

Supporting Information

Mixed Metal Halide Perovskite $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ Quantum Dots: Insight into Photophysics from Photoblinking Studies

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Materials

Cesium carbonate (Cs_2CO_3) 99% (Molychem), Lead Bromide (PbBr_2) 99% (Sigma Aldrich), Tin Bromide (SnBr_2) 92% (Sigma Aldrich), 1-octadecene (ODE) 90% (Thermoscientific), Oleic Acid (OA) 90% (Loba Chemie), Oleylamine(OAm) 95% (SRL), Perylene Dye (Sigma), Hexane HPLC grade 99% (Finar) and Toluene AR Grade 99% (Finar) chemicals are used for synthesis and characterization of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$. All of the reagents were used as received, solvents used in synthesis are degassed and kept under N_2 environment.

Synthesis of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ perovskites: The synthesis of $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ QDs performed using hot Injection method which involves simultaneous preparation of two reaction precursors i.e Oleate precursor and bromide precursors (a) Preparation of Cs-Oleate: Cesium-oleate solution prepared following the method reported by a Protesescu et al¹ with slight modifications. In brief, Cs_2CO_3 (0.62mmol), 0.6 mL of OA, and 10 mL of ODE are loaded in a three-neck flask and degassed under vacuum, followed by gradual heating at 120 °C with constant stirring under a N_2 atmosphere until clear solution of Cs-Oleate observed. This solution kept under N_2 environment at 100 °C for further use. (b) $\text{PbBr}_2/\text{SnBr}_2$ precursor: In another three neck R.B. flask, 0.37 mmol PbBr_2 mixed in the solution containing 10 mL ODE, 1.3 mL oleic acid, and 1.3 mL oleylamine. This mixture dried and degassed for three cycles under constant stirring in N_2 environment. This mixture gradually heated up to 180 °C. 0.8 mL of Cs-oleate, kept at 100 °C quickly injected to the PbBr_2 precursor. In a few seconds, the reaction mixture turned to turbid yellow indicating the progress of the reaction. The reaction was quenched using ice bath and the colour of the mixture turned to yellow- green. Different extent of Sn substitution in the $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ perovskites achieved by varying stoichiometric ratios of the reaction precursors without changing other reaction parameters or conditions. The synthesized material further purified by re-precipitation (as and when required), washing and centrifugation at 6500 rpm for 2-3 times. The purified $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ perovskites dispersed in toluene for further characterization.

