Synergy effect of side-chain and backbone engineering for Thieno[2,3-f]benzofuran-based conjugated polymers for high performance non-fullerene organic solar cells

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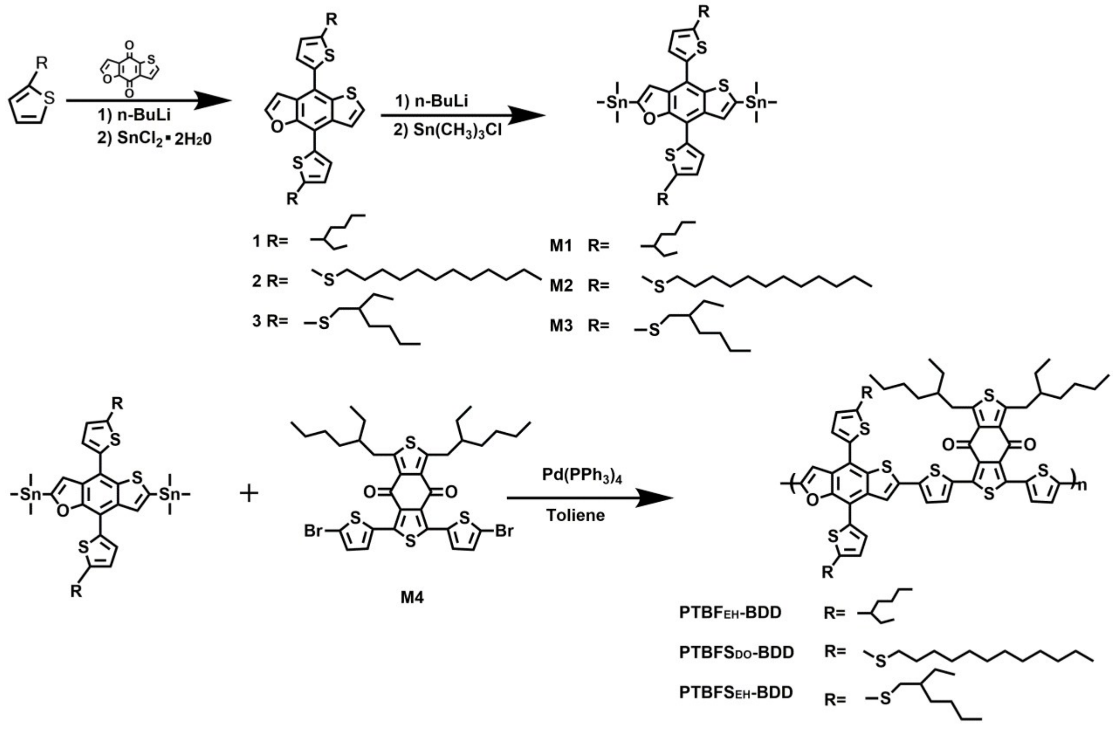
Experimental

All solvent and staring chemical were purchased from commercial source and used without further purification expert for THF and toluene, which were distilled using sodium and benzophenone under the protection of nitrogen atmosphere before used. Thieno[2,3-f]benzofuran-4,8-dione, and M1 were synthesized on the basis of the procedures described in the literature.[1] The synthetic routes for the new monomers and polymers are shown in Scheme S1 and the synthesis details are described below.



Scheme S1 The synthetic routes of the monomers and polymers.

Synthesis of Compound 2: To a solution of 2-(2-ethylhexyl)thiophene (7.65 g, 26.9 mmol) in THF (60 mL) was added n-BuLi in hexane (9.75 mL, 23.4 mmol, 1.6 M) slowly at 0 °C under argon protection, and the mixture was stirred at 0 °C for 3 h. Then thieno[2,3-f]benzofuran-4,8-dione (1.83 g 9.0 mmol) was added in one portion and stirred for 3 h at -78 °C, then followed by slowly warming up to room temperature for 12 h. Subsequently, the mixture was cooled down to room temperature and Tin (II) chloride dihydrate (12.2 g, 54.0 mmol) in 10% HCl (10 mL) was added and then the resulting solution was stirred for an additional 3 h at 50 °C. The reaction was poured into water and then extracted three times with dichloromethane. The organic layer was washed with water, and then dried over anhydrous sodium sulfate. After removal of the solvent, the crude product was purified by column chromatography over silica gel (eluent: petroleum ether) to give compound **2** as light yellow oil (4.65g, yield: 70 %).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, 1H), 7.76 (d, 1H), 7.51 (d, 1H), 7.47 (m, 2H), 7.23 (t, 2H), 7.16 (d, 1H), 2.91 (m, 4H), 1.71 (m , 4H), 1.24 (m, 36H), 0.87 (t, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.74, 146.57, 142.42, 138.56, 136.42, 135.78, 135.64, 133.18, 133.07, 128.95, 127.69, 127.31, 125.22, 123.57, 120.68, 112.75, 106.31, 38.94, 38.89, 31.91, 29.71, 29.66, 29.64, 29.61, 29.53, 29.50, 29.35, 29.18, 28.51, 28.49, 22.69, 14.12.

