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Controllable Transformation Between 3D and 2D Perovskites through Cation Exchange

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Supporting Information

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1. Experimental section

Materials. Lead(II) bromide ($PbBr_2$, 98%, Alfa Aesar), Methylammonium bromide (MABr, Dyesol), n-Octylammonium bromide (OcABr, Dyesol), n-Butylammonium bromide (BABr, Dyesol), Octylamine (OcA, 99%, vapor pressure of 1.3 mbar at 20 °C, Sigma), Oleic acid (OA, 90%, Sigma), N,N-dimethylformamide (DMF, anhydrous, Sigma), methylamine (anhydrous, ≥ 98%, Sigma), Isopropyl Alcohol (IPA, ⩾99.7%, Sigma), Methyl sulfoxide (DMSO, ⩾99%, Sigma).

Synthesis of 3D $MAPbBr_3$ NCs. In a typical synthesis of $MAPbBr_3$ QDs, a mixture of 0.2 mmol MABr and 0.2 mmol $PbBr_2$ was dissolved in 5 mL of DMF with 15 µL of octylamine (or 0.14 mmol of OcABr) and 0.5 mL oleic acid to form a precursor solution. 0.02 mL of precursor solution was dropped into the mixture of 3.5 mL of hexane and 1.5 mL of acetone with vigorous stirring. Along with the mixing, strong green PL emission was observed. The obtained perovskite NCs solution (0.72 µmol in 5 ml) is ready for cation exchange reaction.

Synthesis of 2D $(OcA)_2PbBr_4$ NCs. In a typical synthesis of $(OcA)_2PbBr_4$ QDs, a mixture of 0.4 mmol OcABr and 0.2 mmol $PbBr_2$ was dissolved in 5 mL of DMF with and 0.5 mL oleic acid to form a precursor solution. 0.02 mL of precursor solution was dropped into the mixture of 3.5 mL of hexane and 1.5 mL of acetone with vigorous stirring. Along with the mixing, violet PL emission was observed and the obtained solution (0.72 µmol in 5 ml) is ready for cation exchange reaction.

Cation exchange reactions. In the forward reaction, 2.8 µmol PEABr was dropped into the obtained 3D $MAPbBr_3$ NCs solution (0.72 µmol in 5 ml). Along with the mixing, PL emission change could be observed after vigorous stirring for 15 min. Similarly, 5.6 µmol OcABr or BABr was dropped into the obtained 3D $MAPbBr_3$ NCs solution (0.72 µmol in 5 ml) and PL emission change could be observed after 8-hour vigorous stirring. In the reverse reaction, 1.0 μmol MABr or CsBr was dropped into the obtained 2D $(OcA)_2PbBr_4$ NCs solution (0.72 μmol in 5 ml). Along with the mixing, PL emission change could be observed after vigorous stirring for 15 min. To accurately introduce the certain amount of introduced cations, 20 mg PEABr, OcABr and MABr particles were dissolved in 1mL IPA, respectively. 20 mg CsBr particles were dissolved in the mixture of 0.5 mL DMF and 0.5 mL DMSO.

Time Correlated Single Photon Counting (TCSPC) analysis. Emission lifetimes were measured using a Horiba Jobin Yvon single photon counting system. Life time of the as synthesized perovskite samples and samples with varying addition of octylammonium ion and reverse addition of methylammonium ion had estimated using Time correlated single photon counting analysis. The PL decay curve was fitted with biexponential decay fit. The goodness of fit was judged by χ_{SQ} (1± 0.2) values and residual plots. The average lifetime (τ_{avg}) of perovskite NCs in the presence and absence of 1 mM methyl viologen was calculated using the Equation 1

$$\tau_{avg} = (\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2) / (\alpha_1 \tau_1 + \alpha_2 \tau_2) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{S1}$$

