

# **Influence of Molecular Structure on the Performance of Low $V_{oc}$ Loss Polymer Solar Cells**

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## **Supplementary Information**

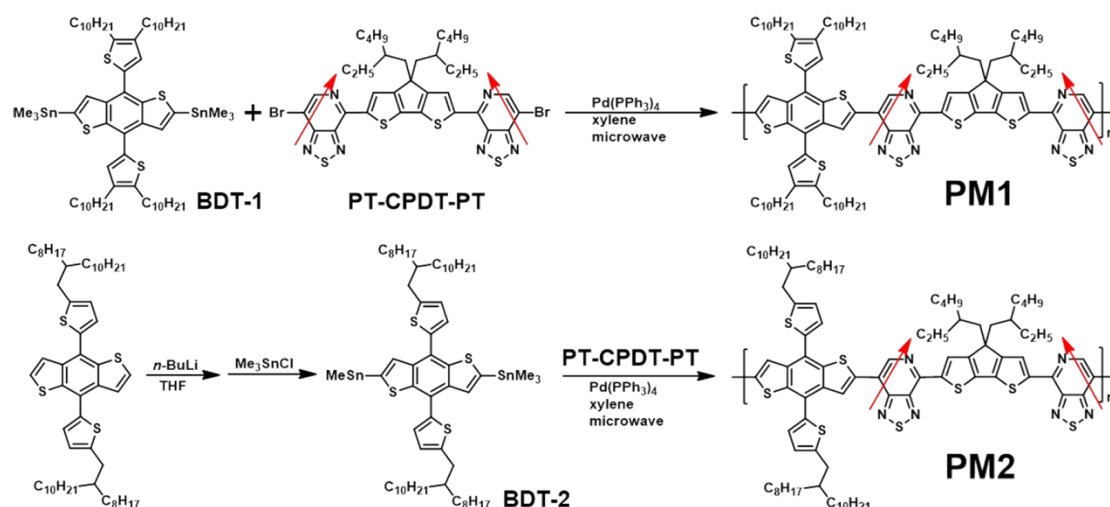
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## 1. General methods

Microwave reactions were performed using a Biotage microwave reactor. Ultraviolet-Visible (UV-Vis) absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained on Varian 500 MHz spectrometer. Gel permeation chromatography (GPC) was performed in chloroform ( $\text{CHCl}_3$ ) on a Waters 2690 Separation Module equipped with a Waters 2414 Refractive Index Detector and a Waters 2996 Photodiode Array Detector. Molecular weights were calculated relative to linear PS standards. Differential scanning calorimetry (DSC) was determined by a TA Instruments DSC (Model Q-20) with about 3 mg polymers samples at a rate of 10 °C / min in the temperature range of 30 to 330 °C. Cyclic voltammetry (CV) measurements were tested on a CHI-730B electrochemistry workstation. 2D grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were performed at the Stanford Synchrotron Radiation Light source (SSRL) on Beamline 11-3, with a MAR345 image plate area detector, at 12.7 keV incident photon energy and an incident angles of 0.12°. The exposure time was set to 300 seconds. Thin film illumination occurred in a helium atmosphere to minimize X-ray beam damage. Transmission Electron Microscopes (TEM) was performed on FEI Tecnai G2 Sphera Microscope system equipped with a LaB6 emitter and S-twin lens for higher resolution at 200kV, and a Gatan UltraScan 1000P CCD camera for image recording. Device characteristics were measured under illumination by a simulated 100 mW/cm<sup>2</sup> AM1.5G light source using a 300 W Xe arc lamp with an AM 1.5 global filter. Solar-simulator irradiance was calibrated using a standard silicon photovoltaic with a protective KG1 filter calibrated by the National Renewable Energy Laboratory. Current density-voltage ( $J$ - $V$ ) characteristics were recorded by a Keithley 236 Source Measure Unit. External quantum efficiencies were determined using a 75W Xe source, monochromator, optical chopper, lock-in amplifier, and a National Institute of Standards and Technology calibrated silicon photodiode was used for power-density calibration. Film thickness was determined on Ambios XP-100 Profilometer.

## 2. Synthesis



Scheme S-1. Synthesis of PM1 and PM2.

2,6-bis{(4-(7-bromo-[1,2,5]thiadiazolo[3,4-c]pyridine))-{4,4-bis(2-ethylhexyl)cyclopenta-[2,1-b:3,4-b']-dithiophene} (**PT-CPDT-PT**)<sup>1</sup> was synthesized as previously reported. 2,6-Bis(trimethyltin)-4,8-bis(4,5-didecyl)thiophen-2-yl)benzo[1,2-b:4,5-b']

dithiophene (**BDT-1**) was synthesized according to the literature.<sup>2</sup> 4,8-bis(5-(2-octyldodecyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene was synthesized from the reported method.<sup>3</sup> Tetrakis(triphenylphosphine) palladium(0) [Pd(PPh<sub>3</sub>)<sub>4</sub>] was purchased from Strem Chemicals Inc. Xylene at the ultra-dry grade were purchased from Acros Organics. All the chemicals were used as received.

*2,6-Bis(trimethyltin)-4,8-bis(5-(2-octyldodecyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene* (**BDT-2**):

4,8-bis(5-(2-octyldodecyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (0.91 g, 1.0 mmol) was dissolved in 20 mL of anhydrous THF in a two-neck flask within argon atmosphere. The solution was cooled to -78 °C, and then a solution of *n*-BuLi (1.6 M in hexane, 1.4 mL, 2.2 mmol) was added dropwise under stirring. The mixture was warmed to room temperature and stirred for 1 hour. Then the mixture was cooled to -78 °C and a Me<sub>3</sub>SnCl solution (1 M in THF, 3 mL, 3 mmol) was added in one portion. The dry-ice/acetone bath was removed and the mixture was warmed to room

