

## Supporting Information for:

# Colloidal CsX (X = Cl, Br, I) Nanocrystals and their Transformation to CsPbX<sub>3</sub> Nanocrystals by Cation Exchange

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### Materials:

Zinc chloride (ZnCl<sub>2</sub>, 99.999%), zinc bromide (ZnBr<sub>2</sub>, 99.999%), zinc iodide (ZnI<sub>2</sub>, 99.999%), cobalt(II) chloride (CoCl<sub>2</sub>, 97%), cobalt(II) bromide (CoBr<sub>2</sub>, 99%), indium (III) chloride (InCl<sub>3</sub>, 99.99%), tetrabutylammonium chloride (TBAC, 97%), tetrabutylammonium bromide (TBAB, 99%), tetrabutylammonium iodide (TBAI, 99%) lead(II) oxide (PbO, 99.999%), lead(II) bromide (PbBr<sub>2</sub>, 99.999% trace metals basis), cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>, reagentPlus, 99%), 1-octadecene (ODE, technical grade, 90%), oleylamine (OLA, 70%), oleic acid (OA, 90%), hexane (anhydrous, 95%) were purchased from Sigma-Aldrich. All chemicals were used without any further purification.

### Methods:

**Preparation of cesium-oleate solution:** 0.325 g Cs<sub>2</sub>CO<sub>3</sub> were dissolved in 5 mL OA by using heat gun until all Cs<sub>2</sub>CO<sub>3</sub> reacted with OA.

**Preparation of PbBr<sub>2</sub> solution:** 0.072g PbBr<sub>2</sub> were solubilized in 2mL ODE, 1mL OA and 1mL OLA in a 20 mL vial on a hotplate at 100°C for 20 minutes.

**Preparation of lead-oleate ( $Pb(OA)_2$ ) solution:** 0.044 g PbO were dissolved in 2 mL OA by using heat gun until all PbO reacted with OA.

**Synthesis of CsX NCs:** All syntheses were carried out in air and without any pre-dried chemicals or solvents. In a typical synthesis, halide precursors (0.4 mmol) were dissolved in 2mL ODE, 1mL OA and 1mL OLA in a 20 mL vial on a hotplate at 100 °C. After complete solubilization of the halide precursors, 500  $\mu$ L of CsOA was added to the solution at optimized temperature (as mentioned in table 1). After 5 minutes, the reaction mixture was slowly cooled to room temperature using a water bath. To collect the CsX NCs, the solution was then centrifuged at 3800 rpm for 10 min. After centrifugation, the supernatant was discarded and the NCs were redispersed in 4mL hexane or ODE (in order to carry out the transformation reactions).

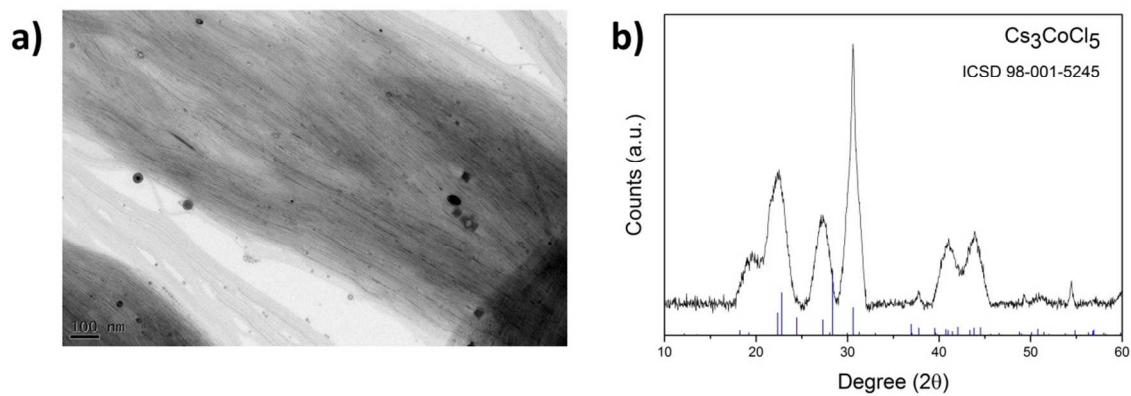
**Transformation reactions:** All experiments were carried out under ambient atmosphere. In the full transformation reactions, 200  $\mu$ L of as-prepared  $Pb(OA)_2$  (40  $\mu$ L for initial stage and 80  $\mu$ L for intermediate stage) were added to the 0.5 mL of CsX NC solutions at room temperature under vigorous stirring for 30 seconds. After the washing step, the perovskite NCs were redispersed in hexane.

