Supporting information

Design and synthesis of the polymers based on alkylthiophenyl side chains and variant acceptor moieties for polymer solar cells

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1. Synthetic processes

*Synthesis of **1-bromo-4-(2-hexyldecyl)thiobenzene (1)***

To a solution of 4-bromobenzenethiol (10 g, 52.89 mmol) and anhydrous potassium carbonate (9.5 g, 68.76 mmol) in dry DMF (150 mL) at room temperature, 1-bromo-2-hexyl-decane (16.1 g, 52.89 mmol) was added dropwise under N_2 atmosphere. After one hour, the mixture was warmed to 80 ^{o} C and stirred for another 24 hours. The reaction mixture was cooled to room temperature, and then extracted by petroleum ether. The organic phase was collected and dried with anhydrous $MgSO_4$, and then the solvent was removed by rotary evaporation. The crude product was purified on silica gel chromatography using petroleum ether as eluent to afford a colorless liquid (20.1 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.38 (d, 2H, J = 8.41 Hz), 7.19 (d, 2H, J = 8.41 Hz), 2.87 (d, 2H, J = 6.19 Hz), 1.62-1.57 (m, 5H), 1.43-1.25 (m, 20H), 0.90-0.86 (m, 6H).

*Synthesis of **SB***

To a solution of 1-bromo-4-(2-hexyldecyl)thiobenzene (15.00 g, 36.28 mmol) in dry THF at -78 ^{o} C, *n*-butyllithium (14.5 mL, 2.5 M in hexane) was added dropwise under N_2 atmosphere. After two hours, benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-dione (3.63 g, 16.49 mmol) was added in one portion and the mixture was stirred overnight. Solution of $SnCl_2$•$2H_2O$ (14.84 g, 65.96 mmol) in 2M HCl was added to the mixture. Two hours later, CH_2Cl_2 and water were added, the organic phase was collected and dried with anhydrous $MgSO_4$. After removing the solvent under reduced pressure, the crude product was obtained, then it was purified on silica gel chromatography using petroleum ether as eluent to obtain purified ***SB*** as a light yellow sticky liquid. (5.78 g, 41%). ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.62 (d, 4H, J = 7.63 Hz), 7.49 (d, 4H, J = 7.64 Hz), 7.40 (d, 2H, J = 5.32 Hz), 7.33 (d, 2H, J = 5.56 Hz), 3.03 (d, 4H, J = 5.59Hz), 1.74 (m, 2H), 1.47−1.30(m, 48H), 0.90 (m,12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 138.40, 138.25, 136.28, 136.21, 129.94, 129.84, 128.45, 127.32, 122.91, 38.12, 37.74, 33.46, 32.12, 30.16, 29.82, 29.57, 26.77, 22.90, 14.32. MALDI-TOF MS ($C_{54}H_{78}S_4$) m/z: calcd for 854.5; found 854.2.

*Synthesis of **M1***

To a solution of **SB** (2.50 g, 2.92 mmol) in dry THF (25 mL), *n*-butyllithium (2.6 mL, 2.5 M in hexane) was added under N_2 atmosphere at-78 ^{o} C. 3 Hours later, trimethyltin chloride (6.7 mL, 1 M in hexane) was added and the mixture was stirred overnight. The solution was poured into 150 mL ice water and extracted by light petroleum for 3 times. The combined organic solution was dried by anhydrous $MgSO_4$. After removing the solvent under reduced pressure, the residue was recrystallized from ethanol to get the monomer (M1) (3.03 g, 88%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.64 (d, 4H, J = 7.01 Hz), 7.49 (d, 4H, J = 7.12 Hz), 7.36 (s, 2H), 3.05 (d, 4H, J = 4.79Hz), 1.76 (m, 2H), 1.48−1.30 (m, 48H), 0.89-0.88 (m, 12H), 0.43-0.29 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 142.53, 142.17, 137.98, 137.07, 136.90, 130.69, 129.97, 128.41, 128.23, 38.00, 37.66, 33.43, 32.05, 31.99, 30.08, 29.74, 29.48, 26.67, 22.83, 14.29, -8.24. Anal. Calcd for $C_{60}H_{94}S_4Sn_2$: C, 61.02; H, 8.02; S, 10.86. Found : C, 60.25; H 8.45; S, 10.66.

