

# **Benzo[1,2-b:4,5-b']dithiophene-dioxopyloothiophene copolymers for high performance solar cells**

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## **Supplementary Information**

## Experimental section

### Instrument

Nuclear Magnetic Resonance spectra were recorded on a Mercury plus 400 MHz machine. Gel permeation chromatography (GPC) analyses were performed on a Perkin Elmer Series 200 gel coupled with UV-Vis detector using THF as eluent with polystyrene as standards. Thermogravimetric analysis (TGA) analyses were conducted with a TA instrument QS000IR at a heating rate of 20 °C min<sup>-1</sup> under nitrogen gas flow. UV-Vis absorption spectra were recorded on a Perkin Elmer model  $\lambda$  20 UV-Vis spectrophotometer. Electrochemical measurements were conducted under nitrogen in a deoxygenated anhydrous acetonitrile solution of *tetra-n*-butylammonium hexafluorophosphate (0.1 M), using a CHI 600 electrochemical analyzer. A platinum electrode was used as a working electrode, a platinum-wire was used as an auxiliary electrode, and an Ag/Ag<sup>+</sup> electrode was used as a reference electrode. Thin film of polymer was coated on platinum electrode and Ferrocene was added as an internal reference. The AFM measurements were performed on SPA300HV instrument with an SPI3800 controller (Seiko Instruments). The TEM images were obtained with a JEOL JEM-1011 transmission electron microscope operated at an acceleration voltage of 100 kV.

### The specimens for TEM measurements were fabricated as following:

A layer of PEDOT: PSS (40 nm) was spin-coated from an aqueous solution onto the pre-cleaned ITO substrate and then was dried at 120 °C for 30 min in air. A solution containing a mixture of polymer:PC<sub>71</sub>BM (5 mg/mL:10 mg/mL) in chloroform with or without DIO (2 vol%) was spin-coated on the top of the PEDOT:PSS layer at 3000 rpm to form a film with thickness of 90–100 nm. After being kept for six hours at room temperature, the film was floated onto a water surface and was transferred to a copper grid for TEM measurements.

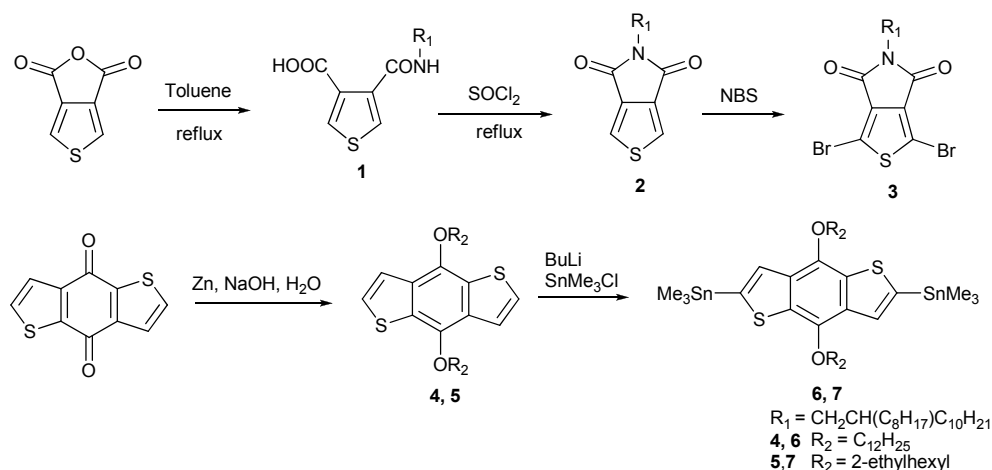
### Device Fabrication and characterization

Polymer solar cells (PSCs) with the device structures of ITO/PEDOT: PSS/polymer: PC<sub>70</sub>BM (1:2, w/w)/LiF/Al were fabricated as follows: A ca. 40-nm-thick PEDOT: PSS (Baytron P AI 4083) was spin-coated from an aqueous solution onto the

pre-cleaned ITO substrates, followed by dried at 120°C for 30 min in air. Then the substrates were transferred into a nitrogen filled glove box. The prepared solution containing a mixture of PBDTDPT: PC<sub>71</sub>BM (5 mg/mL: 10 mg/mL) in chloroform with or without 2 vol% DIO was spin-coated on top of the PEDOT/PSS layer. Finally the samples were transferred into an evaporator and 1-nm-thick LiF and 100-nm-thick Al were thermally deposited under a vacuum of 10<sup>-6</sup> Tor with area of 0.12 cm<sup>2</sup>. The devices were encapsulated in the glove box and measured in the air. Current-voltage characteristics were measured using a computer controlled Keithley 236 source meter. The photocurrent was measured under AM 1.5G illumination at 100 mW/cm<sup>2</sup> from a solar simulator (Oriel, 91160A-1000). The EQE was measured at a chopping frequency of 280 Hz with a lock-in amplifier (Stanford, SR830) during illumination with the monochromatic light from a Xenon lamp.

### Synthesis

4,8-Dihydrobenzoldithiophene-4,8-dione,<sup>1</sup> thiophene-3,4-dicarboxylic anhydride<sup>2</sup> were synthesized according to the literature. Tetrahydrofuran (THF) and toluene were freshly distilled over Na wire under nitrogen prior to use. Other materials used in this work were purchased from Sigma-Aldrich Chemical Company and Alfa Aesar Chemical Company.



Scheme S1. Synthesis of monomers.

