

Supporting Information

The Synergy of Host-Guest Nonfullerene Acceptors Enables 16%-Efficiency Polymer Solar Cells with Increased Open-Circuit Voltage and Fill-Factor

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Materials, methods, and characterizations

Materials. The materials of PBDB-T-SF, IT-4F, Y6, ITCT, PEDOT:PSS and PDINO were purchased from Solarmer company.

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

Cyclic voltammetry measurements. For 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 AFM.

TFM 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 with a sheet resistance of 10 ohm/square and transmission rate of 90% 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 15 min. The PBDB-T-SF:IT-4F:ITCT blends with different weight ratio were dissolved in chlorobenzene (CB) (the concentration of the donor was 7 mg/mL). This solution was stirred at 70°C for about 6 hours. Different ratios of DIO (0.50%, 0.75%, 1.00%) were added into the solution 30 minutes before device fabrication. The blend solution was spin-coated on the top of PEDOT:PSS layer followed by a thermal annealing step (80°C-10 min, 90°C-10 min, 100°C-10 min). The optimal method for active layer was to deposit the solution with 0.75% DIO at 2200 rpm and annealed at 80°C for 10 minutes. The PBDB-T-SF:Y6:ITCT blends with different weight ratio were dissolved in chloroform (CF) (the concentration of the donor was 5.5 mg/mL). This solution was stirred at 60°C for 4 hours. Different ratios of CN (0.25%, 0.50%, 0.75%, 1.00%) were added to the solution before device fabrication. The blend solution was spin-coated on the top of PEDOT:PSS layer followed by a thermal annealing step (80°C-10 min, 90°C-10 min, 100°C-10 min). The optimal method for active layer was to deposit the solution with 0.50% CN at 3000 rpm and annealed at 80°C for 10 minutes.

Atop the active layer, a thin electron transporting layer of PDINO (1.0 mg/mL in methanol, 3000 rpm for 30 s, about 15 nm) was spin-coated. Finally, the Al electrodes were thermally deposited on the top of devices, the thickness of which was about 90 nm. 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 with the as-fabricated solar cell using a QE-R3011 instrument (Enli Technology Co. Ltd., Taiwan).

SCLC measurements. The electron and hole mobilities 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 was 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 cyclic voltammetry (CV) of PBDB-T-SF (a), IT-4F (b), Y6 (c), and ITCT (d) with ferrocene used as a reference.

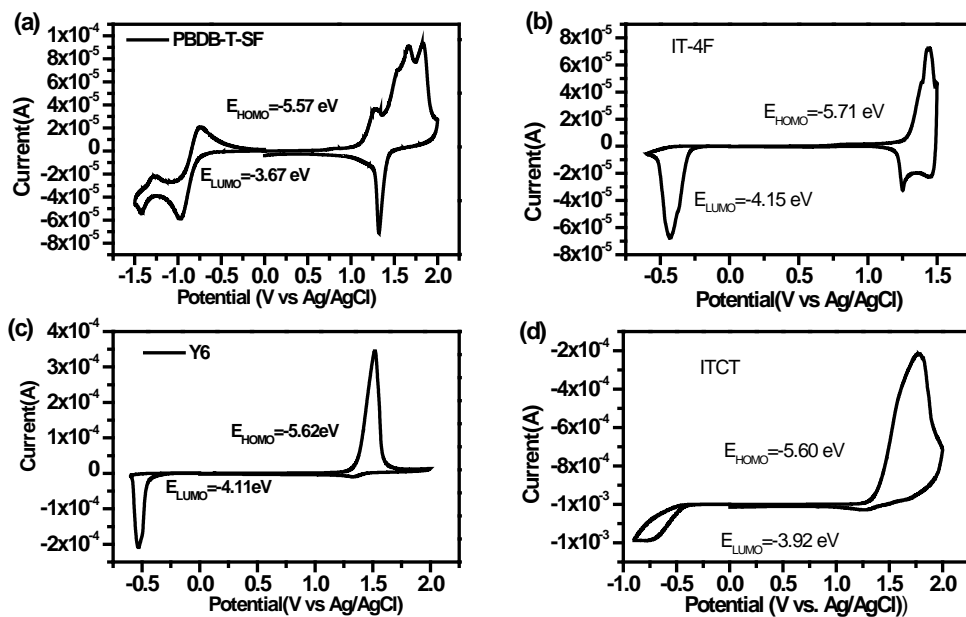


Figure S2. Traces of cyclic voltammetry (CV) of the mixtures of Y6:ITCT (a) and IT-4F:ITCT (b) with ferrocene used as a reference.