Photoluminescence quantum yields of perovskite NCs. The PL quantum yield of perovskite with green emission was measured using rhodamine 6G as standard dye ($\Phi_f = 0.95$) and the blue emissive sample was calculated using 9, 10 diphenyl anthracene in cyclohexane; $\Phi_f = 0.86$ using the below equation

$$\mathbf{\Phi_x = \Phi_{ST} (f_x / f_{ST}) (a_{ST}/a_X) n_x^2 / n_{ST}^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{S2}$$

f_x = Integral over the emission of solution

f_{ST} = Integral over the emission of reference standard

n_x = Refractive index of the solvent of the compound dissolved

n_{ST} = Refractive index of the solvent of the reference standard

a_{ST}= Absorbance of the reference standard

a_X = Absorbance of the solution

***In situ* ambient pressure X-ray photoelectron spectroscopy (AP-XPS).** The *in situ* characterization was performed using a SPECS AP-XPS with a monochromatized Al Kα X-ray source having energy of 1486.61 eV. The $MAPbBr_3$ film was prepared based on a previous reported procedure.[2] Firstly, equimolar $PbBr_2$ and MABr (200 mg) was dissolved in 1mL DMF to form precursor solution, which was then spin-cast at 3000 rpm onto the FTO substrate for 60 s and annealed at 100 °C for 10 min to form a perovskite film. During the forward reaction, 0.5 mbar butylamine (99%, Sigma) vapor was introduced to the reaction chamber and the $MAPbBr_3$ film was treated for 7 hours. After that, the reaction chamber was evacuated for 24 hours to pump out butylamine molecules. 0.5 mbar methylamine gas was subsequently introduced into the chamber for 7 hours to perform the reverse reaction. All photoelectron spectra were recorded at the pass energy of 20 eV and were calibrated to C 1s of the pristine sample, i.e., 285.3 eV.

Characterizations. The absorption spectra were measured using a Varian Cary 50 Bio spectrophotometer. The solution Emission spectra were conducted using a Horiba Jobin Yvon Fluorolog-3 spectrophotometer. Transmission Electron Microscopic (TEM) imaging were carried out using FEI Titan 80-300 (300 kV) high resolution transmission electron microscope. The TEM samples are prepared by drop casting the samples on carbon coated copper grid and dried under vacuum. The X-ray diffraction measurements were performed by using a Bruker D8 Advanced Davinci Powder X-Ray diffractometer (Cu Kα X-ray beam, $\lambda = 1.5406$ Å) with scan rate of 0.025° and acquisition time of 2 sec deg^{-1}. Samples for AFM imaging were prepared by spin-coating the colloidal dispersions onto silicon wafers (Electron microscopy sciences) at a speed of 1500 rpm for 60 s. Before the spin-coating process, silicon wafer substrates were cleaned by soap water initially, and rinsed using distilled water and then ultrasonicated in ethanol for 20 min. Atomic force microscopy (AFM) images were measured with Park Systems XE-70. AFM images were taken in non-contact mode with a PPP-NCHR (Park Systems) probe. AFM image processing and analysis was performed using the software WSxM (WSxM solutions, v5.0).[1]

2. Figures S1-9 and Table S1

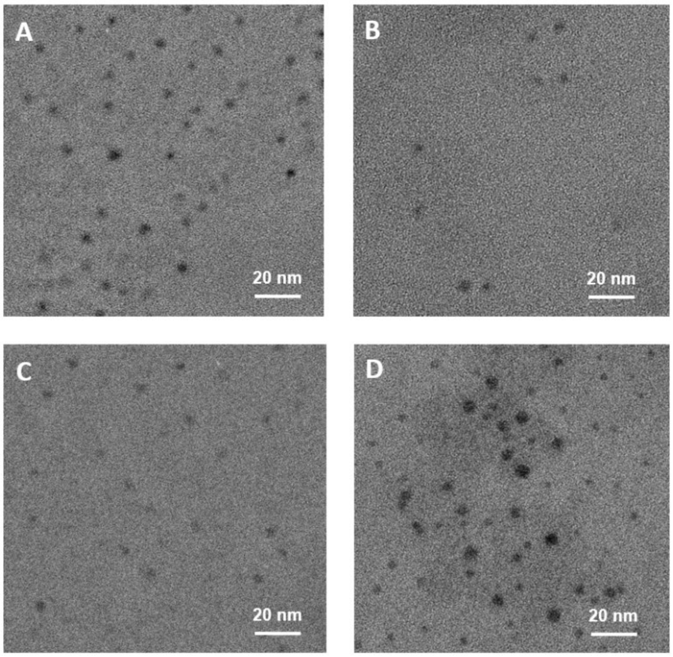

Figure S1. TEM images of (A) the as-synthesized 3D $MAPbBr_3$ sample (0.72 μmol in 5 ml), (B) the as-synthesized 3D sample (0.72 μmol in 5 ml) with the addition of 2.8 μmol of PEA^+, (C) the as-synthesized 2D $(OcA)_2PbBr_4$ sample (0.72 μmol in 5 ml) and (D) the as-synthesized 2D sample (0.72 μmol in 5 ml) with the addition of 1.0 μmol of MA^+.

