

Supporting Information

Toward Efficient Perovskite Solar Cells by Planar Imprint for Improved Perovskite Film Quality and Granted Bifunctional Barrier

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EXPERIMENTAL SECTION

Material: N, N-dimethylformamide (DMF, 99.8% purity), dimethyl sulfoxide (DMSO, 99.9% purity), acetonitrile (99.8% purity), chlorobenzene (CB, 99.8% purity), 4-tert-butyl pyridine (tBP) and CH₃NH₃I (MAI, >98% purity) were purchased from Sigma-Aldrich and used as received without further purification. Lead iodide (PbI₂, 99.9985% purity), tin(IV) oxide (15% in H₂O colloidal dispersion liquid), lithium bis(trifluoromethylsulfonyl) imide (Li-TFSI, >98% purity) and were purchased from Alfa Aesar. Trimethoxy (1H,1H,2H,2H-heptadecafluorodecyl) silane (FAS, 98% purity) was purchased from Innochem. 2,2',7,7'-Tetrakis [N, N -di(4-methoxyphenyl) amino]-9,9'-spirobifluorene (spiro-MeOTAD, 99% purity) was purchased from Luminescence Technology Crop.

Preparation of Solution and Anti-sticking layer: The tin(IV) oxide solution was prepared in a ratio of 1:3. The perovskite solution was prepared by 922 mg of PbI_2 , 318 mg of MAI, 1270 μL DMF and 142 μL DMSO. The spiro-MeOTAD solution was prepared by dissolving 72.3 mg of spiro-MeOTAD, 28.8 μL of TBP and 17.5 μL of Li-TFSI solution (520 mg Li-TFSI in 1 mL acetonitrile) in 1 mL of CB. Finally, FAS was deposited on top of Si stamp by evaporation in high vacuum for 3 hours.

Fabrication of Devices: The indium tin oxide (ITO) glass was cleaned with acetone, detergent, distilled water and isopropanol for 20 min, respectively. SnO_2 was spin-coated on the ITO glass at 3000 rpm for 30 s, annealing at 150°C for 30 min. Then the perovskite solution was deposited on the SnO_2 surface at 4000 rpm for 30 s in N_2 atmosphere and dried 100°C . Simultaneously, 150 μL CB solution was drop-casted fastly in seven seconds. At a pressure of 3 MPa and a preset temperature (100°C , 150°C and 180°C), the perovskite film is placed on the silicon wafer for planar imprint (PiP) for 10 min in air. Finally, the hole transporting layer spiro-MeOTAD solution was spin-coated on top at 4000 rpm for 30 s. Finally, 100 nm Ag was deposited on top by evaporation in high vacuum.

Characterization: FTIR spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. X-ray photoelectron spectroscopy (XPS) was performed in an ESCALAB 250Xi, Thermo Fisher (by using Al $K\alpha$ X-ray source) under high vacuum (10^{-9} mbar). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDS) mapping images were conducted on SU8020 scanning electron microscope operated at an acceleration voltage of 8 kV. Atomic force microscopy (AFM) images were measured by MultiMode 8-HR (Bruker) atomic force microscope. A Rigaku D/Max-B X-ray diffractometer with Bragg-Brentano parafocusing geometry was employed to test X-ray diffraction (XRD) patterns. The ultraviolet-visible (UV-vis) spectra were conducted using a SHIMADZU, UV-2600 spectrophotometer. The steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were recorded by an Edinburgh instruments FLS920 spectrometer (Edinburgh Instruments Ltd.). The current density-voltage ($J-V$) curves of the devices were

measured with a Keithley model 2400 source meter (Abet Solar Simulator Sun2000), equipped with a light source (100 mW cm^{-2}) under AM 1.5 G filter. The active area of the device and the area of the shadow mask are 0.04 cm^2 . The forward scan range is from 0 V to 1.2 V and the reverse scan range is from 1.2 V to 0 V, with 20 mV for each step. The scan rate is 200 mV s^{-1} and the delay time is 30 ms. External quantum efficiency (EQE) values were measured under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with an Oriel 70613NS QTH lamp), and the calibration of the incident light was performed using a monocrystalline silicon diode. Electrical impedance spectroscopy (EIS) of the devices was performed in a frequency range from 1 MHz to 10 mHz using Zahner electrochemical workstation at an applied bias equivalent to the open-circuit voltage of the cell under 1 sun illumination. The trap density of states was deduced from the angular frequency dependent capacitance. The currents were measured under 100 mW cm^{-2} simulated AM 1.5 G irradiation (Abet5 Solar Simulator Sun2000).

