

Organic photovoltaics with 300 nm thick ternary active layer exhibiting 15.6% efficiency

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1. Supplemental Experimental Procedures

Device Fabrication: OPVs were fabricated with a structure ITO/PEDOT:PSS/active layers/PDIN/Al. The patterned indium tin oxide (ITO) glass coated substrates (sheet resistance $15 \Omega/\square$) were pre-cleaned by sequential ultrasonic treatment in detergent, deionized water and ethanol, respectively. The cleaned ITO substrates were blow-dried by high pure nitrogen gas and then treated by oxygen plasma for 1 min to improve its work function and clearance. Subsequently, PEDOT:PSS solution was spin-coated on the ITO substrates at 5000 round per minute (RPM) for 30 s and then annealed at 150°C for 15 min in air. After annealing treatment, the ITO substrates coated PEDOT:PSS films were transferred to a high-purity nitrogen-filled glove box to fabricate active layer. The used PDIN, PM6, BTP-4F-12 were purchased from Solarmer Materials Inc. The acceptors of BP-4F were synthesized according to reported methods¹. The PM6, BTP-4F-12 and BP-4F were dissolved in chloroform to

prepare blend solutions and 0.5 vol% 1-chloronaphthalene was added as the additive. The weight ratios of PM6, BTP-4F-12 and BP-4F are 1:1.2:0, 1:0.96:0.24, 1:0.72:0.48, 1:0.48:0.72, 1:0:1.2. After heated and stirred at 40°C about 3 h, the blend solutions were spin-coated on PEDOT:PSS films. The thickness of active layer was controlled by solution concentrations and spin rates. Next, the active layer on the substrate were placed in a small petri dish to perform solvent vapor annealed (SVA) treatment by carbon disulphide for 20 s and then annealed at 80°C for 5 min. After that, PDIN solution (2 mg/ml in methanol with 0.25 vol% acetic acid) was spin-coated on the top of active layers at 5000 RPM for 30 s to prepare cathode interlayer. Finally, the cathode of Al was deposited by thermal evaporation with a shadow mask under 10^{-4} Pa and the thickness of 100 nm was monitored by a quartz crystal microbalance. The active area is approximately 3.8 mm², which is defined by the overlapping area of ITO anode and Al cathode.

Device Characterization: The current density-voltage (*J-V*) curves of all the OPVs were measured by a Keithley 2400 unit in high-purity nitrogen-filled glove box. The AM 1.5G irradiation was provided by an XES-40S2 (SAN-EI ELECTRIC Co., Ltd) solar simulator (AAA grade, 70×70 mm² photobeam size) with light intensity of 100 mW/cm², which was calibrated by standard silicon solar cells (purchased from Zolix INSTRUMENTS CO. LTD). The external quantum efficiency (EQE) spectra of OPVs were measured in air conditions by a Zolix Solar Cell Scan 100. The ultraviolet-visible (UV-Vis) absorption spectra of neat films were obtained using a Shimadzu UV-3101 PC spectrometer. Photoluminescence (PL) spectra of neat and blend films were measured by a HORIBA Fluorolog®-3 spectrofluorometer system. The active layer thickness was measured using an AMBIOS Technology XP-2 stylus profilometer with less than 3% deviations. Electrochemical impedance spectroscopy (EIS) was measured by a ZAHNER CIMPS electrochemical workstation, Germany. Transmission electron microscopy (TEM) images of active layers were obtained by a JEOL JEM-1400 transmission electron microscope operated at 80 kV. Grazing incidence wide angle X-ray scattering (GIWAXS) measurements were performed at

BL16B1 beamline of Shanghai Synchrotron Radiation Facility in air environment.

The space charge limited current (SCLC) method was employed to investigate the influence of incorporating BP-4F on charge mobility in active layers. The single-charge transport devices were fabricated with the structure of ITO/ZnO/active layer/PDIN/Al or ITO/PEDOT:PSS/active layer/MoO₃/Ag. The fabrication conditions of the active layer films are same with those for the solar cells. The charge mobility was calculated according to the SCLC method. The hole and electron mobility can be calculated from the Mott-Gurney equation with Poole-Frenkel correction as the followings:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3} \exp \left[0.89 \gamma \sqrt{\frac{V}{d}} \right]$$

Here, ε_r is dielectric constant of organic materials, ε_0 is the free space permittivity, μ is charge mobility, V is the applied voltage, and d is the active layer thickness.

