Supporting Information

Restraining Unfavorable Phases via Reduced Spatial Hindrance of Ultrasmall-sized Molecules to Enable High-performance Quasi-two-dimensional Perovskite Solar Cells

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Experimental

Materials. All chemical products are purchased from suppliers and used according to their receipt. Lead (II) iodide (II) (PbI_2, 99.99%), Caesium iodide (CsI,>99.0%) were purchased from TCI, N-carbamoyl-2-propyl-2-ylpent-4-enamide from Aalddin. The methylammonium iodide (MAI), methylamine chloride (MACl), guanidine iodide (GAI) were purchased from Xi'an Polymer Light Technology Corp. Superdehydrated dimethylformamide (DMF, Acros), dimethyl sulfoxide (DMSO, Acros), chlorobenzene (CB, Acros) were purchased from Beijing Innochem Science & Technology co., LTD. Methylamine formate (MAFA), methylamine acetate (MAAc), methylamine propionate (MAPA) were purchased from Aladdin.

Device fabrication. ITO-coated glass substrates were cleaned in an ultrasonic bath containing acetone, deionized (DI) water, and ethanol for 20 min in each step and then dried with a nitrogen (N_2) stream followed by air plasma treatment for 10 min. SnO_x precursor was prepared by mixing the SnO_x colloidal solution with DI water by a ratio of 1:3. The electron transport layer SnO_x solution was spin-coated on ITO glass at 3000 rpm for 30 s in air, followed by annealing at 150 °C for 30 min. The quasi-2D perovskite was then spin-coated on SnO_x with annealing at 100 °C for 5 min. The quasi-2D perovskite precursor solution was prepared according to the stoichiometric composition of $(GA)MA_5Pb_5I_{16}$. Different ionic liquid small molecules are directly added to the perovskite precursor solution. Then the perovskite precursor was spin-coated through a two-step process at 1000 rpm for 10 s and 4000 rpm for 25 s. During the second step, 150 μL of CB was dropped on the spinning substrate 5 s before the end of the second step, then annealing at 100 °C for 10 min. The Spiro-OMeTAD was prepared by dissolving 72.3 mg of Spiro-OMeTAD in 1 mL of chlorobenzene, to which 28.8 μL of 4-tertbutylpyridine (96%, Sigma-Aldrich) and 17.5 μL of lithium bis(trifluoro-methanesulfonyl) imide (Li-TFSI, 98%, Sigma-Aldrich) solution (520 mg Li-TFSI in 1 mL acetonitrile (99.8%, Sigma-Aldrich)) was added. The Spiro-OMeTAD hole-transporting layer was obtained by being spin-coated at 4000 rpm for 20 s, then anneal at 60 °C for 5 min. Finally, 100 nm of Ag electrode was deposited by thermal evaporation under vacuum conditions.

Characterization and measurement. Keithley 2400 was used to characterize the current density-voltage (*J-V*) curves. The currents were measured under 100 $mW \cdot cm^{-2}$ simulated AM 1.5 G irradiation (Abet5 Solar Simulator Sun2000). The active area of the device and the area of the shadow mask are 0.04 cm^2. Devices were stored and tested in the nitrogen-filled glovebox. Scanning electron microscopy (SEM) were conducted on SU8020 scanning electron microscope operated at an acceleration voltage of 8 kV. X-ray diffraction (XRD) spectra were carried out by using X-ray diffractometer (Rigaku D/Max-B). The ultraviolet-visible (UV-Vis) spectra were characterized on UV-2600 spectrophotometer (SHIMADZU). The steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were recorded by an Edinburgh instruments FLS920 spectrometer (Edinburgh Instruments Ltd.). X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) was used for binding energy and element distribution analysis.

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 water contact angle was measured at a Krüss DSA100s drop shape analyser. The dynamic light scattering (DLS) of each solution is measured by a high-resolution laser particle size analyzer (Brookhaven 90 Plus PALS).

