

SUPPORTING INFORMATION

3D Structure Mediated Growth of Zero Dimensional Cs_4SnX_6 Nanocrystals

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Chemicals

Tin(II) iodide (SnI_2 , Sigma-Aldrich, 99.999%), Tin(II) bromide (SnBr_2 , Sigma-Aldrich, 99.999%), Cesium carbonate (Cs_2CO_3 , Aladdin, 99.99%), Oleic Acid (OA, Aladdin, AR), Oleylamine (OLA, Aladdin, 80-90%), Octadecene (ODE, Aladdin, 90%), Octane (Aladdin, AR, 96%), Trioctylphosphine (TOP, Sigma-Aldrich, 97%), Commercial aluminates phosphors ($\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ and $\text{CaAlSiN}_3:\text{Eu}^{2+}$, Shenzhen looking long technology co., LTD), Polymethyl methacrylate (PMMA, Aladdin, Heat resistant injection grade).

Experiments

Cs-OA precursor: Cs_2CO_3 (1.6 g), OA (6 mL) and ODE (60 mL) were added in a 250 mL two-neck flask, and degassed at 110°C with stirring for 2 hours. Then raised the temperature of solution to 150°C with N_2 -protection. Kept heat until the Cs_2CO_3 was dissolved completely and the solution was transparent. Removed the heater and cooled the solution to room temperature naturally. The obtained Cs-OA precursor was stored in glove-box.

Synthesis of Cs_4SnBr_6 NCs: In N_2 glove-box, SnBr_2 (0.4 mmol), TOP (400 μL), OA (50 μL), OLA (50 μL) and ODE (10 mL) were added in a 100 mL two-neck flask, and degassed at 110°C with stirring for 1 hours. When the

SnBr₂ was dissolved completely at 110°C, the color of solution displayed light yellow. Then raised the temperature of solution to 165°C with N₂-protection and the solution became colorless and transparent. 3.48 mL Cs-OA precursor (Cs:Sn=1.3) was taken and dissolved at 100°C. The dissolved Cs-OA precursor was injected in the reaction flask and kept heat for 50 seconds. After the injection, deep red color product formed immediately and then transformed to white color product with the continually heating. After reaction, heater was removed and the reaction flask was put in ice-water bath to cool to room temperature. The reaction flask was transferred to glove-box for Cs₄SnBr₆ NCs purification. The reaction solution was poured in sealed centrifuge tube and centrifuged at 4200 rpm for 5 min. The supernatant was discarded after centrifugation. The precipitate was redispersed in octane and centrifuged at 2000 rpm to remove the undispersed large-size particles. The Cs₄SnBr₆ NCs redispersed in octane was finally obtained.

Cs₄SnBr₃I₃ NCs: In N₂ glove-box, SnBr₂ (0.2 mmol), SnI₂ (0.2 mmol), TOP (400 µL), OA (100 µL), OLA (100 µL) and ODE (10 mL) were added in a 100 mL two-neck flask, and degassed at 110°C with stirring for 1 hours. When the temperature of solution was raised to 180°C, all of the SnBr₂ and SnI₂ can be dissolved completely, and the solution became colorless and transparent. 3.48 mL Cs-OA precursor (Cs:Sn=1.3) was taken and dissolved at 100°C. The dissolved Cs-OA precursor was injected in the reaction flask and kept heat for 50 seconds. After the injection, brown color product formed immediately and then transformed to white color product with the continually heating. After reaction, heater was removed and the reaction flask was put in ice-water bath to cool to room temperature. The following NCs separation and purification was the same with Cs₄SnBr₆ NCs.

Cs₄SnI₆ NCs: In N₂ glove-box, SnI₂ (0.4 mmol), TOP (400 µL), OA (100 µL), OLA (100 µL) and ODE (10 mL) were added in a 100 mL two-neck flask, and degassed at 110°C with stirring for 1 hours. When the temperature of solution was raised to 185°C, SnI₂ can be dissolved completely, and the solution became colorless and

transparent. 3.48 mL Cs-OA precursor (Cs:Sn=1.3) was taken and dissolved at 100°C. The dissolved Cs-OA precursor was injected in the reaction flask and kept heat for 90 seconds. After the injection, black color product formed immediately and then transformed to offwhite color product with the continually heating. After reaction, heater was removed and the reaction flask was put in ice-water bath to cool to room temperature. The following NCs separation and purification was the same with Cs₄SnBr₆ NCs.

White light emitting device (WLED) fabrication: The dried Cs₄SnBr₆ NCs were mixed with the commercial aluminates blue and red phosphors (BaMgAl₁₀O₁₇:Eu²⁺ and CaAlSiN₃:Eu²⁺) with the mass ratio of 2:1:1 to form white light emitting mixture. The mixture were crosslinked by PMMA and then deposited on glass to form white light films. The films were excited by UV LED (350 nm), and bright white light emitting.

