Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2018

Supporting Information

A New Method to Discover Reaction Mechanism of Perovskite Nanocrystals

Chun Sun,[1] *Zhiyuan Gao,*[1] *Hanxin Liu,*[1] *Chong Geng,*[1] *Hua Wu,*[2] *Xiaoyu Zhang,*[2] *Chao Fan*[1] *and Wengang Bi*[1,*]

[1]State Key Laboratory of Reliability and Intelligence of Electrical Equipment, Hebei University of Technology, 5340 Xiping Road, Tianjin, 300401, P. R. China
Tianjin Key Laboratory of Electronic Materials and Devices, School of Electronics and Information Engineering, Hebei University of Technology, 5340 Xiping Road, Tianjin, 300401, P. R. China
[2]State Key Laboratory of Integrated Optoelectronics and College of Electronic Science and Engineering, Jilin University, Changchun, 130012, China
E-mail: wbi@hebut.edu.cn

Experimental Section

Chemicals: Cs_2CO_3 (99.9%), iodotrimethylsilane (95%), bromotrimethylsilane (97%), chlorotrimethylsilane (99%) and CH_3COOCs (99.9%) were attained from J&K. Oleic acid (90%, OA), octadecene (90%, ODE), PbO (99.0%) and Lead stearate (99.9%, $PbSt_2$) were purchased from Alfa Aesar. Oleylamine (80-90%, OLA), $(CH_3COO)_2Pb$ (99.99%) and $Pb(NO_3)_2$ (99.99%) were purchased from Aladdin. Hexane (99.5%) was obtained from Beijing Chemical Factory. PbO (99.0%) was attained from Sigma-Aldrich. All the chemicals were used without further purification.

Synthesis $CsPbBr_3$ NCs: 10 mL ODE, 1mL OA, 1 mL OLA, 0.1mmol Cs_2CO_3 and 0.2 mmol $PbSt_2$ were loaded into a 50 mL three-neck round-bottom flask, degassed under vacuum for 10 min and dried under vacuum for 1 h at 120ºC. Then, the temperature was elevated to 180ºC under N_2 protection and 0.08 mL TMSBr was quickly injected.

5 seconds later, an ice-water bath was applied to cool down the solution to room temperature. Next, the as-prepared solution was centrifuged at 7000 rpm for 10 min. Hexane was added to the precipitate, and then centrifuged at 7000 rpm for 2 min. Finally, the NCs were acquired in the supernatant. The amount of Cs_2CO_3, $PbSt_2$ and TMSBr can be adjusted at will, for example, Cs_4PbBr_6 NCs were synthesized under 0.05mmol $PbSt_2$. Besides, other Cs and Pb monomers can also be used to synthesis perovskite NCs, such as PbO, $(CH_3COO)_2Pb$, CH_3COOCs et al. For the mixed halide perovskite NCs, certain feed ratio of halosilanes (TMSBr, TMSI or TMSCl) were mixed previously with 0.5 ml ODE, then the mixture was vibrated 3 minutes and injected into the Cs and Pb solution.

Characterizations: Fluorescence emission spectra were measured using an Ocean Optics spectrometer. Absorbance spectra of samples were carried out by using a Shimadzu UV-2550 spectrophotometer. The morphology of the NCs was observed by a FEI Tecnai G2 Spirit TWIN transmission electron microscope (TEM) operating at 100 kV. X-ray diffraction (XRD) patterns of NCs were acquired using a Bruker D8 Advance X-ray diffractometer (Cu Kα: λ = 1.5406 Å). Fourier transform infrared spectroscopy (FTIR) was performed on a Thermo-Nicole iS50 FTIR-spectrometer. The absolute PL QYs of the samples were obtained by a fluorescence spectrometer (FLS920P, Edinburgh Instruments) equipped with an integrating sphere with its inner face coated with BENFLEC. Time-resolved PL lifetime measurements were carried out using a time-correlated single-photon counting (TCSPC) lifetime spectroscopy system with a picosecond pulsed diode laser (EPL-380 nm) as the single wavelength excitation light source. The absolute PL quantum yields of samples were determined by standard procedures using a fluorescence spectrometer (FLS920P, Edinburgh Instruments) equipped with an integrating sphere. Atomic force microscopic (AFM) experiments were performed with an Agilent series 5100 AFM/STM. Nuclear Magnetic Resonance (NMR) measurements were recorded on a Bruker Avance 400 Spectrometer operating at a ^1H frequency of 400 MHz.