### **5-(2-Octyldodecyl)thieno[3,4]pyrrole-4,6-dione (2)<sup>3</sup>**

2-Octyldodecylamine (4.64 g, 15.58 mmol) was added to a solution of thiophene-3,4-dicarboxylic anhydride (2.40 g, 15.58 mmol) in toluene (250 mL). The solution was refluxed for 24 h. After cooling to room temperature, the reaction mixture was concentrated and was dried under vacuum to afford a brown solid, compound **1** (6.67g, 95.3%). A solution of compound **1** (2.26 g, 5.00 mmol) in thionyl chloride (200 mL) was refluxed for 5 h. The thionyl chloride was removed under vacuum. The residue was purified by flash chromatography on silica gel with diethyl ether/hexane (1: 15) as eluent to give the titled compound (1.85 g, 85.2%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.80 (s, 2H), 3.50 (d, *J* = 7.6 Hz, 2H), 1.84 (br, 1H), 1.24 (m, 32H), 0.87 (t, *J* = 6.8, 6H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>, δ): 163.13, 136.84, 125.61, 42.95, 37.08, 32.14, 32.11, 31.65, 30.19, 29.85, 29.82, 29.77, 29.57, 29.51, 26.45, 22.91, 22.89, 14.35. (Five peaks in <sup>13</sup>C NMR spectrum overlap).

### **1,3-Dibromo-5-(2-Octyldodecyl)thieno[3,4]pyrrole-4,6-dione (3)<sup>3</sup>**

To a solution of compounds **2** (2.89 g, 6.66 mmol) in concentrated sulfuric acid (12.0 mL) and trifluoroacetic acid (40 mL) was added *N*-bromosuccinimide (NBS) (4.75 g, 26.64 mmol). The reaction mixture was stirred at 55 °C for 24 h. The brown solution was poured into ice water (500 mL) and extracted with dichloromethane. The organic layer was collected and dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure and residue was purified by flash chromatography on silica gel with diethyl ether/hexane (1: 15) as eluent to give the titled compound (2.37 g, 60.2%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 3.47 (d, *J* = 7.2 Hz, 2H), 1.84 (s, 1H), 1.25 (m, 32H), 0.87 (t, *J* = 6.8, 6H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>, δ): 160.85, 134.94, 113.11, 43.30, 37.06, 32.15, 32.12, 31.66, 30.12, 29.86, 29.83, 29.78, 29.58, 29.52, 26.50, 22.92, 22.90, 14.36. (Five peaks in <sup>13</sup>C NMR spectrum overlap).

### **4,8-Didodecyloxybenzol[1,2-b;3,4-b]dithiophene (4)<sup>3</sup>**

Water (40 mL) was added to benzo[1,2-b;3,4-b]dithiophene-4,8-dione ( 2.20 g, 10.0 mmol), zinc power (1.96 g, 30.0 mmol) and sodium hydroxide (8.00 g, 200.0 mmol) in a round bottom flask (150 mL). The mixture was refluxed for 1 h, a catalytic

amount of *tetra-n*-butylammonium bromide (0.032 g, 0.1 mmol) was added, and then the 1-bromododecane (7.50 g, 30 mmol) was added drop-wise to the flask. The reaction was refluxed overnight and then poured into water (200 mL). The mixture was extracted with diethyl ether for three times. The combined organic layer was dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure and residue was purified by flash chromatography on silica gel with dichloromethane/hexane (1: 15) to give the titled compound as white solid (3.61g, 64.7%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.48 (d, *J* = 5.2 Hz, 2H), 7.36 (d, *J* = 5.2 Hz, 2H), 4.27 (t, *J* = 6.4 Hz, 4H), 1.86-1.92 (m, 4H), 1.54 (m, 4H), 1.23-1.37 (m, 32H), 0.88 (t, *J* = 6.4 Hz, 6H).

#### **4,8-Di(2-ethylhexyloxy)benzo[1,2-b;3,4-b]dithiophene (5)<sup>3</sup>**

Same procedure was used as for compound 4. Compound used were benzo[1,2-b;3,4-b]dithiophene-4,8-dione ( 2.20 g, 10.0 mmol), zinc powder (1.96 g, 30.0 mmol), sodium hydroxide (8.00 g, 200.0 mmol), 1-bromo-2-ethylhexane (5.79 g, 30.0 mmol) and a catalytic amount of *tetra-n*-butylammonium bromide (0.032 g, 0.1 mmol) were used in this reaction. A light yellow oil was obtained (2.61 g, 58.2%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.49 (d, *J* = 5.2 Hz, 2H), 7.37 (d, *J* = 5.2 Hz, 2H), 4.19 (d, *J* = 5.6 Hz, 4H), 1.78-1.86 (m, 1H), 1.66-1.74 (m, 1H), 1.56-1.64 (m, 2H), 1.46-1.56 (m, 2H), 1.25-1.45 (m, 12H), 1.03 (t, *J* = 7.2 Hz, 6H), 0.95 (t, *J* = 7.2 Hz, 6H).

#### **2,6-Bis(trimethyltin)-4,8-didodecyloxybenzo[1,2-b; 3,4-b]dithiophene (6)<sup>4</sup>**

A solution of *n*-butyllithium (7.7 ml, 19.25 mmol, 2.5 M in hexane) was added slowly to compound 4 (4.88 g, 8.75 mmol) in tetrahydrofuran (120 mL) at -78 °C. After addition, the mixture was stirred for 1 h at -78 °C. Trimethyltin chloride solution (20.4 mL, 20.4 mmol, 1.0 M in hexane) was added to the mixture. The mixture was warmed to room temperature and stirred overnight. The reaction was quenched with addition of water (150 mL) and was extracted with diethyl ether for three times. The combined organic layer was dried with anhydrous sodium sulfate. Solvent was removed under reduced pressure and residue was purified by re-crystalization in *iso*-propanol to afford white solid (6.37 g, 82.2%). <sup>1</sup>H NMR (400

MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.51 (s, 2H), 4.29 (t,  $J = 6.5$  Hz, 4H), 1.86 (m, 4H), 1.57 (m, 4H), 1.23-1.37 (m, 32H), 0.88 (t,  $J = 6.8$  Hz, 6H), 0.45 (s, 18H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 143.32, 140.68, 134.27, 133.20, 128.27, 73.87, 32.20, 30.77, 29.96, 29.92, 29.76, 29.63, 26.36, 22.99, 14.43, -8.00. (Two peaks in <sup>13</sup>C NMR spectrum overlap).