Compound 3 was prepared by a similar synthetic procedure described above for compound 2

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, 1H), 7.75 (d, 1H), 7.51 (d, 1H), 7.46 (dd, 2H), 7.21 (t, 2H), 7.15 (d, 1H), 2.94 (m, 4H), 1.64 (m,2H), 1.45 – 1.23 (m, 16H), 0.90 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.76, 146.58, 142.08, 138.19, 137.38, 135.80, 135.65, 132.63, 132.48, 128.91, 127.66, 127.31, 125.24, 123.57, 120.69, 112.76, 106.29,43.62 ,43.54,39.21,39.16,32.12,32.09,28.78, 28.76, 25.35, 25.33, 22.97, 22.96, 14.12, 10.78, 10.74.

Synthesis of M2： n-BuLi (5.81mL, 9.31 mmol) was added dropwise to a solution of compound 2(1.96g.2.66mmol) in dry THF (60 mL) at -78 ℃ under nitrogen. The mixture was stirred at -78 ℃ for 2 h and then warmed to room temperature for 1.5 h. After being cooled down to -78 ℃ again, trimethyltin chloride (10.64ml 10.64mmol) was added in one portion. Then the mixture was stirred overnight at room temperature under nitrogen. Water was added to the reaction mixture, and the mixture was extracted by diethyl ether. The organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was recrystallized by ethanol two times. Compound M2 was obtained as a yellow solid (1.75 g, 62%).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (m, 1H), 7.54 (d, 1H), 7.50 (m, 1H), 7.30 (m, 1H), 7.24 (m, 2H), 2.92（m,4H）1.73(m,4H), 1.32 – 1.21 (m, 36H), 0.87 (t, 6H), 0.49 – 0.37 (m, 18H) ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.04, 154.21, 143.51, 141.66, 139.84, 139.77, 136.45, 135.65, 135.63, 133.32, 133.03, 131.23, 128.61, 127.51, 125.54, 118.82, 116.88, 111.21, 39.01, 38.99, 31.91, 29.65, 29.63, 29.61, 29.60, 29.58, 29.56, 29.54, 29.34, 29.23, 29.21, 28.59, 28.54, 22.69, 14.12, -8.27, -8.94.

M3 was prepared by using similar synthetic procedure described above for $\mathbf{M_2}$

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (m, 1H), 7.52 (d, 1H), 7.48 (d, 1H), 7.28 (m, 1H), 7.22 (m,2H), 2.94 (m, 4H), 1.69 – 1.64 (m, 2H), 1.33 – 1.25 (m, 16H), 0.93 – 0.89 (m, 12H), 0.49 – 0.39 (m, 18H).^{13}C NMR (151 MHz, $CDCl_3$) δ 166.98, 153.20, 142.11, 140.62, 138.76, 138.48, 135.58, 135.54, 135.45, 131.73, 131.48, 130.20, 127.55, 126.43, 124.51, 117.79, 115.84, 110.14, 52.39, 42.67, 42.57, 38.14, 31.05, 28.67, 27.73, 27.68, 24.31, 24.29, 21.95, 21.92, 13.11, 13.09, 9.77, 9.74, -9.32, -10.00.

***Synthesis of $PTBF_{EH}$-BDD*:** M1 (0.089g, 0.1 mmol), M4 (0.076 g, 0.1 mmol) and $Pd(PPh3)_4$ (8 mg) were put into a flame-dried and Argon-filled flask. After adding toluene (6 ml), the mixture was carefully heated to 110°C and refluxed for 6h under an argon atmosphere. After the solution was cooled to room temperature, the solution was dropped into methanol. The crude product was collected by filtration and subjected by Soxhlet extraction with methanol, dichloromethane and chloroform. Then, the remaining solid was dropped into methanol again. The final black solid product (99.4mg, yield: 85%) was collected and dried under vacuum overnight at 45

°C.

Synthesis of PTBFS$_{DO}$-BDD: The synthesis was the same as described for the ***PTBF$_{EH}$-BDD*** polymer. A black solid was obtained (112mg, yield:82%).

