## **Supporting information**

Elevated efficiency and stability of hole-transport-layer-free perovskite solar cells induced by phenethylammonium iodide Qingbo Wei<sup>1\*</sup>, Zhangwen Ye<sup>1</sup>, Yixuan Gao<sup>1</sup>, Nannan Wang<sup>1</sup>, Lina Feng<sup>1</sup>, Qingxia Zhao<sup>1</sup>, Xiufang Hou<sup>1</sup>, Lingxing Zan<sup>1</sup>, Feng Fu<sup>1\*</sup>, Dong Yang<sup>2\*</sup> <sup>1</sup> Key Laboratory of Chemical Reaction Engineering of Shaanxi Province, College of Chemistry & Chemical Engineering, Yan'an University, Yan'an 716000, China <sup>2</sup> Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Liaoning, 116023, China \*Corresponding authors E-mail addresses: qbwei@yau.edu.cn; fufeng@yau.edu.cn; dongyang@dicp.ac.cn

## Materials

Methylamine iodine (MAI), lead iodide (PbI<sub>2</sub>), phenylethyl amine iodide (PEAI), carbon slurry, and indium-doped tin oxide (ITO) glasses were obtained from Advanced Electronic Technology Co, Ltd., Yingkou, China. *N*, *N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and chlorobenzene were ordered from Sinopharm Chemical Reagent Co. Ltd. Isopropanol (IPA) was purchased from Sigma-Aldrich Technology Co., Ltd.

## **Device fabrication**

ITO glasses were ultrasonically cleaned with ethanol and treated with UV-ozone for 15 min. To obtain a compact  $SnO_2$  film, a  $SnCl_4 \cdot 5H_2O$  solution precursor was spin-coated on ITO glasses at 3000 rpm for 30 s, and then annealed at 180 °C for 60 min. The precursor perovskite film was made by mixing DMF:DMSO  $(V_{DMF}:V_{DMSO}=9:1)$  containing 0.599 g of PbI<sub>2</sub>, 0.159 g of MAI, and 300 µL of ethyl acetate and then allowing the mixture to drop within 30 s at 3000 rpm. The samples were annealed at 100°C for 10 min. Afterward, the PEAI was spin-coated on the perovskite film at a speed of 5000 rpm for 30 s. The carbon electrode was scraped on the perovskite film with an active area of 0.07 cm<sup>2</sup> and dried for 6 h without any further treatment.

## Measurements and characterization

X-ray diffraction (XRD) measurements were carried out on a DX-2700 diffractometer (Bruker Corp., Germany) using Cu K radiation (0.154181 nm) at 40 kV and 30 mA. PIXEA-CU-1 (AUREA, France) with an Ar<sup>+</sup> excitation light source and an excitation wavelength of 532 nm was used to measure steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL). A PerkinElmer Lambda spectroscopy (950UV/VIS/NIR) was adopted to record UV-vis absorption spectra. The surface morphology was observed on a 7610F scanning electron microscope (SEM, JOEL, Japan). Photocurrent density-voltage (J-V) curves of the perovskite solar cells were measured under AM 1.5G at 100 mW cm<sup>-2</sup> using a solar simulator and NREL traceable Si solar cell.

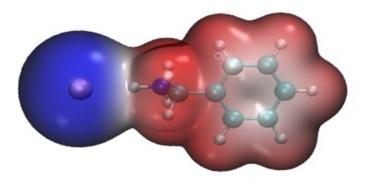


Figure S1. The electrostatic potential surface image of PEAI molecule.

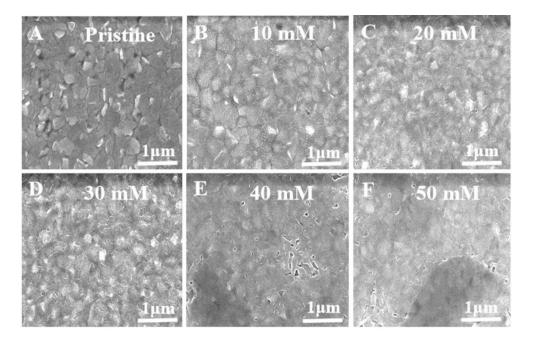


Figure S2. SEM images of the perovskite films treated by PEAI with different concentrations.

