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Over 14.5% efficiency and 71.5% fill factor of ternary organic solar cells with 300 nm thick active layers

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Device Fabrication: OSCs were fabricated with a structure ITO/PEDOT:PSS/active layers/PDIN/Al. The patterned indium tin oxide (ITO) glass coated substrates (sheet resistance 15 Ω/□) 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, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, clevios PVP Al 4083, purchased from H.C. Starck Co., Ltd.) solution was spin-coated on the ITO substrates at 5000 round per minute (RPM) for 30 s and then annealed at 150℃ 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 layers. The used PDIN, PBDB-T-2Cl were purchased from Solarmer Materials Inc. The acceptors of BP-4F, MF1 were synthesized by Yang's group from department of chemistry, Wuhan University. The PBDB-T-2Cl, BP-4F and MF1 were dissolved in chloroform to prepare blend solutions. The weight ratios of PBDB-T-2Cl, BP-4F and MF1 are 1:1.2:0, 1:1.1:0.1, 1:1.0:0.2, 1:0.9:0.3, 1:0.6:0.6, 1:0:1.2. After heated and stirred at 40℃ 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 40 s and then annealed at 80℃ 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 mm^2, 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 organic solar cells 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 mm^2 photobeam size) with light intensity of 100 mW/cm^2, which was calibrated by standard silicon solar cells (purchased from Zolix INSTRUMENTS CO. LTD). The external quantum efficiency (EQE) spectra of organic solar cells were measured in air conditions by a Zolix Solar Cell Scan 100. The ultraviolet-visible (UV-Vis) absorption spectra of neat and blend 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. Transmission electron microscopy (TEM) images of active layers were obtained by a JEOL JEM-1400 transmission electron microscope operated at 80 kV. The energy dispersive X-ray spectroscopy (EDS) for elemental analysis was carried out with a scanning electron microscope (Carl Zeiss) equipped with an energy dispersive X-ray analysis (OXFord).

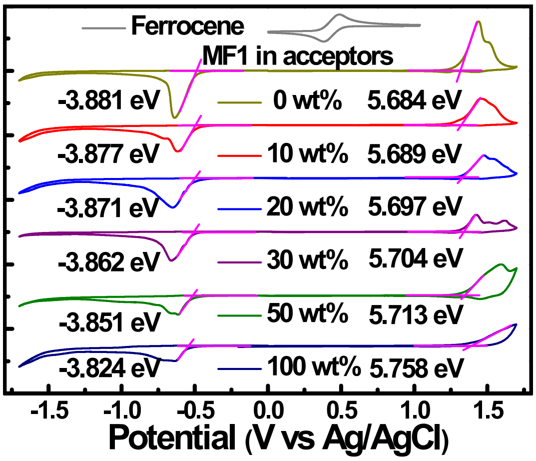

Fig. S1 CV curves of the acceptor blend films with different MF1 content.

Cyclic voltammetry (CV) measurement was carried out on a CHI voltammetric analyzer at room temperature. Tetrabuty-lammonium hexafluorophosphate (n-Bu_4NPF_6, 0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode with a 2 mm diameter, a platinum wire counter electrode, and an Ag/AgCl wire reference electrode. CV curves were obtained at a scan rate of 100 mV s^{-1}. The potentials were determined using ferrocene as the reference. The HOMO and LUMO energy levels were calculated according to the following equations:

$$HOMO =- \left[E_{ox} + (4.88 - E_{Fc})\right] eV$$

$$LUMO =- \left[E_{red} + (4.88 - E_{Fc})\right] eV$$

Where E_{ox} and E_{red} are the onset of oxidation and reduction potential, respectively.

