

Supporting information for

Novel dialkylthio benzo[1,2-b:4,5-b']dithiophene Derivative for High Open-Circuit Voltage in Polymer Solar Cells

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Experimental section

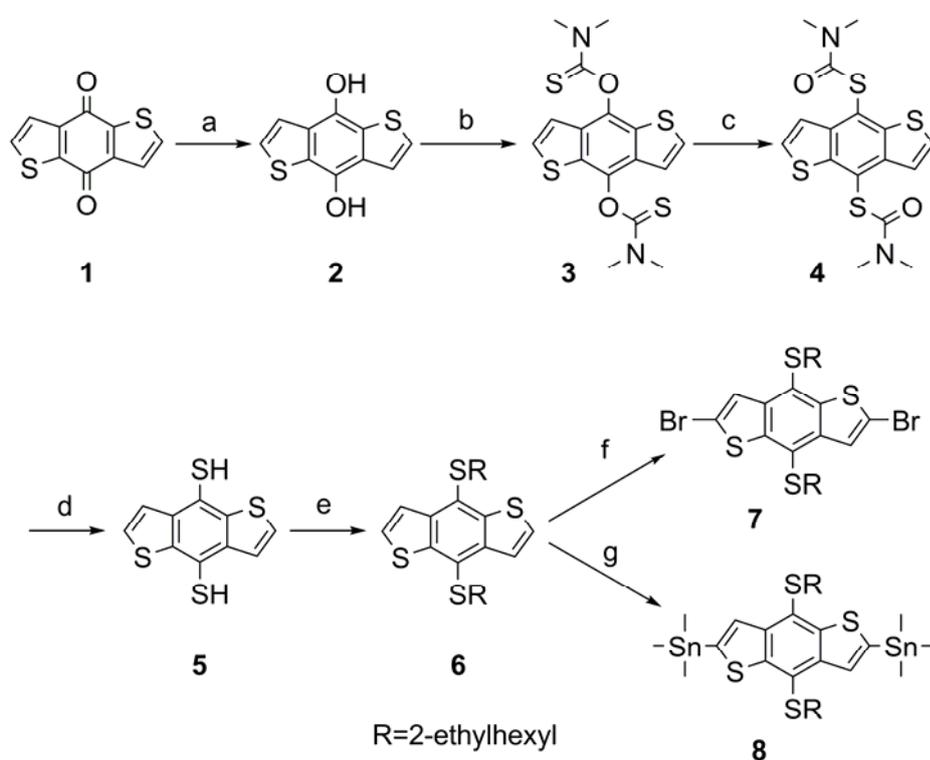
Materials. All chemicals were purchased from Sigma-Aldrich and used without further purification unless otherwise stated. Tetrahydrofuran (THF) and acetonitrile were dried using an MBraun SP Series solvent purification system and their water contents (< 20 ppm) were determined with a Karl-Fisher titrator (Denver Instruments, Model 270). 4,8-Dihydrobenzo[1,2-b:4,5-b']dithiophene-4,8-dione (1) was synthesized according to the reported literature.¹

Characterization. ¹H and ¹³C NMR spectra were recorded with on a JEOL FX-270 MHz NMR spectrometer using CDCl₃ and DMSO-*d*₆ solvent with TMS as the internal standard. Molecular weights and molecular weight distributions of polymers were obtained using the Triple detector gel permeation chromatography (GPC) system (module TDA320, Viscotek) equipped with two ViscoGEL columns (I-MBHMW 3078, Viscotek) and using THF and as the eluting solvent at a flow rate of 1 mL/min at 40 °C and using chloroform and as the eluting solvent at a flow rate of 1 mL/min at 50 °C. Thermal stability of the polymer was measured with thermogravimetric analysis (Perkin Elmer Pyris 1 TGA) under inert gas atmosphere with a heating rate of 10 °C/min. The optical absorption spectra of the polymer were recorded by Perkin Elmer Lambda 900 UV-Vis-NIR Spectrophotometer. High Resolution Mass Spectra (HRMS) were recorded on a Mass Spectrometer operating in positive ESI(+) mode. Tapping Mode Atomic Force Microscopy (TMAFM) studies were conducted on VEECO dimension 5000 scanning probe microscope with Nanoscope software. AFM images were obtained using MPP-12100 tip (Veeco instruments inc.). Image analysis was carried out with Nanoscope 7.30 software.

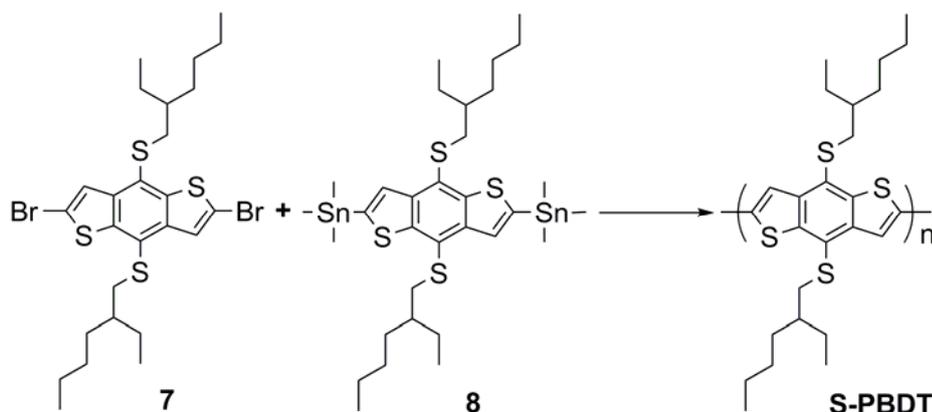
Cyclic voltamograms (CV) were obtained under inert gas atmosphere using a standard three-electrode cell connected to an EG&G Princeton Applied Research Potentiostat/Galvanostat 273A with PowerSuite software. The solution of 0.1M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in dry acetonitrile (AN) was used as the electrolyte. The counter electrode was carbon felt wrapped in Pt mesh and the reference electrode was silver wire in 0.01 M Ag/Ag⁺ (0.1M

Bu₄NPF₆/AN). The polymer film was drop cast from a chloroform solution onto the Pt disc working electrode and CV measurements of the polymer were recorded using a constant scan rate of 100 mV/s. The ionization potential, HOMO level, and electron affinity, LUMO, of the polymer were estimated from onset oxidation potential and onset reduction potential with ferrocene/ferrocinium (Fc/Fc⁺) as an internal reference, assuming the energy level of Fc/Fc⁺ is 4.8 eV below the vacuum level.²⁻⁴

$$\text{HOMO} = -(E_{\text{onset}}^{\text{ox}} + 4.71) \text{ (eV)} ; \text{LUMO} = -(E_{\text{onset}}^{\text{red}} + 4.71) \text{ (eV)}$$



Scheme S1 synthesis of dialkylthio substituted benzodithiophene



Scheme S2 Synthesis route and chemical structure of S-PBDT polymer

4,8-Dihydroxybenzo[1,2-b:4,5-b']dithiophene (2). To a stirred suspension of compound **1** (13.95g, 0.063 mol) in 200 mL of ethanol was added NaBH₄ (5.27g, 0.139 mol) in one portion under ice/water bath cooling, followed by stirring for 3 h at the same temperature. The reaction was quenched by pouring into 1M HCl. The crude product was filtered, washed with large amounts of water, and dried under vacuum at 70 °C. 13.19g of product was obtained as a green solid and used for next step without further purification. Part of the product was purified by recrystallization with glacial acetic acid with about 90 % recovery yield for analysis purposes. mp 260-261 °C (from acetic acid). ¹H NMR (270 MHz, DMSO-*d*₆, Me₄Si), δ (ppm): 9.78 (s, 2H), 7.62 (d, *J* = 5.4 Hz, 2H), 7.55 (d, *J* = 5.4 Hz, 2H). ¹³C NMR (67.5 MHz, DMSO-*d*₆), δ (ppm): 139.8, 127.3, 125.9, 125.2, 121.1. Elemental analysis: Calculated for C₁₀H₆O₂S₂: C, 54.03; H, 2.72. Found: C, 54.03; H, 2.74.

4,8-Bis(N,N'-dimethylthiocarbamoyloxy)benzo[1,2-b:4,5-b']dithiophene (3). In a 250 mL 3-necked round bottom flask was charged with compound **2** (9.5 g, 0.043 mol) and 100 mL of DMF. Sodium hydride (60% in mineral oil, 6.85g, 0.174 mol) was then added slowly within 20 min and the color changed from yellow to dark green. After hydrogen evolution stopped, the reaction solution was cooled down to 10 °C and N,N-dimethyl thiocarbamoyl chloride (21.3 g, 0.174 mol) was added in one portion. The temperature of reaction flask was slowly increased to 80 °C and stirred for 3 h. The oil bath was removed after 3 h and the reaction flask was cooled to room temperature. The reaction mixture was poured slowly into aqueous 1% potassium hydroxide solution (1000 mL) with vigorous stirring and the precipitate was collected by vacuum

filtration and washed with aqueous 1% potassium hydroxide solution followed by 500 mL of water. The product was dried under vacuum at 80 °C to yield 16.26 g (95.5% yield) of yellow solid. The purity of the solid by HPLC was about 90 % and it was used without further purification for the next step. Small amount of sample was purified by silica gel column chromatography with a mixture of dichloromethane/hexane (2:8) for analysis purposes. mp 262-264 °C. ¹H NMR (270 MHz, CDCl₃, Me₄Si), δ (ppm): 7.42 (d, *J* = 5.4 Hz, 2H), 7.26 (d, *J* = 5.4 Hz, 2H), 3.53 (s, 6H), 3.50 (s, 6H). ¹³C NMR (67.5 MHz, CDCl₃), δ (ppm): 185.7, 140.1, 132.7, 131.8, 127.8, 120.1, 43.7, 39.1. HRMS (ESI+) calculated for C₁₆H₁₆N₂O₂S₄: 397.0168 (M+H⁺). Found: 397.0169 (M+H⁺).

