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Supporting information

Self-Assembled Propylammonium Cations at Grain Boundaries and Film Surface to Improve Efficiency and Stability of Perovskite Solar Cells

Chengbin Fei,[a] Meng Zhou,[a] Jonathan Ogle,[b] Detlef-M. Smilgies,[c] Luisa Whittaker-Brooks[b] and He Wang[a]*

[a]Department of Physics, University of Miami, Coral Gables, Florida 33146, United States
[b]Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, United States
[c]Cornell High Energy Synchrotron Source, Cornell University, Ithaca, New York 14853, United States

E-mail: hewang@miami.edu

Experimental

Materials and substrates Tin oxide (SnO_2) aqueous solution (15% wt.) was purchased from Alfa Aesar. All other solvents (anhydrous, ≥99.8%) and liquid reagents were purchased from Millipore Sigma. Fluorine doped tin oxide (FTO) and solid reagents (with purities ≥ 99.9%) including FAI, CsI, MAI, MABr, MACl, $PbBr_2$, and Spiro-OMeTAD were purchased from Advanced Election Technology Co., Ltd. Lead (II) iodide (PbI_2) was purchased from both Advanced Election Technology Co., Ltd and Tokyo Chemical Industry Co., Ltd (TCI). FAI, EAI, PAI and BAI were purchased from Greatcell Solar.

Device fabrication Compact TiO_2 layer was prepared by a chemical deposition method. The cleaned FTO substrates were exposed to UV ozone for 12 min. The substrates were then immersed in 0.2 M $TiCl_4$ aqueous solution for 45 min. Afterwards, the substrates were washed with deionized water and dried in air. The as-prepared substrates were annealed at 450 °C for 30 min and cooled down to room temperature (RT). The mesoporous TiO_2 layer was prepared via spin coating. A 100 μL TiO_2 nanoparticle dispersion (18NRT, 1:15 weight ratio in ethanol solution) was dropped onto the above substrates and spin-coated at 6000 rpm for 20s. The substrates were annealed at 450 °C for 30 min and cooled down to RT. For the cross-sectional SEM samples, a SnO_2 compact layer was prepared by spin coating onto cleaned FTO substrates (UV-ozone by 5 min before use). 60 μL SnO_2 solution was dropped onto the clean FTO substrate and spin-coated at 6000 rpm for 20 s. Afterwards, the substrates were annealed at 150 °C for 30 min, cooled down to RT, and exposed to UV ozone for 3 min.

To prepare the pristine perovskite precursor, 10.0 mg CsI, 86.0 mg FAI, and 11.2 mg MABr were first dissolved in 0.5 mL mixed solution of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) with volume ratio of 10:1. After fully dissolved, 253.6 mg PbI_2 and 36.7 mg $PbBr_2$ were added to the solution, followed by another 13.1 mg MACl. For the EA, PA and BA precursors, 3% EAI/ 3% PAI/ 2% BAI (mol ratio relative to Pb) were directly added into the pristine solution. 50 µL perovskite precursor solution was dropped onto as-prepared TiO_2 or SnO_2 substrates. The substrates were then spun at 4000 rpm for 15-25 s, 30 µL antisolvent (ethyl acetate) was dripped onto the center of the substrate while spinning. The films were thermally processed in a N_2-filled glovebox at 70 °C for 3 min and annealed at 100 °C for 50 min. A thin layer of Spiro-OMeTAD was then coated onto the films following a procedure reported previously (C. Fei, B. Li, R. Zhang, H. Fu, J. Tian and G. Cao, *Adv. Energy Mater.*, 2017, **7**, 1602017). Finally, 90 nm gold was thermally evaporated as the top electrode, with a device active area of 0.105 cm^2.

Characterization The main Linear absorption spectra were obtained using an Agilent UV spectrophotometer (Cary 60). Steady-state and time-solved PL spectra were collected using Horiba fluorescence spectrometers. XRD measurements were carried out on a PANalytical X-ray diffractometer with a step size of 0.01°. GIWAXS experiments were taken at Cornell High Energy Synchrotron Source (CHESS, beamline D1) with an X-ray beam energy of 13.02 KeV. The incident X-ray angle was 0.25° and sample to detector distance was 190 mm. The GIXSGUI graphical user interface was used to process the image and obtain the line cuts (Z. Jiang, *J. Appl. Crystallogr.* 2015, **48**, 917). SEM images were acquired using a Hitachi field-emission scanning electron microscope (SU8020). The J-V curves and steady-state power conversion efficiencies were measured using a Keithley source meter (2612B) under AM 1.5G and 100 mW/cm^2 illumination. Long-term stability studies were acquired on samples stored in a brown desiccator under both low (10-15% RH) and high (45-50% RH) humidity in the dark. The IPCE was measured in the direct current mode using a custom assembled system with a xenon lamp and monochromator. The EIS studies were carried out using a Zahner electrochemical workstation (ZENNIUM) in the dark. Rrec was extracted from the Nyquist plot via Zview software.