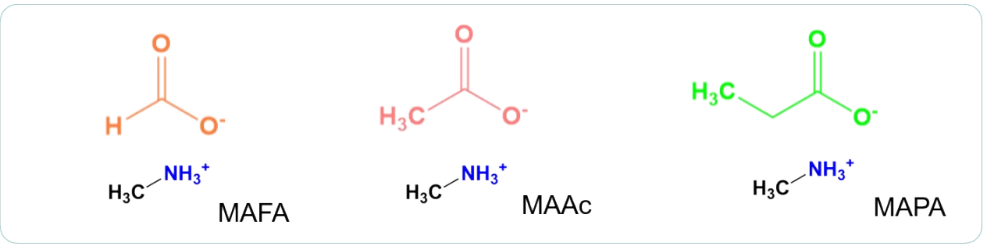

Fig. S1 Molecular structural of MAFA, MAAc, and MAPA.

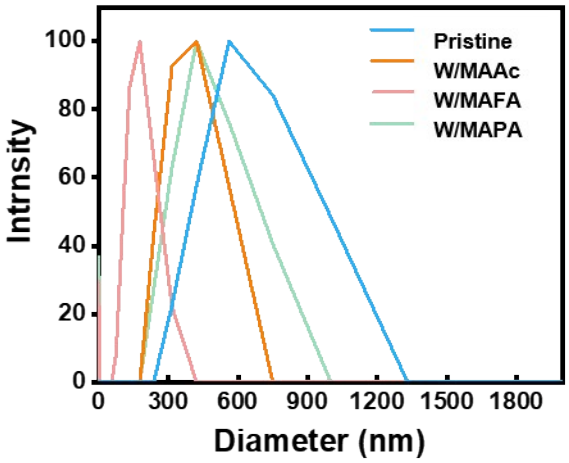

Fig. S2 dynamic light scattering test of pristine, MAFA-based MAAc-based and MAPA-based quasi-2D perovskite precursor solution.

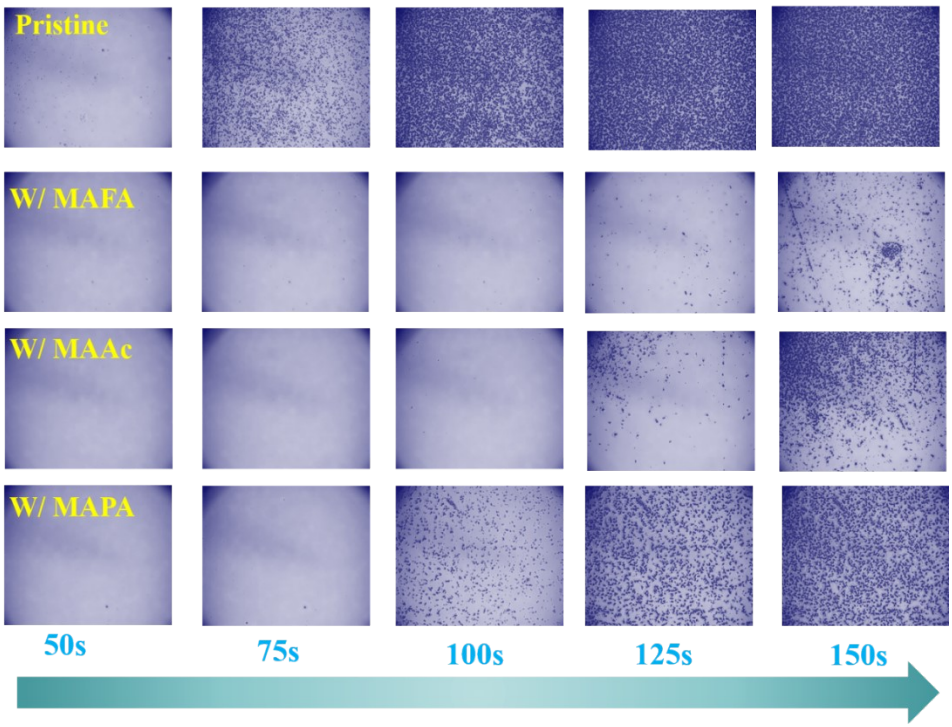

Fig. S3 Optical microscope test of evolution process of wet film growth for pristine, MAAc-based, MAPA-based and MAFA-based 2D perovskite film.

