

Supporting Information

Synthesis of A Polythieno[3,4-b]thiophene Derivative with Low-lying HOMO Level and Its Application in Polymer Solar Cells

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Experimental

Materials: 2,6-Bis(trimethyltin)-4,8-diethylhexyloxybenzo[1,2-b;3,4-b]dithiophene (M2) was prepared according to the adapted literature method.¹³ 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 The synthetic route of **PBDPTT-C** is shown in Scheme 1. The detailed synthetic processes are as follows:

5,9-dimethyldec-1-yne. (1)

Lithium acetylide ethylenediamine complex (10.0g, 97.75 mmol) was suspended in dimethyl sulfoxide (125 mL) under argon protection at 0°C. 1-bromo-3,7-dimethyloctane (20.5g, 92.86 mmol) was added dropwise by a syringe over 30mins and then the temperature was warmed to room temperature and stirred overnight. After 12h, the mixture was cooled to 0°C again and water was added slowly to eliminate the excess lithium salt. Then the mixture was extracted by ethyl ether twice and the organic layer was dried over anhydrous magnesium sulfate and distilled to give colorless liquid (11.8 g, yield 76%). GC-MS: $m/z = 166$. ^1H NMR (δ/ppm , CDCl_3): 2.18 (m, 2H), 1.92 (yne-H, m, 1H), 1.55-1.12 (m, 1H), 0.86 (t, 9H), 1.71 (m, 2H), 1.29-1.20 (m, 6H), 0.95 (t, 3H). ^{13}C NMR (CDCl_3 , 100MHz), δ (ppm): 84.94, 67.92, 39.25, 36.82, 35.65, 31.92, 27.97, 24.63, 22.71, 22.61, 19.14, 16.17.

2,6,13,17-tetramethyloctadec-9-yne. (2)

To a stirred solution of 5,9-dimethyldec-1-yne (11.0 g, 66.1 mmol) in THF (100 mL), a solution of n-butyl lithium (23mL, 66.1 mmol, 2.87M) was added dropwise at -25°C under argon protection. after the mixture was stirred for 20mins at -25°C, anhydrous hexamethylphosphoramide (23.7 g, 132.2 mmol) was added, followed by a dropwise addition of a solution of 1-bromo-3,7-dimethyloctane (13.2 g, 59.5 mmol) in THF (50mL). The mixture was remained at -25°C for an additional 2h, then stirred overnight at room temperature. After 14h, the mixture was

poured into ice water, followed by extraction with ethyl ether. After removal of solvents, the afforded residues was purified by column chromatography on silica gel with hexane as eluent to give colorless liquid (12.74 g, yield 70%). GC-MS: $m/z = 306$. ^1H NMR (δ/ppm , CDCl_3): 2.14 (m, 4H), 1.55-1.13 (m, 20H), 0.86 (m, 18H). ^{13}C NMR (CDCl_3 , 100MHz), δ (ppm): 80.20, 39.28, 36.89, 36.35, 31.95, 27.98, 24.67, 22.72, 22.63, 19.25, 16.54.

3,3'-diiodo-2,2'-bithiophene. (3)

3,3',5,5'-tetraiodo-2,2'-bithiophene (34.4g, 51mmol) and zinc powder (8.6g, 132mmol) were added into the mixture of methanol (350mL) and acetic acid (14ml) by portions at 0°C and stirred for 50mins at 0°C . Then the mixture was filtered and the filter cake was washed with methanol several times. The filtrate was collected and the solvent was removed and the residue was recrystallized from methanol to get white powder (9.8g, yield 45%). GC-MS: $m/z = 418$. ^1H NMR (δ/ppm , CDCl_3): 7.42 (d, 2H), 7.17 (d, 2H).

