

Supporting Information

16.7%-Efficiency Ternary Blended Organic Photovoltaic Cells with PCBM as the Acceptor Additive to Increase Open-Circuit Voltage and Phase Purity

Ming-Ao Pan,^{a,b,c} Tsz-Ki Lau,^d Yabing Tang,^e Yi-Ching Wu,^f Tao Liu,^{b,c} Kun Li,^b Ming-Chou Chen,^f Xinhui Lu,^{*d} Wei Ma^{*e} and Chuanlang Zhan^{*a,b}

^a College of Chemistry and Environmental Science, Inner Mongolia Normal University, Huhhot 010022, China.

^b CAS key Laboratory of Photochemistry, CAS Key Laboratory of Photochemistry, Institute of Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

^c Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China.

^d Department of Physics, Chinese University of Hong Kong, New Territories, Hong Kong, China.

^e State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China.

^f Department of Chemistry and Research Center of New Generation Light Driven Photovoltaic Modules, National Central University, Taoyuan, 32001, Taiwan.

* E-mail: clzhan@iccas.ac.cn (C.Z.)

xinhui.lu@cuhk.edu.hk (X.L.)

msewma@mail.xjtu.edu.cn.

Materials, Methods, and characterizations

Materials. The materials of PBDB-TF (PM6), PBDB-T-2Cl (PM7), IT-4F, Y6, PC₆₁BM and PC₇₁BM were purchased from Companies of Solarmer, Eflexpv, Shenzhen Ruixun, and One-Material. The charge transport material PDINO was bought from Solarmer company. The purity of all the materials was checked with ¹H NMR spectra provided by the company. In fact, this is not enough. We did more about the availability of the commercial materials. Before ordering these commercial materials and starting to use them for the fabrications of solar cells, we had doubly checked their availability by fabricating the solar cells with these materials. First, we got a small amount of a batch of the material from the company, then, we fabricated the solar cell. When the device performance reached the expectation, i.e. the device V_{oc} , J_{sc} , FF and PCE reached the expected values, we then purchased this batch of the material. For example, for PM6 and IT-4F, the PCE of PM6:IT-4F device has to reach over 13%, and for Y6, the PCE of PM6:Y6 device has to be about 15.5%. After getting the batch of the material, we again checked the availability by fabricating the solar cells. After the double checking and when the materials met the expectations, we then started the studies using these materials. PEDOT:PSS (Baytron Clevios P VP AI 4083, Germany) was obtained from Heraeus Group, imported by Solarmer company.

UV-Vis absorption spectra. Absorption spectra of donor polymers and acceptors in solid thin films were prepared by spin-coating their solutions in either chlorobenzene or chloroform atop the quartz glass substrates and measured on a Hitachi U-3010 UV-vis spectrophotometer.

Measurements of the Frontier molecular orbital energy levels. The HOMO/LUMO energy levels of the donor polymer and nonfullerene and fullerene acceptors were measured with differential pulse voltammetry (DPV) in their solutions and with cyclic voltammetry (CV) in their thin films, respectively. Differential pulse voltammetry experiments were performed under N₂ with a conventional three-electrode configuration (a platinum disk working electrode, an auxiliary platinum wire electrode, and a non-aqueous Ag reference electrode, with a supporting electrolyte of 0.1 M tetrabutylammoniumhexafluorophosphate (TBAPF₆) in a dry *o*-C₆H₄Cl₂ solution at the specified temperature using a CHI621C Electrochemical Analyzer (CH Instruments). All electrochemical potentials were referenced to an Fc⁺/Fc internal standard (at 0.6 V). For the CV experiments, the compound was fully dissolved in N₂-degassed anhydrous CHCl₃ with a concentration of 10⁻⁴ M and then the solution was deposited onto the work electrode surface to form a thin solid film. CV traces were measured on an electrochemical workstation (CHI 660) at a scan rate of 50 mV/s using tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) as the supporting electrolyte. A glassy carbon electrode, a Pt wire and an Ag/AgCl electrode were used as the working, counter and reference electrodes, respectively.

AFM characterizations. The AFM images were recorded using a Bruker multimode 8.0 instrument.

TEM characterizations. TEM experiments were performed on a JEM-2100 transmission electron microscope operated at 200 kV. For TEM experiments, the films were obtained by transferring the floated blend films from the water onto the Cu grid.

Solar cell fabrications and characterizations. Devices were fabricated on the Indium tin oxide (ITO) patterned glass with a conventional configuration of ITO/PEDOT:PSS/active layers/PDINO/Al. The ITO substrates were firstly cleaned by detergent, deionized water, acetone