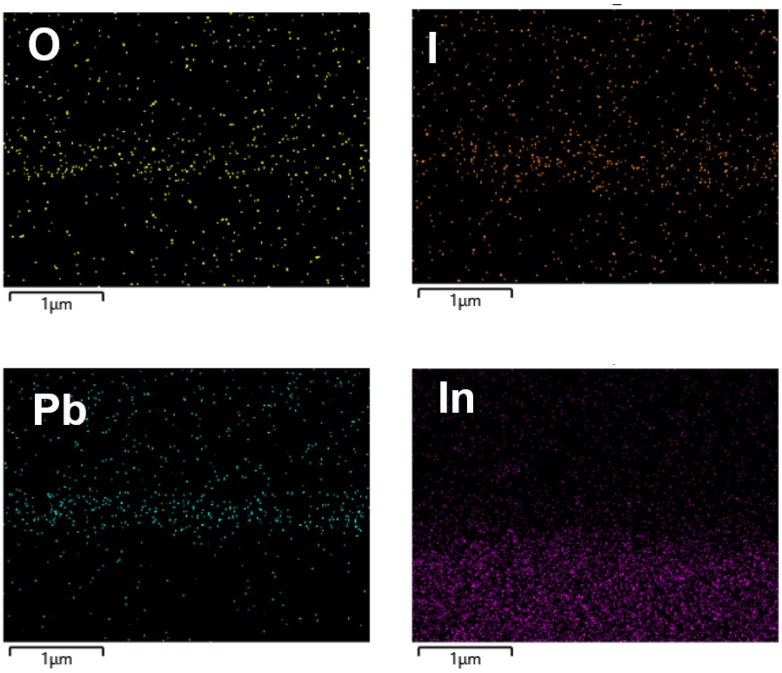

Fig. S4 EDS test of O, I, Pb and ln element for MAFA-based perovskite films on ITO.

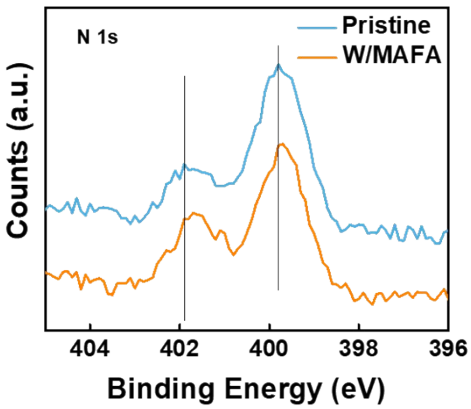

Fig. S5 XPS spectra of N 1s for pristine and MAFA-based perovskite films.

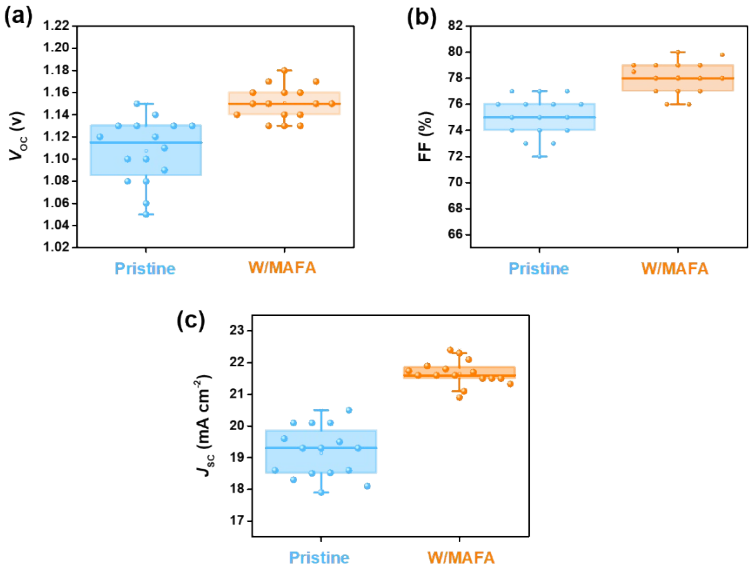

Fig. S6 V_{OC}, FF and J_{SC} distributions of pristine and MAFA-based perovskite devices.