Supporting Information

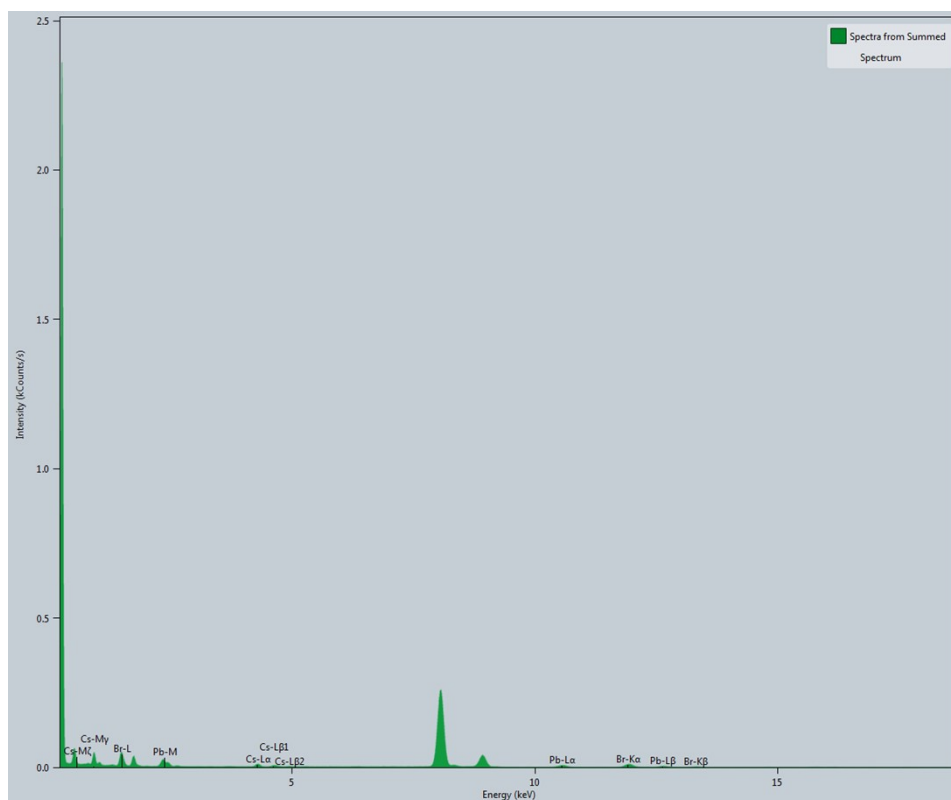


Fig. S1: The energy-dispersive X-ray spectroscopy (EDX) spectrum showing relative elemental mapping for CsPb₁Sn₀Br₃.

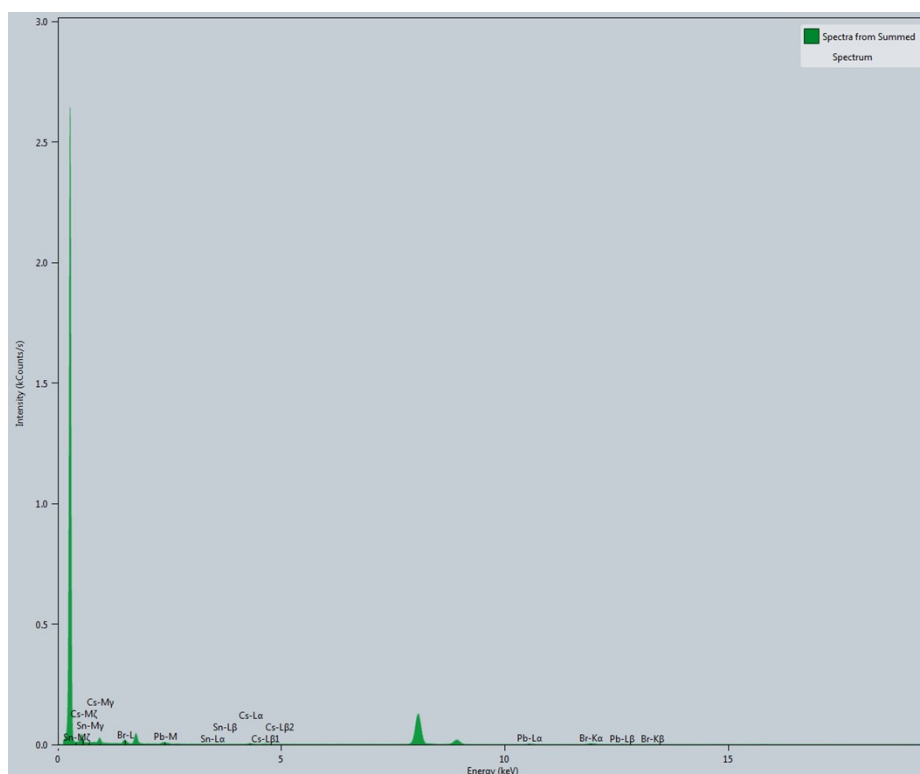


Fig. S2: The energy-dispersive X-ray spectroscopy (EDX) spectrum showing relative elemental mapping for CsPb_{0.9}Sn_{0.1}Br₃.

