

Supporting Information for

Pure Cs₄PbBr₆: Highly Luminescent Zero-Dimensional Perovskite Solids

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Author Contributions

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Synthesis of Cs₄PbBr₆. PbBr₂ (10 mmol) and of CsBr (10 mmol) were dissolved in dimethyl sulfoxide (DMSO, 10 ml) and stirred for one hour. The solution was filtered and heated until 120 °C and kept for 3 h. Then the precipitation was collected with a Buchner funnel, washed with 1 ml DMSO three times, and dried at 100 °C under vacuum overnight. Washing yield is 50% compared to unwashed precipitation.

The powder X-ray diffraction was performed on a Bruker AXS D8 diffractometer using Cu-K α radiation.

The steady-state absorption was recorded using a Cary 6000i UV-Vis-NIR Spectrophotometer with integrated sphere in diffuse-reflectance mode.

The steady-state photoluminescence and PLQY were measured using an Edinburgh Instruments FLS920 Spectrofluorometer, with 465 nm excitation wavelength.

The temperature-dependent photoluminescence spectra were characterized using a Horiba JY LabRAM Aramis spectrometer with an Olympus 50x lens in a Linkam THMS600 stage. A 473 nm laser was used as the excitation source.

Time-resolved photoluminescence measurement was performed using an Ultrafast Systems HALCYONE femtosecond fluorescence spectrometer.

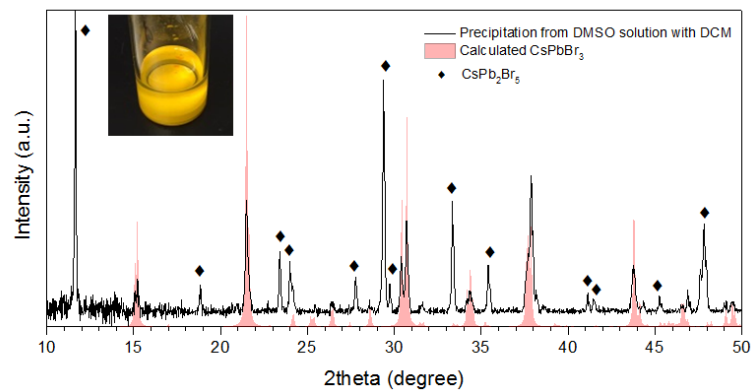


Figure S1. XRD of the powder precipitated from CsBr/PbBr₂ (1/1) - DMSO solution with DCM. It shows that the resultant powder is the mixture of CsPbBr₃ and CsPb₂Br₅. Inset: picture of the precipitation.

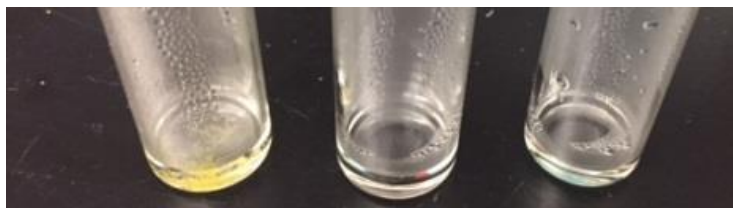


Figure S2. Left to right - filtered solutions of CsBr/PbBr₂ (1/1), (1.25/1) and (1.5/1) in DMSO after keeping at 120 °C for 3 h.

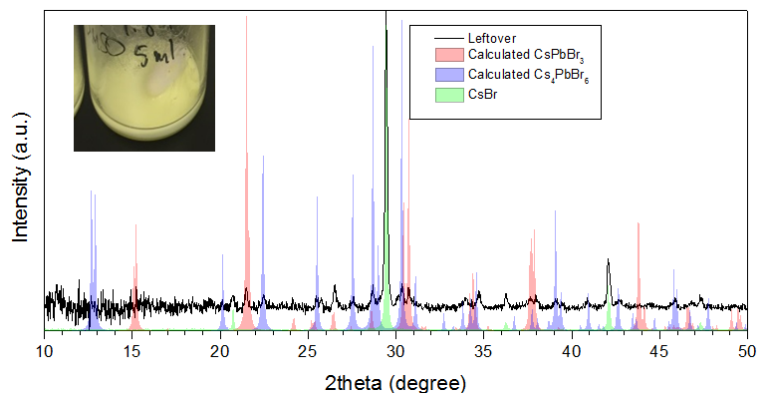


Figure S3. XRD of undissolved powder from CsBr/PbBr₂ (1.5/1) in DMSO. It shows that the leftover powder consists of mainly CsBr, CsPbBr₃ and Cs₄PbBr₆. Inset: the picture of undissolved powder.

CsBr does not dissolve completely, and when precipitated, partially reacts with PbBr₂. This results in decreasing of PbBr₂ concentration. Therefore, the inverse solubility from this solution was not observed.

