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_2CO_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_2CO_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_2CO_3 reacted with OA. For Cs_4PbX_6 and CsX, 0.65 g Cs_2CO_3 were dissolved in 10 mL OA by using heat gun until all Cs_2CO_3 reacted with OA.

Synthesis of $CsPbX_3$ NCs

Synthesis of $CsPbX_3$ 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 ºC 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_4PbX_6 NCs

Synthesis of Cs_4PbX_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 trmperature 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[3]. In brief, halide precursors (0.2 mmol $ZnBr_2$, 0.13 mmol $InCl_3$, 0.2 mmol ZnI_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 $ZnBr_2$, 90-130 °C for $InCl_3$ or 50-90 °C for ZnI_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 $CsPb(Br/X)_3$, $Cs_4Pb(Br/X)_6$ 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 $CsPbBr_3$ and $CsPbCl_3$ or $CsPbI_3$ (Cs_4PbBr_6 and Cs_4PbCl_6 or Cs_4PbI_6; CsBr and CsCl or CsI) were left at room temperature without stirring. The NCs were not further purified.

Reactions of $CsPbX_3$ 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 $CsPbX_3$ NCs with a concentration of 1 μM.

Characterization

UV−vis 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). [4]

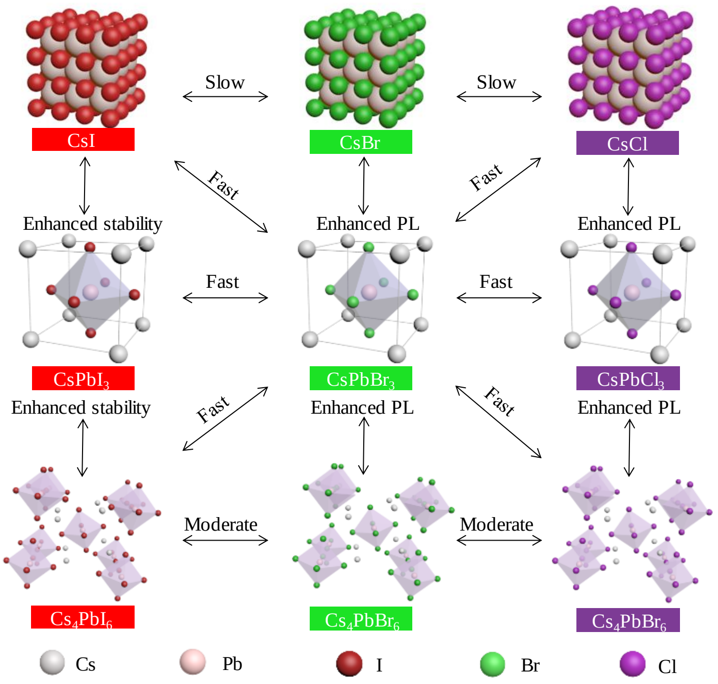

Figure S1, halide exchange reaction in perovskite $CsPbX_3$ NCs and non-perovskite NCs including Cs_4PbX_6 and CsX.

