Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Optimization of processing solvent and film morphology to achieve efficient non-fullerene polymer solar cells processed in the air

Kang An[a], Wenkai Zhong[a], Lei Ying[a,b]*, Peng Zhu[a], Baobing Fan[a,b], Zhenye Li[a], Ning Li[c,]*, Fei Huang[a,b]*, Yong Cao[a]

[a] Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, 510640, P. R. China.

[b] South China Institute of Collaborative Innovation, Dongguan 523808, China.

[c] Institute of Materials for Electronics and Energy Technology (i-MEET), Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058, Erlangen, Germany.

Email: msleiying@scut.edu.cn; ning.li@fau.de; msfhuang@scut.edu.cn

EXPERIMENTAL SECTION

Materials. P2F-EHp, IT-4F, IT-4Cl and PFN-Br was synthesized in our own group. The aqueous dispersion of PEDOT:PSS buffer layer was purchased from Heraeus, Germany. All chemical solvents were purchased from Sigma-Aldrich without further purification.

Devices fabricated with spin-coating. Pre-cleaned indium tin oxide (ITO) glass substrates were treated with oxygen plasma for 2 min. About 40 nm PEDOT:PSS was spun onto the substrates at 4000 r/min for 30 s. After drying at 150 °C on a hot plate for 15 min in air, the substrates were transferred into a nitrogen-filled glove box. All solutions with polymer concentrations of 6.0 mg mL^{-1} were stirred at 50 °C hot plate for 6 h in the glove box before constructed the active layers. The polymer donor:NFA (1:1, wt:wt) blend films were maintained at about 100 nm by the spin-coating methods. Chloroform solvent vapor annealing for 60 s was performed in a glass petri dish. Thermal annealing was conducted at 100 °C for 5 min. 5nm of PFN-Br electronic buffer layer was spin-coated (2000 r/min) onto the active layer from its methanol solution of 0.5 mg mL^{-1}. Finally, 100 nm of silver was thermally deposited atop the interface in a vacuum chamber at a pressure of about 1×10^{-6} mbar.

Devices fabricated with blade-coating. The PEDOT:PSS constructing process are consistent with the fabrication for the spin-coating device. The active layer was blade-coated from the co-solvent solution with a concentration of 12 mg ml^{-1} in ambient conditions. The blade-coating was conducted at the coating speed of 35mm s^{-1} with a gap of 400 mm and substrate temperature at 45 ^{o}C, affording films with thicknesses of

100 ± 5 nm. Then, the buffer layer and silver electrode was performed as above mentioned.

Instruments and characterization. The current density-voltage (*J-V*) characteristics were measured under a computer controlled Keithley 2400 source meter under 1 sun, AM 1.5G solar simulator (Taiwan, Enlitech SS-F5). The EQE spectra was obtained on a commercial EQE measurement system (Taiwan, Enlitech, QE-R3011). The absorption spectra of the active layers deposited on glass substrates were recorded by a UV-Vis-NIR spectrometer (Lambda 950, from Perkin Elmer). Transmission electron microscopy (TEM) images were obtained by using a JEM 2100F Microscope. GIWAXS characterization of the thin films was performed at beamline 7.3.3 of Advanced Light Source, Lawrence Berkeley National Laboratory (LBNL). The X-ray beam energy was 10 k eV. The sample to detector distance was ~280 mm calibrated with Ag behenate and the incidence angle was 0.16^o normalized by a photodiode. All the GIWAXS signals were recorded in Helium atmosphere using a 2D charge-coupled device (CCD) detector (Pilatus 2M) with a pixel size of 0.172 mm by 0.172 mm. Thin film samples were coated atop PEDOT:PSS/silicon wafer substrates. The conditions for the BHJ solutions preparation and film treatment are the same as those for device fabrication. RSoXS was performed at beamline 11.0.1.2 of Advanced Light Source, LBNL.[1] Sample preparation was the same as that of GIWAXS samples. The BHJ films were separated via floating in deionized water and transferred on silicon nitrile windows, and subsequently the samples were loaded onto a holder. After the films were dried in air, the holder was transferred into the vacuum chamber at the beamline endstation. The beam energy was screened ranging from 280 to 290 eV, with a 5 s exposure time per scan. The scattering patterns were collected in vacuum using Princeton Instrument PI-MTE CCD camera with a pixel size of 0.027 mm by 0.027 mm.