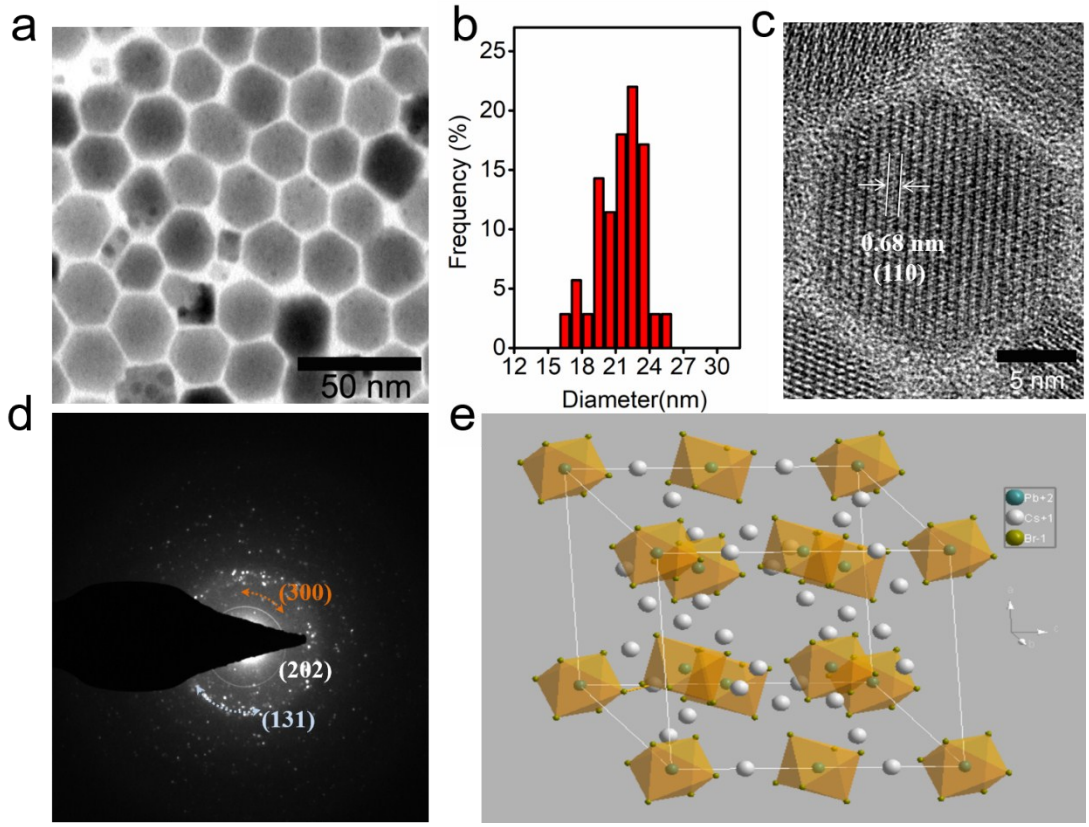

Figure S1. TEM image of Cs_4PbBr_6 perovskite QDs; (b) size distributions of histogram of these QDs in (a); (c) HRTEM image of Cs_4PbBr_6 QDs; (d) SAED pattern Cs_4PbBr_6 QDs (e) Schematic of the cubic Cs_4PbBr_6 perovskite lattice.

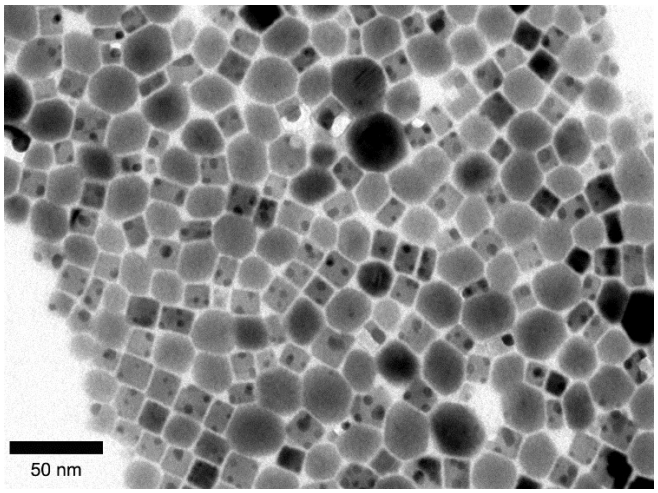

Figure S2. TEM image of the mixture $CsPbBr_3$ and Cs_4PbBr_6 QDs with a Cs:Pb:Br ratio of 1:0.7:3.

