Electronic Supplementary Information

Energy-level modulation of non-fullerene acceptors to achieve high-efficiency polymer solar cells at diminished energy offset

*Zhongqiang Zhang,[a] Wenqing Liu,[a] Tahir Rehman,[a] Huanxin Ju,[b] Jiangquan Mai,[c] Xinhui Lu,[c] Minmin Shi,[a] Junfa Zhu,[b] Chang-Zhi Li,[*a] and Hongzheng Chen[*a]*

1. Materials and Instruments.

All reagents and solvents were purchased from Aldrich and Solarmer Materials Inc. and used without further purification if not mentioned. ^{1}H-NMR spectra was measured on a Bruker Advance DMX300 (400 MHz) nuclear magnetic resonance spectroscope. UV-visible absorption spectra were taken on a Shimadzu UV-2450 spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a WCT-2 thermal balance under protection of nitrogen at a heating rate of 20 °C min^{-1}. Differential scanning calorimetry (DSC) was recorded on a Perkin-Elmer Pyris 1 differential scanning calorimeter under protection of nitrogen at a heating rate of 5 °C min^{-1}. Cyclic voltammetry (CV) was done on a CHI 660C electrochemical workstation with a Pt disk, a Pt plate, and a standard calomel electrode (SCE) as the working electrode, the counter electrode, and the reference electrode, respectively, in a 0.1 mol L^{-1} tetrabutylammonium-hexafluorophosphate (Bu$_4$NPF$_6$) CH$_3$CN solution. Topographic images of the films were obtained using Veeco Multi Mode atomic force microscopy (AFM) in the tapping mode using an etched silicon cantilever at a nominal load of 2 nN, and the scanning rate for a 5 μm × 5 μm image size was 1.0 Hz.

DFT calculation. All calculations were performed in the Density Functional Theory (DFT) framework as implemented in the development version of the GAUSSIAN software suite.[1] We obtained the ground state geometries and electronic structures of the non-fullerene small molecules by using the 6-31G(d) basis set.

SRPES Characterization. Photoemission spectroscopy experiments were performed with the photon energy of 40 eV at the Catalysis and Surface Science endstation in the National Synchrotron Radiation Laboratory (NSRL), Hefei, China. The valence-band spectra were referenced to the Fermi level determined from the Au sample. A sample bias of -5 V was applied in order to observe the secondary electron cut-off.