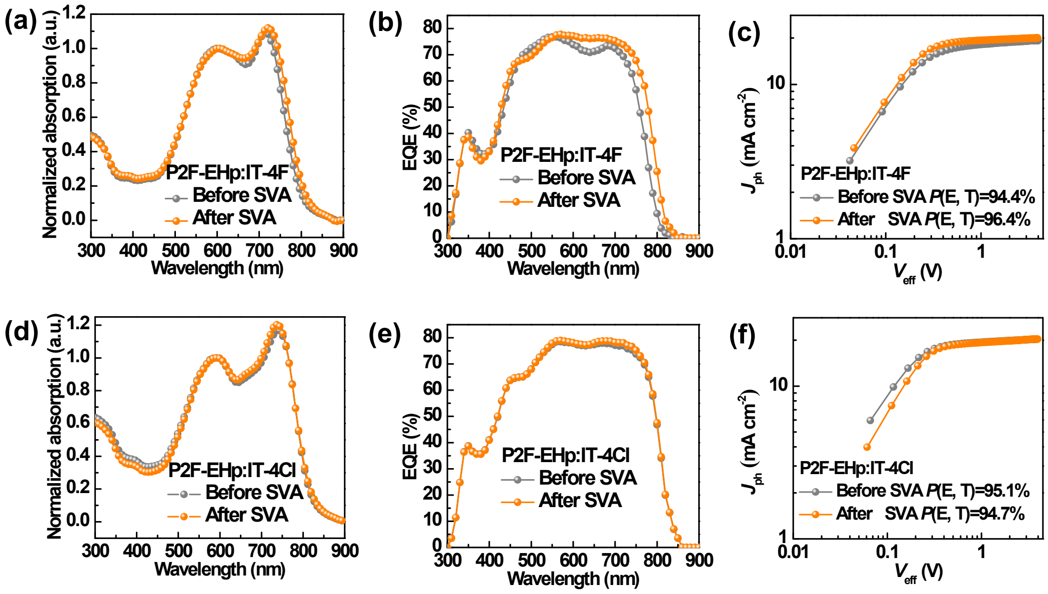

Fig. S1. (a, d) Blend films absorption normalized to the donor peak, (b, e) EQE spectra and (c, f) photocurrent density (J_{ph}) versus effective voltage (V_{eff}) of devices for P2F-EHp:IT-4F and P2F-EHp:IT-4Cl.

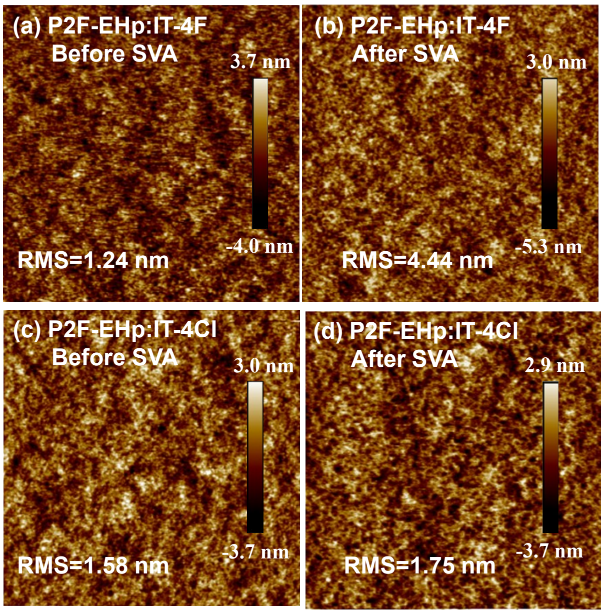

Fig. S2. AFM height images (5 µm × 5 µm) for P2F-EHp:IT-4F (a, b) and P2F-EHp:IT-4Cl (c, d) BHJ films before and after SVA, respectively.