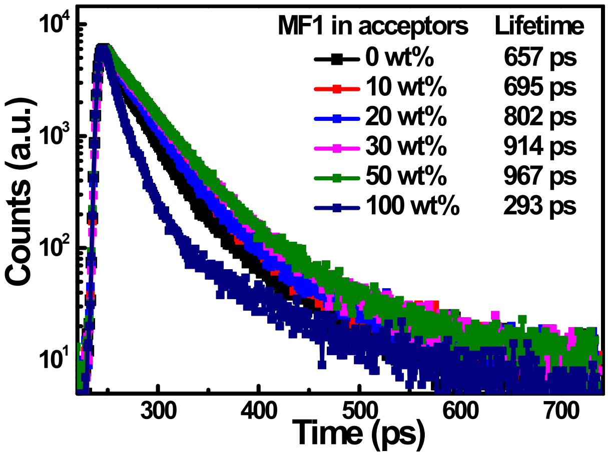

Fig. S2. TRPL spectra of neat and blend BP-4F:MF1 films by monitoring 835 nm light emission.

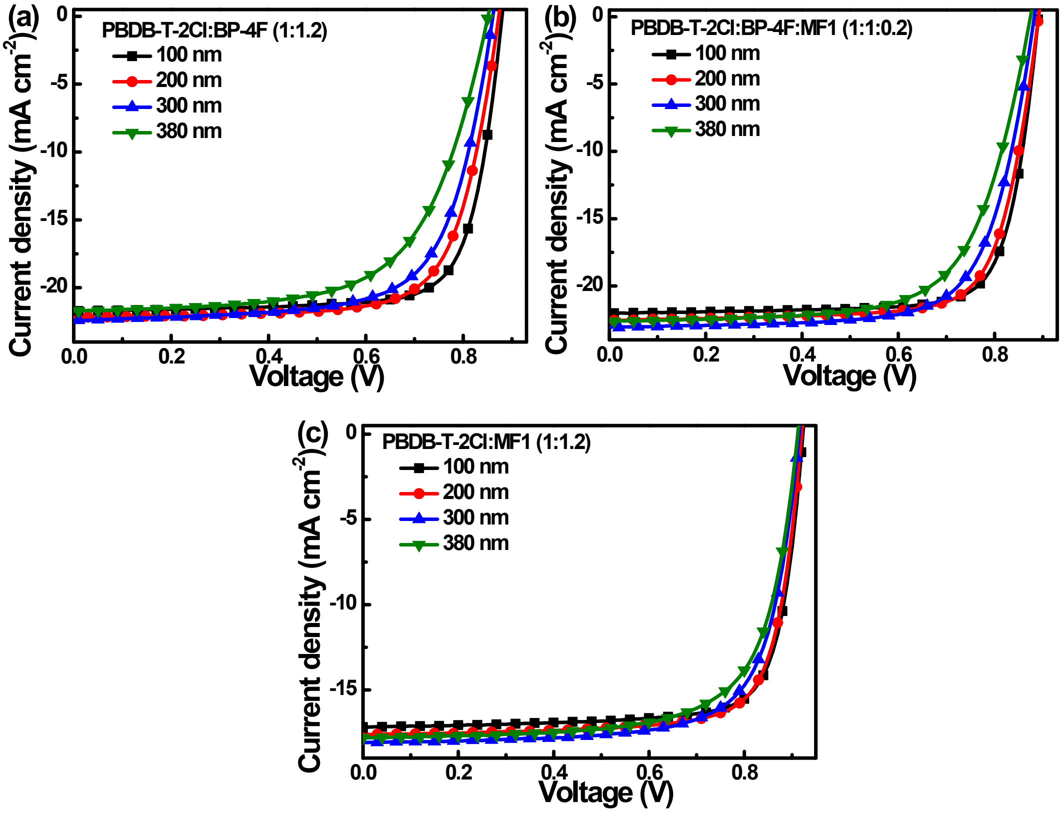

Fig. S3. *J*-*V* curves of typical OSCs with various active layer thicknesses.

