Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Side-chain manipulation on accepting units of two-dimensional benzo[1,2-b:4,5-b']dithiophene polymers for organic photovoltaics

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Content

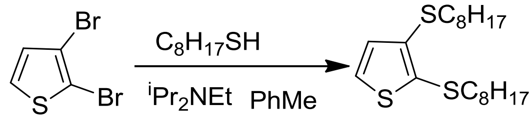
1. Experimental section

1.1 General Details. All regents and chemicals were purchased from common commercial sources (Sigma-Aldrich Co., TCI, or Acros) and used without further purification. Tetrahydrofuran (THF), diethyl ether and toluene were was dried over sodium/benzophenone and freshly distilled prior to use. Dichloromethane and chloroform were purified by refluxing over CaH_2 under nitrogen. All reactions were performed under N_2 atmosphere unless otherwise stated.

^{1}H NMR and ^{13}C NMR spectra were collected on a Bruker AVANCE III 500MHz instrument with tetramethylsilane (TMS) as internal standard. Ultraviolet-visible (UV-Vis) absorption spectra were recorded on a UV-Vis instrument Evolution 220 (Thermo Fisher). For thin film measurements, polymer films were cast from their chloroform solutions on quartz plates. Number average (M_n) and weight average (M_w) molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Waters 717-2410 with polystyrenes as reference standard and THF as an eluent. Thermogravimetric analyses (TGA) were carried out with a TA instrument TGA/SDTA851e with heating rate of 10^{o}C min^{-1} under nitrogen gas flow. The temperature of degradation (T_d) corresponds to a 5% weight loss. Cyclic voltammetry measurements were carried out using a CHI Instruments Model CHI 600D electrochemical workstation equipped with a standard three-electrode configuration. The measurements were taken in anhydrous acetonitrile with tetrabutyl ammonium hexafluorophosphate (0.1 M) as the supporting electrolyte under N_2 atmosphere at a scan rate of 50 mVs^{-1} using ferrocene/ferrocenium (Fc/Fc+) as internal standard.

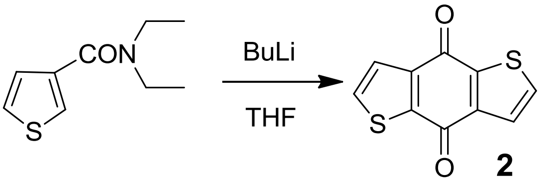
1.2 Synthesis of momoners. The monomer fBT **M3** was synthesized according to the modified procedures in literature.[S1]

2,3-Bis(octylthio)thiophene (1). In a 100 ml dried 2-neck round–bottom flask flask with a condenser, 2,3-dibromothiophene (3.0 g, 12.40 mmol), octane-1-thiol (3.63 g, 24.80 mmol), N,N-diisopropylethylamine (3.53 g, 27,82 mmol) and dry toluene 40 mL were added. The mixture was purged with nitrogen for 30min. Then $Pd_2(dba)_3$ (227 mg) and DPPF (275 mg) was added and the reaction mixture was heated to reflux for 6 hour under N2. The reaction was cooled to room temperature and the solvent was evaporated. The crude oil was purified by column chromatography in hexanes to obtain 4.20 g (11.28 mmol, 91%) of light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 7.28 (d, *J* = 5.5 Hz, 1H), 6.97 (d, J = 5.5 Hz, 1H), 2.89 – 2.85 (m, 2H), 2.84 – 2.80 (m, 2H), 1.64 – 1.57 (m, 4H), 1.39 (s, 4H), 1.28 (dd, *J* = 14.3, 8.1 Hz, 17H), 0.87 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 136.78, 131.74), 129.59, 127.14, 37.60, 34.86, 31.8, 29.96,29.28, 29.16, 28.76, 28.59, 22.65.



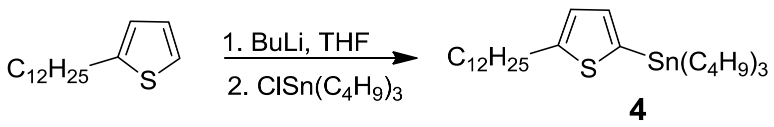
1

4,8-Dihydrobenzo[1,2-b:4,5-b']dithiophen-4,8-dione (2). N,N-diethylthiophene-3-carboxamided (8.0g, 43.65 mmol) was diluted in 80 mL of dry THF, and cooled to 0 ℃ in a nitrogen atmosphere. 45.83 mL of 2.5 M n-BuLi in hexane (0.023 mol, 1.0 eq.) was slowly added. The solution was stirred for 30 minutes at 0 ℃ and then for 1 hours at room temperature. The reaction was poured into 500 mL of ice water, and continued to be stirred for 4 hours. The precipitate was filtered, washed with water, methanol and n-hexane, and finally dried to give a yellow solid (8.07 g, 84 %). ^{1}H NMR (500 MHz, DMSO-$_{d6}$, δ/ppm): 8.15 (d, *J* = 5.0 Hz, 1H), 7.63 (d, *J* = 5.0 Hz, 1H).

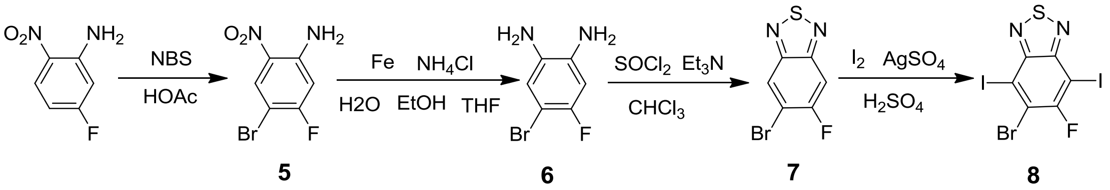


2

Tributyl(5-dodecylthiophen-2-yl)stannane (4). 2-dodecylthiophene (4 g, 15.84 mmol) was diluted in 80 mL of dry THF and purged with nitrogen for 15min. The solution was cooled to -78 ℃ and 7.26 mL of 2.4M n-BuLi in hexane was added drop-wise to the mixture. Then the mixture was warmed to room temperature and stirred for 2h. 4.73 mL of 1.20 g/ml tributyltin chloride was added after the mixture was stirred at -78 ℃. The mixture was warmed to room temperature and stirred overnight, then the solution was poured 200 ml ice water and extracted with ether. The combined extracts were washed with water, brine, dried with anhydrous Mg2SO4 and removed by using a rotary evaporator to obtain 7.38g (13.62 mmol, 86%) of white liquid. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 7.00 (d, *J* = 3.2 Hz, 1H), 6.92 (d, *J* = 3.0 Hz, 1H), 2.87 (t, *J* = 7.7 Hz, 2H), 1.70 (dd, *J* = 15.1, 7.5 Hz, 2H), 1.59 (m, 8H), 1.44 – 1.31 (m, 22H), 1.13 – 1.07 (m, 6H), 0.98 – 0.86 (m, 12H).



4-Bromo-5-fluoro-2-nitroaniline (5). Compound 4 (6.00 g, 38.43 mmol) and NBS (6.84 g, 38.43 mmol) were diluted in 300 ml of HOAc, which was stirred at 118 ℃ for 90 min. Then the reaction was poured into 500 ml of ice water. The mixture was filtered, washed with water and dried to afford 6.86 g (29.14 mmol, 76%) of yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 8.40 (d, *J* = 7.1 Hz, 1H), 6.60 (d, *J* = 9.6 Hz, 1H), 6.24 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 164.04, 162.00, 145.66, 145.42, 131.56 (s), 129.42 (s),104.84, 104.62, 96.41, 96.22.

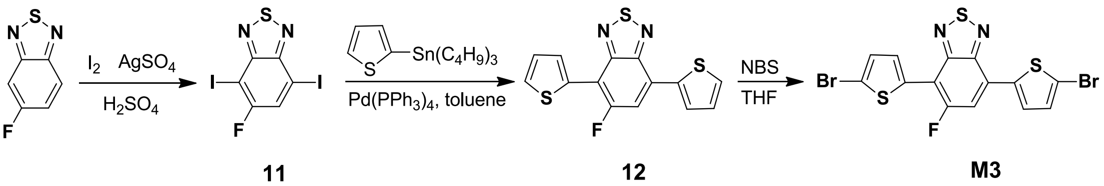


4-Bromo-5-fluro-1,2-diamine (6). In a 100 ml dried 2-neck round–bottom flask with a condenser, Compound 5 (4.0 g, 17.2 mmol) was diluted in EtOH (32 mL), THF (32 mL) and H_2O (16 mL). Then the mixture was added ammonium chloride (1.36 g, 25.6 mmol) and iron powder (4.8 g, 85.2 mmol), which was stirred at 95 ℃ for 4h. The cooled reaction was filtered, and the residue was diluted in EtOAc, washed with H_2O, brine, dried with Na_2SO_4, and filtered. The crude product was recrystallized with Hexane to give 2.79 g (13.6 mmol, 80%) of brown solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 6.84 (d, *J* = 6.5 Hz, 1H), 6.51 (d, *J* = 9.5 Hz, 1H), 3.55 (s, 2H), 3.23 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 154.57, 152.69, 136.18, 136.12, 131.13, 120.41, 104.17, 103.96, 96.48, 96.30.

5-Bromo-6-fluorobenzo[c][1,2,5]thiadiazole (7). Compound 6 (2 g, 9.75 mmol), triethylamine (6.8 ml, 48.7 mmol), and 100ml of $CHCl_3$ were added to a 250 ml round bottom flask under nitrogen atmosphere. Then the solution was cooled to 0 ℃ and dropped Thionylchloride (3.48g, 29.26 mmol) slowly. The reaction then was stirred at 61 ℃ for 5h. After the reaction, the mixture was cooled to room temperature and then was extracted with $CHCl_3$ and water. The organic layer was combined, dried over $MgSO_4$ and evaporated. The crud product was purified by column chromatography in hexane/dichloromethane (1:3 v/v) to obtain 1.59 g (6.83 mmol, 70%) of light gray solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 8.02 (d, *J* =7.5 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 160.16, 158.14, 153.61, 153.51, 151.84, 125.12, 116.13, 115.91, 105.21, 105.01.

5-Bromo-6-fluoro-4,7-diiodobenzo[c][1,2,5]thiadiazole (8). Compound 7 (1 g, 4.29 mmol), Ag_2SO_4 (4.38 g, 21.54 mmol), Iodine (4.36 g, 17.16 mmol) and sulfuric acid (30 mL) were added to a 50 ml round bottom flask and stirred for 30 minutes at room temperature. Then the solution was stirred at 100 ℃ for 5 days. After that the mixture was cooled to room temperature and then was poured into 500 ml of ice water. The mixture was extracted with $CHCl_3$, and the organic layer was combined, dried over $MgSO_4$ and evaporated. The crude product was recrystallized with acetone to give 1.25 g (2.57 mmol, 60%) of light yellow solid. ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm): 160.55, 158.54, 152.16, 124.31, 124.08, 96.68.

5-Fluoro-4,7-diiodobenzo[c][1,2,5]thiadiazole (11).[1] To a round bottom flask (50 mL) was added with 5-fluorobenzo[c][1,2,5]thiadiazole (1 g, 6.49 mmol), Ag_2SO_4 (6.61 g, 32.43 mmol), Iodine (6.59 g, 25.9 5mmol) and sulfuric acid (30 mL). After stirred at room temperature for 0.5 h, then reaction mixture was stirred at 100 ℃ for 5 d. Cooled to room temperature, the reaction mixture was poured into ice water (500 mL). The mixture was extracted with $CHCl_3$, and the organic layer was combined, dried over MgSO4 and evaporated. The crude product was recrystallized with acetone to give the title compound **11** as a light yellow solid (1.65 g, 4.09 mmol, 63%). ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 7.94 (d, *J* = 7.5 Hz, 1H).



