

Supplementary Information

Tuning Nanoscale Morphology using Mixed Solvents and Solvent Vapor Treatment for High Performance Polymer Solar Cells

Dun Wang,^a Fujun Zhang,^{*a} Lingliang Li,^a Jiangsheng Yu,^b Jian Wang,^a Qiaoshi An,^a
Weihua Tang,^{*b}

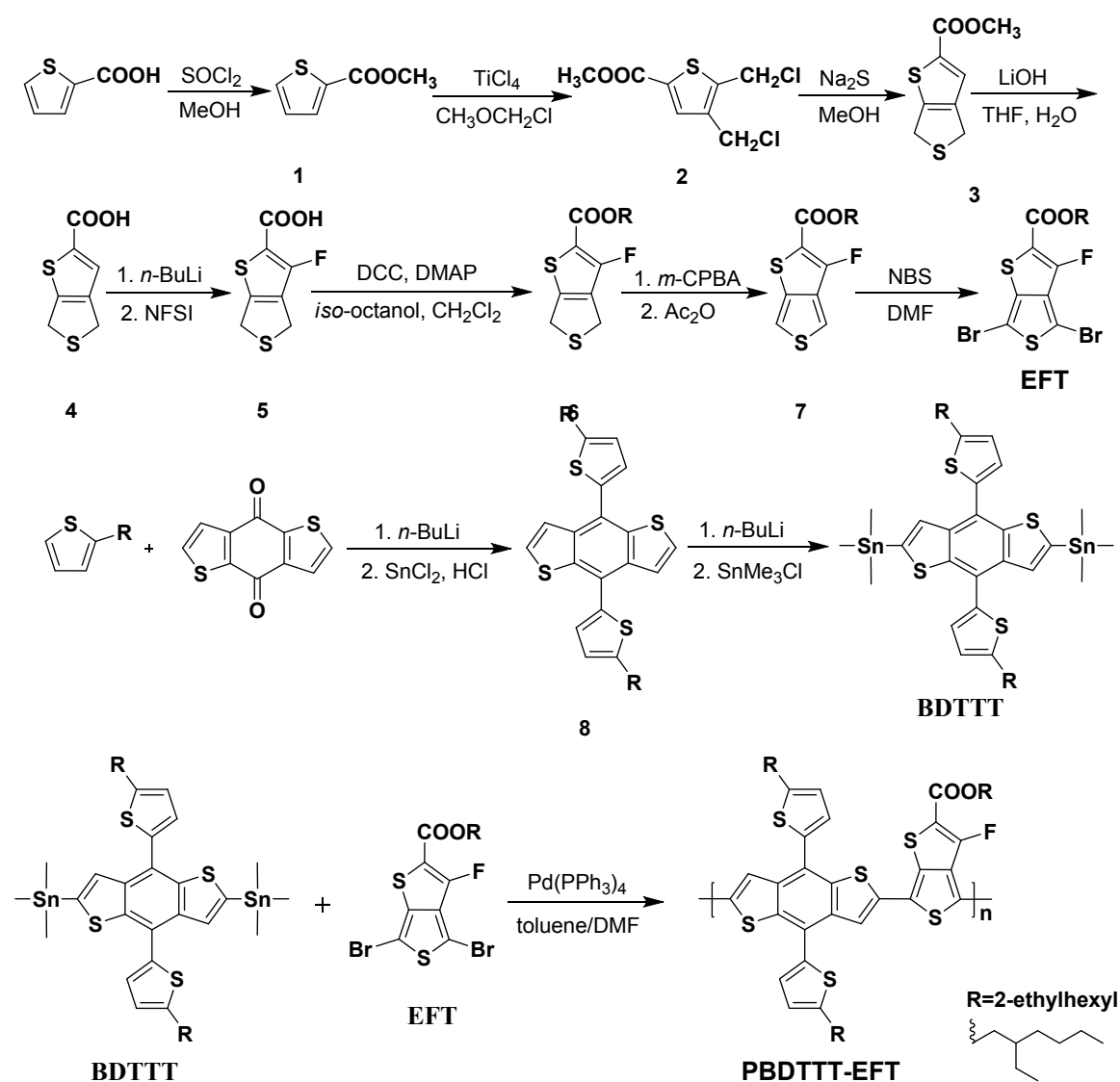
- a.* Key Laboratory of Luminescence and Optical Information, Ministry of Education, Beijing Jiaotong University, Beijing, 100044, PR China
- b.* Key Laboratory of Soft Chemistry and Functional Materials, Ministry of Education, Nanjing University of Science and Technology, Nanjing, 210094, China

List of content

1. Synthetic procedures.....	S2
2. Characterization data of polymer.....	S5
2.1 Molecular weight and thermal properties.....	S5
2.2 Optical and electrochemical properties.....	S6
2.3 NMR spectra.....	S8
2.4 Photovoltaic properties	S9
2.5 XRD spectra.....	S12
2.6 AFM image for CF vapor annealing	S13

1. Synthetic procedures

The synthetic routes for monomers and polymer are shown in Scheme S1.



