

Supporting information for:

Fully Inorganic Ruddlesden-Popper double Cl-I and triple Cl-Br-I Lead Halide Perovskite Nanocrystals

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Additional figures and table:

Table S1. Optical densities (path length 4 mm) and measured PLQYs of the as-synthesized and ammonium thiocyanate-treated (+TCN) CsPbBr₂Cl and CsPb(Cl:Br:I)₃ NC samples.

Nanocrystal samples in toluene	λ_{exc} , nm	OD at λ_{exc}	PLQY ^{obs} , %
CsPbBr ₂ Cl	350	0.18	5.5
CsPb(Cl:Br:I) ₃	350	0.16	~0.1
CsPbBr ₂ Cl + TCN	350	0.23	33
CsPb(Cl:Br:I) ₃ + TCN	350	0.22	~0.2

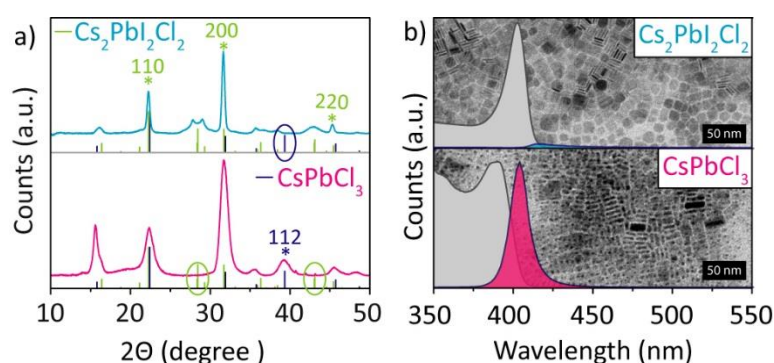


Figure S1. Additional data for Cs₂PbI₂Cl₂ and CsPbCl₃ NCs. (a) XRD patterns of for Cs₂PbI₂Cl₂ and CsPbCl₃ NCs, indicating several differences between the two phases, as well as the strong anisotropic growth indicated by the sharp [xy0] diffractions. (b) Absorption and PL of Cs₂PbI₂Cl₂ and CsPbCl₃ NCs, as well as their respective TEM images.

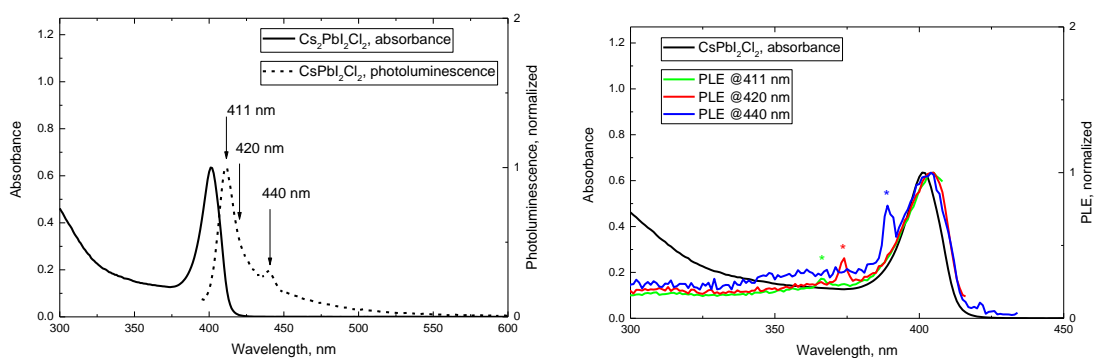


Figure S2. PLE spectra of the Cs₂PbI₂Cl₂ NC sample. **(left)** Steady-state absorption and photoluminescence spectra of Cs₂PbI₂Cl₂ NCs in toluene. Excitation 390 nm. Arrows mark positions on the photoluminescence spectrum at which PLE spectra were recorded. **(Right)** Overlaid steady-state absorption and PLE (recorded at 411 nm, 420 nm, and 440 nm, as indicated in the legend) spectra of Cs₂PbI₂Cl₂ NCs in toluene. Asterisks mark instrumental artifacts.