5-Fluoro-4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (12). Compound **11** (1.5 g, 3.69 mmol) and tributyl(thiophen-2-yl)stannane (3.45 g, 9.24 mmol) were dissolved in anhydrous toluene (30 mL) under nitrogen atmosphere. After the addition of $Pd(PPh_3)_4$ (214 mg, 0.185 mmol), the reaction mixture was bubbled with N_2 for 0.5 h. The reaction was refluxed at 110 ℃ for 2 d. Cooled to room temperature, the reaction mixture was extracted with $CHCl_3$. The combined organic layer was dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography in hexane/dichloromethane (50:1 v/v) to obtain 0.67 g (2.1 mmol, 57%) of light red solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 8.28 (d, *J* = 3.8 Hz, 1H), 8.14 (d, *J* = 3.7 Hz, 1H), 7.80 (d, *J* = 12.8 Hz, 1H), 7.57 (d, *J* = 5.1 Hz, 1H), 7.52 (d, *J* = 5.1 Hz, 1H), 7.25– 7.21 (m, 2H).

4,7-Bis(5-bromothiophen-2-yl)-5-fluorobenzo[c][1,2,5]thiadiazole (M3). Solution of **12** (0.5 g, 1.57 mmol) in anhydrous THF (50 mL) was stirred at 0^{o}C for 0.5 h. N-bromosuccinimide (NBS) (698 mg, 3.92 mmol) was then added in portions. The reaction mixture was stirred at a room temperature for 12 h. After washed with water, the reaction mixture was extracted with CH_2Cl_2. The combined red layer was dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography with hexane/CH_2Cl_2 (20:1 v/v) to obtain 606 mg (1.27 mmol, 81%) of red solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ/ppm): 8.00 (d, *J* = 4.1 Hz, 1H), 7.79 (d, *J* = 4.0 Hz, 1H), 7.66 (d, *J* = 12.9 Hz, 1H), 7.17 – 7.01 (m, 2H).

2. Thermal properties of polymers

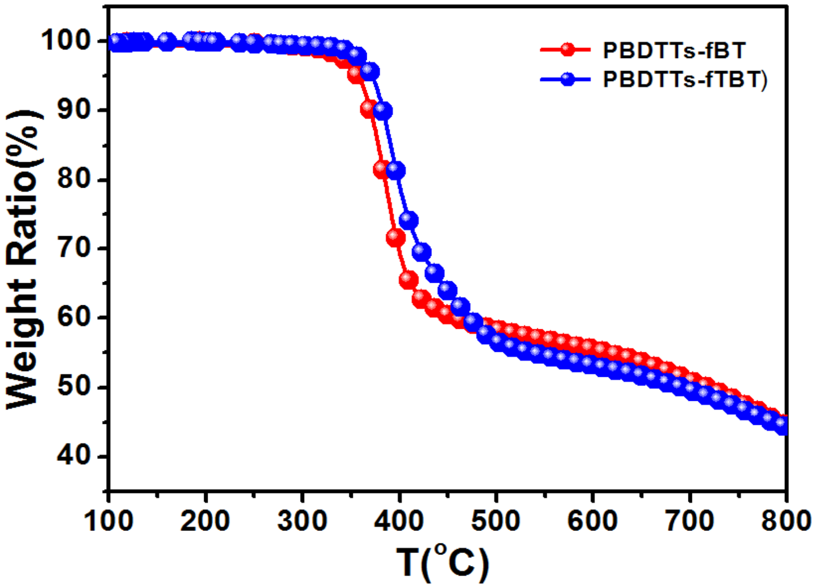


Figure S1. TGA spectra of the as-prepared polymers.

3. Mobility measurement via SCLC method

The SCLC behavior in the trap-free region can be characterized by using the Mott–Gurney square law:[S2]

$$J = {}^{9}/_{8}\, \varepsilon . \mu (V^2 L^{-3}) \qquad (1)$$

where ε is the static dielectric constant of the medium and μ is the carrier mobility. The hole mobilities of **PBDTTs-fBT** evaluated using the above Mott–Gurney law ($\varepsilon = 3\varepsilon_0$) are 9.94×10^{-5} $cm^2V^{-1}s^{-1}$.

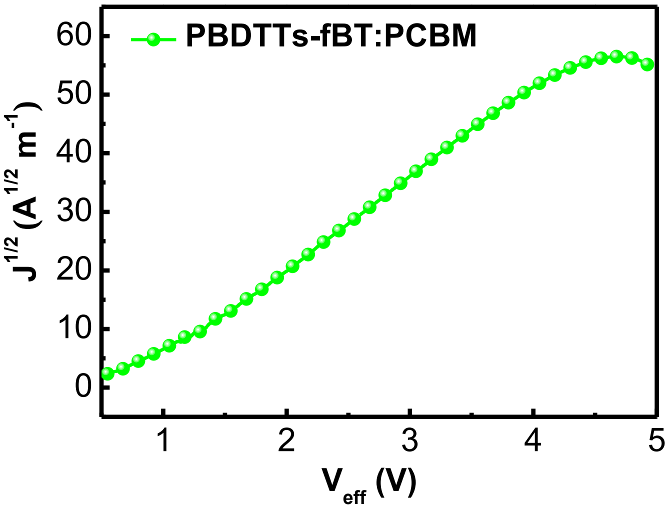


Figure S2. The J - V_{eff} curves of the devices based on ITO (120 nm)/PEDOT:PSS(40 nm)/**PBDTTs-fBT**:$PC_{71}BM$ (1:2)/MoO_3(10 nm)/Al(100 nm).

4. NMR spectra

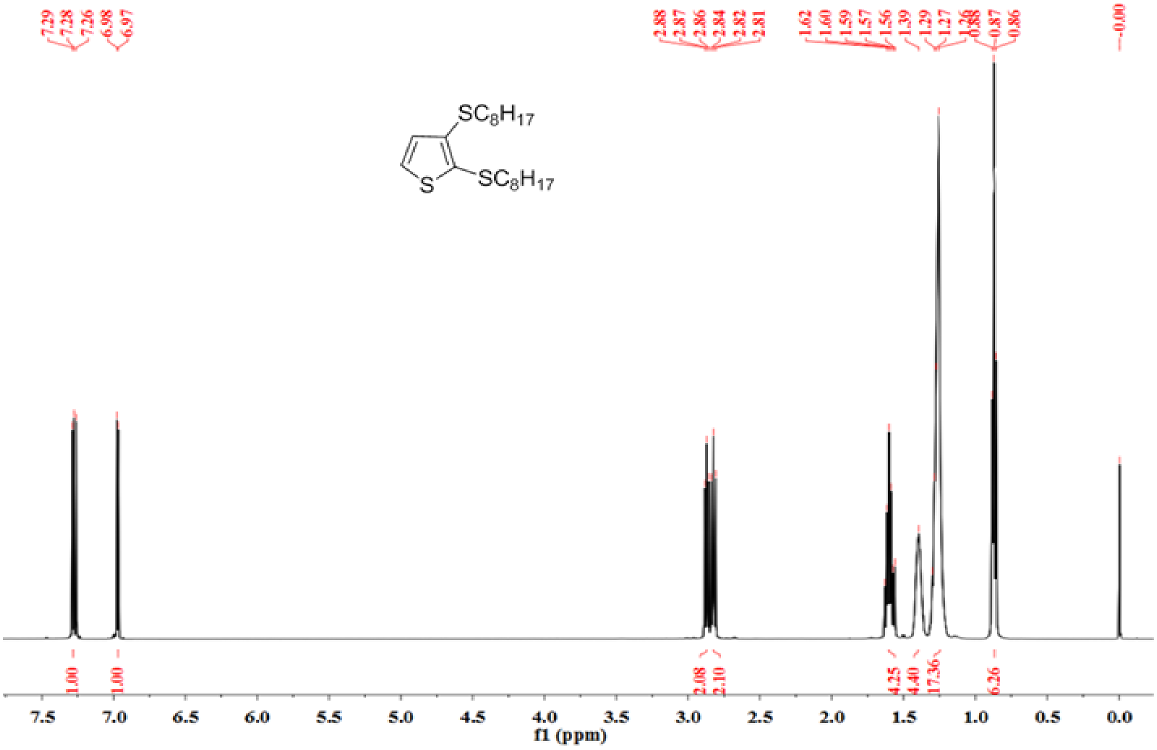


Figure S3. ^{1}H NMR spectrum of **1**.