Scheme S1. Synthetic routes for the monomers and the polymer **PBDTTT-EFT**.

2-Ethylhexyl-4,6-dibromo-3-fluoro-thieno[3,4-b]thiophene-2-carboxylate(EFT).¹

Compound 2-ethylhexyl-3-fluoro-thieno[3,4-b]thiophene-2-carboxylate **7** (8 g, 25.44 mmol) was dissolved in DMF (300 mL) at -30°C . Then NBS (11.32 g, 63.61 mmol)

in 50 mL of DMF was added dropwise in dark. The reaction mixture was stirred at room temperature for 18 h. After diethyl ether/water extraction, the combined organic layers were dried over anhydrous MgSO_4 . After solvent evaporation, the residue was purified by column chromatography on silica gel eluting with petroleum ether to obtain pure compound **EFT** (8.88 g, 18.80 mmol, 74%). ^1H NMR (400 MHz, CDCl_3 , δ): 4.26 (d, $J = 9.6$ Hz, 2H), 1.68-1.67 (m, 1H), 1.44-1.28 (m, 8H), 0.94 (m, 6H).

4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (8).² 40 mL of *n*-butyllithium (100 mmol, 2.5 M) was added dropwise to the solution of compound 2-(2-ethyl-hexyl)thiophene (6.5 g, 33.06 mmol) in 100 mL of anhydrous THF at 0°C under nitrogen atmosphere. The mixture was heated up to 50°C for 2 h. Then the solvent was cooled in ice-water bath. Subsequently, compound 4,8-dihydrobenzo[1,2-*b*:4,5-*b'*]dithiophen-4,8-dione (2.44 g, 11.08 mmol) was added one portion and the mixture was heated for another 2 h. After a mixture of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (20.01 g, 88.62 mmol) in 50 mL of aqueous HCl (10%) was added, the mixture was stirred overnight at room temperature. The reactant was poured into cold water and extracted by 200 mL of diethyl ether two times. The organic layer was washed with water and brine, dried with MgSO_4 , filtered, concentrated via rotary evaporation. Further purification was carried out by column chromatography on silica gel eluting

with petroleum ether to obtain pure compound as a yellow liquid (4.88 g, 8.42 mmol, 76%). ¹H NMR (500 MHz, CDCl₃, δ): 7.66 (d, *J* = 5.7 Hz, 2H), 7.46 (d, *J* = 5.7 Hz, 2H), 7.30 (d, *J* = 3.5 Hz, 2H), 6.90 (d, *J* = 3.5 Hz, 2H), 2.87 (d, *J* = 6.8 Hz, 4H), 1.72-1.67 (m, 2H), 1.43-1.33 (br, 16H), 0.97-0.91 (m, 12H).

2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-

***b*']dithiophene (BDTTT).²** Compound 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene **8** (1.00 g, 1.73 mmol) and 50 mL of anhydrous THF were added into a flask under nitrogen atmosphere. The solution was cooled to -78°C and 1.7 mL of *n*-butyllithium (4.32 mmol, 2.5 M) was added dropwise. The reaction mixture was then stirred for 2 h at room temperature, then the reaction mixture was cooled to 0°C and 4.4 mL of trimethyltin chloride (4.40 mmol, 1.0 M in hexane) was added in one portion and the mixture was stirred at RT overnight. The mixture was quenched by addition of 20 mL of water and extracted by diethyl ether three times. The combined organic phase was dried with MgSO₄, filtered, concentrated via rotary evaporation. Further purification was carried out by recrystallization using ethanol to obtain the pure compound **M2** as pale yellow solid (1.20 g, 1.33 mmol, 77%). ¹H NMR (500 MHz, CDCl₃, δ): 7.69 (s, 2H), 7.32 (d, *J* = 3.5 Hz, 2H), 6.91 (d, *J* = 3.5 Hz, 2H), 2.89-2.86 (m, 4H), 1.72-1.68 (m, 2H), 1.46-

1.35(br, 16H), 0.98-0.86 (m, 12H), 0.40 (s, 18H).

