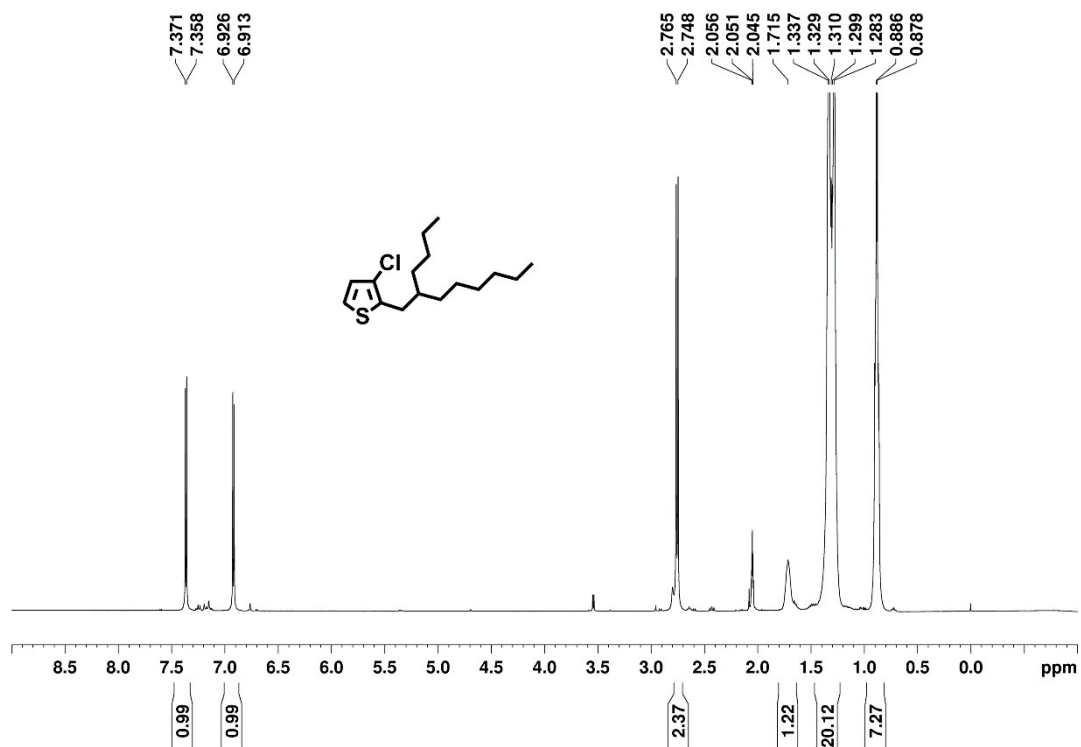


Fig. S7 ^1H NMR spectrum of compound 1.

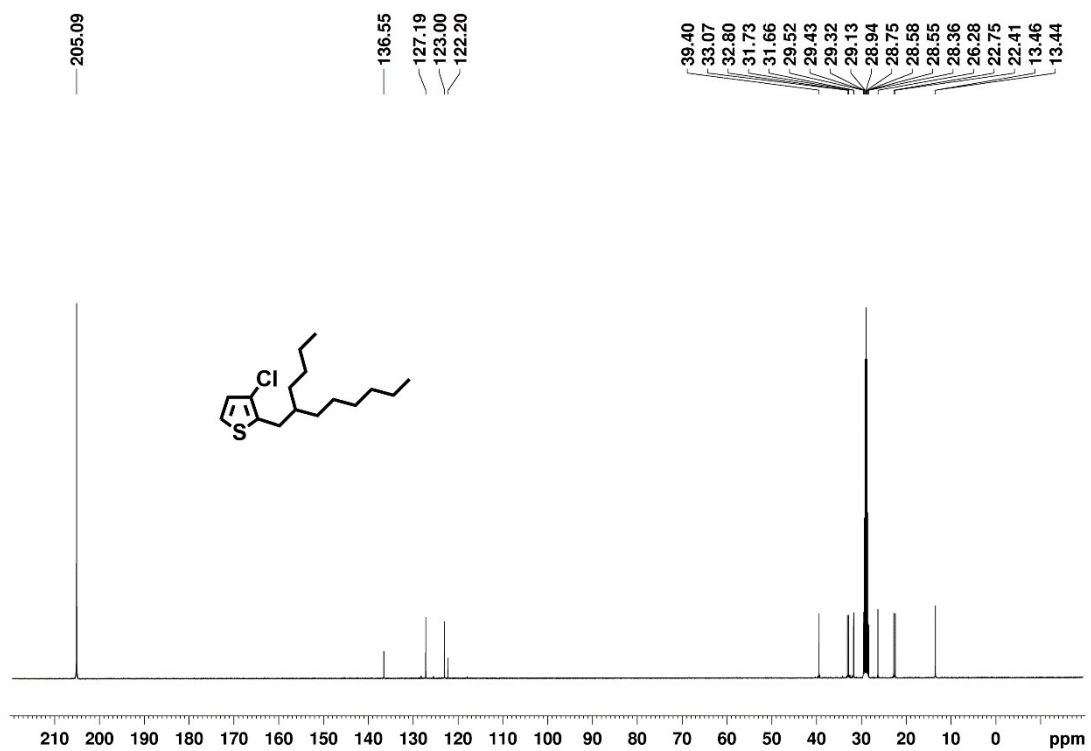


Fig. S8 ^{13}C NMR spectrum of compound 1.

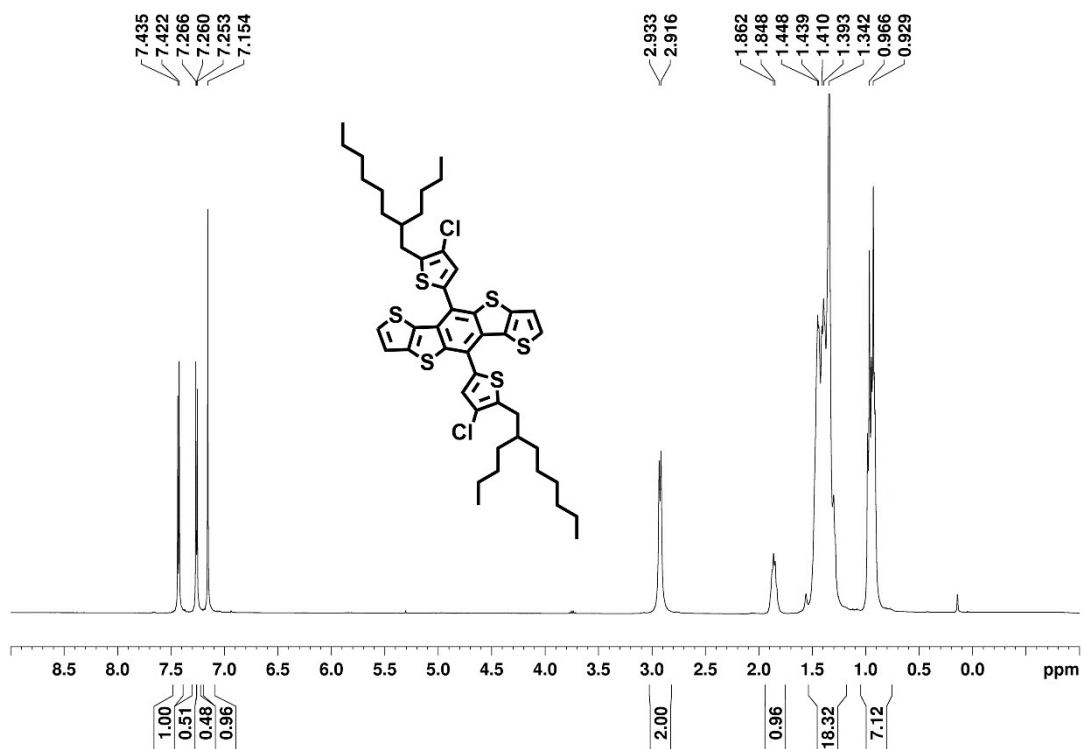


Fig. S9 ¹H NMR spectrum of compound 2.

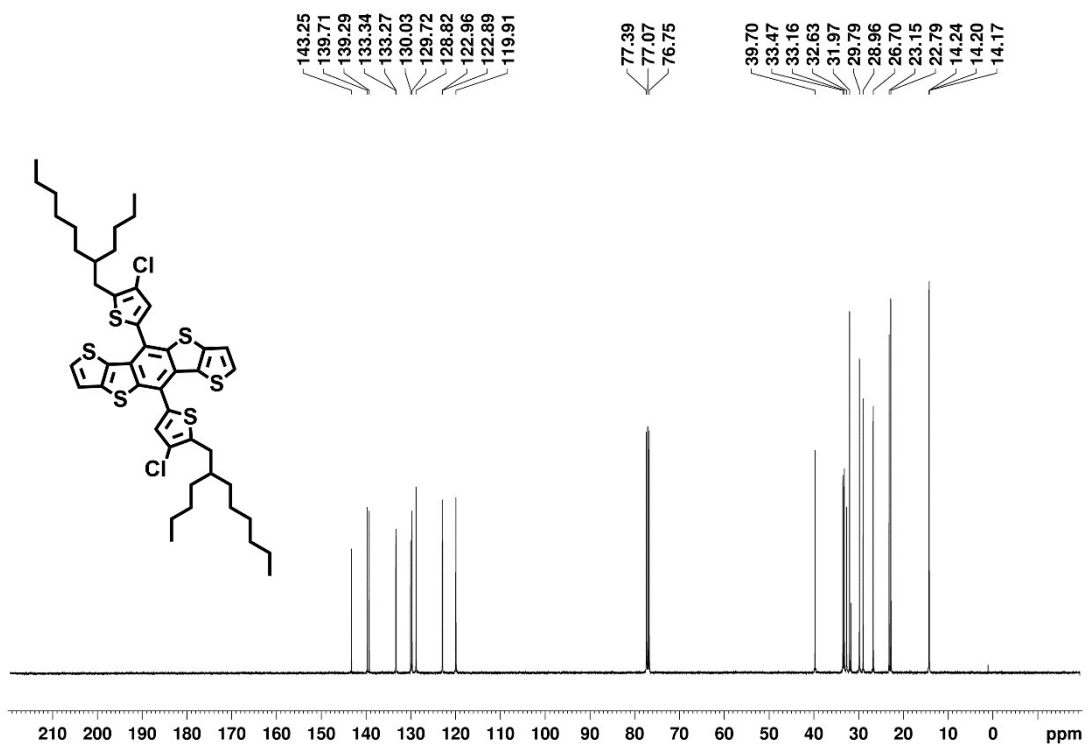


Fig. S10 ¹³C NMR spectrum of compound 2.

