Supporting Information

Surface Modification via Self-Assembling Large Cation for Improved Performance and Modulated Hysteresis of Perovskite Solar Cells

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Experimental section

Materials

Unless specified, otherwise all chemicals were purchased from Alfa Aesar or Sigma-Aldrich and used as received. $SnCl_2 \cdot 2H_2O$ was purchased from Aladdin. Formamidinium iodide (FAI) and methylammonium bromine (MABr) were purchased from Lumtec, Taiwan. Lead iodide (PbI_2) and lead bromine ($PbBr_2$) were purchased from TCI. Phenyl-C61-butyric acid methyl ester (PCBM), n-Butylammonium (BA), tert-butylammonium (tBAI) and Spiro-OMeTAD were purchased from Xi'an Polymer Light Technology Corp.

Preparation of the perovskite precursors.

The CsFAMA mixed perovskite precursor was prepared by dissolving 1.4 M mixture of metal leadsalts which were composed of 0.85 PbI_2 and 0.15 $PbBr_2$, and 1.3 M organic cation which were composed of 0.85 FAI and 0.15 MABr in the mixture solvent of DMF/DMSO (4:1, by volume), and added 34 μL CsI (pre-dissolved as a 2 M stock solution in DMSO) to achieve the desired $Cs_{0.05}(FA_{0.85}MA_{0.15})_{0.95}Pb(I_{0.85}Br_{0.15})_3$ perovskite solution with proper excess lead halide.

Device fabrication

FTO glass was etched by a laser machine (Universal Laser Systems, VLS2.30), and followed by ultrasonic cleaning through detergent, pure water and ethyl alcohol for 20 min, respectively. They were then dried with dry-air gas flow and then treated by plasma for 5 min. The compact SnO_2 film was achieved by chemical bath deposition (CBD). 5g urea was dissolved into 400mL deionized water, followed by the addition of 100 μL mercaptoacetic acid and 5 ml HCl (37 wt%). Finally, $SnCl_2$•$2H_2O$ was dissolved in the solution at 0.012 M and then stored in fridge for 3 days before use. The as cleaned FTO glass was soaked into the diluted $SnCl_2$•$2H_2O$ solution (0.002M) for 2 hours at 70 ℃ and then washed by deionized water and dried by gas gun blowing. The CBD process was repeated for 3 times to achieve the desired thickness, followed by annealing at 180℃ for 1 hour. After cooling down, a 30 uL PCBM/ chlorobenzene (10 mg/mL) solution was spun onto the SnO_2 substrates, and followed by sintered at 70 ℃ for 5 min. The perovskite absorber was deposited on the UV-processed SnO_2 substrates (UV illuminated for 15 min) by spun a 25 μL mixed perovskite solution at 6000 rpm for 30 s with an acceleration speed of 1000 rpm, and 100 μL anti-solvents of ethyl acetate was dropped at the last 5^{th} second. The films were then annealed at 120 ℃ for 45 min, and after cooling down, a 30 uL different concentration of tBAI/ isopropanol solution was spun onto the perovskite films and followed by a sintering for 5 min at 100 °C. After cooling down, a 25 μL Spiro-OMeTAD solution,dissolving 73mg Spiro-OMeTAD into 1 mL chlorobenzene followed by the addition of 18 μL Li-TFSI (pre-dissolved as a 520mg/mL stock solution in acetonitrile) and 29 μL FK209 (pre-dissolved as a 300mg/mL stock solution in acetonitrile) and 30 μL 4-tert-butylpyridine was spun on the corresponding mixed perovskite films at 3000 rpm for 30 s. Finally, a 60 nm of gold was evaporated on the top of Spiro-OMeTAD as the back electrode to complete the whole device.

Characterizations

The surface morphologies and microstructures of the perovskite films and cross-sectional structure of the perovskite solar cells were investigated using a field-emission scanning electron microscopy (FESEM, Zeiss Ultra Plus). The different perovskite films were tested by an X-ray diffractometer (XRD, D8 Advance), UV-vis (lambda 750S, PerkinElmer). Grazing-incidence wide-angle X-ray scattering (GIWAXS) was performed at BL16B1 beamline of Shanghai Synchrotron Radiation Facility. The wavelength of incident X-ray was 0.124 nm and sample-to-detector distance was 283

