Supporting Information

New benzotrithiophene derivative with broad band gap for high performance polymer solar cells

Xiaoli Zhao,^{a,b,c} Dalei Yang,^{a,d} Hongying Lv^{a,b,c} Li Yin^d and Yang Xiaoniu^{a,b}*

^a Polymer Composites Engineering Laboratory, Changchun Institute of Applied

Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, P.

R. China

^b State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of

Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun

130022, P.R. China.

^c Graduate School of the Chinese Academy of Sciences, Beijing 100049, P.R.

China

^d Changchun University of Technology, Changchun 130012, P.R. China

*Corresponding author. E-mail: <u>xnyang@ciac.jl.cn</u>

Material and characterization.

All reagents were used as received without any purification unless otherwise stated. Chlorobenzene (CB, anhydrous, 99+ %) and 1,8-diiodoctane (DIO) were purchased from Sigma-Aldrich Company. PC71BM was purchased from American Dye Source Inc. ¹HNMR spectra were recorded on a Bruker AV-400MHz spectrometer in CDCl₃ $(^{1}H, \delta; 7.26 \text{ ppm})$ with TMS as the internal standard. The starting materials, C11C12 chains grafted BTT^{1, 2} and C6 chain grafted bithiazole^{3, 4}, were synthesized according to the references reported previously, respectively. The number-average molecular weight (Mn) was determined by gel permeation chromatography (GPC) using 1,2,4-trichlorobenzene as eluent at 120°C with a PL-GPC220 instruments. The obtained molecular weight is calibrated with the polystyrene standard. Thermogravimetric analysis (TGA) was investigated using a METTLER TOLEDO TGA/DSC1/1100 LF apparatus operated at a heating rate of 10 °C/min under a N₂ atmosphere. Ultraviolet Photoelectron Spectroscopy (UPS) measurements were performed on a VG ESCALAB using He-I discharge lamp. UV-Vis absorption spectra were taken on a Lambda 750 spectrometer (Perkin-Elmer). The TEM images were acquired with a JEOL JEM-1011 transmission electron microscope operated at an acceleration voltage of 100KV. Surface morphology of the films was observed on an Agilent 5500 AFM by tapping mode in an ambient atmosphere.

Fabrication of polymer solar cells

Polymer solar cells (PSCs) were fabricated under nitrogen conditions with standard device structure of indium-tin oxide (ITO)/poly(ethylenedioxythiophene)(PEDOT):poly(styrenesulfonate)(PSS)/copolyme r:PC₇₁BM/LiF/Al. The PEDOT:PSS layer with ~30 nm of thickness and photoactive layer with ~100 nm of thickness were prepared by spin-coating method, among them, copolymer/PC₇₁BM blend solutions (10mg/mL: 10mg/mL) were made in CB or CB/DIO (1-3vol.%) mixture solvent. The solar cells were completed by evaporation of a layer of LiF(1nm)/Al (100nm) electrodes with an area of 9 mm², as defined by a shadow mask.

Synthesis

2,8-Bis(trimethylstannyl)-5-(2-undecyl-tridecyl)benzo[1,2-b:3,4-b':5,6-d"]trithio phene (BTT-distannylated) (Scheme S1)

5-(2-undecyl-tridecyl)benzo[1,2-b:3,4-b':5,6-d'']trithiophene (0.5 g, 0.86 mmol) was dissolved in 70 mL of anhydrous THF and cooled to -78°C. 1.07 mL (0.86 mmol) of n-butyl lithium solution in hexane (1.6 mol/L) was added slowly to the reaction mixture. After one hour of stirring at low temperature, (1.1 mL, 1.1 mmol) trimethyltin chloride in hexane solution (1 mol/L) were added in one portion and the reaction mixture was allowed to warm to room temperature. The mixture was poured into water and extracted with diethyl ether (3×100mL). The organic phase was dried with MgSO₄. After solvent evaporation under high vacuum, BTT-distannylated was obtained as colorless oil and used without further purification. (703 mg, 90%). ¹H NMR (400 MHz, CDCl₃): δ 7.77 (s, 1H), 7.61 (s, 1H), 7.46 (s, 1H), 3.0 (m, 1H), 1.6 (m, 4H), 1.2 (m, 38H), 0.87 (t, 6H), 0.47 (d, 18H) (Figure S1)