#### **Characterization:**

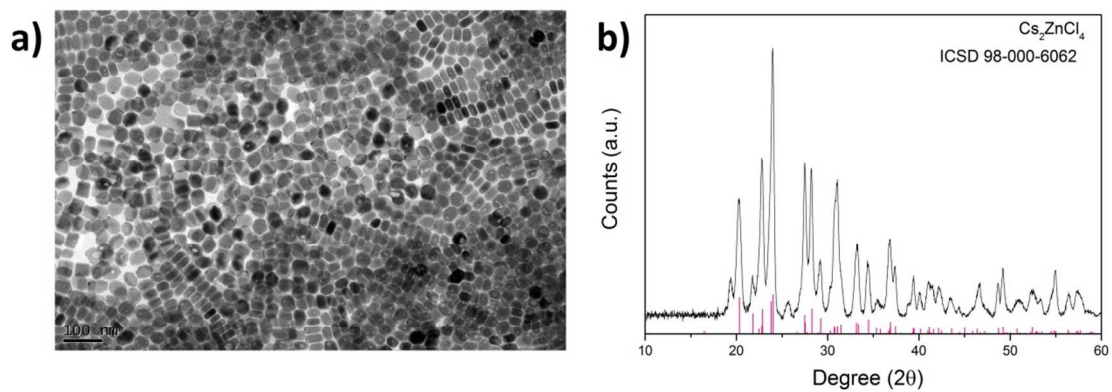
**Transmission Electron Microscopy (TEM).** Conventional TEM images were acquired on a JEOL JEM-1011 microscope equipped with a thermionic gun at 100 kV accelerating voltage. High-resolution TEM (HRTEM) imaging was performed on a JEOL JEM-2200FS microscope equipped with a 200 kV Schottky gun, a CEOS image aberration corrector enabling a spatial resolution of 0.9 Å, and an in column  $\Omega$ -filter. A Bruker Quantax 400 energy dispersive X-ray spectrometry (EDS) system with an XFlash 5060 detector on the same microscope was used for the elemental analysis. EDS analysis was used to identify differences in composition between the central regions and the edge regions of the NCs. First, several EDS spectra were collected from various central and edge regions of NCs. Then, these two sets of spectra were separately summed together. The results are reported in Figure S11. The samples were prepared by drop-casting diluted NC suspensions onto 200 mesh carbon-coated copper grids for conventional TEM imaging, and ultrathin carbon/holey carbon coated 400 mesh copper grids for HRTEM imaging, respectively. Geometrical phase analysis (GPA) was performed on HRTEM images using the FRWRtools plugin [1] for Digital Micrograph® (Gatan, Inc.).

**Powder X-ray Diffraction (XRD) Analysis.** XRD patterns were obtained using a PANalytical Empyrean X-ray diffractometer equipped with a 1.8 kW Cu  $K\alpha$  ceramic X-ray tube, PIXcel3D 2x2 area detector and operating at 45 kV and 40 mA. The diffraction patterns were collected in air at room temperature using Parallel-Beam (PB) geometry and symmetric reflection mode. All XRD samples were prepared by drop casting a concentrated solution on a zero diffraction silicon wafer.

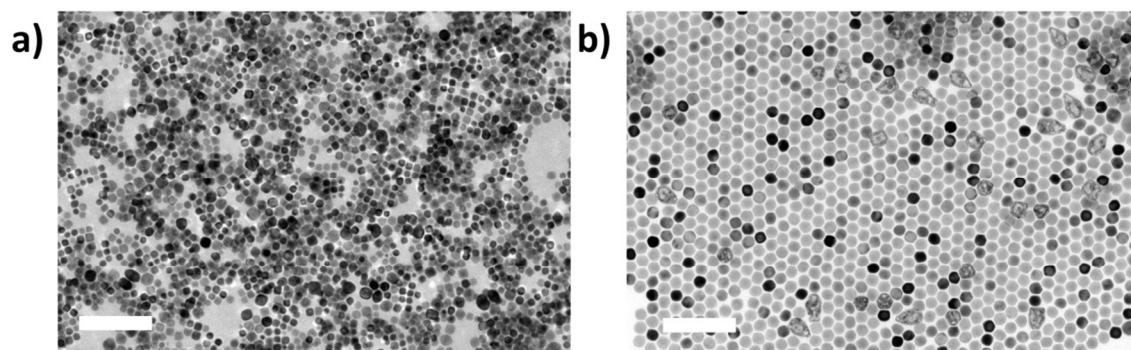
**Optical Absorption and Photoluminescence Spectroscopy.** The optical absorption spectra were taken on a Varian Cary 5000 UV–vis–NIR spectrophotometer. Samples were prepared by diluting the NC solutions in toluene in 1 cm path length quartz cuvettes. Photoluminescence quantum yield (PLQY) measurements of the NCs were carried out with an Edinburgh Instruments fluorescence spectrometer (FLS920) equipped with a Xenon lamp with monochromator for steady-state PL. PLQY values were obtained from CsPbBr<sub>3</sub> NCs toluene solutions in a quartz cuvette and diluted to 0.1 optical density at the excitation wavelength ( $\lambda = 400$  nm) using a calibrated integrating sphere.



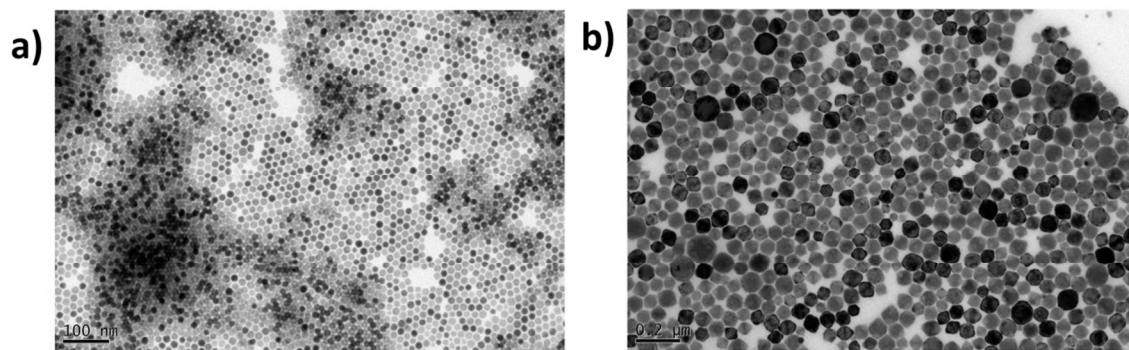
**Figure S1:** a) TEM image and b) XRD pattern of  $\text{Cs}_3\text{CoCl}_5$  NWs