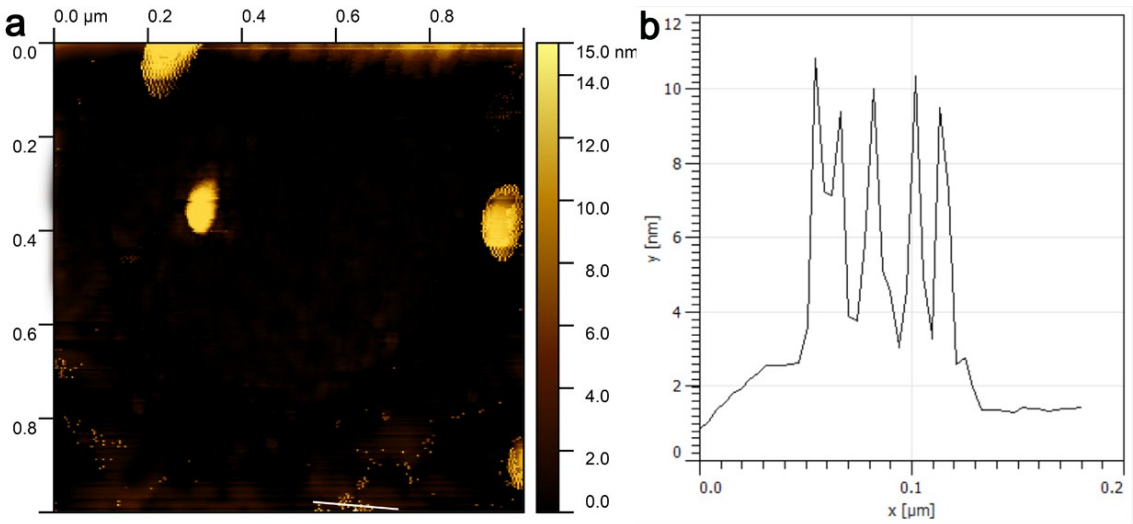

Figure S3. AFM image (**a**) of the mixture $CsPbBr_3$ and Cs_4PbBr_6 QDs with a Cs:Pb:Br ratio of 1:0.7:3 and **(b)** the height distribution.

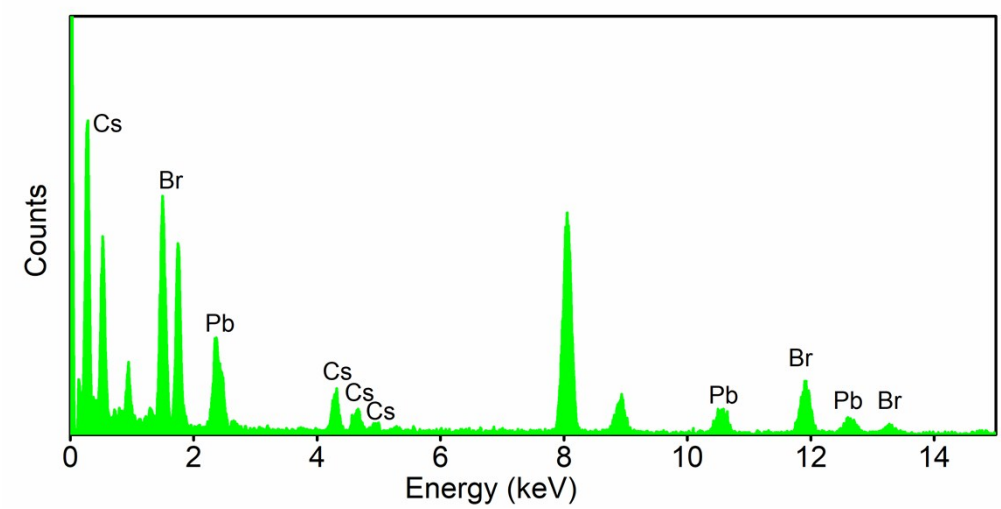

Figure S4. EDX spectrum of $CsPbBr_3$ QDs.

Reaction ratio of Cs:Pb:Br	1:0.25:3	1:0.7:3	1:1:3
Final ratio of Cs:Pb:Br	3.8:1:5.7	1.2:1:3.7	0.85:1:3.1

Table S1. Element ratio acquired from EDX.