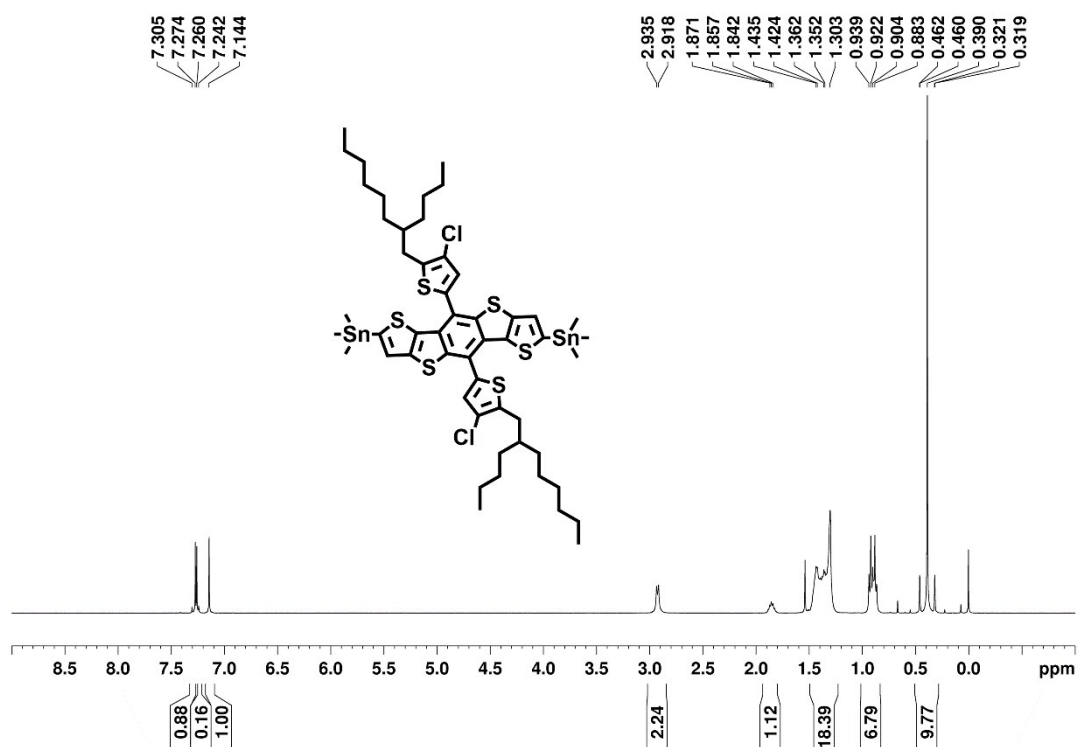


Fig. S11 ¹H NMR spectrum of compound 3.

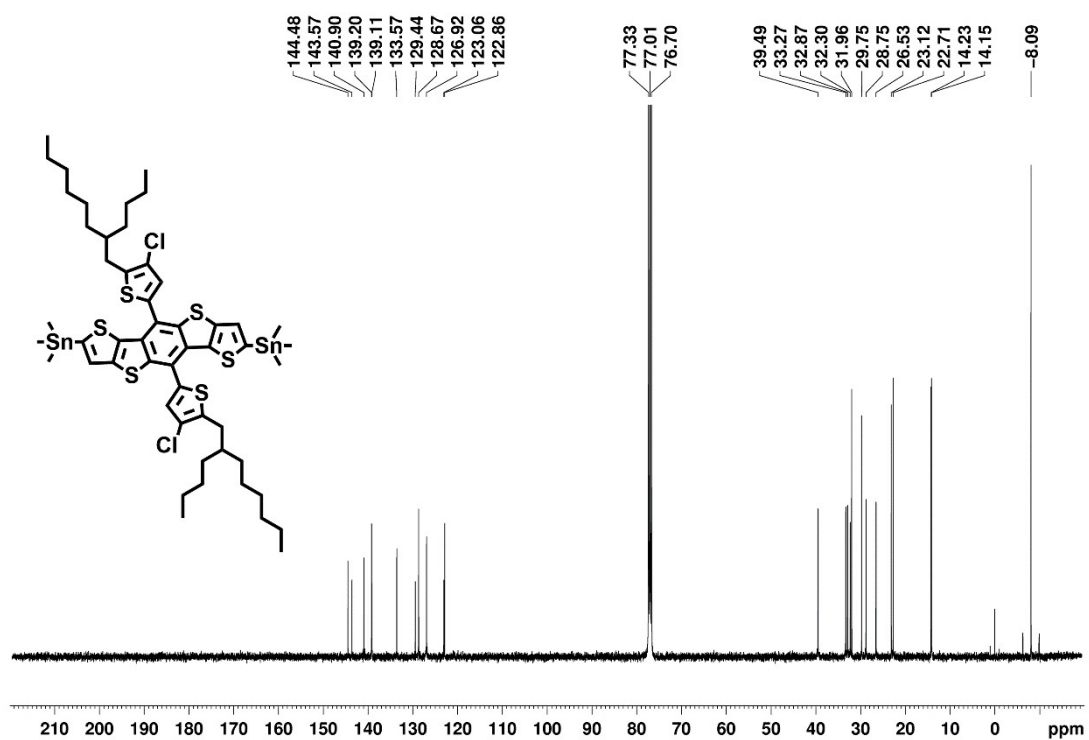


Fig. S12 ¹³C NMR spectrum of compound 3.

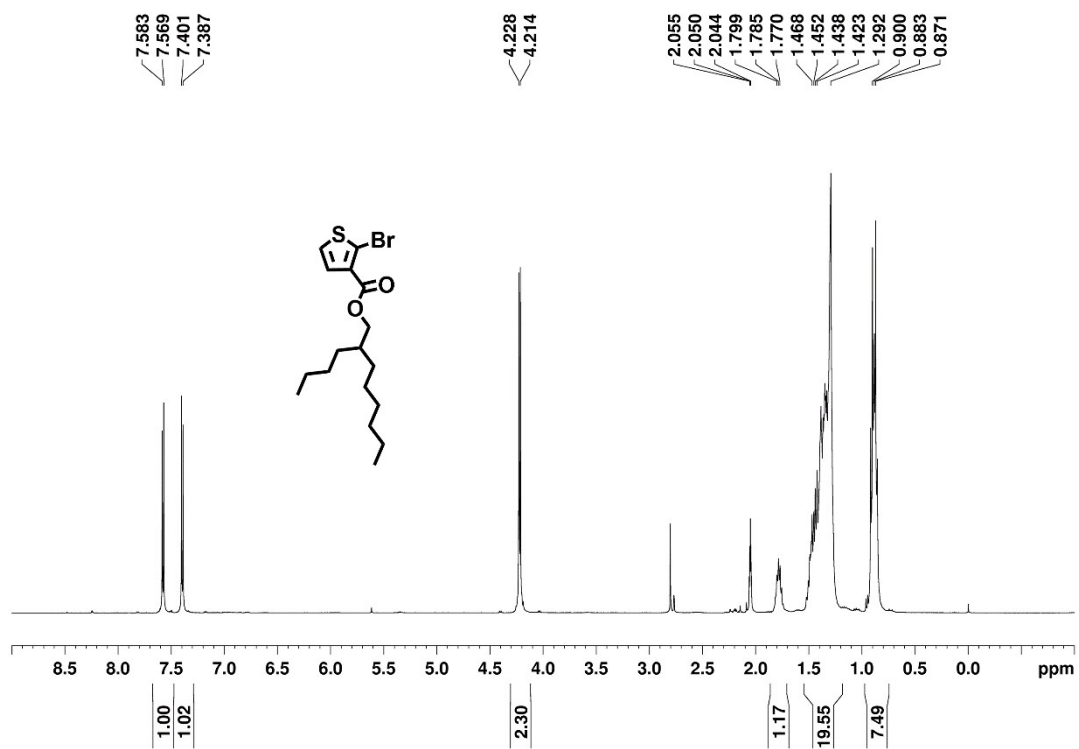


Fig. S13 ¹H NMR spectrum of compound 4.