DFT calculation

All the DFT-based first-principles calculations are performed by using the Vienna Ab-initio Simulation Package¹,² (VASP) with the projector augmented wave³ (PAW) method. Generalized-gradient approximation⁴ (GGA) formulated by Perdew, Burke, and Ernzerhof (PBE) is used as the exchange-correlation functional. And the plane-wave cutoff energy is set to 400 eV. The Gamma-centered k-point mesh with a grid spacing of $2\pi \times 0.03 \text{ \AA}^{-1}$ is used for electronic Brillouin-zone integration.

Characterization

UV-Vis absorption (Abs) spectra: Cs₄SnX₆ (X=Br, I) NCs were dispersed in octane and stored in sealed cuvettes. The Abs spectra were collected with Agilent Cary 5000 UV-Vis-NIR spectrophotometer.

Photoluminescence (PL), PL excitation (PLE) and time-resolved photoluminescence (TRPL) spectra: Cs₄SnX₆ (X=Br, I) NCs were dispersed in octane and stored in sealed cuvettes. The PL and PLE of Cs₄SnX₆ (X=Br, I) NCs were measured by Horiba Fluorolog-3 spectrofluorometer. The TRPL was measured by Time-Correlated Single Photon Counting (TCSPC) system on Fluorolog-3 spectrofluorometer, and the PL was excited by 365 nm laser.

Temperature-dependent PL: Cs_4SnX_6 (X=Br, I) NCs were deposited on quartz glass in glovebox and then transferred into Oxford OptistatDN cryostat. The temperature of samples was cooled down by liquid nitrogen. The nitrogen atmosphere in cryostat ensured that the sample would not be oxidized during the test. The temperature-dependent PL of Cs_4SnX_6 (X=Br, I) NCs was collected by Horiba Fluorolog-3 spectrofluorometer with the same test conditions.

X-ray diffraction (XRD): The XRD pattern of Cs_4SnX_6 (X=Br, I) NCs was characterized by Bruker D8 Advance with Cu K α radiation.

Transmission electron microscopy (TEM) and Energy dispersive spectroscopy (EDS) elemental mapping images: The TEM images of Cs_4SnX_6 (X=Br, I) NCs were measured by JEOL JEM-2100 Plus (200 kV). The samples were prepared on ultra-thin carbon support films in glovebox. The EDS mapping of Cs_4SnBr_6 NCs was measured at STEM model by JEOL JEM-1400 plus (120 kV).

WLED performance measurement: The emission spectra and CRI of WLED was measured by PR 655 spectrophotometer.

Supporting figures

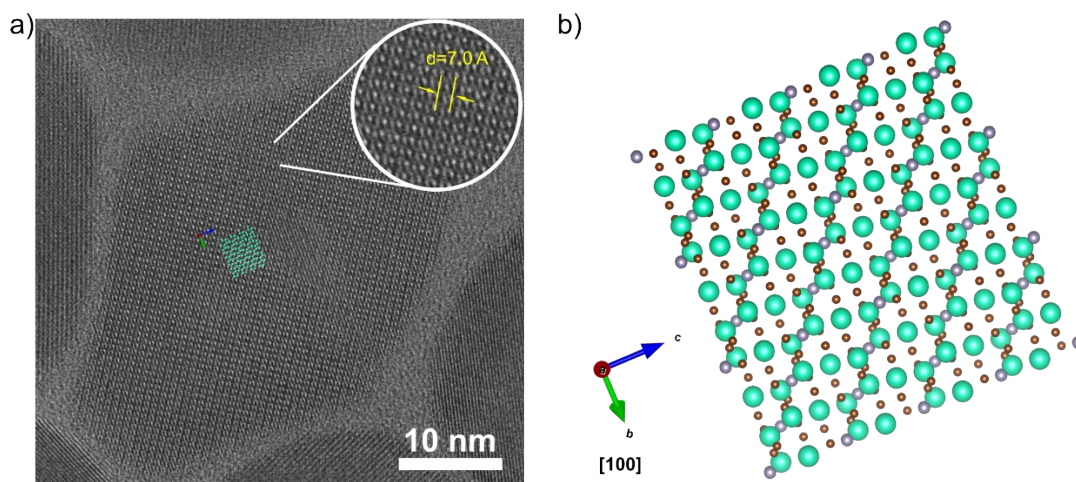


Figure S1 High-resolution TEM images of Cs₄SnBr₆ NCs. The Cs₄SnBr₆ structure is rhombohedral in space group *R*-3c. The d-spacing of 7.0 Å illustrated in (a) corresponds to (012) lattice plane of Cs₄SnBr₆. The clear lattice fringes in (a) were observed in [100] viewing direction. The simulated Cs₄SnBr₆ lattice structure in [100] viewing direction is shown in (b).

