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Supporting Information

Polar-Hydrophobic Ionic Liquid Induces Grain Growth and Stabilization in Halide Perovskites

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Experimental Section

Materials Synthesis and Film Fabrication

All raw chemicals are obtained from Sigma-Aldrich, USA with further purification except when mentioned specifically. MA^+TFA^- ionic liquids (ILs) are synthesized via proton transfer between a Brönsted acid, trifluoroacetic acid and a weak base, methylamine. Anhydrous trifluoroacetic acid (Sigma-Aldrich, USA) and methylamine (MA, 33 wt.% in ethanol solution; Sigma-Aldrich, USA) are reacted in the equimolar amount. Since these reactions are very exothermic, the dropwise addition of the acid to the amine was carried out by cooling the amine solution to 0 °C using an ice water bath. The mixture was then stirred at room temperature for 6 hours. To ensure a complete reaction, an excess of amine was used and then removed in vacuum using a rotary evaporator.

Film Fabrication:

For the deposition of $MAPbI_3$ perovskite thin films with on FTO-coated glass substrates, a 40 wt% PbI_2:MAI (molar ratio 1:1) mixture was dissolved in the N,N-dimethylmethanamide (DMF) solvent, with different amount of MA^+TFA^- as the additive, were prepared. The solutions were spin-coated on the substrates at 4000 rpm for 20 s. The as-formed thin films were then annealed at 130 ºC for 10 min. For obtaining better-quality thin films, the chlorobenzene-solvent-dripping process was introduced during the spin-coating step. Typically, the weight ratios of MA^+TFA^- and $MAPbI_3$ are 1:35, 1:25, 1:15 and 1:10, respectively.

Materials and Thin-Film Characterization. Qualitative analysis of as-synthesized MA^+TFA^- ILs has been carried out by Fourier-transform infrared spectroscopy (FTIR;

iS50, Nicolet, Thermo Scientific, USA) and ^{1}H NMR (Advance Ⅲ HD 400, Bruker, USA). Thermogravimetry and Differential Thermal Analyses (TG-DTA) of the samples were studied via a TG analyzer (DTG-60, Shimadzu, Japan) within the temperature range of 30 to 500 ^{o}C. The measurement process was carried out in the air with a heating rate of 10 ^{o}C/min. X-ray diffraction (XRD) patterns were collected using an X-ray diffractometer (D8 Discover, Bruker, Germany) using Cu Kα radiation (λ=1.5406 Å) at step size of 0.02°. 2D XRD were performed on an X-ray diffractometer with an in-situ heating stage (D8 Advance, Bruker, Germany). UV-vis absorption spectra were obtained on a UV-vis spectrometer (UV-2600, Shimadzu Scientific, Japan). Photoluminescence (PL) spectroscopy was performed on a spectrometer (FluoTime 300, PicoQuant, Germany) using 405 nm laser excitation. The surface and cross-sectional morphology and microstructure of samples were observed by a scanning electron microscopy (SEM; G500, ZEISS, Germany). Energy dispersive X-ray spectrometer (EDS; Octane Elite EDS System, EDAX, USA) attached to the SEM was employed for elemental analyses. The surface chemical compositions were measured using X-ray photoelectron spectroscopy (XPS; K-alpha, Thermo Scientific, USA).