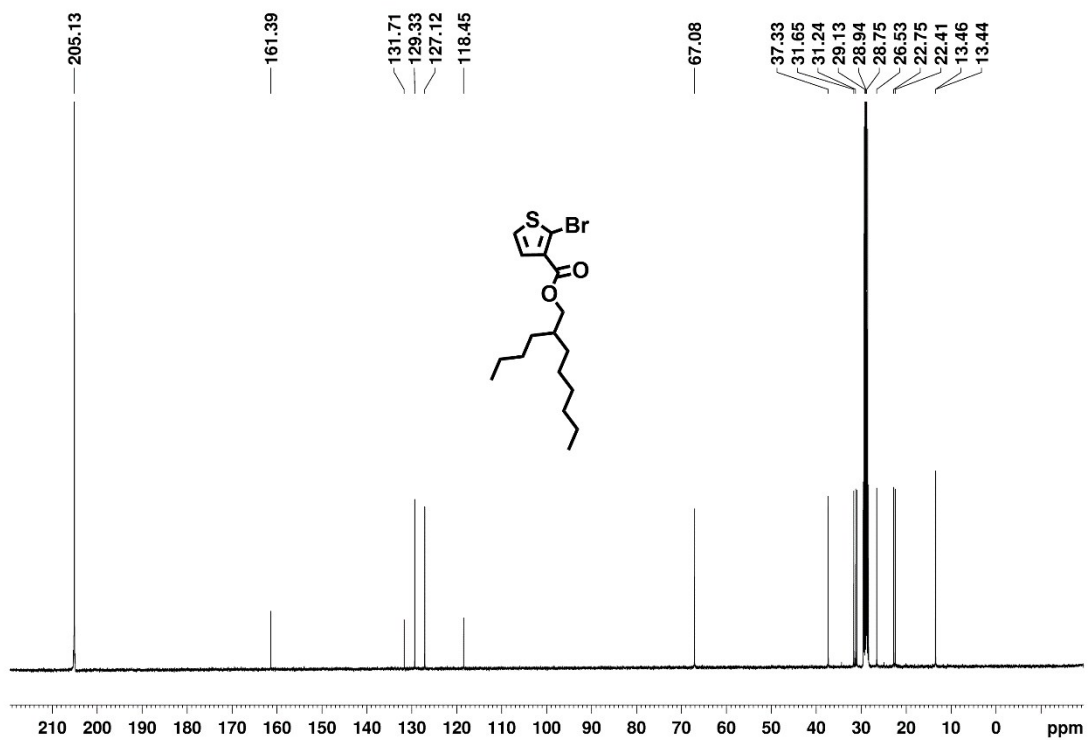


Fig. S14 ¹³C NMR spectrum of compound 4.

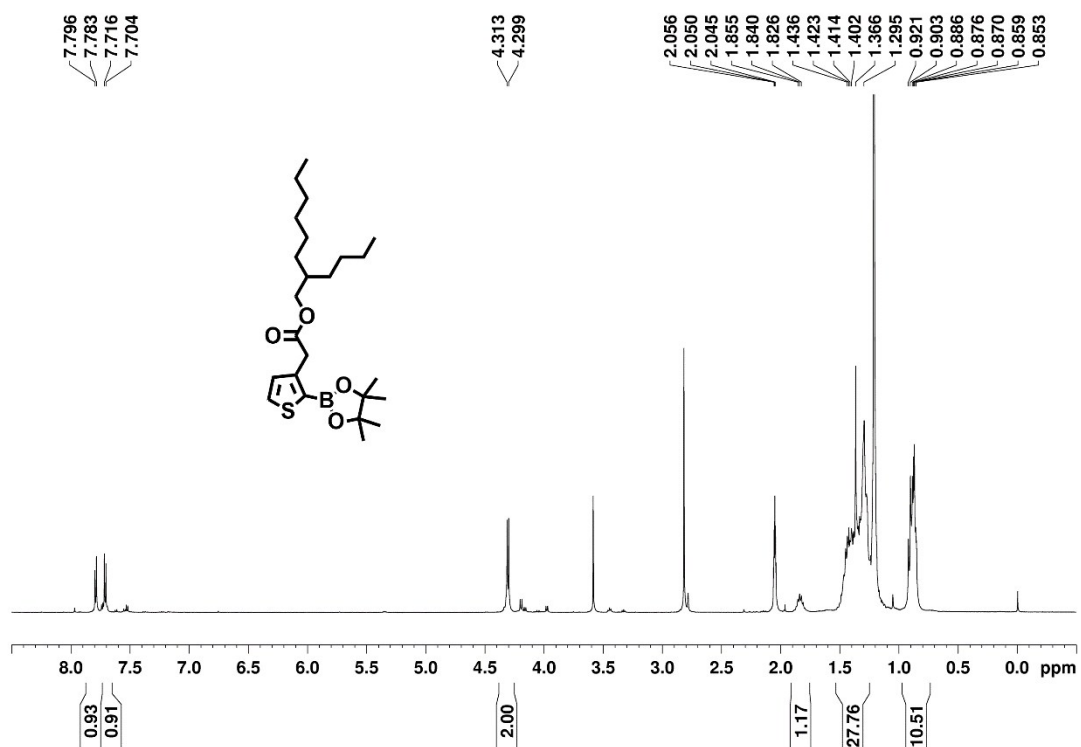


Fig. S15 ¹H NMR spectrum of compound 5.

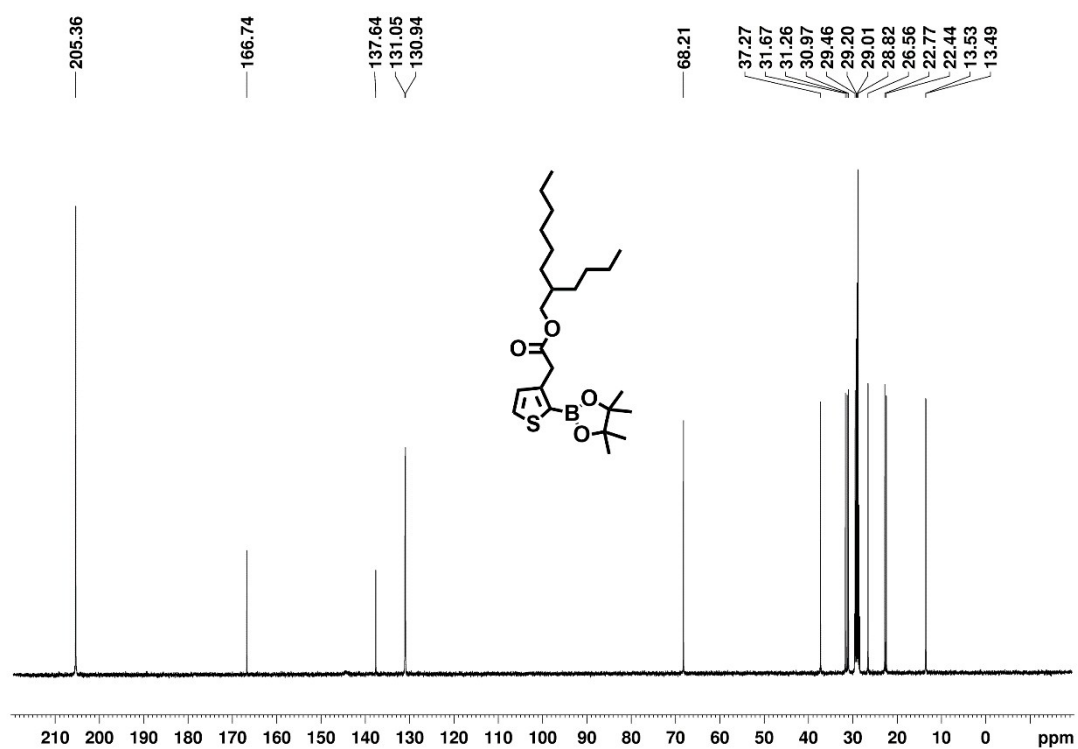


Fig. S16 ¹³C NMR spectrum of compound 5.

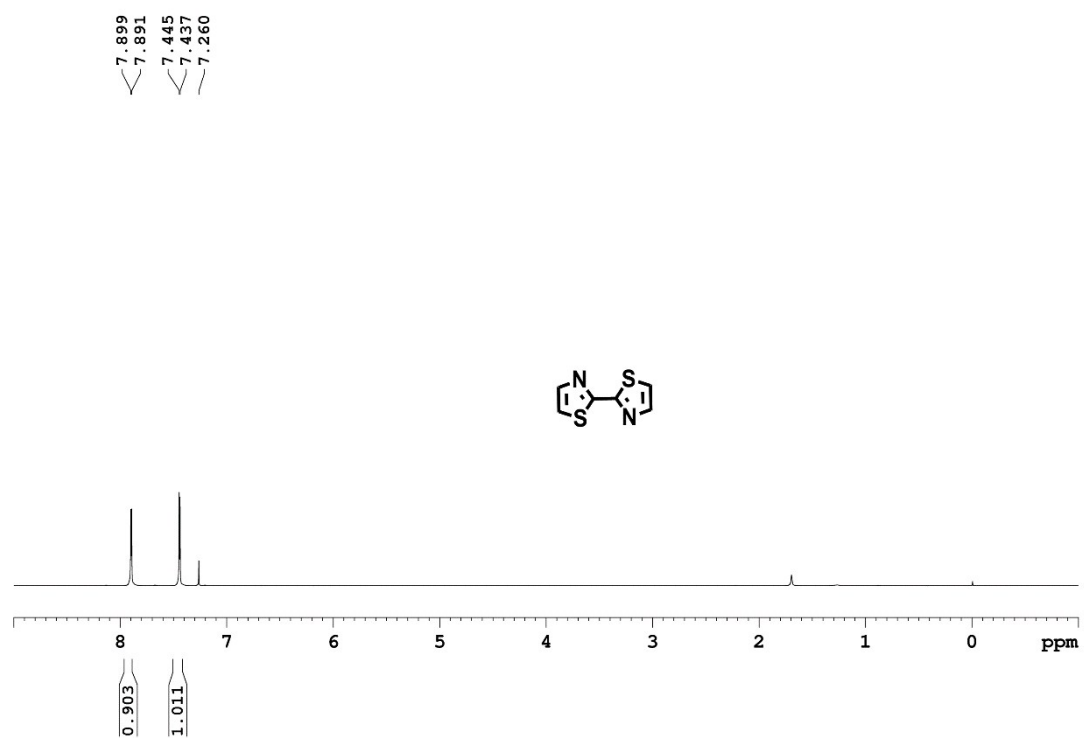


Fig. S17 ¹H NMR spectrum of compound 6.

