Over the past decade, lead halide perovskites (LHPs) have gained much interest in the materials science community owing to their outstanding optoelectronic properties. More recently, research has also expanded to include studies on colloidal LHP nanocrystals (NCs), especially cesium-based ones (CsPbX₃, with X = Cl, Br, I). This has resulted in the successful synthesis of NC samples with tunable compositions, great control over their size and shape, and the fabrication of several different types of LHP NC-based devices. One striking feature of LHP NCs is that they are easy to alloy and dope with other elements, which either improves their optical properties or causes a down-converted emission. For instance, several groups have extended the synthesis of LHP NCs to ternary compositions, such as CsPb(Cl:Br:I)₃, which allows the band gap to be precisely tuned from about 400–700 nm. As is the case in bulk LHPs, mixing Br⁻ with either Cl⁻ or I⁻ anions results in homogenous alloys with a well-defined band gap and narrow PL peak. The formation of homogenous alloys is made possible by small variations in the length of the ionic radius, which only decreases by 8% going from Br⁻ to Cl⁻ and increases by 12% from Br⁻ to I⁻. On the other hand, the difference in the length of the ionic radii between Cl⁻ and I⁻ is apparently too big (19%) to permit homogenous mixing. In the case of CsPbI₃ NCs, the alloying with Cl⁻ is limited to only a few percent. Interestingly, the incorporation of a small amount of Cl⁻ into MAPbI₃ (in which MA = methylammonium) thin films or CsPbI₃ NCs has been found to be beneficial in terms of increasing long-term stability and improving the optical properties. There have not been
any studies on mixing all three halides in LHP NCs, and there have been only few works on the bulk. 19

Here, we have synthesized and studied two types of halide mixing that have not previously been reported for NCs: Cs,Pb,Br,Cl NCs with a Cl/I feed ratio of 1:1 and CsPb(Cl:Br:I) NCs with a Cl/Br/I feed ratio of 1:1:1. In both these cases, the synthesized NCs are nanoplatelet-shaped. In the case of Cs,Pb,Br,Cl the NCs crystallize into a Ruddlesden–Popper phase (RPP), matching the one that previously investigated bulk Cs,Pb,Br,Cl. 20 Even though these NCs are relatively big (5 nm thick by 40 nm in the lateral dimensions), they exhibit an extremely confined excitonic absorption as a result of the individually separated Pb−Cl layers within the RPP. When the Cl/Br/I halides are mixed in a 1:1:1 ratio, perovskite NCs with an optical absorption and crystal lattice similar to those of Cs,Pb,Br,Cl NCs are obtained, and only a small amount of I− is incorporated into the NCs, as was confirmed by elemental analysis. These three halide NCs, however, have a very poor photoluminescence quantum yield (PLQY, well below 1%), which is significantly lower than that of CsPbBr,Cl NCs. By means of high-resolution high-angle annular scanning transmission electron microscopy (HAADF-STEM) analysis, it was found that the CsPb(Cl:Br:I) NCs predominantly crystallize in a perovskite crystal structure, but they contain several planar defects which could be identified as RPP planes. By combining a quantitative high-resolution HAADF-STEM analysis with density functional theory (DFT) calculations, we confirmed that the iodide anions are segregated from the pure LHP structure. Subsequently, they migrate to the RPP interface, forming RPP planes.

### EXPERIMENTAL SECTION

**Chemicals.** Cesium carbonate (Cs2CO3, 99%), lead(II) chloride (PbCl2, 99.99% trace metal basis), lead(II) bromide (PbBr2, 99.999% trace metal basis), ammonium thiocyanate (ATCN, 97.5%), oleylamine (OLAM, 98%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%), and toluene (TOL, 99% trace metal basis) (PbCl2, 98% trace metals basis), lead(II) iodide (PbI2, 99.999% trace metal basis), ammonium thiocyanate (ATCN, 97.5%), oleylamine (OLAM, 98%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%), and toluene (TOL, anhydrous, 99.8%) were purchased from Sigma-Aldrich. All chemicals were used as received, without any further purification.