mm. The incidence light angle was 0.12° and mar165CCD was used to collect the scattering signal. All the samples used for GIWAXS measurements were prepared in the same condition with the device fabrication. The steady-state photoluminescence (PL) spectra were obtained using a PL microscopic spectrometer (Flex One, Zolix, China); The time-resolved photoluminescence (TRPL) was measured at 770 nm using excitation with a 478nm light pulse from Delta Flex Fluorescence Lifetime System (Horiba Scientific Com., Japan)**.** The EIS measurements were carried out by an EC-lab (SP300). The photocurrent density-voltage curves of the perovskite solar cells were measured using a solar simulator (Oriel 94023A, 300 W) and a Keithley 2400 source meter. The intensity (100 mW/cm^2) was calibrated using a standard Si solar cell (Oriel, VLSI standards). All the devices were tested under AM 1.5G sun light (100 mW/cm^2) using a metal mask of 0.16 cm^2 with a scan rate of 10 mV/s.

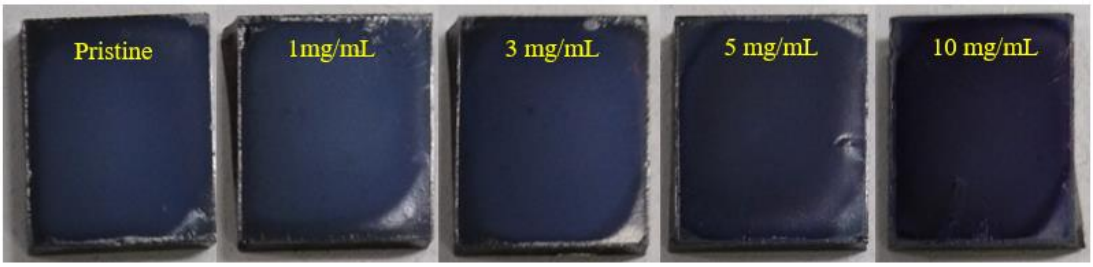

Fig. S1 The photograph of different concentration of tBAI/ IPA solution treated perovskite films.

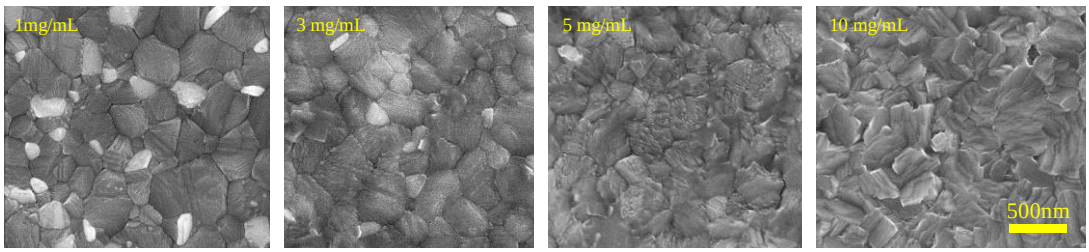

Fig. S2 The SEM images of different concentration of BAI/ IPA solution treated perovskite films.

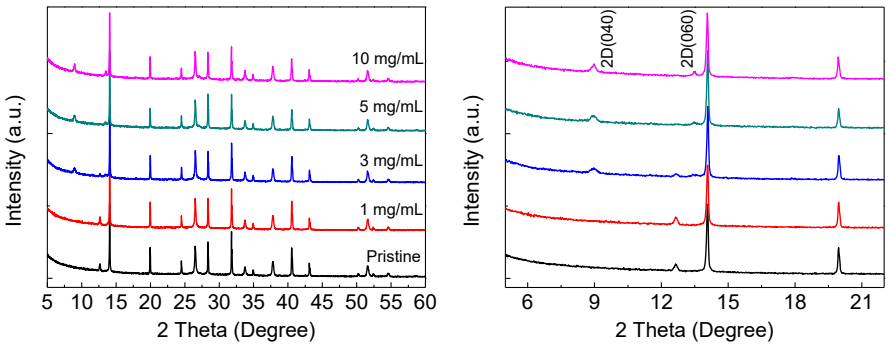

Fig. S3 XRD pattern of different concentration of BAI/ IPA solution treated perovskite films.

