

Supporting Information

Ultrahigh Open-circuit Voltage for High Performance Mixed-cation Perovskite Solar Cells by Acetate Anions

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Experimental Section

Perovskite solar cell fabrication: The methylammonium and formamidinium salts were purchased from Dyesol and the lead compounds were purchased from Sigma. All of them were used as received. The pre-patterned ITO-coated glasses, purchased from TFD (Thin Film Devices), were washed by ultrasonic cleaner using deionized water, acetone, and isopropanol sequentially. A TiO₂ electron transport layer was spin-coated from the colloidal TiO₂ nanocrystal solution and annealed on a hot plate at 150°C for 30 minutes. Then the substrates were transferred to a nitrogen-filled glovebox immediately. Cs_{0.05}FA_{0.81}MA_{0.14}PbI_{2.55}Br_{0.45} precursor solution was prepared in DMF/DMSO (4/1 V/V) solvent, which contains PbI₂ (2.38 M), PbBr₂ (0.42 M), FAI (2.26 M), MABr (0.4 M) and CsI (0.14 M). For low-bandgap devices, the composition is Cs_{0.05}FA_{0.84}MA_{0.11}PbI_{2.80}Br_{0.20}. FAAc additive solution (0.5 M in

DMF/DMSO) was added in the precursor solution with a fixed ratio. The perovskite films were deposited using a two-step program at 2300 and 6000 r.p.m for 10 and 40 s respectively. During the second step, 150 μ L of chlorobenzene was dropped on the spinning substrate at 20 s before the end of the process. After spin-coating, the films were annealed at 100°C for 20 minutes. After that, Spiro-OMeTAD layers were spin-coated from a chlorobenzene solution containing additives of lithium bis (trifluoromethanesulfonyl) imide and 4-TBP at 3000 r.p.m for 45 s. Finally, 80 nm Au electrodes were thermally evaporated under high vacuum ($< 1 \times 10^{-4}$ Pa) to complete the devices.

Device measurements: The J - V curves and steady-state tests were measured using an Aglient B2901 source meter and a 150 W class AAA solar simulator with an AM 1.5G filter (Solar IV-150A, Zolix). A metal mask was used to define the active area during the whole test process. The J - V curves were scanned by reverse (from 1.2 V to -0.1 V) or forward (from -0.1 V to 1.2 V) and the step voltage was fixed at 10 mV. The light intensity of the solar simulator was calibrated by a standard silicon solar cell provided by National Institute of Metrology, China. EQE spectra were tests using an EQE system (SCS100, Zolix).

Other Characterizations: XRD spectra were obtained using Cu K_{α} by an X-ray diffractometer (PANalytical X'Pert3 Powder). TRPL decay was performed by exciting the perovskite samples deposited on glass using a FLS980-S2S2-stm spectrometer. Perovskite films for XRD and TRPL measurements were deposited on bare glasses. The spectra were measured upon excitation at 470 nm. A field emission

SEM (FEI NOVA Nano SEM 430) was used for collecting SEM images. TGA curves of MAAC and FAAC were recorded by a thermogravimetric analyzer Q600-STD in the atmosphere with a heating rate of 10°C per minute.

The impedance spectrum was measured using a potentiostat/galvanostat (SP-150, Bio-Logic, Seyssinet-Pariset, France) at different biases. The ITO side was the negative electrode for biases larger than 0 V, which was the same as for our current–voltage scan. The frequency was tuned from 1 MHz to 0.1 Hz with 60 data points, and at each point 200 measurements were averaged to smooth the impedance spectra. All samples were measured under 10 mW cm⁻² using a 10% optical attenuator.

