Electronic Supplementary Information

Enhancement in the efficiency of an organic–inorganic hybrid solar cell with a doped P3HT hole-transporting layer on a void-free perovskite active layer

Yunlong Guo, Chao Liu, Kento Inoue, Koji Harano, Hideyuki Tanaka,* and Eiichi Nakamura*

Department of Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033.

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1. Materials

Preparation for perovskite precursor

The perovskite precursor was prepared the following procedure in the reference.[1] Thus, 12 ml of hydroiodic acid (57 wt% in water, Sigma-Aldrich) was added dropwise in 2 h to 24 ml of methylamine (33 wt% in ethanol, Sigma-Aldrich) in 100-ml ethanol. Solvent was removed on a rotary evaporator, and the product was recrystallized from diethyl ether to obtain methylammonium iodide (MAI) as a crystalline powder. The powder was dried in a vacuum chamber at 65 °C for 12 h. In a grove box (N_2 atmosphere), MAI and $PbCl_2$ (Aldrich, 99.999%) were dissolved in dimethylformamide (Tokyo Chemical Industry Co., 99.5%) with a molar ratio of 3:1 and stirred for 12 h at 65 °C to obtain a precursor solution. Total material concentration was 20 wt%.

Preparation of TiO$_x$ precursor [2]

To prepare a TiO$_x$ precursor solution, 438 μl of commercially available titanium isopropoxide (Tokyo Chemical Industry Co.) was diluted in isopropanol 3 ml. In a separated flask, 83 μl of a 1 M HCl solution was diluted with isopropanol (3 ml), andwas added dropwise to the titanium precursor solution under rapidly stirring. The solution was filtered through a PTFE membrane filter with 0.2 μm pore size just before use.

Materials for the hole-transporting layer

High purity regioregular P3HT (99.995%) with Mn=30000~60000, Li–TFSI (>99.0%) and D-TBP (97%) were purchased from Aldrich. High purity chlorobenzene was used as solvent for P3HT.

2. Scanning electron microscopy

SEM observations were conducted on an FEI Magellan 400L equipped with AMETEK/EDAX Genesis APEX4 at a landing voltage of 1 kV under a reduced pressure of 5×10^{-5} Pa.
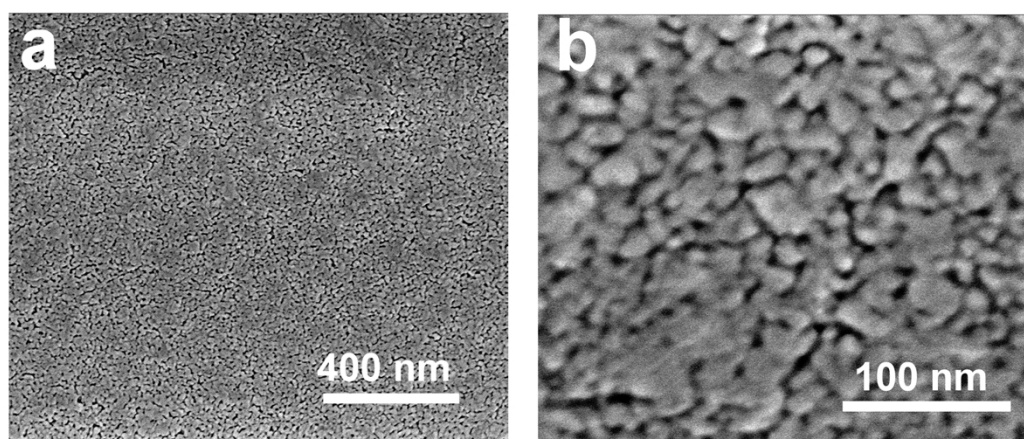

