Electronic Supporting Information (ESI) for:

Observation and Implication of Halide Exchange beyond CsPbX3 Perovskite Nanocrystals

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Experimental section

Materials and chemicals

Lead (II) bromide (PbBr\(_2\), 99.999% trace metals basis), lead (II) chloride (PbCl\(_2\), 99.999% trace metals basis), lead (II) iodide (PbI\(_2\), 99.999% trace metals basis), cesium carbonate (Cs\(_2\)CO\(_3\), 99.9% trace metals basis), oleylamine (OLA, technical grade, 70%) and trioctylphosphine (TOP, Strem, 97%) were purchased from Sigma-Aldrich. 1-Octadecene (ODE, technical grade, 90%) was purchased from J&K Scientific. Oleic acid (OA, A.R.), zinc chloride (ZnCl\(_2\), 99.999%), indium (III) chloride (InCl\(_3\), 99.99%), zinc iodide (ZnI\(_2\), 99.99%), zinc bromide (ZnBr\(_2\), anhydrous, 99.99%) were purchased from Macklin. Hexane (analytical grade, 95%) and acetone (analytical grade, 95%) were purchased from Beijing Chemical Works.

Preparation of Cs-oleate

For CsPbX\(_3\), 0.203 g of Cs\(_2\)CO\(_3\), 10 mL of octadecene (ODE), and 0.8 mL of oleic acid (OA) were added to a 3-necked 50 mL reaction flask, degassed the mixture at 100 °C for 30 minutes under vacuum, and then heated to 150 °C under N\(_2\) for 30 minutes until all Cs\(_2\)CO\(_3\) reacted with OA.

Synthesis of CsPb\(_x\)X\(_3\) NCs

Synthesis of CsPb\(_x\)X\(_3\) NCs was performed according to the method slightly modified from the protocol reported by Protesescu et al.\(^1\) In brief, 0.188 mmol PbX\(_2\) (0.069 g PbBr\(_2\), 0.052 g PbCl\(_2\), 0.087 g PbI\(_2\)), 5 mL ODE, 0.5 mL OA and 0.5 mL OAm were loaded into a 50 mL 3-neck flask, heated to 100°C and purged under vacuum for 30 min. After the PbX\(_2\) was completely dissolved, the temperature was raised to the optimal value (170 °C for PbBr\(_2\), 185 °C for PbCl\(_2\) or 160 °C for PbI\(_2\)), 0.50 mL of Cs-OA was swiftly injected. The reaction mixture was cooled with the ice water bath in 5 seconds. For the synthesis of CsPbCl\(_3\), a higher temperature of 150 °C and 1 mL of trioctylphosphine were required to solubilize PbCl\(_2\). The crude solution was directly washed via centrifugation (at 9000 rpm for 5 minutes), followed by redispersion in 4 mL hexane.

Synthesis of Cs\(_4\)PbX\(_6\) NCs

Synthesis of Cs\(_4\)PbX\(_6\) NCs was performed according to the method slightly modified from the protocol reported by Akkerman et al.\(^2\) Briefly, 0.1 mmol PbX\(_2\) (0.037g PbBr\(_2\), 0.028g PbCl\(_2\), 0.046g PbI\(_2\)), 5 mL ODE, 0.2 mL OA and 1.5 mL OAm were loaded into a 50 mL 3-neck flask, heated to 100°C and purged under vacuum for 30 min. After the PbX\(_2\) was completely dissolved, the temperature was raised to the optimal value (80 °C for PbBr\(_2\), 100 °C for PbCl\(_2\) or 60 °C for PbI\(_2\)), 0.6 mL of Cs-OA was swiftly injected. After about 20 seconds the reaction turned turbid and, depending on the required size, was quickly cooled down after 0-10 min to room temperature with an ice water bath. The crude solution was directly washed via centrifugation (at 5000 rpm for 8 minutes), followed by redispersion in 4 mL hexane.

