

## Supporting Information

# Modifying polymer PM6 by incorporating a third component for enhanced short-circuit current density

Silong Tu, Li Zhang, Xin Lin, Liren Xiao\*, Wen Wang\*, Qidan Ling

Fujian Key Laboratory of Polymer Materials, College of Chemistry and Materials Science, Fujian Normal University, Fuzhou 350007, P. R. China.

\*Corresponding authors.

E-mail addresses: [xlr1966@126.com](mailto:xlr1966@126.com) (L. Xiao), [wangwen@fjnu.edu.cn](mailto:wangwen@fjnu.edu.cn) (W. Wang)

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## Characterization methods

The NMR spectra were recorded on a BRUKER AVIII-400 NMR spectrometer by utilizing deuterated chloroform ( $\text{CDCl}_3$ ) as the solvent and tetramethylsilane (TMS) as the standard. Thermogravimetric analysis (TGA) was performed using a Mettler-Toledo 851e/822e analysis system under  $\text{N}_2$  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  $\text{Ag}/\text{Ag}^+$  electrode as the reference electrode on a CHI660B Electrochemical Workstation in a tetrabutylammoniumhexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) (0.1 M) acetonitrile solution at a scan rate of  $20 \text{ mVs}^{-1}$ . The experiments were calibrated with the standard ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox system and it was assumed that the energy level of  $\text{Fc}/\text{Fc}^+$  was 4.8 eV below vacuum, and the value of 0.36 V was found for  $\text{Fc}/\text{Fc}^+$  vs.  $\text{Ag}/\text{AgCl}$ . 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  $E_{\text{HOMO}} = -e(E_{\text{ox}}^{\text{onset}} + 4.44)\text{V}$ ,  $E_{\text{LUMO}} = -e(E_{\text{red}}^{\text{onset}} + 4.44)\text{V}$ . UV-vis absorption spectra were recorded on a SHIMADZU UV-2600 spectrometer. Grazing-incidence wide-angle X-ray scattering (GIWAXS) was measured at 13A beam line of National Synchrotron Radiation Research Center (NSRRC, Taiwan), and were provided technical support by “Ceshigo Research Service, [www.ceshigo.com](http://www.ceshigo.com)”. All samples for GIWAXS were radiated at 12 keV X-ray with an incident angle of  $0.2^\circ$ . The sample films were prepared by spin-coating of the polymer solutions onto Si substrates (for GIWAXS) and annealed at  $100^\circ\text{C}$  for 5 min. The photoluminescence spectra were recorded on a SHIMADZU RF-5301PC. Time-resolved photoluminescence decay curves were obtained using a FLS920 Fluorescence Spectrometer equipped with an optical maser, which the excitation wavelength is 405 nm. 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.

## Devices fabrication and measurement

The devices were fabricated with a structure of glass/ITO/PEDOT: PSS/active layer/PDINN/Ag. The

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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 O<sub>2</sub>-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 N<sub>2</sub>-filled glove box. Subsequently, the copolymer/Y6 (wt:wt=1:1, 13 mg/mL) blends were dissolved in CHCl<sub>3</sub>, mixed and stirred at 50°C overnight. Afterwards, the blend solutions were filtered (0.45 μm), and then spin-coated on the ITO/PEDOT: PSS substrate at 3000 rpm for 45 s, annealing at 100°C for 5 min. The thickness of the photoactive layer is about 115 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 on 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 mm<sup>2</sup>. Current-voltage (J-V) characteristics were recorded in air, using a Keithley 2400 Source-Measure unit under 100 mW cm<sup>-2</sup> 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.

SCLC mobility was measured using a diode configuration of ITO/PEDOT:PSS/active layer/MoO<sub>3</sub>/Ag for hole and ITO/PFN/active layer/LiF/Al for electron by taking the dark current density in the range of 0-2 V and fitting the results to a space charge limited form, where SCLC is described by:  $J=9\epsilon_0\epsilon_r\mu_0V^2/8L^3$ , where J is the current density, L is the film thickness of the active layer, μ<sub>0</sub> is the hole or electron mobility, ε<sub>r</sub> is the relative dielectric constant of the transport medium, ε<sub>0</sub> is the permittivity of free space (8.85 × 10<sup>-12</sup> Fm<sup>-1</sup>),  $V (V_{appl}-V_{bi})$  is the internal voltage in the device, where  $V_{appl}$  is the applied voltage to the device and  $V_{bi}$  is the built-in voltage due to the relative work function difference of the two electrodes.

## Definition of the parameters

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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<sup>-2</sup> 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 the short-current conditions; charge collection efficiency ( $P_{coll}$ ):  $P_{coll} = J_{MPP} / J_{sat}$ ,  $J_{MPP}$  is the current density under the maximum power point (MPP) conditions.

## EXPERIMENTAL SECTION

### Materials

[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)-4H,8H-benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (BDD) and 2,6-dibromo-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT-T) were purchased from Suna Tech Inc. Y6 was 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 PM6:

BDT-TF monomer (0.053 mmol, 50 mg) and bromide monomer BDD (0.053 mmol, 40.6 mg) added into a 25 mL single-neck round-bottom flask. Pd (PPh<sub>3</sub>)<sub>4</sub> (6 mg) was added into the mixtures in Nitrogen atmosphere glove box. Then, degassed and filled with nitrogen three times (15 minutes) and 10 mL of anaerobic anhydrous toluene was added. The reactions of PM6 were stirred at 100 °C for about 25 h then added 1ml bromobenzene to react 6 h, afterward cooled to room temperature and precipitated from methanol (200 mL) and. 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 91%. GPC: Mn=20.5 kg/mol, Mw=61.7 kg/mol, PDI=3.01. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) 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%.

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#### Synthesis of PM6-T5:

PM6-T5 was synthesized by using similar procedure as mentioned above, with BDT-TF monomer (0.053 mmol, 50mg), bromide monomer BDD (0.0503mmol, 38.6 mg) and bromide monomer BDT-T (0.0027mmol, 2.0 mg) as black solid with a yield of 88%. GPC: Mn=14.7mol, Mw=46.3 kg/mol, PDI=3.15. <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  7.31 (s, 1H), 2.87 (s, 1H), 1.28 (s, 15H). Feed ratio: 95:5, actual ratio: 95.96:4.04. Elemental Anal. Calcd.: C, 69.50%; H, 6.96%; S, 20.90%.

