Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

High-efficiency and stable $FA_{0.75}MA_{0.25}SnI_3$ perovskite solar cell with large-size crystal grains prepared by doping with multifunctional chloride salt

Minghao Wang,*[a] *Wei Wang*,[b]

[a]School of Electronics and Information Engineering, Wuxi University, 333 Xishan Road, Wuxi 214105, China
[b]State Key Laboratory of Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China
*Corresponding author (email: 1239580958@qq.com)

Experimental Section

1. Materials

Tin iodide (SnI_2, 99.99%), tin fluoride (SnF_2, 99%), 1,2,4,5-benzenetetramine tetrahydrochloride ($C_6H_2(NH_2)_4 \cdot 4HCl$, ≥95%), *N*,*N*-dimethylformamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, 99.9%), chlorobenzene (CB, anhydrous, 99.8%), and bathocuproine (BCP, 99.9%). All above-mentioned chemicals were obtained from Sigma-Aldrich. Formamidinium iodide (FAI, 99.99%) and methylammonium iodide (MAI, 99.9%) were purchased from Xi'an Polymer Light Technology Corp. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, PVP AI 4083) was purchased from Heraeus Materials Technology Co. Ltd. Buckminsterfullerene (C_{60}, 99%) was purchased from Nano-C Tech. All chemicals were used as received without further purification.

2. Preparation of perovskite solutions

The perovskite solutions were prepared in a glove box with both H_2O and $O_2 < 0.01$ ppm, which were prepared by dissolving MAI (40 mg), FAI (129 mg), SnI_2 (373 mg) and SnF_2 (16 mg) in a mixed solvent of 800 μL DMF and 200 μL DMSO. Then the as-prepared solutions were stirred for three days. Before use, add x mol $C_6H_2(NH_2)_4 \cdot 4HCl$ ($x = 0.005$, 0.007, and 0.01) to the precursor solutions, and continue stirring until they are dissolved. Finally, the solutions were filtered before use.

3. Device Fabrication

Firstly, the ITO-coated glass substrates (17 mm × 17 mm) were ultrasonically rinsed with acetone, ethanol and deionized water in sequence. After blown with high purity N_2 and dried in a vacuum with an oven, the ITO substrates were treated with UV-ozone for 11 min. Then, The PEDOT:PSS aqueous solution was filtered with a 0.45 μm filter before use, and then it was spin-coated onto the patterned ITO glass substrates at 3500 rpm for 40 s, followed by a 130 °C thermal annealing for 30 min. Then perovskite precursor solution was spin-coated on the PEDOT:PSS-coated ITO substrates at 5000 rpm for 45 s, and 120 μL CB was used as the anti-solvent to treat the perovskite films at the 13th s. After the spin coating was completed, the perovskite film was placed on a 100 °C hot stage to treat for 15 min. The above operations were all done in a glove box filled with N_2. Finally, 35 nm C_{60}, 8 nm of BCP and 110 nm of Ag were sequentially deposited by thermal evaporation under a high vacuum of $>10^{-5}$ Pa, forming a series of PSCs. The active area for all devices is 0.1 cm^{-2}.

4. Device characterization

The scanning electron microscope (SEM) images of $FA_{0.75}MA_{0.25}SnI_3$ perovskite films were obtained by using a Hitachi S-4800 field emission scanning electron microscopy. The X-ray diffraction (XRD) patterns were carried out using a Bruker D8 ADVANCE XRD equipment. The steady-state photoluminescence (PL) and time-resolved PL (TRPL) were measured with a Hamamatsu C12132 fluorescence lifetime spectrometer using a 1.5 ns pulsed laser (frequency 15 kHz) at an excitation wavelength of λ=550 nm and an excitation power of 1 mW. The X-ray photoelectron spectroscopy (XPS) spectra of $FA_{0.75}MA_{0.25}SnI_3$ perovskite films on ITO glass substrate were carried out by using PHI Quantera SXM (ULVAC-PHI) in an ultrahigh-vacuum environment of 5×10^{-11} Pa. The current density-voltage characteristics were carried out using Keithley 2400 under AM 1.5G illuminations (100 mW/cm) from a solar simulator (Oriel Sol3A Class Solar Simulator (94023A)) in a glove box with N_2 atmosphere ($H_2O < 0.1$ ppm and $O_2 < 1$ ppm). The incident photon to current efficiency (IPCE) spectra were carried out by QTest Station 500AD Solar Cell Quantum Efficiency System (CROWNTECH, INC). The ultraviolet photoelectron spectroscopy (UPS) was operated with a He discharged lamp (He I 21.22 eV, Kratos Axis Supra). The electrochemical impedance spectra (EIS) were studied with a CHI660 electrochemical workstation (CH Instrument Inc.), which were measured within a frequency range of 10^5-1 Hz at 0.4 V under dark condition.