Synthesis of CsX NCs

Synthesis of CsX NCs was performed according to the method slightly modified from the protocol
reported by Shamsi et al\textsuperscript{3}. In brief, halide precursors (0.2 mmol ZnBr\textsubscript{2}, 0.13 mmol InCl\textsubscript{3}, 0.2 mmol ZnI\textsubscript{2}) 4 mL ODE, 0.6 mL OA and 0.6 mL OAm were loaded into a 50 mL 3-neck flask, heated to 120°C and purged under vacuum for 30 min. After the halide precursors were completely dissolved, 0.5 mL of Cs-OA was added to the solution at optimized temperature (50-120 °C for ZnBr\textsubscript{2}, 90-130 °C for InCl\textsubscript{3} or 50-90 °C for ZnI\textsubscript{2}). After 5 minutes, the reaction mixture was cooled down to room temperature with a water bath. The crude solution was directly washed via centrifugation (at 4000 rpm for 10 minutes), followed by redispersion in 4 mL hexane.

**Synthesis of CsPb(Br/X)\textsubscript{3}, Cs\textsubscript{4}Pb(Br/X)\textsubscript{6} and Cs(Br/X) (X = Cl, I) NCs via the inter-particle anion-exchange.**

All the anion-exchange reactions were performed in air. In a typical synthesis, equal volumetric amounts (from the purified NC solutions as described above) of CsPbBr\textsubscript{3} and CsPbCl\textsubscript{3} or CsPbI\textsubscript{3} (Cs\textsubscript{4}PbBr\textsubscript{6} and Cs\textsubscript{4}PbCl\textsubscript{6} or Cs\textsubscript{4}PbI\textsubscript{6}; CsBr and CsCl or CsI) were left at room temperature without stirring. The NCs were not further purified.

**Reactions of CsPbX\textsubscript{3} and CsX (X=Br, Cl, I)**

In a typical reaction, 0.05 mL CsX NCs with a concentration of 0.8 mg/mL added into 3 mL CsPbX\textsubscript{3} NCs with a concentration of 1 \textmu M.

**Characterization**

UV-\textvis spectra for colloidal solutions were recorded using a JASCO V-570 spectrophotometer at room temperature. A Cary Eclipse fluorescence spectrophotometer (Varian, Inc.) was used to acquire PL spectra. Transmission electron microscopy (TEM) images of obtained NCs were recorded using a JEM-2100 transmission scanning electron microscope (TEM, JEOL, Japan). X-ray diffraction (XRD) measurements were collected with a D8 Focus X-ray diffractometer. PLQYs were evaluated according to standard procedure using appropriate dye molecules for red, green and blue spectral regions (rhodamine 6G, fluorescein, and coumarine 343).\textsuperscript{4}
Figure S1, halide exchange reaction in perovskite CsPbX₃ NCs and non-perovskite NCs including Cs₄PbX₆ and CsX.

![Diagram showing halide exchange reaction in perovskite and non-perovskite NCs.](image)

Figure S2, XRD patterns of intermediate samples obtained from the internanocrystals anion exchange reaction.