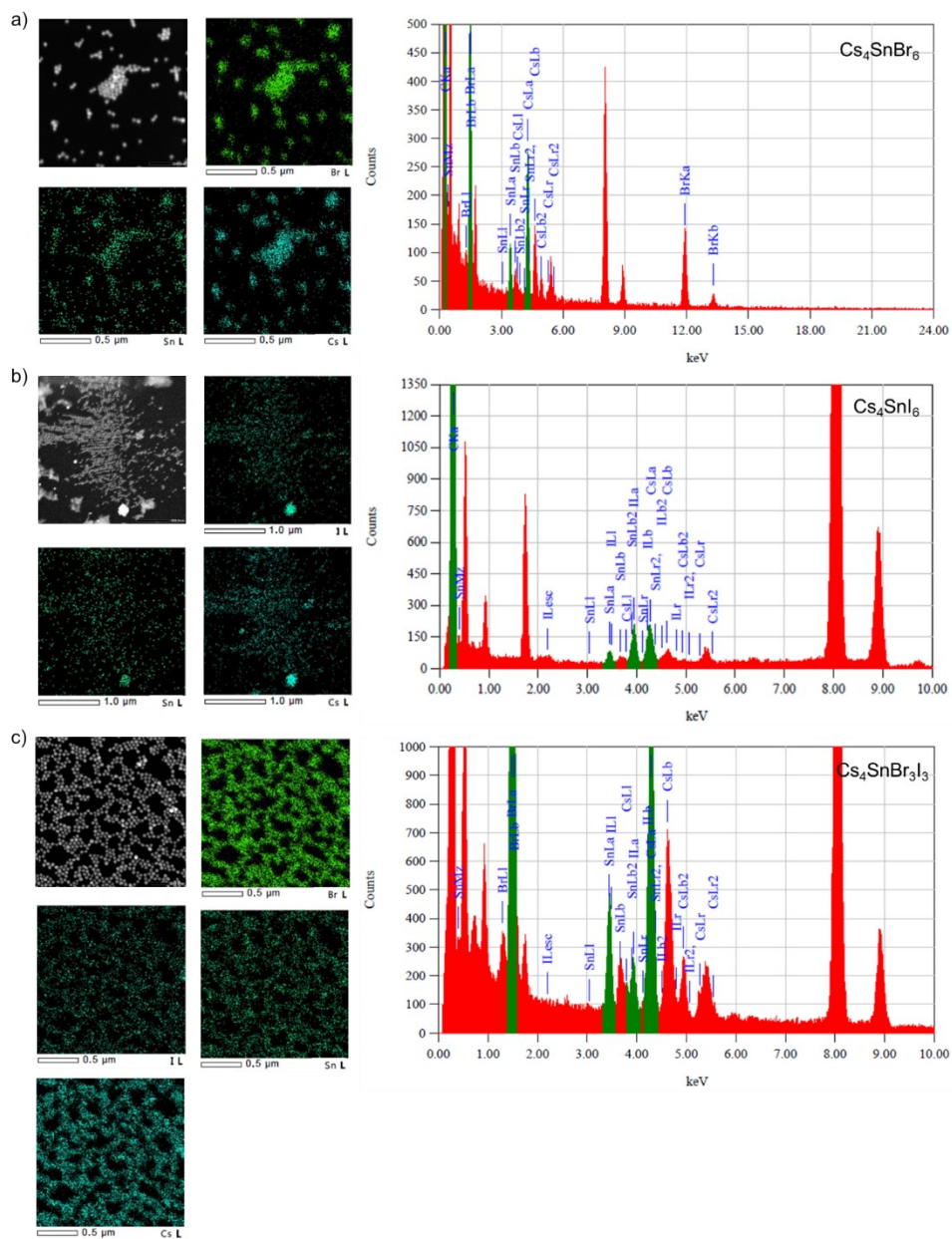


Figure S2 EDS mapping and spectra of a) Cs_4SnBr_6 NCs, b) Cs_4SnI_6 NCs and c) $\text{Cs}_4\text{SnBr}_3\text{I}_3$ NCs.