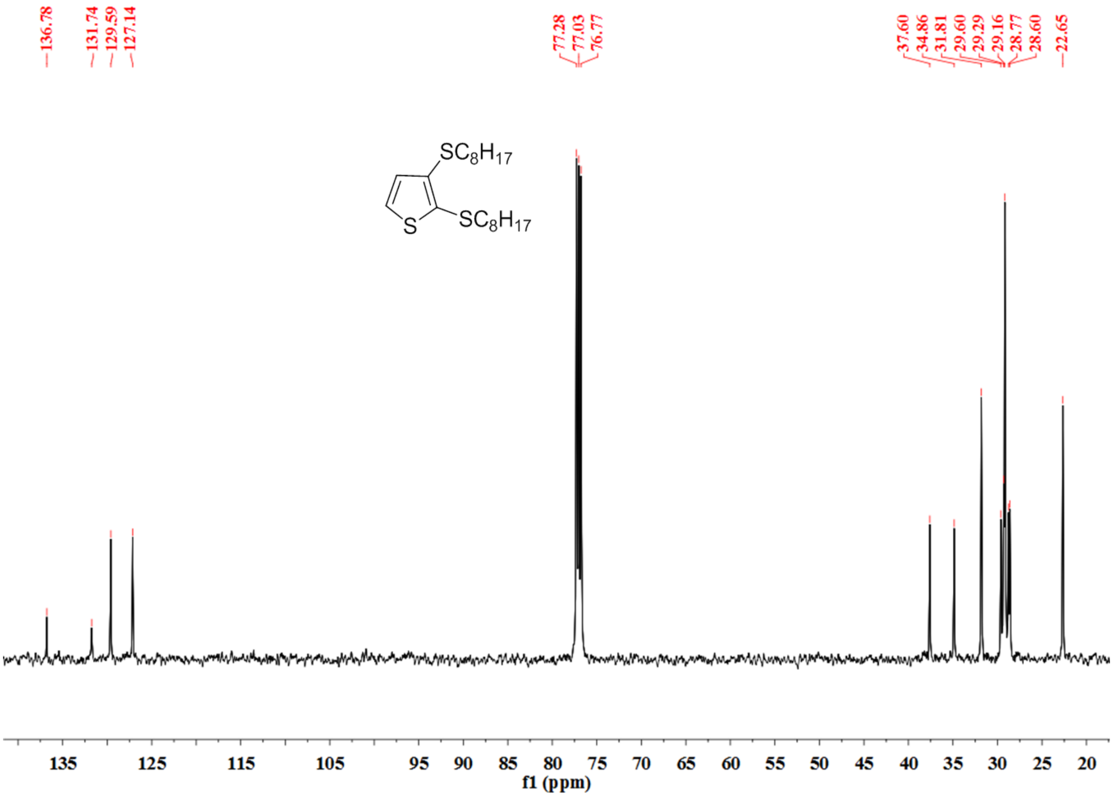


Figure S4. ^{13}C NMR spectrum of **1.**

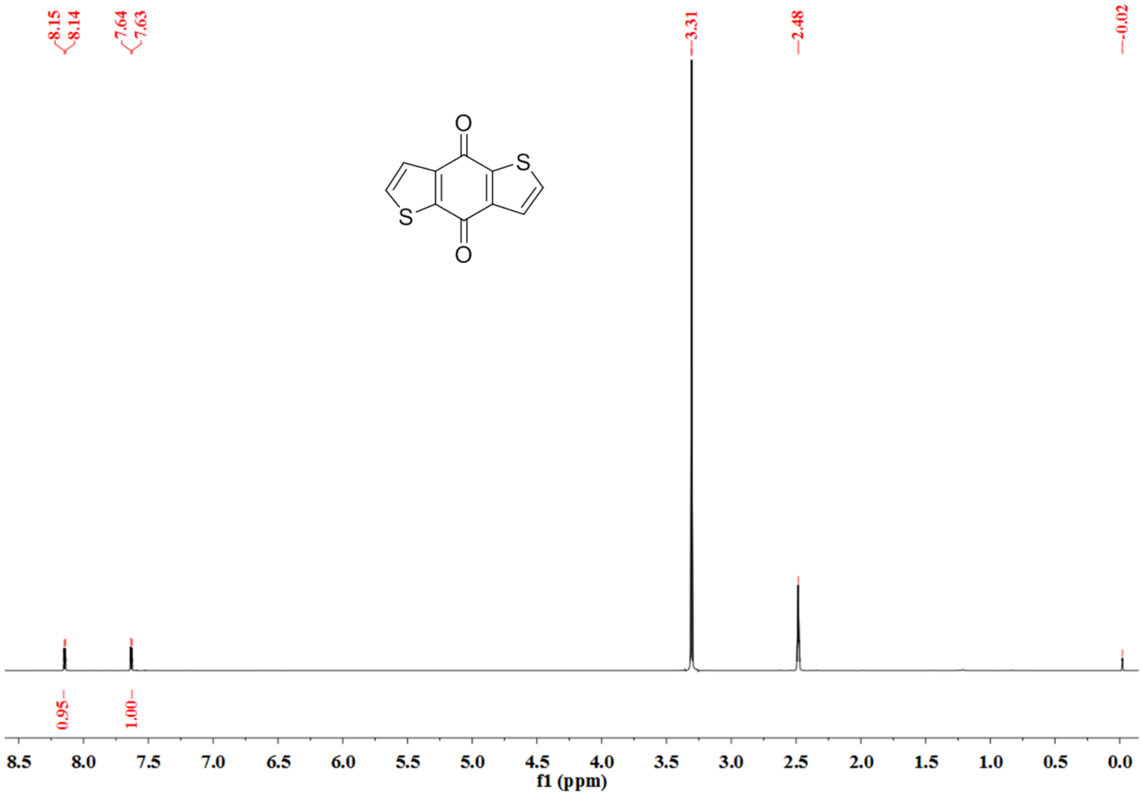


Figure S5. ^{1}H NMR spectrum of **2.**

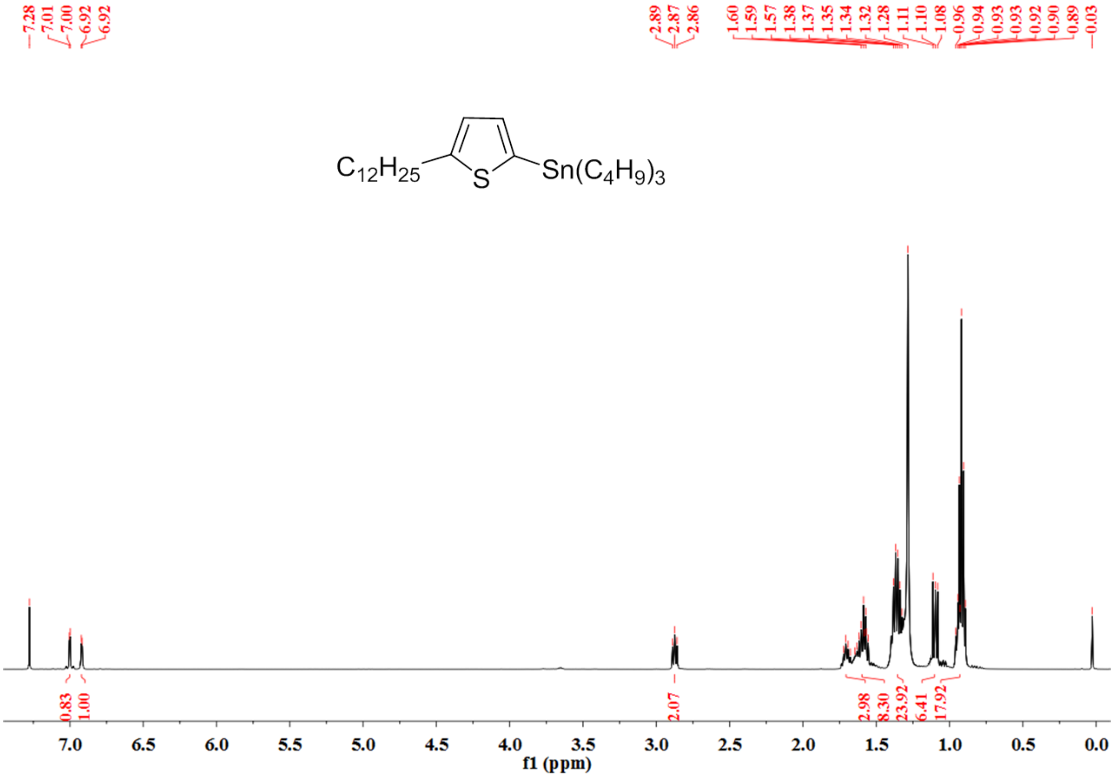


Figure S6. ^{1}H NMR spectrum of **4.**

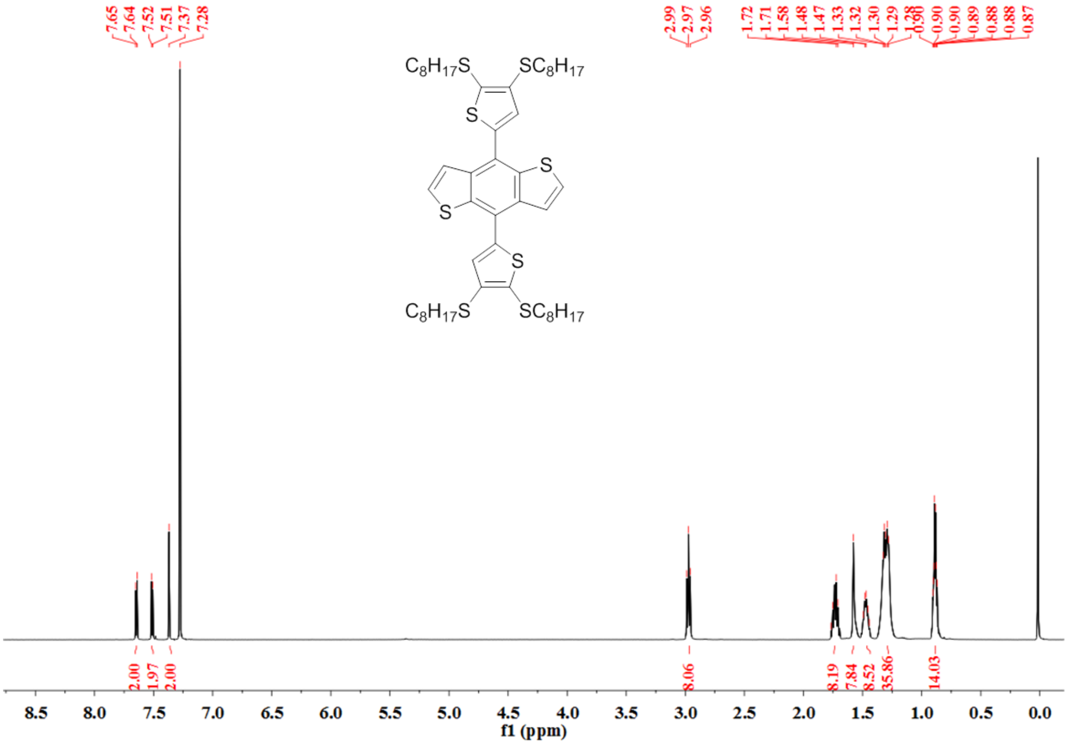


Figure S7. ^{1}H NMR spectrum of **3.**

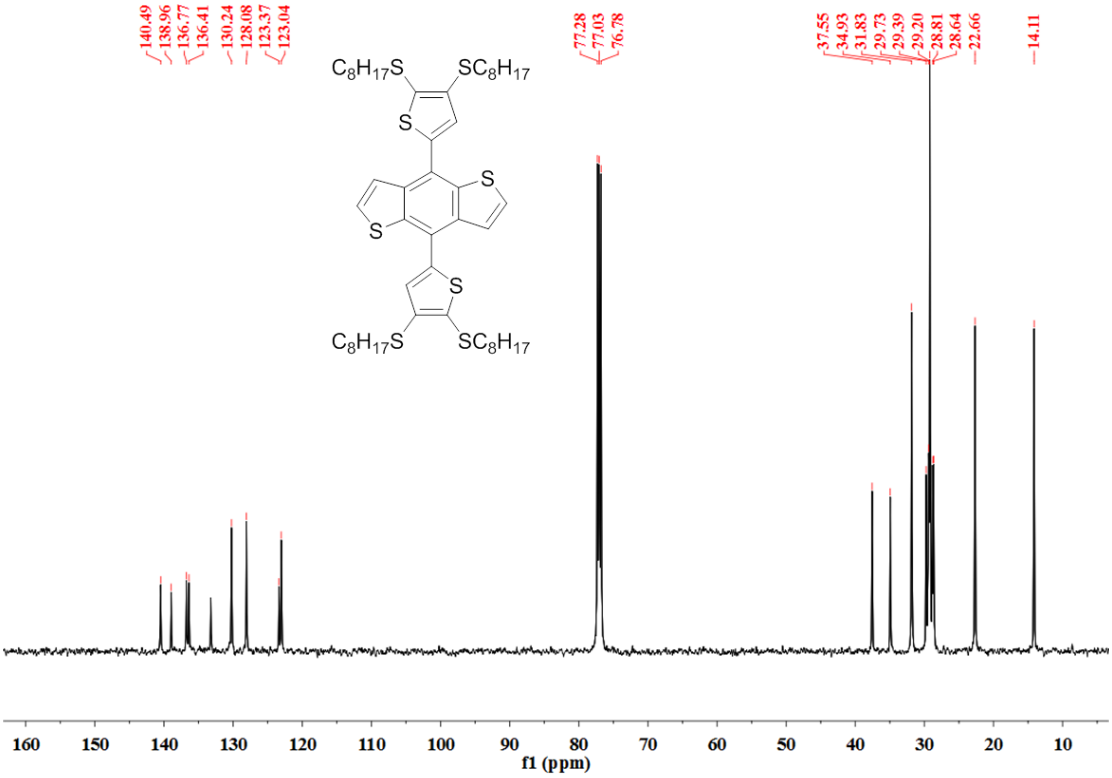


Figure S8. ^{13}C NMR spectrum of **3.**

