

Supporting Information

Low band gap dithieno[3,2-*b*:2',3'-*d*]silole-containing polymers, synthesis, characterization and photovoltaic application

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Experimental

Materials

3,3'-Dibromo-5,5'-bis(trimethylsilyl)-2,2'-bithiophene (1) was prepared according to the adapted literature method.¹ 4,7-Bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (M2) was prepared according to the literature.² Pd(PPh₃)₄ was obtained from Aldrich Chemical Co., Hexane and tetrahydrofuran (THF) were dried over Na/benzophenone ketyl and freshly distilled prior to use. Toluene was dried over molecular sieves and freshly distilled prior to use. The other materials are common commercial level and used as received.

Instruments

¹H NMR spectra were measured on a Bruker DMX-300 spectrometer. Absorption spectra were taken on a Hitachi U-3010 UV-Vis spectrophotometer. Photoluminescence spectra were measured using a Hitachi F-4500 spectrophotometer. The molecular weight of polymers was measured by GPC method, and polystyrene was used as a standard. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with Pt disk, Pt plate, and Ag/Ag⁺ electrode as working electrode, counter electrode and reference electrode respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution.

Synthesis

4,4'-Bis(2-ethylhexyl)-5,5'-bis(trimethylsilyl)-dithieno[3,2-b:2',3'-d]silole.(2)

Compound 1 (4.68g, 10mmol) was dissolved into 60 ml THF in a two-neck round at -78°C under argon protection. butyllithium (7.6 ml, 2.9 mol/L in hexane) was added dropwise in 5 minutes, and the reactant was stirred for another 30 minutes at the same temperature. Subsequently, dichlorodi(2-ethylhexyl)silane (3.9 g, 12 mmol) was added in one portion, and the cooling bath was removed and the reactant was stirred for 2h under ambient temperature. Then, the solution was poured into water and extracted by ethyl ether twice. The solvent were removed under vacuum. The residue was purified by silica gel chromatography using hexane as eluent to obtain compound 4 as light-yellow oil (3.26 g, yield 58%). GC-MS: $m/z = 562$. ^1H NMR (CDCl_3 , 400MHz), δ (ppm): δ 7.06(s, 2H), 1.71(quintuple, 2H), 1.51-1.14(m, 16H), 0.91(t, 6H), 0.85(t, 6H), 0.76(m, 4H), 0.31(s, 18H); ^{13}C NMR (CDCl_3 , 100MHz), δ (ppm): δ 154.13, 144.46, 140.68, 136.72, 35.79, 35.56, 28.94, 28.80, 23.09, 17.60, 14.10, 10.77.

4,4'-Bis(2-ethylhexyl)- 5,5'-dibromo-dithieno[3,2-b:2',3'-d]silole. (3)

Compound 2 (1.69g, 3mmol) was dissolved into 20 ml THF, and N-bromosuccinimide (1.1g, 6.17mmol) was added in one portion. The reactant was stirred at ambient temperature for 2 hours, and then extracted by diethyl ether. The solvent were removed under vacuum, and the residue was purified by silica gel chromatography using hexane as eluent. Compound 5 was obtained as light-yellow oil (1.37g, 2.9mmol, 96%). GC-MS: $m/z = 574$. ^1H NMR (CDCl_3 , 400MHz), δ (ppm): δ 6.97(s, 2H), 1.72(quintuple, 2H), 1.51-1.13(m, 16H), 0.91(t, 6H), 0.83(t, 6H), 0.76(m, 4H). ^{13}C NMR (CDCl_3 , 100MHz), δ (ppm): δ 148.59, 141.95, 132.28, 111.36, 35.81, 35.59, 28.87, 28.83, 22.96, 17.48, 14.13, 10.79.

4,4'-Bis(2-ethylhexyl)-5,5'-bis(trimethyltin)-dithieno[3,2-b:2',3'-d]silole. (M1)

Compound 3 (1.2g, 2.51mmol) and 20ml anhydrous THF were put into a flask and cooled to -78°C . Subsequently, butyllithium (1.9 ml, 2.9 mol/L in hexane) was added

dropwise. After stirring at -78°C for 30 minutes, 7ml trimethyltin chloride was added in one portion, and then the cooling bath was removed. After the reaction temperature warm up to ambient temperature, the reaction was stirred for another 1h and then was poured into water and extracted by diethyl ether for twice. After removing solvent, M2 was obtained as sticky pale green oil (1.78g, yield 95.6%) and used to next step without any further purification. ^1H NMR (CDCl_3 , 400MHz), δ (ppm): δ 7.03(s, 2H), 1.68(m, 2H), 1.4-1.13(m, 16H), 0.90(t, 6H), 0.83(t, 6H), 0.74(m, 4H), 0.33(t, 18H). ^{13}C NMR (CDCl_3 , 100MHz), δ (ppm): δ 154.65, 143.88, 137.91, 137.40, 35.90, 35.60, 28.96, 28.87, 23.02, 17.80, 14.21, 10.85, -8.17.

General synthetic procedure of PSiDTBT6, PSiDTBTEH and PSiDTBT12 by Stille reaction.

The polymers were prepared by a similar procedure of coupling 4,7-Bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (**M2**) and monomers of **M1** with different alkyl side chains respectively. 1.0 mmol of **M1** was put into a three-neck flask. Then 15 mL of degassed toluene and 1.0 mmol of **M2** were added under the protection of argon. The solution was flushed with argon for 10 min, and then 30 mg of $\text{Pd}(\text{PPh}_3)_4$ 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. The yield, ^1H -NMR and molecular weight of polymers are as follows:

Poly[(4,4'-dihexyl-dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl] PSiDTBT6: deep blue solid power, Yield: 72%.
Poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl] PSiDTBTEH: deep blue-green power, Yield: 44%. ^1H -NMR 400 MHz, CDCl_3) 8.86-6.32 (br, 8H), 2.04-1.66 (br, 4H), 1.55-0.73 (m, 30H). $M_w = 8.0\text{K}$, $M_n = 6.7\text{K}$, poly dispersity = 1.2.

