

**A newly designed benzodithiophene building block: tuning of torsional barrier for non-halogenated and non-aromatic solvent-processible photovoltaic polymers**

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## 1. Experimental Section

### Characterization

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$ -NMR spectra were measured using a Bruker Advance III HD system operating at 500, 125, and 470 MHz, respectively. Mass spectra were measured by a MALDI-TOF/TOF™ 5800 system (AB SCIEX) at the Korea Basic Science Institute (Seoul). Cyclic voltammetry (CV) was performed using a Versa STAT 3 electrochemical workstation in 0.1 M tetrabutylammonium tetrafluoroborate in  $\text{CH}_3\text{CN}$  at a scan rate of 0.05  $\text{V s}^{-1}$ . A conventional three-electrode system with a platinum wire as the counter electrode, a platinum electrode as the working electrode, and an  $\text{Ag}/\text{Ag}^+$  electrode as the reference electrode was used. The differential scanning calorimetry (DSC) (PerkinElmer DSC 4000) data were measured in a temperature range of 30–310 °C at a heating rate of 10 °C  $\text{min}^{-1}$ . Thermogravimetric analysis (TGA) measurements were carried out on a SCINCO TGA N-1000 instrument at a heating rate of 10 °C  $\text{min}^{-1}$  from 30 to 600 °C. UV-Vis absorption spectra were obtained in both solution (in chloroform) and film states using a JASCO V-630 spectrophotometer. Temperature-dependent UV-vis absorption spectra in solution (in the range of 30–100 °C) were obtained using a Jasco V-730 spectrophotometer. AFM height, phase and 3D images ( $4 \mu\text{m} \times 4 \mu\text{m}$ ) were obtained using a Veeco Multimode AFM microscope in tapping mode. GIWAXS measurements were conducted at a PLS-II U-SAXS 9A beam line of Pohang Accelerator Laboratory, Republic of Korea.

### Fabrication of Organic Solar Cells and Large Module

Conventional OSC devices were fabricated with a device structure of ITO-coated glass/PEDOT:PSS/polymer:Y6-HU/ZnO/Al. Y6-HU was purchased from Polaron (Ulsan, Korea).<sup>1</sup> The ITO-coated glass substrates were first cleaned using a detergent solution, ultrasonicated in acetone and isopropyl alcohol, and then dried overnight in an oven. Aqueous PEDOT:PSS (Clevious P VPAI 4083Heraeus) solution was spin-cast to produce 40 nm thick film and dried at 140 °C for 10 min in air environment, and then transferred into a nitrogen filled glove box. Blend solutions of donor:Y6-HU (1:1.2, w/w) in THF (total concentration of 13.2  $\text{mg mL}^{-1}$  with 2,2'-(perfluoro-1,4-phenylene)dithiophene (DTBF, 2.2  $\text{mg mL}^{-1}$ ) as a processing additive) or in CF (total concentration of 14  $\text{mg mL}^{-1}$  with DTBF (2.3  $\text{mg mL}^{-1}$ )) were spin-coated on top of the PEDOT:PSS layer. The thickness of optimal PM6, PBDB-T-2F(3/4) and PBDB-T-2F(3) blend films is ~100 nm. After the film was thermally annealed at 100 °C for 10 min, the ZnO nanoparticles were spin cast. An aluminum (Al, 100 nm) electrode was then deposited by thermal evaporation under vacuum ( $2 \times 10^{-6}$  Torr). Device area was 4  $\text{mm}^2$ . The device structure for flexible devices was ITO-coated PET substrate/PEDOT:PSS/PBDB-T-2F(3/4):Y6-HU/ZnO/Al. The flexible OSCs were prepared using a PBDB-T-2F(3/4):Y6-HU solution (in THF) in the same manner as for the devices on glass without thermal annealing of the PEDOT:PSS film. A large-area module was prepared with an architecture of glass substrate coated with five stripes of ITO/ZnO/PBDB-T-2F(3/4):Y6-HU/ $\text{MoO}_3$ /Ag. After the ITO substrates were treated with

UV/ozone for 20 min, the ZnO sol-gel solution was spin-coated at 3000 rpm onto an ITO-coated glass substrate. The ZnO precursor was prepared by mixing zinc acetate dihydrate (99.9%, 1 g; Sigma Aldrich) and ethanolamine (99.5%, 0.28 g; Sigma Aldrich) in 2-methoxyethanol (99.8%, 10 mL), followed by stirring for 12 h in air.<sup>2</sup> The film was thermally annealed at 150 °C for 20 min in air. After the photoactive solution was filtered through a 0.45- $\mu\text{m}$  PTFE filter, a photoactive film was prepared by bar coating (at a moving speed of 15 mm s<sup>-1</sup>) on top of the ZnO layer by dropping a THF solution (20 mL) of PBDB-T-2F(3/4):Y6-HU onto each bar. The coated photoactive films were pre-annealed at 100 °C for 10 min before the deposition of the top electrode. Finally, the module preparation was completed by depositing 10 nm thick MoO<sub>3</sub> and 100 nm thick Ag via thermal evaporation at  $3 \times 10^{-6}$  Torr. The photovoltaic properties were characterized using a mask (area 31.50 cm<sup>2</sup>). For semi-transparent devices, the device structure is ITO/PEDOT:PSS/PBDB-T-2F(3/4):Y6-HU/ZnO/Sb<sub>2</sub>O<sub>3</sub>(2nm)/ Ag(25nm)/Sb<sub>2</sub>O<sub>3</sub>(50nm)/Ag(25nm). Except for the electrode evaporation, OSCs were prepared using a PBDB-T-2F(3/4):Y6-HU solution (in THF) in a same way as for the devices on glass.

### **Solar Cell Characterization**

The Current density–voltage ( $J$ – $V$ ) characteristics of the devices were measured using a Keithley 2365A source measurement unit. The OSC performance was measured using an Air Mass 1.5 global (AM 1.5 G) solar simulator with an irradiation intensity of 1000 W m<sup>-2</sup>, which was calibrated using a standard silicon photodiode (PV Measurements, Inc.). For the shelf storage stability test, the unencapsulated devices were kept in a glove box filled with N<sub>2</sub>. For the ambient-air stability test, the unencapsulated devices were kept in a Petri dish in an ambient environment (25% RH, 25 °C) without light exposure. For the thermal stability test, the unencapsulated devices were placed on a hot plate and heated to 85 °C in a glove box filled with N<sub>2</sub>.

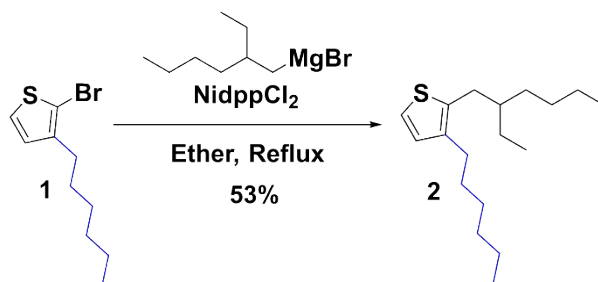
### **Transient-absorption spectroscopy**

We obtained transient-absorption (TA) spectra using the pump-probe method as reported elsewhere.<sup>3</sup> We used an amplified ytterbium-based laser system (Pharos, Light Conversion) as pump and probe sources, which produces IR pulses centered at 1030 nm with a pulse duration of 170 fs at a repetition rate of 200 kHz. We reduced the repetition rate to 10 kHz to completely relax the samples within the pulse interval using a pulse picker divider. Through an optical parametric amplifier (Orpheus, Light Conversion), the pump pulse of 750 nm was generated. The pump fluence was attenuated to 1.6 mJ/cm<sup>2</sup> for exciting the samples to avoid multi-excitonic processes. The resulting pump pulse and the separated IR pulse were directed into the TA spectrometer (Harpia, Light Conversion). The polarization of the pump pulse was set at 54.7° with respect to the polarization of the IR pulse to prevent anisotropic effects. The probe white-light pulses were generated by focusing the IR pulse on a sapphire crystal. Using a data analysis software (Igor, WaveMetrics), TA kinetic profiles were fitted to multi-exponential functions convoluted with the Gaussian-shape instrument response

functions (IRF). Global lifetime analyses were carried out using a data analysis software (CarpetView, Light Conversion). The IRF was typically 210 fs.

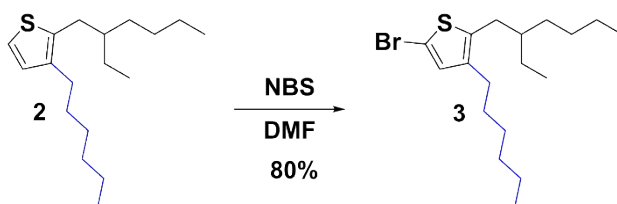
## 2. Synthesis

### 2-Ethylhexyl-3-hexylthiophene (2).



Under nitrogen, turning magnesium (2.24 g, 92.35 mmol), diethyl ether (25 mL) and a piece of iodine were added to a dry 2-neck round bottom flask (RBF) with condenser. 2-Ethylhexylbromide (10.7 g, 55.41 mmol) was added dropwise with strong stirring and then the mixture was heated to reflux for 1 h to obtain the Grignard reagent (dark gray). In another 2-neck RBF with condenser, compound 1 (4.57 g, 18.47 mmol), diethyl ether (70 mL), and [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (NidppCl<sub>2</sub>) (0.4 g, 0.74 mmol) was added at 0 °C. To this solution, the Grignard reagent was added dropwise by syringe. The reaction mixture was heated under reflux for 12 h. Deionized water was added to quench the reaction and the resulting solution was extracted with diethyl ether three times. The organic layer was combined and dried over anhydrous MgSO<sub>4</sub>. After removing the solvent by rotary evaporation, the residual was purified by silica gel column chromatography using hexane as eluent. Colorless oil was obtained. (2.85 g, Yield: 53%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.03 (d, *J* = 5.12 Hz, 1H), 6.81 (d, *J* = 5.12 Hz, 1H), 2.64 (d, *J* = 7.20 Hz, 2H), 2.49 (t, *J* = 7.80 Hz, 2H), 1.59-1.50 (m, 2H), 1.38-1.26 (m, 15H), 0.92-0.87 (m, 9H).

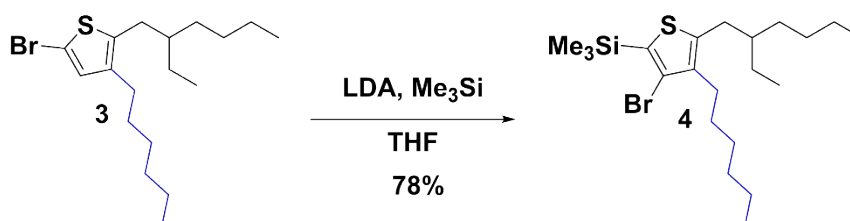
### 5-Bromo-2-(2-ethylhexyl)-3-hexylthiophene (3).



Compound 2 (2.85 g, 10.16 mmol) and *N,N*-dimethylformamide (DMF) (30 mL) was mixed in a 1-neck RBF and cooled to 0 °C using an ice bath. *N*-Bromosuccinimide (NBS) (2.71 g, 15.24 mmol) was then added slowly under a dark condition and followed by stirring at 0 °C for 30 min. After removing the ice bath, the reaction mixture was stirred for another 1 h. After the reaction was completed, deionized water was poured and the mixture was extracted with Et<sub>2</sub>O three times. The organic layer was washed with water and dried over anhydrous MgSO<sub>4</sub>. After removing the solvent by rotary evaporator, the residual was purified by silica

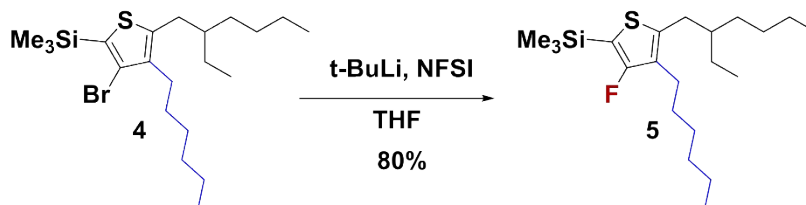
gel column chromatography using hexane as eluent. Yellow oil was obtained. (2.92 g, Yield: 80%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 6.74 (s, 1H), 2.57 (d, *J* = 7.11 Hz, 2H), 2.42 (t, *J* = 7.65 Hz, 2H), 1.52-1.47 (m, 2H), 1.38-1.24 (m, 15H), 0.91-0.86 (m, 9H).

(3-Bromo-5-(2-ethylhexyl)-4-hexylthiophen-2-yl)trimethylsilane (4).



Under a nitrogen atmosphere, compound 4 (2.92 g, 8.13 mmol) and THF (30 mL) were added to a 2-neck RBF and cooled down to 0 °C using an ice bath. Freshly prepared lithium diisopropylamide (LDA) (1.3 M, 21.89 mL) was added dropwise and the resulting mixture was stirred for 30 min. Then, trimethylsilyl chloride (Me<sub>3</sub>SiCl) (1 M in THF, 32.52 mL) was added dropwise at 0 °C. After stirring for 30 min, the solution was allowed to warm to room temperature and stirred for another 1 h. Deionized water was added slowly by syringe and the resulting solution was extracted with Et<sub>2</sub>O three times. The organic layer was combined and dried over anhydrous MgSO<sub>4</sub>. After removing the solvent by rotary evaporator, the residual was purified by silica gel column chromatography using hexane as eluent. Colorless oil was obtained. (2.74 g, Yield: 78%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 2.65 (dd, *J*<sub>1</sub> = 4.37, *J*<sub>2</sub> = 6.84 Hz, 2H), 2.52 (t, *J* = 7.93 Hz, 2H), 1.64-1.55 (m, 1H), 1.50-1.42 (m, 2H), 1.40-1.26 (m, 14H), 0.93-0.86 (m, 9H), 0.37 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 143.5, 139.5, 130.1, 120.0, 41.4, 33.4, 32.7, 31.8, 31.1, 30.0, 29.6, 29.0, 28.5, 25.8, 23.2, 22.8, 14.3, 14.2, 11.0.

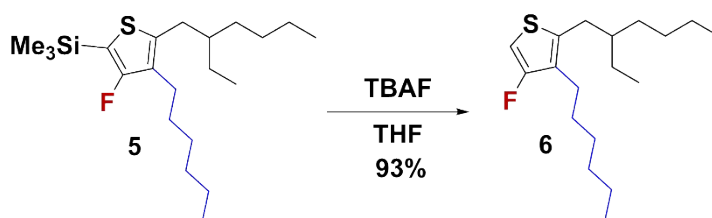
3-Fluoro-5-(2-ethylhexyl)-4-hexylthiophen-2-yl)trimethylsilane (5).



Under a nitrogen atmosphere, Compound 5 (0.5 g, 1.16 mmol) and Et<sub>2</sub>O (4.5 mL) were mixed in a 2-neck RBF. The mixture was cooled down to -80 °C with a cooling bath (Eyela PSL-1810). Then, t-butyllithium (1.7 M in pentane) (2 mL, 3.46 mmol) was added dropwise (to minimize the temperature increase of the reaction solution) and the reaction solution was stirred for 40 min. A solution of *N*-

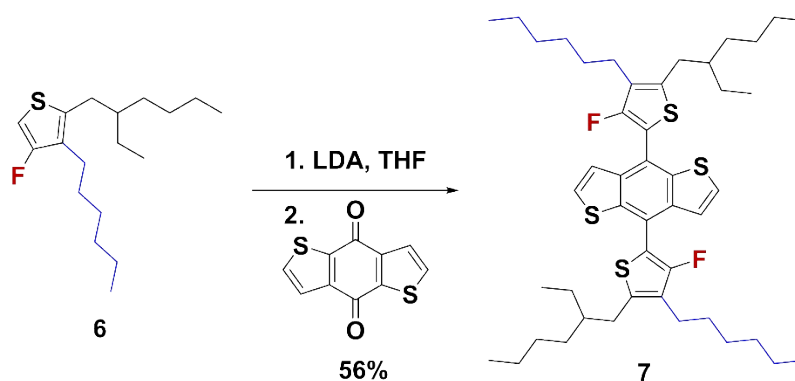
fluorobenzenesulfonimide (1.1 g) in Et<sub>2</sub>O (2.3 mL) was added dropwise by syringe and the mixture was stirred at -80 °C for 1 h. Then, the reaction solution was allowed to warm up to room temperature slowly with stirring overnight. Deionized water was added by syringe to quench the reaction and the mixture was extracted with hexane four times. The organic layer was combined and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed by rotary evaporation and the residual was purified by silica gel column chromatography using hexane as eluent. Colorless oil was obtained. (0.36 g, Yield: 80%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 2.58 (dd, *J*<sub>1</sub> = 2.93, *J*<sub>2</sub> = 6.88 Hz, 2H), 2.40 (t, *J* = 7.82 Hz, 2H), 1.59-1.54 (m, 1H) 1.52-1.44 (m, 2H), 1.40-1.24 (m, 14H), 0.93-0.83 (m, 9H), 0.29 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 162.5, 160.5, 143.1, 143.0, 129.0, 128.8, 110.3, 110.0, 41.2, 33.3, 32.7, 31.8, 29.9, 29.5, 29.0, 25.8, 25.8, 25.7, 23.2, 22.8, 14.3, 14.2, 11.0.

2-(2-Ethylhexyl)-4-fluoro-3-hexylthiophen (6).



