Experimental section

Materials

1-octadecene (ODE, Aladdin, 90%), oleic acid (OA, Aladdin, 90%), oleylamine (OAm, Aladdin, 80-90%), cesium acetate (CsAc, Aladdin, 99.9% metals basis), Cs$_2$CO$_3$ (Aladdin, 99.9%), lead acetate trihydrate (PbAc$_2$·3H$_2$O, Aladdin, 99.9% metals basis), PbBr$_2$ (Aladdin, 99.0%), tetraoctylammonium bromide (TOAB, Aladdin, 98%), cyclohexane (Sinopharm Chemical Reagent Co., Ltd ≥ 99.7%, AR), acetone (Sinopharm Chemical Reagent Co., Ltd ≥ 99.5%, AR), toluene (Sinopharm Chemical Reagent Co., Ltd ≥ 99.5%, AR). All chemicals were used as received without further purification.

Preparation of Cs$_4$PbBr$_6$ NCs

ODE (10 mL), OA (2 mL), OAm (2 mL), CsAc (0.2 mmol) and PbAc$_2$ (0.4 mmol) were loaded into a 50 mL 3-neck flask, then the mixture was dried for 15 min at 90 °C. After complete solubilisation of CsAc and PbAc$_2$, the temperature was decreased to 75 °C, and 3 mL TOAB solution (0.4 mmol TOAB dissolved in 3 mL toluene) was swiftly injected and 10s later the reaction mixture was cooled down by an ice-water bath. After that, acetone with the volume ratio of 1:1 to original dispersion was added to precipitate Cs$_4$PbBr$_6$ NCs. The resulting NCs were collected by centrifugation at 8000 rpm for 3 min, and then re-dispersed into 10 mL cyclohexane.

Water-triggered transformation process

The transformation process was conducted under ambient condition. Typically, 2 mL above Cs$_4$PbBr$_6$ solution was added into a 15 mL centrifuge tube, then 0.5 mL water was directly injected into the dispersion and the mixture was shaken vigorously for 20s to acquire NRs. The resulting product was collected by centrifugation at 8000 rpm for 3 min, and then re-dispersed into 4 mL cyclohexane. This centrifugation process was repeated twice to obtain CsPbBr$_3$ NRs with high purity.

Composition tuning through a halide ion exchange reaction

At first, the halide precursor solutions were prepared by dissolving 0.2 mmol of PbCl$_2$ or PbI$_2$ powder in a mixture of 10 ml of toluene, 0.2 ml of OA and 0.2 ml of OAm at 100 °C under
continuous stirring until the precursor dissolves. Then, the appropriate amount of precursor was added to the CsPbBr$_3$ NRs dispersion to initiate the halide ion exchange. The reaction mixtures were kept under stirring for 30-40 min at 40 °C followed by a centrifugation at 8000 rpm to remove the unreacted reagents. The purified NRs samples were redispersed in cyclohexane for further characterization.

**Growth mechanism research**

First, 0.02 mmol TOAB was dissolved in 2 mL toluene to be used later. Then 2 mL above hot-injection acquired Cs$_4$PbBr$_6$ solution was respectively added into four 15 mL centrifuge tubes, and 0 μL, 10 μL, 20 μL and 100 μL above TOAB solution were respectively added into the centrifuge tubes. Then 0.5 mL water was respectively injected into the centrifuge tubes and the mixture was shaken vigorously for 20s, the resulting products were collected by centrifugation at 8000 rpm for 3 min, and then re-dispersed into 4 mL cyclohexane respectively.

**Characterization**

Transmission electron microscopy (TEM) was measured by Tecnai G$^2$ F20, FEI. The UV-vis absorption spectra and Photoluminescence (PL) emission spectra were measured by the Ocean Optics USB2000+ spectrometer. X-ray powder diffraction (XRD) measurements employed a Bruker AXS D8 X-ray diffractometer equipped with monochromatized Cu Ka radiation ($\lambda=1.5418$ Å). The absolute PL QY was determined using a Quantaurus-QY absolute photoluminescence quantum yield spectrometer (C11347-11, Hamamatsu Photonics, Japan). Time-resolved fluorescence measurements were performed using a time-correlated single photon counting setup (TCSPC, SPC-130-EM, BDL-488-SMN) system.
Fig. S1. TEM image of Cs₄PbBr₆ NCs

Fig. S2. XRD pattern of Cs₄PbBr₆ NCs and CsPbBr₃ NRs.
Fig. S3. PL QY measurements of CsPbBr$_3$ NRs.

Fig. S4. PL decay of CsPbBr$_3$ NRs.
Fig. S5. TEM image of Cs$_4$PbBr$_6$ synthesized by hot-injection.

Fig. S6. (a) Width statistics photo of products that adding 10μL TOAB to Cs$_4$PbBr$_6$ solution and reaction with water. (b) width statistics photo of products that adding 20μL TOAB to Cs$_4$PbBr$_6$ solution and reaction with water. (c) length statistics photo of products that adding 10μL TOAB to Cs$_4$PbBr$_6$ solution and reaction with water. (d) length statistics photo of products that adding 20μL TOAB to Cs$_4$PbBr$_6$ solution and reaction with water.