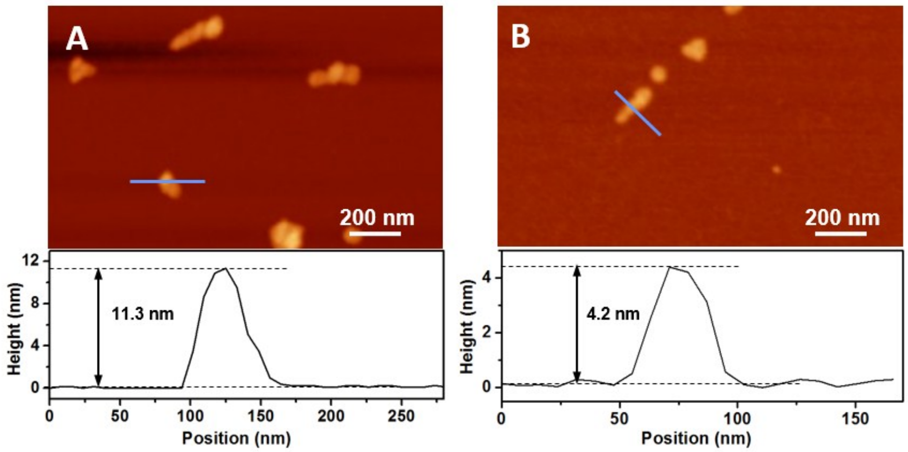

Figure S2. AFM topography images of (A) the as-synthesized 3D $MAPbBr_3$ NCs (0.72 µmol in 5 ml), and (B) the as-synthesized 3D sample (0.72 µmol in 5 ml) with the addition of 2.8 µmol of PEA^+. Similar results were observed in the samples from the reverse (2D-to-3D) reaction.

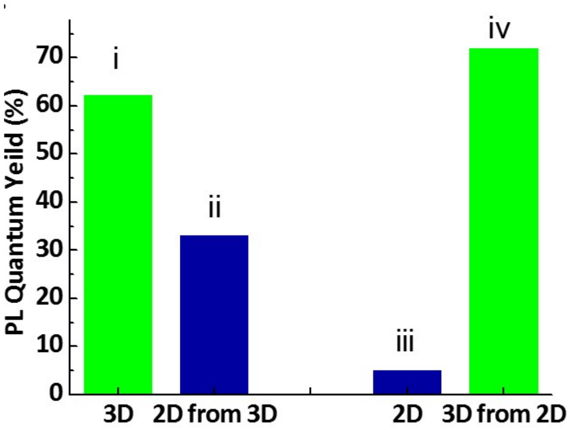

Figure S3. PL quantum yield of the as-synthesized 3D $MAPbBr_3$ NCs (0.72 µmol in 5 ml) (i, Green bar), the as-synthesized perovskite sample (0.72 µmol in 5 ml) with the addition of 2.8 µmol PEA^+ (ii- blue bar), the as-synthesized 2D $(OcA)_2PbBr_4$ NCs (0.72 µmol in 5 ml) (iii- blue bar), and the as-synthesized 2D $(OcA)_2PbBr_4$ NCs (0.72 µmol in 5 ml) with the addition of 1.0 µmol MA^+ (iv- green bar).