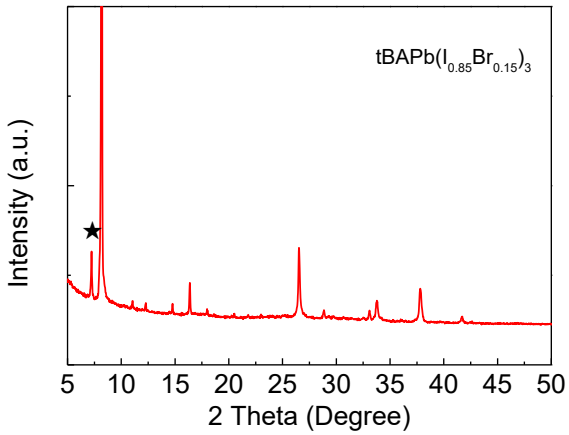

Fig. S4 XRD of tBA based 1D perovskite films.

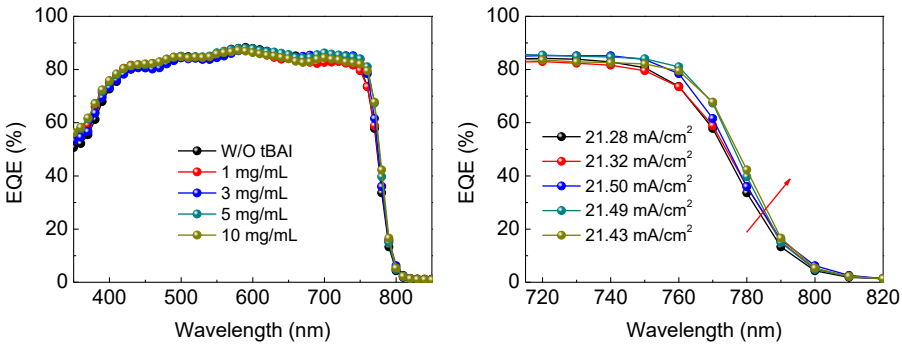

Fig. S5 EQE spectra of different concentration of tBAI/ IPA solution treated perovskite based solar devices.

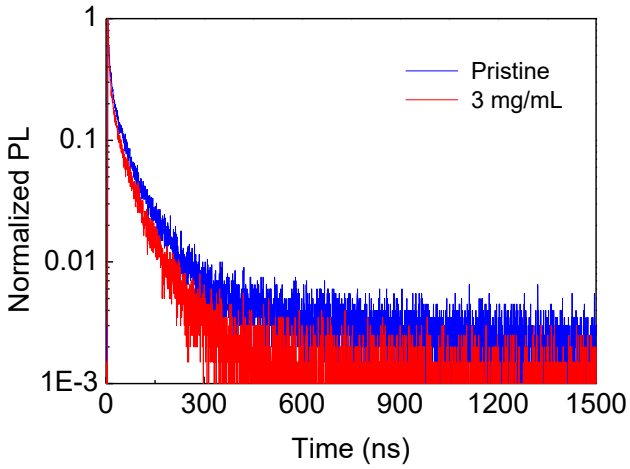

Fig. S6 Normalized TRPL spectra of pristine perovskite and 3mg/mL tBAI treated perovskite films with Spiro-OMeTAD layer.