#### Synthesis of PM6-T10:

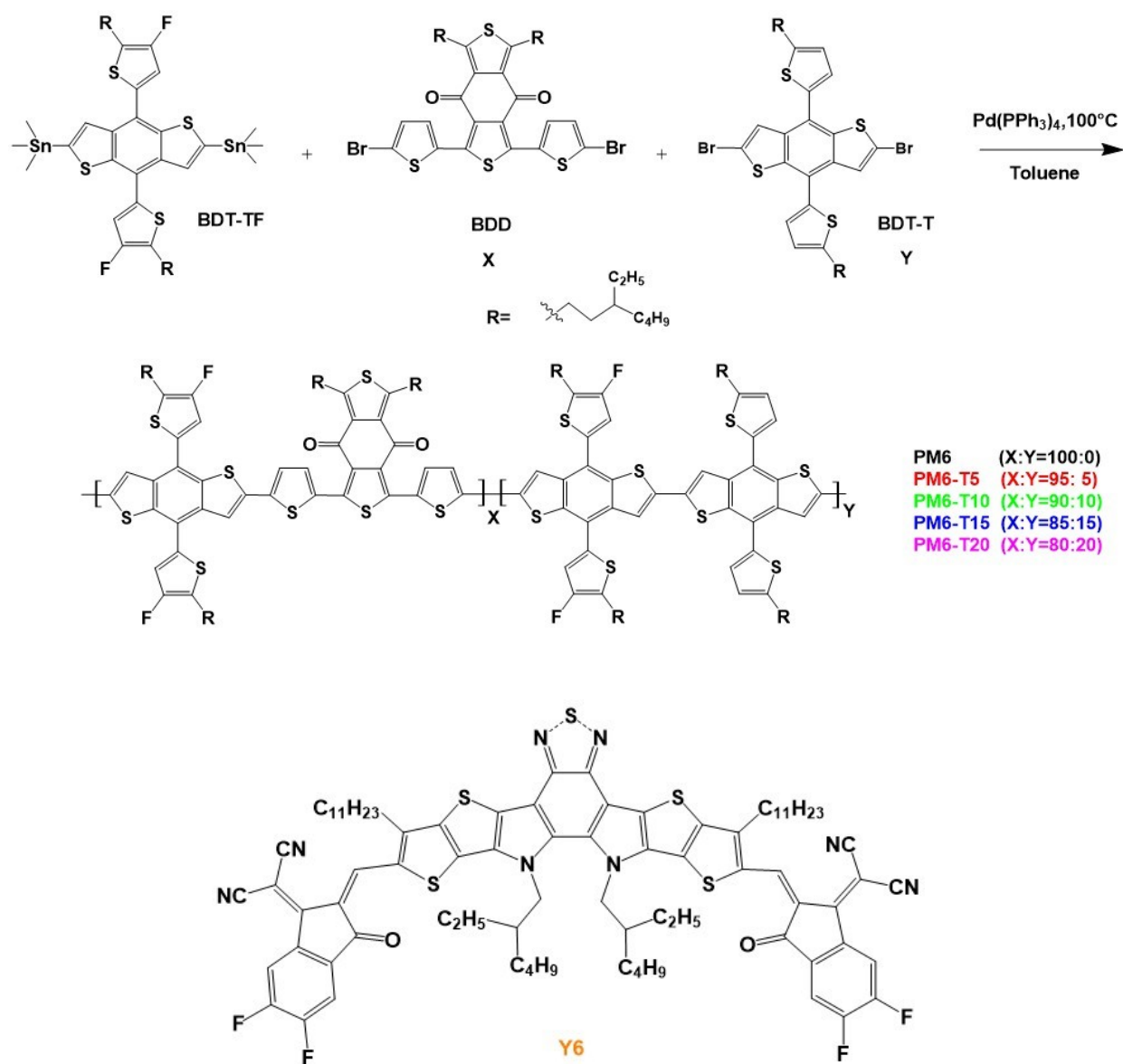
PM6-T10 was synthesized by using similar procedure as mentioned above, with BDT-TF monomer (0.053 mmol, 50mg), bromide monomer BDD (0.0477mmol, 36.6 mg) and bromide monomer BDT-T (0.0053mmol, 3.9 mg) as black solid with a yield of 86%. GPC: Mn=20.0 kg/mol, Mw=68.3 kg/mol, PDI=3.41. <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  7.15 (s, 1H), 2.90 (s, 1H), 1.48 (s, 6H), 0.99 (s, 7H). Feed ratio: 90:10, actual ratio: 92.84:8.16. Elemental Anal. Calcd.: C, 66.90%; H, 7.05% ; S, 19.66%.

#### Synthesis of PM6-T15:

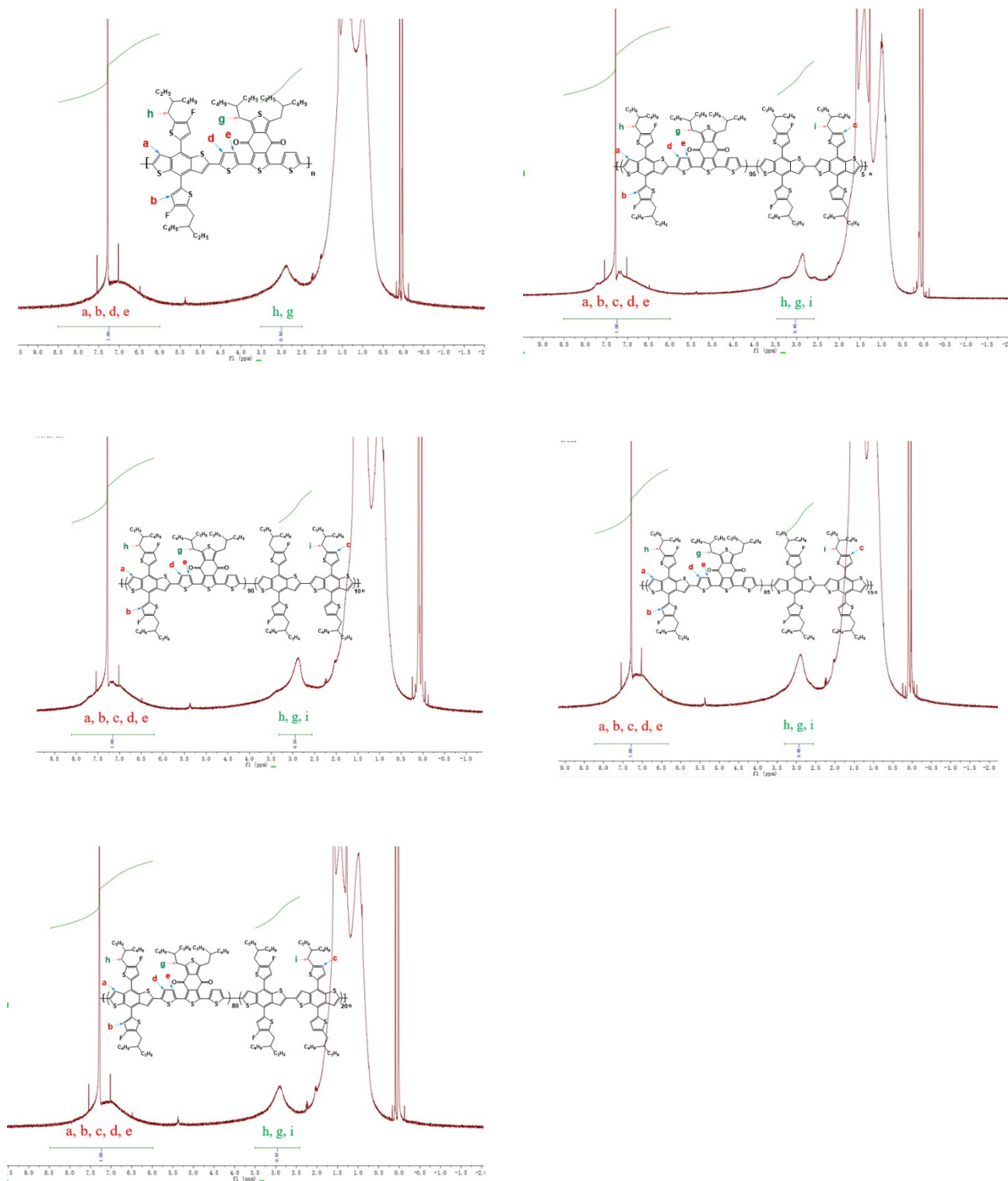
PM6-T15 was synthesized by using similar procedure as mentioned above, with BDT-TF monomer (0.053 mmol, 50mg), bromide monomer of BDD (0.0450mmol, 34.5 mg) and bromide monomer of BDT-T (0.0080mmol, 5.9 mg) as black solid with a yield of 89%. GPC: Mn=14.7 kg/mol, Mw=46.1 kg/mol, PDI=3.13. <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  7.35 (s, 1H), 6.98 (s, 1H), 2.90 (s, 1H), 1.43 (s, 7H), 1.28 (s, 11H), 1.05 (s, 7H), 0.98 (s, 7H). Feed ratio: 85:15, actual ratio: 83.34:16.66. Elemental Anal. Calcd.: C, 69.09%; H, 7.12%; S, 20.33%.