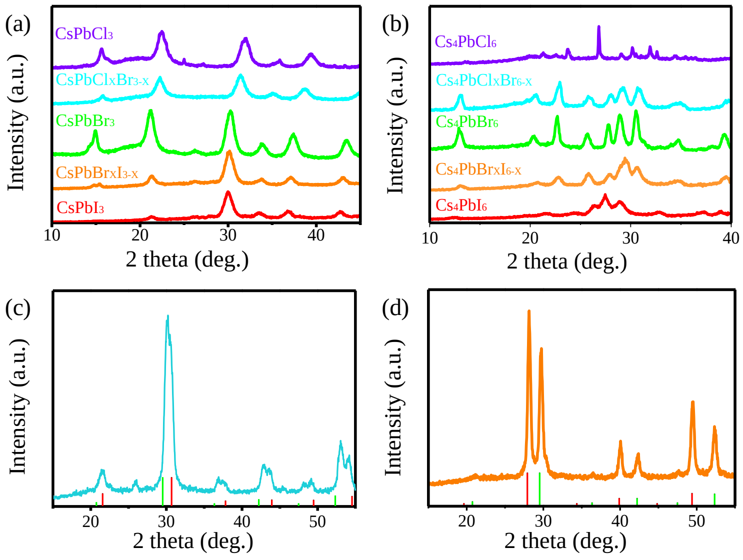

Figure S2, XRD patterns of intermediate samples obtained from the internanocrystal anion exchange (a) The XRD patterns of the perovskite $CsPbCl_3$ NCs, $CsPbBr_3$ NCs and $CsPbI_3$ NCs compared to the XRD patterns of the alloying $CsPbCl_xBr_{3-x}$ NCs and $CsPbBr_xI_{3-x}$ NCs from anion exchange. (b) The XRD patterns of the hexagonal Cs_4PbCl_6 NCs, Cs_4PbBr_6 NCs and Cs_4PbI_6 NCs compared to the XRD patterns of the alloying $Cs_4PbCl_xBr_{6-x}$ NCs and $CsPbBr_xI_{6-x}$ 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.

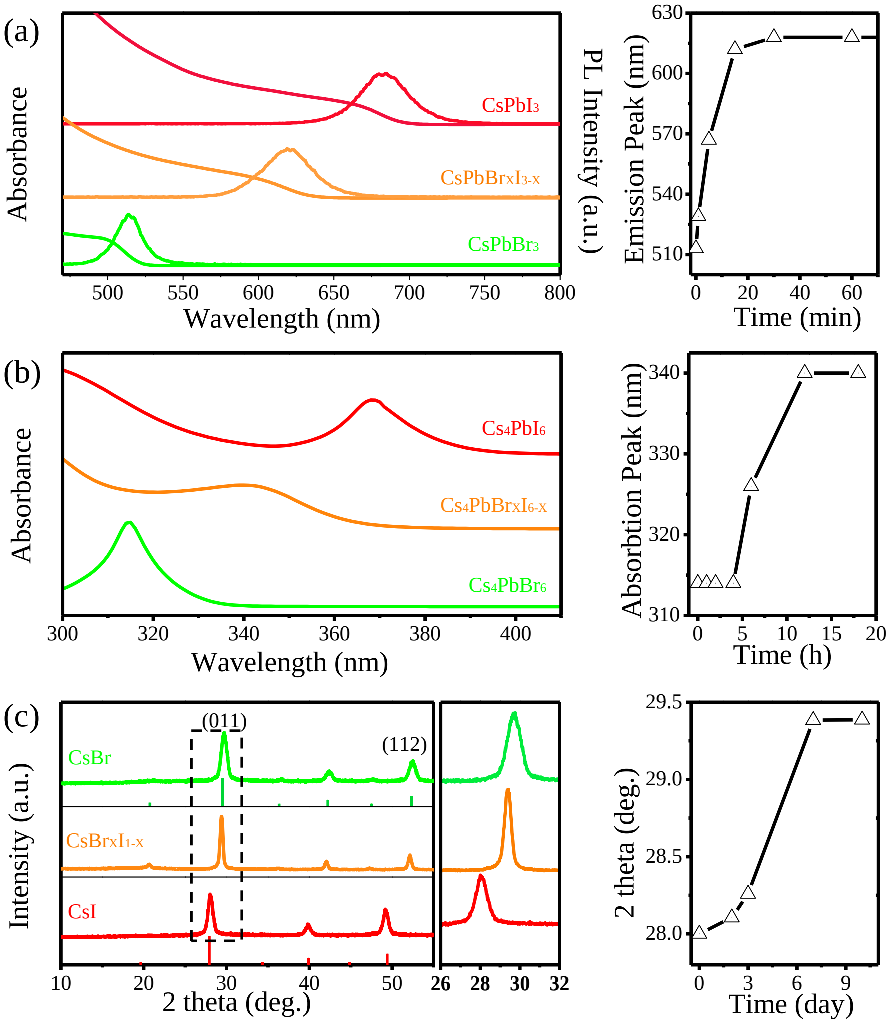

Figure S3, Internanocrystal halide exchange reactions and their dynamics in the case of using pervosksite NCs and non-pervosksite NCs. (a) absorption and PL spectra of initial $CsPbBr_3$ NCs (green line) and $CsPbI_3$ (red line) NCs, and the final alloying $CsPbBr_xCl_{3-x}$ NCs (orange line). The right panel shows the PL peak shift of intermediate alloying $CsPbBr_xI_{3-x}$ NCs relative to pure $CsPbBr_3$ NCs, as function of the exchange time. (b) Absorption spectra of initial Cs_4PbBr_6 NCs (green line) and Cs_4PbI_6 (red line) NCs, and the final $Cs_4PbBr_xI_{6-x}$ NCs (orange line). The panel in the right side shows the absorption peak shift of intermediate $Cs_4PbBr_xI_{6-x}$ NCs relative to pure Cs_4PbBr_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 $CsBr_xI_{1-x}$ 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 $CsBr_xI_{1-x}$ NCs relative to pure CsBr NCs at different exchange time.