Supporting Information

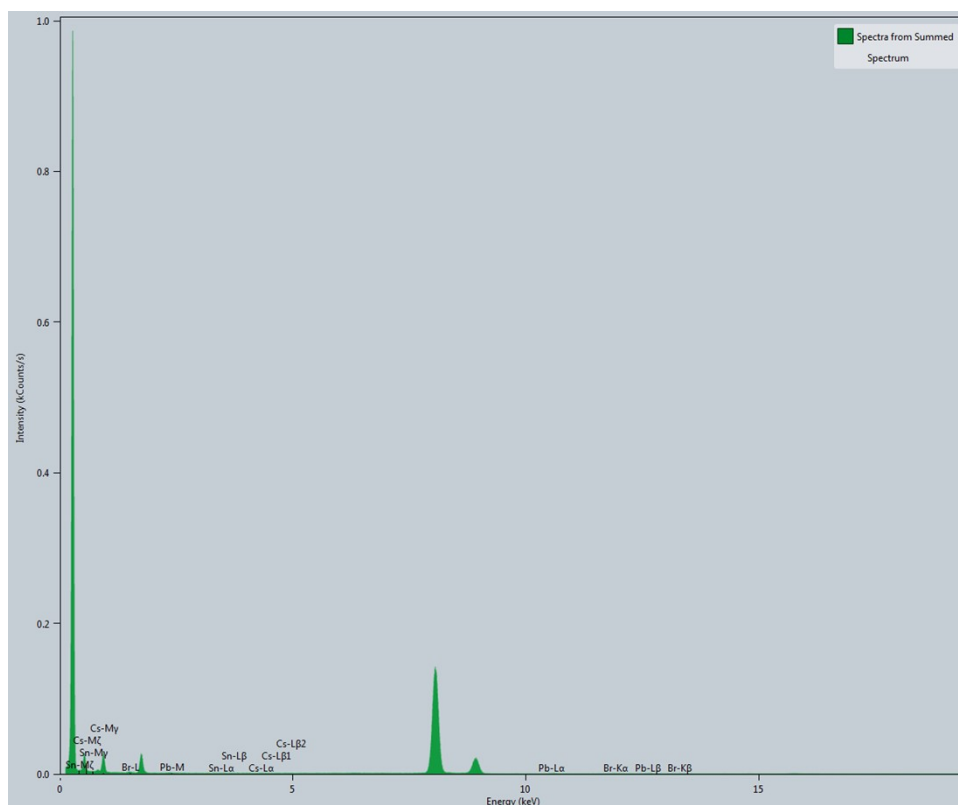


Fig. S3: The energy-dispersive X-ray spectroscopy (EDX) spectrum showing relative elemental mapping for $\text{CsPb}_{0.7}\text{Sn}_{0.3}\text{Br}_3$.

In the EDX spectrum, distinct peaks corresponding to the primary elements Cs, Pb, Sn and Br are observed. The Cs peak is located at approximately 4.29 keV (Cs $L\alpha$), the Pb peaks are at 2.35 keV (Pb $M\alpha$) and 10.6 keV (Pb $L\alpha$), the Sn peaks are at 3.44 keV (Sn $K\alpha$) and the Br peak is at 11.9 keV (Br $K\alpha$) which are in agreement with the literature.^{2, 3} The elemental ratio of every element in $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ ($x=0, 0.1, 0.3$) provided by EDX software are tabulated in the table S1, it clearly state that B^{2+} cations (Pb:Sn) are in 1:0, 0.9:0.1, 0.7:0.3 ratios as expected in all the three perovskites.

| Elements | Atomic Fraction (%) by EDS in $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ | | |
|---------------|---|----------------|------------------|
| | $x=0$ | $x=0.1$ | $x=0.3$ |
| Cs | 19.8 | 19.5 | 12.0 |
| Pb | 20.6 | 20.2 | 36.3 |
| Sn | 0 | 2.09 | 15.8 |
| Br | 59.7 | 58.2 | 35.9 |
| Pb: Sn | 1:0 | 0.9:0.1 | (0.7:0.3) |

Table S1: Data extracted from energy-dispersive X-ray spectroscopy (EDX) to show the elemental composition of different $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ perovskites with varying Sn content in the reaction precursor.