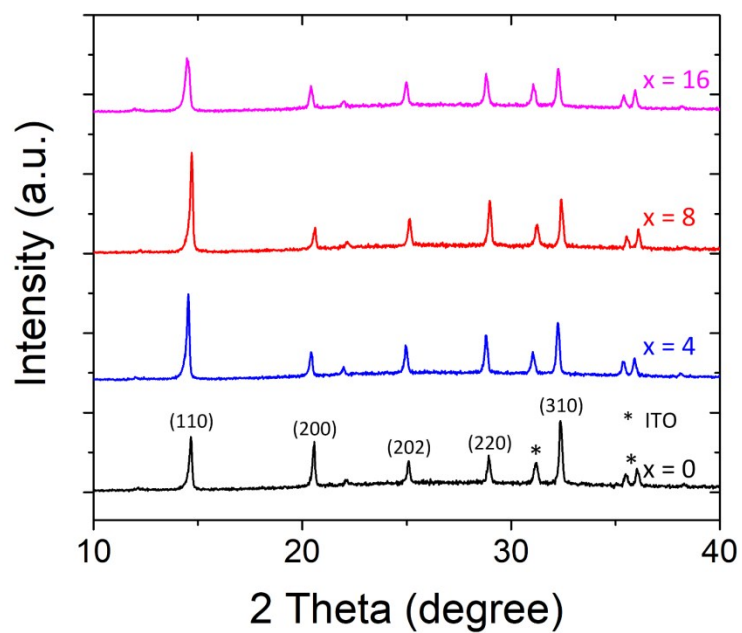


Fig. S1 (a) XRD patterns for perovskite films prepared with different FAAC content.

The patterns are normalized based the substrate peaks (denoted as *).

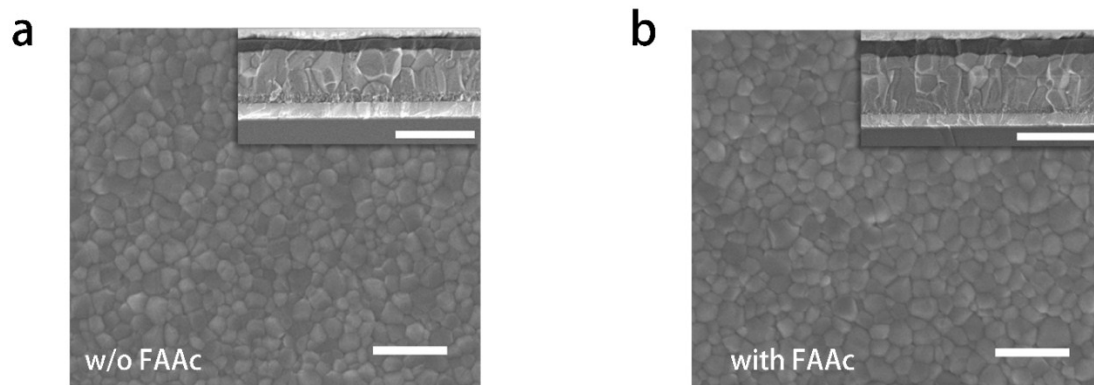


Fig. S2 (a, b) Top-view SEM images of perovskite films without and with FAAC additive ($x = 8$). Insets: Cross-section SEM images of corresponding solar cell devices. Scale bar: 1 μm .