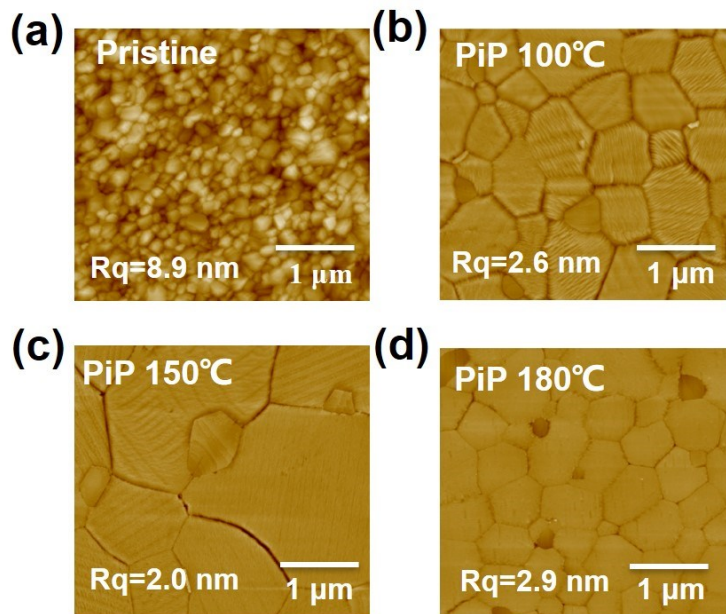


Figure S1. AFM height images of (a) the pristine, (b) PiP 100°C, (c) PiP 150°C and (d) PiP 180°C perovskite film.

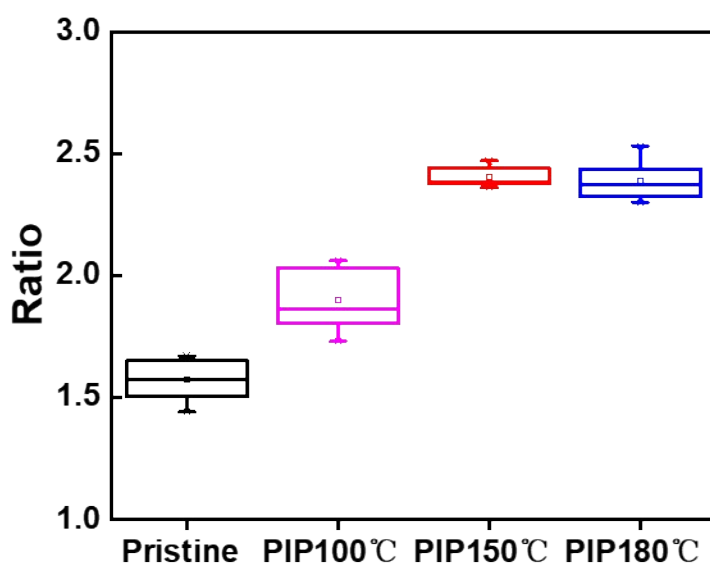


Figure S2. The distribution histogram of XRD patterns from different batches are exhibited (with temperature of 100°C, 150°C, 180°C, respectively).

