

Supporting Information

Boosting overall stability of organic solar cells by crosslinking vinyl-functionalized polymer derived from PM6

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Characterization methods

The ^1H NMR and ^{13}C NMR spectra were recorded on a BRUKER AVIII-400 NMR spectrometer by utilizing deuterated chloroform (CDCl_3) as the solvent and tetramethylsilane (TMS) as the standard. Mass data were obtained using a Bruker Microflex MALDI-TOF mass spectrometer. Thermogravimetric analysis (TGA) was performed using a Mettler-Toledo 851e/822e analysis system under N_2 at a heating rate of $10^\circ\text{C min}^{-1}$. Cyclic voltammetric (CV) measurements were carried out in a conventional three-electrode cell using a platinum plate as the working electrode, a platinum wire as the counter electrode, and a Ag/Ag^+ electrode as the reference electrode on a CHI760E Electrochemical Workstation in a tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) (0.1 M) acetonitrile solution at a scan rate of 20 mVs^{-1} . The experiments were calibrated with the standard ferrocene/ferrocenium (FOC) redox system and it was assumed that the energy level of FOC was 4.8 eV below vacuum, and the value of 0.36 V was found for FOC vs. Ag/AgCl . The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were calculated from the onset oxidation potential and the onset reduction potential, using the equation $E_{\text{HOMO}} = -e(E_{\text{onset ox}} + 4.44)$, $E_{\text{LUMO}} = -e(E_{\text{onset red}} + 4.44)$. UV-vis absorption spectra were recorded on a SHIMADZU UV-2600 spectrometer. The sample polymer neat films and blend films were prepared by spin-coating from the polymer solutions onto glass substrate. Atomic-force microscopy (AFM) images were obtained using a Bruker-Dimension Icon microscope in the ScanAsyst mode, the sample films were prepared under optimal conditions for device fabrication, and were provided technical support by “Ceshigo Research Service, www.ceshigo.com”.

Experimental section

Materials

ITO glass substrates were purchased from Advanced Election Technology Co., Ltd. [4,8-bis[5-(2-ethylhexyl)-4-fluorothiophen-2-yl]-2-trimethylstannylthieno[2,3-*f*] (BDT-TF), 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (BDD) were purchased from Suna Tech Inc. Y6, 2,6-dibromobenzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (BDTO-2Br) and 10-bromo-1-decene were purchased from Nanjing Zhiyan Technology Co.Ltd. PEDOT:PSS (Baytron PVP A1 4083) was purchased from J&K Scientific Ltd. Hexane,

dichloromethane, petroleum ether, toluene, chloroform, methanol, and acetone were purchased from Sinopharm and must be distilled in order to exclude water and oxygen in the reaction. PDINN was obtained from the laboratory of Zhang Z G' group.

Synthesis of monomer and polymers

Synthesis of BDTOA-2Br

BDTO-2Br (200 mg, 0.53 mmol), Zinc (346 mg, 5.3 mmol) powder after activation, K_2CO_3 (732 mg, 5.3 mmol) and TBAB (15 mg) added into a 25 mL single-neck round-bottom flask. Then, degassed and filled with nitrogen three times (15 minutes). Afterwards, 10-bromo-1-decene (1.16 g, 5.3 mmol) and 10 mL THF were added. The reaction of BDTOA-2Br was stirred at 70°C for about 8 h. The mixture was cooled to room temperature, poured into saturated NaCl aqueous solution. The organic products were extracted by CH_2Cl_2 and dried over anhydrous $MgSO_4$ as white solid with a yield of 78%. 1H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 2H), 5.85 (ddt, $J = 16.9, 10.1, 6.7$ Hz, 2H), 5.03 (dq, $J = 17.2, 1.8$ Hz, 2H), 4.96 (ddt, $J = 10.1, 2.3, 1.3$ Hz, 2H), 4.21 (t, $J = 6.6$ Hz, 4H), 2.08 (tdd, $J = 6.6, 5.3, 1.4$ Hz, 4H), 1.97 – 1.80 (m, 4H), 1.62 – 1.31 (m, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.56 (s), 139.20 (s), 131.18 (s), 130.91 (s), 123.15 (s), 115.00 (s), 114.20 (s), 74.17 (s), 33.82 (s), 30.44 (s), 29.42 (s), 29.36 (s), 29.08 (s), 28.92 (s), 25.97 (s).

Synthesis of PM6

BDT-TF monomer (0.053 mmol, 50 mg) and bromide monomer of BDD (0.053 mmol, 40.6 mg) added into a 25 mL single-neck round-bottom flask. $Pd(PPh_3)_4$ (6 mg) was added into the mixtures in nitrogen atmosphere glove box. Then, degassed and filled with nitrogen three times (15 mins) and 10 mL of anaerobic anhydrous toluene was added. The reactions of PM6 were stirred at 100°C for about 24 h then add 1ml bromobenzene to react 6 h, afterward cooled to room temperature and precipitated from methanol (200 mL) and filtrated. The solid was sequentially purified via Soxhlet extraction using methanol, acetone, hexane, dichloromethane and chloroform. The chloroform fraction was concentrated. The polymer was then precipitated in methanol (150 mL) and dried under vacuum for 24 h as black solid with a yield of 90%. GPC: $M_n=20.5$ kg/mol, $M_w=61.7$ kg/mol, $PDI=3.01$. 1H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 1H), 2.89 (s, 1H), 1.43 (s, 14H), 1.00 (s, 6H). Elemental Anal. Calcd.: C, 70.05%; H, 6.89%; S, 20.74%.

Synthesis of PM6-A5

BDT-TF monomer (0.053 mmol, 50.0 mg), bromide monomer of BDD (0.0503 mmol, 38.6 mg) and BDTOA-2Br (0.0027 mol, 1.7 mg) added into a 25 mL single-neck round-bottom flask. Pd (PPh₃)₄ (6 mg) was added into the mixtures in Nitrogen atmosphere glove box. Then, degassed and filled with nitrogen three times (15mins) and 10 mL of anaerobic anhydrous toluene was added. The reactions of PM6 were stirred at 100°C for about 7 h then add 1ml bromobenzene to react 2h, afterward cooled to room temperature and precipitated from methanol (200 mL) and filtrated. The solid was sequentially purified via Soxhlet extraction using methanol, acetone, hexane, dichloromethane and chloroform. The chloroform fraction was concentrated. The polymer was then precipitated in methanol (150 mL) and dried under vacuum for 24 h as black solid with a yield of 88%. GPC: *M_n*=32.9 kg/mol, *M_w*=81.9 kg/mol, PDI=2.71. ¹H NMR (400 MHz, CDCl₃) δ 8.17 – 6.28 (m, 1H), 2.88 (s, 1H), 0.99 (s, 16H). Elemental Anal. Calcd.: C, 72.38%; H, 13.88%; S, 22.39%. Feed ratio: 95:5, actual ratio: 95.96:4.04.

Synthesis of PM6-A15

PM6- A15 was synthesized by using the similar procedure as mentioned above, with BDT-TF monomer (0.053 mmol, 50mg), bromide monomer of BDD (0.0450 mmol, 34.5 mg) and bromide monomer of BDT-T (0.0080 mmol, 5.2 mg) as black solid with a yield of 87%. GPC: *M_n*=35.5 kg/mol, *M_w*=101.3 kg/mol, PDI=2.85. ¹H NMR (400 MHz, CDCl₃) δ 7.02 (s, 1H), 2.88 (s, 1H), 1.43 (s, 1H), 1.00 (s, 15H). Elemental Anal. Calcd.: C, 71.82%; H, 12.24%; S, 24.06%. Feed ratio: 85:15, actual ratio: 83.34:16.66.