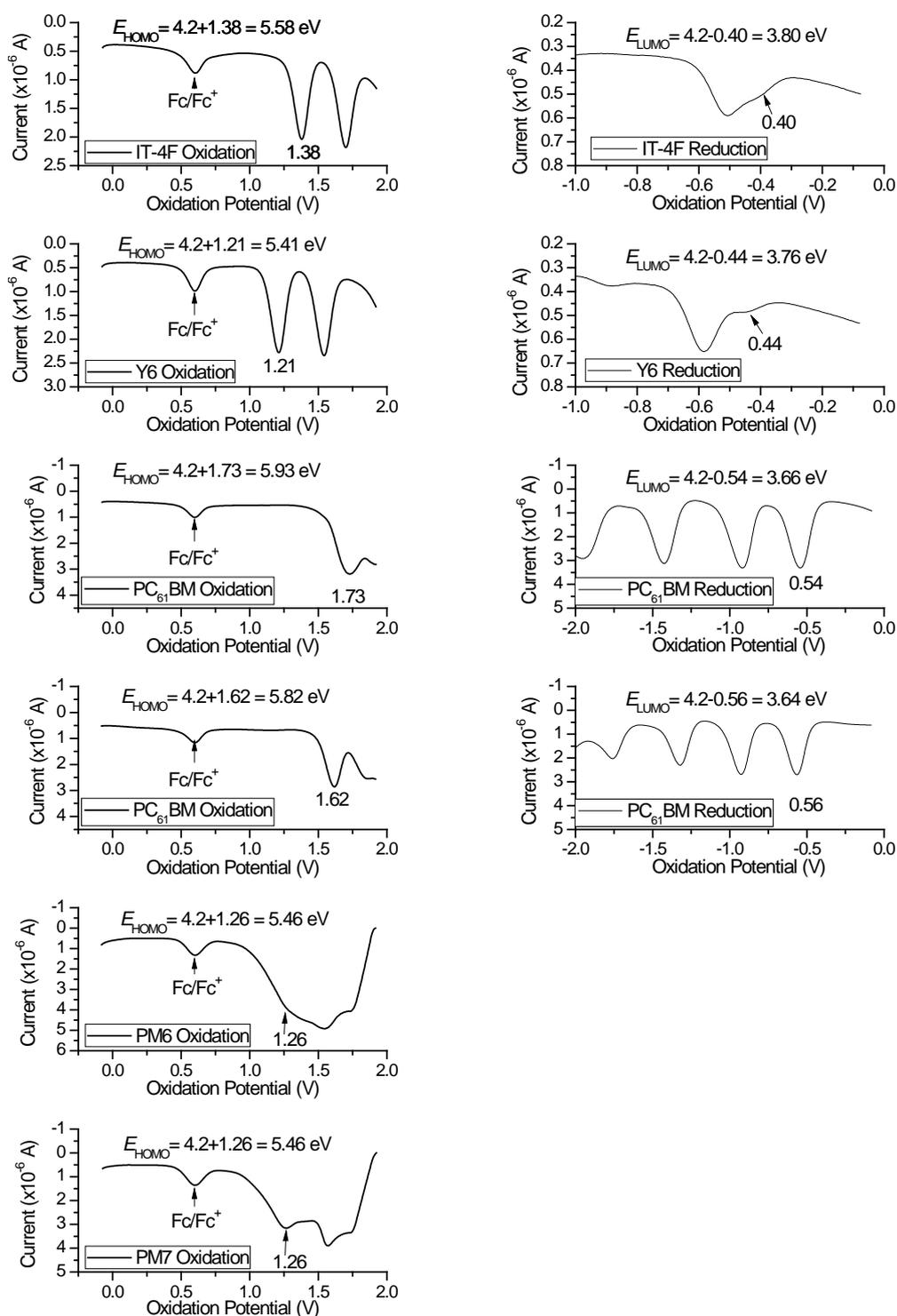
and isopropanol in turn with sonication for 30 min respectively. The substrates were dried by nitrogen gas and then treated by UV-Ozone for 30 min before use. PEDOT:PSS was spin-coated onto the ITO substrates at 6000 rpm for 30 s, then the substrates were moved to oven and dried at 150 °C for 20 min. The PM6:IT-4F:PC₇₁BM blends with different weight ratio were dissolved in chlorobenzene (CB) (the concentration of the donor was 10 mg mL⁻¹). This solution was stirred at 50°C for about 10 hours. Different ratios of DIO (1,8-diiodooctane, 0.75%, 1.0%, 1.25%) were added to the solution before device fabrication. The blend solution were spin-coated on the top of PEDOT:PSS layer followed by a thermal annealing step (90°C-10min, 100°C-10min, 110°C-10min). The optimal method for active layer was to deposit the solution with 1.0% DIO at 2500 rpm and annealed at 100°C for 10 minutes. The PM6:Y6:PC₇₁BM blends with different weight ratio were dissolved in chloroform (CF) (the concentration of the donor was 7 mg mL⁻¹). This solution was stirred at 50°C for no less than 3 hours. Different ratios of CN (1-chloronaphthalene, 0.25%, 0.5%, 0.75%) were added to the solution before device fabrication. The blend solution were spin-coated on the top of PEDOT:PSS layer followed by a thermal annealing step (80°C-10min, 90°C-10min, 100°C-10min). The optimal method for active layer was to deposit the solution with 0.5% CN at 3000 rpm and annealed at 90°C for 10 minutes. PM7 was then used to replace the PM6 to fabricate the devices with the same procedure. The optimal thickness of the active layer measured by a Bruker Dektak XT stylus profilometer was about 100 nm. Atop the active layer, a thin electron transporting layer of PDINO (1.0 mg mL⁻¹ in methanol, 3000rpm for 30 s, about 15 nm) was spin-coated, and the optimal rotating speed was about 3000 rpm. Finally, the Al electrodes (ca. 90 nm) were thermally deposited on the top of devices. The effective device area is 4 mm² with a mask. The current density-voltage (J-V) curves were measured in a nitrogen glove box and were conducted on a computer-controlled Keithley 2400 source measure unit under AM 1.5G (calibrated to be 100 mW/cm² with a reference silicon cell) using a solar illumination (AAA grade, XES-70S1). The EQE measurements were performed under the ambient condition with the as-fabricated solar cell using a QE-R3011 instrument (Enli Technology Co. Ltd., Taiwan).