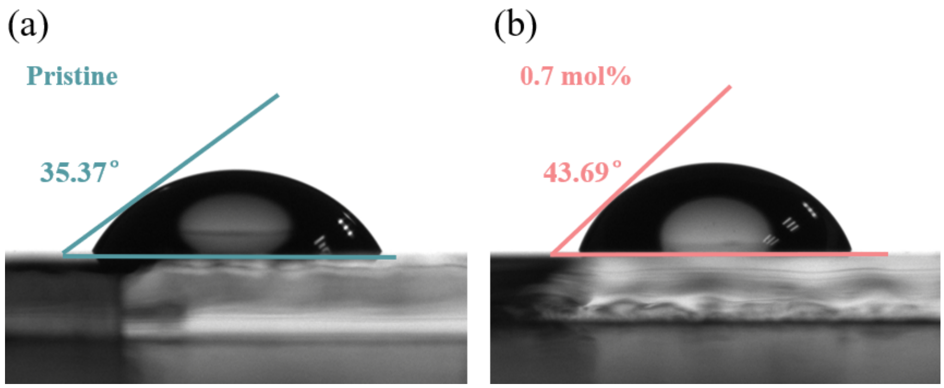

Fig. S1. (a) Contact angle of H_2O on pristine and (b) $C_6H_2(NH_2)_4 \cdot 4HCl$-doped $FA_{0.75}MA_{0.25}SnI_3$ films.

