Supporting Information for

Pure Cs₄PbBr₆: Highly Luminescent Zero-Dimensional Perovskite Solids

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Author Contributions

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Synthesis of Cs$_4$PbBr$_6$. PbBr$_2$ (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-Kα 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/PbBr$_2$ (1/1) - DMSO solution with DCM. It shows that the resultant powder is the mixture of CsPbBr$_3$ and CsPb$_2$Br$_5$. Inset: picture of the precipitation.

Figure S2. Left to right - filtered solutions of CsBr/PbBr$_2$ (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 Cs$_4$PbBr$_6$. Inset: slow scan XRD at $2\theta$=13.5-18° of washed Cs$_4$PbBr$_6$ in neat and with 2% CsPbBr$_3$ nanocrystals. This experiment demonstrates that our washed Cs$_4$PbBr$_6$ is pure and free of any presence of CsPbBr$_3$ 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]

\[ I_T = \frac{I_0}{1 + A \exp(-\frac{E_B}{k_BT})} \]

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