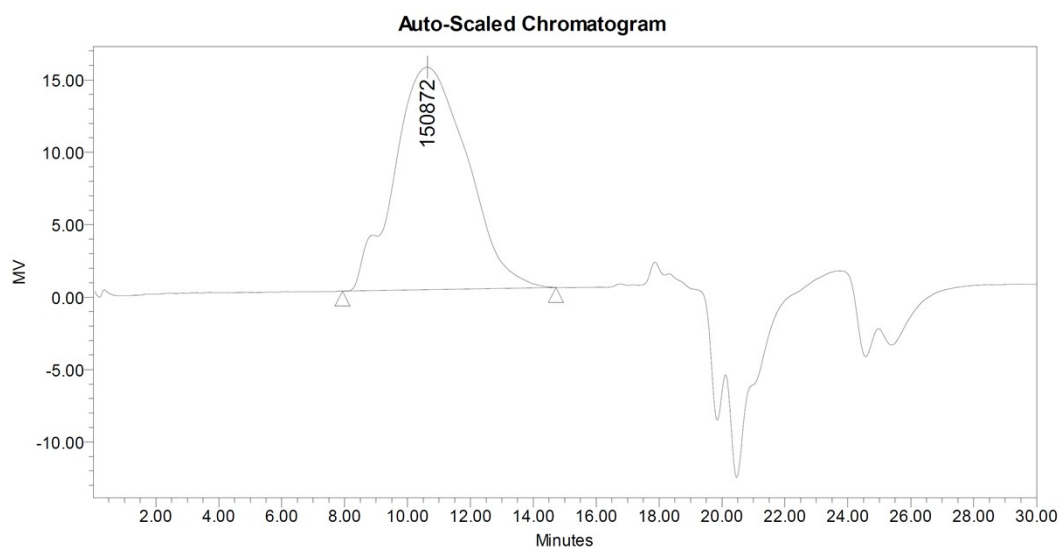
temperature overnight. The mixture was poured into water and extracted twice with hexane. The organic layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to afford the yellow oil. Then it was dried under the vacuum overnight for polymerization, 1.18 g, yield 95%. <sup>1</sup>H NMR (500 MHz, chloroform-d,  $\delta$ ) 7.69 (s, 2H), 7.31 (d, 2H), 6.90 (d, 2H), 2.86 (d, 4H), 1.74 (m, 2H), 1.15-1.45 (m, 64H), 0.87 (t, 12H), 0.40 (s, 18H). <sup>13</sup>C NMR (125 MHz, chloroform-d,  $\delta$ ) 145.33, 143.27, 142.17, 137.98, 137.29, 131.15, 127.50, 125.25, 122.40, 40.04, 34.71, 33.42, 31.91, 30.04, 29.70, 29.69, 29.65, 29.36, 29.35, 26.72, 26.67, 22.69, 22.68, 14.10, -8.37

**PM1** 2,6-Bis(trimethyltin)-4,8-bis(4,5-didecyl)thiophen-2-yl]benzo[1,2-b:4,5-b']dithiophene (130 mg, 0.105 mmol), **PT-CPDT-PT** (83 mg, 0.1 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (5.8 mg, 0.005 mmol), xylene (4 mL) were added to a 2-5 mL microwave tube in the nitrogen atmosphere glovebox. The tube was sealed and subjected to the following reaction conditions in the microwave reactor: 80 °C for 2 min, 130 °C for 2 min, 160 °C for 2 min, 180 °C for 40 min. The reaction was allowed to cool to room temperature, then xylene (1 mL) and 2-bromothiophene (0.2 mL) was added and sealed in the glovebox. The end-capping reaction was subjected to the microwave reactor under the following reaction condition: 80 °C for 2 min, 130 °C for 2 min, 160 °C for 20 min. After the reaction was cooled to room temperature, the polymer was precipitated in methanol. The precipitates were collected by a cellulose extraction thimble and extracted with methanol, dichloromethane, chloroform and chlorobenzene respectively via a Soxhlet extractor. The chlorobenzene fraction was concentrated on the rotovaper under vacuum, and then concentrated polymer solution was added dropwise to the methanol under the stirring. The polymer was precipitated and collected via filter paper, dried over in the vacuum line to give 130 mg dark solid, yield 82%. <sup>1</sup>H NMR (500 MHz, tetrachloroethane-d<sub>2</sub>, 80 °C,  $\delta$ ) 8.96 (s, 2H), 8.72 (s, 2H), 7.51 (s, 2H), 7.39 (b, 2H), 2.96 (b, 4H), 2.76 (b, 4H), 0.50-2.5 (m, 110);  $M_n$ =83,000 g/mol,  $M_w$ =182,000 g/mol,  $PDI$ =2.2