Synthesis of PTBFS$_{EH}$-BDD: The synthesis was the same as described for the ***PTBF$_{EH}$-BDD*** polymer. A black solid was obtained (90.1mg, yield:73%).

characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 600 MHz spectrometer. TGA and DSC measurements were performed using a SDT Q600 V20.9 Build 20 at a heating rate of 10°Cmin^{-1}. The absorption spectra were recorded using a Hitachi U-4100 UV-Vis-NIR scanning spectrophotometer. The molecular weight of the polymer was measured by gel permeation chromatography (GPC) performed using an ELEOS system, and polystyrene was used as the standard (40°C, tetrahydrofuran (THF) as the eluent). Cyclic voltammetry (CV) measurements were performed on a CHI660D electrochemical workstation, which is equipped with a three-electrode cell consisting of a platinum working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire as counter electrode. The measurements were carried out in anhydrous acetonitrile containing 0.1 M n-Bu$_4$NPF$_6$ as a supporting electrolyte under an argon atmosphere at a scan rate of 100 mV s^{-1}. Thin films were deposited from chloroform solution onto the working electrodes.

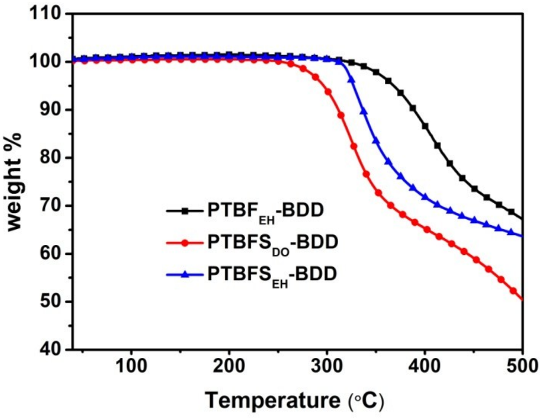


Fig. S1 Thermogravimetric analysis (TGA) of the polymers.

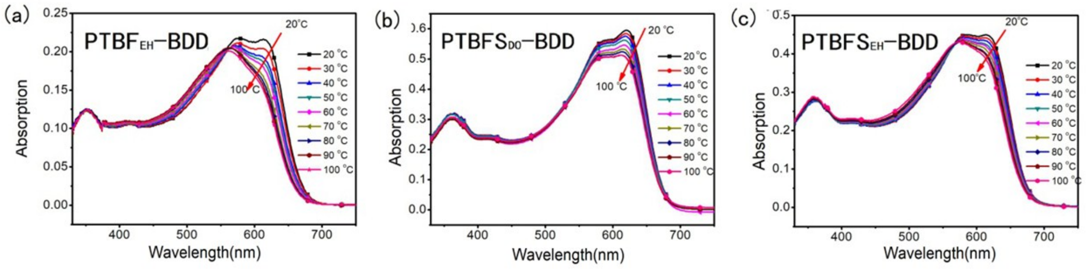


Fig.S2 The temperature-dependent UV-vis absorption spectra of (a) PTBF$_{EH}$-BDD and (b) PTBFS$_{DO}$-BDD and (c) PTBFS$_{EH}$-BDD in CHCl$_3$ dilute solution.

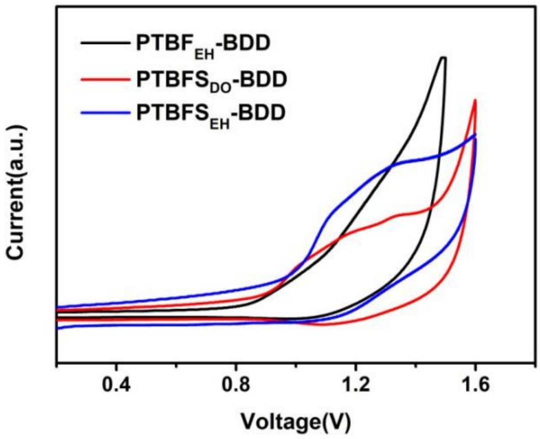


Fig.S3 CV curves of the polymers.

