

## **Supporting Information**

### **Crystalline Conjugated Polymer Containing Fused**

### **2,5-Di(thiophen-2-yl)thieno[2,3-*b*]thiophene and**

### **Thieno[3,4-*c*]pyrrole-4,6-dione Units for Bulk Heterojunction Solar**

### **Cells**

**Guan-Yu Chen, Yu-Hsin Cheng, Yi-Jen Chou, Ming-Shin Su, Chia-Min Chen,**

**and Kung-Hwa Wei \***

Department of Material Science and Engineering, National Chiao Tung University,

300 Hsinchu, Taiwan

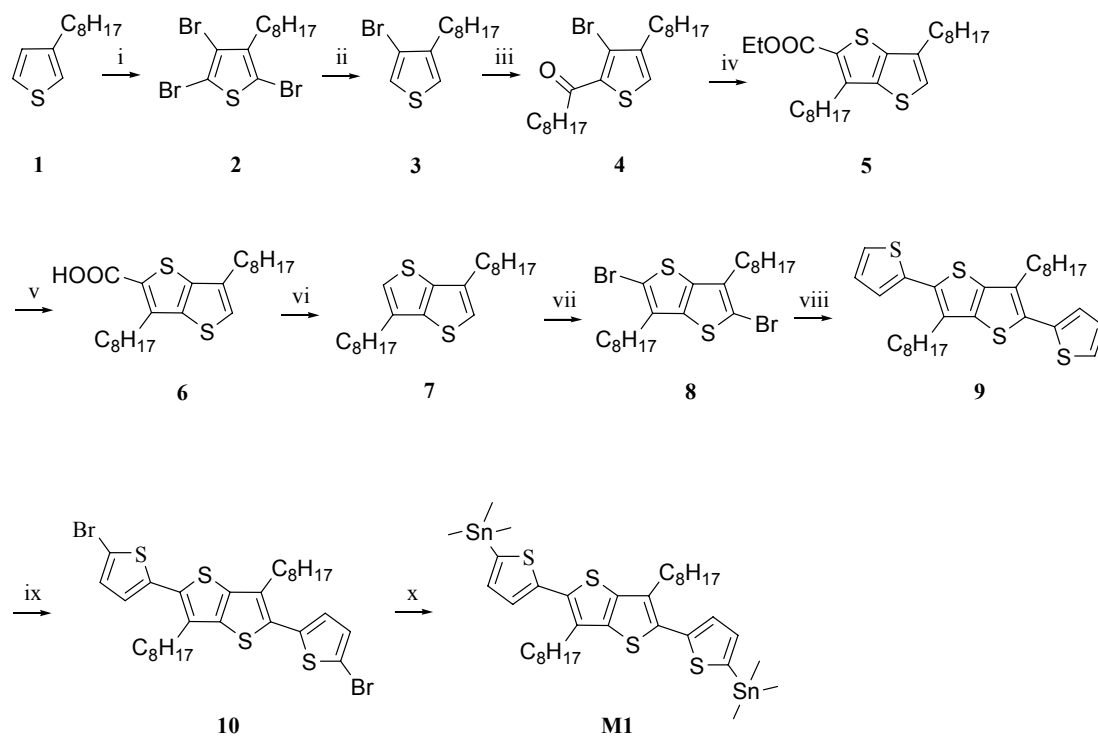
E-mail address: [khwei@mail.nctu.edu.tw](mailto:khwei@mail.nctu.edu.tw)

## Experimental

### Materials.

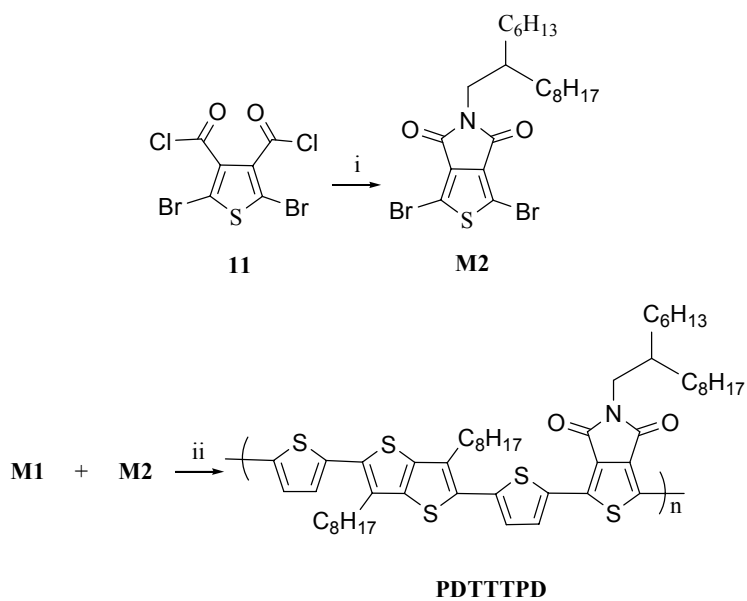
3-Octylthiophene (**1**),<sup>1</sup> 2,5-dibromothiophene-3,4-dicarboxylic acid chloride (**11**),<sup>2</sup> and 2-hexyldecan-1-amine<sup>3</sup> were prepared according to reported procedures. PCBM and PC<sub>71</sub>BM were purchased from Solenne. All other reagents were used as received from commercial sources, without further purification.

