

<Supporting Information>

**Efficient Planar-Heterojunction Perovskite Solar Cells Achieved via Interfacial Modification of Sol-gel ZnO Electron Collection Layer**

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## Experimental

### *Synthesis of materials*

The synthesis of  $\text{CH}_3\text{NH}_3\text{I}$  has been reported elsewhere.<sup>1</sup> Briefly, the  $\text{CH}_3\text{NH}_3\text{I}$  was synthesized by reacting 27.86 mL methylamine (40% in methanol, Sigma-Aldrich) and 30 mL hydroiodic acid (57 wt%, Sigma-Aldrich) in a 250 mL round-bottomed flask at 0 °C for 2 h with stirring. A yellowish raw product ( $\text{CH}_3\text{NH}_3\text{I}$ ) was obtained using a rotary evaporator and re-dissolved in 80 mL absolute ethanol; a white-colored powder ( $\text{CH}_3\text{NH}_3\text{I}$ ) was formed via addition of 300 mL ethyl acetate. After filtration, the powder was washed repeatedly with ethyl acetate. Recrystallization from ethanol yielded a pure crystal of  $\text{CH}_3\text{NH}_3\text{I}$ . The crystal was collected and dried at 60 °C in a vacuum oven for 24 h. For the ZnO precursor solution, zinc acetate dehydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ , Sigma-Aldrich, 99.9%, 1 g) and ethanolamine ( $\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$ , Sigma-Aldrich, 99.8%, 0.28 g) were dissolved in 2-methoxyethanol ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ , Sigma-Aldrich, 99.8%, 10 mL) and the solution was vigorously stirred in air for 12 h.<sup>2</sup>

### *Fabrication of planar-heterojunction perovskite solar cells*

Patterned ITO/glass substrates (15  $\Omega/\text{sq}$ ) were cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried overnight in an oven. For the electron-selective layer of the PHJ perovskite solar cells, a sol-gel ZnO precursor solution was spin-cast in air onto the pre-cleaned and UV/ozone-treated ITO/glass substrates at 3,000 rpm for 30 s (~ 30 nm thickness). Then, the films were pre-heated on a hot plate at 150 °C for 10 min and further annealed in a covered glass Petri dish at 290 °C for 10 min in air. After cooling to room temperature, the ZnO films were rinsed with deionized water and ethanol, and then dried in air for 10 min at 200 °C. For interfacial modification of the top surface of the ZnO layer, PCBM (10 mg  $\text{mL}^{-1}$  in chlorobenzene), were spin-coated onto the ZnO film and then annealed at 80 °C for 5 min. The thickness of the PCBM is about 10 nm. Then, the substrates transferred into a  $\text{N}_2$ -filled glove box, where the thin  $\text{PbI}_2$  films were spin-coated from a solution of 460 mg/mL  $\text{PbI}_2$  in DMF at 2,500 - 3,000 rpm for 15 s and annealed at 150 °C for 10 min, after which the films were dried for approximately 15 min. The  $\text{PbI}_2$  films were dipped in a solution of  $\text{CH}_3\text{NH}_3\text{I}$  in 2-propanol (10 mg  $\text{mL}^{-1}$ ) to form  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite films. The HTL was then deposited by spin coating a solution of PTB7-Th in chlorobenzene (20 mg  $\text{mL}^{-1}$ ) at 1,000 rpm for 30 s. For our optimized devices, a spiro-OMeTAD-based HTL (80 mg spiro-OMeTAD, 28.8  $\mu\text{L}$  4-tert-butylpyridine, 17.5  $\mu\text{L}$  of a stock solution of 520 mg  $\text{mL}^{-1}$  lithium bis(trifluoromethylsulphonyl)imide in acetonitrile, and 29  $\mu\text{L}$  of a stock solution of 300 mg  $\text{mL}^{-1}$  tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) bis(trifluoromethylsulphonyl)imide in acetonitrile in 1 ml chlorobenzene) was deposited by spin coating at 4,000 rpm for 30s. Finally, those samples were pumped down to a vacuum

( $1 \times 10^{-7}$  Torr; 1 Torr  $\approx$  133 Pa), and an approximately 5 nm-thick MoO<sub>x</sub> and 110 nm-thick Ag electrode (active area: 4.64 mm<sup>2</sup>) was deposited on top of the devices.

