

Supporting Information for

Precise Control of Quantum Confinement in Cesium Lead Halide Perovskite Quantum Dots via Thermodynamic Equilibrium

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Materials

Cesium carbonate (Cs_2CO_3 , puratronic, 99.994%, metals basis, Alfa Aesar), Lead (II) bromide (PbBr_2 , puratronic, 99.999% metals basis, Alfa Aesar), Lead (II) chloride (PbCl_2 , puratronic 99.999% metals basis, Alfa Aesar), Lead (II) iodide (PbI_2 , 99.9985% metals basis, Alfa Aesar), Lead (II) acetate trihydrate ($\text{Pb}(\text{Ac})_2 \cdot 3\text{H}_2\text{O}$, puratronic, 99.995% metals basis, Alfa Aesar), Zinc bromide (ZnBr_2 , 99.9%, metals basis, Alfa Aesar), Cobalt (II) bromide (CoBr_2 , 97%, anhydrous, Alfa Aesar), Hydrobromic acid (HBr , 47-49%, J.T.Baker), Zinc Chloride (ZnCl_2 , ACS grade), Zinc Iodide (ZnI_2 , ultra-dry, 99.995%, Alfa Aesar), Zinc stearate ($\text{Zn}(\text{St})_2$, Alfa Aesar), Oleylamine (OAm, technical grade 70%, Aldrich), Propionic acid ($\text{C}_2\text{H}_5\text{COOH}$, >99%, J.T. Baker), Oleic acid (OA, technical grade 90%, Aldrich), 1-Octadecene (ODE, technical grade 90%, Aldrich), Trioctylphosphine (TOP, 97%, Aldrich), Acetone (Certified ACS, Fischer), Hexane (HPLC grade, Millipore), Methyl acetate (99%, BeanTown Chemical), Ethyl acetate (ACS grade), Cyclohexane (HPLC grade, BDH), Poly(styrene-divinylbenzene) (cross-linked with 2% DVB 200-400 mesh, BeanTown Chemical).

Purification of QDs

Once the reaction was cooled to room temperature, the QD solution was centrifuged at 3500 rpm for 10 min to remove the unreacted salt. Two different cleaning methods were used for the

reactions conducted at high (140-190 °C) and low temperatures (80-120 °C). For reactions conducted at higher temperatures (140-190 °C), less unreacted salts remained in solution from a greater reaction yield. In this case, ~8 mL of acetone was directly added into the supernatant to precipitate the QD followed by centrifuging at 3500 rpm for 3 mins. The precipitants were collected and dissolved in ~1 mL of hexane. For reactions conducted at lower temperatures (80-120 °C), larger amount of unreacted salt remained in the supernatant after centrifuging. In this case, the supernatant was left on the bench top under ambient conditions for ~ 2 hours until the salts precipitated. Then the mixture was centrifuged again. This procedure could be repeated if necessary. When the supernatant remained clear, ~ 8 mL of acetone was slowly added until the mixture became turbid to avoid decomposition of the QD. Then the QD was centrifuged at 3500 rpm for 3 min and the precipitate was collected and dissolved in ~1 mL of hexane.

Synthesis of CsPbBr₃ QDs with CoBr₂

The Cs-oleate precursor was made as described in the Experimental Section. The precursor solution of Pb and Br was prepared by dissolving PbBr₂ (75 mg), CoBr₂ (250 mg) in a mixture of ODE (5 mL), OA (2 mL) and OAm (2 mL) in a 25-mL three necked round bottomed flask under N₂ atmosphere at 120 °C for 1 min. Then the temperature was raised to 180 °C followed by a swift injection of 0.4 mL Cs-oleate precursor. The reaction was quenched with an ice bath after ~10 s. Purification of the obtained QD is the same as mentioned above.

Effect of Zn²⁺ on size control

To determine whether the cation influenced the size of the QD, a control experiment was conducted at 160 °C with a non-halide Zn source. Keeping the concentration of Zn²⁺ the same, an equivalent amount of Zn(St)₂ was used to replace ZnBr₂. For Fig. S1, ~700 mg of Zn(St)₂ was used while following the procedure described in the Experimental section.