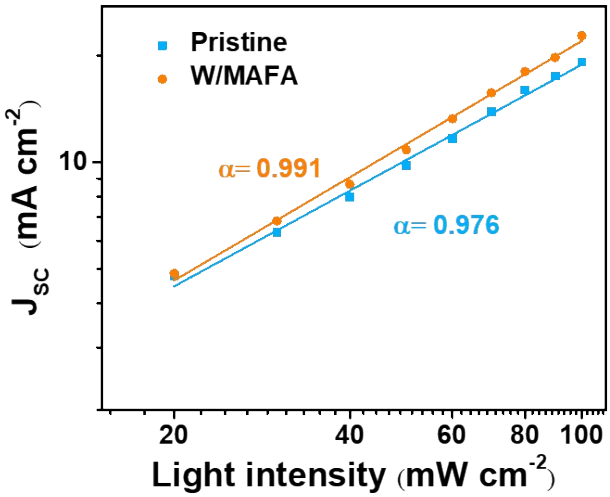

Fig. S7 J_{SC} values of the corresponding devices versus light intensity on a double-logarithmic scale.

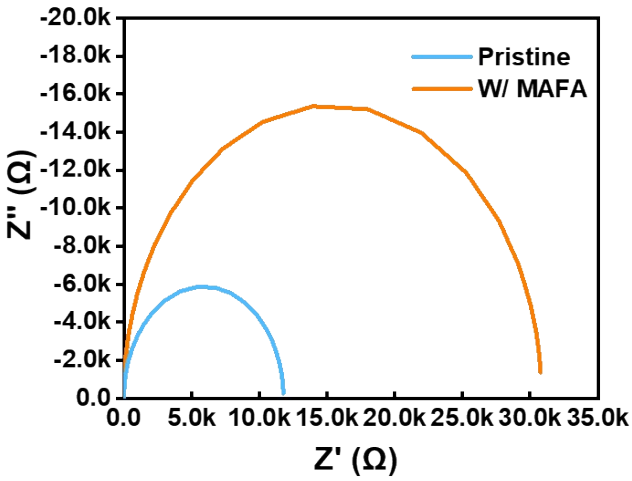

Fig. S8 Nyquist plots of pristine and MAFA-based perovskite devices.

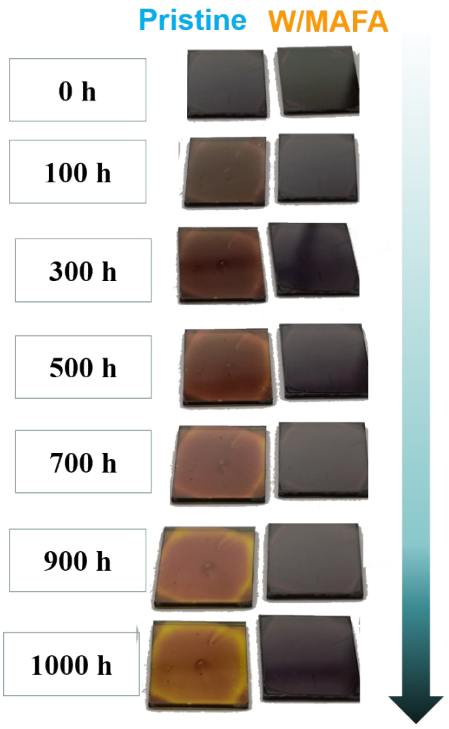

Fig. S9 Pictures of fresh and aged pristine and MAFA-based 2D films by being stored in air with a relative humidity of 85% at 25 °C at room temperature from 0 h to 1000 h. The yellow part in the XRD pattern indicates the peak of PbI_2.

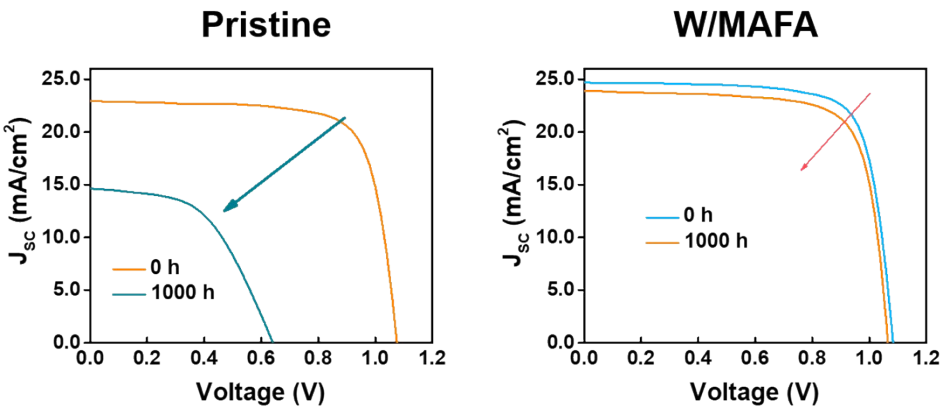

Fig. S10 *J-V* curve of pristine and MAFA-based perovskite solar cells before and after aging in air at room temperature at 85 % RH for 1000 h.

