

## Electronic Supplementary Information

(ESI)

### Insight into the effect of ion source for the solution processing of perovskite films

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### Experimental Section

**Perovskite Solution and Substrate Preparation.** Methylammonium iodide (MAI) was synthesized by reacting 27.6 mL methylamine, 27 ~ 32 wt% in ethanol (Sinopharm, China), with hydroiodic acid (HI), 45 wt% in water (Sinopharm, China) at 0°C for 2 h under argon atmosphere. HI was added dropwise while stirring. Methylammonium acetate (MAAc) was synthesized by reacting 30.3 mL methylamine, 27 ~ 32 wt% in ethanol (Sinopharm, China), with 10mL glacial acetic acid (98 wt%, Sinopharm, China) at 0 °C for 2 h. The acid was added dropwise while stirring. After complete reaction, the powder was collected by rotary evaporation, which was washed and purified with a mixture of ethanol and diethyl by air-pump filtration. The resulting powder was dried at 60 °C under vacuum before use. All the solutions were generated by dissolve reagents in anhydrous N,N-Dimethylformamide (Aldrich-Sigma, U.S.A.) with final concentration of ~ 40 wt%. Other reagents were purchased from Sinopharm, China.

Fluorine-doped tin oxide (FTO) coated glass was patterned by etching with 1 M HCl diluted in Milli-Q water and Zn powder. The etched substrate was then cleaned subsequently in water, saturated KOH solution in isopropanol, ethanol and acetone. The substrate was cleaned in oxygen plasma before use. A 30 nm thick dense TiO<sub>2</sub> hole-blocking layer (prepared as we reported before) was deposited on the FTO glass by spin-coating (4000 rpm, 30 s), and annealed at 150°C for 30 min in air. Afterwards, a 300 nm thick TiO<sub>2</sub> mesoporous layer was deposited on the TiO<sub>2</sub> dense layer by spin-coating (4000 rpm, 30 s) a diluted commercial TiO<sub>2</sub> paste (1:4 with ethanol by weight), followed by a sintering heat-treatment of 550 °C for 30 min in air.

**Device Fabrication and Testing.** The fresh films were prepared by spin-coating a 40 wt% perovskite solution at 4000 rpm in a nitrogen-filled glovebox. After that, the films were annealed at 100 °C for 5 min. The spiro-OMeTAD hole-transporting layer was prepared by dissolving 72.3 mg of spiro-MeOTAD in 1 mL of chlorobenzene (99.8%, Aldrich-Sigma, U.S.A.), to which 28.8  $\mu$ L of 4-tert-butylpyridine (96%, Aldrich-Sigma, U.S.A.) and 17.5  $\mu$ L of lithium bis (trifluoro-methanesulfonyl) imide (LITSFI, Aldrich-Sigma, U.S.A.) solution (520 mg LITSFI (98%) in 1 mL acetonitrile (99.8%, Aldrich-Sigma, U.S.A.) were added and then deposited by spin-coating (3000 rpm, 30 s). Finally, silver electrodes were thermally evaporated under vacuum to complete the PSCs fabrication.

Current density (J)–voltage (V) characteristics of the PSCs were measured using a 2400 Sourcemeater (Keithley, U.S.A.) under simulated one-sun AM 1.5G 100 mW/cm<sup>2</sup> intensity (Oriel Sol3A Class AAA, Newport, U.S.A.), under both reverse (from V<sub>OC</sub> to J<sub>SC</sub>) and forward (from J<sub>SC</sub> to V<sub>OC</sub>) scans. The step voltage was 50 mV with a 10 ms delay time per step. The maximum-power output stability of the PSCs was measured by monitoring the J output at the maximum-power V bias (deduced from the reverse-scan J–V curves). The J output is converted to PCE output using the following relation: PCE = {J (mA cm<sup>-2</sup>) × V (V)}/(100 (mW cm<sup>-2</sup>)). A shutter was used to switch on and off the one-sun illumination on the PSC. Typical, active area of the PSCs is 0.09 cm<sup>2</sup> defined using a non-reflective metal mask.

**Material and Film Characterization.** X-ray diffraction (XRD) patterns were obtained on a diffractometer (D8 Advance, Bruker, Germany) using Cu K $\alpha$  radiation, with 0.02° step. UV–vis absorption spectra of the perovskite films were recorded using a spectrometer (U-4100, Hitachi, Japan). A field-emission SEM (S-4800, Hitachi, Japan) was used to observe the top surfaces and cross sections. All films for XRD, SEM, and UV–vis were deposited on FTO/glass substrates with a 30 nm layer of dense TiO<sub>2</sub> and a 300 nm layer of mesoporous TiO<sub>2</sub>. The precursor solutions with or without additives were spin-coated on these substrates at 4000 rpm for 40 s.

**Table S1.** Calculated J<sub>sc</sub> of devices made from S-NH<sub>4</sub>Ac, S-MAAc and S-PbAc<sub>2</sub> precursor solutions.