Computational details

Density function theory (DFT) calculations with methyl groups in replacing alkyl substituents to simplify the calculations were performed with the Gaussian 09 program. Full geometry optimizations in water were performed to locate all the stationary points, using B3LYP-D3/6-31+G (d, p)¹⁻³. Geometry optimizations were performed with full relaxation of all atoms in gas phase without solvent effects. Vibration frequency calculation was performed to check that the stable structures had no imaginary frequency.

Devices fabrication and measurement

The devices were fabricated with a structure of glass/ITO/PEDOT: PSS/active layer/PDINN/Ag. The ITO-coated glass substrates were cleaned by ultrasonic treatment in detergent, distilled water, acetone, and isopropyl alcohol under ultra-sonication for 30 minutes each and subsequently dried by a nitrogen blow, and then treated with an O₂-plasma. A thin layer of PEDOT: PSS (Baytron PVP A1 4083, filtered at 0.45 μm) was spin-coated (3000 rpm for 30 s) on ITO glass and then dried at 150°C for 15 min on a hotplate in air. Then, the substrates were transferred into an N₂-filled glove box. Subsequently, the copolymer/Y6 (wt:wt=1:1.2, 16 mg/mL) blends were dissolved in CHCl₃, mixed and stirred at 50°C overnight. Then spin-coated on the ITO/PEDOT: PSS substrate at 3000 rpm for 45 s, annealing at 100°C for 5 min or no annealing and continuous annealing at 150°C. The thickness of the photoactive layer is about 120 nm measured by probe type profile thickness analyzer (D-500 Stylus Profilometer). Then, the PDINN solution (1 mg/mL, dissolved in methanol) was spin-coated onto the top of active layers at 3000 rpm. Finally, the counter electrode of Ag (80 nm) was deposited under high vacuum onto the cathode-buffer layer inside a nitrogen glove box. The effective active areas of the cells between the cathode and anode were 4 mm². Current-voltage (J - V) characteristics were recorded in air, using a Keithley 2400 Source-Measure unit under 100 mW cm⁻² illumination simulated AM 1.5G irradiation. The external quantum efficiency (EQE) values of the solar cells were measured using Enlitech QE-R3011 at room temperature in air. A calibrated silicon detector was used to determine the absolute photo sensitivity at different wavelength. The light-intensity dependence was measured using a Keithley 2400 Source-Measure Unit. An Oriel Sol3A solar simulator (Newport) was used as a light source. The light intensity was calibrated by a NREL certified Si reference cell. The white LED (Xingliang 4000 K, 100 W, OSRAM) was used to evaluate the photostability of PVSCs, and their irradiation intensity on the samples was obtained from an illuminometer (AccuMAX XRP-3000).

Definition of the parameters

Photocurrent densities (J_{ph}), defined as $J_L - J_D$, where J_L and J_D are the current densities under AM 1.5G 100 mW·cm⁻² illumination and in the dark, respectively; effective voltage (V_{eff}), defined as $V - V_0$, where V is the applied voltage and V_0 is the voltage when J_{ph} equals to zero. Saturated photocurrent density (J_{sat}); the exciton dissociation efficiency (P_{diss}): $P_{diss} = J_{sc} / J_{sat}$, J_{sc} is the current density under

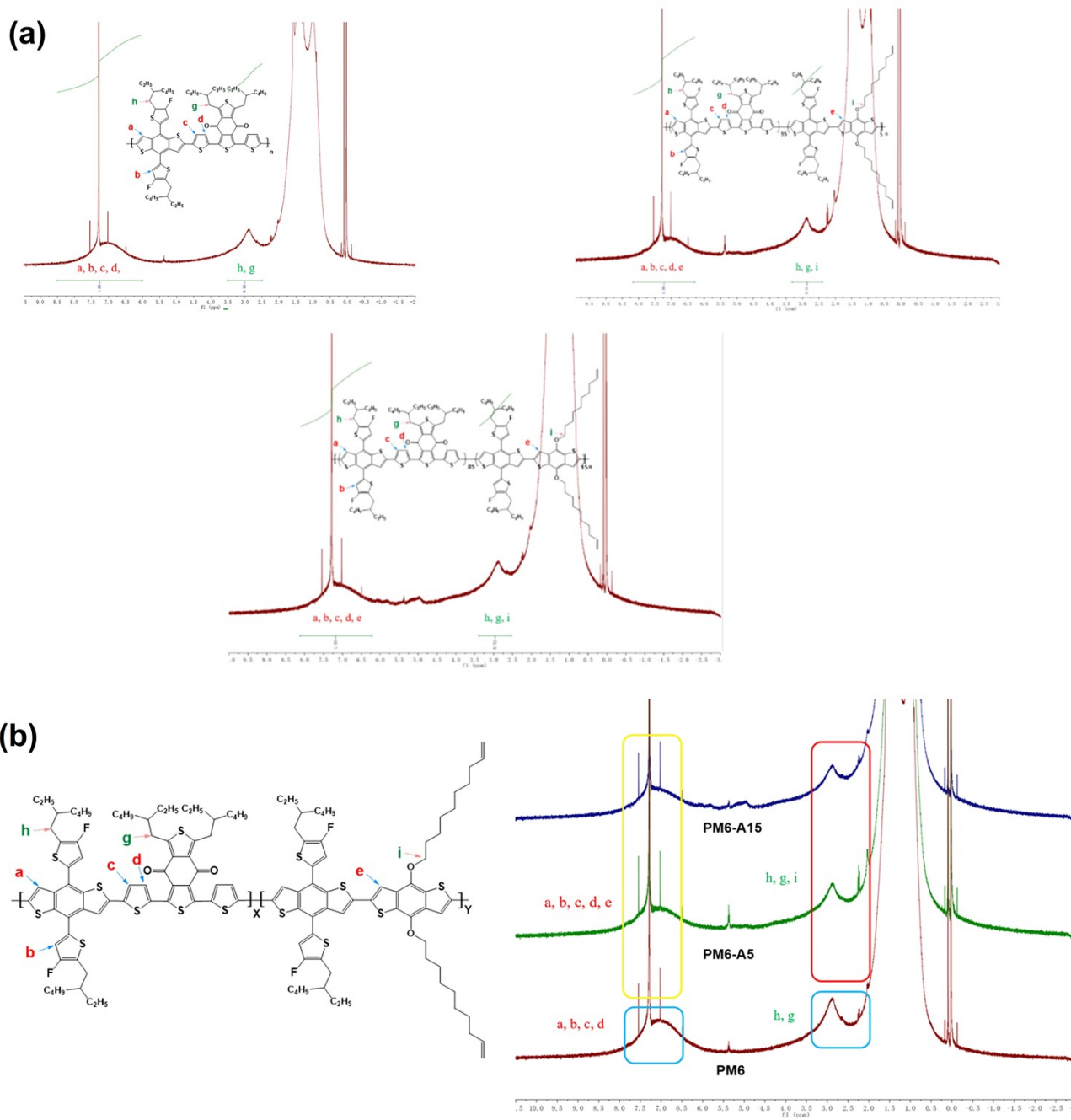


Fig. S3 (a) ^1H NMR spectra of PM6, PM6-A5, and PM6-A15 (b) Comparison of ^1H NMR spectra of PM6 (X:Y=100:0), PM6-A5 (X:Y=95:5) and PM6-A15 (X:Y=85:15)