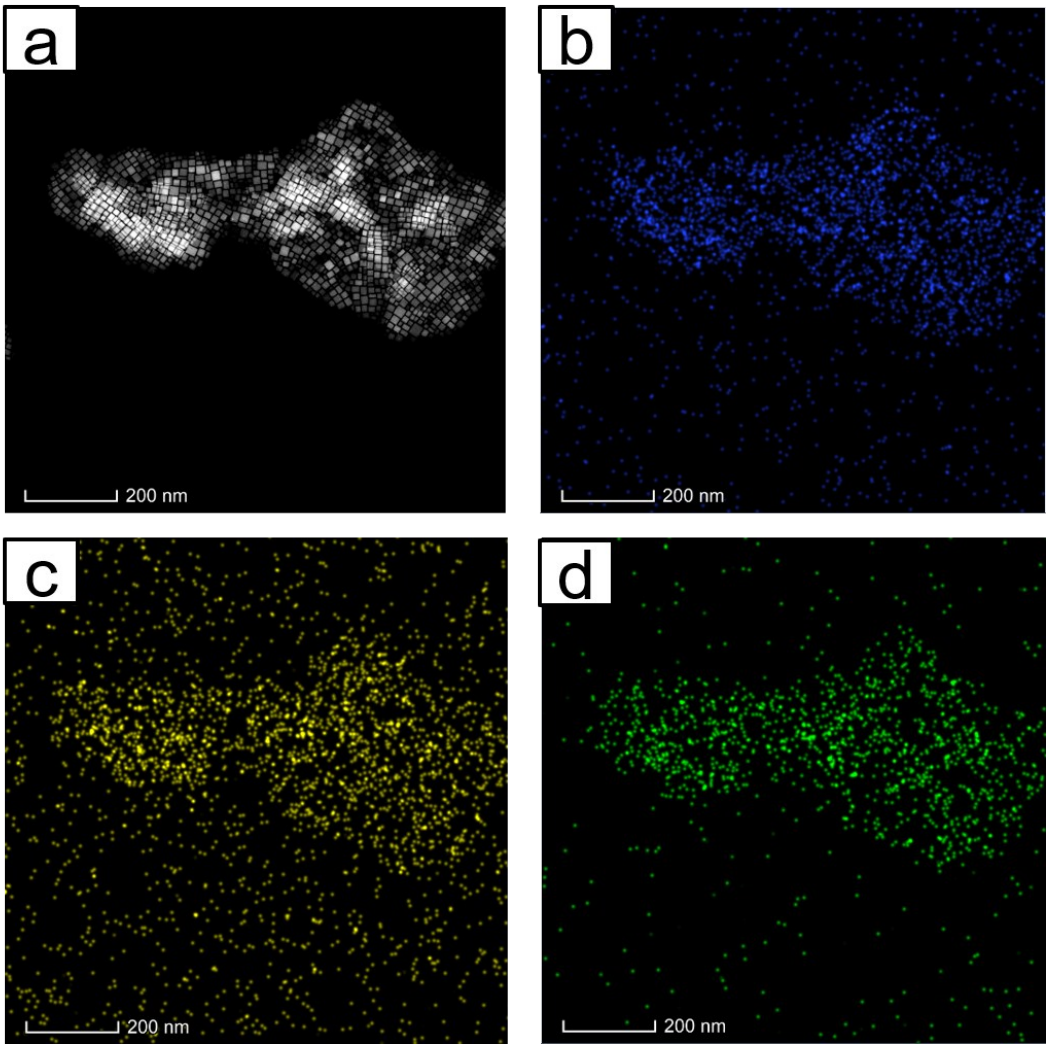

Figure S5. Mapping images of $CsPbBr_3$ QDs. (a) High-angle annular dark-field scanning TEM (HAADF-STEM) image of $CsPbBr_3$ QDs, cesium (b), lead (c), bromine (d) elemental maps.