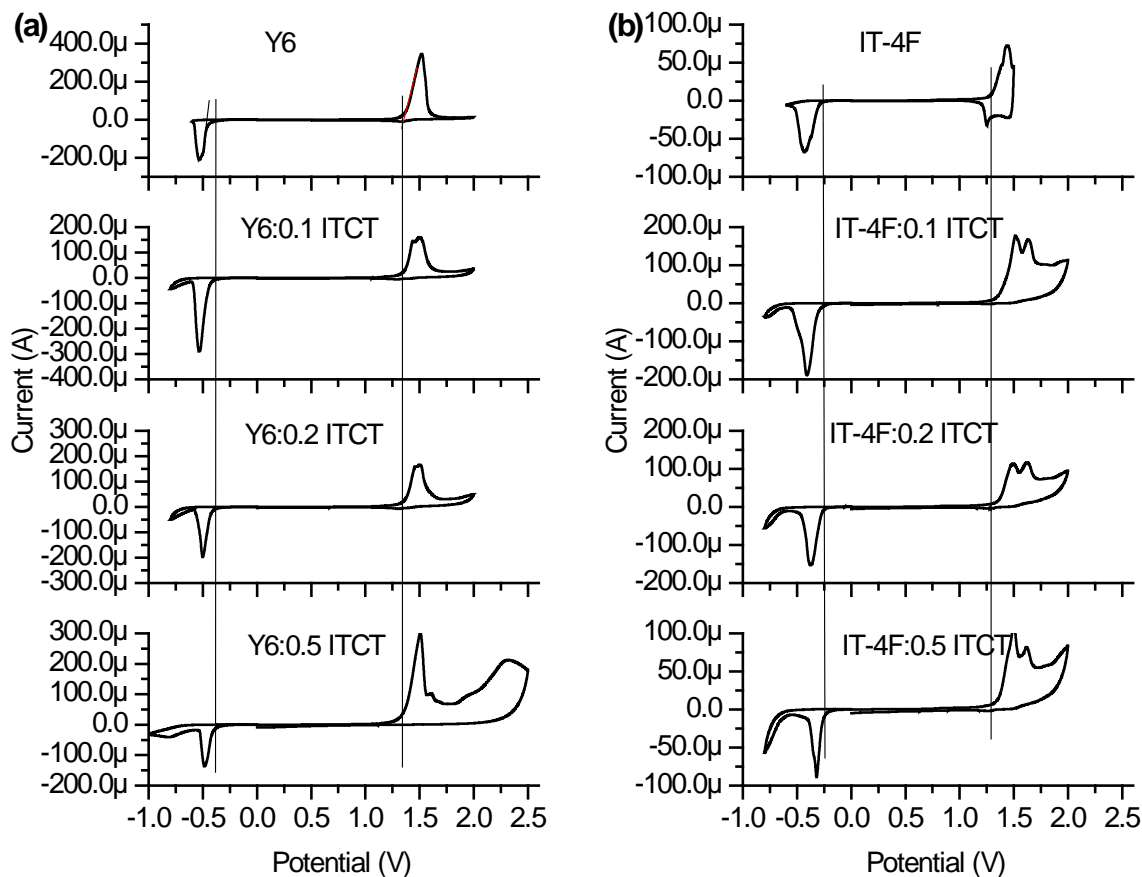


Figure S3. Scanning copy of the certificate report of a solar cell device with PBDB-T-SF:Y6:ITCT (1:1.1:0.1) as the active layer and PDINO as the ETL obtained from the National Institute of Metrology (NIM), China.

