Supporting Information

Heterovalent Substitution in Mixed Halide Perovskite Quantum Dots for Improved and Stable Photovoltaic Performance

Dibyendu Ghosh,[#] Md. Yusuf Ali,[#] Anima Ghosh, Arnab Mandal and Sayan Bhattacharyya*

Department of Chemical Sciences, and Centre for Advanced Functional Materials, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur - 741246, India

*Email for correspondence: sayanb@iiserkol.ac.in
#Equal contribution

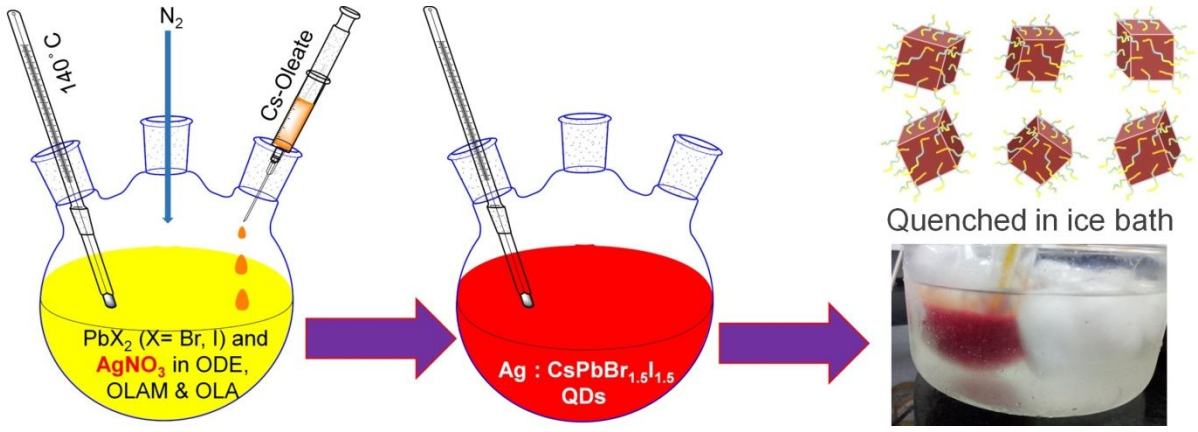

Figure S1. Schematic representation of the synthesis of $CsPb_{1-x}Ag_xI_{1.5}Br_{1.5}$ QDs *via* hot injection method.

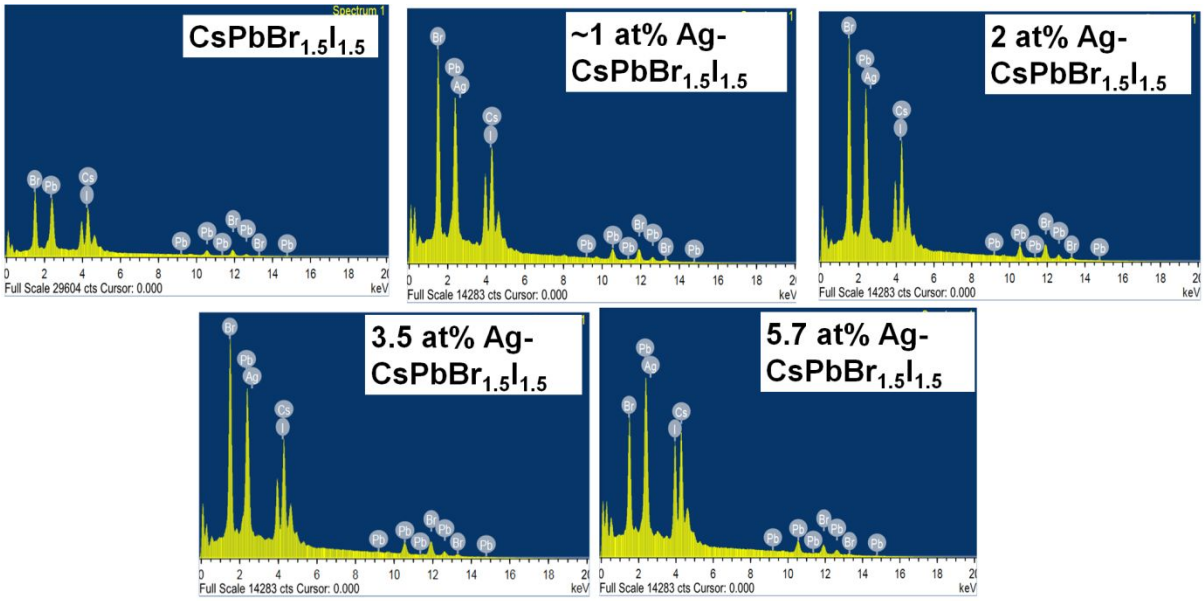

Figure S2. EDAX spectra of pristine and Ag-doped CPBI QDs.