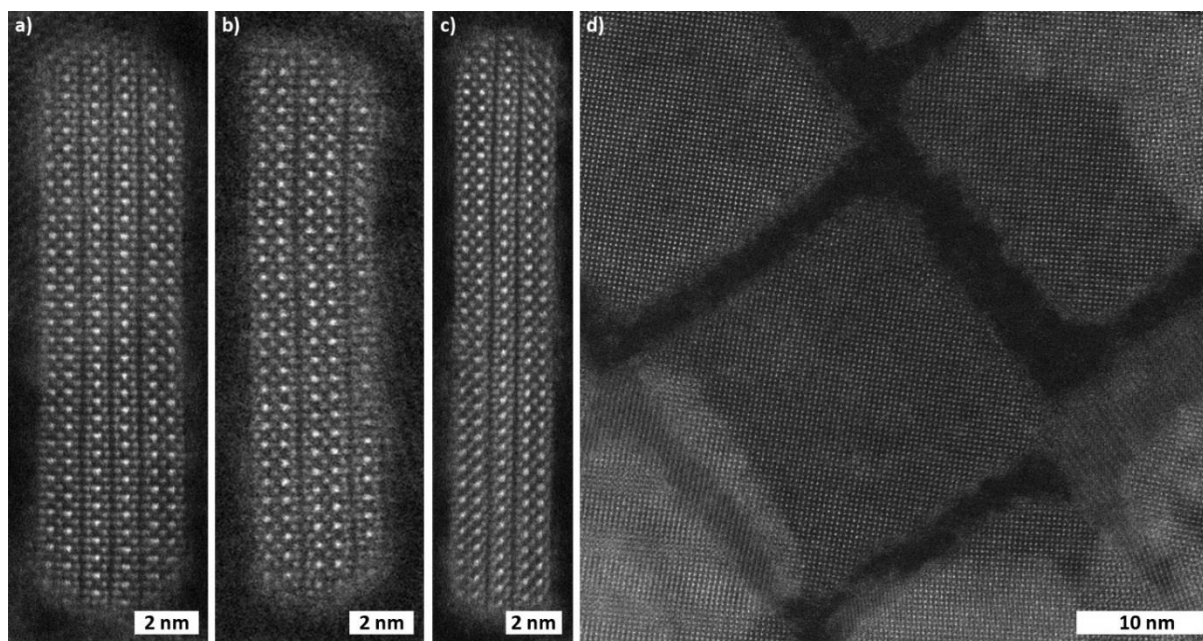


Figure S3. Additional HAADF-STEM images of Cs₂PbI₂Cl₂ NCs. (a-c) NCs observed from the side, laying perpendicular to the substrate. (d) NCs observed from the top, laying parallel to the substrate.

