

Benzothiadiazole Based Conjugated Polymers for High Performance Polymer Solar Cells

Xue Gong, Guangwu Li, Cuihong Li,^{} Jicheng Zhang and Zhishan Bo^{*}*

Beijing Key Laboratory of Energy Conversion and Storage Materials, College of
Chemistry, Beijing Normal University, Beijing 100875, China

Email Addresses: licuihong@bnu.edu.cn; zsbo@bnu.edu.cn;

Experimental Part

Materials and Instruments. Unless otherwise noted, all chemicals were purchased from Aldrich or Acros and used without further purification. The catalyst precursor Pd(PPh₃)₄ was prepared according to the literature and stored in a Schlenk tube under nitrogen atmosphere. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium with benzophenone as an indicator under nitrogen atmosphere. Hexane and dichloromethane (DCM) were distilled from CaH₂. Chloroform (CF) was distilled before use. All reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC) on silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200-300 mesh). ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 spectrometer. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. Elemental analyses were performed on a Flash EA 1112 analyzer. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA2100 and Perkin-Elmer Diamond DSC

instrument, respectively, under a nitrogen atmosphere at a heating rate of 10 °C/min to record TGA and DSC curves. The gel permeation chromatography (GPC) measurements were performed at 150 °C on a PL-220 (Polymer Laboratories) chromatography connected to a differential refractometer with 1,2,4-trichlorobenzene (TCB) as an eluent. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode. The thickness of the blend films was determined by a Dektak6 M surface profilometer. The powder X-ray diffraction (XRD) patterns were collected using a PANalytical X'Pert PRO MPD diffractometer with Cu KR radiation. The electrochemical behavior of the polymers was investigated using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 M Bu₄NPF₆ solution in CH₃CN at room temperature under an atmosphere of nitrogen with a scanning rate of 0.1 V/S. A Pt plate working electrode, a Pt wire counter electrode, and an Ag/AgNO₃ (0.01 M in CH₃CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (F_c) redox system and assumption that the energy level of F_c is 4.8 eV below vacuum.

Hole mobilities of blend film measured by SCLC

Blend films were fabricated with the device configuration of ITO/PEDOT:PSS/Polymer:PC₇₁BM/Au. The conductivity of ITO was 20 Ω/□. PEDOT:PSS is Baytron Al 4083 from H.C.Starck and was filtered with a 0.45 μm polyvinylidene difluoride (PVDF) film before use. A thin layer of PEDOT:PSS was

spin-coated on top of cleaned ITO substrate at 3000 rpm/s for 60 s and dried subsequently at 130 °C for 15 min on a hotplate before transferred into a glove box. The thickness of the PEDOT:PSS layer was about 40 nm. The blend of polymers and PC₇₁BM was dissolved in 1,2-dichlorobenzene (DCB) and heated at 100 °C for overnight to ensure the sufficient dissolution, and then spin-coated onto PEDOT:PSS layer. The processing conditions are exactly same with the best condition used for solar cells. The top electrode was thermally evaporated, with a 100 nm of gold at a pressure of 10⁻⁴ Pa through a shadow mask. The measurement of devices was conducted in air without encapsulation. Dark Current-voltage characteristics were recorded using an Agilent B2902A Source in a dark circumstances with a range of 0 V to 5.0 V. The temperature while measuring the dark *J-V* curves was approximately 25 °C. The hole mobilities was calculated according to the Mott-Gurney equation:

$$\mu = \frac{8d^3}{9\epsilon_0\epsilon_r} \left(\frac{\sqrt{J}}{V} \right)^2$$

, which *d* was the thickness of active layer, ϵ_0 is the vacuum dielectric constant, ϵ_r is the relative dielectric constant of polymer.