Table S1. EDAX data of the individual elements in Ag loaded CBPI QDs.

Sample	Cs at%	Pb at%	Br at%	I at%	Ag at%	*x* in $CsPb_{1-x}Ag_xBr_{1.5}I_{1.5}$	*d* spacing in Å (XRD)	QD size (nm)*
CPBI	20.4	20.1	29.6	29.9	0	0	4.2573	8.4 ± 0.5
$Ag_{0.01}$-CPBI	20.5	19.8	30.1	29.75	0.15	0.01 (1 %)	4.2213	8.3 ± 0.3
$Ag_{0.02}$-CPBI	20.3	19.5	30.3	29.5	0.4	0.02 (2%)	4.1937	8.3 ± 0.6
$Ag_{0.035}$-CPBI	20.4	19.2	30.4	29.3	0.7	0.035 (3.5%)	4.1858	8.1 ± 0.4
$Ag_{0.057}$-CPBI	20.2	18.5	29.8	30.4	1.1	0.057 (5.7%)	4.1937	8.3 ± 0.5

*Error is estimated for 10 samples

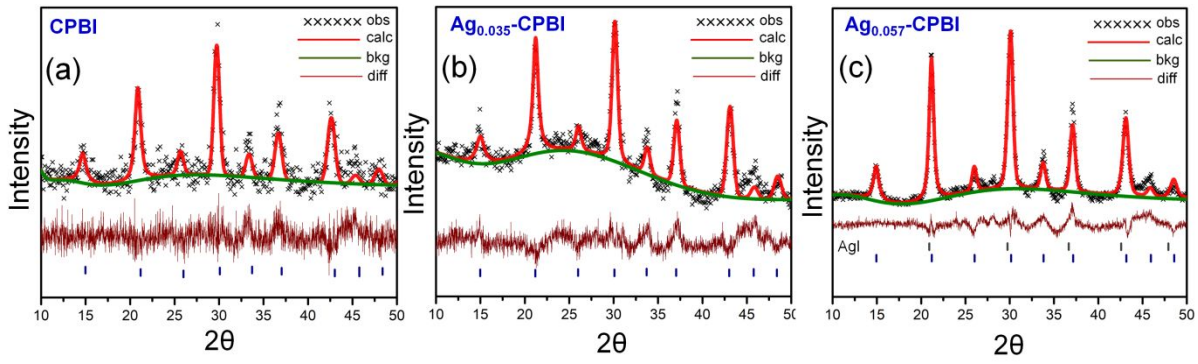

Figure S3. Rietveld refinement of XRD patterns of (a) CPBI, (b) $Ag_{0.035}$-CPBI and (c) $Ag_{0.057}$-CPBI QDs.

Table S2. Rietveld refinement results.

QD	Major Phases	Space Group	Volume (Å^3)	Lattice parameter (Å)	GOF	R_{wp}
CPBI	$CsPbBr_{1.5}I_{1.5}$	*Pm-3m*	212.028 ± 1.383	5.963 ± 0.013	1.03	14.0*
$Ag_{0.035}$-CPBI	$CsPbBr_{1.5}I_{1.5}$	*Pm-3m*	211.389 ± 0.312	5.957 ± 0.003	1.33	5.8
$Ag_{0.057}$-CPBI	$CsPbBr_{1.5}I_{1.5}$ (97.5%) AgI (2.5%)	*Pm-3m*	207.579 ± 1.741	5.921 ± 0.016	1.58	6.3

*The R_{wp} is high because of the scattered experimental data points in Figure S3a.

