

## Supporting Information for

### Side-chain engineering improve molecular stacking and enhanced miscibility for efficient fullerene organic solar cells

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#### Experimental Section

All starting materials and reagents were purchased from commercial sources and used without further purification, unless otherwise mentioned.

#### Instrumentation

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker Advance III 600 spectrometer with tetramethylsilane (TMS,  $\delta = 0$  ppm) as an internal standard. All GPC analyses were made using 1,2,4-trichlorobenzene (TCB) as eluent at 150 °C and polystyrene standard as reference. The UV-vis absorption spectra were measured by PerkinElmer Lambda 25 UV/Vis Spectrometer. Cyclic voltammetry (CV) measurements were implemented on a electrochemical workstation (CHI660D). Thermalgravimetric analysis (TGA) measurements were performed on STA-409 at a heating rate of 10 °C/min. The current-density ( $J-V$ ) curves of the APSCs were tested with a Keithley 2420 source meter under AM1.5G solar simulator. The light intensity was 100 mW cm<sup>-2</sup> that standardized by a standard silicon detector. External quantum efficiencies (EQEs) spectra were measured by incident photon conversion efficiency (IPEC)

measurement system. And the morphologies were observed by atomic force microscope (AFM) and transmission electron microscope (TEM). Grazing incidence wide-angle X-ray scattering (GIWAXS) patterns were collected by beamline BL16B1 workstation (Shanghai Synchrotron Radiation Facility).

### **Photovoltaic device fabrication**

The PSCs were fabricated based on traditional device structure of ITO/PEDOT:PSS/active layer/PDINO/Al. And the specific fabricating procedure was as follows: Cleaned the ITO-coated glass substrates with deionized water, acetone and isopropyl alcohol by ultrasonic bath sequentially for 15 min in turn. After cleaning, the ITO-coated glass substrates were dried by N<sub>2</sub>, and then treated with O<sub>2</sub> plasma for 6 min. PEDOT:PSS was spin coated on ITO-coated glass with 4000 rpm and dried in an oven. Afterwards, and the blend solution was spin-coated on the PEDOT:PSS film in glove box. After that the PDINO solution was spin-coated on the active layer at 4000rpm as buffer layer. In the end, an aluminum layer was thermally evaporated below  $4 \times 10^{-4}$  Pa as the cathode. And the effective areas of the solar cells were 0.1 cm<sup>2</sup> as defined by shadow masks. The blend solution of polymer: PC<sub>71</sub>BM was prepared with ratio 1:1.5, and stirring 6 h in chlorobenzene.



## Materials

All the reagents, unless otherwise specified, were purchased from J&K and Tokyo Chemical Industry Co., Ltd., and were used without further purification. PC<sub>71</sub>BM was purchased from Solarmer Materials Inc. BDT-ThS and BDT-PhS were purchased from Derthon Optoelectronic Materials Science Technology Co., Ltd, and the purity of the two materials were both 98%. The general synthetic routes from monomers to polymers are shown in **Scheme S1**. The detailed synthesized procedures are as follows.

### 4-bromothiophene-3-carbaldehyde (1)

5-3,4-dibromothiophene (12.10 g, 50 mmol) was added to a 250 mL single-topped flask, and evacuate with argon gas for three times. Then 100 mL of ether with anhydrous and oxygen-free was added and dissolved. And 2.4 M of n-BuLi (20.8 mL, 50 mmol) was slowly added to the solution at -78°C, and after holding for 1 h, DMF (3.65 g, 50 mmol) was added. After slowly returning to room temperature, continue to stir for 2 h. Then add saturated ammonium chloride solution to quench the reaction. The combined organic phases were extracted twice with ether and dried with anhydrous sodium sulfate. The organic phase was concentrated and purified by column chromatography to give a pale yellow oily liquid in 80% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ ( ppm ) : 9.94 (s, 1H), 8.16 (d, J=3.6Hz, 1H), 7.37 (d, J=3.6 Hz, 1H).

