

Supporting Information

In-Situ Formation of Low-Dimensional Perovskite Structure for Efficient Single-Crystal MAPbI₃ Solar Cells with Enhanced Ambient Stability

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Experimental Section

Materials: Lead (II) iodide (PbI₂, 99.9%), gamma-butyrolactone (GBL, 99%), hydroiodic acid (HI) (57 wt.%, stabilized with 1.5% hypophosphorous acid), methylamine (CH₃NH₂, 40 wt.% in water), N, N-dimethylformamide (DMF, 99.9%) and isopropanol (IPA, 99.7%) were purchased from Aladdin Reagent Ltd. Methylammonium iodide (MAI) was synthesized as the following. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl) amine (PTAA), fullerene (C₆₀), bathocuproine (BCP) and 2-phenylethylamine hydroiodide (PEAI) were purchased from Xi'an Polymer Light Technology Corp. Chlorobenzene (CB, 99.5%) and PEDOT: PSS (2.7 wt % in H₂O) were purchased from Sigma-Aldrich. Indium tin oxide glass (ITO) substrate was purchased from Advanced Election Technology (China). Au (99.999%) and Cu (99.999%) were purchased from ZhongNuo Advance Material Technology (China). All commercial materials were used without any further purification.

1. Preparation of CH₃NH₃I (MAI)

The mass fraction of 57 wt. % HI with a mass fraction of 40 wt. % of CH₃NH₂ in water were mixed in the amount of 1:1 of the substance. The solution was stirred for 2 hours with ice water bath, then transferred to the flask of the rotary evaporator, and evaporated in vacuum at a temperature of 50 °C. Then the white precipitate was taken out, dissolved in ethanol, and then recrystallized with anhydrous ether. This evaporation-dissolution-recrystallization process was repeated for three times to obtain MAI with high purity. Afterwards, the prepared MAI was dried in a vacuum drying oven at 60 °C for 12 hours.

2. Preparation of MAPbI₃ single-crystal thin films

2.1 Preparation of MAPbI₃ bulk single-crystals

The MAI prepared in procedure 1 was mixed with PbI₂ of with equal molar amount and dissolved in GBL to prepare 1.5 M MAPbI₃ solution. This solution was stirred and heated at 72 °C until the solid particles were completely dissolved. After that, the solution was transferred to the hot stage, and the temperature continued to rise at a rate of 2 °C h⁻¹. As the temperature increased, MAPbI₃ crystals gradually precipitated from solution. When the temperature reached 120 °C, the crystals in the solution were taken out and was cooled to room temperature.

2.2 Preparation of MAPbI₃ precursor solution

MAPbI₃ crystals prepared in 2.1 were dissolved in GBL and a clear yellow transparent solvent was obtained. This precursor solution was kept on a hot plate at 60 °C before use.

2.3 Preparation of substrates

2 mg mL⁻¹ PTAA (its structure shown in Figure S1) solution in chlorobenzene was prepared and spin-coated on ITO glass (5 cm × 5 cm, have been washed with soap, deionized water, and anhydrous ethanol, followed by an ultraviolet-zone surface treatment for 15 min). Then the ITO glass was annealed on a hot plate at 100 °C for 10 min.

2.4 Growth of MAPbI₃ single-crystal thin films

The annealed cooled PTAA/ITO glass was placed on a 60 °C temperature-controlled stage for preheating, then 75 µL of perovskite precursor solution was dropped on it. After that, the PTAA/ITO glass was covered by another PTAA/ITO glass, with the precursor solution between them. The hot stage program was set for crystal growth with a rapid temperature increase of 30 °C h⁻¹ in the range of 60 - 74 °C and a slow temperature increase of 2 °C h⁻¹ in the range of 74 - 110 °C. The crystals nucleated and grew laterally between the two substrates. The MAPbI₃ single-crystal film with a lateral dimension of 3 - 6 mm and a thickness of 32 µm.

