

## Electronic Supplementary Information

### **Self-assembly of interfacial and photoactive layers via one-step solution processing for efficient inverted organic solar cells**

Hongkyu Kang, Jinho Lee, Suhyun Jung, Kilho Yu, Sooncheol Kwon, Soonil Hong, Seyoung Kee, Seongyu Lee, Dongwon Kim, and Kwanghee Lee\*

*School of Materials Science and Engineering, Department of Nanobio Materials and Electronics, Heeger Center for Advanced Materials, Research Institute for Solar and Sustainable Energies, Gwangju Institute of Science and Technology, Gwangju 500-712, Republic of Korea.*

*Fax: +82-62-970-2304; Tel: +82-62-970-2325; E-Mail: klee@gist.ac.kr*

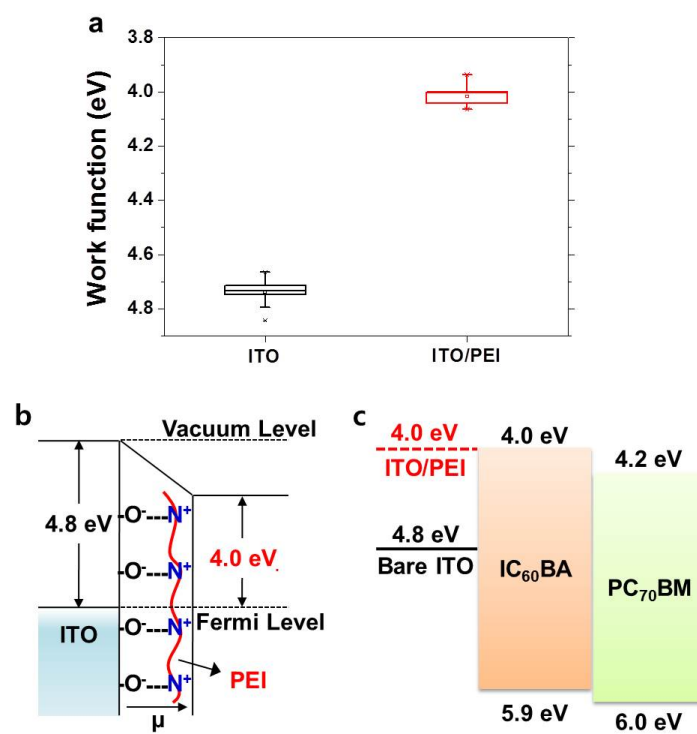
## Experimental

Materials: PEI (50 wt% in H<sub>2</sub>O) was diluted in alcohols (IPA, 2-ME or BtOH) to 0.05 and 0.1 wt%. For the preparation of the P3HT:IC<sub>60</sub>BA solution, 20 mg of P3HT, 20 mg of IC<sub>60</sub>BA, and 1 ml of DCB were mixed. The PTB:PC<sub>70</sub>BM solution consisted of a blend of PTB and PC<sub>70</sub>BM (1:1.5 by weight) in CB solvent with a 1,8-diiodooctane (DIO) additive (3% by volume) with a total concentration of 20 mg/ml. The DTS-F:PC<sub>70</sub>BM solution was prepared by mixing 17.5 mg of DTS-F, 17.5 mg of PC<sub>70</sub>BM, and 1 ml of CB. An additive (0.4% by volume), DIO, was added to the DTS-F:PC<sub>70</sub>BM solution. We prepared the PEI:BHJ solutions by mixing 50 mg of the dilute PEI solutions (0.1 wt%) and 450 mg of the BHJ solutions. We used a dilute PEDOT:PSS (VPAI 4083, H. C. Starck) solution mixed with IPA in a 1:5 mass ratio to directly coat the hydrophilic PEDOT:PSS onto the hydrophobic BHJ and PEI:BHJ surfaces.