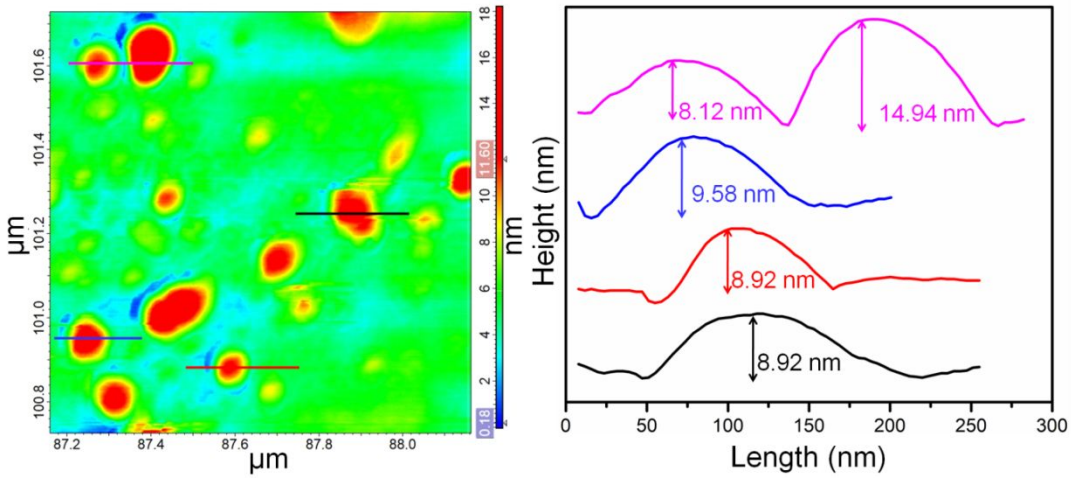

Figure S4. AFM image of $Ag_{0.035}$-CPBI after 2 weeks of ageing (left panel) and its line profile (right panel).

Table S3. Transient PL parameters of pristine and Ag-doped CPBI QDs.

Sample	PLQY (%)	B1	τ_1 (ns)	B_2	τ_2 (ns)	B_3	τ_3 (ns)	χ^2	$\langle\tau\rangle$ (ns)*
CPBI	72	34.72	2.95	46.23	12.2	19.05	0.66	1.07	10.60 ± 0.03
$Ag_{0.01}$-CPBI	74	30.60	3.49	56.68	13.4	12.72	0.79	1.04	12.04 ± 0.08
$Ag_{0.02}$-CPBI	75	27.85	3.14	57.00	14.4	15.15	0.68	1.19	13.17 ± 0.12
$Ag_{0.035}$-CPBI	78	18.32	3.84	73.91	17.7	7.71	0.72	1.08	16.92 ± 0.06
$Ag_{0.057}$-CPBI	73	41.65	2.14	25.16	7.8	33.19	0.53	1.04	5.07 ± 0.14

*Error is estimated on 5 samples.

τ: lifetime, B: corresponding amplitude, $\langle\tau\rangle$: average lifetime, $\langle\ \tau\ \rangle = \frac{\sum_{t=1}^{3} B * \tau^2}{\sum_{t=1}^{3} B * \tau}$

Measurement of PL Quantum Yield (PLQY):

To measure PLQY the samples were dispersed in hexane and with the help of standard dye, according to the following formula:[S1,S2]

$$(QY)_S = (QY)_R \frac{\eta_S^2}{\eta_R^2} \frac{I}{A} \frac{A_S}{I_R}$$

Here,
$(QY)_S$ = Quantum Yield of sample
$(QY)_R$ = Quantum Yield of reference
η_S = Refractive Index of the sample
η_R = Refractive Index of the reference
I_R = Integrated fluorescence Intensity of the reference
I_S = Integrated fluorescence Intensity of the sample
A_R = the absorbance of the reference at the excitation wavelength
A_S = the absorbance of the sample at the excitation wavelength

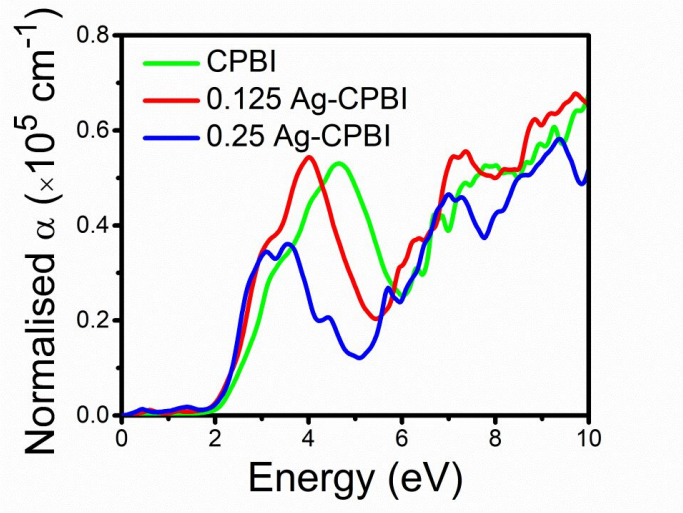

Figure S5. Calculated absorption coefficient (α) plots of $CsPb_{1-x}Ag_xI_{1.5}Br_{1.5}$ (x = 0, 0.125, 0.25) structures.