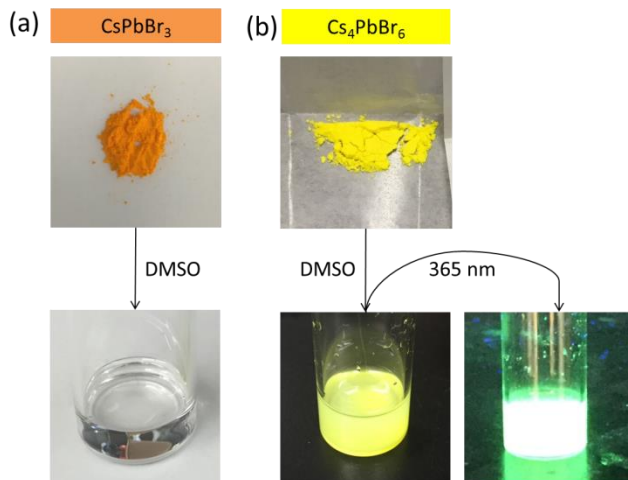


Figure S4. Demonstration of (a) good solubility of CsPbBr₃ and (b) poor solubility of Cs₄PbBr₆ in DMSO. This observation allowed us to clean the Cs₄PbBr₆ from CsPbBr₃.

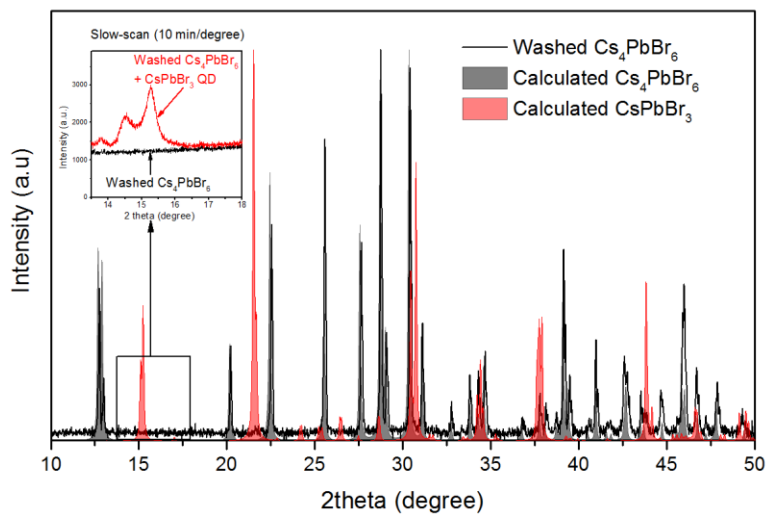


Figure S5. XRD of washed Cs₄PbBr₆. Inset: slow scan XRD at 2θ=13.5-18° of washed Cs₄PbBr₆ in neat and with 2% CsPbBr₃ nanocrystals. This experiment demonstrates that our washed Cs₄PbBr₆ is pure and free of any presence of CsPbBr₃ in any form, including nanocrystals.

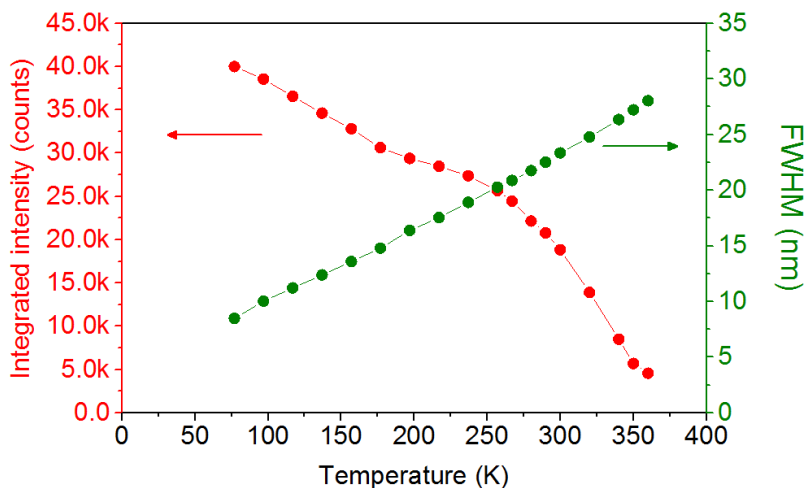


Figure S6. Analysis of temperature-dependent PL. The integrated PL peak at 300 K is 20k, extrapolated at 0K it reaches 45k. Thus, the PLQY at 300 K is 20k/45k = 40%.

FWHM decreases by decreasing the temperature, reaching 10 nm at 77K.

Exciton binding energy was estimated using the following fitting:^[1]

$$I_T = \frac{I_0}{1 + A \exp\left(-\frac{E_B}{k_B T}\right)}$$

Where I_T is the integrated intensity at T K, E_B is the binding energy, and k_B is the Boltzmann constant.

References

- [1] K. Wu, A. Bera, C. Ma, Y. Du, Y. Yang, L. Li, T. Wu, *Phys. Chem. Chem. Phys.* **2014**, *16*, 22476.