

# Synthesis and Characterization of Dithienylbenzobis(thiadiazole)-Based Low Band-Gap Polymers for Organic Electronics

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## Electronic Supplementary Information (ESI)

### Materials

10 All chemicals were purchased from Sigma-Aldrich unless stated otherwise. Anhydrous solvents used were stored over molecular sieves under argon. All manipulations and reactions were carried out under argon atmosphere. 4,4-Bis(2-ethylhexyl)-2,6-bis(tributylstannanyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (**1**)<sup>1</sup>, 2,7-bis(4,4,5,5-tetramethyl[1,3,2]dioxo-borolan-2-yl)-9,9-bis(2-ethylhexyl)fluorene (**2**)<sup>2</sup>, 4,7-dibromo-2,1,3-benzothiadiazole (**3**)<sup>3</sup>, 4,7-bis(5-bromo-2-thiophenyl)-benzo[*c*][1,2,5]-thiadiazole (**4**)<sup>4</sup> and 4,8-bis(5-bromo-2-thiophenyl)-2,7-*d*-[1,2-*c*:4,5-*c'*]bis[1,2,5]thiadiazole (**5**)<sup>5</sup>  
15 were synthesized according to the literature procedures.

### Instruments

<sup>1</sup>H NMR spectra were recorded on a Varian Inova-500 Instrument (500 MHz). GPC analysis was carried out on Viscotek's GPC Max with two Olexis columns (Polymer Laboratories, Varian Inc.) and TDA302 Tetrade detector Array system which contained refractive index, UV, low and right angle light scattering modules. THF was used as a carried solvent at 30°C.  
20 Thermal decomposition temperature of the prepared polymer was determined by a Netzsch Thermisch Analyser TG 209. For the thermogravimetric tests (TGA) was used with a nitrogen flow of 15 mL/min from room temperature to 300°C with a heating rate of 20°C/min. The differential scanning calorimeter (DSC) equipment used was a Netzsch DSC 204 F1. All samples were heated from 20 to 250 C with a rate of 10 C/min in a nitrogen atmosphere. The UV/vis spectra were taken in a Shimadzu spectrophotometer model NIR 3101. A potentiostat/galvanostat PAR 273A was used for the electrochemical  
25 characterization, with a three electrode cell. Working electrode (Pt), reference electrode (Ag/Ag<sup>+</sup> in acetonitrile), counter electrode (Pt), supporting electrolyte (0.1M tetrabutyl ammonium hexafluorophosphate in acetonitrile) and scanning rate 50 mV/s. Atomic force microscopy (AFM) was performed using a Digital Instruments Nanoscope IV operated in tapping mode (~ 350 kHz frequency, Si tip). X-ray diffraction of the polymers was taken on a Rigaku X-ray Diffractometer using a Cu<sub>k</sub> wavelength of 0.154 nm. An accelerating voltage of 50 kV and a current of 80 mA were used. Scans were taken from  
30 2θ = 3 ~ 60° with a step size of 0.2° and a step time of 10 min/step.

**Synthesis of poly[2,6-(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPBDT)** The compound **1** (0.98 g, 1.0 mmol) and **3** (0.29 g, 1.0 mmol) were dissolved in toluene (20 mL). After the reaction was purged with Ar<sub>2</sub>, tris(dibenzylideneacetone)dipalladium(0) (0.03 g) and triphenylphosphine (0.06 g, 0.02 mmol) were added. The mixture was refluxed for 3 days under Ar<sub>2</sub>. The solvent was removed under reduced pressure and  
35 the residue was dissolved in chloroform. The solution was dropwise dropped into stirred methanol, the blue precipitate obtained was collected with Soxhlet thimble, washed with methanol, dried, extracted in a Soxhlet extractor with acetone for

12 hours. The insoluble remainders were re-dissolved in chloroform and precipitated into MeOH. After filtration and evaporation, the solid was dried in vacuo at room temperature overnight to obtain the polymer, **PCPBTB**, as a blue solid (54% yield).  $T_g = 122^\circ\text{C}$ ;  $M_n = 12,000$ ,  $M_w = 28,000$ ,  $\text{PDI} = 2.32$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.14 (s, br, 2H), 7.89 (s, br, 2H), 2.08 (s, br, 4H), 1.04 (m, 16H), 0.88-0.74 (m, 12H), 0.68 (m, 12H). Anal. calcd. for  $(\text{C}_{31}\text{H}_{40})_n$ : C, 69.21; H, 7.55. Found: C, 69.35; H, 7.51.