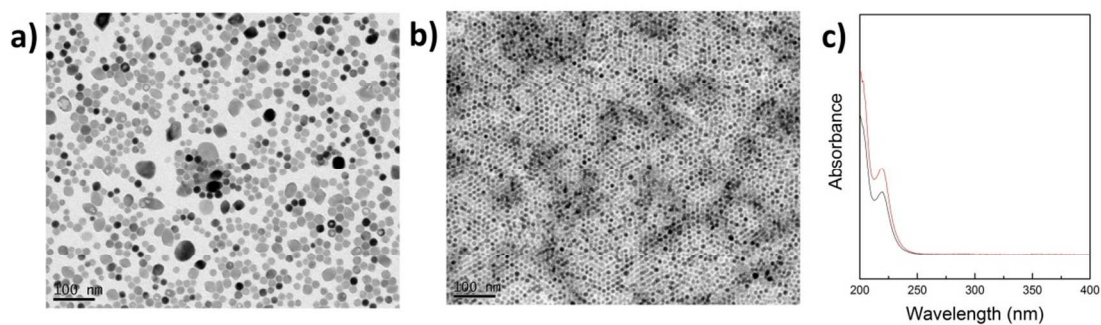
**Figure S2:** a) TEM image and b) XRD pattern of  $\text{Cs}_2\text{ZnCl}_4$  NCs



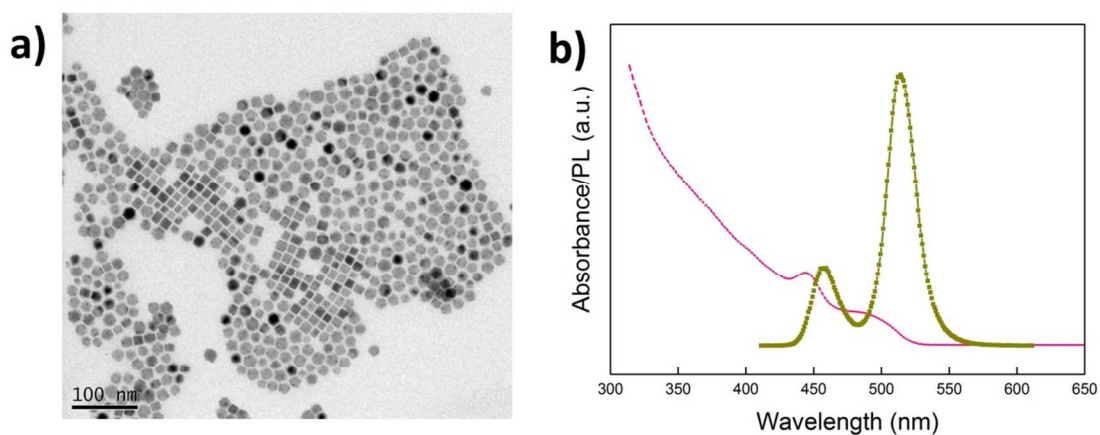
**Figure S3:** TEM images of CsCl NCs; a) by using TBAC at 90 °C; b) by using  $\text{InCl}_3$  at 90 °C (scale bars correspond to 100 nm)



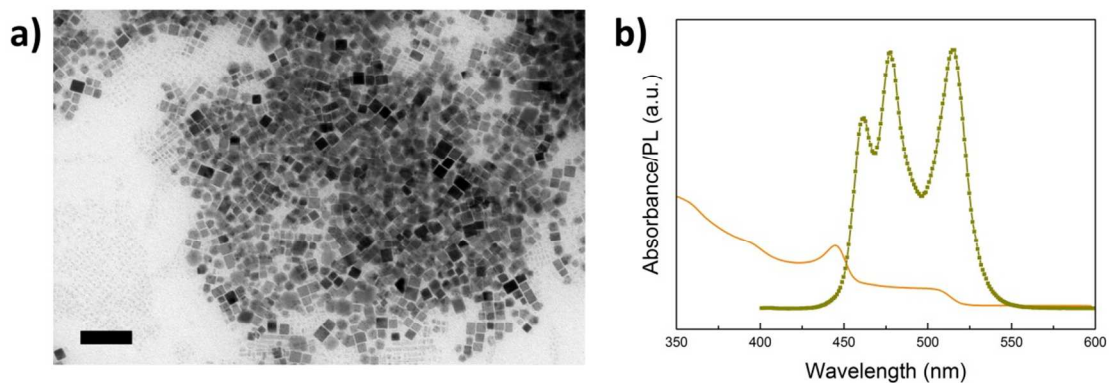
**Figure S4:** TEM images of CsBr NCs; a) by using  $\text{CoBr}_2$  and b) by using TBAB (scale bars correspond to 100 nm)