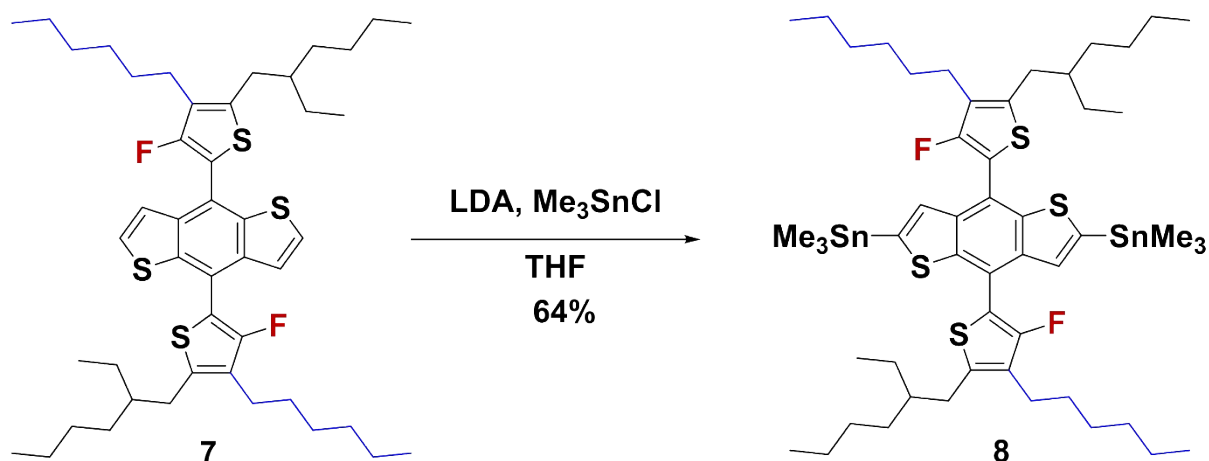
Under nitrogen, compound 6 (0.36 g, 0.97 mmol) and THF (4 mL) was added into a 2-neck RBF and the mixture was cooled to 0 °C. To the above solution, 1 M tetrabutylammonium fluoride solution in THF (2.91 mL) was added dropwise at 0 °C. After stirring for 15 min, ice bath was removed and the reaction solution was allowed to warm up to room temperature and stirred for another 1 h. Deionized water was added by syringe and the mixture was extracted with ethyl acetate three times. The organic layer was combined and dried over anhydrous MgSO<sub>4</sub>. After removing the solvent, the residual was purified by silica gel column chromatography using hexane as eluent. Colorless oil was obtained (0.27 g, Yield: 93%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 6.44 (s, 1H), 2.58 (d, *J* = 7.16 Hz, 2H), 2.42 (t, *J* = 7.78 Hz, 2H), 1.55-1.45 (m, 3H), 1.37-1.24 (m, 14H), 0.95-0.83 (m, 9H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 157.5, 155.4, 137.9, 137.8, 127.9, 127.7, 99.1, 99.0, 77.4, 77.2, 76.9, 41.3, 33.1, 32.6, 31.8, 29.9, 29.3, 29.0, 25.8, 25.6, 25.6, 23.2, 22.8, 14.3, 14.2, 11.0.

4,8-Bis(5-(2-ethylhexyl)-3-fluoro-4-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (7).



Under nitrogen, compound 6 (0.3 g, 1 mmol) and THF (1.3 mL) was added to a 2-neck RBF and the mixture was cooled down to 0 °C. A freshly prepared LDA (1 M, 6.5 eq) was added dropwise, and the reaction solution was stirred at room temperature for 15 min and heated at 45 °C for 1 h to form a brown solution. Under nitrogen, benzo[1,2-b:4,5-b']dithiophene-4,8-dione (73.8 mg, 0.34 mmol) and THF was mixed in a RBF and then cooled down to -80 °C, to which the above solution was transferred by syringe dropwise. After removing a cooling bath, the reaction mixture was allowed to warm up to room temperature and stirred for 1.5 h. After the solution was cooled down to 0 °C with an ice bath, degassed SnCl<sub>2</sub>/HCl solution (SnCl<sub>2</sub> 0.53 g, 10% HCl 1.1 mL) was added and stirred for 13 h. After extraction the resulting solution with hexane three times, the organic layer was dried over anhydrous MgSO<sub>4</sub>. After removing the solvent using a rotary evaporator, the residual was purified by silica gel column chromatography using hexane as eluent. A sticky liquid was obtained (0.12 g, Yield: 56%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.50 (d, *J* = 5.61 Hz, 2H), 7.44 (dd, *J*<sub>1</sub> = 1.95, *J*<sub>2</sub> = 5.61 Hz, 2H), 2.74 (d, *J* = 7.10 Hz, 4H), 2.59 (t, *J* = 7.78 Hz, 4H), 1.71-1.61 (m, 6H), 1.48-1.31 (m, 28H), 0.99-0.90 (m, 18H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 153.8, 151.7, 139.5, 138.2, 138.1, 137.2, 128.5, 128.3, 127.6, 123.5, 123.5, 120.2, 113.1, 113.0, 41.4, 33.2, 32.8, 31.8, 30.0, 29.4, 29.1, 26.1, 25.9, 23.2, 22.8, 14.3, 14.2, 11.1.

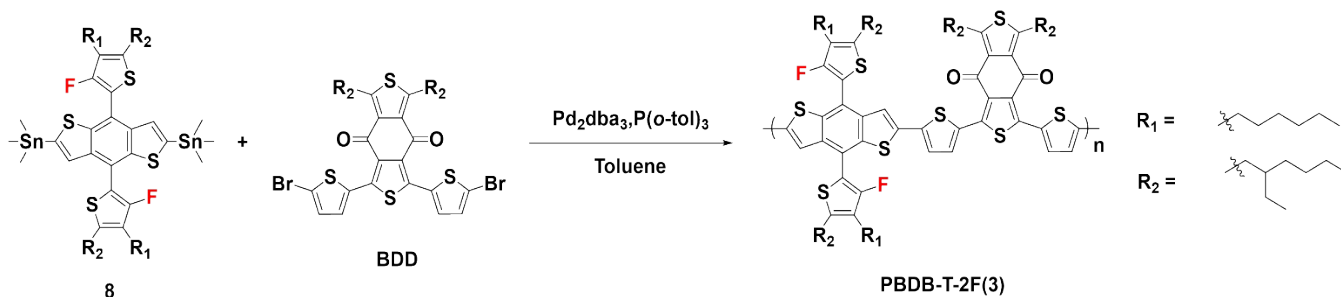
(4,8-Bis(5-(2-ethylhexyl)-3-fluoro-4-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (8).



To a 2-neck RBF, compound 7 (0.12 g, 0.15 mmol) and THF (1.2 mL) was added and cooled down to 0 °C. Freshly prepared LDA solution (1.3 M, 0.71 mL) was added dropwise by syringe. The resulting mixture was stirred for 15 min, and then allowed to warm up to room temperature. After stirring for another 1 h, the solution was cooled down to -78 °C. Trimethyltin chloride (1M in THF, 0.975 mL) was added dropwise by syringe. After stirring for 1 h, the reaction solution was allowed to warm up to room temperature. The mixture was stirred for 12 h, followed by quenching with water. After extraction with ethyl acetate three times, the organic phase was combined and dried over anhydrous  $\text{MgSO}_4$ . After removing solvent by rotary evaporation, the residual was dissolved in hexane and the insoluble solid was filtered off. After hexane was removed under reduced pressure, the residual was washed with acetone and isopropanol at ca. -15 °C in sequence. A white solid was obtained (0.11 g, Yield: 64%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.43 (d,  $J = 2.12$  Hz, 2H), 2.79-2.67 (m, 4H), 2.59 (t,  $J = 7.55$  Hz, 4H), 1.69-1.60 (m, 6H), 1.45-1.27 (m, 28H), 0.98-0.89 (m, 18H), 0.39 (s, 18H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 153.6, 151.5, 143.7, 142.4, 137.9, 137.8, 137.7, 131.3, 128.4, 128.2, 118.4, 113.8, 113.6, 47.7, 41.3, 33.3, 32.8, 31.9, 29.9, 29.3, 29.1, 26.2, 25.8, 23.2, 22.8, 19.5, 14.3, 14.3, 11.2, -8.2. MS (MALDI-TOF)  $m/z$ :  $[\text{M}^+]$  Calcd for  $\text{C}_{52}\text{H}_{80}\text{F}_2\text{S}_4\text{Sn}_2$ , 1108.87; found: 1108.0529.

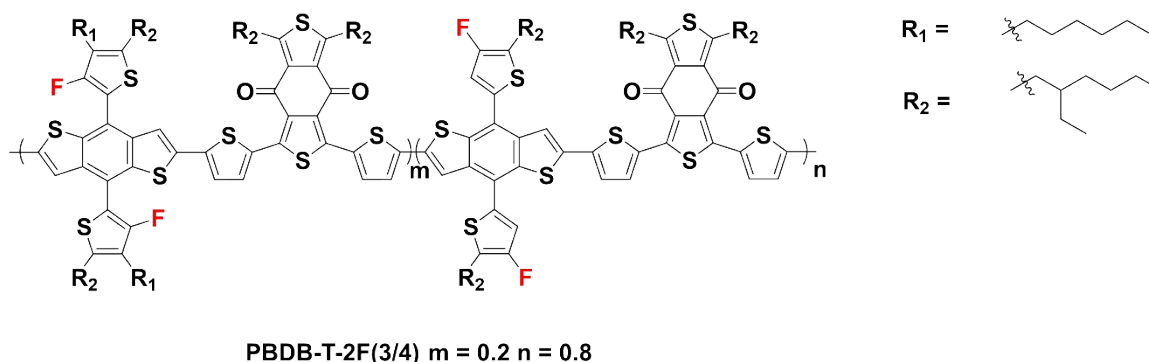
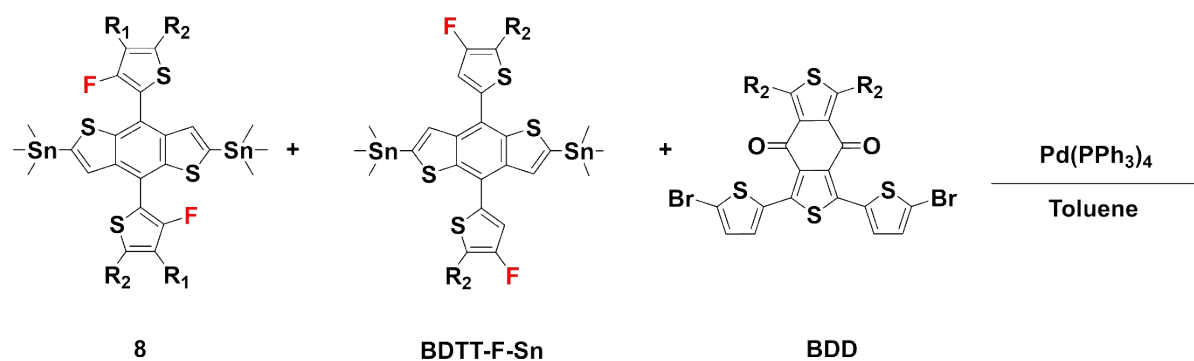


PBDB-T-2F(3).



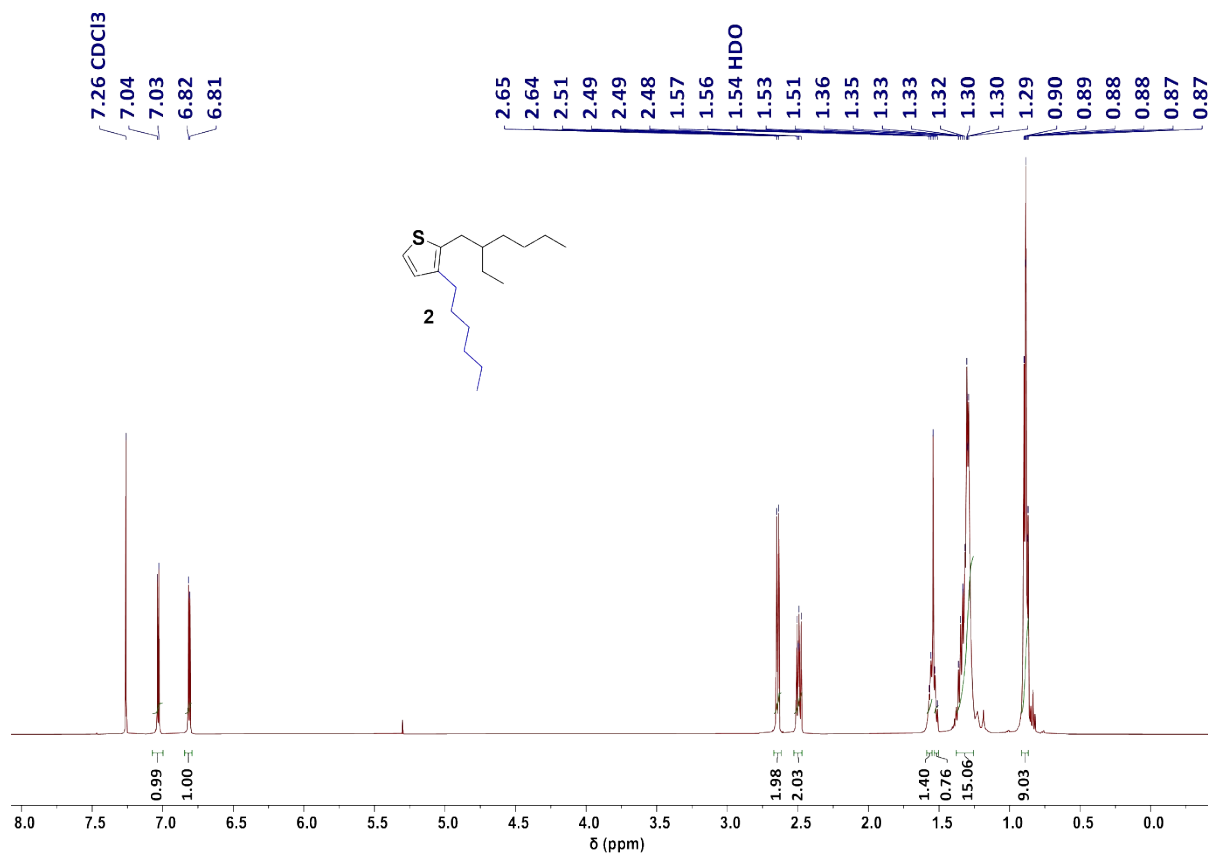
In a nitrogen filled glove box, compound **8** (103.6 mg, 0.094 mmol), 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo[1,2-c:4,5-c']dithiophene-4,8-dione (**BDD**, 72.45 mg, 0.094 mmol),  $\text{Pd}_2(\text{dba})_3$  (2 mol%, 1.72 mg), and  $\text{P}(o\text{-tol})_3$  (16 mol%, 4.58 mg) were added into a microwave reaction vial (Biotage® 0.5–2.0 mL). The reaction vial was sealed with cap and then anhydrous toluene (2 mL) was injected by syringe. In a microwave reactor (Biotage® Initiator<sup>+</sup>), the reaction solution was heated with stirring at 80 °C for 3 min, 110 °C for 3 min, 140 °C for 50 min, and 150 °C for 55 min. The resulting solution was precipitated into a mixture of methanol (100 mL) and HCl solution (12 M, 2 mL). The crude polymer was filtered using a Soxhlet thimble and purified by Soxhlet extraction with hexane, dichloromethane (DCM), and THF in sequence. The extracted portion in THF was precipitated into methanol, filtered, and dried under vacuum, yielding a deep blue solid (94.5 mg, 71%). GPC (*o*-DCB, 80 °C):  $M_n = 26.9$  kg/mol (dispersity = 2.31). <sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.75 (br, 2H), 7.56 (br, 2H), 7.31 (br, 2H), 3.36–3.31 (br, 4H), 2.77–2.63 (br, 6H), 1.67–1.29 (br, 55H), 0.95 (br, 29H).

PBDB-T-2F(3/4).