SCLC measurements. The electron and hole mobility were measured by using the method called space-charge limited current (SCLC) for electron-only and hole-only devices. The structure of electron-only devices was ITO/titanium (diisopropoxide) bis(2,4-pentanedionate) (TIPD)^[1]/active layer/PDINO/Al and the hole-only devices were fabricated with the structure of ITO/PEDOT:PSS/active layer/Au. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the Mott–Gurney law: $J = 9\epsilon_0\epsilon_r\mu V^2/8L^3$, where J is the measured current density, L is the film thickness of the active layer, μ is the mobility of charge carrier, ϵ_r is the relative dielectric constant of the transport medium component, and ϵ_0 is the permittivity of vacuum (8.85419×10^{-12} CV⁻¹m⁻¹), V is the difference of applied voltage (V_{app}) and offset voltage (V_{BI}). The mobility of charge carriers can be calculated from the slope of the $J^{1/2} \sim V$ curves.

GIWAXS measurements. GIWAXS data were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and Pilatus3R 300K detector. The incidence angle is 0.2°.

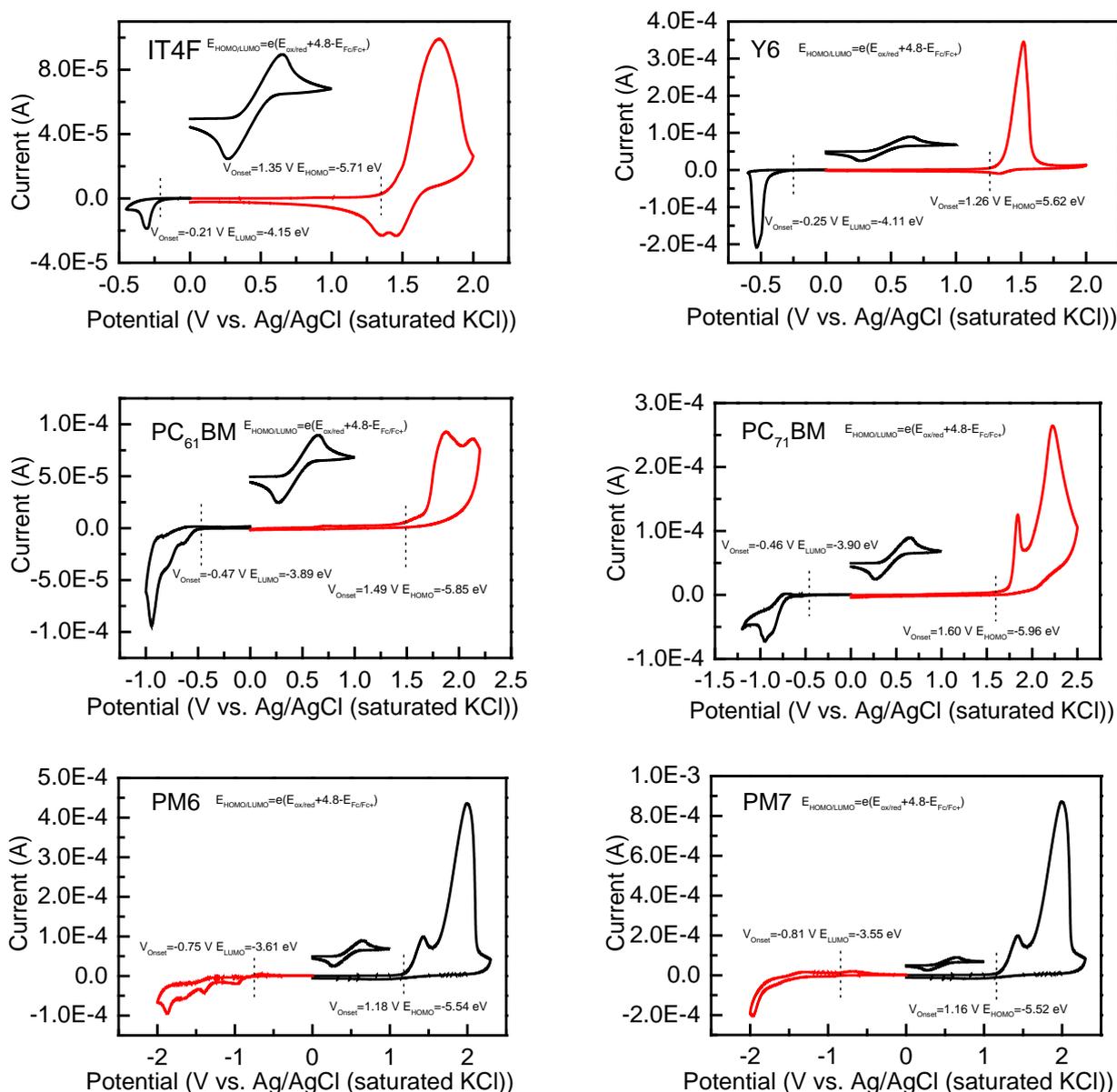
Supporting figures

Figure S1. Traces of differential pulse voltammetry (DPV) of IT-4F, Y6, PC₆₁BM, PC₇₁BM, PM6, and PM7.