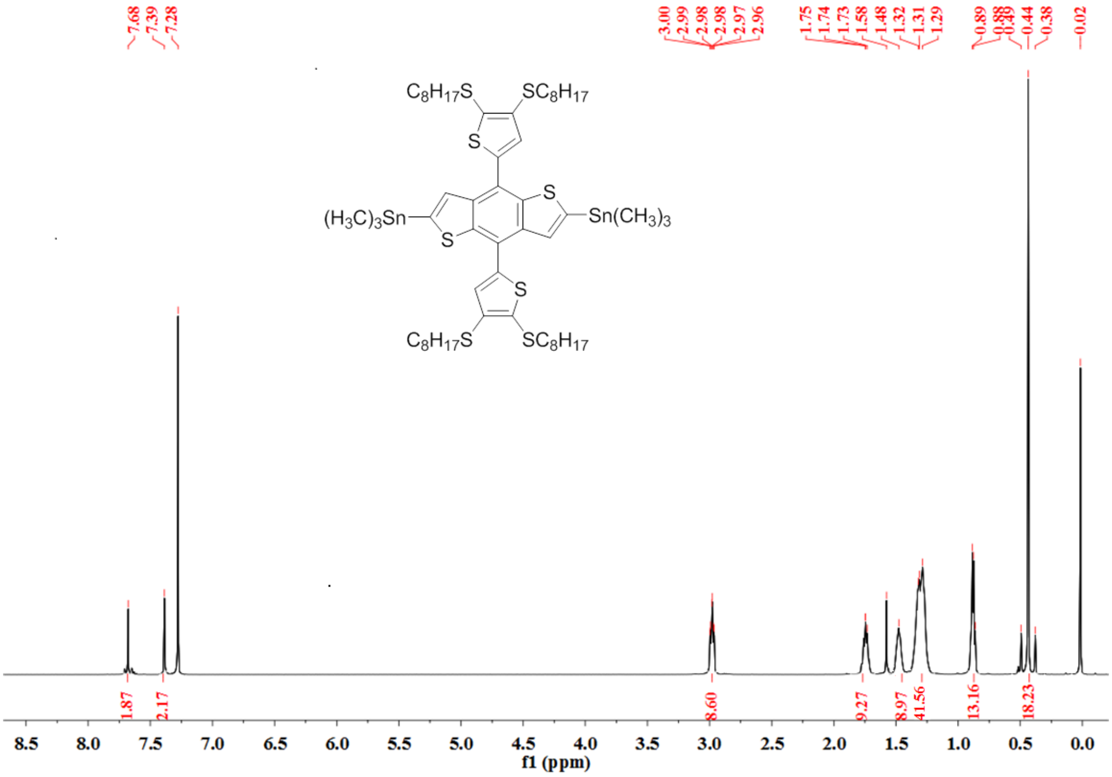


Figure S9. ^{1}H NMR spectrum of **M1.**

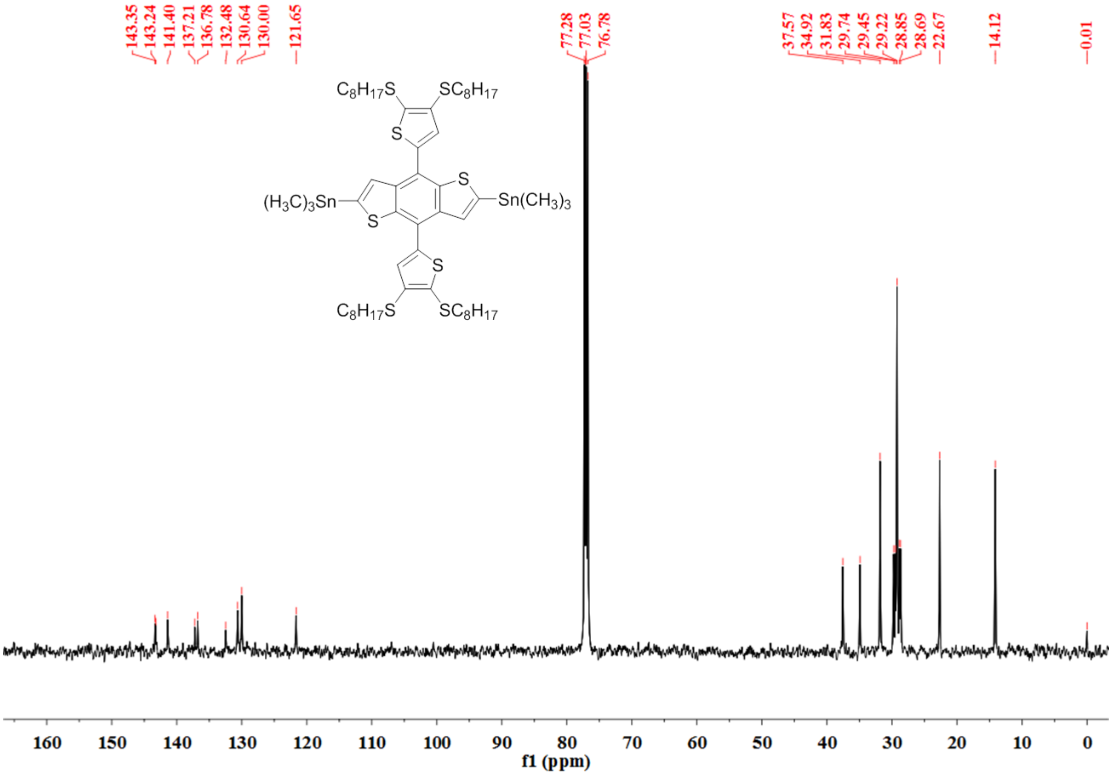


Figure S10. ^{13}C NMR spectrum of **M1.**

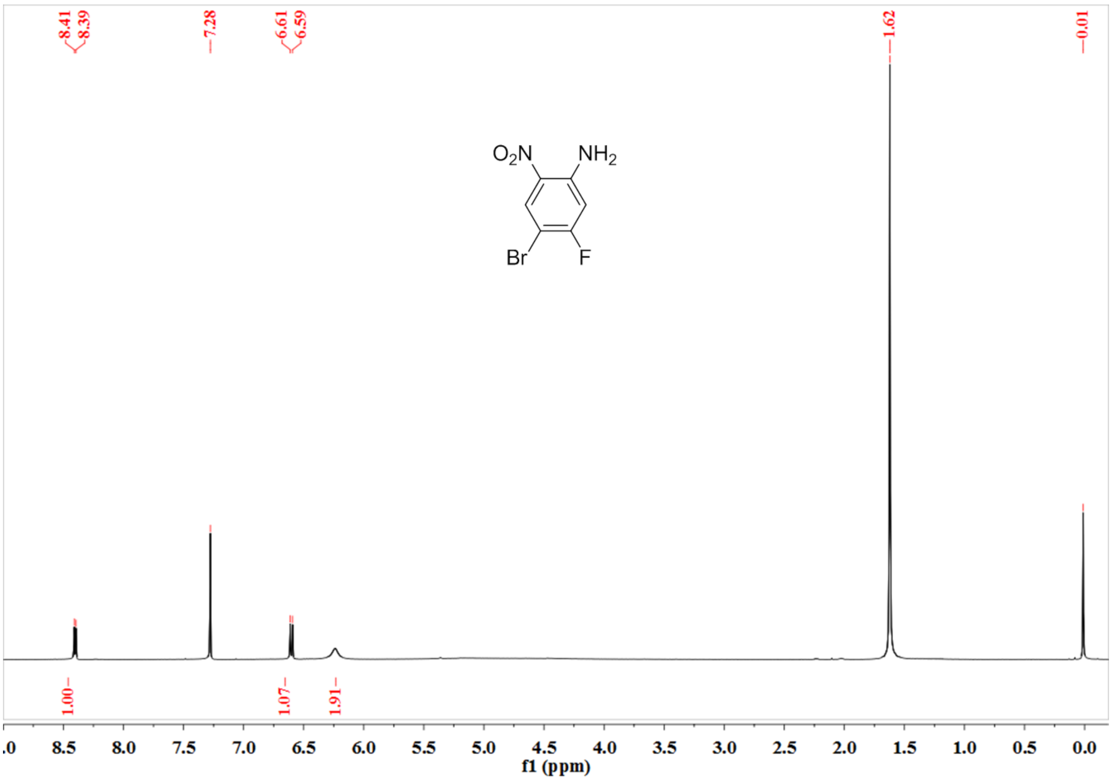


Figure S11. ^{1}H NMR spectrum of **5.**

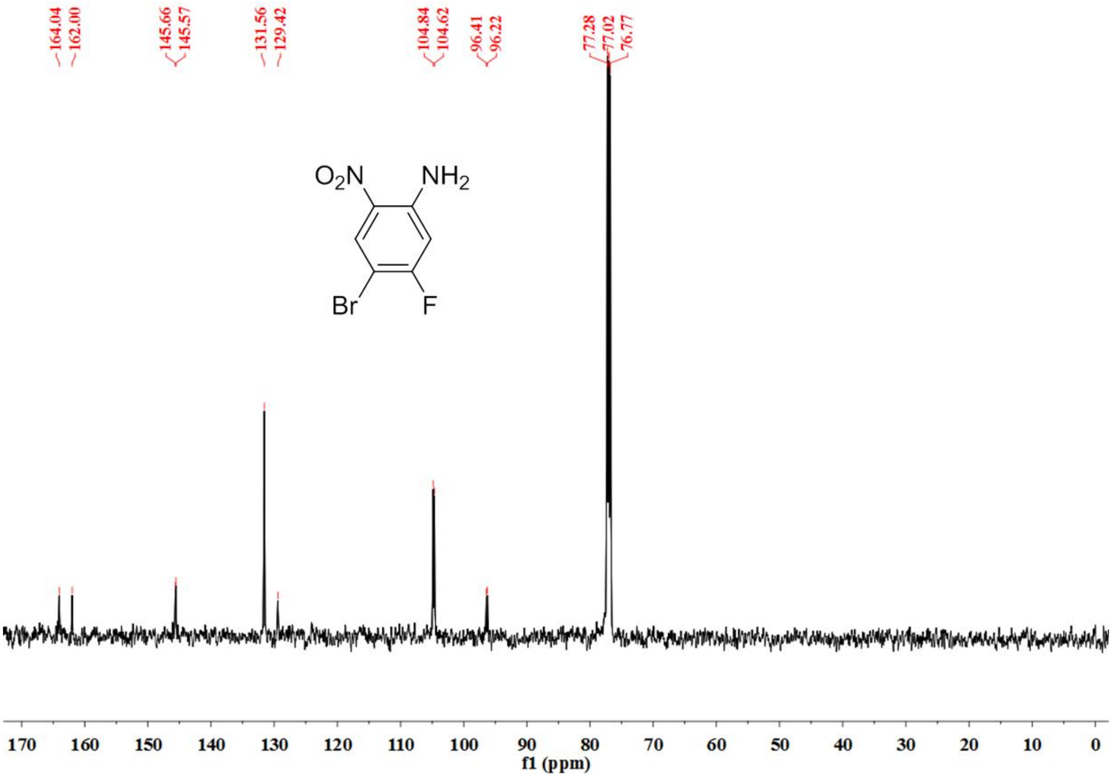


Figure S12. ^{13}C NMR spectrum of **5.**

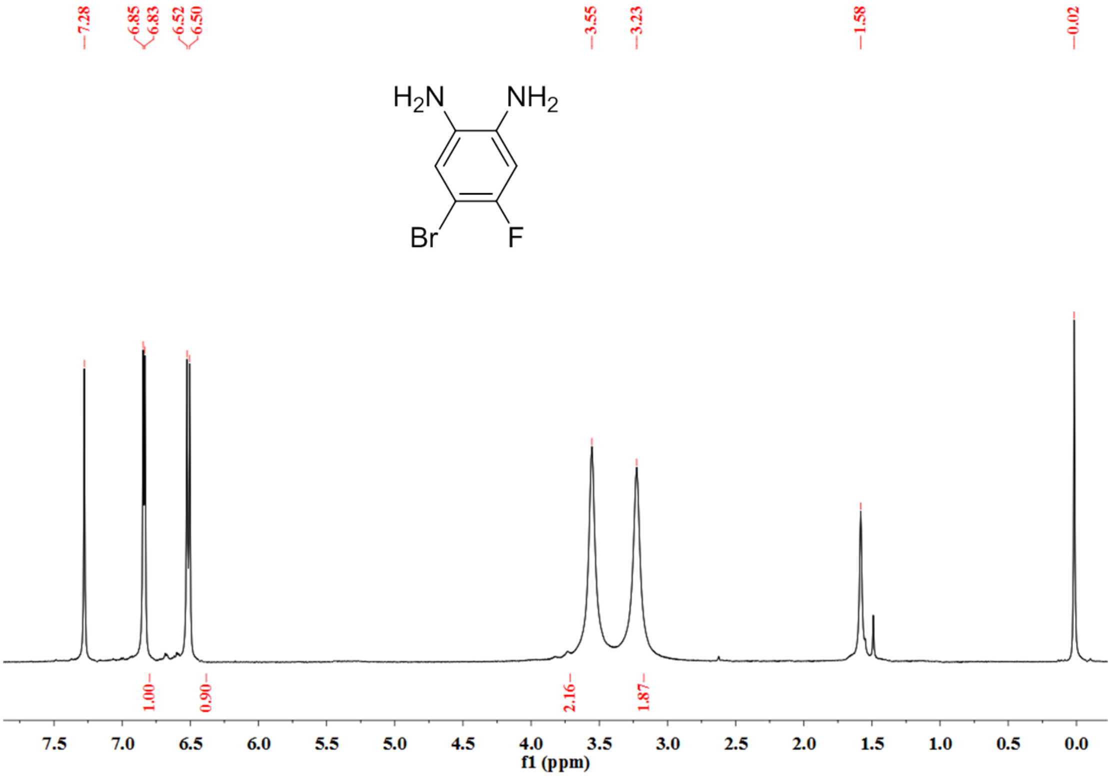