PSC Fabrication and Testing. Patterned FTO-glass substrates were cleaned ultrasonically with an alconox (detergent) solution, followed by sonication in deionized water, acetone, and isopropyl alcohol sequentially for 20 min each. A 30-nm compact-TiO_2 layer was deposited on top of the etched FTO/glass substrates using the procedure described earlier. A 250-nm mesoporous-TiO_2 layer was then deposited by spin-coating followed by a sintering heat-treatment of 500 ˚C for 30 min in air. A 1.5 wt % solution of $SnCl_4$ he distilled water was spin-coated at 3000 rpm for 30 s. This is followed by annealing at 200 °C for 30 min, forming an ultrathin compact SnO_2 layer. The addition of SnO_2 coating is for purpose of enhancing the overall device open-circuit voltage and does not have an obvious effect on the solution wetting. The thin films of $MAPbI_3$ modified with or without the MA^+TFA^- additive were then deposited according to the procedure described above. A solution of Spiro-MeOTAD (Merck Group, Germany) hole-transporting material (HTM) coating was prepared by dissolving 72.3 mg of Spiro-MeOTAD in 1 mL of chlorobenzene (99.8%), to which 28.8 μL of 4-tert-butyl pyridine (96%) and 17.5 μL of lithium bis(trifluoromethanesulfonyl)imide (LITSFI) solution (520 mg LITSFI in 1 mL acetonitrile were added. The HTM was deposited by spin-coating (3000 rpm, 30 s). Finally, a 100 nm Au electrode was thermally-evaporated to complete the solar cells. The current density-voltage (J-V) of the solar cells were measured using a Keithley 2400 sourcemeter under simulated AM1.5 illumination (100 mW cm^{-2}) simulated using a solar simulator (Sol3A Class AAA, Oriel, USA). A non-reflective mask (0.09 cm^2) was used to define the PSC area. The stabilized maximum-power outputs of the PSCs were measured by monitoring the J outputs at the maximum-power V bias (deduced from the reverse-scan J−V curves). The external quantum efficiency (EQE) spectra were recorded with an EQE measurement system (Newport, USA).

Supplementary Figures

Figure S1. Photograph of 70 wt% clear solution of $MA^{+}TFA^{-}$ in DMF, demonstrating the high solubility.

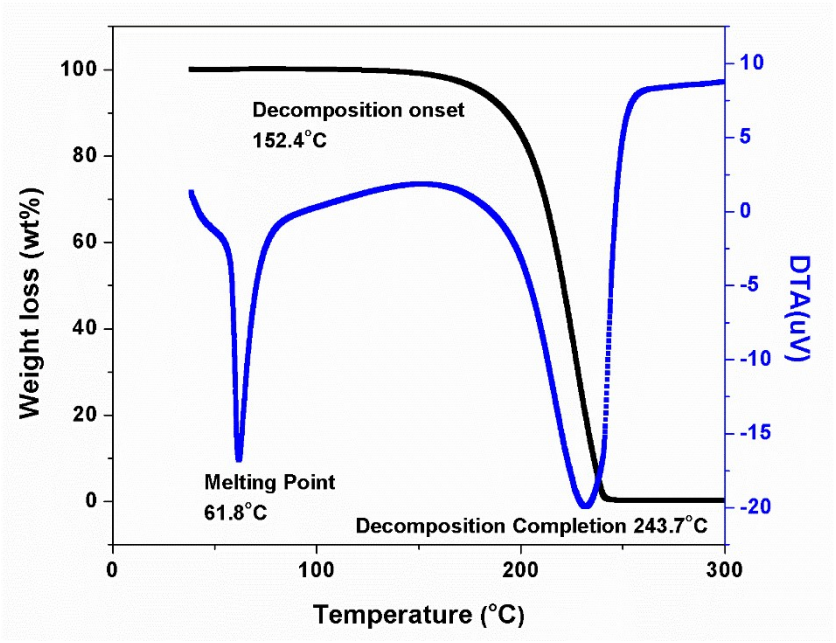


Figure S2. TG-DTA result of $MA^{+}TFA^{-}$, showing the melting point of 61.8 °C, and the decomposition onset at152.4 °C and completion at 243.7 °C.