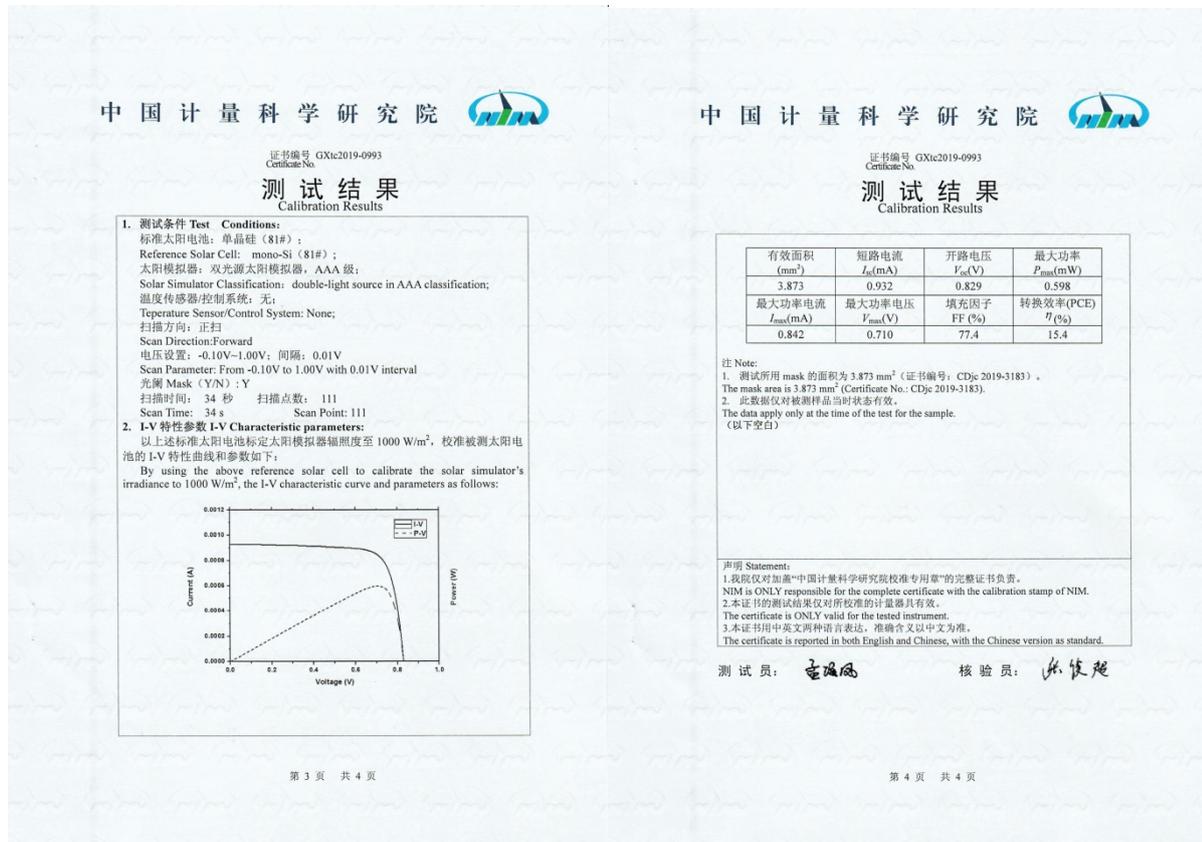
The HOMO energy was calculated from the first oxidation peak potential and the LUMO energy is estimated from the first reduction peak potential. Ferrocene was used as the internal reference compound which gives an oxidation peak at 0.6 V. For IT-4F, Y6, PC₆₁BM, and PC₇₁BM, the DPV experiments were performed in a *o*-C₆H₄Cl₂ solution at the room temperature. While for polymers PM6 and PM7, the DPV experiments were carried out at 100°C (5 mg in 30 mL) of *o*-C₆H₄Cl₂ since the polymers do not dissolve well at room temperature.

Figure S2. Traces of cyclic voltammetry (CV) of IT-4F, Y6, PC₆₁BM, PC₇₁BM, PM6, and PM7.