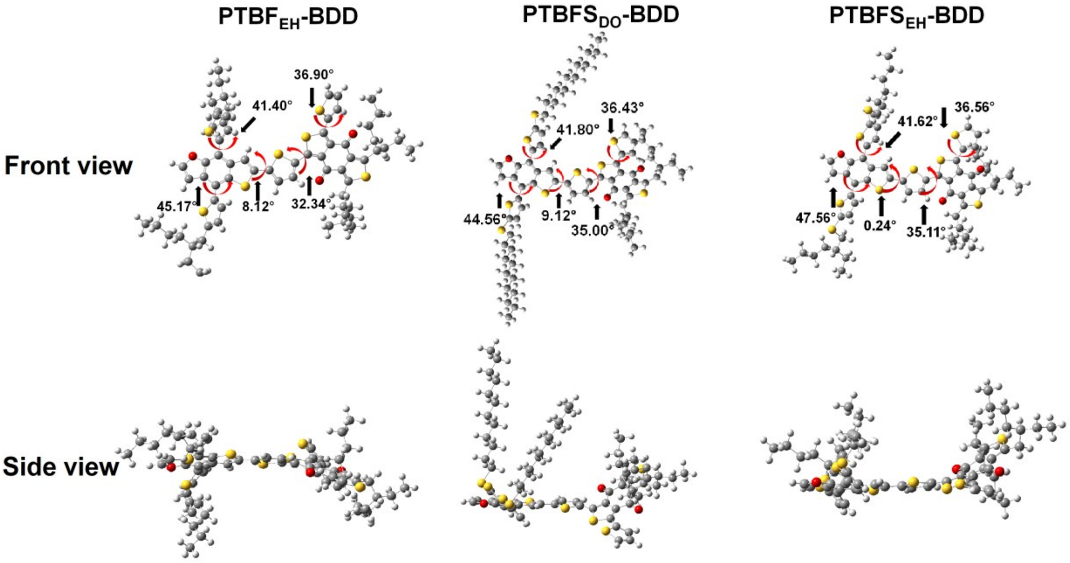


Fig. S4 Density functional theory (DFT) calculations.

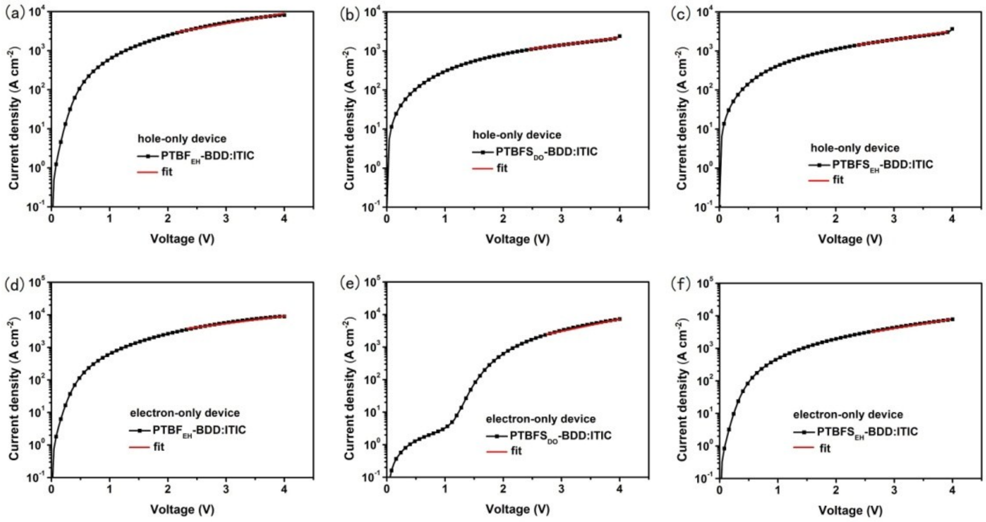


Fig. S5 The SCLC curves based hole-only(top) and electron-only(bottom) devices of PTBF$_{EH}$-BDD (a,d) PTBFS$_{DO}$-BDD (b,e) and PTBFS$_{EH}$-BDD(c,f).

