Electronic Supplementary Information

Experimental Section

Instruments and measurements: ^{1}H and ^{13}C NMR spectra were measured on a Bruker DMX-400 spectrometer. Chemical shifts were reported in ppm relative to the singlet of $CDCl_3$ at 7.26 and 77 ppm for ^{1}H and ^{13}C NMR, respectively. The absorption spectra were obtained from a TU-1901 UV/Vis spectrameter (PERSEE). Electrochemical cyclic voltammetry was conducted on a Zahner IM6e electrochemical workstation with Pt dist, Pt wire, and Ag/Ag^{+} electrode (0.01 M $AgNO_3$, 0.09 M Bu_4NPF_6 in acetonitrile) as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammnium hexafluorophosphaste (Bu_4NPF_6) *o*-dichlorobenzene/acetonitrile (5:1) solution. A trace amount of ferrocene was used as reference material. Thermograms were obtained on Mettler differential scanning calorimeter (DSC). Thermogravimetric analysis (TGA) was carried on Pyris 1 Perkin-Elmer.

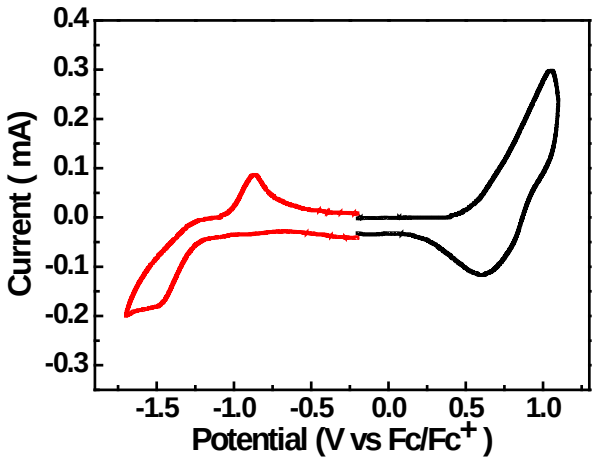

Fig.1 Cyclic voltammogram of the PBDTTT-S films on a platinum electrode in acetonitrile solution containing 0.1 mol/L Bu_4NPF_6 at a scan rate of 20 mV/s.

Computational Method: The DFT calculations were carried out using the hybrid B3LYP functiona.[1,2] All DFT calculations were performed using the Gaussian 03 package.[3]

Device fabrication: To evaluate the effect of the introduction of sulfone group on the optical-electric properties of PBDTTT-S, polymer solar cell devices with the structure ITO/PEDOT-PSS/polymer:$PC_{71}BM$/Ca/Al were fabricated as follows: After spin-coating a 30 nm layer of poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) onto a precleaned indium-tin oxide (ITO) coated glass substrate, the additive of 1,8-Diiodooctane (purchased from Sigma Aldrich, used as received with 3% volume ratio) was added to the PBDTTT-S/$PC_{71}BM$ (1:1.5, w/w) solution in dichlorobenzene, the concentration of the polymer in the solutions is 10 mg/mL and the solution was spin-coated and then were completed by evaporating Ca/Al metal electrodes with an area of 4 mm^2, which was defined by masks. To optimize device performance, different donor/acceptor (D/A) weight ratios (1:1 to 1:4) were used during the device fabrication process. However, it was found that the 1:1.5 D/A weight ratio gave the best device performance. The thickness of the active layer was approximately 100 nm.

Synthesis: **2-(2-ethylhexylthio)thiophene (1)** thiophene-2-thiol (5.8 g, 50 mmol), 1-bromo-2-ethylhexane (11.58 g, 60 mmol) and sodium carbonate (6.36 g, 60 mmol) were dissolved into 50 mL DMF. The mixture was stirred for 1h at 110^{o}C and cooled to room temperature. Then 200 mL water was added and extracted by ethyl ether

twice. The solvent were removed under vacuum, and the residue was purified by silica gel chromatography using hexane as eluent to obtain compound 1 as light-yellow liquid (10.28 g, yield 90%). GC-MS: m/z = 228. ^{1}H NMR ($CDCl_3$, 400MHz), δ (ppm): δ 7.29 (d, 1H), 7.08 (d, 1H), 6.94 (m, 1H), 2.79 (t, 2H), 1.24-1.53 (m, 9H), 0.87(m, 6H).

2-(2-ethylhexylsulfonyl)thiophene (2) Compound 1 (5.7 g, 25 mmol) was dissolved into 100 mL $CHCl_3$ and m-CPBA (8.6 g, 50 mmol) was added by portions at room temperature. After being stirred for 1h, diluted sodium hydroxide solution was added and the mixture was extracted by ethyl ether twice. The combined organic phase was evaporated to remove the solvent under vacuum, and the residue was purified by silica gel chromatography using hexane:acetic ester (30:1) as eluent to obtain compound 2 as stick yellow liquid (4.35 g, yield 67%). GC-MS: m/z = 260. ^{1}H NMR ($CDCl_3$, 400MHz), δ (ppm): δ 7.62 (d, 1H), 7.56 (d, 1H), 7.04 (m, 1H), 3.02 (d, 2H), 1.85 (m, 1H), 1.36-1.06 (m, 8H), 0.74 (m, 6H).