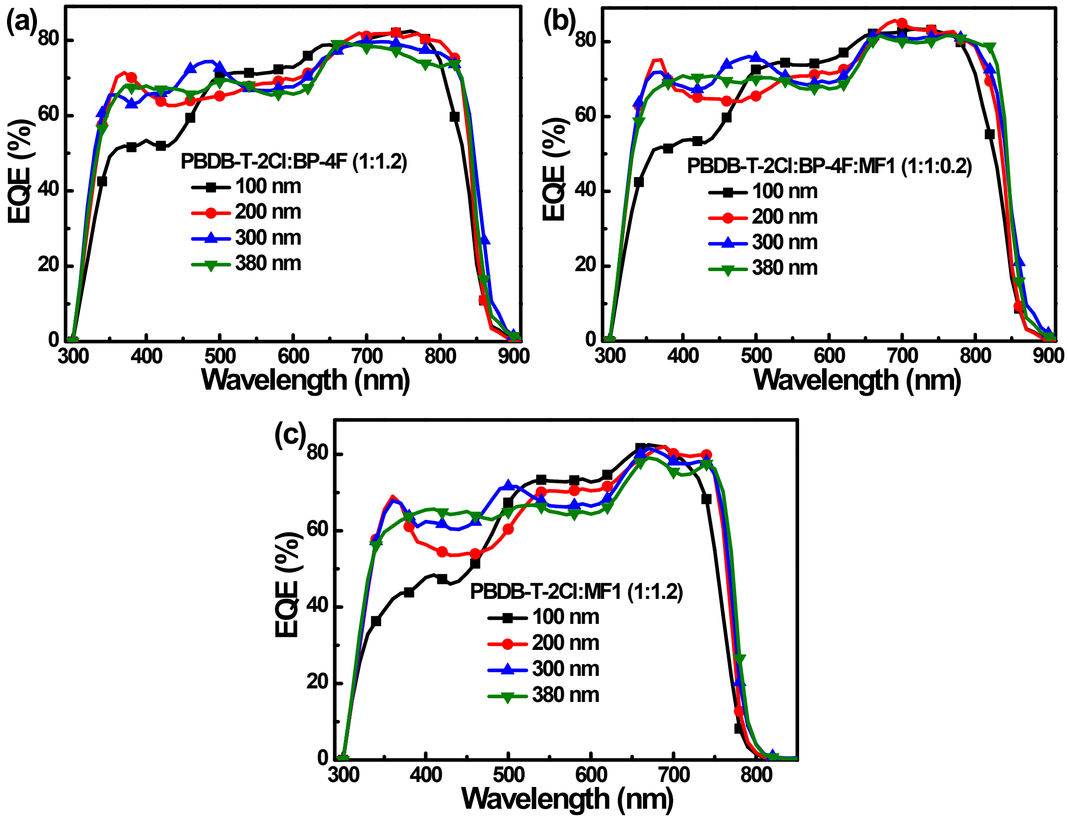

Fig. S4. EQE spectra of typical OSCs with various active layer thicknesses.