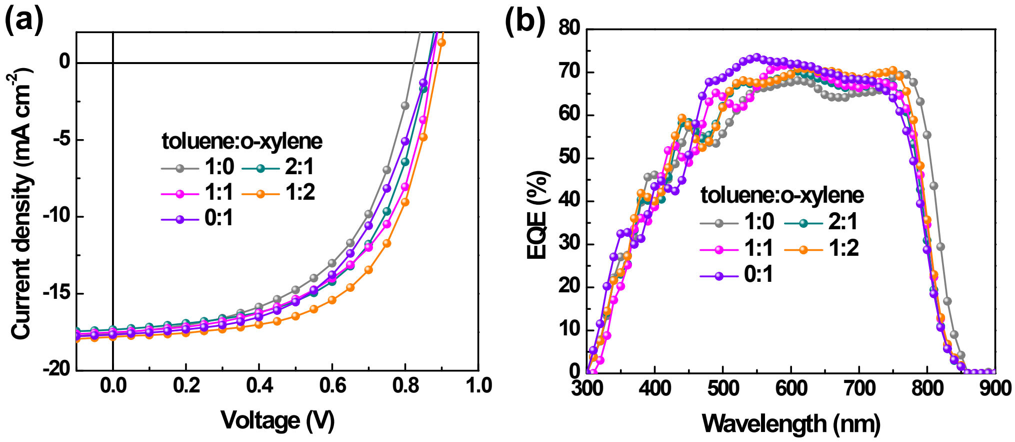

Fig. S3. *J-V* characteristics (a) and EQE spectra (b) for P2F-EHp:IT-4Cl devices according to the composition of co-solvents.

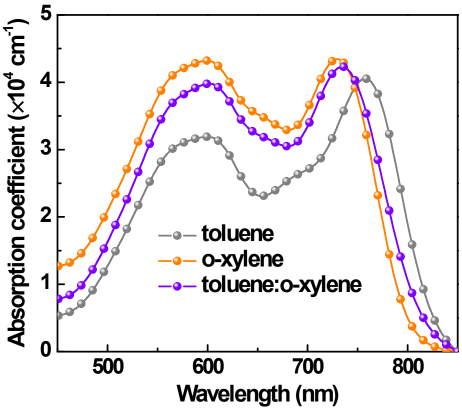

Fig. S4. Absorption profiles of P2F-EHp:IT-4Cl bend films processed from the solution of toluene, o-xylene and toluene:o-xylene (v:v of 1:2).