### ethyl thieno[3,4-b]thiophene-2-carboxylate (2)

In a mixture of compound 1 (6.69 g, 35 mmol), ethyl thioglycolate (4.63 g, 38.5 mmol), copper oxide nanoparticles (334 mg), potassium carbonate (7.26 g, 52.5 mmol), added 100 mL DMF to dissolve. The reaction was carried out at 80°C for 12 h. At the end of the reaction, the solution was poured into ice water and extracted twice with ether. Then the organic phases were dried with anhydrous sodium sulfate, concentrated and purified by column chromatography to give a clear yellow solid in 48% yield. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ ( ppm ) : 7.70 (s, 1H), 7.59 (d, J=3.0 Hz, 1H), 7.28 (d, J=3.0 Hz, 1H), 4.37 (q, J=7.2 Hz, 2H), 1.39 (t, J=7.2 Hz, 3H).

### thieno[3,4-b]thiophene-2-carboxylic acid (3)

To a solution of compound 2 (3.18 g, 15 mmol), NaOH (1.2 g, 30 mmol) in ethanol (100 mL), dissolved and distilled back overnight. After the reaction was completed, the solution was poured into ice water and extracted with petroleum ether. Then adjust the aqueous phase to 2-3 using dilute hydrochloric acid, at which time a large amount of yellow solid was seen to precipitate. The resulting solid was filtered and recrystallized using ethanol to give a yellow solid in 91% yield. <sup>1</sup>H NMR (600 MHz, DMSO-d<sub>6</sub>), δ (ppm) : 13.87 (brs, 1H), 7.53 (s, 1H)

#### **2-octyldodecyl thieno[3,4-b]thiophene-2-carboxylate (4)**

Under light-proof conditions, a mixture of compound 3 (3.20 g, 17.37 mmol), DMAP (0.11 g, 0.87 mmol) was dissolved by 200 mL of dichloromethane. DCC (3.94 g, 19.11 mmol) was slowly added in batches, stirred for 30 min, then added 2-octyldodecanol (5.71 g, 19.11 mmol) and stirred for 20 h. After the reaction, the solids in the reaction solution were filtered out and the filter cake was washed with a small amount of dichloromethane. Then the filtrate was concentrated and purified by column chromatography to obtain a light yellow liquid, which condensed to a white solid at low temperature with a yield of 70%.

#### **2-octyldodecyl 4,6-diiodothieno[3,4-b]thiophene-2-carboxylate (5)**

Compound 4 (6.24 g, 13.43 mmol) was dissolved with 100 mL of chloroform under light-proof conditions. Then NIS (6.35 g, 28.2 mmol) was slowly added in batches, followed by 2 mL of trifluoroacetic acid. After reacting for 30 min, the solution was spun to dry and purified by column chromatography under light-proof conditions. And a light red liquid was obtained, which congealed to a light red solid with a yield of 73% at low temperature.

#### **4-methyl-2-(tributylstannyl)thiazole (6)**

Methylthiazole (1.20 g, 10 mmol) was added to a 200 mL flask and pumped under argon protection. Then 50 mL of anhydrous oxygen-free treated ether was added. Then n-BuLi (6.9 ml, 1.6 M) was added slowly drop by drop at -78°C. After maintaining at low temperature for 1 h, tributyltin chloride (3.58 g, 11 mmol) was added and slowly recovered to room temperature overnight. After completion, the

reaction was quenched with water and extracted twice with ether. The organic phase was de-watered with anhydrous sodium sulfate and spun dry to yield a pale yellow oily liquid, which was ready for the next step. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ 7.03 (s, 1H), 2.55 (s, 3H), 1.62-1.56 (m, 6H), 1.34 (dd, J=14.8, 7.4 Hz, 6H), 1.23-1.18 (m, 6H), 0.89 (t, J=7.4 Hz, 9H).

**2-Octyldodecyl4,6-bis(4-methylthiazol-2-yl)thieno[3,4-b] thiophene-2-carboxylate (7)**

A mixture of compound 5 (2.15 g, 3.00 mmol), compound 6 (3.80 g, 9.00 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (170 mg, 0.15 mmol) in 40 mL of toluene under argon protection. The reaction solution was heated at 100°C for 8 h. After the reaction, the toluene was dried and the product was extracted by column chromatography to give a yellow solid with a yield was 56%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>), δ 8.15 (s, 1H), 6.95 (d, J = 0.4 Hz, 2H), 4.28 (d, J = 5.8 Hz, 2H), 2.53 (d, J = 6.7 Hz, 6H), 1.85 - 1.79 (m, 1H), 1.43 - 1.24 (m, 32H), 0.86 (t, J = 6.9 Hz, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 162.74, 158.50, 158.42, 154.40, 154.36, 142.65, 142.21, 138.83, 128.80, 123.94, 123.92, 114.10, 113.84, 68.87, 37.40, 31.92, 31.42, 29.97, 29.69, 29.66, 29.62, 29.58, 29.37, 29.35, 26.77, 22.69, 17.14, 17.13, 14.12.