The TA experiments were performed using a commercial Ti:sapphire laser at a repetition rate of 5 kHz (Coherent Astrella) with details reported elsewhere (C. Fei, J. S. Sarmiento and H. Wang, *J. Phys. Chem. C*, 2018, **122**, 17035-17041.). A small portion of the fundamental beam at 805 nm was focused on a sapphire plate to generate a white continuum probe pulse (430-780 nm). A large portion of the 805 nm pulse was sent to a collinear optical parametric amplifier (Light conversion) to generate a pump pulse at 400 nm, which was chopped at 2.5 kHz and attenuated by a neutral density filter. Pump and probe pulses were focused and overlapped on the sample and the time resolution was about 100 fs. The TA spectra were collected on a commercial pump-probe spectrometer (Helios Fire, Ultrafast Systems). The TR was collected on the same setup, with the probe pulse reflected from the surface of the film at an incident angle of 45°. The polarization of the pump pulse was adjusted by a half-wave plate. The chirp of the white light was corrected using the software Surface Xplorer (Ultrafast systems).

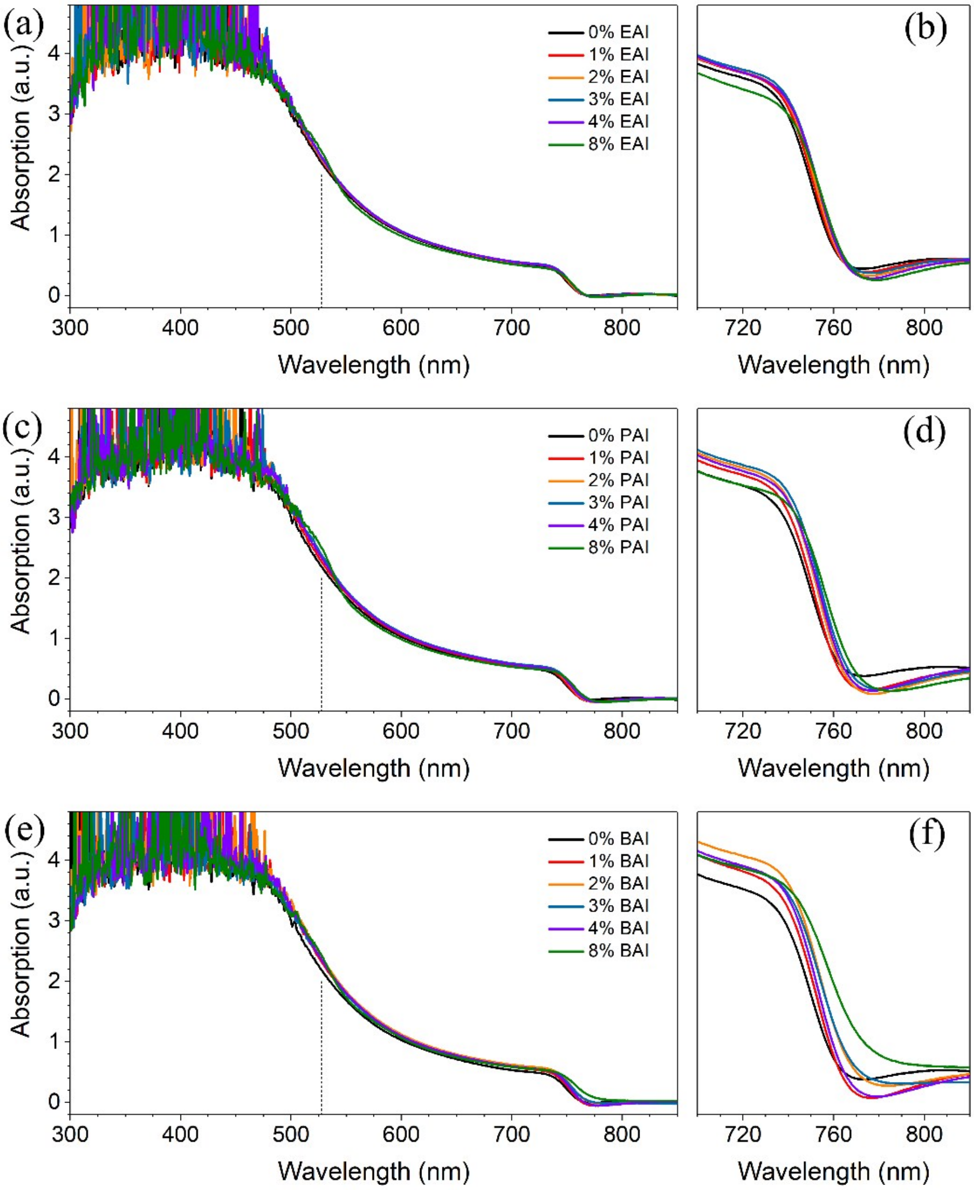

Fig. S1 Optical absorption spectrum of the multiple ion perovskite with different ratio large-size organic ion: (a)-(b) EA^+, (c)-(d) PA^+, (e)-(f) BA^+.

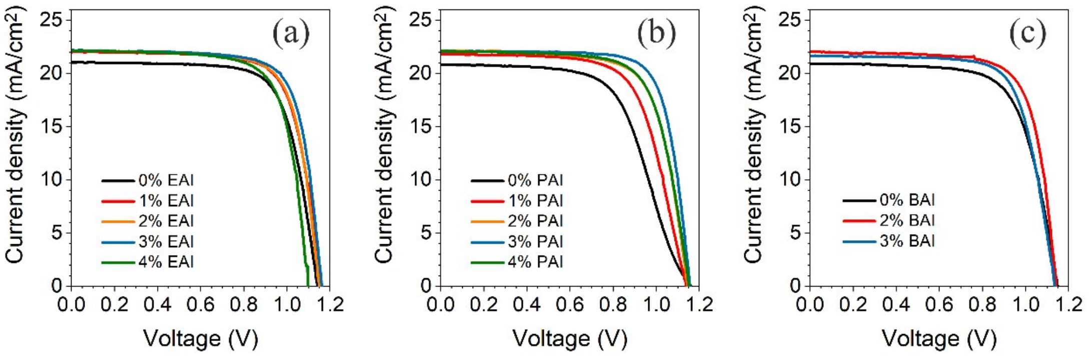

Fig. S2 J-V curves of perovskite solar cells with different ratio cations: (a) EAI, (b) PAI and (c) BAI.

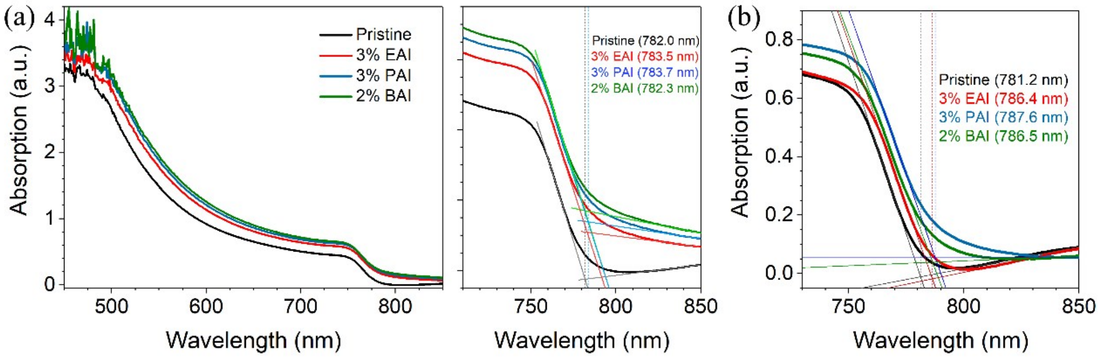

Fig. S3 UV-vis absorption spectra of perovskite films with different cations: (a) $MAPbI_3$ and (b) multiple ion perovskite.