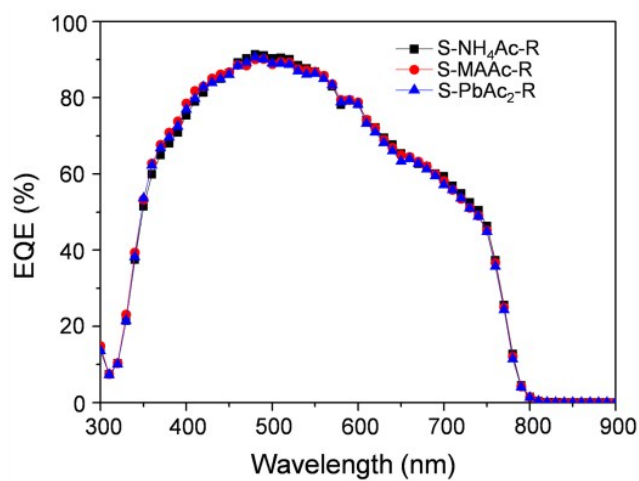
Routes	S-NH <sub>4</sub> Ac	S-MAAc	S-PbAc <sub>2</sub>
Calculated J <sub>sc</sub> (mA/cm <sup>2</sup> )	18.11	18.10	18.05

**Table S2.** PCE statistics of PSCs fabricated from S-NH<sub>4</sub>Ac, S-MAAc and S-PbAc<sub>2</sub> precursor solutions.

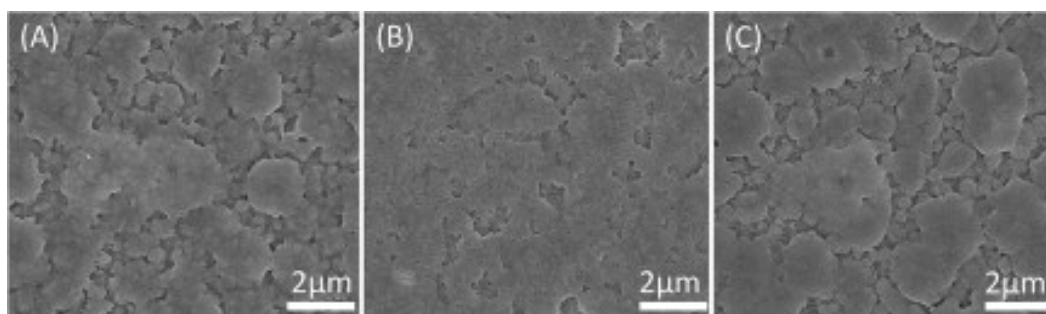
PSC No.		$J_{SC}$ (mA/cm <sup>2</sup> )	$V_{OC}$ (V)	FF (%)	PCE (%)
S-NH <sub>4</sub> Ac	1	19.08	0.942	57.22	10.28
	2	19.11	0.936	57.15	10.22
	3	19.02	0.944	57.21	10.27
S-MAAc	1	19.12	0.947	55.23	10.00
	2	19.08	0.945	55.31	10.00
	3	19.03	0.942	55.80	9.70
S-PbAc <sub>2</sub>	1	19.17	0.939	57.25	10.30
	2	19.05	0.938	57.33	10.24
	3	19.11	0.941	56.98	10.25

**Table S3.** Compositions of different precursor solutions.

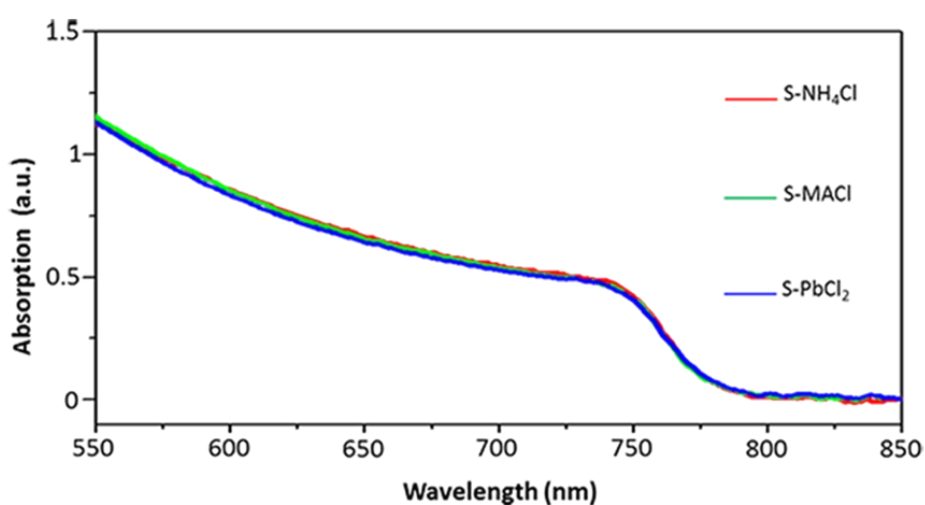
S-NH <sub>4</sub> Cl	S-MAcI	S-PbCl <sub>2</sub>
NH <sub>4</sub> Cl:MAI:PbI <sub>2</sub> =1:1:1	NH <sub>4</sub> I:MAcI:PbI <sub>2</sub> =1:1:1	MAI: NH <sub>4</sub> I:PbCl <sub>2</sub> :PbI <sub>2</sub> =1:1:0.5:0.5