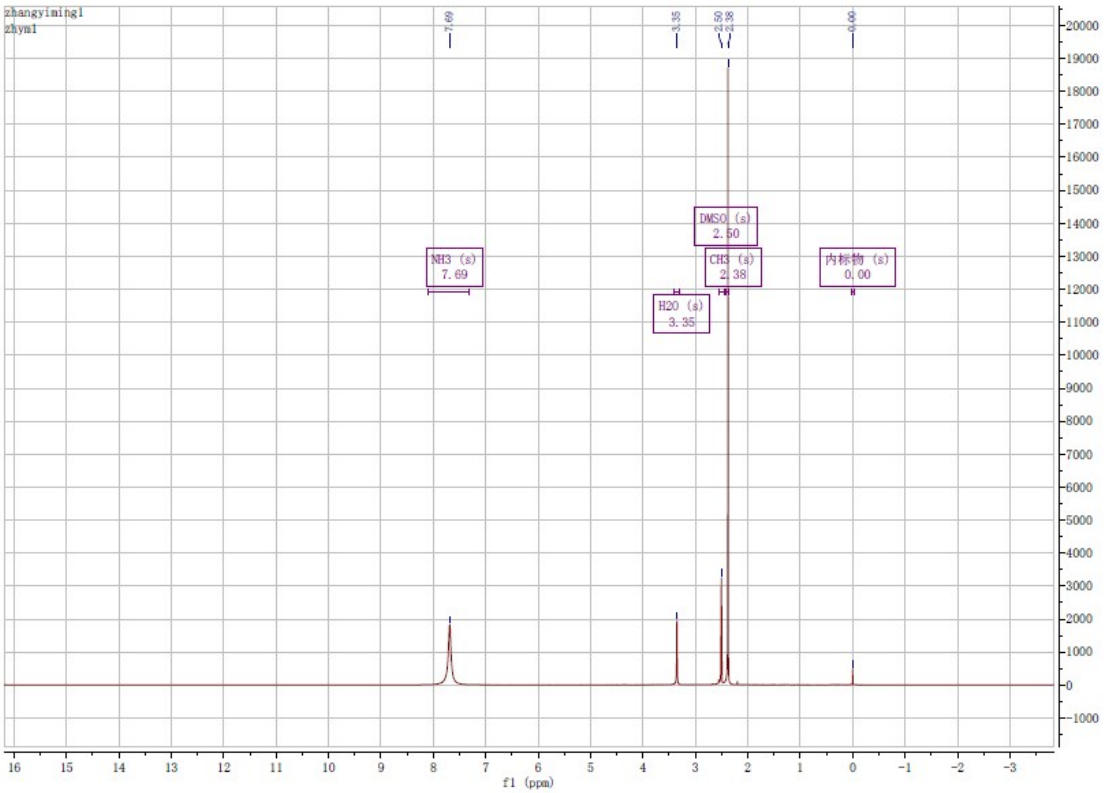


Figure S3. ^{1}H NMR spectrum (DMSO-d6, 400 MHz, TMS) of $MA^{+}TFA^{-}$.

^{1}H NMR**:** δ 7.69 (s, 4H), 2.38 (s, 3H), demonstrating the existing of $CH_3NH_3^{+}$ cation in DMSO.

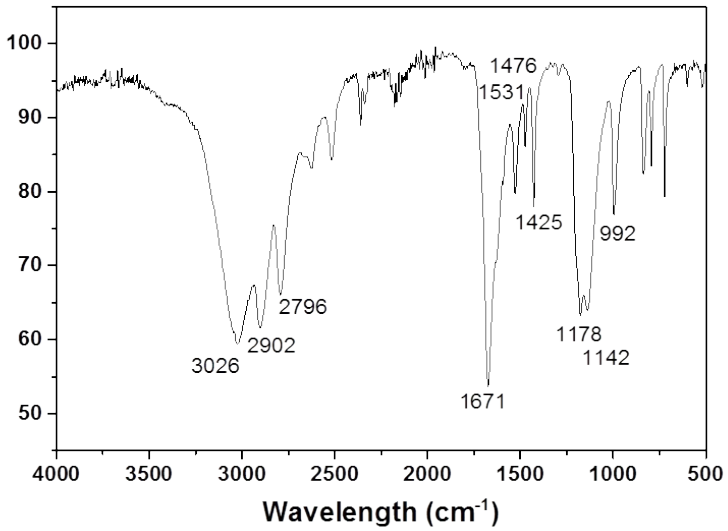


Figure S4. FTIR spectrum of MA^+TFA^-. The valleys are assigned as below: 3026 cm^{-1} for ν N-H, which confirms the existing of $-NH_3$; 2902 cm^{-1} for ν^s C-H, 2796 cm^{-1} for ν^{as} C-H, 1476 cm^{-1} for δ^{as} C-H; 992 cm^{-1} for ν C-H, suggesting the existence of methyl group; 1425 cm^{-1} for δ^s C-H in $-N-CH_3$, which confirms N atom is adjacent to methyl group, all above demonstrate the existence of $CH_3NH_3^+$ cation. 1178 and 1142 cm^{-1} for ν C-F, 1671 cm^{-1} for ν C=O, 1531 cm^{-1} for ν C-O, all these prove the existing of the anion CF_3COO^- .