Device fabrication: I-OSCs were fabricated with structures of ITO/BHJ/PEDOT:PSS or MoO<sub>x</sub>/Ag, ITO/PEI/BHJ/PEDOT:PSS or MoO<sub>x</sub>/Ag, and ITO/PEI:BHJ/PEDOT:PSS or MoO<sub>x</sub>/Ag. The ITO-coated glass substrates were cleaned with detergent, ultrasonicated in deionized water, acetone, and IPA, and then dried overnight in an oven at 100 °C. The cleaned ITO-coated glass substrates were UV/ozone treated before device fabrication. For the fabrication of the ITO/PEI/BHJ/PEDOT:PSS or MoO<sub>x</sub>/Ag devices, the dilute PEI solution (0.05 wt%) was spin cast onto the ITO at 5000 rpm and then dried at 100 °C. After the substrates were transferred into a glove box, the BHJ solutions were spin coated onto the PEI layer at 1000 rpm, 2500 rpm, and 1500 rpm for P3HT:IC<sub>60</sub>BA, PTB:PC<sub>70</sub>BM, and DTS-F:PC<sub>70</sub>BM, respectively. The PTB:PC<sub>70</sub>BM and DTS-F:PC<sub>70</sub>BM films were annealed at 70 °C. The P3HT:IC<sub>60</sub>BA film was annealed in a glass Petri dish at 50 °C and then dried at 80 °C. For the fabrication of the ITO/BHJ/PEDOT:PSS or MoO<sub>x</sub>/Ag and ITO/PEI:BHJ/PEDOT:PSS or MoO<sub>x</sub>/Ag devices, the UV/ozone-treated ITO glass substrates

were transferred into a glove box for the direct coating of the BHJ and PEI:BHJ layers. The BHJ and PEI:BHJ solutions were spin coated onto the ITO at 1000 rpm, 2500 rpm, and 1500 rpm for P3HT:IC<sub>60</sub>BA, PTB:PC<sub>70</sub>BM, and DTS-F:PC<sub>70</sub>BM, respectively. The PTB:PC<sub>70</sub>BM and DTS-F:PC<sub>70</sub>BM films were annealed at 70 °C, and the P3HT:IC<sub>60</sub>BA films were annealed in a glass Petri dish at 50 °C and then dried at 80 °C. For the P3HT:IC<sub>60</sub>BA and PTB:PC<sub>70</sub>BM devices, the dilute PEDOT:PSS solution was spin coated onto the photoactive layer at 2000 rpm in air and then annealed at 80 °C. For the DTS-F:PC<sub>70</sub>BM devices, the MoO<sub>x</sub> films were deposited onto the photoactive layer by thermal evaporation in a high vacuum of  $1 \times 10^{-6}$  Torr. Finally, for all devices, the Ag (thickness of 120 nm and area of 14.5 mm<sup>2</sup>) electrodes were deposited onto the PEDOT:PSS or MoO<sub>x</sub> films by thermal evaporation under a high vacuum of  $1 \times 10^{-6}$  Torr. The finished I-OSCs were post-annealed at 150 °C (P3HT:IC<sub>60</sub>BA and PTB:PC<sub>70</sub>BM devices) or 130°C (DTS-F:PC<sub>70</sub>BM devices).

Measurements: The J-V characteristics were measured using a Keithley 236 source-measure unit (SMU) under AM 1.5 G illumination from a calibrated solar simulator with an irradiation intensity of 100 mW/cm<sup>2</sup>. To minimize measurement errors, we cross-checked the photocurrents that were obtained from the IPCE spectra with those that were obtained from the J-V plots. The depth-profile data were obtained with a TOF-SIMS (ION-TOF, Germany) instrument; a 25 keV Bi<sub>1</sub><sup>+</sup> beam was used for the analyses, and a 3 keV Cs<sup>+</sup> beam was used for sputtering. The absorption spectra and RMS roughness of the samples were characterized using an absorption spectrophotometer (Lambda 750, Perkin Elmer) and AFM measurements, respectively. The WF analysis was conducted using Kelvin probe measurements.



**Fig. S1.** (a) WFs of the bare ITO and ITO/PEI samples. (b) Dipole formation between the oxygen anions of ITO and the protonated amines of PEI. (b) Energy-level diagram of the ITO/PEI cathode and acceptors.

