

Electronic supplementary information for

High-performance fullerene-free polymer solar cells with 6.31% efficiency

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Experimental details

Materials. Unless stated otherwise, all the solvents and chemical reagents used were obtained commercially and were used without further purification. Toluene was distilled from sodium benzophenone under nitrogen prior to use. Compound **1**¹ was synthesized according to a literature procedure. Compounds **2**, **3** and PTB7-TH were purchased from SunaTech, TCI and Solarmer Materials Inc., respectively.

Measurements. The NMR spectra were measured using Bruker AVANCE 400 MHz and 600 MHz spectrometers. Mass spectra were measured using a Bruker Daltonics Biflex III MALDI-TOF Analyzer in the MALDI mode. Elemental analyses were carried out using a Flash EA1112 elemental analyzer. Solution (dichloromethane) and thin film (on a quartz substrate) UV-vis absorption spectra were recorded using a Jasco V-570 spectrophotometer. Photoluminescence (PL) spectra of thin films on a quartz substrate were measured using a Hitachi F4500 spectrofluorometer. Electrochemical

measurements were carried out under nitrogen in a deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M) in CH₃CN using a computer-controlled CHI660C electrochemical workstation, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and an Ag/AgCl as a reference electrode. The potential scan rate was 100 mV s⁻¹. The potentials were referenced to ferrocenium/ferrocene (FeCp₂⁺⁰) couple by using ferrocene as an internal standard. Thermogravimetric analysis (TGA) measurements were performed using a Shimadzu thermogravimetric analyzer (Model DTG-60) under a nitrogen flow at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) measurements were performed using a Mettler differential scanning calorimeter (DSC822e) under nitrogen at a heating rate of 10 °C min⁻¹. X-ray diffraction (XRD) of thin film was performed in the reflection mode at 40 kV and 200 mA with Cu-Kα radiation using a 2 kW Rigaku D/max-2500 X-ray diffractometer. The UPS was analysed on the Kratos AXIS ULTRA DLD. The gas discharge lamp was used for UPS, with helium gas admitted and the HeI (21.22 eV) emission line employed. The helium pressure in the analysis chamber during analysis was about 3.0 × 10⁻⁸ Torr. The data were acquired with -9 V bias. The nanoscale morphology of blended film was observed using a Veeco Nanoscope V atomic force microscope (AFM) in the tapping mode. The transmission electron microscopy (TEM) characterization was carried out using a JEM-2200FS. The samples for the TEM measurements were prepared as follows: The active-layer films were spin-casted on ITO/PEDOT:PSS substrates, and the ITO glass with the active layers were submerged in deionized water (10 min) to make the active layers float onto the air–water interface. Then the floated films were picked up on unsupported 200 mesh copper grids for

the TEM measurement. The initial stability of PSC device was measured under continuous AM1.5G illumination in nitrogen atmosphere.

Mobility measurements. Hole-only or electron-only diodes were fabricated using the architectures ITO/PEDOT: PSS/PTB7-TH: IEIC/Au for holes and Al/IEIC or PTB7-TH: IEIC/Al for electrons. The Mobility was extracted by fitting the current density–voltage curves using the space charge limited current method (SCLC).² The J – V curves of the devices were plotted as $J^{0.5}$ versus V using the equation $J = 9\epsilon_0\epsilon_r\mu_h(\mu_e)V^2/8d^3$ for holes and electrons, where J is the current density, d is the film thickness of active layer, μ_h is the hole mobility, μ_e is the electron mobility, ϵ_r is the relative dielectric constant of the transport medium, and ϵ_0 is the permittivity of free space (8.85×10^{-12} F m⁻¹). $V = V_{\text{appl}} - V_{\text{bi}}$, where V_{appl} is the applied voltage, V_{bi} is the offset voltage (for hole-only diodes, V_{bi} is 0.2 V; for electron-only diodes, V_{bi} is 0 V).