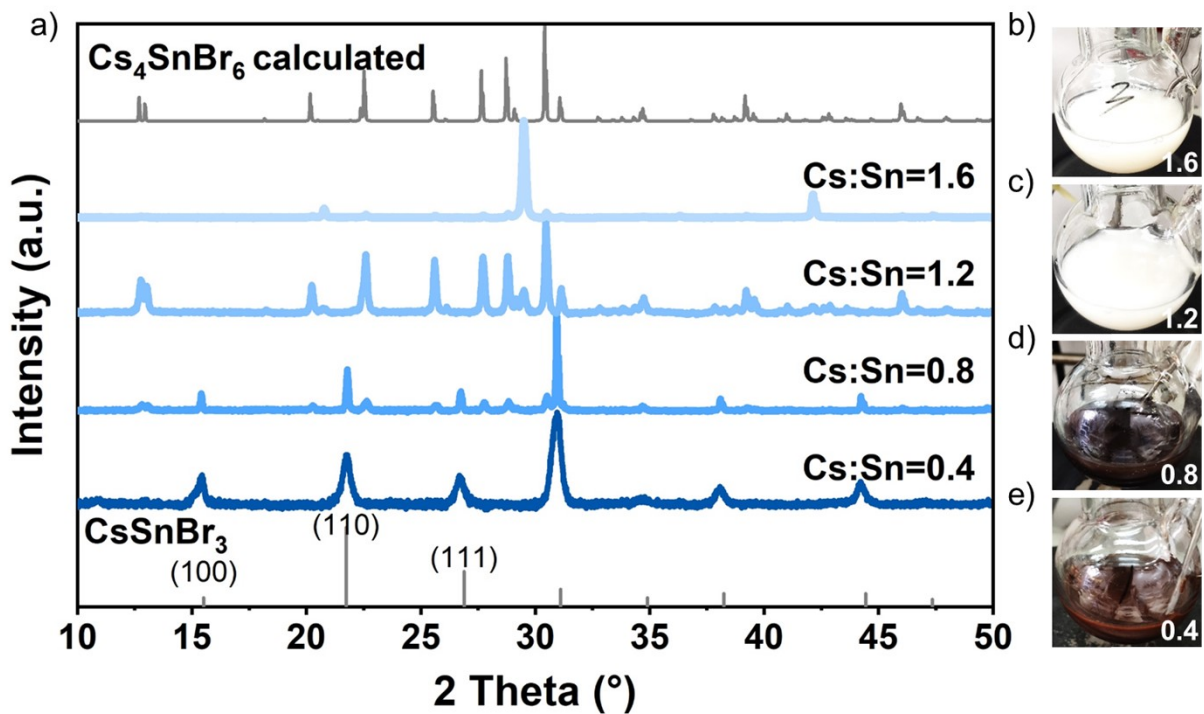


Figure S3. Synthesis of Cs_4SnBr_6 NCs with different Cs:Sn feed mole ratio. a) XRD patterns of produce synthesized at different Cs:Sn feed mole ratio. b~e) Digital images of the produce at different Cs:Sn feed mole ratio. The proper Cs:Sn feed mole ratio for CsSnBr_3 and Cs_4SnBr_6 NCs by 3D assisted method was 0.4 and 1.3, respectively. When the Cs:Sn feed mole ratio was 1.6, CsBr was dominant in product.