Synthesis of CsPbBr₃ QDs with HBr

The Cs-oleate precursor was made as described in the Experimental Section. The precursor solution of Pb and Br was prepared by dissolving PbBr₂ (75 mg), 0.5 mL OAm, and 171 µL of HBr in a mixture of ODE (5 mL), OA (1 mL) and OAm (1 mL) in a 25-mL three necked round bottomed flask under N₂ atmosphere at 120 °C for 1 min. Then the temperature was raised to 160 °C followed by a swift injection of 0.4 mL Cs-oleate precursor. The reaction was quenched with an ice bath after ~10 s. Purification of the obtained QD is the same as mentioned above. The control experiment was conducted using propionic acid instead of HBr to protonate the OAm.

Anion exchange reaction of CsPbBr₃ QDs

The anion exchange reactions of CsPbBr₃ QDs were performed by mixing the QD solution in hexane and ~0.3 mL of PbX₂ precursor solution under vigorous stirring. PbX₂ (X=Cl, Br, I) precursors were prepared by adding 100 mg of PbX₂ into 5 mL of ODE in a 25-mL three necked round bottom flask. After 10 min of vacuum drying at 120 °C, ~1 mL (2.5 mL for PbCl₂) of dried OA/OAm mixture was injected to dissolve the salt. The precursor solution was used after cooling down to room temperature.

Statistics

The size distribution of CsPbBr₃ QDs was obtained by measuring the edge-to-edge lengths of the nanocubes in the TEM images. The edges of the QDs were determined from the half maximum of the peaks from the TEM line profile. The size of the nanocubes was obtained by averaging the two-dimensional edge-to-edge lengths for each cube. More than 100 particles were measured for each sample.

Additional Figures

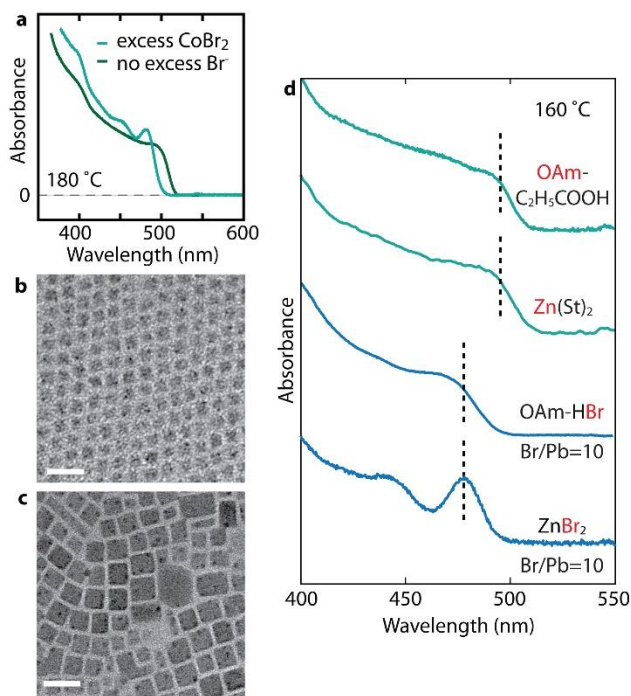


Figure S1. Comparison of the effects of Br⁻, Zn²⁺ and organic ligands on the size control. (a) Absorption spectra of quantum confined CsPbBr₃ QDs synthesized using excess Br⁻ with CoBr₂ as the bromine source. The control sample was made without excess Br⁻ following a previously reported method.¹ (b, c) TEM images of QDs (b) made with CoBr₂ and (c) control CsPbBr₃ nanocrystals. Both scale bars are 20 nm. (d) Absorption spectra of QD samples made with protonated OAm, ZnSt₂, OAm-HBr, and ZnBr₂. The protonated OAm and ZnSt₂ both lack the ability to control the size and distribution of the synthesized QDs while the OAm-HBr and ZnBr₂ show control over the size of the NC. This verifies that the cation is not the species responsible for controlling the size of the NC. The excess Br⁻ that is introduced into the reaction is responsible for controlling the size and distribution of the NC.