PBDTTT-EFT. M1 (0.5415 g, 1.15 mmol), **M2** (1.04 g, 1.15mmol), dry toluene (20 mL) and dry dimethylformamide (4 mL) were added in a flask under nitrogen atmosphere. The catalyst Pd(PPh₃)₄ (39.8 mg, 0.0345mmol, 3%) was added quickly. After another flushing with for 15 minutes, the reaction mixture was heated to reflux at 110°C for 16 h. The reactant was cooled down to room temperature and poured into 200 mL methanol. The precipitate was collected and Soxhlet-extracted in sequence with methanol, hexane and chloroform. Polymer was recovered from the chloroform fraction by rotary evaporation and precipitated in methanol. The purple polymer **PBDTTT-EFT** was collected by filtration and dried under vacuum with a yield of 85%. Anal. Calcd for (C₄₉H₅₇FO₂S₆)_n: C, 66.17; H, 6.46. Found: C, 66.22; H, 6.46. $M_n = 23.4$ KDa, $M_w = 81.9$ KDa, PDI = 3.5.

2. Characterization data of polymer

2.1 Molecular weight and thermal properties

Table S1. Molecular weights and thermal properties of **PBDTTT-EFT**.

Polymer	M_n (kDa) ^a	M_w (kDa) ^a	PDI ^a	T_d (°C) ^b
PBDTTT-EFT	23.4	81.9	3.5	343

a) Determined by GPC in THF on the basis of polystyrene standards.

b) DSC measurement of the polymer with a ramping rate of 10 °C/min

Thermal stability of the polymer was investigated with thermogravimetric analysis (TGA). As shown in **Figure S1** and **Table S1**, the polymer shows good thermal stability under nitrogen atmosphere with the 5% weight-loss temperature (T_d) at 343 °C. The thermal stability of PBDTTT-EFT is good enough for the applications

in optoelectronic devices. From the differential scanning calorimetry (DSC) traces shown as inset in **Figure S1**, neither melting point nor glass transition temperatures was observed, suggesting that the polymer tends to be amorphous.

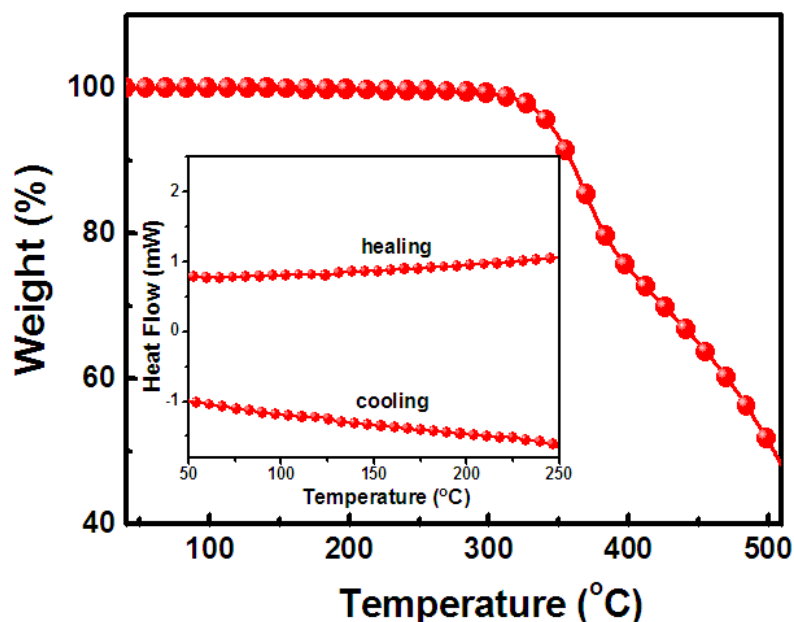


Figure S1. TGA curve of PBDTTT-EFT with a heating rate of 10 °C/min under nitrogen; the inset shows the DSC curve of PBDTTT-EFT.

2.2 Optical and electrochemical properties

The ultraviolet-visible (UV-vis) absorption data of PBDTTT-EFT and PC₇₁BM dilute solution in dichlorobenzene and the polymer film spin-coated on quartz substrate are summarized in **Table S2**.

Table S2. Optical and electrochemical properties of PBDTTT-EFT.