### Scheme S1 Synthesis of M1<sup>a</sup>



<sup>a</sup>Reagents and conditions: (i) Br<sub>2</sub>, 70 °C, overnight; (ii) *n*-BuLi, -78 °C, 10 min; (iii) nonanoyl chloride, AlCl<sub>3</sub>, rt, 2 h; (iv) ethyl mercaptoacetate, K<sub>2</sub>CO<sub>3</sub>, [18]crown-6, 70 °C, overnight; (v) NaOH, tetrabutylammonium iodide, MeOH, reflux, 5 h; (vi) Cu powder, quinoline, 250 °C, 3 h; (vii) NBS, rt, 5 h; (viii) 2-tributylstannylthiophene, Pd<sub>2</sub>dba<sub>3</sub>, tri(*o*-tolyl)phosphine, 80 °C, 3 h; then reflux, 1 h; (ix) NBS, rt, 3 h; (x) *n*-BuLi, -78 °C, 2 h; then trimethylstannyl chloride, rt, overnight.

### Scheme S2 Syntheses of **M2** and **PDTTTPD**<sup>a</sup>



<sup>a</sup>Reagents and conditions: (i) 2-hexyldecan-1-amine, 140 °C, 12 h; (ii) Pd<sub>2</sub>dba<sub>3</sub>, Ph<sub>3</sub>P,

135 °C, 24 h.

### **2,3,5-Tribromo-4-octylthiophene (2)**

Br<sub>2</sub> (3.90 mL, 76.9 mmol) was added dropwise to a solution of **1** (10.0 g, 23.3 mmol) in AcOH (20 mL). After stirring at room temperature for 4 h, the mixture was heated at 70 °C overnight. The solution was then poured into ice water and neutralized with 6 M NaOH. The mixture was extracted with EtOAc (3 × 100 mL) and the combined organic phases dried (MgSO<sub>4</sub>). The solvent was evaporated under reduced pressure; the crude product was purified through column chromatography (SiO<sub>2</sub>, hexane) to obtain **2** (31.6 g, 95%). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) : δ 14.1, 22.7, 28.5, 29.1, 29.2, 29.3, 29.7, 31.8, 108.0, 109.4, 115.7, 141.5.

### **3-Bromo-4-octylthiophene (3)**

*n*-BuLi (1.85 mL, 4.62 mmol) was added dropwise into a mixture of **2** (1.00 g, 2.31 mmol) in dry THF (10 mL) at -78 °C. After stirring at -78 °C for 10 min, the reaction mixture was poured into water and extracted with EtOAc (3 × 100 mL). The combined organic phases were dried (MgSO<sub>4</sub>) and the solvent evaporated under reduced pressure. The crude product was purified through column chromatography (SiO<sub>2</sub>, hexane) to obtain **3** (0.51 g, 80%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.25–1.31 (m, 10H), 1.57–1.62 (m, 2H), 2.55 (t, *J* = 8.1 Hz, 2H), 6.93 (s, 1H), 7.20 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) : δ 14.1, 22.7, 29.2, 29.3, 29.4, 29.7,

29.9, 31.9, 112.8, 120.5, 122.6, 141.7

#### **1-(3-Bromo-4-octylthiophen-2-yl)nonan-1-one (4)**

Nonanoyl chloride was added dropwise to a mixture of **3** (10.0 g, 36.4 mmol) and AlCl<sub>3</sub> (9.60 g, 72.7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 mL). After stirring at room temperature for 2 h, the mixture was poured into 6 M HCl (200 mL) and extracted with EtOAc (3 × 100 mL). The combined organic phases were dried (MgSO<sub>4</sub>) and the solvent evaporated under reduced pressure to obtain **4** as a crude product that was used in the next step without further purification.

#### **3,6-Dioctylthieno[3,2-*b*]thiophene-2-carboxylic acetate (5)**

Ethyl mercaptoacetate (1.34 mL, 12.5 mmol) was added dropwise to a mixture of **4** (5 g, 12.0 mmol), K<sub>2</sub>CO<sub>3</sub> (3.41 g, 24.7 mmol), and [18]crown-6 (50 mg) in DMF (15 mL) at 70 °C and then the reaction mixture was stirred overnight. After cooling to room temperature, the mixture was poured into water, extracted with EtOAc (3 × 100 mL), and then the combined organic phases were dried (MgSO<sub>4</sub>). The solvent was evaporated under reduced pressure to obtain **5** as a crude product that was used in the next step without further purification.

### **3,6-Dioctylthieno[3,2-*b*]thiophene-2-carboxylic acid (6)**

A mixture of **5** (5.61 g, 12.8 mmol), NaOH (10 wt%, 10 mL), tetrabutylammonium iodide (50 mg), and MeOH (3.5 mL) in THF (21 mL) was heated under reflux for 5 h. After evaporating the solvent under reduced pressure, the mixture was acidified with concentrated HCl and then extracted with EtOAc (3 × 100 mL). The combined organic phases were dried and the solvent evaporated under reduced pressure. The crude product was purified through column chromatography (SiO<sub>2</sub>, hexane) to obtain **6** (1.25 g, 24%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.92 (t, *J* = 6.9 Hz, 6H), 1.22–1.38 (m, 20H), 1.61–1.79 (m, 4H), 2.76 (t, *J* = 7.8 Hz, 2H), 3.20 (t, *J* = 7.8 Hz, 2H), 7.31 (s, 1H).