4,8-Bis(N,N'-dimethylthiocarbamoylthio)benzo[1,2-b:4,5-b']dithiophene (4). In a 500 mL three-necked round bottom flask, compound **3** (0.5 g, 1.26 mmol) in 250 mL of diphenyl ether was heated at 245 °C under nitrogen protection. After 3 hours at this temperature, the reaction flask was allowed to cool to room temperature and the mixture was poured into 500 mL of hexane. The suspension was cooled in ice/water bath and the product was filtered under reduced pressure and washed with hexane. The collected solid was dried under vacuum at 70 °C to yield 7.88 g of brown solid with 78.8 % recovery yield. The purity of the product was > 95% by HPLC and it was used directly for the next step without further purification. A small amount of sample was purified by silica gel column chromatography with a mixture of dichloromethane/ethyl acetate (7:3) for analysis purposes. mp 245-247 °C. ¹H NMR (270 MHz, CDCl₃, Me₄Si), δ (ppm): 7.58 (d, *J* = 5.4 Hz, 2H), 7.51 (d, *J* = 5.4 Hz, 2H), 3.24 (s, 6H), 3.04 (s, 6H). ¹³C NMR (67.5 MHz, CDCl₃), δ (ppm): 164.1, 145.9, 141.7, 128.8, 123.8, 118.3, 37.2. HRMS (ESI+) calculated for C₁₆H₁₆N₂O₂S₄: 397.0168 (M+H⁺). Found: 397.0169 (M+H⁺).

4,8-Dimercaptobenzo[1,2-b:4,5-b']dithiophene (5). A lithium aluminum hydride (LiAlH₄) solution (2M in THF, 21.6 mL, 43.2 mmol, 4 equiv.) was added into a 250 mL three-necked round bottom flask and stirred under nitrogen. The reaction flask was cooled in ice/water bath and compound **4** (4.29 g, 10.8 mmol) in THF (100 mL) was added into reaction flask in one portion. After the addition was complete, the ice/water bath was removed and the reaction mixture was stirred for 3.5 h at ambient temperature and then cooled in an ice/water bath and then quenched by slowly adding a 3 M HCl solution under nitrogen protection. The product was collected by vacuum filtration and washed with a large amount of water. After drying under

vacuum at 80 °C, 2.59 g of a yellow solid was obtained with 94.3 % yield and it was used without further purification for the next step. mp 175-177 °C. ¹H NMR (270 MHz, CDCl₃, Me₄Si), δ (ppm): 7.60 (d, *J* = 5.4 Hz, 2H), 7.54 (d, *J* = 5.4 Hz, 2H), 3.76 (s, 2H). ¹³C NMR (67.5 MHz, CDCl₃), δ (ppm): 140.7, 137.8, 128.0, 123.4, 116.1.

4,8-Bis(2-ethylhexylthio)benzo[1,2-b:4,5-b']dithiophene (6). Compound **5** (2.20g, 8.7 mmol) and 50 mL of DMSO were added into 100 mL three-necked round bottom flask and stirred under nitrogen, followed by the addition of anhydrous K₂CO₃ (3.6 g, 26.1 mmol, 3 equiv.). The reaction mixture was stirred at room temperature for 30 min and the color changed from orange to red. 2-Ethylhexyl bromide (5.03 g, 26.1 mmol) was added into the flask and the reaction mixture was stirred at ambient temperature for overnight (color changed to dark yellow). The product was extracted with diethyl ether and the combined organic layer was washed with water, dried with anhydrous MgSO₄, and the solvent was evaporated under reduced pressure to yield crude product as brown oil. The crude product was purified by silica gel column chromatography with hexane as eluent solvent to yield 2.25 g of pale yellow oil with 54 % yield. R_f = 0.34. ¹H NMR (270 MHz, CDCl₃, Me₄Si), δ (ppm): 7.74 (d, *J* = 5.4 Hz, 2H), 7.53 (d, *J* = 5.4 Hz, 2H), 2.98 (d, *J* = 5.4 Hz, 4H), 1.45 (m, 10H), 1.15 (m, 8H), 0.80 (m, 6H). ¹³C NMR (67.5 MHz, CDCl₃), δ (ppm): 144.8, 140.5, 128.4, 124.0, 123.7, 40.2, 39.9, 32.2, 28.8, 25.6, 23.0, 14.1, 10.8. HRMS (ESI+) calculated for C₂₆H₃₈S₄: 478.1851 (M⁺). Found: 478.1850 (M⁺).

2,6-Dibromo-4,8-bis(2-ethylhexylthio)benzo[1,2-b:4,5-b']dithiophene (7). Compound **6** (1.44 g, 3.0 mmol) was dissolved into 100 mL of methylene chloride and placed in a 250 mL one-neck flask under nitrogen protection. Bromine (1.06 g, 6.6 mmol) was dissolved in 10 mL of methylene chloride and slowly added into the reaction flask cooled in an ice/water bath and the mixture was stirred for overnight at ambient temperature. All of the volatile substances were removed by vacuum and the residue was purified by silica gel column chromatography with hexane as eluent solvent to yield 1.687 g of a pale yellow sticky oil (88 % yield). R_f = 0.53, ¹H NMR (270 MHz, CDCl₃, Me₄Si), δ (ppm): 7.67 (s, 2H), 2.91 (d, *J* = 5.4 Hz, 4H), 1.44 (m, 10H), 1.20 (m, 8H), 0.85 (m, 6H). ¹³C NMR (67.5 MHz, CDCl₃), δ (ppm): 146.2, 140.0, 126.7, 122.0, 117.9, 40.4, 39.9, 32.2, 28.8, 25.6, 23.0, 14.1, 10.8. Elemental analysis: Calculated for C₂₆H₃₆Br₂S₄: C, 49.05; H, 5.70. Found: C, 49.49; H, 5.51.

2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexylthio)benzo[1,2-b:4,5-b']dithiophene (8).

Compound **6** (0.20 g, 0.418 mmol) was added into a 50 mL three necked round bottom flask and flushed with nitrogen for 10 min. Anhydrous THF (7 mL) was added into the reaction flask and cooled to -78 °C. *n*-Butyllithium solution (0.42 mL, 1.035 mmol, 2.5 M in hexane) was added dropwise into the flask and the mixture was stirred in an acetone/liquid nitrogen bath for 30 min and then at room temperature for 30 min, and white precipitate was formed in the flask. After cooling the flask to -78 °C, trimethyltin chloride solution (1.24 mL, 1.24 mmol, 1 M in hexane) was added *via* syringe in one portion and the reaction mixture quickly turned clear. The cooling bath was removed and the reaction mixture was stirred for overnight at room temperature. The reaction was quenched by pouring into 50 mL of water, extracted with diethyl ether, and dried with anhydrous magnesium sulfate. The organic solvent was removed by rotary evaporation to yield 0.321 g of crude product (~95.5% yield) as pale yellow oil and it was used for polymerization without further purification. ¹H NMR (270 MHz, CDCl₃, Me₄Si), δ (ppm): 7.78 (s, 2H), 2.99 (d, *J* = 5.4 Hz, 4H), 1.44 (m, 10H), 1.20 (m, 8H), 0.85 (m, 6H), 0.45 (s, 18H). Integration of protons includes peaks on 0.55(d) and 0.35(d) due to coupling with ¹¹⁷Sn and ¹¹⁹Sn). ¹³C NMR (67.5 MHz, CDCl₃), δ (ppm): 148.8, 143.6, 141.3, 131.8, 121.7, 40.2, 39.9, 32.3, 28.9, 25.7, 23.0, 14.2, 10.9, 8.3.