	Absorption spectra				Cyclic voltammetry	
	Solution ^a	Film ^b				
Polymer	λ_{\max} (nm)	λ_{\max} (nm)	λ_{onset} (nm)	$E_{\text{g}}^{\text{opt}}$ (eV) ^c	HOMO (eV)	LUMO (eV)
PBDTTT-EFT	705	707	790	1.57	-5.45	-3.54

^aMeasured in DCB solution. ^bCast from DCB solution. ^cBandgap estimated from the onset wavelength (λ_{onset}) of the optical absorption in the solid state: $E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{onset}}$.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of PBDTTT-EFT were determined by electrochemical cyclic voltammetry (CV). **Figure S2** shows the CV trace of polymer film on Pt electrode in Bu_4NPF_6 (0.1 M) acetonitrile solution at a scan rate of 100 mV/s with respect to the Ag/Ag⁺ electrode. The potential of Fc/Fc⁺ was measured in the same solution and found to be located at 0.23 V. On the basis of 4.8 eV below vacuum for the energy level of Fc/Fc⁺, the HOMO and LUMO energy level of the polymer is calculated from the onset oxidation potentials ($E_{\text{ox}}^{\text{onset}}$) and reduction potentials ($E_{\text{red}}^{\text{onset}}$), according to the following equations:

$$E_{\text{HOMO}} = -e(E_{\text{ox}}^{\text{onset}} + 4.57) \text{ (eV)} \quad (1)$$

$$E_{\text{LUMO}} = -e(E_{\text{red}}^{\text{onset}} + 4.57) \text{ (eV)} \quad (2)$$

The $E_{\text{ox}}^{\text{onset}}/E_{\text{red}}^{\text{onset}}$ of PBDTTT-EFT occurred at 0.88/-1.03 eV. The HOMO/LUMO energy levels were then estimated to be -5.45/-3.54 eV. Compared to the high HOMO level of P3HT (-4.76 eV), the PBDTTT-EFT with a deep-lying HOMO energy level indicate that the electron-withdrawing BDT unit into the polymer backbone is a good choice to lower the HOMO level and therefore result in the higher V_{oc} with PC₇₁BM as the acceptor.

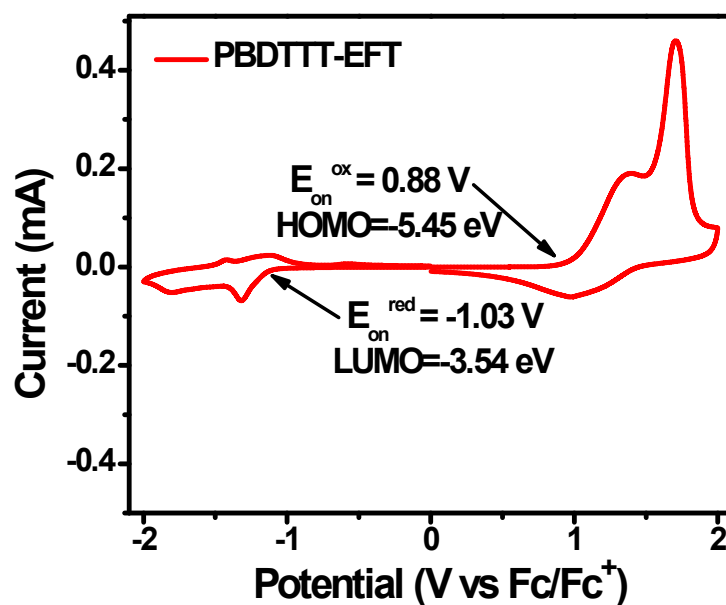


Figure S2. Cyclic voltammograms of PBDTTT-EFT film cast on a platinum electrode in $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NPF}_6$ acetonitrile solution at a scan rate of 100 mV/s .