Polymer Solar Cell Fabrication and Characterization. PSCs were fabricated with the device configuration of ITO/PEDOT:PSS/Polymer:PC₇₁BM/LiF or FN-C60/Al. The conductivity of ITO was 20 Ω/□. PEDOT:PSS is Baytron Al 4083 from H.C. Starck and was filtered with a 0.45 mm polyvinylidene difluoride (PVDF) film before use. A thin layer of PEDOT:PSS was spin-coated on top of cleaned ITO substrate at 3000 rpm/s for 60 s and dried subsequently at 130 °C for 15 min on a hotplate before transferred into a glove box. The thickness of the PEDOT:PSS layer was about 40 nm. The blend of polymers and PC₇₁BM was dissolved in 1,2-dichlorobenzene (DCB) and

heated at 100 °C for overnight to ensure the sufficient dissolution, and then spin-coated onto PEDOT:PSS layer. The top electrode was thermally evaporated, with a 0.6 nm LiF layer, then followed by 100 nm of aluminum at a pressure of 10^{-4} Pa through a shadow mask. Five cells were fabricated on one substrate with an effective area of 0.04 cm². The measurement of devices was conducted in air without encapsulation. Current-voltage characteristics were recorded using an Agilent B2902A Source Meter under an AM1.5G AAA class solar simulator (model XES-301S, SAN-EI) with an intensity of 100 mWcm⁻² as the white light source and the intensity was calibrated with a standard single-crystal Si photovoltaic cell. The temperature while measuring the *J-V* curves was approximately 25 °C.

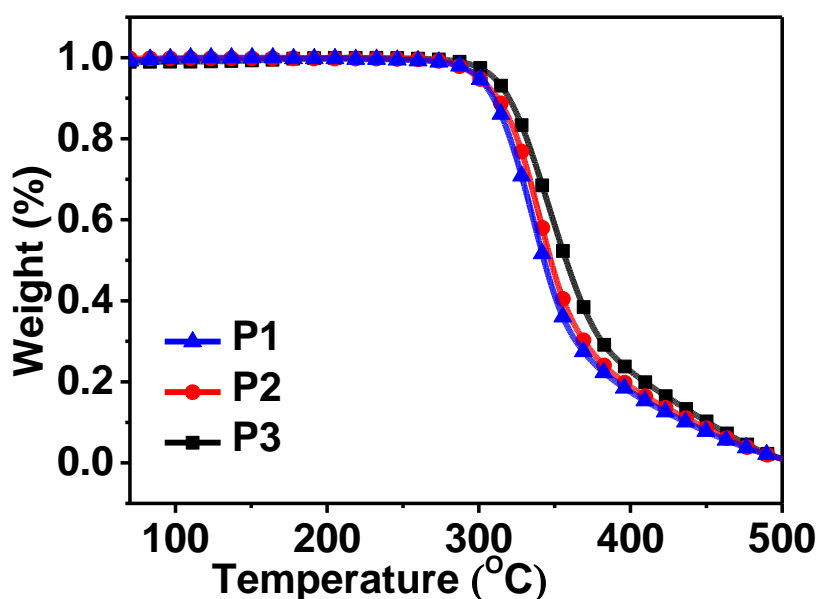


Fig. S1 TGA plots of **P1**, **P2** and **P3** with a heating rate of 10 °C/min under N₂ atmosphere.

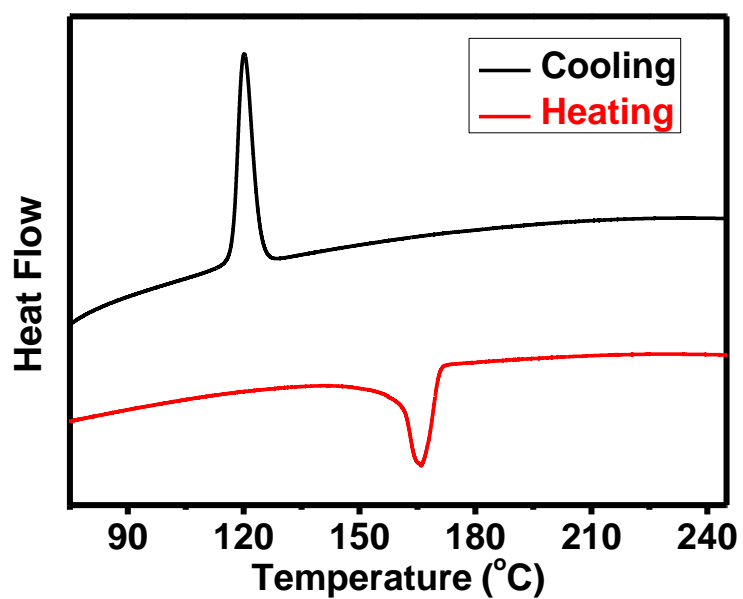


Fig. S2 DSC plot of **P3** with a heating rate of 10 °C/min under N₂ atmosphere.