Figure S1. SEM image of TiO$_x$ coated on ITO substrate (a), and enlarge image (b)
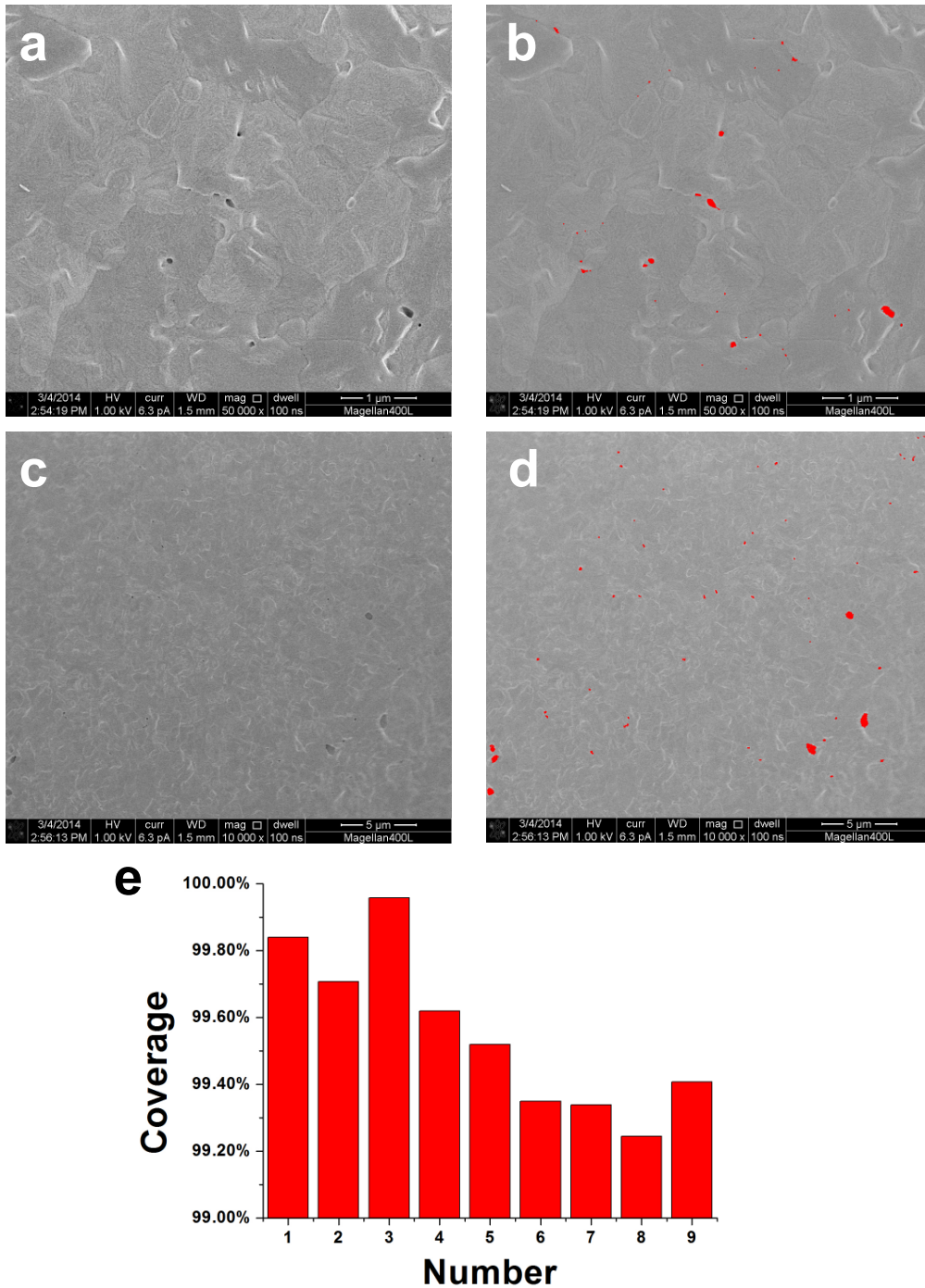
Figure S2. Original SEM images (a,c) and void-labeled SEM images (b, d) of the rapidly cooled perovskite layer. Estimated coverage is 99.84% based on the integration of the red area in (b), and 99.71% estimated from (d). (e) Statistical analysis the coverage based on 9 different samples. The average value is 99.55% (± 0.24%).
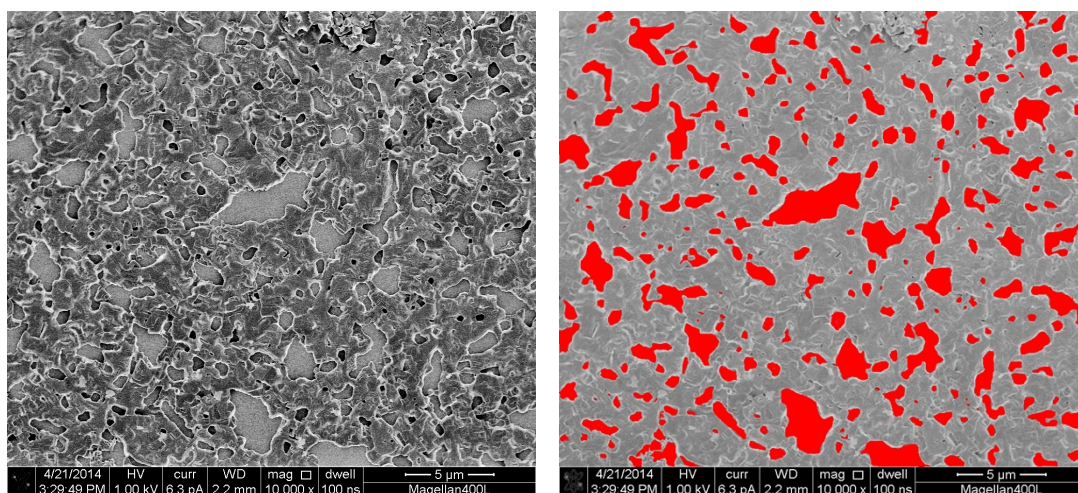
Figure S3. Original SEM images (left) and void-labeled SEM images (right) of the rapidly cooled perovskite layer of slowly cooled perovskite layer. Estimated coverage is here 82.2%.

