Supporting Information

Pure Zero-dimensional Cs₄PbBr₆ Single Crystal Rhombohedral Microdisks with High Luminescence and Stability

Haihua Zhang,^{a,b} Qing Liao,^{*,c} Yishi Wu,^{*,a} Jianwei Chen,^{a,b} Qinggang Gao,^c Hongbing Fu^{*a,c,d}

^{*a*} Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.

^b University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

^c Beijing Key Laboratory for Optical Materials and Photonic Devices, Department of Chemistry, Capital Normal University, Beijing 100048, P. R. China

^d Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, P.R. China

† E-mail: hongbing.fu@iccas.ac.cn

Experimental Section

1. Materials: All starting materials were purchased from Sigma-Aldrich and used as received without further purification. The N,N-Dimethylformamide (DMF, HPLC grade) and dichloromethan were purchased from Beijing Chemical Agent Ltd., China.

2. Preparation of Cs₄PbBr₆ MDs: We synthesized high-quality Cs₄PbBr₆ MDs using a facile one-step solution self-assembly method without any ligands involved. Stock solution 1 of CsBr (0.03 M) and solution 2 of CsBr+PbBr₂ (0.03 M) in N,N-dimethylformamide (DMF) was prepared independently. Two solutions were mixed at room temperature with a 3:1 volume ratio (solution 1: solution 2), a CsBr·PbBr₂ solution with a concentration ratio at 4:1 has been formed. 100 μ L of mixed solution was dip-coated over a 2 × 2 cm² glass slide, which was placed on a teflon stage in a beaker. This beaker contained CH₂Cl₂ leveled below the Teflon stage, and was sealed by a porous Parafilm in order to control the evaporation rate of solution. Diffusion of CH₂Cl₂ vapor into solution induced the nucleation and subsequent growth of Cs₄PbBr₆ MDs.

CsBr, CsPbBr₃ and the phase separation products were obtained by using a mixture of stock solutions **1** and **2** at different volume ratios in the same methods above.

3. Morphology and Structure Measurements: The morphologies and sizes of Cs₄PbBr₆ MDs were examined using field emission scanning electron microscopy (FESEM, Hitachi S-4300) at acceleration voltages of 10-15 kV. Prior to analysis, the samples were coated with a thin platinum layer using an Edwards Sputter Coater. Transmission electron microscopy (TEM) images were obtained by a JEOL JEM-1011. TEM measurement was performed at room temperature at an accelerating voltage of 100 kV. X-ray diffraction patterns weremeasured by a D/max 2500 X-ray diffractometer with Cu Karadiation ($\lambda = 1.54050$ Å) operated in the 2 θ range from 5 to 45.

4. Optical Measurement: The reflectance, emission spectra and PLQY were measured on Shimidazu UV-3600 UV-VIS-NIR and Horiba FluoroMax-4-NIR spectrophotometers, respectively. The temperature-dependence PL spectra were collected by using an Edinburgh Instruments FLS920 Spectrofluorometer, with 380 nm excitation wavelength.

Single MDs PL spectra was investigated at room temperature in air by a home-made optical microscopy equipped with a 50 X 0.9NA excitation objective shown in Fig. S5. A 405-nm laser was focused to a 2-µm-diameter spot to excite the selected individual Cs₄PbBr₆ MDs or CsPbBr₃ MDs. Then PL spectra were collected underneath by using a 50 X 0.9NA objective that was mounted a 3D movable stage. A long-wave pass dielectric filter was used to block any scattered excitation light. Finally the collected PL was coupled to an optical fiber and detected using a liquid-nitrogen-cooled CCD (SPEC-10-400B/LbN, Roper Scientific) attached to a polychromator (Spectropro-550i, Acton).

5. Additional Information



Fig. S1

Fig. S1 The PL images(a) and size distribution(b) of large amounts of Cs_4PbBr_6 MDs according to (a), respectively.





Fig. S2 Energy-dispersive X-ray spectroscopy (EDS) analysis of a single Cs_4PbBr_6 MDs shown in the SEM image. As shown in the insert table, the Cs/PB/Br ratio is determined to be ~ 4/1/6, in good agreement with a Cs_4PbBr_6 stoichiometry.



Fig. S3

Fig. S3 Optical image of the obtained CsBr MDs under white light (left) and UV light (right), no PL was observed from this structure.

10 µm

Fig. S4



Fig. S4 (a,b)Serious phase separation between Cs_4PbBr_6 and $CsPbBr_3$ MD under white light (left) and UV light (right).(c) Increased decuple exposure time to obtain the CsPbBr₃ MDs PL image whereas rhombohedral Cs_4PbBr_6 MDs were overexposure.





Fig. S5 Schematic illustration of (a) the home-build optical microscopy and (b) the transmittance optical path for the μ -spectra measurements..





Fig. S6 Schematic illustration o the crystal structure of Cs₄PbBr₆.



Fig. S7

Fig. S7 Bright-field and PL images of Cs₄PbBr₆ MDs and CsPbBr₃ QDs film heating for 0 hour, 0.5 hour and 5 hour, respectively.