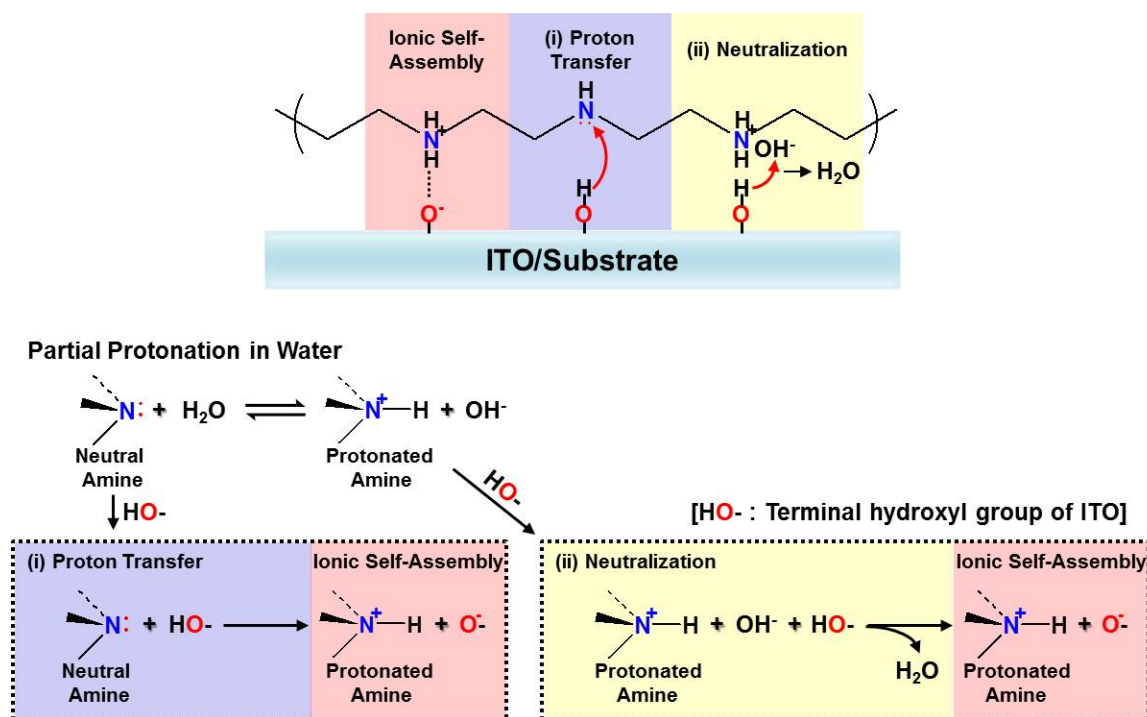
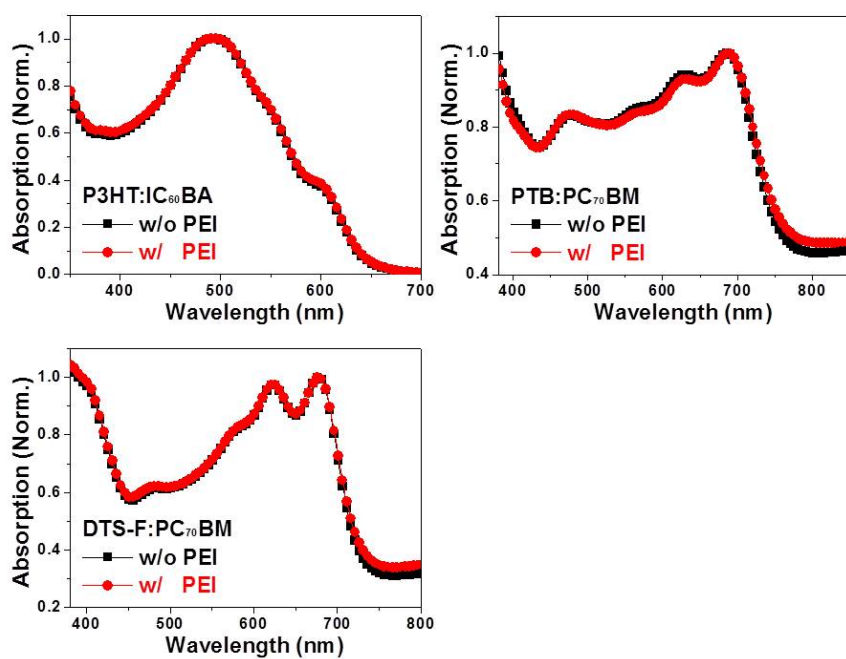
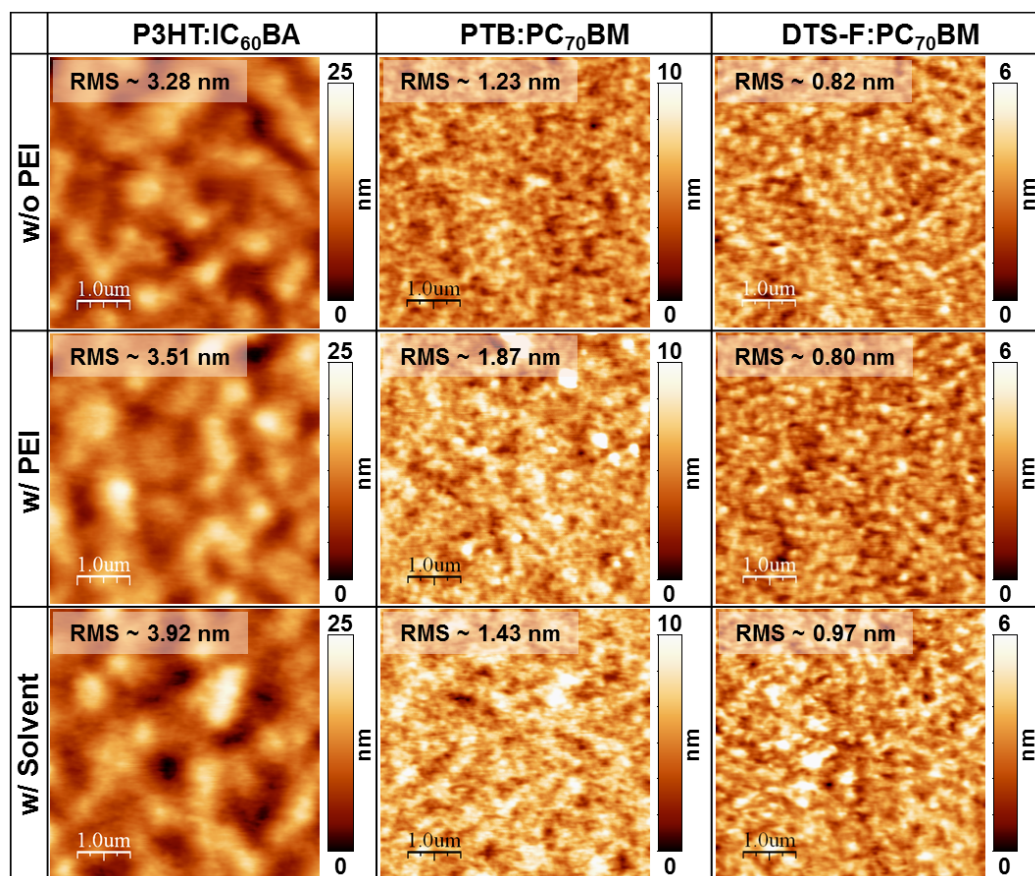