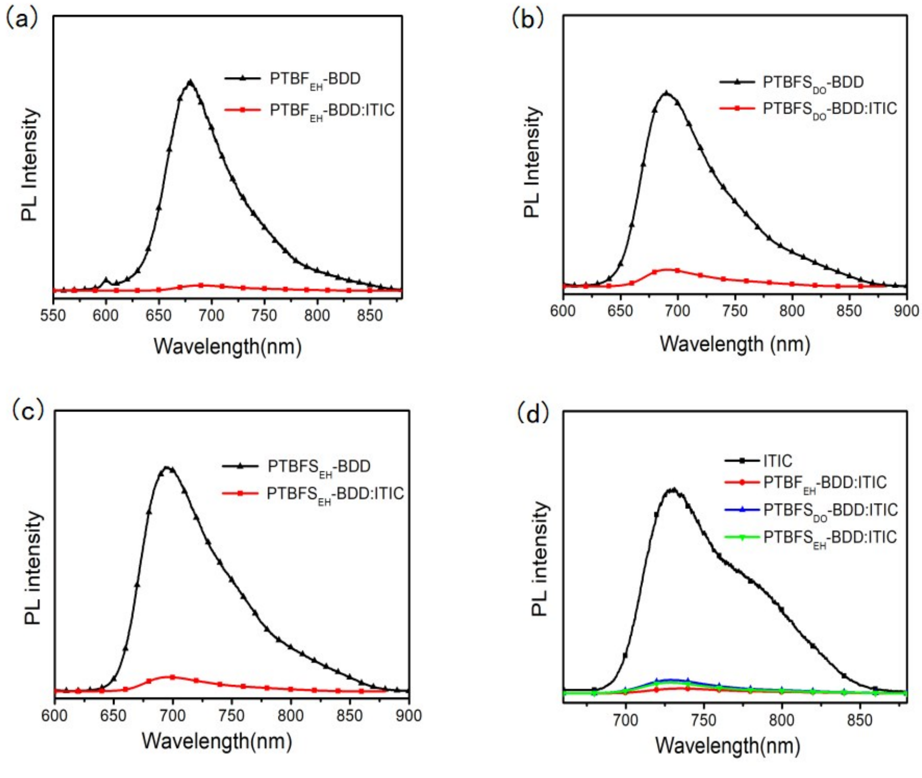


Fig. S6 PL emission spectra of pure polymers PTBF$_{EH}$-BDD PTBF$_{DO}$-BDD PTBFS$_{EH}$-BDD and blend films.