#### *Characterization of planar-heterojunction perovskite solar cells*

The J-V characteristics were measured using a Keithley 237 source measure unit in an N<sub>2</sub> atmosphere. The solar-cell parameters were obtained using an AM 1.5 G solar simulator with an irradiation intensity of 100 mW·cm<sup>-2</sup>. The lamp was calibrated with an NREL-calibrated KG5 filtered silicon reference cell. The light intensity of the lamp was modulated by using neutral density filters with a various optical density. The IPCE measurement was carried out by using QEX10 solar cell instrument (PV Measurement, Inc., USA) with chopping frequency of 100 Hz. The surface morphology of films were measured by AFM measurement (Park systems corp., XE-100). SEM measurement were performed by S-4700 SEM instrument (Hitachi, Japan).

For TEM measurement, PbI<sub>2</sub> film was first formed by drop casting PbI<sub>2</sub> solution (0.5 M in DMF) on 200 mesh copper grids (Electron Microscopy Sciences). The PbI<sub>2</sub> film was transformed into CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite film by drop CH<sub>3</sub>NH<sub>3</sub>I solution (10 mg/ml in IPA) onto the PbI<sub>2</sub> film. TEM images of the sample films were recorded using a Tecnai G2 F30 S-Twin microscope at an acceleration voltage of 300 kV.

For the impedance spectroscopy measurement of the devices, the frequency response analyzer (FRA) system of the AUTOLAB instrument was used. Sinusoidal voltage signals V(t) over the frequency range of 1 Hz ~ 1 MHz, were applied to the perovskite devices by the potentiostat at different applied bias (0 V ~ 8 V) under 1-sun illumination.

To reveal the electronic structure of ITO, ZnO, PCBM, and ZnO/PCBM, the UPS measurements were performed by using an AXIS-NOVA instrument (Kratos Analytical Ltd, England) with a He I (21.2 eV) excitation source at an ultrahigh vacuum of 1.0 x 10<sup>-10</sup> Torr, at the Deajeon Center of Korea Basic Science Institute (KBSI).

Figure S1.