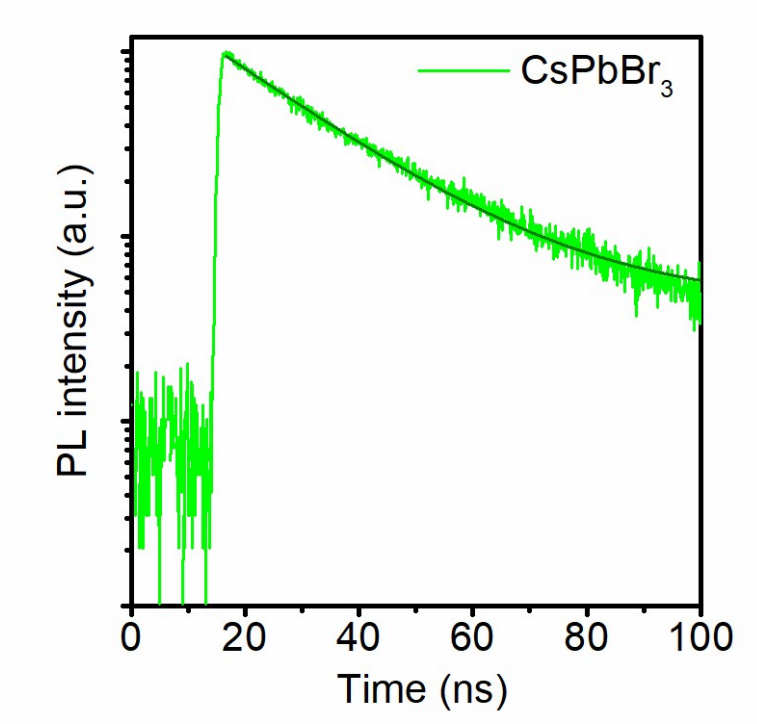

Figure S6. Time-resolved PL decay of $CsPbBr_3$ QDs.

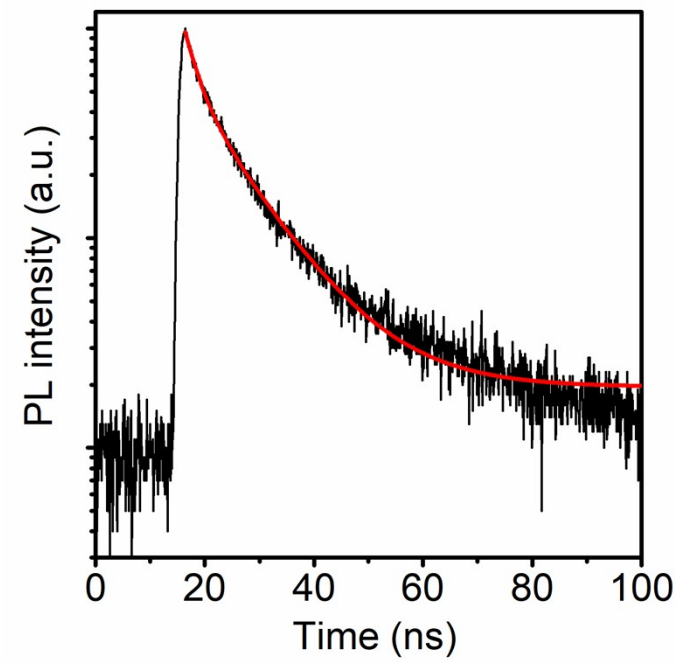

Figure S7. Time-resolved PL decay for the mixture of $CsPbBr_3$ and Cs_4PbBr_6 QDs.

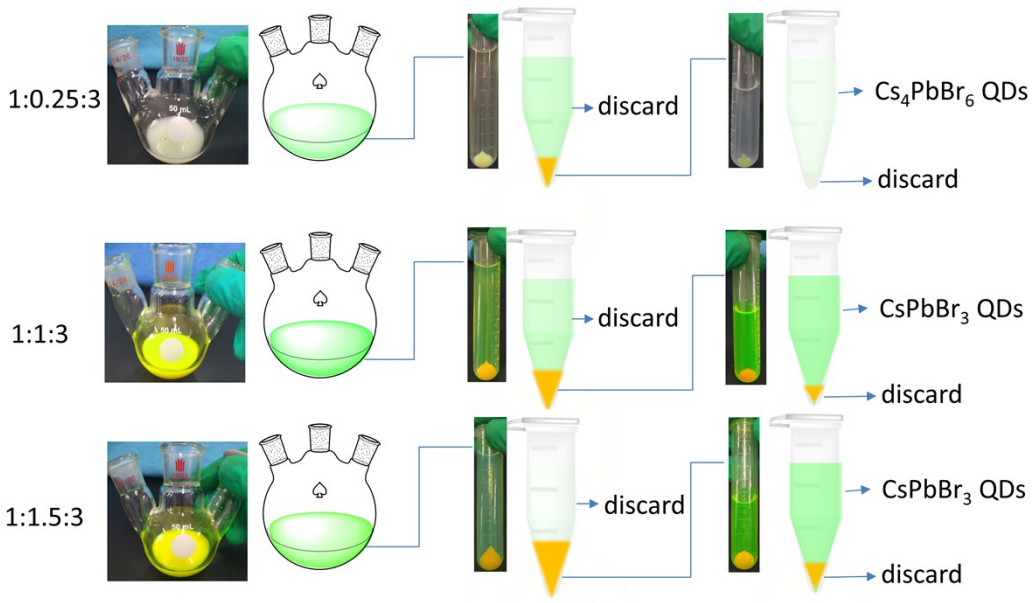

Figure S8. Schematic for centrifugation procedure with increased Pb content (the Cs:Pb:Br ratio is shown in the left).