GIWAXS measurement. The GIWAXS measurements were conducted at 23A SWAXS beamline of a superconductor wiggler at the National Synchrotron Radiation Research Center, Hsinchu, Taiwan. We probed the samples with 0.15° incident angle, using a 10 keV beam of 0.15 mm in height and 0.2 mm in width and C9728DK area detector.
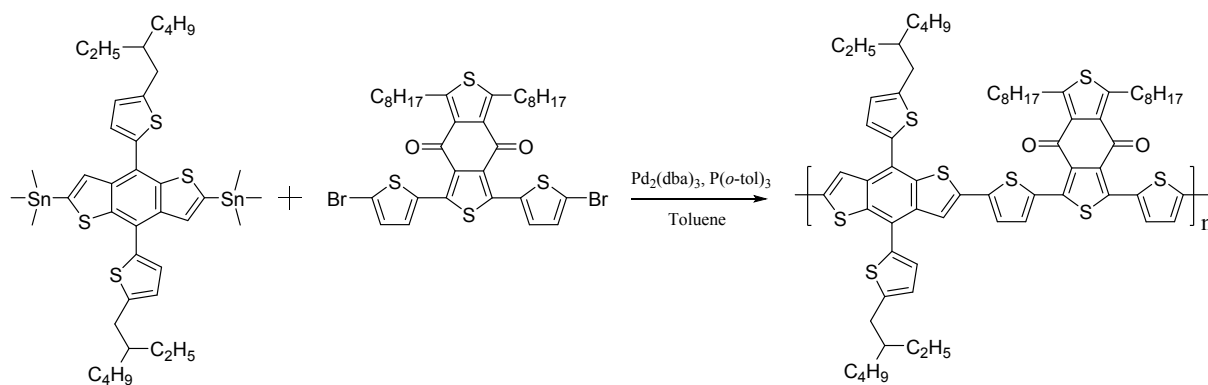
2. Synthesis.
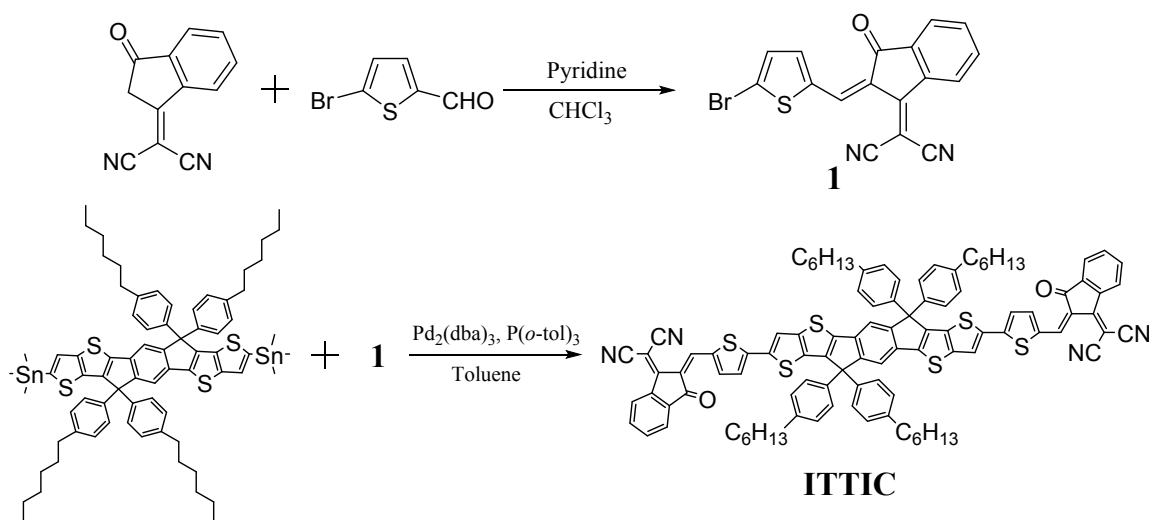
Scheme S1. Synthetic route of ITTIC.

2-(2-((5-Bromothiophen-2-yl)methylene)-3-oxo-2,3-dihydro-1H-inden-1ylidene)malono-nitrile. Under N_2 atmosphere, 5-bromothiophene-2-carbaldehyde (1 g, 5.23 mmol), 2-(3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (1.5 g, 7.73 mmol), 30 mL chloroform and 1 mL pyridine were added to a three-necked flask. The mixture was fluxed for 12 h. After cooling to room temperature, the precipitate was filtered and washed by chloroform/triethylamine (50/1, v/v) to get an orange solid (1.32 g, yield 69%). ^{1}H NMR (400

2

MHz, DMSO) δ 8.64 (s, 1H), 8.54 (d, J = 8.0 Hz, 1H), 7.97 (ddd, J = 23.2, 14.7, 7.2 Hz, 3H), 7.82 (d, J = 4.1 Hz, 1H), 7.57 (d, J = 4.1 Hz, 1H).

ITTIC. Under N_2 atmosphere, 2-(2-((5-bromothiophen-2-yl)methylene)-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (120 mg, 0.33 mmol), IDTT-ditin (200 mg, 0.15 mmol) and 10 mL anhydrous toluene were added to a three-necked flask. After deoxygenating for 30 min, $Pd_2(dba)_3$ (10 mg) and P(o-tol)$_3$ (13 mg) were added and the mixture was heated to 110 °C for 24 h. After cooling to room temperature, the mixture was precipitated in methanol and the precipitate was purified by column using chloroform, giving a dark blue solid which was further purified by recrystallization in chloroform. 180 mg dark blue solid was obtained as final product (yield 75%). ^{1}H-NMR (400 MHz, CDCl$_3$) δ 8.84 (s, 2H), 8.70 (d, J = 6.7 Hz, 2H), 7.93 (d, J = 7.1 Hz, 2H), 7.83 - 7.69 (m, 6H), 7.56 (s, 2H), 7.33 (d, J = 4.2 Hz, 2H), 7.14 (ddd, J = 14.8, 11.4, 8.0 Hz, 16H), 2.57 (s, 8H), 1.63 - 1.25 (m, 32H), 0.86 (t, J = 6.5 Hz, 12H). Exact Mass = 1592.20, MS (MALDI-TOF) = 1592.86.