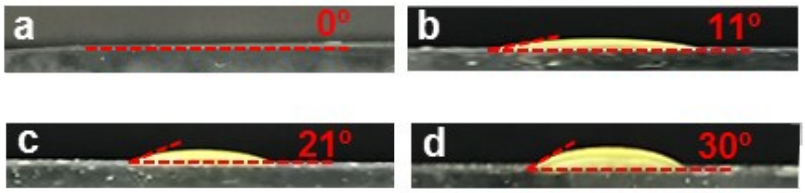


Figure S5. Cross-sectional optical images of $MAPbI_3$ perovskite solution droplets on compact-TiO_2-coated FTO-glasses with the increasing weight ratio of MA^+TFA^- to $MAPbI_3$: (a) 0; (b) 1:35; (c) 1:15, (d) 1:10.

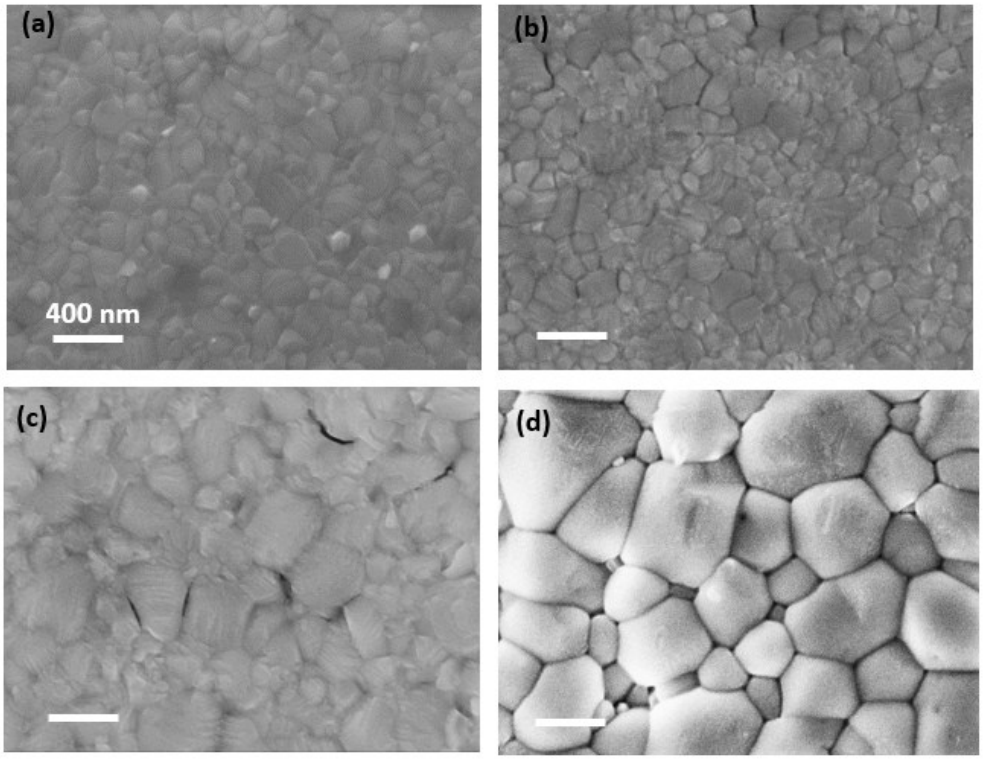


Figure S6. SEM images of $MAPbI_3$ perovskite thin films on compact-TiO_2-coated FTO-glasses made with different weight ratios of MA^+TFA^- to $MAPbI_3$: (a) 0; (b) 1:35; (c) 1:15; (d) 1:10. Note that (a) and (d) are reproduced from Figure 1c and 1d.