2.3 NMR spectra

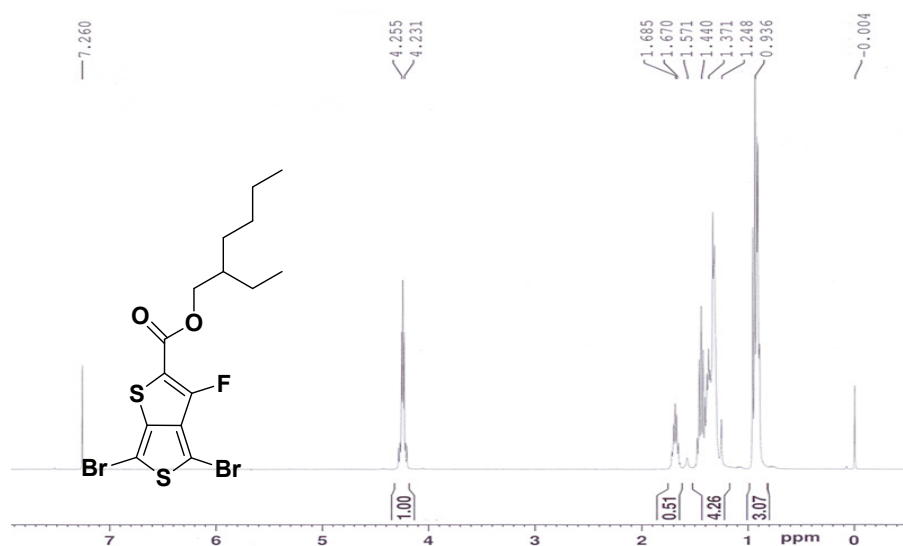


Figure S3. ^1H NMR spectrum of EFT.

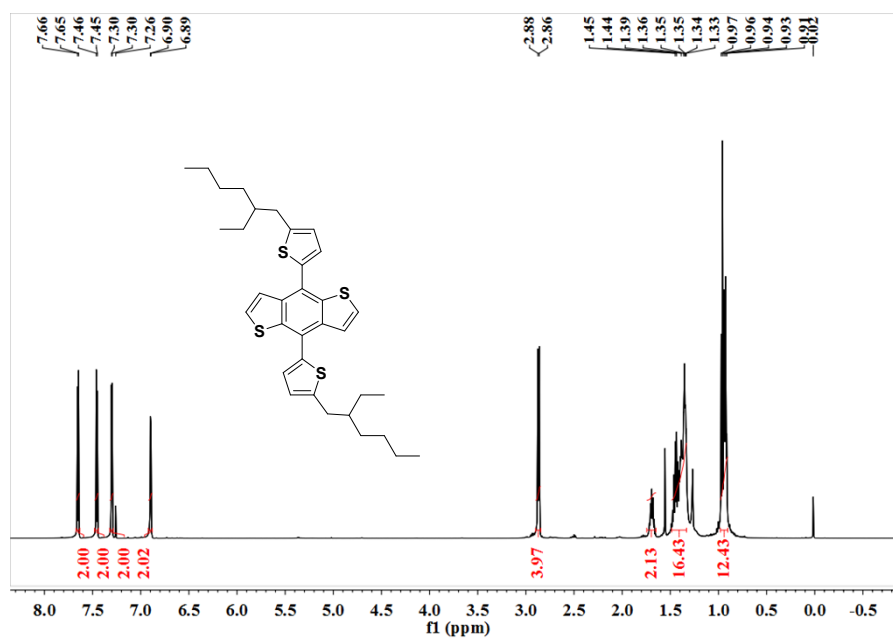


Figure S4. ^1H NMR spectrum of 4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene.

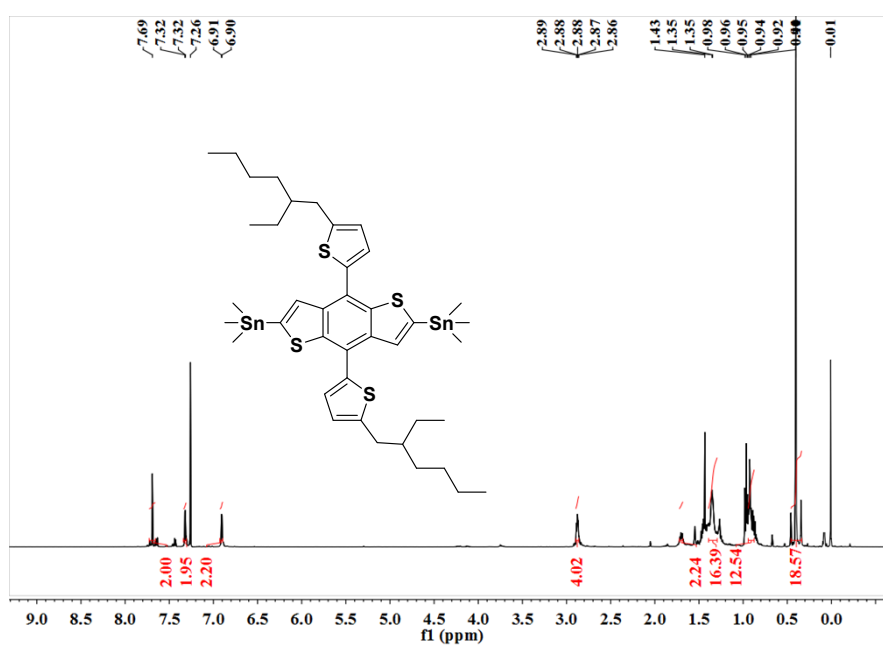


Figure S5. ^1H NMR spectrum of BDTTT.