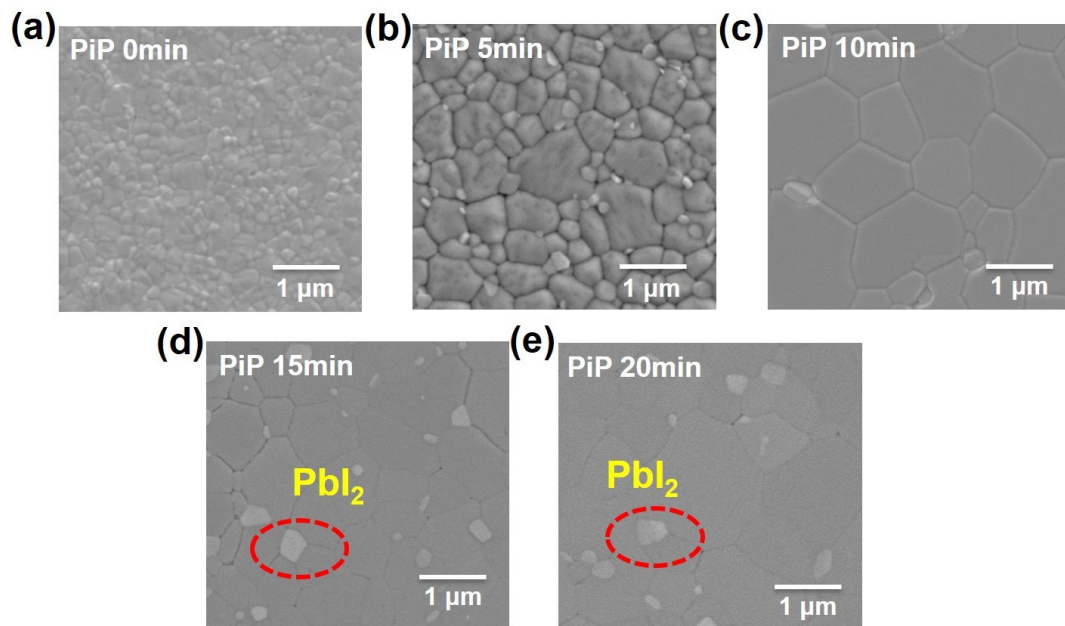


Figure S3. The growth process of perovskite grain in the PiP process with different PiP time (0 min, 5 min, 10 min, 15 min, 20min) under 150°C. PbI₂ accumulation layers are indicated by circles.

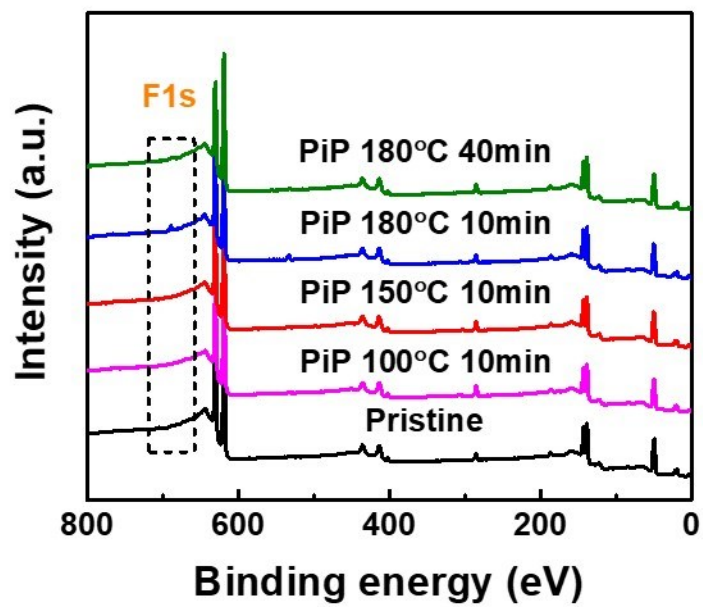


Figure S4. XPS spectra of perovskite film with different PiP time and PiP temperature.

Density function theory calculation were performed by using the CP2K package.¹ PBE functional² with Grimme D3 correction³ was used to describe the system. Unrestricted Kohn-Sham DFT has been used as the electronic structure method in the framework of the Gaussian and plane waves method.^{4, 5} The Goedecker-Teter-Hutter (GTH) pseudopotentials,^{6,7} DZVPMOLOPT-GTH basis sets⁴ were utilized to describe the molecules. A plane-wave energy cut-off of 500 Ry has been employed.

The adsorption energies of molecule is about -0.70 eV when vertically adsorbed on the surface and about -1.07 eV when parallelly adsorbed.

The charge density difference is defined as

$$\Delta \rho = \rho_{mol/sur} - \rho_{mol} - \rho_{sur} \quad (1)$$

Where $\rho_{mol/sur}$, ρ_{mol} and ρ_{sur} are the electron density of the molecule adsorbed on surface, and the individual electron density of molecule and surface.

The binding energy is defined as

$$E_b = E_{mol/sur} - E_{mol} - E_{sur} \quad (2)$$

Where $E_{mol/sur}$, E_{mol} and E_{sur} are the energies of the molecule adsorbed on surface, and the individual electron density of molecule and surface.