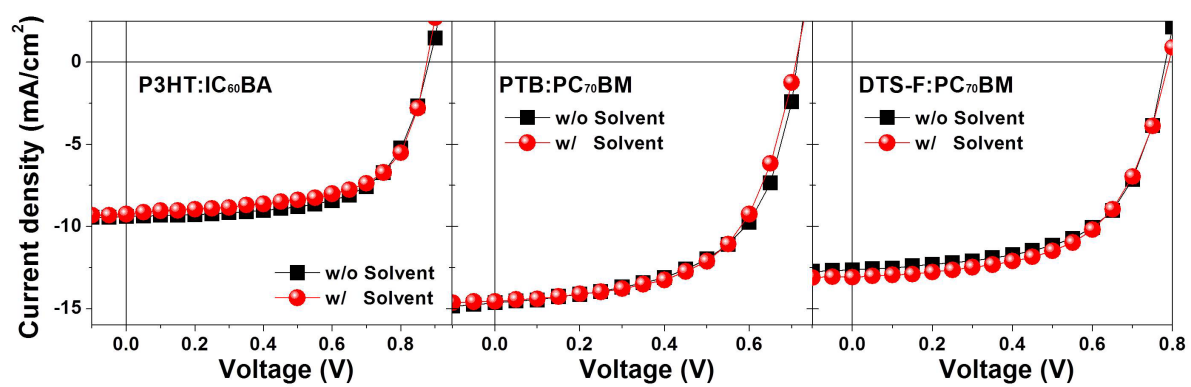
Fig. S2. Chemical reactions and ionic self-assembly between PEI and ITO.