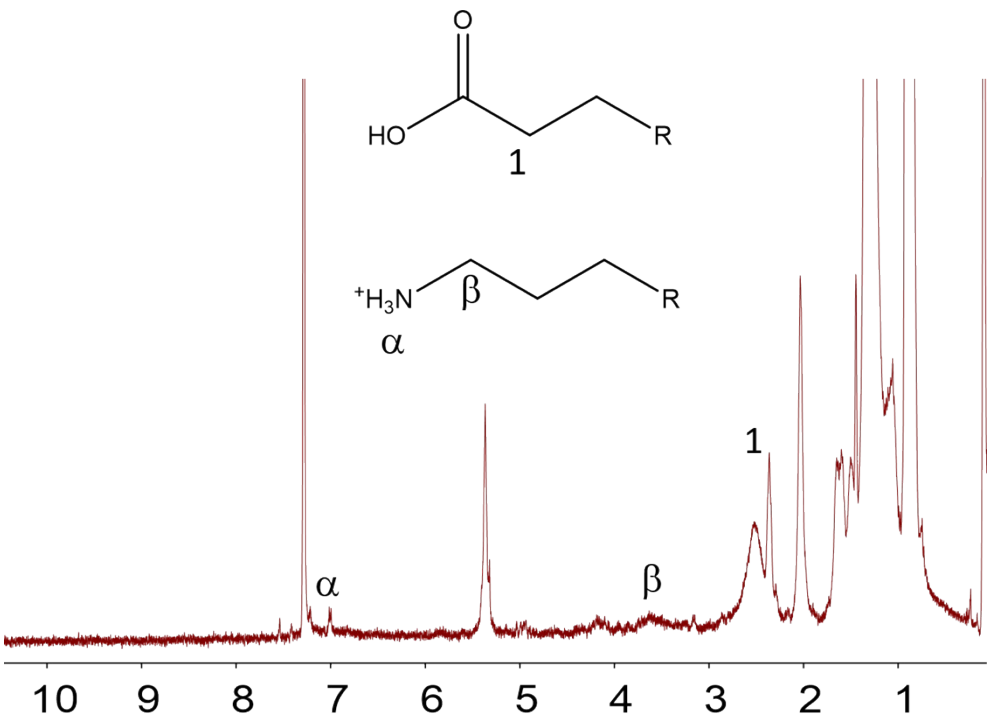

Figure S9. 1H NMR spectrum of $CsPbBr_3$ NCs.

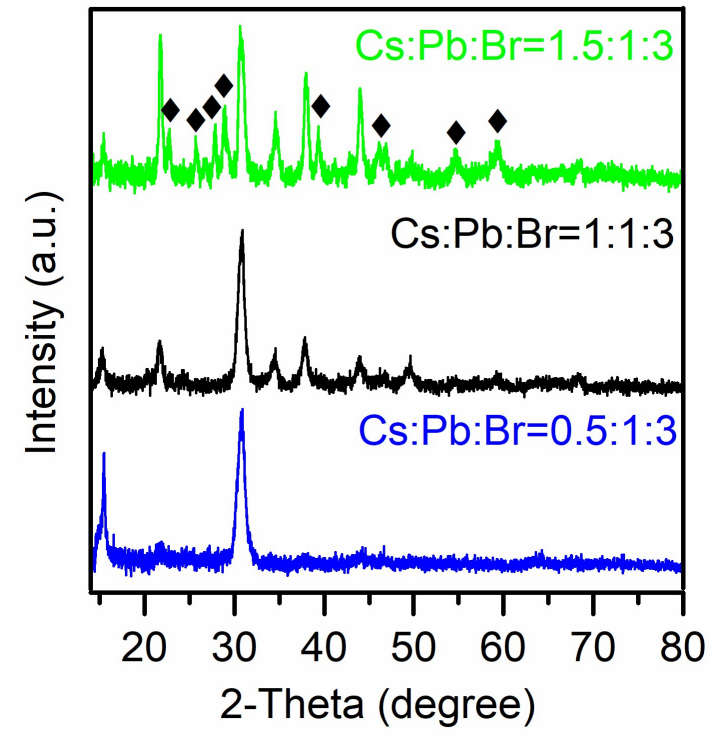

Figure S10. XRD patterns with increased Cs content (the black rhombus represents the peak of Cs_4PbBr_6)..