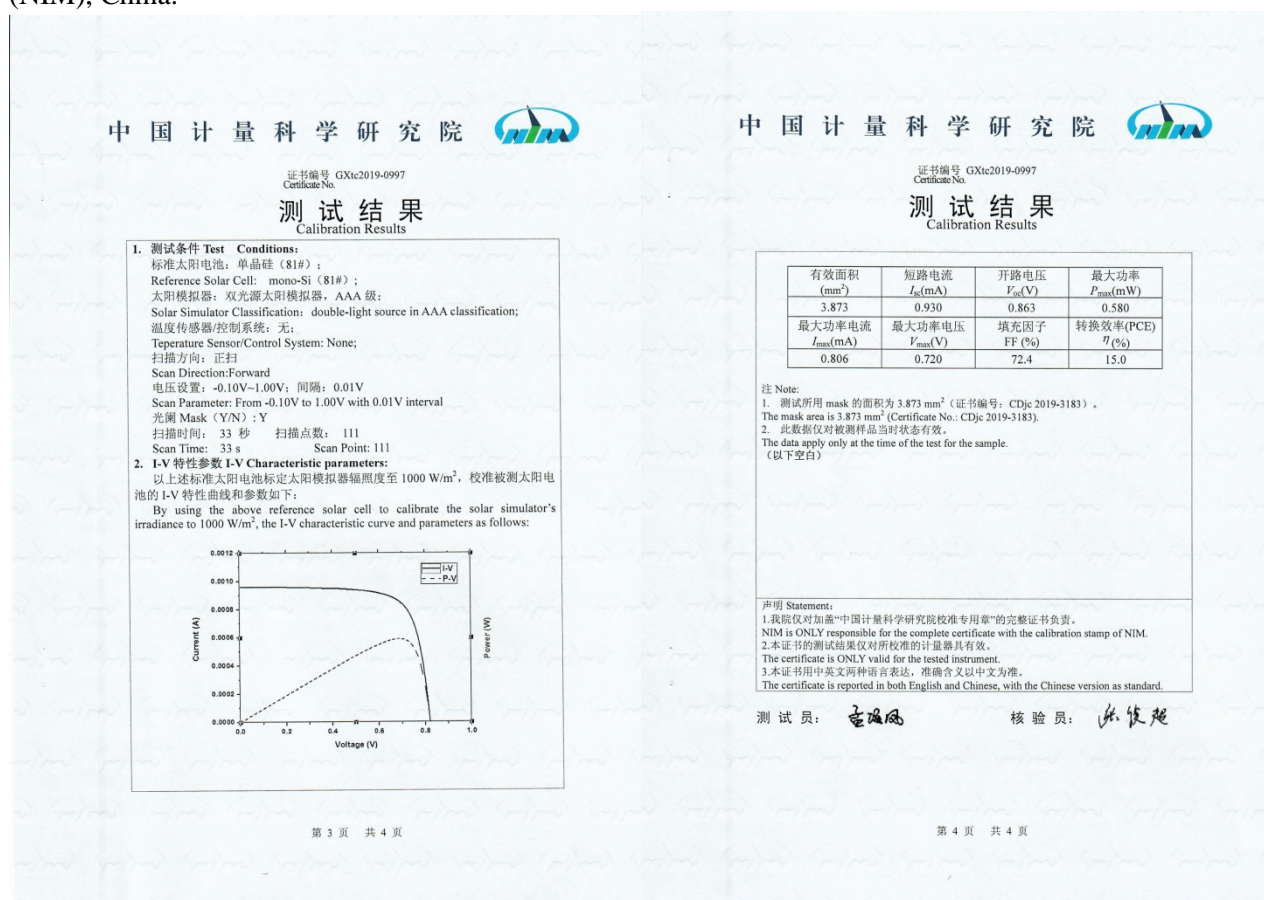


Figure S4. The $J^{0.5} - V$ plots for calculations of the electron (a and c) and hole (b and d) mobilities: IT-4F (a and b) Y6 based (c and d) binary and ternary blends.