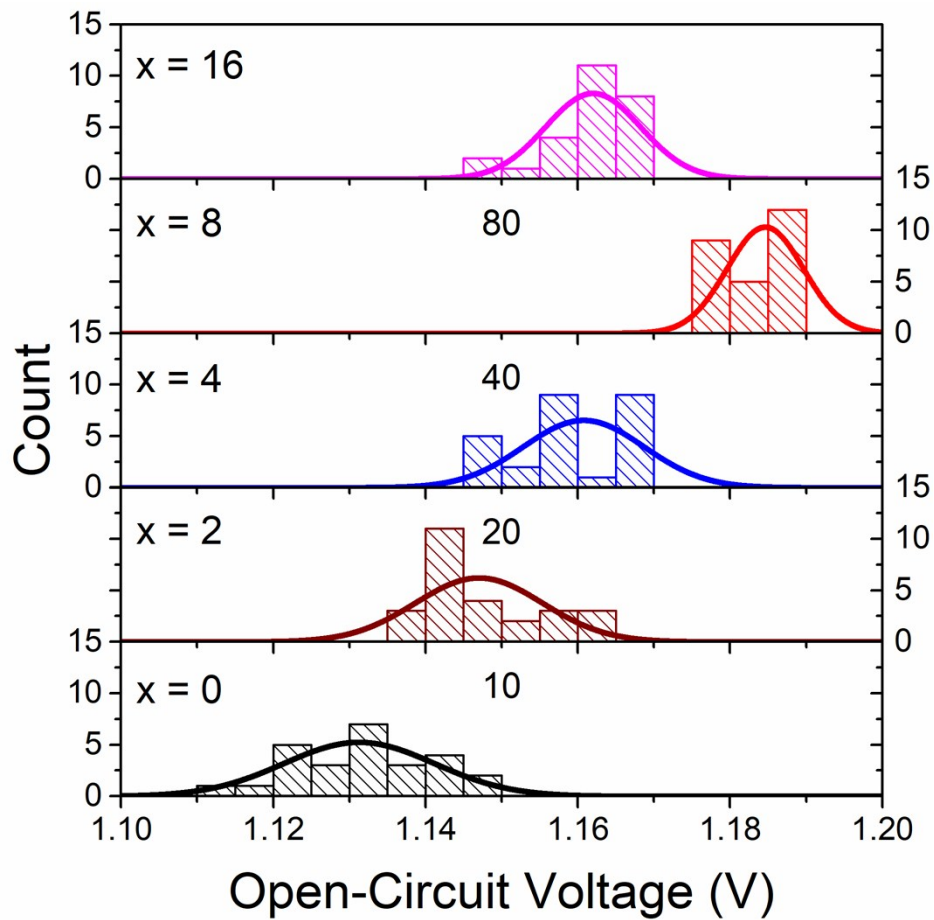


Fig. S3 Histograms of V_{OC} among 130 devices in total with different content of FAAC additive, fitted to a Gaussian distribution.

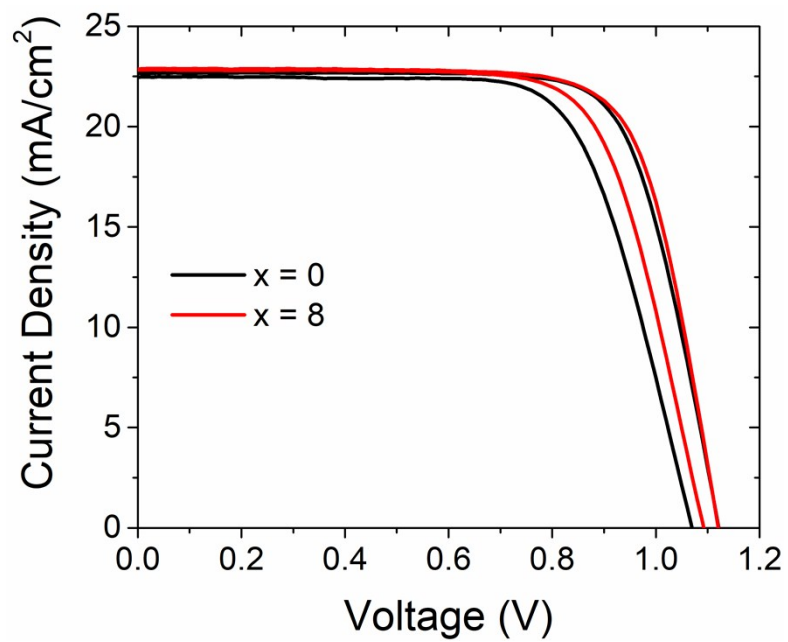


Fig. S4 J-V curves of solar cell devices measured with forward and backward scans using FAAC method and control sample.