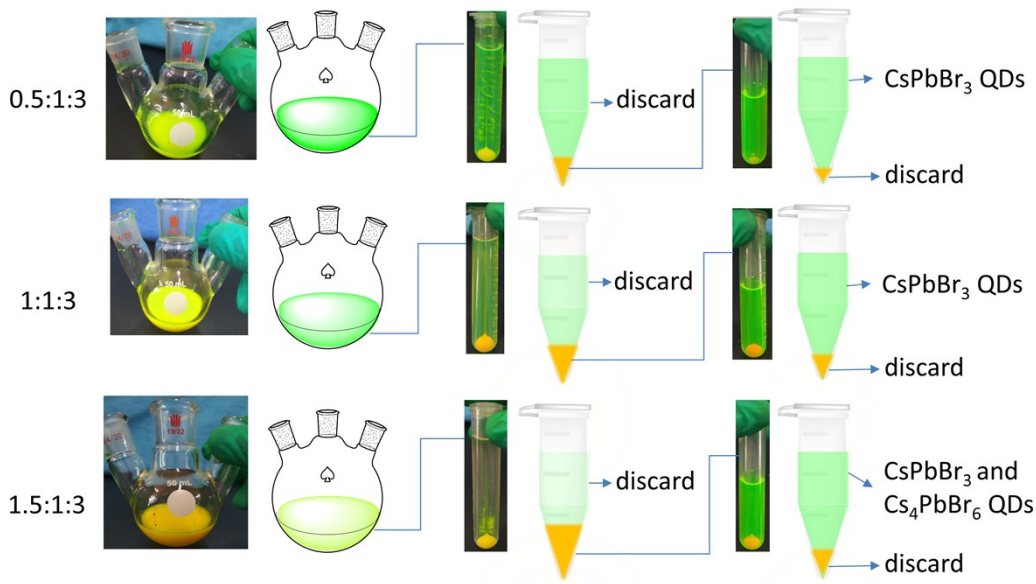

Figure S11. Schematic for centrifugation procedure with increased Cs content (the Cs:Pb:Br ratios are shown in the left).

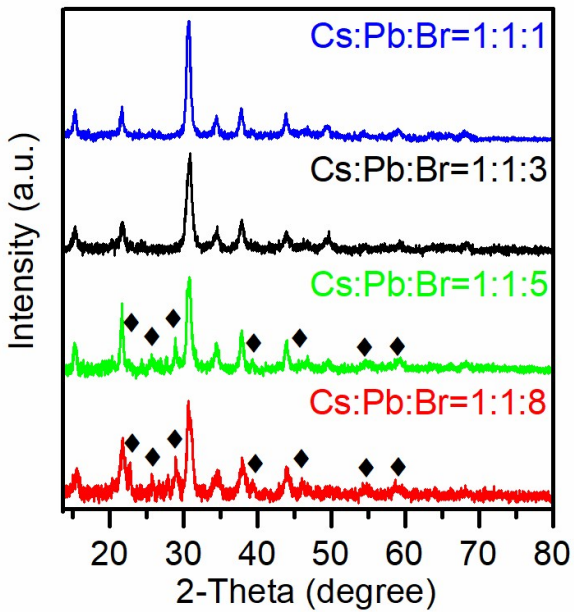

Figure S12. XRD patterns with increased Br content (the black rhombus represents the peak of Cs_4PbBr_6)..