Ferrocene was used as the reference. Its CV curve was measured under the same conditions. The reversible curve of the CV of ferrocene is shown in the middle of each figure. The LUMO and HOMO energy levels of each compound were calculated according to Eq. $E_{\text{HOMO/LUMO}} = e(E_{\text{ox/red}} + 4.8 - E_{\text{Fc/Fc}^+})$, here, $E_{\text{ox/red}}$ is the oxidation/reduction onset obtained from the CV curve for each compound; $E_{\text{Fc/Fc}^+}$ is 0.44 eV, the average of oxidation and reduction peak potentials of ferrocene; 4.8 eV is the energy difference between the energy level of ferrocene and the vacuum.

Figure S3. Scanning copy of the certificate report of the best device with PM6:Y6:PC₇₁BM (1:1.2:0.2) as the active layer and PDINO as the ETL obtained from the National Institute of Metrology (NIM), China.



The certificated value is obtained with the encapsulation of the solar cell device and measured under the ambient condition. The value is lower than that measured from the unencapsulated device in the nitrogen-filling glove box. The decreased performance can be due to the effects from the encapsulation process.

Figure S4. Traces of cyclic voltammetry of the binary blends of IT-4F:PC₆₁BM (a), IT-4F:PC₇₁BM (b), and Y6:PC₇₁BM (c) with the ratios changing from 1:0 to 1:0.1, 1:0.2, and 1:0.3, respectively.

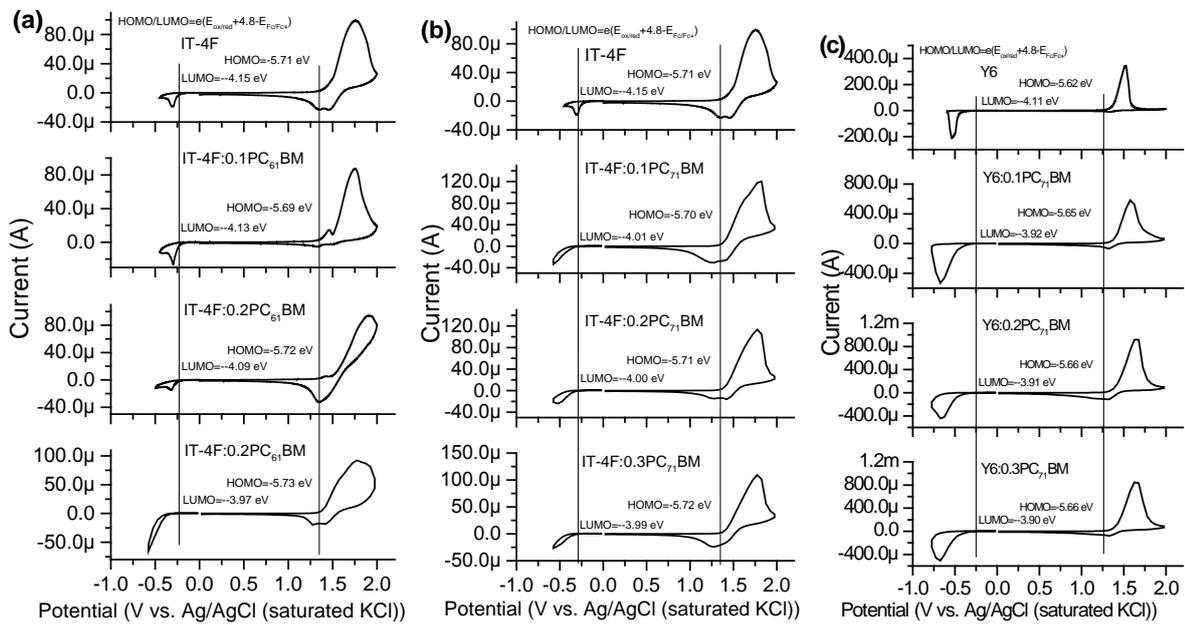
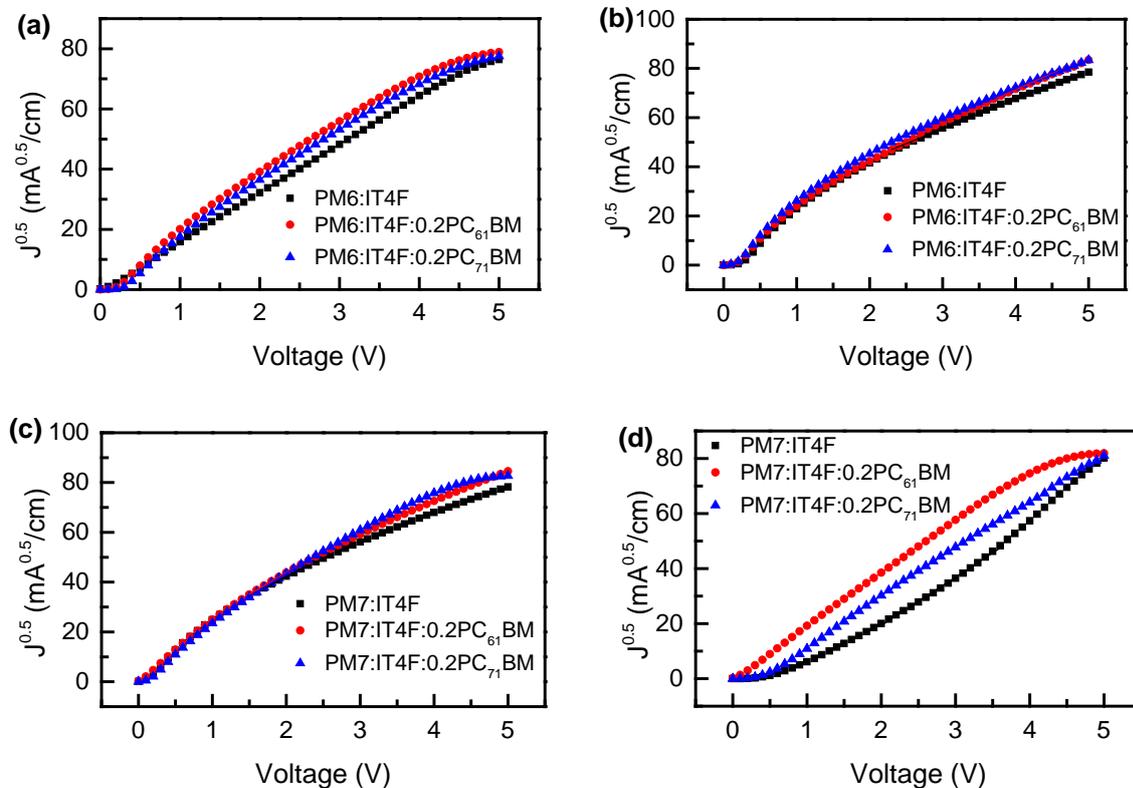