**Compound M1.**

Dissolve compound 7 (1.26 g, 2 mmol) with 40 mL of chloroform. Then NBS (0.8 g, 4.5 mmol) was added slowly in batches. After the reaction was stirred for 4 h at room temperature, The solvent was concentrated and purified by column chromatography. A yellow solid was obtained in 84% yield. H NMR (600 MHz, CDCl<sub>3</sub>), δ 7.95 (s, 1H), 4.26 (d, J = 5.9 Hz, 2H), 2.44 (d, J = 6.6 Hz, 6H), 1.85-1.79 (m, 1H), 1.41 - 1.24 (m, 32H), 0.86 (t, J = 6.9 Hz, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 162.33, 157.65, 157.53, 153.21, 153.15, 142.70, 142.55, 139.01, 128.22, 123.53, 123.27, 105.03, 104.74, 69.05, 37.38, 31.93, 31.92, 31.43, 29.99, 29.70, 29.67, 29.64, 29.59, 29.38, 29.36, 26.78, 22.70, 15.68, 15.66, 14.13.

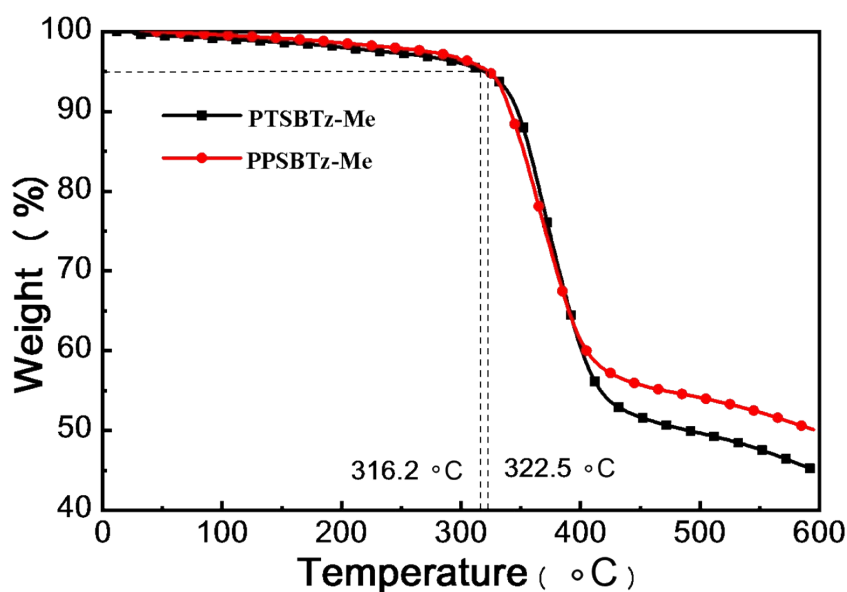
**Polymer PTSBTz-Me Synthesis**

A mixture of BDT (96.9 mg, 0.1 mmol), compound M1 (81.7 mg, 0.1 mmol),

$\text{Pd}(\text{PPh}_3)_4$  (5.8 mg, 0.005 mmol) were pumped and exchanged three times under argon protection. Then add 4 mL of anhydrous toluene and 1 mL of dry DMF. The reaction was stopped after 1 h of distillation at  $110^\circ\text{C}$ . When the reaction solution was brought to room temperature, drop into methanol drop by drop, and get the precipitated polymer. Then the solids were extracted with methanol, acetone, dichloromethane, trichloromethane and chlorobenzene in order. The polymer was obtained in 64% yield. Mn: 63.7 kDa, PDI: 3.54.

#### Polymer PPSBTz-Me Synthesis

A mixture of BDT (95.7 mg, 0.1 mmol), compound M1 (81.7 mg, 0.1 mmol),  $\text{Pd}(\text{pPh}_3)_4$  (5.8 mg, 0.005 mmol) was pumped and exchanged three times under argon protection. Then add 4 mL of anhydrous toluene and 1 mL of dry DMF. The reaction was stopped after 30 min of distillation at  $110^\circ\text{C}$ . When the reaction solution was brought to room temperature, drop into methanol drop by drop, and get the precipitated polymer. Then the solids were extracted with methanol, acetone, dichloromethane, trichloromethane and chlorobenzene in order. The polymer was obtained in 61% yield. Mn: 87.2 kDa, PDI: 3.14.