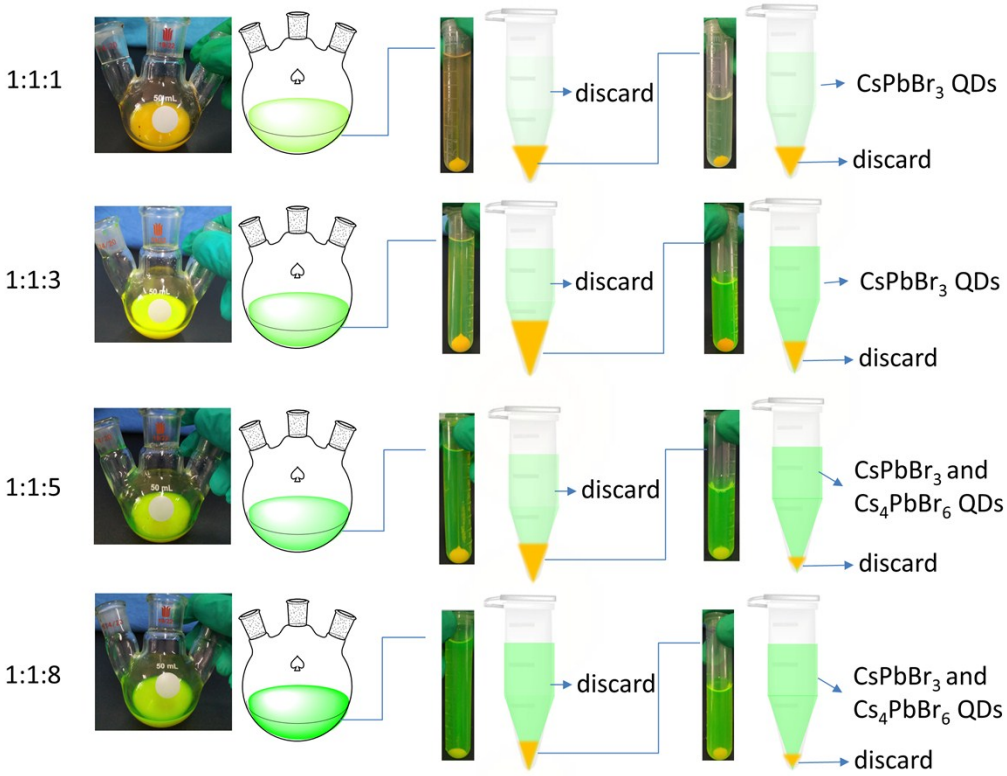

Figure S13. Schematic for centrifugation procedure with increased Br content (the Cs:Pb:Br ratio is shown in the left).

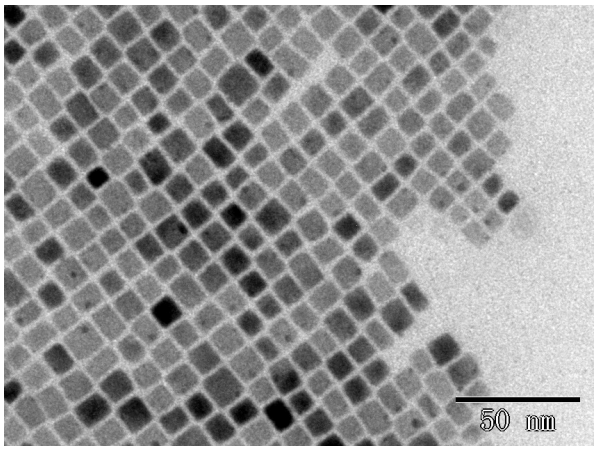

Figure S14. TEM image of $CsPbBr_3$ QDs with a Cs:Pb:Br ratio of 1:1:5.

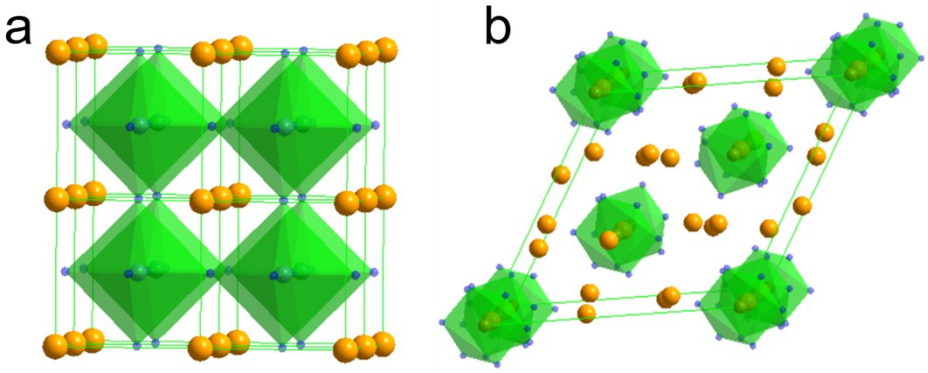

Figure S15. Schematic of the $CsPbBr_3$ (a) and Cs_4PbBr_6 (b) perovskite lattices.