### **3,6-Dioctylthieno[3,2-*b*]thiophene (7)**

A mixture of **6** (1.00 g, 2.44 mmol) and Cu powder (0.100 g, 1.57 mmol) in quinoline (5 mL) was stirred at 250 °C for 3 h. After cooling to room temperature, the mixture was added to hexane (100 mL) and then washed with 2 M HCl. The organic phase was dried (MgSO<sub>4</sub>) and the solvent evaporated under reduced pressure. The crude product was purified through column chromatography (SiO<sub>2</sub>, hexane) to obtain **7** as a colorless oil (0.57 g, 64%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.86 (t, *J* = 6.3 Hz, 6H), 1.24–1.32 (m, 20H), 1.67–1.75 (m, 4H), 2.69 (t, *J* = 7.8 Hz, 4H), 6.93 (s, 2H). <sup>13</sup>C

NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  14.1, 22.7, 28.7, 29.2, 29.4, 29.7, 29.8, 31.9, 120.8, 135.4, 139.2.

### **2,5-Dibromo-3,6-dioctylthieno[3,2-*b*]thiophene (8)**

NBS (1.5 g, 8.43 mmol) was added in three portions to a solution of **7** (1.40 g, 3.84 mmol) in CHCl<sub>3</sub> (60 mL) and AcOH (20 mL). After stirring at room temperature for 5 h, the mixture was poured into water and extracted with EtOAc (3  $\times$  100 mL). The combined organic phases were washed with brine and dried (MgSO<sub>4</sub>). The solvent was evaporated under reduced pressure and the crude product purified through column chromatography (SiO<sub>2</sub>, hexane) to provide **8** as a colorless oil (1.4 g, 70%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.88 (t, *J* = 6.6 Hz, 6H), 1.27–1.31 (m, 20H), 1.63–1.68 (m, 4H), 2.67 (t, *J* = 8.1 Hz, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  14.1, 22.6, 28.1, 28.9, 29.1, 29.3, 29.7, 31.9, 109.4, 134.4, 136.0.

### **3,6-Dioctyl-2,5-di(thiophen-2-yl)thieno[3,2-*b*]thiophene (9)**

Tris(dibenzylideneacetone)dipalladium (35.1 mg, 0.038 mmol) was added to a mixture of **8** (1 g, 1.91 mmol), 2-tributylstannylthiophene (1.52 mL, 4.79 mmol), and tri(*o*-tolyl)phosphine (93.2 mg, 0.310 mmol) in dry toluene (10 mL), which had been degassed at 60 °C for 10 min. The mixture was stirred at 80 °C for 3 h and then heated



under reflux for another 1 h. After cooling to room temperature and evaporating the solvent, the crude product was purified through column chromatography (SiO<sub>2</sub>, hexane) and recrystallization (hexane) to yield **9** (0.9 g, 90%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.88 (t, *J* = 7.2 Hz, 6H), 1.27–1.40 (m, 20H), 1.71–1.81 (m, 4H), 2.87 (t, *J* = 8.1 Hz, 4H), 7.09 (dd, *J* = 1.5, 5.1 Hz, 2H), 7.17 (dd, *J* = 1.2, 3.6 Hz, 2H), 7.34 (dd, *J* = 1.2, 5.1 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 14.1, 22.6, 28.7, 29.1, 29.2, 29.3, 29.7, 31.9, 125.7, 126.1, 127.5, 131.3, 131.9, 136.5, 138.5.

#### **2,5-Bis(5-bromothiophen-2-yl)-3,6-dioctylthieno[3,2-*b*]thiophene (10)**

NBS (1.01 g, 5.67 mmol) was added in three portions to a mixture of **9** (1.47g, 2.78 mmol) in AcOH (40 mL) and CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The mixture was stirred at room temperature for 3 h, poured into water, and then extracted with EtOAc (3 × 100 mL). The combined organic phases were dried (MgSO<sub>4</sub>) and then the solvent was evaporated under reduced pressure. The crude product was purified through chromatography (SiO<sub>2</sub>, hexane) and recrystallization (hexane) to yield **10** (1.5 g, 80%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.88 (t, *J* = 6.6 Hz, 6H), 1.28–1.39 (m, 20H), 1.70–1.75 (m, 4H), 2.82 (t, *J* = 8.4 Hz, 4H), 6.9 (d, *J* = 3.9 Hz, 2H), 7.04 (d, *J* = 3.9 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 14.1, 22.7, 28.7, 29.0, 29.2, 29.3, 29.6, 31.9, 112.4, 126.5, 130.3, 130.6, 132.4, 137.9, 138.6.