## ***PM2***

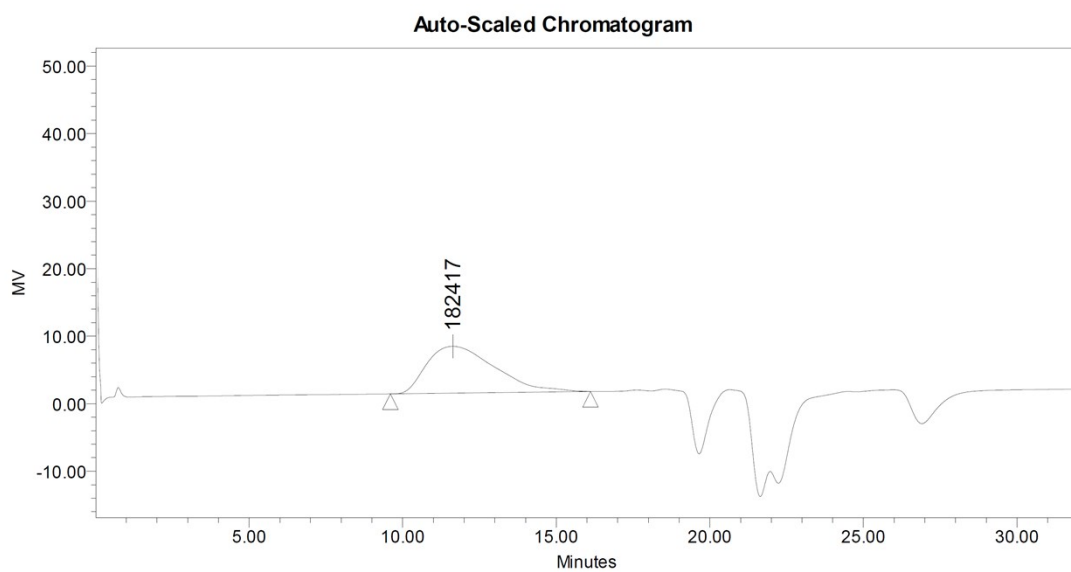
2,6-Bis(trimethyltin)-4,8-bis(5-(2-octyldodecyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (130 mg, 0.105 mmol), **PT-CPDT-PT** (83 mg, 0.1 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (5.8 mg, 0.005 mmol), xylene (4 mL) were added to a 2-5 mL microwave tube in the nitrogen atmosphere glovebox. The tube was sealed and subjected to the following reaction conditions in the microwave reactor: 80 °C for 2 min, 130 °C for 2 min, 160 °C for 2 min, 180 °C for 2 min and 200 °C for 40 min. Then it was followed by the same post treatment procedure of **PM1** to give 120 mg of **PM2** polymer, yield 76 %. <sup>1</sup>H NMR (500 MHz, tetrachloroethane-d<sub>2</sub>, 80 °C, δ) 8.87 (b, 2H), 8.71(b, 2H), 7.57 (b, 2H), 7.10 (b, 4H), 3.10 (b, 4H), 0.50-2.5 (m, 112); *M<sub>n</sub>*=83,000 g/mol, *M<sub>w</sub>*=167,000 g/mol, *PDI*=2.0

1. Welch, G. C.; Bakus, II, R. C.; Teat, S. J.; Bazan, G. C. *J. Am. Chem. Soc.*, **2013**, *135*, 2298.
2. Wang, M.; Hu, X. W.; Liu, P.; Li, W.; Gong, X.; Huang, F.; Cao, Y. *J. Am. Chem. Soc.* **2011**, *133*, 9638.
3. Xu, X. P.; Wu, Y. L.; Fang, J. F.; Li, Z. J.; Wang, Z. G.; Li, Y.; Peng, Q. *Chem.-Eur. J.* **2014**, *20*, 13259.



GPC Results										
	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		83239	182303	150872	324395	472635		2.190111		
2										

Figure S-1 GPC measurement of PM1 in chloroform.



GPC Results										
	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		82780	166923	182417	243156	303569		2.016457		
2										

Figure S-2 GPC measurement of PM2 in chloroform.

### 3. UV-vis absorption

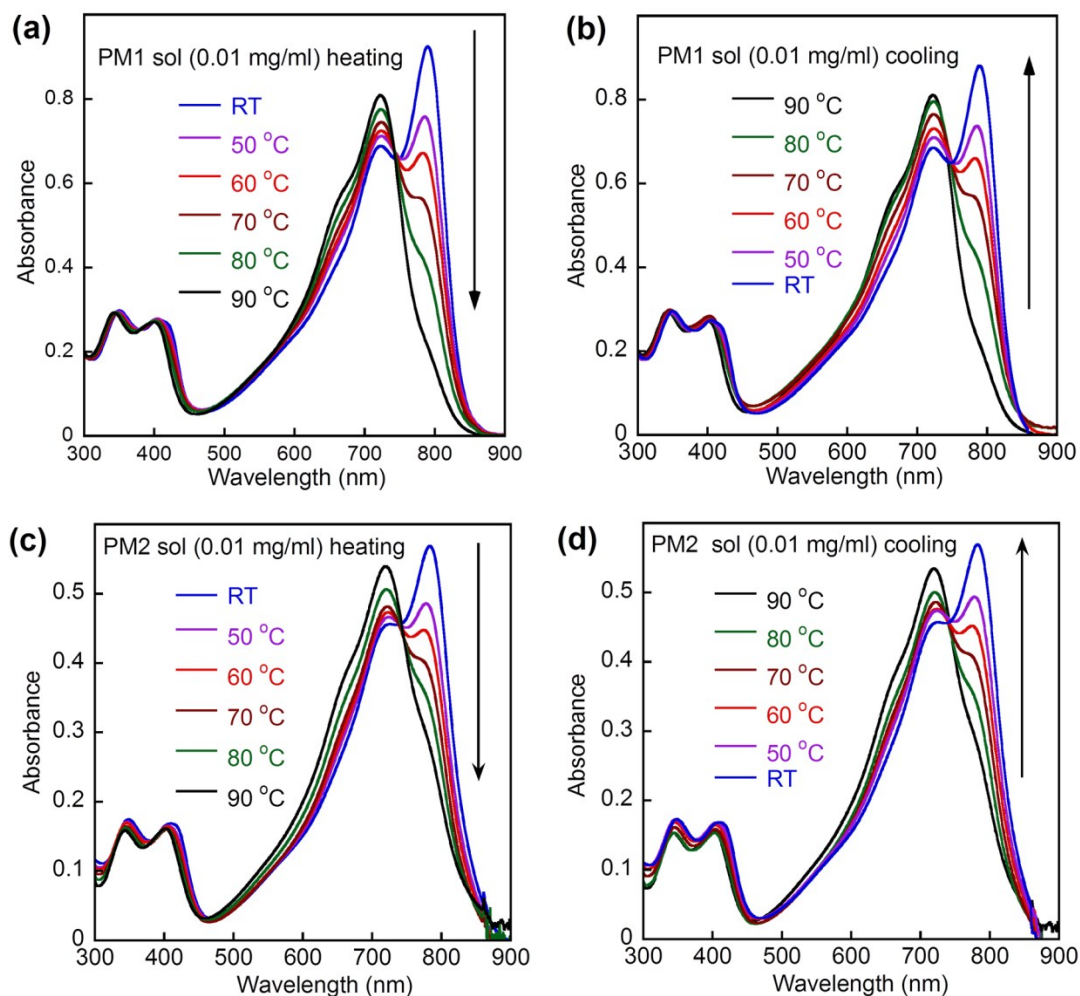


Figure S-3. UV-vis absorption in chlorobenzene solution at different temperatures.