**Synthesis of poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene)-*alt*-5,5-(4,8-di-2-thienyl-2,2'-[1,2-*c*:4,5-*c'*]bis[1,2,5]thiadiazole)] (PCPBBT)** The compound **1** (0.98 g, 1.0 mmol) and **5** (0.51 g, 1.0 mmol) were dissolved in dry DMF (50 mL). After the reaction was purged with  $\text{Ar}_2$ , palladium tetrakis(triphenylphosphine) (0.03 g) and triphenylphosphine (0.06 g, 0.02 mmol) were added. The reaction mixture was refluxed for 3 days. The reaction was cooled down to the room temperature and the solution was concentrated. After re-dissolving in  $\text{CHCl}_3$ , the solution was dropped into stirred MeOH to obtain a crude product. The solid was filtered, washed with methanol and dried. It was then dissolved in chlorobenzene and an aqueous solution of sodium diethyldithiocarbamate trihydrate (6.3 g in 84 mL water) was added. The mixture was stirred at  $80^\circ\text{C}$  under  $\text{Ar}_2$  for overnight. The organic layer was separated and was passed through a column packed with alumina, Celite and silica gel. The column was eluted with chlorobenzene. The combined polymer solution was concentrated and was poured into methanol. The precipitates were collected, extracted by Soxlet extractor for 8 hours in acetone solvent, dried under the vacuum at room temperature for overnight to obtain polymer, **PCPBBT**, as a brownish solid (61% yield).  $T_g = 119^\circ\text{C}$ ;  $M_n = 27,000$ ,  $M_w = 44,000$ ,  $\text{PDI} = 1.63$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500MHz):  $\delta$  8.99 (br, 2H), 7.76-6.66 (br, 4H), 1.94 (br, 4H), 1.03 (m, 16H), 0.77 (m, 10H), 0.65 (m, 4H). Anal. calcd. for  $(\text{C}_{39}\text{H}_{42})_n$ : C, 61.67; H, 5.60. Found: C, 61.70; H, 5.58.

**Synthesis of poly[2,7-(9,9-bis(2-ethylhexyl)fluorene)-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PFTBTD)** A mixture of **2** (0.64 g, 1.0 mmol), **4** (0.45 g, 1.0 mmol) and Aliquat 336 (0.04 g) was degassed three times with  $\text{Ar}_2$  before dry toluene (10 mL) was added. Tetrakis(triphenylphosphine)palladium(0) (0.01 g) and aqueous sodium carbonate solution (2 M, 3.0 mL) was added under  $\text{Ar}_2$ . The mixture was stirred vigorously and refluxed for 3 days. The highly viscous reaction mixture was re-dissolved with  $\text{CHCl}_3$  and washed with  $\text{H}_2\text{O}$ , dried with  $\text{Na}_2\text{SO}_4$ , and filtered through Celite. The solution was then concentrated and poured into hot methanol to obtain a pale-green crude polymer. The polymer was collected, extracted by Soxlet extractor for 8 hours in acetone solvent, dried under the vacuum at room temperature for overnight to obtain polymer, **PFTBTD** (49% yield).  $T_g = 88^\circ\text{C}$ ;  $M_n = 30,000$ ,  $M_w = 37,000$ ,  $\text{PDI} = 1.23$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  8.18 (s, br, 2H), 7.94 (s, br, 2H), 7.23 (s, br, 6H), 7.48 (m, 2H), 2.13 (br, 4H), 1.00-0.75 (m, 18H), 0.68 (m, 6H), 0.59 (m, 6H); Anal. calcd. for  $(\text{C}_{43}\text{H}_{48})_n$ : C, 74.79; H, 7.21. Found: C, 74.95; H, 7.02.

**Synthesis of poly[2,7-(9,9-bis(2-ethylhexyl)fluorene)-*alt*-5,5-(4,8-di-2-thienyl-2,2'-[1,2-*c*:4,5-*c'*]bis[1,2,5]thiadiazole)] (PFTBBT)** A mixture of **2** (0.64 g, 1.0 mmol), **5** (0.51 g, 1.0 mmol) and Aliquat 336 (0.04 g) was degassed three times with  $\text{Ar}_2$  before dry toluene (10 mL) was added. Tetrakis(triphenylphosphine)palladium (0.01 g) and aqueous sodium carbonate solution (2 M, 3.0 mL) was added under  $\text{Ar}_2$ . The mixture was stirred vigorously and refluxed for 3 days. The highly viscous reaction mixture was re-dissolved with  $\text{CHCl}_3$  and washed with  $\text{H}_2\text{O}$ , dried with  $\text{Na}_2\text{SO}_4$ , and filtered through Celite. The solution was then concentrated and poured into hot methanol to obtain a pale-green crude polymer. The polymer was collected, extracted by Soxlet extractor for 8 hours in acetone solvent, dried under the vacuum at room temperature for overnight to obtain polymer, **PFTBBT** (55% yield).  $T_g = 100^\circ\text{C}$ ;  $M_n = 4,600$ ,  $M_w = 11,000$ ,  $\text{PDI} = 2.39$ ;  $^1\text{H}$