#### Synthesis of PM6-T20:

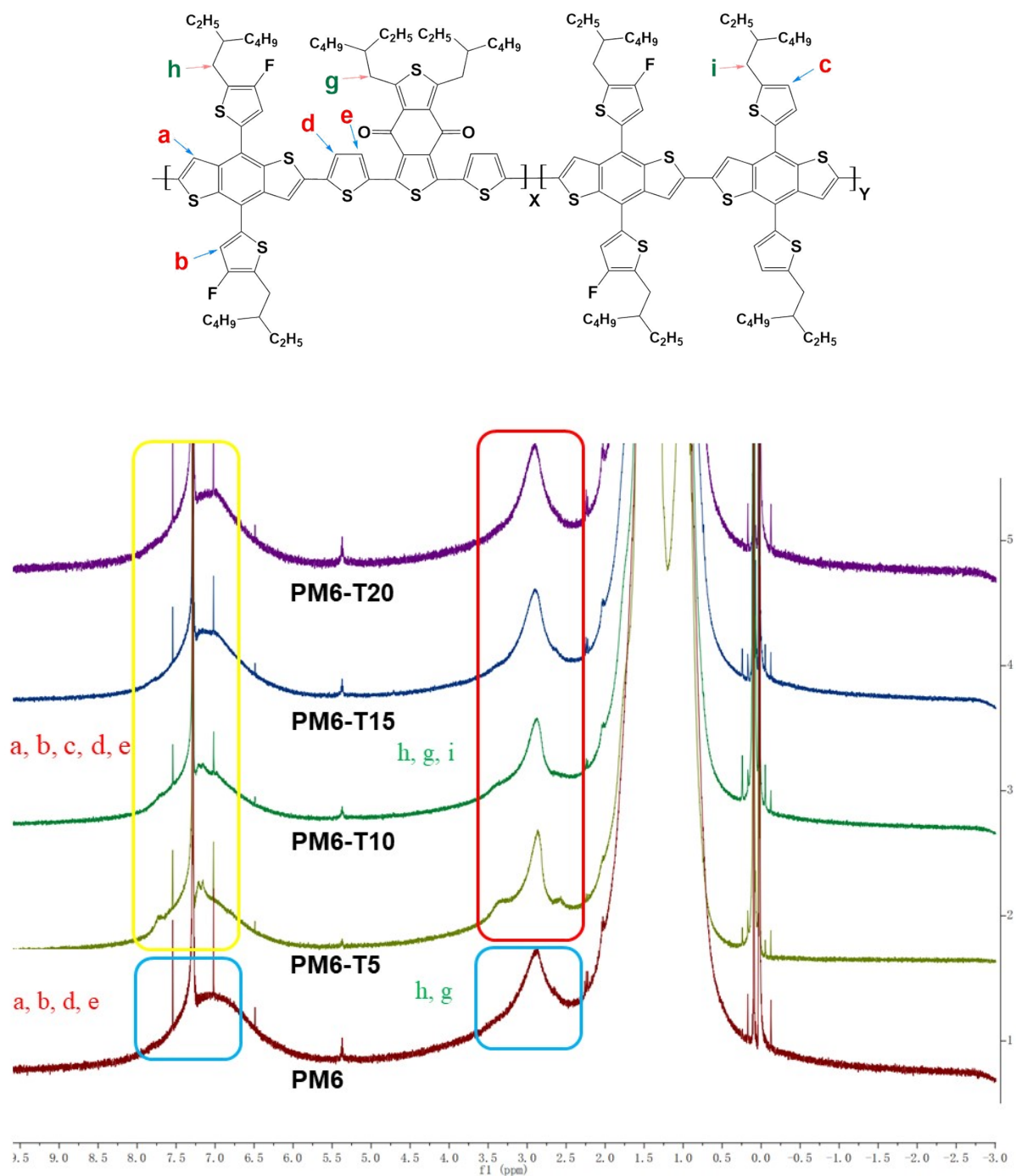
PM6-T20 was synthesized by using similar procedure as mentioned above, with BDT-TF monomer (0.053 mmol, 50mg), bromide monomer of BDD (0.0424mmol, 32.5 mg) and bromide monomer of BDT-T (0.0011mmol, 7.8 mg) as black solid with a yield of 85%. GPC: Mn=14.0 kg/mol, Mw=38.5 kg/mol, PDI=2.75. <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  7.18 (s, 1H), 2.90 (s, 1H), 1.46 – 1.39 (m, 11H), 0.98 (s, 7H). Feed ratio: 80:20, actual ratio: 78.95:21.05. Elemental Anal. Calcd.: C, 69.32%; H, 7.04%; S, 21.04%