**Synthesis of Cs,Pb,Br,Cl, CsPb(Cl:Br,I) NCs, CsPbBr,Cl, and Cs,Pb,Cl NCs.** The Cs,Pb,Br,Cl, CsPb(Cl:Br,I), CsPbBr,Cl, and Cs,Pb,Cl NCs were synthesized based on a hot plate synthesis that had previously been used to prepare Cs,Pb,X and CsPbBr,Cl NCs. 21,22 All syntheses were performed in air and without any predried chemicals or solvents. In a typical synthesis, PbX2 salts (in total 0.2 mmol, with 1:1 PbCl2/PbI2 for Cs,Pb,Br,Cl and Cs,PbBr,Cl, and 1:2 PbCl2/PbBr2 for Cs,Pb,Cl) were dissolved in 5 mL ODE, 0.125 mL OA, and 0.5 mL OLAM in a 20 mL vial on a hot plate set at 250 °C. When the temperature reached 185 °C (for CsPb(Cl:Br,I) and CsPbBr,Cl) or 165 °C (for Cs,Pb,Br,Cl), 0.5 mL of Cs−OA (0.4 g Cs2CO3 dissolved in 15 mL ODE) was quickly injected, and the reaction was swiftly injected, and the reaction was quickly cooled down with a cold water bath. The NCs were directly washed via centrifugation (at 6000 rpm for 10 min), followed by redispersion in 5 mL TOL. For high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD), the NCs were rinsed several times with TOL, as previously reported. 23

**Transmission Electron Microscopy.** Conventional TEM images were acquired on a JEOl JEM-1011 microscope equipped with a high-resolution gun at an accelerating voltage of 100 kV. The samples were prepared by drop-casting diluted NC solutions onto 200 mesh carbon-coated copper grids.

**Energy-Dispersive Spectroscopy.** STEM-EDS was performed on a JEOl JEM-2200FS microscope equipped with a Schottky emitter operating at 200 kV, a CEP0 spherical aberration corrector for the objective lens, an in-column energy filter (Omega-type), and a Bruker Quantax 400 EDS system with an XFlash 5060 detector.

**High-Resolution High-Angle Annular Dark-Field Imaging Scanning Transmission Electron Microscopy.** High-resolution HAADF-STEM images were acquired using a FEI Titan microscope operating at 300 kV. A probe semiconvergence angle of ~20 mrad was used. The quantitative HAADF-STEM analysis was performed using StatSTEM. 24 The intensity values of the halide-containing atomic columns are calculated by fitting a Gaussian function to each individual column. The intensity value equals the volume of the Gaussian peak.

**Powder XRD Analysis.** XRD patterns were obtained using a PANalytical Empyrean X-ray diffractometer equipped with a 1.8 kW Cu Kα ceramic X-ray tube and a PANalytical X’Pert MD 2 X 2 area detector operating at 45 kV and 40 mA. The diffraction patterns were collected in air at room temperature using parallel-beam geometry and symmetric reflection mode. All XRD samples were prepared by drop-casting a concentrated solution on a zero-diffraction quartz wafer.

**Steady-State Absorbance, Photoluminescence, and Photoluminescence Excitation Spectra.** Absorbance spectra from solutions of NCs were recorded using a Cary-300 spectrophotometer. The photoluminescence (PL) and PL excitation (PLE) spectra were recorded using a FLS920 Edinburgh Instruments spectroradiometer. Concentrated NC solutions were diluted with TOL in 4 mm × 10 mm quartz cuvettes, as described below.

**PLQY Measurements.** The PLQYs of as-synthesized and thioucyanate-treated Cs,Pb,Br,Cl and CsPb(Cl:Br:I) NCs were measured on freshly made samples using a FLS920 Edinburgh Instruments spectroradiometer equipped with an integrating sphere. The samples for PLQY were prepared in air by diluting 13−25 μL of the concentrated NC solutions with 1 mL of anhydrous TOL in 4 mm × 10 mm quartz cuvettes capped with white PTFE stops (Hellma Analytics, part number 114F-10-40). Dilutions were performed shortly before the measurements. The samples were excited at 350 nm using the xenon lamp (Xe900) with an excitation slit width set at 10 nm. The emission slit width was set at 0.40 nm. The cuvettes were oriented inside the sphere such that the excitation was through the 4 mm path length. The photon number spectra for the samples and TOL solvent reference were collected over the 325−550 nm spectral range with a step size of 1 nm, and a dwell time of 0.2 s per step. Five consecutive scans were added together to obtain the data for PLQY calculations. Corrections for the background, PMT detector sensitivity, and the lamp reference detector were applied automatically during the data collection by the software. For PLQY calculations, the photon number spectra were integrated in the range of 335−365 nm in order to determine the total number of scattered photons (sc photons), and in the ranges 435−500 nm (CsPbBr2Cl) or 435−500 nm [CsPb(Cl:Br:I)] to determine the total number of emitted photons (em photons). The values of PLQY were calculated using the following formula: PLQY, % = 100 × (Nsample − Nbackground) / Nsample. Report values with 1−2 significant figures.