#### **2,6-Bis(trimethyltin)-4,8-di(2-ethylhexyloxy)benzo[1,2-b; 3,4-b]dithiophene (7)<sup>5</sup>**

Same procedure was used as for compound **6**. Compound used were *n*-butyllithium (10.56 ml, 26.4 mmol, 2.5 M in hexane), compound **5** (5.35 g, 12 mmol), trimethyltin chloride solution (27.96 mL 27.96 mmol, 1M in hexane). After workup, product was obtained as pale needle (7.07 g, 76.3%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.51 (s, 2H), 4.18 (d, 5.2 Hz, 4H), 1.78-1.86 (m, 1H), 1.66-1.74 (m, 1H), 1.56-1.64 (m, 2H), 1.46-1.56 (m, 2H), 1.28-1.45 (m, 12H), 1.02 (t,  $J = 7.2$ , 6H), 0.92 (t,  $J = 7.2$ , 6H), 0.45 (s, 18H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 143.46, 140.81, 134.10, 133.10, 128.19, 75.84, 40.88, 30.75, 29.47, 24.12, 23.42, 14.45, 11.60, -8.11.

**Synthesis of polymers PBDTDPT1.** Tris(dibenzylideneacetone)dipalladium (0.018 g, 0.02 mmol), triphenylsine (0.012 g, 0.04 mmol) were added to a solution of 1,3-dibromo-5-(2-octyldodecyl)thieno[3,4]pyrrole-4,6-dione (**3**) (0.59 g, 1.0 mmol) and 2,6-bis(trimethyltin)-4,8-didodecyloxybenzo[1,2-b; 3,4-b]dithiophene (**6**) (0.89, 1.0 mmol) in toluene (15 mL) under nitrogen. The solution was subjected to three cycles of evacuation and admission of nitrogen. The mixture was heated to 110 °C for 24 h. After cooled to room temperature, the mixture was poured into methanol (100 mL) and stirred for 2 h. A purple precipitate was collected by filtration. The product was purified by washing with methanol and hexane in a Soxhlet extractor for 24 h each. It was extracted with hot chloroform in an extractor for 24 h. After removing solvent, a purple solid was collected (0.9 g, 90.9%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.00 – 8.50 (br, 2H), 3.50-5.02 (br, 6H), 1.01-2.52 (br, 73H), 0.72-1.01 (br, 12H). Mn = 43,521; PDI = 3.62.

#### **Synthesis of polymers PBDTDPT2**

**PBDTDPT2** are synthesized according to the same procedure for **PBDTDPT1**.

Compound used were tris(dibenzylideneacetone)dipalladium (0.019 g, 0.021 mmol), triphenylsine (0.013 g, 0.042 mmol), 1,3-dibromo-5-(2-octyldodecyl)thieno[3,4]-

pyrrole-4,6-dione (**3**) (0.8 g, 1.04 mmol) and 2,6-bis(trimethyltin)-4,8-di(2-ethylhexyloxy)benzo[1,2-b; 3,4-b]dithiophene (**7**) (0.8 g, 1.04 mmol). After workup, a purple solid was obtained (0.83 g, yield, 91.3%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.80-8.58 (br, 2H), 3.50-5.02 (br, 6H), 1.10-2.50 (br, 51H), 0.75-1.10 (br, 18H). M<sub>n</sub> = 91,110; PDI = 6.59.

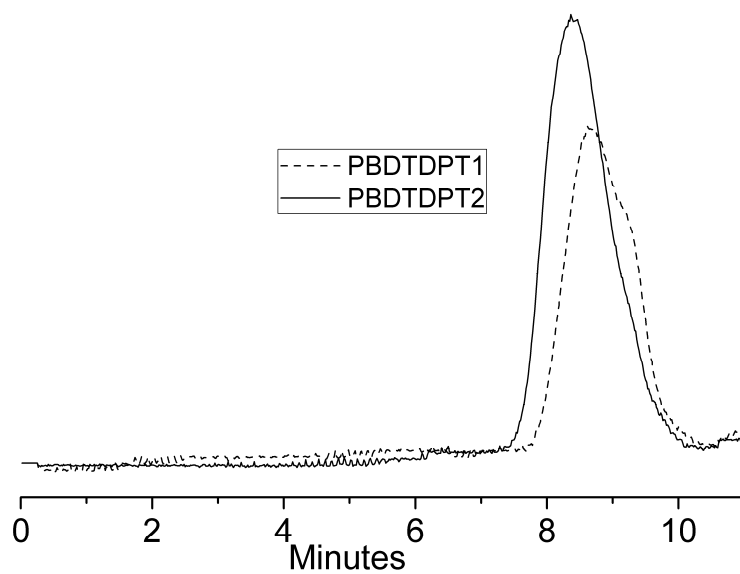


Fig S1. GPC curves of **PBDTDPT1** and **PBDTDPT2**.