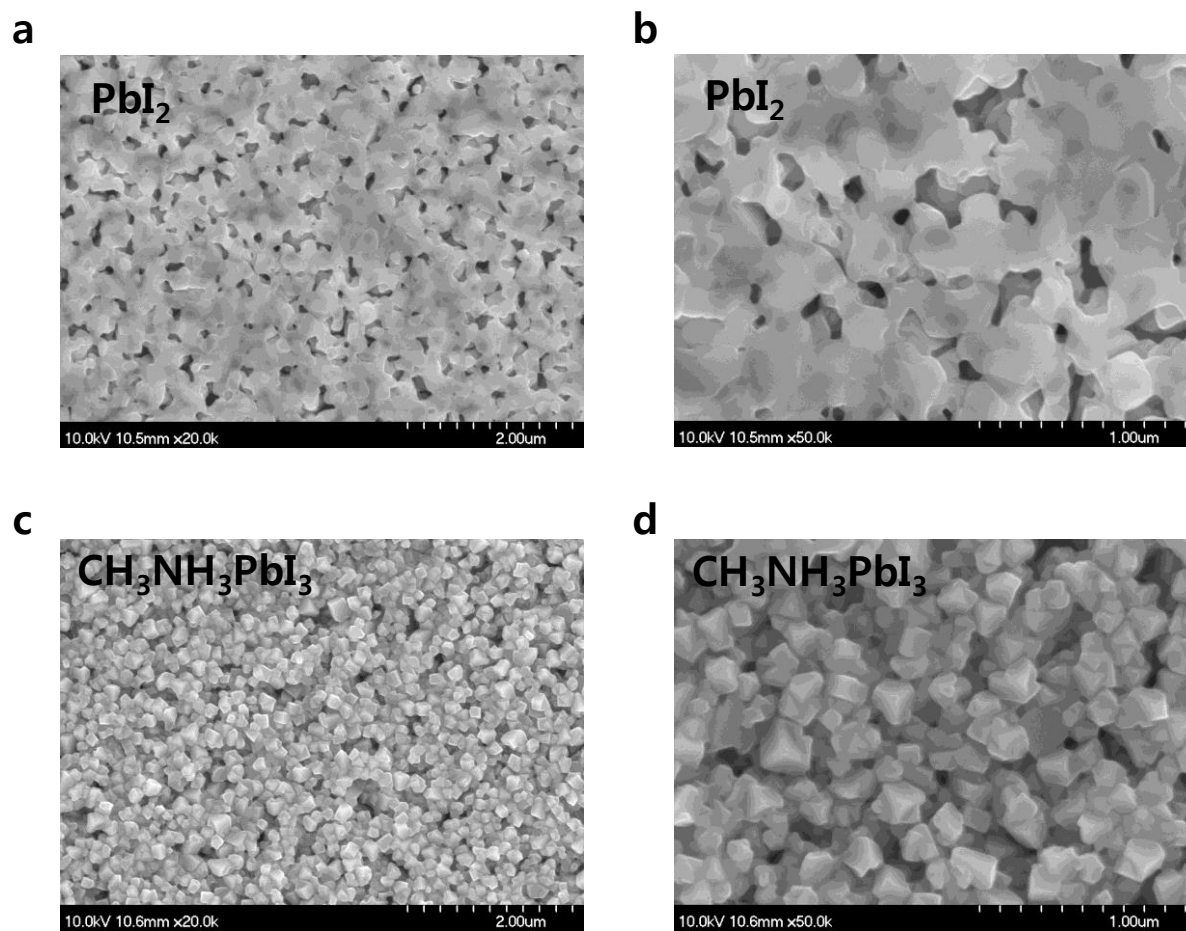


Figure S1. SEM top views of (a) a  $\text{PbI}_2$  and (c) a  $\text{CH}_3\text{NH}_3\text{PbI}_3$  film. (b), (d) High magnification SEM images of the  $\text{PbI}_2$  and the  $\text{CH}_3\text{NH}_3\text{PbI}_3$  film, respectively.

Figure S2.