*Synthesis of the polymer **PSB-DFBT***

M1 (236 mg, 0.20 mmol) and **M2** (66 mg, 0.20 mmol) were dissolved in 5 mL of dry toluene, and the solution was flushed with argon for 15 min; then 15 mg of $Pd(PPh_3)_4$ was added into the solution. The mixture was flushed with argon for 30 min again. The polymerization was carried out at 110 °C for 36 h. Finally, the reaction mixture was cooled to room temperature and slowly added to methanol (250 mL). The precipitate was purified by Soxhlet extraction with methanol, hexane, and chloroform in sequence. The chloroform fraction was evaporated by rotary evaporation. After drying under vacuum for 24 h, the polymer **PSB-DFBT** was obtained as a purple-black solid. Yield: 160 mg, 78.2%. Anal. Calcd for $C_{60}H_{76}F_2N_2S_5$: C, 70.40; H, 7.48; N, 2.74; S, 15.66. Found: C, 70.46; H, 7.59; N, 2.70; S, 14.43.

*Synthesis of the polymer **PSB-DTDFBT** and **PSB-FTT***

By following the similar method used for **PSB-DTDFBT**, the polymer **PSB-DTDFBT** was synthesized with the monomers **M1** (236 mg, 0.20 mmol) and **M3** (120 mg, 0.20 mmol). The final product was obtained as a dark-red solid. Yield: 208mg, 76.8%. Anal. Calcd for $C_{80}H_{104}F_2N_2S_7$: C, 70.85; H, 7.73; N, 2.07; S, 16.55. Found: C, 70.73; H, 7.97; N, 2.18; S, 15.66.

The polymer **PSB-FTT** was synthesized with the monomers **M1** (236 mg, 0.20mmol) and **M4** (94 mg, 0.20 mmol). The final product was obtained as a dark blue solid. Yield: 191 mg, 81.6%. Anal. Calcd for $C_{69}H_{93}FO_2S_6$: C, 71.08;

H, 8.04; S, 16.50. Found: C, 71.43; H, 7.98; S, 14.96.