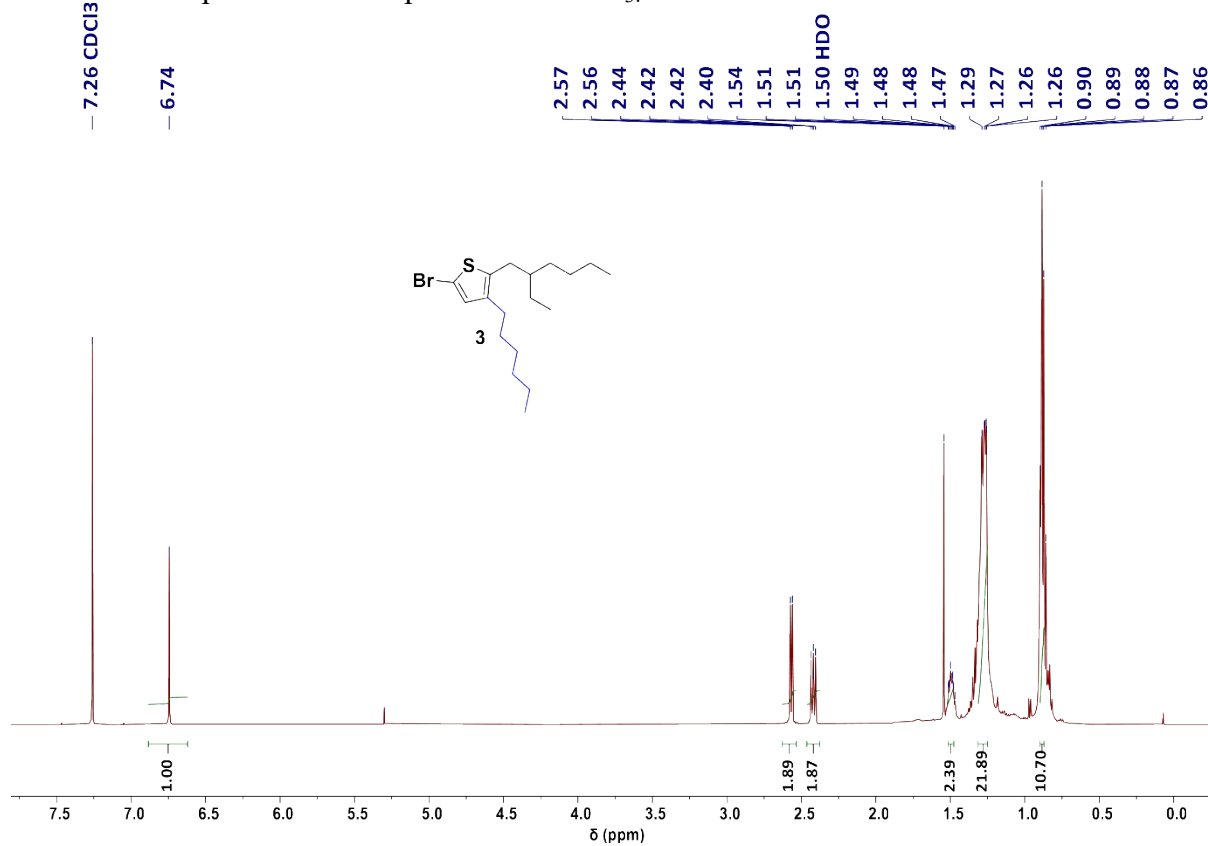


In a nitrogen filled glove box, compound **8** (13.1 mg, 0.0118 mmol), 2,6-bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (BDTT-F-Sn, 100.2 mg, 0.1065 mmol), BDD (90.8 mg, 0.1184 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (4 mol%, 5.5 mg) were added into a microwave reaction vial. The reaction vial was sealed with cap and then anhydrous toluene (2.4 mL) was injected. The mixture was heated at 80 °C for 30 min with stirring in an oil bath, and then further reacted at 110 °C for 5.5 h. The resulting solution was precipitated into a mixture of methanol (100 mL) and HCl solution (12 M, 2 mL). The precipitated solid was filtered using a Soxhlet thimble and purified by Soxhlet extraction with hexane, DCM, THF and chloroform in sequence. The extracted portion in chloroform was precipitated into methanol, filtered, and dried under vacuum, yielding a deep blue solid (82 mg, 55.1%). GPC (*o*-DCB, 80 °C):  $M_n = 22.6$  kg/mol (dispersity = 3.06). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.67-7.48 (br, 1.2H), 7.21-6.83 (br, 6.4H), 3.34-3.28 (br, 0.83H), 2.96-2.59 (br, 7.6H), 1.77-1.46 (br, 29H), 1.01-0.83 (br, 25.8H)

## Supplementary Figures



**Figure S1.** <sup>1</sup>H-NMR spectrum of compound **2** in CDCl<sub>3</sub>.



**Figure S2.** <sup>1</sup>H-NMR spectrum of compound **3** in CDCl<sub>3</sub>.

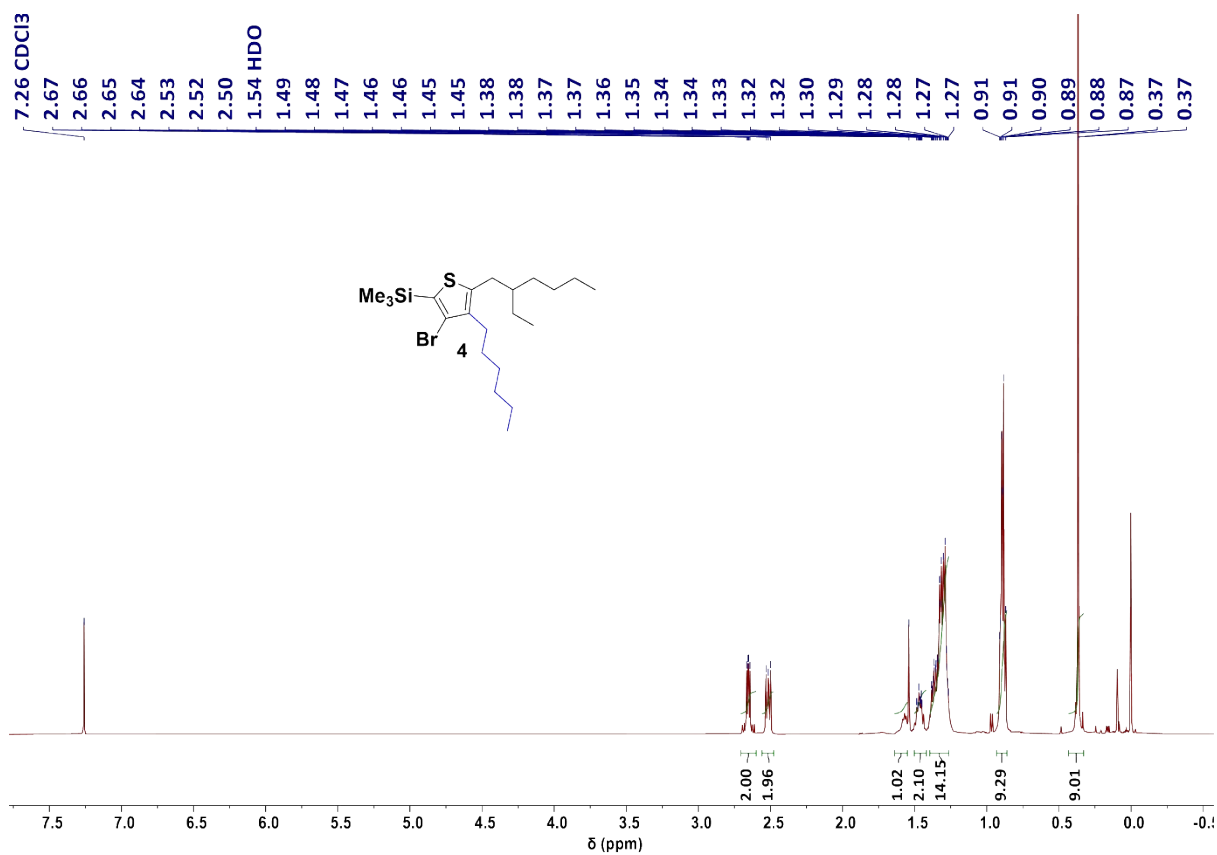


Figure S3. <sup>1</sup>H-NMR spectrum of compound 4 in CDCl<sub>3</sub>.

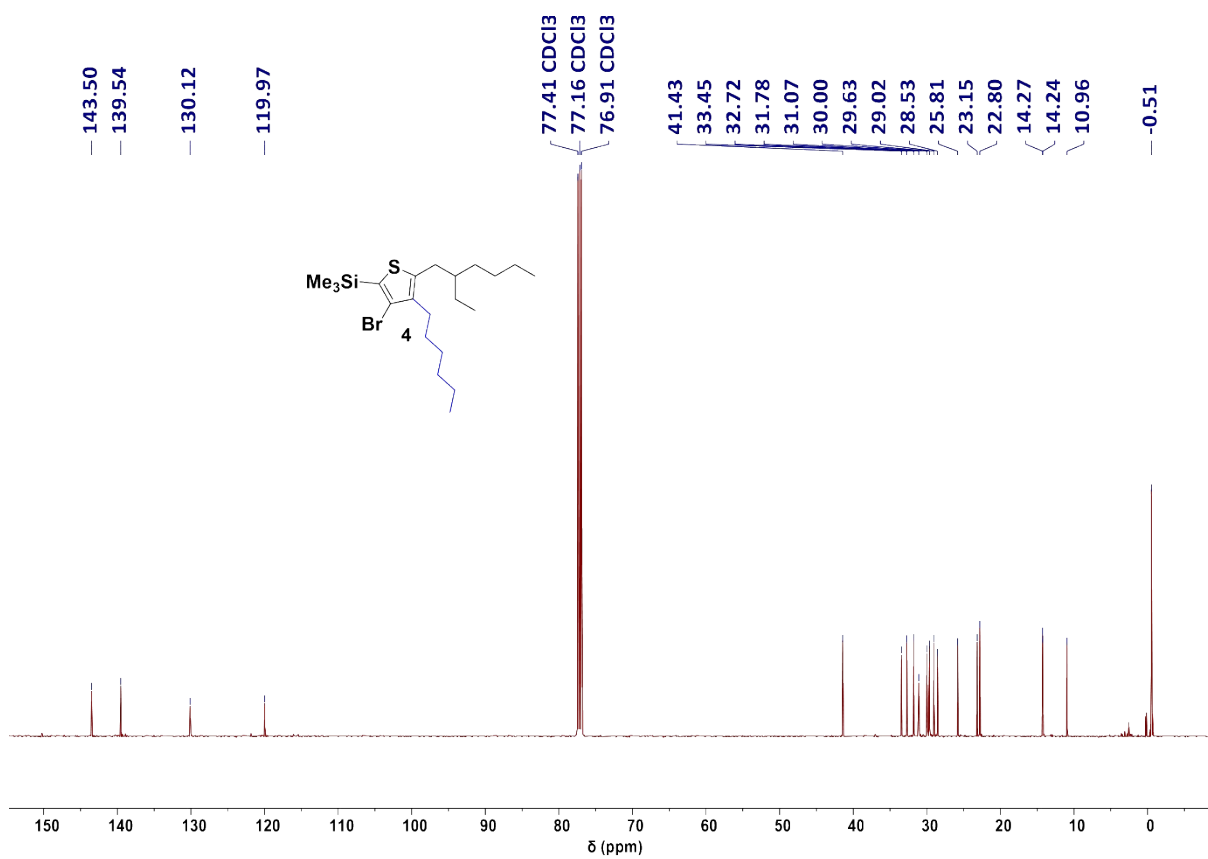


Figure S4. <sup>13</sup>C-NMR spectrum of compound 4 in CDCl<sub>3</sub>.

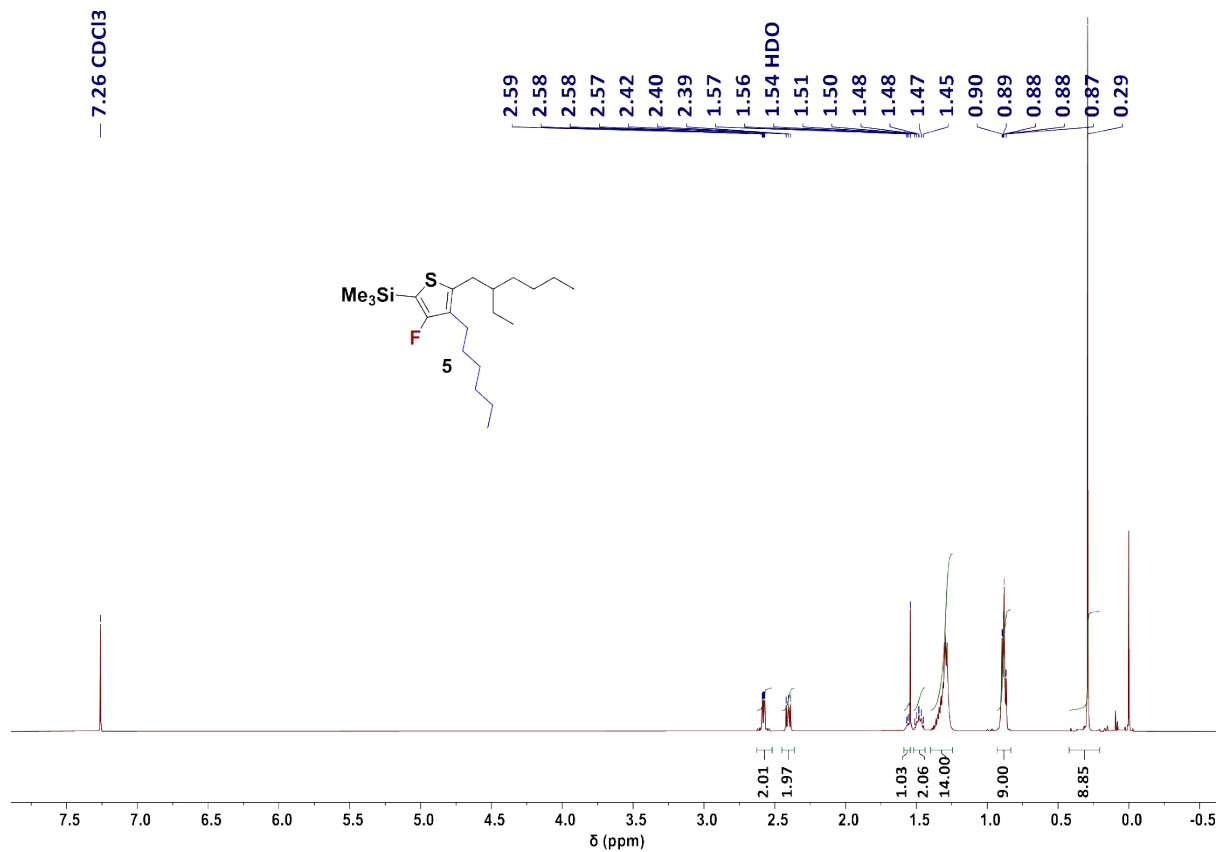


Figure S5.  $^1\text{H-NMR}$  spectrum of compound **5** in  $\text{CDCl}_3$ .

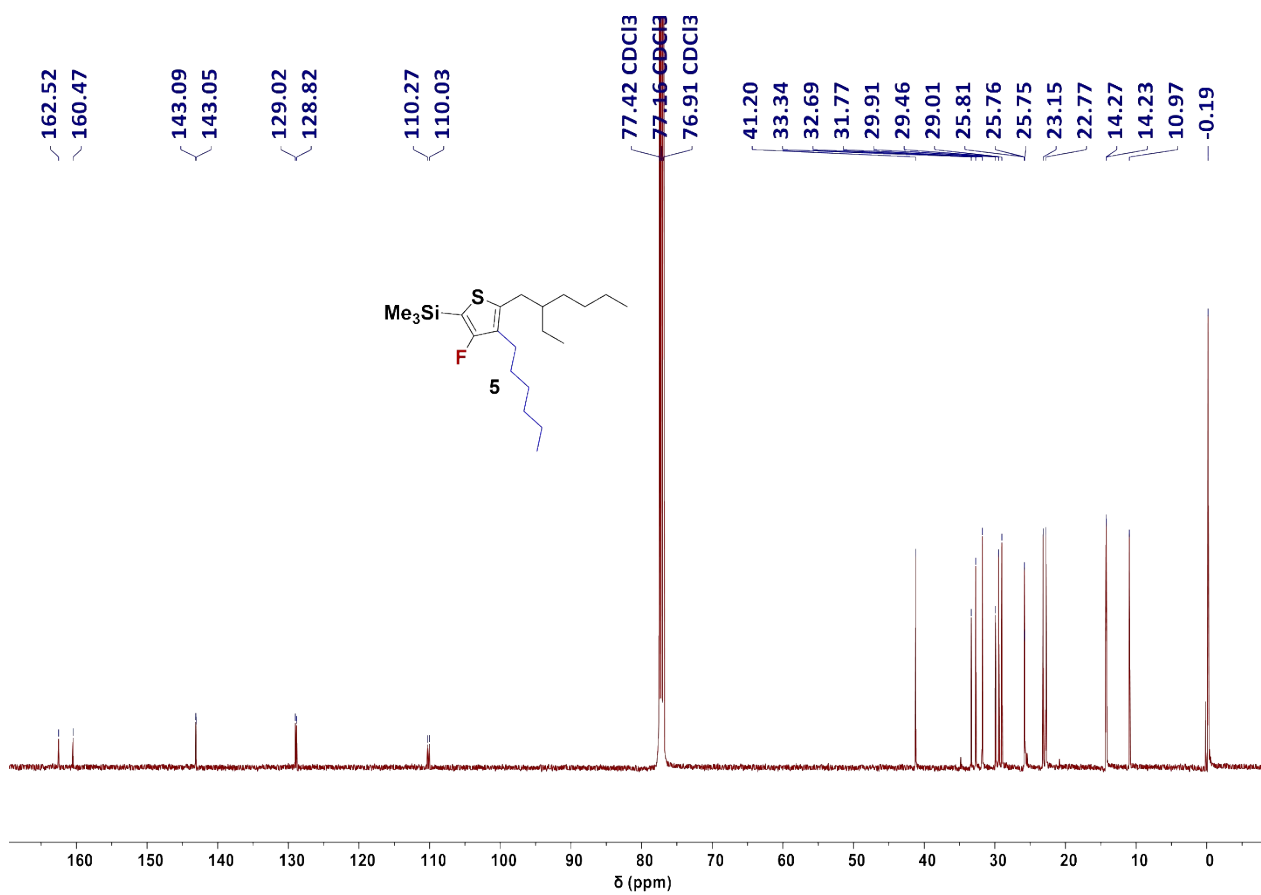


Figure S6.  $^{13}\text{C-NMR}$  spectrum of compound **5** in  $\text{CDCl}_3$ .