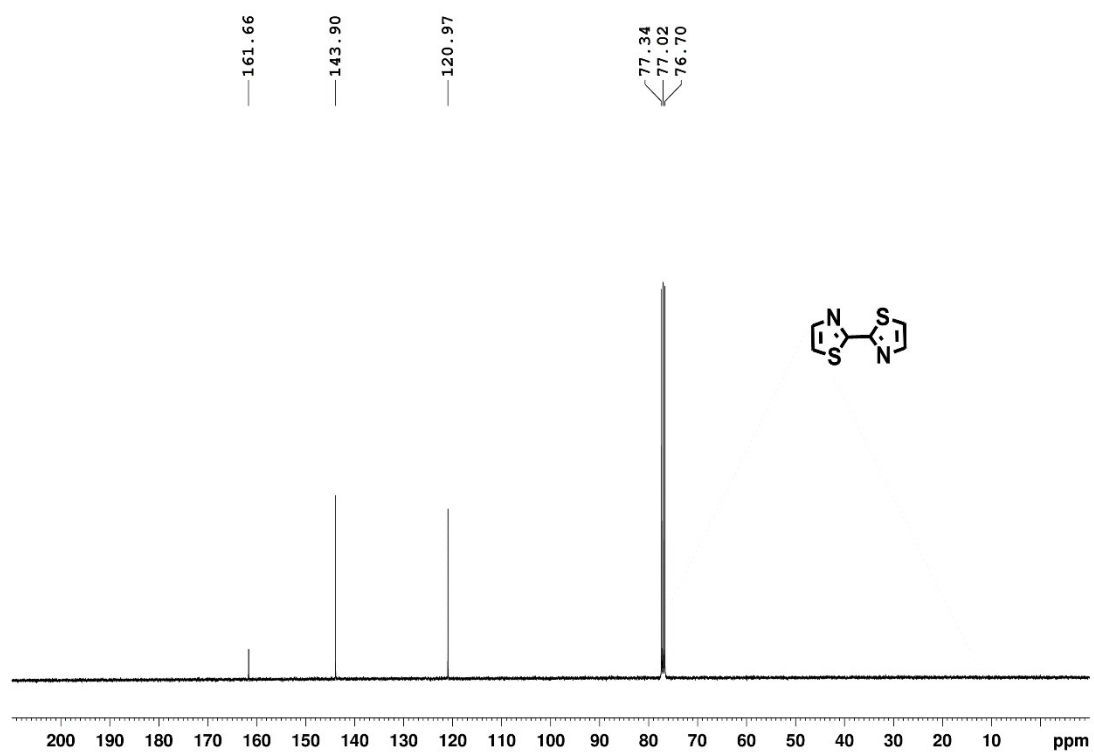


Fig. S18 ¹³C NMR spectrum of compound 6.

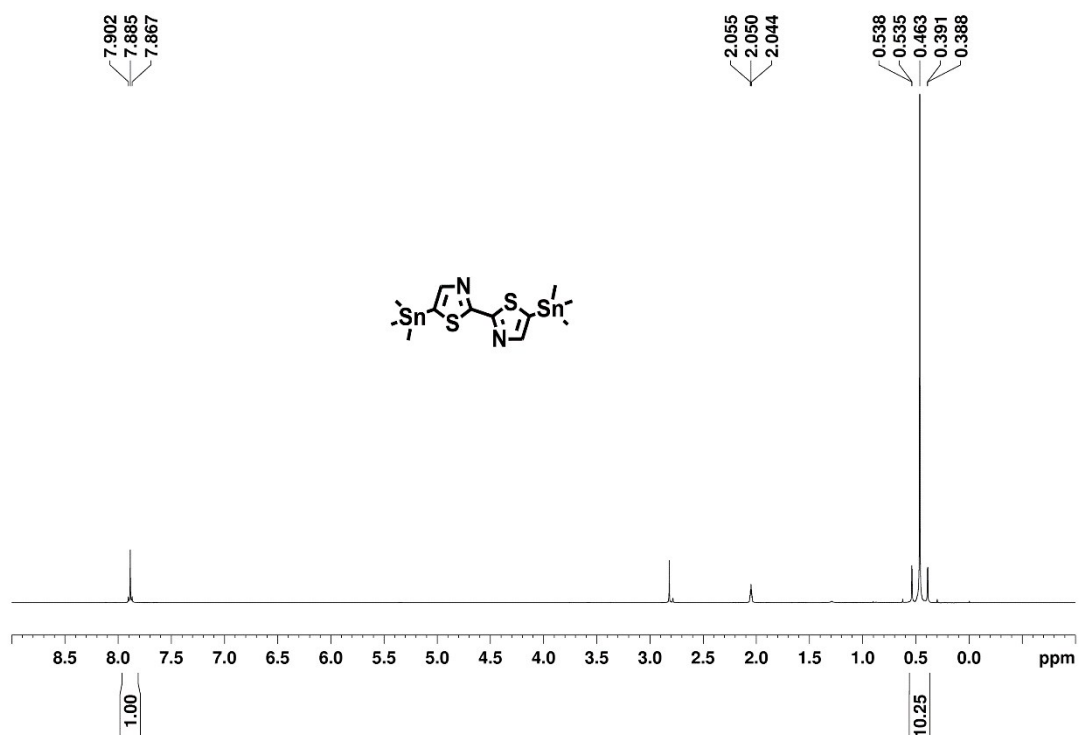


Fig. S19 ^1H NMR spectrum of compound 7.

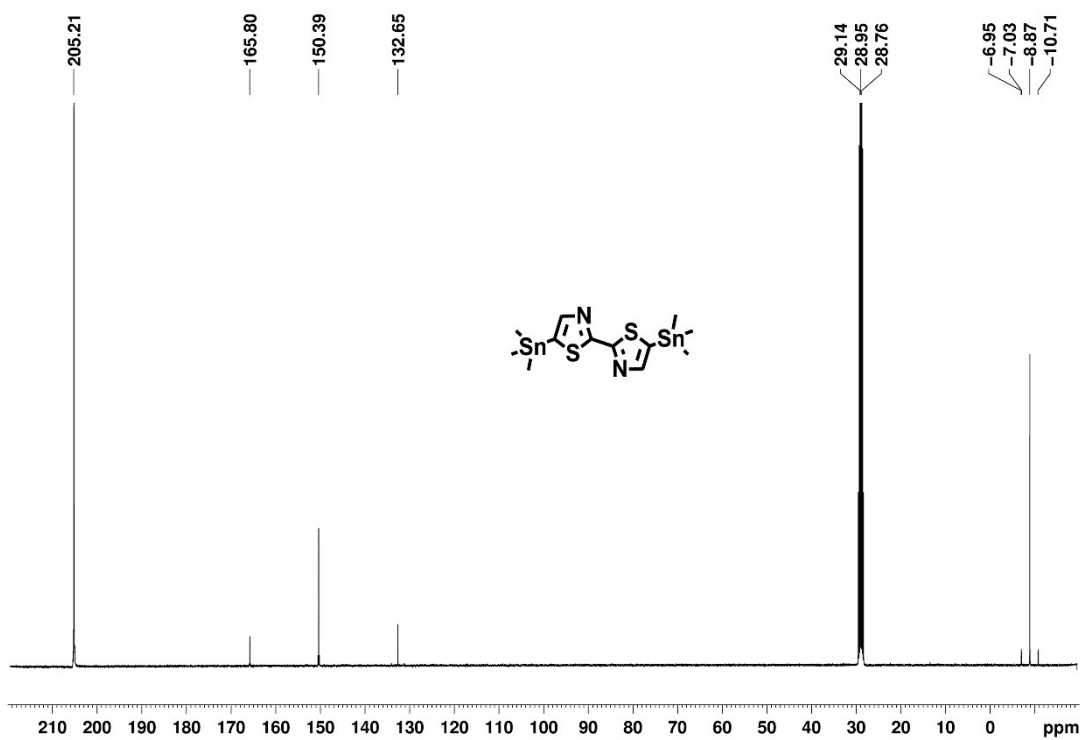


Fig. S20 ^{13}C NMR spectrum of compound 7.

