

# **Structural Similarity Induced Improvement in the Performance of Organic Solar Cells Based on Novel Terpolymer Donors**

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## Materials and Methods

### General Information

All reactions and manipulations were operated under argon atmosphere and all the starting materials were purchased from commercial suppliers and used without further purification. Chloroform, Al (99.999%), Y6 and other materials were purchased from Alfa, Aldrich, Solarmer Materials Inc. And used without further purification. Indium-tin oxide (ITO) glass was purchased from Delta Technologies Limited. 4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']-dithiophene (BDT-2F) and 1,3-bis(thiophen-2-yl)-5,7-bis(2-ethyl-hexyl)benzo-[1,2-c:4,5-c']dithiophene-4,8-dione (BDD) were purchased from Solarmer Materials Inc. Pd(PPh<sub>3</sub>)<sub>4</sub> was obtained from J&K.

The <sup>1</sup>H spectra were recorded in deuterated solvents on a Bruker ADVANCE 400 NMR Spectrometer. <sup>1</sup>H NMR chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer TGA 7 instrument for thermal analysis at a heating rate of 10 °C/min under nitrogen. Number-average (*M<sub>n</sub>*) and weight-average (*M<sub>w</sub>*) molecular weights were determined with Agilent 1260 infinity II high temperature gel permeation chromatography (GPC) system.

### Optical characterizations

UV-vis absorption spectra were recorded on an Agilent series UV-Vis-NIR spectrophotometer. All film samples were spin-cast on quartz slice substrates. The photoluminescence spectra (PL) were measured by photoluminescence spectroscopy (Hitachi F-7000).

### Electrochemical characterizations.

Cyclic voltammetry (CV) was performed by a Zahner IM6e electrochemical work station, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. Polymers were drop-cast onto the

electrode from chloroform solutions to form thin films. 0.1 mol L<sup>-1</sup> tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the supporting electrolyte. The scan rate was 0.05 V s<sup>-1</sup>. The E<sub>HOMO</sub> and E<sub>LUMO</sub> are calculated as refer to the eqs (1) and (2).

$$E_{\text{HOMO}} = -(E_{\text{ox}} + 4.4) \text{ eV (1),}$$

$$E_{\text{LUMO}} = -(E_{\text{red}} + 4.4) \text{ eV (2).}$$

### **AFM characterizations.**

The specimen for AFM measurements was prepared using the same procedures those for fabricating devices but without PDINO/Al on top of the active layer.

### **GIWAXS measurements.**

The GIWAXS measurement was carried out at the PLS-II 6A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea. The X-rays coming from the in-vacuum undulator (IVU) were monochromated (wavelength  $\lambda = 1.10994 \text{ \AA}$ ) using a double crystal monochromator and focused both horizontally and vertically (450 (H) x 60 (V)  $\mu\text{m}^2$  in FWHM @ the sample position) using K-B type mirrors. The grazing incidence wide-angle X-ray scattering (GIWAXS) sample stage was equipped with a 7-axis motorized stage for the fine alignment of the sample, and the incidence angles of the X-ray beam were set to be 0.11°-0.13° for the neat and blend films. The GIWAXS patterns were recorded with a 2D CCD detector (Rayonix SX165) and an X-ray irradiation time within 100 s, dependent on the saturation level of the detector. Diffraction angles were calibrated using a sucrose standard (monoclinic, P21,  $a=10.8631 \text{ \AA}$ ,  $b=8.7044 \text{ \AA}$ ,  $c=7.7624 \text{ \AA}$ , and  $\beta=102.938 \text{ \AA}$ ) and the sample-to-detector distance was ~231 mm.

### **Electron and Hole mobility measurements.**

Hole and electron mobilities were measured using the space charge limited current (SCLC) method, with hole-only device of ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS)/active layer (copolymer:Y6 for 1.0:1.2, w/w)/MoO<sub>3</sub>/Ag for hole mobility measurement and the electron-only devices used a diode configuration of ITO/ZnO/active layer

(copolymer:Y6 for 1.0:1.2, w/w)/PDINO/Al by taking current-voltage curve in the range of -5-5 V. The SCLC mobilities were calculated by MOTT-Gurney equation, which is described by:

$$J = 9\epsilon_0\epsilon_r u V^2 / 8L^3$$

where  $J$  is the current density,  $L$  is the film thickness of active layer,  $\epsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-12}$  F m<sup>-1</sup>),  $\epsilon_r$  is the relative dielectric constant of the transport medium,  $u$  is the hole or electron mobility,  $V$  is the internal voltage in the device and  $V = V_{appl} - V_r - V_{bi}$ , where  $V_{appl}$  is the applied voltage to the device,  $V_r$  is the voltage drop due to contact resistance and series resistance across the electrodes, and  $V_{bi}$  is the built-in voltage due to the relative work function difference of the two electrodes.

### **Device Fabrication and Characterizations.**

All the devices were manufactured with the structure of Glass ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS)/active layer/PDINO/Al. The conductive ITO substrates were sequentially cleaned with ultrasonication in acetone, detergent, water and isopropanol. After drying the ITO substrates and treating the surface with UV ozone for 20 min, The PEDOT:PSS precursor was spin-coated at 4000 rpm. for 50s onto the ITO surface. After being baked at 150 °C for 20 min in air, the PEDOT:PSS-coated substrates were transferred into a nitrogen-filled glove box. The optimal conditions for preparation of the PM6:Y6, PM6-SiCl-10%:Y6, PM6-SiCl-15%:Y6 and PM6-SiCl-20%:Y6 blend films were found to spin-coating a total blend concentration of 16.5 mg/ml in chloroform at 3000 rpm. (D/A mass ratio 1:1.2, w/w) with the addition of 0.5% 1-CN as an additive followed by thermal annealing at 110 °C for 10 min in a nitrogen-filled glove box. The interlayer of PDINO (1.0 mg/mL, in methanol) was generally deposited on the active layer via spin-coating at 3000 rpm for 30s. Subsequently, the structure of Al (100 nm) was deposited over the interlayer by thermal evaporation under a vacuum chamber with a mask to accomplish the device fabrication. The effective area of one cell was 0.04 cm<sup>2</sup>. The current-voltage ( $J$ - $V$ ) characteristics were measured by a Keithley 2400 Source Meter under simulated solar light (100 mW cm<sup>-2</sup>, AM 1.5 G, Abet Solar Simulator Sun 2000). All the measurements

were performed at room temperature under ambient atmosphere.