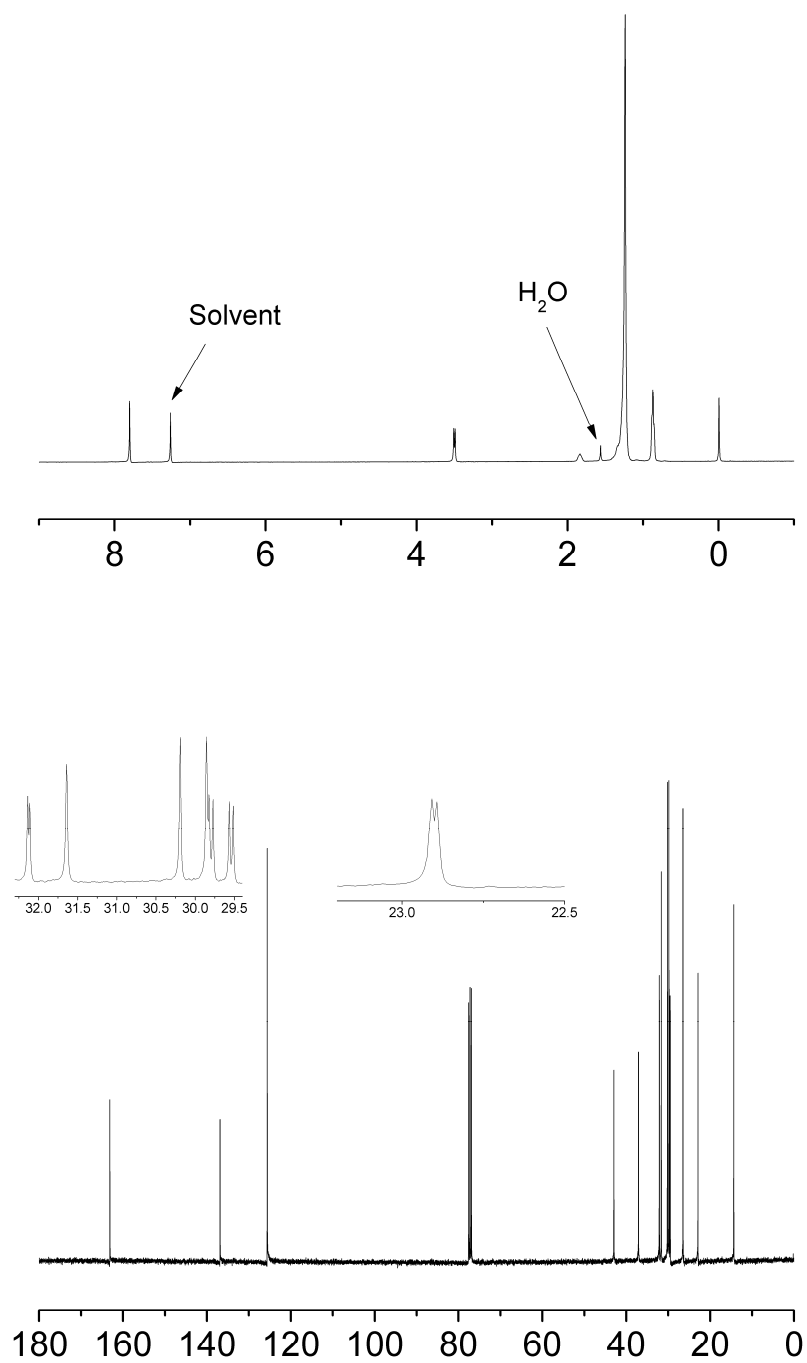


Fig S2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound 2.

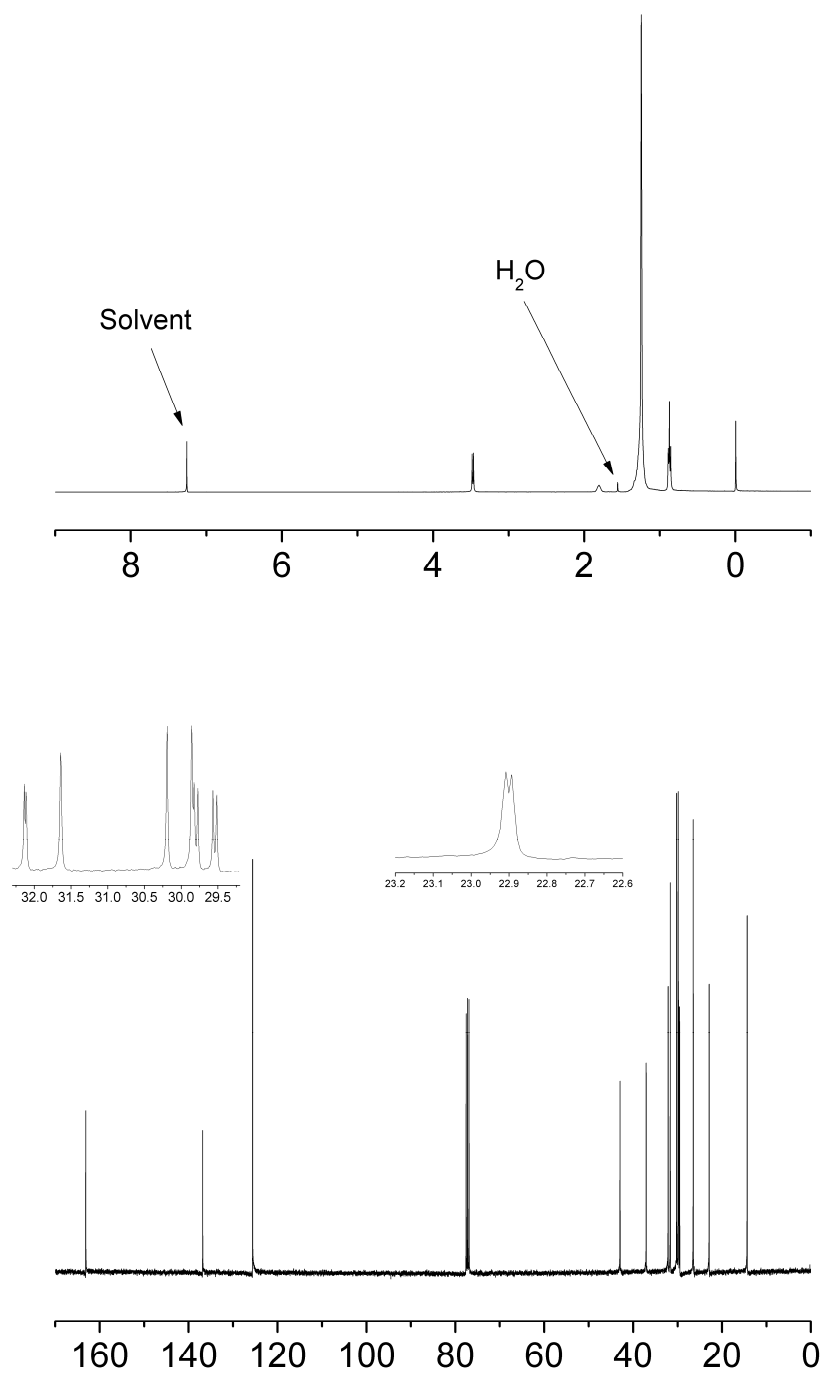


Fig S3.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound 3.