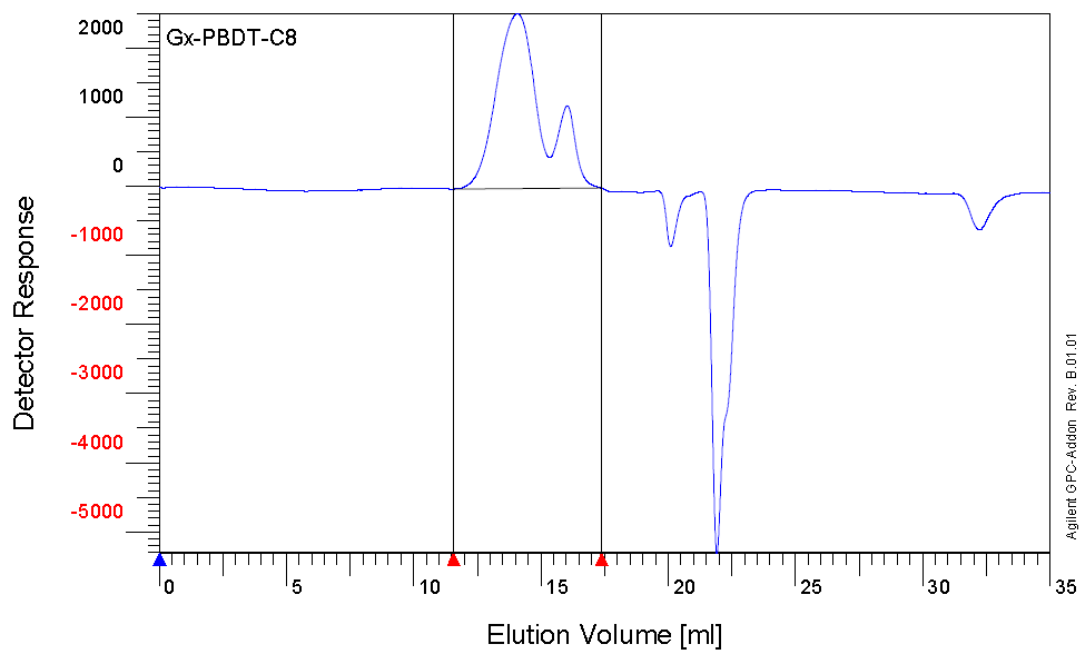


Figure S3. GPC elution curve of **P1**.