### **Detailed $E_{\text{loss}}$ measurements.**

Electroluminescence (EL) and photoluminescence (PL) spectra were taken using a Kymera-328I spectrograph and an EMCCD purchased from Andor Technology (DU970P). Injection current used for EL was  $1 \text{ mA cm}^{-2}$ , and excitation wavelength used for the PL measurements was 610 nm.  $\text{EQE}_{\text{EL}}$  measurements were done using a home built setup taking a Keithley 2400 to inject current to the solar cells. Emission photon-flux from the solar cells was recorded using a Si detector (Hamamatsu s1337-1010BQ) and a Keithley 6482 picoammeter. Sensitive EQE measurements were recorded using a halogen lamp light source, chopped at a frequency of 173 Hz, a monochromator (Newport CS260), a Stanford SR830 lock-in amplifier, a Stanford SR570 current amplifier, and a set of long pass filters. Lamp intensity was calibrated using a Si detector (Hamamatsu s1337-1010BQ).

### **Synthetic procedures**

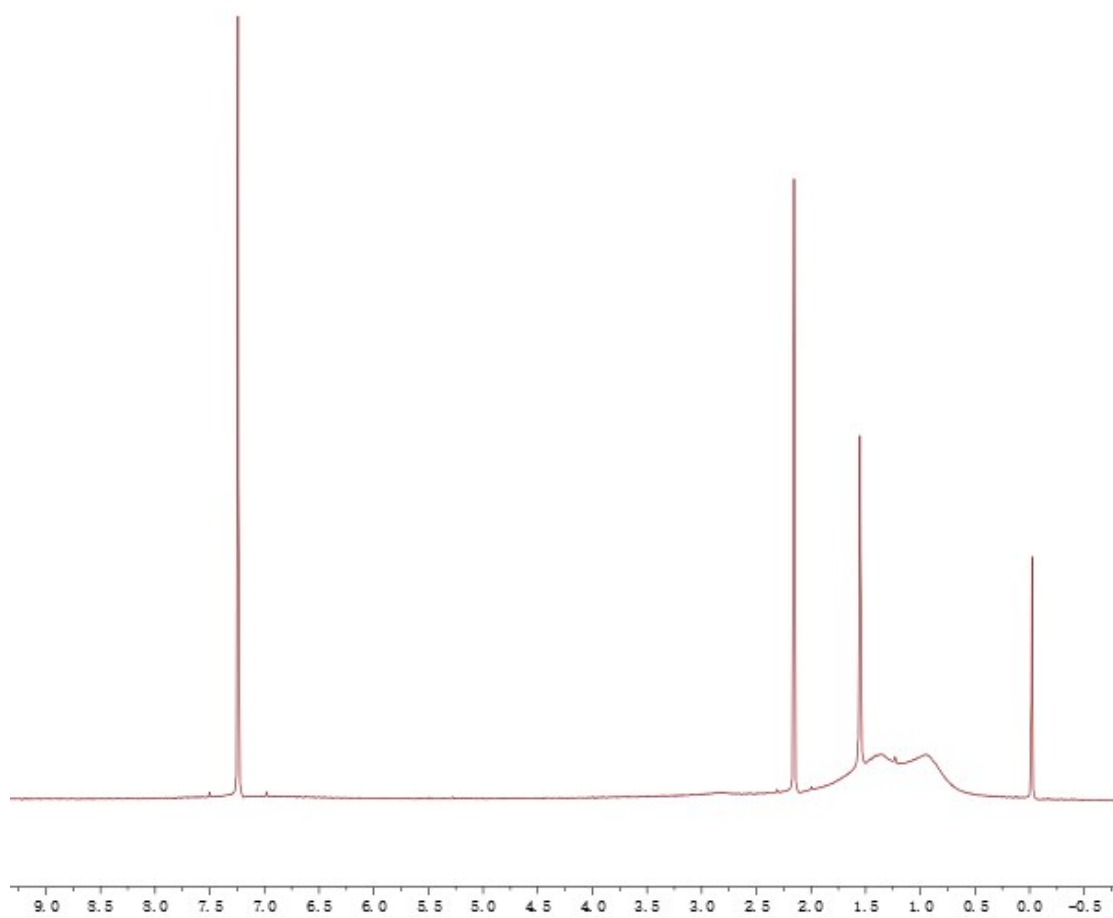
0.1 mmol monomer of BDD and 0.05 mmol bromide monomer of BDT-2F and BDT-SiCl at distinct content (0.1 BDT-2F:0 BDT-SiCl, 0.09 BDT-2F:0.01 BDT-SiCl, 0.085 BDT-2F:0.015 BDT-SiCl and 0.08 BDT-2F:0.02 BDT-SiCl) were dissolve in toluene (10 mL).  $\text{Pd}(\text{PPh}_3)_4$  (9.2 mg) was added into the mixtures after being flushed with argon for five minutes. Then the reaction container was purged with argon for another ten minutes. The reactions were stirred at  $110 \text{ }^\circ\text{C}$  for six hours. The reactant was cooled down to room temperature and poured into MeOH (200ml), then precipitated the crude product in methanol, followed by Soxhlet extraction with hexane, acetone and chloroform, respectively. Last purified by silica gel column and dried under vacuum for 12 h before use. The yields are around 55%.

Elemental analysis calculated (%) for PM6-SiCl-10% ( $\text{C}_{68.2}\text{H}_{76.8}\text{Cl}_{0.2}\text{F}_{1.8}\text{O}_2\text{S}_8\text{Si}_{0.2}$ ): F=2.78%, Si=0.46%. Found: F=2.80%, Si=0.51%.

