## **Supporting Information**

## Synergetic Effects of DMA Cation Doping and Cl Anion Additive Induced Re-growth of MA<sub>1-x</sub>DMA<sub>x</sub>PbI<sub>3</sub> Perovskite

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## **Experimental Methods**

*Materials and Precursor Preparation:* The MAI, PbI<sub>2</sub> and MACl were purchased from Alfa Aesar. N,N-dimethylformamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, 99.8%) and chlorobenzene (CB, anhydrous, 99%) were purchased from J&K Scientific Ltd. The powder DMACl was synthesized by reacting dimethylamine (DMA, 40 wt.% in H<sub>2</sub>O) and hydrochloric acid (HCl, 36.0~38.0 wt.% in H<sub>2</sub>O) with a molar ratio of 1:1.3 at 60°C for 2 h. The precipitate was collected by rotary evaporation then recrystallized with ethanol, washed with ethanol three times and vacuum dried. The MAPbI<sub>3</sub> precursor solutions were prepared by firstly dissolving 1.4 mM MAI and PbI<sub>2</sub> powders into mL DMF and DMSO mixed solvent (4:1 volume ratio) to form a 1.4 M precursor solution and then MACl or DMACl powder was added to the MAPbI<sub>3</sub> precursor solutions, the molar ratio between MACl/DMACl and PbI<sub>2</sub> was 0.15:1.

Device fabrication: A ~20 nm thick compact TiO<sub>2</sub> was deposited on the patterned fluorine-doped tin oxide (FTO, TEC-7) by spray pyrolysis 0.2 M Ti (IV) bis(ethyl acetoacetate)-diisopropoxide 1-butanol solution at 450 °C followed by annealing at 450 °C for 1h. SnO<sub>2</sub> was deposited on c-TiO<sub>2</sub>/FTO substrate by coat-spinning Tin (IV) oxide colloid precursor (15% in H<sub>2</sub>O colloidal dispersion) in ammonium hydroxide at 3000 rpm for 30 s, and was then annealed at 180 °C for 30 min in air. The perovskite layers were deposited on SnO<sub>2</sub>/c-TiO<sub>2</sub>/FTO substrate by coat-spinning fresh precursor at 5000 rpm for 20 s with an accelerating rate of 5000 rpm·s<sup>-1</sup>. 600 µL CB was dripped on spinning substrate at 15 s. The obtained perovskite film was then annealed at 100 °C for 20 min. After that, a hole-transport material (HTM) solution contain 0.1 M spiro-MeOTAD, 0.035 M bis (trifluoromethane) sulfonimide lithium salt (Li-TFSi), and 0.12 M 4-tert-butylpyridine (TBP) in chlorobenzene solution was then spin coated onto the perovskite film at 4000 rpm for 20 s. Finally, a 100 nm thick Ag was deposited as contact layer via thermal evaporator.

*Characterization:* The crystal structures of perovskite films were characterized by Shimadzu XRD 6100 diffractometer with Cu Ka radiation. UV-vis spectra were collected on Cary-60 UV-vis spectrophotometer. PL spectra were measured at room temperature on a fluorescence spectrophotometer (FLS1000). Time-resolved photoluminescence (TRPL) spectra were measured on FLS/1000 а spectrofluorometer. The surface morphologies were characterized by a SEM (JEOL JSM-7800F Prime). X-ray photoelectron spectroscopy (XPS) was performed by AXIS UltraDLD. Electrochemical impedance spectroscopy (EIS) was recorded on an electrochemical workstation (ZAHNER ZENNIUM PP211, Germany) at a bias of 0.9 V under dark condition with a frequency range of 0.1 Hz - 1 M Hz and amplitude (V) = 0.01. Atomic force microscope (AFM) was carried out on Agilent SPM 5500. Mass spectra of perovskite films were characterized by Time-of-flight secondary ion mass spectrometry (ToF-SIMS, ION ToF SIMS 5-100). The TPC and TPV (Zahner PP211 and Zahner Zennium) were generated by a microsecond pulse of a white light incident on solar cells under short circuit condition and open circuit condition. The J-V curves of perovskite solar cells were measured by a Keithley 2401 source meter with scan rate of 0.05 V s<sup>-1</sup> under simulated AM 1.5 G illumination (100 mW cm<sup>-2</sup>; Enlitech

Class AAA Solar Simulator) at temperature between 50°C~55°C. IPCE was measured on an Enlitech QE-3011 system.



Figure S1. Normalized photoluminescence spectra of MACl/MAPbI<sub>3</sub> and DMACl/MAPbI<sub>3</sub> films.



Figure S2. The XPS spectra (Cl 2p core level) of  $MACl/MAPbI_3$  and  $DMACl/MAPbI_3$  films.



Figure S3. AFM images of the MACl/MAPbI3 and DMACl/MAPbI3 films. The size of each image is 5  $\times$  5  $\mu m^2.$ 



Figure S4. (a) and (b) UV-vis spectra of MACl/MAPbI<sub>3</sub> and DMACl/MAPbI<sub>3</sub> films before and after placing in the environment of 70% relative humidity for 9 days.



Figure S5. (a) and (b) UV-vis spectra of MACl/MAPbI<sub>3</sub> and DMACl/MAPbI<sub>3</sub> films before and after annealing at 70 °C for 14 days.



Figure S6. (a) XRD patterns, (b) UV-vis spectra and (c) Normalized PL spectra of

 $MAPbI_3$  with different amount of DMACl additive.



Figure S7. Typical J-V curves of MAPbI<sub>3</sub> with different ratio DMACl additive.



Figure S8. XRD patterns of MAPbI $_3$  with 0.15 M MACl, DMAI and DMACl additive.



Figure S9. SEM images of MAPbI<sub>3</sub> films with the addition of 0.15 M DMAI additive.



Figure S10. XRD patterns of MAPbI<sub>3</sub> and DMAPbI<sub>3</sub>.



Figure S11. The zoom-in of normalized XRD patterns of DMACl/MAPbI<sub>3</sub> films annealing for different time at 100 °C.



Figure S12. Normalized PL spectra of DMACl/MAPbI<sub>3</sub> films annealing for different time at 100 °C.



Figure S13. Steady state photoluminescence spectra of MACl/MAPbI<sub>3</sub> and DMACl/MAPbI<sub>3</sub> films.



Figure S14. Nyquist plots of MACl/MAPbI<sub>3</sub> and DMACl/MAPbI<sub>3</sub> based PSC devices in a frequency range from 0.1 Hz to 1 M Hz at 0.9 V bias voltage under darkness.



Figure S15. Dark J-V curves of MACl/MAPbI $_3$  and DMACl/MAPbI $_3$  based PSC devices.



Figure S16. Forward and reverse scan of DMACl/MAPbI<sub>3</sub> perovskite solar cell devices.



Figure S17. The stable output of champion solar cells based on DMACl/MAPbI<sub>3</sub> at a maximun power point of 0.94 V.



Figure S18. The photostability of unencapsulated MACl/MAPbI<sub>3</sub> and DMACl/MAPbI<sub>3</sub> based PSC devices under continuous illumination of 100 mW cm<sup>-2</sup> white LED light in  $N_2$  atmosphere.

Table S1: PV parameters of devices based on MACl/MAPbI<sub>3</sub> and DMACl/MAPbI<sub>3</sub> perovskite.

	$J_{SC}$ (mA cm <sup>-2</sup> )	V <sub>OC</sub> (V)	FF	PCE (%)
MACl	21.734±0.449	1.063±0.011	0.748±0.019	17.262±0.536
DMACl	22.843±0.444	1.081±0.010	0.793±0.022	19.961±0.482