**PL Lifetime Measurements.** Time-dependent PL intensity decays were measured after the PLQY measurements on the same samples using the time-correlated single-photon counting technique using a FLS920 Edinburgh Instruments spectroradiometer. The PL intensity decay curves are shown on a logarithmic scale. The samples were excited with a 401.2 nm picosecond pulsed diode laser (EPL-405, Edinburgh Instruments) and a 500 ns pulse period. The PL decays were collected at the peak of the emission spectra with an emission slit width of 3–5 nm.

**DFT Calculations.** All DFT calculations were performed using the CP2K quantum chemistry code, 25 employing the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional and double ξ basis set plus polarization functions. 26,27 Scalar relativistic effects have been incorporated with an effective core potential, while spin–orbit
coupling effects were not added in the calculations. Charge-balanced NC models were built according to previous receipt from some of us. Time-dependent calculations were carried out using the simplified Tamm–Dancoff approach that allows the simultaneous computation of hundreds of excited states. This methodology has been implemented within the QMflow-namd software package and is suitable to compute the optical absorption spectrum of the mixed lead halide model systems until approximately 4.0 eV.

## RESULTS AND DISCUSSION

The Cs$_2$PbI$_2$Cl$_2$ and CsPb(Cl:Br)I$_3$ NCs were synthesized based on the previously reported synthesis of CsPbBr$_3$ NC. Here, a Cs$^+$-oleate solution was injected into a solution of ODE, OLAM, and OA containing either 1:1 PbCl$_2$/$\text{PbI}_2$ or 1:1 PbCl$_2$/PbBr$_2$/$\text{PbI}_2$ (see the Supporting Information, for more details). In the case of a 1:1 ratio of PbCl$_2$/$\text{PbI}_2$, NCs that were about 4.2 ± 0.6 nm thick and 21 ± 3 nm wide were produced, as is shown in Figure 1a. As depicted in Figure 1b, these NCs crystallized in the RPP Cs$_2$PbI$_2$Cl$_2$ phase (K$_2$NiF$_4$-type phase), which consists of corner-sharing $[\text{PbI}_2\text{Cl}_4]^{4-}$ octahedra layers. In the Cs$_2$PbI$_2$Cl$_2$ phase, the Cl$^-$ ions occupy the equatorial halide sites and the I$^-$ ions occupy the axial halide sites, as is depicted in Figure 1c. Although the Cs$_2$PbI$_2$Cl$_2$ crystal lattice shares similar diffraction peaks with the CsPbCl$_3$ crystal lattice, it has several additional peaks, as is demonstrated in Figure S1a. Furthermore, because of the breaking of symmetry in the z direction of the lattice, the diffraction from the $\{112\}$ family of planes normally observed in CsPbCl$_3$ cannot be observed in the Cs$_2$PbI$_2$Cl$_2$ XRD pattern. As will be further discussed later on, the XRD pattern also confirmed that the NCs grow anisotropically, as several peaks, notably those of the $\{xy0\}$ plane family are significantly sharper than the other diffraction peaks. This further indicates that the NCs are essentially formed by stacked layers of corner-sharing $[\text{PbI}_2\text{Cl}_4]^{4-}$ octahedra which are charge-balanced by Cs$^+$ counterions. The strong confinement of carriers inside these single layers of lead chloride perovskites is also evident from the optical absorption spectrum, which is presented in Figure 1d. Here, the Cs$_2$PbI$_2$Cl$_2$ NCs exhibit a narrow excitonic absorption around 400 nm (3.1 eV), which matches a band gap of 3.04 eV that was reported by Kanatzidis’ group. This is a sharper absorption than that of CsPbCl$_3$ NCs (Figure S1b). However, the PL of the Cs$_2$PbI$_2$Cl$_2$ NCs is significantly broader than that of CsPbCl$_3$, NCs, and it exhibits a broad tail that is similar to what has been reported previously (Figure 1d). This broad PL was too weak to determine a PLQY, but the PLE, which is shown in Figures 1d and S2, matches the absorption, indicating that the broad asymmetric PL indeed originates from the Cs$_2$PbI$_2$Cl$_2$ NCs.