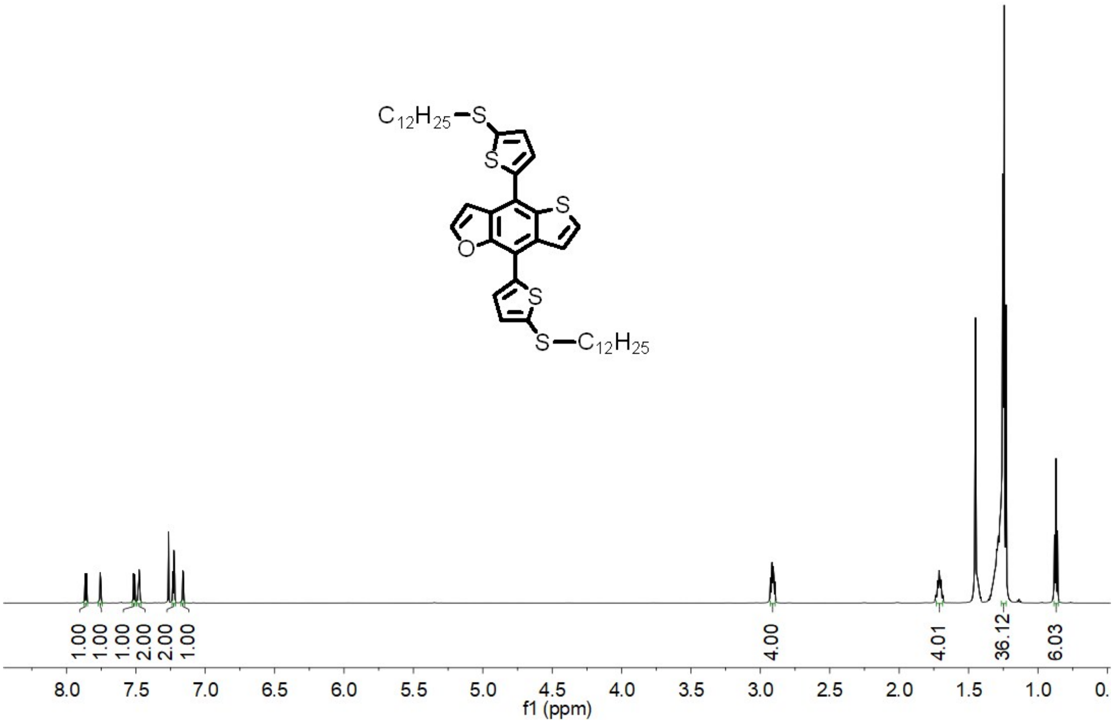


Fig. S7 ^{1}H NMR spectrum of compound **2.**

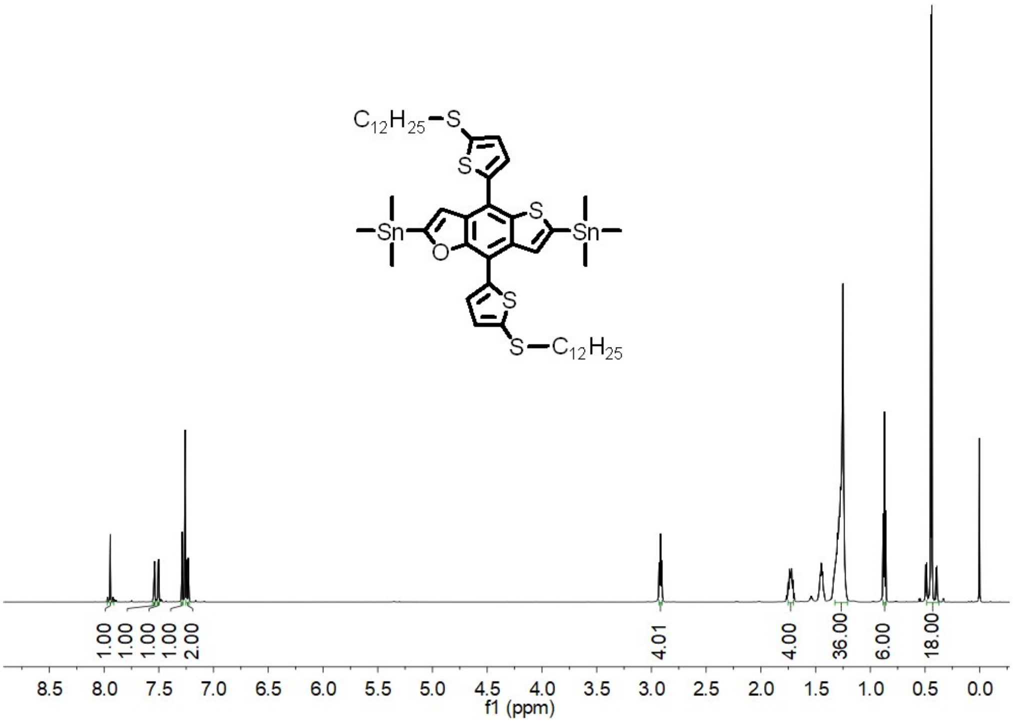


Fig. S8 ^{1}H NMR spectrum of compound M2.

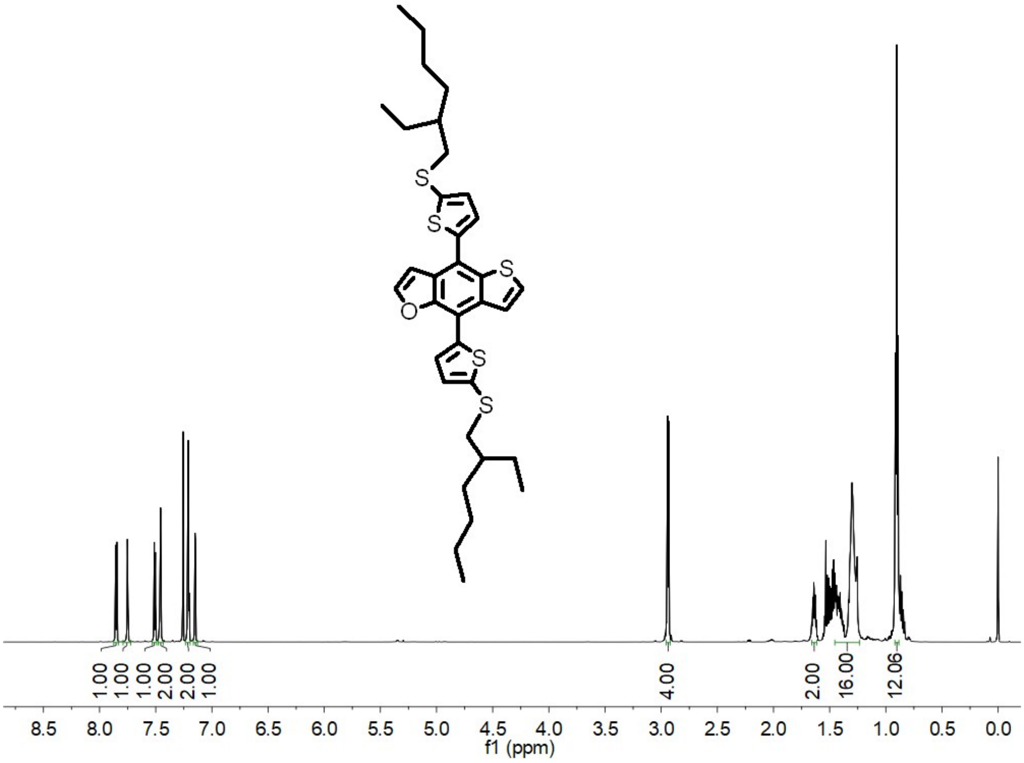


Fig. S9 ^{1}H NMR spectrum of compound 3.