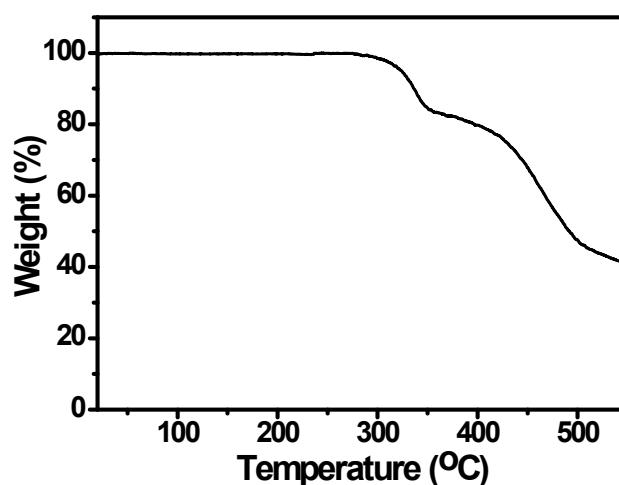


Fig. S1. TGA curve of IEIC.

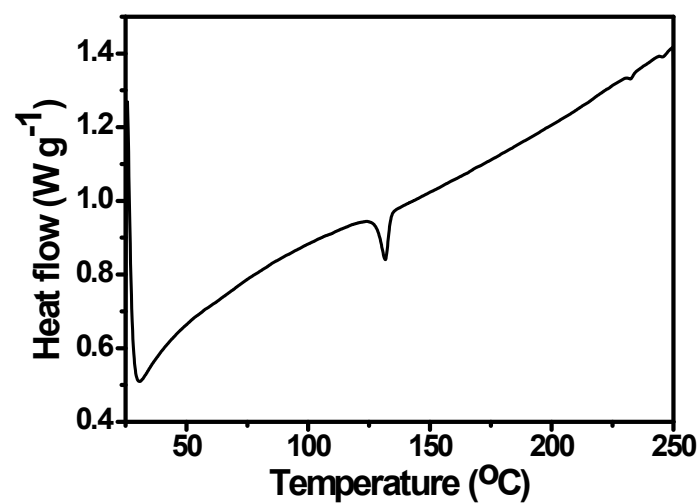


Fig. S2. DSC curve of IEIC.

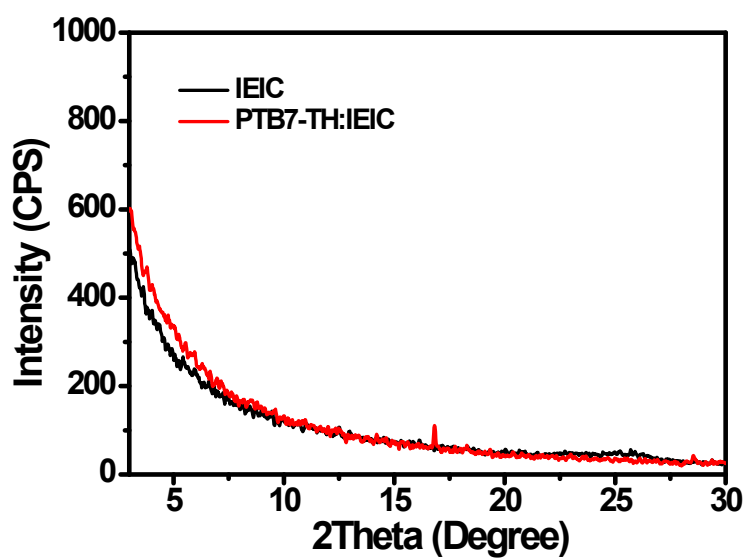


Fig. S3. Out-of-plane XRD patterns of IEIC film and PTB7-TH: IEIC (1: 1.5, w/w) blended film on Si substrates.

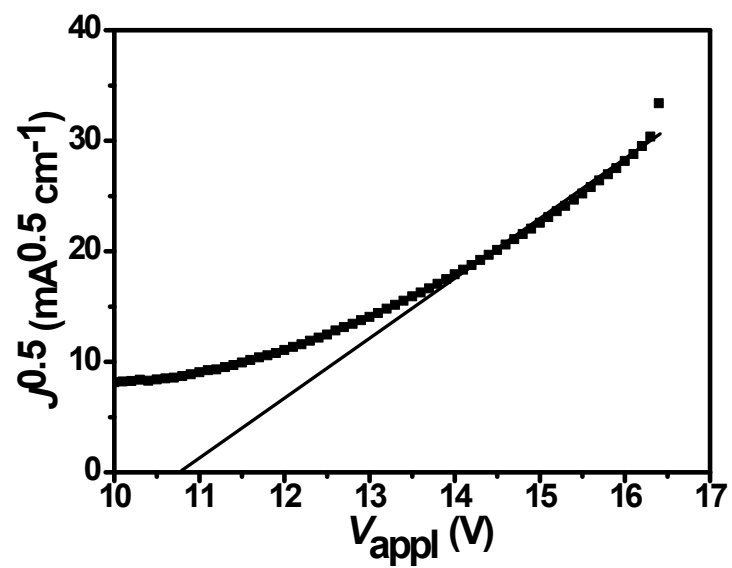


Fig. S4. $J_{0.5}$ - V plots for the IEIC-based electron-only device.