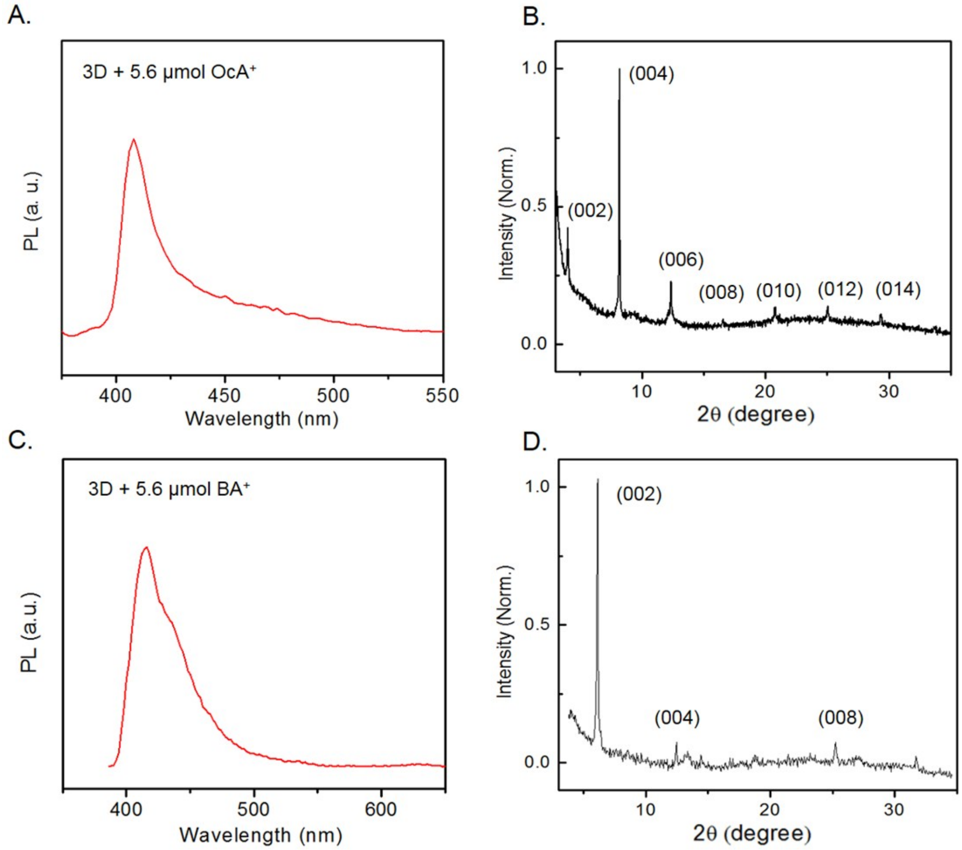

Figure S4. (A) PL emission spectrum of the as-synthesized 3D sample (0.72 µmol in 5 ml) with the addition of 5.6 µmol of OcA$^+$. And (B) XRD patterns of the as-synthesized 3D sample (0.72 µmol in 5 ml) with the addition of 5.6 µmol of OcA$^+$, (C) PL emission spectrum of the as-synthesized 3D sample (0.72 µmol in 5 ml) with the addition of 5.6 µmol of BA$^+$. And (B) XRD patterns of the as-synthesized 3D sample (0.72 µmol in 5 ml) with the addition of 5.6 µmol of BA$^+$.

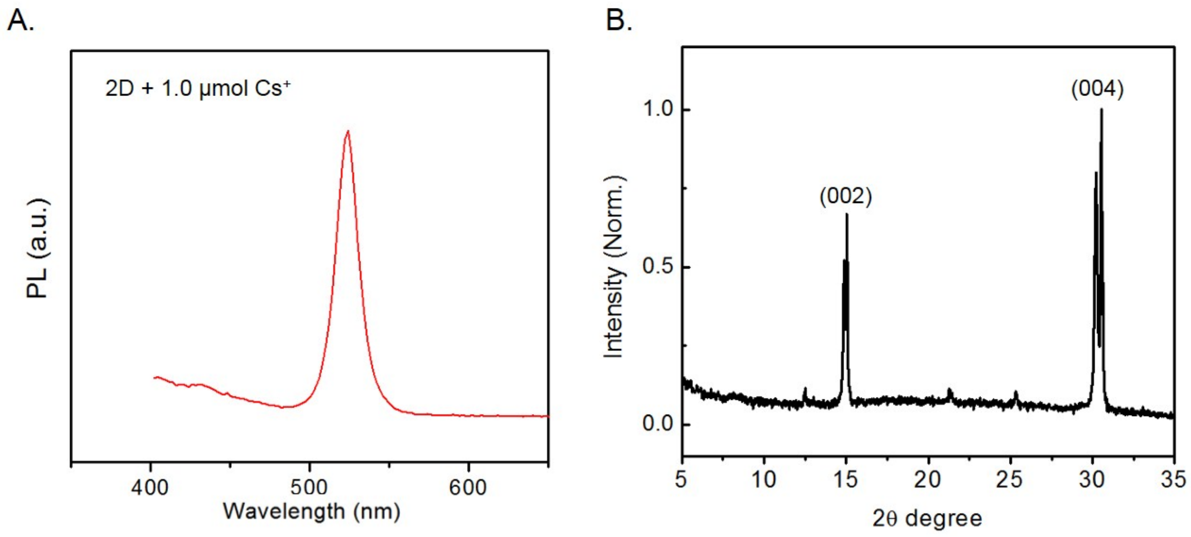

Figure S5. (A) PL emission spectrum of the as-synthesized 2D sample (0.72 µmol in 5 ml) with the addition of 1.0 µmol of Cs^+. And (B) XRD patterns of the as-synthesized 2D sample (0.72 µmol in 5 ml) with the addition of 1.0 µmol of Cs^+.