**Fig.S1** TGA plots of two polymers with a heating rate of  $10^\circ\text{C}/\text{min}$  under the protection of nitrogen

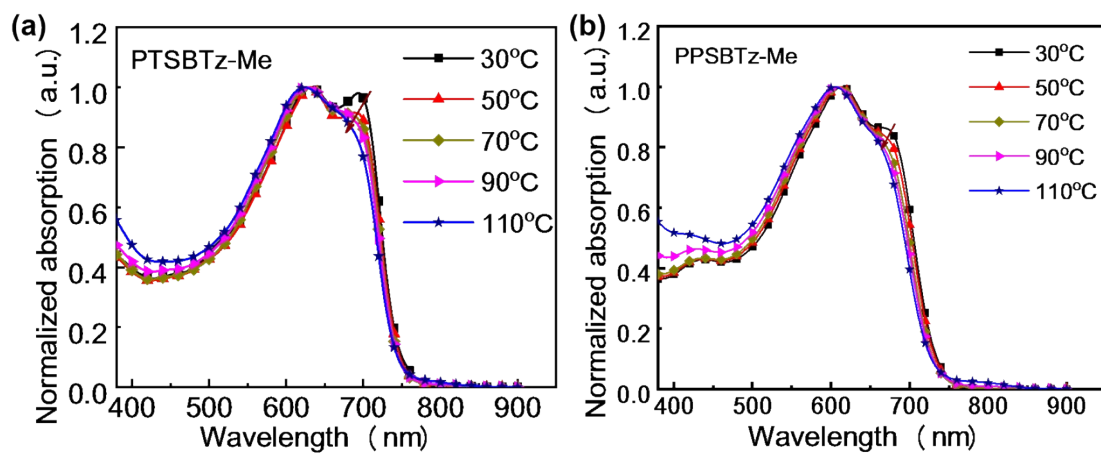


Fig.S2 Temperature-dependent UV-vis absorption spectra of the two polymers in chlorobenzene solution