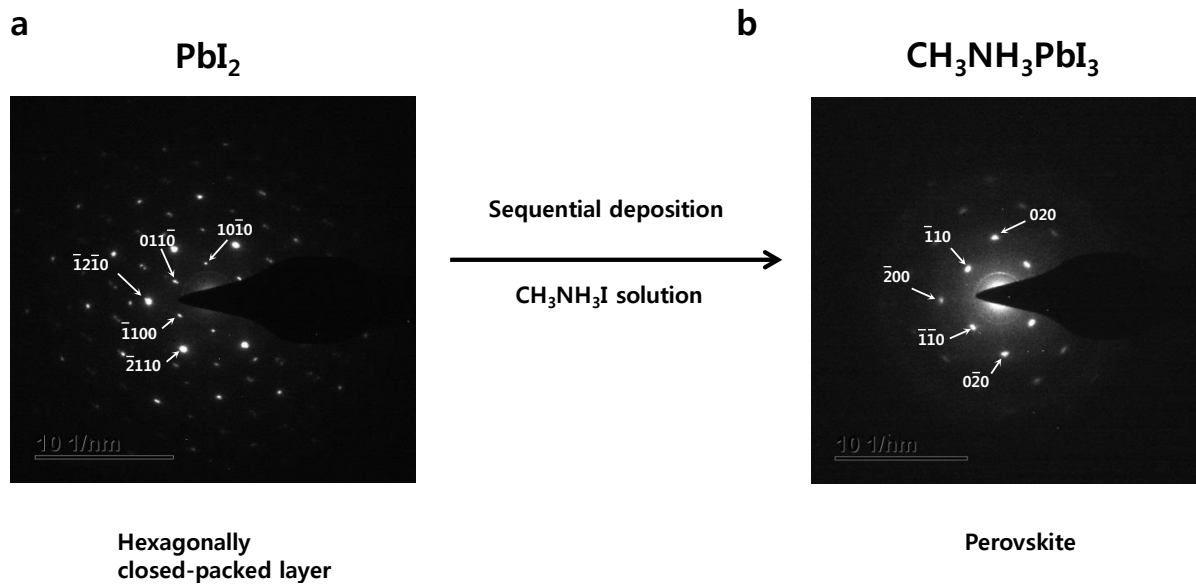


Figure S2. Selected area electron diffraction (SAED) patterns of (a) a PbI<sub>2</sub> and (b) a CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film. Estimated crystalline structure of the films are described in below.

**Figure S3.**

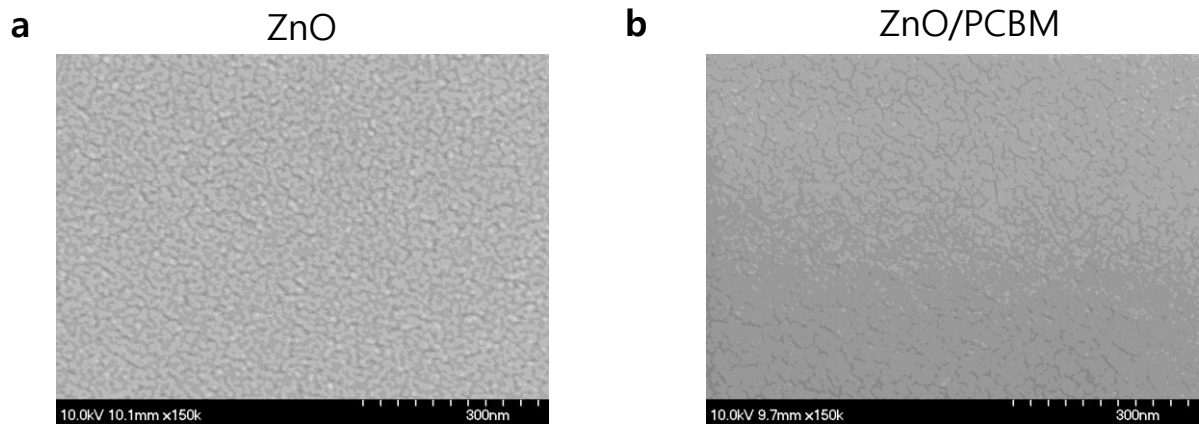


Figure S3. SEM top views of (a) a ZnO and (b) ZnO/PCBM substrates.

**Figure S4.**

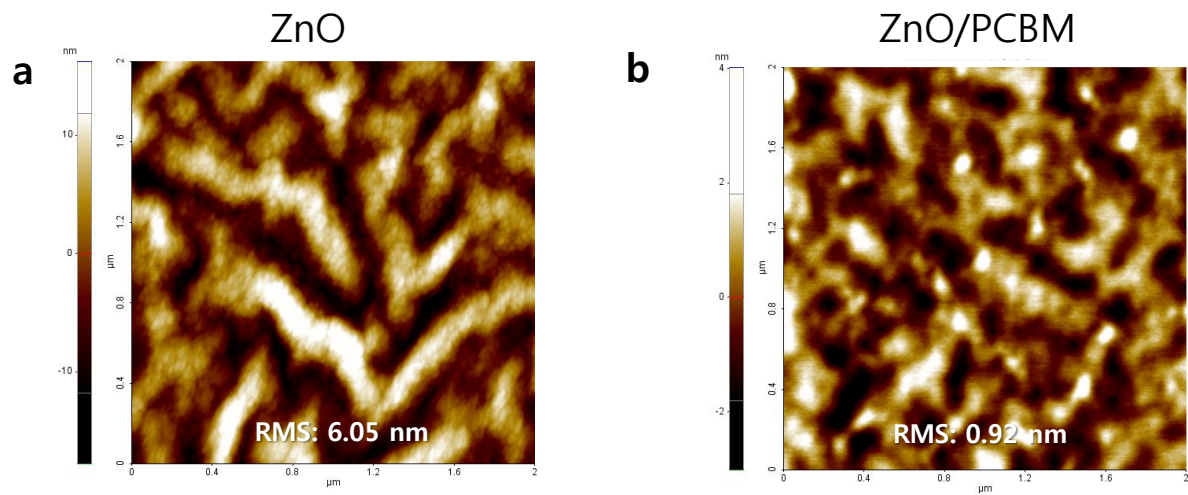


Figure S4. AFM topographic images of (a) a ZnO and (b) ZnO/PCBM substrates.