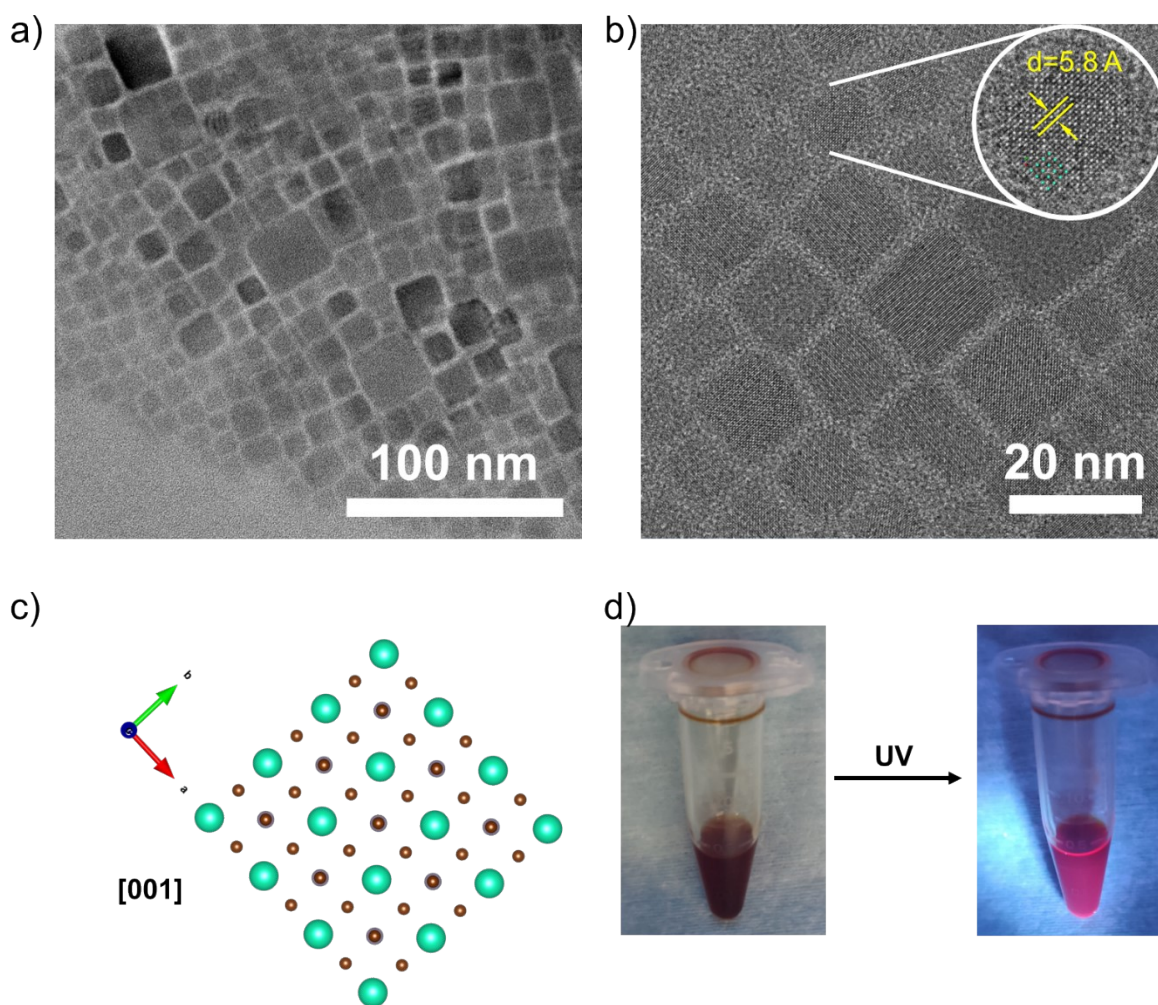


Figure S4. TEM images of CsSnBr_3 NCs synthesized at $\text{Cs}:\text{Sn}=0.4$. a) Low magnification TEM image; b) High magnification TEM image; c) Simulated CsSnBr_3 lattice structure in $[001]$ viewing direction; d) Digital photos of CsSnBr_3 NCs solution under daylight and UV irradiation. The shape of CsSnBr_3 NCs was square, different with the Cs_4SnBr_6 NCs. The CsSnBr_3 structure is cubic in space group $Pm-3m$. The d-spacing of 7.0 \AA illustrated in (b) corresponds to (100) lattice plane of Cs_4SnBr_6 . The clear lattice fringes in (b) were observed in $[001]$ viewing direction.

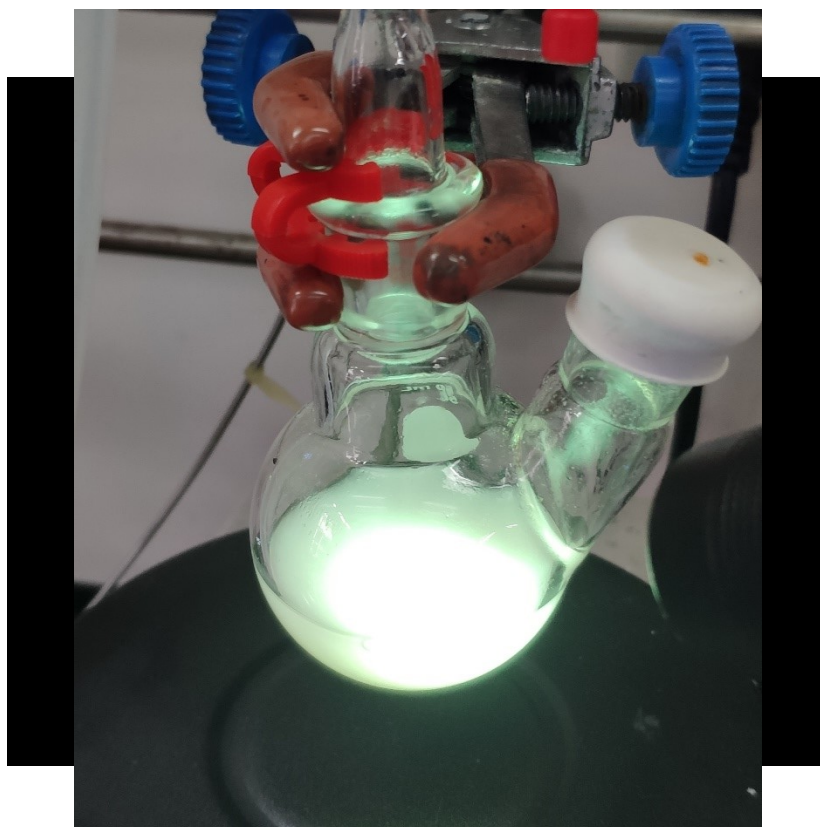


Figure S5. Digital photo of the Cs_4SnBr_6 NCs emitting bright PL under UV illumination as the reaction time extended to 50 s.