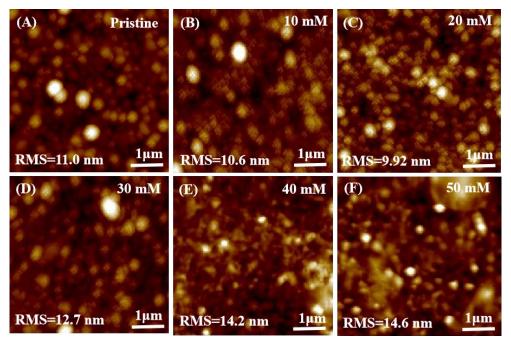


Figure S3. AFM images of the perovskite films treated by PEAI with different

concentrations.

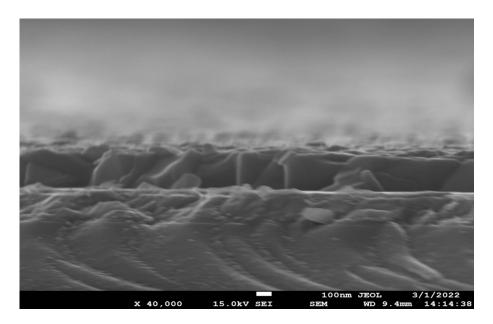


Figure S4. Cross-sectional SEM image of perovskite films treated by 10 mM.

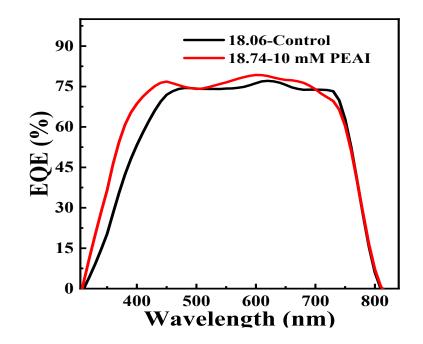
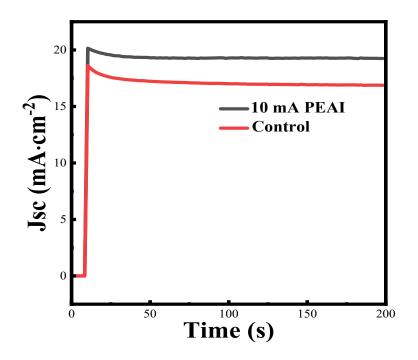
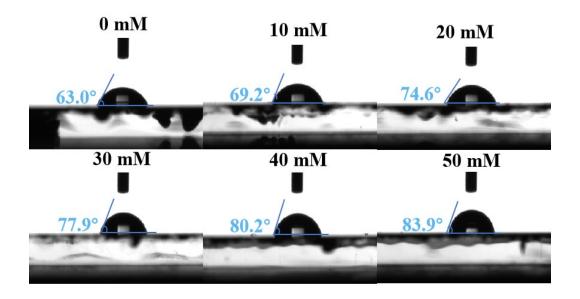


Figure S5. EQE data of the perovskite devices with and without PEAI treatment.



**Figure S6.** Maximal steady-state power output at the maximum power point for the PSCs prepared with and without PEAI treated at 0.7V.



**Figure S7.** Water contact angle of the perovskite films treated by PEAI with different concentrations.

Cycle index	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
1	1.17	19.57	68.19	15.67
2	1.17	19.54	68.51	15.72
3	1.17	19.56	68.13	15.64
4	1.17	19.57	68.21	15.65
5	1.17	19.55	68.32	15.64
6	1.17	19.52	68.18	15.57
7	1.17	19.51	68.04	15.52
8	1.17	19.54	68.00	15.52
9	1.17	19.55	67.80	15.47
10	1.17	19.54	67.74	15.44
11	1.17	19.52	67.67	15.40
12	1.16	19.51	67.53	15.36
13	1.16	19.55	67.50	15.39
14	1.16	19.53	67.32	15.32
15	1.16	19.54	67.18	15.29
16	1.16	19.52	67.21	15.29
17	1.16	19.51	67.13	15.25
18	1.16	19.51	66.95	15.21
19	1.16	19.50	66.90	15.20
20	1.16	19.50	66.84	15.17

**Table S1.** Device parameters for 20 cycles under the optimum concentration.

Bias voltage (V)	$V_{oc}(V)$	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
1.2	1.18	19.93	63.35	14.84
1.4	1.17	19.94	63.94	14.98
1.6	1.17	19.93	64.28	15.03
1.8	1.17	19.97	64.85	15.20
2.0	1.17	19.96	65.07	15.22
2.2	1.17	19.93	65.33	15.23
2.4	1.17	19.89	65.66	15.27
2.6	1.16	19.87	65.78	15.23
2.8	1.16	19.80	65.39	15.06
3.0	1.16	19.77	65.20	14.96

 Table S2. Device parameters under various scan voltages at the optimum concentration.