It is important to stress that, from the structural point of view, these “all-inorganic” RPP Cs$_2$PbI$_2$Cl$_2$ NCs are very different from the previously reported organic–inorganic RPPs (including organic–inorganic RPP NCs), in which bulky organic ligands act as spacers between the stacked lead halide layers [such as (BA)$_2$(MA)$_x$PbI$_{3x+1}$, with BA = butylammonium]. In our RPP Cs$_2$PbI$_2$Cl$_2$ NCs, the individual layers are not separated by bulky ligands (acting as cations) but rather by the large size difference of the Cl$^-$ and I$^-$ anions. Therefore, their periodicity along the stacking direction is much smaller than that of the organic–inorganic RPP phase. As a consequence, we do not observe low-angle XRD diffractions, originating from large periodicities along the stacking direction (Figure 1b). Our all-inorganic RPP Cs$_2$PbI$_2$Cl$_2$ NCs are also different from the ligand-passivated ultrathin two-dimensional LHP NCs (nanosheets and nanoplatelets), which can have thickness down to a few unit cells and thus can exhibit superstructure effects at low diffraction angles which arise from the stacking of the ligand-coated nanosheets on top of each other.

The Cs$_2$PbI$_2$Cl$_2$ NCs, even though they are coated with organic ligands, are too thick for such periodicities to be appreciated by low-angle XRD diffraction (see again Figure 1b). Finally, because the individual layers in these Cs$_2$PbI$_2$Cl$_2$ NCs are not separated by bulky ligands, the NCs are expected to have an electronic structure and optical properties that are significantly different from those of the organic–inorganic RPPs and of the ligand-coated ultrathin LHP nanosheets.

The crystal structure of the Cs$_2$PbI$_2$Cl$_2$ NCs was further studied via high-resolution HAADF-STEM imaging. The Cs$_2$PbI$_2$Cl$_2$ NCs were observed while they were lying parallel to the substrate, as can be seen in Figure 2a. Here, only slight intensity differences are present in the atomic columns in these NCs (Figure S1b). However, the PL of the Cs$_2$PbI$_2$Cl$_2$ NCs is much smaller than that of the organic–inorganic RPP phase. As a consequence, we do not observe low-angle XRD diffractions, originating from large periodicities along the stacking direction (Figure 1b).

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Optical and structural data of Cs$_2$PbI$_2$Cl$_2$ NCs. (a) TEM image of monodisperse Cs$_2$PbI$_2$Cl$_2$ NCs. (b) XRD pattern of Cs$_2$PbI$_2$Cl$_2$ NCs matching that of bulk Cs$_2$PbI$_2$Cl$_2$. (c) Crystal structure of Cs$_2$PbI$_2$Cl$_2$ RPP. (d) Strong excitonic absorption from Cs$_2$PbI$_2$Cl$_2$ and broad PL of Cs$_2$PbI$_2$Cl$_2$ NCs. PLE spectra of Cs$_2$PbI$_2$Cl$_2$ NCs (red line, recorded at 411 nm) overlapping with the absorption spectrum, indicating that the PL originates from Cs$_2$PbI$_2$Cl$_2$. The asterisk marks the instrumental artifact. XRD reference patterns correspond to ref 20.
Cs$_2$Pb$_2$I$_5$Cl$_2$ (see the bottom part of Figures 2d as well as S3a–c).

To further prove that the I$^-$ ions occupy the axial halide sites, and that the Cl$^-$ ions occupy the equatorial (perovskite) halide sites (see Figure 1c), we performed a quantitative high-resolution HAADF-STEM analysis. Using StatSTEM, we calculated the intensities of the halide atomic columns by fitting a Gaussian function to each individual atomic column, calculating the alternating layers of the RPP. Figure 2c shows a Cs$_2$Pb$_2$I$_5$Cl$_2$ NC that is parallel to the substrate, within the inset, a highlighted view of the atomic arrangement. (b) Side view of a Cs$_2$Pb$_2$I$_5$Cl$_2$ NC, which clearly matches the alternating layers of the RPP. (c) Volume of the fitted Gaussian peaks of the halide columns of the NC as shown in Figure 2b. The significant increase in the intensity values measured at the axial positions matches the expected iodide positions. (d) Cs$_2$Pb$_2$I$_5$Cl$_2$ NC observed perpendicular to the substrate overlaid with the crystal structure of Cs$_2$PbI$_2$Cl$_2$ (Cs$^+$ = purple, Pb$^{2+}$ = black, Cl$^-$ = blue, I$^-$ = red, and [PbI$_2$Cl$_4$]$^{2-}$ octahedra = gray), indicating a single layer of Cs$_2$Pb$_2$I$_5$Cl$_2$ in between two bilayers of Cs$_2$PbI$_2$Cl$_2$. For additional HAADF-STEM data, see Figures S3 and S4.