3. Photovoltaic performances

Table S1. The details of photovoltaic performance of solar cell using HTLs H-1 to H-6 containing P3HT, Li–TFSI and D-TBP in a variety of ratios.

HTL	P3HT[a] (mg)	Li–TFSI[b] (mg)	D-TBP[c] (mg)	Jsc (mA·cm^{-2})	Voc (V)	FF (%)	PCE (%)	R_S (Ω·cm^2)	σ (S·m^{-1})
H-1	15	0	0	17.7	0.92	56.2	9.2	12.4	5.4×10^{-4}
H-2	15	0.54	0	19.3	0.94	61.5	11.2	8.9	5.4×10^{-2}
H-3	15	0.54	8.8	19.1	0.98	66.3	12.4	8.5	6.4×10^{-2}
H-4	15	0	8.8	17.5	0.89	41.6	6.5	48.3	3.4×10^{-3}
H-5	15	0.07	2.9	18.8	0.94	57.8	10.2	12.5	4.3×10^{-2}
H-6	15	0.19	2.9	19.9	0.96	61.2	11.7	11.3	5.0×10^{-2}

[a]P3HT dissolved in 1 ml chlorobenzene, [b]Li–TFSI dissolved in 6.8 μl acetonitrile, [c]D-TBP (3.4 μl (2.9 mg) or 10.2 μl (8.8 mg)) was added into the P3HT:Li–TFSI mixture solution.
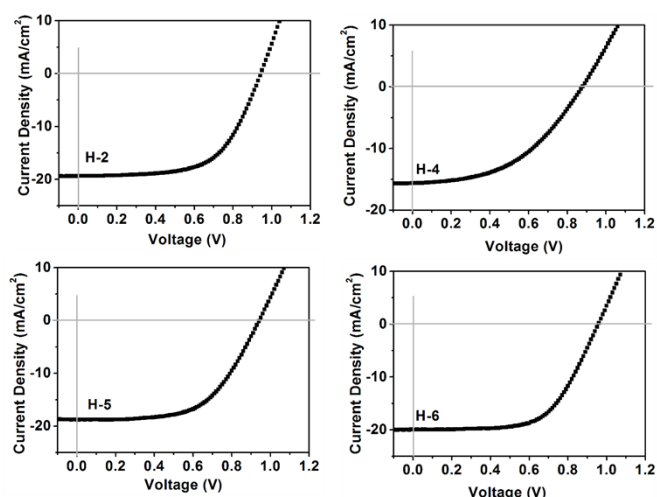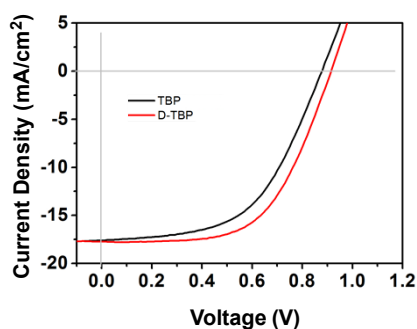
Figure S4. J-V curves of the cell using H-2, H-4, H-5, and H-6 as HTL.