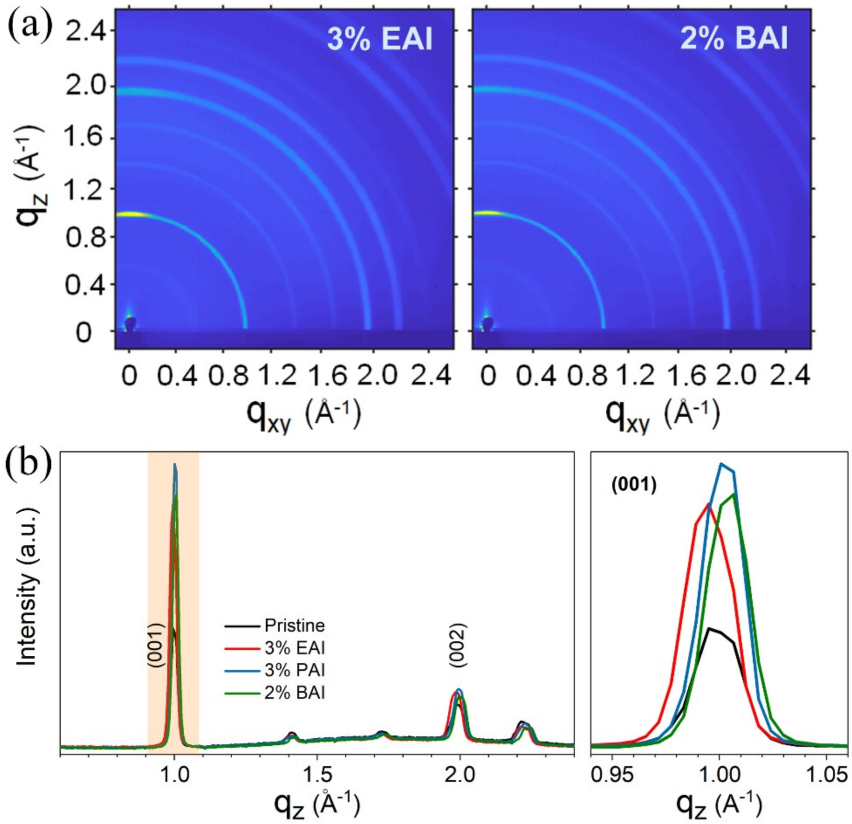

Fig. S4 (a) GIWAXS images of 3% EAI and 2% BAI perovskite films; (b) vertical line cut of the GIWAXS images.

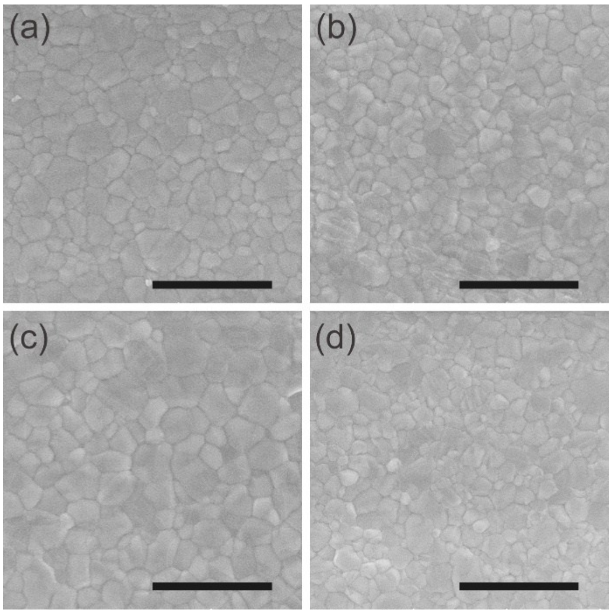

Fig. S5 Low magnification SEM images of perovskite films with different cations: (a) pristine; (b) 3% EAI; (c) 3% PAI; (d) 2% BAI. All of the scale bars are 2μm.