Figure S5.

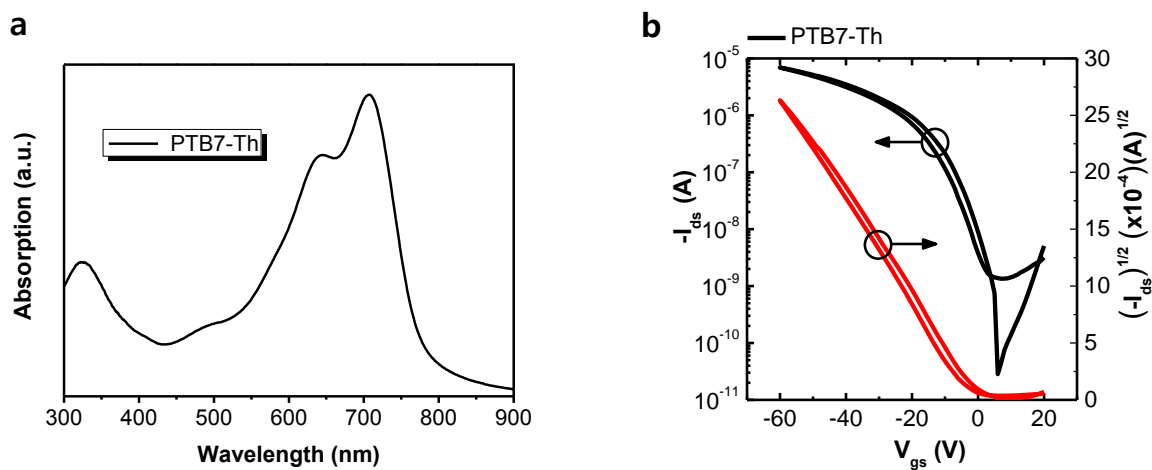


Figure S5. (a) UV-Vis absorption spectrum of PTB7-Th polymer on fused silica substrate. (b) Transfer characteristics of OFETs on a heavily n-doped Si/SiO<sub>2</sub> silicon wafer ( $t_{\text{ox}} \sim 200$  nm) using PTB7-Th semiconductor. The device structure is n-doped Si/SiO<sub>2</sub> silicon/PTB7-Th/Au (top contact and bottom gate device).



Figure S6.