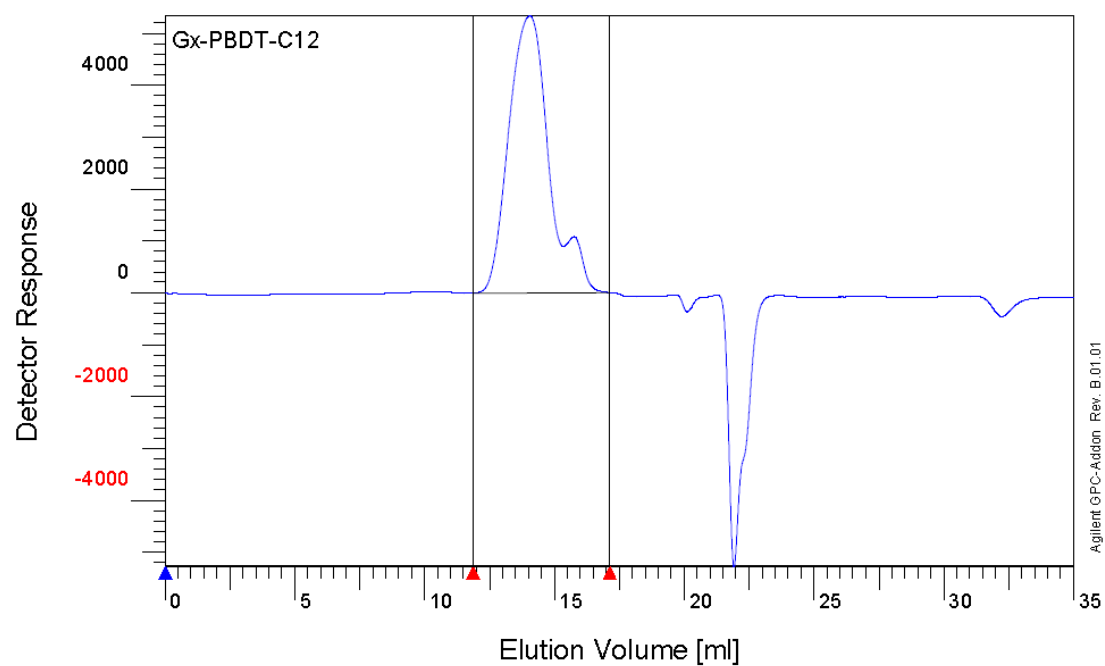


Figure S4. GPC elution curve of **P2**.

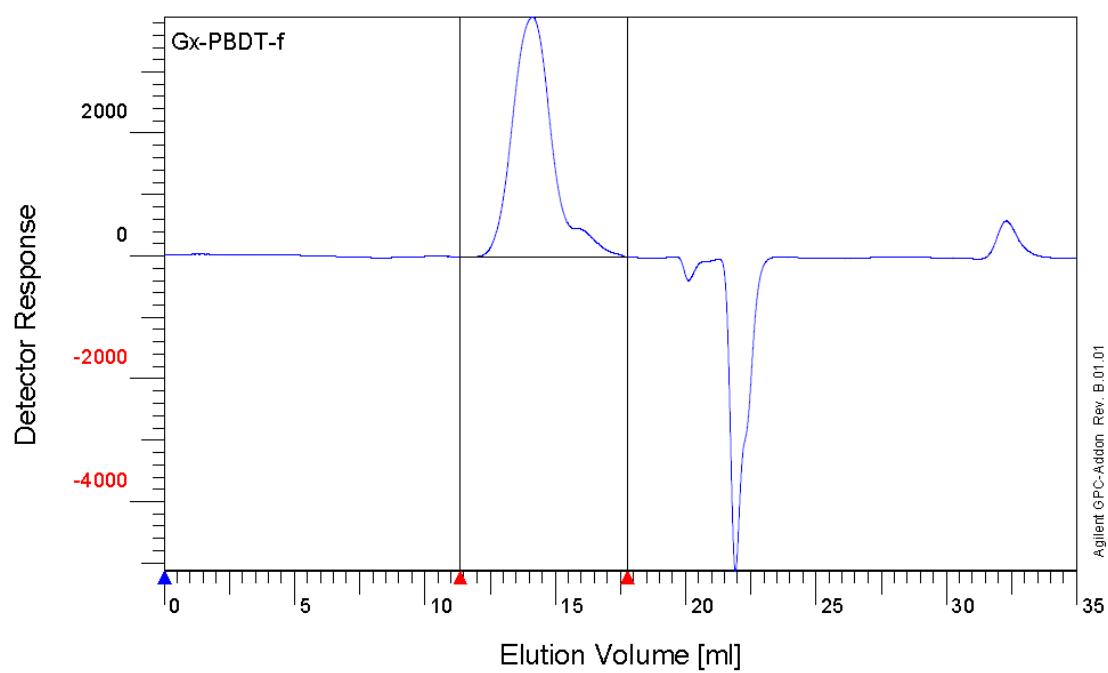


Figure S5. GPC elution curve of **P3**.