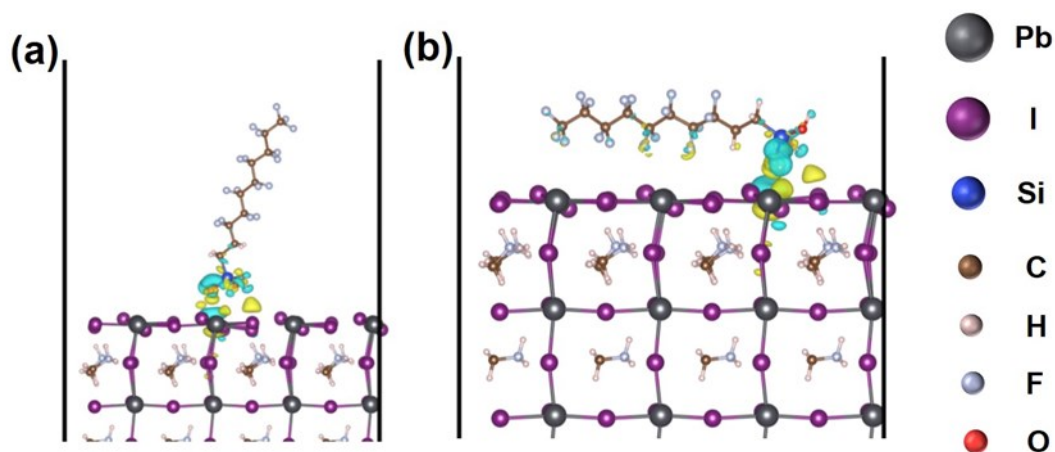


Figure S5. Charge difference analysis between molecule and MAPbI₃. Isovalue = 0.001 a.u.

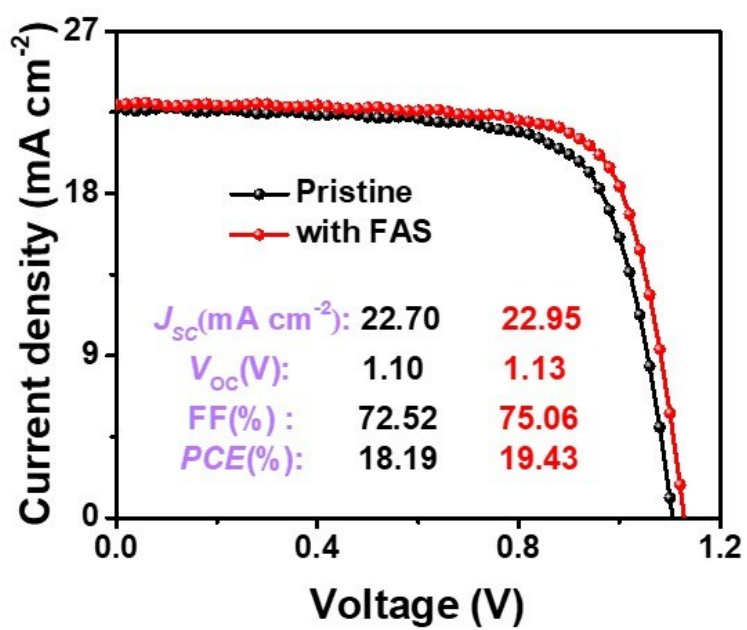


Figure S6. The current density–voltage (J – V) curves of devices based on pristine and modified film with FAS.

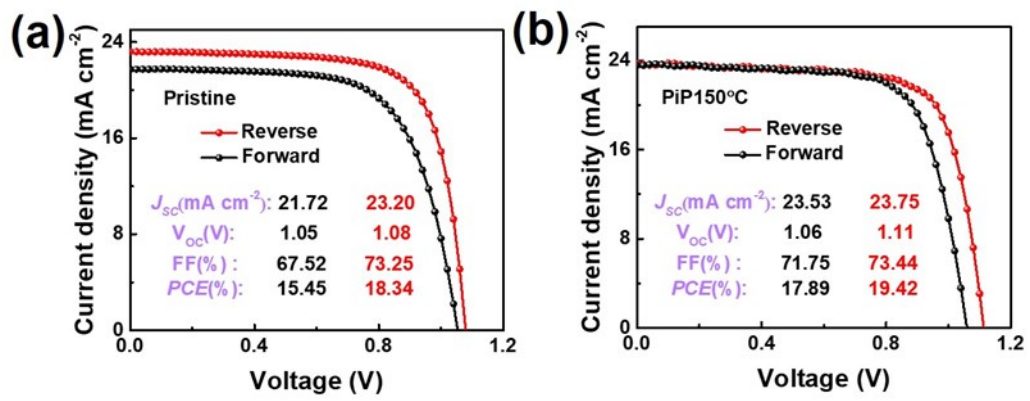


Figure S7. Typical J - V curves of (a) pristine and (b) PiP 150°C devices under reverse and forward scans.

