

Supporting Information for

Blended Additive Manipulated Morphology and Crystallinity Transformation toward High Performance Perovskite Solar Cells

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Experimental Section

Materials: The synthesis of methylammonium iodide (MAI) is by stirring methylamine (30 mL, 27% in ethanol, 0.156 mol), hydroiodic acid (25 mL, 45% in water, 0.132 mol) and 50 mL ethanol in three-necked flask under the atmosphere of nitrogen. After stirring for 2 h, the reactants were fully reacted and the primary product was recovered at 60 °C for 2 h by rotary evaporation. Then the obtained white solid was dissolved by ethanol and recrystallization at -10 °C. The final product was washed by anhydrous ether, and dried at 60 °C for 12 h in a vacuum oven.

The synthesis of methylammonium acetate (MAAc) is by stirring glacial acetic acid (10 mL, 99.5%, 0.174 mol), methylamine (34 mL, 27% in ethanol, 0.195 mol) and 20 mL ethanol. The synthesis of methylammonium chlorinated (MACl) by stirring hydrochloric acid (7.5 mL, 36% in water, 0.00871 mol), methylamine (16 mL, 27% in ethanol, 0.0920 mol) and 20 mL ethanol. The further purification is the same as the MAI. And the final products were transparent viscous and white powdery solid, respectively. PbI_2 (TCI 0.461 g, 1 mmol) and MAI (0.159 g, 1 mmol) were dissolved in anhydrous N,N-Dimethylformamide (DMF) to form MAPbI_3 precursor solution. The two additives of MAAc and MACl were added into precursor solutions according to molar ratio to PbI_2 by 1:0:1, 0:1:1, 0.8:0.2:1, recorded as MAPI-MAAc, MAPI-MACl, MAPI-BOAs, respectively.

Devices Fabrication and Characterization.

Polyimide tape wrapped glass substrates (coated fluorine-doped tin oxide (FTO)) were etched by 6 M HCl and Zn powder. The substrate was washed successively by saturated KOH solution in isopropanol, water, acetone and ethanol. After dried at 150 °C for 10 min in an oven, the

washed substrates were deposited with TiO₂ layer (20 nm thick) by atomic layer deposition (ALD). A 300 nm thick mesoporous TiO₂ layer was then deposited by spin-coating a dilute commercial TiO₂ paste (1:4 with ethanol by weight) at 4000 rpm for 30 s, afterward, annealed at 500 °C for 30 min in air. Three precursor solutions were spin-coated onto the prepared substrates at 3000 rpm for 30 s, after that, the fresh films of **MAPI-MAAc**, **MAPI-BOAs**, **MAPI-MACl** were heated-treated at 100 °C for 5 min, 15 min, 30 min in a nitrogen-filled glovebox, respectively. Then, the solution of hole-transporting layer (HTM) was spin-coated at 3000 rpm for 30 s. The solution of HTM is comprised of 72.3 mg of spiro-MeOTAD (99%) in 1 mL anhydrous of chlorobenzene, 28.8 μL of 4-tert-butylpyridine (99.8%) and 17.5 μL of lithium bis (trifluoro-methanesulfonyl) imide (LITSFI) solution (520 mg LITSFI (98%) in 1 mL acetonitrile). Finally, 80 nm thick Au electrode was thermally evaporated to complete the device with shadow mask after storing in the glovebox for 12 hours. The active area of solar cells was 0.09 cm².

The Keithley 2400 Sourcemeter was employed to measure the J-V characteristics (both reverse and forward scans) of solar cells under simulated one-sun AM 1.5G 100 mW cm⁻² intensity (Oriel Sol3A Class AAA, Newport, USA). The step voltage was 50 mV with a 10 ms delay time per step. The J output is converted to PCE output using the following relation: $PCE = \{J \text{ (mA cm}^{-2}) \times V \text{ (V)}\} / (100 \text{ (mW cm}^{-2})\}$. The testing condition of the device efficiency is air condition with a relative humidity of 40% without any light soaking. The stability comparison is tested under one-sun illumination with a relative humidity of 40%. The interval between tests is kept under illumination with an open circuit condition to speed up the degradation of the device. The hole and electron space-charge-limited-current (SCLC) regime is measured by the electron-only devices following the structure of FTO/TiO₂/perovskite layer/PCBM/Ag.

Perovskite Film Characterization.

Hitachi S-4800 scanning electron microscope (SEM) was used to study the morphologies. Hitachi U-4100 spectrometer was employed to study the UV-vis absorption spectra of the perovskite films. The surface in situ crystallization process of perovskite films was obtained by optical microscope (BX51). X-ray diffraction (XRD) analysis was performed by using a Bruker D8 Advance with the Cu K α radiation. Size distributions of perovskite precursors were measured by Malvern Zetasizer Nano-S90. FLS980 (Edinburgh Instruments Ltd) were used to measure the steady-state photoluminescence (PL) spectra and time-resolved photoluminescence (TRPL) spectroscopy (PL) with an excitation at 445 nm. The Newport measurement system was employed to detect the External quantum efficiencies.