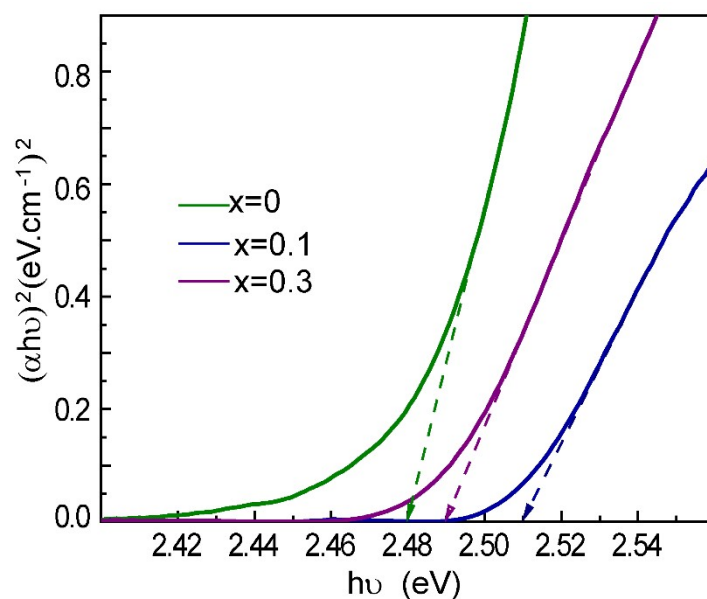


Fig. S4: Tauc plot (solid lines) constructed from the absorption spectra represented in Fig. 1 (d-f) of the main text. The band gap energy from these plots estimated for different $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ as shown in the Fig..

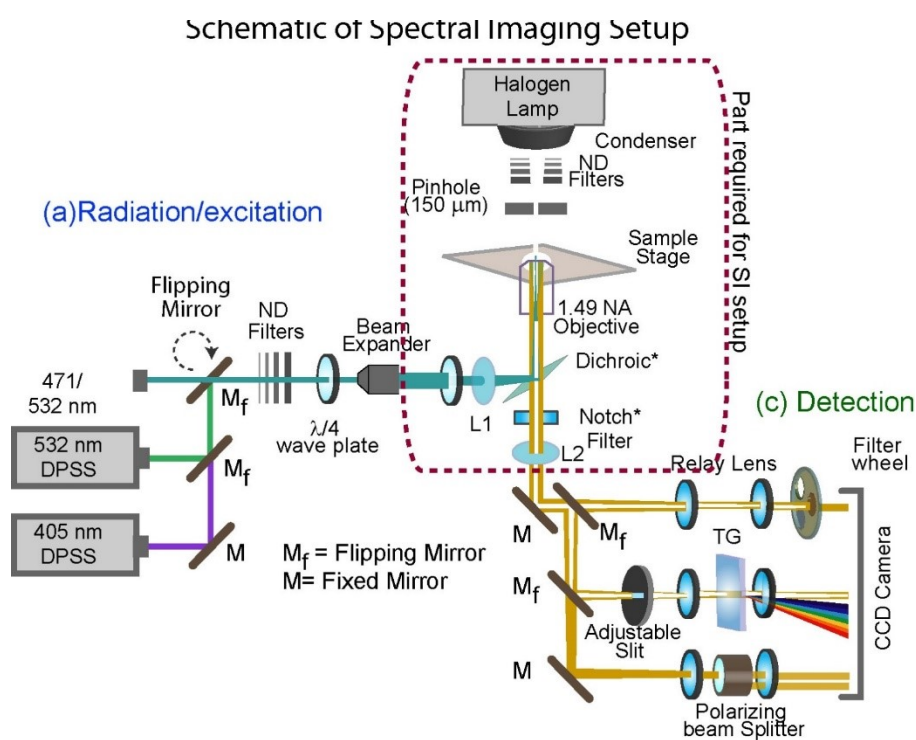


Fig. S5: Schematic of home-built experimental setup for PL measurements at single particle level.

