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Version: Supplemental Material

# 13.9% Efficiency Ternary Nonfullerene Organic Solar Cells Featuring Low-structural Order

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**Materials**

m-INPOIC was synthesized as in our previous work.[1] PBDB-T, IT-M were purchased from Solarmer Materials (Beijing) Inc. The molecular weight and polydispersity index of PBDB-T are 11.5K ($M_n$) and 1.18, respectively. ZnO precursor solution was prepared according to a previous literature report.[2] The processing solvents used in the fabrication processes were of reagent grade.

**Device Fabrication**

All organic solar cells were fabricated in an inverted structure. The prepatterned indium tin oxide (ITO)-glass substrates (resistance ≈15 Ω per square) were cleaned by sequential sonication in water, ethanol, and isopropyl alcohol for 10 min each, and dried at 100 °C on a hotplate before use. These substrates were further treated with ultraviolet/ozone for 15 min before solution processing. The 30 nm thick ZnO films were spin-coated onto cleaned ITO substrates and then heated at 200 °C for 30 min in air. The photoactive layer solutions were prepared by dissolving the PBDB-T:m-INPOIC:IT-M with the weight ratios of 1:1:0, 1:0.9:0.1, 1:0.8:0.2 in chlorobenzene respectively (20mg/ml with 0.5 vol% 1,8-diiodooctane (DIO)). Subsequently, the prepared blend solutions were spin-coated on ZnO modified ITO substrates at 2200 rpm for 40 s to give the film

with thickness of about 105 nm, in a nitrogen-filled glove box. After the casting of the active layer, all devices were further treated with thermal annealing at 100 °C for 10 min. Then 10 nm $MoO_3$ and 100 nm Ag were thermally evaporated forming the anode and counter electrode under high vacuum to finish the device preparation. The size of the photoactive area defined by the overlapping of anode and cathode is 4 mm$^2$.

**Instruments and Characterization**

Film thickness was measured using a spectroscopic ellipsometer (J. A. Woollam, USA). The surface morphologies of the active layers were characterized by TEM (JEOL, Japan). GIWAXS was conducted with 10 keV X-rays and an incidence angle of 0.16° using the I07 beamline at Diamond Light Source synchrotron (UK) as part of session SI22651-1. Synchrotron GISAXS measurements were conducted using the beamline BL16B1 at the Shanghai Synchrotron Radiation Facility in China. Film absorption spectra were measured using a UV–visible spectrophotometer (HITACHI, Japan). PL was obtained using a PL microscopic spectrometer (Flex One, Zolix, China) with a 532 nm CW laser as the excitation source. Device J–V characterization was performed under AM 1.5G (100 mW/cm$^2$) illumination using a Newport 3A solar simulator (USA) in air at room temperature. The light intensity was calibrated using a standard silicon reference cell certified by the National Renewable Energy Laboratory (NREL, USA). J-V characteristics were recorded using J-V sweep software developed by Ossila Ltd. (UK) and a Keithley 2612B (USA) source meter unit. EQE was measured with a Zolix (China) EQE system equipped with a standard Si diode. Impedance measurements were performed on an XM-studio electrochemical workstation (Solartron, UK).

Hole-only and electron-only devices were fabricated to measure the hole and electron mobilities of devices using the space charge limited current (SCLC) method with hole-only devices of ITO/PEDOT:PSS/Active layer/$MoO_3$/Ag and electron-only devices of ITO/ZnO/Active layer/Ca/Ag. The mobilities ($\mu_h$ or $\mu_e$) were determined by fitting the dark current to the model of a single carrier SCLC, described by the equation 1:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3} \qquad (1)$$

Where J is the current, $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the material relative permittivity, d is the thickness of the active layer and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage ($V_{bi}$) from the applied voltage ($V_{appl}$), V=$V_{appl}$-$V_{bi}$. The mobility can be calculated from the slope of the $J^{1/2}$-V curves.

To quantify and compare the phase separation in the non-fullerene photovoltaic blends, the 1D GISAXS profiles were fitted using a universal model expressed in Equation 2 using the fitting software SASView (Version 3.1.2). The first term of the equation is the so-called Debye−Anderson−Brumberger (DAB) term, where q is the scattering wave vector, $A_1$ is an independent fitting parameter, and $\xi$ is the average correlation length of the PBDB-T domain. The second term represents the contribution from fractal-like aggregations of m-INPOIC. Here, P (q, R) is the form factor of m-INPOIC. S (q, R, η, D) is the fractal structure factor, which describes the interaction between primary particles (defined as 4 nm in our fitting) in this fractal-like aggregation system, with R the mean radius of primary m-INPOIC aggregates, and η the correlation length of the fractal-like structure. The average correlation length of the clustered m-INPOIC phases can be defined by the Guinier radius ($R_g$) of the network, where $R_g = \sqrt{\frac{D(D+1)}{2}}\,\eta$.