3. Surface modification of MAPbI₃ single-crystal films

PEAI solution in IPA was prepared and spin-coated on a MAPbI₃ single-crystal thin film substrate. PEA solution with the concentration of 0.5 mg mL⁻¹, 0.75 mg mL⁻¹, 1 mg mL⁻¹ and 1.5 mg mL⁻¹ was prepared. In order to explore the state of PEA's existence on the surface of perovskite single-crystals, (PEA)₂PbI₄ two-dimensional perovskite films were made by mixing PEA and PbI₂ in DMF solvent with a molar ratio of 2:1 and a concentration of 0.5 M, and spin-coating on a glass substrate with PEDOT: PSS layer. After spin-coating, the sample was annealed at 50 °C for 30 min and a (PEA)₂PbI₄ two-dimensional perovskite film was obtained.

4. Fabrication of MAPbI₃ perovskite single-crystal solar cells

The single-crystal thin films grown in procedure 2 and modified films in 3 were fabricated into single-crystal cells, respectively. The high-temperature tape was used to cover part of the edges of the single-crystal film to prevent a short circuit between the surface and ITO during the evaporation of the electrode. Finally, 20 nm C60, 3 nm BCP and 80 nm Cu electrodes were evaporated sequentially on the single-crystal film to prepare perovskite single-crystal solar cell.

5. Characterization

Phase and surface analysis

The Smart Lab 9KW X-ray diffraction platform (from Rigaku, Japan) with Cu target, K α wavelength was utilized for determining perovskite crystals. The morphology and surface roughness of MAPbI₃ single-crystal films with and without surface modification was examined using SEM (ZEISS, G300 FE-SEM System) and AFM (Bruker Dimension Icon). The contact angle was measured by a surface tension meter (Sigma 700, Biolin Scientific).

Spectroscopy analysis

Fourier Transform Infrared Spectroscopy (FTIR) was employed to detect organic functional groups in PEA powder and the perovskite single-crystal thin films with/without PEA modification. The NEXUS 670 FTIR-Raman spectrometer from Thermo Nicolet was used, which has a maximum resolution of 0.09 cm⁻¹ and a detection range of 7500 - 400 cm⁻¹. *X-ray photoelectron spectroscopy (XPS)*: Thermo Fisher Scientific's ESCALAB 250 X-ray photoelectron spectrometer (optimal energy resolution 0.45 eV, optimal spatial resolution 3 µm, optimal sensitivity of monochromatic light source: 1,000,000 cps, ion gun spot < 150 µm) was used to analyze the elemental compositions and chemical states of the crystal surfaces. *Photoluminescence (PL) and Time-Resolved Photoluminescence (TRPL)*: Steady-state PL spectra were measured using a fluorescence spectrometer (FLS1000, Edinburgh Instruments). TRPL spectra were

measured using a nanosecond pulsed diode laser (405 nm) with a repetition frequency of 1 MHz as an excitation source. *UV-Vis absorption spectrum*: The ultraviolet–visible absorption spectra were recorded using a spectrophotometer (U-3500, HITACHI).

J-V Curve

By using a solar simulator with the light intensity of 100 mW cm^{-2} (Sun 2000, ABET Technologies), the MAPbI₃ single-crystal solar cell was scanned for voltage from 1.2 V to -0.1 V at a rate of 10 mV s^{-1} . A metal photomask with an area of 0.02 cm^2 was placed on top of the solar cell to define the active area. The *J-V* curve can be measured by a Keithley 2450 source meter platform. The external quantum efficiency (EQE) spectra were measured by a QTEST HIFINITY 5 system (CROWNTECH, INC. USA) using a monochromatic light beam, calibrated by a reference silicon photodiode.

Electrical conductivity measurement

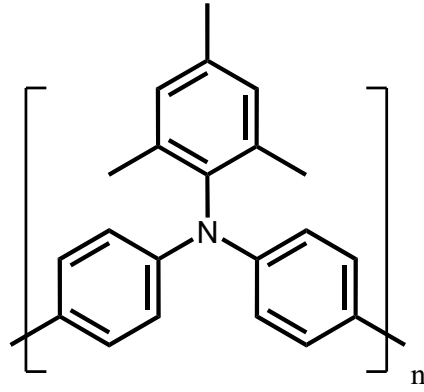
For temperature-dependent electrical conductivity measurement, devices with lateral structure of Au/single crystals/Au were fabricated. One sample is with the spin-coating of PEAI solution on the single crystal, which the other is not. A metal mask with gap width of $40 \mu\text{m}$ and length of 1 mm was covered on the MAPbI₃ thin single crystals and then 80 nm Au electrode was deposited by thermal evaporation. The electrical conductivity at different temperatures was tested by a Keithley 4200 source meter. The applied voltage is from 0 to 8 V, with a temperature range of 180 to 300 K.