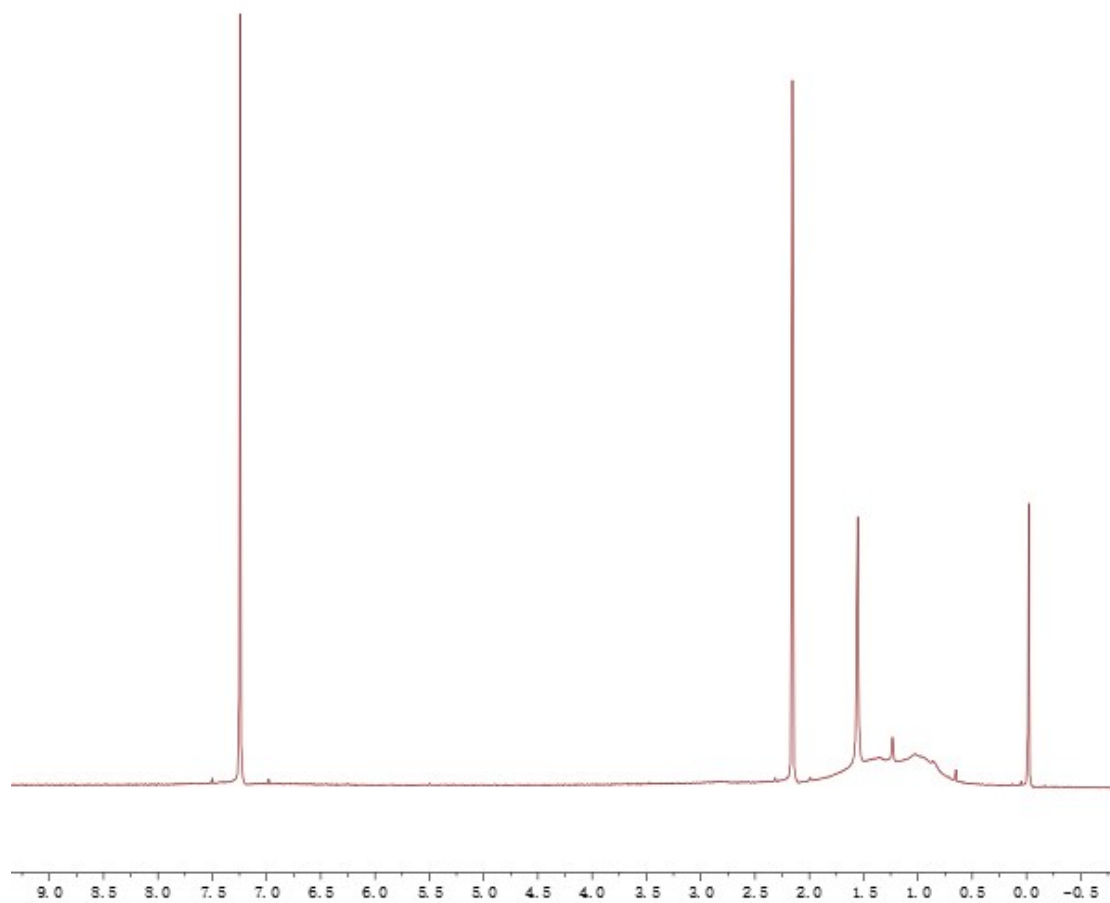
Elemental analysis calculated (%) for PM6-SiCl-15% ( $\text{C}_{68.3}\text{H}_{77.2}\text{Cl}_{0.3}\text{F}_{1.7}\text{O}_2\text{S}_8\text{Si}_{0.3}$ ): F=2.61%, Si=0.68%. Found: F=2.58%, Si=0.66%.

Elemental analysis calculated (%) for PM6-SiCl-20% ( $\text{C}_{68.4}\text{H}_{77.6}\text{Cl}_{0.4}\text{F}_{1.6}\text{O}_2\text{S}_8\text{Si}_{0.4}$ ):

F=2.45%, Si=0.90%. Found: F=2.45%, Si=0.88%.