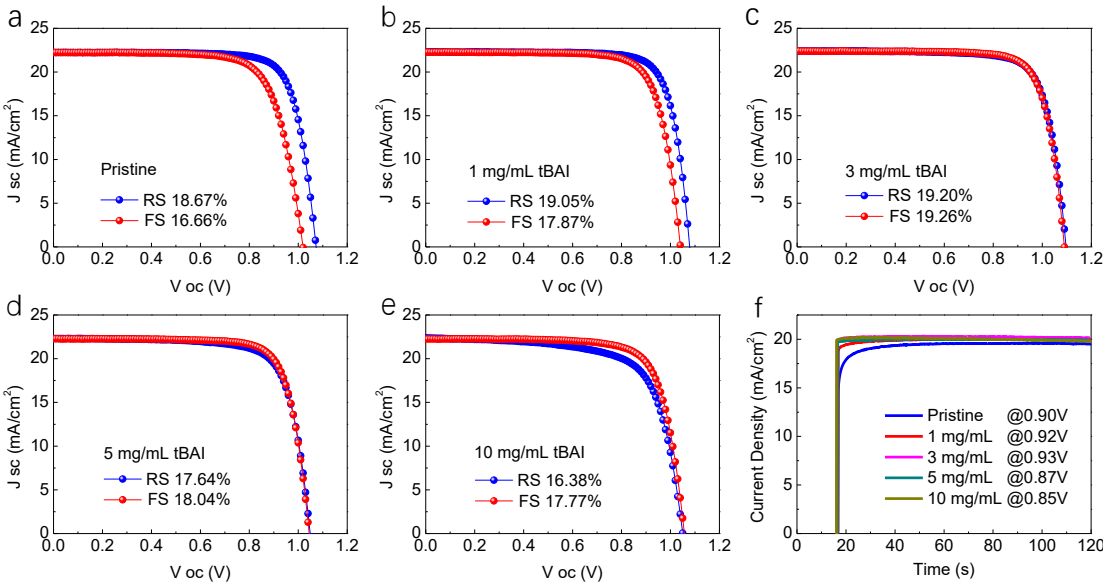

Fig. S7 The typical *J-V* curves of PSCs with different concentration of tBAI/ IPA solution treatment. (a) 0 mg/mL, (b) 1 mg/mL, (c) 3 mg/mL, (d) 5 mg/mL, (e) 10 mg/mL and (f) the corresponding steady state output current density under maximum power point.

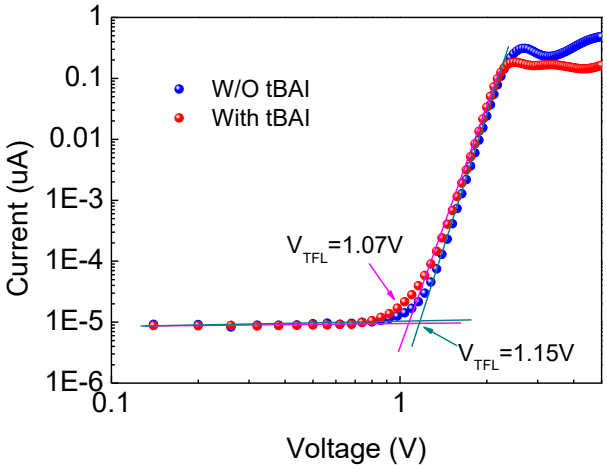

Fig. S8 Dark *J-V* characteristics of electron-only devices with and without tBAI treatment.

Table S1. The average parameters derived from the *J-V* curves of PSCs with different concentration of tBAI/ IPA solution treatment.

tBAI (mg/mL)	sweep	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
0	RS	1.069±0.011	22.04±0.15	0.771±0.011	18.37±0.26
	FS	1.019±0.032	22.03±0.17	0.690±0.031	15.58±0.65
1	RS	1.072±0.014	22.16±0.16	0.780±0.006	18.62±0.41
	FS	1.029±0.018	22.16±0.16	0.752±0.015	17.09±0.62
3	RS	1.089±0.015	22.33±0.31	0.777±0.010	18.92±0.53
	FS	1.083±0.016	22.32±0.32	0.782±0.011	18.93±0.44
5	RS	1.053±0.012	22.12±0.34	0.741±0.022	17.54±0.55
	FS	1.056±0.033	22.12±0.33	0.767±0.014	18.07±0.28
10	RS	1.040±0.021	21.90±0.26	0.734±0.034	16.92±0.64
	FS	1.044±0.018	21.91±0.25	0.764±0.018	17.66±0.23

Table S2. The fitted parameters of perovskite films with different concentration of tBAI/ IPA solution treatment from TRPL spectra. $y = A1\exp\left(-\frac{t}{\tau 1}\right) + A2\exp\left(-\frac{t}{\tau 2}\right)$,$\tau\text{eff} = \frac{A1\tau 1 + A2\tau 2}{A1 + A2}$.

Lifetime（ns）	Prinstine	1 mg/mL	3 mg/mL	5 mg/mL	10 mg/mL
A_1	0.37	0.28	0.24	0.37	0.43
τ_1	41.06	61.15	83.90	47.68	36.59
A_2	0.40	0.47	0.61	0.39	0.35
τ_2	588.12	822.46	1034.06	507.65	523.23

τ_{eff}	250.44	403.68	650.91	215.63	198.86

Table S3. The fitted parameters of pristine perovskite and 3mg/mL tBAI treated perovskite films with Spiro-OMeTAD from TRPL spectra. $y = A1\exp\left(-\frac{t}{\tau 1}\right) + A2\exp\left(-\frac{t}{\tau 2}\right)$,$\tau eff = \frac{A1\tau 1 + A2\tau 2}{A1 + A2}$.

Lifetime（ns）	A_1	τ_1	A_2	τ_2	τ_{eff}
Prinstine	0.72	4.95	0.27	51.74	17.55
3 mg/mL	0.75	3.78	0.25	41.64	13.24