In Situ Identification of Cation-Exchange-Induced Reversible Transformations of 3D and 2D Perovskites

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Supporting Information

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- 1. Experimental section
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- 3. Reversible cation exchange reactions occurred in the film

1. EXPERIMENTAL SECTION

The materials used in this work are listed below. Lead (II) bromide (PbBr₂, 98%, Alfa Aesar), methylammonium bromide (MABr, Dyesol), N,N-dimethylformamide (DMF, anhydrous, Sigma), octylamine (OcA, 99%, vapor pressure of 1.3 mbar at 20 °C, Sigma), methylamine (anhydrous, \geq 98%, Sigma).

Preparation of MAPbBr₃ films. Fluorine-doped tin-oxide (FTO)-coated glass substrates were cleaned with detergent solution and then ultrasonicated in 1:1 solution of deionized water (DI H₂O) and ethanol for 30 min. After drying, the FTO substrates were exposed to air plasma for 15 min. The MAPbBr₃ precursor (200 mg/ml) was composed of an equimolar solution of PbBr₂ and MABr at 200 mg/mL in DMF stirred for 2 h at 70 °C. Then, this solution was spin-cast onto the FTO substrate at 3000 rpm for 60 s and annealed at 70 °C for 15 min to form a MAPbBr₃ film structure. All steps were conducted in a dry nitrogen glove box.

In situ ambient pressure X-ray photoelectron spectroscopy (AP-XPS). The *in situ* characterization of the surface chemistry of perovskites was performed under 0.7 mbar pressure of octylamine or methylamine using a SPECS AP-XPS with a monochromatized Al K α X-ray source and an *in situ* reaction chamber, through which the reactant gas was allowed to flow during data acquisition. The perovskite film on FTO was mounted on a stainless steel sample holder by using a carbon tape. Silver paint (SPI supplies) was applied to the edges of the perovskite film to prevent charging of the glass substrates. For the forward reaction, 0.7 mbar octylamine vapor was introduced to the reaction chamber and the MAPbBr₃ film was treated for 6 hours. After that, the reaction chamber was evacuated for 24 hours to pump out

octylamine and eliminate the surface-adsorbed octylamine molecules. 0.7 mbar methylamine gas was subsequently introduced into the chamber for 6 hours to perform the reverse reaction. During the forward and reverse reactions, all photoelectron spectra were recorded at room temperature at the pass energy of 20 eV.

In order to determine the concentrations of different elements in the perovskite film

quantitatively, the ratios of N/Pb and C/Pb were estimated using the relation, $\frac{N_1}{N_2} = \frac{I_1 S_2}{I_2 S_1}$, where N is the concentration of the elements, I is the peak area of the elements, and S is the atomic sensitivity factor. All spectra were calibrated to their corresponding C 1s of the pristine sample, i.e., 285.3 eV. The uncertainty of the binding energy values for all assigned spectral peaks was in the range of 0.1-0.2 eV.

Other characterizations. The absorption spectra were measured using a Varian Cary 50 Bio spectrophotometer. The X-ray diffraction measurements were performed by using a Bruker D8 Advanced Davinci Powder X-Ray diffractometer (Cu K α X-ray beam, $\lambda = 1.5406$ Å) with scan rate of 0.025° and acquisition time of 2 sec deg⁻¹. The morphology of perovskite samples was characterized using a field emission scanning electron microscopy (FESEM) (FEI, Magellan-400) operating at an accelerating voltage of 5 kV.

2. Figures S1-4



Figure S1. N 1s photoelectron spectra of the pristine MAPbBr₃ film, the MAPbBr₃ film recorded after OcA treatment, and the OcA-treated MAPbBr₃ film recorded after MA treatment.



Figure S2. (A) C 1s, (B) N 1s, (C) Pb 4f and (D) Br 3d photoelectron spectra of the MAPbBr₃ film at a OcA pressure of 0.7 mbar for 6 h, in vacuum for 24 h, at a MA pressure of 0.7 mbar for 6 h, and then in vacuum for 3 h. Peak assignments: (I) 285.3 eV \pm 0.1 eV (adventitious carbon, OcA⁺ ion, surface adsorbed OcA), (II) 286.6 eV \pm 0.1 eV (C-N⁺), (III) 402.5 \pm 0.1 eV (C-N⁺), (IV) 400.8 \pm 0.1 eV (OA/MA gas phase), and (V) 397.7 \pm 0.1 eV (surface absorbed OcA).



Figure S3. Time evolution of nitrogen (N) content relative to lead (Pb) in the MAPbBr₃ film, in which the sample was continuously kept under the exposure of OcA for 6 h, in vacuum for

24 h, under the exposure of MA for 6 h and in vacuum for 3 h.



Figure S4. Proton transfer mechanism of reversible conversion between OcA⁺ and MA⁺ ions.

3. Reversible cation exchange reactions

$$MAPbBr_3 + OcA \leftrightarrow 1/2(OcA)_2PbBr_4 + 1/2Pb-Br_2 + MA$$
(S1)