Figure S13. ^{13}H NMR spectrum of **6.**

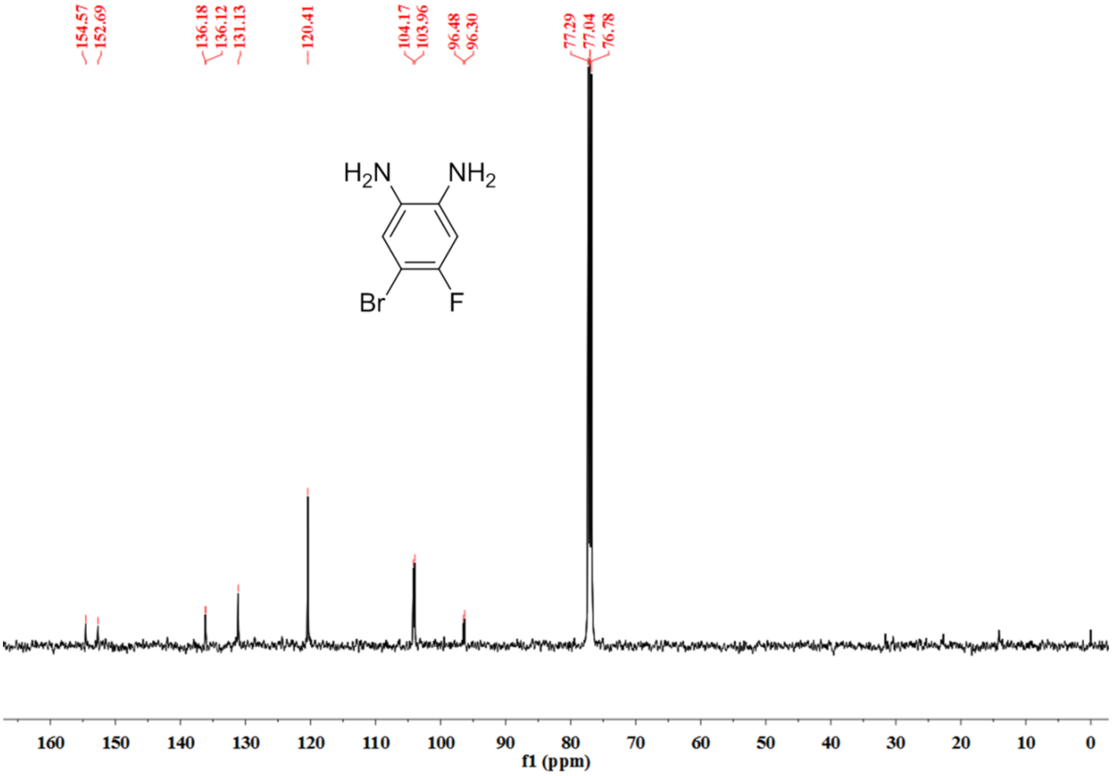


Figure S14. ^{13}C NMR spectrum of **6.**

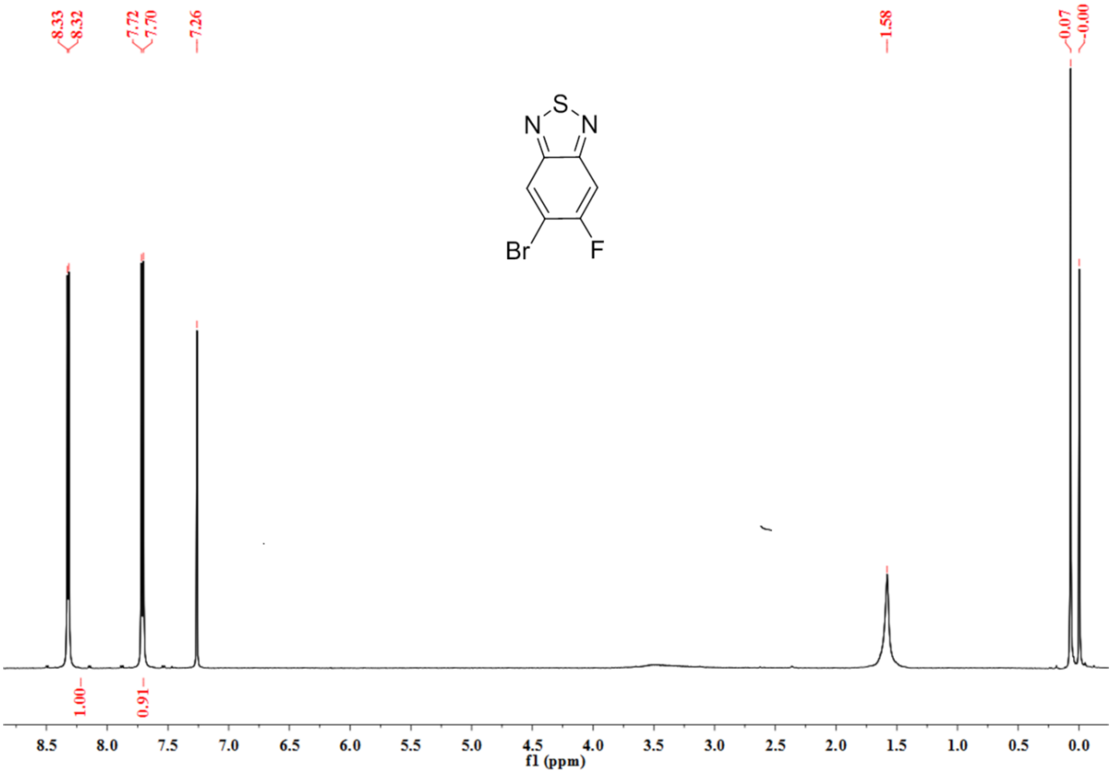


Figure S15. ^{1}H NMR spectrum of **7.**

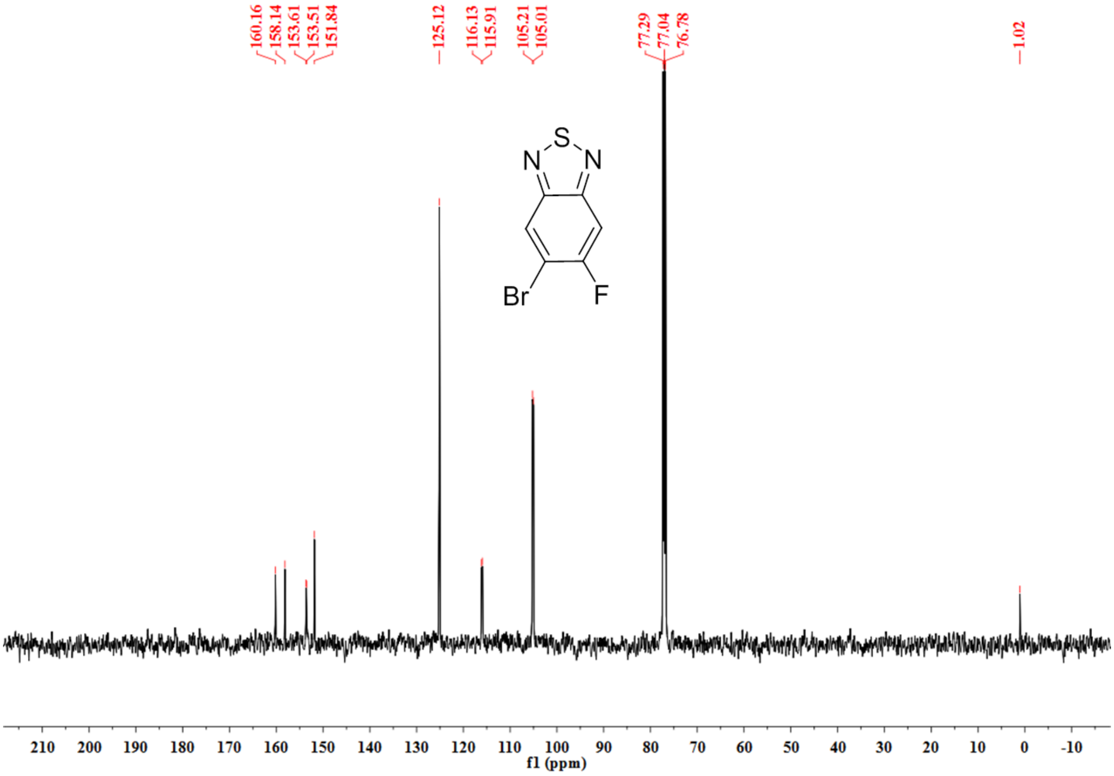


Figure S16. ^{13}C NMR spectrum of **7.**

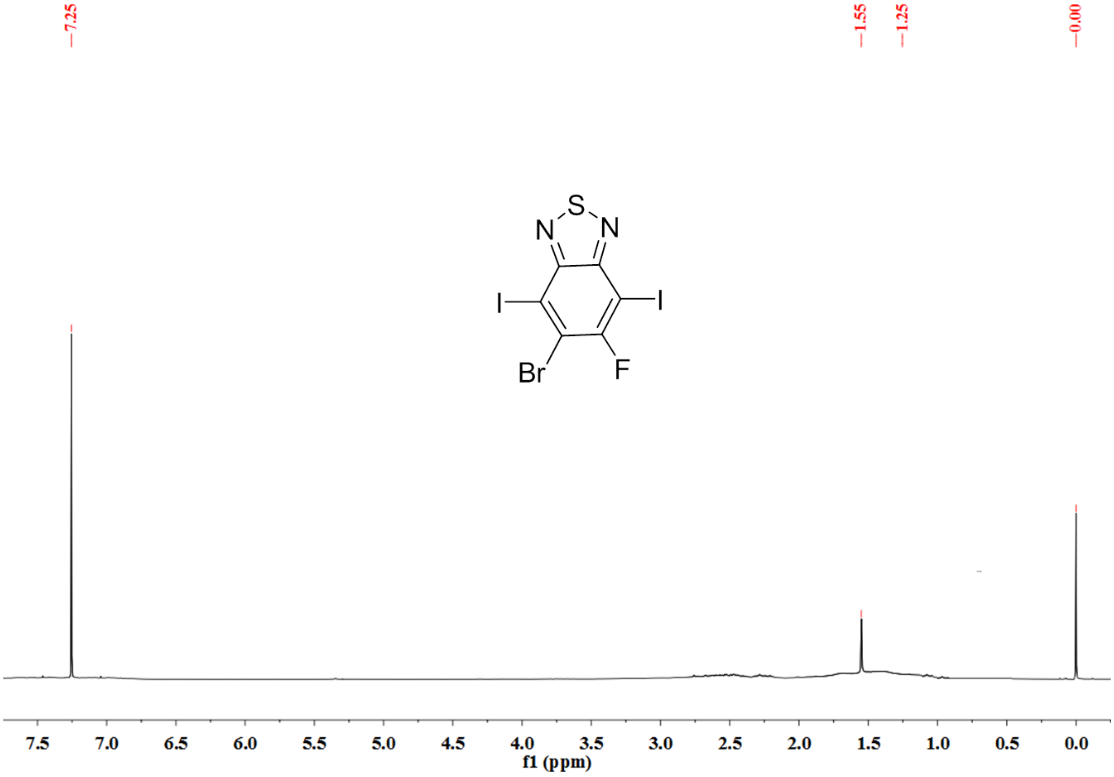


Figure S17. ^{1}H NMR spectrum of **8.**

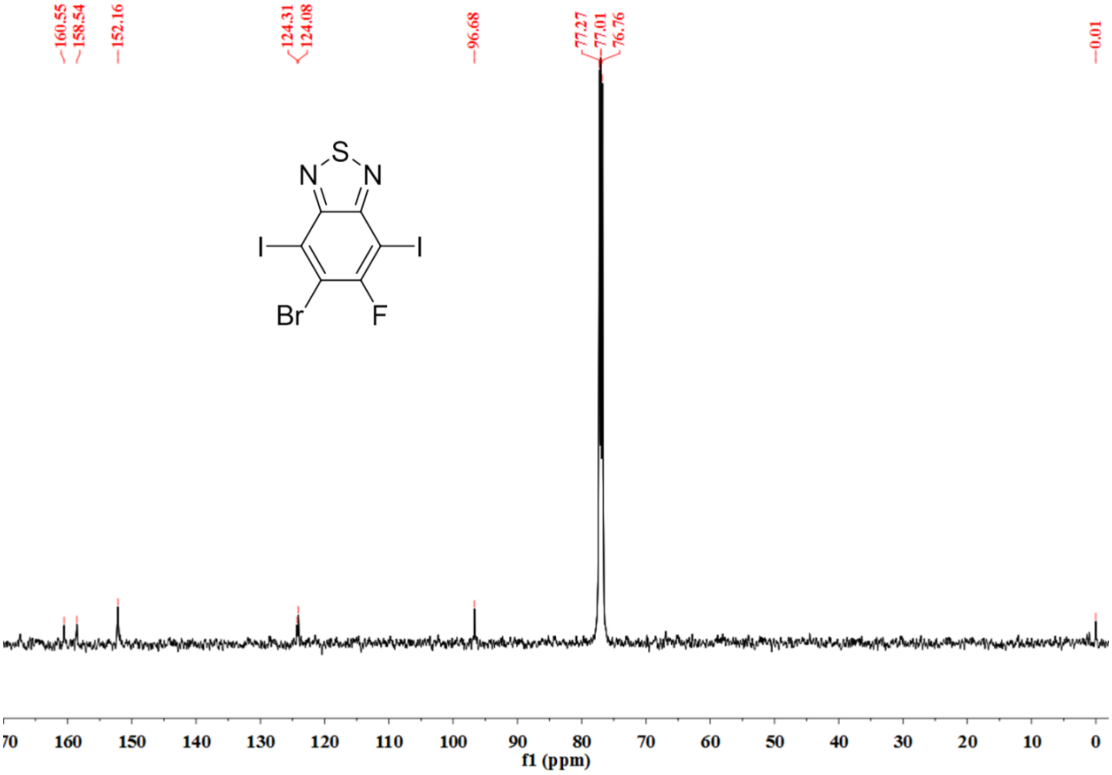