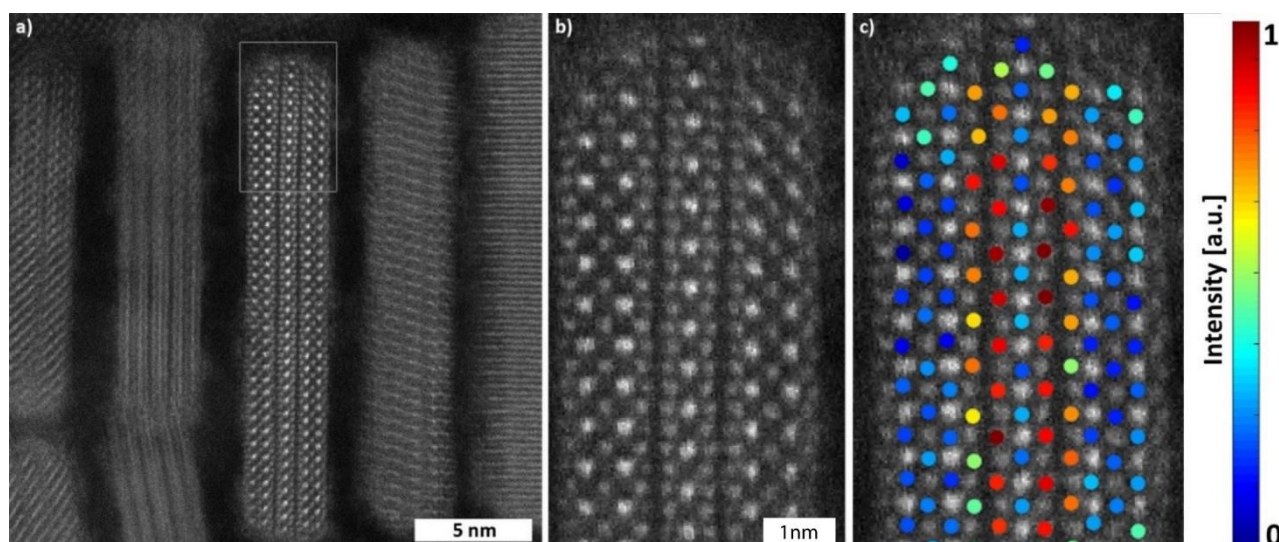


Figure S4. Additional StatTEM image of $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ NC laying perpendicular to substrate, indicating that the halide columns at the RPP interface consist of heavier halides, proving that these positions are indeed occupied by iodide halides.

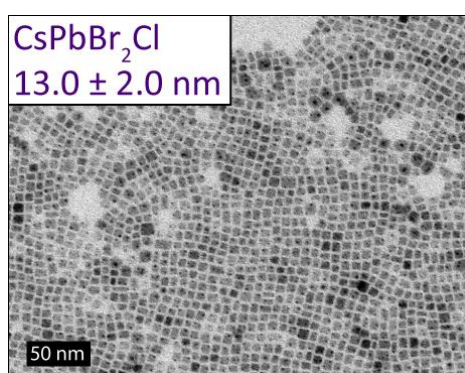


Figure S5. TEM image of CsPbBr_2Cl NCs with an average size of 13 nm.

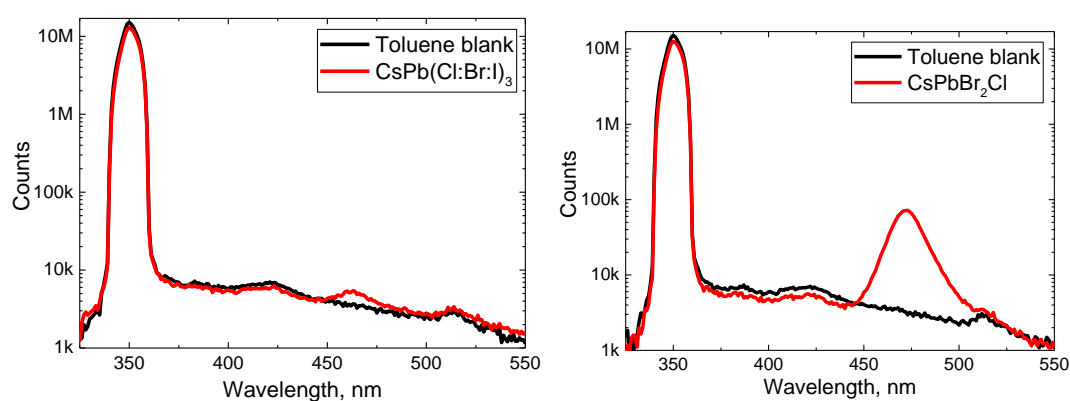


Figure S6. Photon number spectra of $\text{CsPb}(\text{Cl}:\text{Br}:\text{I})_3$ NCs (left panel, PLQY $\sim 0.1\%$) and CsPbBr_2Cl NCs (right panel, PLQY $\sim 5.5\%$) in toluene recorded in the integrating sphere under 350 nm excitation.