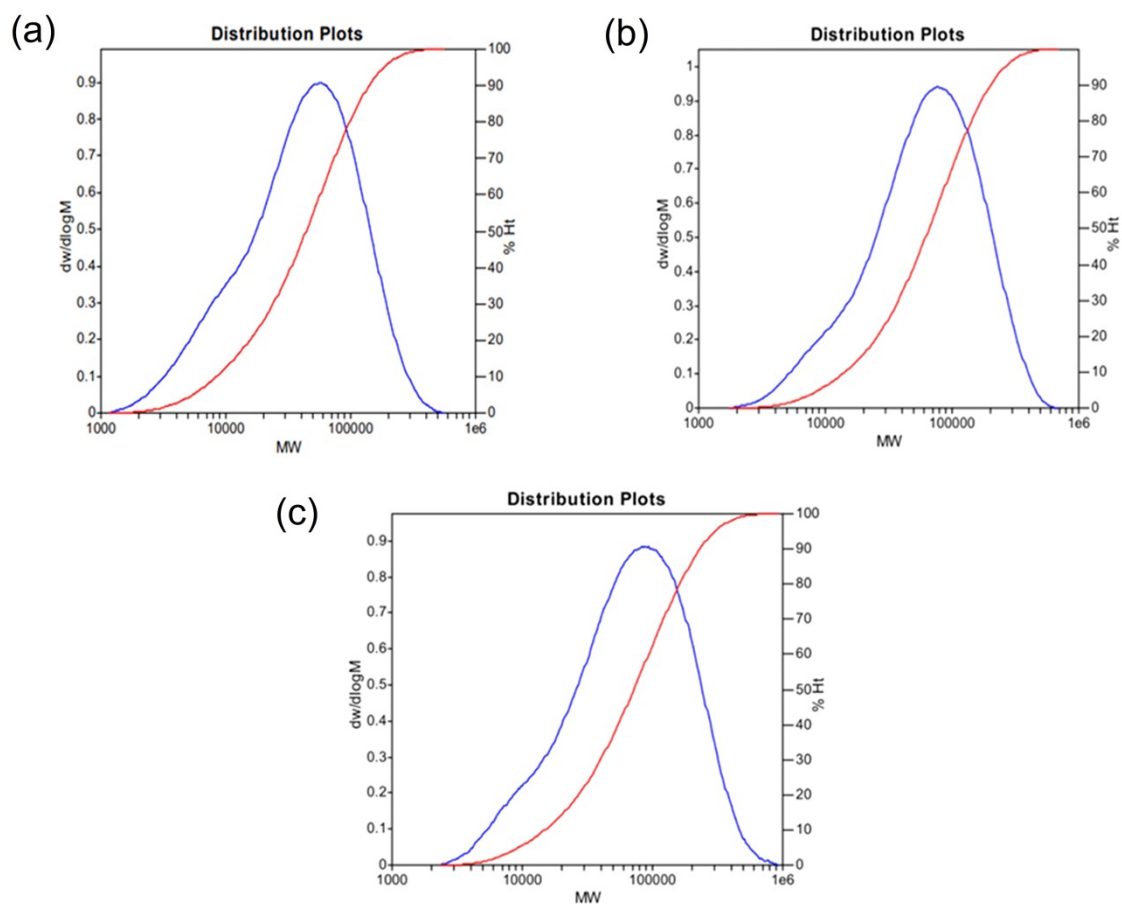


Fig. S4 GPC traces of polymers: (a) PM6; (b) PM6-A5; (c) PM6-A15; High temperature GPC with 1,2,4-trichlorobenzene as the eluent and polystyrene as a standard at 150 °C

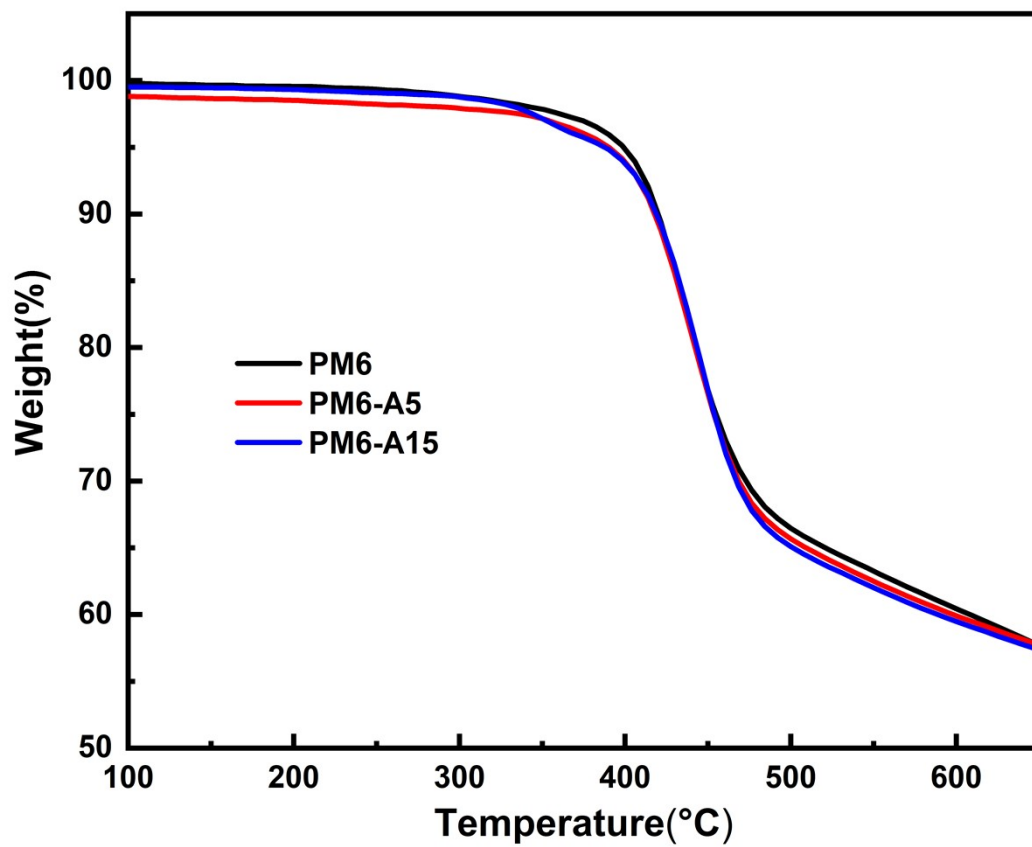


Fig. S5 TGA curves of polymer donors at a scan rate of 10 °C/min under nitrogen atmosphere