Figure S5. The $J^{0.5} - V$ plots for calculations of the electron (a, c, e, and g) and hole (b, d, f, and h) mobilities: PM6:IT-4F based (a and b), PM7:IT-4F based (c and d), and PM6:Y6 based (e and f).



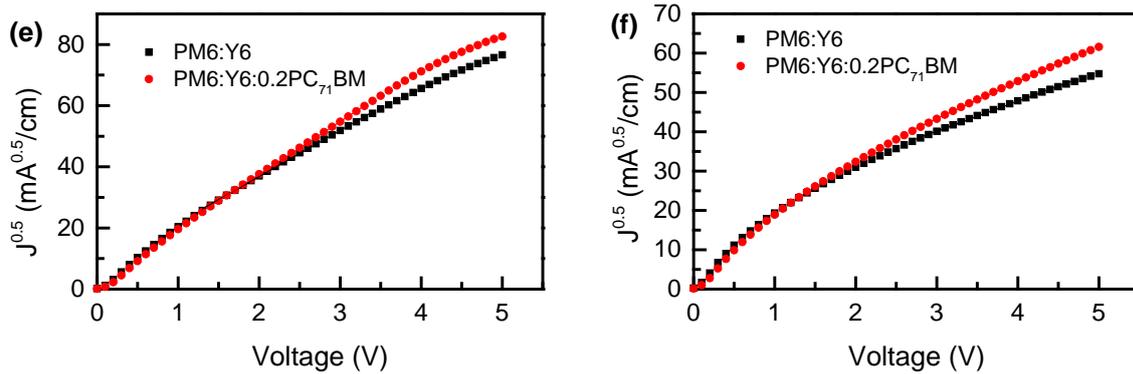


Figure S6. Photocurrent-density (J_{ph}) – effective voltage (V_{eff}) curves of the optimized binary and ternary devices: PM6:IT-4F based (a), PM7:IT-4F based (b), PM6:Y6 based (c), and PM7:Y6 based (d).