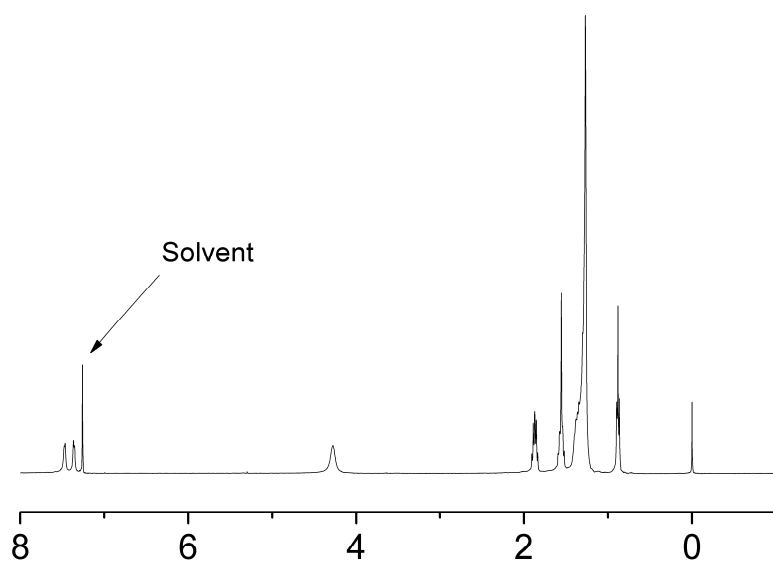


Fig S4.  $^1\text{H}$  NMR spectra of compound 4.

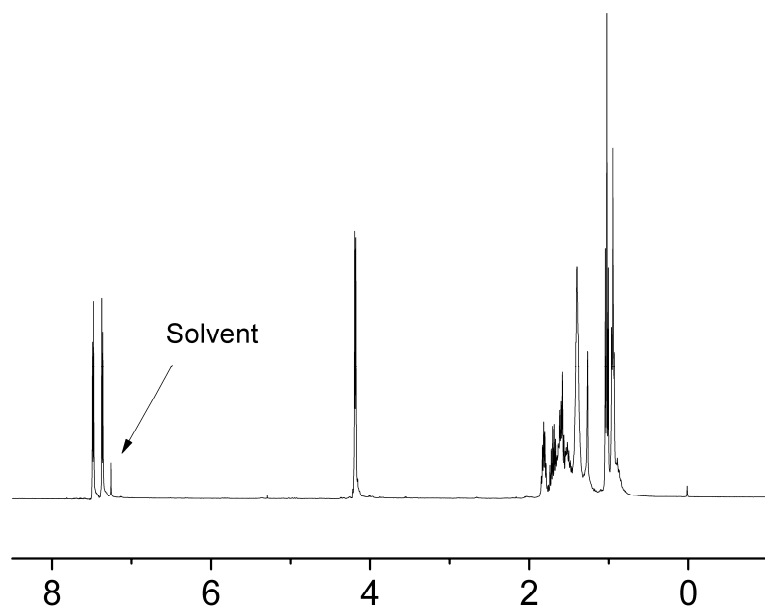


Fig S5.  $^1\text{H}$  NMR spectra of compound 5.

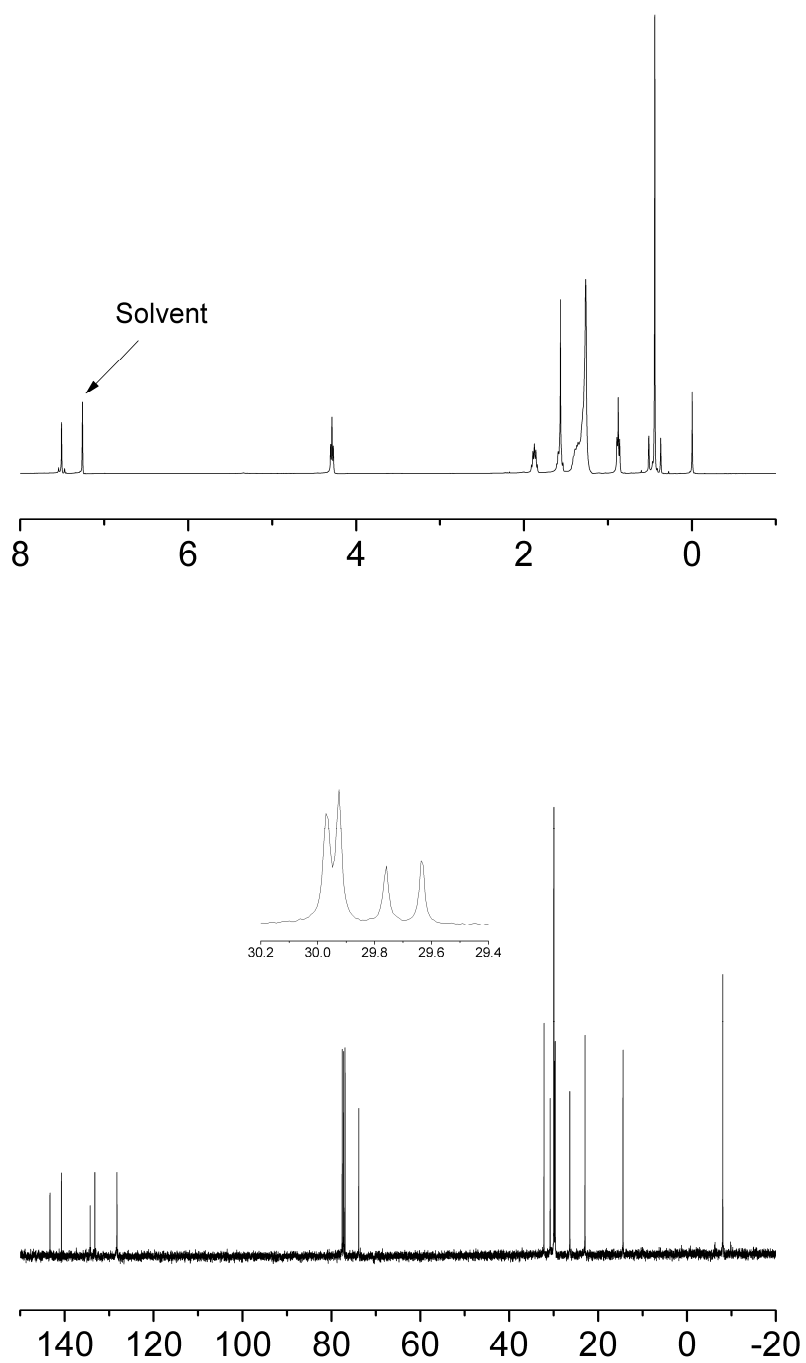


Fig S6.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound 6.