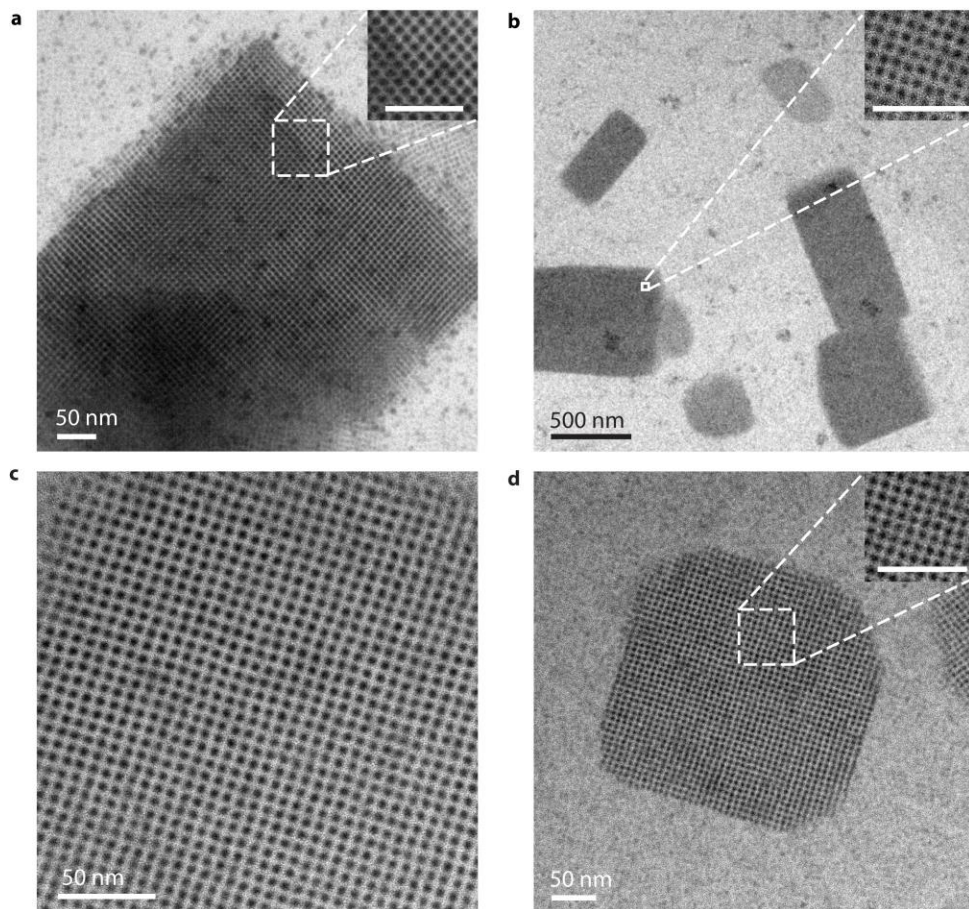


Figure S2. Extensive survey of TEM images of CsPbBr₃ QDs showing ordered QDs and superlattices. (a, b) TEM images of the superlattice formed by highly homogeneous 5.3 nm CsPbBr₃ QDs with wide view of superlattices. (c, d) Close view (c) and wide view (d) TEM images of another CsPbBr₃ QD sample. These are the representative TEM images of all the QDs showing no sign of contamination from particles of other morphology such as nanoplatelets or nanowires. All scale bars in insets are 50 nm.