**Figure S1.** Synthetic scheme for the polymers and chemical structure of Y6

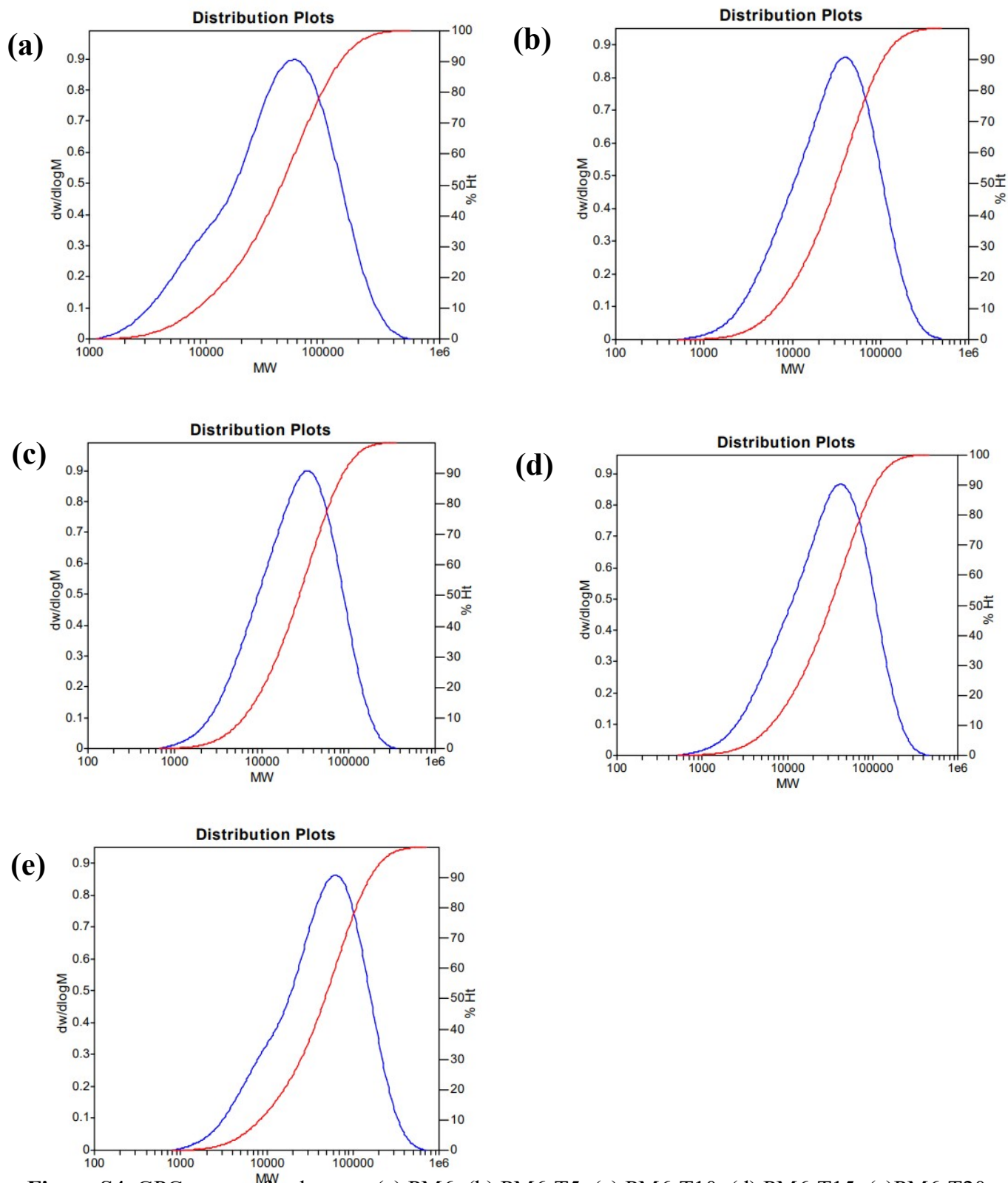


**Figure S2.** <sup>1</sup>H NMR spectra of PM6, PM6-T5, PM6-T10, PM6-T15 and PM6-T20

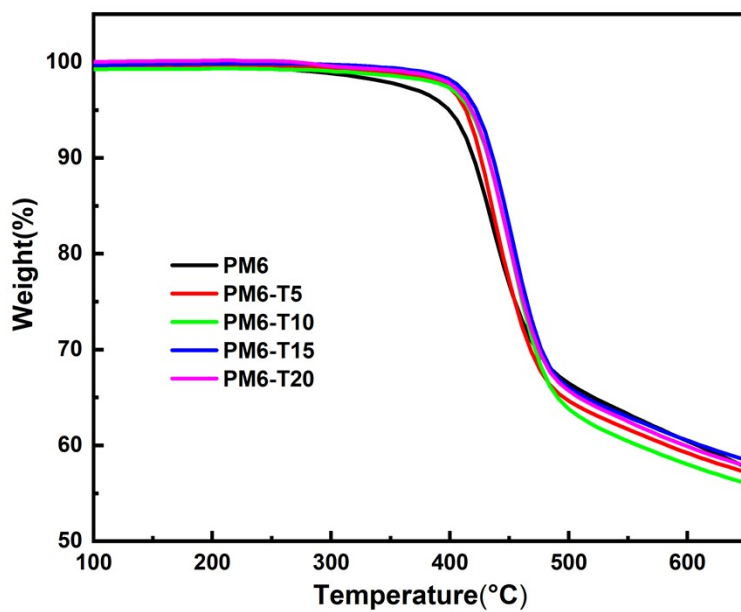


**Figure S3.** Comparison of <sup>1</sup>H NMR spectra of PM6 (X:Y=100:0), PM6-T5 (X:Y=95:5), PM6-T10 (X:Y=90:10), PM6-T15 (X:Y=85:15) and PM6-T20 (X:Y=80:20)

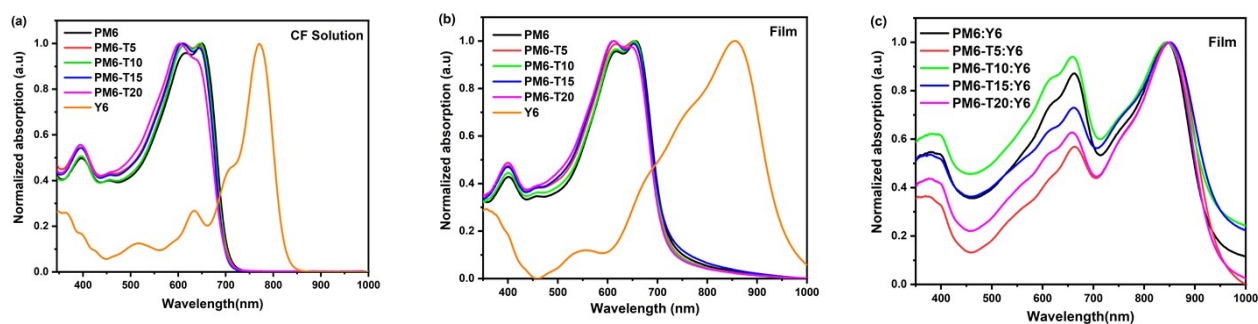




**Figure S4.** GPC traces of polymers: (a) PM6; (b) PM6-T5; (c) PM6-T10; (d) PM6-T15; (e) PM6-T20. High temperature GPC with 1, 2, 4-trichlorobenzene as the eluent and polystyrene as a standard at 150 °C