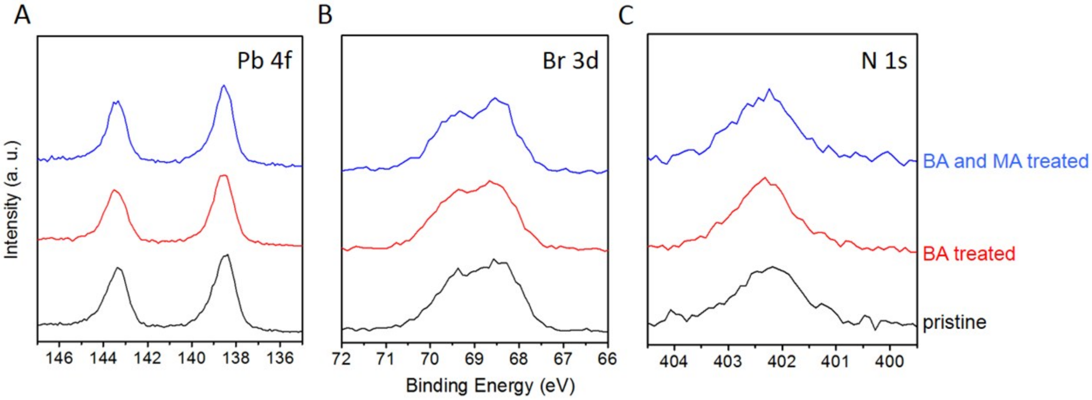

Figure S6. (A) Pb 4f, (B) Br 3d, and (C) N 1s photoelectron spectra of the pristine $MAPbBr_3$ film, (ii) the $MAPbBr_3$ film obtained after the exposure of BA, and (iii) the $MAPbBr_3$ film obtained after consecutive exposure to BA and MA.

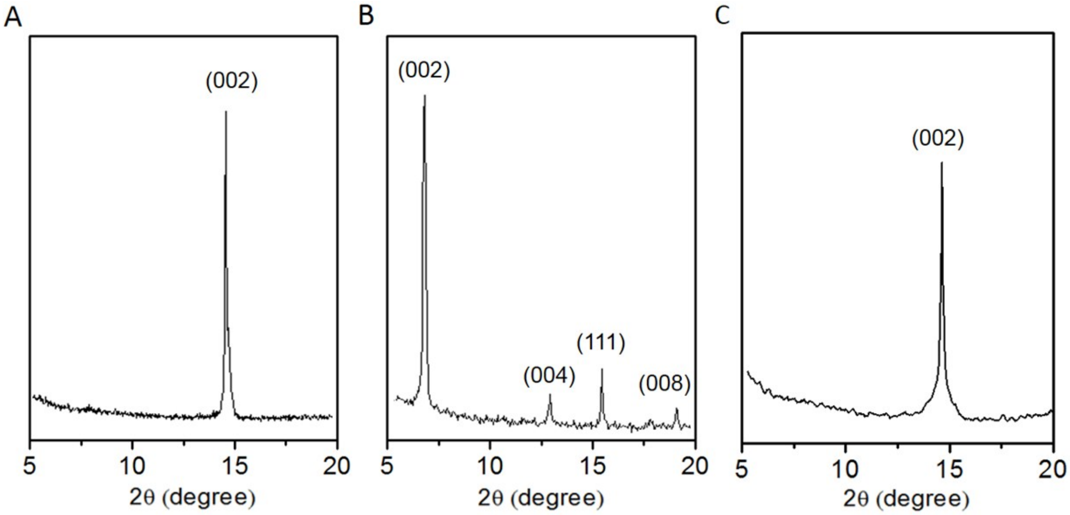

Figure S7. XRD pattern of (i) the pristine $MAPbBr_3$ film, (ii) the $MAPbBr_3$ film obtained after the exposure of BA, and (iii) the $MAPbBr_3$ film obtained after consecutive exposure to BA and MA.