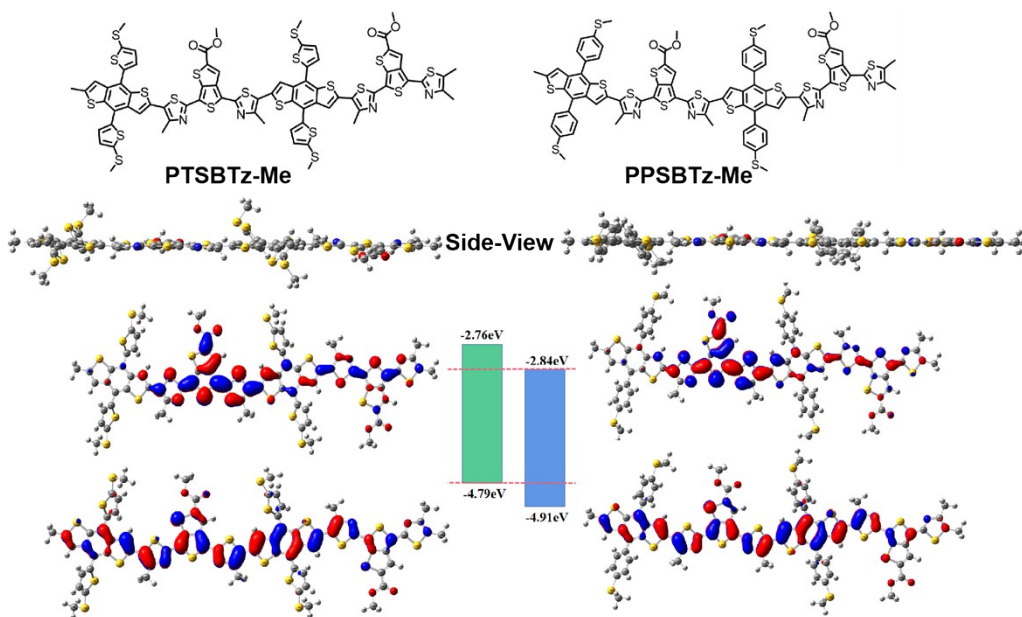


Fig.S3 HOMO and LUMO energy levels of the polymer PTSBTz-Me and PPSBTz-Me

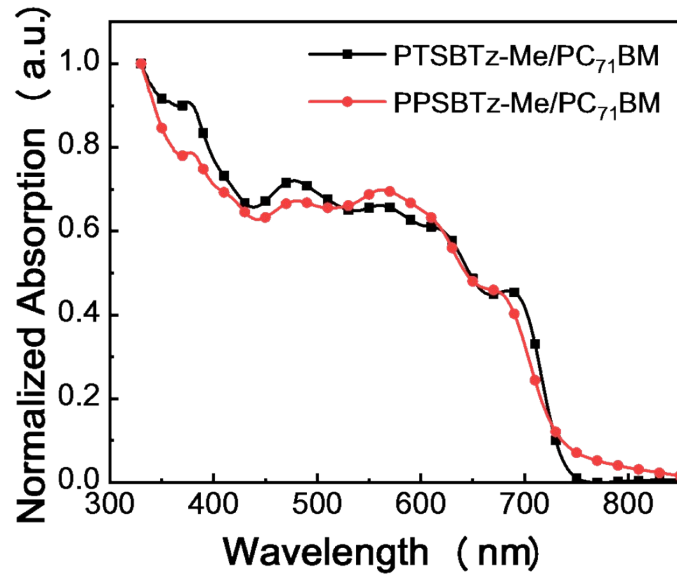


**Table S1.** The photovoltaic performance of PTSBTz-Me/PC<sub>71</sub>BM under different conditions

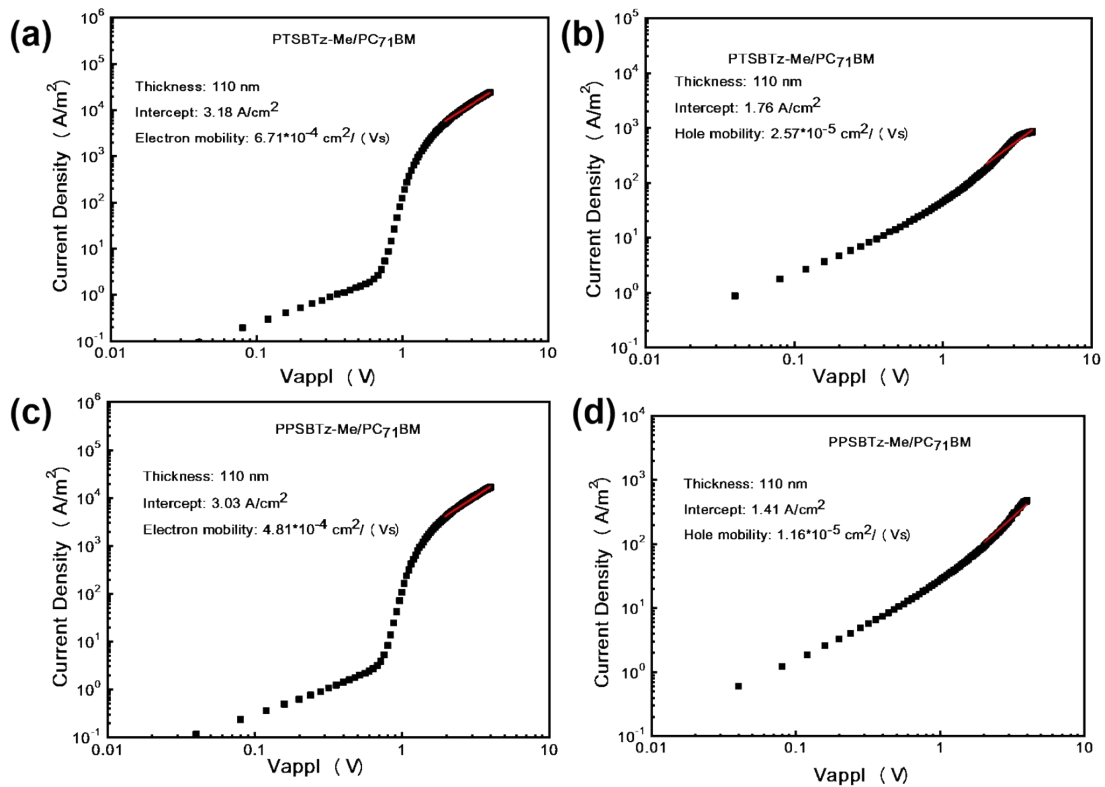
D/A ratios (w/w)	Concentration (mg/mL)	Additive	Interface layer	V <sub>oc</sub> (V)	J <sub>SC</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)	Anneal
1:1	9	DIO 1.5%	PDINO	0.88	16.39	64.08	9.29	No
1:2	9	DIO 1.5%	PDINO	0.87	15.75	67.78	9.24	No
1:1.5	9	DIO 1.5%	PDINO	0.86	16.53	71.02	10.14	No
1:1.5	8	DIO 2%	PDINO	0.89	17.34	67.39	10.36	No
1:1.5	8	DIO 2%	PDINO	0.90	13.68	67.77	8.32	TA80°C
1:1.5	8	DIO 2%	PDINO	0.89	14.32	63.97	8.19	TA100 °C
1:1.5	8	DIO 2%	PDINO	0.90	13.01	67.09	7.89	TA120 °C
1:1.5	8	DIO 2%	PFN	0.88	14.79	67.70	8.85	No
1:1.5	8	DIO 2%	PFN-Br	0.88	13.54	71.54	8.50	No
1:1.5	8	DIO 0%	PDINO	0.91	8.85	56.45	4.57	No
1:1.5	8	DIO 3%	PDINO	0.89	15.84	69.82	9.81	No
1:1.5	8	CN 2%	PDINO	0.88	15.34	67.02	9.02	No
1:1.5	8	DPE 2%	PDINO	0.87	16.60	68.57	9.87	No