Additive	Jsc (mA·cm^{-2})	Voc (V)	FF (%)	PCE (%)
D-TBP	17.7	0.91	59.0	9.1
TBP	17.6	0.94	54.0	8.4

Fig

ure S5. J-V curves and the photovoltaic parameters of the cell using D-TBP or TBP (3.4 μl) added P3HT (15mg dissolved in 1 ml chlorobenzene) with the Li-TFSI (6.8 μl acetonitrile).
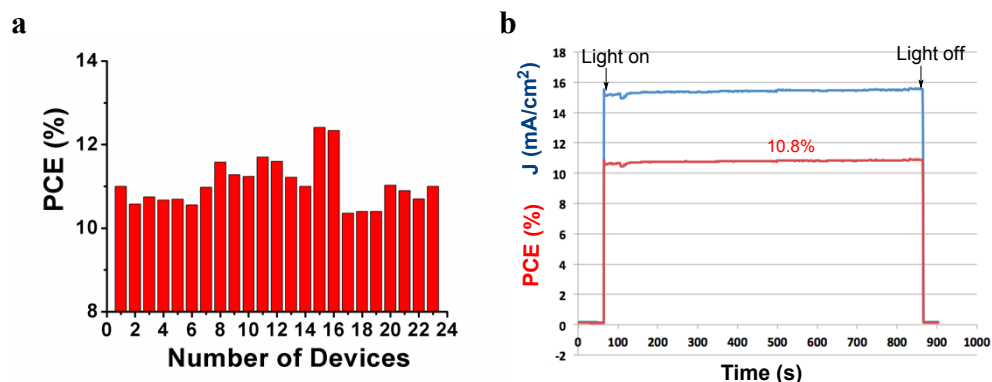

Figure S6. Solar cell performances of the H-3 devices. (a) Statistical distribution of 23 devices. The average value of PCE is 11.1% (± 0.55%). (b) Photocurrent density and power conversion efficiency at 0.7 V applying voltage under the irradiation of 10.8% device.

4. Absorption and photoluminescence spectra

Absorption spectrum of the perovskite thin films was recorded on a Jasco V-670 spectrophotometer, and photoluminescence was examined on a fluorescence spectrophotometer (HITACHI, F-4500).
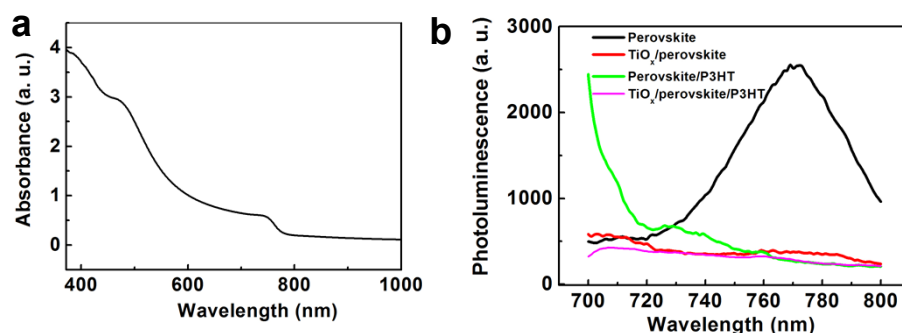

Figure S7. Absorption spectrum of the perovskite thin films (a), and the photoluminescence (b) from the perovskite on the different configuration perovskite/pristine P3HT, TiO$_x$/perovskite and TiO$_x$/perovskite/pristine P3HT. All thin films were coated on to the quartz substrate.