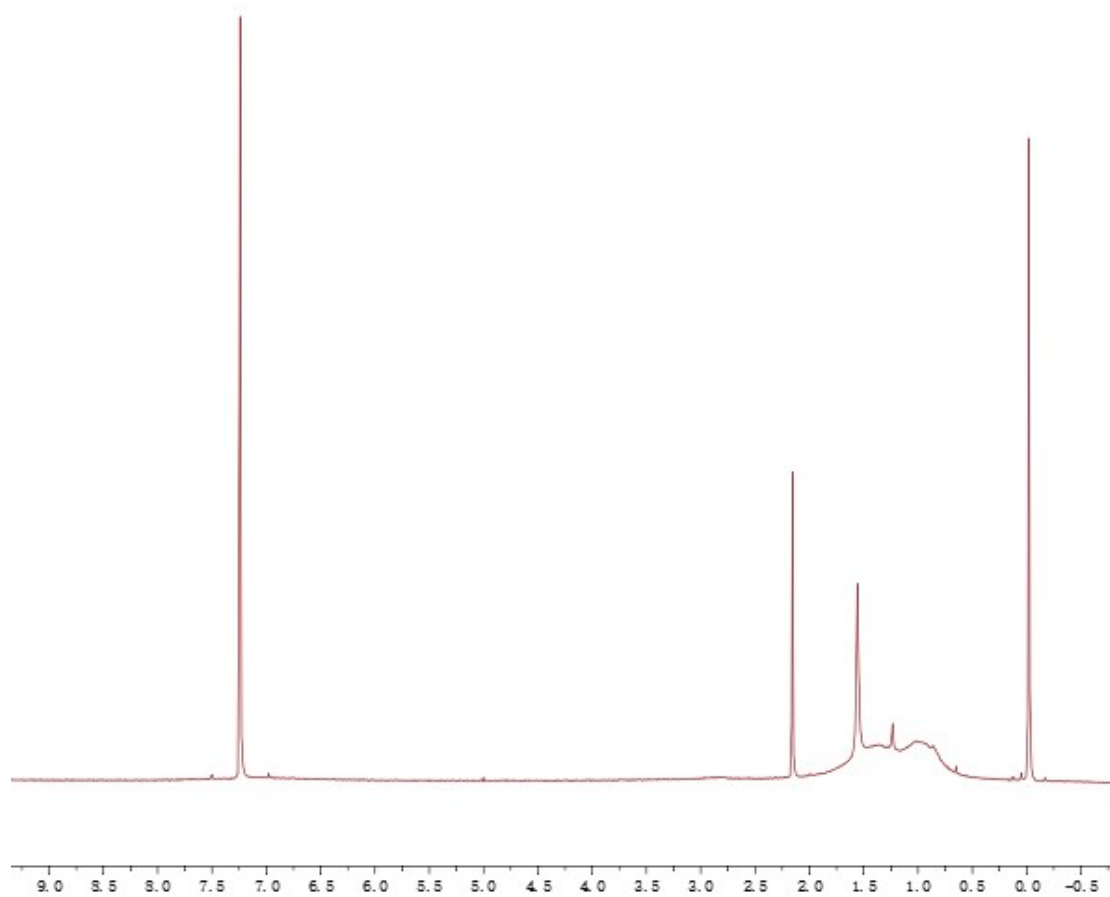


**Figure S1.**  $^1\text{H}$  NMR of PM6 ( $\text{CDCl}_3$ ).

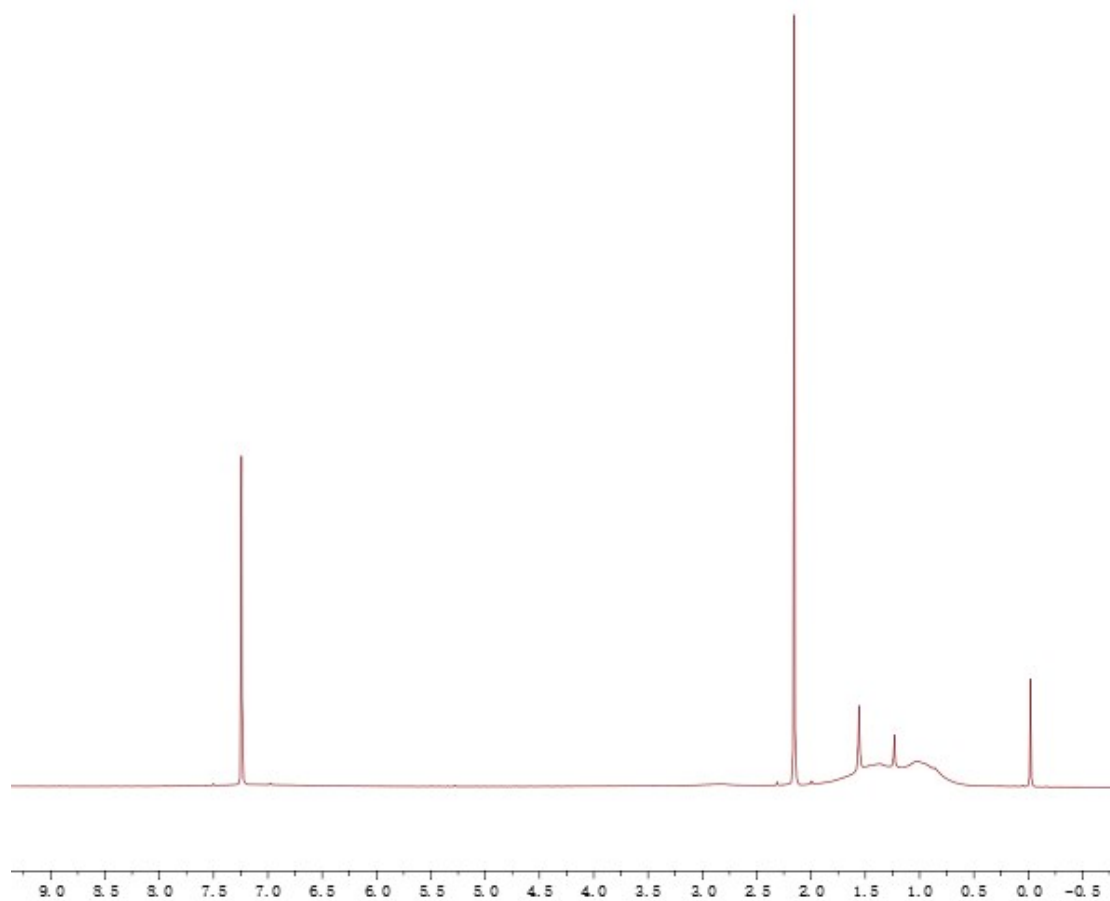


**Figure S2.**  $^1\text{H}$  NMR of PM6-SiCl-10% ( $\text{CDCl}_3$ ).

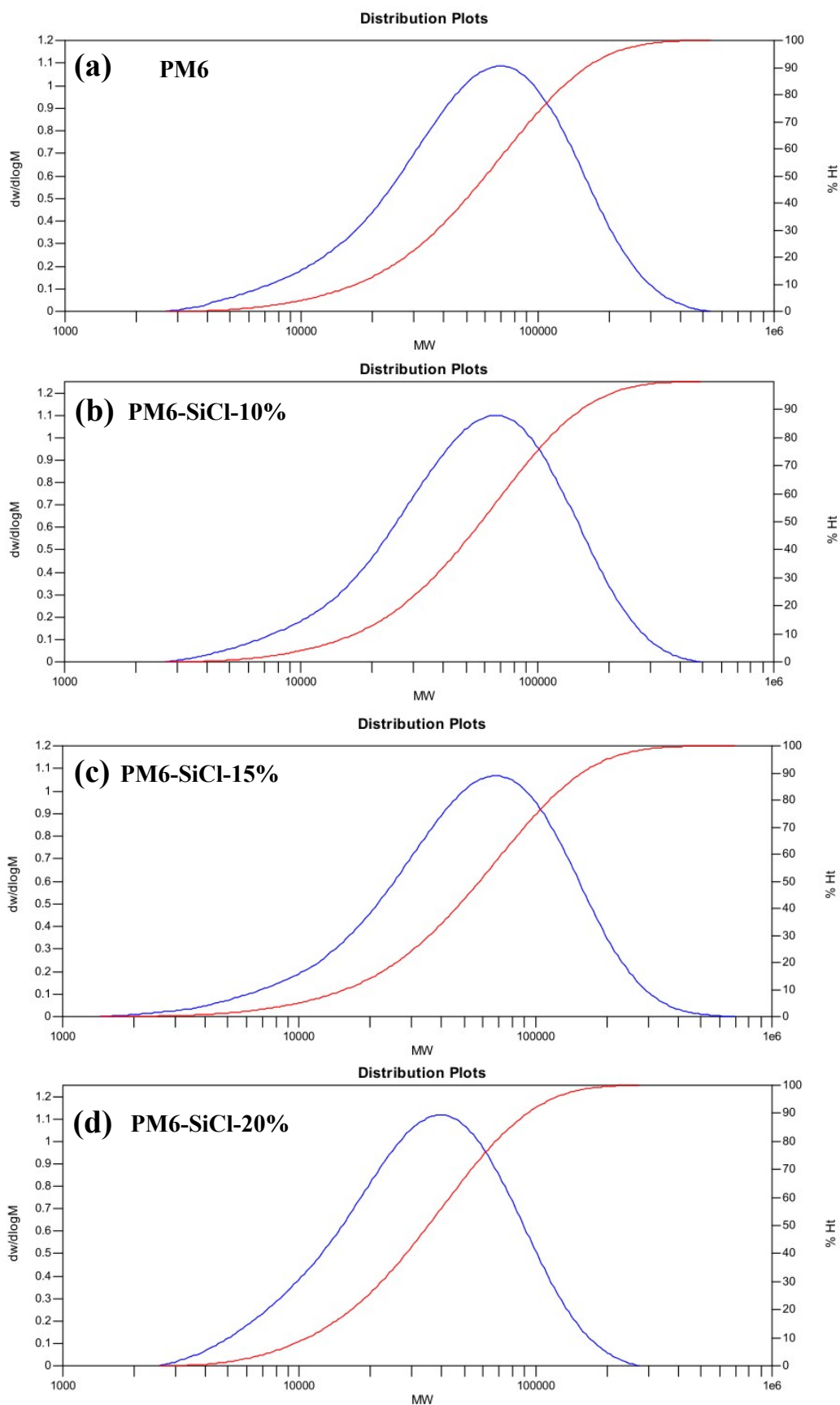




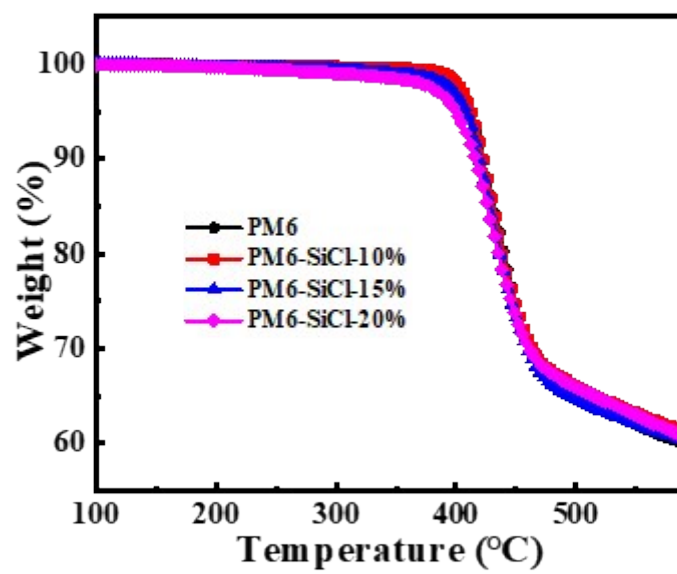
**Figure S3.**  $^1\text{H}$  NMR of PM6-SiCl-15% ( $\text{CDCl}_3$ ).



**Figure S4.