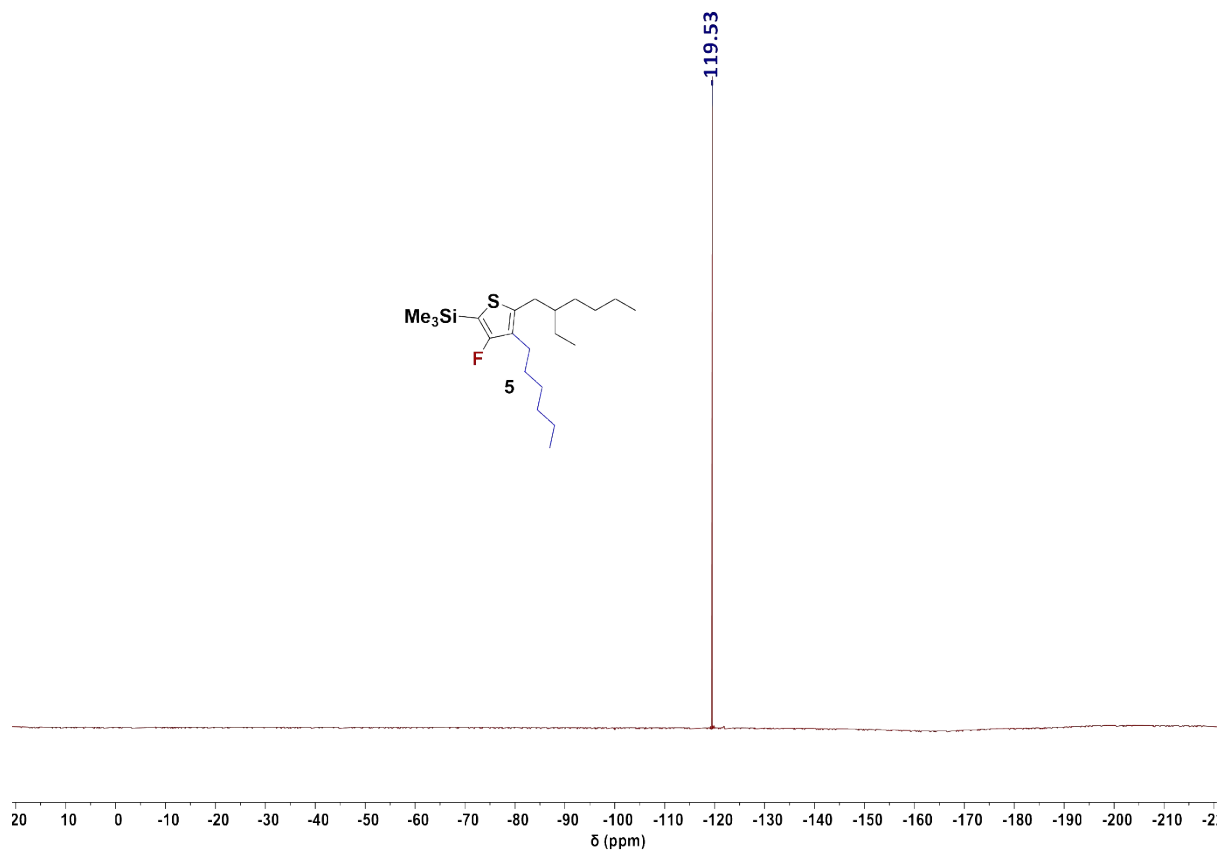


Figure S7.  $^{19}\text{F}$ -NMR spectrum of compound 5 in  $\text{CDCl}_3$ .

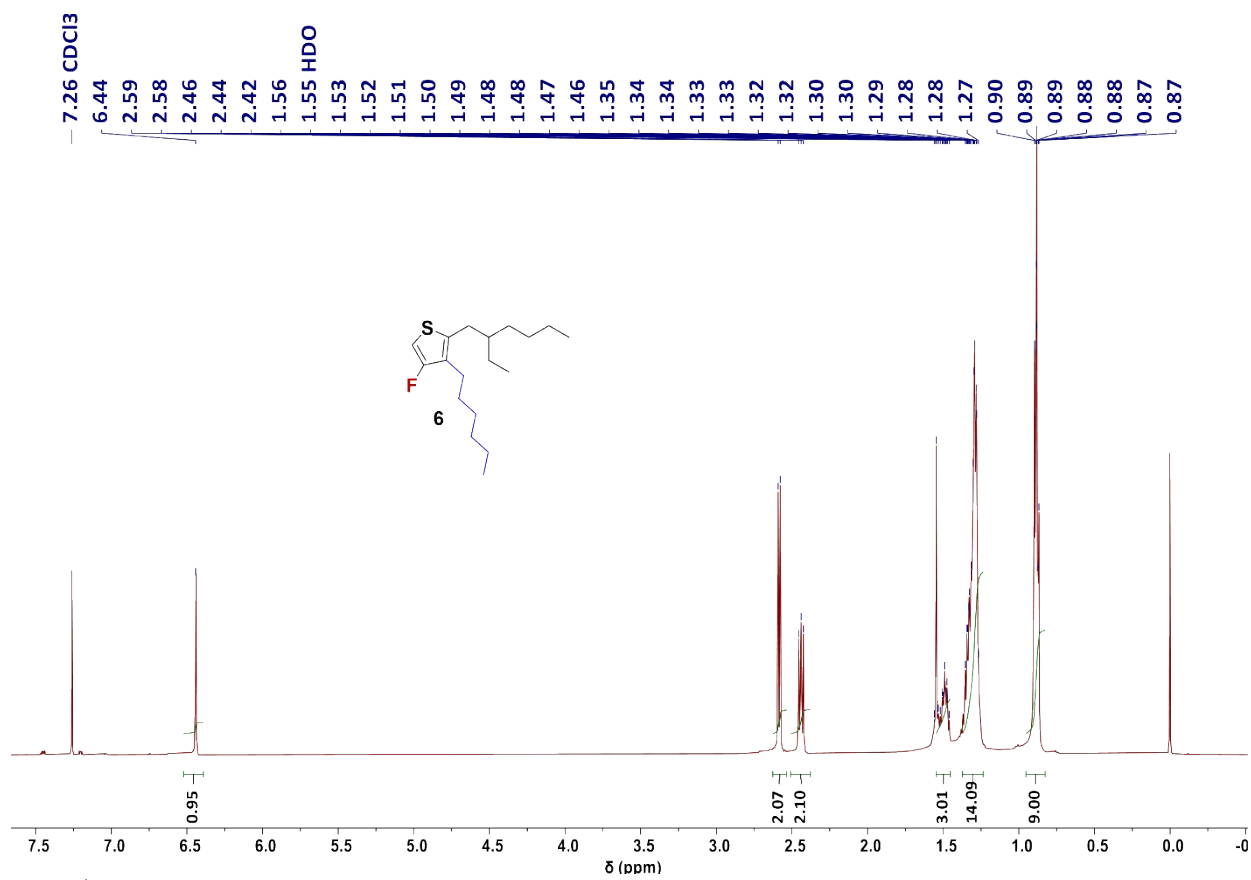


Figure S8.  $^1\text{H}$ -NMR spectrum of compound 6 in  $\text{CDCl}_3$

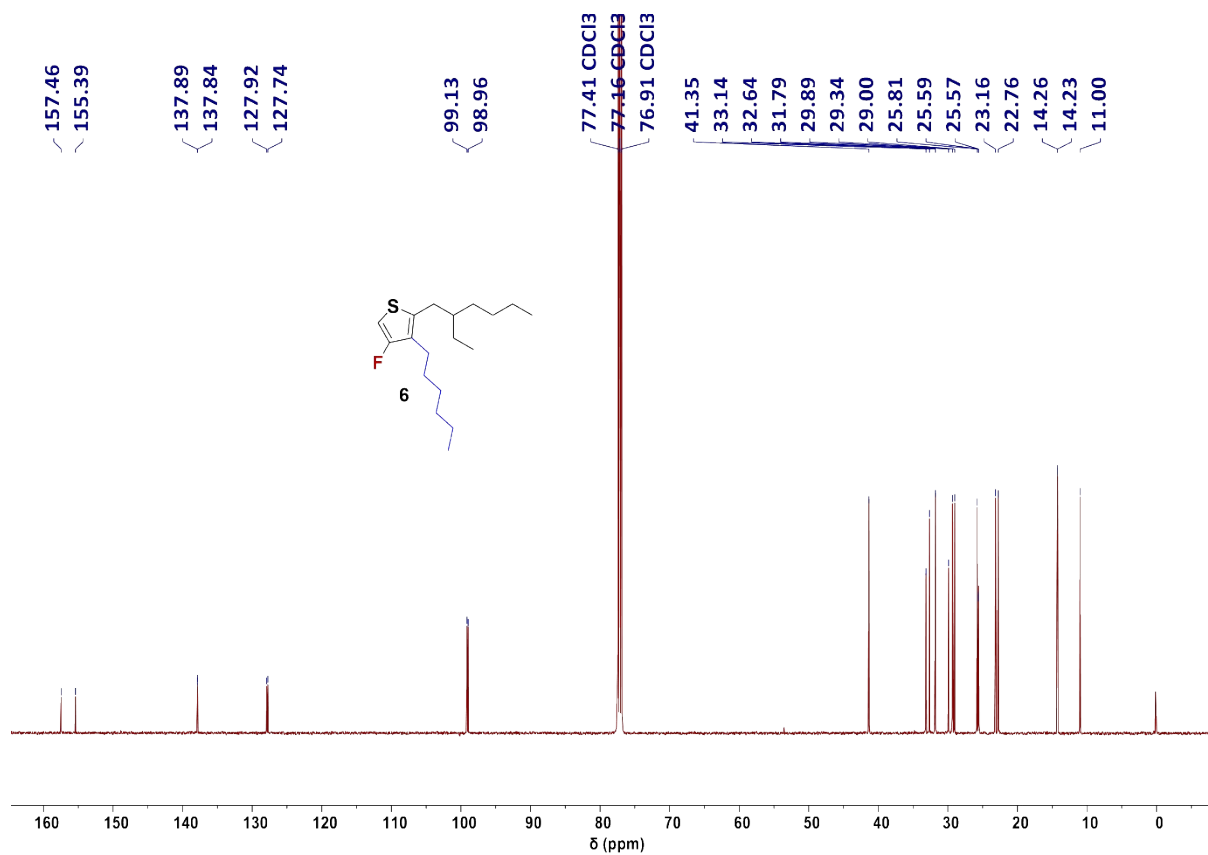


Figure S9.  $^{13}\text{C}$ -NMR spectrum of compound 6 in  $\text{CDCl}_3$

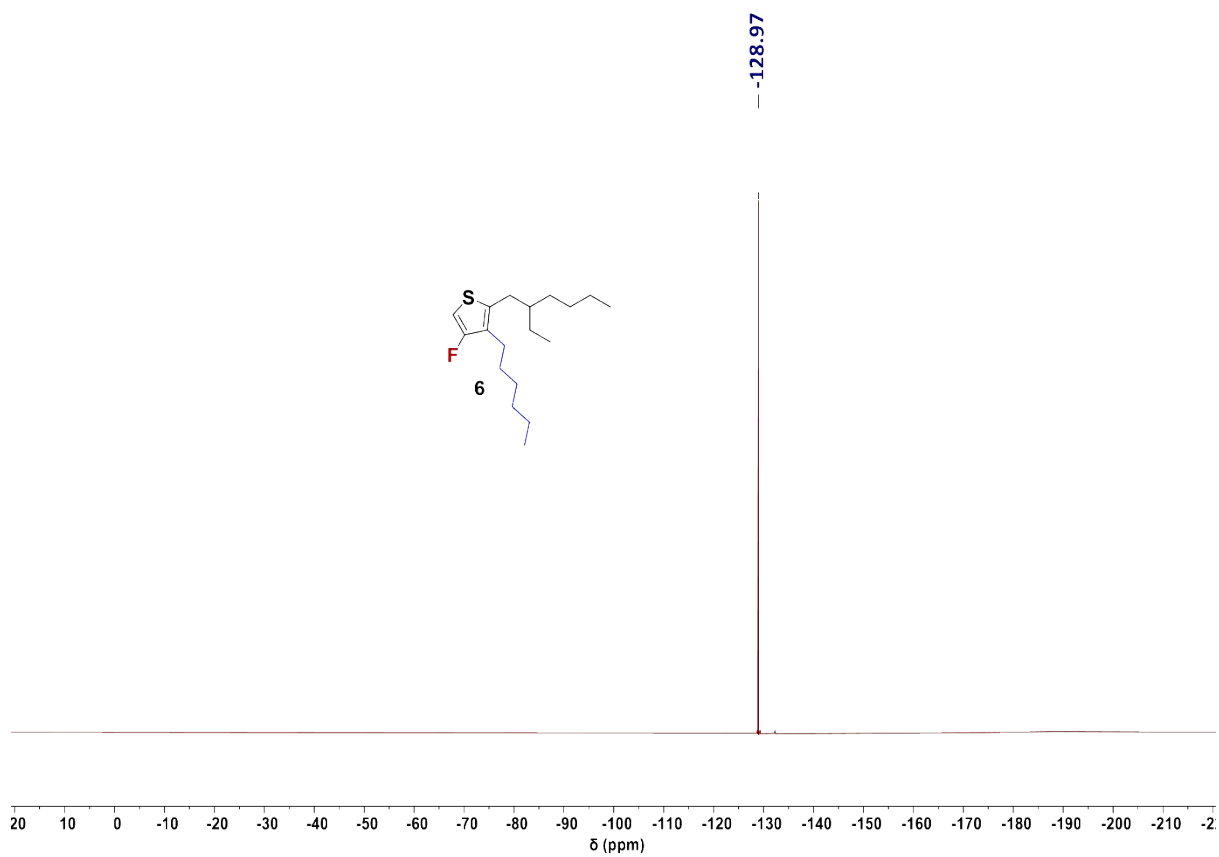
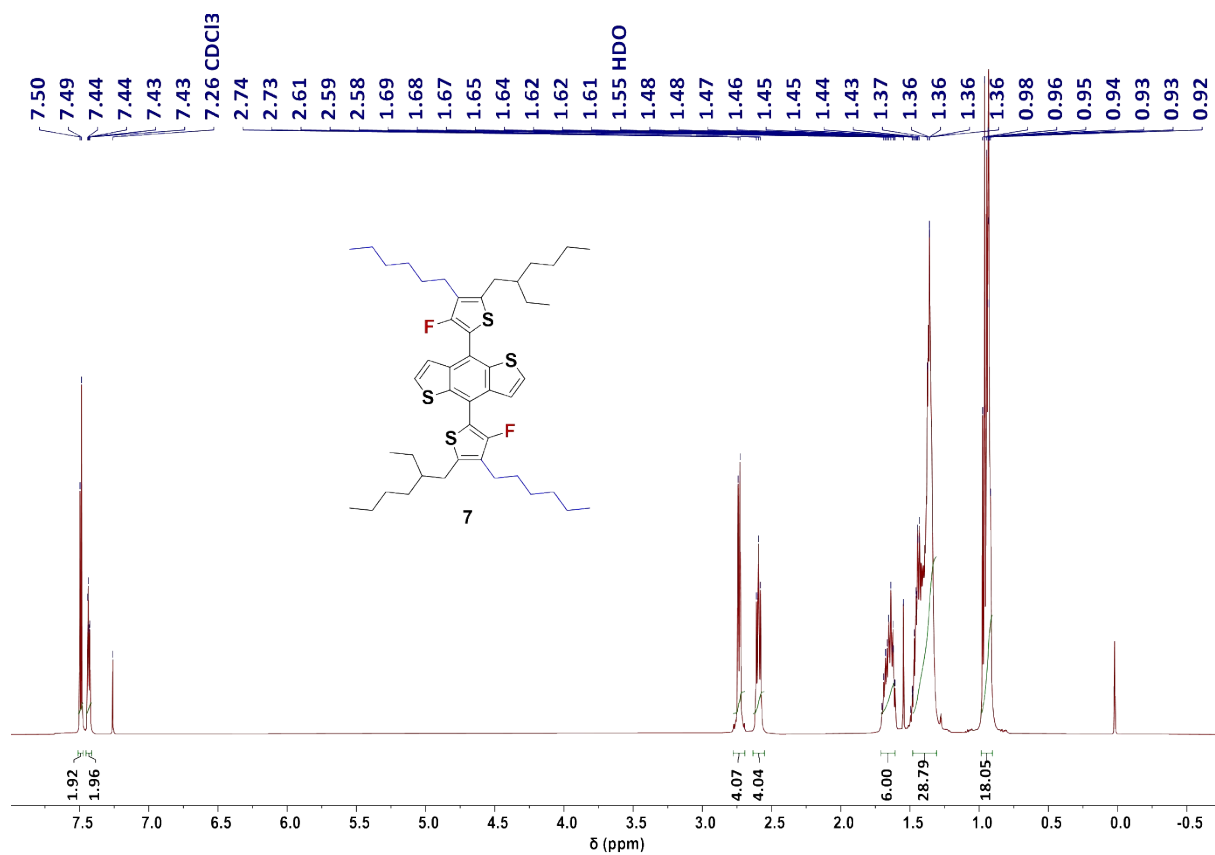
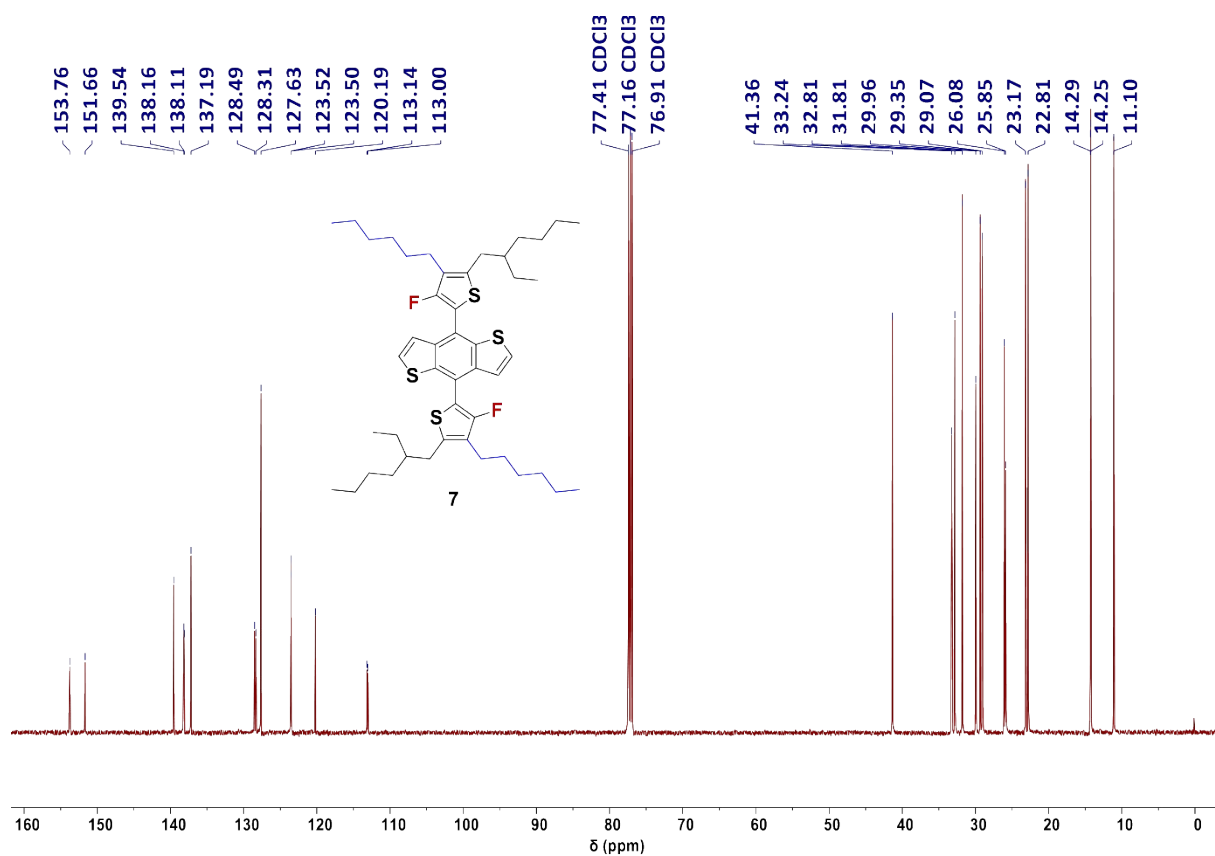