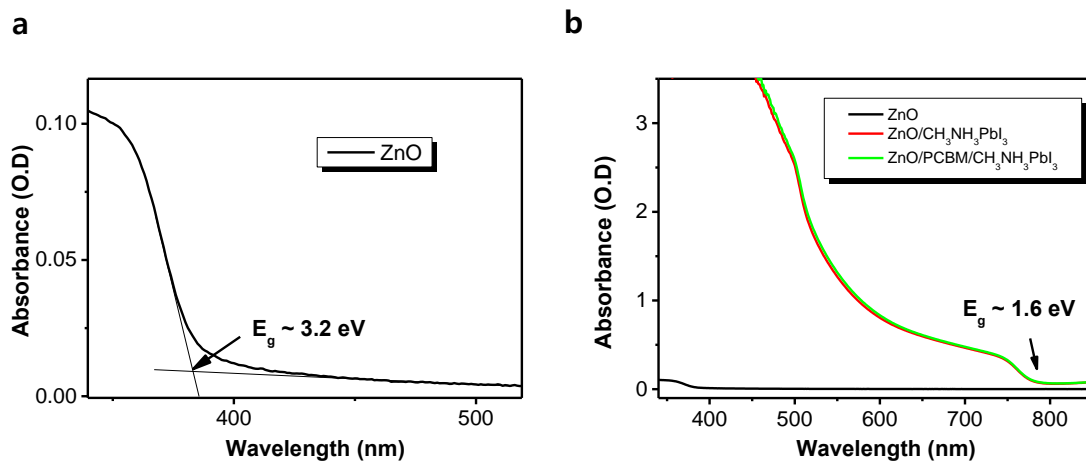


Figure S6. UV-Vis absorption spectrum of (a) ZnO film on fused silica substrate and (b)  $\text{CH}_3\text{NH}_3\text{PbI}_3$  on ZnO and ZnO/PCBM substrates. Optical band gap ( $E_g$ ) values are indicated in the both graphs.

Figure S7.

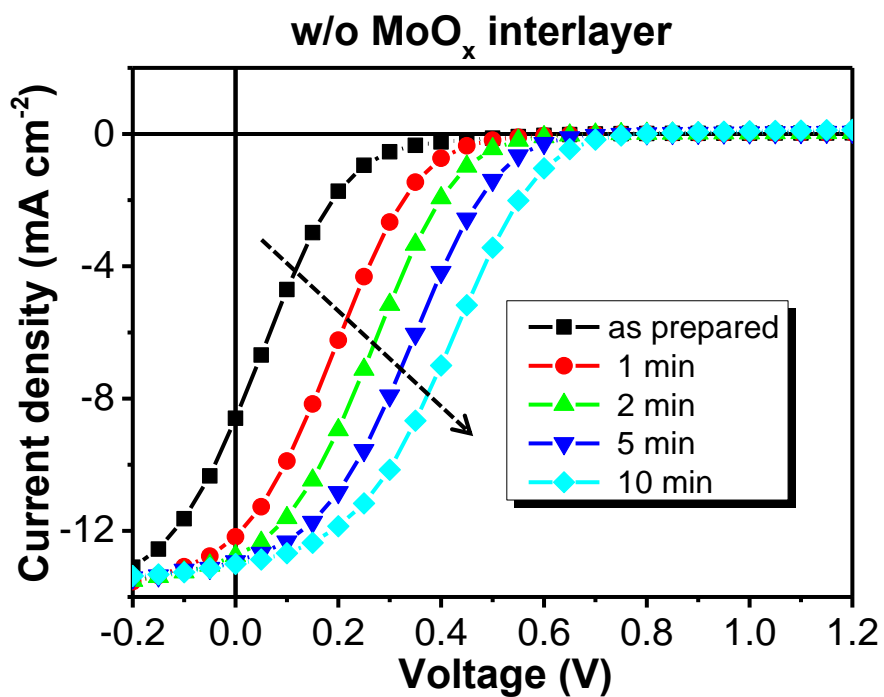


Figure S7. Current density-voltage characteristics of the planar-heterojunction perovskite solar cells with a structure of ITO/sol-gel ZnO/PCBM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PTB7-Th/Ag measured under AM 1.5G irradiation at 100 mW cm<sup>-2</sup>. The devices were measured with illumination time and the performances of the device increase with the illumination time.

Figure S8.