**  $^1\text{H}$  NMR of PM6-SiCl-20% ( $\text{CDCl}_3$ ).



**Figure S5.** GPC spectra of (a) PM6, (b) PBDB-TF-SiCl-10%, (c) PBDB-TF-SiCl-15% and (d) PBDB-TF-SiCl-20% in trichlorobenzene.



**Figure S6.** TGA analysis (heating ramp: 10 °C min<sup>-1</sup>) of polymers in nitrogen.

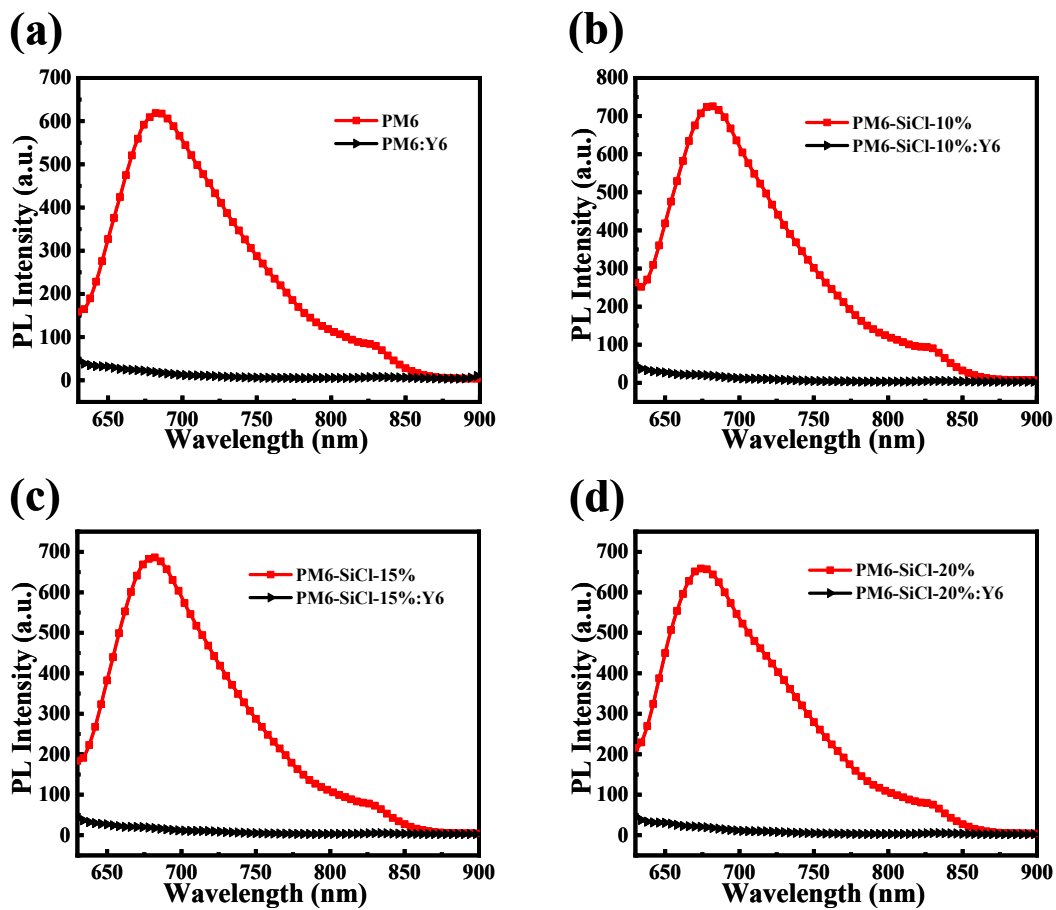
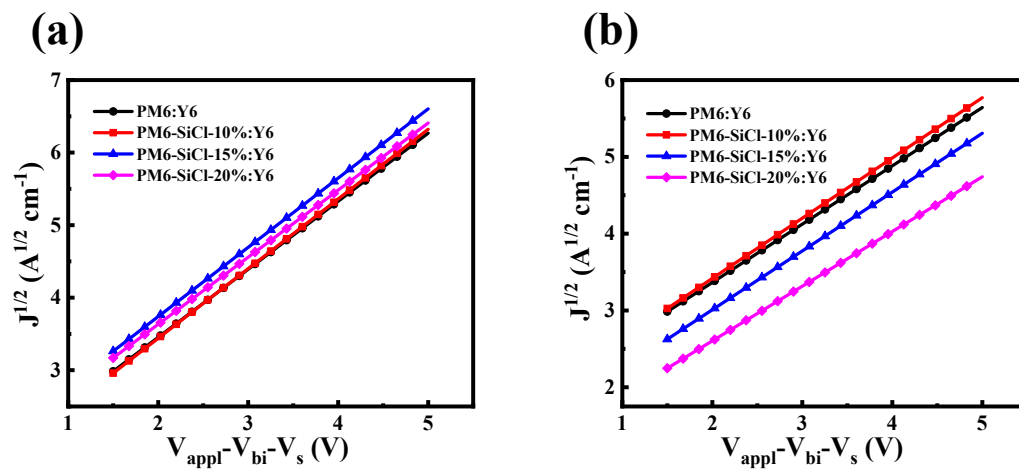
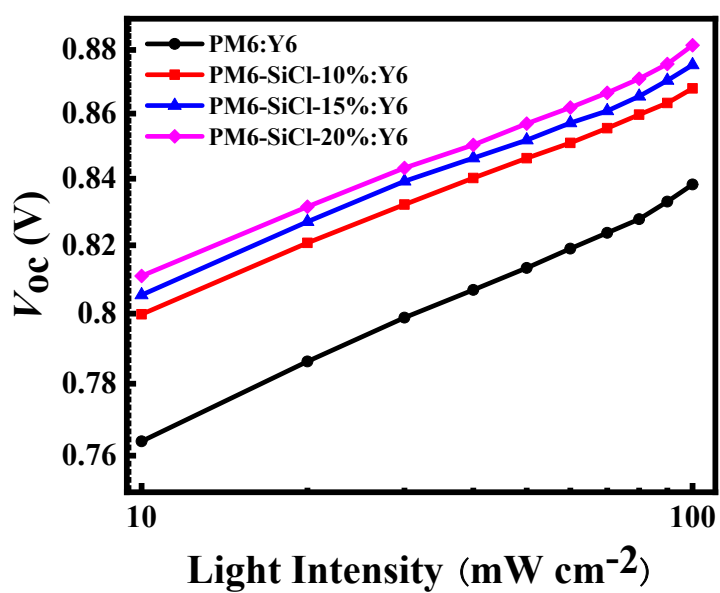