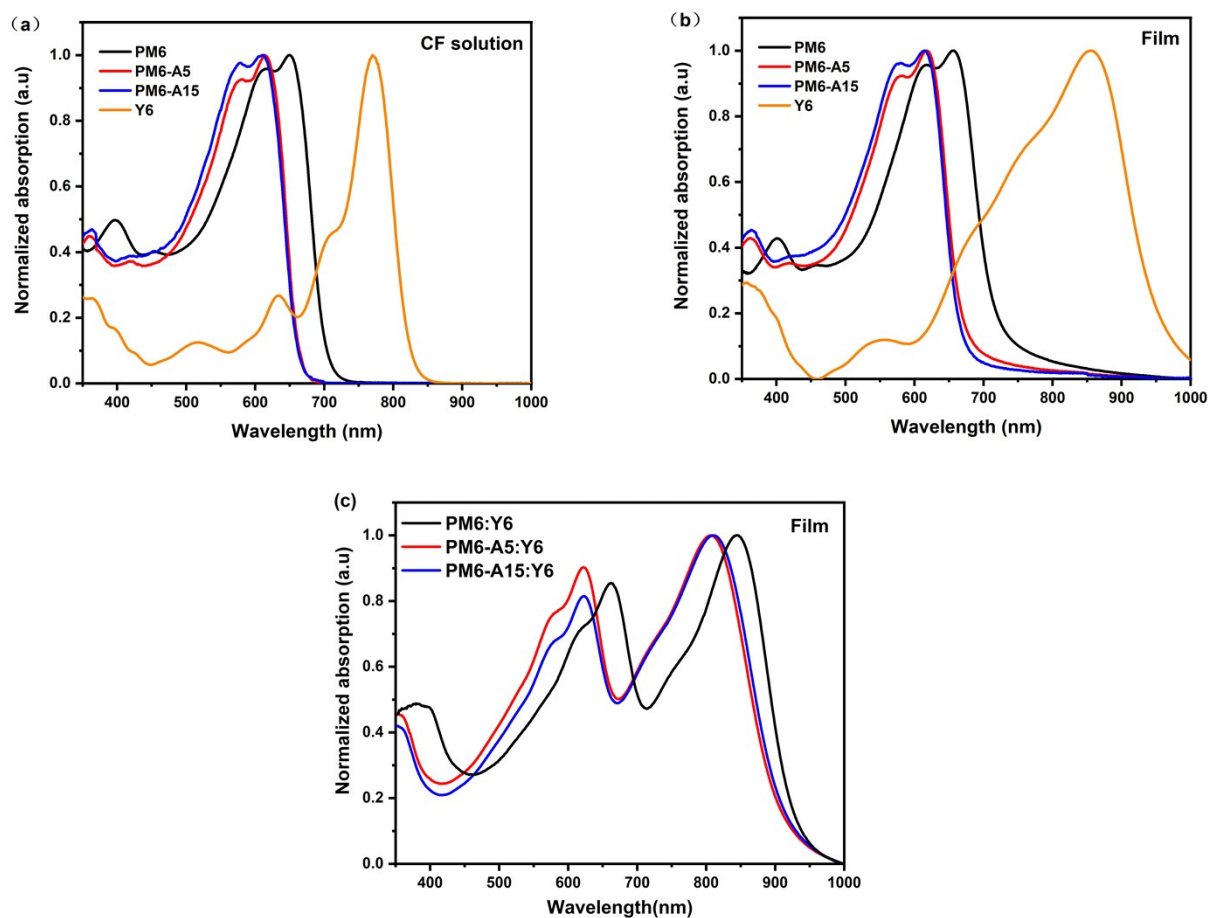


Fig. S6 (a) Normalized absorption spectra of polymers and Y6 in chloroform. (b) normalized absorption spectra of polymers and Y6 in film. (c) UV-vis absorption spectra of the polymer: Y6 blend films

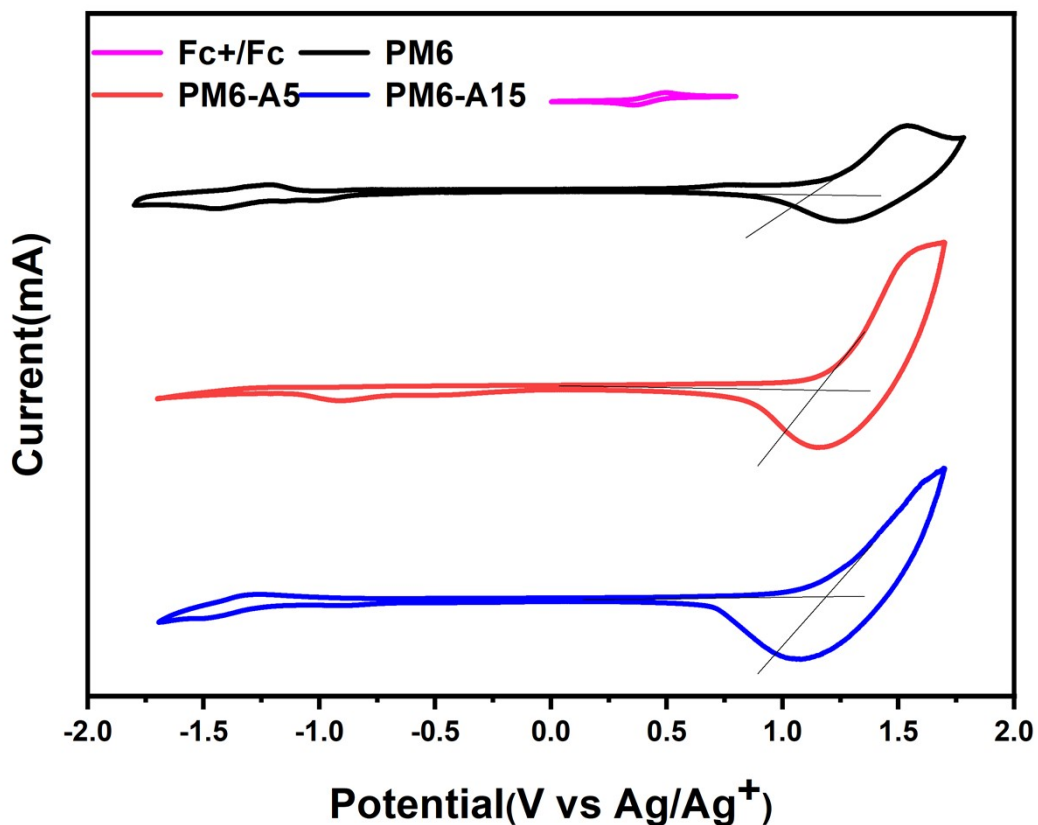


Fig. S7 Cyclic voltammogram (CV) curves of polymers. Cyclic voltammetry (CV) was performed on name of device electrochemical workstation with a three-electrode system in $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NPF}_6$ acetonitrile solutions at a scan rate of 100 mV s^{-1} . The three-electrode system included glassy carbon disk, platinum wire and Ag/Ag^+ electrode as the working electrode, counter electrode, and reference electrode, respectively. The potential of the Ag/Ag^+ reference electrode was internally calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc^+), and the Ag/Ag^+ reference electrode possessed an energy level of 4.44 eV