Defect Density Testing

The bulk defect density of the single crystal was calculated using the Mott-Gurney law. The current-voltage curves data of the manufactured ITO/PTAA/Perovskite/Au devices were measured in dark using the 2400 source meter from Keithley (U.S.A.) voltage scanned from 0 - 12V.

Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy (Nyquist plots) were measured using an impedance analyzer (PGSTAT 302N, Autolab, Eco-Chemie, The Netherlands) in the dark at -0.6 V bias, with the magnitude and frequency of the alternative signal being 10 mV and $10^{-1} - 10^5 \text{ Hz}$, respectively. Impedance spectra were analyzed using an equivalent circuit model, and the model parameters were obtained by Nova software.



PTAA

Figure S1. Molecule structure of PTAA.

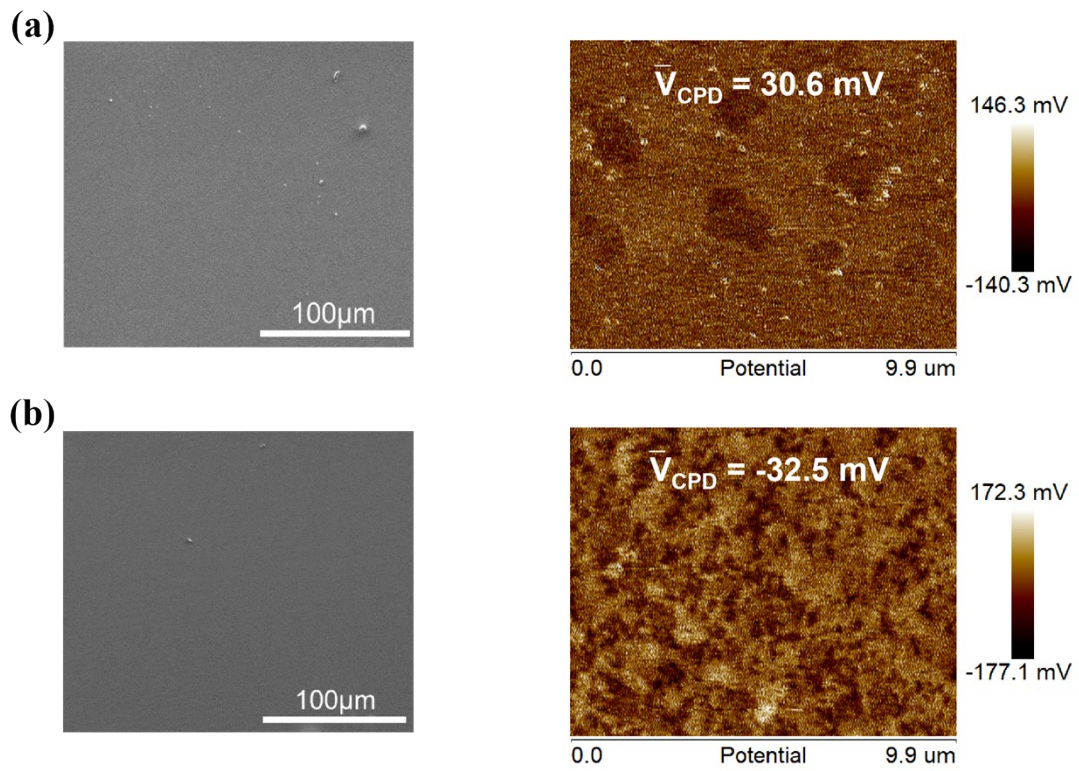


Figure S2. SEM and AFM images of MAPbI₃ single crystal film surface before (a) and after (b) PEAI modification.