Figure S7. Photoluminescence (PL) spectra of the four neat polymer films and the four blend films.



**Figure S8.** (a)  $J^{1/2}-V$  plots of hole-only devices with active layer. (b)  $J^{1/2}-V$  plots of electron-only devices with active layer. (in dark)

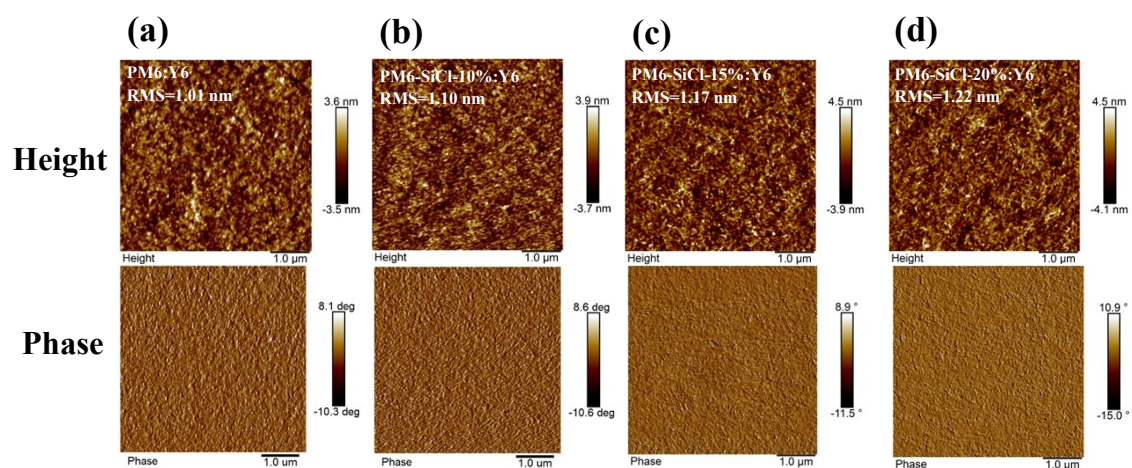


**Figure S9.** Dependence of  $V_{oc}$  on the light intensity of the OSC devices studied in this work

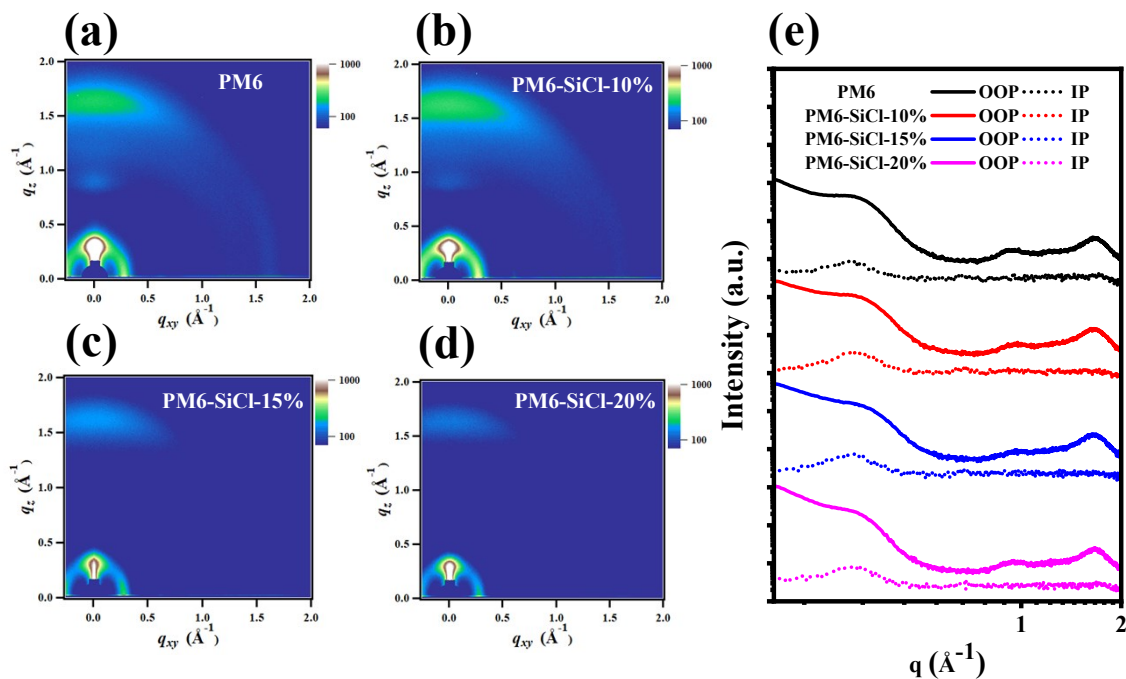
**Table S1.** Hole and electron mobilities of PM6, PM6-SiCl-10%, PM6-SiCl-15% and PM6-SiCl-20%-based devices in the dark.