S-PBDT using Stille coupling reaction. Compound **7** (0.130 g, 0.204 mmol), compound **8** (0.165 g, 0.204 mmol), and 15 mL anhydrous toluene were added into 100 mL three-necked round bottom flask under inert atmosphere and stirred for 20 min. Pd(PPh₃)₄ catalyst (7 mg) was added into the reaction mixture and flushed with nitrogen for another 20 min. The reaction temperature was increased slowly to 115 °C and stirred for 16 h under inert gas atmosphere. The reaction solution was cooled to room temperature and precipitated by pouring into 300 mL of methanol. The suspension was filtered through a Soxhlet thimble, and then extracted with methanol and further with hexane for 24 h each. The residue was then extracted into chloroform to afford 0.143 mg (74 % yield) of dark red solid. ¹H NMR (270 MHz, CDCl₃, Me₄Si), δ (ppm): 7.65 (br, 2H), 2.95 (m, 4H), 1.60-1.10 (m, 18H), 0.85 (m, 12H). *M_n* = 16.1 K, *M_w* = 61.6 K, PDI = 3.81 (using THF), *M_n* = 15.7 K, *M_w* = 71.0 K, PDI = 4.52 (using chloroform)

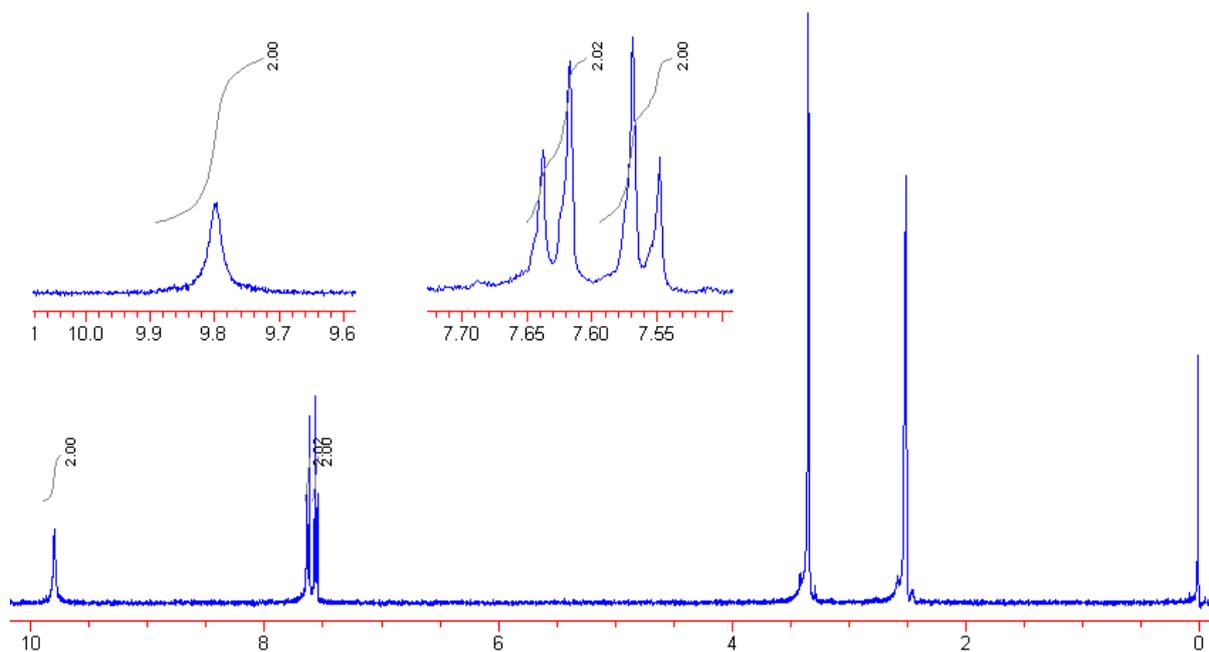


Fig. S1 ¹H NMR spectrum of 4,8-dihydroxybenzo[1,2-b:4,5-b']dithiophene (**2**)

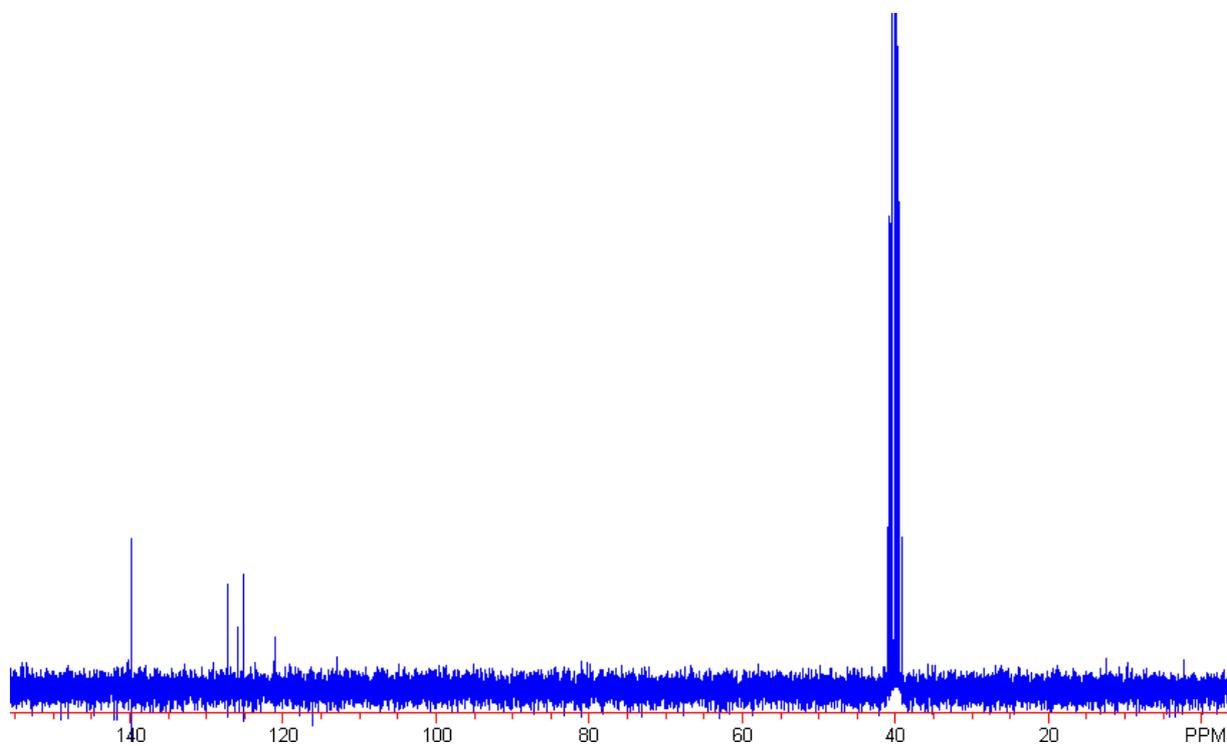


Fig. S2 ¹³C NMR spectrum of 4,8-dihydroxybenzo[1,2-b:4,5-b']dithiophene (**2**)

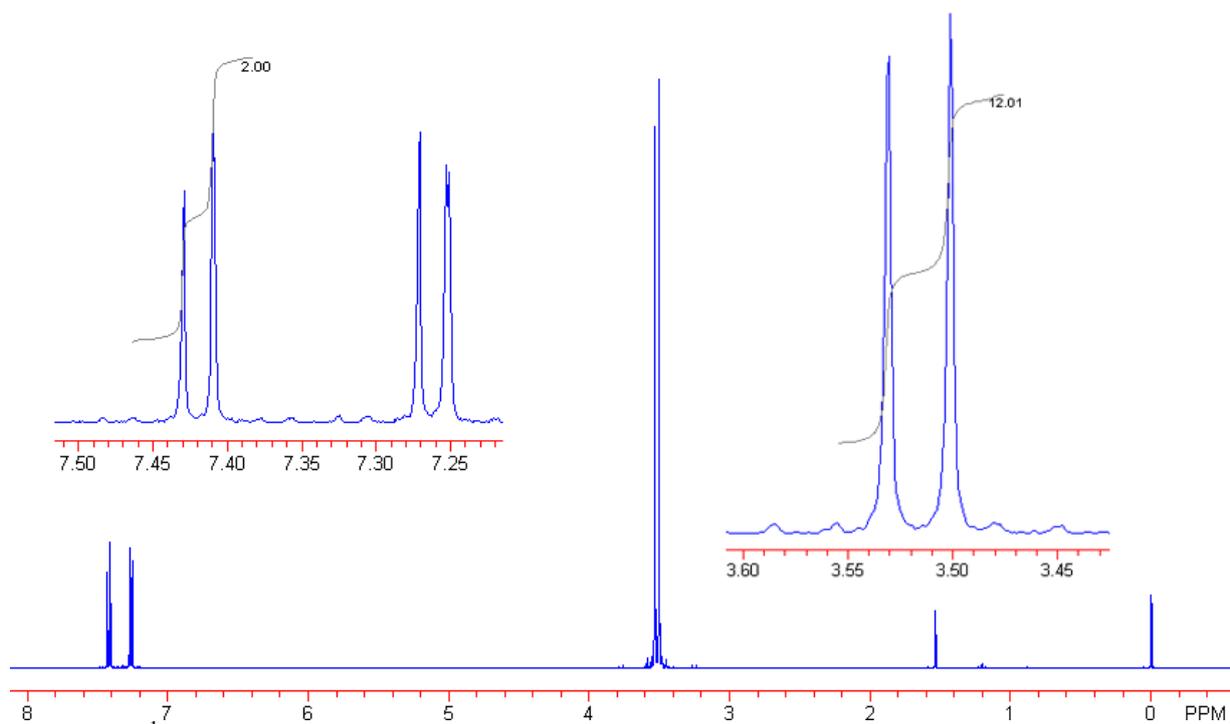


Fig. S3 ^1H NMR spectrum of 4,8-Bis(N,N'-dimethylthiocarbamoyloxy)benzo[1,2-b:4,5-b']dithiophene (**3**)