Scheme S1. Synthetic route of PBDB-T1.

The synthesis of 1,3-Bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)benzo[1,2-c:4,5-c']dithiophene-4,8-dione (BDD-C8) will be reported in another work.

Polymerization of PBDB-T1. BDD-C8 (100mg, 0.13 mmol) and (4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl) bis(trimethylstannane) (118mg, 0.13 mmol) were dissolved in 2 mL of toluene. the solution was flushed with nitrogen for 15 min, and then 6 mg $Pd_2(dba)_3$ and 7.8 mg P(o-tol)$_3$ were added into the

solution. The mixture was again flushed with nitrogen for 15 min. The reaction solution was heated to 110 °C for 24 h. The reaction mixture was cooled to room temperature and added dropwise into 100 mL of methanol. The precipitate was collected and further purified by Soxhlet extraction with methanol, acetone, hexane, and chloroform in order. The chloroform fraction was concentrated and added dropwise into methanol. Subsequently, the precipitates were collected and dried under vacuum overnight to get polymer as dark blue solid (100 mg, 65% yield). The number-average molecular weight (M_n) and the polydispersity index (PDI) estimated by GPC are 66.4 kDa and 2.55, respectively

3. Fabrication and characterization of PSCs.

An inverted structure of ITO/ZnO/Active layers/MoO$_3$/Ag was adopted for the device fabrication. First, the ITO glass substrates were pre-cleaned using detergent, deionized water, acetone, isopropanol and ethanol consecutively for every 20 min, and then treated in an ultraviolet ozone generator for 20 min. Then, a thin layer of ZnO ($\approx$ 40 nm) was spin coated from its sol-gel precursor solution (1 g zinc acetate dihydrate and 0.28 g ethanolamine were dissolved in 10 mL 2-methoxyethanol with stirring for 12 h in air) onto pre-cleaned ITO-coated glass substrates with post-annealing at 170 °C for 20 min in air. In the following, the ZnO-coated ITO substrates were transferred into glovebox for the active layer deposition. The active layer solutions were pre-prepared by dissolving PBDB-T1:ITTIC or PBDB-T1:ITIC (1:1.2 weight ratio) with total concentration of 10 mg/ml in *o*-dichlorobenzene (or with 0.5 % volume ratio DIO) and stirred for 6 h at an temperature of 100-110 °C. Both the active layer solutions and ZnO-coated ITO substrates were pre-heated to about 100-110 °C before casting. Subsequently, the ZnO-coated ITO substrates were transferred onto the spincoater and the warm solution is added onto the substrate. The active layers were cast under dynamic spin coating process with 2000 rpm s^{-1} for 120s. The PBDB-T1:ITTIC samples were annealled at

110 °C for 10 min. Lastly, the samples were loaded into a vacuum deposition chamber (background pressure $\approx 5\times10^{-4}$ Pa) to deposit 10-nm-thick MoO_3 (0.2 Å s^{-1}) and 100-nm-thick Ag (2 Å s^{-1}) through a shadow mask, giving an active area of 5.5 mm^2 per device.

The current density-voltage (*J-V*) curves of PSCs were measured with Keithley 2400 measurement source units at room temperature in air. The photocurrent was measured under a calibrated solar simulator (Enli Technology) at 100 mW cm^{-2} and the light intensity was calibrated with a standard photovoltaic (PV) reference cell. External quantum efficiency (EQE) spectrum was measured with a Stanford lock-in amplifier 8300 unit.