Device	$\mu_h$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_e$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_h/\mu_e$
PM6:Y6	3.08×10 <sup>-3</sup>	2.02×10 <sup>-3</sup>	1.52
PM6-SiCl-10%:Y6	3.23×10 <sup>-3</sup>	2.15×10 <sup>-3</sup>	1.50
PM6-SiCl-15%:Y6	3.19×10 <sup>-3</sup>	2.05×10 <sup>-3</sup>	1.55
PM6-SiCl-20%:Y6	2.99×10 <sup>-3</sup>	1.77×10 <sup>-3</sup>	1.68

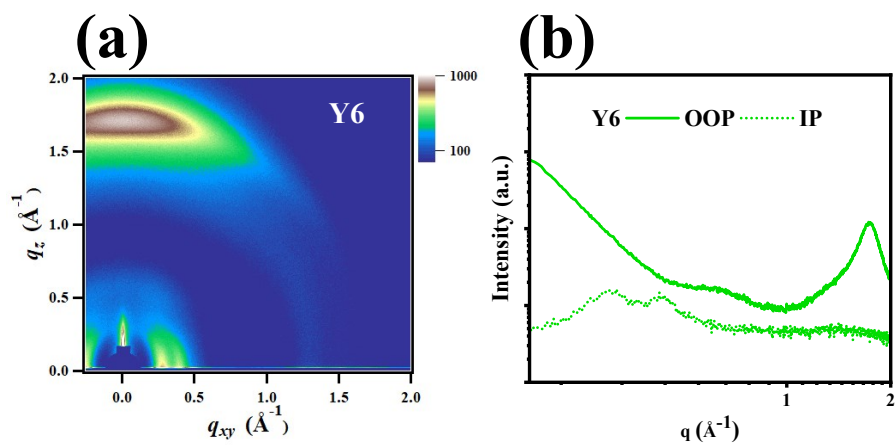




**Figure S10.** AFM height images and phase images of the blend films for (a) PM6-Y6, (b) PM6-SiCl-10%:Y6, (c) PM6-SiCl-15%:Y6 and (d) PM6-SiCl-20%:Y6.



**Figure S11.** Film-forming properties of the corresponding neat films. 2D GIWAXS profiles for (a) PM6, (b) PM6-SiCl-10%, (c) PM6-SiCl-15% and (d) PM6-SiCl-20% based films. (e) 1D GIWAXS line curves with respect to the in-plane (IP) direction and out-of-plane (OOP) direction.



**Figure S12.** (a) 2D GIWAXS profiles and (b) 1D GIWAXS line curves with respect to the in-plane (IP) direction and out-of-plane (OOP) direction for Y6 neat film.

**Table S2.** The parameters of exciton dissociation efficiency and charge collection efficiency.

Device	$J_{\text{sat}}$ (mA cm <sup>-2</sup> )	$J_{\text{ph}}^*$ (mA cm <sup>-2</sup> )	$J_{\text{ph}}^{\&}$ (mA cm <sup>-2</sup> )	$\eta_{\text{diss}}$ (%)	$\eta_{\text{coll}}$ (%)
PM6:Y6	26.20	25.18	21.22	96.1	81.5
PM6-SiCl-10%:Y6	26.32	25.37	22.19	96.4	84.3
PM6-SiCl-15%:Y6	26.23	25.26	21.25	96.3	81.7
PM6-SiCl-20%:Y6	26.10	24.88	20.09	95.3	77.3

$J_{\text{sat}}$ : The  $J_{\text{ph}}$  under condition of  $V_{\text{eff}}=2$  V.

$J_{\text{ph}}^*$ : The  $J_{\text{ph}}$  under short circuit conditions.

$J_{\text{ph}}^{\&}$ : The  $J_{\text{ph}}$  under maximum power output conditions.

**Table S3.** Summarized parameters for the ordering structures of neat films.

	Out-of-Plane				In-Plane			
	$\pi$ - $\pi$ stacking cell axis (010)				Unit cell long axis (100)			
	q ( $\text{\AA}^{-1}$ )	d-spacing ( $\text{\AA}$ )	FWHM ( $\text{\AA}^{-1}$ )	Coherence length ( $\text{\AA}$ )	q ( $\text{\AA}^{-1}$ )	d-spacing ( $\text{\AA}$ )	FWHM ( $\text{\AA}^{-1}$ )	Coherence length ( $\text{\AA}$ )
Y6	1.71	3.67	0.243	23.55	0.31	20.35	0.084	67.08
PM6	1.67	3.76	0.295	19.42	0.30	20.87	0.093	64.02
PM6-SiCl-10%	1.67	3.76	0.247	23.14	0.31	20.32	0.100	56.59
PM6-SiCl-15%	1.66	3.79	0.316	18.09	0.31	20.52	0.085	66.85
PM6-SiCl-20%	1.66	3.79	0.317	18.01	0.32	19.95	0.092	61.26

**Table S4.** Summarized parameters for the ordering structures of blend films.

	Out-of-Plane				In-Plane			
	$\pi$ - $\pi$ stacking cell axis (010)				Unit cell long axis (100)			
	q ( $\text{\AA}^{-1}$ )	d-spacing ( $\text{\AA}$ )	FWHM ( $\text{\AA}^{-1}$ )	Coherence length ( $\text{\AA}$ )	q ( $\text{\AA}^{-1}$ )	d-spacing ( $\text{\AA}$ )	FWHM ( $\text{\AA}^{-1}$ )	Coherence length ( $\text{\AA}$ )
PM6:Y6	1.72	3.65	0.233	24.52	0.31	20.15	0.067	85.08
PM6-SiCl-10%:Y6	1.72	3.65	0.234	24.36	0.32	19.89	0.064	87.82
PM6-SiCl-15%:Y6	1.72	3.65	0.245	23.40	0.32	19.94	0.070	80.78
PM6-SiCl-20%:Y6	1.71	3.67	0.247	23.16	0.32	19.86	0.074	76.31

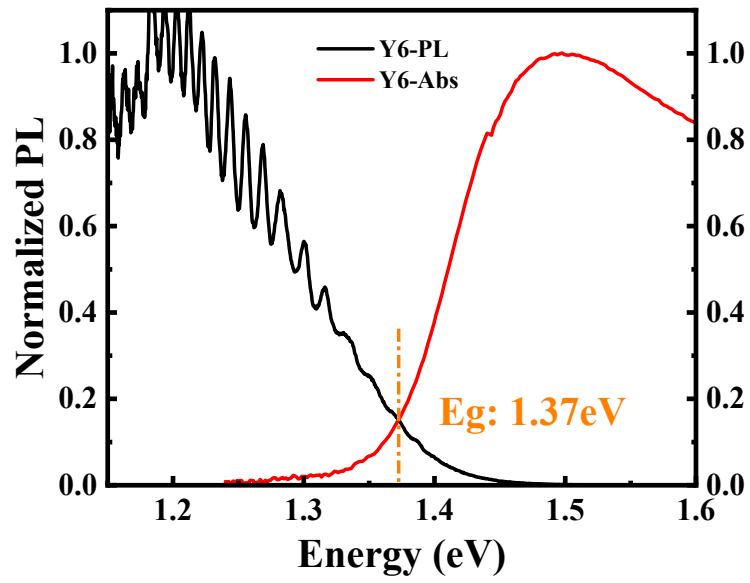
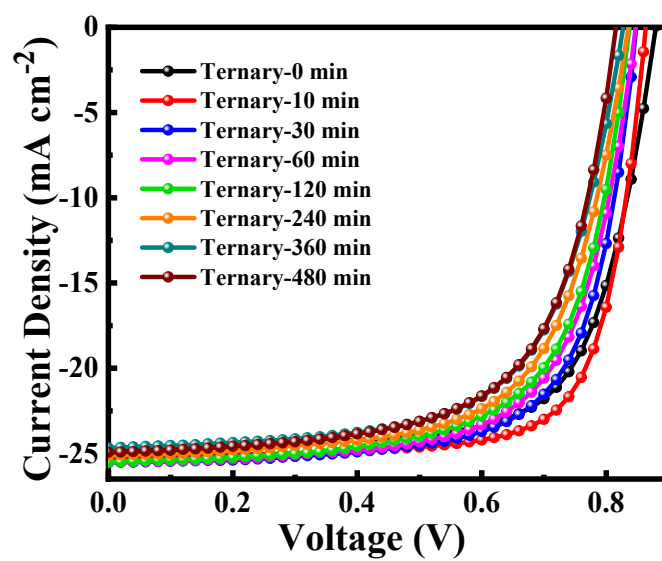