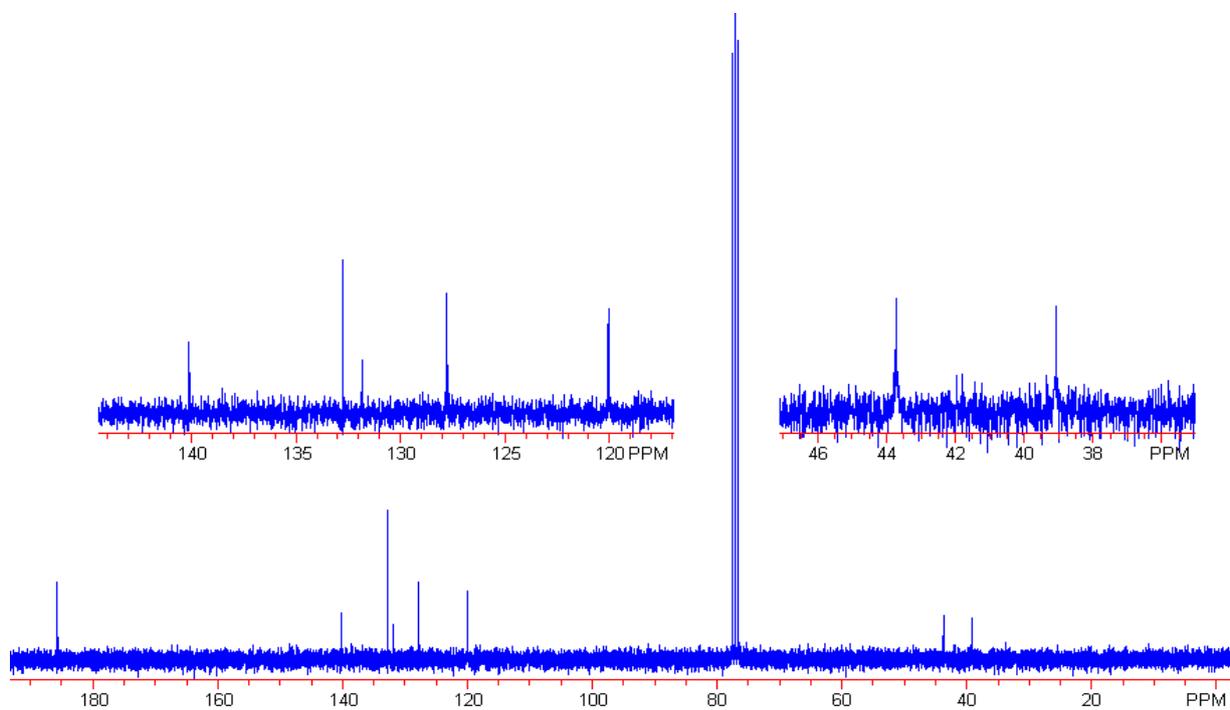


Fig. S4 ^{13}C NMR spectrum of 4,8-Bis(N,N'-dimethylthiocarbamoyloxy)benzo[1,2-b:4,5-b']dithiophene (**3**)

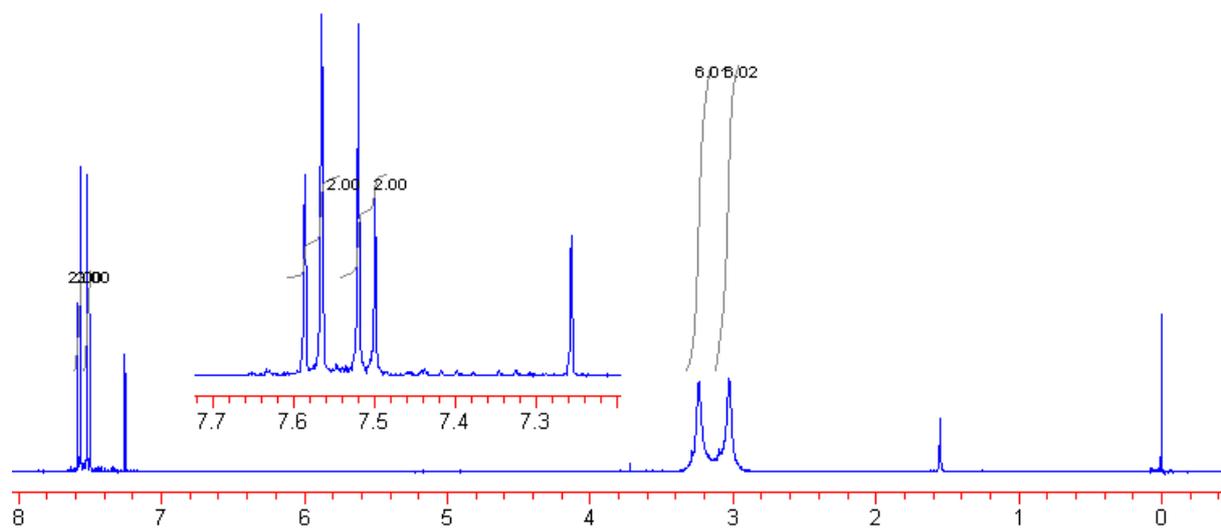


Fig. S5 ¹H NMR spectrum of 4,8-Bis(N,N'-dimethylthiocarbamoylthio)benzo[1,2-b:4,5-b']dithiophene (**4**)

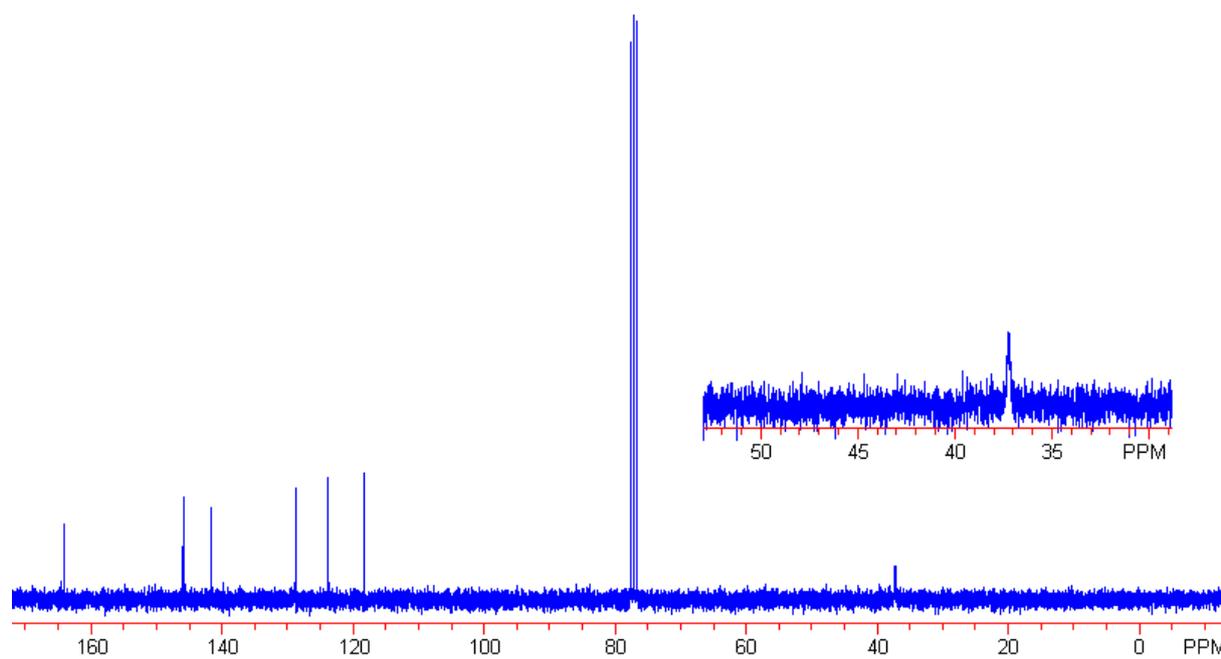


Fig. S6 ¹³C NMR spectrum of 4,8-Bis(N,N'-dimethylthiocarbamoylthio)benzo[1,2-b:4,5-b']dithiophene (**4**)