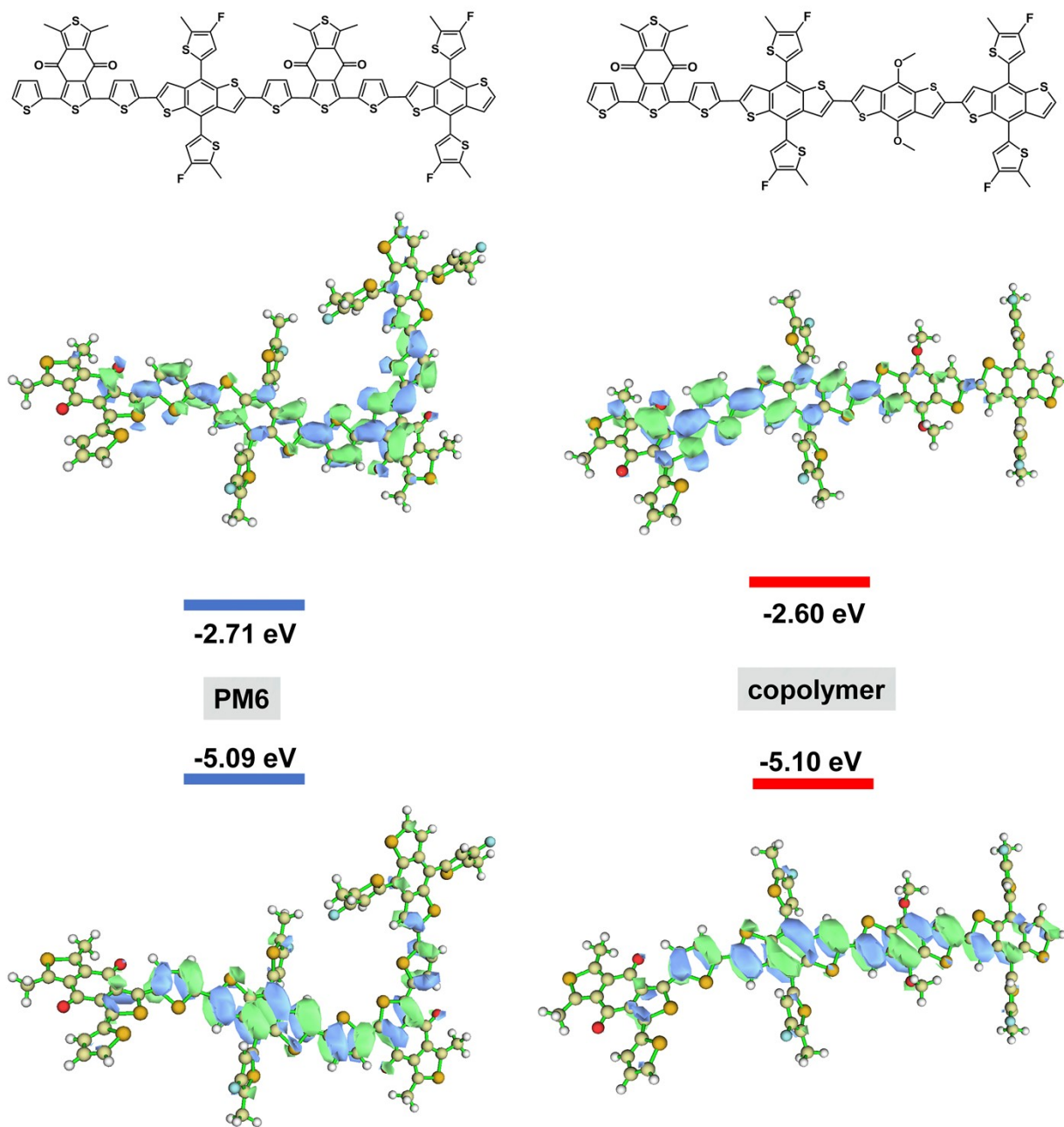


Fig. S8 Molecular energy levels and wavefunction distributions of the frontier orbitals for by polymer models calculated by Density functional theory (DFT) with methyl groups in replacing alkyl substituents to simplify the calculations

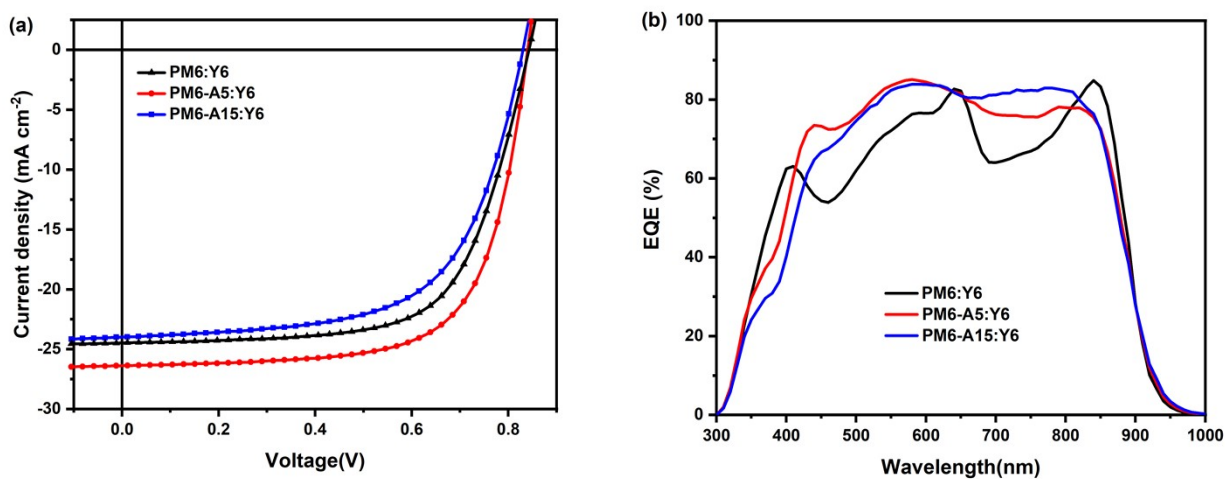


Fig. S9 (a) J - V plots of the Y6-based OSCs with different polymer donors under the illumination of AM1.5G, 100mWcm^{-2} , and (b) EQE curves of the corresponding OSCs

Energy Loss calculation⁴

$$E_{\text{loss}} = E_{g}^{opt} - qV_{oc}$$

Table S1. The parameters of energy loss calculation

Devices	V_{oc}	E_{g}^{opt} (acceptor)	E (loss)
	(V)	(eV) ^a	(eV)
PM6:Y6	0.84		0.44
PM6-A5:Y6	0.84	1.28	0.44
PM6-A15:Y6	0.83		0.45

a

$$E_{g}^{opt} = 1240/\lambda_{\text{onset}}$$

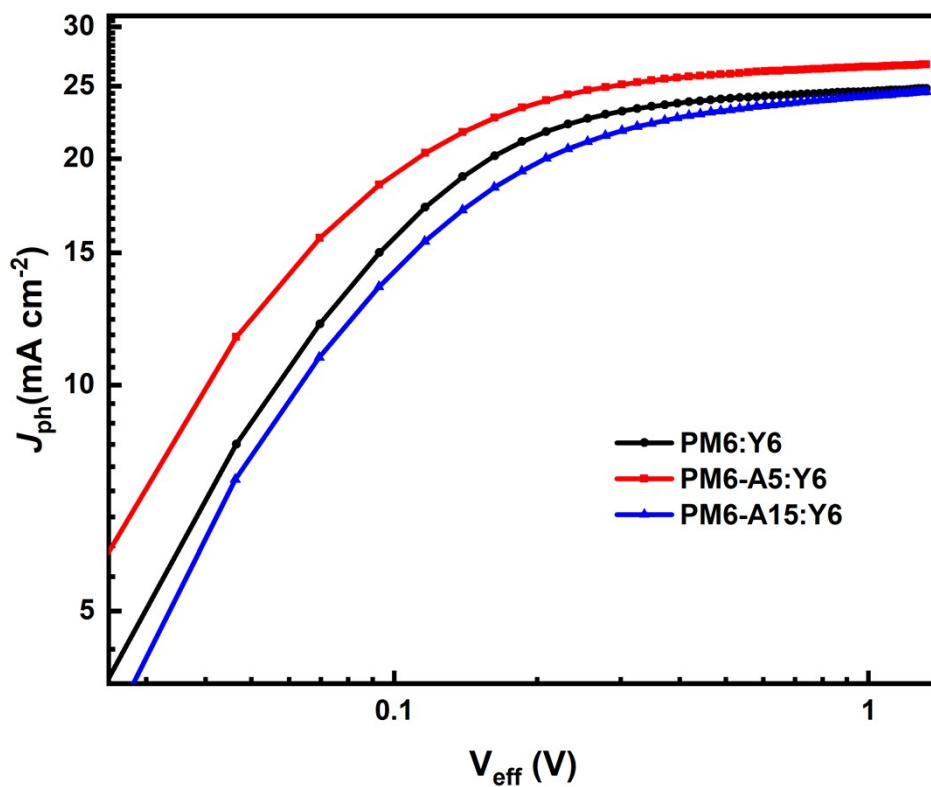


Fig. S10 J_{ph} versus V_{eff} curves of the optimized devices

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

Devices	J_{sat} (mA/cm ²)	J_{sc} (mA/cm ²)	J_{MPP} (mA/cm ²)	P_{diss} (%)	P_{coll} (%)
PM6:Y6	24.82	24.45	22.12	98.51	89.12
PM6-A5:Y6	26.69	26.36	24.19	98.76	90.63
PM6-A15:Y6	24.56	23.95	22.02	97.52	89.65

