## **Supporting Information**

## Impact of Cesium in Methylammonium Lead Bromide Perovskites: Insights from the Microstructures, Stability and Photophysical Properties

S. Premkumar,<sup>1</sup> Kaushik Kundu,<sup>1\*</sup> and Siva Umapathy,<sup>1,2\*</sup>

 <sup>1</sup> Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India.
<sup>2</sup> Indian Institute of Science Education and Research, Bhopal Bhopal Bypass Road, Bhauri, Bhopal 462 066, Madhya Pradesh, India.

## **Corresponding Author Information:**

E-mail: kaushik.isi@gmail.com / siva.umapathy@gmail.com



Fig. S1. Photograph of colloidal dispersions of  $MA_{1-x}Cs_xPbBr_3$  ( $0 \le x \le 1$ ) perovskites in cyclohexane under room light.



Fig. S2. (A) Calculated effective tolerance factors and (B) structural distortion in MA<sub>1-x</sub>Cs<sub>x</sub>PbBr<sub>3</sub> ( $0 \le x \le 1$ ) perovskites with cell volume per formula unit and the c/a ratio as a function of composition.



Fig. S3. Gaussian deconvolution of low-frequency Raman spectra of the synthesized (A)  $MA_{0.2}Cs_{0.8}PbBr_3$ , and (B)  $MA_{0.8}Cs_{0.2}PbBr_3$  perovskites. (C and D panels) Raman frequency shift of the individual deconvoluted peaks as a function of composition along with the (D) FWHM of  $MA_{1-x}Cs_xPbBr_3$  ( $0 \le x \le 1$ ) perovskites.



Fig. S4. (A and B panels). Raman spectra of the synthesized  $MA_{1-x}Cs_xPbBr_3$  ( $0 \le x \le 1$ ) perovskites over the high-frequency region (2700-3300 cm<sup>-1</sup>), i.e., where the C-H and N-H vibrations of methylammonium appear.



**Fig. S5.** The size distribution histogram of the MA<sub>1-x</sub>Cs<sub>x</sub>PbBr<sub>3</sub> ( $0 \le x \le 1$ ) perovskites.



Fig. S6. SAED patterns of the synthesized (A) MAPbBr<sub>3</sub>, (B)  $MA_{0.8}Cs_{0.2}PbBr_3$ , (C)  $MA_{0.6}Cs_{0.4}PbBr_3$ , (D)  $MA_{0.4}Cs_{0.6}PbBr_3$ , (E)  $MA_{0.2}Cs_{0.8}PbBr_3$  and (F) CsPbBr<sub>3</sub> perovskites.



Fig. S7. (A) Photoluminescence (PL) spectra of the synthesized  $MA_{1-x}Cs_xPbBr_3$  ( $0 \le x \le 1$ ) perovskites. (B) UV-vis absorption and PL spectra of the synthesized  $MA_{1-x}Cs_xPbBr_3$  ( $0.6 \le x \le 1$ ) perovskites. (C) Gaussian deconvolution of PL spectra of the synthesized  $MA_{0.8}Cs_{0.2}PbBr_3$  perovskite. (D) FWHM of the PL spectra of the synthesized  $MA_{1-x}Cs_xPbBr_3$  ( $0 \le x \le 1$ ) perovskites.

Name/unit cell parameters	<i>a</i> / Å	<i>b</i> / Å	<i>c</i> / Å	Volume/ Å <sup>3</sup>
CsPbBr <sub>3</sub>	8.306058	8.203634	11.79377	803.6259
MA <sub>0.2</sub> Cs <sub>0.8</sub> PbBr <sub>3</sub>	8.338306	8.276673	11.62543	802.3109
$MA_{0.4}Cs_{0.86}PbBr_3$	8.326415	8.326415	11.68876	808.8815
$MA_{0.6}Cs_{0.4}PbBr_{3}$	8.43999	11.88780	8.312142	833.9816
MA <sub>0.8</sub> Cs <sub>0.2</sub> PbBr <sub>3</sub>	8.436164	11.91719	8.397279	844.2238
MAPbBr <sub>3</sub>	8.493311	12.01103	8.536381	870.8253

**Table S1**. Unit cell parameters of  $MA_{1-x}Cs_xPbBr_3$  ( $0 \le x \le 1$ ) perovskite samples.

Sample	$\tau_1$ (ns)	$\tau_2$ (ns)	A1	A2	$\tau_{avg}$ (ns)	$\chi^2$
CsPbBr <sub>3</sub>	2.92	31.61	0.12	0.88	31.25309637	1.32
MA <sub>0.2</sub> Cs <sub>0.8</sub> PbBr <sub>3</sub>	3.55	31.96	0.14	0.86	31.45540893	1.39
MA <sub>0.4</sub> Cs <sub>0.6</sub> PbBr <sub>3</sub>	4.20	32.09	0.14	0.86	31.50816259	1.17
MA <sub>0.6</sub> Cs <sub>0.4</sub> PbBr <sub>3</sub>	5.09	26.43	0.23	0.77	25.26918919	1.18
MA <sub>0.8</sub> Cs <sub>0.2</sub> PbBr <sub>3</sub>	4.39	24.14	0.17	0.83	23.4307771	1.23
MAPbBr <sub>3</sub>	1.06	39.82	0.63	0.37	38.13935641	1.22

**Table S2.** Fitted lifetime values using a bi-exponential decay model along with the respective % contribution of each component of  $MA_{1-x}Cs_xPbBr_3$  ( $0 \le x \le 1$ ) perovskite series.