### **2,5-Bis[5-(trimethylstannyl)thiophen-2-yl]-3,6-dioctylthieno[3,2-*b*]thiophene**

#### **(M1)**

*n*-BuLi (2.5 M, 0.64 mL, 1.60 mmol) was added dropwise to a solution of **10** (0.50 g, 0.73 mmol) in dry THF (10 mL) at  $-78\text{ }^{\circ}\text{C}$ . After stirring at  $-78\text{ }^{\circ}\text{C}$  for 2 h, trimethylstannyl chloride (1 M, 1.82 mL, 1.82 mmol) was added to the reaction mixture at  $-78\text{ }^{\circ}\text{C}$  and then the mixture was warmed to room temperature overnight. The mixture was poured into water and extracted with hexane ( $3 \times 100\text{ mL}$ ). The combined organic phases were washed with water and dried ( $\text{MgSO}_4$ ). The solvent was evaporated under reduced pressure to provide **M1** (0.2 g, 35%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.41 (s, 18H), 0.87 (t, 6.4 Hz, 6H), 1.25–1.42 (m, 20H), 1.74–1.76 (m, 4H), 2.88 (t,  $J = 8.1\text{ Hz}$ , 4H), 7.16 (d,  $J = 3.3\text{ Hz}$ , 2H), 7.27 (d,  $J = 3.3\text{ Hz}$ , 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$   $-8.2$ , 14.1, 22.7, 28.8, 29.0, 29.2, 29.3, 29.7, 31.9, 127.0, 131.4, 131.5, 135.5, 138.4, 138.5, 142.3. Anal. Calcd: C, 50.60; H, 6.61. Found: C, 50.88; H, 6.70.

#### **1,3-Dibromo-5-(2-hexyldecyl)-5*H*-thieno[3,4-*c*]pyrrole-4,6-dione (M2)**

A mixture of **11** (0.500 g, 1.37 mmol) and 2-hexyldecan-1-amine (0.350 g, 1.45 mmol) was stirred at  $140\text{ }^{\circ}\text{C}$  for 12 h. After cooling to room temperature, the solid was

dissolved in EtOAc (100 mL) and washed with  $\text{NaHCO}_{3(\text{aq})}$  ( $2 \times 100$  mL). The organic phase was dried ( $\text{MgSO}_4$ ) and the solvent evaporated under reduced pressure. The crude product was purified through column chromatography ( $\text{SiO}_2$ ; EtOAc/hexane, 1:9) to yield **M2** (0.53 g, 72%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.81–0.94 (m, 6H), 1.10–1.40 (m, 24H), 1.75–1.85 (m, 1H), 3.48 (d,  $J = 7.2$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  14.1, 22.6, 26.2, 29.3, 29.5, 29.9, 31.4, 31.8, 36.8, 43.1, 112.9, 134.7, 160.6. Anal. Calcd: C, 49.36; H, 6.21; N, 2.62. Found: C, 49.64; H, 6.16; N, 2.62.

### **PDTTTPD**

A mixture of **M1** (250 mg, 0.292 mmol), **M2** (156 mg, 0.292 mmol), and triphenylphosphine (12.2 mg, 16.0 mol%) in dry chlorobenzene (3.7 mL) was degassed at 60 °C for 10 min. Tris(dibenzylideneacetone)dipalladium (6.4 mg, 2.0 mol%) was added to the mixture, which was then heated at 135 °C for 24 h. 2-Tributylstannylthiophene (0.19 mL) was added and then the mixture was stirred for 3 h. Subsequently, 2-bromothiophene (0.06 mL) was added to the mixture, which was then stirred for another 3 h. After cooling to room temperature, the solution was poured into MeOH (100 mL) and the solid filtered off. The crude polymer was dissolved in  $\text{CHCl}_3$ , filtered through a 0.5- $\mu\text{m}$  polytetrafluoroethylene (PTFE) filter,

and then reprecipitated from MeOH. The precipitated material was purified by washing with MeOH, hexane, and acetone in a Soxhlet system. The pure polymer was collected and dried to yield **PDTTTPD** (205 mg, 78%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.87 (s, 12H), 1.23–1.56 (m, 49H), 2.62 (br, 4H), 3.56 (br, 2H), 7.01 (br, 2H), 7.89 (br, 2H). Anal. Calcd: C, 69.21; H, 7.93; N, 1.55. Found: C, 68.17; H, 8.09; N, 0.99.

**PDTTTPD** exhibited a number-average molecular weight ( $M_n$ ) of  $9.2 \text{ kg mol}^{-1}$ .

To further increase the molecular weights of the synthesized polymers, we would attach more or longer alkyl chains to fused thiophene for improving their solubility.

### Measurements and Characterization

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Varian Unity-300 NMR spectrometer.