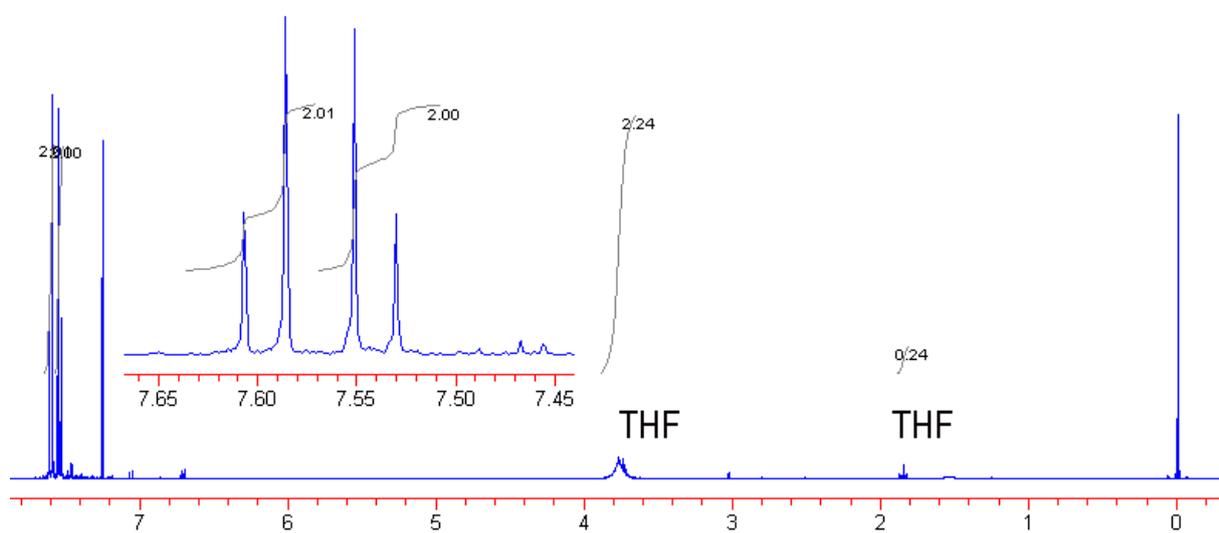


Fig. S7 ¹H NMR spectrum of 4,8-Dimercaptobenzo[1,2-b:4,5-b']dithiophene (**5**)

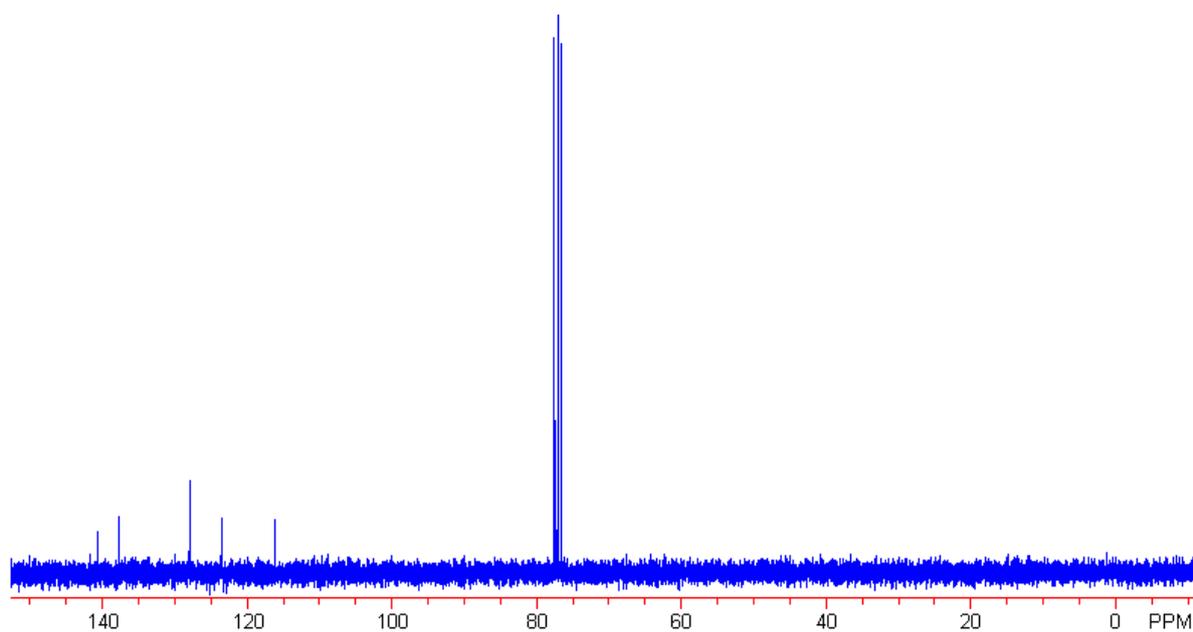


Fig. S8 ¹³C NMR spectrum of 4,8-Dimercaptobenzo[1,2-b:4,5-b']dithiophene (**5**)

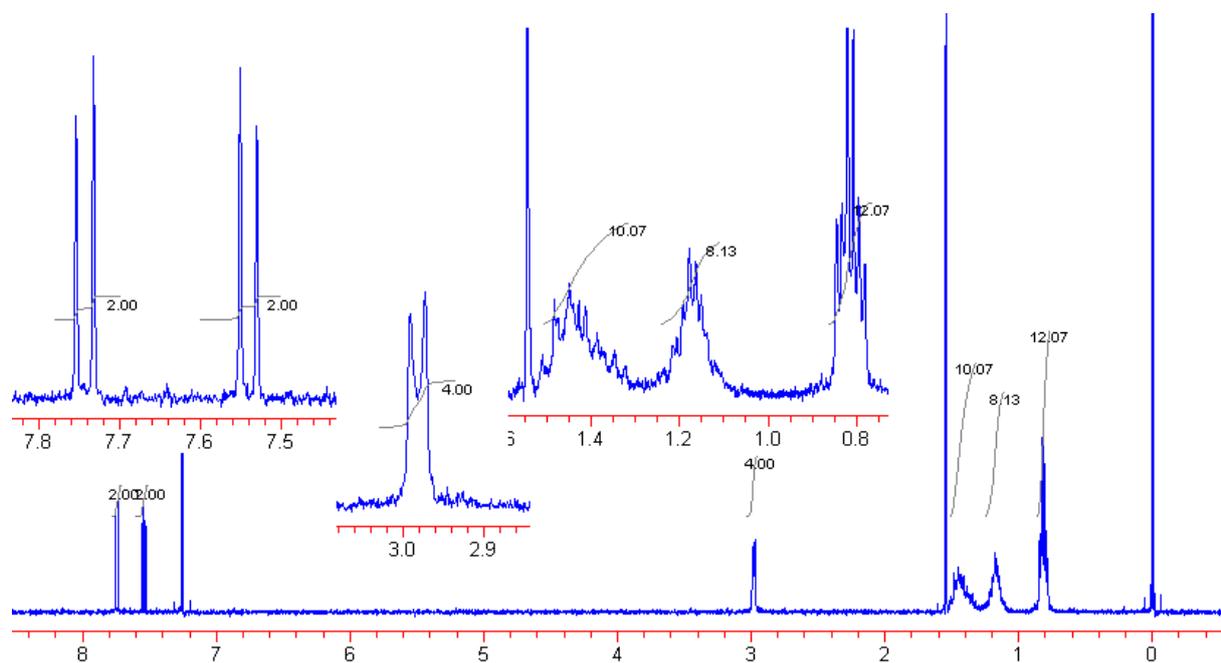


Fig. S9 ^1H NMR spectrum of 4,8-bis(2-ethylhexylthio)benzo[1,2-b:4,5-b']dithiophene (**6**)

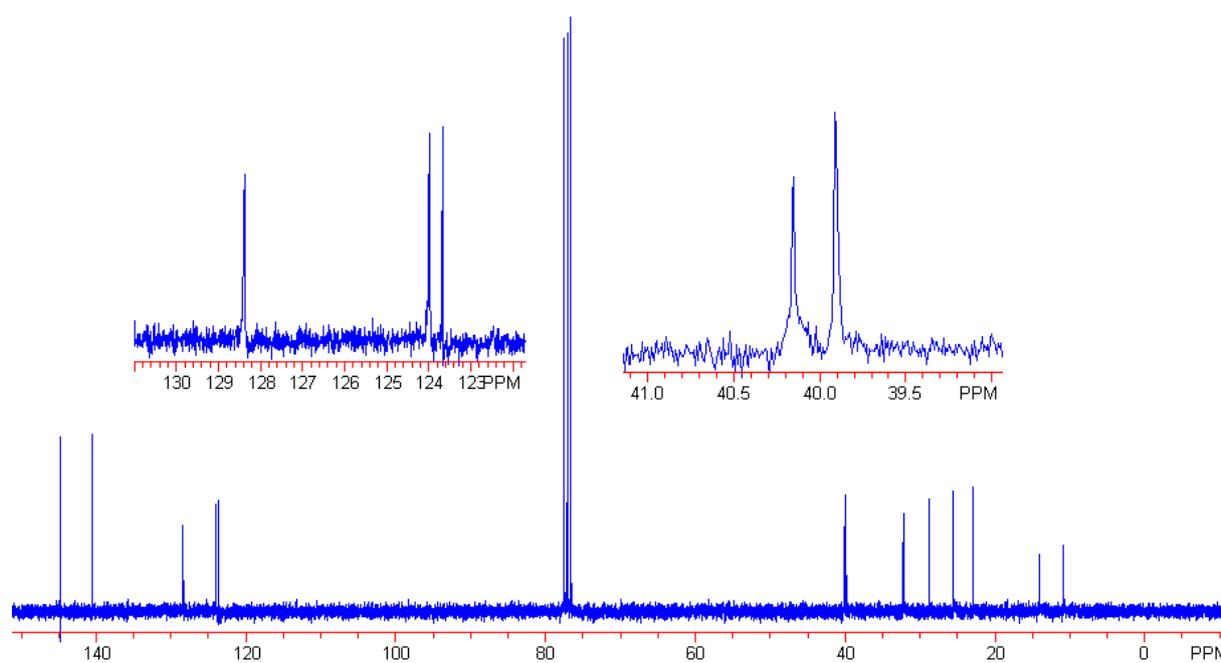


Fig. S10 ^{13}C NMR spectrum of 4,8-bis(2-ethylhexylthio)benzo[1,2-b:4,5-b']dithiophene (**6**)