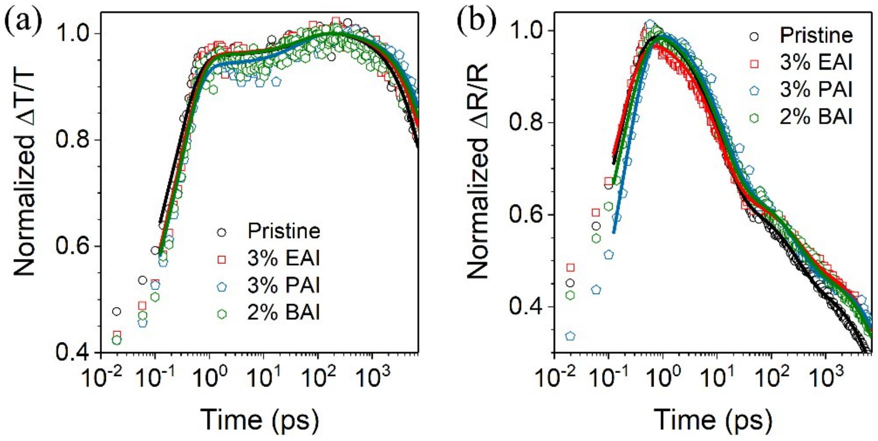

Fig. S6 Fitting results of the (a) transient absorption (TA) and (b) transient reflection (TR) lifetime from the perovskite films with different large-size organic cations.

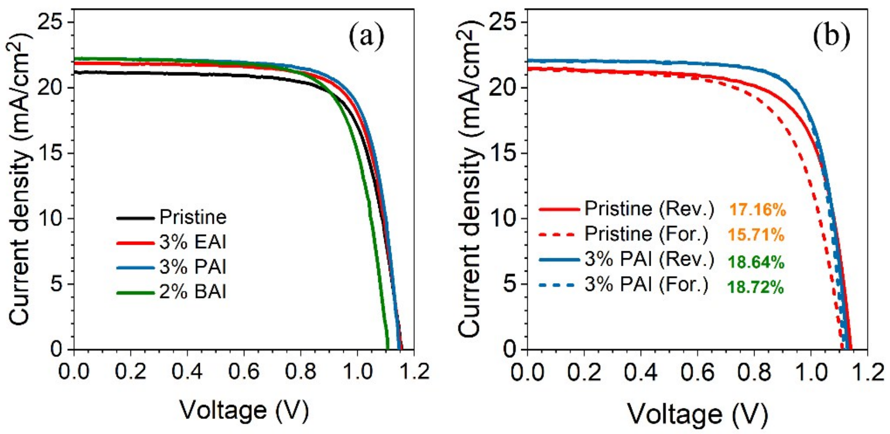

Fig. S7 (a) Different precursor-based perovskite solar cells with FTO/SnO_2/perovskite/Spiro-OMeTAD/Au device structure; (b) Reverse and forward J-V scan of pristine and 3% PAI perovskite solar cells.

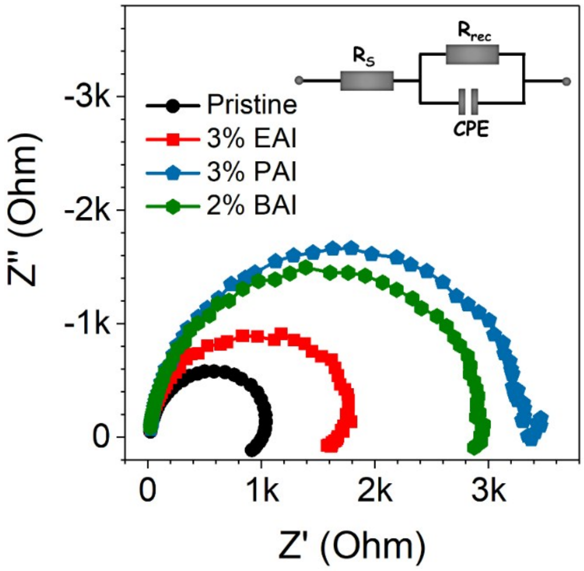

Fig. S8 Nyquist curves of the perovskite solar cells with different large-size organic ions at the bias of 1.0V in dark condition.

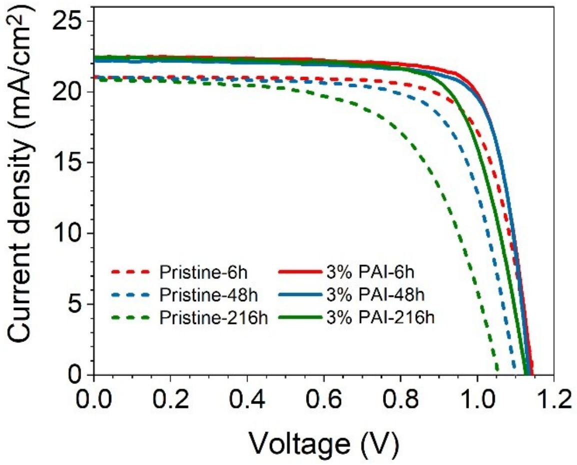

Fig. S9 J-V curves of pristine (dash lines) and 3% PAI (solid lines) perovskite solar cells with different precursor aging time.