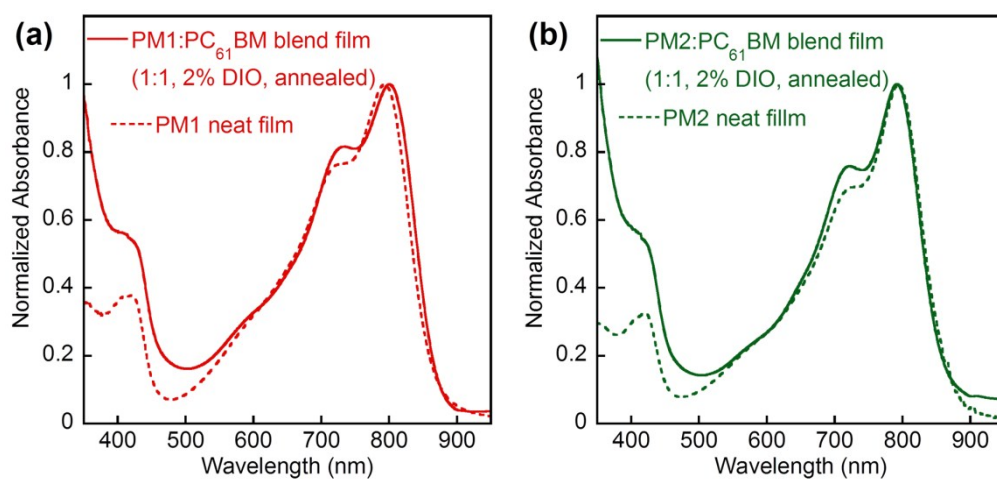


Figure S-4. UV-vis absorption of neat polymer films and optimized polymer:PC<sub>61</sub>BM blend films: (a) PM1; (b) PM2

#### 4. Differential scanning calorimetry

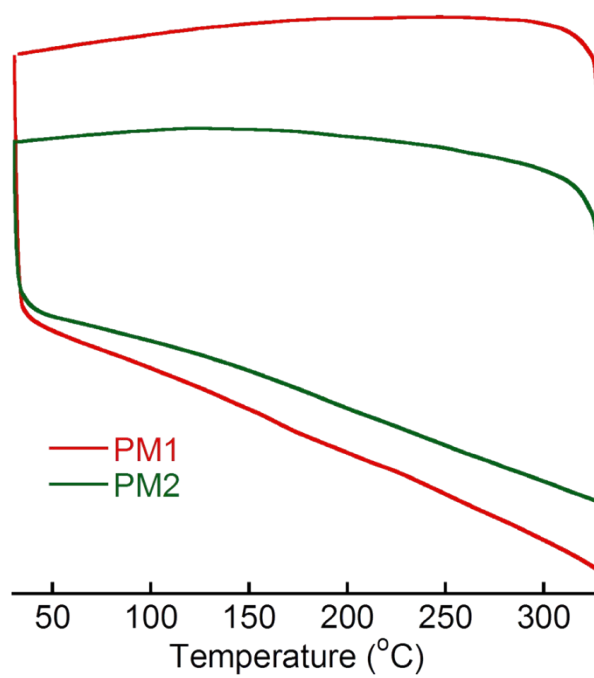


Figure S-5. Differential scanning calorimetry measurements of PM1 and PM2.

## 5. Cyclic voltammetry

Cyclic voltammetry (CV) measurements were conducted using a standard three-electrode configuration under an argon atmosphere. A three-electrode cell equipped with a glassy carbon working electrode, an Ag wire reference electrode and a Pt wire counter-electrode. The measurements were performed in absolute acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte at a scan rate of 50 mV/s. Polymer films for CV test were drop-casted onto the glassy carbon working electrode from the chlorobenzene solution, and concentrations are 5 mg/mL for neat films and 10 mg/mL for blend films. For PM1 and PM2 blend films, polymer:PC<sub>61</sub>BM ratio is 1/1 (w/w). For PIPCP blend, polymer:PC<sub>61</sub>BM ratio is 1:2 (w/w). The absolute energy level of ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was set to be 4.8 eV below vacuum. The HOMO level was calculated from the equation:  $E_{HOMO} = -4.8 \text{ eV} - E_{onset}^{ox}$ , and the LUMO level was calculated from:  $E_{LUMO} = E_{HOMO} + E_g^{opt}$ .

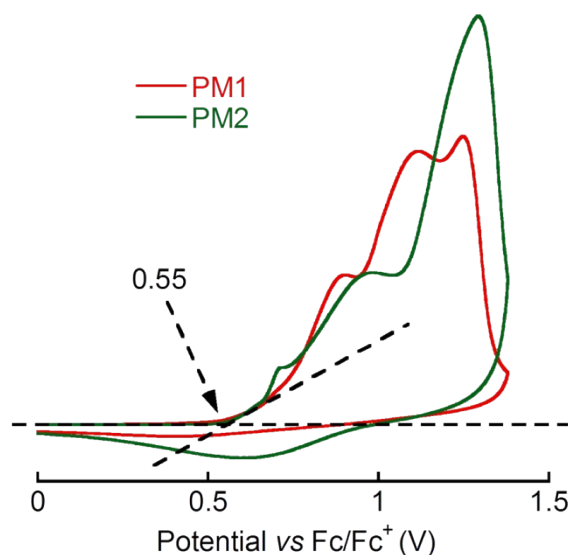


Figure S-6. Oxidation measurements of PM1 and PM2 films.