Figure 3. Overview of structural and optical data of CsPb(Cl:Br:I)$_3$ NCs. (a) TEM image of CsPb(Cl:Br:I)$_3$ NCs. (b) XRD pattern of CsPb(Cl:Br:I)$_3$ NCs that matches that of CsPbBr$_2$Cl NCs. (c) Optical properties of CsPb(Cl:Br:I)$_3$ NCs, evidencing an absorption edge at around 460 nm and a weak but narrow emission around 470 nm, matching the same band gap of CsPbBr$_2$Cl NCs. (d) Absorption-corrected PL of CsPb(Cl:Br:I)$_3$ NCs compared to brightly emitting CsPbBr$_2$Cl NCs, with a photo of CsPbBr$_2$Cl and CsPb(Cl:Br:I)$_3$ NCs under UV excitation, showing no visible PL for the CsPb(Cl:Br:I)$_3$ NCs. CsPbBr$_2$Cl (cubic) and CsPbBr$_2$Cl (orthorhombic) XRD reference patterns correspond to 98-002-9076 and 96-451-0746.

To further study the crystal lattice of these CsPb(Cl:Br:I)$_3$ NCs, and to further understand why their PLQY is so low, we used all three halides (Cl, Br, and I) in the synthesis of LHP NCs. As is shown in Figure 3a, this combination resulted in NCs with lateral dimensions of approximately 13 nm and thicknesses of about 5 nm. Different to the Cs$_x$Pb$_x$I$_x$NCs, the CsPb(Cl:Br:I)$_3$ NCs crystallized in the perovskite crystal lattice, with a lattice spacing of about 5.8 Å, which matches that of CsPbBr$_2$Cl NCs (see Figures 3b and S5). Furthermore, the CsPb(Cl:Br:I)$_3$ NCs have an absorption edge (around 460 nm) and PL peak (around 470 nm) that are similar to those of CsPbBr$_2$Cl NCs. The optical properties of CsPb(Cl:Br:I)$_3$ NCs that matches that of CsPbBr$_2$Cl NCs. (c) Optical properties of CsPb(Cl:Br:I)$_3$ NCs, evidencing an absorption edge at around 460 nm and a weak but narrow emission around 470 nm, matching the same band gap of CsPbBr$_2$Cl NCs. (d) Absorption-corrected PL of CsPb(Cl:Br:I)$_3$ NCs compared to brightly emitting CsPbBr$_2$Cl NCs, with a photo of CsPbBr$_2$Cl and CsPb(Cl:Br:I)$_3$ NCs under UV excitation, showing no visible PL for the CsPb(Cl:Br:I)$_3$ NCs. CsPbBr$_2$Cl (cubic) and CsPbBr$_2$Cl (orthorhombic) XRD reference patterns correspond to 98-002-9076 and 96-451-0746.