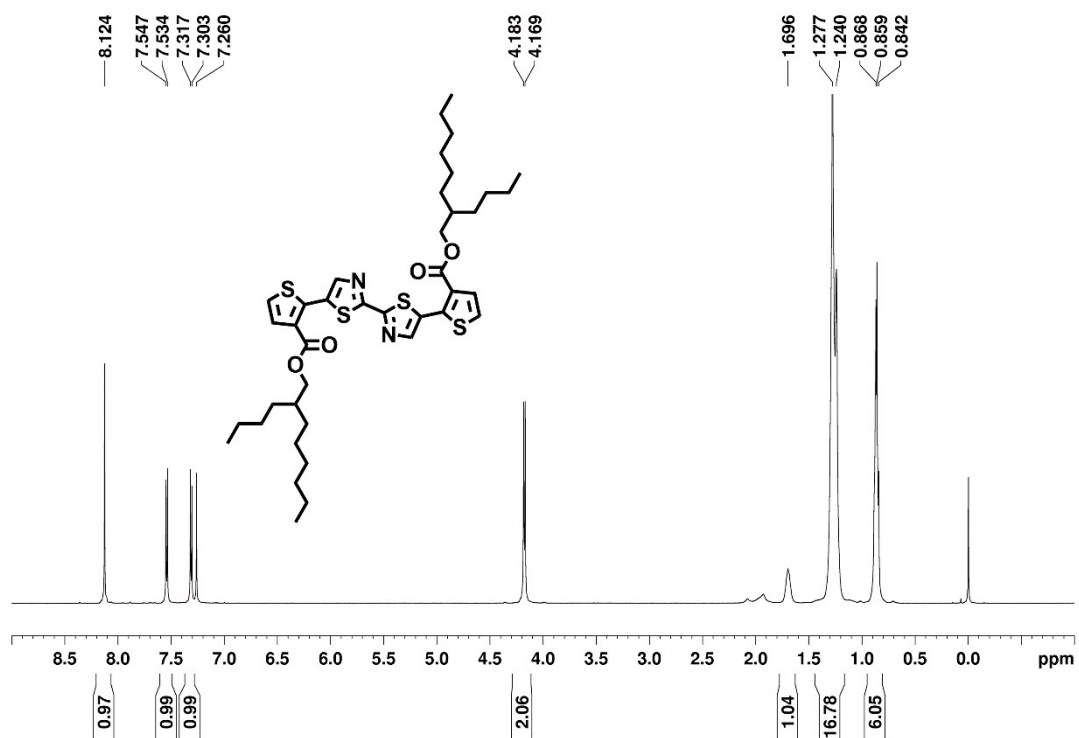


Fig. S21 ¹H NMR spectrum of compound 8.

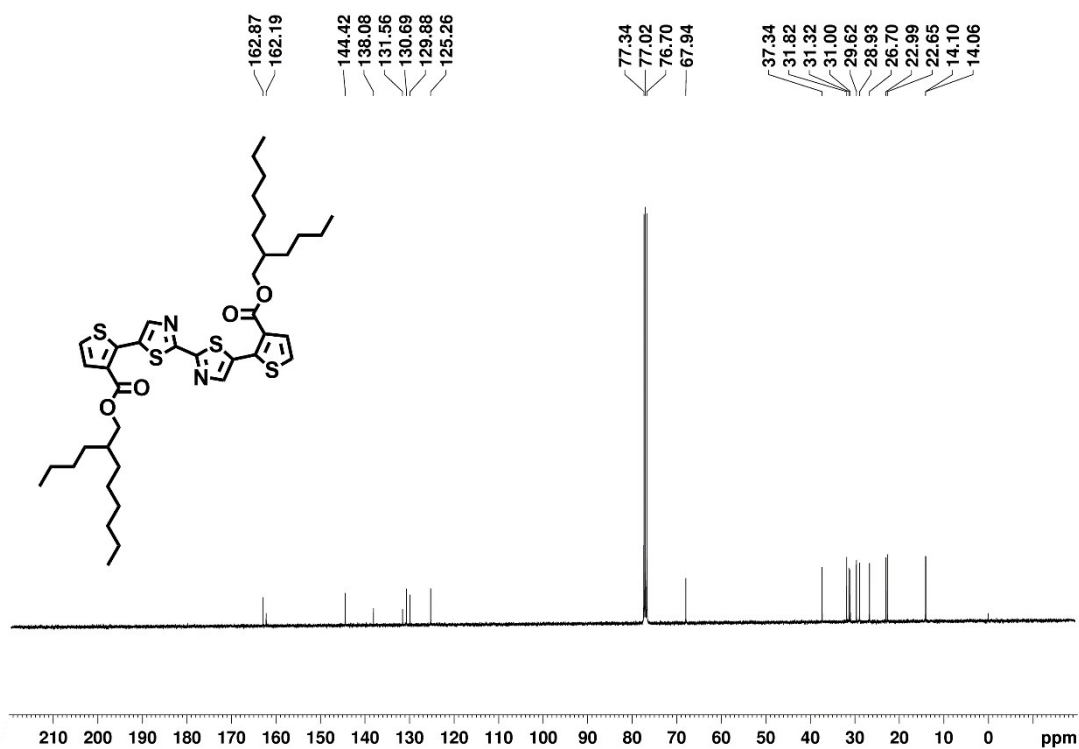


Fig. S22 ¹³C NMR spectrum of compound 8.

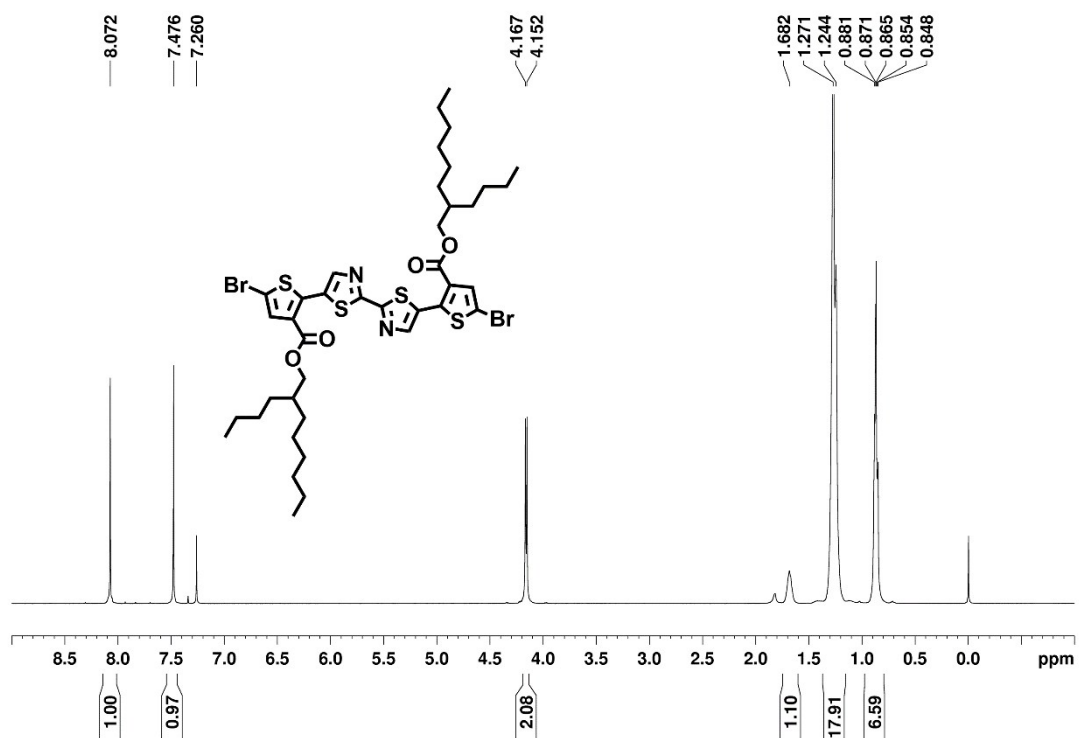


Fig. S23 ^1H NMR spectrum of compound 9.