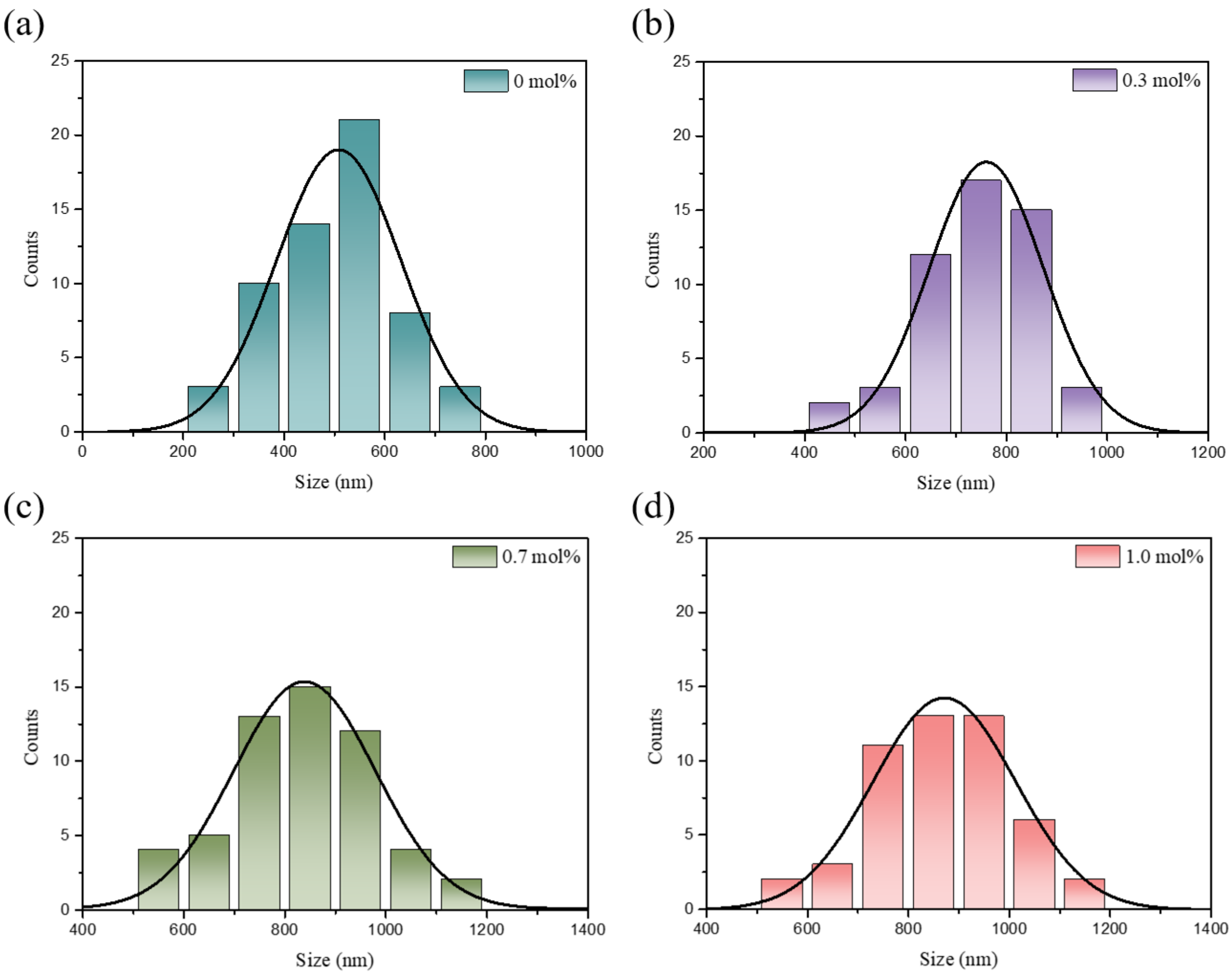

Fig. S2. Grain size statistics of the pristine perovskite and $C_6H_2(NH_2)_4 \cdot 4HCl$-incorporated perovskites with different doping concentration from top-view SEM images: (a) 0 mol%, 507 nm, (b) 0.5 mol%, 760 nm, (c) 0.7 mol%, 853 nm, (d) 1.0 mol%, 872 nm.

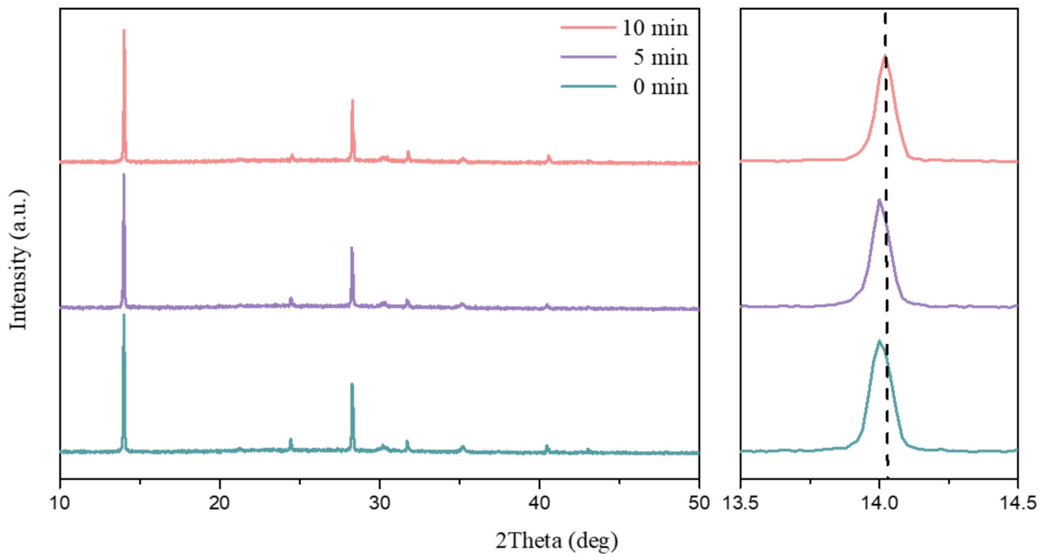

Fig. S3. XRD patterns for the precursor films annealed for 0 min, 5 mins and 10 mins.

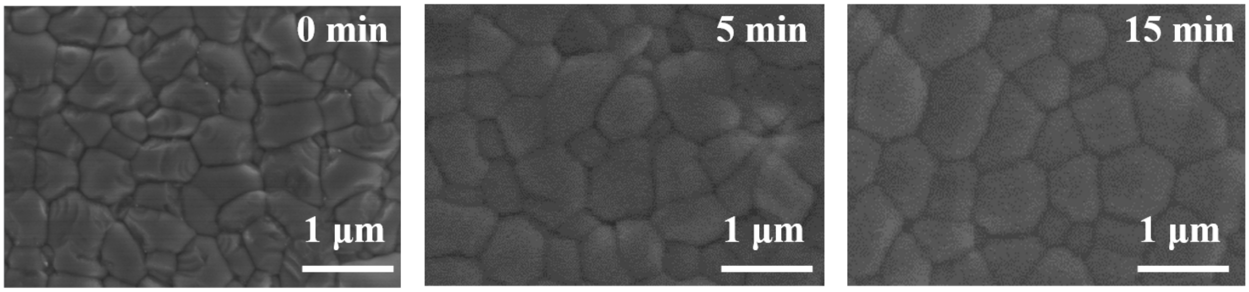

Fig. S4. SEM patterns for the $FA_{0.75}MA_{0.25}SnI_3$ films annealed for 0 min, 5 mins and 15 mins.