Figure S18. ^{13}C NMR spectrum of **8.**

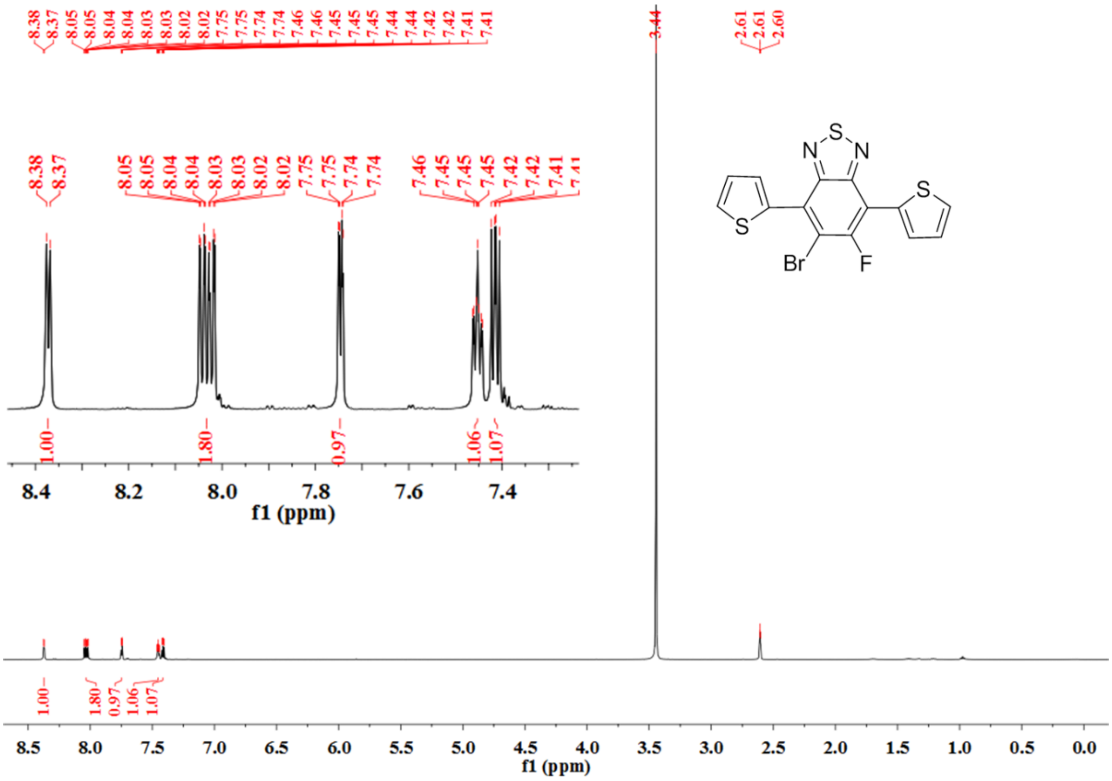


Figure S19. ^{1}H NMR spectrum of **9.**

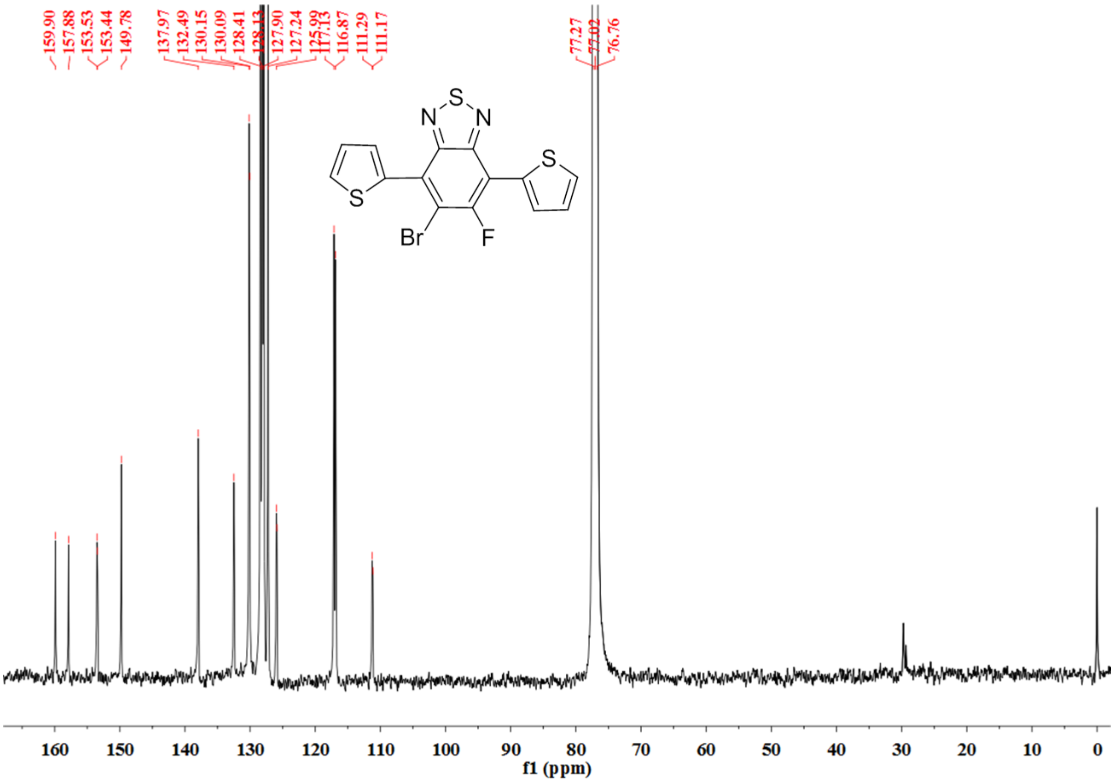


Figure S20. ^{13}C NMR spectrum of **9.**

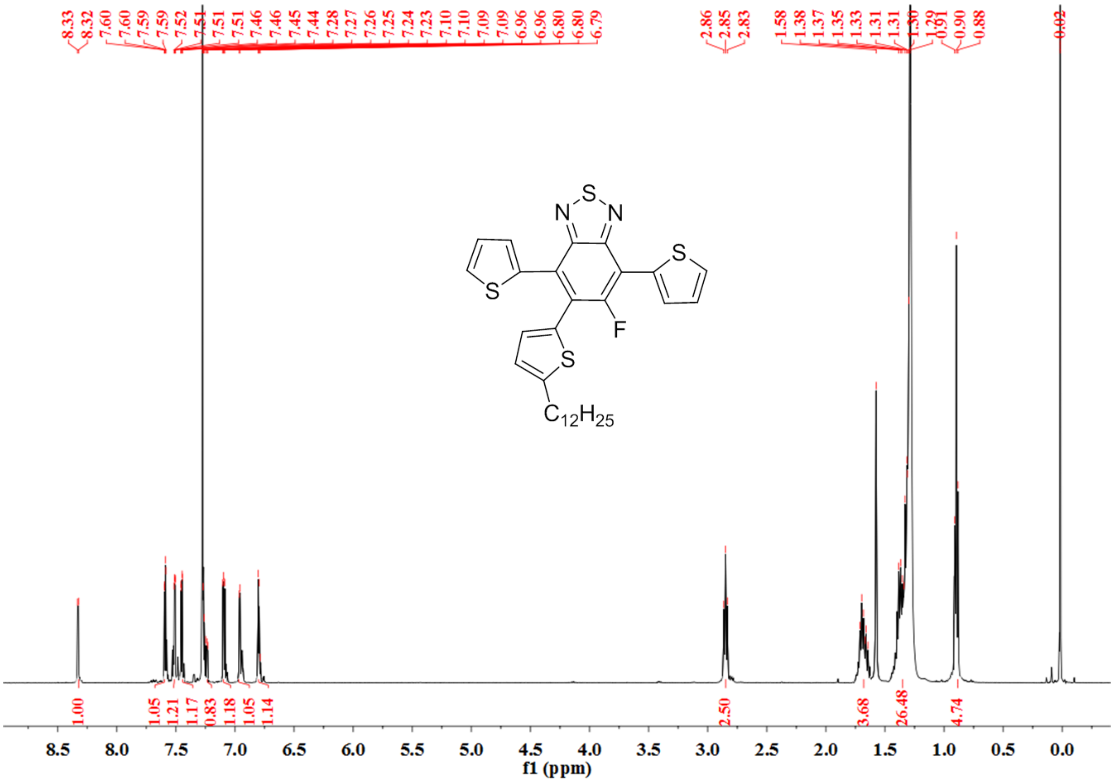


Figure S21. ^{1}H NMR spectrum of **10.**

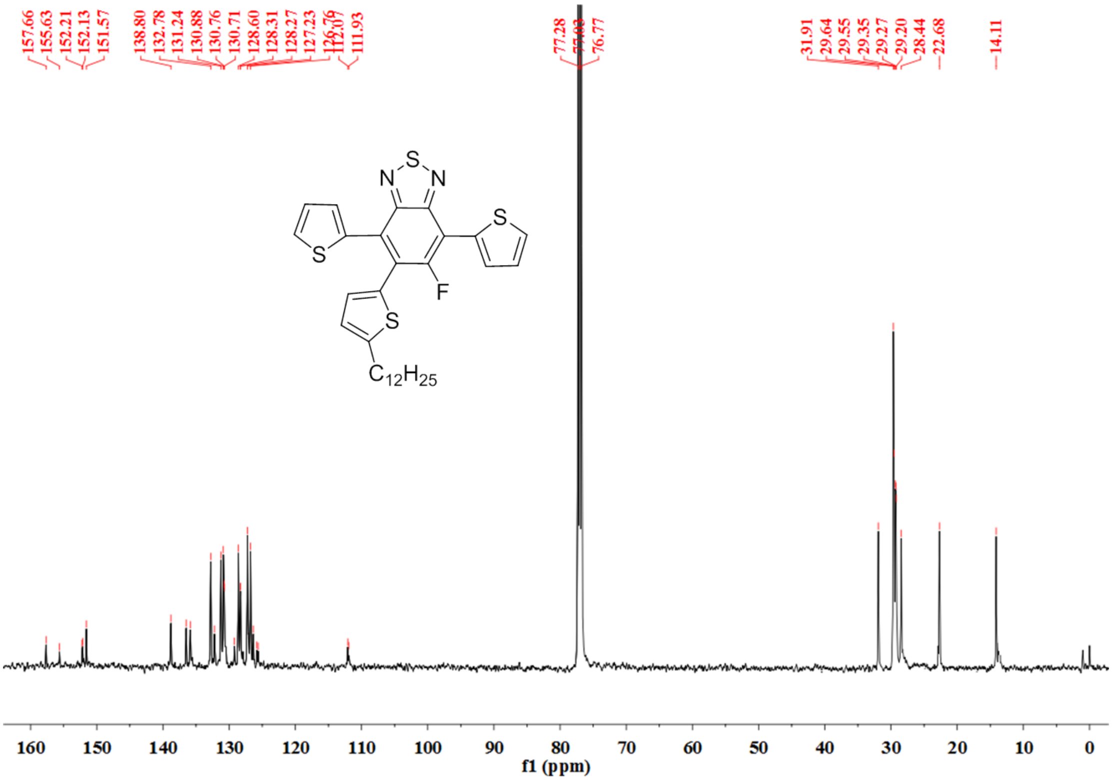


Figure S22. ^{13}CNMR spectrum of **10.**