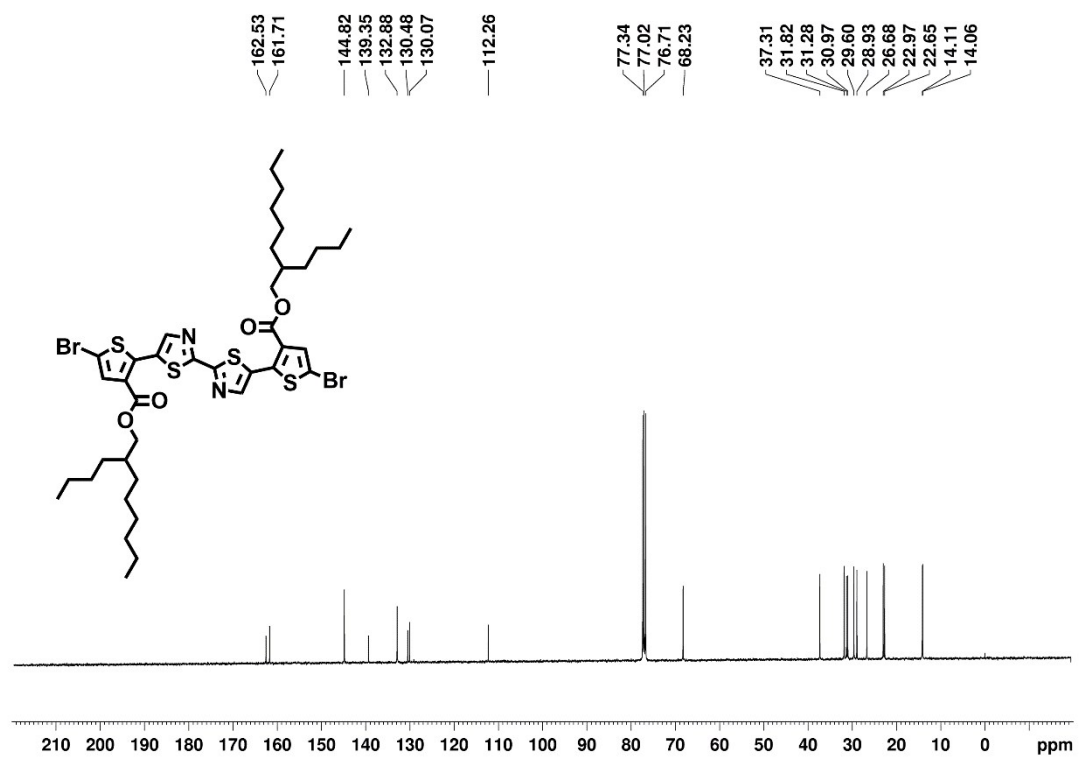


Fig. S24 ^{13}C NMR spectrum of compound 9.

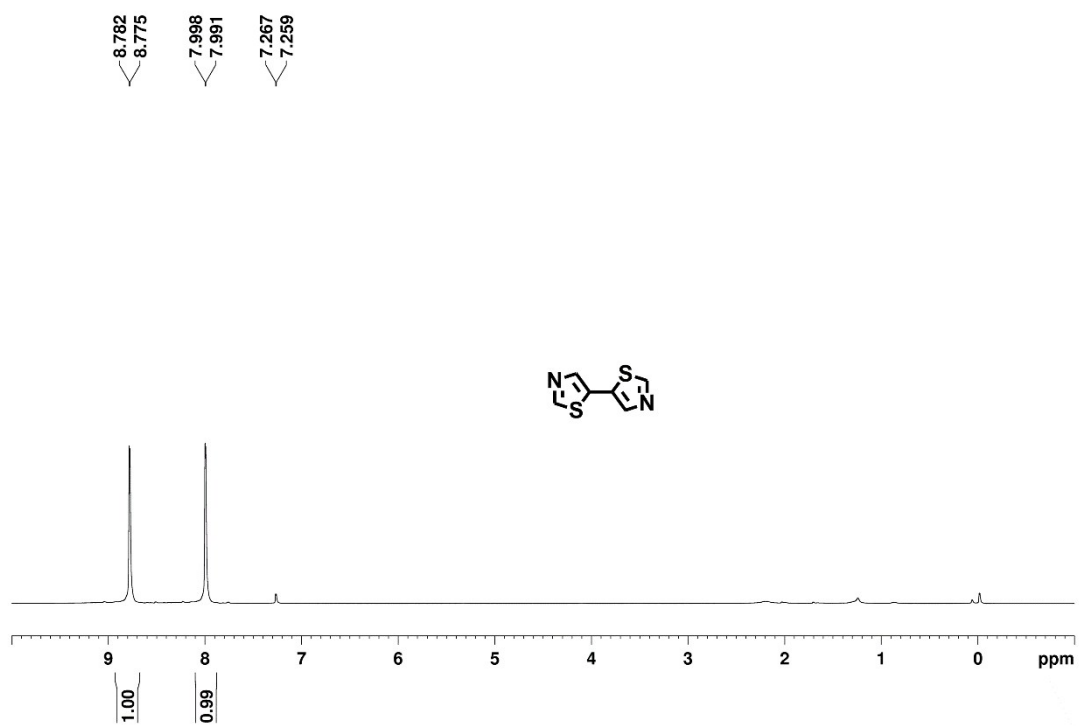


Fig. S25 ¹H NMR spectrum of compound 10.

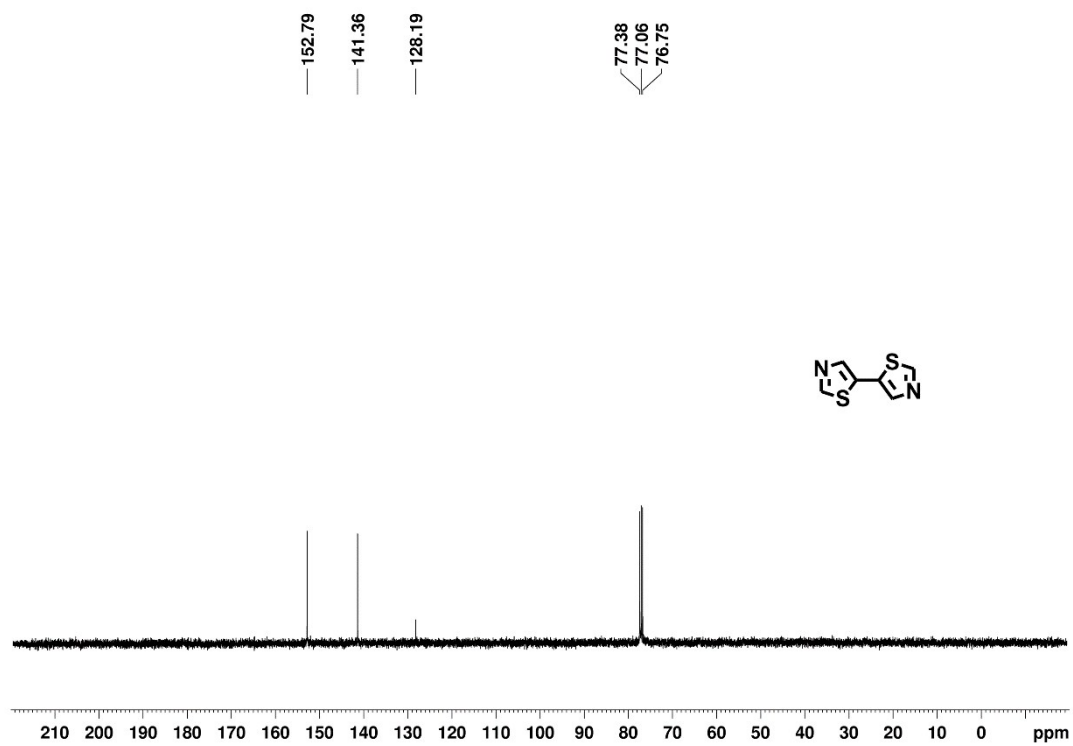


Fig. S26 ¹³C NMR spectrum of compound 10.

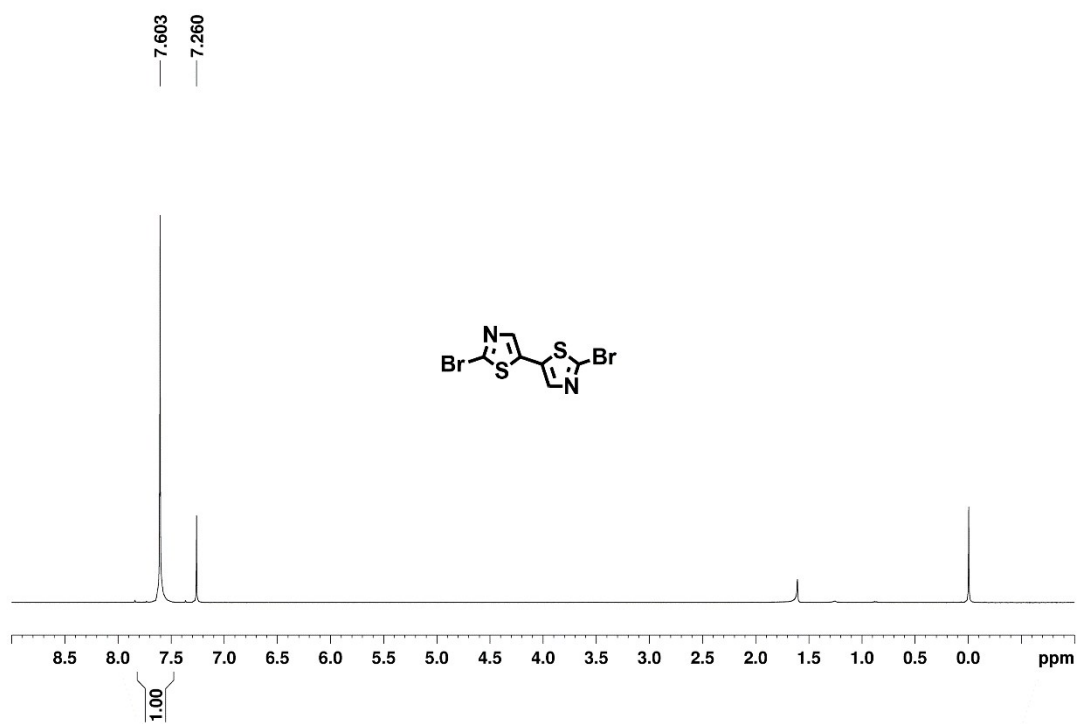


Fig. S27 ¹H NMR spectrum of compound 11.