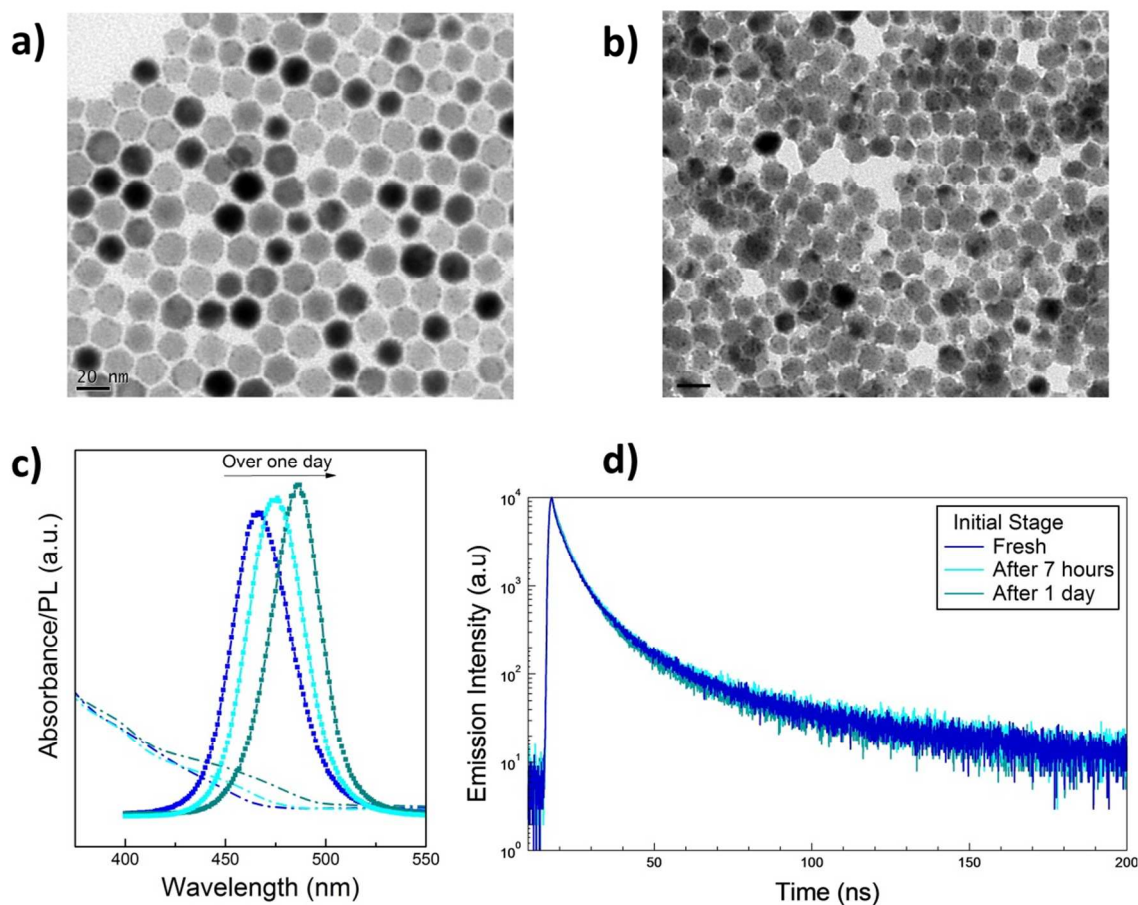
**Figure S5.** a) TEM image of CsI NCs prepared at 90 °C by using TBAI; b) TEM image of 10 nm CsI NCs synthesized at 50 °C by using  $\text{ZnI}_2$ ; c) absorption spectra for two different sizes (10 nm (panel b) and 22 nm (figure 1c)).



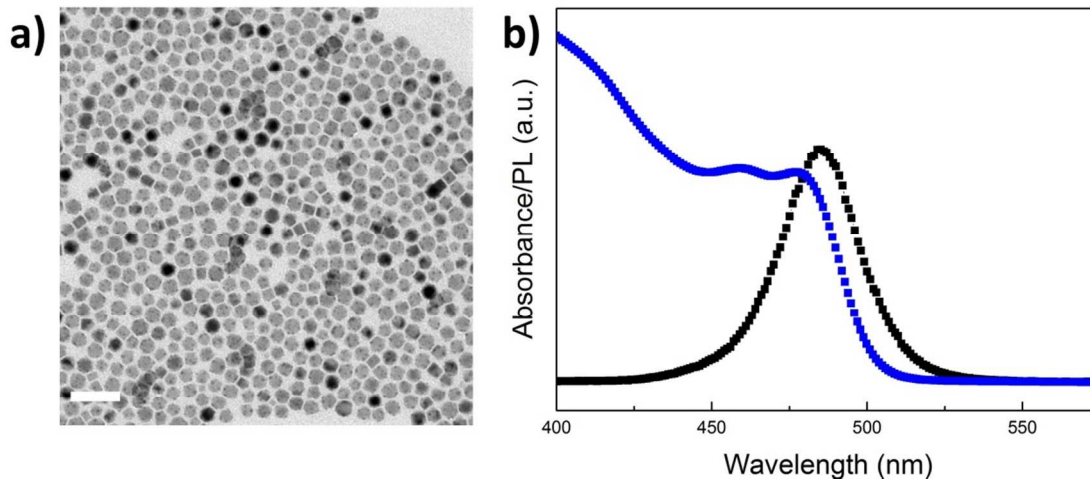
**Figure S6.** Results of transformations induced by exposing the CsBr NCs to an excess amount of  $\text{PbBr}_2$  at room temperature, overnight: a) TEM image; b) optical absorption (violet) and emission (green) spectra.