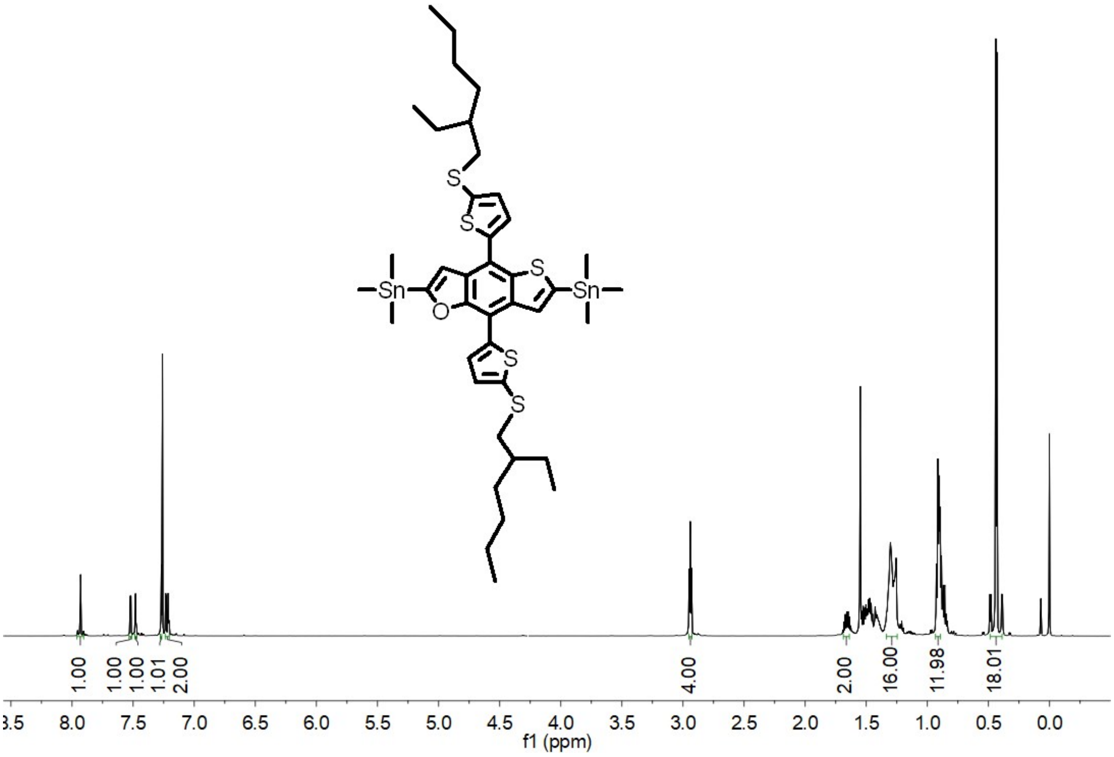


Fig. S10 ^{1}H NMR spectrum of compound M3.

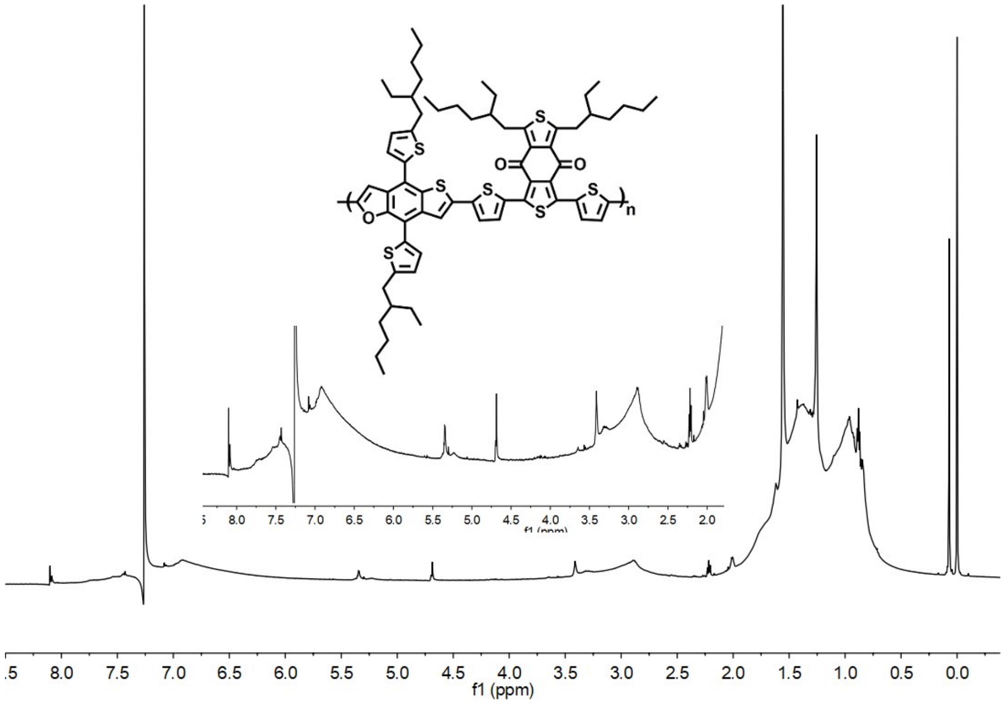


Fig. S11 ^{1}H NMR spectrum of compound ***PTBF$_{EH}$-BDD***.