Figure S10.  $^{19}\text{F}$ -NMR spectrum of compound 6 in  $\text{CDCl}_3$ .



**Figure S11.**  $^1\text{H-NMR}$  spectrum of compound **7** in  $\text{CDCl}_3$ .



**Figure S12.**  $^{13}\text{C-NMR}$  spectrum of compound **7** in  $\text{CDCl}_3$ .



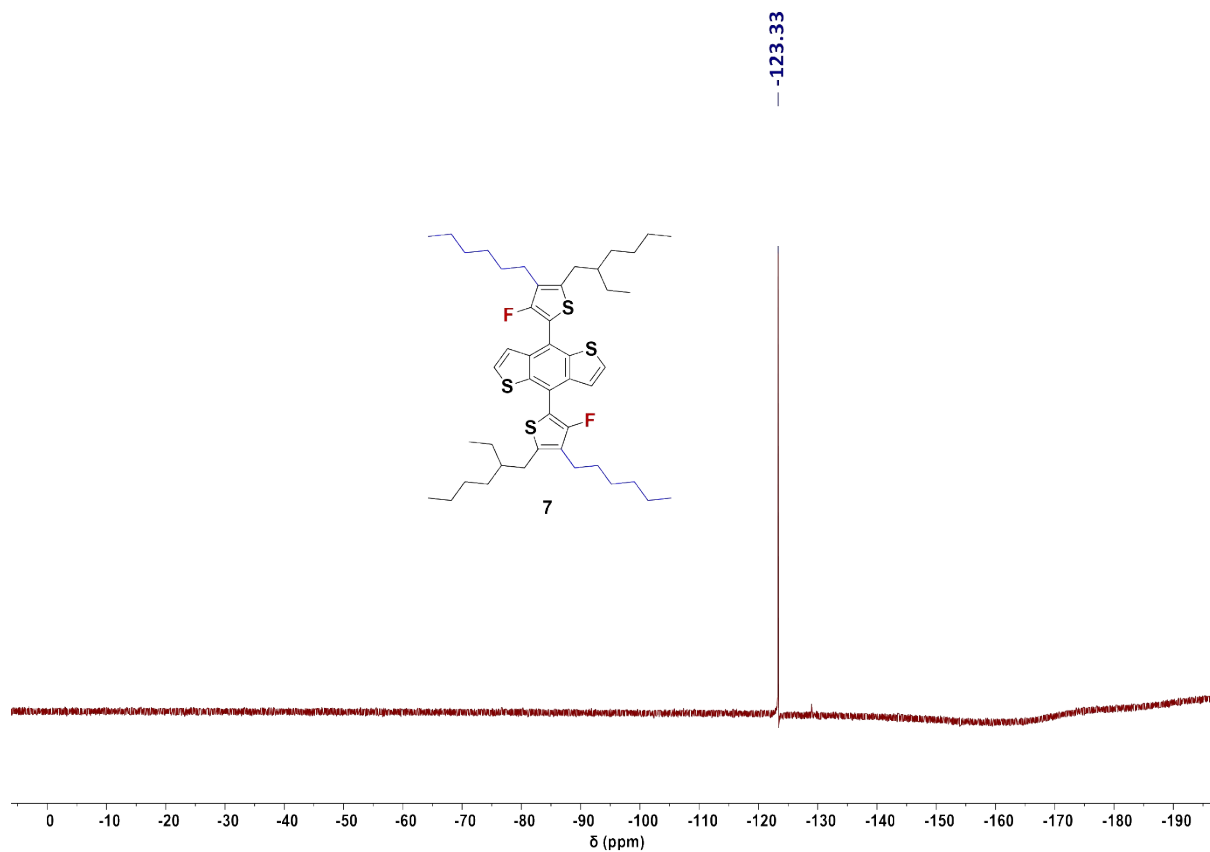


Figure S13.  $^{19}\text{F}$ -NMR spectrum of compound **7** in  $\text{CDCl}_3$ .

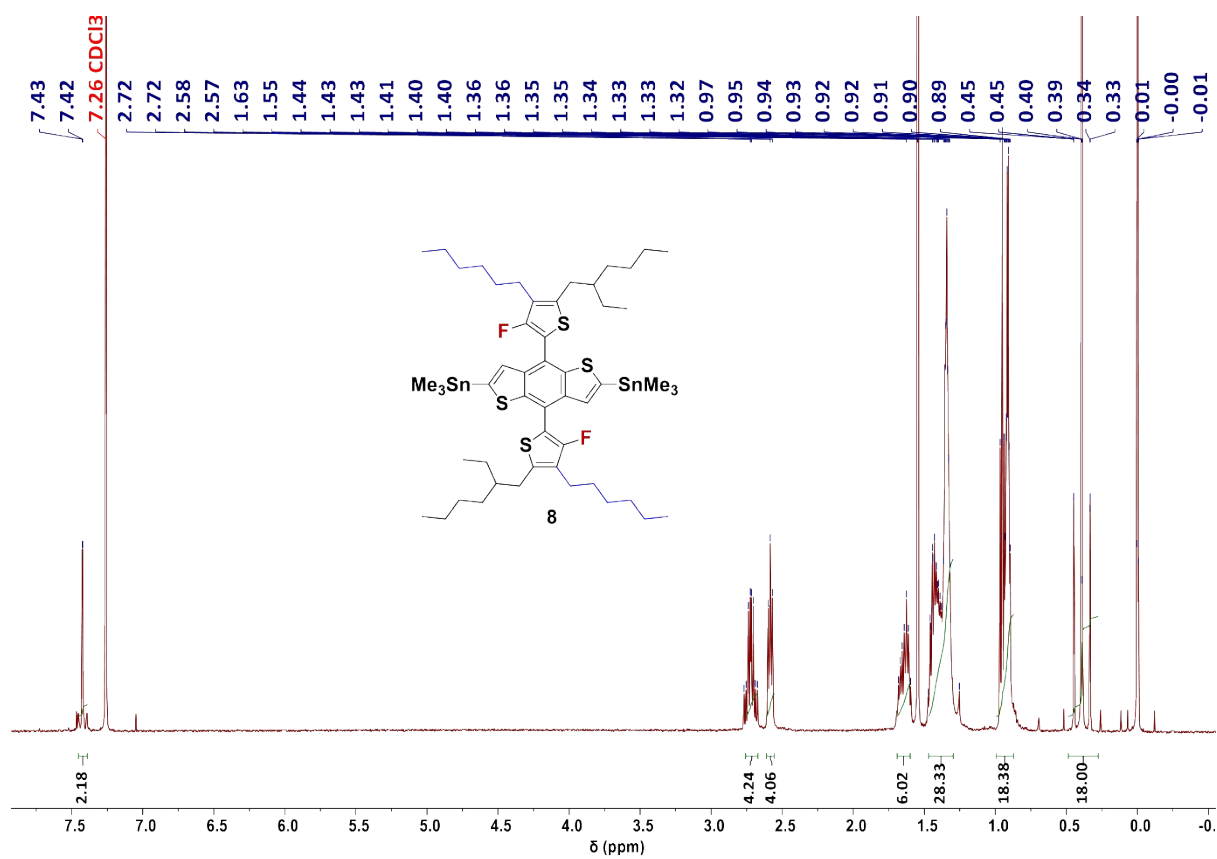
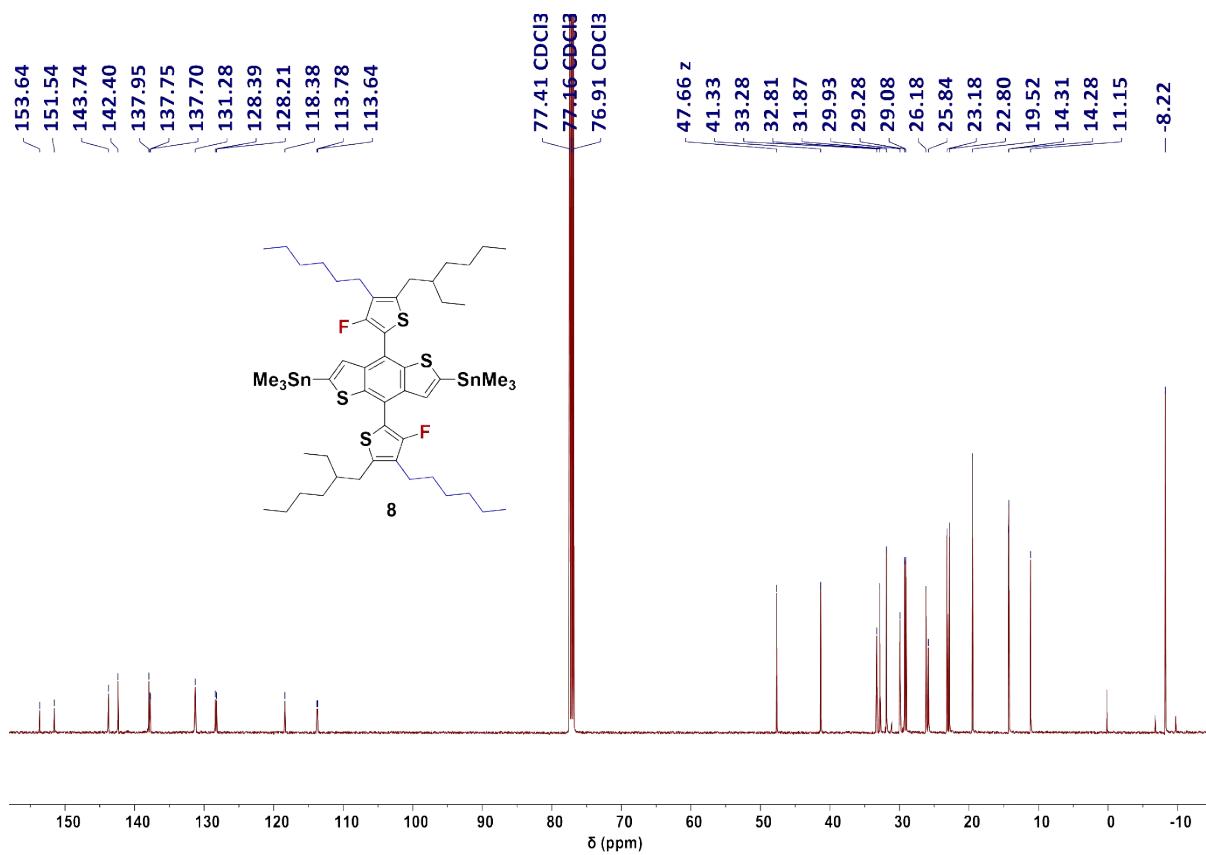
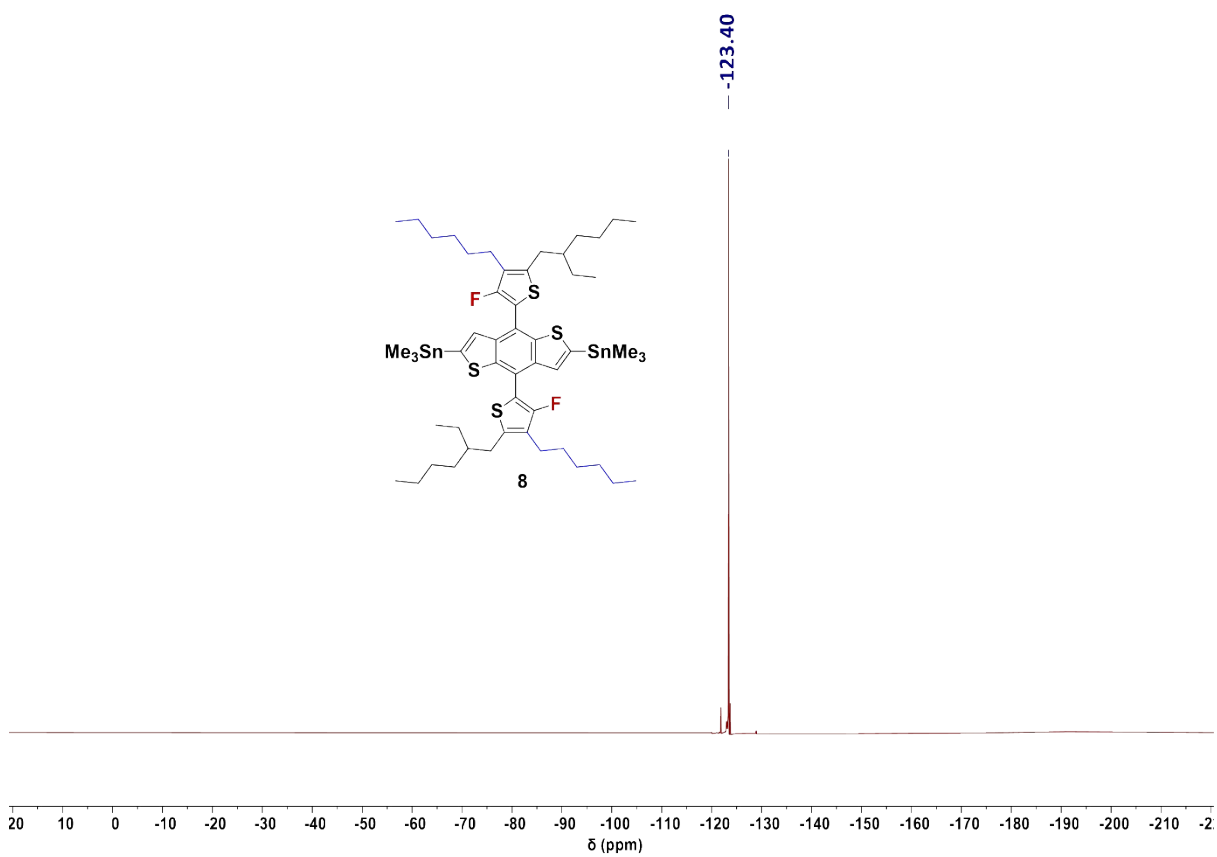


Figure S14.  $^1\text{H}$ -NMR spectrum of compound **8** in  $\text{CDCl}_3$ .