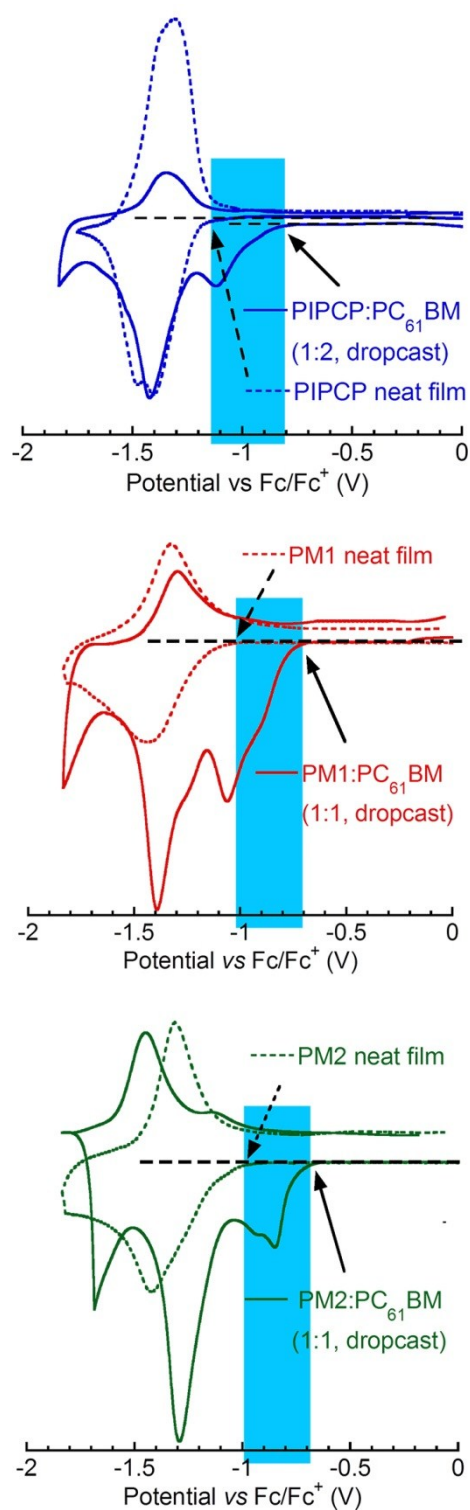


Figure S-7. Reduction measurements of PIPCP, PM1, PM2 neat films and PIPCP:PC<sub>61</sub>BM, PM1:PC<sub>61</sub>BM and PM2:PC<sub>61</sub>BM blend films.

## 6. GIWAXS

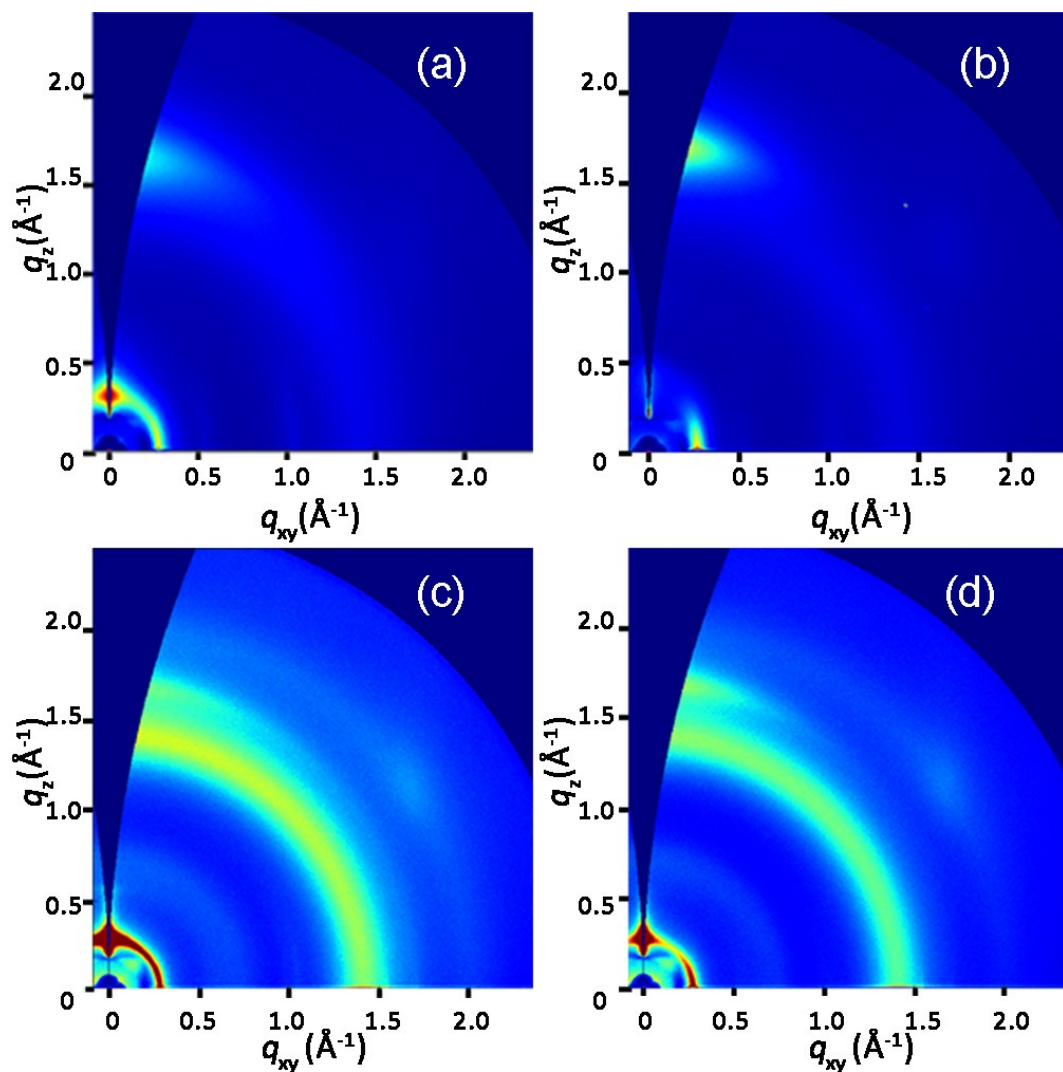


Figure S-8. GIWAXS of neat polymer and blend films: (a) PM1; (b) PM2; (c) PM1:PC<sub>61</sub>BM (1:1, 2% DIO, 100 °C/10 minutes); (d) PM2:PC<sub>61</sub>BM (1:1, 2% DIO, 100 °C/10 minutes).