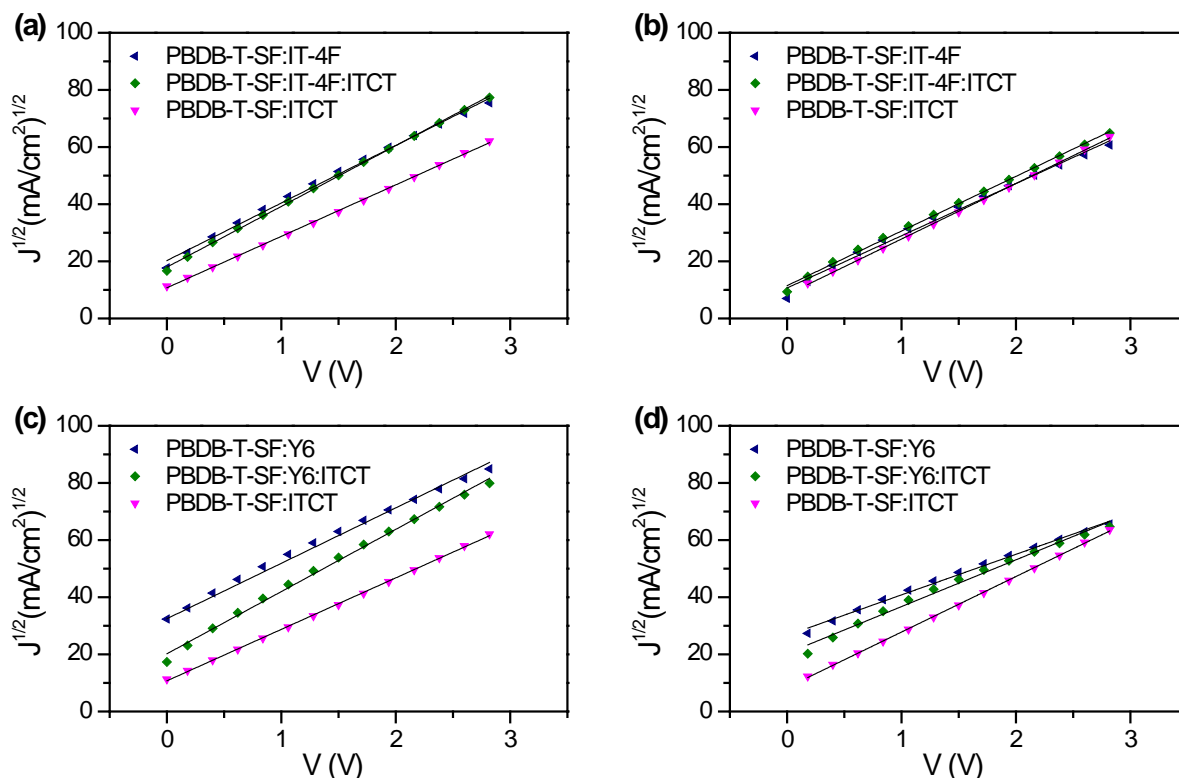


Figure S5. The plots of short-circuit current-density (J_{sc}) (a and c) and open-circuit voltage (V_{oc}) (b and d) vs. light intensity of the optimized binary and ternary devices: The IT-4F based (a and b) and the Y6 based (c and d).