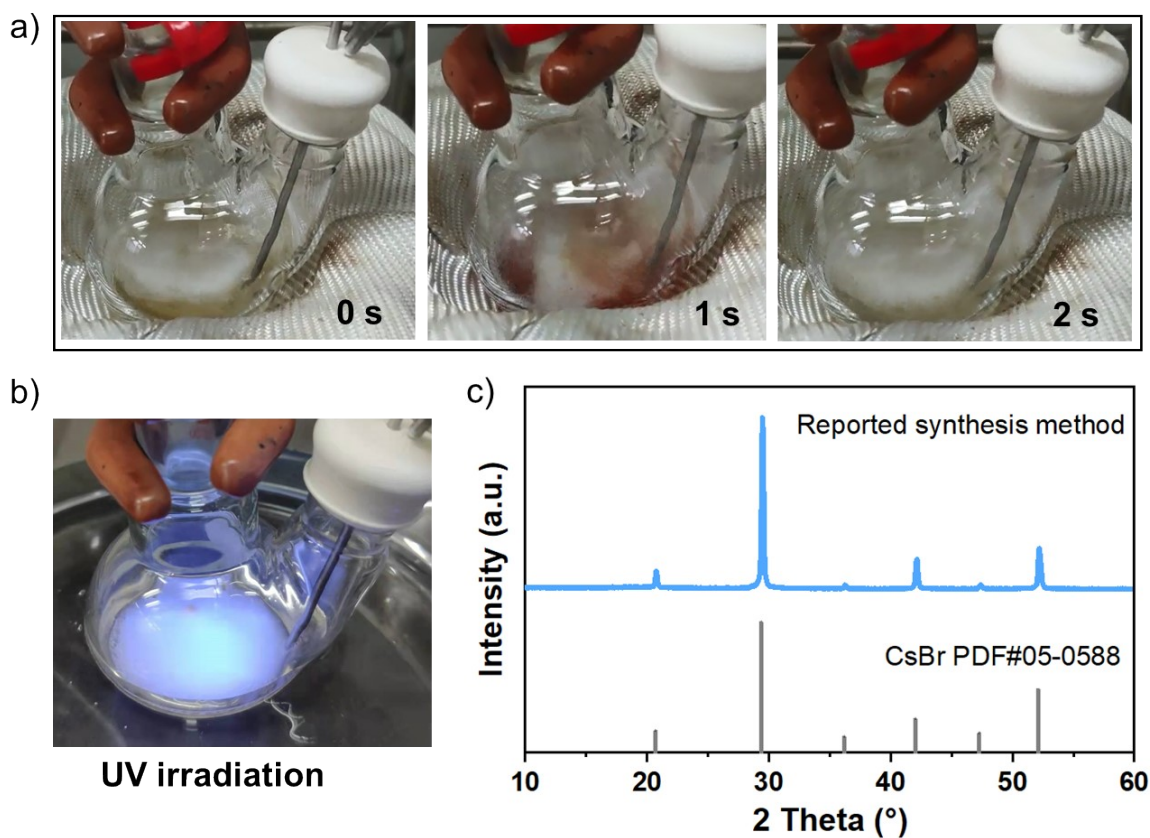


Figure S6. Cs_4SnBr_6 NCs synthesis by injecting Sn(II) precursor into Cs-OA as reported.⁵ Cs-OA was in the flask. The Cs:Sn feed mole ratio was 1.3 that was the same as 3D assisted method. a) Digital photos of the reaction solution at 0, 1 and 2 s after Sn(II) precursor injection. CsSnBr_3 formed when the Sn(II) precursor contacted with Cs-OA, but immediately decompose into CsBr after 1 s. b) Digital photo of the product under UV irradiation. The product by the reported method showed weak light emission. c) XRD of the product. The product synthesized by injecting Sn(II) precursor into Cs-OA was CsBr instead of Cs_4SnBr_6 .

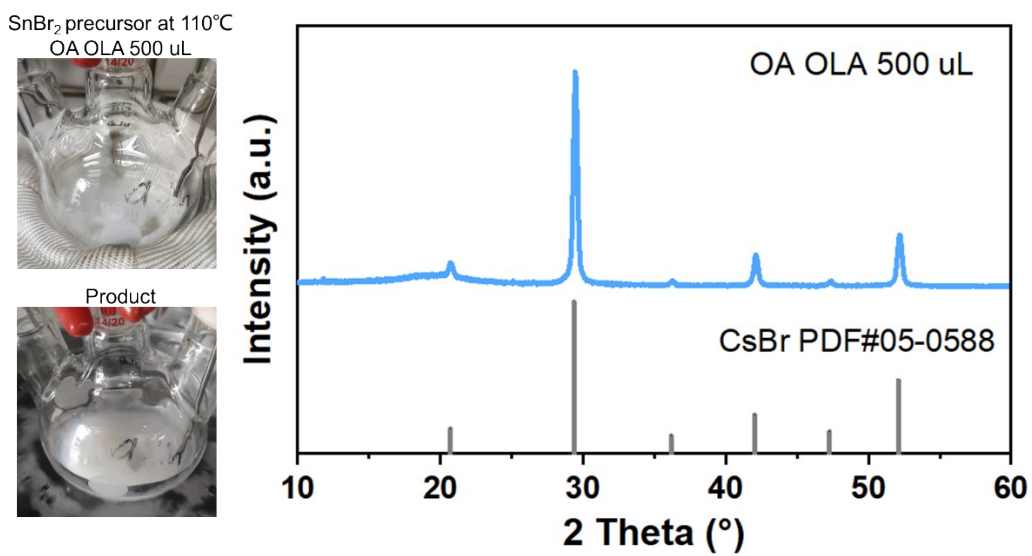


Figure S7. The synthesis of Cs₄SnBr₆ NCs when the amount of ligands was excess. The The OA and OLA was 500 uL when the SnBr₂ was 0.4 mmol. When the Cs-OA was injected into flask, non perovskite product was formed but CsBr.