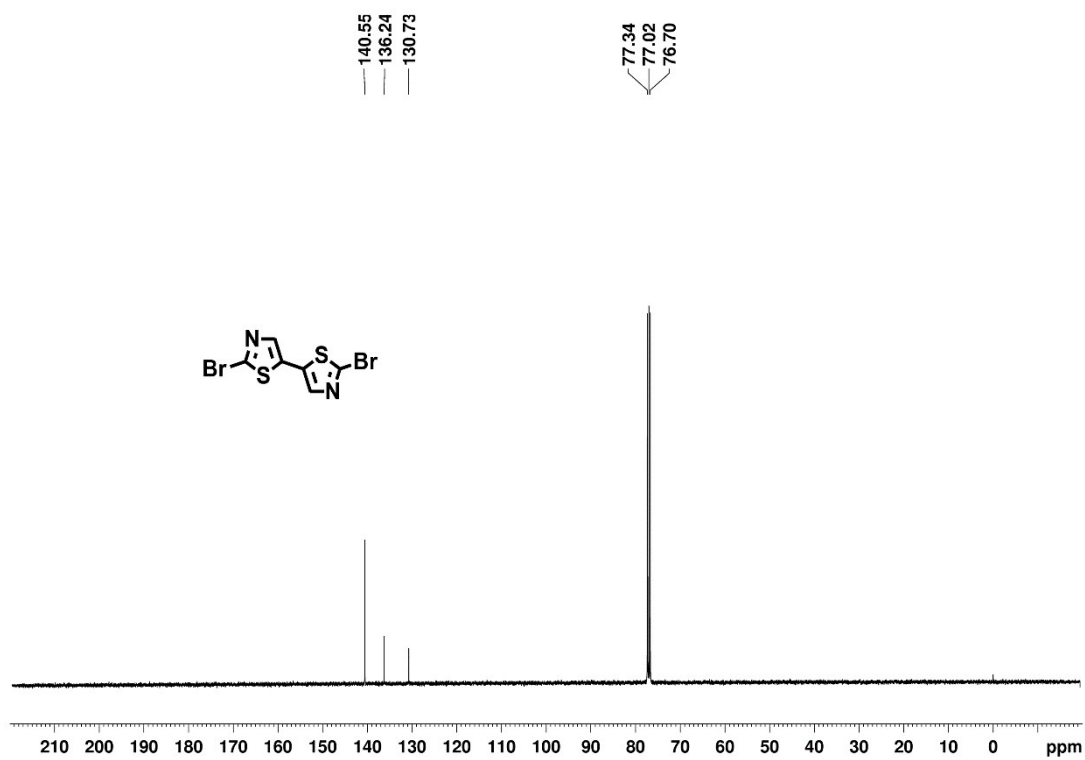


Fig. S28 ¹³C NMR spectrum of compound 11.

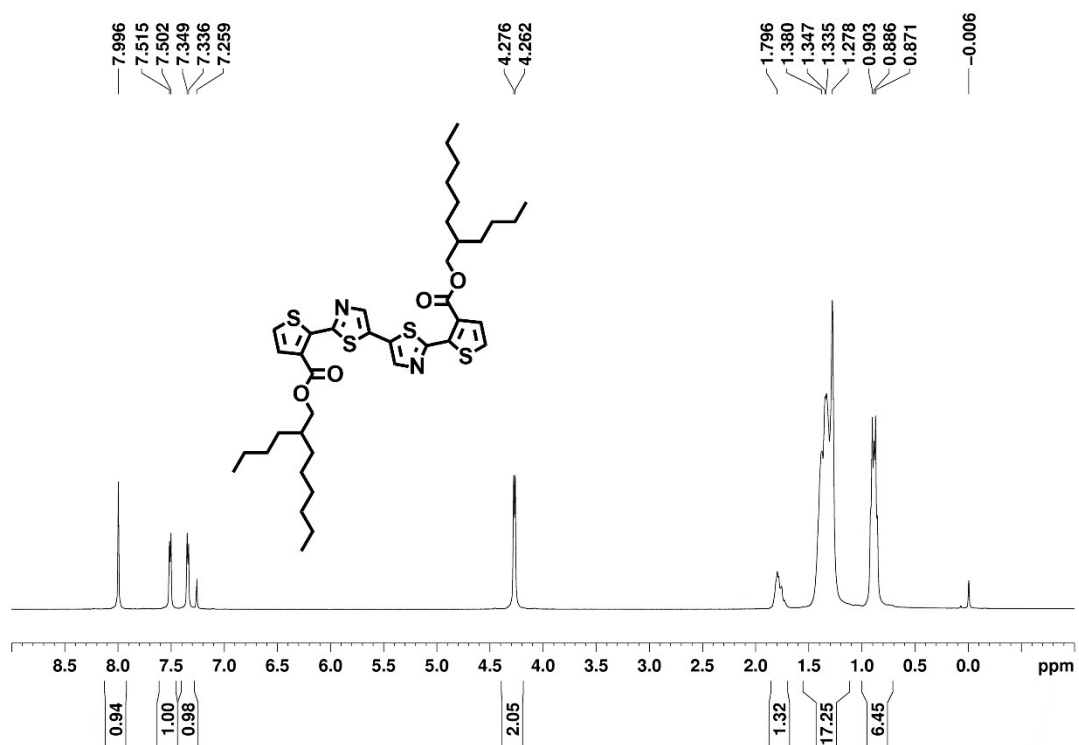


Fig. S29 ¹H NMR spectrum of compound 12.

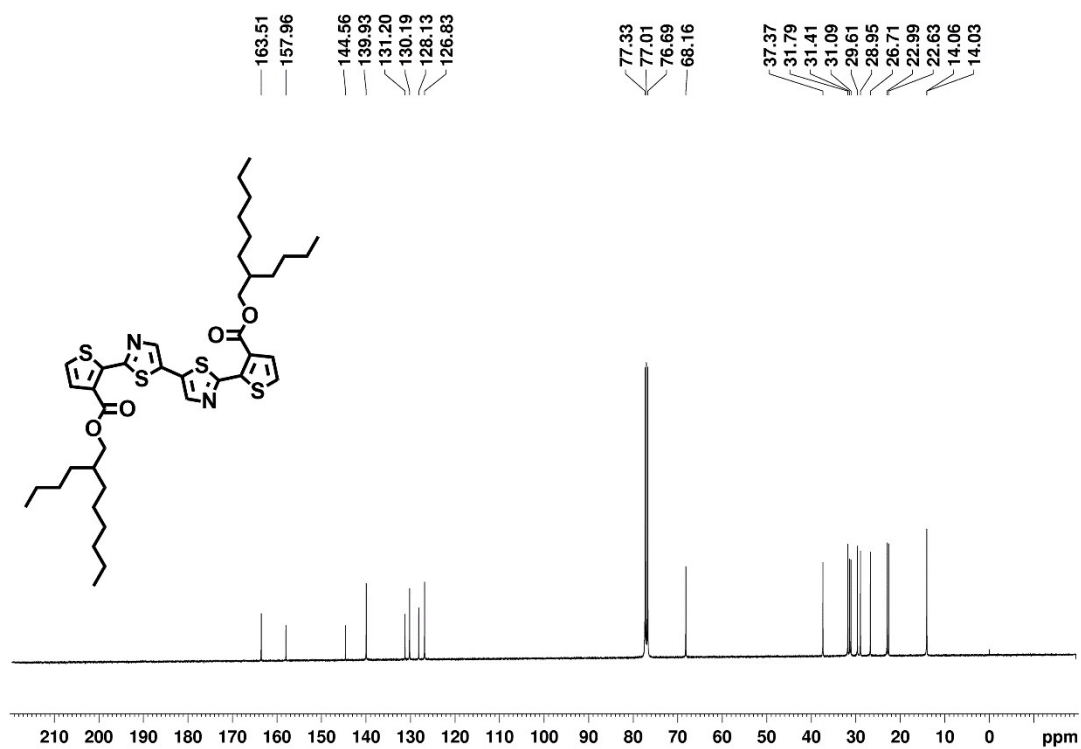


Fig. S30 ¹³C NMR spectrum of compound 12.

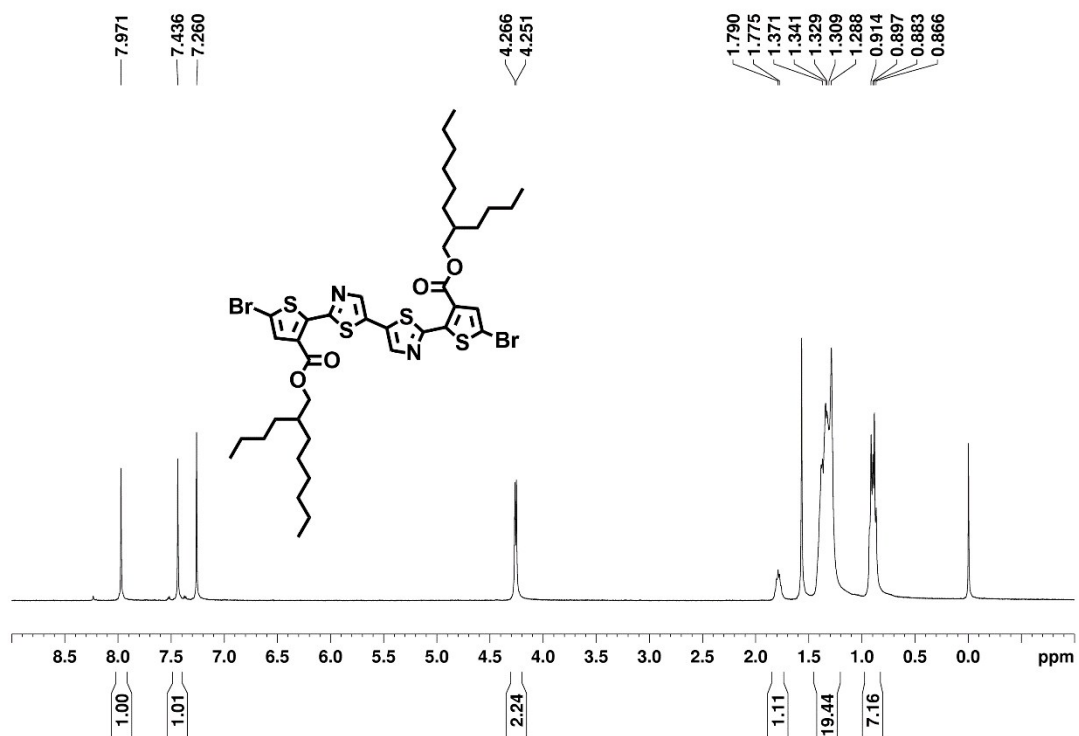


Fig. S31 ^1H NMR spectrum of compound 13.