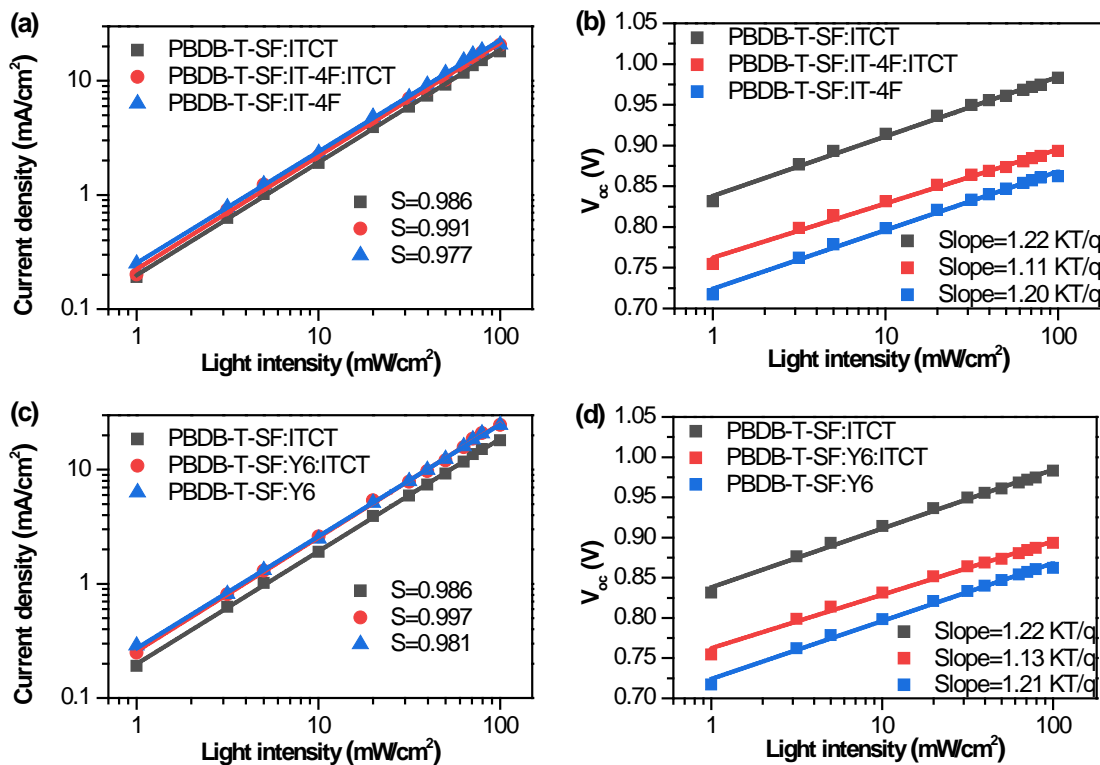


Figure S6. Photocurrent-density (J_{ph}) – effective voltage (V_{eff}) curves of the optimized binary and ternary devices: The IT-4F based (a) and the Y6 based (b).

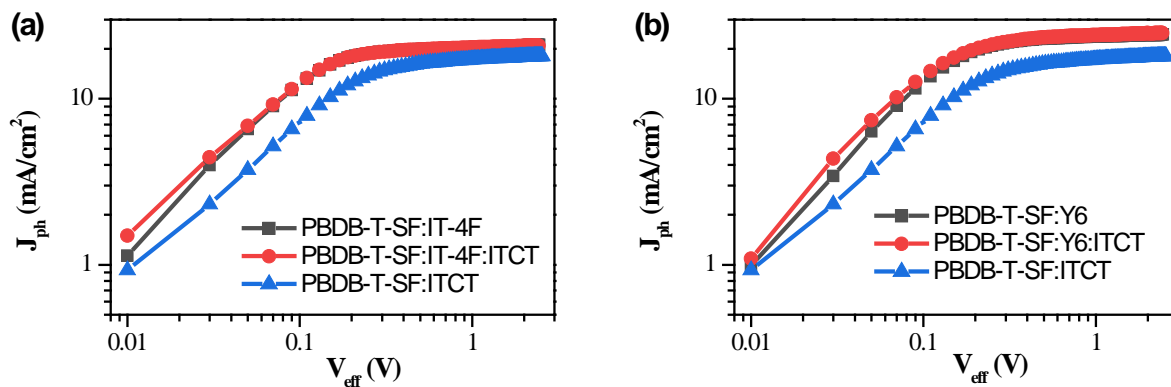
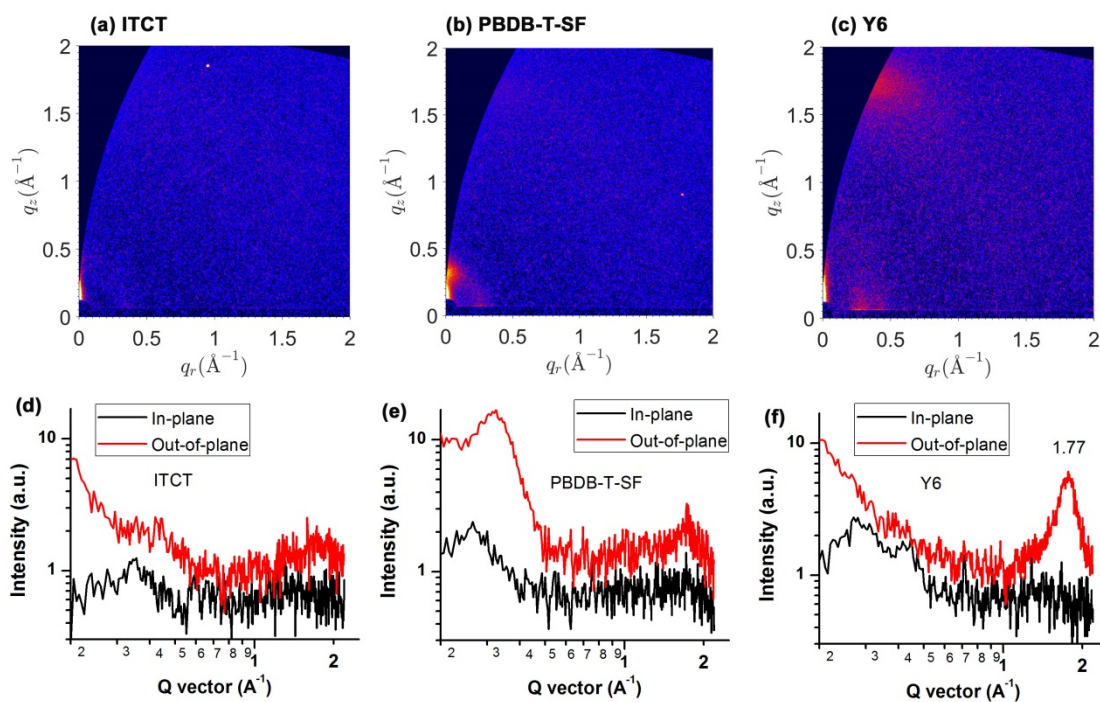