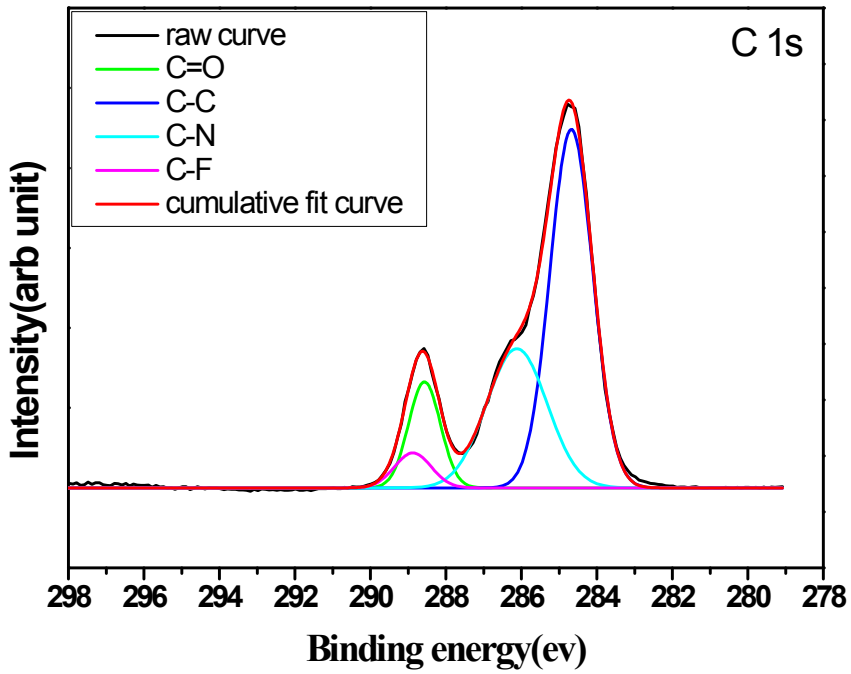


Figure S7. C 1s XPS of $MAPbI_3$ perovskite thin film made with MA^+TFA^-.

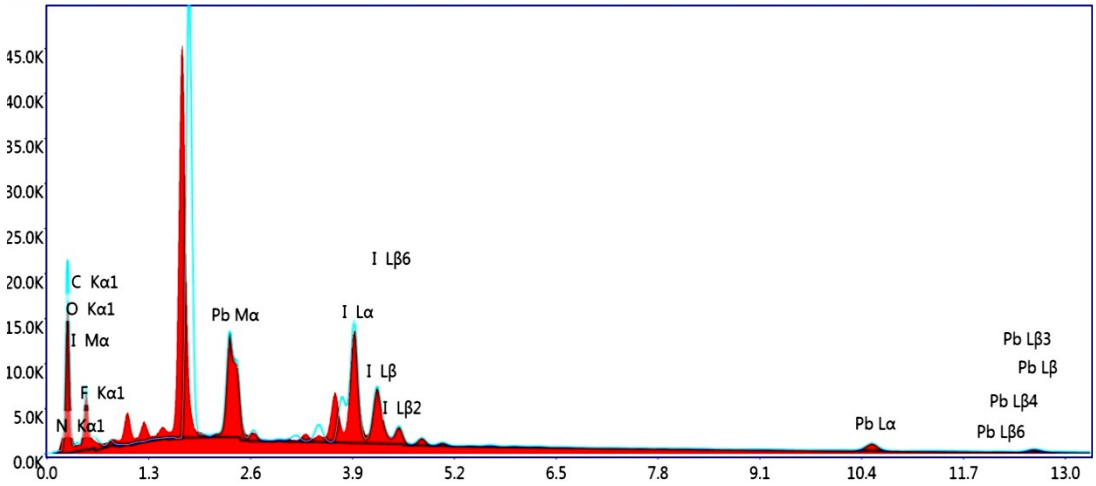


Figure S8. EDX spectrum of $MAPbI_3$ perovskite thin film made with $MA^{+}TFA^{-}$.

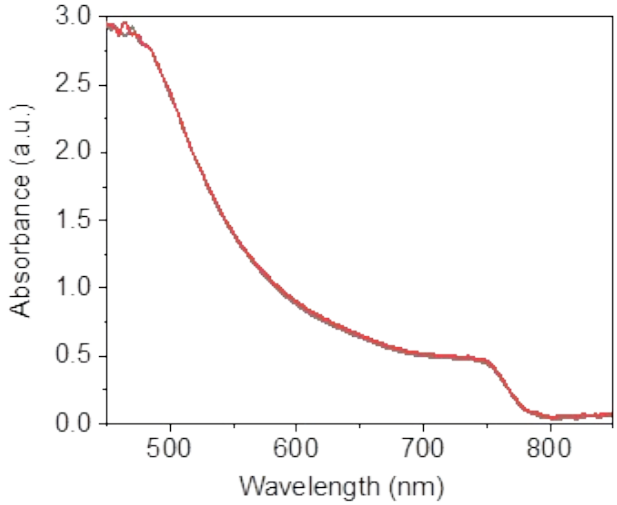


Figure S9. UV-vis absorption spectra of $MAPbI_3$ perovskite thin films made without (grey solid line) and with (red solid line) MA^+TFA^- additive.