For the second type of halide alloying that we investigated, we used all three halides (Cl, Br, and I) in the synthesis of LHP NCs. As is shown in Figure 3a, this combination resulted in
Figure 4. HAADF-STEM analysis of Cs(Cl:Br:I)₃ NCs. HAADF-STEM images of Cs(Cl:Br:I)₃ NCs, showing (a) the perovskite lattice and (b,c) NCs with several plane shifts. (d) Volume of the fitted Gaussian peaks of the halide columns of the NC as shown in (c) indicates increased intensity values of the halide columns around the RPP planes, confirming an increased concentration of iodide ions at these positions. (e) RPP plane shift model (Cs⁺ = purple, Pb²⁺ = black, Cl⁻/Br⁻ = blue, I⁻ = red, and PbX₆ octahedra = gray) overlapping an HAADF-STEM image of a CsPb(Cl:Br:1)₃ NC. For additional HAADF-STEM data, see Figures S7–S9.
performed a high-resolution HAADF-STEM analysis. As is reported in Figure 4a, the CsPb(Cl:Br:I)\textsubscript{3} NCs consist predominantly of a perovskite crystal structure with a lattice spacing of (5.9 ± 0.1) Å, which is in agreement with the XRD measurements. Large grain boundaries were observed in many of the CsPb(Cl:Br:I)\textsubscript{3} NCs, as is shown in Figures 4b and S7. These grain boundaries are made of shifted lattice planes over half of the unit cell along the [100] planes. These types of lattice shifts are similar to those of the Cs\textsubscript{2}PbI\textsubscript{4}Cl\textsubscript{2} RPP NCs but consist of only a single-shifted plane between two layers of 3D perovskites. The same was observed in large CsPbBr\textsubscript{3} nanosheets, which sometimes contained RPPs caused by the alternating layers of a RPP, as is shown in Figure 5a. All halide atoms at the RPP boundary were then replaced by iodine, while the CsI unit was kept constant, as is highlighted in a different color. (c) Absorption spectrum of CsPbBr\textsubscript{2}Cl and CsPb(Cl:Br:I)\textsubscript{3} NCs. (a) Relaxed CsPbBr\textsubscript{2}Cl structures (left) and CsPb(Cl:Br:I)\textsubscript{3} structures (right) shown from different directions and computed at the DFT/PBE levels of theory. (b) Electronic structure near the conduction and valence band regions. Each molecular orbital is decomposed in terms of atomic type contributions and is highlighted in a different color. (c) Absorption spectrum of each system computed using the simplified time-dependent (TDDFT/PBE) methodology.

Figure 5. DFT studies performed on the CsPbBr\textsubscript{2}Cl and CsPb(Cl:Br:I)\textsubscript{3} NCs. (a) Relaxed CsPbBr\textsubscript{2}Cl structures (left) and CsPb(Cl:Br:I)\textsubscript{3} structures (right) shown from different directions and computed at the DFT/PBE levels of theory. (b) Electronic structure near the conduction and valence band regions. Each molecular orbital is decomposed in terms of atomic type contributions and is highlighted in a different color. (c) Absorption spectrum of each system computed using the simplified time-dependent (TDDFT/PBE) methodology.

In some cases, the formation of RPP planes can also be observed from the [001] direction, as can be seen in Figure S8. If the lattice shift is located in the middle of the NCs, half of the crystal is shifted, which leads to mixed Pb and Cs atomic columns with equal amounts of Pb and Cs throughout the atomic columns. Thus, the RPP shift results in averaging of the Pb and Cs intensities in the Pb- and Cs-containing columns, which leads to comparable intensity values because not all-Cs or all-Pb atomic columns are present. This was observed for several NCs, which exhibited regions which did not show separate different intensities for Pb–X and Cs columns but rather only columns with a comparable intensity. This is not caused by the alternating layers of a RPP, as is shown in Figure 2b,d but by a single RPP plane shift. The same was observed in large CsPbBr\textsubscript{3} nanosheets, which sometimes contained RPP domains. Because the iodide ions tend to occupy the axial halide positions in the RPP Cs\textsubscript{2}PbI\textsubscript{4}Cl\textsubscript{2} phase, it is likely that the small amount of incorporated iodine species in the CsPb(Cl:Br:I)\textsubscript{3} NCs are segregated at the RPP halide positions. To confirm that the iodide halides segregate at the RPP, we again performed a quantitative high-resolution HAADF-STEM analysis to investigate the intensities of the halide columns using StatSTEM, and we found that all the halide columns that are directly positioned in the RPP exhibit significantly higher intensities compared to those outside the RPP planes (see Figures 4c,d and S9). This indicates that the iodide halides do tend to segregate into the RPP planes. This is in accordance with the small amount of iodide that was observed in the elemental analysis, but the NCs generally have the same properties as CsPbBr\textsubscript{2}Cl NCs.