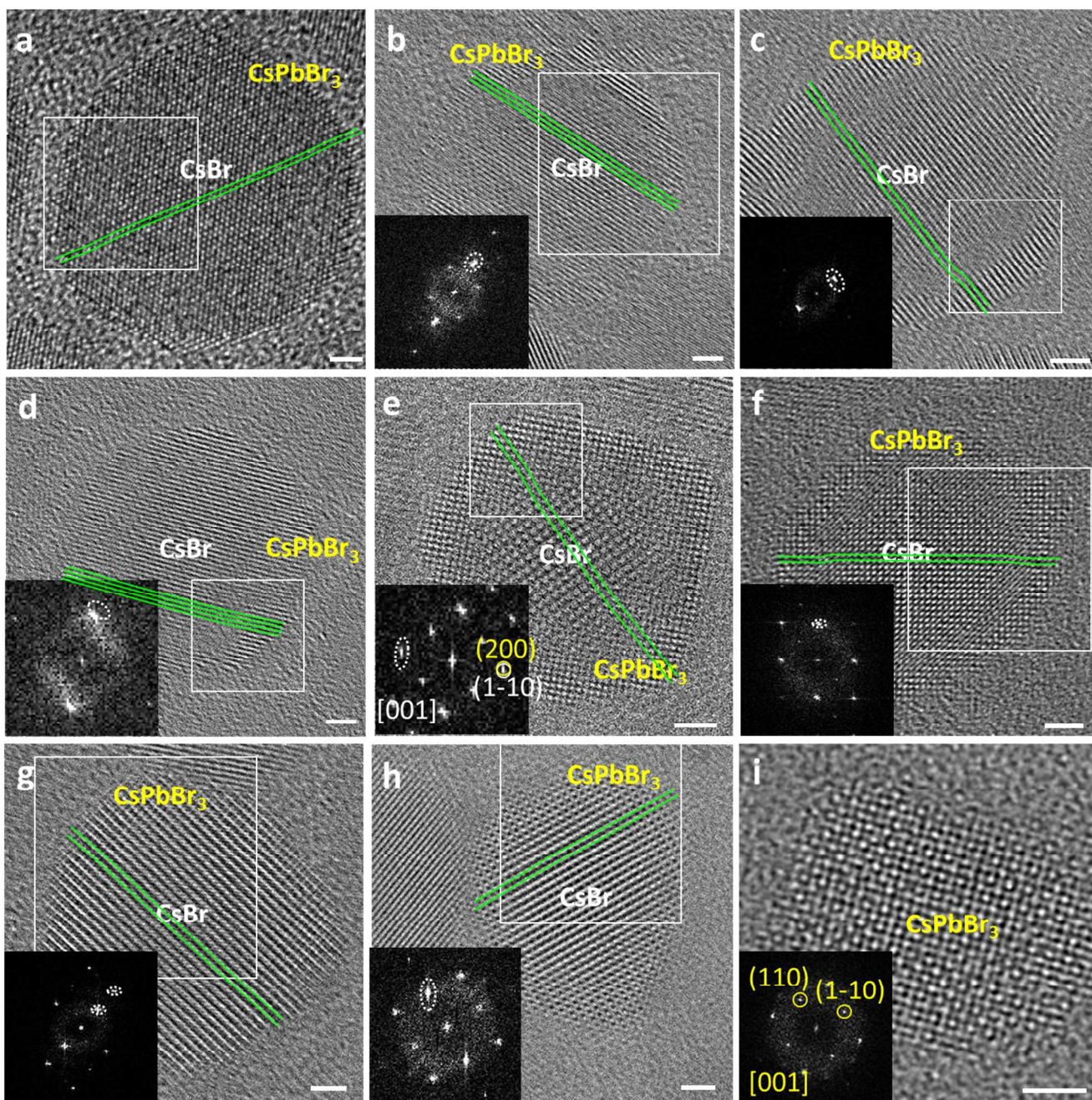
**Figure S7.** Results of transformations induced by exposing the CsBr NCs to an excess amount of  $\text{PbBr}_2$  at  $70^\circ\text{C}$  for 1 minute: a) TEM image (scale bar is 100 nm); b) optical absorption (violet) and emission (green) spectra.



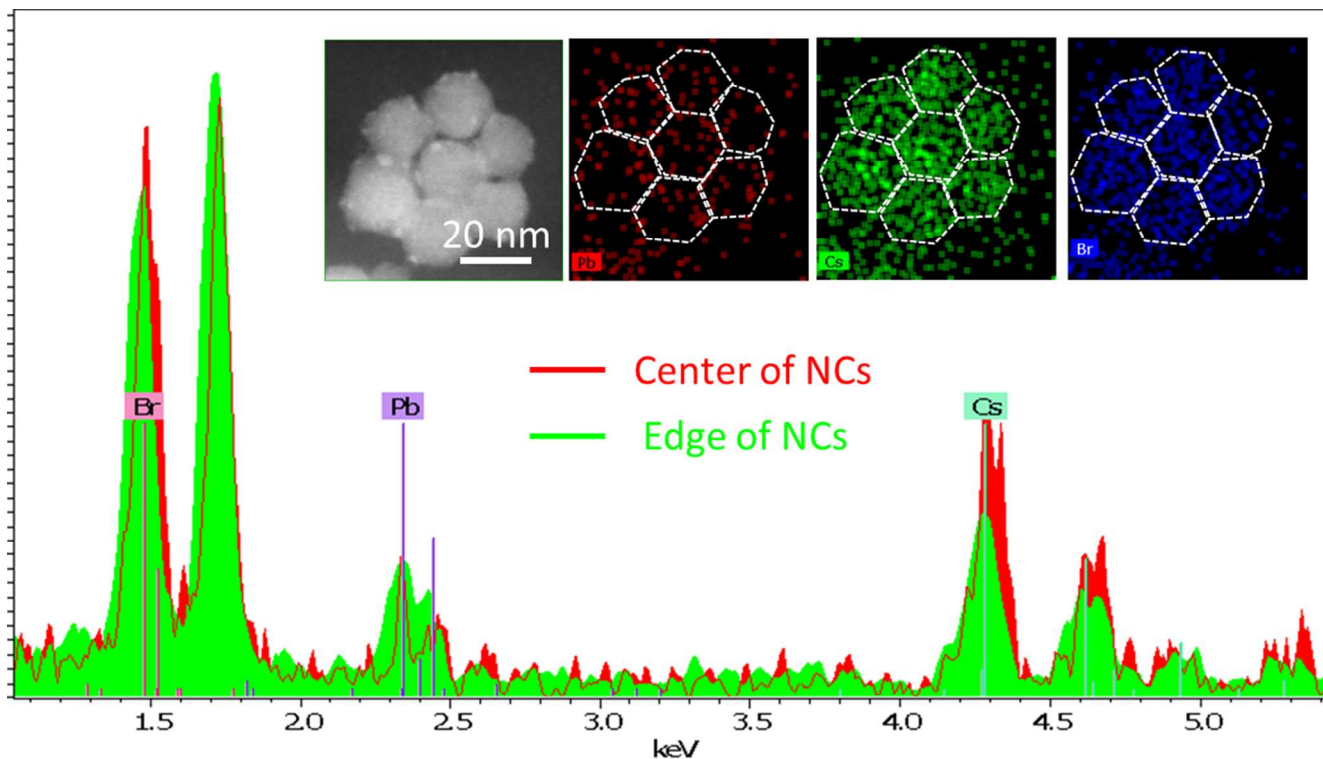
**Figure S8.** Initial stage of the CsBr to  $\text{CsPbBr}_3$  transformation: TEM images of a) fresh sample and b) aged sample (scale bars are 20 nm); c) optical spectra of confined domain over one day (the PL peak position varies from 468 nm to 486 nm); d) corresponding time-resolved PL decays for the confined  $\text{CsPbBr}_3$  domain over one day (PL decay slightly increased from 4.49 ns to 4.81 ns).