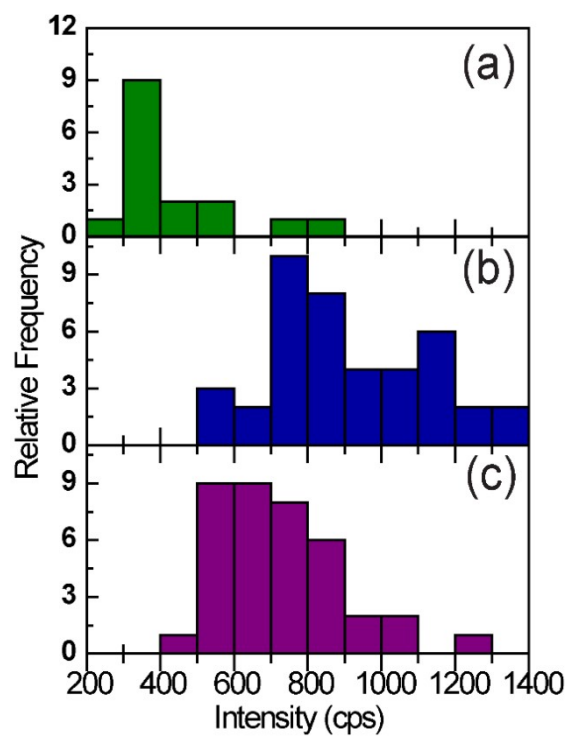


Fig. S6: Spatial distribution of the intensity for $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ perovskites for different 'x' values at single particle level.

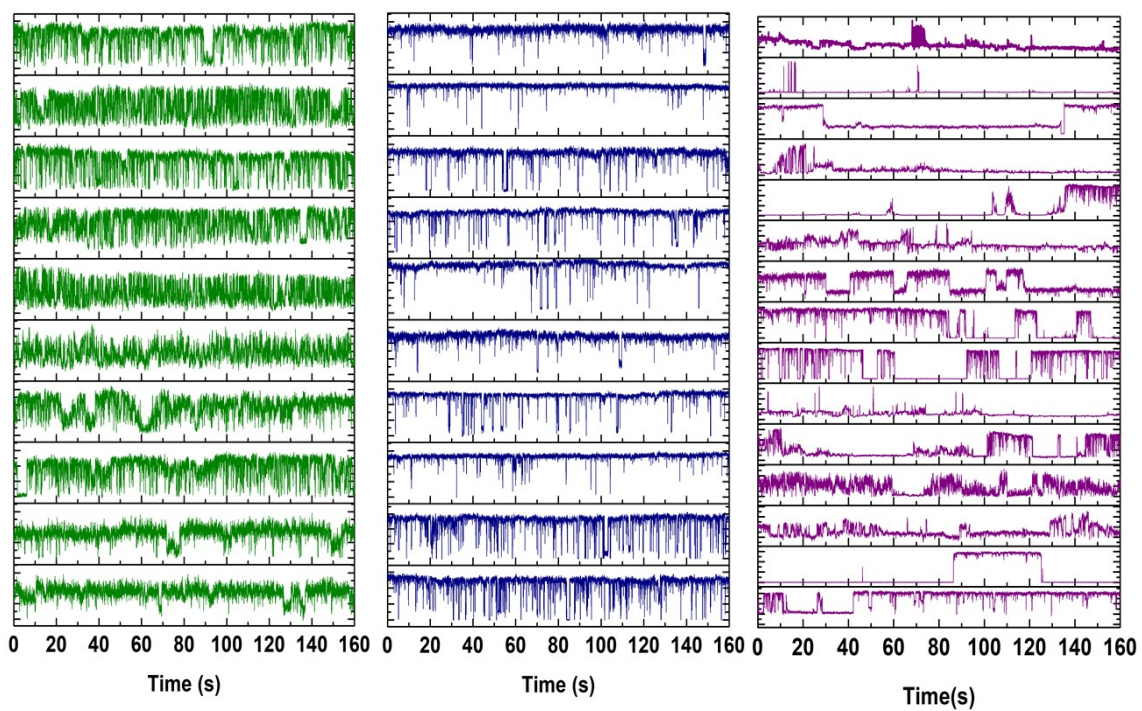


Fig. S7: Examples of intensity time traces of individual $\text{CsPb}_{1-x}\text{Sn}_x\text{Br}_3$ perovskites for $x=0$ (green), 0.1 (blue) and 0.3 (purple) respectively.