**Table S2.** The photovoltaic performance of PPSBTz-Me/PC<sub>71</sub>BM under different conditions

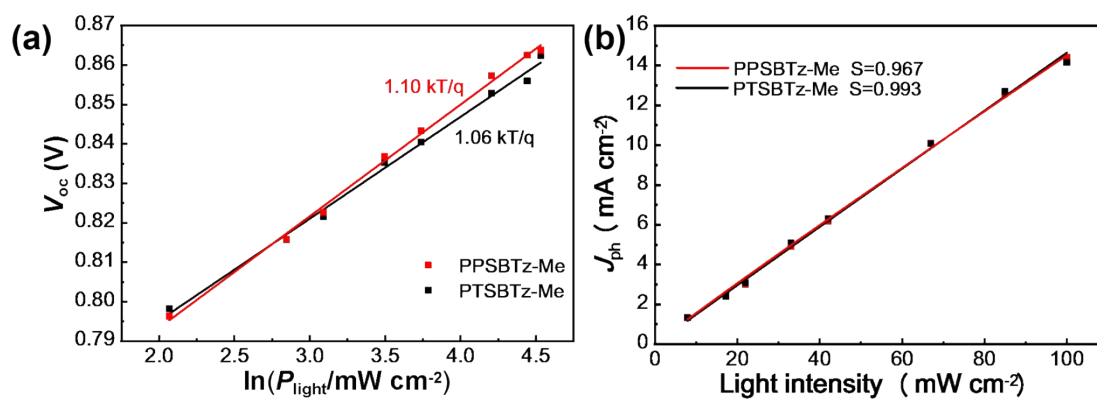
D/A ratios(w/w)	Concentration (mg/mL)	Additive	Interface layer	V <sub>oc</sub> (V)	J <sub>SC</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)	Anneal
1:1	8	DIO 3%	PDINO	0.90	12.32	59.06	6.53	No
1:1.5	8	DIO 3%	PDINO	0.90	15.38	64.71	8.95	No
1:2	8	DIO 3%	PDINO	0.90	12.96	63.37	7.40	No
1:1.5	8	DIO 3%	PDINO	0.89	11.81	58.08	6.11	TA60 ℃
1:1.5	8	DIO 3%	PDINO	0.87	11.64	58.46	5.95	TA80 ℃
1:1.5	8	DIO 3%	PFN	0.89	13.05	61.08	7.11	No
1:1.5	8	DIO 3%	PFN-Br	0.90	12.77	67.56	7.75	No
1:1.5	8	DIO 0%	PDINO	0.91	3.93	57.54	2.05	No
1:1.5	8	DIO 1%	PDINO	0.88	14.60	65.81	8.41	No
1:1.5	8	DIO 2%	PDINO	0.90	13.87	67.23	8.36	No
1:1.5	8	CN 3%	PDINO	0.88	14.05	58.97	7.31	No
1:1.5	8	DPE 3%	PDINO	0.88	14.55	63.61	8.15	No