The number-average molecular weights ( $M_n$ ) was measured through gel permeation chromatography (GPC) using a Waters chromatography unit interfaced with a Waters 2414 differential refractometer. Three 5- $\mu\text{m}$  Waters styragel columns were connected in series in decreasing order of pore size (104, 103, and 102  $\text{\AA}$ ); THF was the eluent and standard polystyrene samples were used for calibration. Differential scanning calorimetry (DSC) was performed using a Perkin–Elmer Pyris DSC1 instrument operated at a heating rate of  $20 \text{ }^\circ\text{C min}^{-1}$  under a  $\text{N}_2$  purge. Thermogravimetric analysis (TGA) was performed using a TA Instrument Q500 apparatus operated at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  under a  $\text{N}_2$  atmosphere. UV–Vis spectra of the dilute

$\text{CHCl}_3$  solution ( $1 \times 10^{-5}$  M) and the thin solid film were recorded using an HP Agilent-8453 diode array spectrophotometer. The solid film for UV–Vis spectroscopic analysis was obtained by spin-coating a 1,2-dichlorobenzene (DCB) solution of the polymer ( $10 \text{ mg mL}^{-1}$ ) onto a quartz substrate. Electrochemical cyclic voltammetry (CV) was performed using a BAS 100 electrochemical analyzer and solutions in MeCN containing 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) as the electrolyte; the scan rate was  $100 \text{ mV s}^{-1}$ . A glassy disk carbon electrode coated with a thin film of polymer was used as the working electrode; a Pt wire was the counter electrode;  $\text{Ag}/\text{Ag}^+$  ( $0.01 \text{ M AgNO}_3$ ) was the reference electrode; ferrocene was the internal standard. The X-ray diffraction pattern of the pristine polymer film, prepared by drop-casting the polymer solution onto a Si substrate, was measured using a Bruker D8 high-resolution X-ray diffractometer operated in grazing incidence mode. Topographic images of the active layers were obtained using a Digital Instruments Nanoscope III atomic force microscope operated in the tapping mode under ambient conditions.

### **Device Fabrication and Characterization**

An indium tin oxide (ITO)–coated glass substrate was cleaned sequentially with detergent, DI water, acetone, and isopropyl alcohol and then dried in an oven. Before use, the substrate was treated with UV ozone for 30 min.

Poly(ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS, Baytron P VP AI 4083) was spin-coated (5000 rpm) onto the ITO substrates. After baking at 140 °C for 20 min in air, the substrates were transferred to a N<sub>2</sub>-filled glove box. The active layers were prepared by dissolving the polymer and PCBM at different weight ratios, but with a fixed total concentration (30 mg mL<sup>-1</sup>), in DCB and then spin-coating the solutions onto the ITO/PEDOT:PSS (30 nm) substrates for 60 s. The blend solution of **PDTTTPD** was stirred continuously for 12 h at 130 °C. The films were dried at room temperature for 30 min and then subjected to thermal annealing at 90 °C for 20 min. Finally, Al (100 nm) was thermally evaporated through a shadow mask to result in a device area of 0.04 cm<sup>2</sup>. The active layers of the devices based on **PDTTTPD**/PC<sub>71</sub>BM were prepared by dissolving **PDTTTPD** and PC<sub>71</sub>BM with a concentration of 25 mg mL<sup>-1</sup> in DCB, and DIO (1 vol%) was added as an additive. The blend solution was stirred continuously for 12 h at 130 °C and then spin-coated onto the ITO/PEDOT:PSS (30 nm thick) substrates using spin coating rate of 600, 800 and 1000 rpm to prepare active layers with thickness of 103, 83 and 62 nm, respectively. The films were dried at room temperature for 30 min and then subjected to thermal annealing at 90 °C for 20 min. Finally, Al (100 nm) was thermally evaporated through a shadow mask to form top electrode, and the device area is 0.04 cm<sup>2</sup>. The devices were measured under AM 1.5 radiation (100 mW cm<sup>-2</sup>) using a Xe

lamp-based Newport 66902 150W solar simulator. A calibrated Si photodiode with a KG-5 filter was employed to check the illumination intensity. The external quantum efficiency (EQE) was measured using an Optosolar system. Monochromatic light from a 500-W Xe lamp source was passed through a monochromator. The photocurrent of the device was detected using a lock-in amplifier under short-circuit conditions by illuminating the monochromatic incident beam. A calibrated mono silicon diode exhibiting a response at 300–800 nm was used as a reference. The theoretical short-circuit density was calculated through following equations:

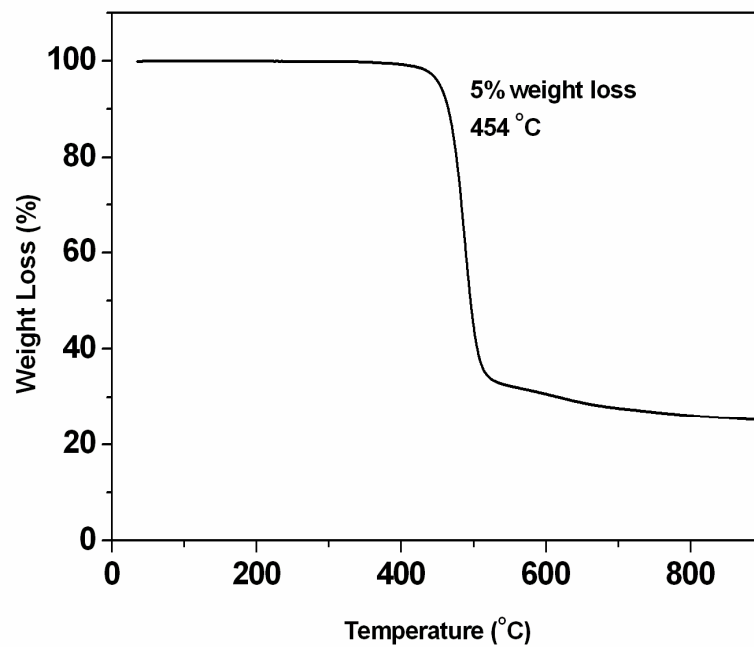
$$S_T(\lambda) = \frac{q\lambda}{hc} EQE(\lambda)$$
$$J_{sc} = \int_{\lambda_2}^{\lambda_1} E_{Ref}(\lambda) S_T(\lambda) d\lambda$$