The charge carrier mobilities were measured using the space-charge-limited current (SCLC) method.[2] Hole-only devices were fabricated in a structure of ITO/PEDOT:PSS/Active layers/MoO_3/Al, electron-only devices were fabricated in a structure of Al/Active layers/Al. The device characteristics were extracted by modeling the dark current under forward bias using the SCLC expression described by the Mott-Gurney law:

$$J = \frac{9}{8}\varepsilon_r\varepsilon_0\mu\frac{V^2}{L^3}$$

Here, $\varepsilon_r \approx 3$ is the average dielectric constant of the blend film, ε_0 is the permittivity of the free space, μ is the carrier mobility, $L \approx 100$ nm is the thickness of the film, and V is the applied voltage.
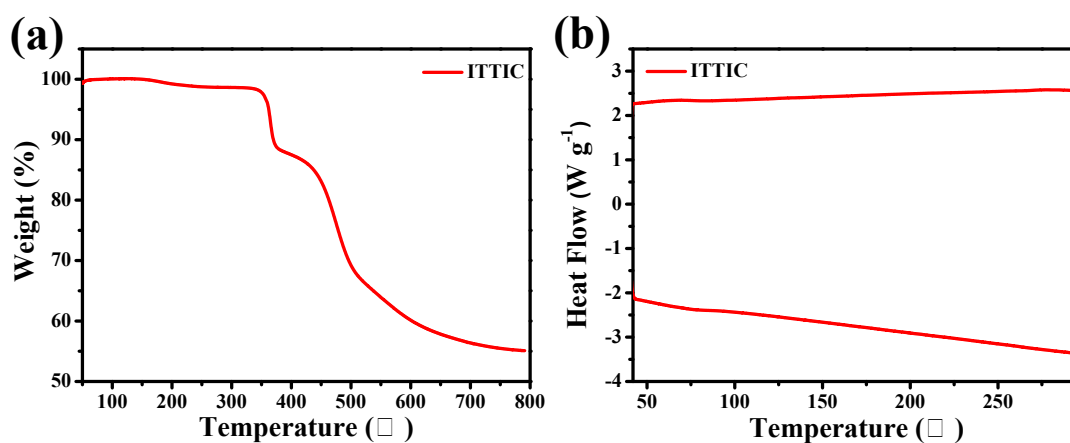
4. Figures and Tables.

Figure S1. (a) TGA traces of ITTIC with a heating rate of 20 °C min^{-1}. (b) DSC curve of ITTIC with a heating and cooling rate of 10 °C min^{-1}.
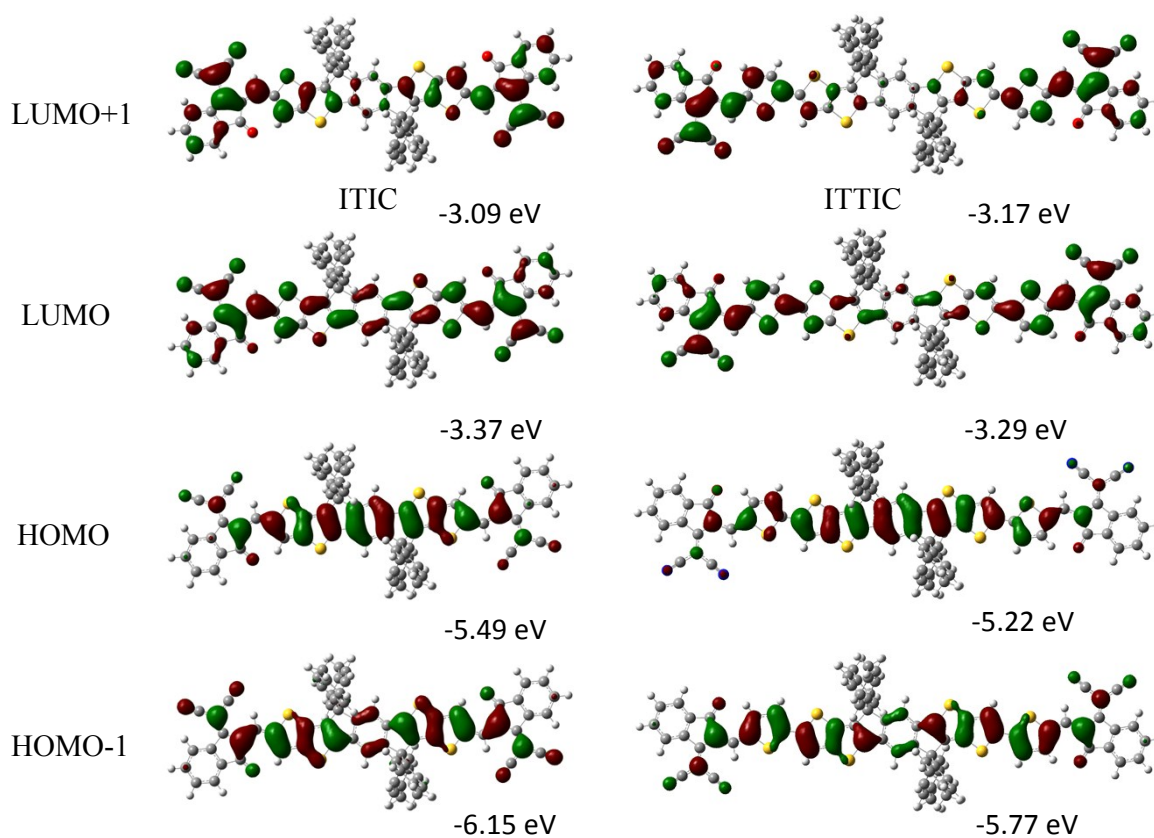