Table S1. Devices properties of P1 and P2 with or without solvent addition.

polymer	Solvent	Voc [V]	Jsc [mA/cm ²]	FF	PCE [%]
P1	DCB	0.74	11.60	0.63	5.4
P1	DCB+2% DIO	0.73	10.87	0.63	5.0
P2	DCB	0.76	11.26	0.72	6.1
P2	DCB+2% DIO	0.75	11.13	0.72	6.0

Table S2. Devices properties of **P3** and **P2** with different thick active layers.

P3, DCB + 2% DIO	89 nm	PCE (%) (Average)	Standard deviation	PCE (%)	J_{sc} (mA/cm²)	V_{oc} (V)	FF
		7.11	0.19	7.02	11.78	0.82	0.73
				6.94	11.59	0.81	0.74
				7.36	12.38	0.81	0.73
				7.40	12.28	0.82	0.73
				6.96	11.80	0.81	0.73
				6.97	11.68	0.81	0.74
P3, DCB + 2% DIO	180 nm	PCE (%) (Average)	Standard deviation	PCE (%)	J_{sc} (mA/cm²)	V_{oc} (V)	FF
		7.33	0.17	7.27	13.18	0.80	0.69
				7.61	13.71	0.80	0.70
				7.13	13.24	0.80	0.68
				7.41	13.37	0.79	0.70
				7.24	13.15	0.80	0.69

P3, DCB + 2% DIO	250 nm	PCE (%) (Average)	Standard deviation	PCE (%)	J_{sc} (mA/cm²)	V_{oc} (V)	FF
		7.61	0.10	7.58	14.28	0.79	0.67
				7.61	14.08	0.79	0.69
				7.43	14.33	0.79	0.66
				7.75	14.33	0.79	0.69
				7.54	14.31	0.78	0.67
				7.69	14.38	0.79	0.67
				7.67	14.29	0.79	0.68
				7.50	14.31	0.79	0.67
				7.73	14.42	0.78	0.68
P3, DCB + 2% DIO	378 nm	PCE (%) (Average)	Standard deviation	PCE (%)	J_{sc} (mA/cm²)	V_{oc} (V)	FF
		7.03	0.23	7.25	14.62	0.79	0.62
				6.74	15.14	0.80	0.55
				6.86	14.88	0.80	0.58
				7.25	15.12	0.80	0.60
P3, DCB+ 2% DIO	480 nm	PCE (%) (Average)	Standard deviation	PCE (%)	J_{sc} (mA/cm²)	V_{oc} (V)	FF
		6.38	0.19	6.31	14.26	0.79	0.56
				6.64	14.84	0.79	0.57
				6.34	14.70	0.78	0.55
				6.64	14.34	0.78	0.59

				6.50	14.24	0.78	0.59
				6.21	14.19	0.78	0.56
				6.07	14.51	0.78	0.54
				6.47	14.29	0.78	0.58
				6.22	13.94	0.78	0.58
P2, DCB	217 nm	PCE (%) (Average)	Standard deviation	PCE (%)	J_{sc} (mA/cm²)	V_{oc} (V)	FF
		5.42	0.22	5.74	13.18	0.73	0.59
				5.34	12.38	0.72	0.60
				5.11	12.74	0.72	0.56
				5.60	12.79	0.72	0.61
				5.31	12.84	0.72	0.57

Standard deviation was calculated through the formula below. In this formula, σ means standard deviation, μ means the average PCE, N means the number of devices, P_i means one of measured PCEs.

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (P_i - \mu)^2}$$

Synthesis of monomer M4 and copolymers P1-3

4,8-bis(4-((2-ethylhexyl)thio)phenyl)benzo[1,2-b:4,5-b']dithiophene (2)

To a solution of (4-bromophenyl)(2-ethylhexyl)sulfane (13.31 g, 44.2 mmol) in THF at -78 °C, *n*-butyllithium (18.4 mL, 2.4 M in hexane) was added dropwise under N₂ atmosphere. After 1 hour, benzo[1,2-b:4,5-b']dithiophene-4,8-dione (3.12 g, 14.2 mmol) was added in one portion and the mixture was stirred overnight. Solution of