Where  $S_T(\lambda)$  is the spectral responsivity of the test device, the constant term  $q/hc$  is  $8.0655 \times 10^5$ ,  $E_{Ref}(\lambda)$  is the reference spectral irradiance (AM1.5). Hole-only mobility measurement was performed using a device having the structure ITO/PEDOT:PSS/**PDTTTPD**:PCBM/Au. The hole mobility was determined by fitting the dark  $J$ - $V$  curve into the space-charge-limited current (SCLC) model, based on the equation

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_h \frac{V^2}{L^3}$$

where  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  is the dielectric constant of the material,  $\mu_h$  is the hole mobility,  $V$  is the voltage drop across the device, and  $L$  is the thickness

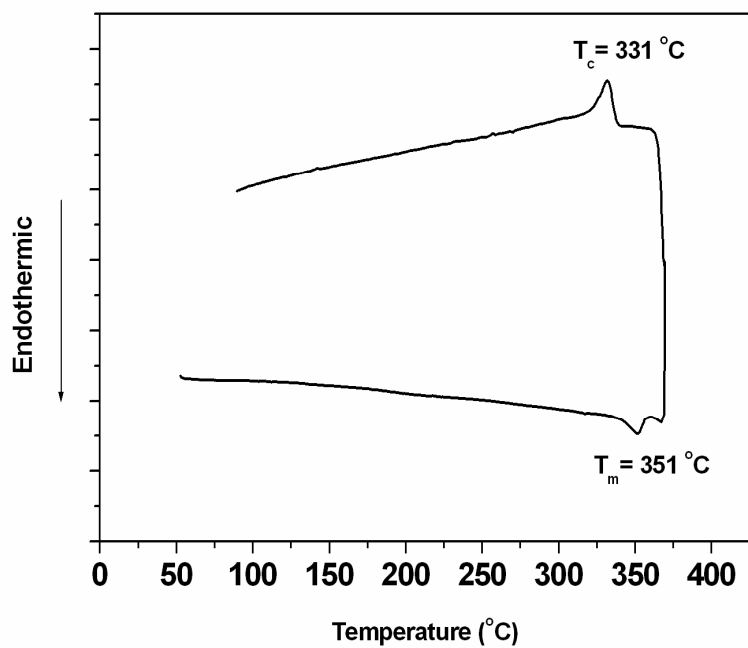
of the active layer.



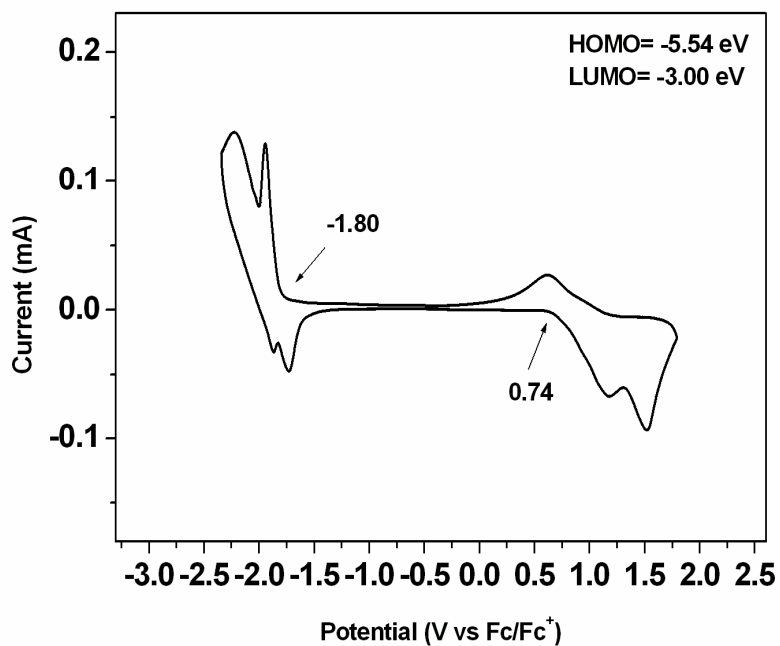
**Fig. S1** TGA thermogram of **PDTTTPD**, recorded at a heating rate of  $10\text{ °C min}^{-1}$

under a  $\text{N}_2$  atmosphere.