2.4 Photovoltaic properties

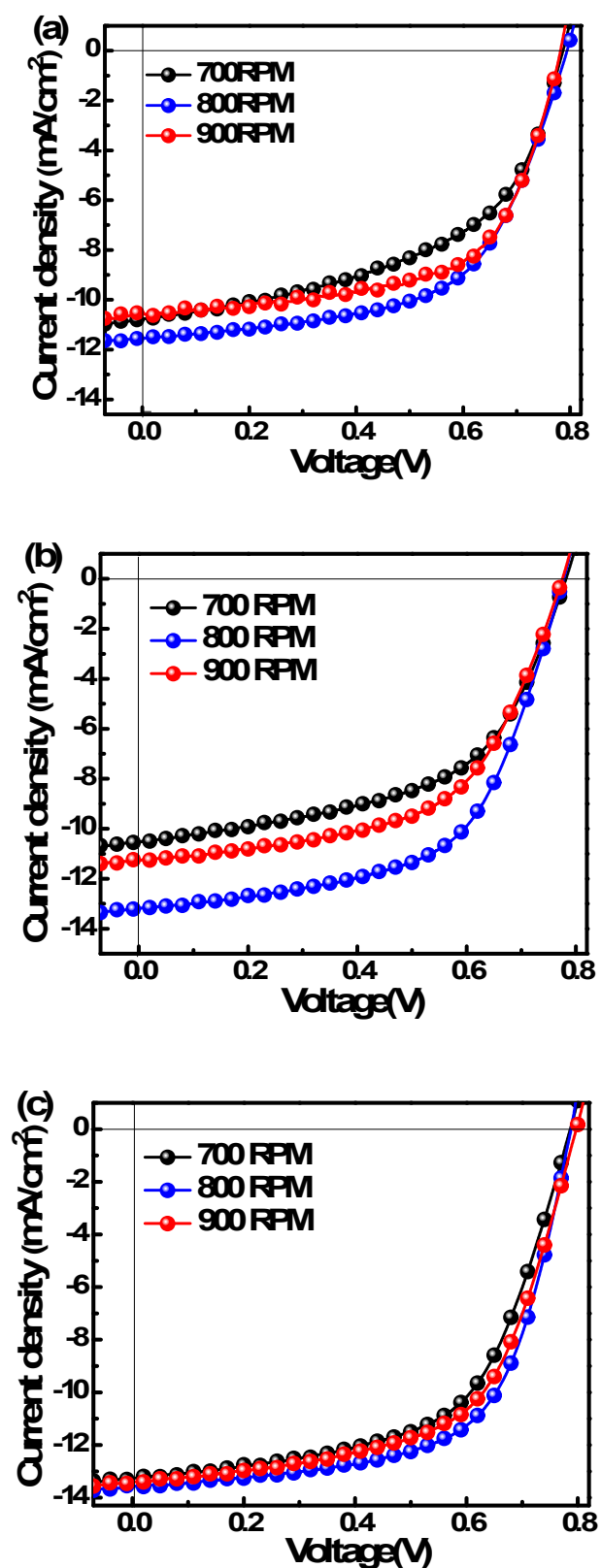


Figure S6. J - V characteristics curves of PSCs processed with DCB (a), CB (b) and DCB/CB (c) solvent (DIO was added into solutions before the spin-coating process,

v/v of solvent/DIO is 97:3) under illumination 100 mW/cm² AM 1.5 G simulated solar light.

Table S3. Key parameters of three kinds of PSCs under illumination 100 mW/cm² AM 1.5 G simulated solar light.

Solvent	Spin rate (RPM)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	Best PCE (%)	*Ave.PCE (%)
DCB 3% DIO	700	0.79	10.78	51.3	4.37	4.31±0.06
	800	0.79	11.54	59.1	5.39	5.30±0.09
	900	0.78	10.55	62.1	5.11	4.94±0.07
CB 3% DIO	700	0.78	10.55	54.3	4.47	4.40±0.07
	800	0.78	13.18	58.3	5.99	5.86±0.13
	900	0.78	11.31	56.1	4.95	4.90±0.05
DCB/CB 3% DIO	700	0.80	13.25	57.8	6.13	6.07±0.06
	800	0.79	13.63	62.9	6.77	6.70±0.07
	900	0.80	13.39	59.7	6.40	6.30±0.10

*The average PCE was evaluated based on 30 cells.