5. Transporting property and X-ray diffraction

To measure the field-effect mobility, we fabricated bottom-gate/bottom contact field-effect transistor devices on SiOx/Si wafer. Highly doped Si and SiOx (300 nm) formed gate electrode and gate dielectrics, respectively. The source and drain electrodes based on gold were prepared by photolithography. The channel length and width were 9 μm and 325 μm, respectively. A hole transporting material containing different additives (15 mg/ml, in chlorobenzene) was spin-coated its surface in a glove-box and encapsulated before the measurements. The I-V characteristics were obtained on a Keithley SCS 4200 in air and the linear region mobility was calculated according to the following formula:

$$\mu = \frac{\partial I_{DS}}{\partial V_{GS}} \frac{L}{W C_i V_{DS}}$$

Here, the I_{DS} is the current collected by drain electrode and V_{GS} is gate voltage, L is the channel length and W is the channel width. The C_i is the captaincy of gate dielectrics and V_{DS} is the voltage between drain and source.

The XRD experiment was performed on a Rigaku SmartLab X-Ray diffractometer equipped with a D/teX Ultra detector. The measurement employed the Cu-Kα line focused radiation at a 9 kW (45 kV, 200 mA) power using a 0.02° 2θ step scan from 3.0–30.0° with a scanning speed of 10° min^{-1}.
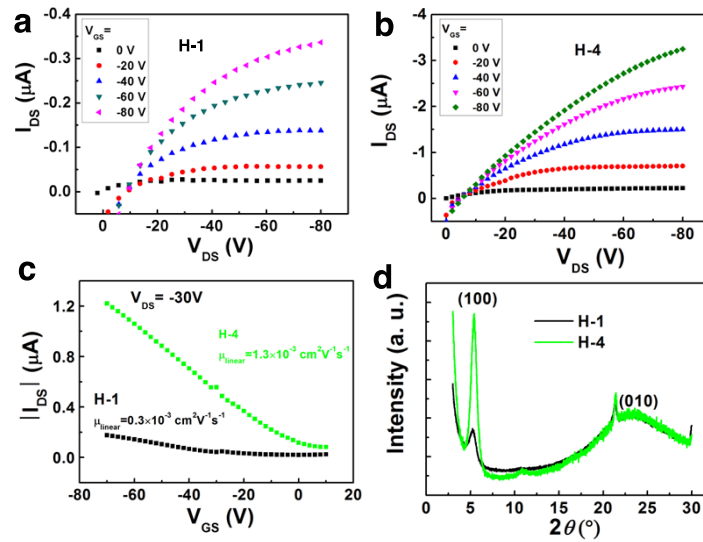
Figure S8. The I-V characteristics of field-effect transistor devices (a–c) and XRD (d) of different HTL layers. The output curves of H-1 (a) and H-4 thin films (b), and its corresponding transfer curves (c).
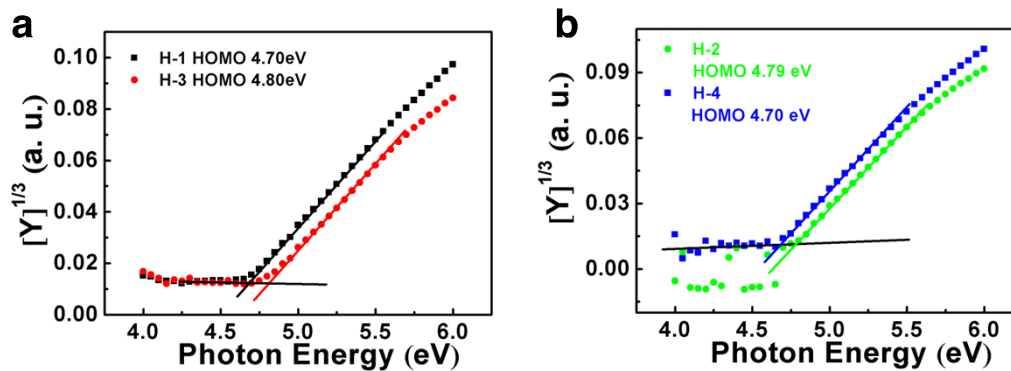
6. Photoemission yield spectroscopy