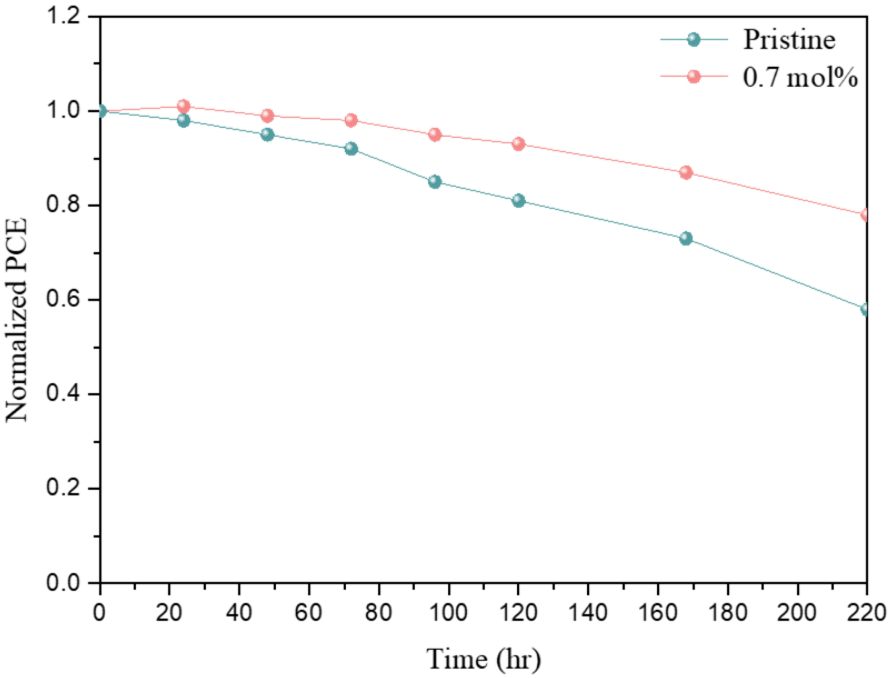

Fig. S5. Stabilities of devices based on pristine and $C_6H_2(NH_2)_4{\cdot}4HCl$-doped $FA_{0.75}MA_{0.25}SnI_3$ perovskites were measured under AM 1.5 real working condition.

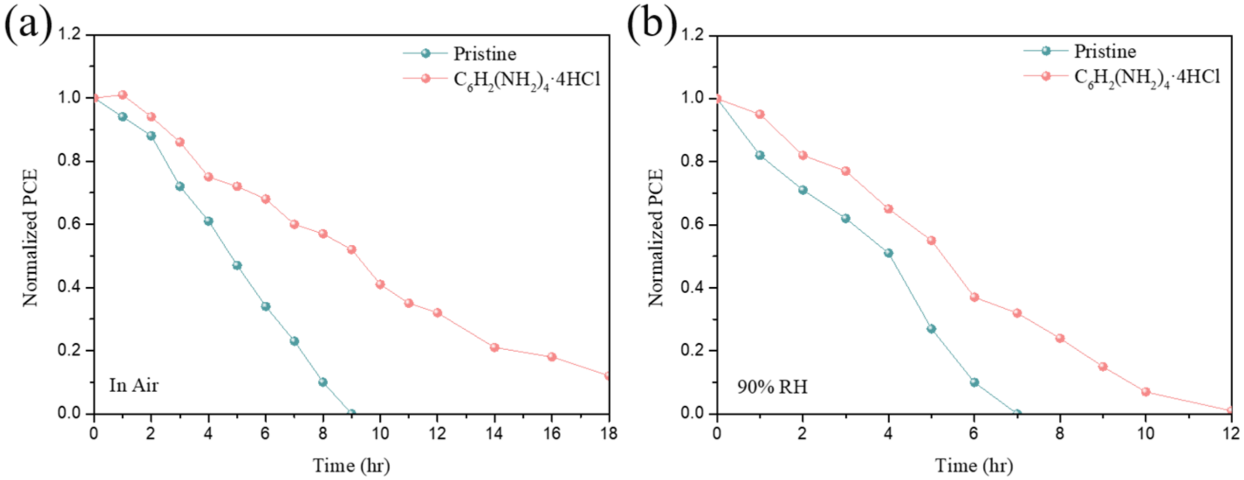

Fig. S6. Stabilities of devices based on pristine and $C_6H_2(NH_2)_4{\cdot}4HCl$-doped $FA_{0.75}MA_{0.25}SnI_3$ perovskites were measured in (a) air and (b) 90% high humidity environment.

Table S1. Fitted photoluminescence lifetimes for pristine and 0.7 mol% $C_6H_2(NH_2)_4{\cdot}4HCl$-doped $FA_{0.75}MA_{0.25}SnI_3$ perovskite films with a bi-exponential decay model. Here, A_1 and A_2 are fractional intensities, and τ_1 and τ_2 are lifetimes. The average carrier lifetime was calculated with $\tau_{avr} = A_1\tau_1+A_2\tau_2$.

Sample	τ_1 (ns)/A_1 (%)	τ_2 (ns)/A_2 (%)	χ^2	τ_{avr} (ns)
Pristine	0.46/35.82	2.18/64.18	0.914	1.56
0.7 mol% $C_6H_2(NH_2)_4 \cdot 4HCl$	0.99/32.84	3.93/67.16	1.106	2.97