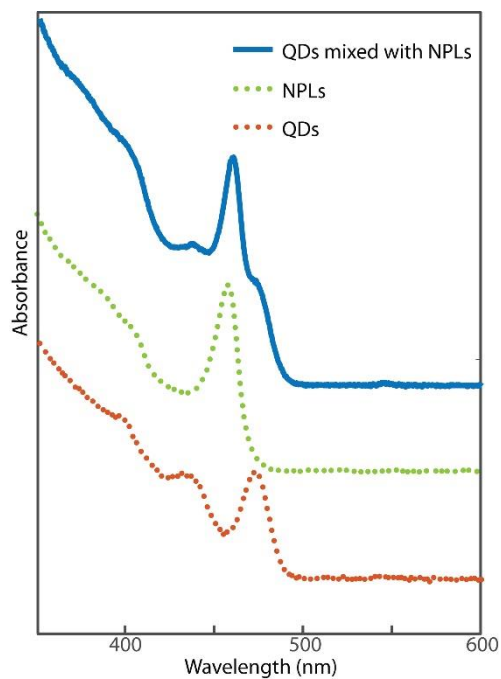


Figure S3. Comparison of the absorption spectra of pure QDs and QDs contaminated with nanoplatelets. Absorption spectra of CsPbBr₃ QDs mixed with nanoplatelets (NPLs) (blue), pure CsPbBr₃ NPLs (green) and pure QDs (red). The pure NPLs were made by a modified version of the method reported in this work performed at room temperature. The morphology of NPLs was confirmed by TEM imaging.