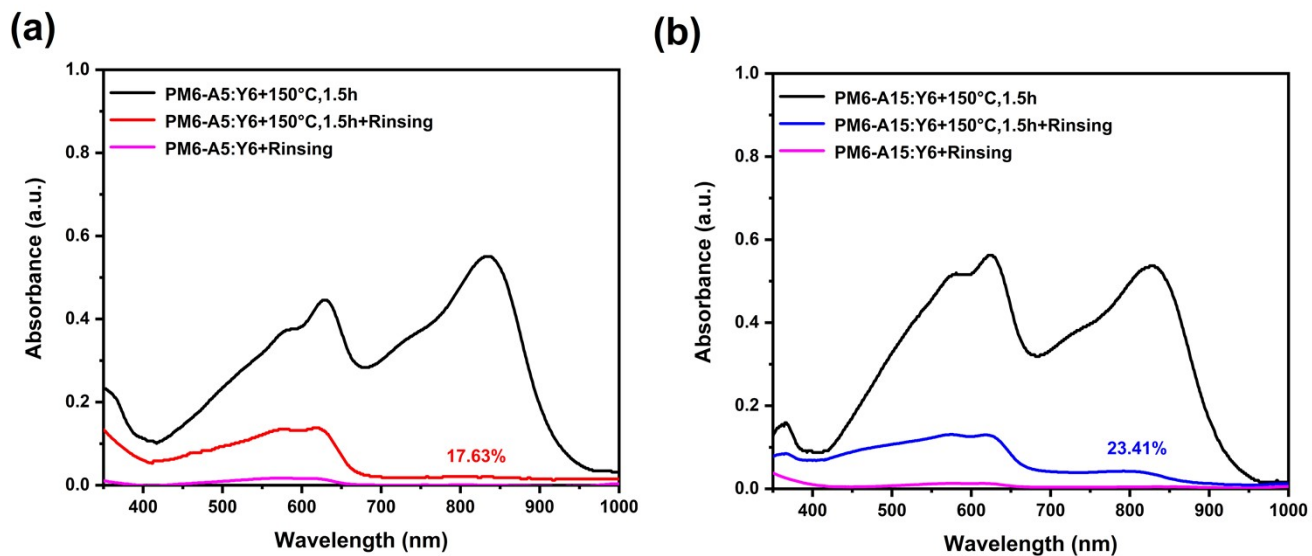


Fig. S11 a) UV-vis absorption spectra of the PM6-A5:Y6 blend film before and after rinsing and b) UV-vis absorption spectra of the PM6-A15:Y6 blend film before and after rinsing.

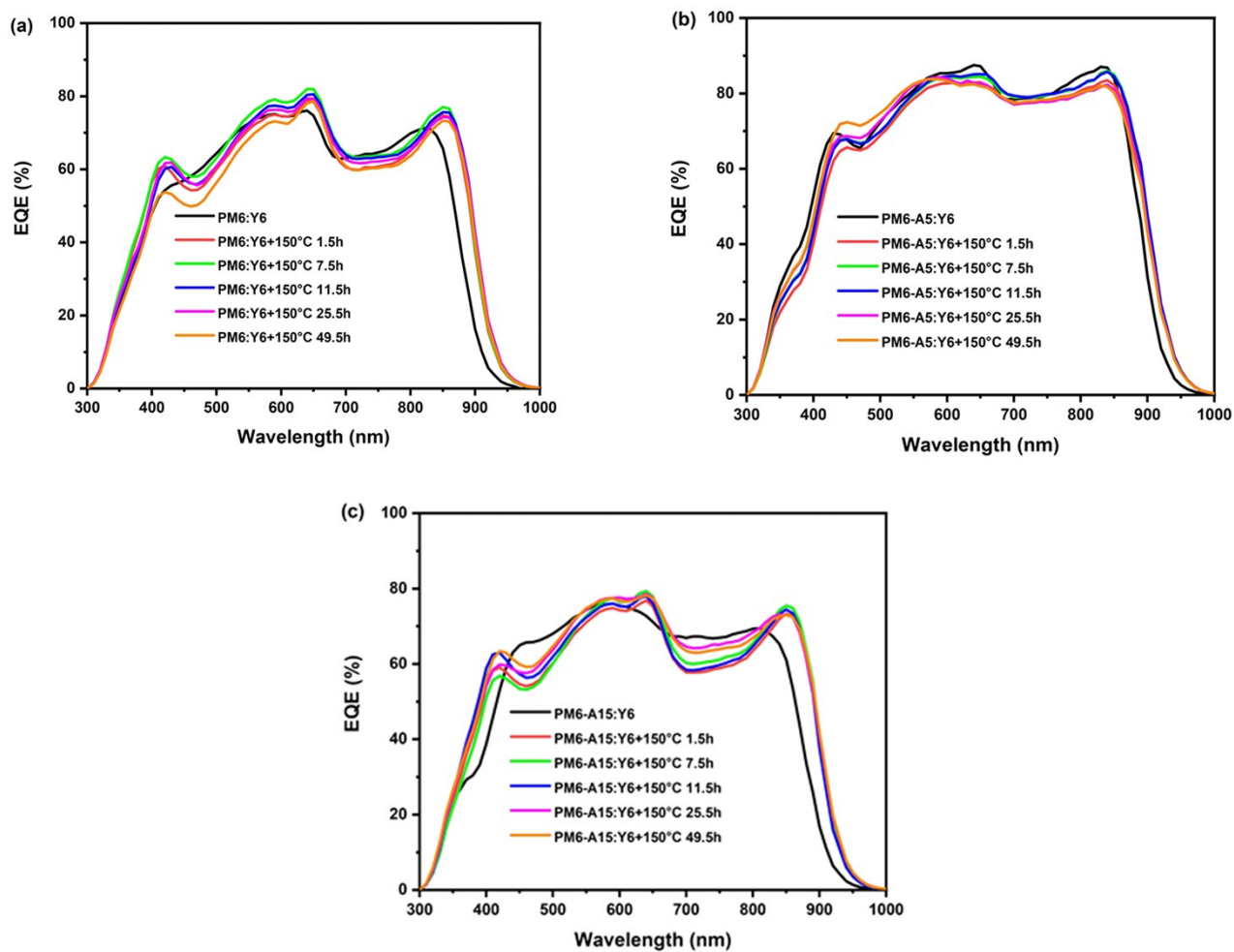


Fig. S12 EQE curves of the devices based Y6 for three systems (a) PM6, (b) PM6-A5 and (c) PM6-A15 against the annealing time for 150°C.