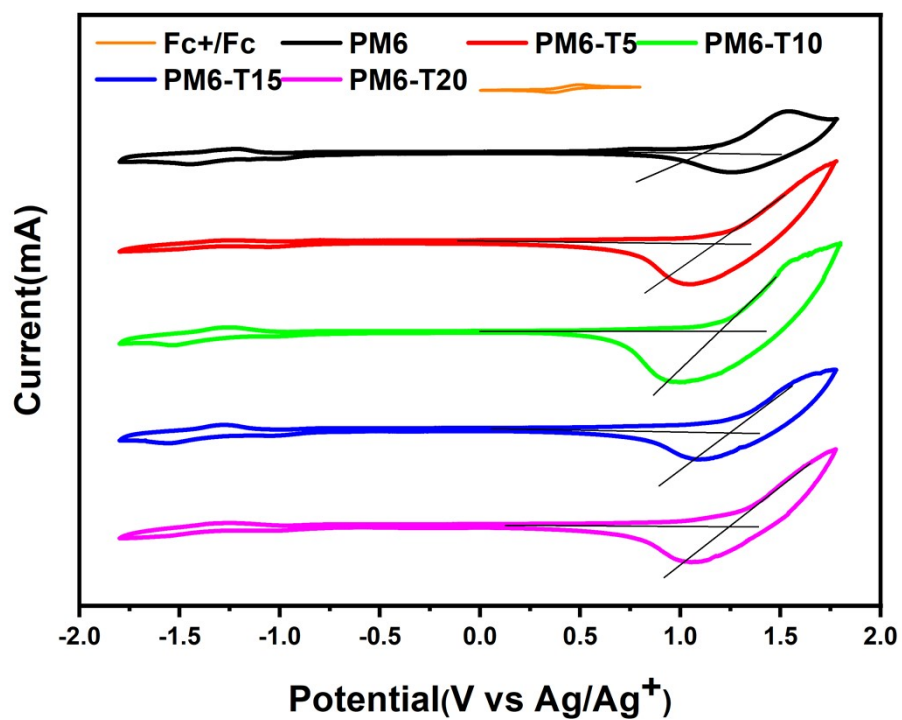
**Figure S5.** TGA curves of polymer donors at a scan rate of 10 °C/min under nitrogen atmosphere



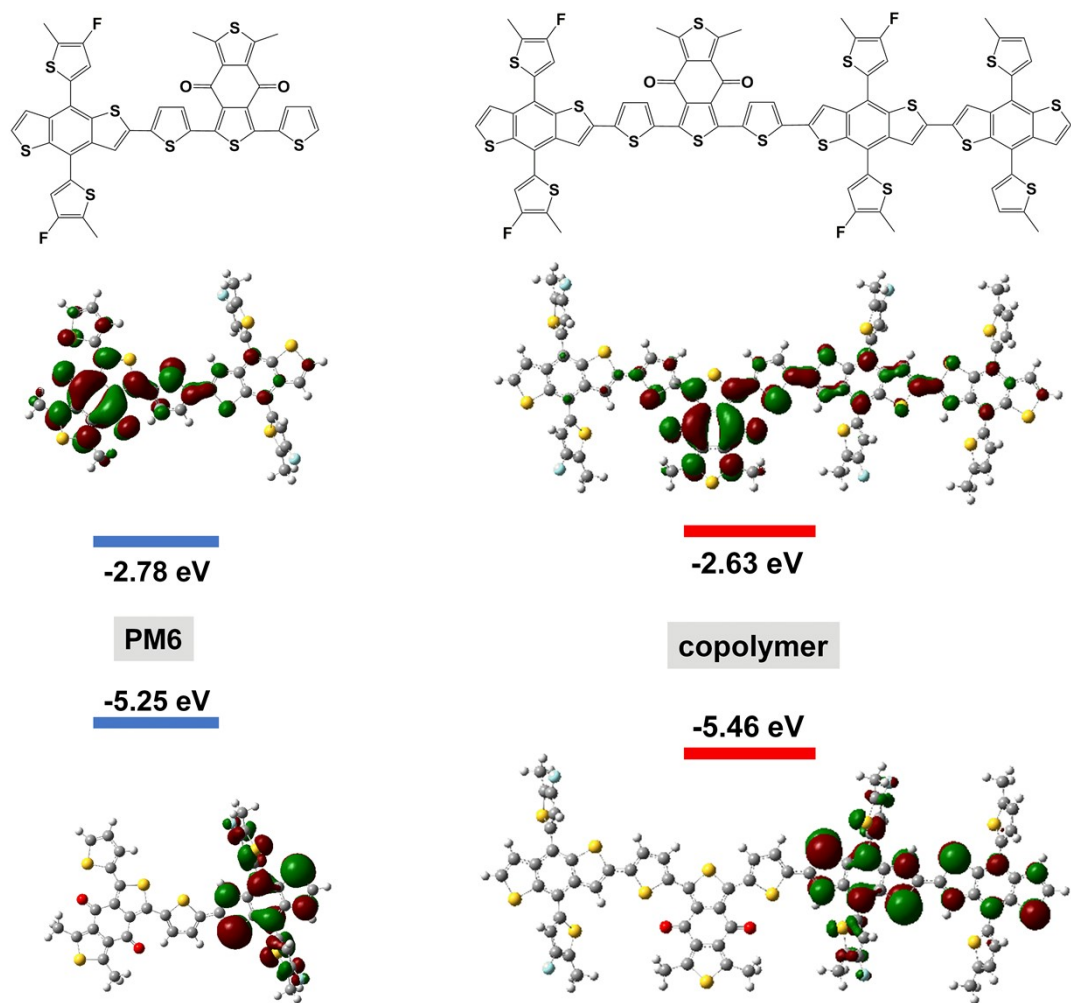
**Figure S6.** (a) Normalized absorption spectra of polymers in chloroform. (b) the absorption coefficients of neat polymer films (c) UV-vis absorption spectra of the polymer: Y6 blend films

**Table S1** Device data with different proportions of additives

Active layer	Additive ratio	$V_{oc}$ [V]	$J_{sc}$ [mA cm <sup>-2</sup> ]	FF[%]	PCE[%]
	No addition	0.85	25.98	65.92	14.61
PM6-T15:Y6	0.5%CN	0.87	26.47	71.09	16.31
	0.7%CN	0.86	27.02	71.14	16.60