2. Additional experimental results

Table S1. Photovoltaic parameters of typical OPVs with various active layer thickness.

PM6:BTP-4F-12:BP-4F (wt:wt)	Thickness (nm)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
1:1.2:0	100	25.47	0.849	76.64	16.57
	200	26.34	0.837	71.40	15.74
	300	26.73	0.827	66.13	14.62
1:0.48:0.72	100	25.24	0.858	77.91	16.87
	200	26.17	0.849	73.81	16.40
	300	26.57	0.840	70.03	15.63
1:0:1.2	100	23.01	0.870	75.79	15.17
	200	23.85	0.861	72.75	14.94
	300	24.12	0.857	68.41	14.14

Table S2 The J_{ph} s and the ratios of the typical thick-film OPVs under different conditions.

BTP-4F-12:BP-4F (wt:wt)	J_{ph}^* (mA cm ⁻²)	$J_{ph}^\#$ (mA cm ⁻²)	J_{sat} (mA cm ⁻²)	J_{ph}^*/J_{sat} (%)	$J_{ph}^\#/J_{sat}$ (%)
1.2:0	26.73	22.52	27.87	95.91	80.80
0.72:0.48	26.57	23.45	27.17	97.79	86.31
0:1.2	24.12	20.77	25.30	95.33	82.09

Table S3 The fitted parameters of typical OPVs with 300 nm thick active layers according to the impedance spectroscopy.

BTP-4F-12:BP-4F (wt:wt)	R_S (Ω)	R_{trans} (Ω)	R_{rec} (Ω)
1:1.2:0	39.1	20.8	15.3
1:0.72:0.48	39.3	17.8	19.6
1:0:1.2	40.5	18.1	17.2