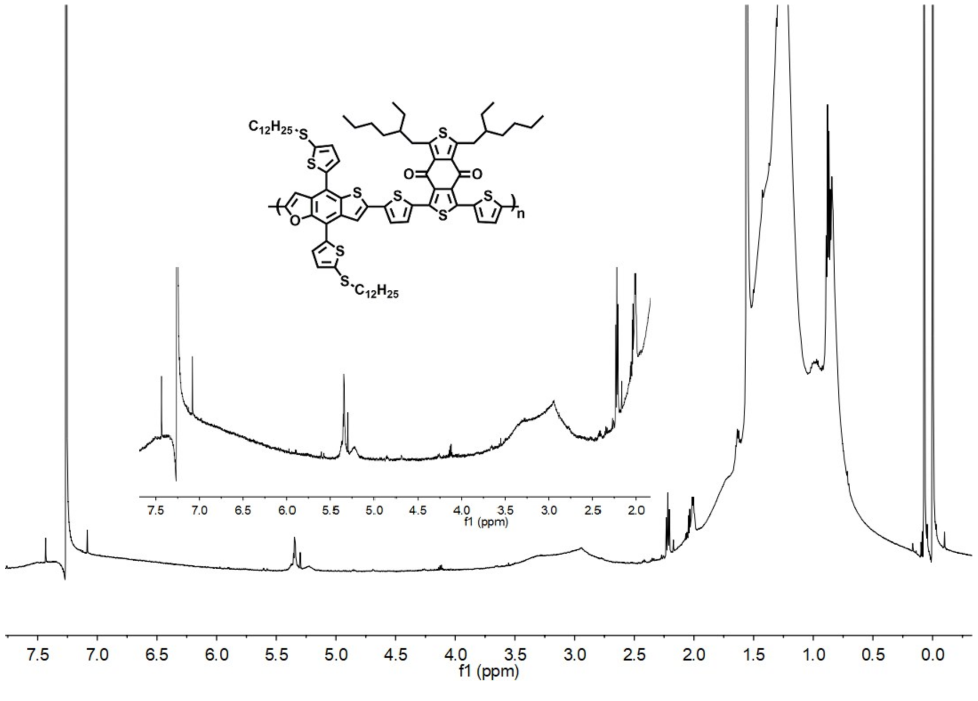


Fig. S12 ^{1}H NMR spectrum of compound ***PTBFS$_{DO}$-BDD***

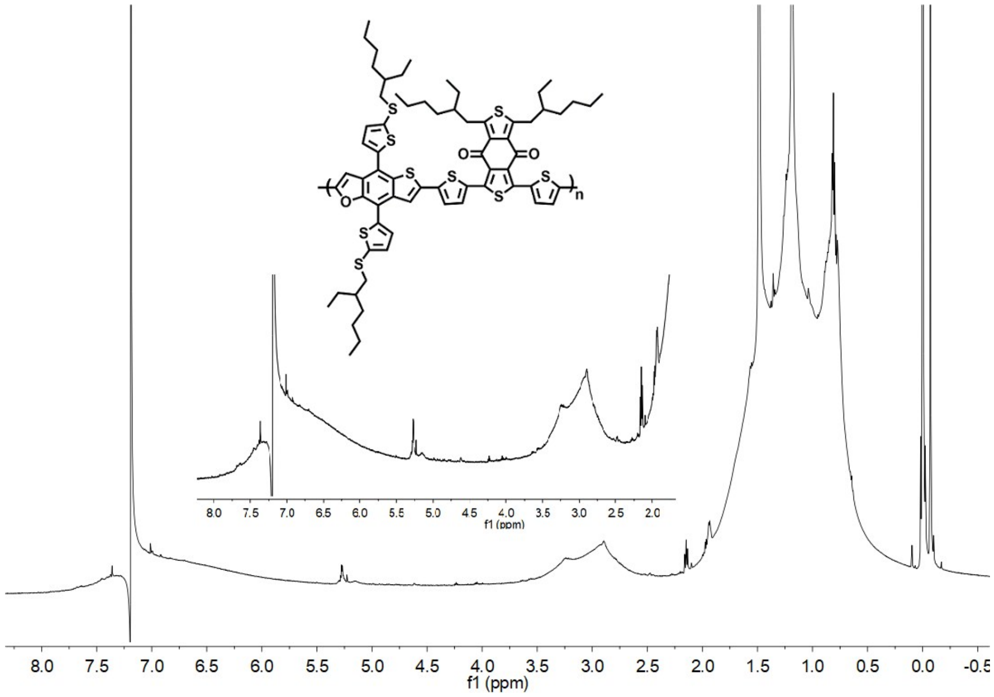


Fig. S13 ^{1}H NMR spectrum of compound ***PTBFS$_{EH}$-BDD***.

References

1 L. Fan, R. Cui, Q. Zhang, X. Gao, D. Qian, B. Qiu, J. Yuan, Y. Li, W. Huang, J. Yang, W. Liu, X. Xu, L. Li, Y. Zou, *J. Mater. Chem. C* 2014, **2**, 5651-5659