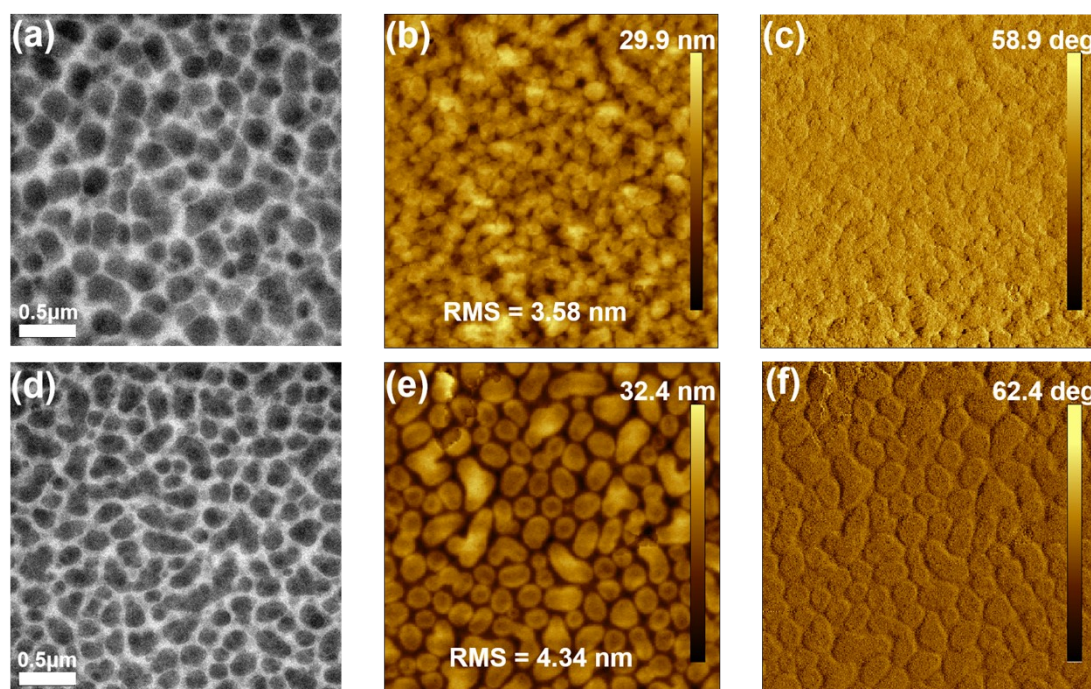
**Fig.S4** UV-vis absorption spectra of the blend film of PTSBTz-Me/PC<sub>71</sub>BM and PPSBTz-Me/PC<sub>71</sub>BM



**Fig.S5** J-V characteristics of the blend films. The symbols are experimental data for the transport of holes and electrons, and the solid lines are fitted according to the SCLC model.



**Fig.S6**  $V_{oc}$ - $P_{light}$  (a) and  $J_{sc}$ - $P_{light}$  (b) of PTSBTz-Me/ $PC_{71}BM$  and PPSBTz-Me/ $PC_{71}BM$



**Fig.S7** Morphology of blend film of PTSBTz-Me/ $PC_{71}BM$  without DIO (a-c) and PPSBTz-Me/ $PC_{71}BM$  without DIO (d-f) : AFM images of height (b, e) and phase (c, f). TEM images (a, d).

**Table S3.** Contact angles and surface energy of the net films.

Material	[Water] (°)	[Diiodomethane] (°)	$\gamma$ (mN/m)	$\gamma_{\text{average}}$ (mN/m)
PTSBTz-Me	102.47	42.68	41.96	41.95
	102.89	42.35	42.37	
	103.23	43.41	41.76	
	102.76	43.10	41.78	
	102.53	42.82	41.88	
	100.13	45.85	38.85	
PPSBTz-Me	99.79	45.10	39.25	39.13
	99.52	46.26	38.37	
	100.46	44.67	39.78	
	100.36	45.17	39.40	
	78.57	20.26	47.71	
	76.53	19.86	47.84	
PC <sub>71</sub> BM	76.06	20.31	47.73	47.84
	75.10	19.56	47.99	
	75.02	19.74	47.94	