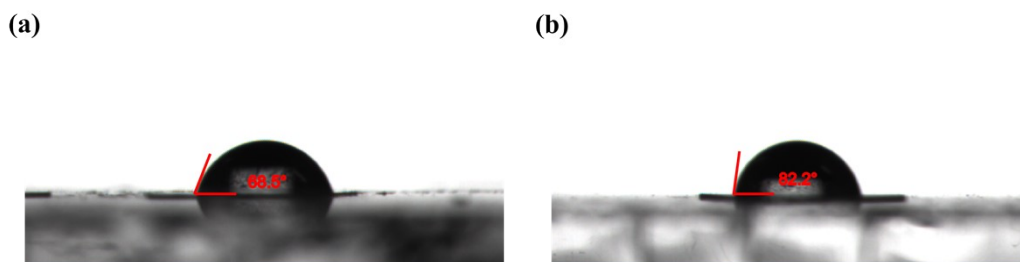


Figure S3. Contact angle of MAPbI₃ single crystal before (a) and after (b) PEAI modification.

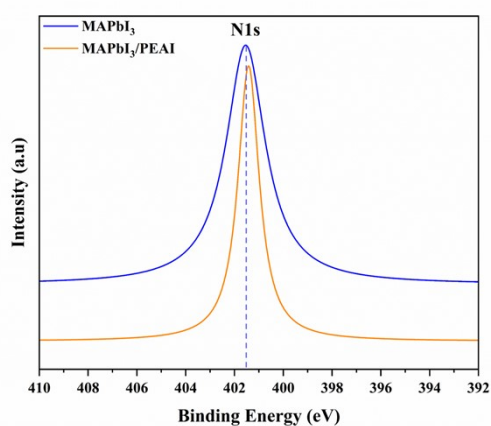


Figure S4. N1s orbit on the surface of MAPbI₃ single-crystal film before and after PEAI modification.

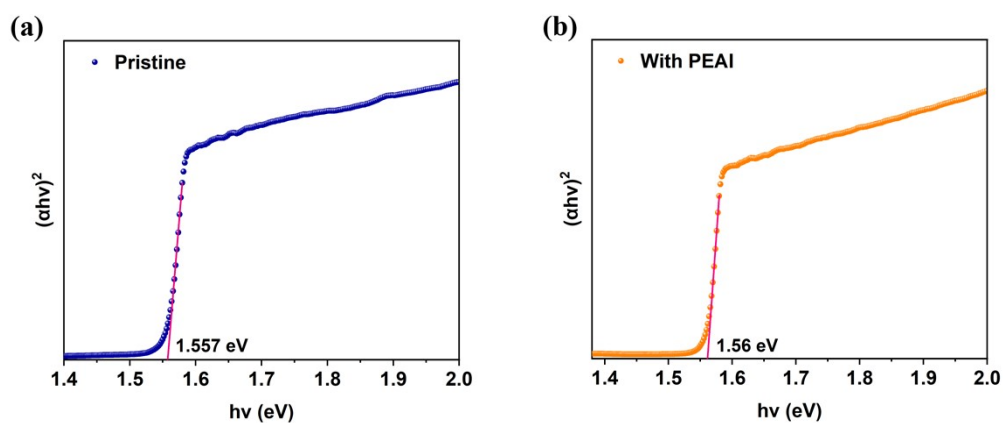


Figure S5. Bandgap of MAPbI₃ single crystal film before (a) and after (b) PEAI surface modification.

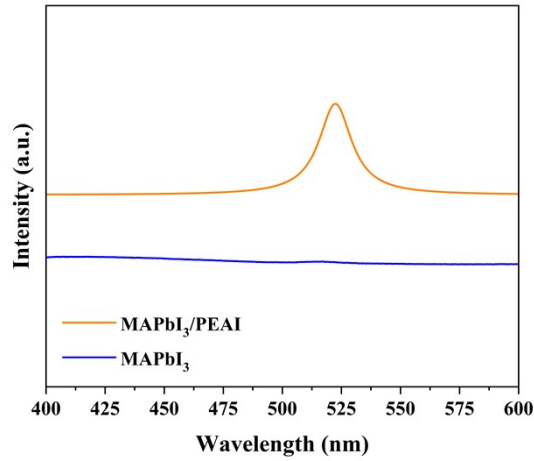


Figure S6. Steady-state PL spectra of MAPbI₃ single-crystal film before and after PEAI surface modification. The excitation wavelength is 375 nm.