Figure S2. Front orbitals of ITIC and ITTIC obtained by theoretical calculation.
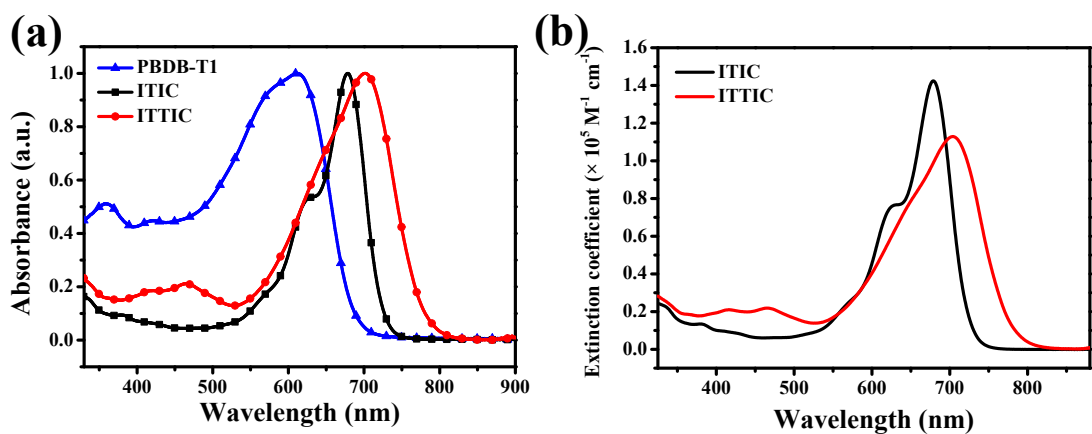
Figure S3. (a) UV-vis absorption spectra of PBDB-T1, ITIC and ITTIC in dilute chloroform solution. (b) Extinction coefficient of ITIC and ITTIC in 10^{-5} M chloroform solution.
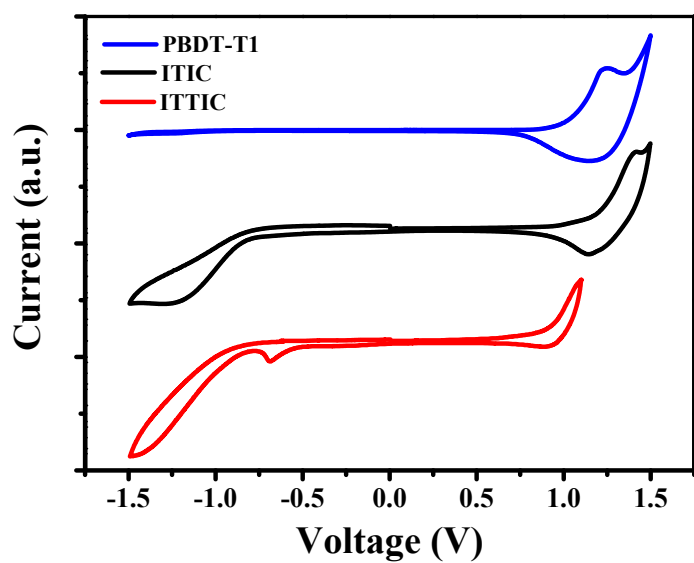