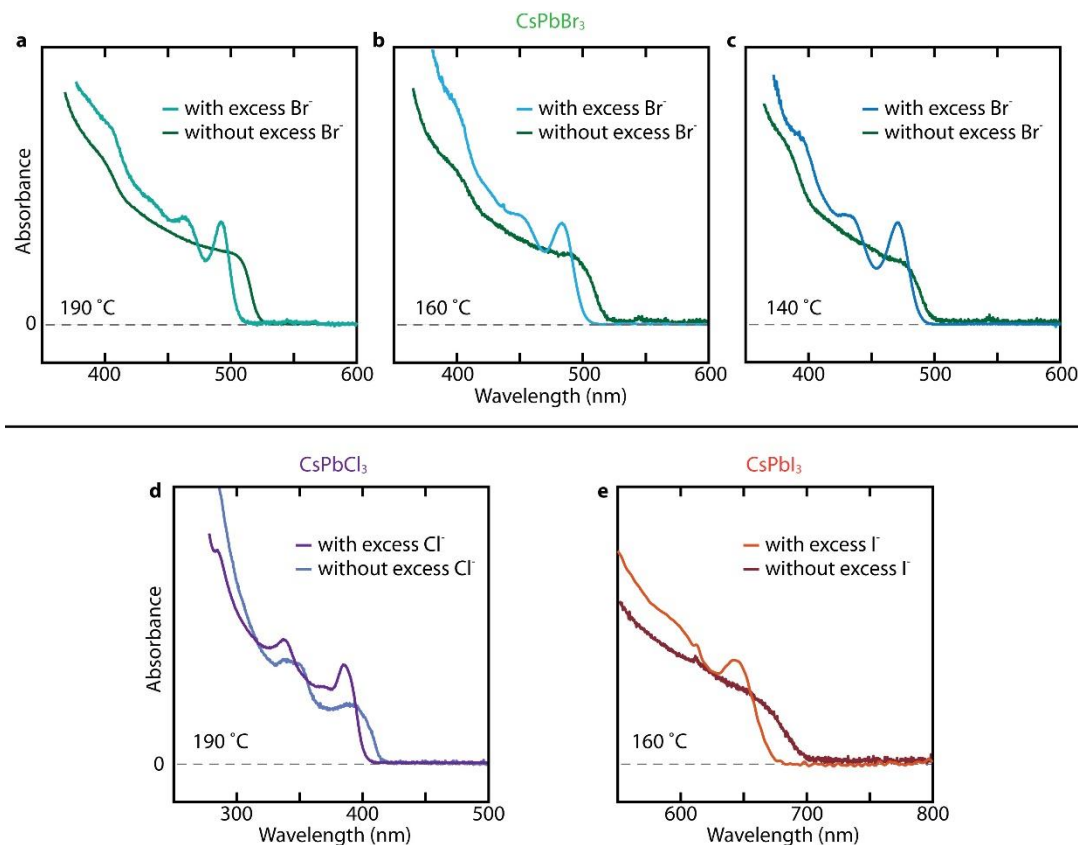


Figure S4. Comparison of the optical spectra of CsPbX₃ nanocrystals synthesized using new and previous methods at various temperatures. (a-c) Comparison of the absorption spectra of CsPbBr₃ nanocrystals synthesized using the new method reported here utilizing the thermodynamic equilibrium under high Br/Pb ratio condition and without excess X⁻ at the same reaction temperature. (d, e) Comparison of the absorption spectra of CsPbCl₃ (d) and CsPbI₃ (e) QDs synthesized with and without excess halide ions.

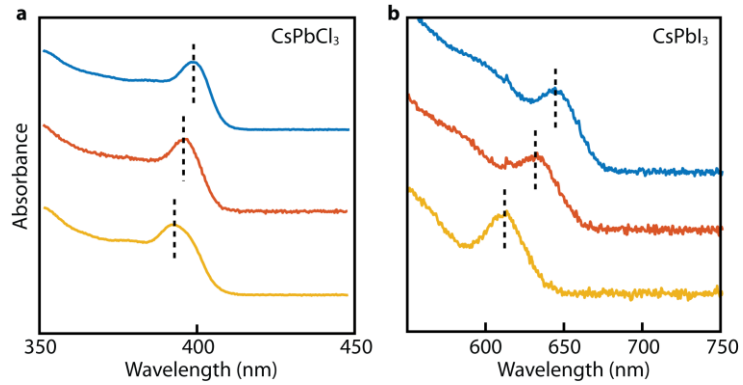


Figure S5. Absorption spectra of CsPbCl₃ and CsPbI₃ QDs with size control achieved in this study. (a) Absorption spectra of CsPbCl₃ QDs of several different sizes. Peak wavelength for the exciton absorption (λ_{peak}) is $\lambda_{\text{peak}} = 392$ nm, 389 nm, and 385 nm in decreasing order. (b) Absorption spectra of CsPbI₃ QDs of several different sizes. $\lambda_{\text{peak}} = 643$ nm, 630 nm, and 611 nm in decreasing order.

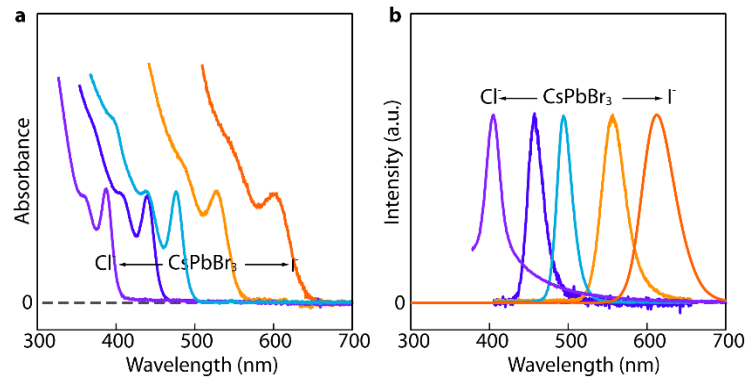


Figure S6. Absorption spectrum of anion-exchanged QD. (a) Absorption and (b) PL spectra of anion-exchanged ~ 4 nm CsPbBr₃ QDs with Cl⁻ and I⁻.

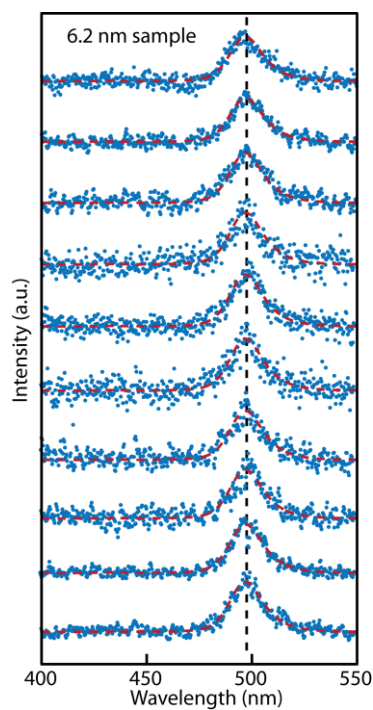


Figure S7. Additional single-particle PL spectra of 6.2 nm CsPbBr₃ QDs.