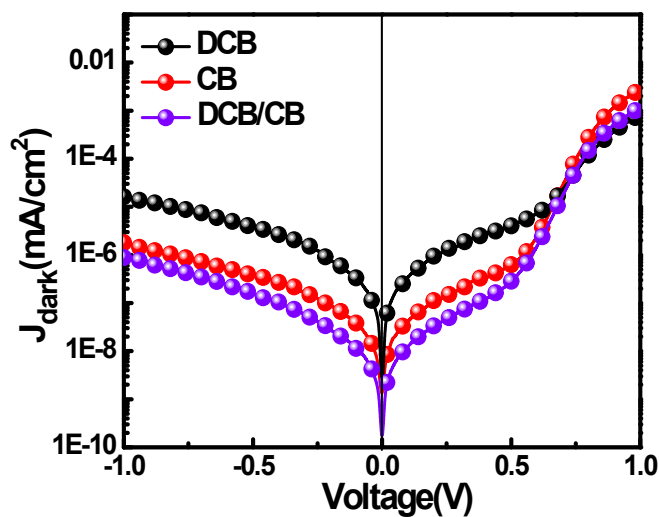


Figure S7. Single logarithmic of J - V characteristics curves of PSCs processed with different solvents.

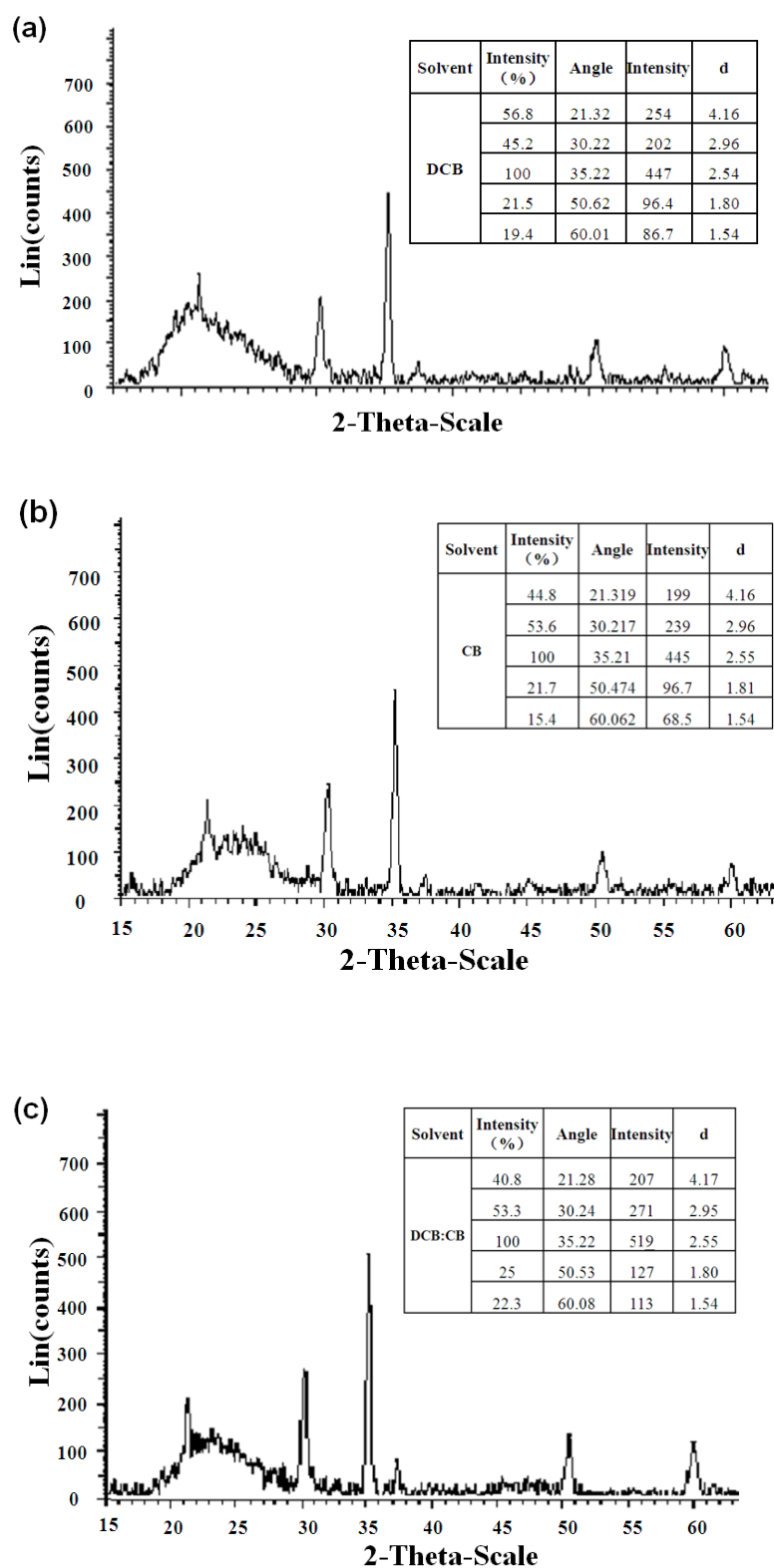


Figure S8. XRD patterns of the PBDTTT-EFT:PC₇₁BM blend films processed with different solvents.

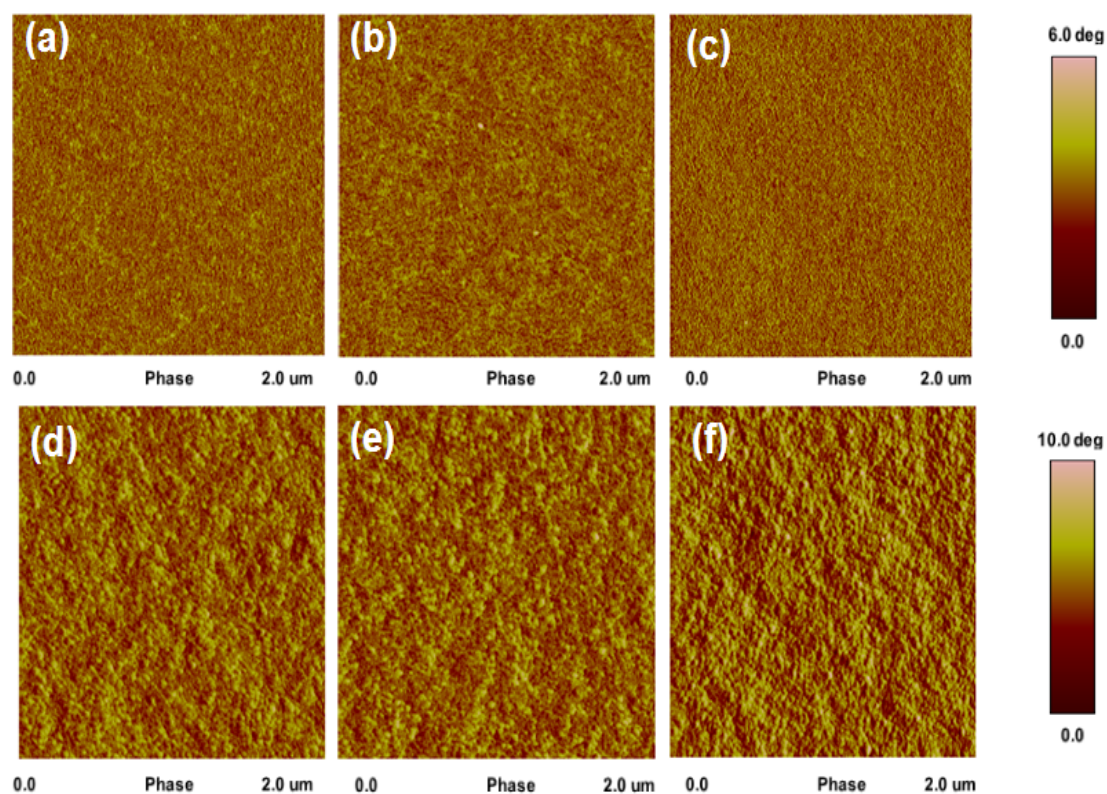


Figure S9. AFM phase images of PBDTTT-EFT:PC₇₁BM blend films under different time (30s, 60s, 90s, 120s, 180s, 360s) CF vapor annealing treatment.

References:

1. Y. Y. Liang, D. Q. Feng, Y. Wu, S. T. Tsai, G. Li, C. Ray and L. P. Yu, *J Am Chem Soc*, 2009, **131**, 7792.
2. L. J. Huo, S. Q. Zhang, X. Guo, F. Xu, Y. F. Li and J. H. Hou, *Angew Chem Int Edit*, 2011, **50**, 9697.