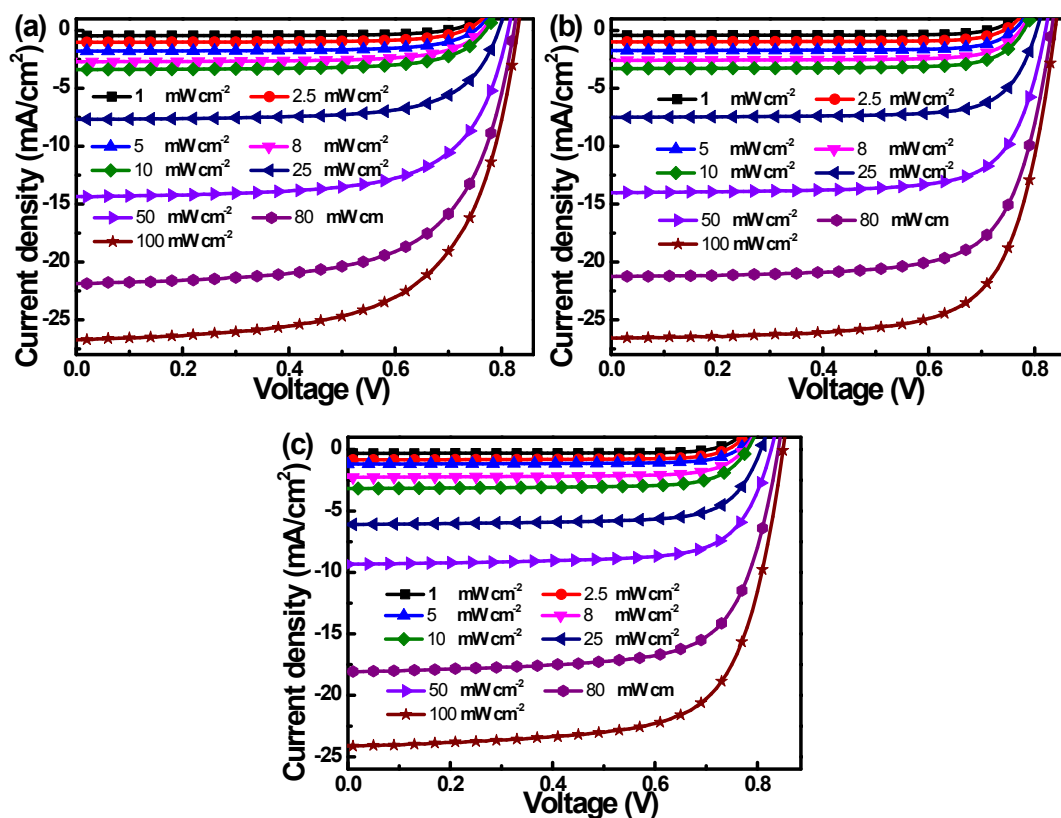


Fig. S1 J - V curves of the typical thick-film OPVs under AM 1.5G illumination with light intensity of 100, 80, 50, 25, 10, 8, 5, 2.5, 1 mW/cm², respectively: (a) BTP-4F-

12 based binary OPVs, (b) optimized ternary OPVs, (c) BP-4F based binary OPVs.

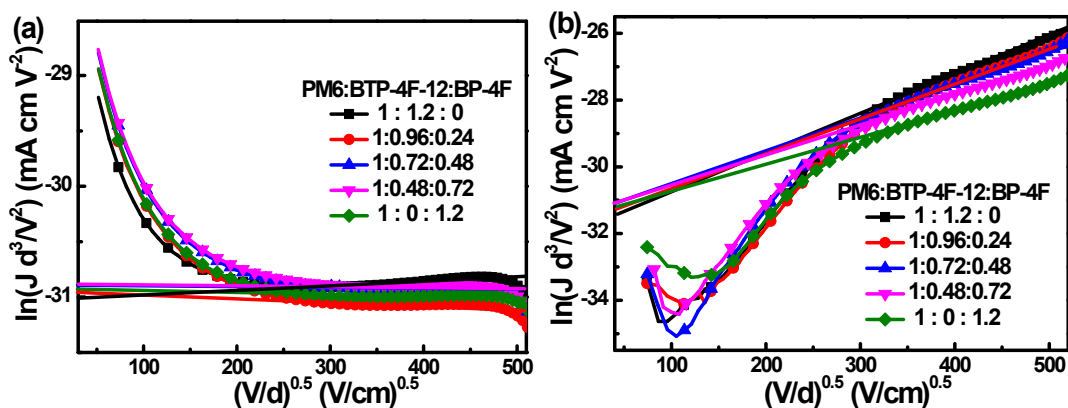


Fig. S2 The $\ln(Jd^3/V^2)$ versus $(V/d)^{0.5}$ curves of (a) hole-only devices and (b) electron-only devices.

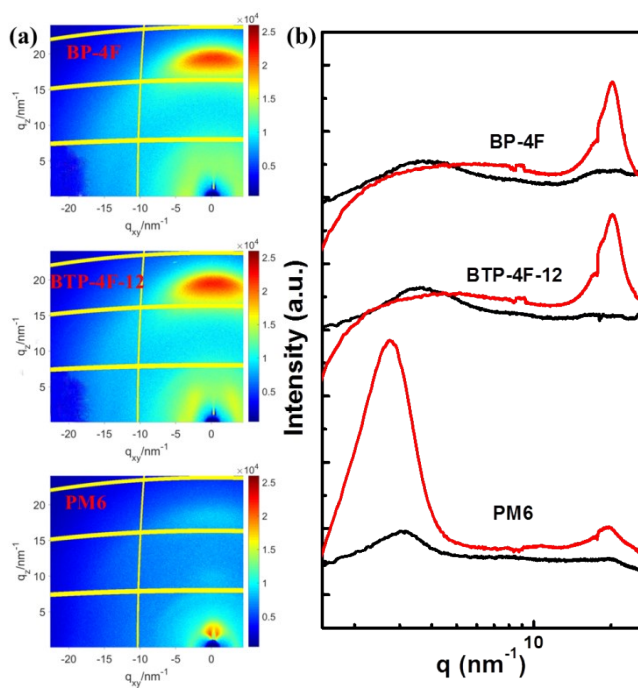


Fig. S3 (a) 2D-GIWAXS patterns; (b) corresponding scattering profiles along IP and OOP directions of neat PM6, BTP-4F-12 and BP-4F.

References

1. W. Gao, X. Ma, Q. An, J. Gao, C. Zhong, F. Zhang and C. Yang, *J. Mater. Chem. A*, 2020, **8**, 14583-14591.