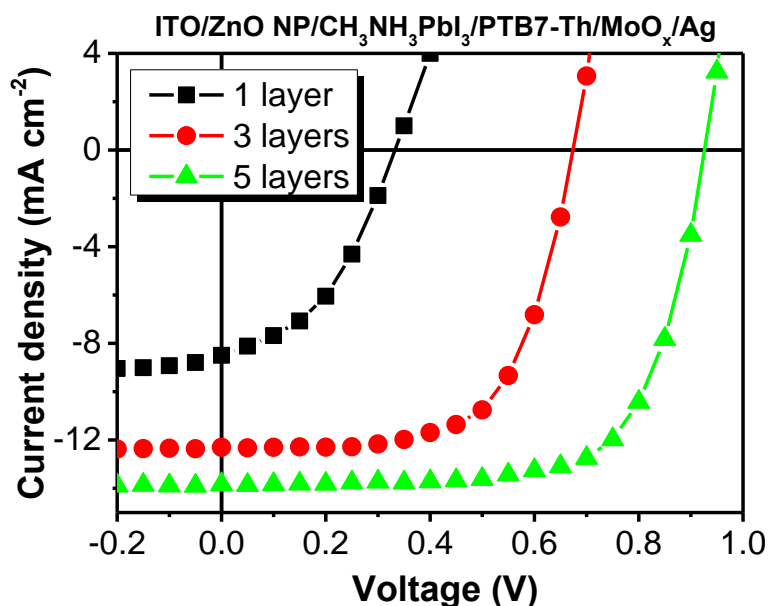


Figure S8. Current density-voltage characteristics of the planar-heterojunction perovskite solar cells with a structure of ITO/ZnO NP/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PTB7-Th/Ag measured under AM 1.5G irradiation at 100 mW cm<sup>-2</sup>.

# of layers (mean ± s.d.)	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF	PCE (%)	R <sub>s</sub> (Ω·cm <sup>2</sup> ) <sup>[a]</sup>
1	0.30 ± 0.02	8.20 ± 0.22	0.41 ± 0.02	1.01 ± 0.15 (1.21)	15.8 ± 1.5
3	0.66 ± 0.02	12.1 ± 0.34	0.64 ± 0.01	5.12 ± 0.25 (5.38)	8.0 ± 0.77
5	0.90 ± 0.04	14.16 ± 0.35	0.68 ± 0.02	8.55 ± 0.41 (8.98)	6.4 ± 1.28

[a] The R<sub>s</sub> of the perovskite solar cells were calculated using (dJ/dV)<sup>-1</sup> at V = V<sub>oc</sub>.

Figure S9.