**Figure S15.**  $^{13}\text{C}$ -NMR spectrum of compound **8** in  $\text{CDCl}_3$ .



**Figure S16.**  $^{19}\text{F}$ -NMR spectrum of compound **8** in  $\text{CDCl}_3$ .

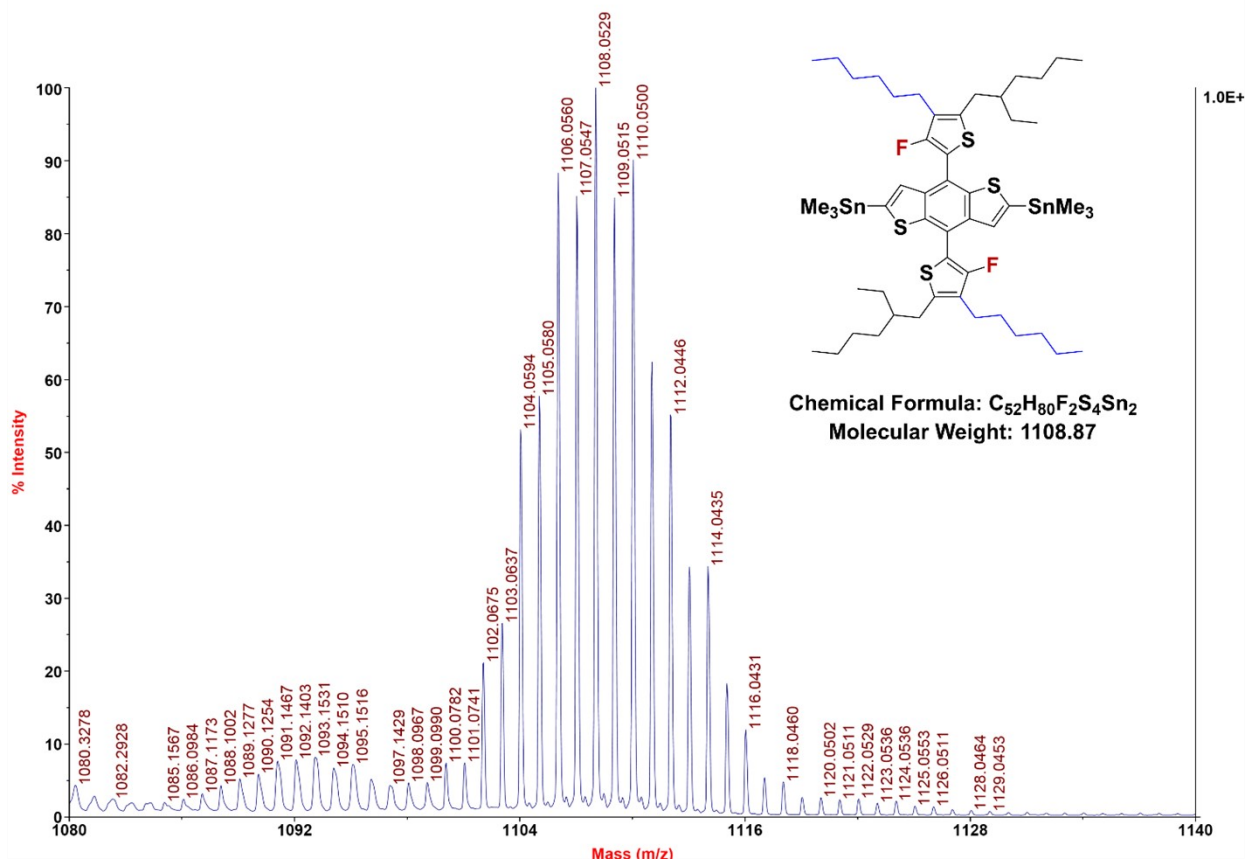


Figure S17. MALDI-TOF spectrum of compound 8.

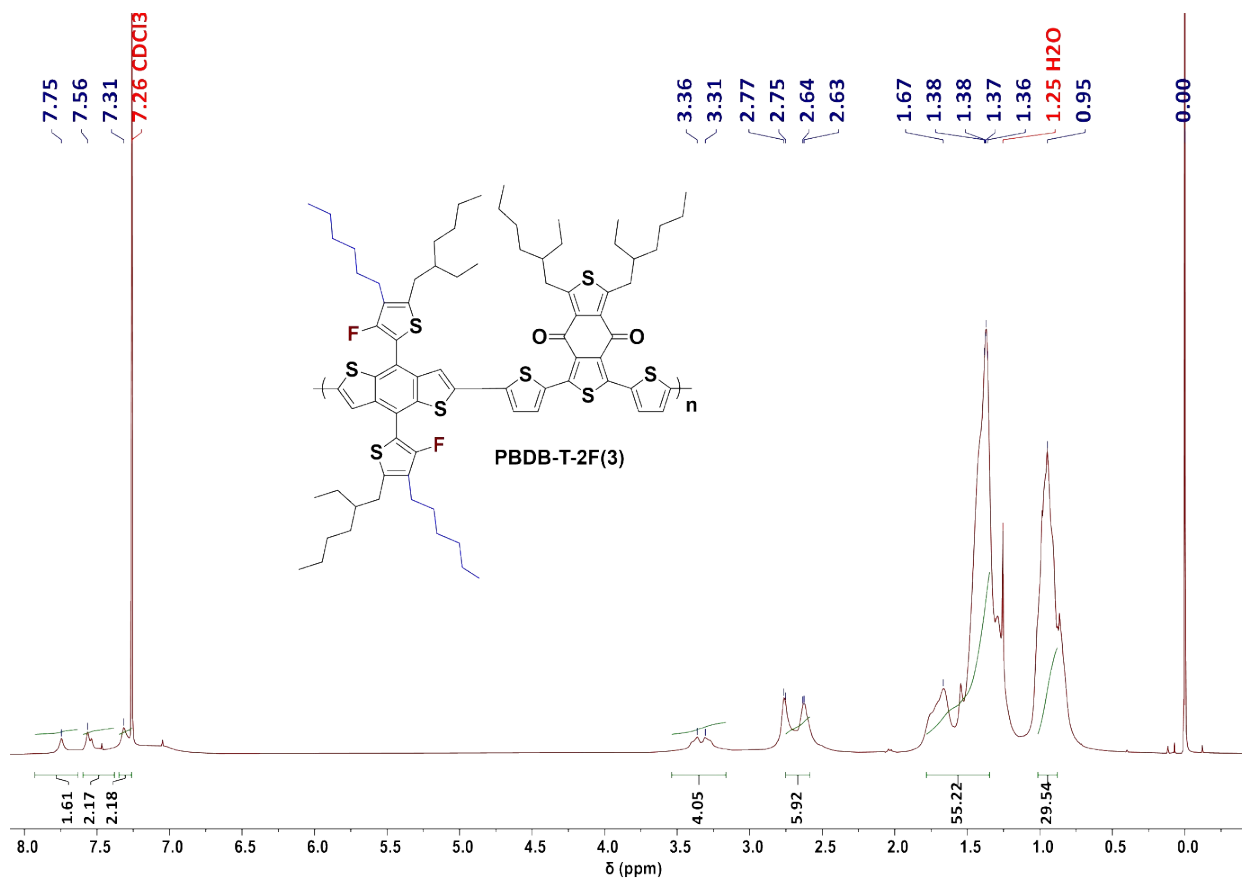
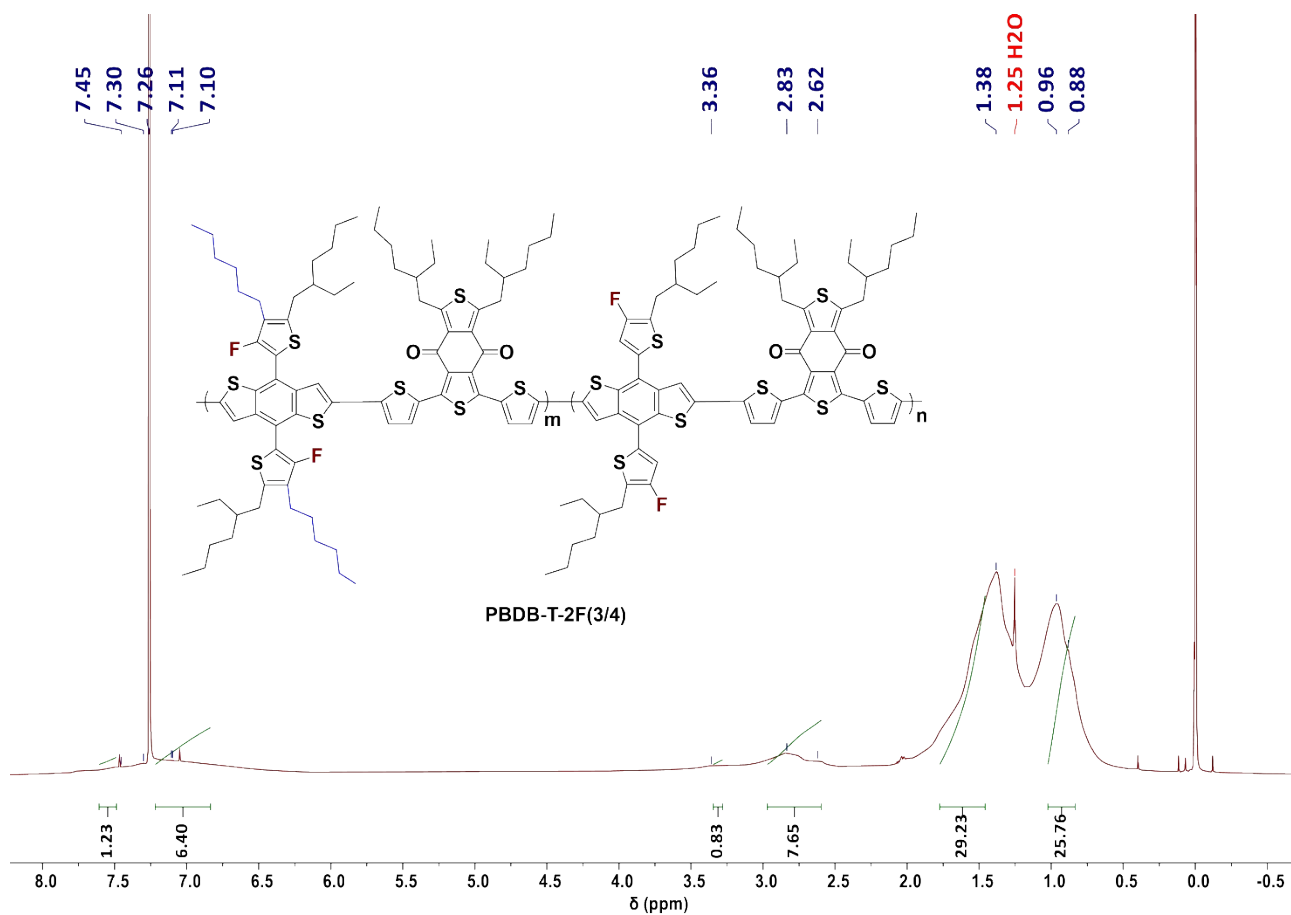
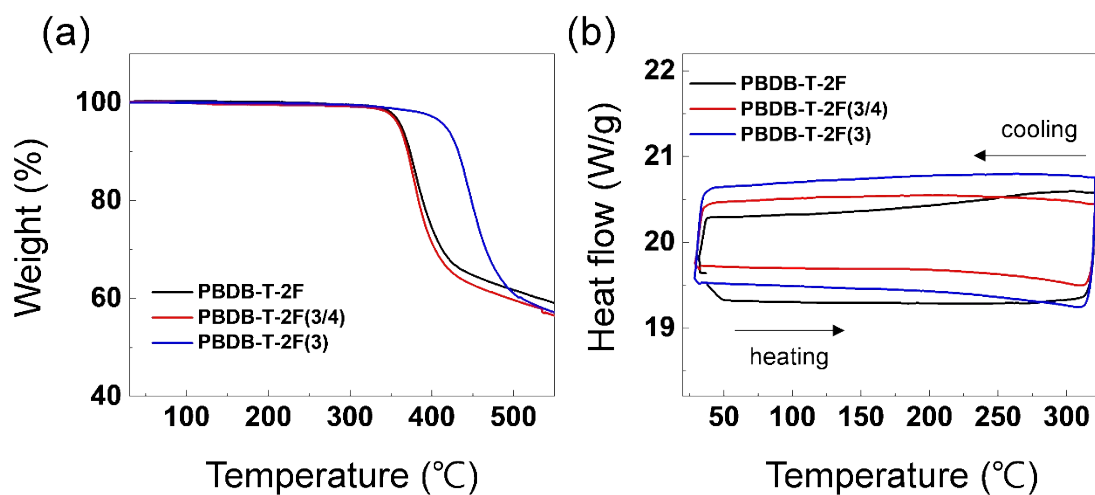


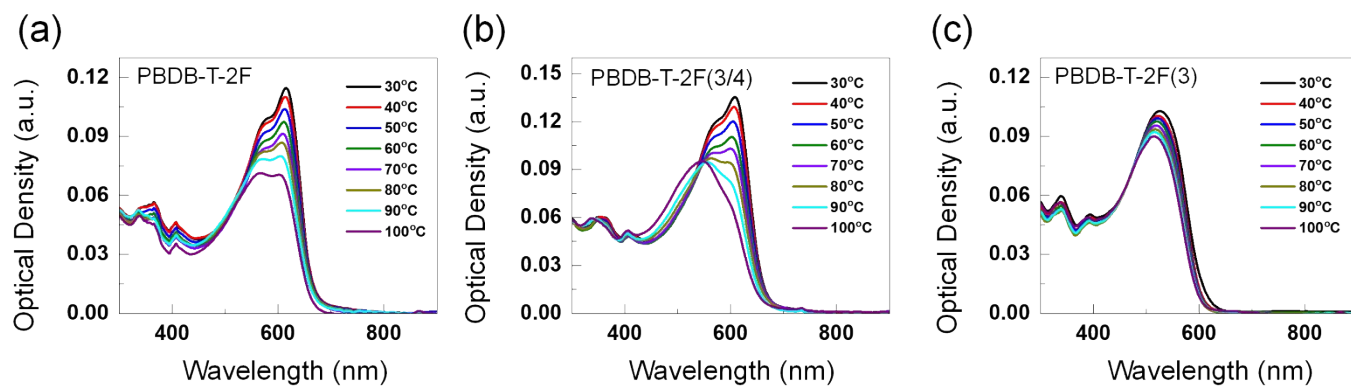
Figure S18. <sup>1</sup>H-NMR spectrum of PBDB-T-2F(3) in CDCl<sub>3</sub>.



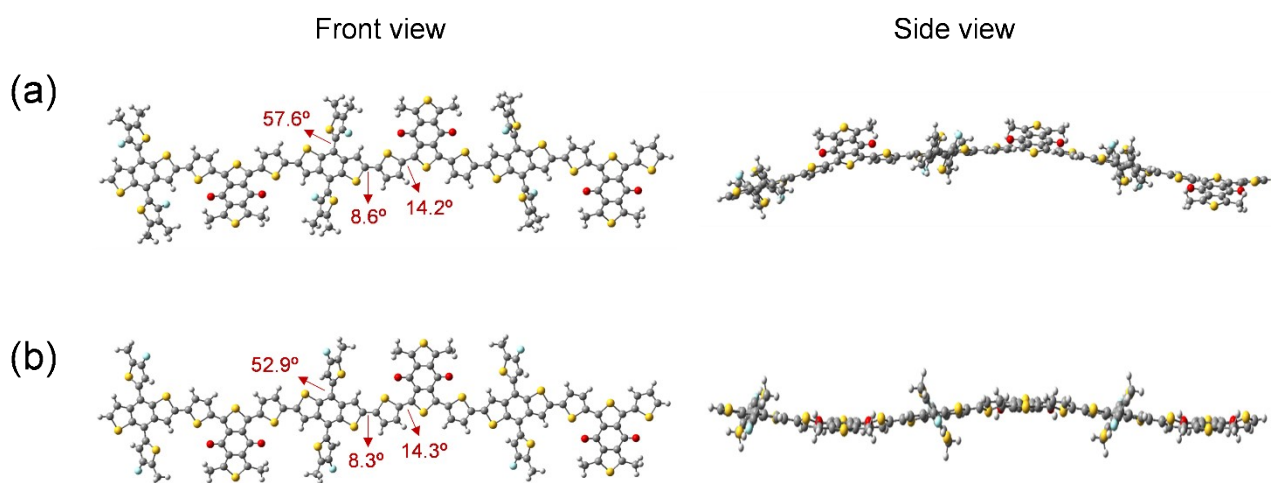
**Figure S19.**  $^1\text{H-NMR}$  spectrum of PBDB-T-2F(3/4) in  $\text{CDCl}_3$ .