NMR (CDCl<sub>3</sub>, 500 MHz): 9.05 (m, 2H), 7.89-7.57 (m, 8H), 2.11 (br, 4H), 1.00-0.76 (m, 18H), 0.75-0.52 (m, 12H). Anal. calcd. for (C<sub>43</sub>H<sub>46</sub>)<sub>n</sub>: C, 68.95; H, 6.25. Found: C, 69.13; H, 6.21.

**Polymer film morphology and microstructure** Tapping mode AFM was employed to study the surface morphology of the polymer films on glass substrates. The annealed thin films of the polymers showed a relatively smooth surface with rms roughness of 3 ~ 10 nm and maximum height within 30 nm (Figure 1). Small crystallites (~ 50 nm) were homogeneously dispersed for **PCPBTD**, **PFTBTD**, and **PFTBBT**. This result suggests an extended conjugation length from thiophene units at the core bridges provides easy crystalline packing of the polymers compared to **PCPBTD**. The microstructure of the two polymers, **PFTBTD** and **PCPBTD**, were studied by wide-angle X-ray diffraction. From the Bragg reflections shown in Figure 2, the out-of-plane *d* spacings are estimated to be 15.2 Å induced by extended alkyl chains for both polymers. In the in-plane profiles, both polymers also shows  $\pi$ - $\pi$  stacking spacing of ~ 4.0 Å indicated as (100) signals.

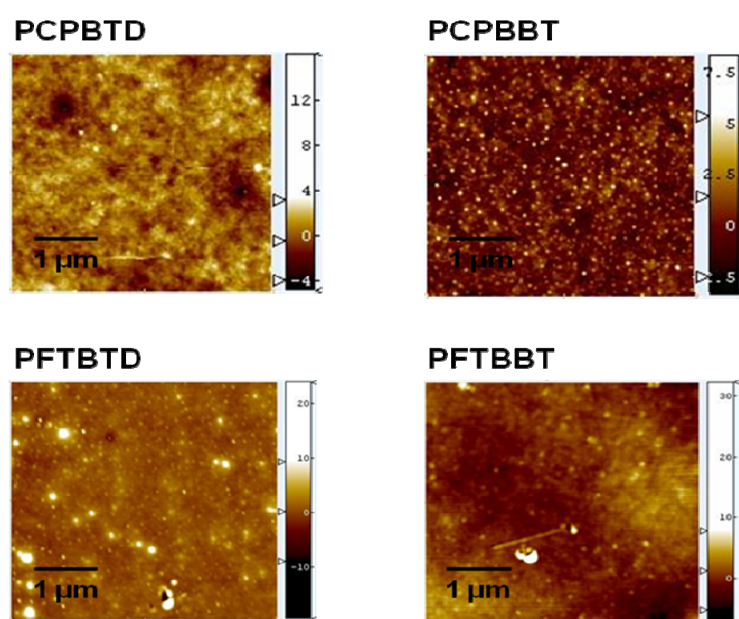


Figure 1. AFM height images (5 × 5 μm) of (a) **PCPBTD**, (b) **PCPBTT**, (c) **PFTBTD**, and (d) **PFTBBT**

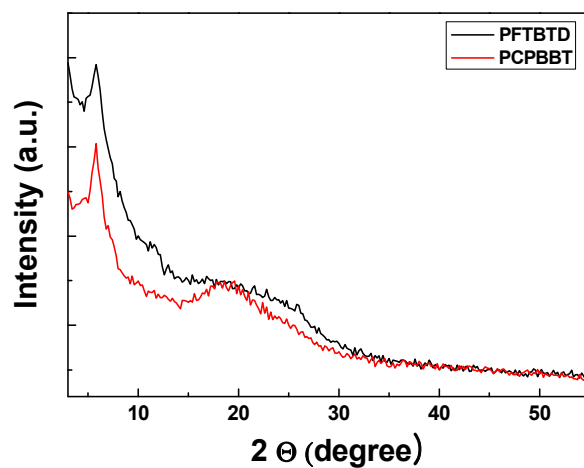


Figure 2. Wide-angle X-ray diffractions for **PFTBTD** (black line) and **PCPBBT** (red line)

## References

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