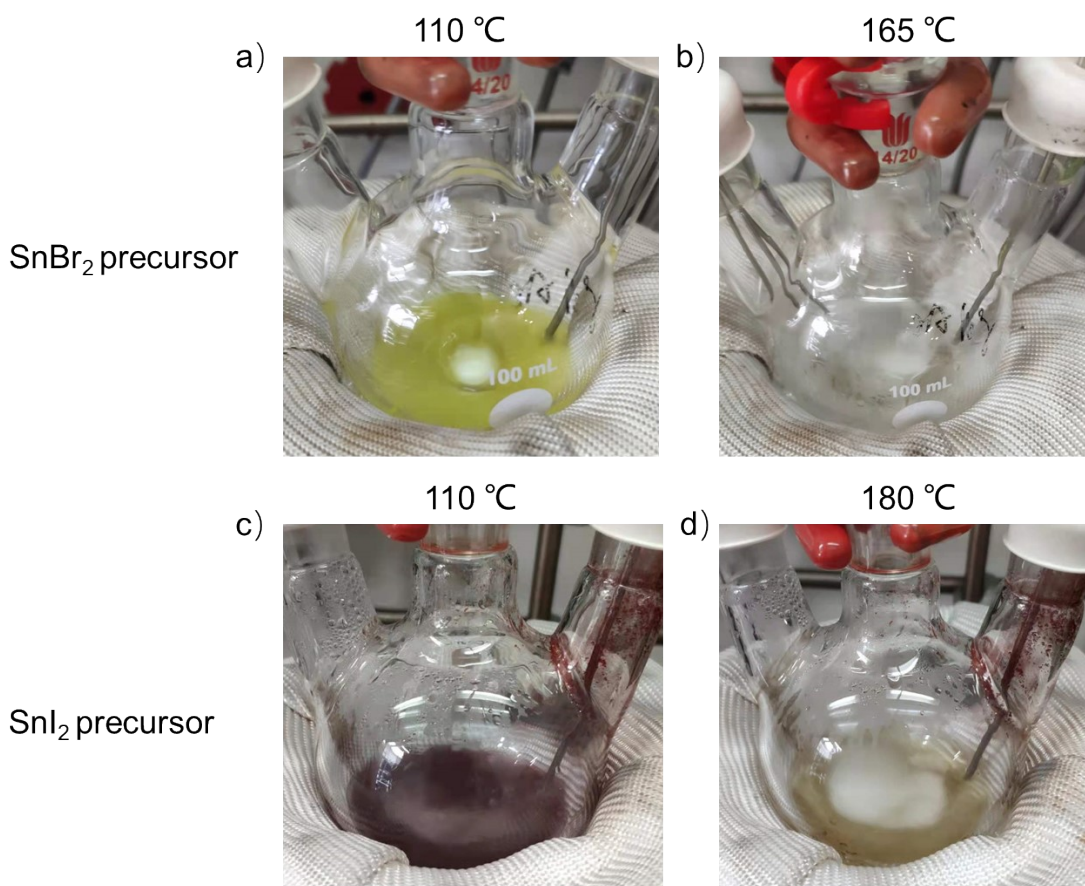


Figure S8. Digital photos of the SnX₂ precursors at different temperature. When the SnX₂ precursors were degassed at 110°C, SnX₂ can not be dissolved totally. The SnBr₂ or SnI₂ precursor should be heated to 165°C or 180°C so that can be dissolved completely.

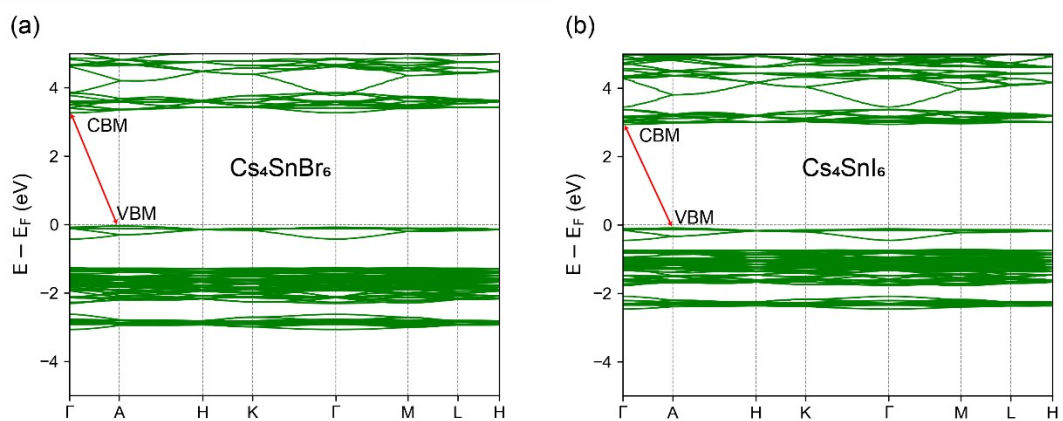


Figure S9. Calculated band structure of (a) Cs_4SnBr_6 , and (b) Cs_4SnI_6 .