**Figure S7.** Cyclic voltammograms of polymers and standard ferrocene/ferrocenium ((Fc/Fc<sup>+</sup>)).



**Figure 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

Energy Loss calculation<sup>1</sup>

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

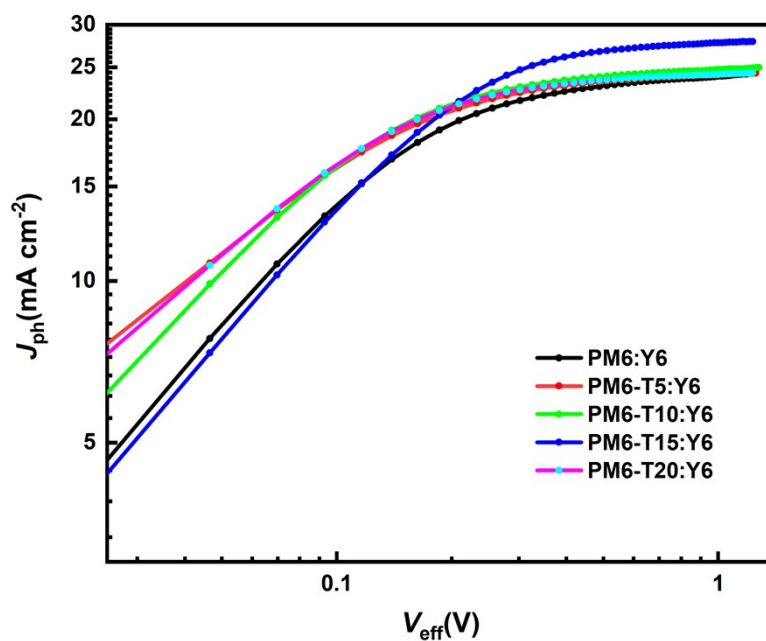
Table S2. The parameters of energy loss calculation

Devices <sup>a)</sup>	$V_{OC}$ (V)	$E_{g}^{opt}$ (accpetor) (eV) <sup>b</sup>	E (loss) (eV)
PM6: Y6	0.88		0.40
PM6-T5: Y6	0.89		0.39
PM6-T10: Y6	0.87	1.28	0.41
PM6-T15: Y6	0.86		0.42
PM6-T20: Y6	0.88		0.40

<sup>a</sup>0.70%CN.

<sup>b</sup>

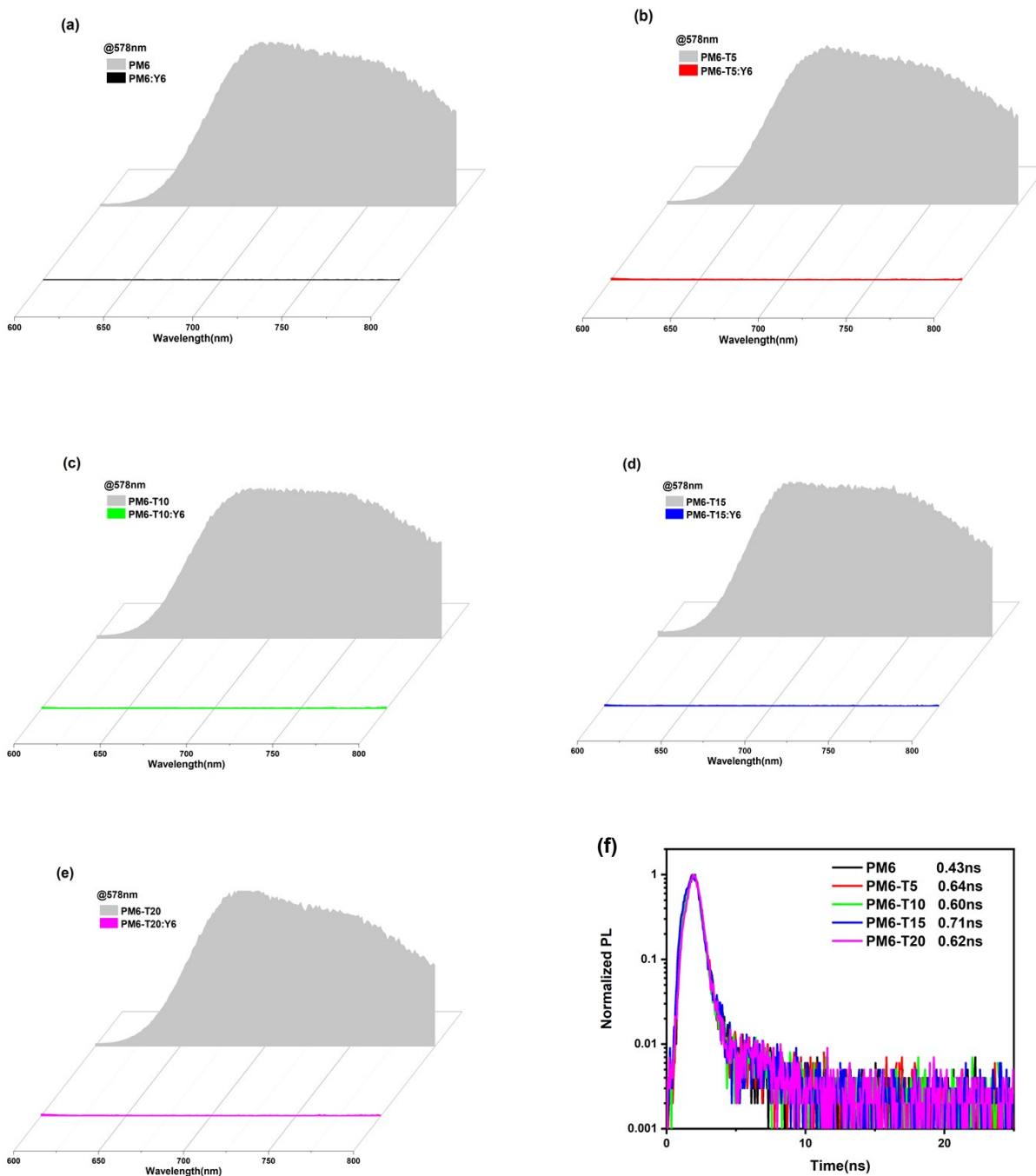
$$E_{g}^{opt} = 1240/\lambda_{\text{onset}}(\text{eV})$$



**Figure S9.**  $J_{\text{ph}}$  versus  $V_{\text{eff}}$  curves of the optimized devices

**Table S3.** The parameters of exciton dissociation efficiency and charge collection efficiency

Devices	$J_{\text{sat}}$ (mA/cm <sup>2</sup> )	$J_{\text{sc}}$ (mA/cm <sup>2</sup> )	$J_{\text{MPP}}$ (mA/cm <sup>2</sup> )	$P_{\text{diss}}$ (%)	$P_{\text{coll}}$ (%)
PM6: Y6	24.52	23.93	20.67	97.6	84.3
PM6-T5: Y6	24.38	23.68	20.38	97.1	83.6
PM6-T10: Y6	24.99	24.50	21.67	98.0	86.7
PM6-T15: Y6	27.91	27.38	24.91	98.1	89.3
PM6-T20: Y6	24.40	23.87	20.53	97.8	84.1