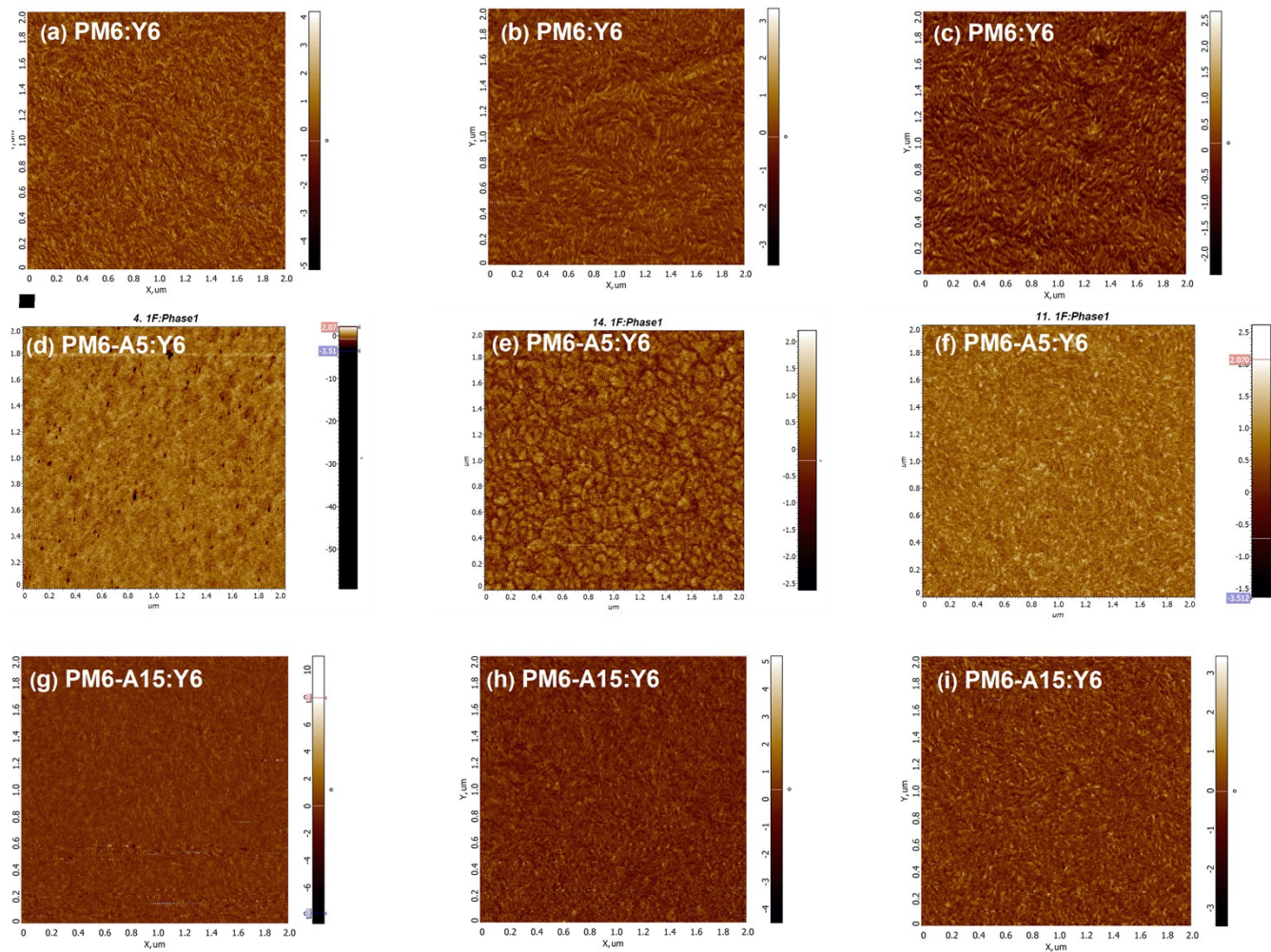


Fig. S13 AFM phase images of blend films based on PM6:Y6 (a, b, c), PM6-A5Y6 (d, e, f), PM6-A15 (g, h, i) with different annealing time at 150 °C. Annealing time; 0 h: (a, d, g); 1,5 h for thermal-crosslinking: (b, e, h); then 49.5h: (c, f, i).

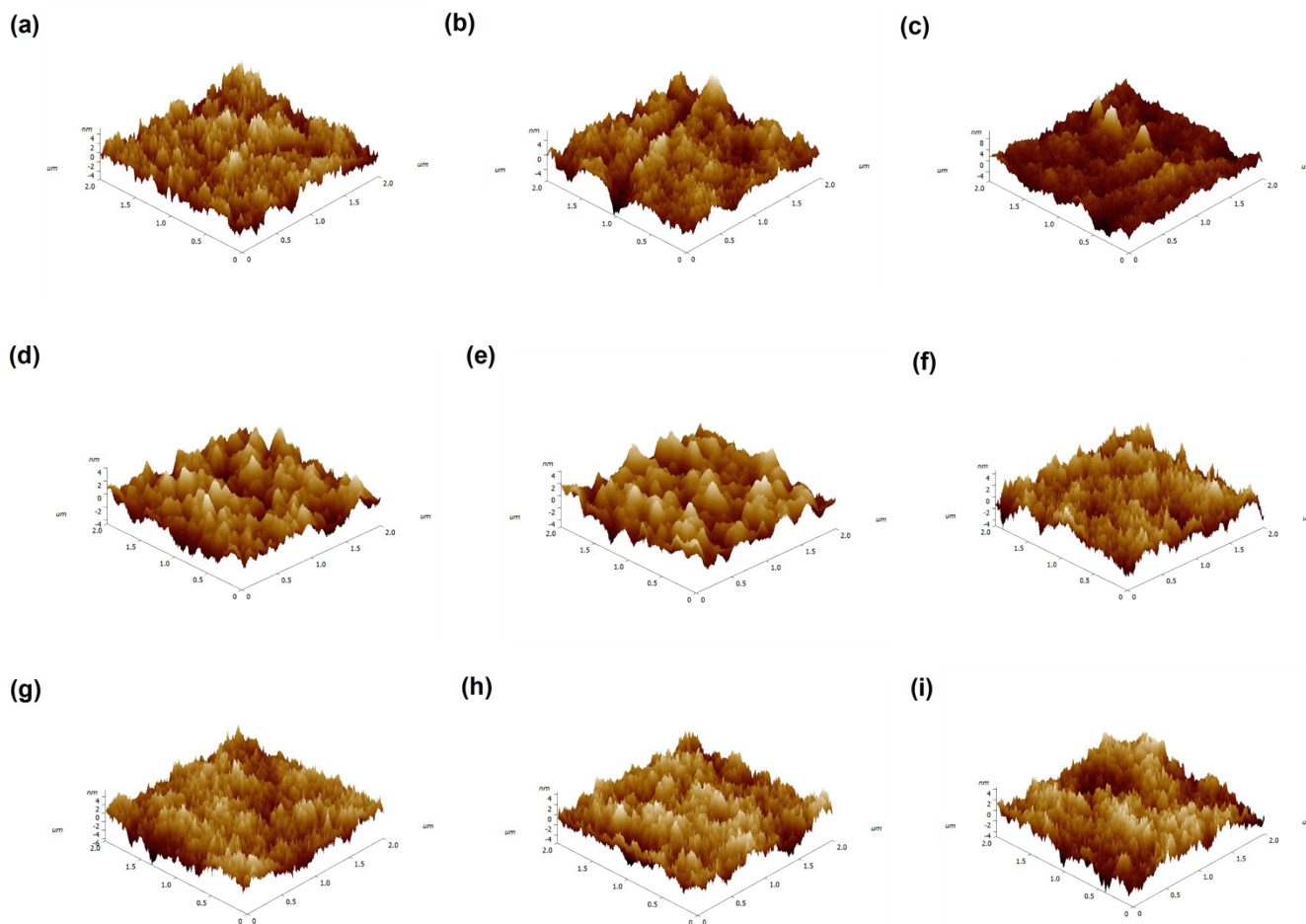


Fig. S14 AFM 3D images of blend films based on PM6:Y6 (a, b, c), PM6-A5Y6 (d, e, f), PM6-A15 (g, h, i) with different annealing time at 150 °C. Annealing time; 0 h: (a, d, g); 1,5 h for thermal-crosslinking: (b, e, h); then 49.5h: (c, f, i).