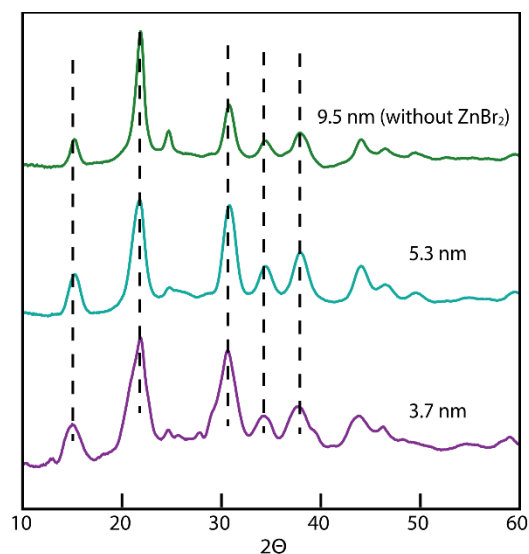


Figure S8. XRD patterns X-ray diffraction (XRD) patterns of CsPbBr₃ QDs. The top pattern was obtained from the large CsPbBr₃ nanocrystals synthesized in the absence of excess Br⁻ from ZnBr₂.

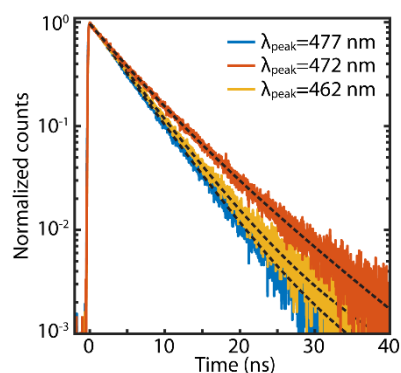


Figure S9. PL Lifetime of the QDs. PL lifetime of three different CsPbBr₃ QDs with exciton absorption peak (λ_{peak}) at 477 nm, 472 nm and 462 nm. The average PL lifetime is 4.6 ns, 5.9 ns and 4.9 ns respectively.

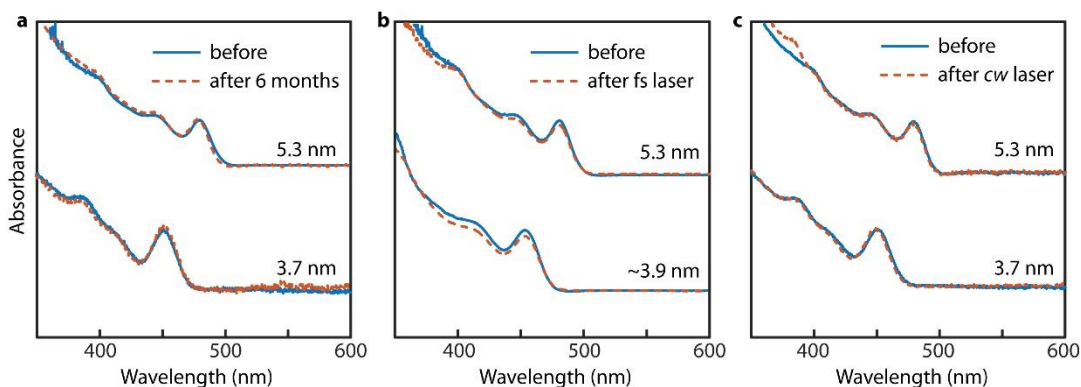


Figure S10. Stability of the QDs. (a) Comparison of absorption spectra of 5.3 nm and 3.7 nm CsPbBr₃ QDs when they were freshly made and after storing for 6 months in hexane. Both of this two samples were exposed to air and kept at room temperature. (b) Comparison of absorption spectra of 5.3 nm and 3.9 nm CsPbBr₃ QDs before and after exposure to femtosecond UV excitation for 6 hours ($\lambda=400$ nm, 70 fs pulse width, 40 μ W, 3kHz). (c) Comparison of absorption spectra of 5.3 nm and 3.7 nm CsPbBr₃ QDs before and after exposure to cw UV excitation for 10 hours ($\lambda=405$ nm, 10 mW)