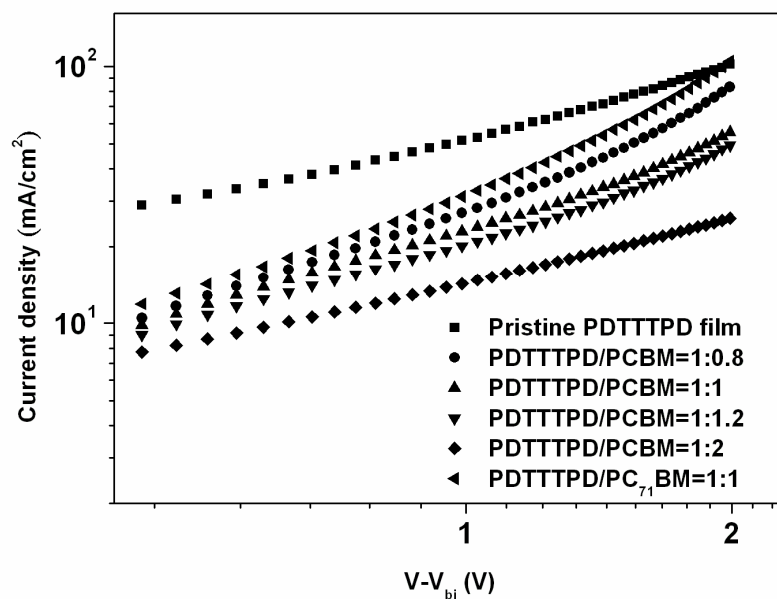




**Fig. S2** DSC trace of **PDTTTPD**, recorded at a heating rate of  $20\text{ }^\circ\text{C min}^{-1}$  and a cooling rate of  $40\text{ }^\circ\text{C min}^{-1}$ , under a  $\text{N}_2$  atmosphere.



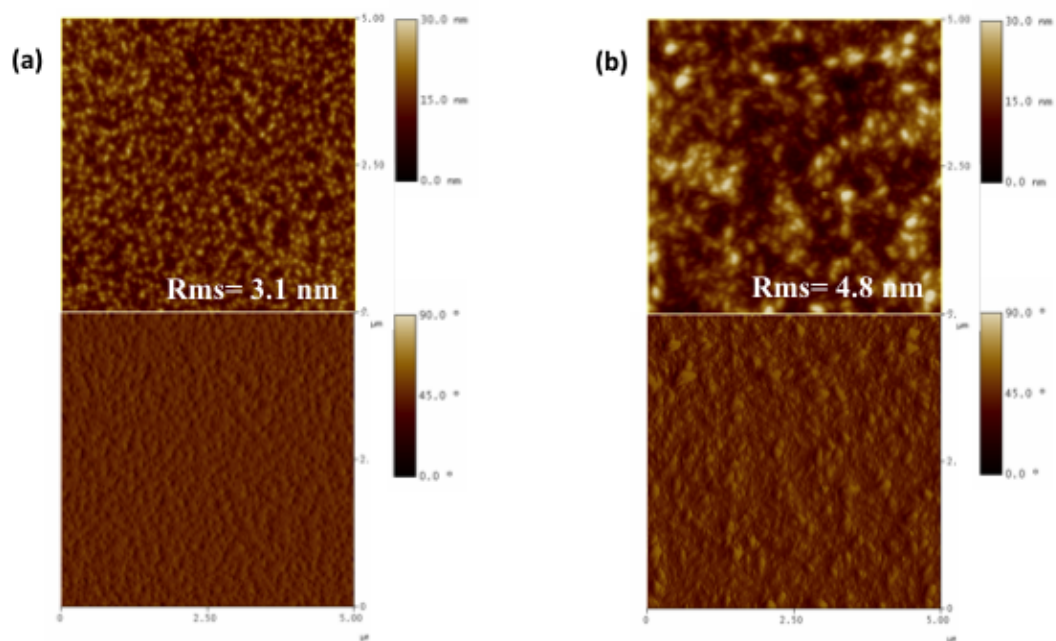
**Fig. S3** CV trace of **PDTTTPD**.



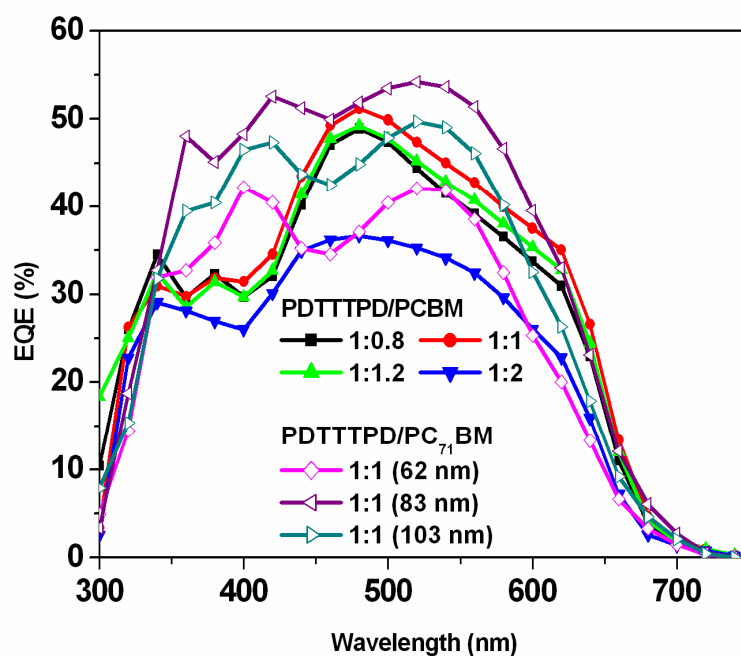
**Fig. S4** Dark  $J$ - $V$  curves for hole-dominated carrier devices incorporating the pristine and blend films at various blend weight ratios.