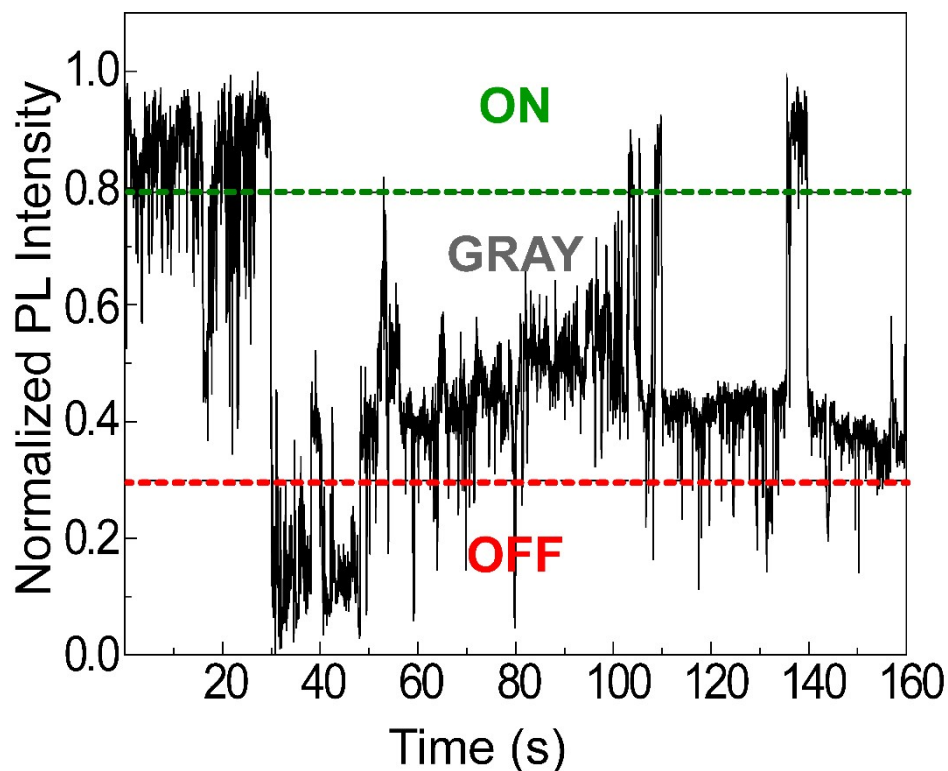


Fig. S8: Criteria for determining ON, GRAY and OFF states for blinking analysis.

Reference:

- 1 L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, Nanocrystals of Cesium Lead Halide Perovskites (CsPbX_3 , $X = \text{Cl, Br, and I}$): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut, *Nano Lett.*, 2015, **15**, 3692–3696.
- 2 O. Nazarenko, M. R. Kotyrba, S. Yakunin, M. Wörle, B. M. Benin, G. Rainò, F. Krumeich, M. Kepenekian, J. Even, C. Katan and M. V. Kovalenko, Guanidinium and Mixed Cesium-Guanidinium Tin(II) Bromides: Effects of Quantum Confinement and Out-of-Plane Octahedral Tilting, *Chem. Mater.*, 2019, **31**, 2121–2129.
- 3 H. V Vishaka, G. K. Jesna, P. Altaf, K. Sarina and B. R. Geetha, Lattice constriction and trapped excitons: a structure–property relationship unveiled in CsPbBr_3 perovskite QDs, *J. Mater. Chem. C*, 2020, **8**, 17090–17098.