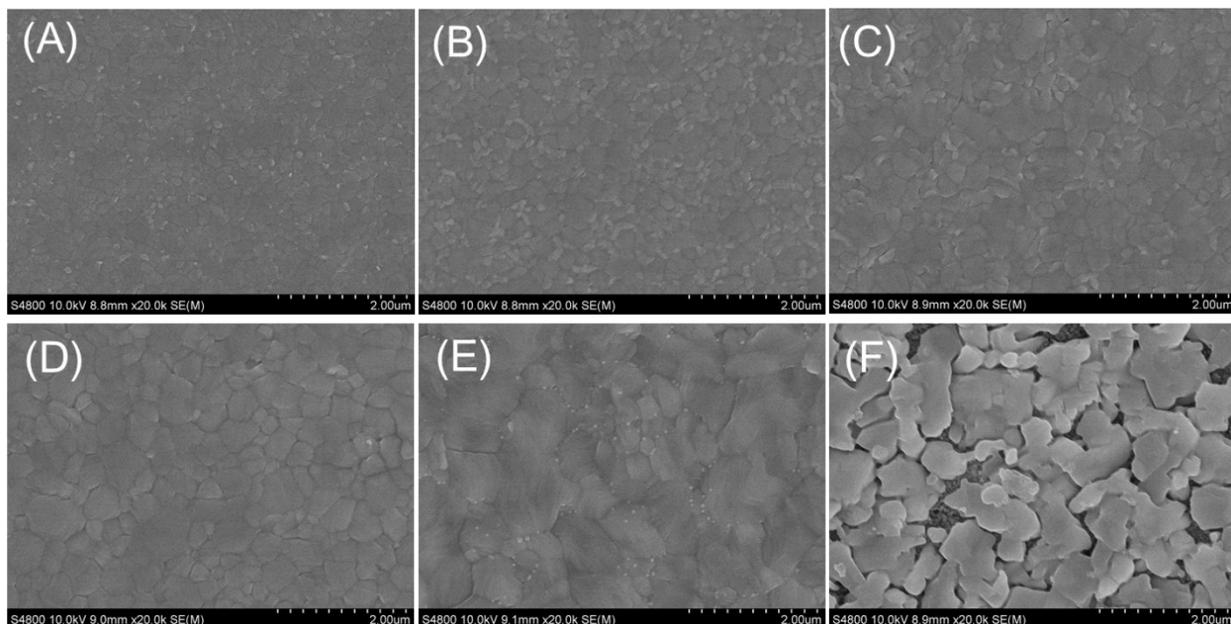


Figure S1. (A-F) Top-view SEM images of MAPbI₃ perovskite films with different blended additives MAAc_{1-x}MACl_x (x=0, 0.2, 0.4, 0.6, 0.8, 1, respectively).

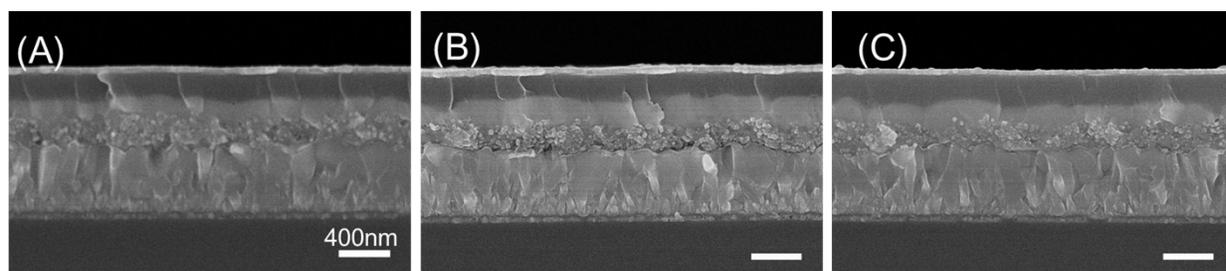


Figure S2. Cross-sectional SEM micrographs of (A) MAPI-MAAc, (B) MAPI-MACl, and (C) MAPI-BOAs perovskite solar cell devices.