**Table S1** Hole mobilities of the pristine and blend films incorporating various blend weight ratios.

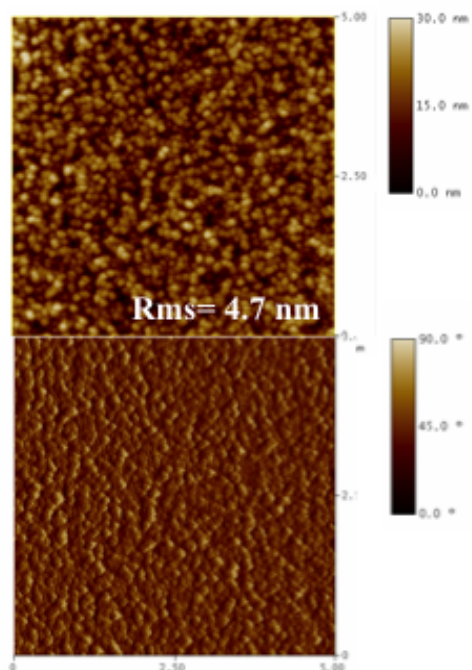
Weight ratio of active layer	Thickness (nm)	$\mu_h$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )
Pristine <b>PDDTTPD</b> film	103	$2.2 \times 10^{-4}$
<b>PDDTTPD</b> /PCBM = 1:0.8	117	$1.7 \times 10^{-4}$
<b>PDDTTPD</b> /PCBM = 1:1	120	$1.5 \times 10^{-4}$
<b>PDDTTPD</b> /PCBM = 1:1.2	119	$1.3 \times 10^{-4}$
<b>PDDTTPD</b> /PCBM = 1:2	109	$7.1 \times 10^{-5}$
<b>PDDTTPD</b> /PC <sub>71</sub> BM = 1:1	110	$1.5 \times 10^{-4}$



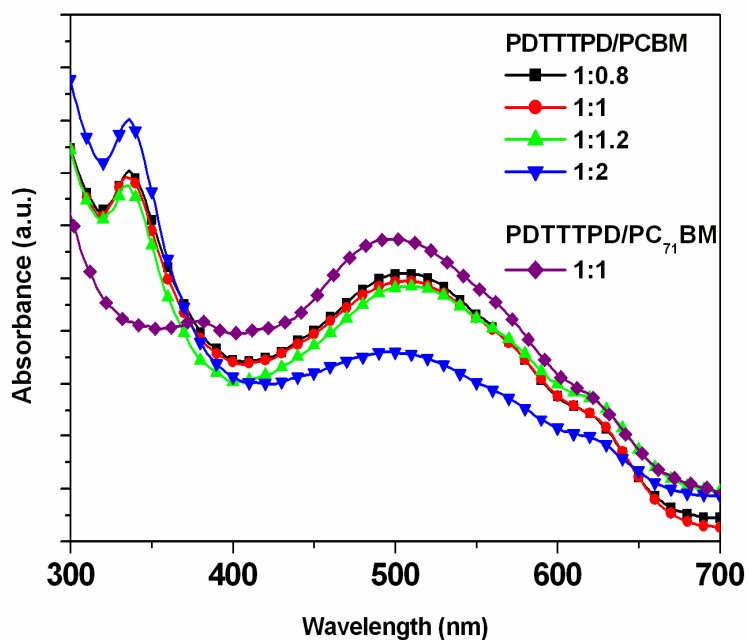
**Fig. S5** Height and phase images of **PDDTTPD/PCBM** blends prepared at weight ratios of (a) 1:1 and (b) 1:2.



**Fig. S6** EQE spectra of BHJ solar cells incorporating **PDDTTPD/PCBM** blends at various weight ratios and **PDDTTPD/PC<sub>71</sub>BM** at a blend weight ratio of 1:1.



**Fig. S7** Height and phase images of **PDTTTPD/PC<sub>71</sub>BM** at a blend weight ratio of 1:1, with DIO (1 vol%) added as an additive.



**Fig. S8** Absorption spectra of **PDTTTPD/PCBM** and **PDTTTPD/PC<sub>71</sub>BM** blend films.

## References

- 1 R. D. McCullough, R. D. Lowe, M. Jayaraman and D. L. Anderson, *J. Org. Chem.*, 1993, **58**, 904.
- 2 Q. T. Zhang and J. M. Tour, *J. Am. Chem. Soc.*, 1997, **119**, 5065.
- 3 J. Liu, R. Zhang, I. Osaka, S. Mishra, A. E. Javier, D. M. Smilgies, T. Kowalewski and R. D. McCullough, *Adv. Funct. Mater.*, 2009, **19**, 3427.