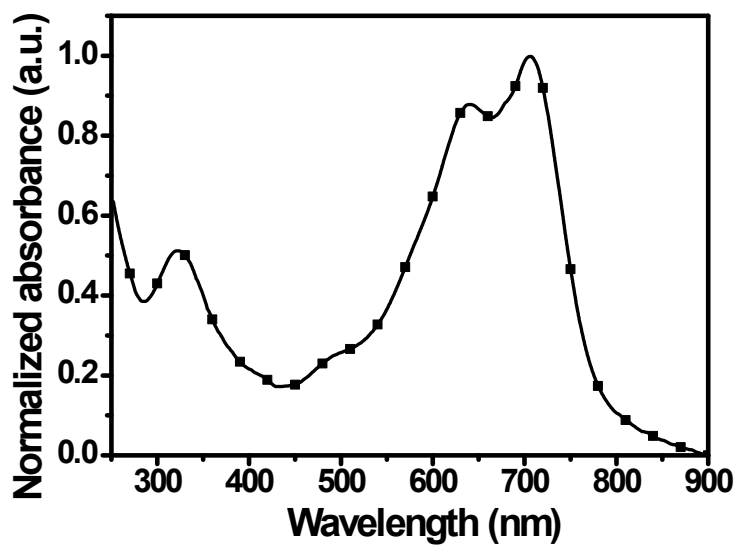


Fig. S5. UV-vis absorption spectra of PTB7-TH in thin film.

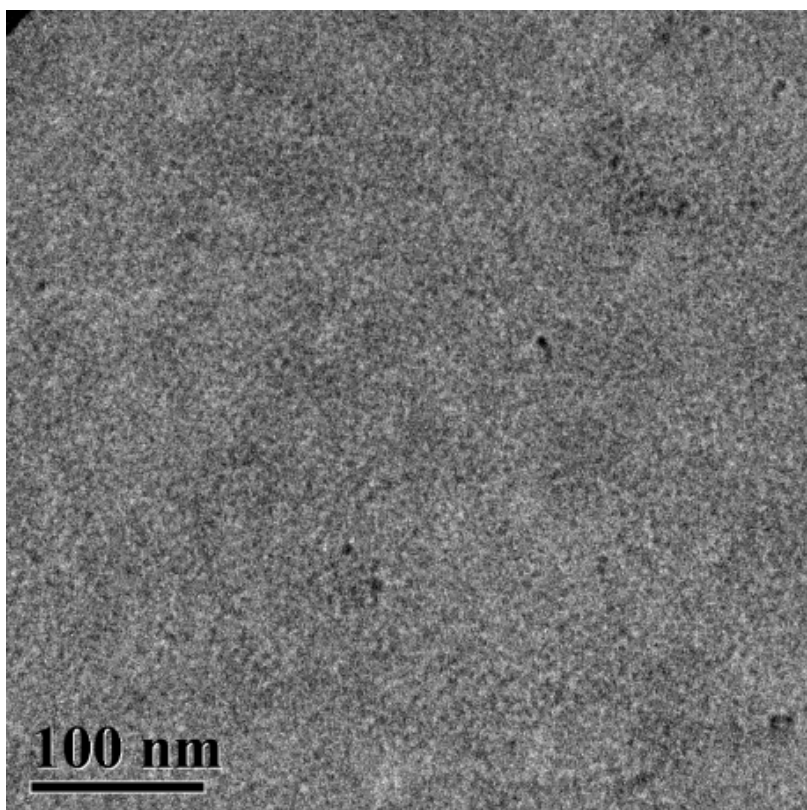


Fig. S6. TEM image of PTB7-TH: IEIC (1:1.5, w/w) blended film.