4,5-bis(3,7-dimethyloctyl)-benzo[2,1-b:3,4-b']dithiophene. (4)

3,3'-diiodo-2,2'-bithiophene (0.5 g, 1.2 mmol) and 2,6,13,17-tetramethyloctadec-9-yne (1.1 g, 3.6 mmol) and $\text{Pd}(\text{OAc})_2$ (27 mg, 0.12 mmol) were added into a flask under argon protection. Then tributylamine (0.67 g, 3.6 mmol) and anhydrous DMF (5mL) was added and warmed up to 130°C . After 12h the reaction was cooled to room temperature and pour into water and extracted by ethyl ether, the solvent was removed and the residue was purified by column chromatography on silica gel with hexane as eluent to get colorless stick liquid (0.35 g, yield: 62%). GC-MS: $m/z = 470$. ^1H NMR (δ/ppm , CDCl_3): 7.45 (d, 2H), 7.38 (d, 2H), 2.98(m, 4H), 1.54-1.19(m, 20H), 0.86 (m, 18H).

^{13}C NMR (CDCl_3), δ (ppm): δ 137.43, 131.67, 131.35, 123.55, 123.41, 39.37, 38.78, 36.36, 33.71, 28.03, 27.99, 24.92, 22.75, 22.65, 19.78.

2,7-dibromo-4,5-bis(3,7-dimethyloctyl)-benzo[2,1-b:3,4-b']dithiophene. (5)

NBS(2.2 g, 12.3 mmol) was added into a solution of 4,5-bis(3,7-dimethyloctyl)-benzo[2,1-b:3,4-b']dithiophene (2.4 g, 5.1 mmol) in DMF (40mL) by portions at room temperature. After 15h, the mixture was washed by water and extracted by ethyl ether and further purified by column chromatography on silica gel with hexane as eluent to get white solid (2.66 g, yield:83%). GC-MS: m/z = 628. ^1H NMR (δ /ppm, CDCl_3): 7.37 (s, 2H), 2.91(m, 4H), 1.60-1.06(m, 20H), 0.90 (t, 18H). ^{13}C NMR (CDCl_3), δ (ppm): δ 137.24, 131.55, 131.39, 126.12, 112.64, 39.35, 38.63, 37.02, 33.65, 28.07, 27.93, 24.92, 22.78, 22.70, 19.74.

2,7-bis(trimethyltin)-4,5-bis(3,7-dimethyloctyl)-benzo[2,1-b:3,4-b']dithiophene. (6)

Compound 2,7-dibromo-4,5-bis(3,7-dimethyloctyl)-benzo[2,1-b:3,4-b']dithiophene (0.57g, 0.90mmol) and 20ml anhydrous THF were put into a flask and cooled to -78°C . Subsequently, butyllithium (0.69 ml, 2.9 mol/L in hexane) was added dropwise. After stirring at -78°C for 30 minutes, trimethyltin chloride (2.2mL, 1M) 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 light yellow oil (0.68g, yield 94.5%) and used to next step without any further purification. ^1H NMR (CDCl_3 , 400MHz), δ (ppm): δ 7.52(s, 2H), 3.03(m, 4H)1.71-1.34(m, 18H), 0.90(t, 12H), 0.36(t, 18H). ^{13}C NMR (CDCl_3 , 100MHz), δ (ppm): δ 138.43, 137.07, 135.88, 131.34, 130.92, 40.27, 35.81, 32.52, 28.96, 25.77, 23.09, 14.13, 11.01, -8.08.

**poly[(4,5-bis-(3,7-dimethyloctyl)-benzo[2,1-b:3,4-b']dithiophene-2,7-diyl)-alt-(2-(2-ethyl-hexa
noyl)-thieno[3,4-b]thiophene-4,5-diyl)], PBDPTT-C.** Two Monoemrs, M1 (0.5mmol), M2
(0.5mmol), toluene (10ml) and DMF (2ml) were mixed in a 50ml two-neck flask. The reactant
was purged by argon for 5 minutes, and then 25 mg of Pd(PPh₃)₄ was added. After being purged
for 20 minutes, the reactant was heated up to 110°C under protection of inert atmosphere. After 24
hours, the sticky reactant was poured into methanol. The target polymer was precipitated as black
powder and filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction
with methanol and chloroform. The polymer was recovered from the chloroform fraction as black
solid. The solid was dried under vacuum for 1 day to get the final product. The yield was 40%.