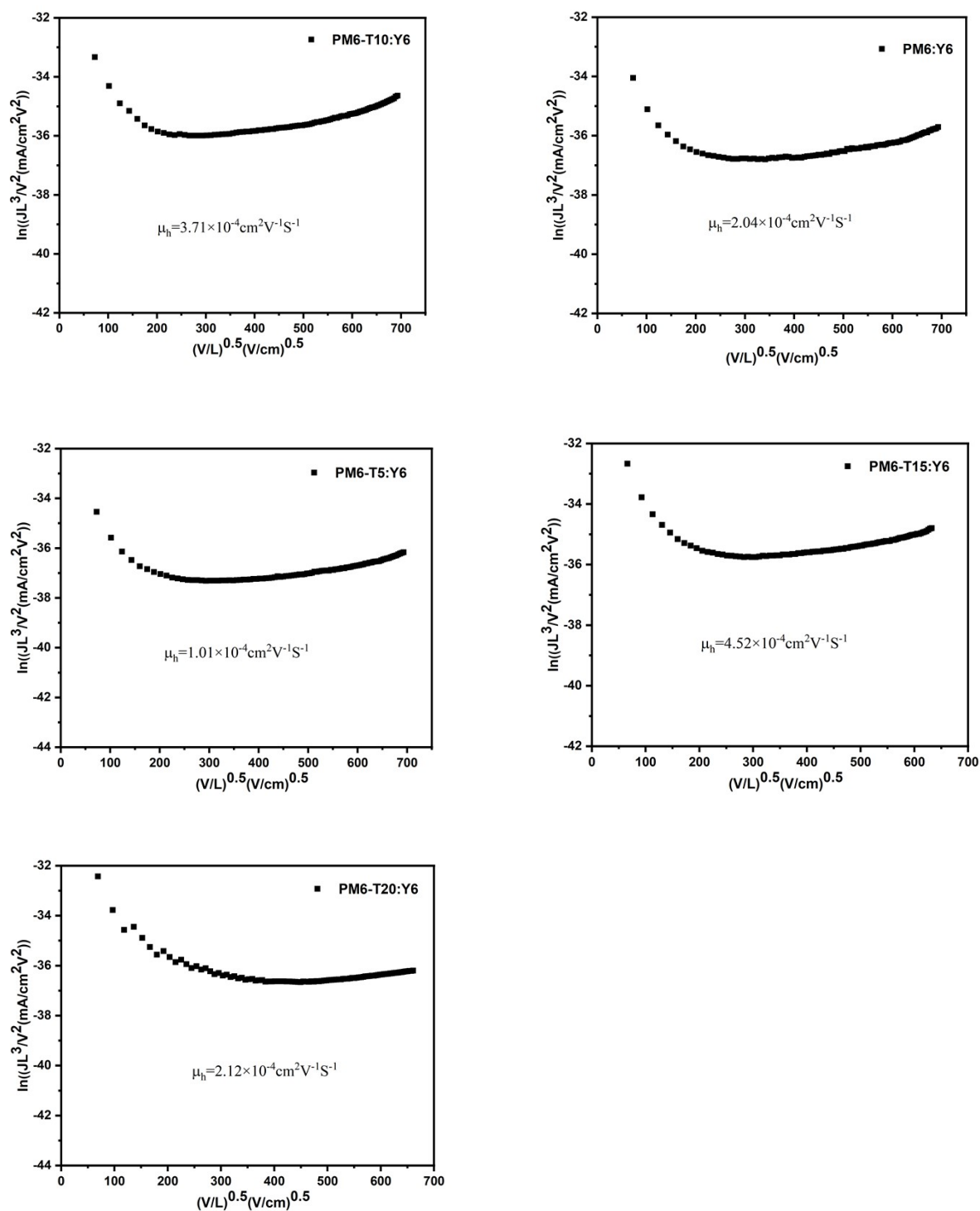


**Figure S10.** The PL spectra of (a) the PM6 pure film and related PM6:Y6 blend film, (b) the PM6-T5 pure film and related PM6-T5:Y6 blend film, (c) the PM6-T10 pure film and related PM6-T10:Y6 blend film, (d) the PM6-T15 pure film and related PM6-T15:Y6 blend films, (e) the PM6-T20 pure film and related PM6-T20:Y6 blend films, and (f) TRTPL spectra (excited at 405nm) of PM6, PM6-T5, PM6-T10, PM6-T15, and PM6-T20 neat films were obtained using a FLS920 Fluorescence Spectrometer equipped with a optical maser