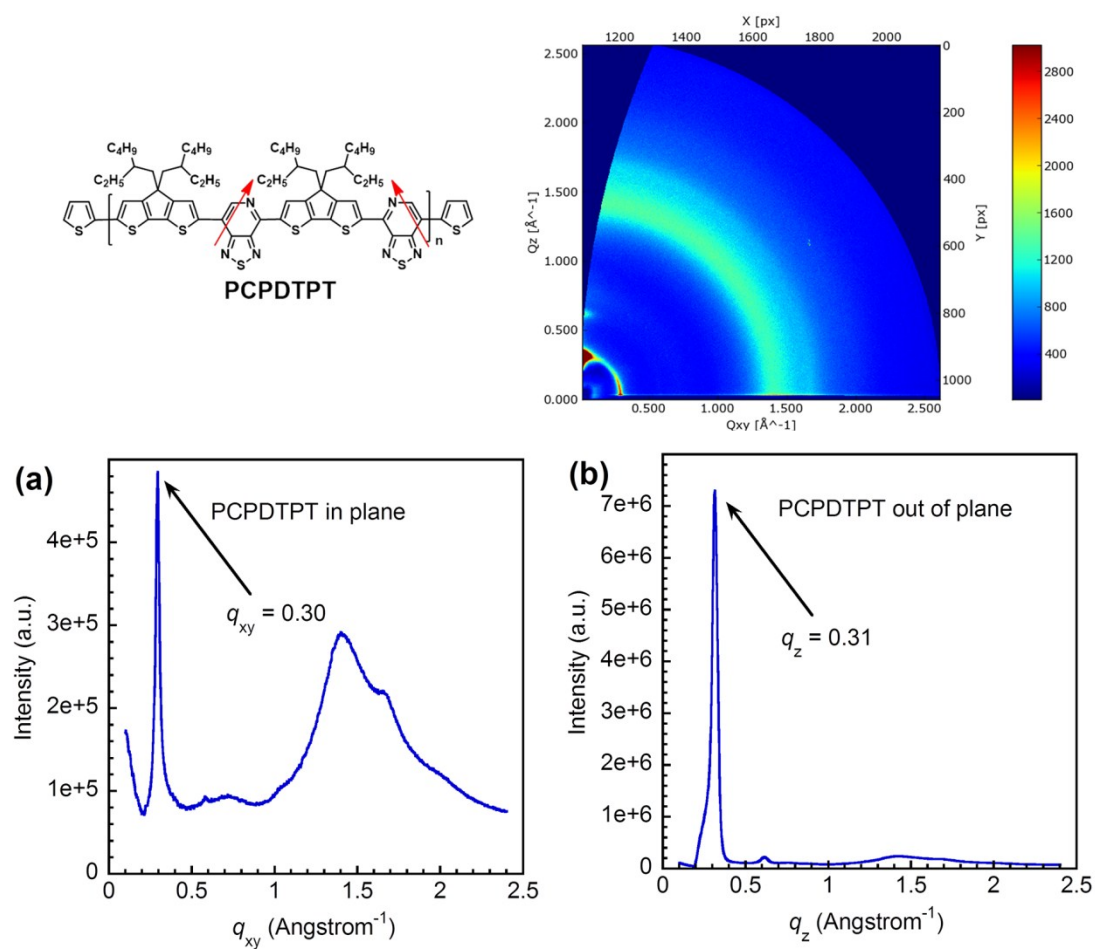


Figure S-9. Structure and GIWAXS analysis of PCPDTPT polymer.

PCPDTPT film shows a lamella distance of 2.0 - 2.1 nm, which is shorter than the polymer PM1 or PM2.

## 7. Mobility measurements by space charge limited current

Hole-only devices were fabricated to measure the hole mobility using the space charge limited current (SCLC) method. The device structure is ITO/MoO<sub>3</sub>/polymer or blend/Au. Polymer films were then spin-coated from the chlorobenzene solutions at the concentration. And the blend films were used the same solution for the OPV device fabrications and thermal annealed at 100 °C for 10 minutes. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is

described by equation: 
$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{(V - V_{bi})^2}{d^3}$$
, where  $J$  is the current,  $\epsilon_0$  is the permittivity of free space,  $\epsilon_r$  is the relative permittivity of the material,  $\mu$  is the zero-field mobility,  $d$  is the thickness of the polymer layer,  $V$  is the applied voltage and the  $V_{bi}$  is the built-in voltage. Then hole mobilities were calculated from the slope of the  $J^{1/2}$ - $V$  curves below.

Table 1. Neat polymer films mobilities

Neat PM1 Thickness	Neat PM1 Mobility	Neat PM2 Thickness	Neat PM2 Mobility
140 nm	$1.6 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$	150 nm	$2.9 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$

Table 2. Blend films mobilities (Blend films processing conditions were same as the PSCs, with 2% DIO and thermal annealing.)

PM1 Blend Thickness	PM1 Blend Mobility	PM2 Blend Thickness	PM2 Blend Mobility
150 nm	$3.1 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$	175 nm	$4.5 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$

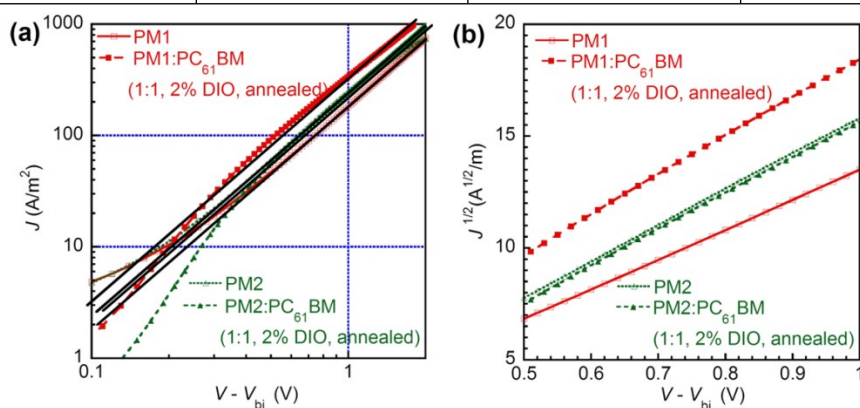


Figure S-10. SCLC mobility measurements (a)  $J$ - $V$  curves (b)  $J^{1/2}$ - $V$  curves.