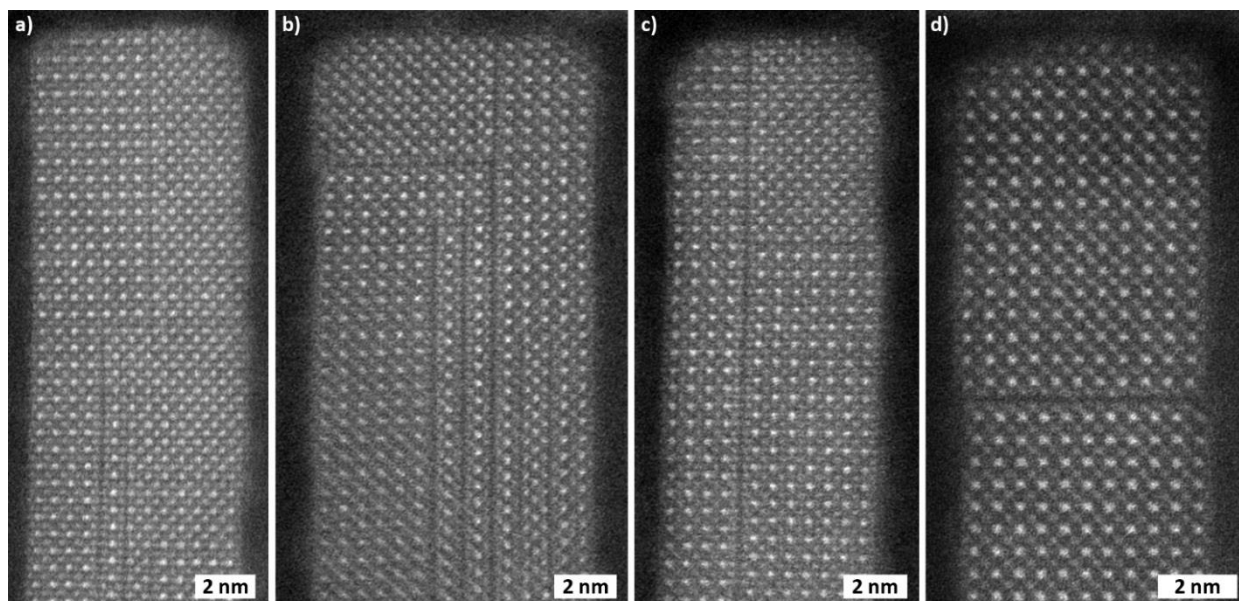


Figure S7. Several different observed RPP planes in $\text{CsPb}(\text{Cl}:\text{Br}:\text{I})_3$ NCs.

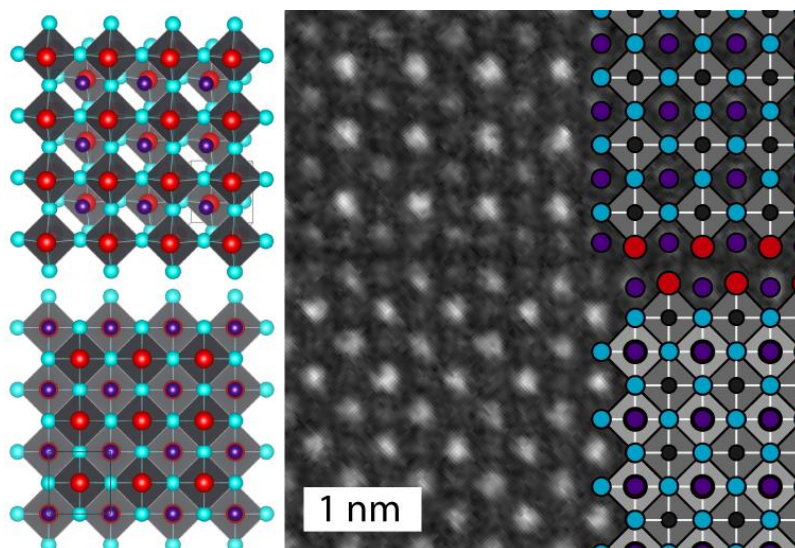


Figure S8. RPP plane observed from the z-axis resulting in the homogenization of the Pb-X and Cs columns.