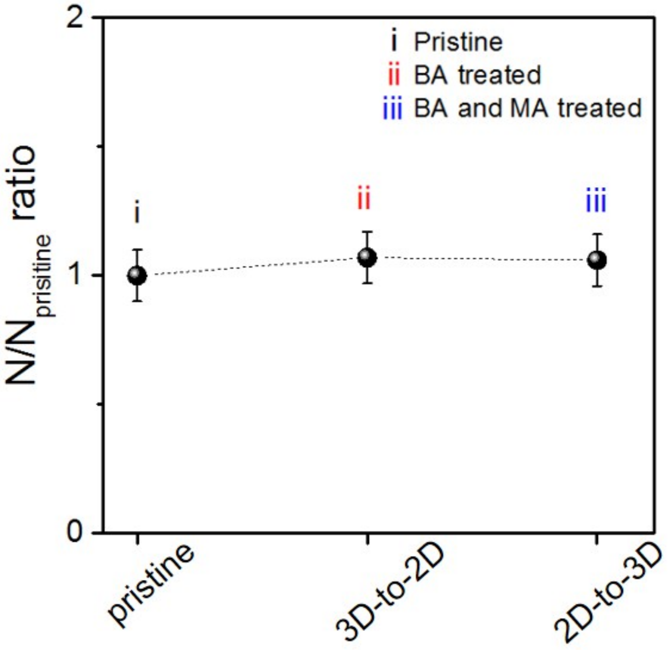

Figure S8. The change of nitrogen content in (i) the pristine $MAPbBr_3$ film, (ii) the $MAPbBr_3$ film obtained after the exposure of BA, and (iii) the $MAPbBr_3$ film obtained after consecutive exposure to BA and MA.

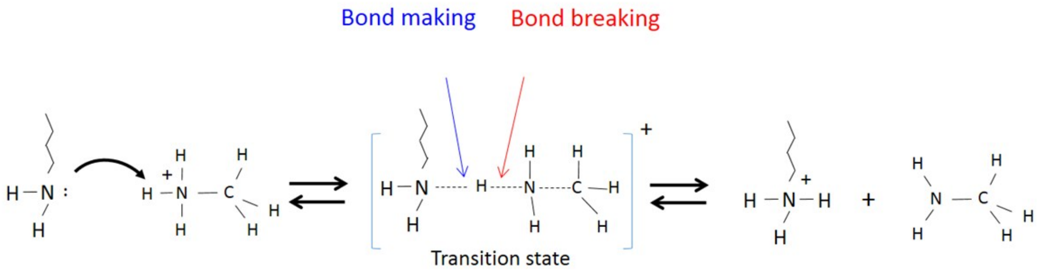

Figure S9. Proton transfer mechanism of reversible conversion between BA^+ and MA^+.

Table S1. Average Lifetime of Perovskite nanocrystals

Perovskite samples	**T_1 (ns)** **α_1**	**T_2 (ns)** **α_2**	**χ_{SQ}**	**T_{avg} (ns)**
3D sample **(λ_{max}:520 nm)**	6.11 (41.05)	20.23 (59.95)	1.32	17.83
(2D from 3D) **(λ_{max}:432 nm)**	3.80 (36.93)	6.21 (63.07)	0.95	5.57

Perovskite samples	**T_1 (ns)** **α_1**	**T_2 (ns)** **α_2**	**χ_{SQ}**	**T_{avg} (ns)**
2D sample **(λ_{max}:415 nm)**	1.079 (88.62)	6.75 (11.38)	1.5	0.37
3D from 2D **(λ_{max}:515 nm)**	8.65 (31.5)	13.55 (68.5)	1.9	12.43

τ_1 and τ_2 Life time of first and second; α_1 and α_2 are the percentage of first and second components; χ_{SQ} is goodness of fit; T_{avg} is the average lifetime calculated using the above equation.

3. Cation exchange reactions occur in solution

(i) Forward reaction (3D-to-2D):

$$MAPbBr_3 + 2PEABr \rightarrow (PEA)_2PbBr_4 + Br^- + MA^+ \qquad (S1)$$

(ii) Reverse reaction (2D-to-3D):

$$(OcA)_2PbBr_4 + MABr \rightarrow MAPbBr_3 + 2Br^- + 2OcA^+ \qquad (S2)$$

REFERENCE

1. Horcas, I.; Fernández, R.; Gómez-Rodríguez, J. M.; Colchero, J.; Gómez-Herrero, J.; Baro, A. M. *Rev. Sci. Instrum.* **2007**, *78*, 13705.

2. C.-G. Wu, C.-H. Chiang and S. H. Chang, *Nanoscale,* **2016**, 8, 4077–4085.