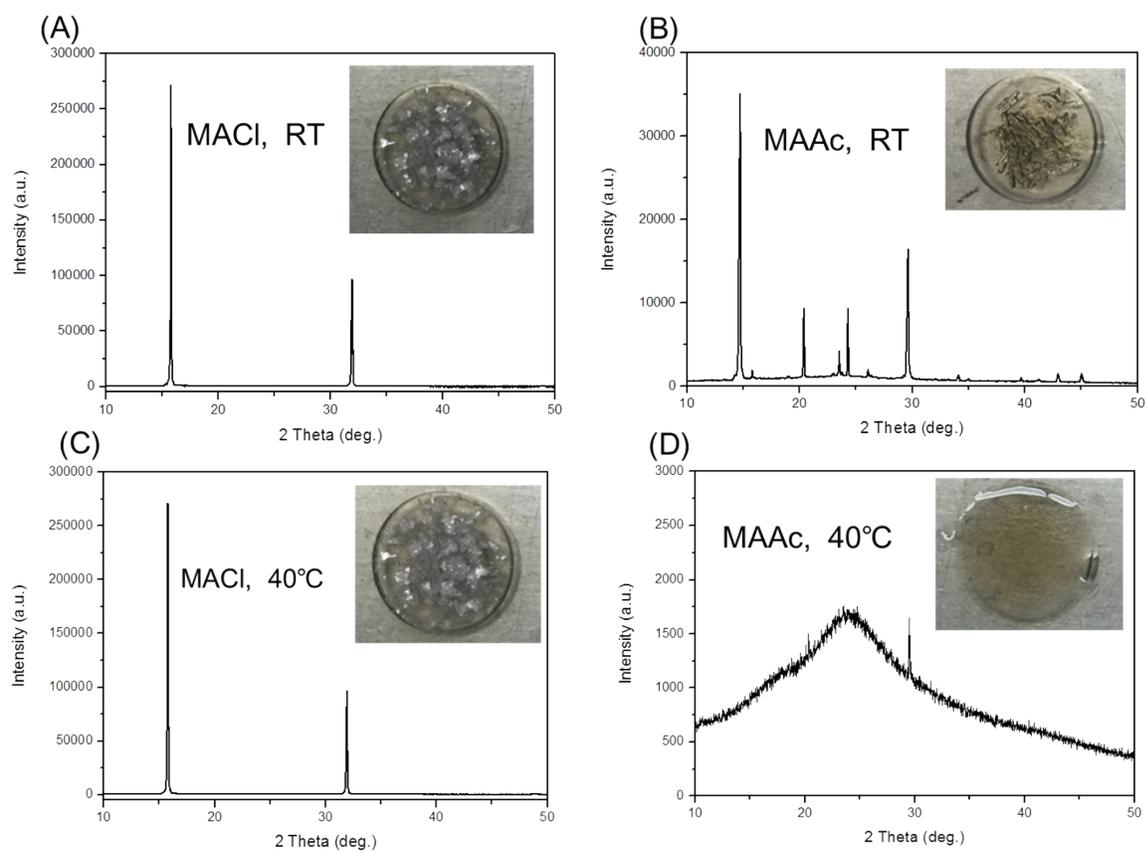


Figure S3. XRD patterns of (A) MACl and (B) MAAc at room temperature. Inserted pictures are their corresponding powder images. (C-D) XRD patterns of the two samples heated at 40 °C and their powder images.

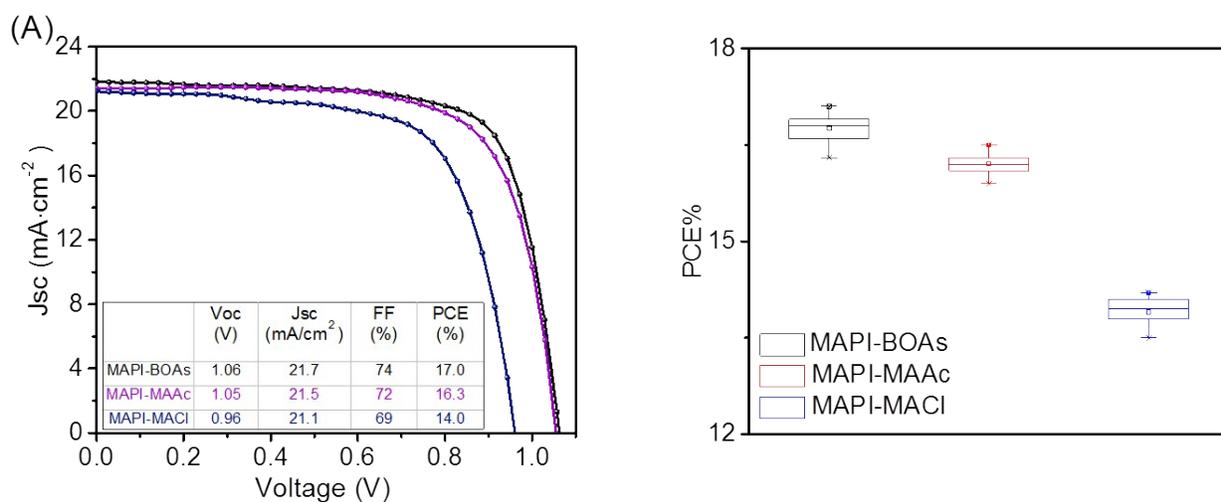


Figure S4. (A) J–V curves of devices fabricated by MAPI-MACl, MAPI-BOAs, MAPI-MAAc precursor solutions. (B) Box charts of PCE distributions of MAPI-MACl, MAPI-BOAs, MAPI-MAAc devices. 20 devices are measured for each precursor.