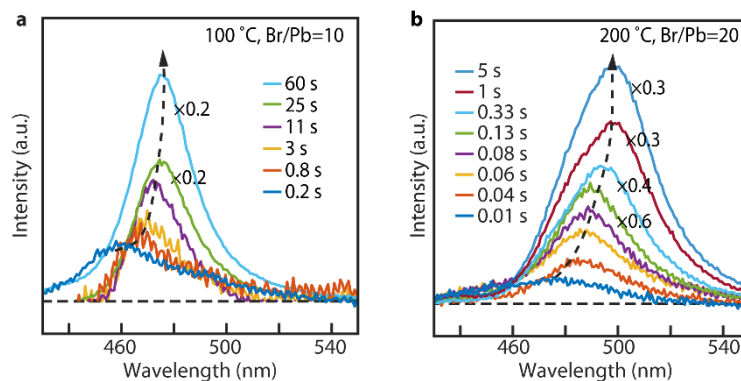


Figure S11. Time-dependent PL during the growth. Time-dependent PL spectra during the early phase of the reaction showing the growth of the QD that was not clearly visible in the contour plots of the time-dependent PL spectra shown in Figure 3 in the main text. (a) $T=100\text{ }^{\circ}\text{C}$, $\text{Br/Pb}=10$ and (b) $T=200\text{ }^{\circ}\text{C}$, $\text{Br/Pb}=20$.

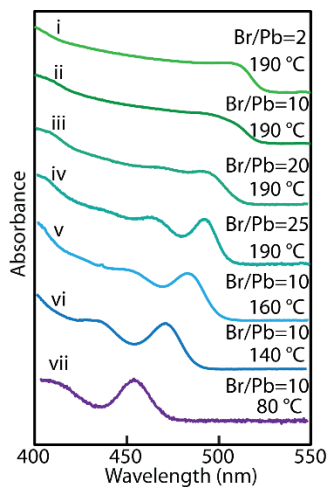


Figure S12. Additional absorption spectra of CsPbBr_3 QDs. Dependence of the absorption spectra of CsPbBr_3 QDs on Br/Pb ratio in the reactant at a fixed reaction temperature (i-iv) and on the reaction temperature at a fixed Br/Pb ratio in the reactant (v-vii).

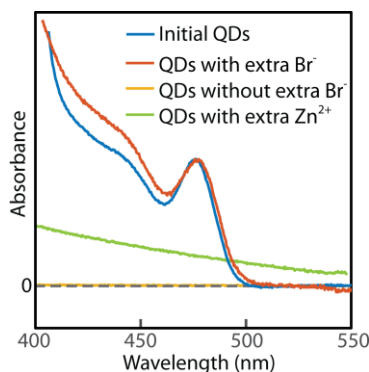


Figure S13. Comparison of the effects of Br^- and Zn^{2+} on high-temperature stability. Absorption spectra of the initial CsPbBr_3 QDs (blue) and the same QD sample redispersed in ODE containing ZnBr_2 and OA/OAM mixture after heating at 140°C for 5 mins (red). In the absence of ZnBr_2 in ODE, CsPbBr_3 QDs disintegrate completely forming a colorless solution upon heating (yellow). Adding zinc stearate does not improve the high-temperature stability of the QDs (green). Adding Cs_2CO_3 and $\text{Pb}(\text{Ac})_2$ as the source of extra Cs^+ and Pb^{2+} results in QD degradation.

Reference

1. Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. *Nano Lett.* **2015**, *15*, (6), 3692-3696.