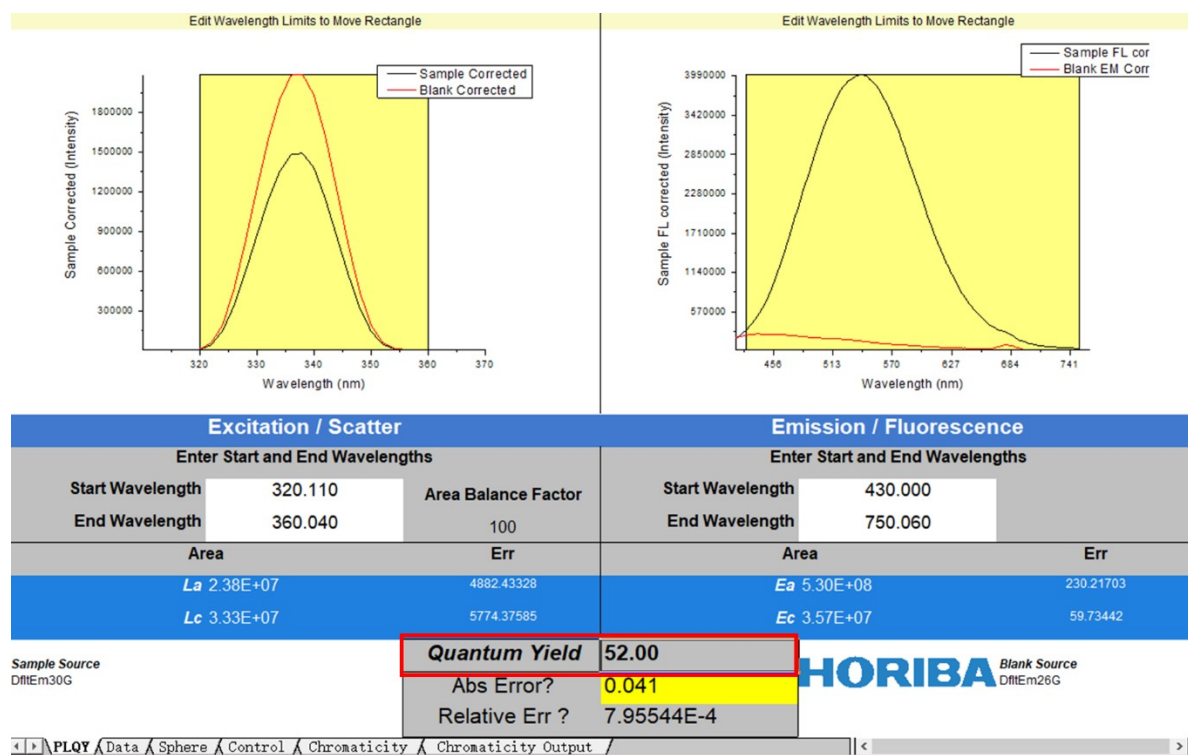


Figure S10. PLQY measurement of Cs₄SnBr₆ NCs.



Figure S11. PLQY measurement of Cs₄SnI₆ NCs.

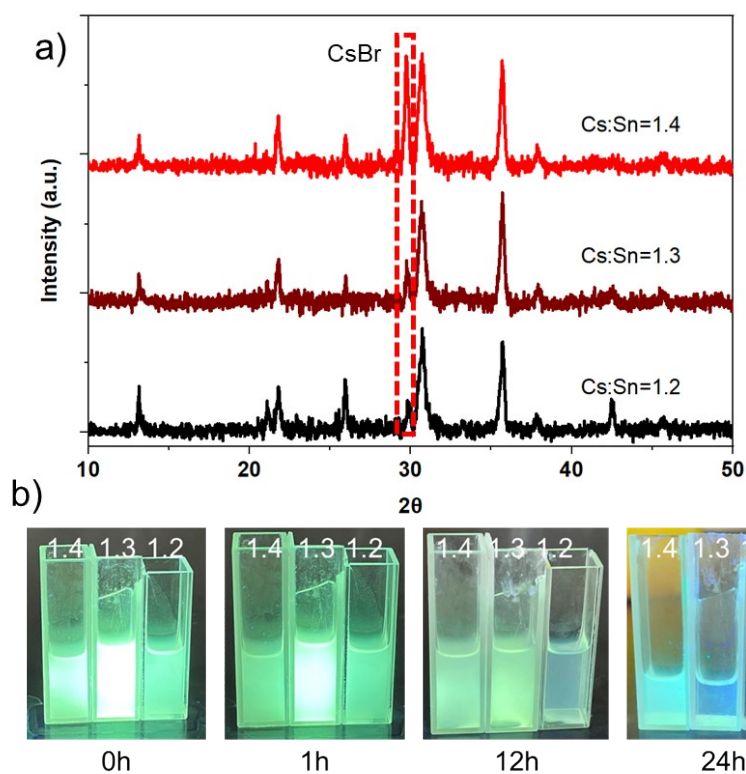


Figure S12. Stability characterization of Cs_4SnBr_6 NCs with different CsBr containing. a) XRD patterns of Cs_4SnBr_6 NCs with different Cs:Sn feed mole ratio. b) Cs_4SnBr_6 NCs with different amount of CsBr.

Reference

1. Kresse, G.; Furthmuller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys Rev B Condens Matter* **1996**, *54*, 11169-11186.
2. Kresse, G.; Furthmuller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* **1996**, *6*, 15-50.
3. Blochl, P. E., Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953-17979.
4. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Physical Review Letters* **1996**, *77*, 3865-3868.
5. Chiara, R.; Ciftci, Y. O.; Queloz, V. I. E.; Nazeeruddin, M. K.; Grancini, G.; Malavasi, L., Green-Emitting Lead-Free Cs₄SnBr₆ Zero-Dimensional Perovskite Nanocrystals with Improved Air Stability. *J Phys Chem Lett* **2020**, *11*, 618-623.