S7 Optical bandgap:

The calculation of the optical bandgap is carried out according to the Tauc formula ^[1,2]:

$$(\alpha h\nu)^{1/n} = B(h\nu - E_g)$$

Among them, α is the absorbance coefficient, which is proportional to the absorbance in the absorption spectrum, $h\nu$ is the energy of the photon at different wavelengths, E_g is the optical bandgap of the thin film. The value of n is related to the type of semiconductor, since CH₃NH₃PbI₃ is a direct bandgap semiconductor, 1/2 is taken. Taking $(\alpha h\nu)^2$ as the ordinate and $h\nu$ as the abscissa to plot, and the intersection point of the linear part with the X-axis is the optical band gap value of the material.

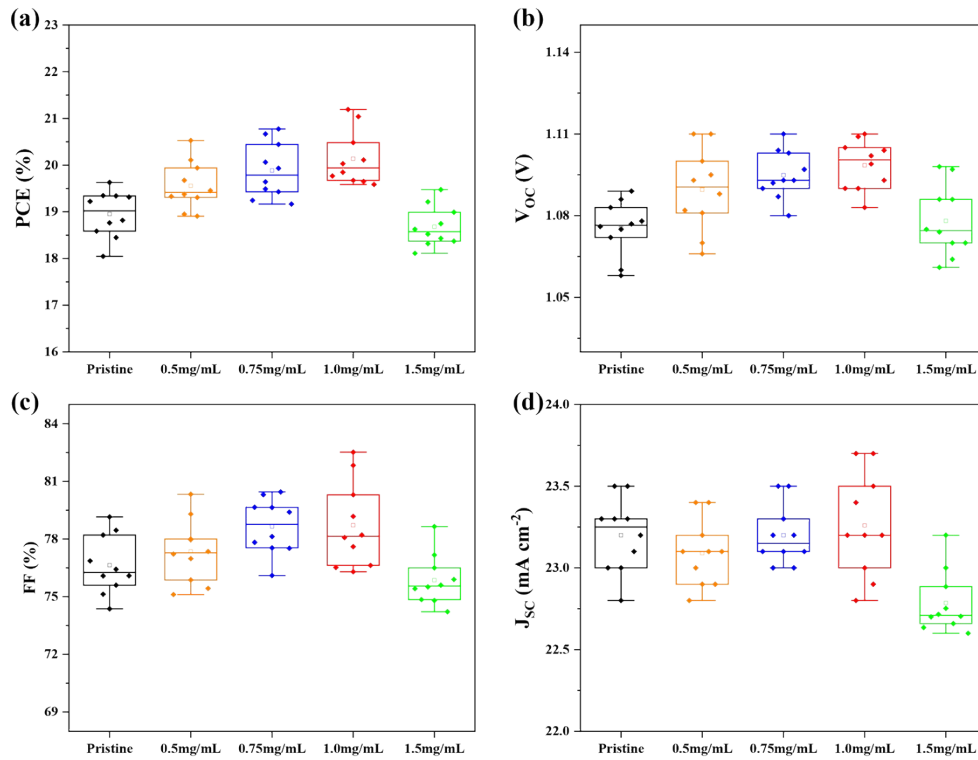


Figure S8. Statistical distribution of (a) PCE, (b) V_{OC} , (c) FF, (d) J_{SC} based on 10 solar cell devices.