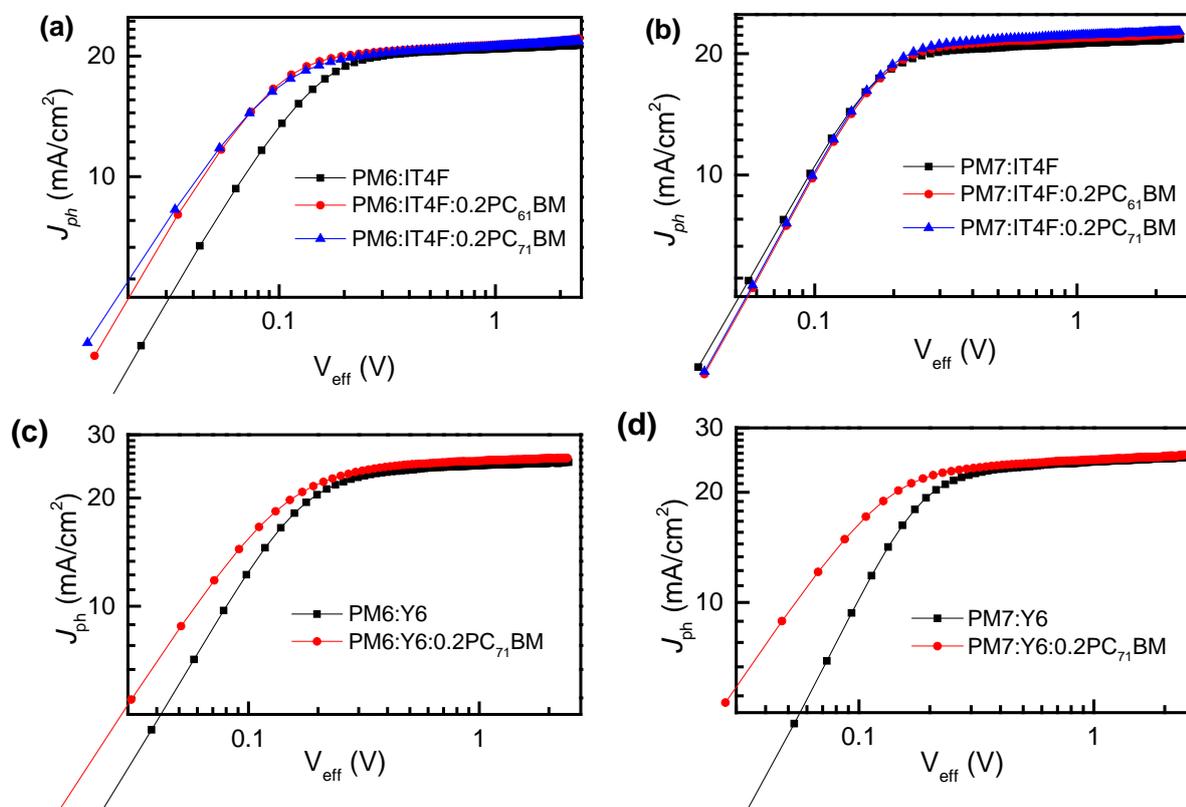


Figure S7. The plots of short-circuit current-density (J_{sc}) (a, c, e, and g) and open-circuit voltage (V_{oc}) (b, d, f, and h) vs. light intensity of the optimized binary and ternary devices: PM6:IT-4F based (a and b), PM7:IT-4F based (c and d), PM6:Y6 based (e and f), and PM7:Y6 based (g and h).