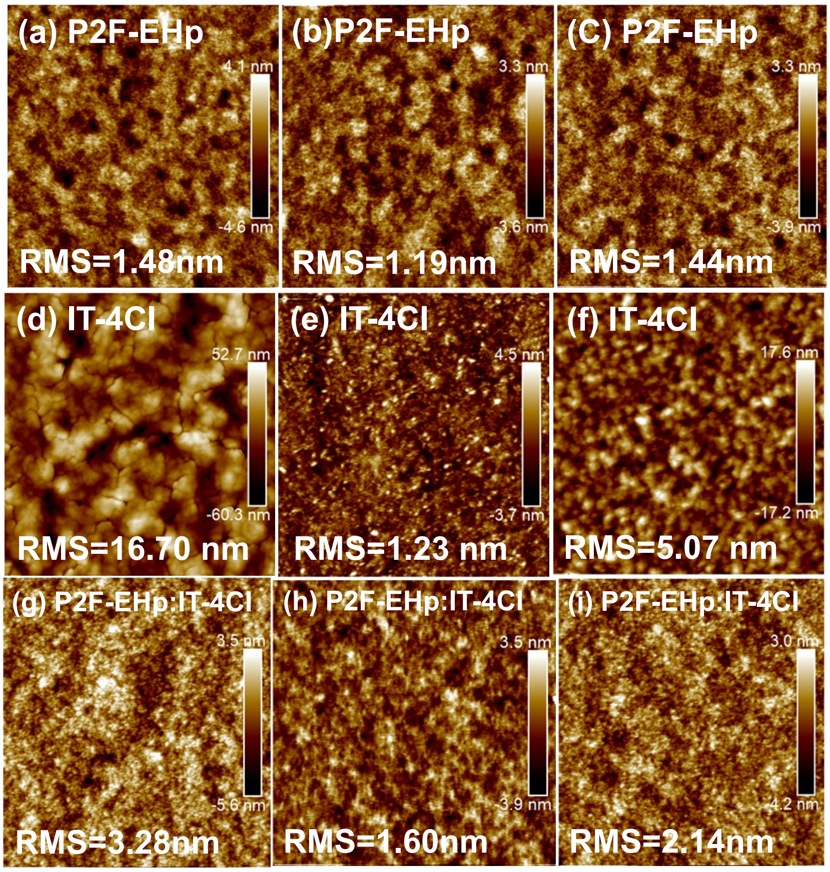

Fig. S5. AFM height images (5 μm × 5 μm) of P2F-EHp, IT-4Cl and P2F-EHp:IT-4Cl films dissolved in toluene (a, d, g), o-xylene (b, e, h) and toluene:o-xylene = 1:2 (c, f, i), respectively.

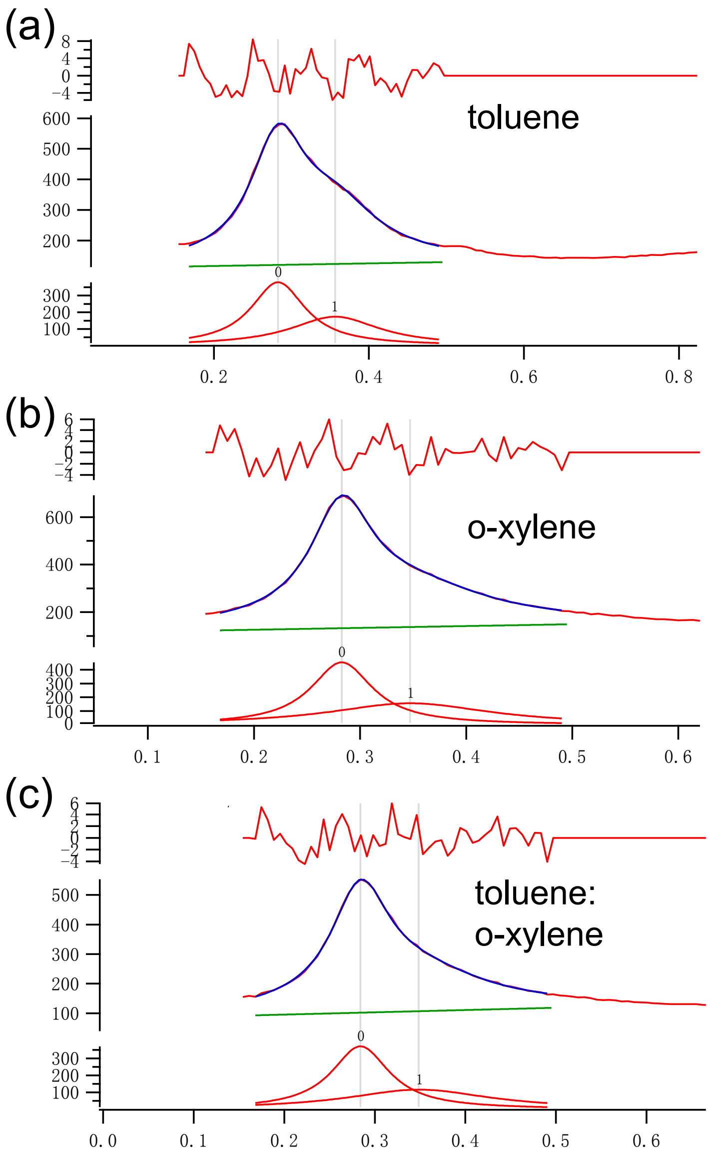

Fig. S6. Curves fitting results of GIWAXS (100) peaks of the P2F-EHp:IT-4Cl blend films produced using toluene, o-xylene and toluene:o-xylene = 1:2.