2. NMR

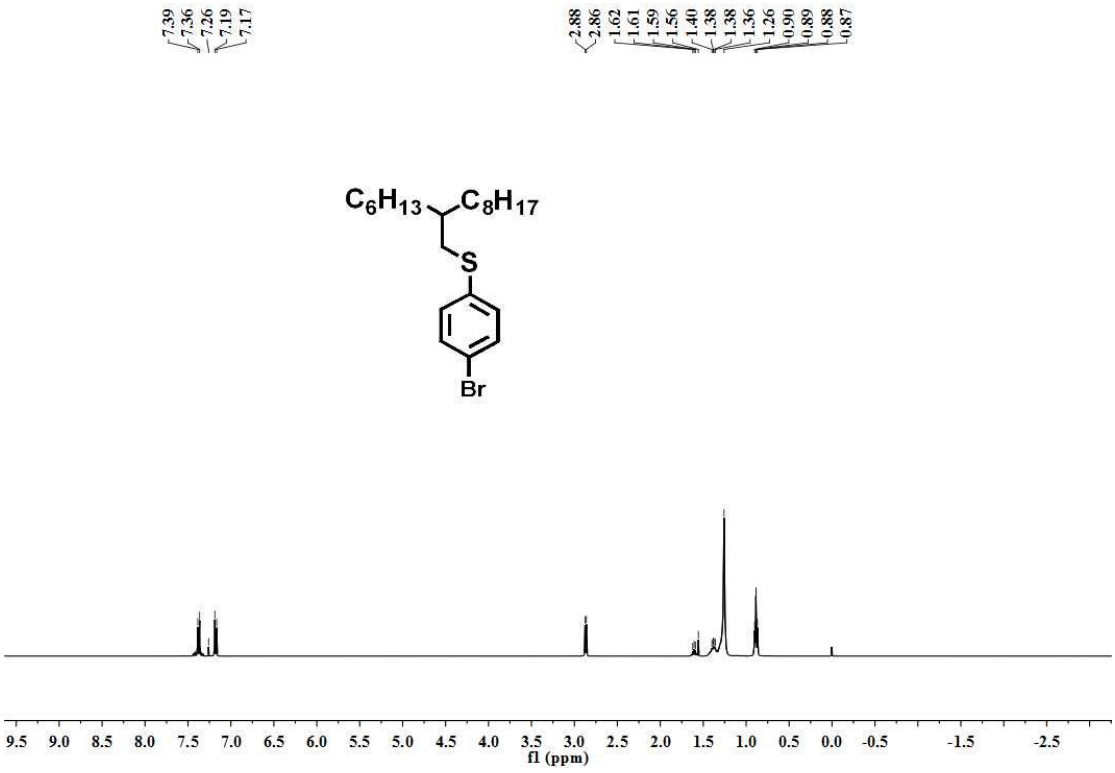

Fig. S1 ^{1}H spectrum of compound 1

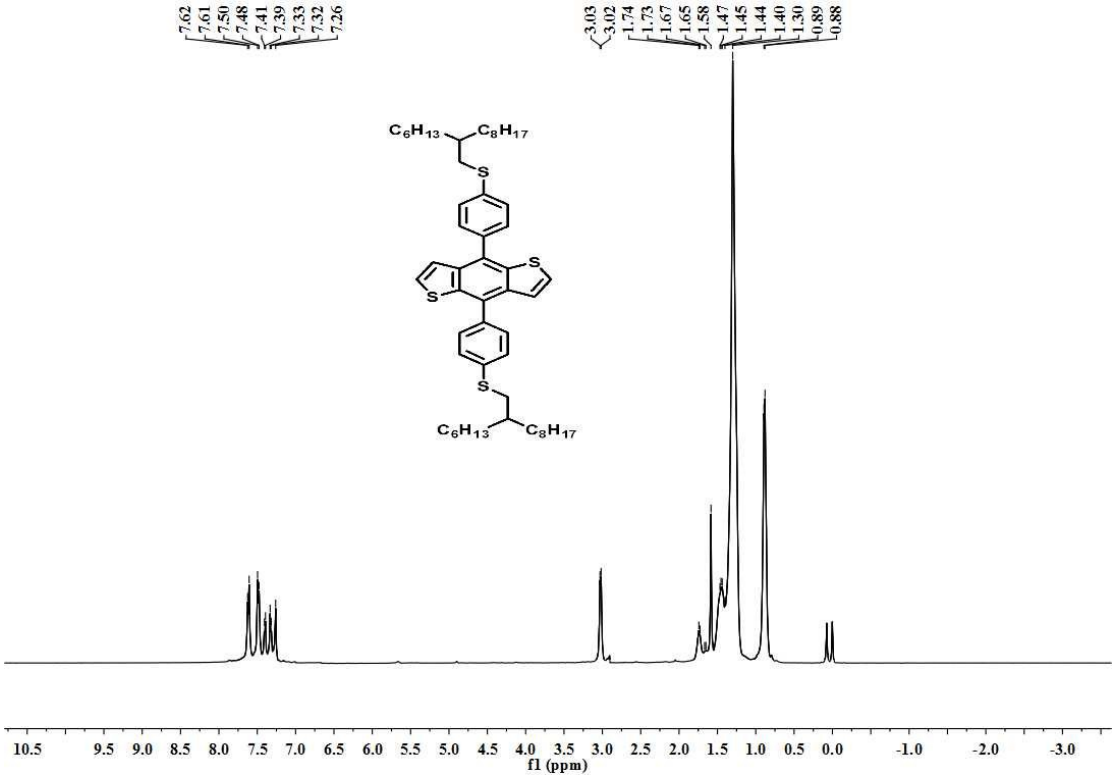

Fig. S2 ^{1}H-NMR spectrum of compound SB

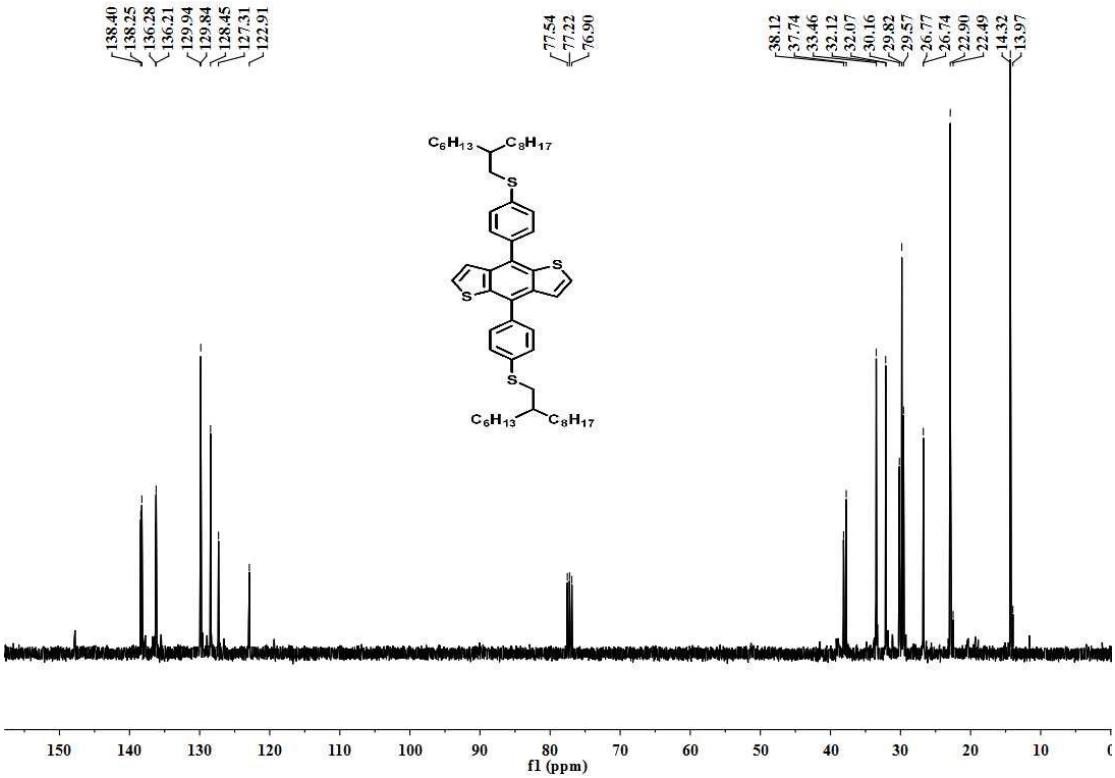

Fig. S3 ^{13}C-NMR spectrum of compound SB

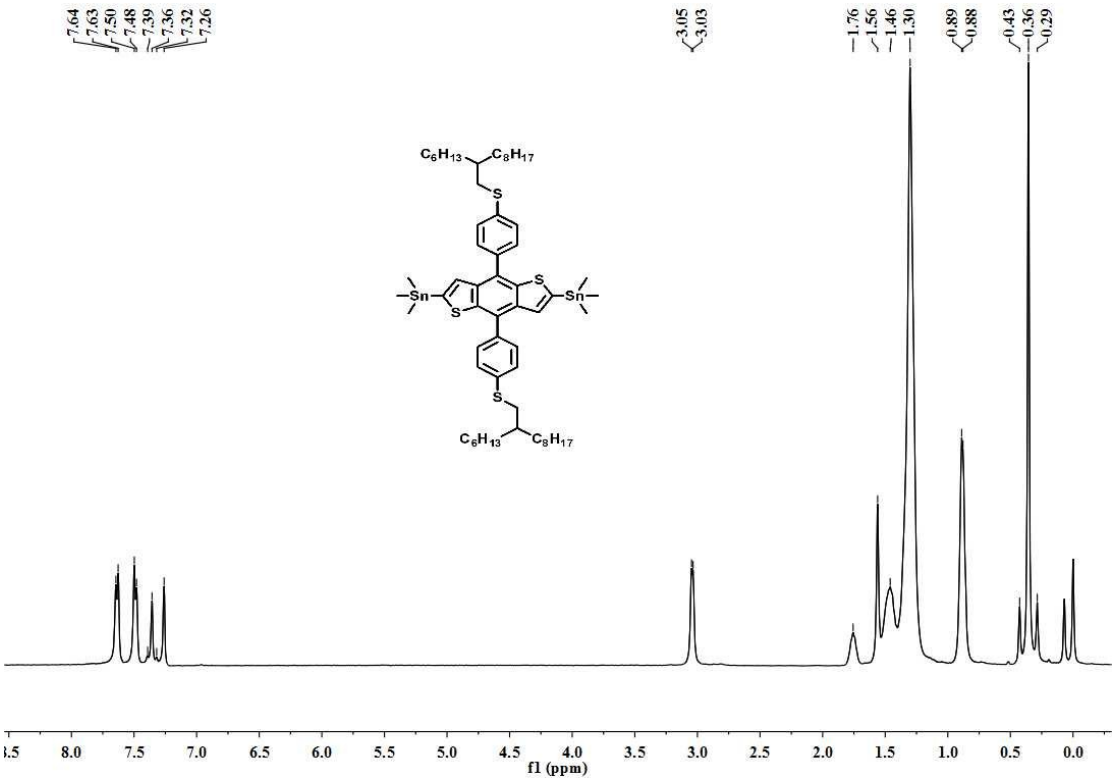

Fig. S4 ^{1}H-NMR spectrum of compound M1