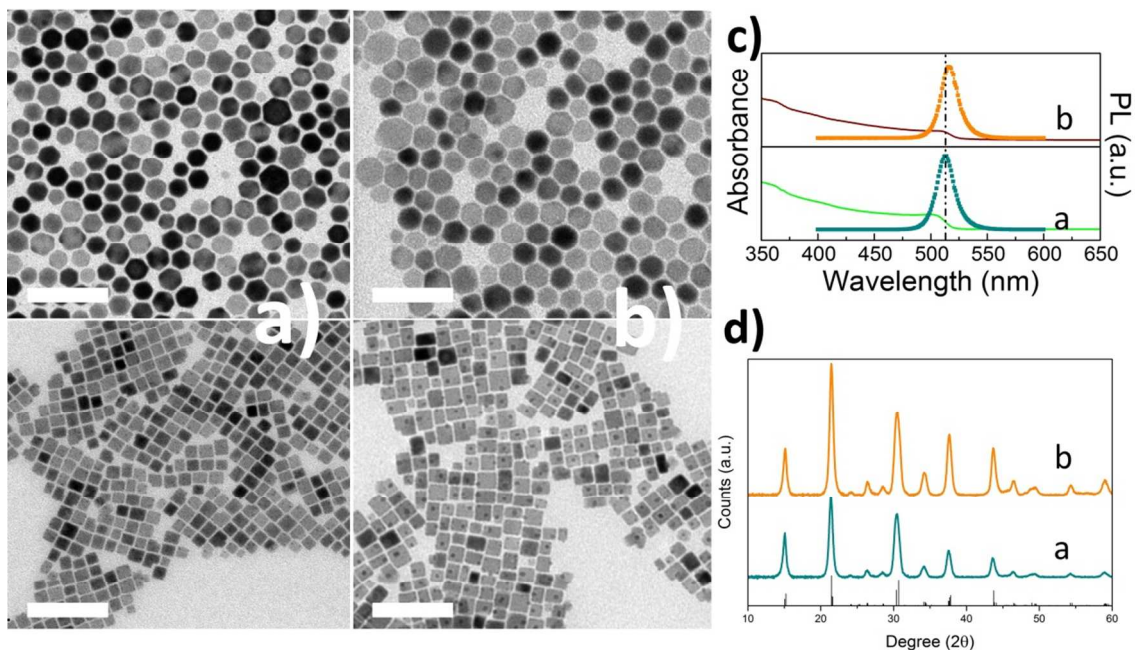
**Figure S9.** Intermediate stage of CsBr to CsPbBr<sub>3</sub> transformation a) TEM image and b) optical spectra; two absorption peaks and wide FWHM (31 nm) of PL present poor control over the shell thickness at intermediate stage (scale bar corresponds to 50 nm).



**Figure S10.** A set of HRTEM images related to intermediate stages (a-h) and final stage (i) of the transformation of CsBr NCs to CsPbBr<sub>3</sub> NCs (scale bar is 2 nm in all images). Green lines are drawn along the fringes.