Poly[(4,4'-didodecyl-dithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazole)-5,5'-diyl] **PSiDTBT12**: deep blue-green power, Yield: 57%. $^1\text{H-NMR}$ 400 MHz, CDCl_3) 8.68-6.13 (br, 8H), 2.01-1.58 (br, 4H), 1.33-0.74 (m, 46H). $M_w = 13.3\text{K}$, $M_n = 8.9\text{K}$, poly dispersity = 1.5.

Hole mobility measurement.

we used a device structure of ITO/PEDOT:PSS/ polymer/Au for the hole mobility measurement, based on the space-charge-limited current (SCLC) model.¹¹ The thickness of the PSiDTBTEH and PSiDTBT12 films is 73 nm and 61 nm, respectively. According to the following equation:

$\text{Ln}(JL^3/V^2) \cong 0.89(1/E_0)^{0.5}(V/L)^{0.5} + \text{Ln}(9 \epsilon \epsilon_0 \mu_0/8)$, Where μ_0 is the zero-field mobility, E_0 is the characteristic field, J is the current density, ϵ is the dielectric constant of the polymer, ϵ_0 is the permittivity of the vacuum, L is the thickness of the polymer layer, $V = V_{\text{appl}} - V_{\text{bi}}$, V_{appl} is the applied potential, and V_{bi} is the built-in potential (in this device structure, $V_{\text{bi}} = 0.2$ V). According to the equation, hole mobility can be calculated. The hole mobility obtained for the PSiDTBTEH film is ca. $6.3 \times 10^{-6} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, which is similar with that of PSiDTBT12 of $3.6 \times 10^{-6} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ under the same conditions.

Fabrication of polymer solar cell devices.

polymer solar cell devices with the structure of TO/PEDOT-PSS/polymer:PC[70]BM (1:1, w/w) /Ca/Al were fabricated under conditions as follows: After spin-coating a 30 nm layer of poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) onto a pre-cleaned indium-tin oxide (ITO) coated glass substrates, the polymer/PCBM blend solution was spin-coated. Typical concentration of the polymer/PC[70]BM(1:1, w/w) blend solution used in this study for spin-coating active layer was 10mg/ml, and chlorobenzene was used as solvent. The thickness of the active layer was ~80 nm. The devices were completed by evaporating Ca/Al metal electrodes with area of 12.5mm^2 defined by masks. Testing was done in N_2 under simulated AM1.5G irradiation (100mW/cm^2) using a xenon-lamp-based solar simulator (Oriol 96000

150W Solar Simulator) with an AM 1.5G filter (obtained from Newport Corporation).
In order to ensure accuracy, the simulated light-source and device area were calibrated
through the method in our previous work².

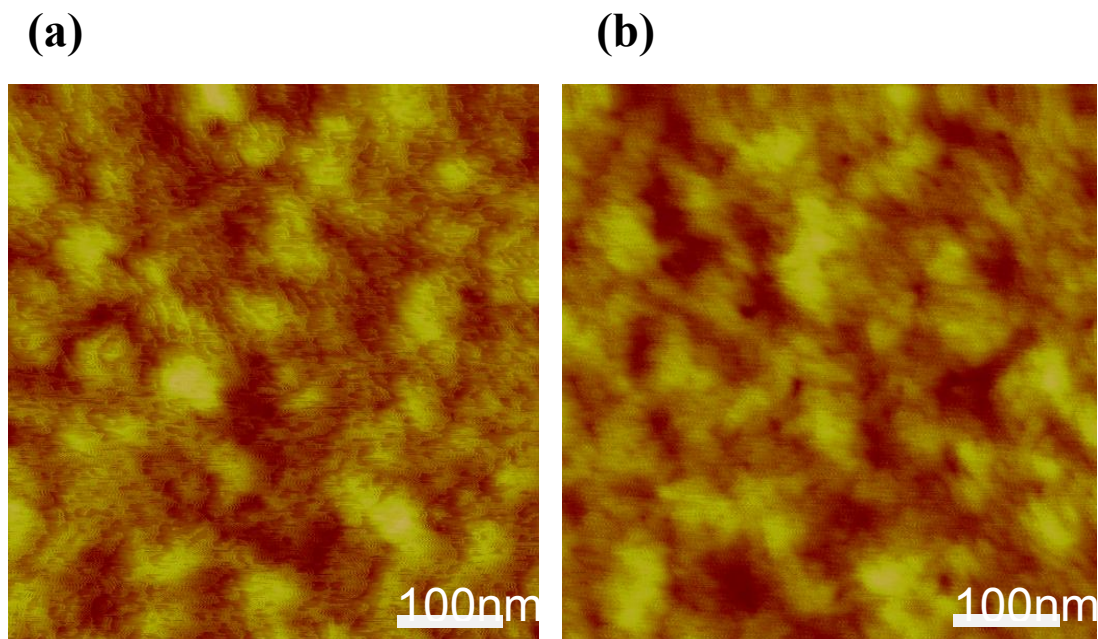


Fig 1. AFM images of the topography (a) **PSiDTBTEH / PC[70]BM** and
(b) **PSiDTBT12 / PC[70]BM**, spin-coated from chlorobenzene solution.

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