To identify whether the PL quenching originates from the presence of RPP planes in the inorganic cores of the CsPb(Cl:Br:I)\textsubscript{3} NCs, or is mainly related to surface trapping effects, the NCs were subjected to a surface treatment that is in accordance with the small amount of iodide that was observed in the XPS measurements. Large CsPbBr\textsubscript{2}Cl NCs before, but they originated from a post synthesis treatment on the CsPb(Cl:Br:I)\textsubscript{3} NCs, as is shown in Figures 4b and S7. Measurements. Large grain boundaries were observed in many of the CsPb(Cl:Br:I)\textsubscript{3} NCs, as is shown in Figures 4b and S7. These grain boundaries are made of shifted lattice planes over half of the unit cell along the [100] planes. These types of lattice shifts are similar to those of the Cs\textsubscript{2}PbI\textsubscript{4}Cl\textsubscript{2} RPP NCs but consist of only a single-shifted plane between two layers of 3D perovskites. The same was observed in large CsPbBr\textsubscript{3} nanosheets, which sometimes contained RPPs caused by the alternating layers of a RPP, as is shown in Figure 5a. All halide atoms at the RPP boundary were then replaced by iodine, while the CsI unit was kept constant, as is highlighted in a different color. (c) Absorption spectrum of each system computed using the simplified time-dependent (TDDFT/PBE) methodology.
meV below. This behavior is surprising because the iodine orbitals are expected to contribute at higher energies compared to the other halides. This effect, however, can be explained by the lack of the PbX₂ layer at the RPP interface that breaks the connection between the corner edge octahedra, lifting their electronic connection. This tells us that the interface resembles rather a wide band gap CsI structure, with the iodine orbitals pushed below the valence band edge. 49 This configuration, however, discards the idea that the segregation of iodine at the RPP interface alone localizes the hole carrier at the RPP interface, reducing the electron–hole overlap, and thus the emission efficiency. A most likely explanation to the loss of PLQY is that the RPP interface itself is defective, presumably due to some halide vacancies, which could form deep traps in the core region of the NCs that cannot be directly accessed postsynthetically via a surface treatment.

We also computed the optical spectrum of the CsPbBr₂Cl and CsPb(Cl:Br:I)₃ NCs at a time-dependent DFT level of theory, analyzing the lowest 700 electronically excited states (Figure 5c). This revealed that the triple halide system maintains excitonic features in the band gap region, which is in agreement with our experiments.

To understand how the presence of the three types of halide atoms at different locations in the perovskite lattice can lead to iodine segregation at the RPP interface, we studied several isomeric CsPb(Cl:Br:I)₃ NC structures with equal amounts of the three halogen atoms with DFT. First, we designed a symmetric NC which was built from a CsPb(Cl:Br:I)₃ unit cell that was replicated evenly along the three axes by 2 unit cells (the size of the NC was about 3 nm). Using this configuration as a point of reference, we then swapped, for example, the chloride ions at the surface with the iodide ions that are present in the core so as to provide a qualitative picture of the diffusion of this latter ion type to the surface. The difference in the total energy of this structure compared to the one used as a point of reference provides us with a rough estimate of the likelihood that segregation will occur. An inspection of the DFT data shows that the segregation of iodide ions into the surface leads to an overall stabilization with respect to the likelihood that segregation will occur. The presence of iodine in the CsPb(Cl:Br:I)₃ NCs, even in very small amounts, systematically produces the RPP type shifts because of its size difference with respect to the other halides in the structure. Thus, these ions migrate outward and fill the halide positions at the plane interfaces. This work thus expands the list of LHP NCs consisting of multiple anions, a list that is strongly limited by the structural constraints imposed by size differences between the different anions. These new types of lead halide NCs will deserve further scrutiny in terms of mechanism of their formation, optoelectronic properties, as well as their use in optoelectronic applications. For instance, the Cs₂PbI₂Cl₂ NCs, because of their incorporation of heavy iodide ions, should be suitable for alpha particle detection, but at the same time, unlike the classical iodide perovskites, they do not absorb much in the visible region of the spectrum. 50 Furthermore, the Cs₃PbI₅Cl NCs could be the predecessors of other interesting RPP NCs, such as mixed halide–pseudo halide Cs₂PbI₂(thiocyanate) NCs. 50 Although the reported NCs in this work exhibit low PLQYS, they could be exploited for photodetectors. Finally, the reported NCs in this work may act potential hosts for various dopant atoms, with emission properties that could be different from those of doped halide perovskite NCs.

ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.9b00489.

Additional details including XRD patterns, TEM images, and PL and absorption spectra of CsPbCl₃ and CsPbBr₂Cl NCs; PLE data from Cs₃PbI₂Cl₂ NCs; PLQY data on CsPb(Cl:Br:I)₃ and CsPbBr₂Cl NCs; additional HAADF-STEM images and StatSTEM data; and surface treatment data from CsPb(Cl:Br:I)₃ and CsPbBr₂Cl NCs (PDF)

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Notes
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