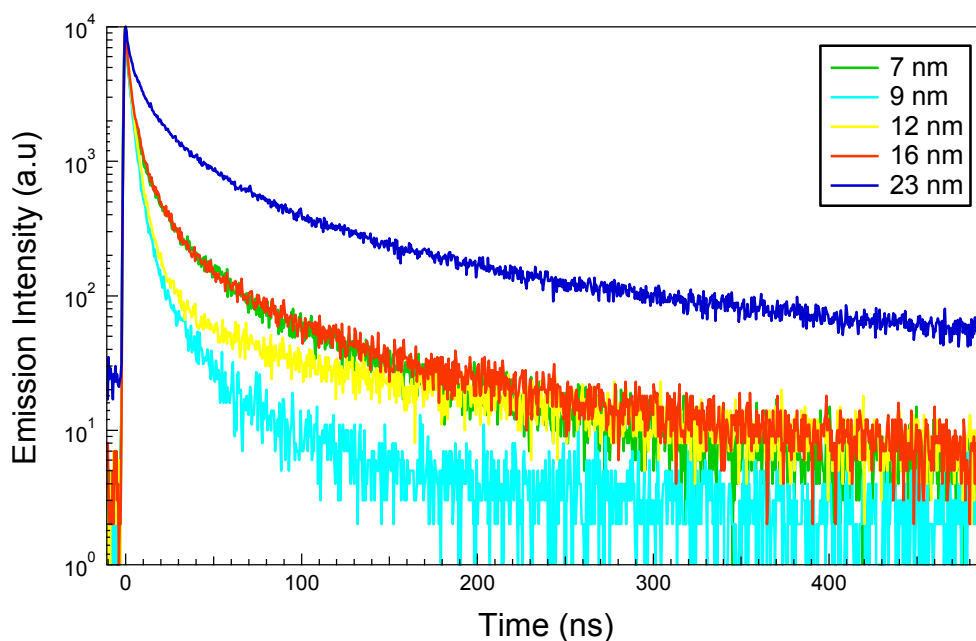


**Figure S11.** EDS analysis of CsBr NCs that had been partially converted to CsPbBr<sub>3</sub>. **The Main plot** reports EDS spectra. The red signal corresponds to a sum of several EDS spectra collected from the edge regions of the NCs. The green signal corresponds instead to a sum of several EDS spectra collected from the edge regions of the NCs. The central regions are richer in Cs and poorer in Pb compared to the edge regions. This fits into a model of a core/shell CsBr/CsPbBr<sub>3</sub> for these partially converted NCs. **Insets:** from left to right: HAADF-STEM image and corresponding elemental maps of Pb, Cs, and Br.



**Figure S12.** (a, b) TEM images of CsBr NCs of two additional sizes (24 and 30 nm, top panels) and corresponding TEM images of the resulting CsPbBr<sub>3</sub> NCs (16 and 23 nm, bottom panels). Scale bars correspond to 100 nm in all images; (c) Optical spectra and (d) XRD patterns of the resulting CsPbBr<sub>3</sub> NCs (ICSD reference pattern: 98-009-7851).