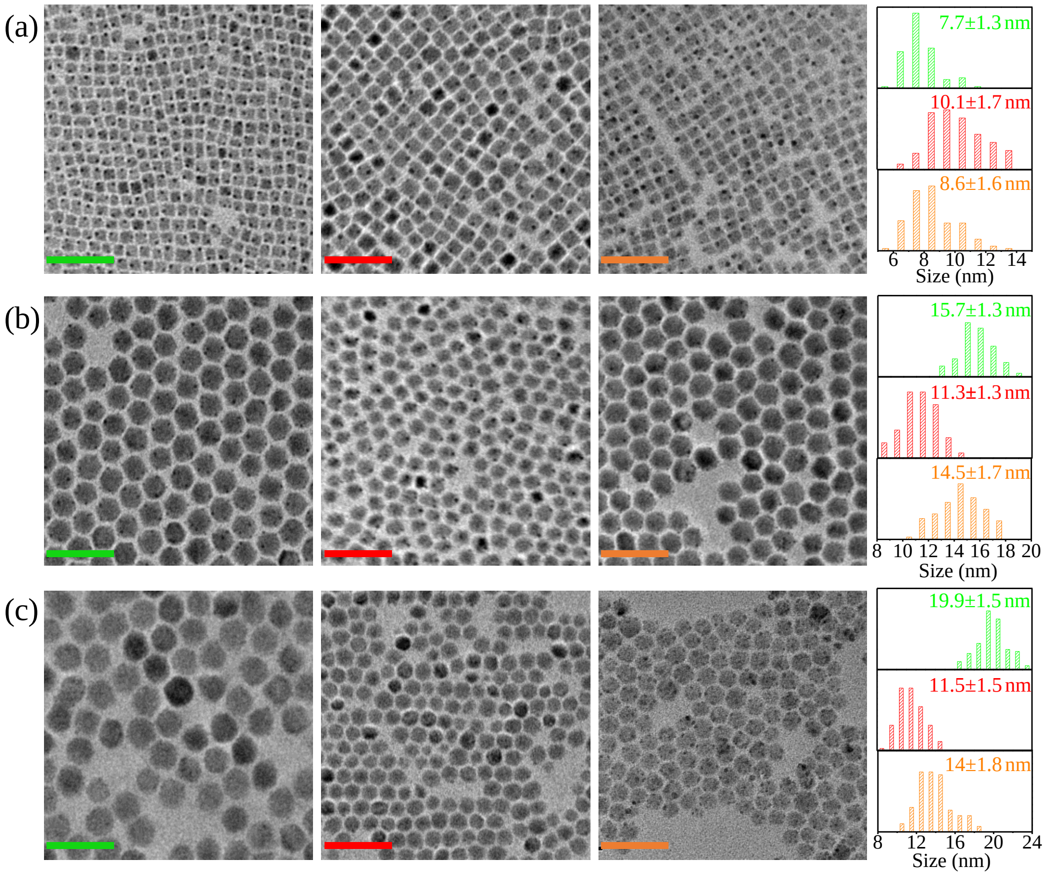

Figure S4, The size and morphology evolution of a variety of NCs during the intentional anion exchange was evaluated by transmission electron microscopy (TEM). (a) TEM images of initial $CsPbBr_3$ NCs (green scale bar), $CsPbI_3$ (red scale bar) NCs and the final alloying $CsPbBr_xI_{3-x}$ NCs (orange scale bar). (b) TEM images of initial Cs_4PbBr_6 NCs (green scale bar), Cs_4PbI_6 NCs (red scale bar) and the final alloying $Cs_4PbBr_xI_{6-x}$ NCs (orange scale bar). (c) TEM images of initial CsBr NCs (green scale bar), CsI (red scale bar) NCs and the final alloying $CsBr_xI_{1-x}$ NCs (orange scale bar).The panel at the left of each set of TEM images, shows the size distribution of each samples.