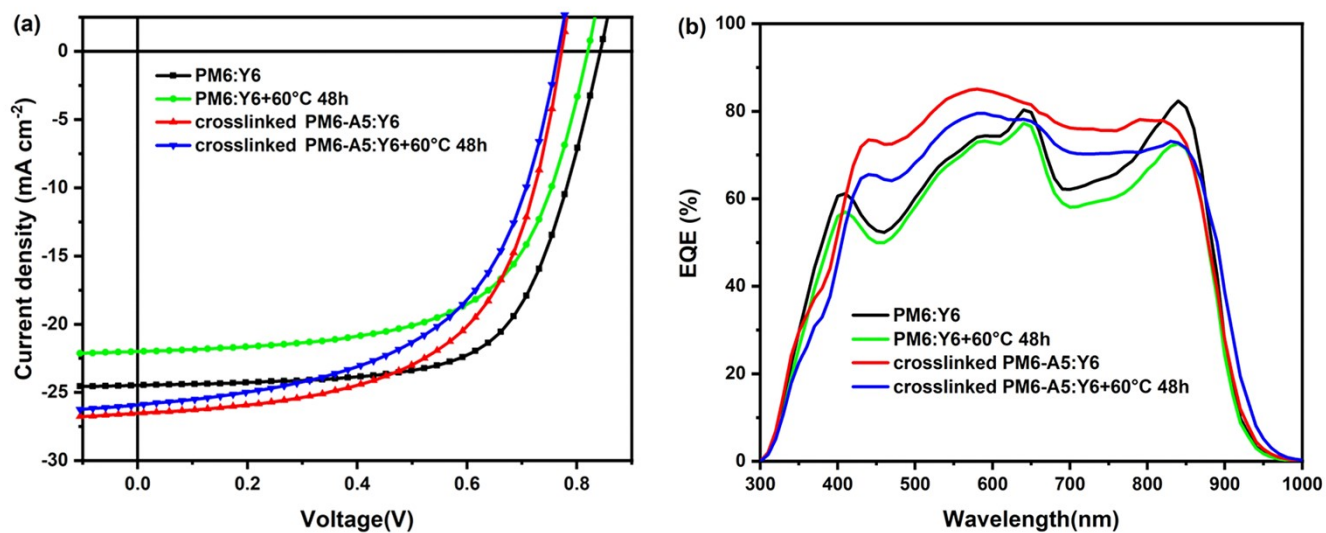


Fig. S15 (a) J-V plots of the Y6-based OSCs for PM6 and PM6-A5 (crosslinked) with and without annealing at 60°C under the illumination of AM1.5G, 100 mWcm⁻² (b) EQE curves of the devices with the PM6 as-cast blend film, PM6-A5 crosslinked blend film.

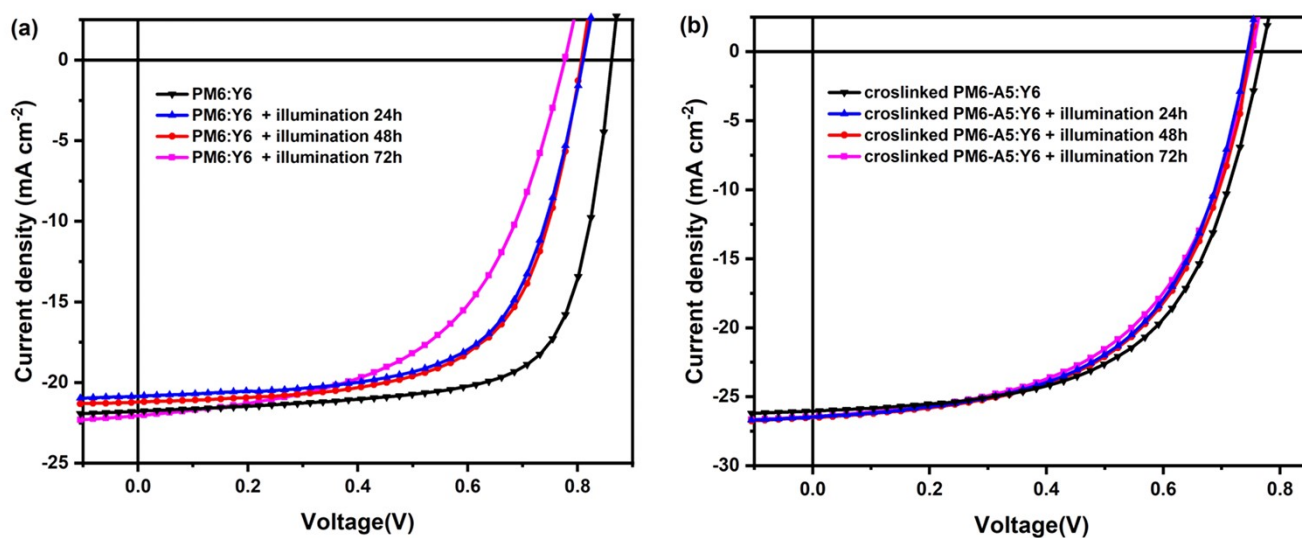


Fig. S16 (a) J-V plots of the Y6-based OSCs for PM6 by LED white light (the light intensity of white LED is 12 mW cm^{-2}) illumination under the illumination of AM1.5G, 100 mW cm^{-2} (b) J-V plots of the Y6-based OSCs for and PM6-A5 (crosslinked) by LED white light (12 mW cm^{-2}) illumination under the illumination of AM1.5G, 100 mW cm^{-2}

Table S3. Characteristic photovoltaic parameters of Shelf-life stability of the OSCs with the PM6 as-cast blend film, PM6-A5 and PM6-A15 crosslinked blend film.

Devices	Day	$V_{oc}(V)$ ^a	$J_{sc}(mA\ cm^{-2})$ ^a	FF(%) ^a	PCE _{avg} (%) ^a
PM6:Y6 ^b	-	0.85	22.60	69.60	13.37
	6	0.75	22.46	69.22	11.66
	13	0.74	21.91	69.45	11.26
	27	0.75	21.73	67.89	11.08
	38	0.73	22.00	64.31	10.28
	52	0.72	22.12	62.16	9.90
	60	0.72	22.29	57.01	9.15
PM6-A5:Y6 ^c	-	0.77	26.04	58.90	11.81
	6	0.78	25.74	57.78	11.60
	13	0.77	25.55	58.51	11.51
	27	0.77	25.34	57.35	11.19
	38	0.75	25.27	56.35	10.68
	52	0.76	25.21	55.55	10.64
	60	0.76	24.96	55.88	10.60

^a Average values are obtained from 6 devices

^b No annealing

^c Thermal-annealing at 150°C for 1.5h (crosslinked)

No.	Weight [mg]	Name	Method	N [%]	C [%]	H [%]	S [%]	Date	Time
41	4.7880	TO-A1	5mg90s	0.03	70.05	6.89	20.74	2021/1/23	4:23

No.	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	Date	Time
22	4.8680	A5	5mg90s	1 569	81 831	19 351	8 781	0.02	72.38	13.88	22.39	2021/9/11	0:33

No.	Weight [mg]	Name	Method	N Area	C Area	H Area	S Area	N [%]	C [%]	H [%]	S [%]	Date	Time
23	4.8090	A1s	5mg90s	982	80 252	17 697	9 256	0.00	71.82	12.24	24.06	2021/9/11	0:44

Fig. S17 Elemental analysis

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