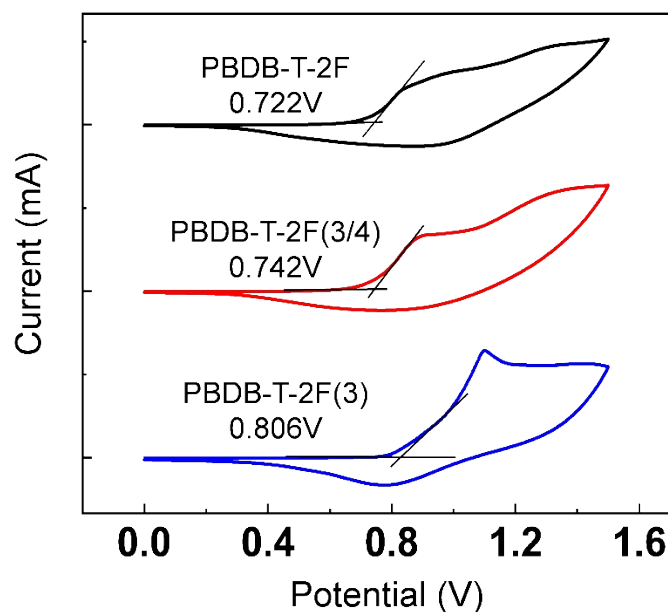
**Figure S20.** TGA (a) and DSC heating and cooling (b) thermograms of PBDB-T-2F, PBDB-T-2F(3/4), PBDB-T-2F(3).



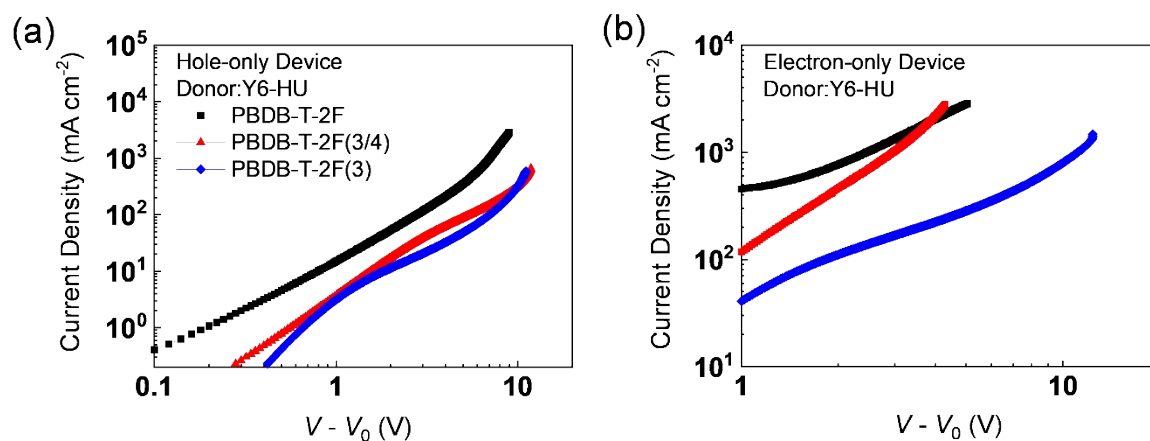
**Figure S21.** Temperature-dependent UV-vis absorption spectra of PBDB-T-2F, PBDB-T-2F(3/4) and PBDB-T-2F(3) in chlorobenzene.



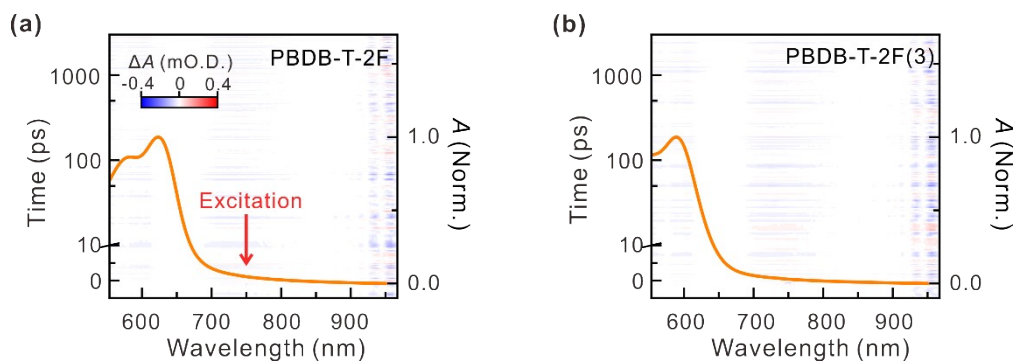
**Figure S22.** Energy-minimized geometries of (a) PBDB-T-2F(3) and (b) PBDB-T-2F based on three repeating units.



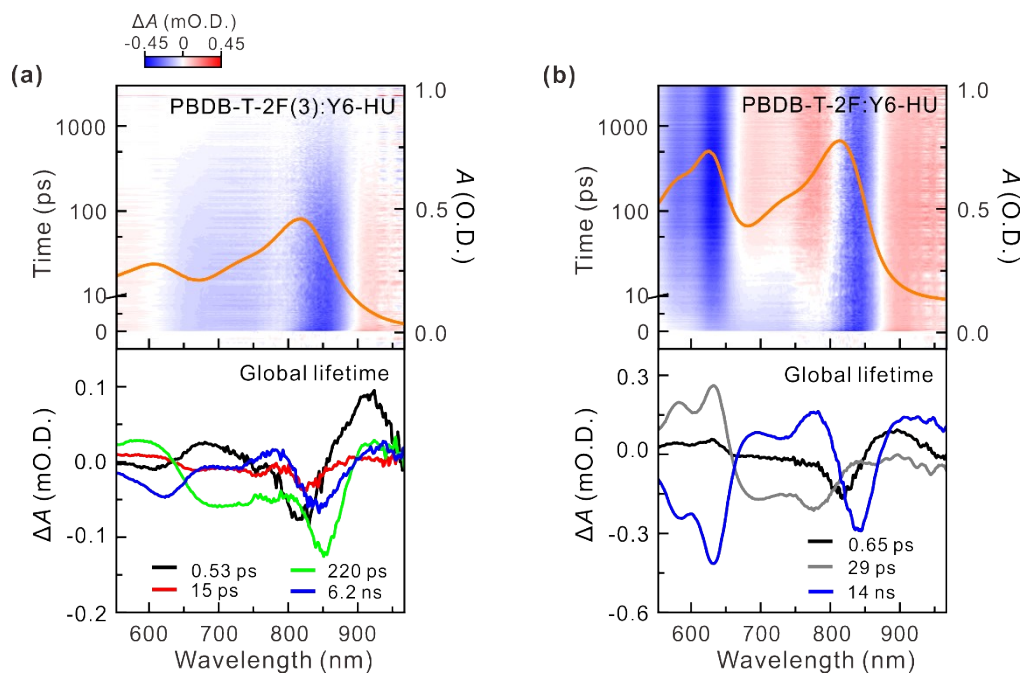
**Figure S23.** Cyclic voltammograms of PBDB-T-2F, PBDB-T-2F(3/4) and PBDB-T-2F(3) in 0.1 M tetrabutylammonium tetrafluoroborate ( $\text{Bu}_4\text{NBF}_4$ ) acetonitrile solution.



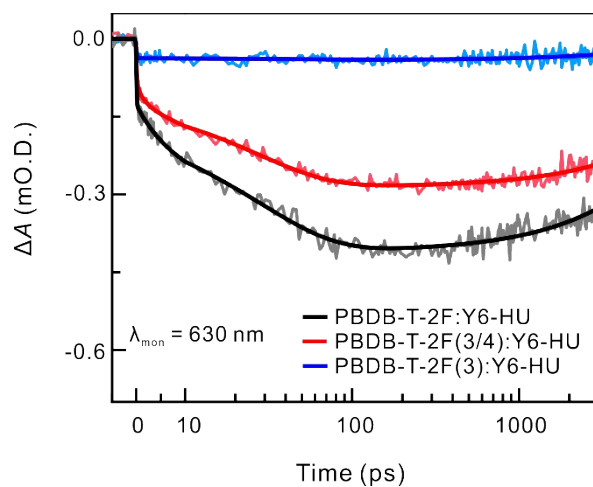
**Figure S24.** Dark current density versus voltage characteristics of (a) hole-only and (b) electron-only devices.



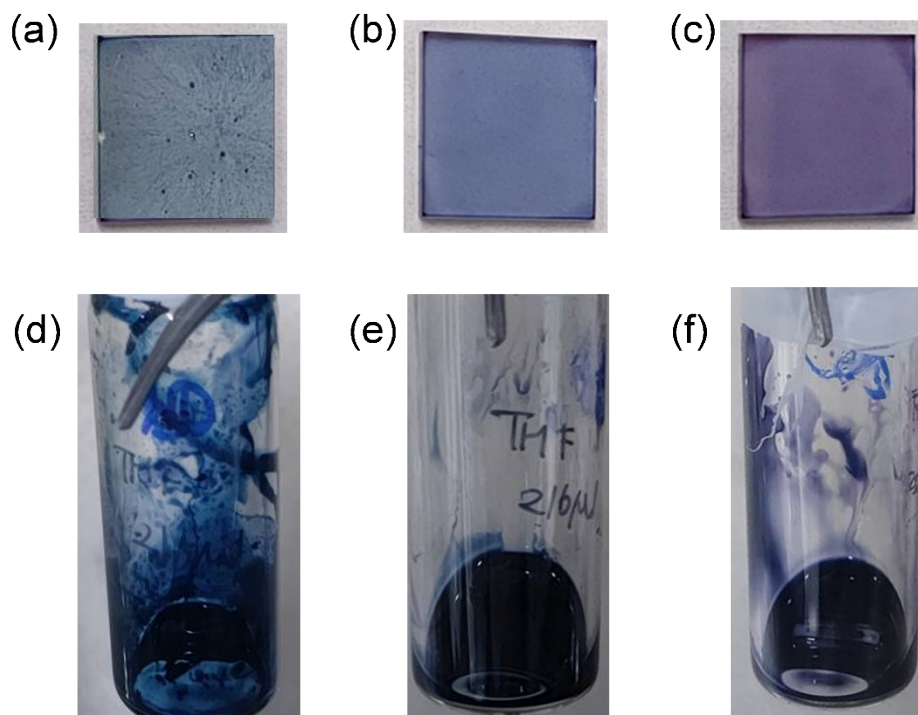
**Figure S25.** TA maps of pristine (a) PBDB-T-2F and (b) PBDB-T-2F(3) films with excitation at 750 nm. The steady-state absorption spectrum of each sample is presented (orange solid line).



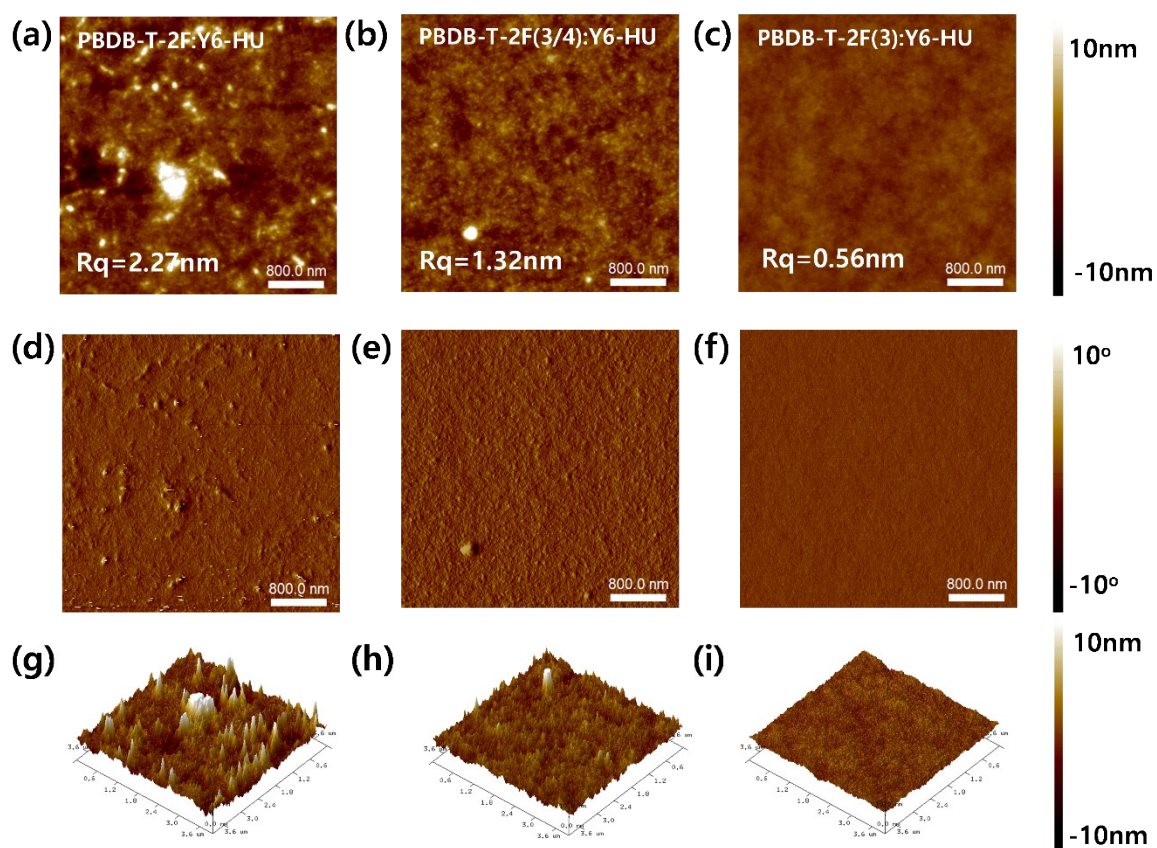
**Figure S26.** Two-dimensional TA maps and results of global lifetime analysis of TA spectra of (a) PBDB-T-2F(3):Y6-HU and (b) PBDB-T-2F:Y6-HU films with excitation at 750 nm. The steady-state absorption spectrum of each sample is presented (orange solid line) on each upper panel.



**Figure S27.** Kinetic profiles of PBDB-T-2F:Y6-HU (black), PBDB-T-2F(3/4):Y6-HU (blue), and PBDB-T-2F(3):Y6-HU (green) probed at 630 nm.

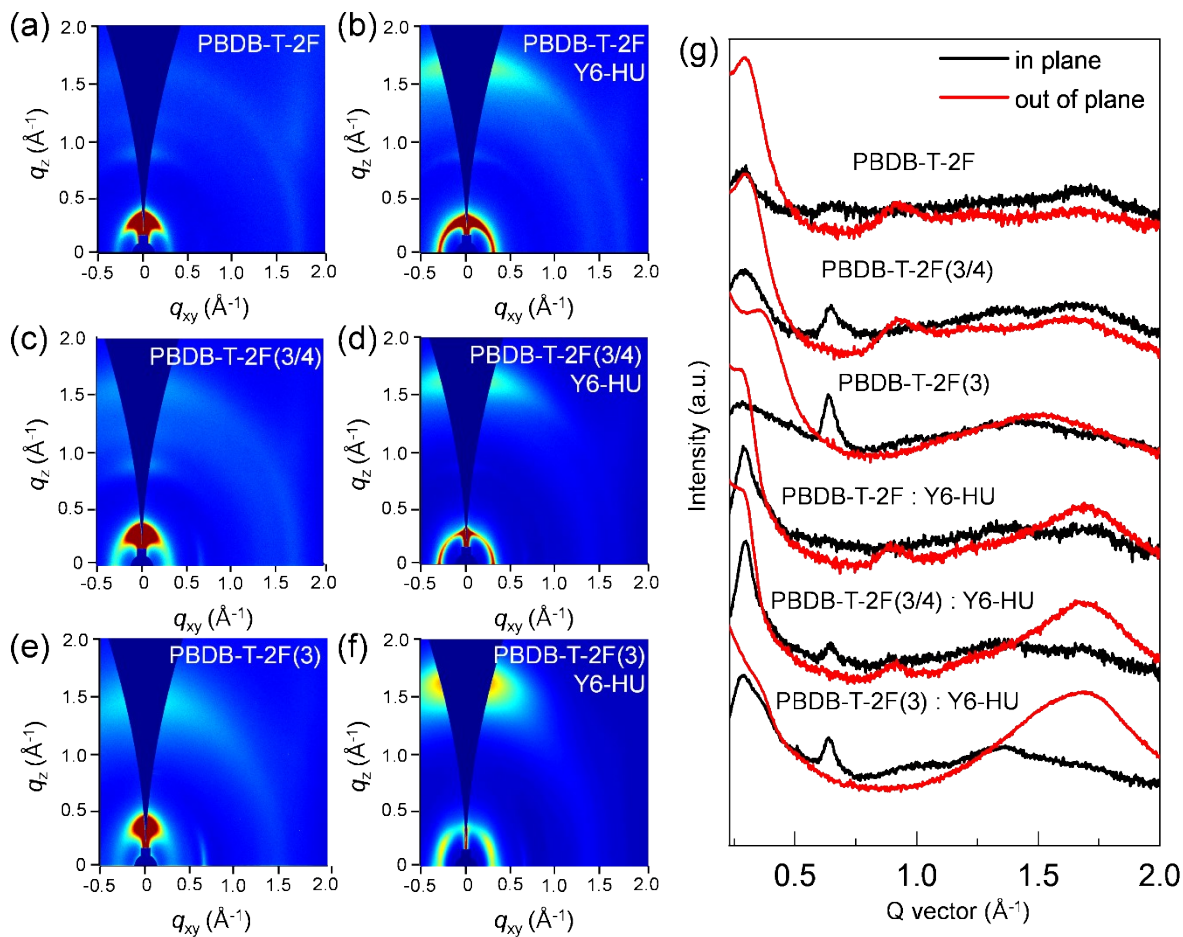


**Figure S28.** Film and solution pictures of (a,d) PBDB-T-2F:Y6-HU, (b,e) PBDB-T-2F(3/4):Y6-HU, and (c,f) PBDB-T-2F(3):Y6-HU.