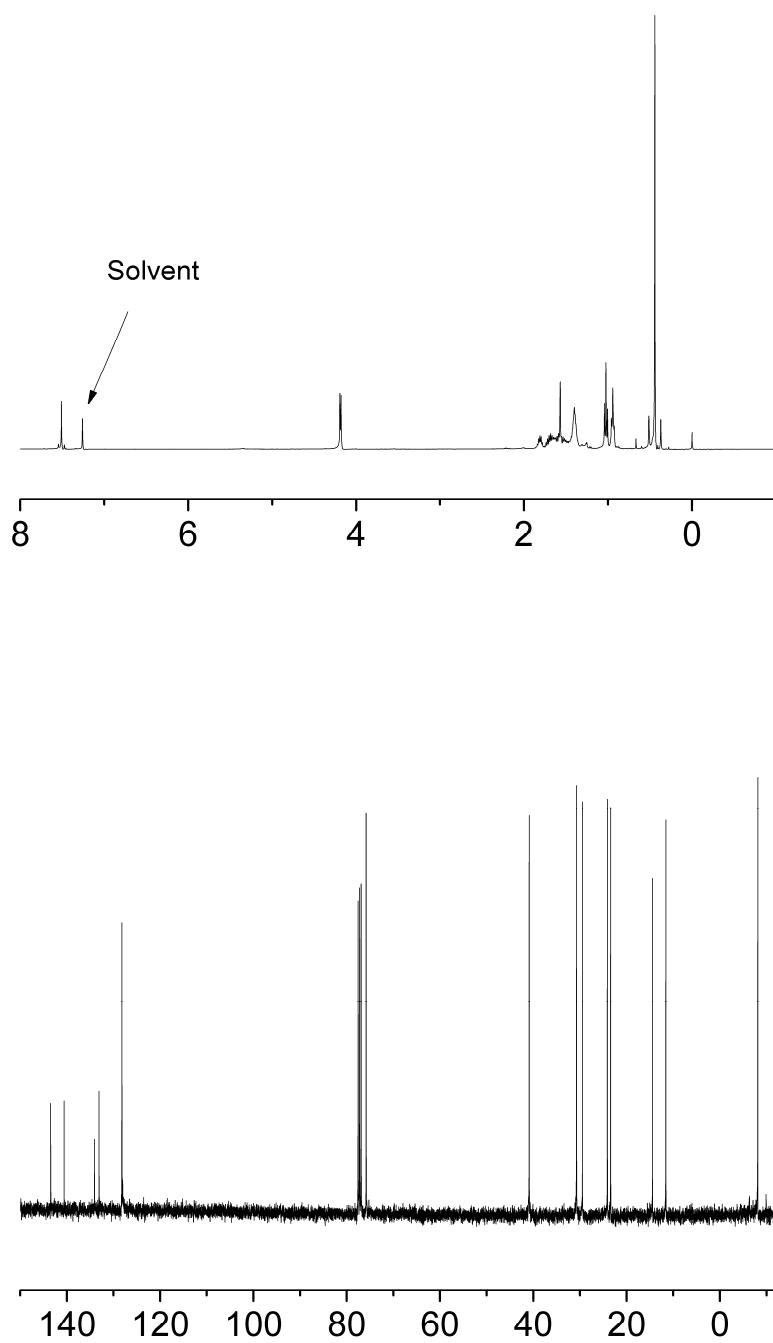


Fig S7.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound 7.

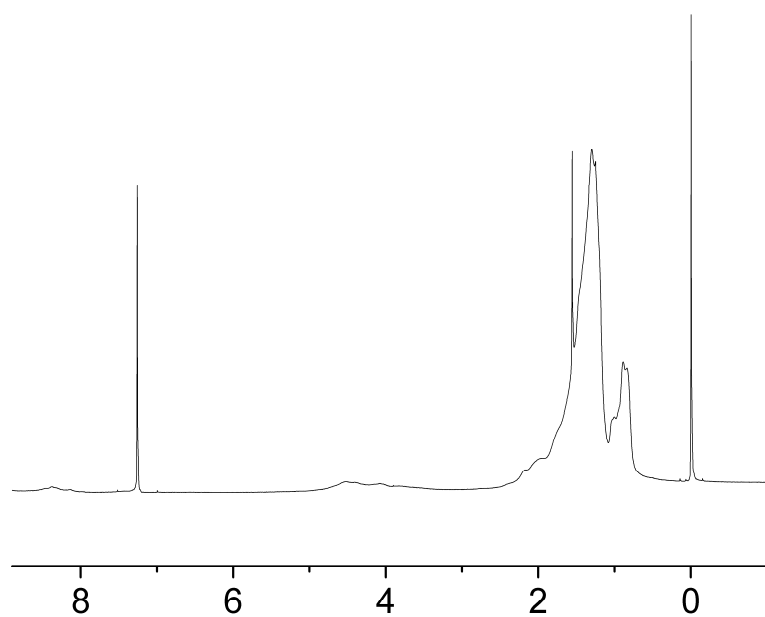


Fig S8.  $^1\text{H}$  spectra of polymer **PBDTDPT1**.