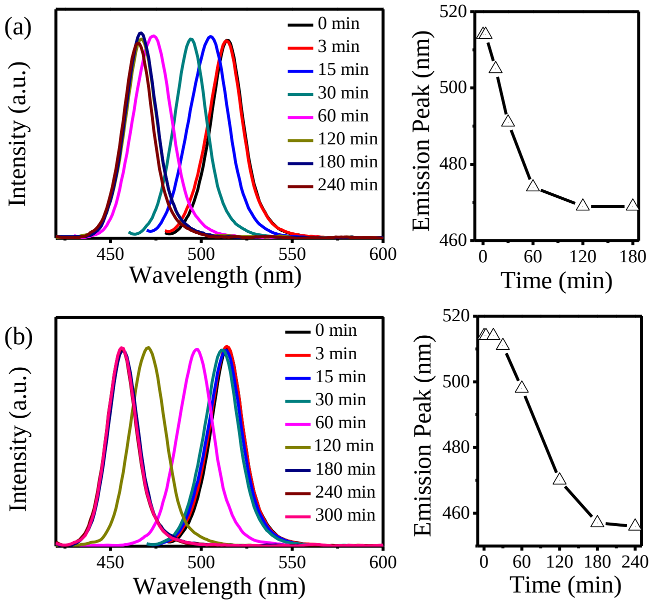

Figure S5, Internanocrystals anion exchange reaction between perovskite and non-perovskite NCs. (a) PL spectra changes of the $CsPbBr_3$ NCs after mixing with Cs_4PbCl_6 NCs, the right panel shows the PL peak shifts as function of the reaction time. (b) PL spectra changes of the $CsPbBr_3$ NCs after mixing with CsCl NCs, the right panel shows the PL peak shifts as function of the reaction time.

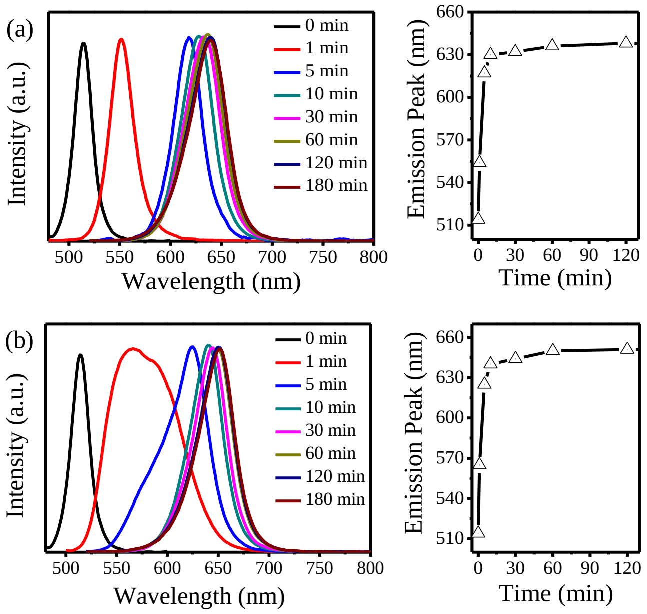

Figure S6, Internanocrystals anion exchange reaction between perovskite and non-perovskite NCs. (a) PL spectra changes of the $CsPbBr_3$ NCs after mixing with Cs_4PbI_6 NCs, the right panel shows the PL peak shifts as function of the reaction time. (b) PL spectra changes of the $CsPbBr_3$ NCs after mixing with CsI NCs, the right panel shows the PL peak shifts as function of the reaction time.

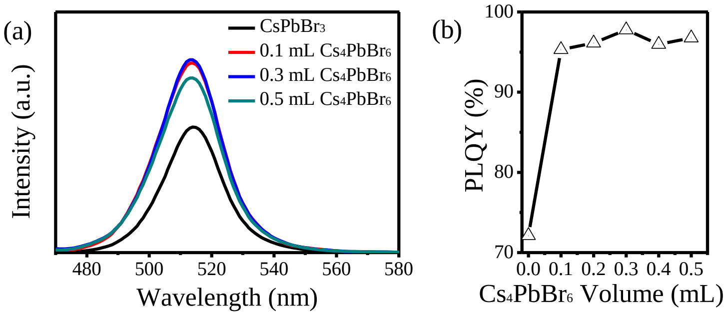

Figure S7, Internanocrystals anion exchange reaction between perovskite $CsPbBr_3$ NCs and non-perovskite Cs_4PbBr_6 NCs. The PL intensity (a) and the PL QY (b) of $CsPbBr_3$ NCs as function of the amount of the added Cs_4PbBr_6 NCs.