## 8. Solar cell performance.

Table 3. PM1 and PM2 devices average performance based on 16 devices.

	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
PM1:PC <sub>61</sub> BM (1:1)	13.6 ± 0.2	0.80	0.58 ± 0.02	6.2 ± 0.2
PM2:PC <sub>61</sub> BM (1:1)	13.9 ± 0.4	0.79	0.65 ± 0.01	7.2 ± 0.1

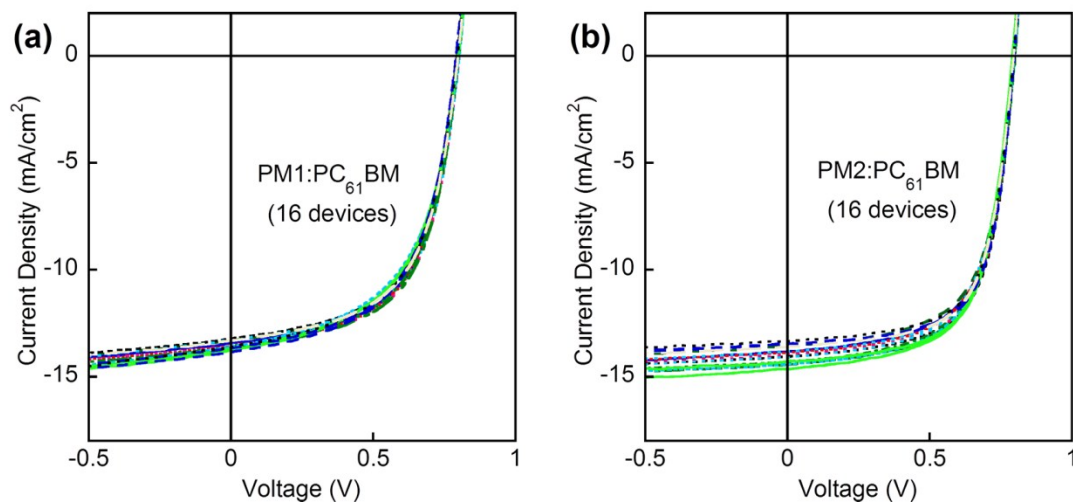


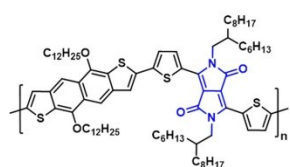
Figure S-11.  $J$ - $V$  curves of 16 devices for: (a) PM1:PC<sub>61</sub>BM (1:1, 2% DIO, annealed); (b) PM2:PC<sub>61</sub>BM (1:1, 2% DIO, 100 °C/10 minutes).

Table 4. PM1 and PM2 devices results based on the D/A ratio of 1:2 and 1:3

	D/A Ratio	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
PM1:PC <sub>61</sub> BM	1:2	12.4 ± 0.1	0.77 ± 0.01	0.62 ± 0.01	5.9 ± 0.1
PM1:PC <sub>61</sub> BM	1:3	8.5 ± 0.4	0.76	0.64	4.2 ± 0.2
PM2:PC <sub>61</sub> BM	1:2	12.5 ± 0.2	0.78	0.68 ± 0.01	6.6 ± 0.1
PM2:PC <sub>61</sub> BM	1:3	10.1 ± 0.2	0.77	0.64 ± 0.01	5.0 ± 0.1

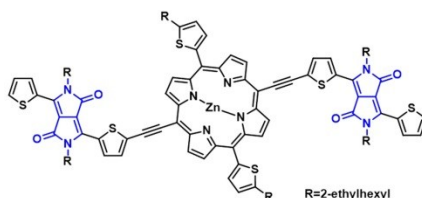
(Films processing conditions of 1:2 and 1:3 devices were identical to the 1:1 devices, with 2% DIO and same thermal annealing condition of 100 °C/10 minutes.)

## 9. Donor structures of $E_{loss}$ below 0.7 eV.



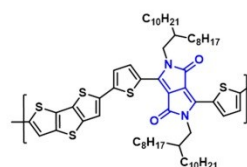
**PNDTDP**

$E_g=1.36$  eV,  $V_{oc}=0.76$  eV,  $E_{loss}=0.60$  eV  
 $J_{sc}=13.34$  mA/cm<sup>2</sup>, FF=60%, PCE=6.92%  
 Peng et al. *Chem. Commun.* **2012**, 48, 11452



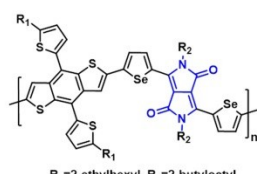
**DPPEZnP-TEH**

$E_g=1.37$  eV,  $V_{oc}=0.78$  eV,  $E_{loss}=0.59$  eV  
 $J_{sc}=16.76$  mA/cm<sup>2</sup>, FF=61.8%, PCE=8.08%  
 Peng et al. *J. Am. Chem. Soc.* **2015**, 137, 7282



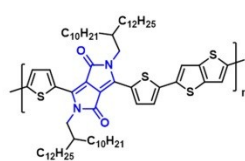
**PDTTDP**

$E_g=1.22$  eV,  $V_{oc}=0.66$  eV,  $E_{loss}=0.56$  eV  
 $J_{sc}=13.7$  mA/cm<sup>2</sup>, FF=66.1%, PCE=6.05%  
 Jo et al. *Energy Environ. Sci.* **2012**, 5, 6857