SnCl₂·2H₂O in 3M HCl was added to the mixture. Two hours later, CH₂Cl₂ and water were used for extraction, the organic phase was collected and dried with anhydrous MgSO₄. After removing the solvent under reduced pressure, the product was afforded by column chromatography. (3.5g, 39%). ¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, J = 8.3 Hz, 4H); δ 7.49 (d, J = 8.3 Hz, 4H); δ 7.40 (d, J = 5.7 Hz, 2H); δ 7.33 (d, J = 8.3 Hz, 2H); δ 3.03 (d, J = 6.3 Hz, 4H); δ 1.70 (m, 2H); δ 1.54 (m, 8H); δ 1.34 (m, 8H); δ 0.93 (m, 12H). ¹³C NMR (400 MHz, CDCl₃): δ 138.18, 138.14, 136.22, 136.133, 129.90, 129.76, 128.40, 127.33, 122.88, 39.00, 37.63, 32.50, 28.82, 25.73, 23.00, 14.14, 10.84. Anal. Calcd for C₃₈H₄₆S₆: C 72.33, H 7.35. Found: C 72.36, H 7.35.

(4,8-bis(4-((2-ethylhexyl)thio)phenyl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (M4)

To a solution of **1** (0.88g, 1.4mmol) in THF (50 ml), n-butyllithium (1.3 mL, 2.4 M in hexane) was added under N₂ atmosphere at -40 °C. 1 hour later, trimethyltin chloride (3.1mL, 1 M in hexane) was added and the mixture was stirred overnight. The solution was poured into 100 ml water and extracted by dimethyl ether for 3 times. The combined organic solution was dried by anhydrous MgSO₄, after removing the solvent under reduced pressure. The residue was recrystallized from hexane to get the monomer (**M4**) (1.2g, 90%) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.88 (d, J = 8.3 Hz, 4H); δ 7.86 (s, 2H); δ 7.54 (d, J = 8.3 Hz, 4H); δ 2.91 (d, J = 6.2 Hz, 4H); δ 1.70 (m, 2H); δ 1.52 (m, 8H); δ 1.32 (m, 8H); δ 1.01 (t, J = 7.0, 6H); δ 0.92 (t, J = 7.4, 6H); δ 0.25 (s, 18H). ¹³C NMR (400 MHz, CDCl₃): δ 142.43, 142.15, 137.79, 136.97, 136.89, 130.57, 129.88, 128.32, 128.29, 39.02, 37.57, 32.52, 28.83, 25.75, 23.00,

14.15, 10.85, 8.34. Anal. Calcd for $C_{44}H_{62}S_6Sn_2$: C 55.24, H 6.53. Found: C 55.24, H 6.35.

General procedures for prepare polymers P1-3

To a solution of **M4** (0.02 mmol) and **M1-3** (0.02 mmol) in a mixture solvent of toluene (10 mL) and DMF (2 mL), then $Pd(PPh_3)_4$ (5 mg) was added under N_2 atmosphere. After two days of heating at 120 °C, tributyl(thiophen-2-yl)stannane and 2-bromothiophene were successively added for end capping. Then the mixture was cooled to room temperature and poured into 50 mL methanol, the precipitated solid was subjected to Soxhlet extractor successively with methanol, acetone, dichloromethane and chloroform. The residue was further dissolved in hot 1-chlorobenzene and filtered, the polymers was recovered by participate in methanol from the corresponding solutions.

P1 was recovered from 1-chlorobenzene solutions (170 mg, 72%). Anal. Calcd for $C_{68}H_{84}N_2O_2S_7$: C 69.63, H 7.47. N 2.26. Found: C 68.71, H 7.14. N 2.30.

P2 was recovered from 1-chlorobenzene solutions (160 mg, 62%). Anal. Calcd for $C_{76}H_{100}N_2O_2S_7$: C 70.32, H 7.76. N 2.16. Found: C 69.75, H 7.66. N 2.07.

P3 was recovered from chloroform solutions (250 mg, 96%). Anal. Calcd for $C_{76}H_{99}FN_2O_2S_7$: C 70.21, H 7.68. N 2.15. Found: C 70.21, H 7.77. N 2.10.