Molecular weigh by GPC: $M_w = 16.5K$, $PDI = 2.8$.

Hole mobility measurement. We used a device structure of ITO/PEDOT:PSS/polymer:PC₇₀BM/Au for the hole mobility measurement, based on the space-charge-limited current (SCLC) model. According to the following equation: $\ln(JL^3/V^2) \cong 0.89(1/E_0)^{0.5}(V/L)^{0.5} + \ln(9\varepsilon\varepsilon_0\mu_0/8)$, 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.

Device fabrications

Polymer solar cell devices with the structure of ITO/PEDOT-PSS/Polymers:PC₇₀BM /Ca/Al were fabricated under conditions as follows: After spin-coating a 30 nm layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) onto a pre-cleaned indium-tin oxide (ITO) coated glass substrates, the polymer/PCBM blend solution was spin-coated. The typical concentration of the blend solution used in this study for spin-coating the active layer was 10 mg/ml, and dichlorobenzene was used as the solvent. The thickness of the active layer was ~80 nm. The devices were completed by evaporating Ca/Al metal electrodes with an area of 12.5 mm² as defined by masks.

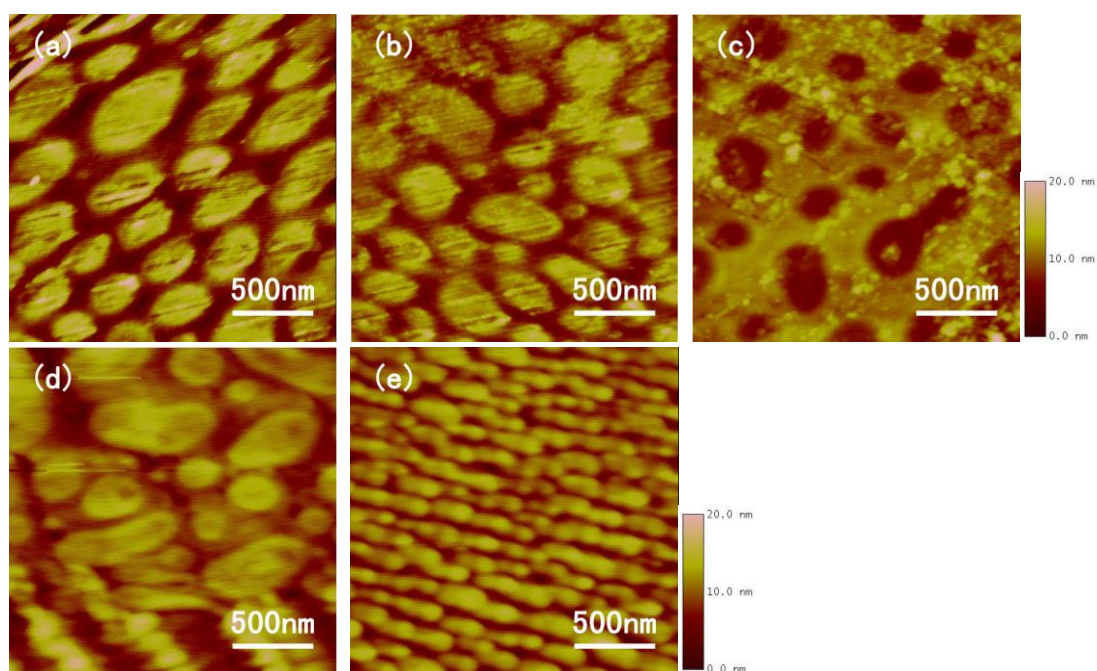


Fig. 1 AFM images ($2 \times 2 \mu\text{m}^2$) of the active layers from PBDPTT-C:PC₇₀BM with weight ratio: (a)1:1; (b) 1:2; (c) 1:3; (d) 1:2, annealed; (e) 1:2, additive (3% DIO).