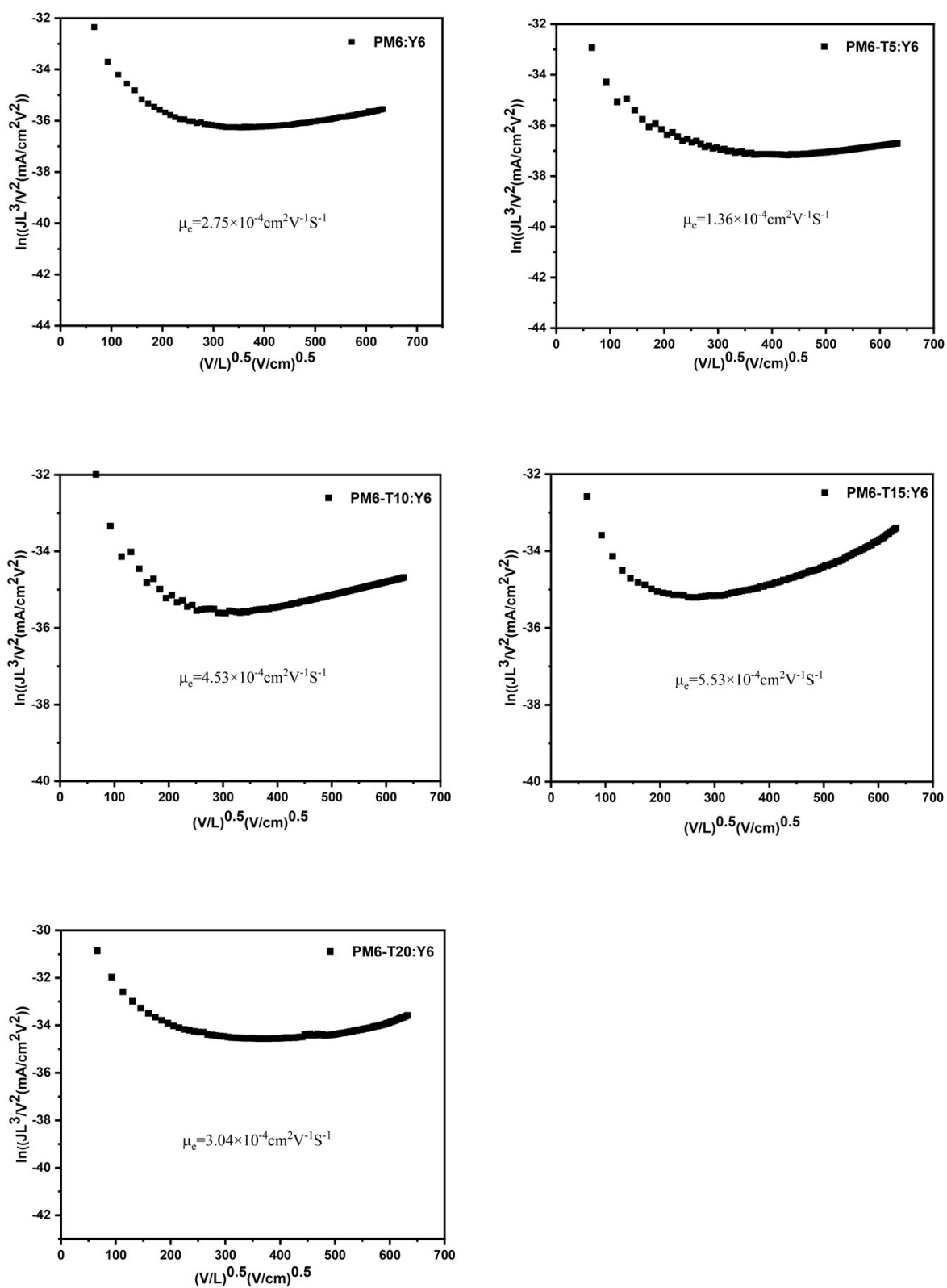


**Table S4.** Lifetime of PM6, PM6-T5, PM6-T10, PM6-T15, and PM6-T20

polymer	$\lambda_{em}$ (nm)	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_{av}$ (ns)	$\chi^2$
PM6	405	0.43 (100%)		0.43	1.060
PM6-T5	405	0.41 (94.18%)	4.43 (5.82%)	0.64	1.067
PM6-T10	405	0.40 (94.17%)	3.78 (5.83%)	0.60	1.091
PM6-T15	405	0.44 (94.06%)	4.98 (5.94%)	0.71	1.190
PM6-T20	405	0.42 (94.46%)	4.11 (5.54%)	0.62	1.184



**Figure S11-1.** The hole mobility of active layer for five polymers by SCLC



**Figure S11-2.** The electron mobility of active layer for five polymers by SCLC

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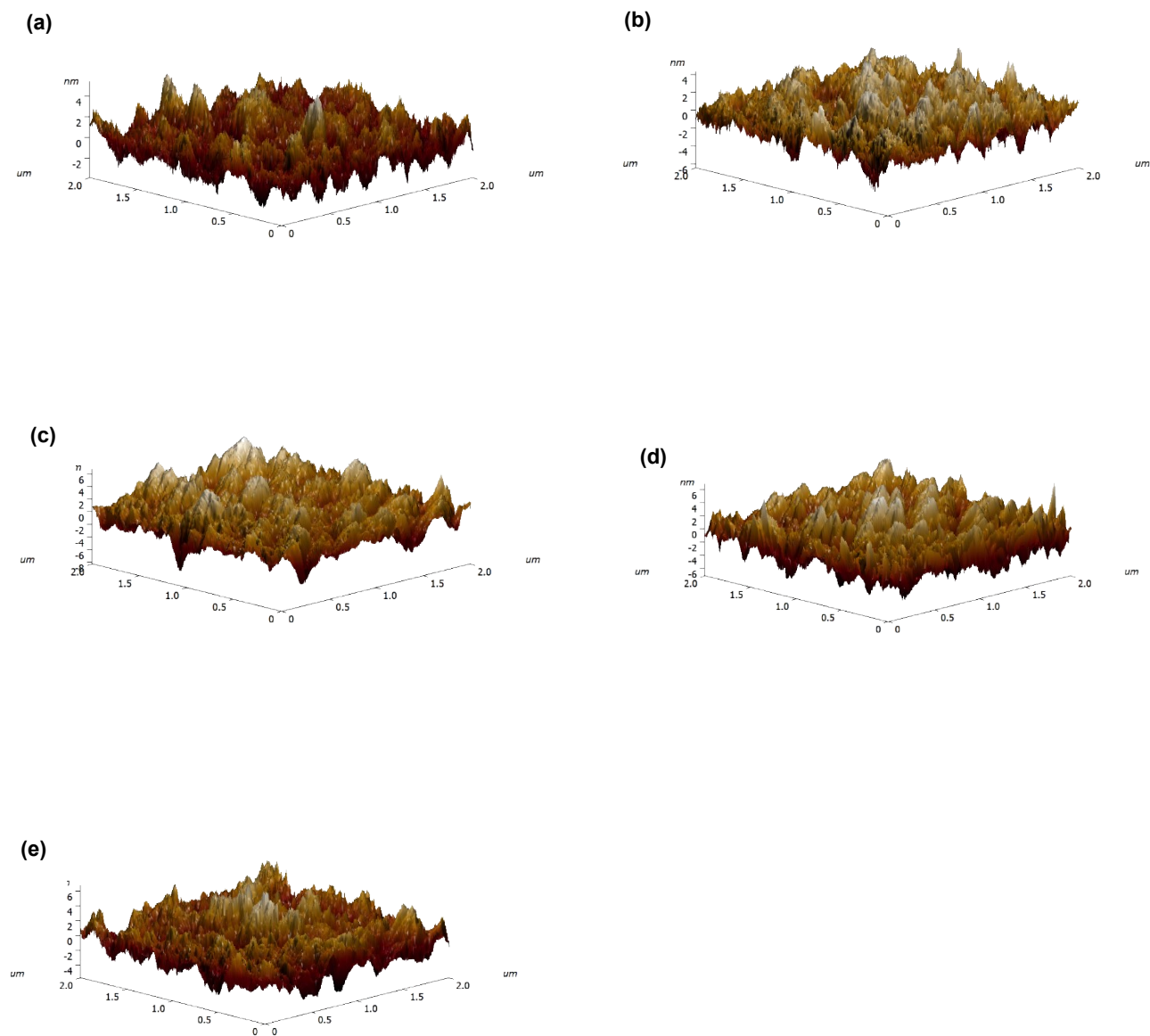
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analytic functional testing  
varioELcube  
serial number: 19181051

**Text report**

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
42	4.9940	T5-A2	5mg90s	0.00	69.50	6.96	20.90	2021/1/23	4:34
43	4.7930	T10-A3	5mg90s	0.00	66.90	7.05	19.66	2021/1/23	4:44
44	4.8280	T15-A4	5mg90s	0.01	69.09	7.12	20.33	2021/1/23	4:54
45	4.7080	T20-A5	5mg90s	0.00	69.32	7.04	21.04	2021/1/23	5:04

**Figure S12.** Elemental analysis



**Figure S13.** AFM 3D images of blends (a) PM6:Y6; (b) PM6-T5:Y6 (c) PM6-T10:Y6; (d) PM6-T15:Y6 and (e) PM6-T20:Y6

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1. F. Qi, K. Jiang, F. Lin, Z. Wu, H. Zhang, W. Gao, Y. Li, Z. Cai, H. Y. Woo, Z. Zhu and A. K. Y. Jen, *ACS Energy Lett.*, 2020, **6(1)**, 9-15.