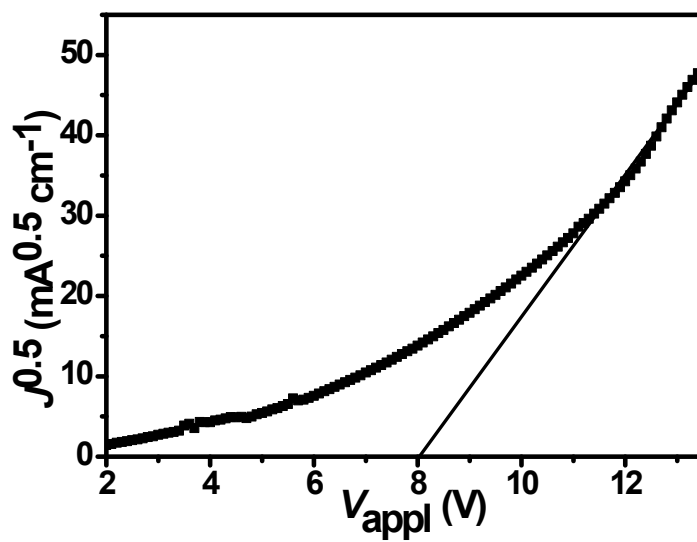


Fig. S7. $J^{0.5}$ - V plots for the PTB7-TH: IEIC (1:1.5, w/w)-based hole-only device.

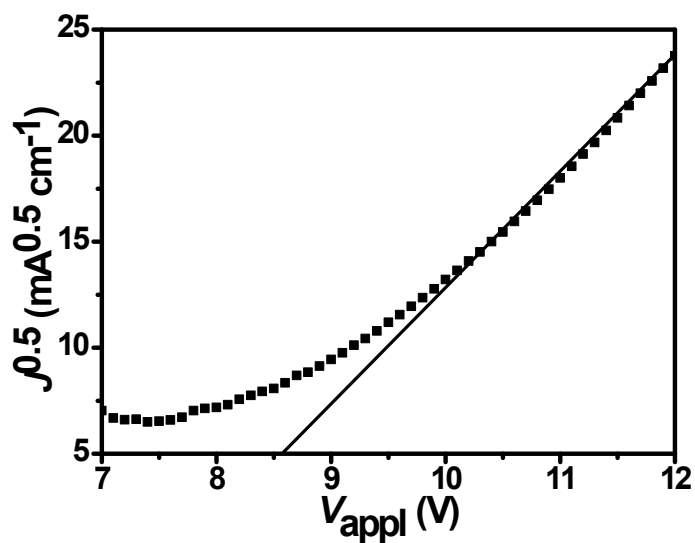


Fig. S8. $J^{0.5}-V$ plots for the PTB7-TH: IEIC (1:1.5, w/w)-based electron-only device.

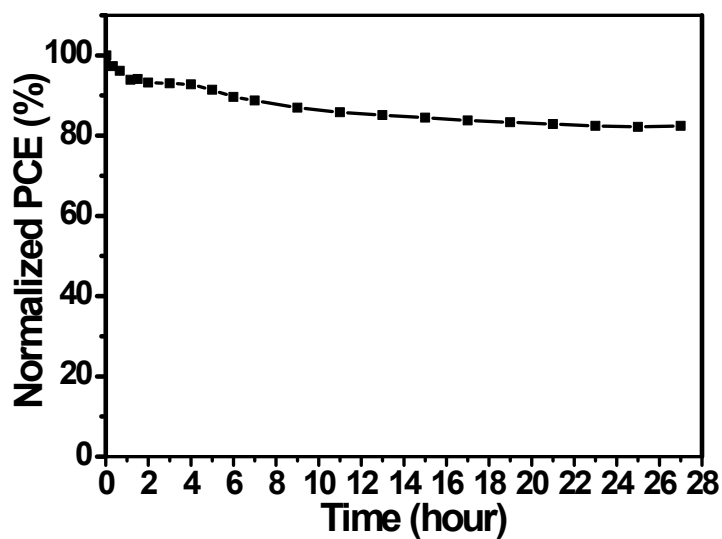


Fig. S9. Plot of PCE vs. time under continuous AM1.5G illumination for ITO/PEDOT:

PSS/PTB7-TH: IEIC (1:1.5, w/w)/PDIN/Al.

References

1. Y.-C. Chen, C.-Y. Yu, Y.-L. Fan, L.-I. Hung, C.-P. Chen and C. Ting, *Chem. Commun.*, 2010, **46**, 6503-6505.

2. G. G. Malliaras, J. R. Salem, P. J. Brock and C. Scott, *Phys Rev B*, 1998, **58**, 13411-13414.