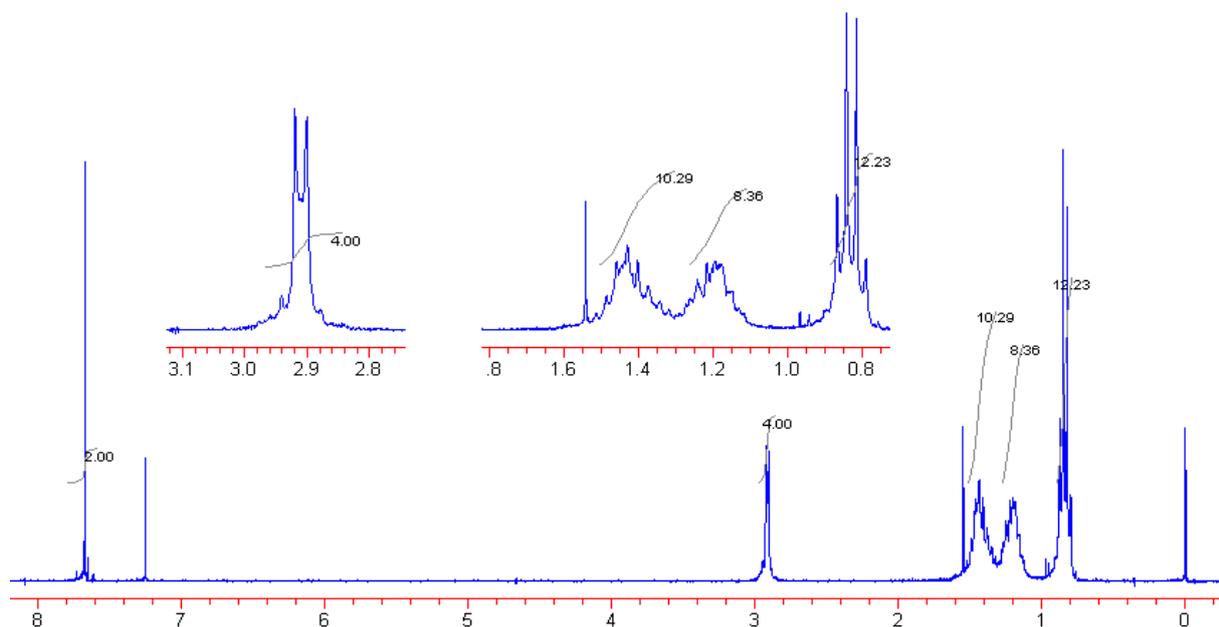


Fig. S11 ^1H NMR spectrum of 2,6-dibromo-4,8-bis(2-ethylhexylthio)benzo[1,2-b:4,5-b']dithiophene (**7**)

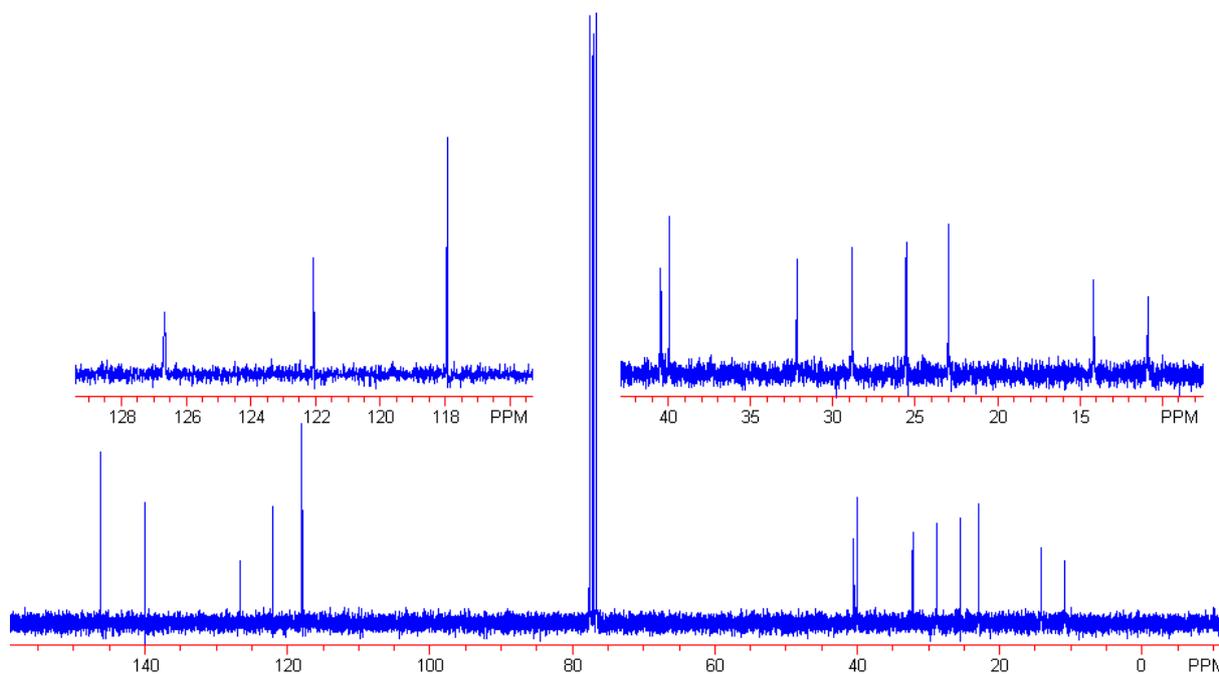


Fig. S12 ^{13}C NMR spectrum of 2,6-dibromo-4,8-bis(2-ethylhexylthio)benzo[1,2-b:4,5-b']dithiophene (**7**)

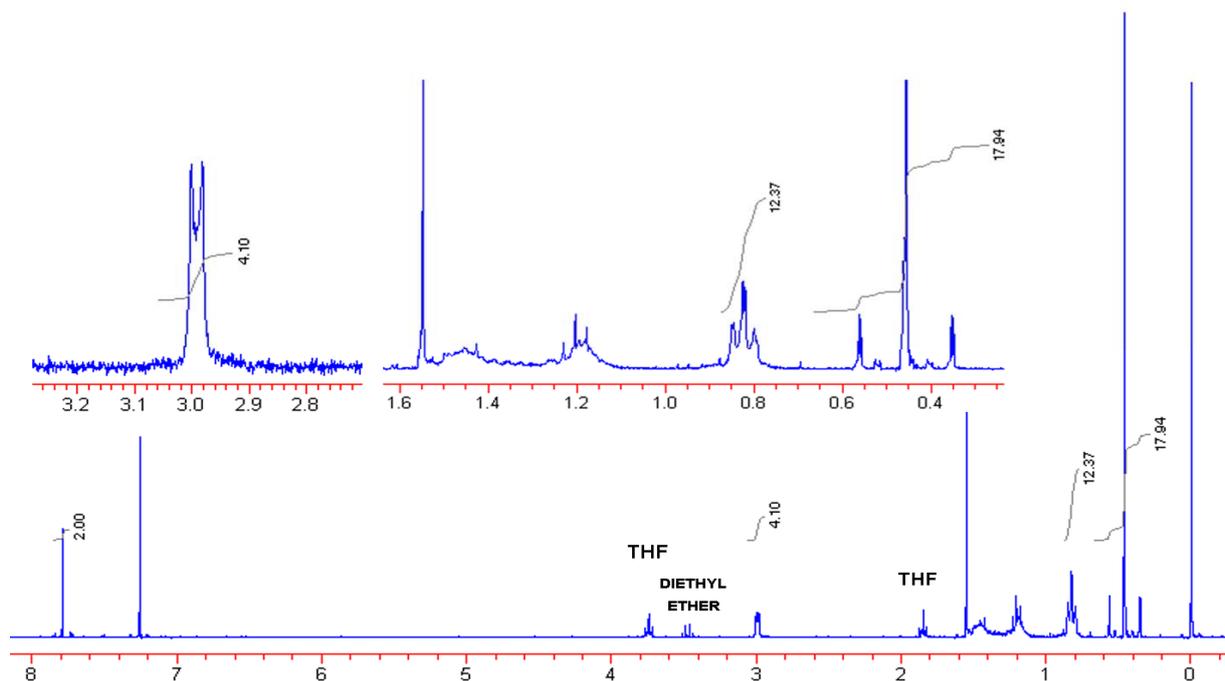


Fig. S13 ^1H NMR spectrum of 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexylthio)benzo[1,2-b:4,5-b']dithiophene (**8**)