Figure S7. 2-D GIWAXS images (a-c) and the linecut profiles (d-f) of the neat ITCT (a and d), PBDB-T-SF (b and e), and Y6 (c and f) films, respectively.



Supporting Tables

Table S1. The photovoltaic data of Y6 based binary and ternary solar cells with different optimized conditions.

Conditions		V_{oc}^a [V]	J_{sc}^a [mA/cm ²]	FF^a [%]	PCE_{ave}^a [%]
CN (%)	0.25	0.867 (0.863±0)	24.21 (19.06±0.15)	70.16 (69.24±1.58)	14.73 (14.41±0.24)
	0.50	0.864 (0.856±0)	24.68 (24.37±0.29)	71.19 (70.75±1.38)	15.18 (14.96±0.22)
	0.75	0.852 (0.847±0)	23.48 (19.69±0.21)	72.05 (71.84±1.36)	14.41 (14.15±0.17)
Annealing temperature (°C)	80	0.869 (0.862±0)	24.14 (24.00±0.17)	69.98 (69.25±1.45)	14.68 (14.39±0.20)
	90	0.864 (0.856±0)	24.68 (24.37±0.29)	71.19 (70.75±1.38)	15.18 (14.96±0.22)
	100	0.861 (0.855±0)	24.36 (24.14±0.14)	70.89 (70.27±1.42)	14.87(14.55±0.25)
Spin coating speed (rpm)	2700	0.860 (0.854±0)	25.14 (24.92±0.28)	70.13 (69.57±1.42)	15.16 (15.01±0.14)
	3000	0.864 (0.856±0)	24.68 (24.37±0.29)	71.19 (70.75±1.38)	15.18 (14.96±0.22)
	3300	0.867 (0.864±0)	24.16 (23.85±0.34)	71.35 (70.88±1.27)	14.95 (14.72±0.20)

Conditions		V_{oc}^a [V]	J_{sc}^a [mA/cm ²]	FF^a [%]	PCE_{ave}^a [%]
D:A ratio	1:1.2:0	0.864 (0.856±0)	24.68 (24.37±0.29)	71.19 (70.75±1.38)	15.18 (14.96±0.22)
	1:1.1:0.1	0.885 (0.880±0)	24.61 (24.21±0.20)	73.67 (72.39±1.42)	16.04 (15.83±0.18)
	1:1.0:0.2	0.897 (0.891±0)	23.49 (23.14±0.27)	71.46 (70.46±1.63)	15.06 (14.79±0.17)
	1:0.9:0.3	0.907 (0.901±0)	23.01 (22.25±0.22)	68.95 (67.97±1.58)	14.39 (14.07±0.21)
	1:0:1	0.981 (0.979±0)	18.11 (17.79±0.28)	61.45 (60.05±1.36)	10.92 (10.53±0.18)
CN (%)	0.25	0.887 (0.892±0)	23.95 (23.54±0.21)	71.46 (70.89±1.45)	15.18 (14.87±0.28)
	0.50	0.885 (0.880±0)	24.61 (24.21±0.20)	73.67 (72.39±1.42)	16.04 (15.83±0.18)
	0.75	0.881 (0.878±0)	23.46 (23.11±0.15)	72.37 (71.69±1.84)	14.96 (14.58±0.31)
Annealing temperature (°C)	70	0.891 (0.886±0)	24.23 (23.95±0.19)	71.15 (70.85±1.34)	15.36 (15.04±0.32)
	80	0.885 (0.880±0)	24.61 (24.21±0.20)	73.67 (72.39±1.42)	16.04 (15.83±0.18)
	90	0.879 (0.872±0)	24.04 (23.78±0.23)	73.39 (72.17±1.65)	15.51 (15.39±0.26)
Spin coating speed (rpm)	2700	0.880 (0.876±0)	25.01 (24.72±0.18)	71.47 (70.84±1.38)	15.72 (15.42±0.34)
	3000	0.885 (0.880±0)	24.61 (24.21±0.20)	73.67 (72.39±1.42)	16.04 (15.83±0.18)
	3300	0.889 (0.884±0)	23.96 (23.78±0.17)	73.95 (73.11±1.57)	15.75 (15.53±0.21)

Table S2. The photovoltaic data of IT-4F based binary and ternary solar cells with different optimized conditions.