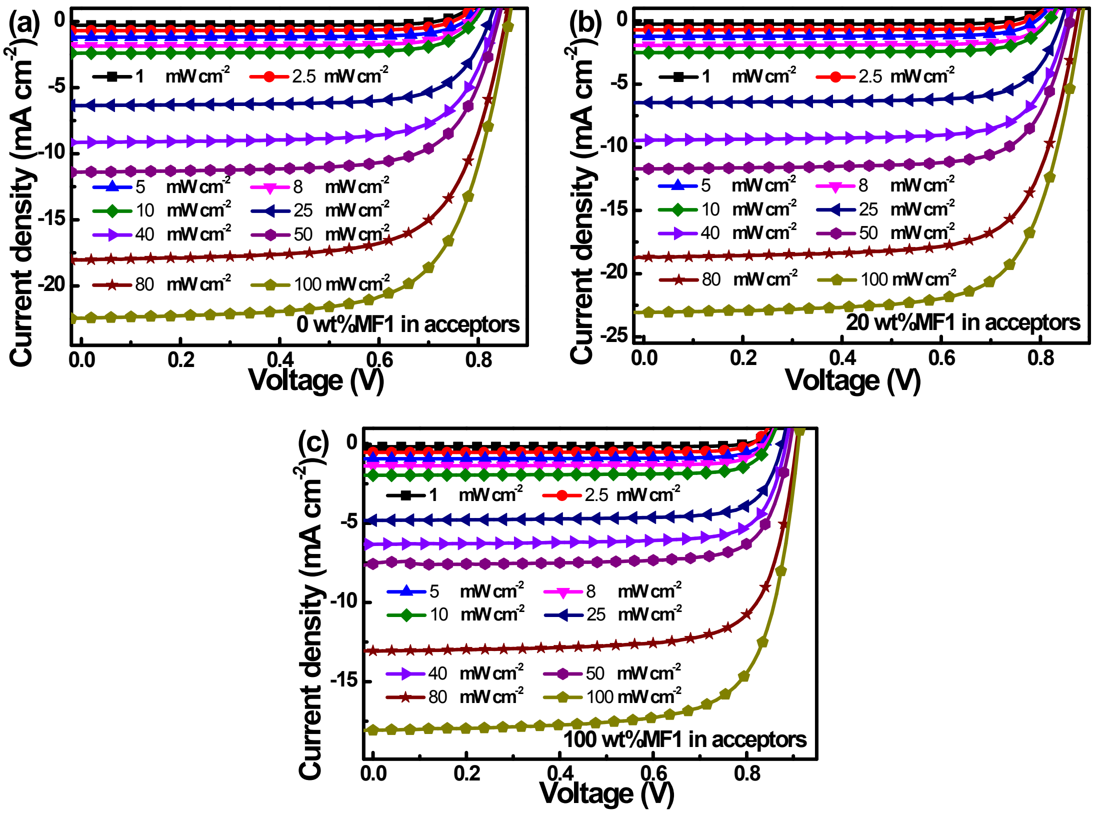

Fig. S5. The *J-V* curves of the typical OSCs under different light illumination intensity, obtained from standard AM 1.5G (100 mW cm^{-2}) illumination using a set of neutral optical filters.

Table S1 J_{ph}, J_{sat}, and J_{ph}/J_{sat} values of typical OSCs with 300 nm thick active layers.

MF1 in acceptors [wt%]	J_{ph}* (mA cm^{-2})	J_{ph}# (mA cm^{-2})	J_{sat} (mA cm^{-2})	J_{ph}*/J_{sat} (%)	J_{ph}#/J_{sat} (%)
0	22.42	19.59	23.75	94.40	82.48
20	23.06	20.47	24.04	95.93	85.15
100	18.09	16.14	18.71	96.68	86.26

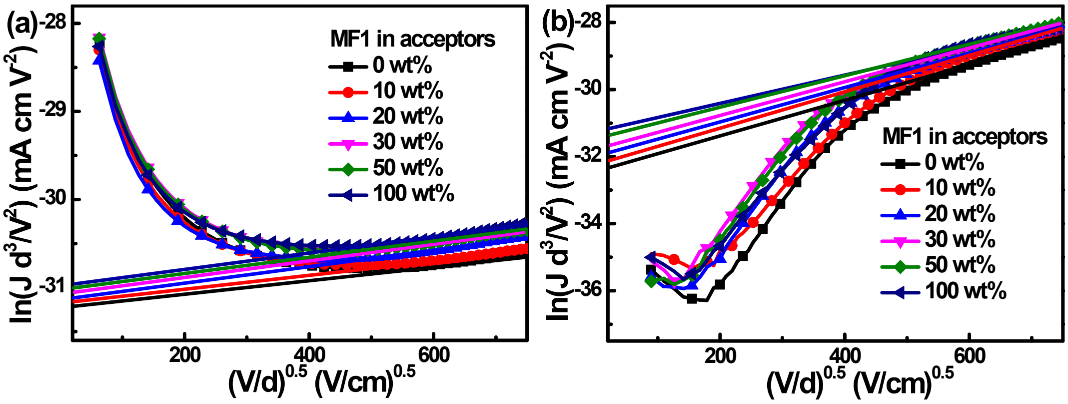

Fig. S6. The ln(Jd^3/V^2) versus (V/d)$^{0.5}$ curves of (a) hole-only devices and (b) electron-only devices.

The structure of electron-only devices is ITO/ZnO/active layer/PDIN/Al and the structure of hole-only devices is ITO/PEDOT:PSS/active layer/MoO_3/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 space charge limited current (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.

Table S2 The hole mobility (μ_h), electron mobility (μ_e) values of the active layers with various MF1 content.