$$I(q) = \frac{A_1}{[1+(q\xi^2)]^2} + A_2\langle P(q,R)\rangle S(q,R,\eta,D) + B \qquad (2)$$

$$S(q) = 1 + \frac{\sin[(D-1)\tan^{-1}(q\eta)]b\pm\sqrt{b^2-4ac}}{(qR)^D} \frac{D\Gamma(D-1)}{\left[1+\frac{1}{(q\eta)^2}\right]^{(D-1)/2}} \qquad (3)$$
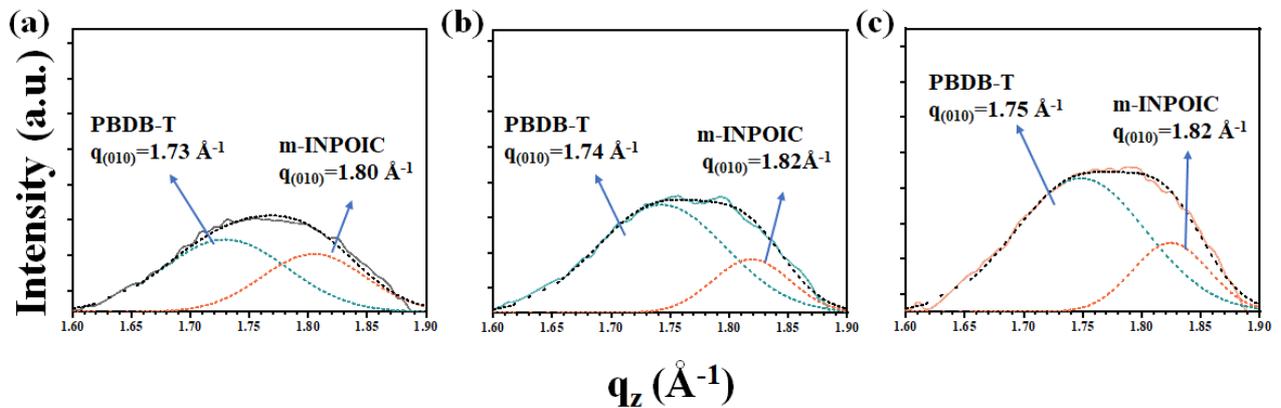


**Figure S1.** Multi-peak fits of the out-of-plane GIWAXS line cuts at the high q region for the blend films of (a) PBDB-T:m-INPOIC, (b) PBDB-T:m-INPOIC:IT-M (10wt%), (c) PBDB-T:m-INPOIC:IT-M (20 wt%).
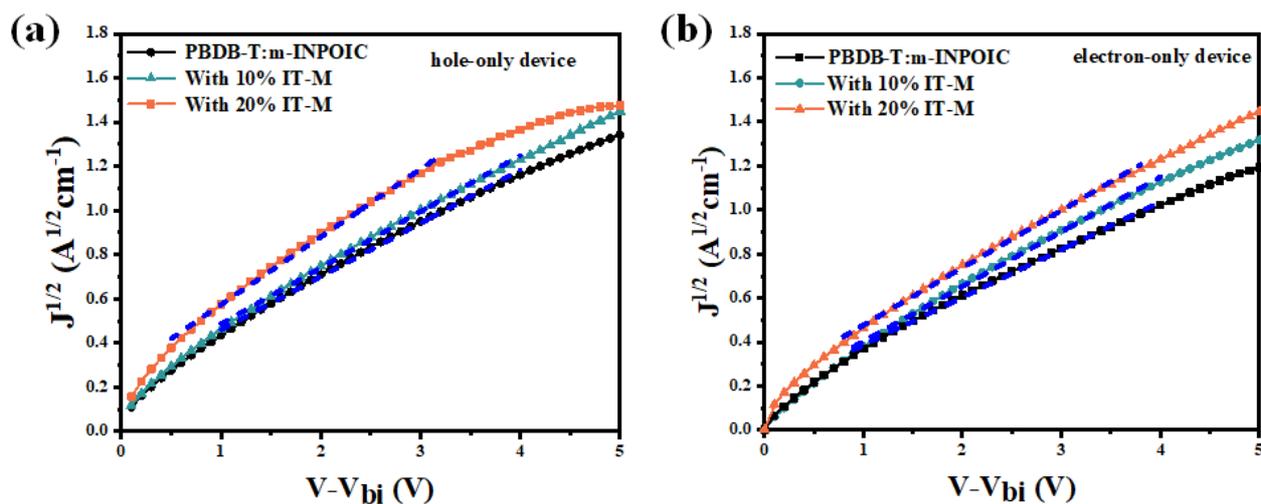
**Figure S2.** (a) Hole mobility and (b) electron mobility based on PBDB-T:m-INPOIC and its ternary devices with different amounts of IT-M.

**Reference**

(1)  Feng, H.; Song, X.; Zhang, Z.; Geng, R.; Yu, J.; Yang, L.; Baran, D.; Tang, W. Molecular Morientation Unified Nonfullerene Acceptor Enabling 14% Efficiency As-Cast Organic Solar Cells. *Adv. Funct. Mater.* **2019**, https://doi.org/10.1002/adfm.201903269.

(2)  Sun, Y.; Seo, J. H.; Takacs, C. J.; Seifter, J.; Heeger, A. J. Inverted Polymer Solar Cells Integrated with a Low-Temperature-Annealed Sol-Gel-Derived ZnO Film as an Electron Transport Layer. *Adv. Mater.* **2011**, *23*, 1679–1683.