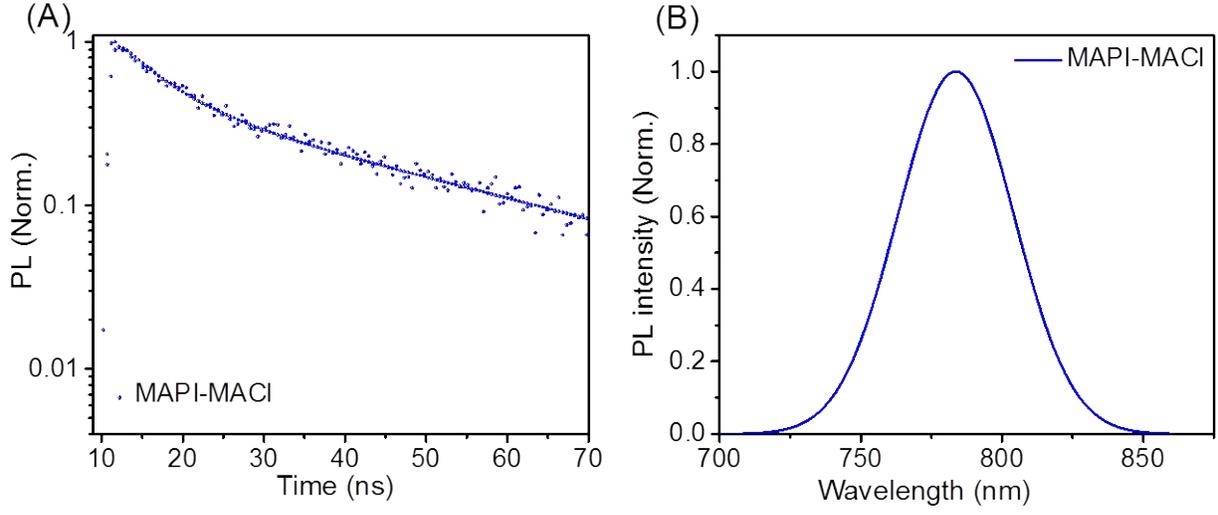


Figure S5. Time-resolved photoluminescence decay (A) and normalized steady-state photoluminescence spectra (B) of MAPI-MACl perovskite film.

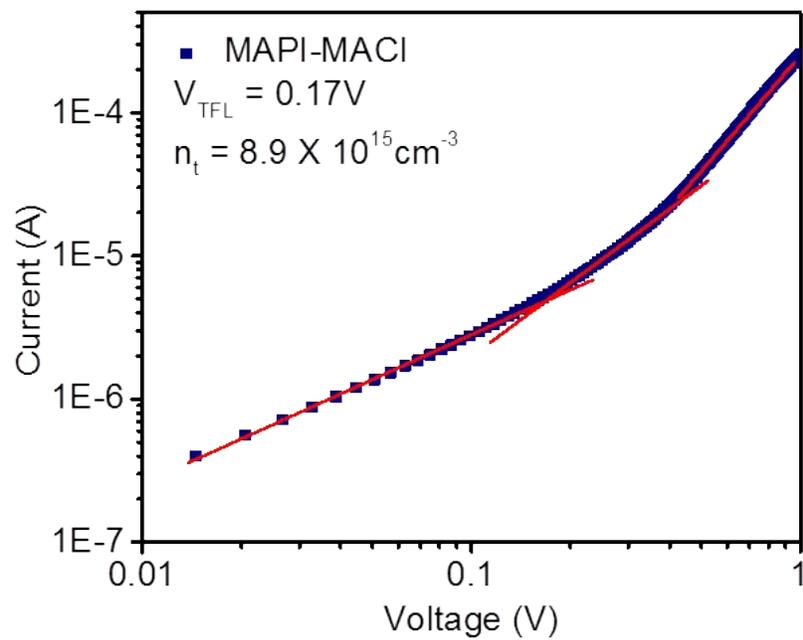


Figure S6. I-V curve of MAPI-MACl device in space-charge-limited-current (SCLC) regime.

The device employs FTO/com-TiO₂/perovskite/PCBM/Ag configuration.