Supporting Information

Over 13%-Efficiency Quaternary Polymer Solar Cells Enabled by Improving Film-Morphologies via Binary Mixed Fullerene Additive

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1. Experimental details

1.1. Materials and Instruments

The materials of PBDB-T, ITIC, PCBM, and ICBA were purchased from One Material and Solarmer company. N719 and PrC₆₀MAI were bought from LumTec Company (Taiwan). PEDOT:PSS (Baytron Clevios P VP AI 4083, Germany) was obtained from Heraeus Group. Absorption spectra were measured on a Hitachi U-3010 UV–vis spectrophotometer at room temperature. TEM measurements were performed on a JEM-2100F transmission electron microscope operated at 200 kV. The thickness of the solid films was measured using a Dektak Profilometer.

1.2. Sample preparations and characterizations

Film samples for measurements of absorption and TEM were all prepared atop the pre-coated ITO/PEDOT:PSS substrate via the spin-coating method. The pure donor film was spun-cast from an CB solution of 10 mg/ml and the pure acceptor film was spin-coated from a chloroform solution of 10 mg/ml. All the blend films were fabricated under the optimal conditions. For UV–vis absorption, an ITO/PEDOT:PSS substrate was used as the reference. For TEM, the films were obtained by transferring the floated blend films from the water onto the Cu grid. For GIXRD measurements, the blend films were prepared on the silicon substrate. The BHJ composite films were spin-coated on the top of the SiO₂/PEDOT:PSS substrates under exactly the same conditions as those for the fabrication of solar cell devices. The 1D GIXRD data were measured on the 1W1A beam line at the Beijing Synchrotron Radiation Facility (BSRF). The 1D GIXRD data, either along the out-of-plane or the in-plane directly recorded by a silicon drift detector on a 5-circle Huber diffractometer. The authors gratefully acknowledge the assistance of the scientists at the 1W1A station during the experiments.

1.3. Measurements of the hole and electron mobility by the space-charge limited current (SCLC) method

The hole-only devices were fabricated with configuration of ITO/PEDOT:PSS/blend/Au. The electron-only devices were fabricated with a configuration of ITO/titanium (diisopropoxide) bis(2,4-pentanedionate) (TIPD)/blend/CBL/Al. The TIPD buffer layer was prepared by spin-coating a 3.5 wt % TIPD isopropanol solution onto the pre-cleaned ITO substrate and then baked at 150 °C for 10 min to convert TIPD into TOPD.¹ Subsequently, the blend was spin-coated on it under the same condition as preparation of the optimal solar cell. The Au or Al layer was thermally deposited on the top of the blend in vacuum. The Au layer was deposited under a low speed (1 Å/10 s) to

avoid the penetration of Au atoms into the active layer. The Al layer was deposited at a speed of 1 Å/ s. The hole and electron mobility was extracted by fitting the current density–voltage curves using the Mott–Gurney law

$$J_{\rm SCL} = 9\varepsilon\varepsilon_0 \mu V^2 / (8L^3) \tag{1}$$

where ε is the dielectric constant of the organic component, ε_0 is the permittivity of the vacuum $(8.85419 \times 10^{-12} \text{ CV}^{-1} \text{m}^{-1})$, μ is the zero-field mobility, *J* is the current density, *L* is the thickness of the active layer, and $V = V_{app} - V_{bi}$, here V_{app} is the applied potential, and V_{bi} the built-in potential which results from the difference in the work function values of the anode and the cathode (in the hole-only device, $V_{bi} = 0.2$ V, and in the electron-only device, $V_{bi} = 0.4$ V). The hole and electron mobility of the solar cell blend are deduced from the intercept value of $9\varepsilon\varepsilon_0\mu/(8L^3)$ by linearly plotting $\ln(J) vs$. $\ln(V)$ (the slope of $\ln(J) vs$. $\ln(V)$ is ≈ 2).

2. Supporting Figures and Tables.

PBDB-T:ITIC:IC ₆₀ BA	$V_{ m oc}{}^{[b]}[{ m V}]$	$J_{\rm sc}$ ^[b] [mA/cm ²]	$FF^{[b]}$	$PCE_{ave}^{[b]}[\%]$	$PCE_{\max}[\%]$
1:1:0	0.952±0.007	16.59±0.32	0.675±0.013	10.66±0.39	11.15
1:1:0.1	0.956±0.007	16.80±0.28	0.682±0.013	10.95±0.32	11.35
1:1:0.2	0.956±0.006	17.21±0.35	0.705±0.011	11.60±0.35	12.06
1:1:0.3	0.959±0.006	16.99±0.37	0.709±0.012	11.55±0.36	12.00

Table S1. The photovoltaic properties of the ternay cells by introducing $IC_{60}BA$ as the third component. All data are obtained under illumination of AM 1.5G, 100mW/cm² light source.