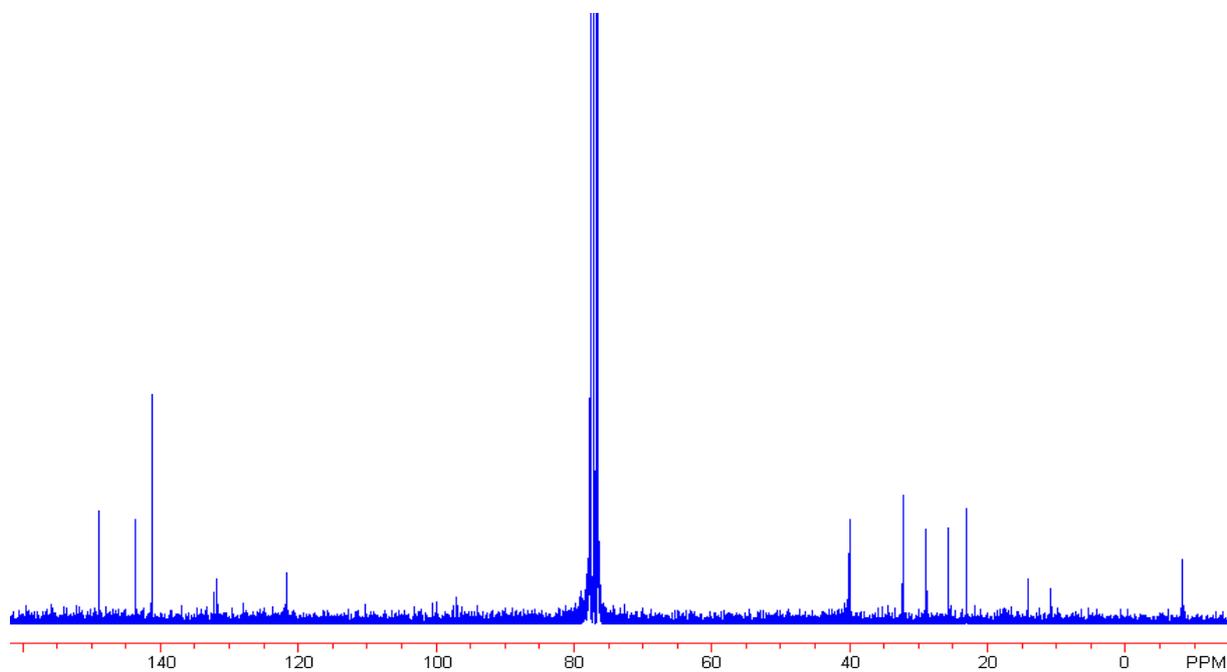


Fig. S14 ^{13}C NMR spectrum of 2,6-bis(trimethylstannyl)-4,8-bis(2-ethylhexylthio)benzo[1,2-b:4,5-b']dithiophene (**8**)

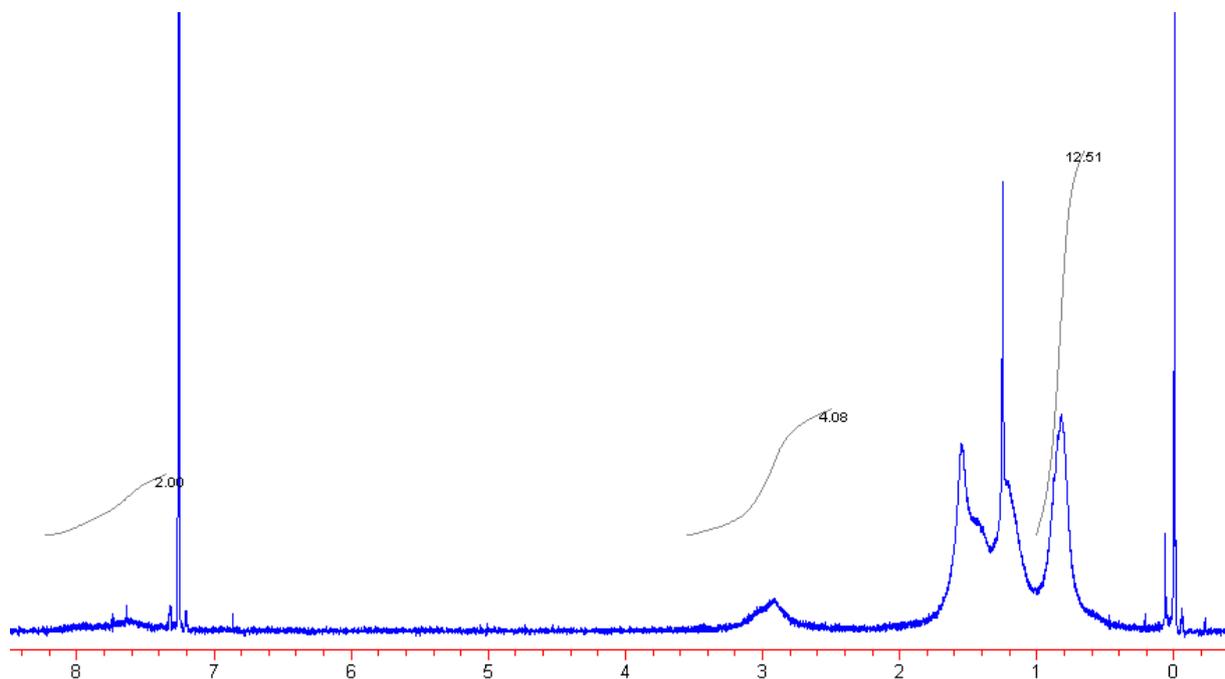


Fig. S15 ^1H NMR spectrum of S-PBDT polymer

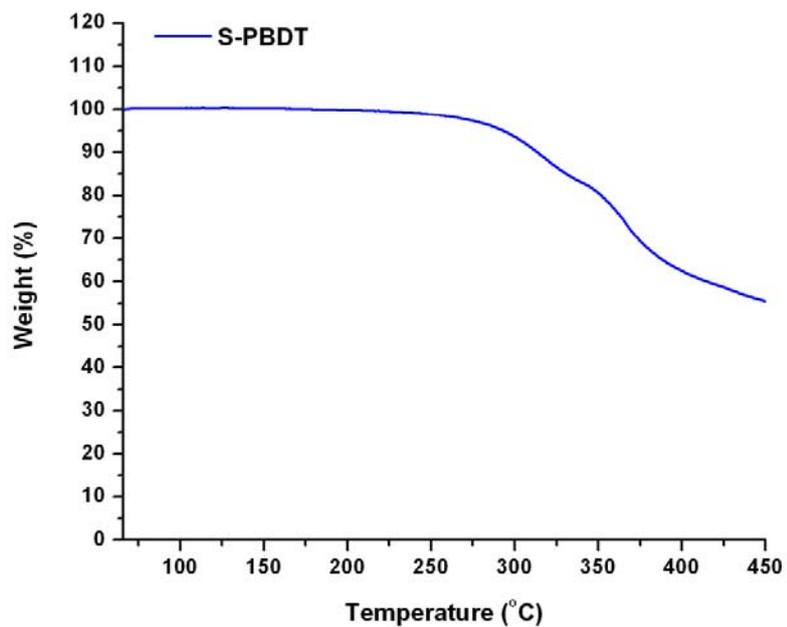


Fig. S16 TGA plot of S-PBDT polymer with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under inert atmosphere

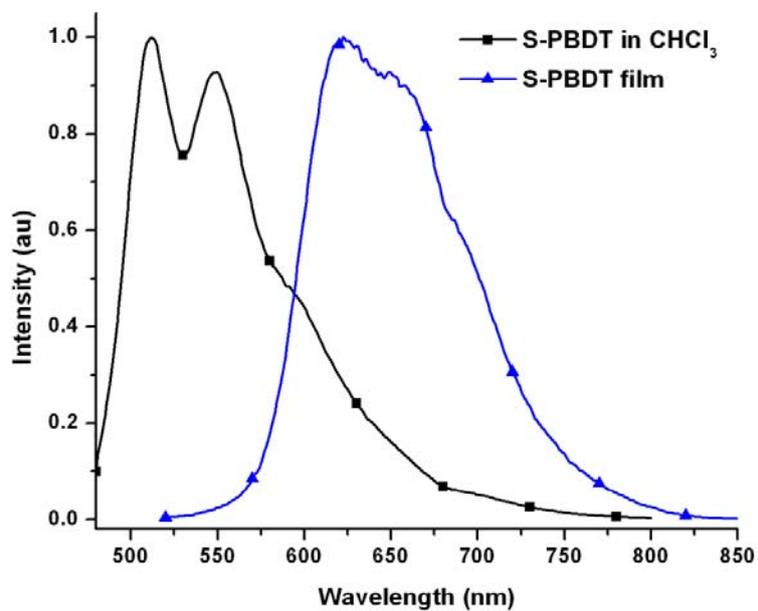


Fig. S17 Photoluminescence spectrum of S-PBDT polymer in chloroform (excitation wavelength of 470 nm) and in the solid state (excitation wavelength of 490 nm)