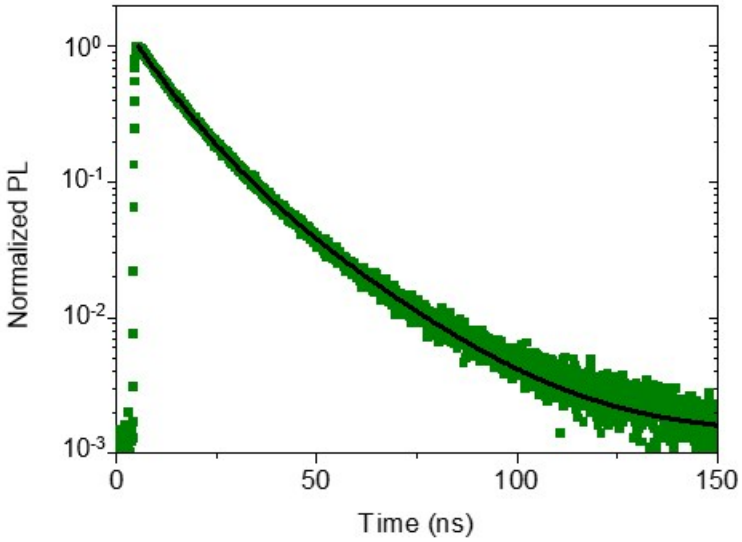


Figure S10. Time-resolved PL spectrum of the $MAPbI_3$ perovskite thin film that is made using solvent annealing method [ref: doi:10.1002/adma.201401685] and exhibit a similar grain size to the film made with MA^+TFA^- additive in this study. The spectrum is fit using a bi-exponential function and the fitting parameters are included in Table S1.