Table S1 Photovoltaic parameters of the perovskite solar cells with different concentration EA/PA/BA cations

PSCs		Jsc (mA/cm^2)	Voc (V)	FF	PCE (%)	Maximum PCE (%)
EA	0%	21.05±0.31	1.14±0.01	0.71±0.02	16.95±0.42	17.44
	1%	21.96±0.36	1.14±0.02	0.71±0.01	18.02±0.66	18.72
	2%	21.99±0.29	1.15±0.01	0.72±0.01	18.19±0.53	18.83
	3%	21.92±0.35	1.14±0.01	0.73±0.02	18.38±0.69	19.43
	4%	22.03±0.24	1.10±0.01	0.72±0.02	17.39±0.48	17.76
PA	0%	20.75±0.12	1.15±0.01	0.58±0.04	13.93±0.50	14.60
	1%	21.80±0.21	1.14±0.01	0.66±0.02	16.37±0.44	16.71
	2%	22.08±0.26	1.14±0.01	0.69±0.01	17.17±0.82	18.07
	3%	22.12±0.31	1.14±0.01	0.73±0.01	18.65±0.51	19.41
	4%	22.01±0.25	1.14±0.02	0.70±0.02	17.46±0.68	18.09
BA	0%	20.83±0.20	1.15±0.01	0.68±0.02	16.29±0.47	16.67
	2%	22.02±0.34	1.14±0.01	0.72±0.01	18.00±0.55	18.53
	3%	21.59±0.19	1.14±0.02	0.70±0.02	17.32±0.46	17.79

*The devices were fabricated with a structure of FTO/SnO_2/perovskite/Spiro-OMeTAD/Au. Each of the average data was collected from 8 to 12 solar cells.

Table S2 Simulated parameters of the lifetime of the transient absorption traces

Sample	Pristine	3% EAI	3% PAI	2% PAI
τ_1 (ps)	0.25	0.28	0.27	0.29
τ_2 (ps)	55.76	57.39	45.72	49.93
τ_3 (ns)	27.55	34.48	44.58	38.66

* The amplitude of τ_1 and τ_2 are negative, demonstrating the rising ranges.

Table S3 Simulated parameters of the lifetime of the transient reflection traces

Sample	Pristine	3% EAI	3% PAI	2% PAI
τ_1 (ps)	0.16	0.15	0.20	0.19
τ_2 (ps)	11.40	10.95	12.98	11.76
τ_3 (ps)	277.89	319.13	285.49	304.63
τ_4 (ns)	13.63	20.80	23.65	18.97

* The amplitude of τ_1 is negative, demonstrating the rising ranges.

Table S4 Photovoltaic parameters and simulated photoluminescence lifetimes of the perovskite prepared from different precursors (FTO/TiO_2 substrate)

PSCs	Jsc (mA/cm^2)	Voc (V)	FF	PCE (%)	Maximum PCE (%)	τ (ns)
Pristine	21.27±0.43	1.11±0.01	0.73±0.02	17.23±0.49	17.62	143.1
3% EAI	21.81±0.45	1.12±0.01	0.75±0.01	18.30±0.63	18.92	206.4
3% PAI	22.26±0.29	1.13±0.01	0.78±0.01	19.65±0.56	20.25	267.0
2% BAI	22.01±0.40	1.11±0.02	0.76±0.02	18.72±0.78	19.43	238.8

* Each of the average data was collected from 8 to 12 solar cells.

Table S5 Photovoltaic parameters of the perovskite solar cells with FTO/SnO_2/perovskite/Spiro-OMeTAD/Au device structure

PSCs	Jsc (mA/cm^2)	Voc (V)	FF	PCE (%)	Maximum PCE (%)
Pristine	21.27±0.16	1.15±0.01	0.73±0.01	17.92±0.25	18.19
3% EAI	21.91±0.45	1.15±0.01	0.74±0.01	18.69±0.63	19.36
3% PAI	22.15±0.29	1.15±0.01	0.74±0.01	18.82±0.56	19.65
2% BAI	21.98±0.40	1.11±0.02	0.72±0.02	17.49±0.61	18.18

* Each of the average data was collected from 8 to 12 solar cells.