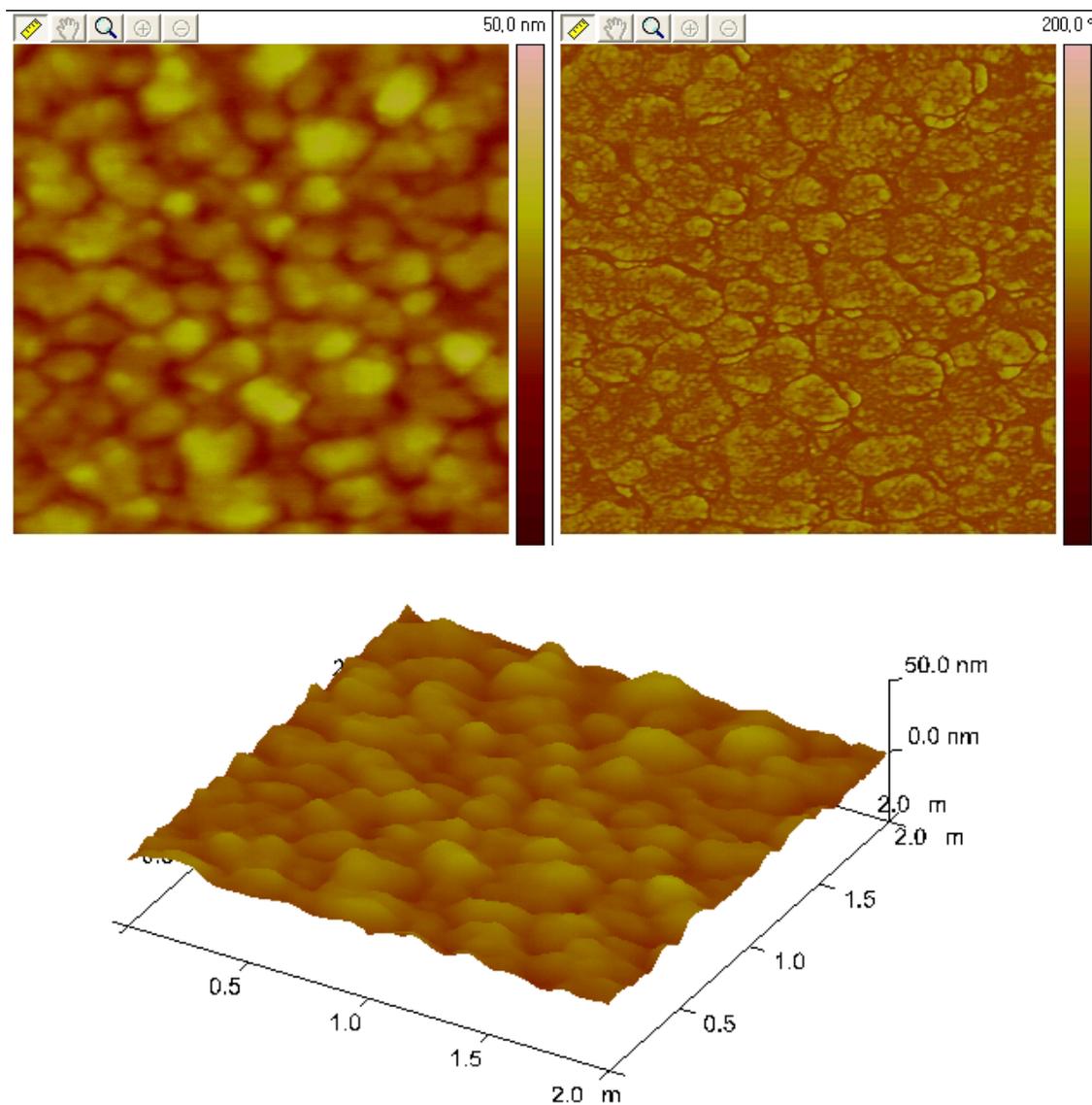


Fig. S18 The AFM tapping mode height (top left) and phase (top right) images (2 μ m x 2 μ m) of S-PBDT:PCBM (1:2) film and 3D height image(bottom)

Device Fabrication. The S-PBDT polymer and PCBM were codissolved in *o*-dichlorobenzene in the weight ratios from 1:1, 1:2 and 1:3, respectively. The concentration of the solution mixture of polymer and PCBM was 30 mg/mL in total. The polymer solar cells were fabricated by spin-casting of the polymer active layer sandwiched between a transparent indium tin oxide (ITO) anode and an aluminum metal cathode. Before fabrication of device, the ITO-coated glass substrates (about 15 Ω/\square with > 85 % light transmission) were patterned by photolithography and cleaned in ultrasonic bath in acetone, toluene, methanol, acetone and isopropyl alcohol sequentially.

Polyethylenedioxythiophene/polystyrenesulphonate (PEDOT/PSS, H.C. Starck) was spin-coated onto the patterned ITO substrate (21 x 21 mm²) at 3000 rpm for 40 s to create a ca. 30 nm thick layer. The substrate was dried at 150 °C for 10 min in a N₂ filled glove box. The active layer was spun cast onto the ITO/PEDOT:PSS substrate without further special treatments at various spin rates. Calcium (10 nm) and aluminum (100 nm) layers were then deposited under high vacuum (<10⁻⁶ torr). The active area (9 mm²) of device was defined by shadow mask. Ambios XP-1 stylus profilometer was used to measure film thickness.

Current-Voltage Measurements. The PSC devices were tested in a N₂ filled glove box. The current density-voltage (*J-V*) curves were measured with a Keithley 2400 source-measure unit and Spectra Physics 91160 solar simulator fitted with Oriel AM 1.5G filter. NREL calibrated silicon solar cell fitted with a KG-5 filter (Newport M465440) was used to calibrate the solar simulator to 100 mW/cm² AM1.5G illumination.

External quantum efficiencies (EQEs) were measured by using a lock-in amplifier (SR830, Stanford Research Systems) under short-circuit conditions. The devices structure was ITO/PEDOT:PSS(30nm)/Active layer/Al(100nm). The devices were illuminated by monochromatic light from a xenon lamp passing through a monochromator (Cornerstone 74000, Oriel Instruments) with a typical intensity of 30mW/cm². Prior to incident on the device, the monochromic incident beam is chopped with a mechanical chopper connected to the lock-in amplifier and then focused on the testing pixel of the device. The photocurrent signal is then detected with the SR830. A calibrated mono silicon diode with known spectral response is used as a reference.

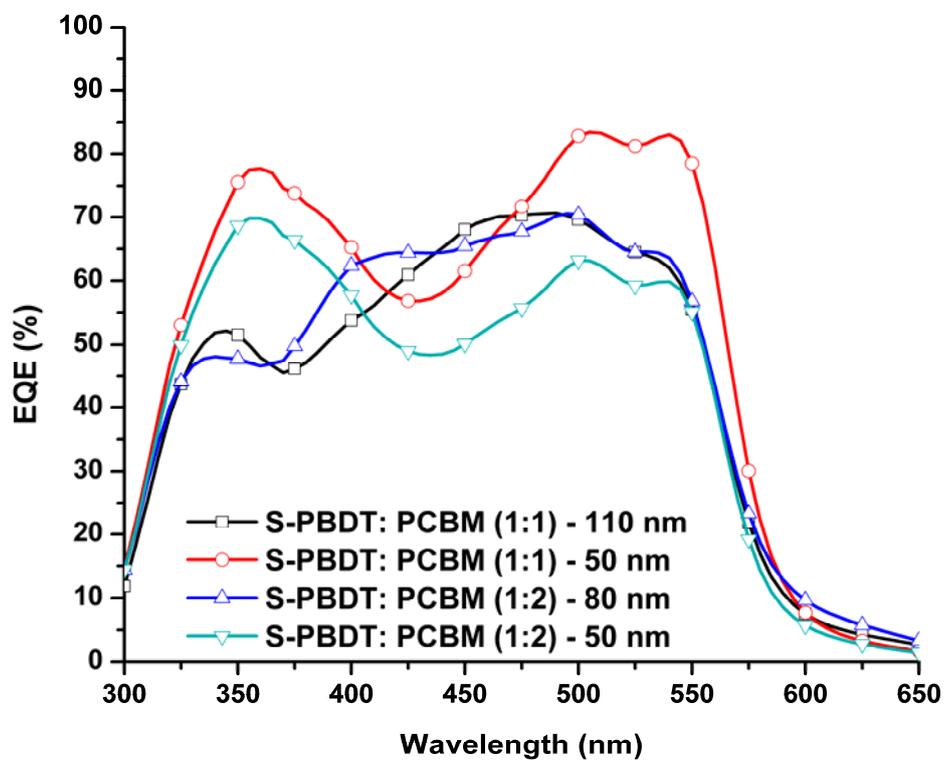


Fig. S19 External quantum efficiency of S-PBDT:PCBM with the ratio of 1:1 and 1:2.

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