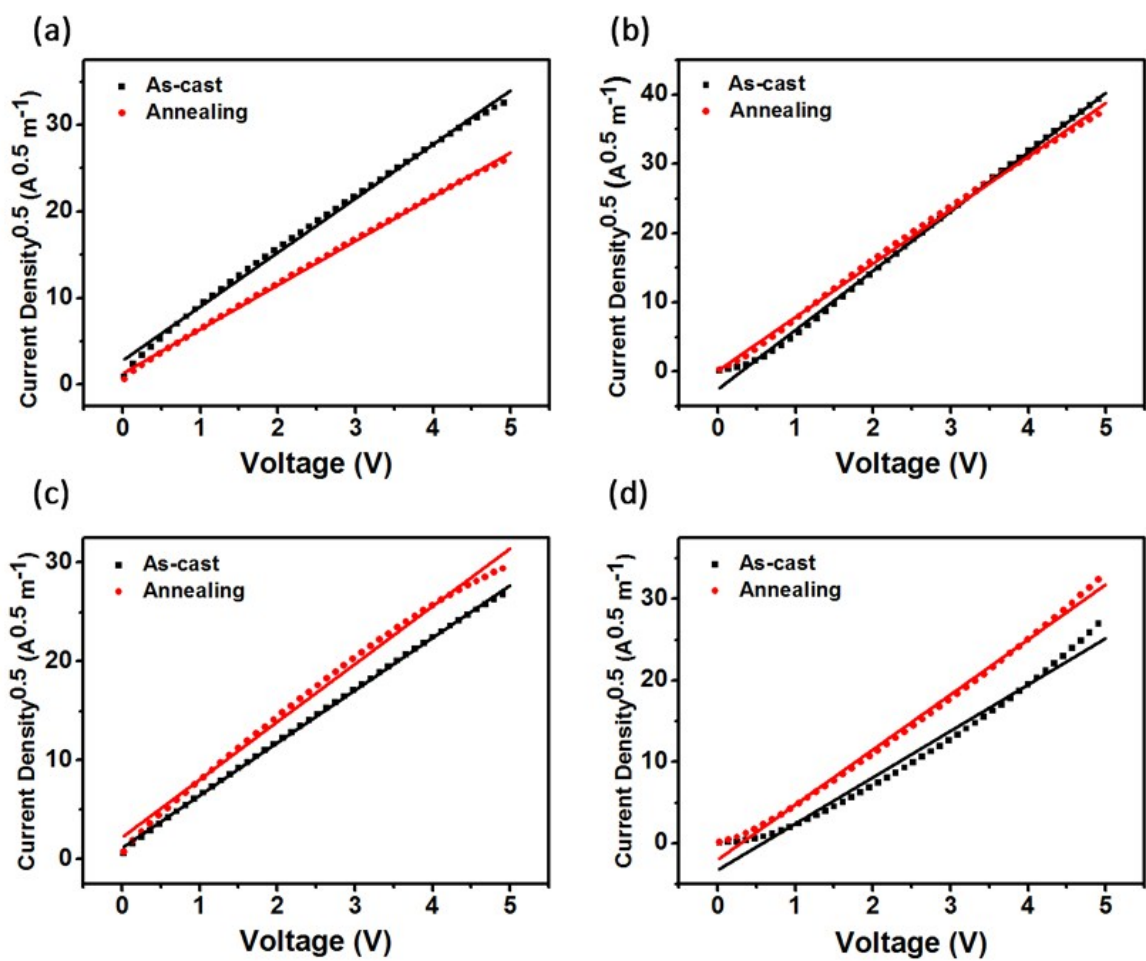**Figure S4.** CV curves of PBDB-T1, ITIC and ITTIC.