Figure S9. Photoemission spectra of different P3HT thin-films, (a) H-1 (black square, pristine P3HT) and H-3 (red circle, P3HT doped with Li–TFSI and D-TBP), and (b) H-2 (green circle, P3HT doped with Li–TFSI) and H-4 (blue square, P3HT mixed with D-TBP) coated on ITO substrate. The HOMO level was estimated from the intersection of base line (black) and liner fit lines.
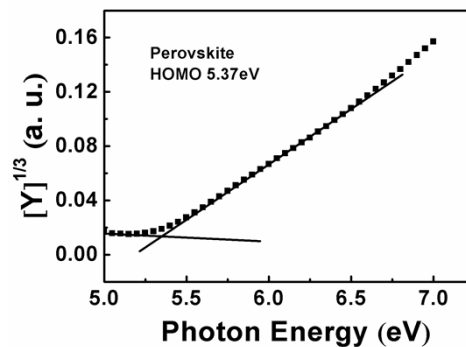

Figure S10. Phtoemission spectrum of perovskite thin-film coated on ITO substrate.

7. Solar cell fabrication and measurement

An indium tin oxide (ITO) layer on the glass substrate used for this study was 145 nm thick with a sheet resistance of 8 Ω/square. The surface roughness, R_a, was 0.7 nm and the R_{max} was 8.1 nm. Prior to the formation of the buffer layer, the patterned ITO glass was ultrasonically cleaned using a surfactant, rinsed with water, and then finally given UV–ozone treatment. A 45-nm thick electron-transporting layer TiO_x was deposited by spin-coating (3000 rpm for 30s) of the precursor solution (see materials section) and annealed at 500 °C for 30 min in air atmosphere. To form the $CH_3NH_3PbCl_xI_{3-x}$ layer, a 20 wt% precursor solution was spin-coated on the TiO_x layer at 500 rpm for 60s and annealed at 95 °C for 100 min in a nitrogen-filled glove box. The hole-transporting layer (see materials section) was then deposited by spin coating (2500 rpm for 30s). The top electrode (Ag, 150 nm) was deposited through a metal shadow mask, which defined a 2 mm stripe pattern perpendicular to the ITO stripe. Finally, the fabricated cell was encapsulated with backing glass using a UV-curable resin under nitrogen atmosphere.

The encapsulated cells were subjected to *J–V* measurements under both dark and irradiated conditions. Current–voltage sweeps were taken on a Keithley 2400 source measurement unit controlled by a computer. The light source used to determine the PCE was an AM1.5G solar simulator system (Sumitomo Heavy Industries Advanced Machinery) with intensity of 100 mW/cm^2. The solar cells were masked with a metal aperture to define the active area, typically 4 mm^2. The details of J–V curve test were as follows: step-size, 0.01V; dwelling time, 0.01s; the scanning range from 1.2 V to – 0.3 V. For the external quantum efficiency measurement, a constant power mode was employed using monochromatized photons from halogen or xenon lamps. And for the estimation of IQE spectrum, one-time reflection spectrum from the cell was measured by V-670 spectrophotometer.
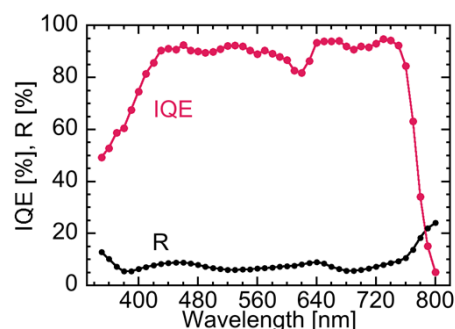

Figure S11. The IQE and reflectance spectra of optimized perovskite solar cells using hole-transporting H-3.

[1] Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J. *Science* **2012,** *338,* 643.
[2] Docampo, P.; Ball, J. M.; Darwich, M.; Eperon, G. E.; Snaith, H. J. *Nat. Commun.* **2013,** *4:2761* doi: 10.1038/ncomms3761.