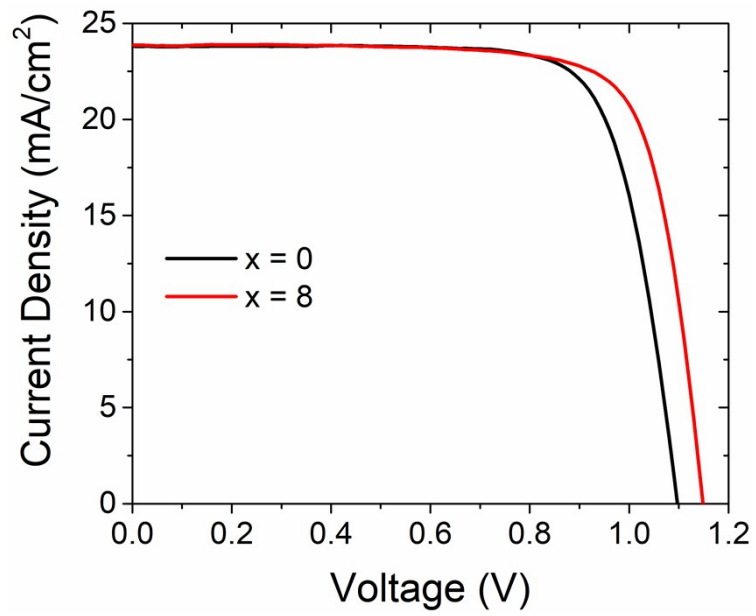


Fig. S5 J-V results for low-bandgap $\text{Cs}_{0.05}\text{FA}_{0.84}\text{MA}_{0.11}\text{PbI}_{2.80}\text{Br}_{0.20}$ perovskite solar cells with and without FAAc additive.

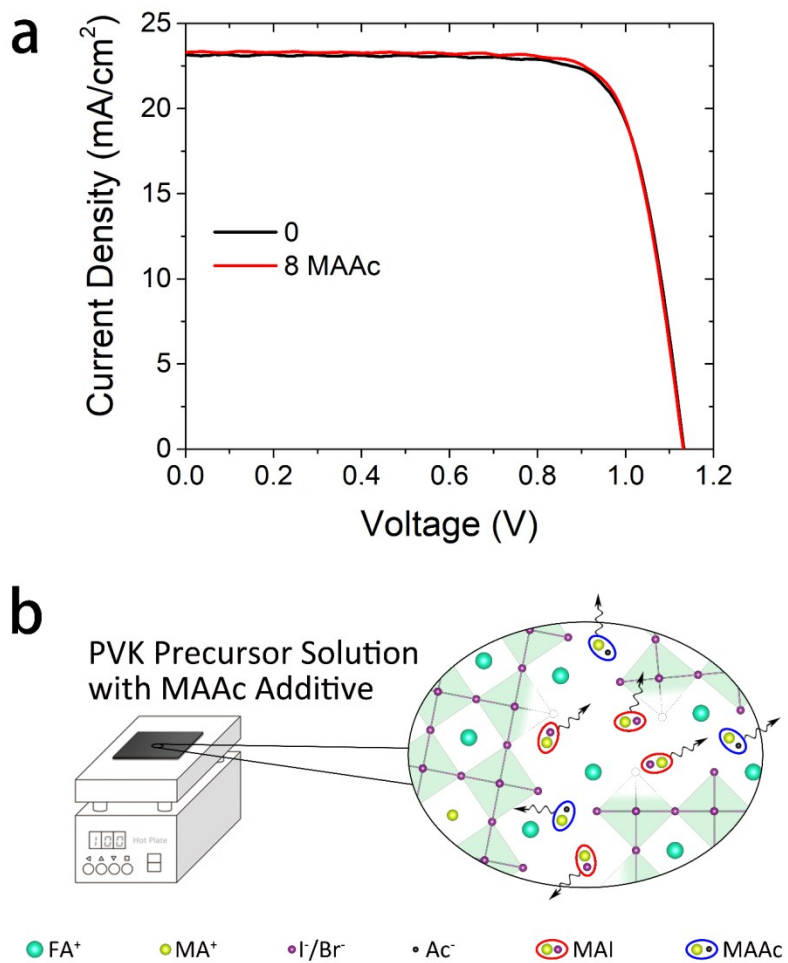


Fig. S6 (a) J-V results for devices fabricated using the same manner except for choosing MAAc as the Ac⁻ source provider instead of FAc. **(b)** Schematic illustration of the annealing process for perovskite thin film with MAAc additive.