Figure S13. Absorption and PL spectra of Y6 acceptor.



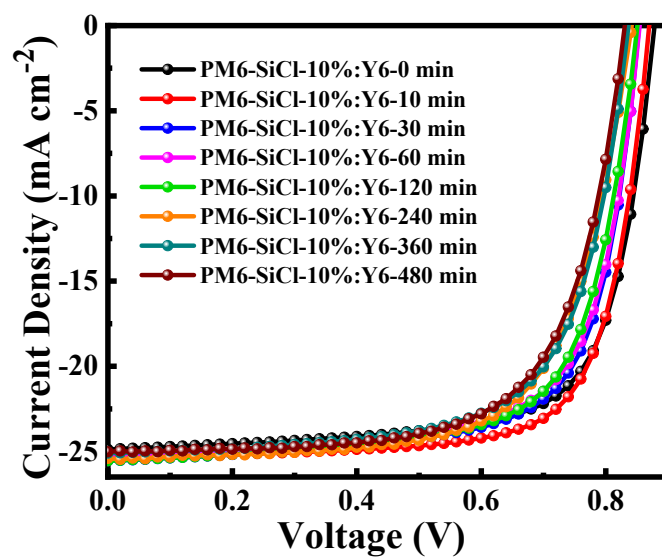
**Figure S14.** The  $J$ - $V$  characteristics of dual-donor ternary blend devices of different annealing times at 110 °C.



**Table S5.** The dual-donor ternary blend devices parameters of different annealing times at 110 °C.

Active Layer	Annealing time (min)	$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE <sup>a</sup> (%)
Ternary	0	0.880	24.74	70.09	15.26 (15.15±0.11)
	10	0.863	25.30	74.04	16.17 (16.04±0.13)
	30	0.848	25.52	69.71	15.09 (14.97±0.12)
	60	0.847	25.53	67.22	14.54 (14.42±0.12)
	120	0.837	25.51	66.33	14.17 (14.05±0.12)
	240	0.835	25.11	65.31	13.71 (13.59±0.12)
	360	0.827	24.68	64.56	13.18 (13.06±0.12)
	480	0.815	24.93	64.61	13.14 (13.02±0.12)

<sup>a</sup> Average PCEs are based on 10 independent devices.



**Figure S15.** The  $J$ - $V$  characteristics of PM6-SiCl-10%:Y6 blend devices of different annealing times at 110 °C.

**Table S6.** The PM6-SiCl-10%:Y6 blend devices parameters of different annealing times at 110 °C.

Active Layer	Annealing time (min)	$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE <sup>a</sup> (%)
PM6-SiCl-10%:Y6	0	0.878	24.87	71.72	15.66 (15.55±0.11)
	10	0.870	25.37	73.48	16.22 (16.11±0.11)
	30	0.854	25.54	70.41	15.35 (15.23±0.12)
	60	0.854	25.36	69.39	15.03 (14.91±0.12)
	120	0.851	25.54	69.13	15.02 (14.90±0.12)
	240	0.842	25.40	67.47	14.43 (14.31±0.12)
	360	0.836	25.09	67.61	14.20 (14.08±0.12)
	480	0.831	25.02	67.45	14.01 (13.89±0.12)

<sup>a</sup> Average PCEs are based on 10 independent devices.

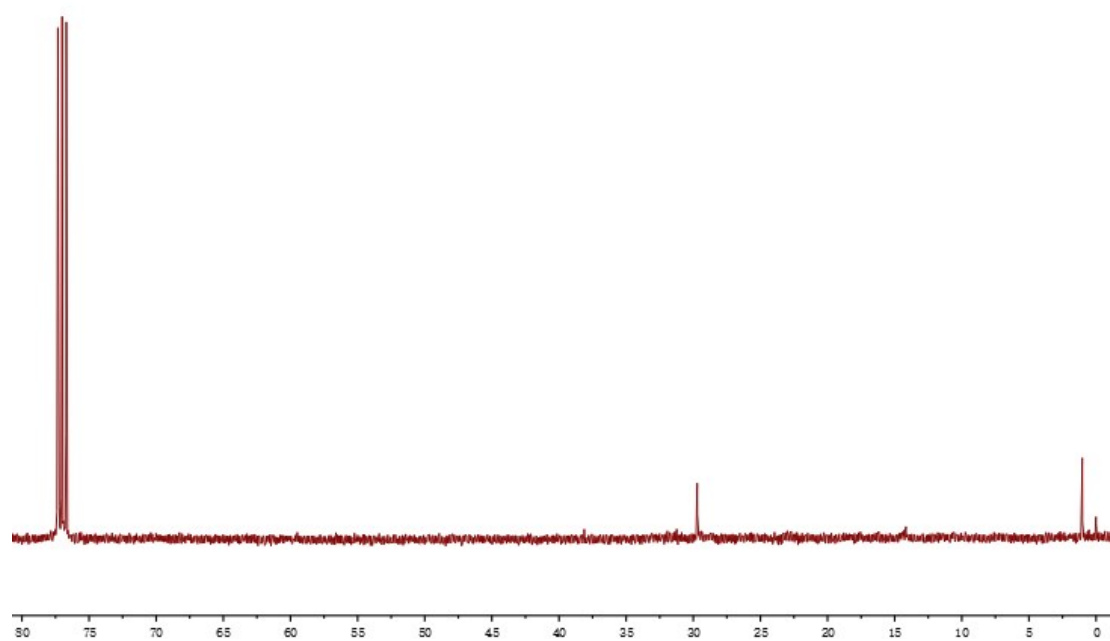


Figure S16.  $^{13}\text{C}$  NMR of PM6-SiCl-10% ( $\text{CDCl}_3$ ).