2,3-bis(chloromethyl)-5-(ethylhexylsulfonyl)thiophene (3) Compound 2 (5.8g, 22.4 mmol) was dissolved into chloromethyl ethyl ether (12.7 g, 134.4 mmol) and Tin(IV) chloride (10.5 g, 40.3 mmol) was added dropwise at 0^{o}C. Then the reaction was kept at the ice bath for about 40 mins. The orange liquid was poured into ice-water and extracted by ethyl ether three times. The combined organic phase was evaporated to remove the solvent under vacuum, and the residue was purified by silica gel chromatography using hexane:acetic ester (30:1) as eluent to obtain compound 3 as stick brown liquid (7.7 g, yield 96.6%). ^{1}H NMR ($CDCl_3$, 400MHz), δ (ppm): δ 7.56

(s, 1H), 4.76 (s, 2H), 4.57 (s, 2H), 3.12 (d, 2H), 1.98 (m, 1H), 1.49-1.17 (m, 8H), 0.84 (m, 6H).

2-(2-ethylhexylsulfonyl)-4,6-dihydrothieno[3,4-b]thiophene (4) Compound 3 (2.86 g, 8.0 mmol) was dissolved into 100 mL methanol and the sodium sulfide (0.62 g, 8.0 mmol) in 20 mL methanol was added dropwise at 60^{o}C for about 30 mins. After being stirred for another 30 mins at 60^{o}C, the mixture was cooled to room temperature and the solvent was evaporated to obtain the coarse product. The further purification was finished by silica gel chromatography using hexane:acetic ester (30:1) as eluent to obtain compound 4 as brown yellow solid (1.34 g, yield 27%). GC-MS: m/z = 318. ^{1}H NMR ($CDCl_3$, 400MHz), δ (ppm): δ 7.34(s, 1H), 4.18 (s, 2H), 4.04 (s, 2H), 3.08 (d, 2H), 1.93 (m, 1H), 1.47-1.16 (m, 8H), 0.83 (m, 6H).

2-(2-ethylhexylsulfonyl)-4,6-dihydrothieno[3,4-b]thiophene-5-oxide (5) Compound 4 (0.64 g, 2.0 mmol) was dissolved into 25 mL acetic ester and m-cPBA (0.34 g, 2.0 mmol) was added by portions at -70^{o}C, then the mixture was warmed to room temperature slowly and stirred for 6h. The solvent was removed and the coarse product 5 was obtained as brown solid and used to next step without further purification.

2-(2-ethylhexylsulfonyl)thieno[3,4-b]thiophene (6) Compound 5 was added to 5 mL acetic anhydride and stirred for 30 mins at reflux temperature. Then the mixture was evaporated to remove the solvent and the residue was purified by silica gel chromatography using hexane:acetic ester (5:1) as eluent to obtain compound 6 as brown solid (0.35 g, yield 98%). GC-MS: m/z = 316. ^{1}H NMR ($CDCl_3$, 400MHz), δ

(ppm): δ 7.68(s, 1H), 7.61 (s, 1H), 7.36 (s, 1H), 3.16 (d, 2H), 2.02 (m, 1H), 1.2-1.51 (m, 8H), 0.86 (m, 6H).

4,6-dibromo-2-(2-ethylhexylsulfonyl)thieno[3,4-b]thiophene (M1) Under argon protection and dark against light, NBS (0.45 g, 2.5 mmol) was added to the solution of DMF (10 mL) with compound 6 (0.32 g, 1.0 mmol) at 0^oC, after the mixture was stirred for 5h at 0^oC, the reactants were poured into the diluted solution of sodium thiosulfate and extracted by ethyl ether twice. The solvent was removed under vacuum and the coarse product was purified by silica gel chromatography using hexane:acetic ester (10:1) as eluent to obtain compound 6 as light-yellow solid (0.38 g, yield 81%). ^{1}H NMR ($CDCl_3$, 400MHz), δ (ppm): δ 7.46(s, 1H), 3.16(d, 2H), 2.06 (m, 1H), 1.55-1.23(m, 8H), 0.88(m, 6H). ^{13}C NMR ($CDCl_3$, 400MHz), δ (ppm): δ= 148.30, 144.07, 139.88, 123.83, 103.84, 98.12, 60.63, 34.26, 32.37, 28.17, 25.76, 22.69, 13.96, 10.19.

Poly[4,8-diethylhexyloxybenzo[1,2-b;3,4-b]dithien-2,6-yl-alt-2-(2-ethylhexylsulfonyl)thieno[3,4-b]thiophene] PBDTTT-S.

The polymer of **PBDTTT-S** was prepared by Stille coupling reaction. The monomers of M1 (142.2mg, 0.3mmol) and M2 (232.3mg, 0.3mmol) were put into a three-neck flask. Then 8 mL of toluene and 0.6 mL of DMF were added under the protection of argon. The solution was flushed with argon for 10 min, and then 15 mg of $Pd(PPh_3)_4$ was added. After another flushing with argon for 20 min, the reactant was heated to reflux for 18 h. Then the reactant was cooled to room temperature, and the polymer

was precipitated by adding 50 mL methanol, and filtered through a Soxhlet thimble, then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer was recovered as solid from the chloroform fraction by rotary evaporation. The solid was dried under vacuum for 1 day. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): δ 7.46(br, 1H), 7.01(br, 2H), 3.65~2.90 (br, 6H), 2.40~0.80(m, 45H). Anal. Calcd for [$C_{42}H_{62}O_4S_5$]: C, 63.75; H, 7.9; O, 8.09; S, 20.26. Found: C, 64.63; H, 6.61. M_w=18.0K; Polydispersity=1.8.

References:

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