Conditions		V_{oc}^a [V]	J_{sc}^a [mA/cm ²]	FF^a [%]	PCE_{ave}^a [%]
DIO(%)	0.25	0.868 (0.863±0)	19.21 (19.06±0.15)	69.79 (68.56±1.68)	11.64 (11.51±0.14)
	0.50	0.864 (0.858±0)	20.10 (19.57±0.19)	73.51 (72.49±1.59)	13.07 (12.91±0.18)
	0.75	0.861 (0.855±0)	19.86 (19.69±0.21)	72.46 (71.84±1.36)	12.09 (11.88±0.09)
Annealing temperature (°C)	80	0.869 (0.864±0)	20.27 (20.15±0.08)	71.97 (70.05±1.34)	12.68 (12.47±0.13)
	90	0.864 (0.858±0)	20.10 (19.57±0.19)	73.51 (72.49±1.59)	13.07 (12.91±0.18)
	100	0.860 (0.857±0)	19.85 (19.64±0.11)	71.46 (70.59±1.21)	12.20 (12.05±0.19)
Spin coating speed (rpm)	2000	0.861 (0.856±0)	20.51 (20.32±0.08)	71.53 (70.57±1.29)	12.63 (12.51±0.17)
	2200	0.864 (0.858±0)	20.10 (19.57±0.19)	73.51 (72.49±1.59)	13.07 (12.91±0.18)
	2500	0.868 (0.861±0)	19.76 (19.35±0.14)	74.09 (73.38±1.82)	12.71 (12.53±0.10)

Conditions		V_{oc}^a [V]	J_{sc}^a [mA/cm ²]	FF^a [%]	PCE_{ave}^a [%]
D:A ratio	1:1:0	0.864 (0.858±0)	20.10 (19.57±0.19)	73.51 (72.49±1.59)	12.77(12.31±0.18)
	1:0.9:0.1	0.888 (0.882±0)	20.19 (19.73±0.21)	76.23 (75.47±1.66)	13.67 (13.23±0.26)
	1:0.8:0.2	0.908 (0.903±0)	19.65 (19.13±0.24)	72.46 (71.89±1.23)	12.93 (12.49±0.07)
	1:0.7:0.3	0.913 (0.909±0)	19.01 (18.67±0.18)	69.95 (68.56±1.46)	12.14 (11.79±0.14)
	1:0:1	0.981 (0.977±0)	18.11 (17.79±0.28)	61.45 (60.05±1.36)	10.92 (10.53±0.18)
DIO (%)	0.5	0.898(0.892±0)	19.95 (19.79±0.19)	72.06 (71.89±1.37)	12.91 (12.57±0.08)
	0.75	0.888 (0.882±0)	20.19 (19.73±0.21)	76.23 (75.47±1.66)	13.67 (13.23±0.26)
	1	0.884 (0.878±0)	19.66 (19.26±0.17)	75..26 (74.39±1.57)	13.08 (12.88±0.09)
Annealing temperature (°C)	70	0.894 (0.889±0)	20.23 (20.05±0.08)	75.07 (74.58±1.25)	13.58 (13.23±0.12)
	80	0.888 (0.882±0)	20.19 (19.73±0.21)	76.23 (75.47±1.66)	13.67 (13.23±0.26)
	90	0.886 (0.881±0)	20.06 (19.74±0.11)	75.99 (74.79±1.32)	13.51 (13.35±0.18)
Spin coating speed (rpm)	2000	0.884 (0.879±0)	20.60 (20.52±0.08)	74.67 (73.69±1.39)	13.60 (13.31±0.12)
	2200	0.888 (0.882±0)	20.19 (19.73±0.21)	76.23 (75.47±1.66)	13.67 (13.23±0.26)
	2500	0.890 (0.884±0)	19.86 (19.67±0.14)	76.50 (75.12±1.62)	13.52 (13.23±0.10)

1. Z. Tan, W. Zhang, Z. Zhang, D. Qian, Y. Huang, J. Hou and Y. Li, *Adv. Mater.*, 2012, **24**, 1476-1481.