MF1 in acceptors [wt%]	μ_h **(cm^2 V^{-1} s^{-1})**	μ_e **(cm^2 V^{-1} s^{-1})**	μ_h/μ_e
0	9.43×10^{-5}	3.25×10^{-5}	2.91
10	1.01×10^{-4}	3.98×10^{-5}	2.53
20	1.03×10^{-4}	5.17×10^{-5}	1.98
30	1.09×10^{-4}	6.31×10^{-5}	1.73
50	1.15×10^{-4}	8.36×10^{-5}	1.38
100	1.21×10^{-4}	9.82×10^{-4}	1.23

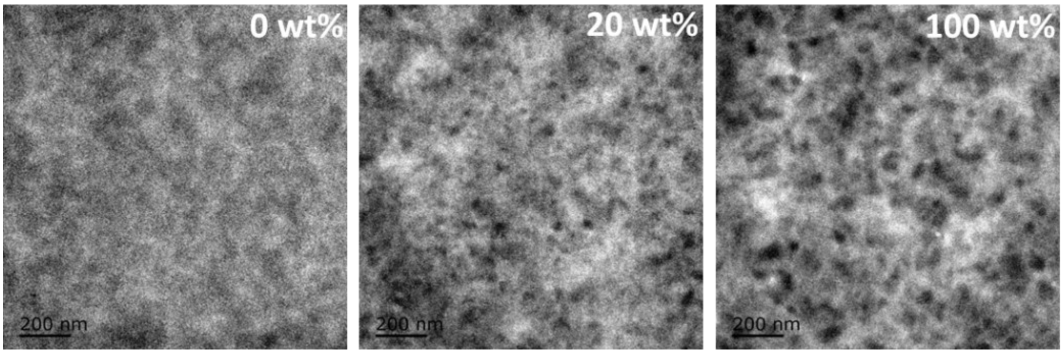

Fig. S7. TEM images of blend films with varied MF1 content.

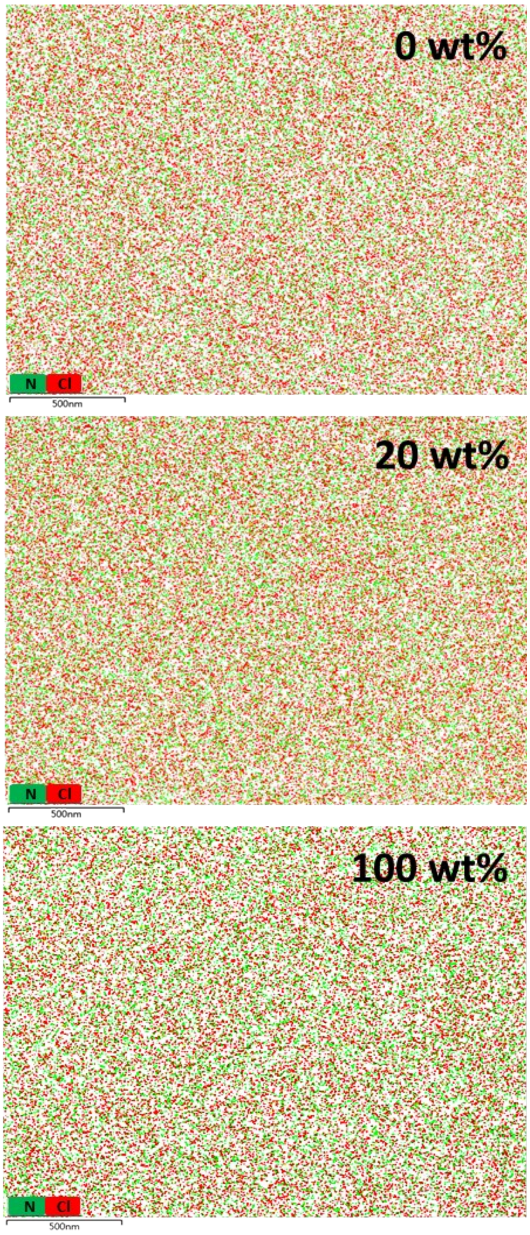

Fig. S8. EDS element mappings of blend films with varied MF1 content. The featured elements are Cl (red) of PBDB-T-2Cl and N (green) of acceptors, respectively.