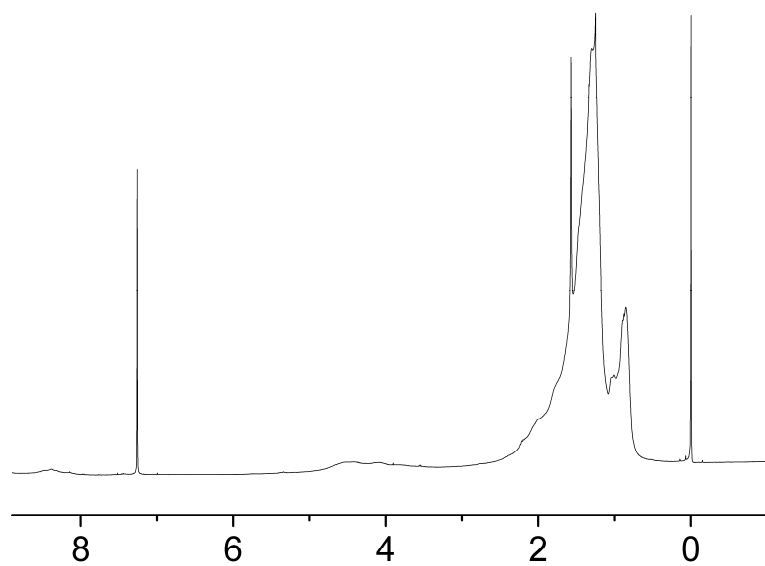


Fig S9.  $^1\text{H}$  spectra of polymer **PBDTDPT2**.

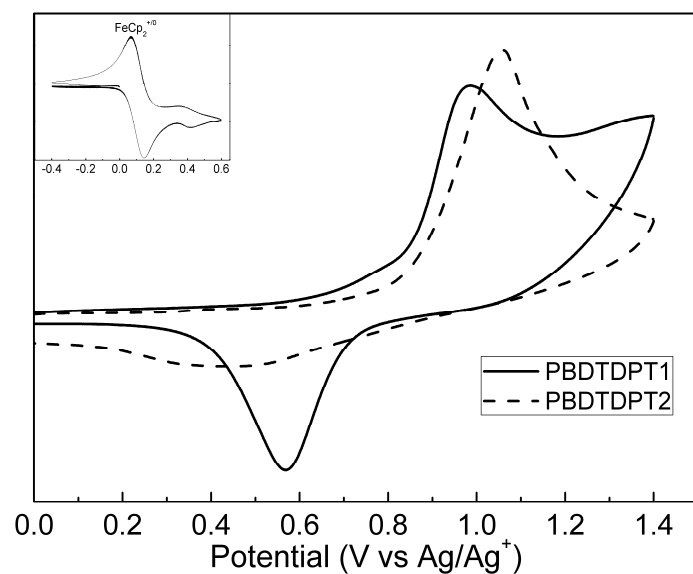


Fig S10. Cyclic voltammogram of copolymers film cast on a platinum electrode in 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>/MeCN at a scan rate of 50 mV/s.

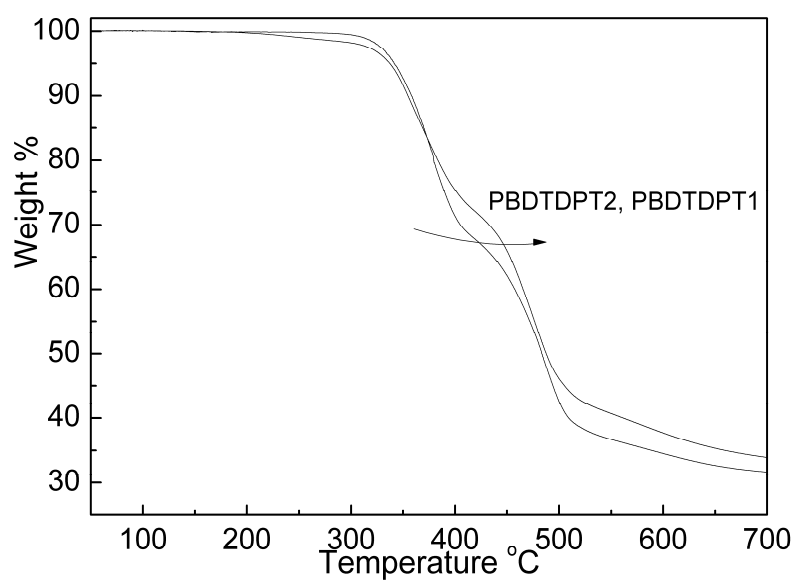


Fig S11. TGA plot of the copolymers.

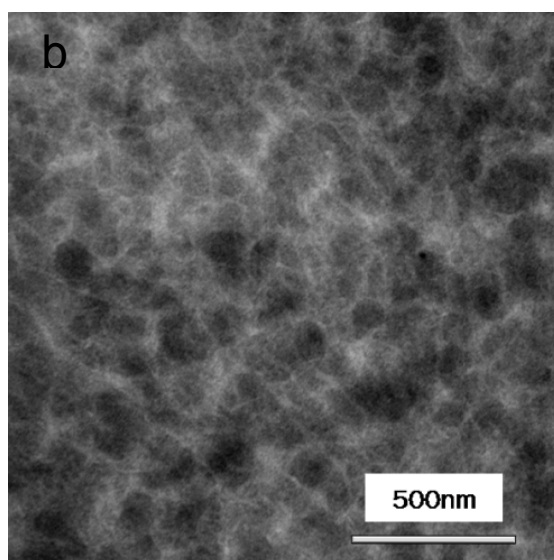
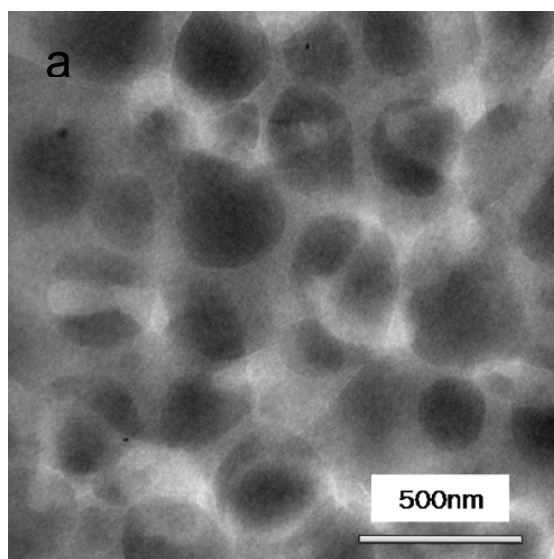


Fig S12. TEM images of **PBDTDPT2**/ $\text{PC}_{71}\text{BM}$  (1:2) blend films, a) without 2% DIO and b) with 2% DIO.