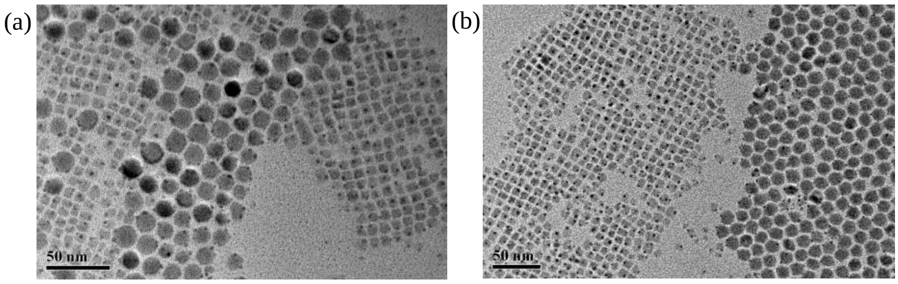

Figure S8, Internanocrystals anion exchange reaction between perovskite $CsPbBr_3$ NCs and non-perovskite. The TEM images of the obtained samples after mixing $CsPbBr_3$ NCs with CsBr NCs (a) and Cs_4PbBr_6 NCs (b) for 2 days.

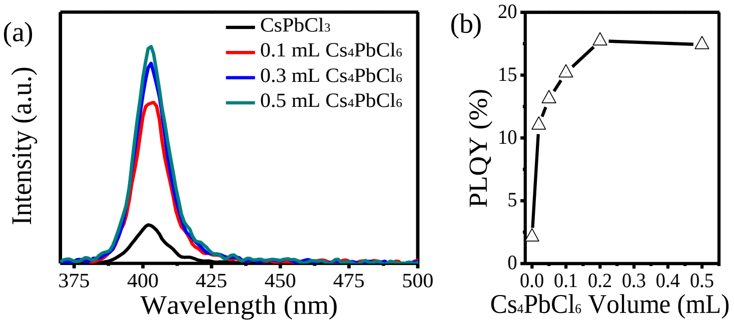

Figure S9, Internanocrystals anion exchange reaction between perovskite $CsPbCl_3$ NCs and non-perovskite Cs_4PbCl_6 NCs. The PL intensity (a) and the PL QY (b) of $CsPbCl_3$ NCs as function of the amount of the added Cs_4PbCl_6 NCs.

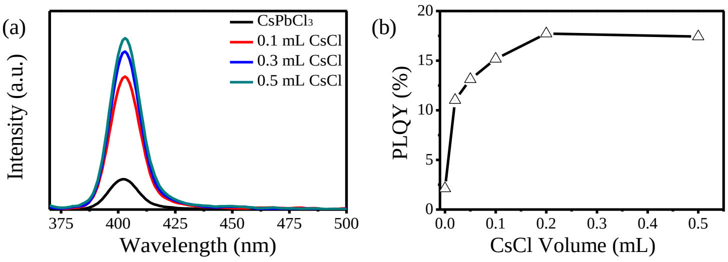

Figure S10, Internanocrystals anion exchange reaction between perovskite $CsPbCl_3$ NCs and CsCl NCs. The PL intensity (a) and the PL QY (b) of $CsPbCl_3$ NCs as function of the amount of the added CsCl NCs.

Reference：

1. Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V., Nanocrystals of Cesium Lead Halide Perovskites (CsPbX3, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Letters* **2015,** *15* (6), 3692-3696.
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3. Shamsi, J.; Dang, Z.; Ijaz, P.; Abdelhady, A. L.; Bertoni, G.; Moreels, I.; Manna, L., Colloidal CsX (X = Cl, Br, I) Nanocrystals and Their Transformation to CsPbX3 Nanocrystals by Cation Exchange. *Chemistry of Materials* **2017,** *30* (1), 79-83.
4. Di Stasio, F.; Christodoulou, S.; Huo, N.; Konstantatos, G., Near-Unity Photoluminescence Quantum Yield in CsPbBr3 Nanocrystal Solid-State Films via Postsynthesis Treatment with Lead Bromide. *Chemistry of Materials* **2017,** *29* (18), 7663-7667.