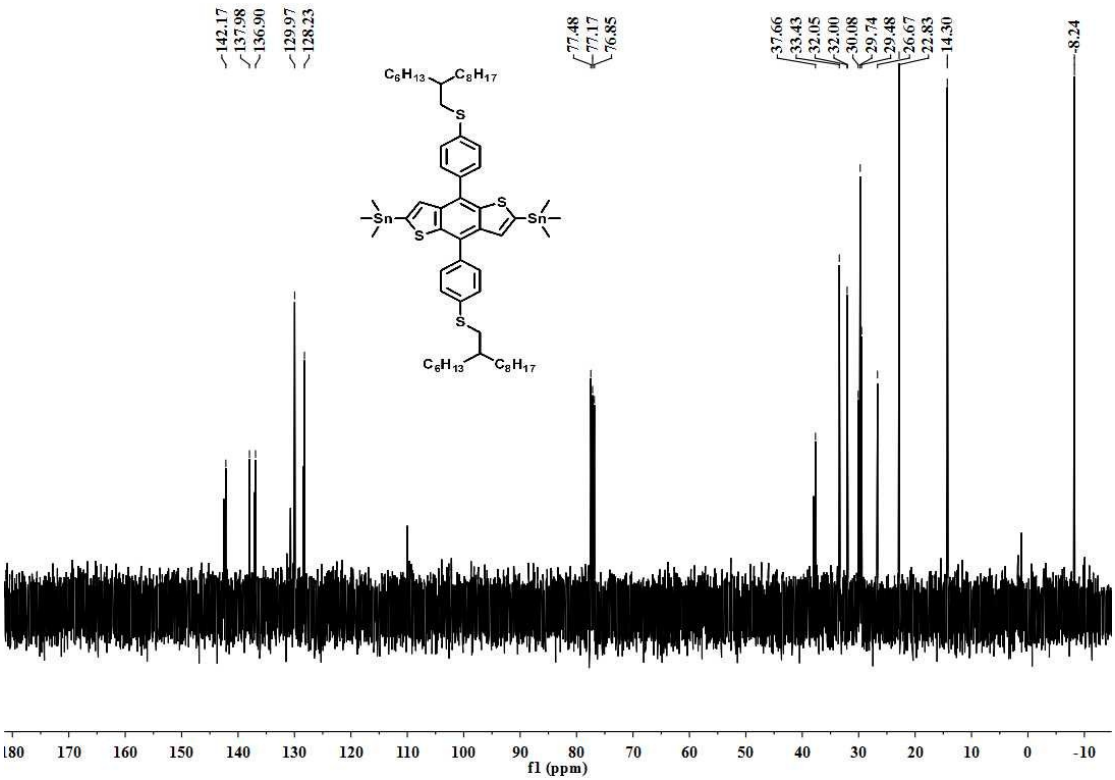

Fig. S5 ^{13}C-NMR spectrum of compound M1

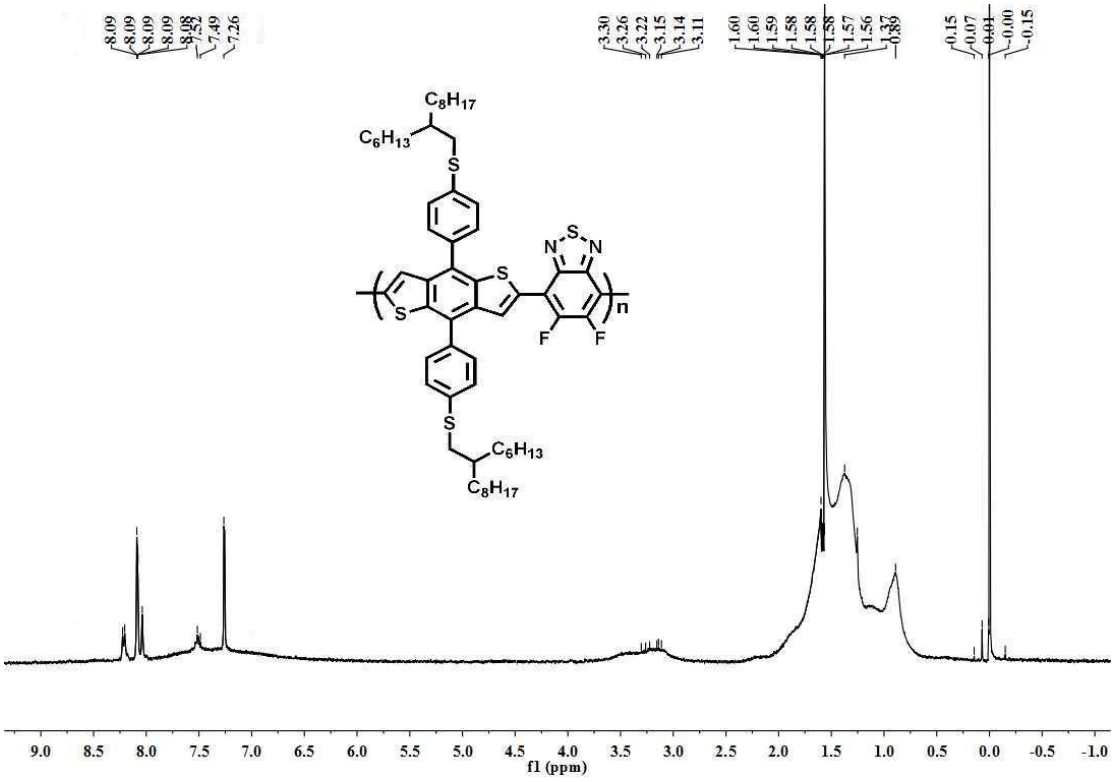

Fig. S6 ^{1}H-NMR spectrum of PSB-DFBT

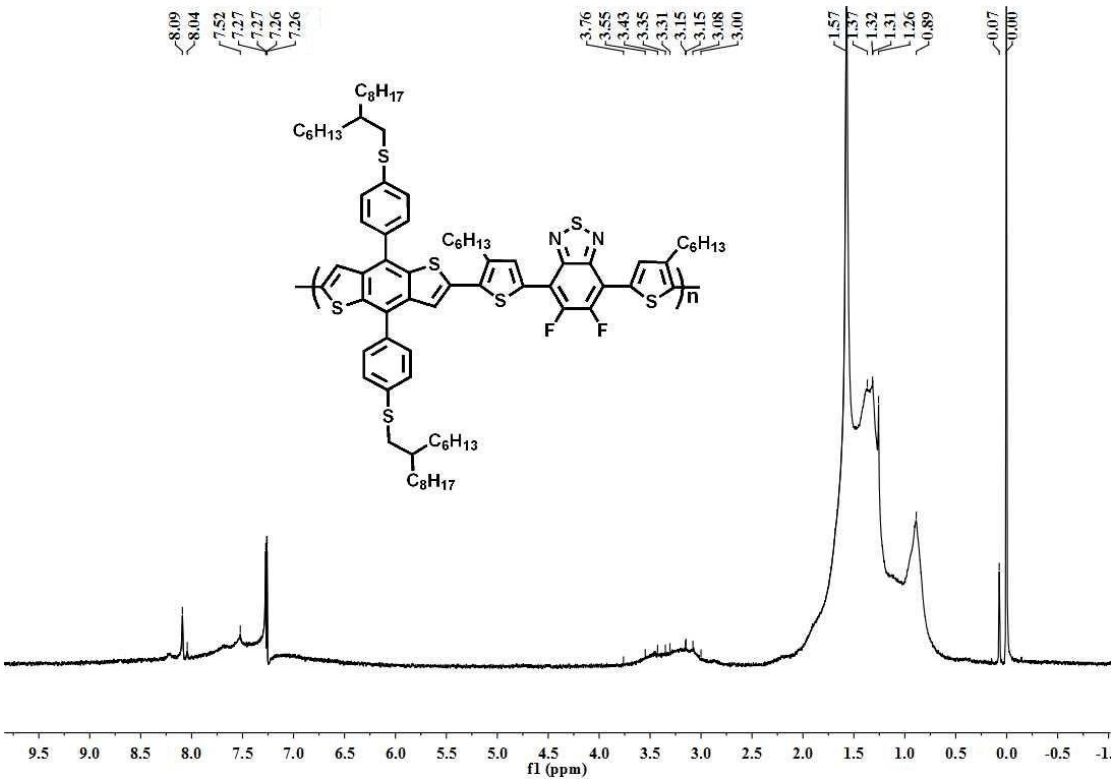

Fig. S7 ^{1}H-NMR spectrum of PSB-DTDFBT

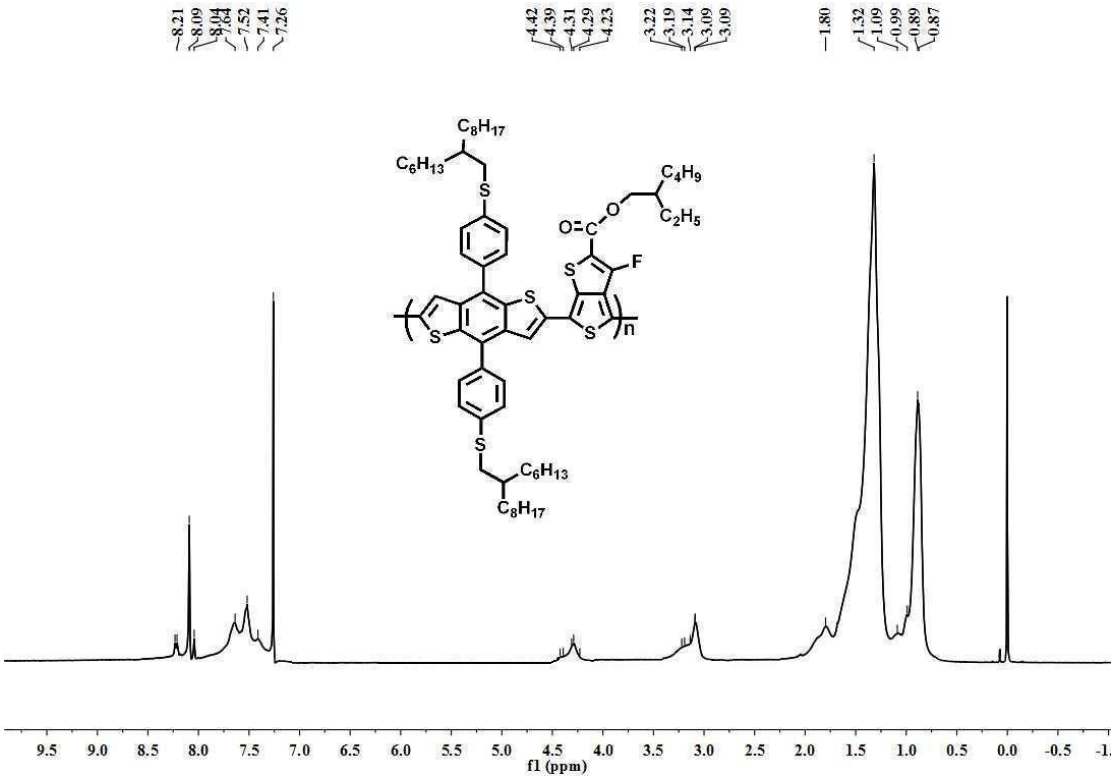

Fig. S8 ^{1}H-NMR spectrum of PSB-FTT

3. GPC Traces

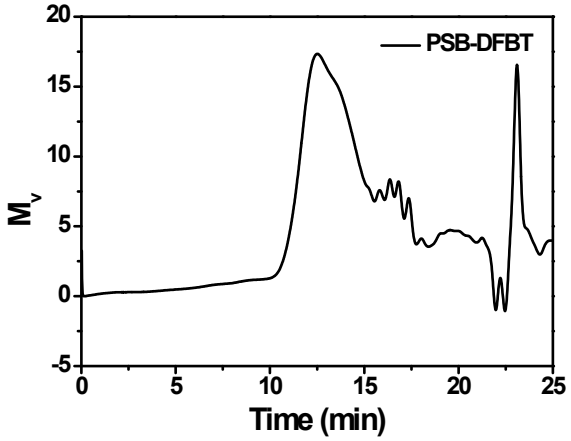