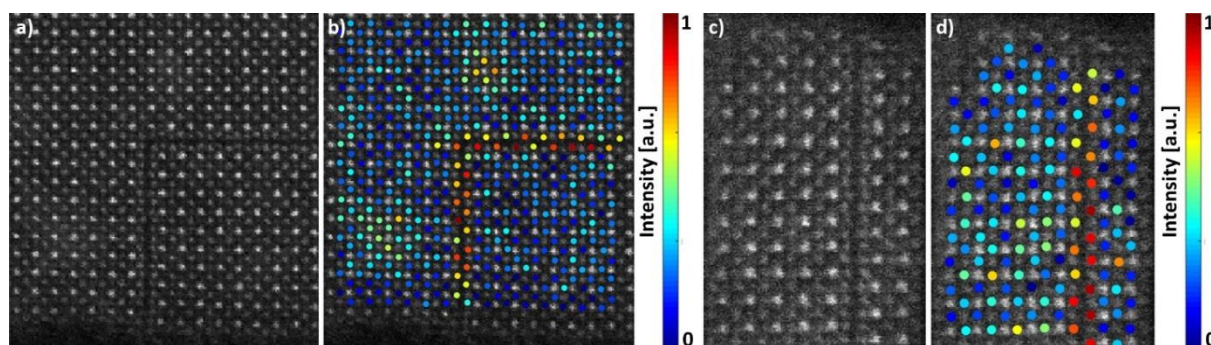


Figure S9. Additional StatSTEM images of $\text{CsPb}(\text{Cl}:\text{Br}:\text{I})_3$ NC confirming the agglomeration of iodide ions towards the RPP planes.

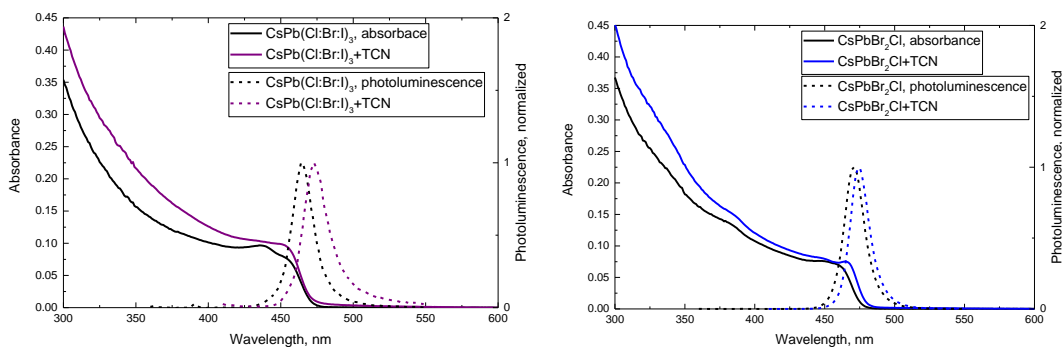


Figure S10. Steady-state absorption and photoluminescence spectra of (left) $\text{CsPb}(\text{Cl}:\text{Br}:\text{I})_3$ and $\text{CsPb}(\text{Cl}:\text{Br}:\text{I})_3$ + ammonium thiocyanate (TCN) NCs in toluene with excitation at 350 nm [$\text{CsPb}(\text{Cl}:\text{Br}:\text{I})_3$] and 400 nm [$\text{CsPb}(\text{Cl}:\text{Br}:\text{I})_3$ + TCN], and (right) CsPbBr_2Cl and CsPbBr_2Cl + TCN NCs in toluene with excitation at 350 nm.