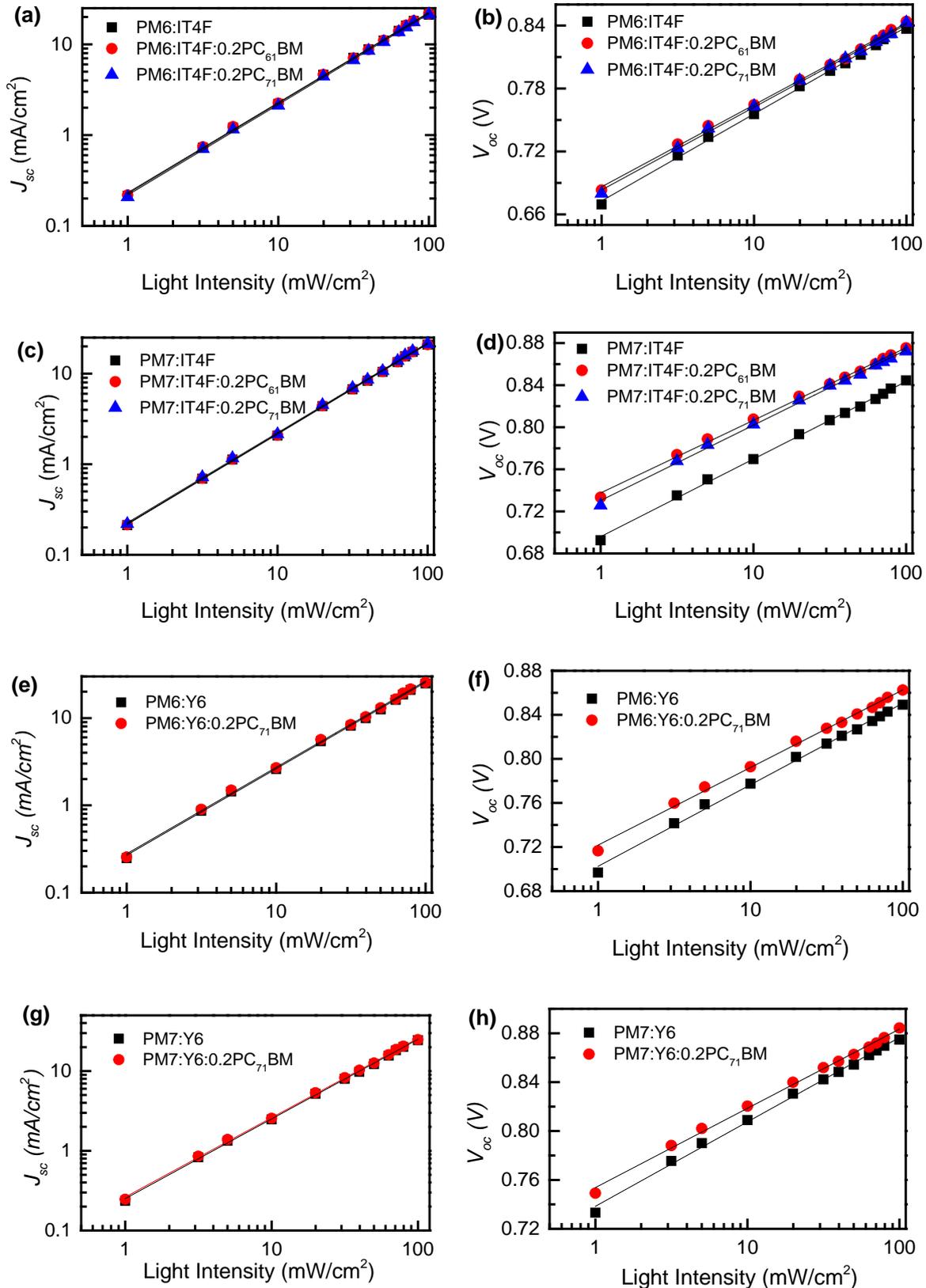


Figure S8. Two-dimensional pictures of the GIWAXS data (a-d) and the linecut profiles (e-h) of the pure Y6 (a and e), PC₇₁BM (b and f), IT-4F (c and g), and PM6 (d and h) films.

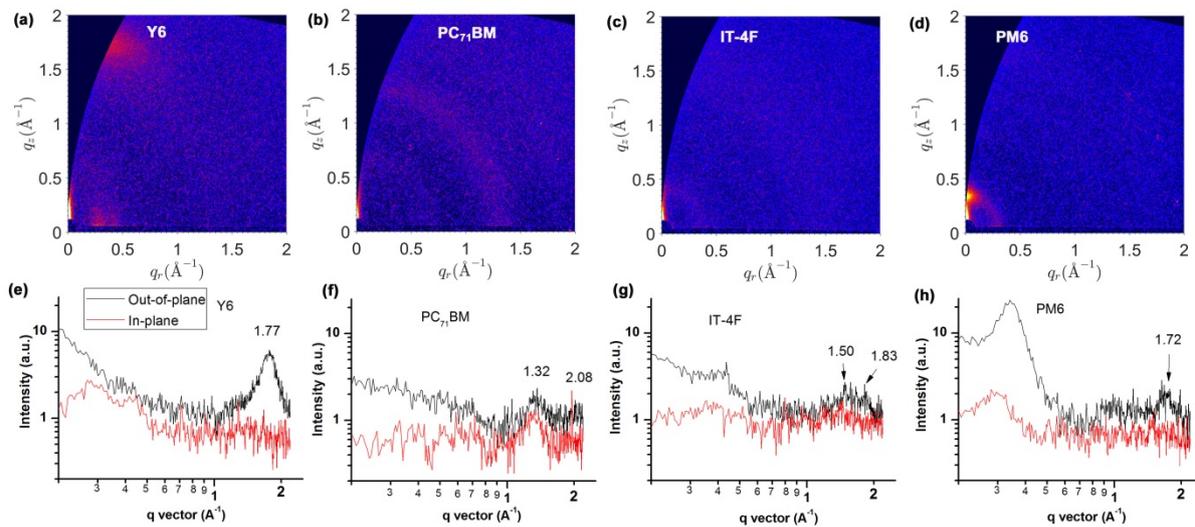


Table S1. The Optimization of the Solar Cell Devices.

Entries	IT4F:PC ₇₁ BM	DIO%	Annealing temperature (°C)	V _{oc} (V)	PCE (%)	FF (%)	J _{sc} (mA/cm ²)
1.1	1.0:0	1	100	0.843	13.06	75.16	20.63
1.2	1.0:0.1	1	100	0.850	13.51	75.56	21.03
1.3	1.0:0.2	1	100	0.858	13.92	76.74	21.15
1.4	1.0:0.3	1	100	0.865	13.61	74.66	21.07
2.1	1.0:0.2	0.75	100	0.863	13.41	74.66	20.89
2.2	1.0:0.2	1	100	0.857	13.92	76.72	21.11
2.3	1.0:0.2	1.25	100	0.853	13.10	73.05	21.03
3.1	1.0:0.2	1	90	0.866	12.97	72.13	20.77
3.2	1.0:0.2	1	100	0.859	13.90	76.59	21.13
3.3	1.0:0.2	1	110	0.851	13.77	76.07	21.28

Entries	Y6:PC ₇₁ BM	CN%	Annealing temperature (°C)	V _{oc} (V)	PCE (%)	FF (%)	J _{sc} (mA/cm ²)
1.1	1.2:0	0.5	90	0.848	15.47	74.58	24.47
1.2	1.2:0.1	0.5	90	0.853	16.11	76.17	24.78
1.3	1.2:0.2	0.5	90	0.861	16.70	77.24	25.16
1.4	1.2:0.3	0.5	90	0.864	16.31	75.63	24.97
2.1	1.2:0.2	0.25	90	0.865	16.11	74.86	24.88
2.2	1.2:0.2	0.5	90	0.859	16.69	77.19	25.18
2.3	1.2:0.2	0.75	90	0.856	16.49	76.15	25.29
3.1	1.2:0.2	0.5	80	0.863	16.28	75.83	24.87
3.2	1.2:0.2	0.5	90	0.860	16.65	77.05	25.13
3.3	1.2:0.2	0.5	100	0.854	16.40	76.72	25.02

Reference

- [1] Z. Tan, W. Zhang, Z. Zhang, D. Qian, Y. Huang, J. Hou, Y. Li, *Adv. Mater.* 2012, 24, 1476.