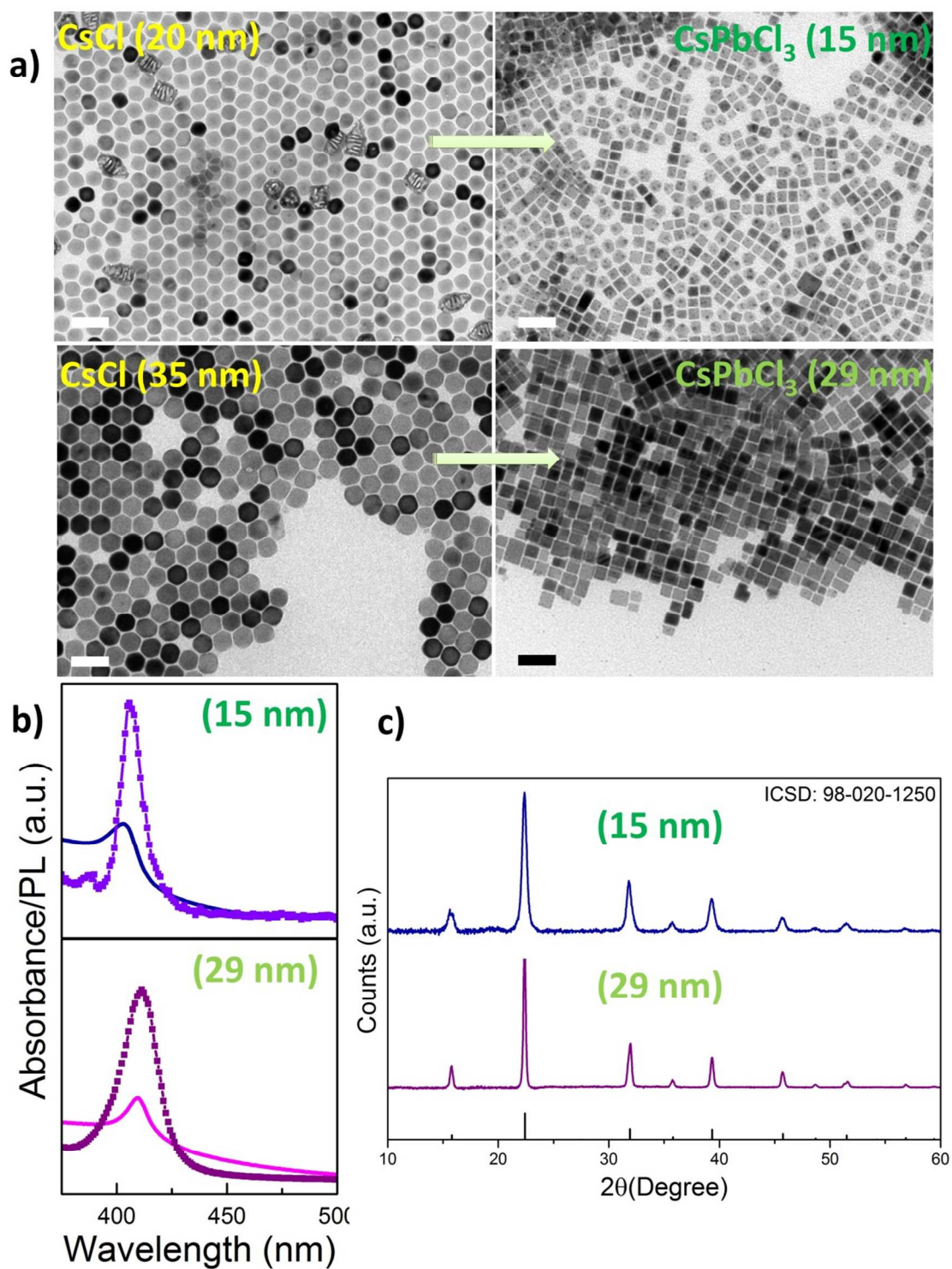




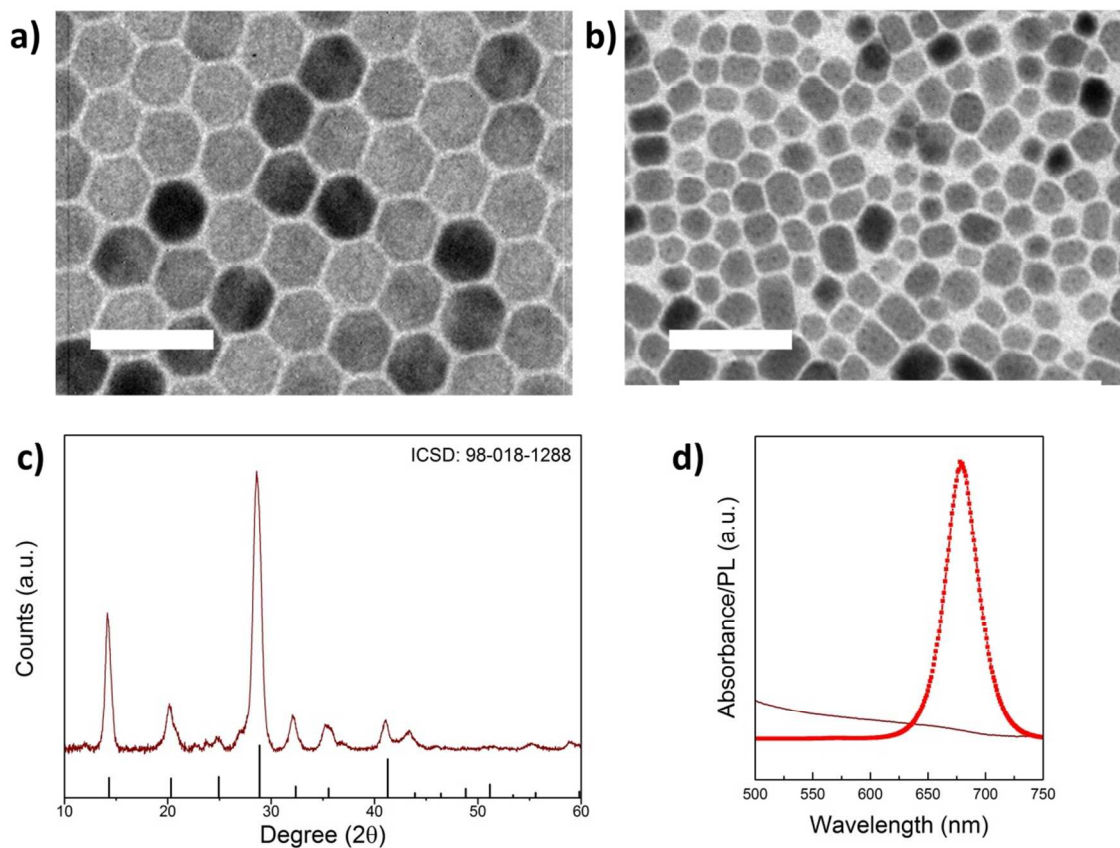
**Figure S13.** Time-resolved PL decays for all different sizes of CsPbBr<sub>3</sub> NC samples (shown in table S1). The numbers in the legend refer to the size of the NCs.

**Table S1.** Dataset of full transformation of CsBr NCs.

Sample	Reaction Temperature of CsBr (°C)	Size of CsBr (nm)	Size of CsPbBr <sub>3</sub>	PL Peak (nm)	FWHM (nm)	PLQY % (pretreatment)	Average PL lifetime (ns)
Figure 3a	50	13 ± 1	7 ± 0.5	500	20.6	49.1	4.48
Figure 3b	80	16 ± 1	9 ± 1	504	22.6	50.9	2.91
Figure 3c	90	20 ± 1	12 ± 1	509	21.7	50.1	3.89
Figure S8a	100	24 ± 3	16 ± 3	512	20.1	38.1	5.02
Figure S8b	120	30 ± 4	23 ± 3	517	20	32.5	17.16



**Figure S14.** A) TEM images of initial CsCl NCs (two different sizes, 20 nm (synthesized at 90 °C) and 35 nm (synthesized at 130 °C)) and the corresponding CsPbCl<sub>3</sub> NCs (15 and 29 nm, respectively). Scale bars correspond to 50 nm; b) optical spectra and c) XRD patterns of the two samples of CsPbCl<sub>3</sub> NCs.



**Figure S15.** a-b) TEM images of a sample of a) CsI NCs (22 nm, synthesized at 90 °C) and; b) corresponding CsPbI<sub>3</sub> NCs after the transformation. Scale bars correspond to 50 nm in both images; c) XRD pattern and d) optical spectra of the CsPbI<sub>3</sub> NCs.

## References

- (1) [https://www.physics.hu-berlin.de/en/sem/software/software\\_frwrtools](https://www.physics.hu-berlin.de/en/sem/software/software_frwrtools)