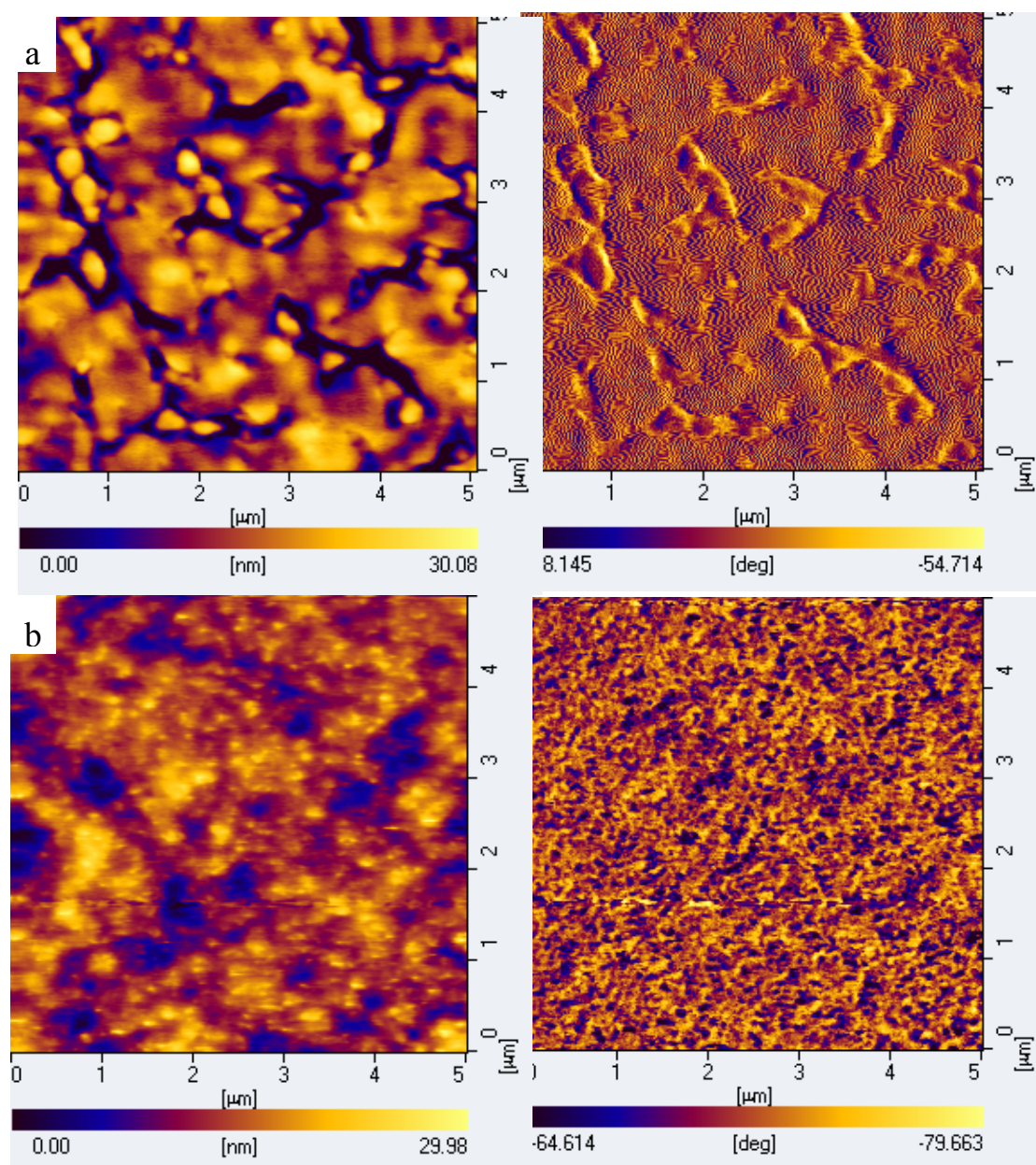


Fig S13. AFM images of the **PBDTDPT2**: PC<sub>71</sub>BM (1:2) bulk heterojunction films processed from chloroform (a) without and (b) with 2% DIO. The topography of each film is shown in the left panels, and the corresponding phase image in the right panels.

Table S1. Optical and redox properties of **PBDTDPT1** and **PBDTDPT2**.

Polymer	Solution		Film			Film		
	$\lambda_{\max}^{abs}$ (nm)	$\lambda_{\max}^{abs}$ (nm)	$\lambda_{\text{onset}}^{abs}$ (nm)	$E_g^{opt}$ (eV)	$E_{\text{onset}}^{ox}$ (V)	HOMO <sup>a</sup> (eV)	$E_{\text{onset}}^{red}$ <sup>b</sup> (V)	LUMO <sup>c</sup> (eV)
<b>PBDTDPT1</b>	605	625	675	1.84	0.73	-5.44	-1.11	-3.60
<b>PBDTDPT2</b>	607	615	674	1.84	0.71	-5.42	-1.13	-3.58

a) HOMO =  $-(4.71 + E_{\text{onset}}^{ox})$ , b)  $E_{\text{onset}}^{red} = E_{\text{onset}}^{ox} - E_g^{opt}$ , c) LUMO =  $-(4.71 + E_{\text{onset}}^{red})$ .

#### References for Supporting Information

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