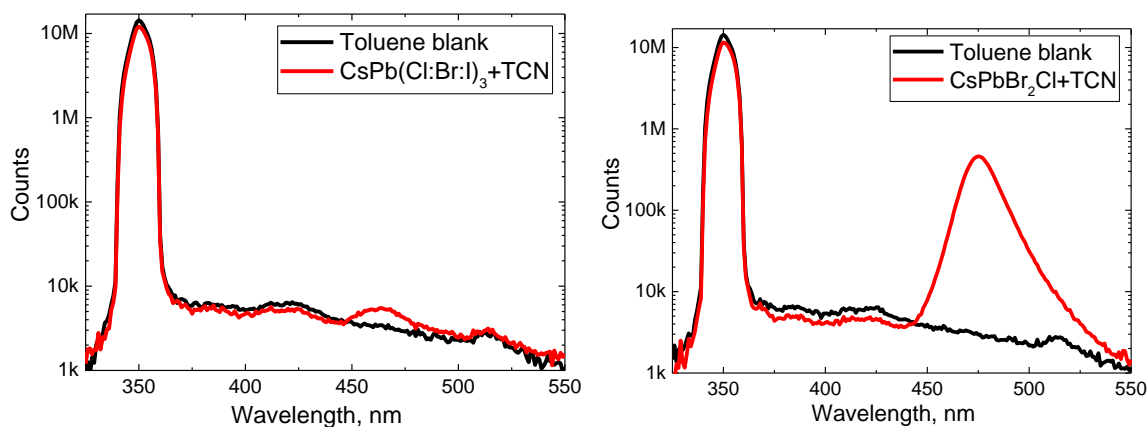


Figure S11. Photon number spectra of ammonium thiocyanate (+TCN) treated $\text{CsPb}(\text{Cl}:\text{Br}:\text{I})_3$ NCs (left panel, PLQY $\sim 0.2\%$) and CsPbBr_2Cl NCs (right panel, PLQY = 33%) NCs in toluene recorded in the integrating sphere under 350 nm excitation.

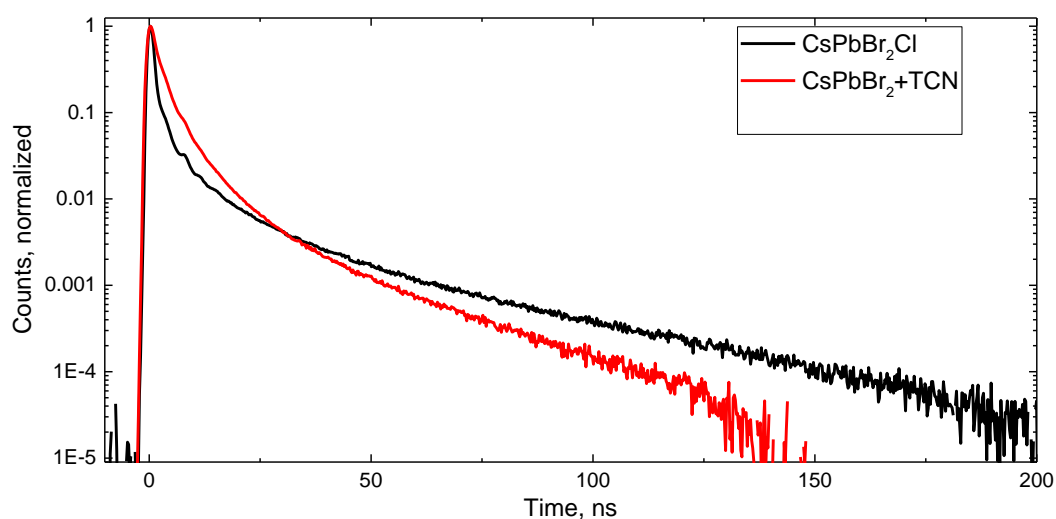


Figure S12. PL intensity decays for as-synthesized and thiocyanate-treated (+ TCN) samples of CsPbBr_2Cl NCs in toluene.