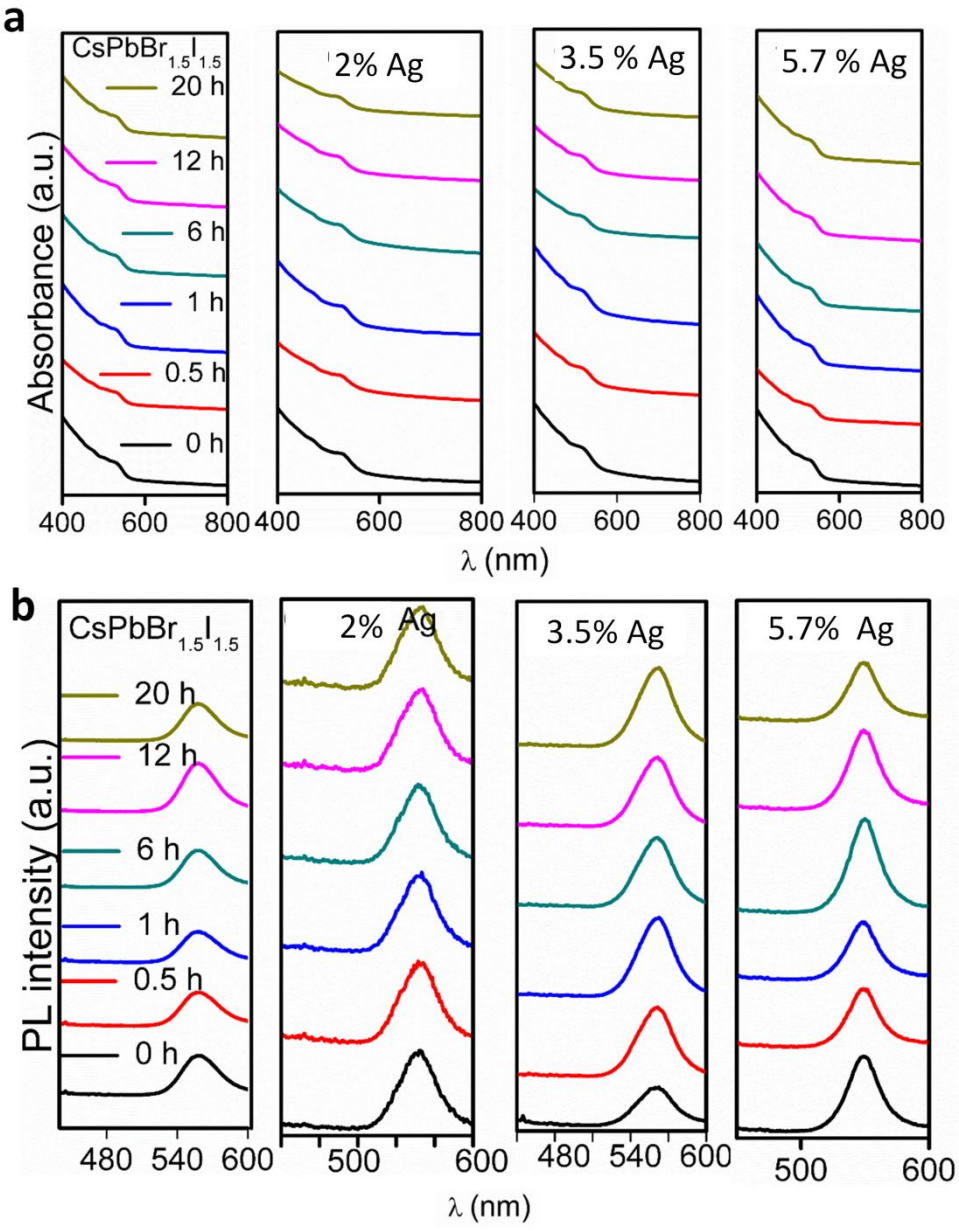

Figure S6. Stability test of pristine and Ag-doped CPBI QDs with respect to (a) optical absorbance and (b) PL intensity. The QD solutions were monitored in 20h continuous measurement under ambient conditions.

References

(S1) Brouwer, A. M. Standards for Photoluminescence Quantum Yield Measurements in Solution (IUPAC Technical Report), *Pure Appl. Chem.* **2011**, *83*, 2213–2228.

(S2) Su, Y.; Chen, X.; Ji, W.; Zeng, Q.; Ren, Z.; Su, Z.; Liu, L. Highly Controllable and Efficient Synthesis of Mixed-Halide $CsPbX_3$ (X = Cl, Br, I) Perovskite QDs toward the Tunability of Entire Visible Light, *ACS Appl. Mater. Interfaces* **2017**, *9*, 33020–33028.