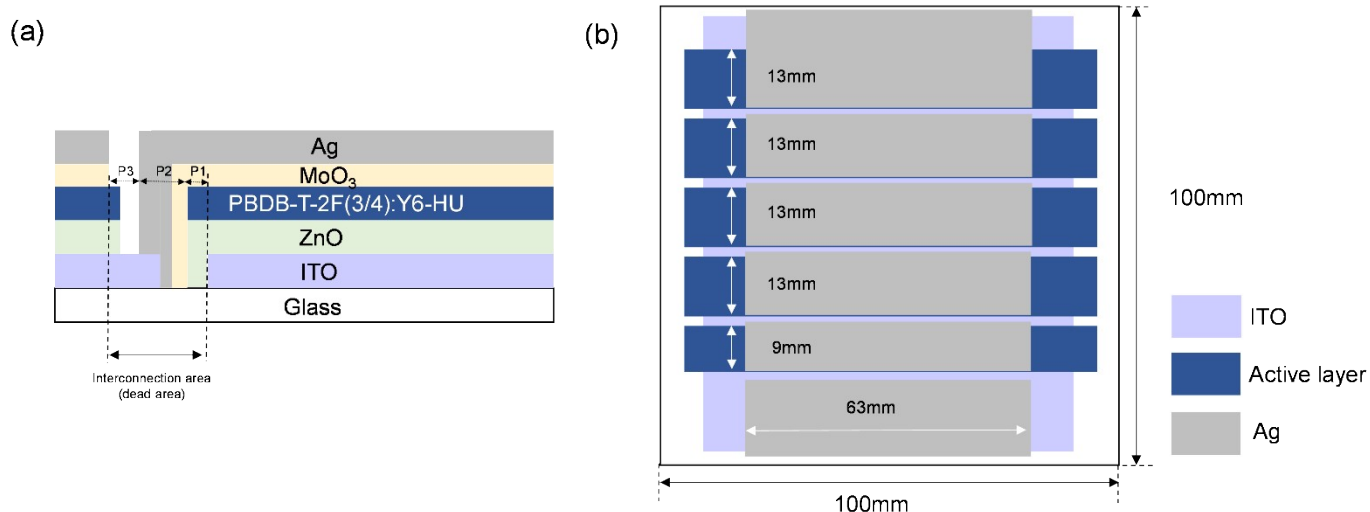


**Figure S29.** AFM height, phase and 3D images of (a,d,g) PBDB-T-2F:Y6-HU, (b,e,h) PBDB-T-2F(3/4):Y6-HU, and (c,f,i) PBDB-T-2F(3):Y6-HU films.

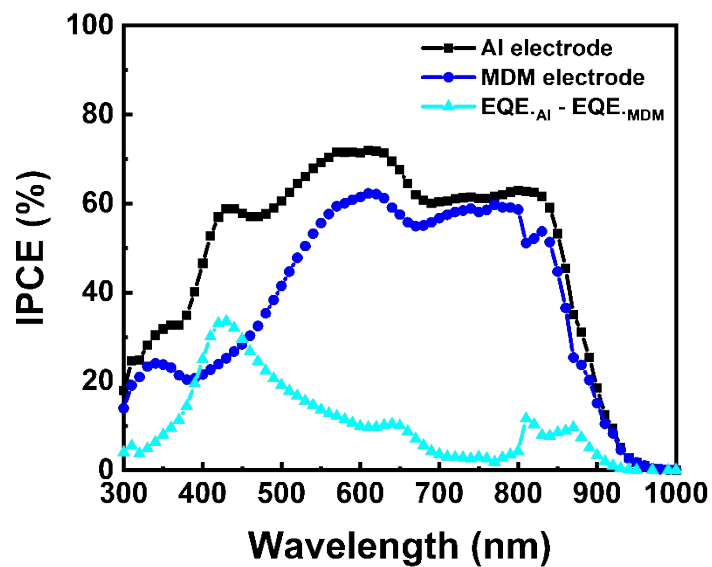




**Figure S30.** 2D GIWAXS images of pristine and blend films processed with THF: (a,b) PBDB-T-2F, (c,d) PBDB-T-2F(3/4), and (e,f) PBDB-T-2F(3). (g) IP and OOP line-cuts for pristine donor films and blend films.



**Figure S31.** (a) Device structure of large area module. (b) The module consists of five series-connected sub-cells. The total device area is 100 cm<sup>2</sup> and the active area is 38.43 cm<sup>2</sup>. For measurement of photovoltaic characteristics, a shadow mask (31.50 cm<sup>2</sup>) was used.



**Figure S32.** EQE spectra of PBDB-T-2F(3/4):Y6-HU based OSCs with Al electrode and MDM electrode. Graph with cyan colored line shows the EQE difference of devices with Al electrode and MDM electrode.

## Supplementary Tables

**Table S1.** Toxicity of commonly used organic solvents.

Solvent	Median lethal dose (LD50) <sup>a</sup>	Price (KRW L <sup>-1</sup> )
Ethanol	10470 mg Kg <sup>-1</sup>	240,200
Methanol	5628 mg Kg <sup>-1</sup>	123,400
Acetone	5800 mg Kg <sup>-1</sup>	95,100
Toluene	5580 mg Kg <sup>-1</sup>	118,500
2-Methyltetrahydrofuran	300-2000 mg Kg <sup>-1</sup>	349,300
Tetrahydrofuran	1650 mg Kg <sup>-1</sup>	234,000
1-Methyl-2-pyrrolidone	4150 mg Kg <sup>-1</sup>	319,400
Anisole	3700 mg Kg <sup>-1</sup>	225,400
o-Xylene	3523 mg Kg <sup>-1</sup>	196,500
1-Chloronaphthalene	1540 mg Kg <sup>-1</sup>	290,800
Chlorobenzene	1110 mg Kg <sup>-1</sup>	241,300
Chloroform	908 mg Kg <sup>-1</sup>	136,900
1,2-Dichlorobenzene	500 mg Kg <sup>-1</sup>	227,600

<sup>a</sup> Median lethal dose (LD50): the amount of the substance required (per body weight) to kill 50% of the test population. The LD50 values for rats by oral ingestion were obtained from the MSDS provided by Sigma Aldrich Co.

**Table S2.** SCLC mobility measurements in pristine donor and blend films determined by single-carrier devices.

Donor	Pristine donor $\mu_h$ [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	Blend $\mu_h$ [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	Blend $\mu_e$ [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]	$\mu_h/\mu_e$ [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]
PBDB-T-2F	8.30E-04	3.32E-04	1.55E-03	0.21
PBDB-T-2F(3/4)	5.11E-04	6.59E-05	1.81E-03	0.036
PBDB-T-2F(3)	3.87E-05	7.25E-06	2.94E-04	0.025

**Table S3.** Charge generation, extraction, and recombination characteristics of OSC devices fabricated using CF.

Blend	$P_{\text{diss}}$	$P_{\text{coll}}$	$\alpha$	$S$
PBDB-T-2F:Y6-HU	99.2%	87.6%	0.99	1.03 kTq <sup>-1</sup>
PBDB-T-2F(3/4):Y6-HU	95.3%	75.8%	0.99	1.37 kTq <sup>-1</sup>
PBDB-T-2F(3):Y6-HU	90.3%	65.2%	0.99	1.13 kTq <sup>-1</sup>

**Table S4.** Summary of GIWAXS packing parameters for pristine and blend films processed by CF.

Samples (CF)	In-Plane (100)				Out-of-Plane (010)				
	$q$ [Å <sup>-1</sup> ]	$d$ -spacing [Å]	FWHM	CCL [Å]	$q$ [Å <sup>-1</sup> ]	$d$ -spacing [Å]	FWHM	CCL [Å]	
Pristine	PBDB-T-2F	0.29	21.66	0.09602	58.89	1.65	3.81	0.27583	20.50
	PBDB-T-2F(3/4)	0.29	21.66	0.10824	52.24	1.64	3.83	0.30439	18.57
	PBDB-T-2F(3)	0.30	20.94	0.18012	31.39	1.52	4.13	0.34429	16.42
Blend with Y6-HU	PBDB-T-2F	0.29	21.66	0.04974	113.69	1.67	3.76	0.21700	26.05
	PBDB-T-2F(3/4)	0.30	20.94	0.05608	100.83	1.67	3.76	0.25443	22.23
	PBDB-T-2F(3)	0.30	20.94	0.10481	53.95	1.66	3.78	0.33423	16.92

**Table S5.** Fit parameters for bleach recovery kinetic profiles at the GSB peak of PBDB-T-2F.<sup>a</sup>

Samples	$\Delta A_1$ (mO.D.)	$\tau_1$ (ps)	$\Delta A_2$ (mO.D.)	$\tau_2$ (ps)	$\Delta A_3$ (mO.D.)	$\tau_3$ (ps)
PBDB-T-2F:Y6-HU	0.050 ± 0.015 <sup>b</sup>	4.2 ± 1.9	0.23 ± 0.02	30 ± 2	-0.41 ± 0.00	13000 ± 1000
PBDB-T-2F(3/4):Y6-HU	0.034 ± 0.006	1.1 ± 0.4	0.17 ± 0.00	27 ± 1	-0.29 ± 0.00	18000 ± 1000
PBDB-T-2F(3):Y6-HU	0.0036 ± 0.0016	50 ± 69	-0.041 ± 0.001	10000 ± 3000		

<sup>a</sup> All transients were fitted to  $I(t) = \sum_i A_i \exp(-t/\tau_i)$  convoluted with the Gaussian instrument response function (IRF) of 150 fs. <sup>b</sup> Fitting error.

**Table****S6.**

Functional Group	Occurrences	$\Sigma V$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\Sigma F_{di}$ (J <sup>1/2</sup> cm <sup>3/2</sup> mol <sup>-1</sup> )	$\Sigma F_{pi}$ (J <sup>1/2</sup> cm <sup>3/2</sup> mol <sup>-1</sup> )	$\Sigma U_{hi}$ (J <sup>1/2</sup> cm <sup>3/2</sup> mol <sup>-1</sup> )
CH <sub>3</sub>	8	268	3360	0	0
-CH <sub>2</sub> -	20	322	5400	0	0
>CH-	4	-4	320	0	0
=CH-	8	108	1600	0	0
=C<	26	-143	1820	0	0
>C=O	2	21.6	580	1185800	4000
-S-	8	64	3632	1048352	1768
-F	2	36	0	587528	0
Total		672.6	16712	2821680	5768

Functional group contribution terms used for calculating HSPs of PBDB-T-2F.



**Table S7.** Functional group contribution terms used for calculating HSPs of PBDB-T-2F(3).

Functional Group	Occurrences	$\Sigma V$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\Sigma F_{di}$ (J <sup>1/2</sup> cm <sup>3/2</sup> mol <sup>-1</sup> )	$\Sigma F_{pi}$ (J <sup>1/2</sup> cm <sup>3/2</sup> mol <sup>-1</sup> )	$\Sigma U_{hi}$ (J <sup>1/2</sup> cm <sup>3/2</sup> mol <sup>-1</sup> )
CH <sub>3</sub>	10	335	4200	0	0
-CH <sub>2</sub> -	30	483	8100	0	0
>CH-	4	-4	320	0	0
=CH-	6	81	1200	0	0
=C<	28	-154	1960	0	0
>C=O	2	21.6	580	1185800	4000
-S-	8	64	3632	1048352	1768
-F	2	36	0	587528	0
Total		862.6	19992	2821680	5768

**Table S8.** Calculated  $\delta_D$ ,  $\delta_P$ , and  $\delta_H$  parameters for PBDB-T-2F and PBDB-T-2F(3).

	$\delta_D$ (MPa <sup>1/2</sup> )	$\delta_P$ (MPa <sup>1/2</sup> )	$\delta_H$ (MPa <sup>1/2</sup> )
PBDB-T-2F	24.85	2.50	2.93
PBDB-T- 2F(3)	23.18	1.94	2.59

**Table S9.** Radius of interaction of PBDB-T-2F and PBDB-T-2F(3) with different solvents.

	PBDB-T-2F $R_a$	PBDB-T-2F(3) $R_a$
Chloroform (CF)	14.38	11.25
Dichlorobenzene (DCB)	16.93	14.20
Tetrahydrofuran (THF)	17.18	14.35
Anisole	14.77	11.84
Acetone	20.70	18.07
Methanol	29.72	27.99

$R_a$  refers to the distance between two compounds' coordinate position in Hansen solubility space, which is calculated using 3 HSP components of target compounds and solvents.

$$R_a = \sqrt{a(\delta_{D2} - \delta_{D1})^2 + b(\delta_{P2} - \delta_{P1})^2 + c(\delta_{H2} - \delta_{H1})^2}$$

$\delta_D$ ,  $\delta_P$ , and  $\delta_H$  refer to the dispersion interaction, permanent dipole-permanent dipole interaction, and hydrogen bonding interaction, respectively. All the parameter values are obtained from the literature.<sup>4,5</sup> Weighting factors: a = 4 and b = c = 1.

**Table S10.** Photovoltaic parameters of PBDB-T-2F(3/4):Y6-HU with different concentrations of donor (without additive).

Donor Concentration	$J_{sc}$ [mA cm <sup>-2</sup> ]	$V_{oc}$ [V]	FF	PCE [%]
6 mg/mL	22.55	0.86	0.66	12.70
8 mg/mL	21.73	0.88	0.61	11.73

**Table S11.** Photovoltaic parameters of PBDB-T-2F(3/4):Y6-HU with and without thermal treatment (without additive).

Thermal treatment	$J_{sc}$ [mA cm <sup>-2</sup> ]	$V_{oc}$ [V]	FF	PCE [%]
None	20.70	0.89	0.65	11.90
100 °C/10 min	22.55	0.86	0.66	12.70

**Table S12.** Photovoltaic parameters of PBDB-T-2F(3/4):Y6-HU with different additives.

Additive treatment	$J_{sc}$ [mA cm <sup>-2</sup> ]	$V_{oc}$ [V]	FF	PCE [%]
None	22.55	0.86	0.66	12.70
CN 0.5%	19.98	0.86	0.69	11.85
DTBF 30wt%	23.28	0.86	0.69	13.86
DTT 25wt%	22.37	0.86	0.69	13.20
DTT 25wt%+CN 0.5%	20.01	0.86	0.69	11.93

**Table S13.** Charge generation, extraction, and recombination characteristics of OSC devices fabricated using THF.

Blend	$P_{diss}$	$P_{coll}$	$\alpha$	$S$
PBDB-T-2F:Y6-HU	92.66%	83.65%	1.02	1.33 kTq <sup>-1</sup>
PBDB-T-2F(3/4):Y6-HU	96.63%	85.19%	1.03	1.36 kTq <sup>-1</sup>
PBDB-T-2F(3):Y6-HU	90.15%	66.40%	1.02	1.71 kTq <sup>-1</sup>

**Table S14.** GIWAXS packing parameters for pristine and blend films processed by THF.

Samples (THF)	In-Plane (100)				Out-of-Plane (010)				
	$q$ [Å <sup>-1</sup> ]	$d$ -spacing [Å]	FWHM	CCL [Å]	$q$ [Å <sup>-1</sup> ]	$d$ -spacing [Å]	FWHM	CCL [Å]	
Pristine	PBDB-T-2F	0.29	21.66	0.12809	44.14	—	—	—	—
	PBDB-T-2F(3/4)	0.29	21.66	0.14893	37.97	—	—	—	—
	PBDB-T-2F(3)	0.30	20.94	0.24501	23.08	1.50	4.18	0.30140	18.76
Blend with Y6-HU	PBDB-T-2F	0.30	20.94	0.05844	96.76	1.69	3.72	0.26130	21.64
	PBDB-T-2F(3/4)	0.27	23.27	0.05142	109.97	1.68	3.74	0.22404	25.24
	PBDB-T-2F(3)	0.30	20.94	0.11335	49.89	1.65	3.81	0.35879	15.76

**Table S15.** Photovoltaic parameters of PBDB-T-2F(3/4):Y6-HU blend with different substrates (processed

with THF).

Blend	Substrate	$J_{sc}$ [mA cm <sup>-2</sup> ]	$V_{oc}$ [V]	FF	PCE [%]
PBDB-T-2F(3/4):Y6-HU	PET/ITO	18.26	0.85	0.67	10.39
	Glass/ITO	23.28	0.86	0.69	13.86

**Table S16.** Photovoltaic parameters of PBDB-T-2F(3/4):Y6-HU module.

Blend	Substrate	$J_{sc}$ [mA cm <sup>-2</sup> ]	$V_{oc}$ [V]	FF	PCE [%]
PBDB-T-2F(3/4):Y6-HU	Module	2.83	4.21	0.53	6.26

**Table S17.** Photovoltaic parameters of PBDB-T-2F(3/4):Y6-HU with a blue MDM electrode.

Top electrode	$J_{sc}$ [mA cm <sup>-2</sup> ]	$J_{sc,cal}$ [mA cm <sup>-2</sup> ]	$V_{oc}$ [V]	FF	PCE [%]
Sb <sub>2</sub> O <sub>3</sub> /Ag/Sb <sub>2</sub> O <sub>3</sub> /Ag	17.79	16.47	0.85	0.68	10.31

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