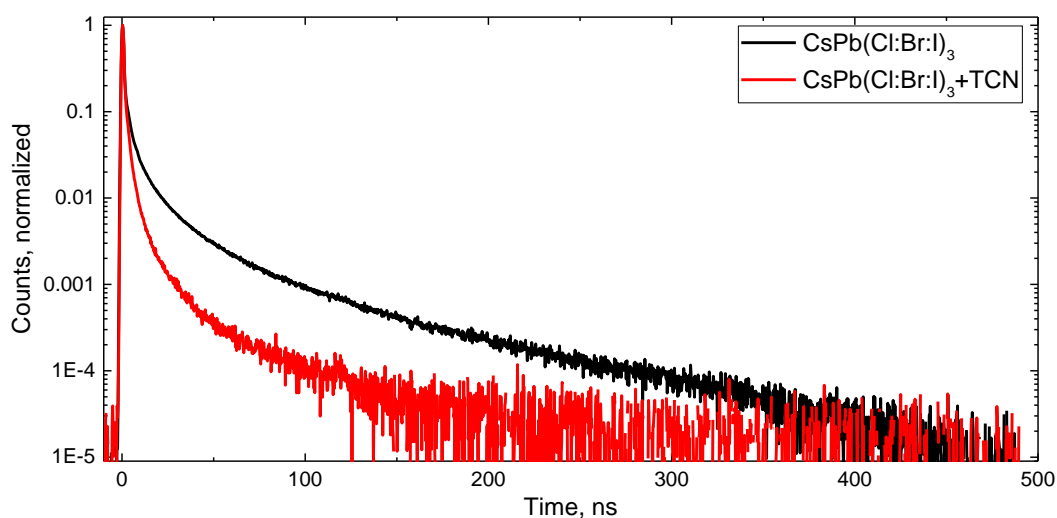


Figure S13. PL intensity decays for as-synthesized and thiocyanate-treated (+ TCN) samples of $\text{CsPb}(\text{Cl}:\text{Br}:\text{I})_3$ NCs in toluene.

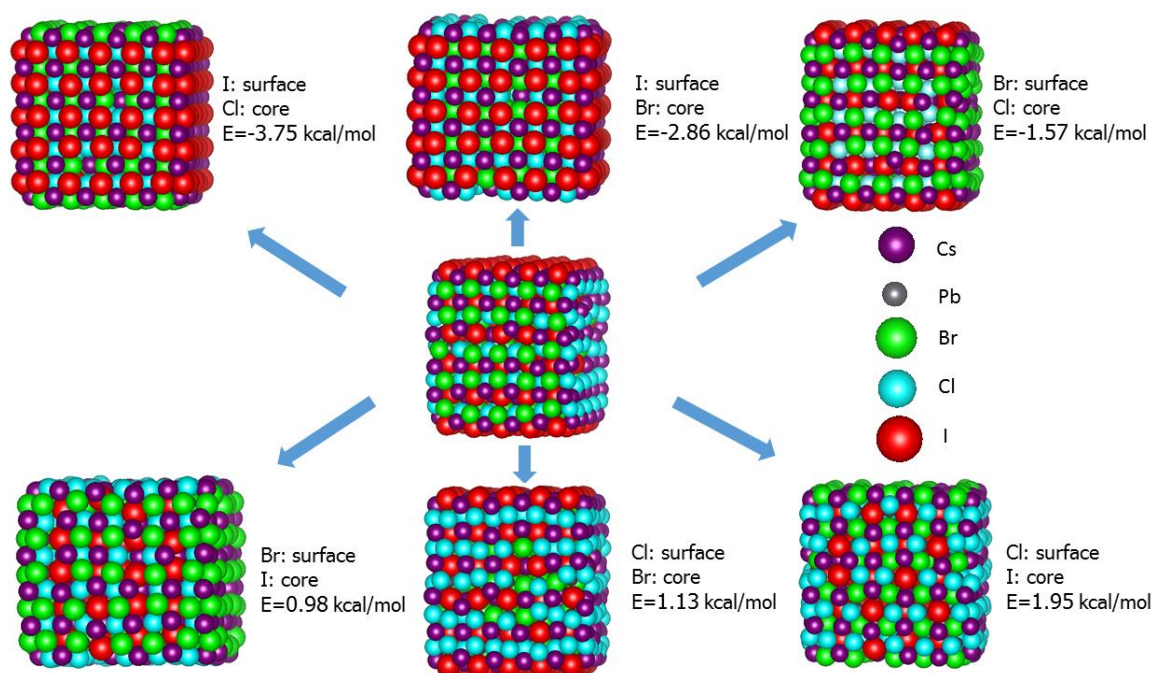


Figure S14. Relaxed structures used to study the diffusion of halogens in the crystal. All geometries were obtained at the DFT/PBE level of theory. In the central structure all three halogens are distributed uniformly through the NC. Starting from this configuration, we studied diffusion by exchanging 62 halogen atoms of one type with halogens of a second type, keeping the third type of halogen in its starting configuration. The swaps are carried out so that one type of halogen terminates four facets and the other type of halogen is confined at the core of the nanocrystal. The structures are ordered energetically, from left to right and from top to bottom, from the most to least stable. All structures have the same stoichiometry and their total energies can be compared. In the Figure we provide the energy per swap required to exchange one halogen type vs another type with respect to the reference (central) structure.