Fig. S9 GPC Traces of polymer PSB-DFBT

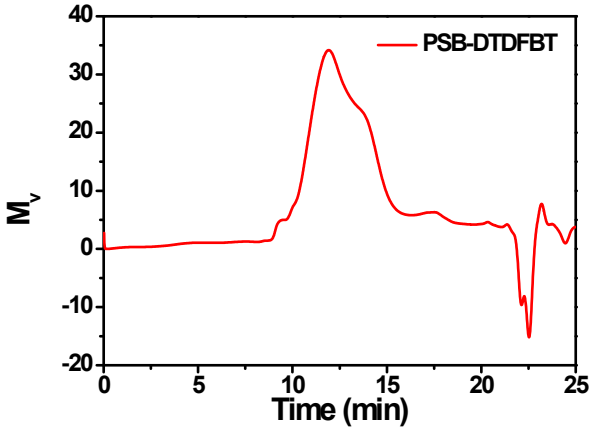

Fig. S10 GPC Traces of polymer PSB-DTDFBT

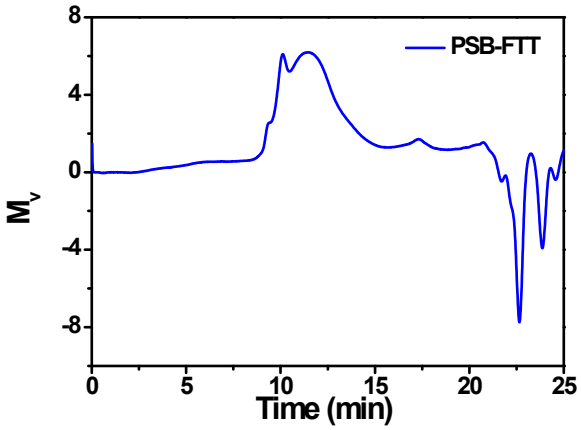

Fig. S11 GPC Traces of polymer PSB-FTT

3. TGA curves

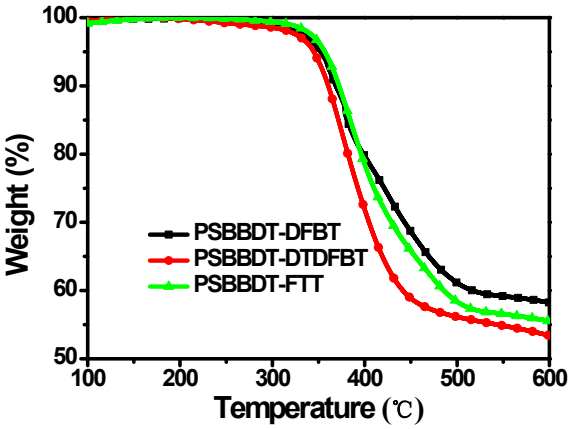

Fig. S12 TGA curves of the polymers with a scan rate of 20 °C min^{-1} under nitrogen atmosphere.