[a] Average values from 10-35 devices.

Table S2. The photovoltaic properties of the ternay cells by introducing $PC_{61}BM$ as the third component. All data are obtained under illumination of AM 1.5G, 100mW/cm² light source.

PBDB-T:ITIC:PC ₆₁ BM	$V_{ m oc}{}^{[b]}[{ m V}]$	$J_{\rm sc}$ ^[b] [mA/cm ²]	$FF^{[b]}$	$PCE_{ave}^{[b]}[\%]$	$PCE_{\max}[\%]$
1:1:0	0.952±0.007	16.59±0.32	0.675±0.013	10.66±0.39	11.15
1:1:0.1	0.950±0.006	17.19±0.33	0.688±0.012	11.24±0.32	11.63
1:1:0.2	0.948 ± 0.005	17.38±0.36	0.709±0.010	11.68±0.32	12.09
1:1:0.3	0.939±0.006	17.11±0.35	0.703±0.011	11.29±0.30	11.67

[a] Average values from 10-35 devices.

Table S3. The photovoltaic properties of the ternay cells by introducing $IC_{60}BA$ as the forth component. All data are obtained under illumination of AM 1.5G, 100mW/cm² light source.

PBDB-T:ITIC:bis- PC ₇₁ BM:IC ₆₀ BA	$V_{ m oc}^{ m ~[b]}$ [V]	$J_{\rm sc}^{[b]}$ [mA/cm ²]	FF ^[b]	PCE _{ave} ^[b] [%]	PCE _{max} [%]
1:1:0.2:0	0.959 ± 0.008	16.79±0.30	0.726±0.012	11.69±0.32	12.11
1:1:0.2:0.1	0.967 ± 0.008	17.18±0.28	0.728±0.011	12.09±0.30	12.49
1:1:0.2:0.2	0.968±0.006	18.21±0.33	0.731±0.011	12.89±0.37	13.31
1:1:0.2:0.3	0.970±0.006	17.49±0.37	0.730±0.012	12.38±0.35	12.83

[a] Average values from 10-35 devices.

Table S4. The photovoltaic properties of the ternay cells by introducing $PC_{61}BM$ as the forth component. All data are obtained under illumination of AM 1.5G, 100mW/cm² light source.

BDB-T:ITIC:bis- PC ₇₁ BM:PC ₆₁ BM	$V_{ m oc}^{ m [b]}$ [V]	$J_{\rm sc}^{[b]}$ [mA/cm ²]	FF ^[b]	PCE _{ave} ^[b] [%]	PCE _{max} [%]
1:1:0.2:0	0.959 ± 0.008	16.79±0.30	0.726±0.012	11.69±0.32	12.11
1:1:0.2:0.1	0.958 ± 0.007	17.69±0.33	0.729±0.012	12.35±0.33	12.79
1:1:0.2:0.2	0.957±0.007	18.38±0.31	0.730±0.010	12.86±0.35	13.28
1:1:0.2:0.3	0.949±0.006	17.44±0.35	0.728±0.010	12.05±0.32	12.47

[a] Average values from 10-35 devices.

а 10² PBDB-T:IT-M +bis-PC₇₁BM 10⁰ +IC₆₀BA J (mA/cm²) +PC₆₁BM 10⁻² 10⁻⁴ +bis-PC71BM:IC BA +bis-PC71BM:PC₆₁BM 10⁻⁶ 0.0 -0.5 0.5 1.0 1.5 V(V)

Figure S1. Dark *J–V* Characteristics of the Binary, Ternary, and Quaternary Devices.

Figure S2. The dark J-V curves in the electron-only (a) and the hole-only (b) devices of the binary, ternary, and quaternary solar cell blend films.



Figure S3. The multi-peaks fitting of the OOP-direction's 1D-GIXRD data at the 1.4–2.3 Å region: (a) PBDB-T:IT-M; (b) +Bis-PC₇₁BM; (c) +IC₆₀BA; (d) +PC₆₁BM; (e) +Bis-PC₇₁BM:IC₆₀BA; (f) (e) +Bis-PC₇₁BM:PC₆₁BM. The relative intensity inserted in each figure is calculated with equation Intensity_{1.83-1.86}/Intensity_{1.70-1.73}.



References

(1) Tan, Z.; Zhang, W.; Zhang, Z.; Qian, D.; Huang, Y.; Hou, J.; Li, Y. High-Performance Inverted Polymer Solar Cells with Solution-Processed Titanium Chelate as Electron-Collecting Layer on ITO Electrode. *Advanced Materials* **2012**, *24* (11), 1476-1481, DOI: 10.1002/adma.201104863.