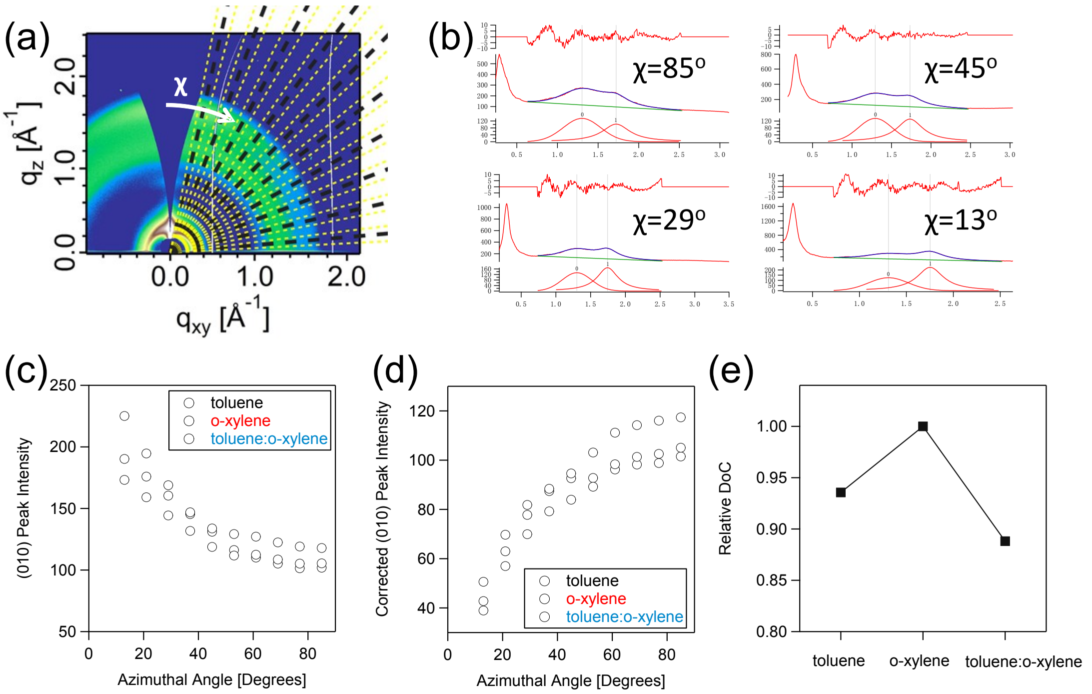

Fig. S7. Illustration of the sectors with angular width of 4° for the line-cut profiles as a function of the azimuthal angle χ (a) and 4 samples of the peak fitting of the line-cut profiles for extracting the (010) peak intensities at each χ (b). As the exposure time, film thickness, and the experimental setup in the beamline for each sample are nearly identical, the (010) peak intensity and the corrected intensity, I(χ)sin(χ), as a function of χ are plotted (c and d). Finally, the relative degree of crystallinity (DoC) is calculated by $\int_{\chi_1}^{\chi_2} \sin(\chi) I(\chi) d\chi$, and the results of films prepared by different processing solvents are depicted (e).

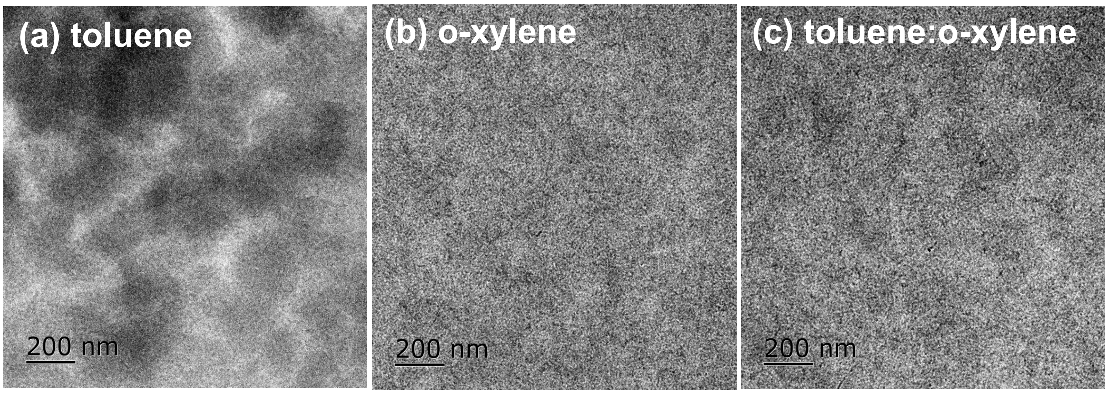

Fig. S8. TEM images for P2F-EHp:IT4Cl BHJ dissolved in toluene (a), o-xylene (b) and toluene:o-xylene = 1:2 (c).