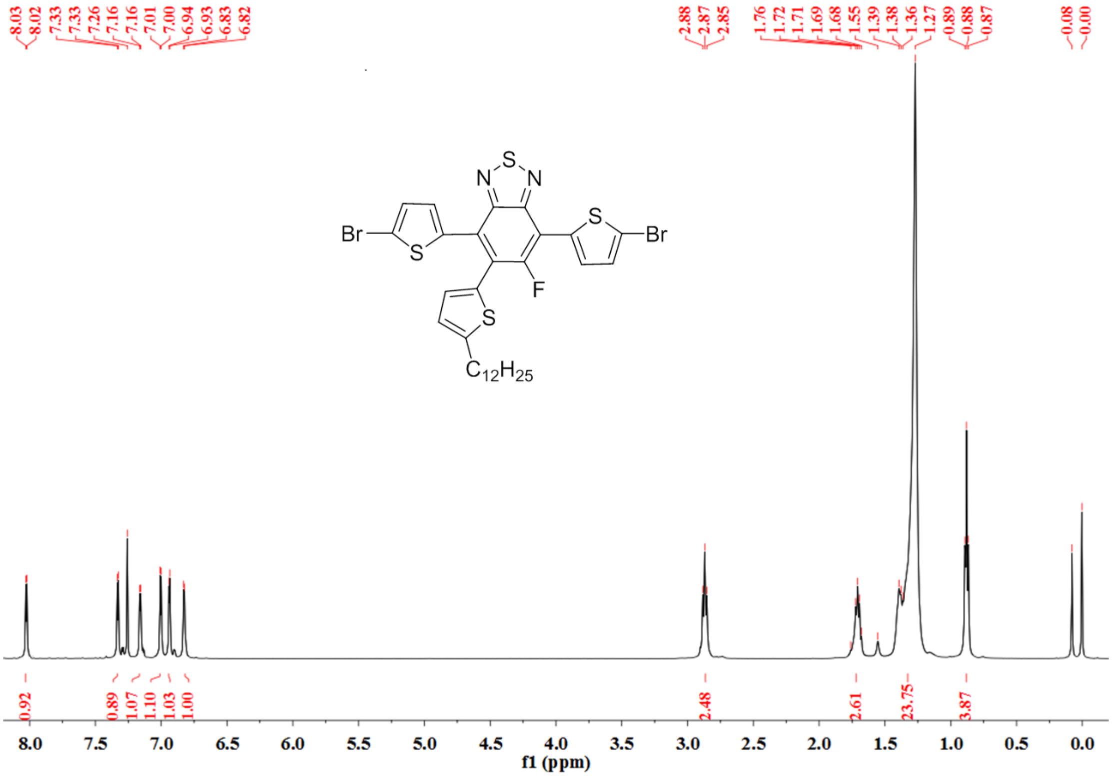


Figure S23. ^{1}H NMR spectrum of **M2.**

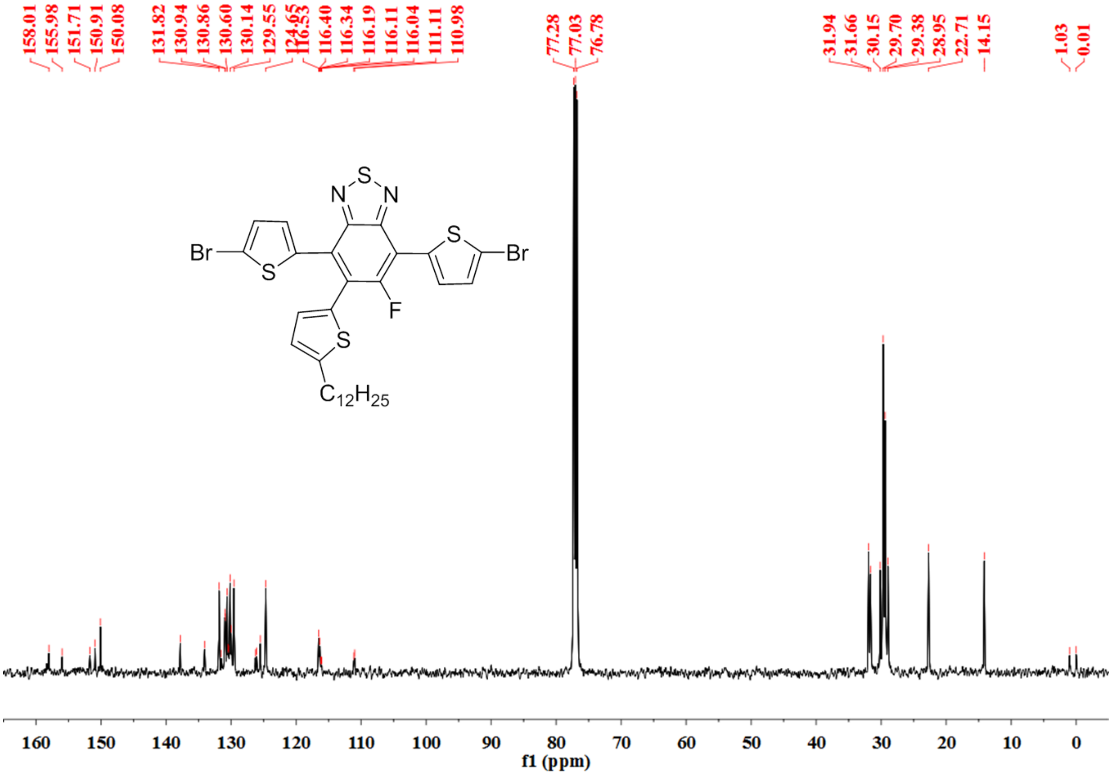


Figure S24. ^{13}C NMR spectrum of **M2.**

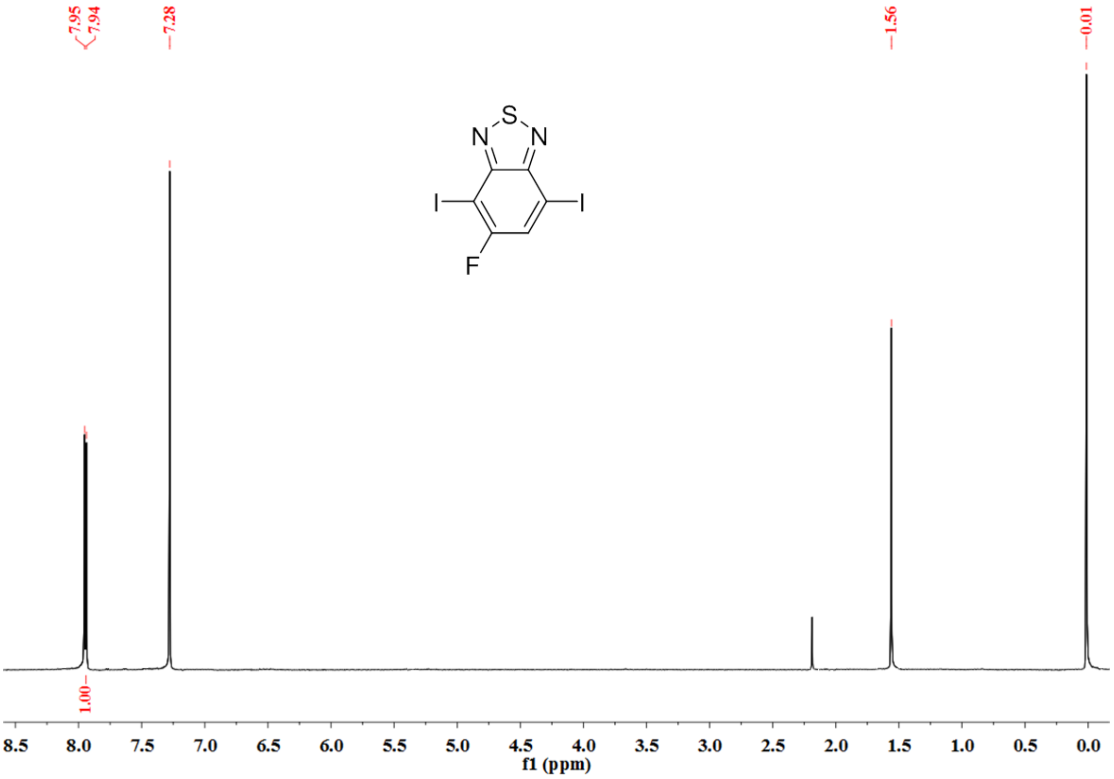


Figure S25. ^{1}H NMR spectrum of **11.**

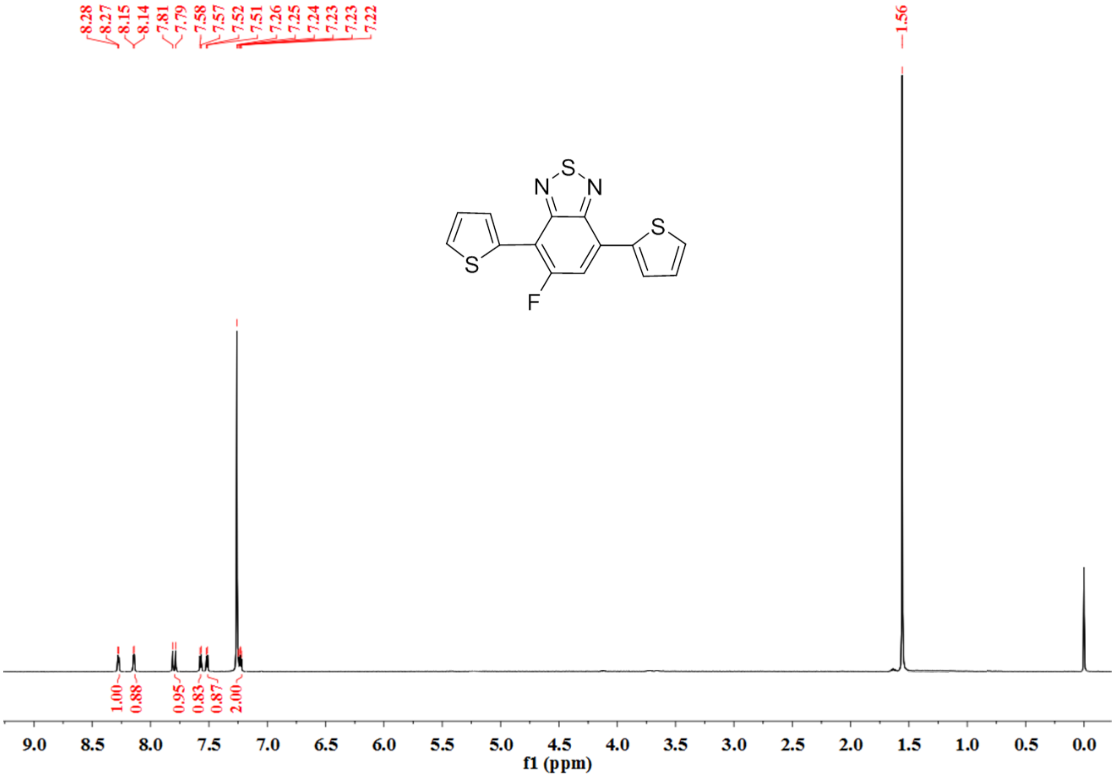


Figure S26. ^{1}H NMR spectrum of **12**.

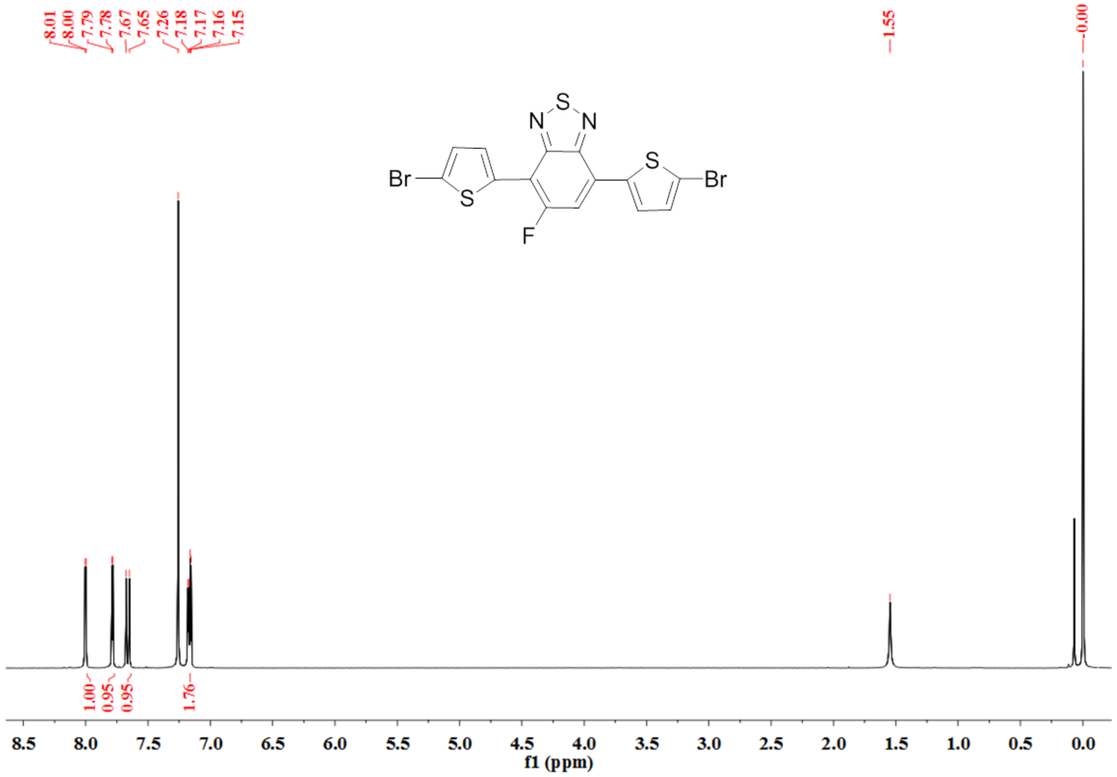


Figure S27. ^{1}H NMR spectrum of **M3.**