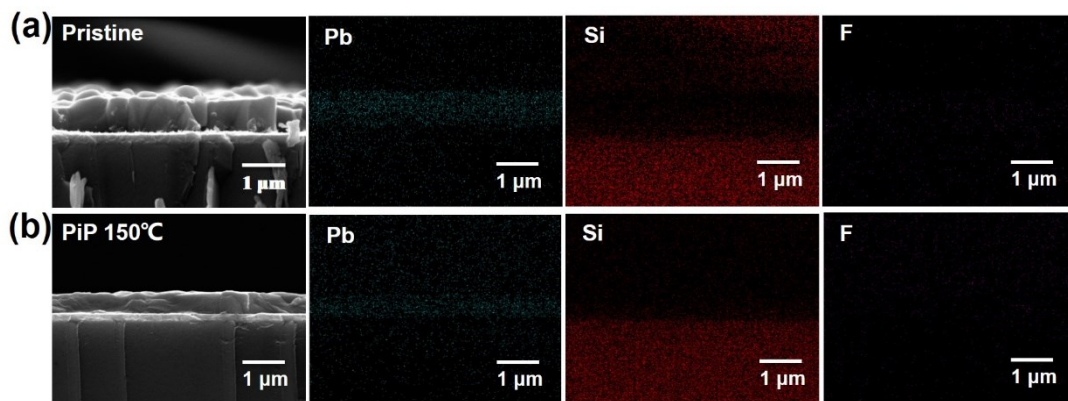


Figure S8. Cross-SEM-EDS mappings of Pb, F, and Si for the (a) Pristine and (b) PiP 150°C film onto ITO.

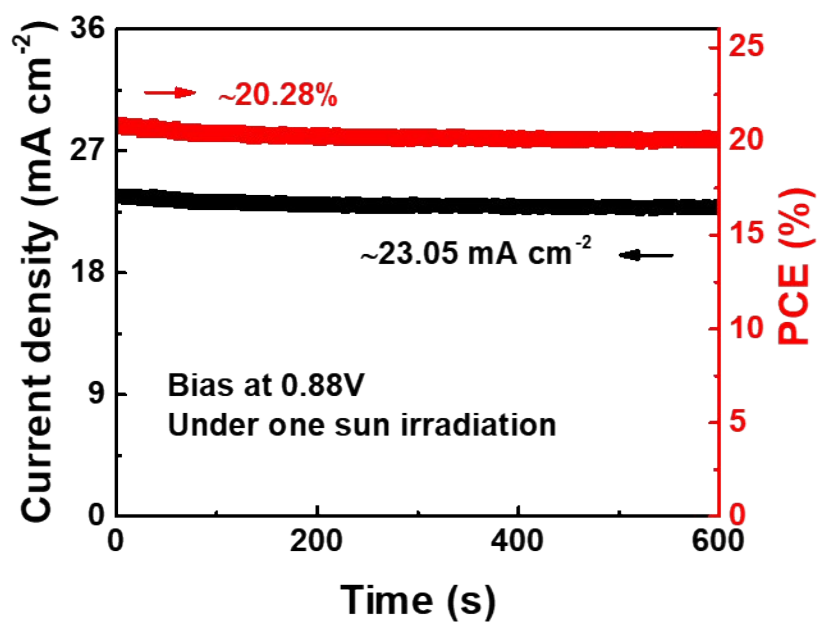


Figure S9. The steady-state photocurrent and output PCE of PiP 150°C device at the maximum power point of 0.88V.

Table S1. F content of perovskite film with different PiP temperature and PiP time.

| Temperature (°C) | Time (min) | F (%) |
|------------------|------------|-------|
| 100 | 10 | 0.21 |
| 150 | 10 | 1.04 |
| 180 | 10 | 6.03 |
| 150 | 40 | 2.49 |

Table S2. A comparison of PSCs based on modified MAPbI₃ with different pressure conditions.

| Device structure | Template type | V_{oc} (V) | J_{sc} (mA cm ⁻²) | FF (%) | PCE (%) | Ref. |
|--|------------------------|--------------|---------------------------------|--------------|--------------|------------------|
| FTO/TiO ₂ /MAPbI ₃ /spiro-MeOTAD/Ag | PUA stamp | 1.05 | 23.24 | 78.27 | 19.16 | 8 |
| FTO/TiO ₂ /MAPbI ₃ /spiro-MeOTAD/Au | DVD stamp | 1.11 | 23.11 | 76.75 | 19.71 | 9 |
| ITO/PEDOT:PSS/MAPbI ₃ /PC ₇₁ BM/C ₆₀ /BCP | Hot isostatic pressing | 0.67 | 18.90 | 67 | 11.80 | 10 |
| FTO/TiO ₂ /MAPbI ₃ /spiro-MeOTAD/Ag | Flat stamp | 0.96 | 22.51 | 0.742 | 16.07 | 11 |
| iTO/SnO₂/MAPbI₃/spiro-MeOTAD/Ag | Flat stamp | 1.13 | 23.57 | 77.19 | 20.52 | This work |

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