(a) The XRD patterns of the perovskite CsPbCl₃ NCs, CsPbBr₃ NCs and CsPbI₃ NCs compared to the XRD patterns of the alloying CsPbClₓBr₃₋ₓ NCs and CsPbBrₓI₃₋ₓ NCs from anion exchange. (b) The XRD patterns of the hexagonal Cs₄PbCl₆ NCs, Cs₄PbBr₆ NCs and Cs₄PbI₆ NCs compared to the XRD patterns of the alloying Cs₄PbClₓBr₆₋ₓ NCs and Cs₄PbBrₓI₆₋ₓ NCs from anion exchange. (c, d) The XRD patterns of intermediate sample obtained from internanocrystals anion exchange reaction between CsBr and CsCl (or CsI NCs) after 2 days reaction time.
Figure S3, Internanocrystal halide exchange reactions and their dynamics in the case of using pervoskite NCs and non-pervoskite NCs. (a) absorption and PL spectra of initial CsPbBr\(_3\) NCs (green line) and CsPbI\(_3\) (red line) NCs, and the final alloying CsPb\(_{x}\)Br\(_{3-x}\) NCs (orange line). The right panel shows the PL peak shift of intermediate alloying CsPb\(_{x}\)Br\(_{3-x}\) NCs relative to pure CsPbBr\(_3\) NCs, as function of the exchange time. (b) Absorption spectra of initial Cs\(_4\)PbBr\(_6\) NCs (green line) and Cs\(_4\)PbI\(_6\) (red line) NCs, and the final Cs\(_4\)PbBr\(_{x}\)I\(_{6-x}\) NCs (orange line). The panel in the right side shows the absorption peak shift of intermediate Cs\(_4\)PbBr\(_{x}\)I\(_{6-x}\) NCs relative to pure Cs\(_4\)PbBr\(_6\) NCs at different exchange time. (c) Powder X-ray diffraction (XRD) patterns of CsBr NCs (green line) and CsI (red line) NCs, and the final alloying CsBr\(_{1-x}\) NCs (orange line). The inserted panel shows the enlarged (011) diffraction peaks shift from 29.66 to 30.35 degree. The right panel shows the (011) diffraction peak shift of intermediate CsBr\(_{1-x}\) NCs relative to pure CsBr NCs at different exchange time.
Figure S4, The size and morphology evolution of a variety of NCs during the intentional anion exchange was evaluated by transmission electron microscopy (TEM). (a) TEM images of initial CsPbBr$_3$ NCs (green scale bar), CsPbI$_3$ (red scale bar) NCs and the final alloying CsPbBr$_x$I$_{3-x}$ NCs (orange scale bar). (b) TEM images of initial Cs$_4$PbBr$_6$ NCs (green scale bar), Cs$_4$PbI$_6$ NCs (red scale bar) and the final alloying Cs$_4$PbBr$_x$I$_{6-x}$ NCs (orange scale bar). (c) TEM images of initial CsBr NCs (green scale bar), CsI (red scale bar) NCs and the final alloying CsBr$_x$I$_{1-x}$ NCs (orange scale bar). The panel at the left of each set of TEM images, shows the size distribution of each samples.
Figure S5, Internanocrystals anion exchange reaction between perovskite and non-perovskite NCs. (a) PL spectra changes of the CsPbBr$_3$ NCs after mixing with Cs$_4$PbCl$_6$ NCs, the right panel shows the PL peak shifts as function of the reaction time. (b) PL spectra changes of the CsPbBr$_3$ NCs after mixing with CsCl NCs, the right panel shows the PL peak shifts as function of the reaction time.

Figure S6, Internanocrystals anion exchange reaction between perovskite and non-perovskite NCs. (a) PL spectra changes of the CsPbBr$_3$ NCs after mixing with Cs$_4$PbI$_6$ NCs, the right panel shows the PL peak shifts as function of the reaction time. (b) PL spectra changes of the CsPbBr$_3$ NCs after mixing with CsI NCs, the right panel shows the PL peak shifts as function of the reaction time.
Figure S7, Internanocrystals anion exchange reaction between perovskite CsPbBr$_3$ NCs and non-perovskite Cs$_4$PbBr$_6$ NCs. The PL intensity (a) and the PL QY (b) of CsPbBr$_3$ NCs as function of the amount of the added Cs$_4$PbBr$_6$ NCs.

Figure S8, Internanocrystals anion exchange reaction between perovskite CsPbBr$_3$ NCs and non-perovskite. The TEM images of the obtained samples after mixing CsPbBr$_3$ NCs with CsBr NCs (a) and Cs$_4$PbBr$_6$ NCs (b) for 2 days.

Figure S9, Internanocrystals anion exchange reaction between perovskite CsPbCl$_3$ NCs and non-perovskite Cs$_4$PbCl$_6$ NCs. The PL intensity (a) and the PL QY (b) of CsPbCl$_3$ NCs as function of the amount of the added Cs$_4$PbCl$_6$ NCs.
Figure S10, Internanocrystals anion exchange reaction between perovskite CsPbCl$_3$ NCs and CsCl NCs. The PL intensity (a) and the PL QY (b) of CsPbCl$_3$ NCs as function of the amount of the added CsCl NCs.

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