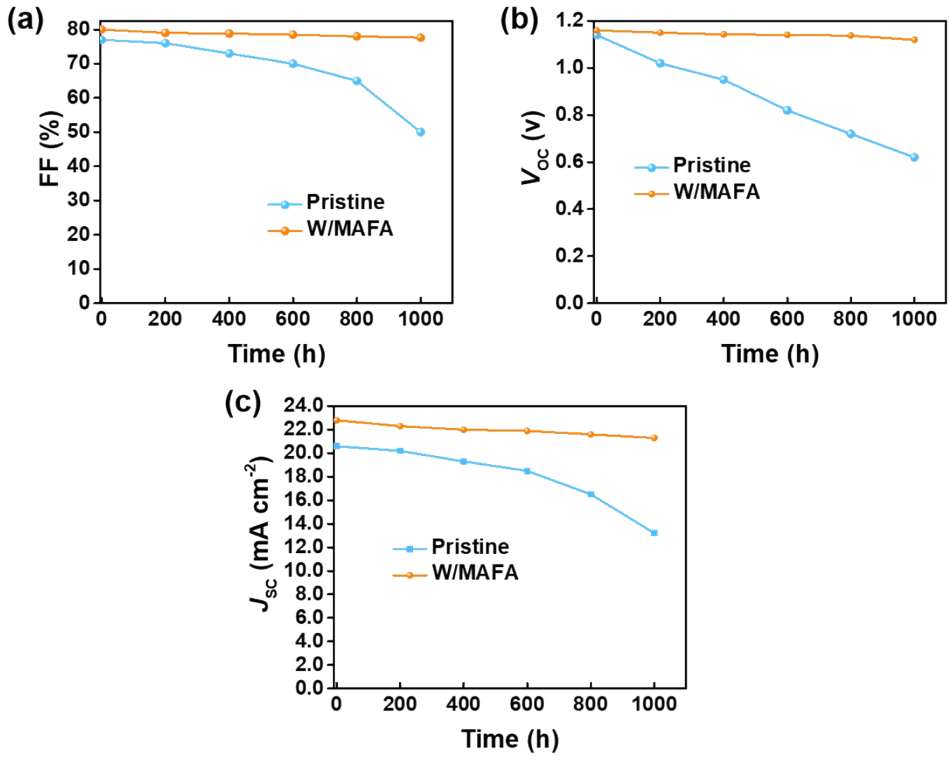

Fig. S11 FF, V_{OC} and J_{SC} variation curves of pristine and MAFA-based perovskite devices before and after aging in air at room temperature at 85 % RH for 1000 h.