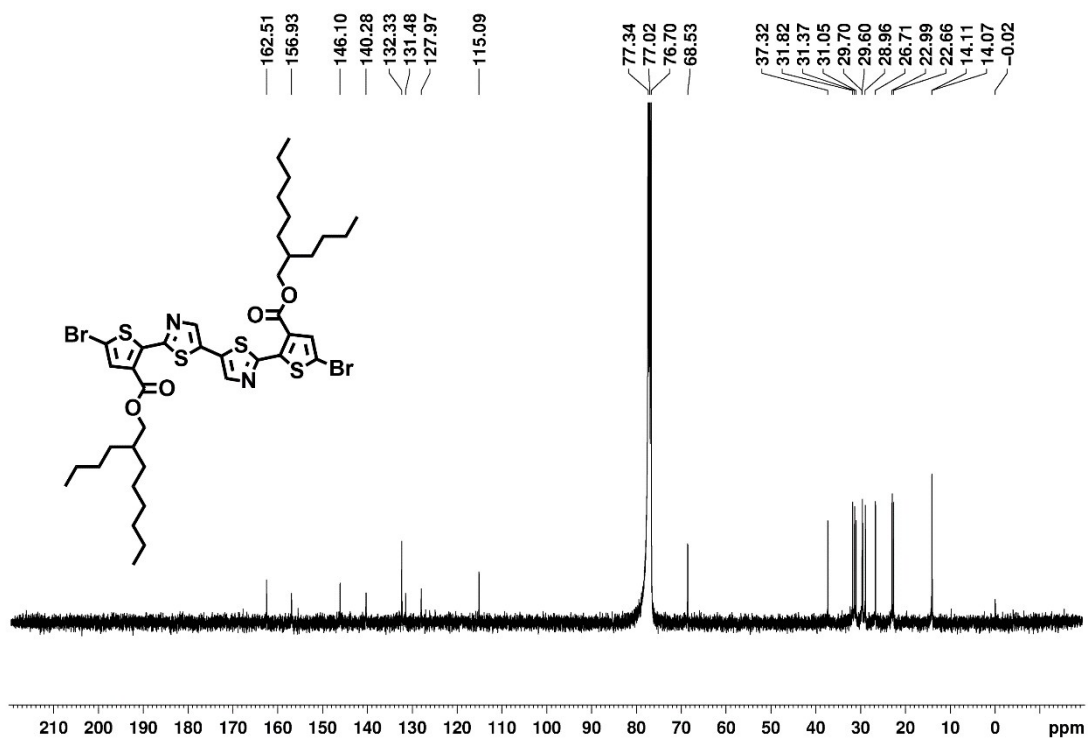


Fig. S32 ^{13}C NMR spectrum of compound 13.

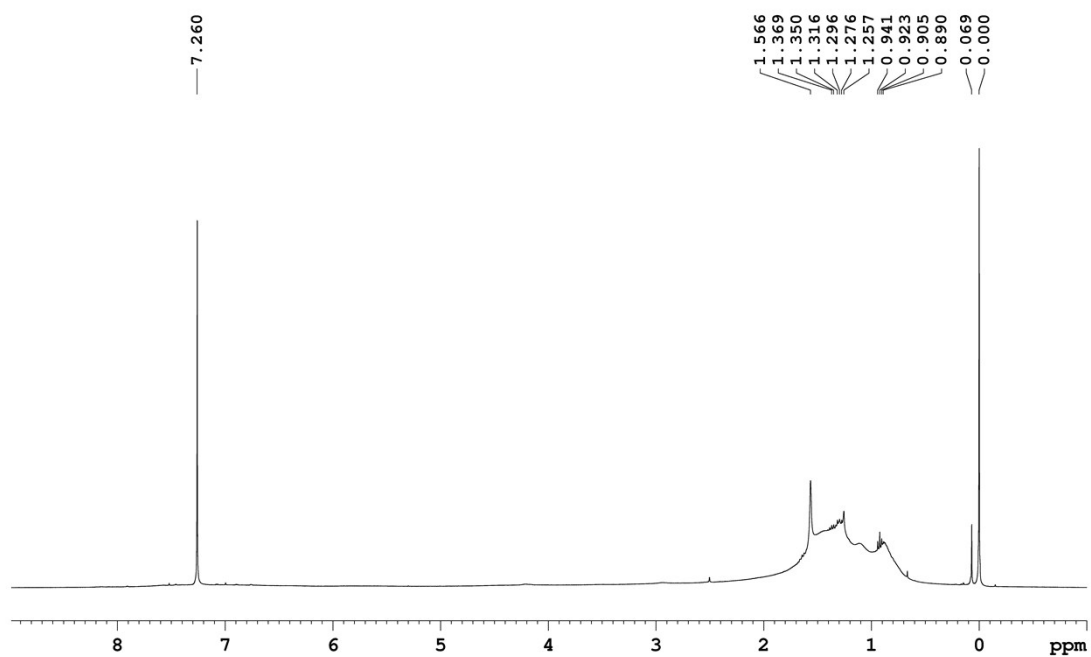


Fig. S33 ^1H NMR spectrum of compound PDBT(E)BTz-*p*.

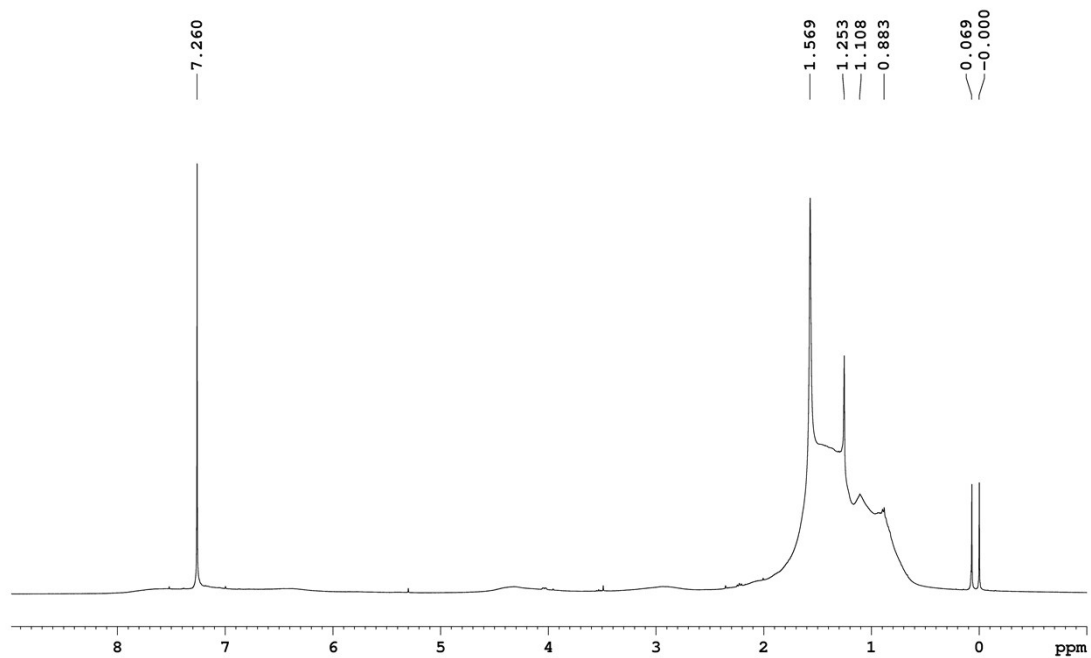


Fig. S34 ^1H NMR spectrum of compound PDBT(E)BTz-*d*.

References

- 1 a) H.-J. Yun, Y.-J. Lee, S.-J. Yoo, D. S. Chung, Y.-H. Kim, S.-K. Kwon, *Chemistry – A European Journal* **2013**, 19, 13242; b) T. T. Do, K. Rundel, Q. Gu, E. Gann, S. Manzhos, K. Feron, J. Bell, C. R. McNeill, P. Sonar, *New Journal of Chemistry* **2017**, 41, 2899; c) M. Pomerantz, A. S. Amarasekara, H. V. R. Dias, *The Journal of Organic Chemistry* **2002**, 67, 6931.
- 2 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2009.