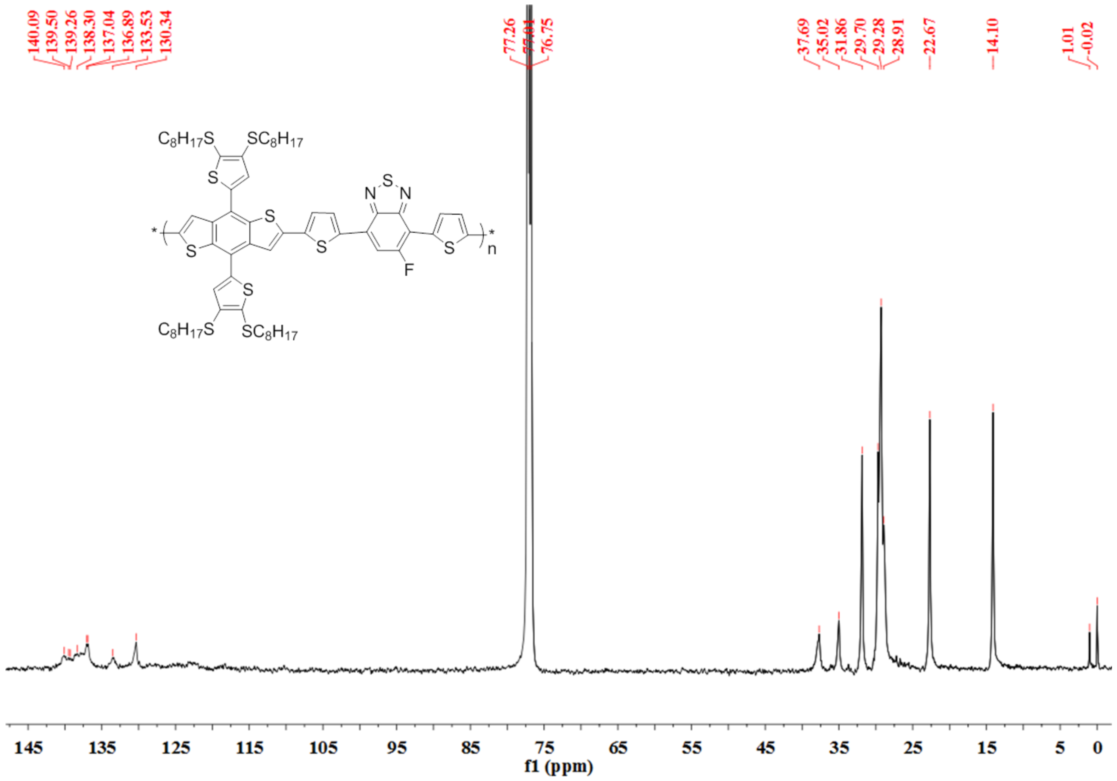


Figure S28. ^{13}C NMR spectrum of **PBDTTs-fBT**.

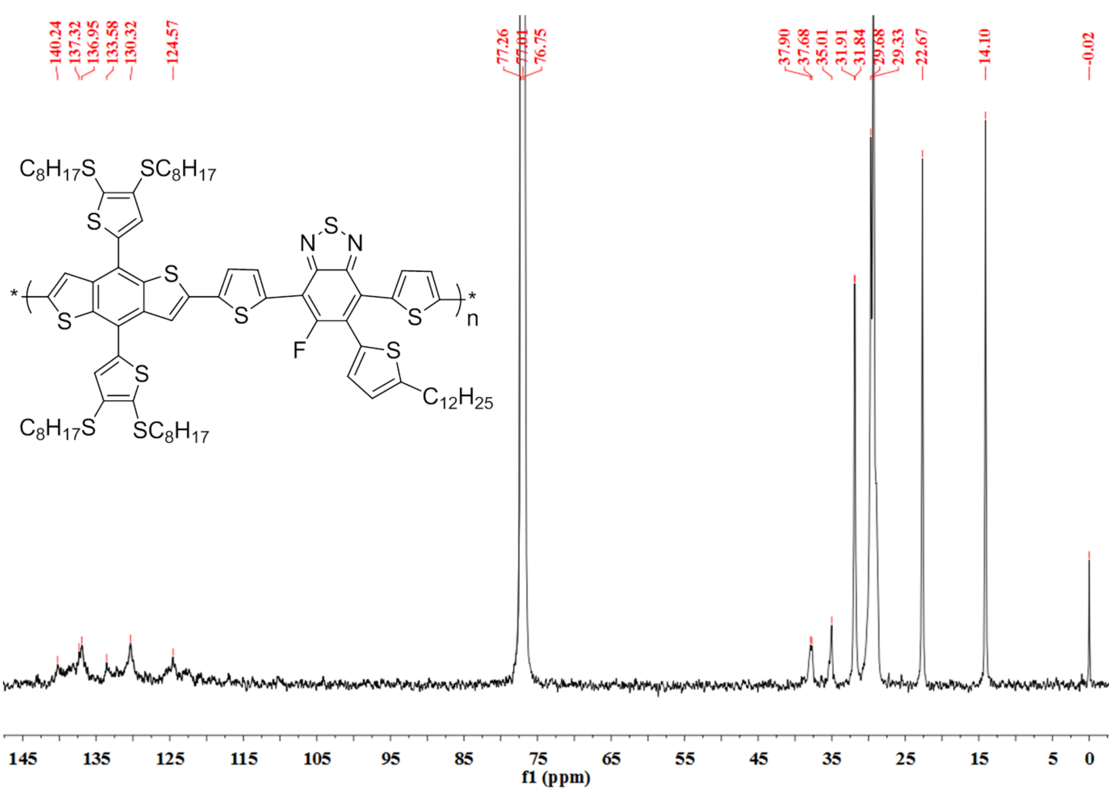


Figure S29. ^{13}C NMR spectrum of **PBDTTs-fTBT**.

Reference

S1. N. Cho, K. Song, J. K. Lee, J. Ko, *Chem. Eur. J.*2012, ***18***, 11433.

S2. V. D. Mihailetchi, H. Xie, B. Boer, L. J. A. Koster, P. W. M. Blom, *Adv. Funct. Mater*. 2006, **16**, 699.