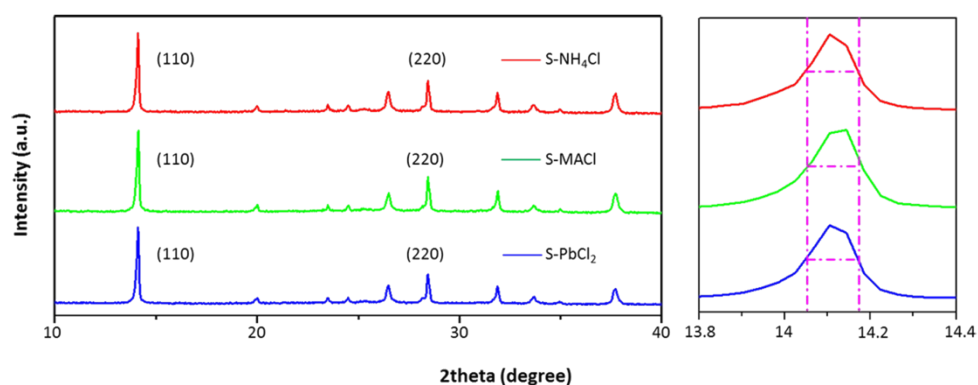
**Figure S1.** EQE for devices made from S-NH<sub>4</sub>Ac, S-MAAc and S-PbAc<sub>2</sub> precursor solutions.



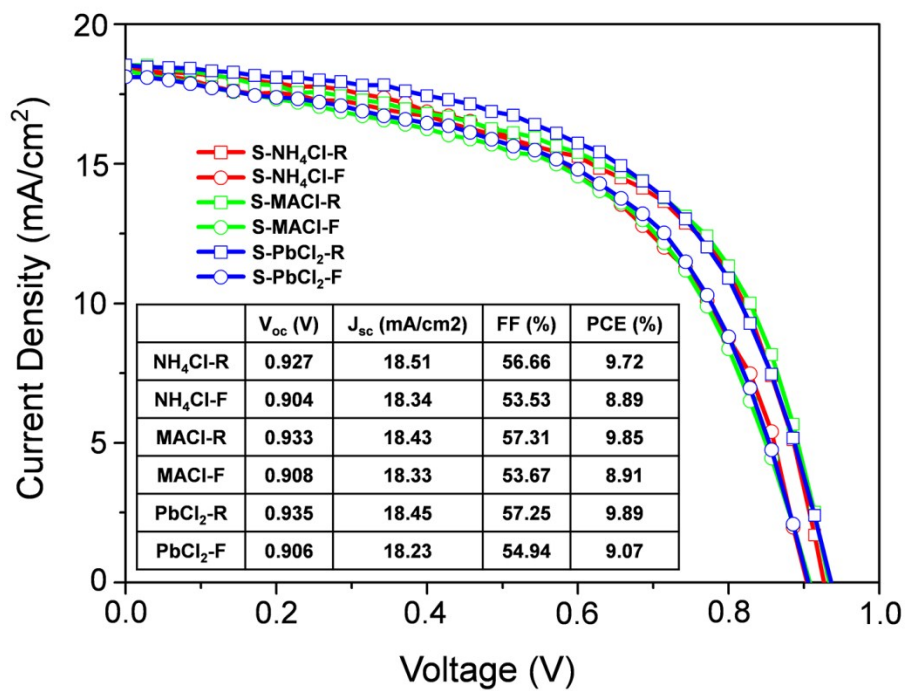
**Figure S2.** (A-C) SEM images of perovskite films made from S-NH<sub>4</sub>Ac, S-MAAc and S-PbAc<sub>2</sub> precursor solutions. (A) MAI, PbI<sub>2</sub> and NH<sub>4</sub>Ac (1:1:1 molar ratio) or S-NH<sub>4</sub>Ac; (B) NH<sub>4</sub>I, PbI<sub>2</sub> and MAAc (1:1:1 molar ratio) or S-MAAc; (C) NH<sub>4</sub>I, MAI, PbAc<sub>2</sub> and PbI<sub>2</sub> (1:1:0.5:0.5 molar ratio) or S-PbAc<sub>2</sub>.



**Figure S3.** UV-vis absorption spectra of perovskite films made from S-NH<sub>4</sub>Cl, S-MACl and S-PbCl<sub>2</sub> precursor solutions.



**Figure S4.** X-ray diffraction spectra of perovskite films made from S-NH<sub>4</sub>Cl, S-MACl and S-PbCl<sub>2</sub> precursor solutions.



**Figure S5.** J–V curves of devices made from S-NH<sub>4</sub>Cl, S-MACl and S-PbCl<sub>2</sub> precursor solutions with forward and reverse scan.