S9 Hysteresis Index:

Since there are some differences in the J-V curves of different scanning directions, the hysteresis index [3] was introduced in order to assess the degree of hysteresis between the J-V curves obtained from the positive and negative scanning directions.

$$\text{Hysteresis index} = \frac{PCE_{Reverse} - PCE_{Forward}}{PCE_{Reverse}}$$

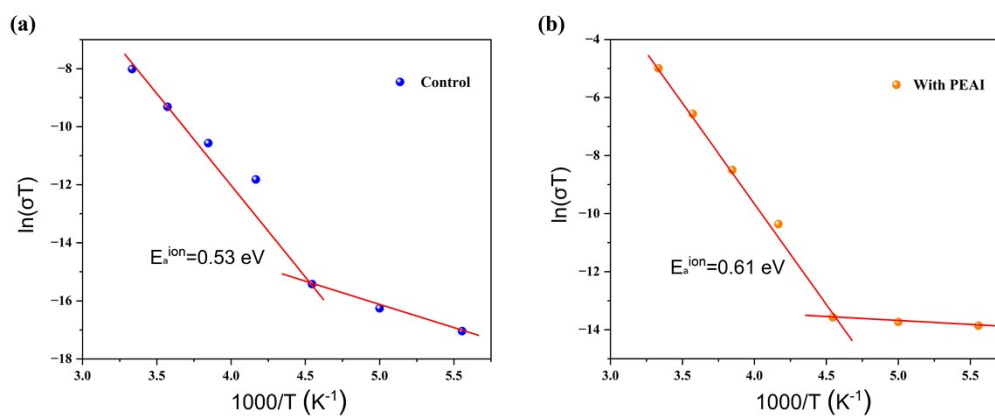


Figure S10. Temperature-dependent electrical conductivity of the MAPbI₃ single crystals (a) without and (b) with PEAI modification.

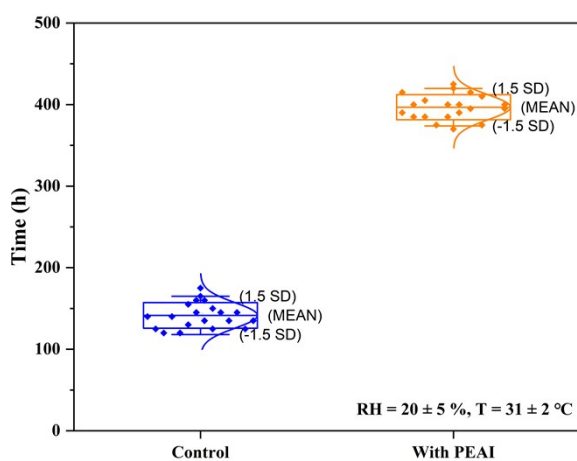


Figure S11. Statistical distribution of air stability T90 (decay time to retain 90% of initial efficiency) for 20 MAPbI₃ devices and 20 PEAI modification devices. Samples are placed in the air with $T = 31 \pm 2 \text{ }^\circ\text{C}$ and $RH = 20 \pm 5 \%$.

Table S1. Fitting parameters of TRPL spectra for MAPbI₃ single crystal films before and after PEAI modification.

Sample	A1(%)	τ_1 (ns)	A1(%)	τ_2 (ns)	τ_{avg} (ns)
Glass/PTAA/MAPbI ₃	88	0.75	12	6.15	3.61
Glass/PTAA/MAPbI ₃ /PEA	71	4.5	29	8.42	6.31

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Table S2. Performance parameters of MAPbI₃ single crystal solar cells before and after PEAI surface modification.

Condition	Scan direction	$J_{SC}/mA \cdot cm^{-3}$	V_{OC}/V	FF/%	PCE/%	Hysteresis index
Pristine	Reverse	23.8	1.053	78.66	19.71	7.46%
	Forward	23.1	1.061	74.42	18.24	
With PEAI	Reverse	23.9	1.096	80.93	21.20	5.24%
	Forward	23.6	1.092	77.81	20.05	

Reference

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- [2] D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y. Losovyj, X. Zhang, P. A. Dowben, O. F. Mohammed, E. H. Sargent, O. M. Bakr, *Science (New York, N.Y.)*, **2015**, 347, 519-522.
- [3] Severin N. Habisreutinger, Nakita K. Noel, Henry J. Snaith, *ACS Energy Lett.*, **2018** 3 (10), 2472-2476