4. Device optimization

Table S1 Photovoltaic properties of the polymers and PCBM (1:1.5, w/w)

polymers	Blend	solvent	J_{sc} (mA·cm^{-2})	V_{oc} (V)	*FF*	PCE (%)
PSBDT-DFBT	Polymer/$PC_{61}BM$	CB	4.52	0.75	0.34	1.15
PSBDT-DFBT	Polymer/$PC_{61}BM$	97%CB+3%DIO	5.32	0.72	0.36	1.38
PSBDT-DFBT	Polymer/$PC_{71}BM$	97%CB+3%DIO	6.39	0.76	0.39	1.88
PSBDT-DFBT	Polymer/$PC_{61}BM$	ODCB	4.45	0.77	0.30	1.03
PSBDT-DFBT	Polymer/$PC_{61}BM$	97%ODCB+3%DIO	5.60	0.73	0.36	1.47
PSBDT-DTDFBT	Polymer/$PC_{61}BM$	CB	1.42	0.56	0.21	0.17
PSBDT-DTDFBT	Polymer/$PC_{61}BM$	97%CB+3%DIO	1.52	0.54	0.21	0.18
PSBDT-DTDFBT	Polymer/$PC_{71}BM$	97%CB+3%DIO	2.97	0.58	0.28	0.48
PSBDT-DTDFBT	Polymer/$PC_{61}BM$	ODCB	1.83	0.56	0.19	0.19
PSBDT-DTDFBT	Polymer/$PC_{61}BM$	97%ODCB+3%DIO	1.75	0.58	0.21	0.21
PSBDT-FTT	Polymer/$PC_{61}BM$	CB	5.92	0.92	0.36	1.97
PSBDT-FTT	Polymer/$PC_{61}BM$	97%CB+3%DIO	8.95	0.82	0.44	3.21
PSBDT-FTT	Polymer/$PC_{71}BM$	97%CB+3%DIO	9.50	0.82	0.57	4.45
PSBDT-FTT	Polymer/$PC_{61}BM$	ODCB	5.11	0.90	0.38	1.74
PSBDT-FTT	Polymer/$PC_{61}BM$	97%ODCB+3%DIO	7.66	0.82	0.37	2.30