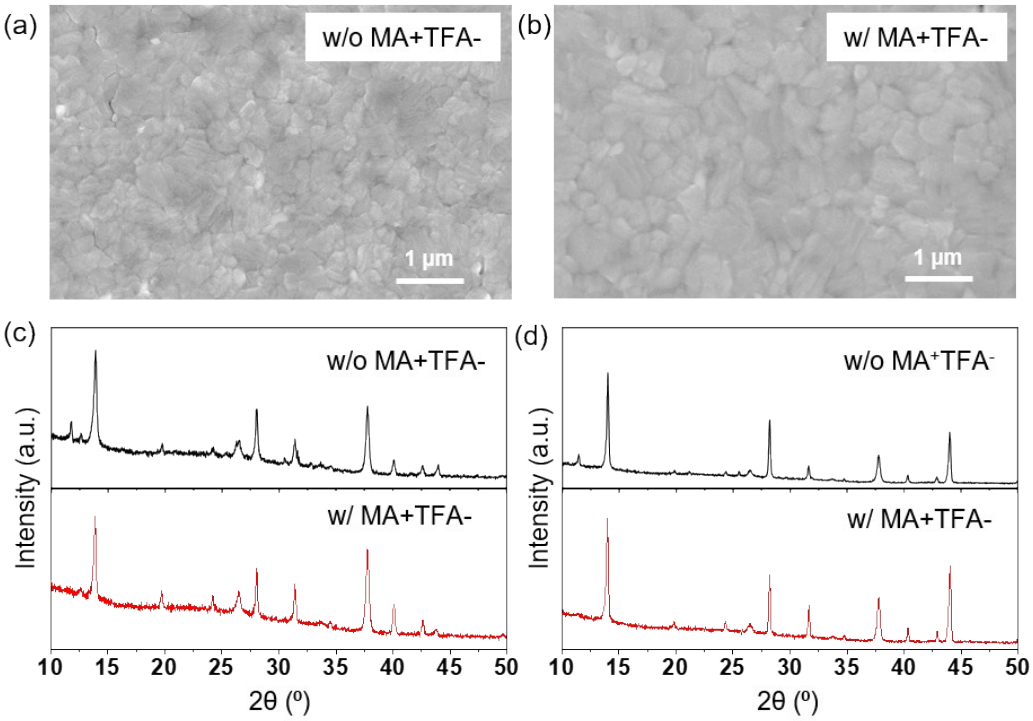
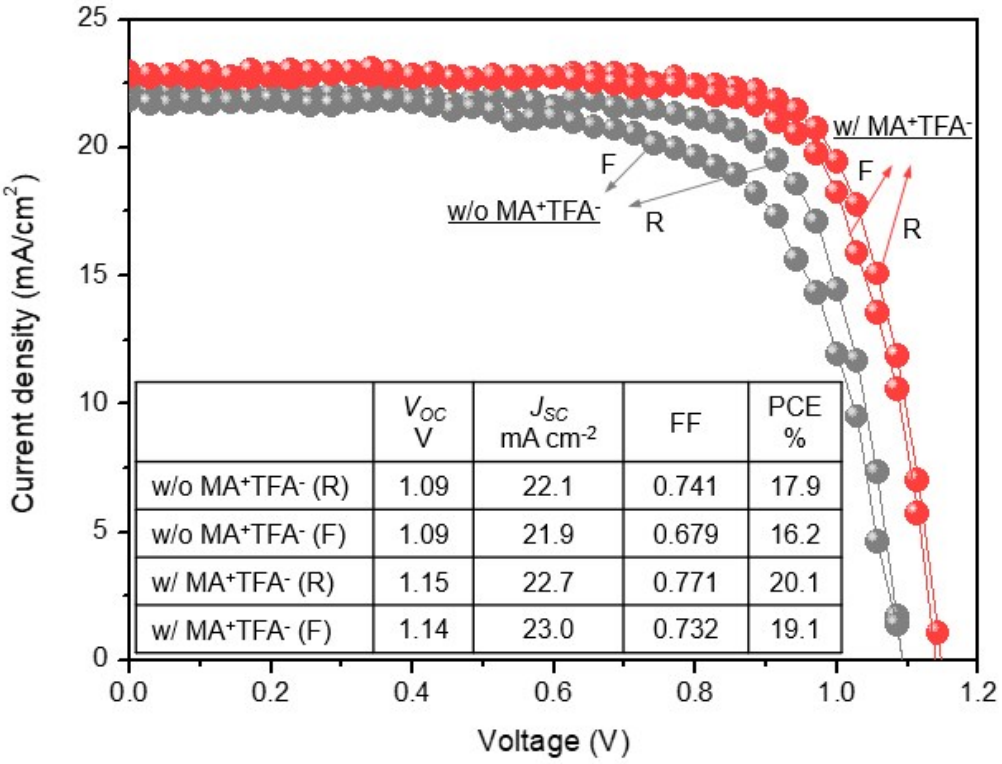


Figure S11. SEM images of the $FAPbI_3$ perovskite thin film made (a) without and (b) with MA^+TFA^- additive. (c) XRD patterns of the $FAPbI_3$ perovskite thin film made without and with MA^+TFA^- additive after storage 48-h exposure to the controlled humid condition (70% RH, RT). (d) XRD patterns of the $MA_{0.7}FA_{0.3}PbI_3$ perovskite thin film made without and with MA^+TFA^- additive after storage 48-h exposure to the controlled humid condition (70% RH, RT).



	V_{OC} V	J_{SC} mA cm^{-2}	FF	PCE %
w/o MA$^+$TFA$^-$ (R)	1.09	22.1	0.741	17.9
w/o MA$^+$TFA$^-$ (F)	1.09	21.9	0.679	16.2
w/ MA$^+$TFA$^-$ (R)	1.15	22.7	0.771	20.1
w/ MA$^+$TFA$^-$ (F)	1.14	23.0	0.732	19.1

Figure S12. J-V curves at both forward (F) and reverse ® scans for the best PSCs made without and with MA$^+$TFA$^-$ additive. Inset shows the extracted J-V parameters.

Table S1. Time constants for fitting the PL decays in Figure 3b using bi-exponential functions. τ_{avg} is the amplitude average PL lifetime.

	τ_1	τ_2	τ_{avg}
w/ MA^+TFA^-	10.9 ns	20.6 ns	15.6 ns
w/o MA^+TFA^-	6.1 ns	24.0 ns	6.3 ns
w/ MA^+TFA^- (solvent-annealed)	8.8 ns	20.5 ns	12.2 ns