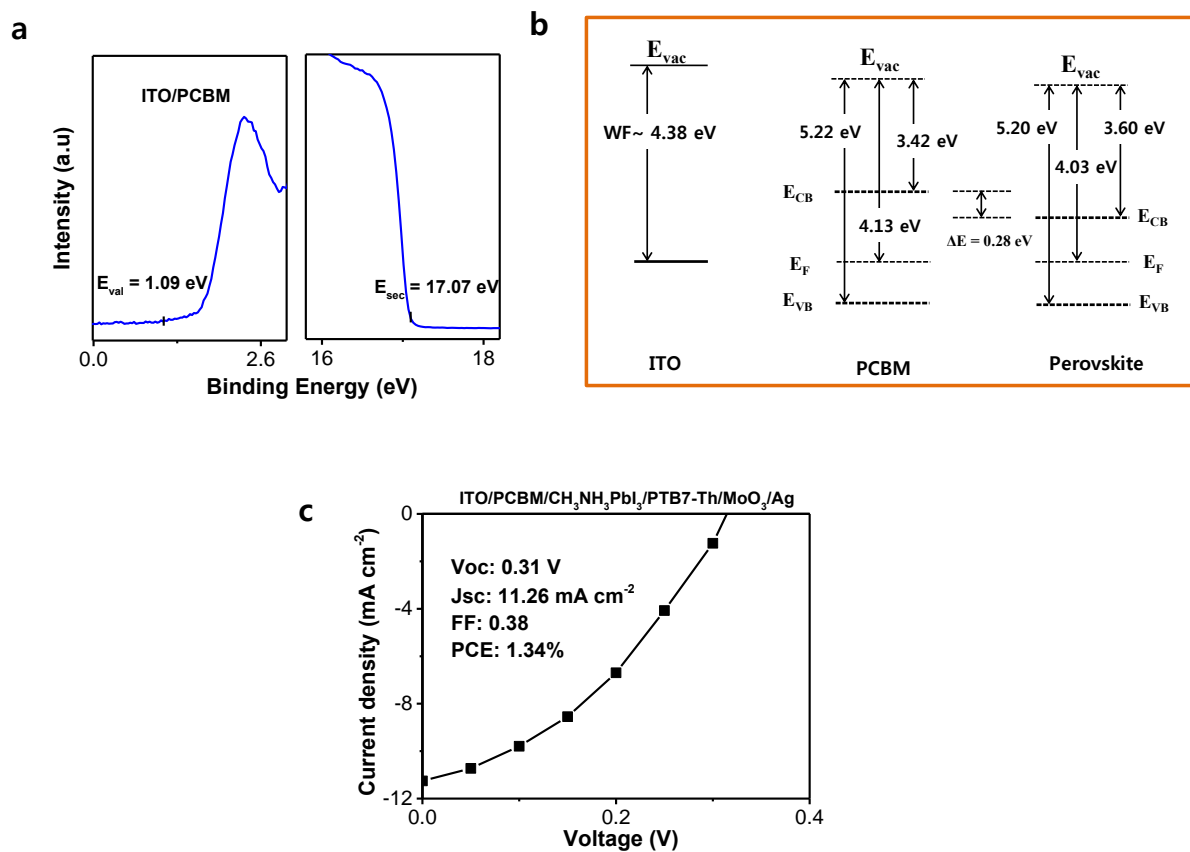


Figure S9. (a) UPS spectra of ITO/PCBM substrate. (left) the valence band edge and (right) magnified section of the photoemission onset. (b) Energy-level diagrams of ITO, ITO/PCBM, perovskite films resulting from the UPS studies. (c) Current density-voltage characteristics of the planar-heterojunction perovskite solar cells with a structure of ITO/PCBM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PTB7-Th/Ag measured under AM 1.5G irradiation at 100 mW cm<sup>-2</sup>.

Figure S10.

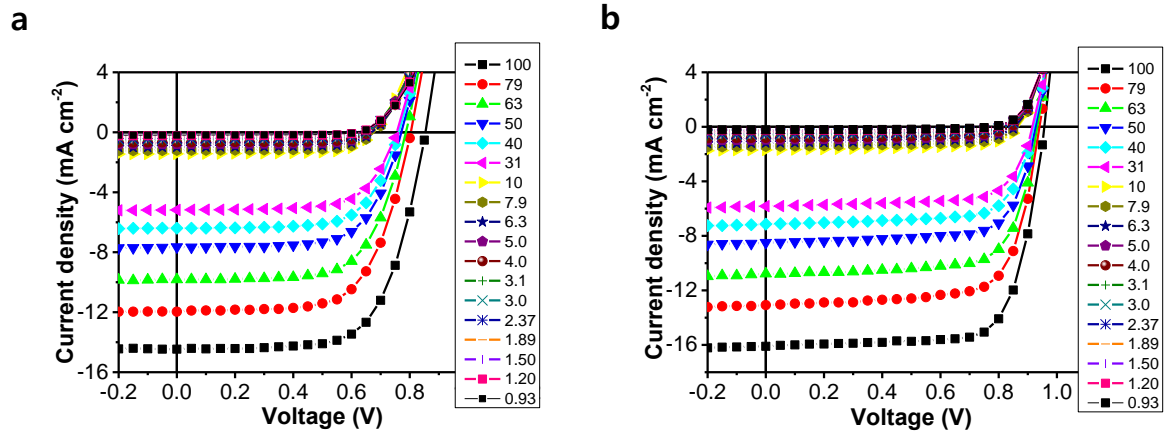


Figure S10. Current density-voltage characteristics of the planar-heterojunction perovskite solar cells with (a) only ZnO and (b) ZnO/PCBM ECL with light intensity.

Table S1. Photoemission parameters obtained from UPS measurement and optical bandgap ( $E_g$ ) of various substrates.

Substrate	$E_{\text{valence}}$	High B.E	WF	HOMO	LUMO	$\Delta E_g$
ITO	-	16.82	4.38	-	-	-
ITO/ZnO	3.1	17.41	3.79	6.89	3.69	3.2
ITO/ZnO/PCBM	1.50	17.46	3.74	5.24	3.44	1.8
ITO/ZnO/Perovskite	1.17	17.17	4.03	5.2	3.6	1.6

1. D. Liu and T. L. Kelly, *Nat. Photon.*, 2014, **8**, 133-138.
2. Y. Sun, J. H. Seo, C. J. Takacs, J. Seifter and A. J. Heeger, *Adv. Mater.*, 2011, **23**, 1679-1683.