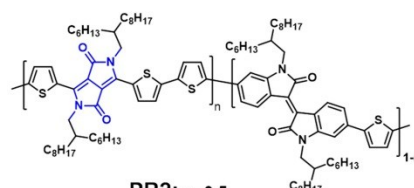
**PBDT-SeDPP**

$E_g=1.38$  eV,  $V_{oc}=0.69$  eV,  $E_{loss}=0.69$  eV  
 $J_{sc}=16.8$  mA/cm<sup>2</sup>, FF=62%, PCE=7.2%  
 Yang et al. *Adv. Mater.* **2013**, 25, 825



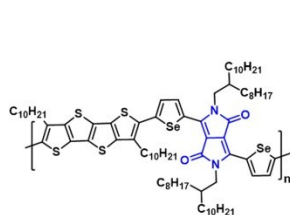
**DT-PDPP2T-TT**

$E_g=1.35$  eV,  $V_{oc}=0.68$  eV,  $E_{loss}=0.67$  eV  
 $J_{sc}=12.3$  mA/cm<sup>2</sup>, FF=74%, PCE=6.1%  
 Janssen et al. *Adv. Mater.* **2013**, 25, 3182



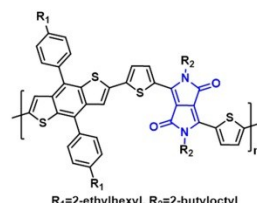
**PR2: n=0.5**

$E_g=1.40$  eV,  $V_{oc}=0.77$  eV,  $E_{loss}=0.63$  eV  
 $J_{sc}=13.52$  mA/cm<sup>2</sup>, FF=58%, PCE=6.04%  
 Jo et al. *Energy Environ. Sci.* **2013**, 6, 3301



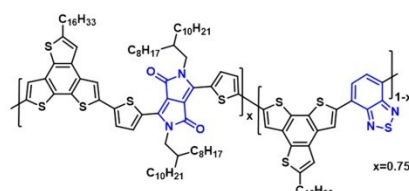
**PTDDPPSe**

$E_g=1.28$  eV,  $V_{oc}=0.58$  eV,  $E_{loss}=0.70$  eV  
 $J_{sc}=15.62$  mA/cm<sup>2</sup>, FF=62%, PCE=5.68%  
 Peng et al. *J. Mater. Chem. A*, **2014**, 2, 653



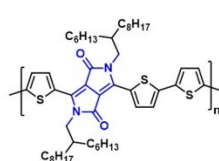
**PBDTP-DPP**

$E_g=1.46$  eV,  $V_{oc}=0.76$  eV,  $E_{loss}=0.70$  eV  
 $J_{sc}=13.6$  mA/cm<sup>2</sup>, FF=60%, PCE=6.20%  
 Yang et al. *J. Am. Chem. Soc.* **2012**, 134, 10071



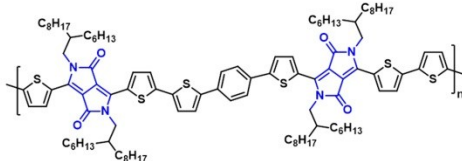
**P1**

$E_g=1.36$  eV,  $V_{oc}=0.68$  eV,  $E_{loss}=0.68$  eV  
 $J_{sc}=10.95$  mA/cm<sup>2</sup>, FF=69%, PCE=5.14%  
 McCulloch et al. *Chem. Commun.*, **2012**, 48, 5832



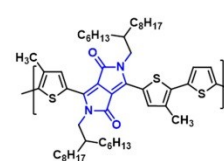
**PDPP3T**

$E_g=1.33$  eV,  $V_{oc}=0.67$  eV,  $E_{loss}=0.66$  eV  
 $J_{sc}=15.4$  mA/cm<sup>2</sup>, FF=69%, PCE=7.10%  
 Janssen et al. *Angew. Chem. Int. Ed.* **2013**, 52, 8341



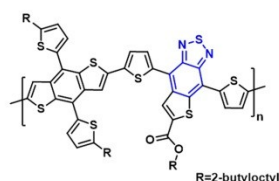
**PDPP3TaltTPT**

$E_g=1.43$  eV,  $V_{oc}=0.75$  eV,  $E_{loss}=0.68$  eV  
 $J_{sc}=15.9$  mA/cm<sup>2</sup>, FF=67%, PCE=8.0%



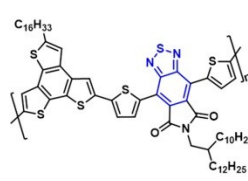
**PMDPP3T**

$E_g=1.30$  eV,  $V_{oc}=0.60$  eV,  $E_{loss}=0.70$  eV  
 $J_{sc}=17.8$  mA/cm<sup>2</sup>, FF=66%, PCE=7.0%  
 Janssen et al. *J. Am. Chem. Soc.* **2013**, 135, 5529



**PBTT-TBDDT**

$E_g=1.45$  eV,  $V_{oc}=0.75$  eV,  $E_{loss}=0.70$  eV  
 $J_{sc}=12.63$  mA/cm<sup>2</sup>, FF=53%, PCE=5.10%  
 Qin et al. *Chem. Mater.* **2014**, 26, 3495



**BBTI-1**

$E_g=1.5$  eV,  $V_{oc}=0.80$  eV,  $E_{loss}=0.70$  eV  
 $J_{sc}=16.45$  mA/cm<sup>2</sup>, FF=63%, PCE=8.3%  
 McCulloch et al. *Adv. Mater.* **2015**, 27, 948



**PDPT-DFBT**

$E_g=1.38$  eV,  $V_{oc}=0.70$  eV,  $E_{loss}=0.68$  eV  
 $J_{sc}=18.0$  mA/cm<sup>2</sup>, FF=63.4%, PCE=8.0%  
 Yang et al. *Macromolecules* **2013**, 46, 3384