**Fig. S3.** Absorption spectra of the BHJ films coated with the BHJ and PEI:BHJ solutions.

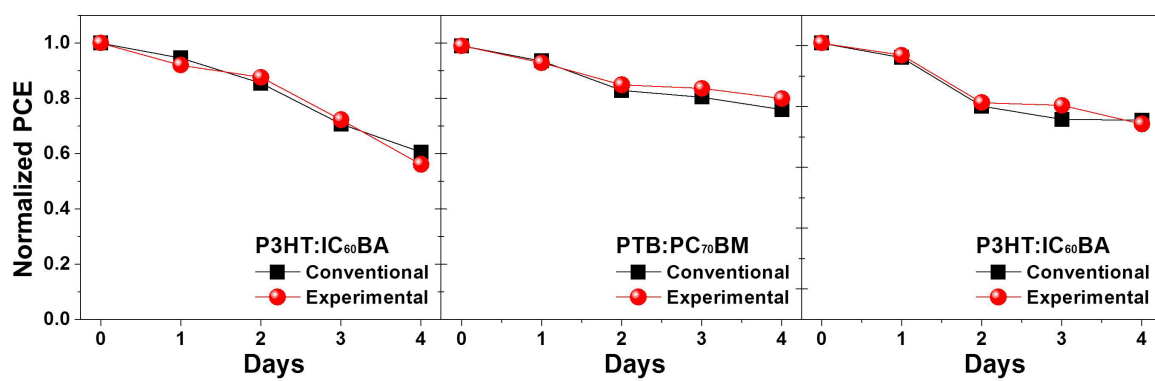


**Fig. S4.** Topographies of the BHJ films coated with the BHJ, PEI:BHJ, and solvent:BHJ solutions.

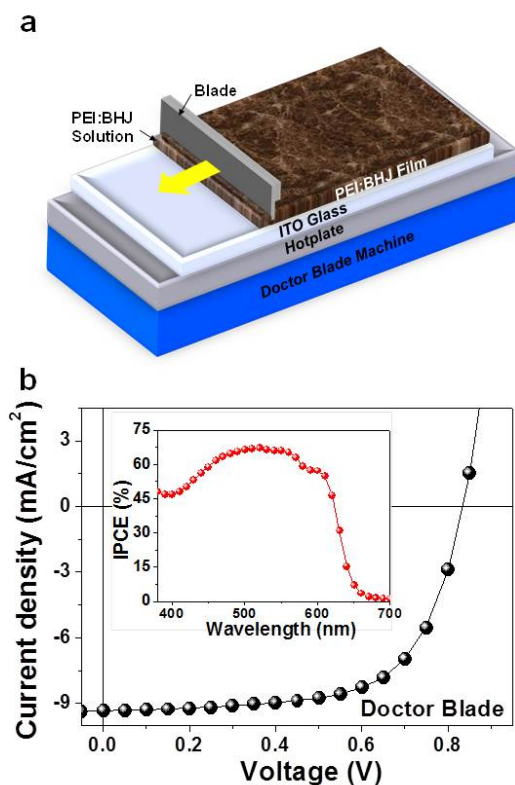


**Fig. S5.**  $J$ - $V$  characteristics of the I-OSCs using the BHJ films coated with the BHJ and solvent:BHJ solutions.





**Fig. S6.** Normalized PCEs as a function of storage time for the I-OSCs in the ambient air.



**Fig. S7.** (a) Schematic representation of the doctor-blade coating process. (b)  $J$ - $V$  characteristics and IPCE spectra of the I-OSCs based on P3HT:IC<sub>60</sub>BA.

For the doctor-blade-coated PEI:BHJ film, the P3HT:IC<sub>60</sub>BA solution was mixed with a dilute PEI solution (0.1 wt%) in a 7:1 mass ratio. The doctor-blade-coated PEI:BHJ film was obtained with a coating speed of 10 mm/s and a gap distance (i.e., the distance between the blade and the substrate) of 0.2 mm in air at room temperature; the film was annealed in a glass Petri dish.