5,5'-Dibromo-4,4'-dihexyl-2,2'-bithiazole (BTz-dibromo) (Scheme S2)

Bithiazole (1 g, 2.97 mmol) and N-bromosuccinimide (1.5 g, 8.43 mmol) were dissolved in a mixture of 10 mL glacial acetic acid and 10 mL N-dimethylformamide.

After 12 h of stirring in the dark at room temperature, the mixture was poured into water and extracted with CH₂Cl₂ (3×100 mL). The organic phase was dried with MgSO₄. After solvent evaporation, the crude product was purified by silica gel chromatography using hexane/CH₂Cl₂=3:1 as eluent to give the dibromo product (1.15g, 82%). ¹H NMR (400 MHz, CDCl3): δ 2.72 (t, 4H), 1.70 (m, 4H), 1.42 - 1.26 (m, 12H), 0.89 (t, 6H) (Figure S2).

Poly[benzo[1,2-b:3,4-b':5,6-d"]trithiphene-alt-4,4'-dihexyl-2,2'-bithiazole] (BTT-BTz)

BTT-distannylated (0.703 g, 0.77 mmol) and BTZ-dibromo (0.38 g, 0.77 mmol) were dissolved in 150mL of anhydrous toluene. The mixture was purged by argon for 15 min, then Pd₂(dba)₃ (18.4 mg) and P(o-Tolyl)₃ (48.9 mg) were added. After being degassed with argon for another 15 min, the reaction medium was then heated and allowed to stand at 110 °C under argon for 24h. The crude product was end-capped with 2-bromothiophene (20 μ L) and 2-(tributylstannyl)-thiophene (20 μ L) and subsequently the reaction medium precipitated into methanol. The mixture was collected by filtration, and purified by Soxhlet extraction using methanol, acetone, hexane, tetrahydrofuran and chloroform. The pure polymer was recovered from chloroform and dried (vacuum) to afford the BTT-BTz (600 mg, 85%) as dark purple solid. ¹H NMR (400 MHz, CDCl₃): δ 7.6-6.5 (br, 3H), 3.2-3.0 (br, 1H), 2.7-0.5 (br, 48H) (Figure S3). GPC: Mw=42K, Mn=23K, Mw/Mn=1.8.



Scheme S1. Synthesis of BTT-distannylated monomer.

Scheme S2. Synthesis of BTz-dibromo monomer.





Fig. S1. ¹H NMR spectrum of BTT-distannylated monomer.



Fig. S2. $^1\!\mathrm{H}$ NMR spectrum of BTz-dibromo monomer.



Fig. S3. ¹H NMR spectrum of BTT-BTz copolymer.



Fig. S4. TGA thermogram of BTT-BTz copolymer.



Fig. S5. UPS curve of BTT-BTz copolymer film.

Notes and references

- C. B. Nielsen, J. M. Fraser, B. C. Schroeder, J. Du, A. J. P. White, W. Zhang and I. McCulloch, Org. Lett., 2011, 13, 2414-2417.
- 2 B. C. Schroeder, C. B. Nielsen, Y. J. Kim, J. Smith, Z. G. Huang, J. Durrant, S. E. Watkins, K. Song, T. D. Anthopoulos and I. McCulloch, *Chem. Mat.*, 2011, **23**, 4025-4031.
- 3 J. Lee, B. J. Jung, S. K. Lee, J. I. Lee, H. J. Cho and H. K. Shim, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 1845-1857.
- 4 M. Zhang, H. Fan, X. Cuo, Y. He, Z. Zhang, J. Min, J. Zhang, G. Zhao, X. Zhan and Y. Li, *Macromolecules*, 2010, **43**, 5706-5712.