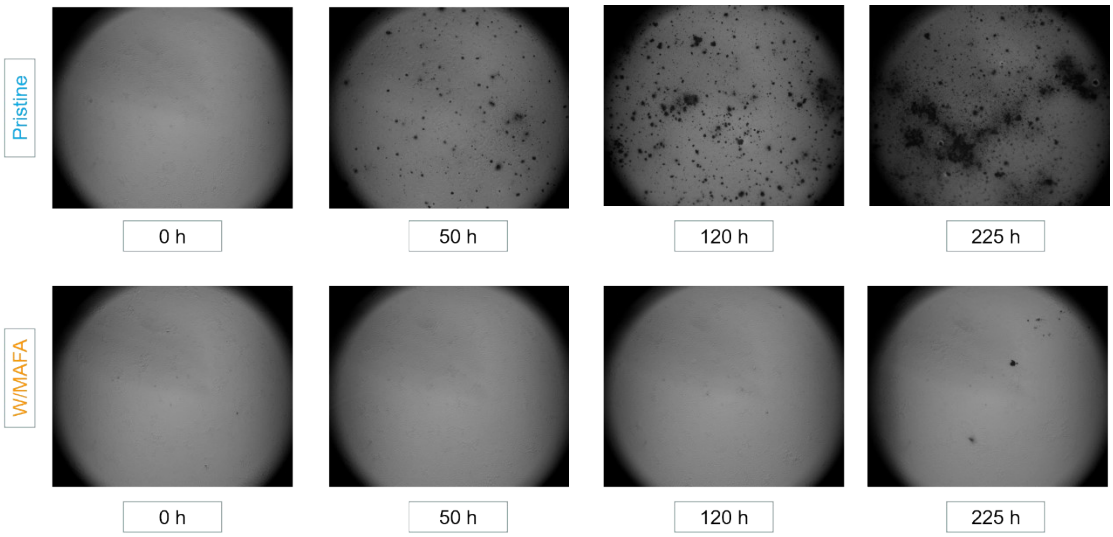

Fig. S12 Optical microscope photographs of Ag electrodes for pristine and MAFA-based perovskite devices, in their initial state and after aging at 75 °C in air with 40 ± 5% RH in dark from 0 h to 225 h.

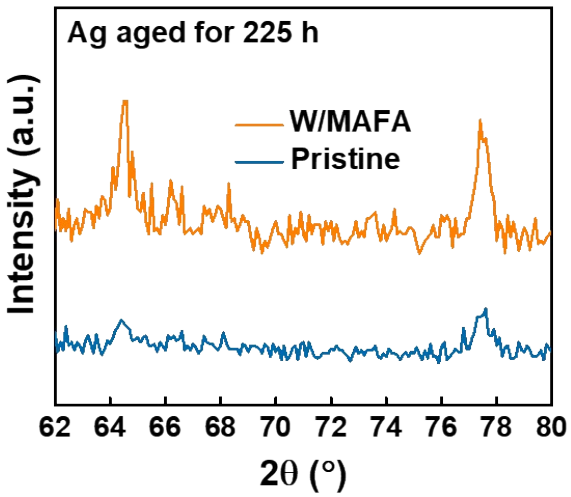

Fig. S13 XRD of Ag electrodes for pristine and MAFA-based perovskite devices, in their initial state and after aging at 75 °C in air with 40 ± 5% RH in dark for 225 h.

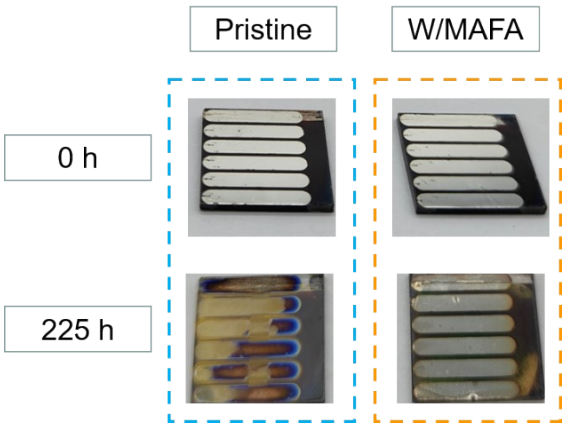

Fig. S14 Images of pristine and MAFA-based perovskite devices, in their initial state and after aging at 75 °C in air with 40 ± 5% RH in dark for 225 h.

Table S1 Calculated binding energy by using DFT.

	Energy (eV)	Binding Energy (eV)
PbI_2	-7.4020385	
MAFA	-28.956074	
MAAc	-40.520298	
MAPA	-61.897841	
MAFA@PbI_2	-39.175122	-2.8170095
MAAc@PbI_2	-50.426432	-2.5040955
MAPA@PbI_2	-71.650888	-2.3510085

Table S2 The content of Pb, I, C, O and N elements in EDS test for MAFA-based film.

element	Wt%	Wt% Sigma
N	2.49	0.24
O	22.49	1.40
C	10.51	3.45
I	43.37	3.60
Pb	20.14	1.28
total：	100.00	

Table S3 Photovoltaic parameters of the pristine and MAFA-based PSCs with different n values.

	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE
W/MAFA	1.17 (1.15 ± 0.02)	22.82 (22.54 ± 0.18)	78.49 (78.47 ± 0.02)	21.13 (20.62 ± 0.51)
Pristine	1.14 (1.10 ± 0.04)	20.81 (20.49 ± 0.32)	75.87 (75.72 ± 0.15)	18.03 (16.93 ± 1.10)