Figure S5. $J^{0.5}$-V curves of hole only devices (a, c) and electron only devices (b, d) of PBDB-T1:ITIC blended film (a, b) and PBDB-T1:ITTIC blended film (c, d) with or without annealing.
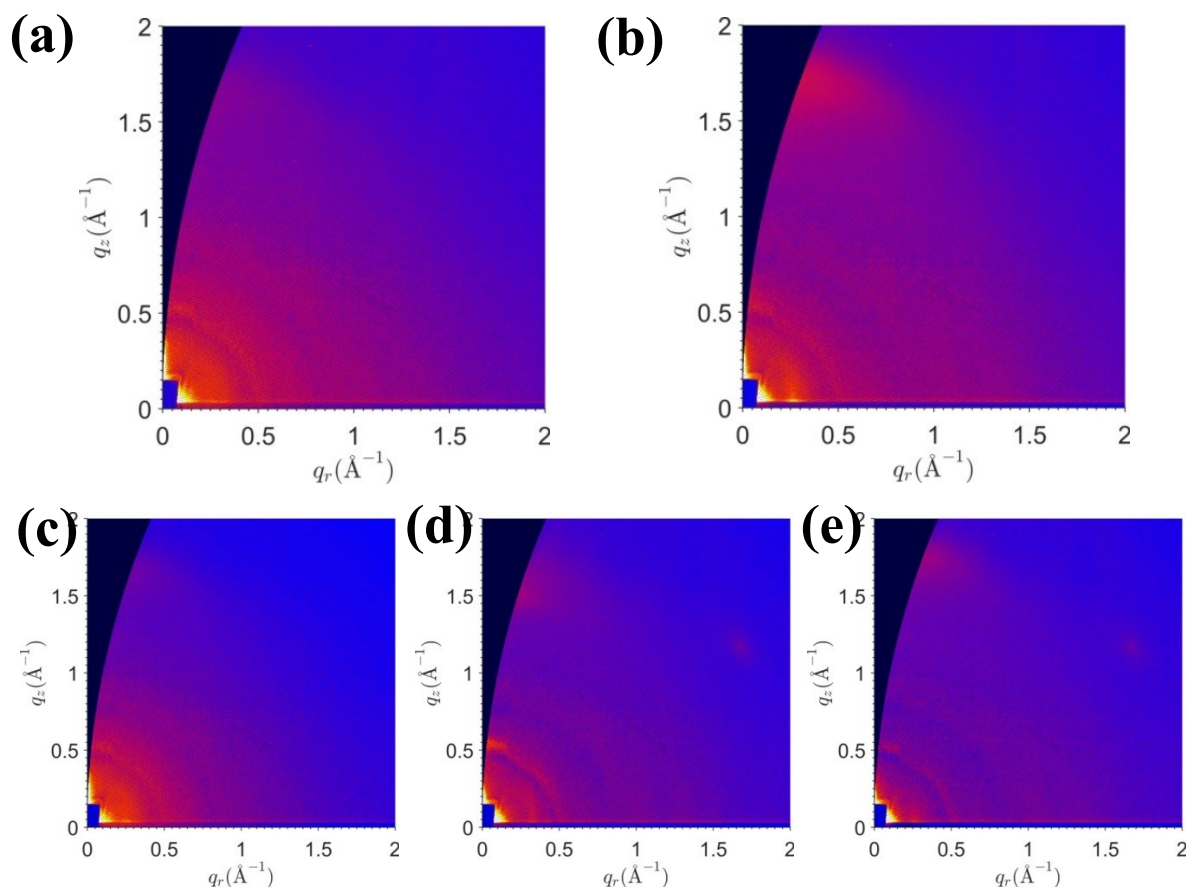
Figure S6. GIWAXS images of (a) PBDB-T1:ITIC, (b) PBDB-T1:ITTIC, (c) PBDB-T1, (d) ITIC and (e) ITTIC films.

References

1 Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., et al. Gaussian Development Version Revision H.13, Gaussian Inc.: Wallingford, CT, 2010.

2 G.G. Malliaras, J.R. Salem, P.J. Brock, C. Scott, Electrical characteristics and efficiency of single-layer organic light-emitting diodes, Phys. Rev. B 58 (1998)R13411–R13414.