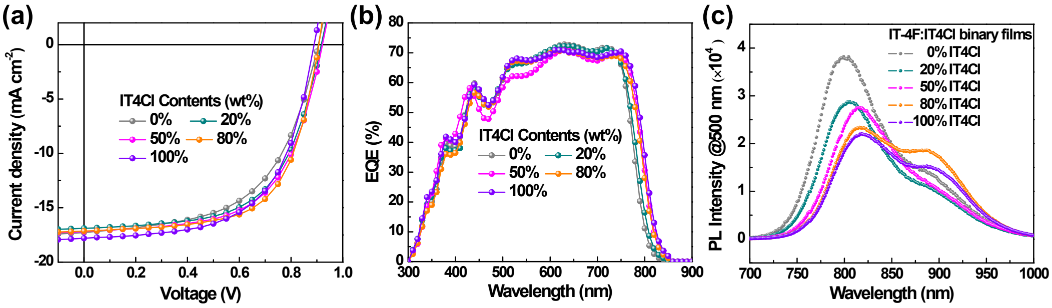

Fig. S9. *J-V* characteristics (a) and EQE spectra (b) for P2F-EHp:IT-4F:IT-4Cl ternary devices with the optimized co-solvent. (c) Photoluminescence (PL) emission spectra of various IT-4F:IT-4Cl binary films.

Table S1. Photovoltaic parameters for P2F-EHp:IT-4Cl devices according to the composition of co-solvents.

toluene : o-xylene [a]	V_{OC} (V)	J_{SC} (mA cm^{-2})	$J_{SC,\ EQE}$ [b] (mA cm^{-2})	FF (%)	PCE (avg [c]/max) (%)
1:0	0.825	17.58	17.60	53.83	7.81 (7.67 ± 0.14)
2:1	0.864	17.33	17.14	57.44	8.60 (8.42 ± 0.18)
1:1	0.877	17.50	17.29	55.51	8.44 (8.30 ± 0.14)
1:2	0.890	17.80	17.59	60.00	9.51 (9.30 ± 0.21)
0:1	0.865	17.66	17.18	54.03	8.26 (8.00 ± 0.26)

[a] Devices with area of 0.104 cm^2. [b] $J_{SC,\ EQE}$ represents the integrated current density obtained from EQE spectra. [c] Statistical data obtained from 10 devices.

Table S2. Photovoltaic parameters for ternary devices with the optimized co-solvent.

IT4Cl Contents [a] (wt %)	V_{OC} (V)	J_{SC} (mA cm^{-2})	$J_{SC,\ EQE}$ [b] (mA cm^{-2})	FF (%)	PCE (avg [c]/max) (%)
0	0.906	17.28	16.72	55.00	8.76 (8.49 ± 0.27)
20	0.918	16.88	16.86	60.00	9.33 (9.25 ± 0.08)
50	0.923	17.18	16.97	60.23	9.55 (9.51 ± 0.04)
80	0.908	17.14	17.08	63.86	9.94 (9.83 ± 0.11)
100	0.890	17.80	17.59	59.90	9.51 (9.30 ± 0.21)

[a] Devices with area of 0.104 cm^2. [b] $J_{SC,\ EQE}$ represents the integrated current density obtained from EQE spectra. [c] Statistical data obtained from 10 devices.

References

---

(1) Gann, E.; Young, A. T.; Collins, B. A.; Yan, H.; Nasiatka, J.; Padmore, H. A.; Ade, H.; Hexemer, A.; Wang, C. Soft X-Ray Scattering Facility at the Advanced Light Source with Real-Time Data Processing and Analysis. *Rev. Sci. Instrum.* **2012**, *83*, 045110.