Alloy CsCd$_x$Pb$_{1-x}$Br$_3$ Perovskite Nanocrystals: The Role of Surface Passivation in Preserving Composition and Blue Emission

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**ABSTRACT:** Various strategies have been proposed to engineer the band gap of metal halide perovskite nanocrystals (NCs) while preserving their structure and composition and thus ensuring spectral stability of the emission color. An aspect that has only been marginally investigated is how the type of surface passivation influences the structural/color stability of AMX$_3$ perovskite NCs composed of two different M$^{2+}$ cations. Here, we report the synthesis of blue-emitting Cs-oleate capped CsCd$_x$Pb$_{1-x}$Br$_3$ NCs, which exhibit a cubic perovskite phase containing also Cd-rich domains of Ruddlesden-Popper phases (RP-phases). The RP domains spontaneously transform into pure orthorhombic perovskite ones upon NC ageing and the emission color of the NCs shifts from blue to green over days. On the other hand, post-synthesis ligand exchange with various Cs-carboxylate or ammonium bromide salts, right after NC synthesis, provides monocrystalline NCs with cubic phase, highlighting the metastability of the RP domains. When the NCs are treated with Cs-carboxylates (including Cs-oleate), most of the Cd$^{2+}$ ions are expelled from the NCs, the NCs’ phase evolves from cubic to orthorhombic and their emission color changes from blue to green. Instead, when the NCs are coated with ammonium bromides, the loss of Cd$^{2+}$ ions is suppressed and the NCs tend to retain their blue emission (both in colloidal dispersions and in electroluminescent devices), as well as their cubic phase, over time. The improved compositional and structural stability in these latter cases is ascribed to the saturation of surface vacancies, which may act as channels for the expulsion of Cd$^{2+}$ ions from the NCs.

Halide perovskite nanocrystals (NCs) exhibit many exciting optical properties, such as near-unity photoluminescence quantum yield (PLQY), narrow emission line widths and band gap tunability. The latter can be achieved by regulating the size of the NCs and/or by adjusting their chemical composition. Unfortunately, (and contrary to more traditional semiconductor NCs, such as CdSe) halide perovskite NCs have much lower colloidal stability, and small NCs, with sizes around 4-5 nm or below, are very unstable. To take the case of CsPbBr$_3$, as an example, 4-5 nm size NCs of this material have blue photoluminescence (PL), but their rapid coalescence and ripening, even when they are deposited in dry films, makes their emission shift toward the green. Tuning the emission color by adjustments in the chemical composition comes with its own shortcomings as well. Mixed halide anion compositions, for instance APb(BrCl)$_3$, or APb(BrI)$_3$ (here A is typically Cs$, methylammonium or formamidinium and also as bulk crystals, tend to undergo halide segregation under conditions such an electrical potential bias or high irradiation flux, and their emission color changes with time.
Even perovskites with mixed A or B cation composition undergo cation segregation. Recent studies have shown that divalent cation (Mn$^{2+}$) substitution leads to the formation of Ruddlesden-Popper (RP) phases in Mn-doped CsPbCl$_3$ NCs. Mixed cation strategies based on alloying univalent or divalent cations have been widely used in polycrystalline thin films, to enhance the stability and power conversion efficiency of solar cells. Also in those cases, the resulting polycrystalline films are prone to ion segregation. Various studies on thin-films have revealed that ion migration (both cation and anion) is dominant at the grain boundaries and can be significantly reduced by efficient grain boundary passivation. In comparison, the impact of surface coatings on the ion segregation, phase homogeneity and color stability remains unclear for the NCs counterpart.

In the present work, we synthesize blue emitting CsCd$_{1-x}$Pb$_{x}$Br$_3$ NCs and show that the as-prepared NCs, which are coated with Cs-oleate ligands (one of the standard ligand shells they have as they are delivered from a typical synthesis) are spectrally unstable and evolve into green emitting NCs upon ageing. Atomically resolved high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) reveals that the as-synthesized NCs are not structurally uniform: in addition to the perovskite phase, these NCs also contain Ruddlesden-Popper (RP) phases. This phase heterogeneity likely emerges at the synthesis step. We also demonstrate that Cd$^{2+}$ ions, although distributed in the whole NCs, tend to accumulate in the RP domains by contracting the lattice parameters in those regions (Scheme 1, sketch-a). Over ageing, the RP regions undergo a transition to the perovskite phase and the NCs become monocrystalline. The same transition is accelerated when the NCs are treated, post-synthesis, with Cs-carboxylates (such as Cs-oleate or Cs-phenylacetate) or with various alkyl/arylammonium salts (Scheme 1, sketches b and c). Apparently, these RP domains form a metastable state that, thanks to the softness of the NC lattice, can structurally reorganize easily.

**Scheme 1. Structural/compositional evolution of perovskite CsCd$_{1-x}$Pb$_x$Br$_3$ NCs coated with Cs-carboxylate ligands (a, b) or with ammonium bromide ligands (c). The specific CsCd$_{0.25}$Pb$_{0.75}$Br$_3$ case is amply studied in this work.**

Upon ageing, two different fates are observed for the NCs depending on their surface ligands composition: (1) both the pristine sample (i.e. not treated post-synthesis with ligands) and the Cs-carboxylate treated samples expel most of the Cd$^{2+}$ ions, likely due to an unstable surface ligand passivation of the NCs under such circumstances. This loss of Cd$^{2+}$ ions leads to a phase transformation of the NCs from cubic perovskite to orthorhombic perovskite and to a shift in the emission color from blue to green (Scheme 1, sketches a and b); (2) when the NCs are treated with primary or quaternary ammonium bromide ligands, they retain a uniform cubic CsCd$_{1-x}$Pb$_x$Br$_3$ perovskite phase, from which Cd$^{2+}$ ions are not expelled, so that they are able to preserve their blue emission over time both in colloidal dispersions and in electroluminescent devices (Scheme 1, sketches-c). A likely explanation for this structural (and emission color) stability is that ammonium bromide ligands are better able to saturate the surface AX vacancies, and this suppresses a potential channel for the expulsion of Cd$^{2+}$ ions from the NCs.

**EXPERIMENTAL SECTION**

**Chemicals.** Cadmium acetate dehydrate ((CdAc$_2$·2H$_2$O), 99.99%), Lead acetate trihydrate ((PbAc$_2$·3H$_2$O), 99.99%), cesium carbonate (Cs$_2$CO$_3$, reagent Plus, 99%), benzoyle bromide (C$_6$H$_5$COBr, 97%), ethyl acetate (98.8%), toluene (anhydrous, 99.5%), phene-
thylammonium bromide (≥98%) Didodecylidimethylammonium bromide (DDABr), octadecene (ODE, technical grade, 96%), dimethyl sulfoxide-d6 (DMSO, 99 atom. % D) toluene-d8 (99 atom. % D), oleic acid (OA, 90%), ITO patterned substrates, polystyrene sulphonate (PEDOT:PSS, AL 4083), poly (N,N₂-bis(4-butylphenyl)-N,N₂-bis(phenyl)-benzidine) (poly-TPD) and 2,2',2''-1,3,5-Benzenetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) were acquired from Ossila Ltd. Poly(9-vinylcarbazole) (PVK) and LiF were purchased from Sigma-Aldrich. Diodocelamine (97%) was purchased from TCI. Oleic acid was dried at 120 °C for an hour and stored in a nitrogen filled glove box. All other chemicals were used with no further purification.

Preparation of oleylammonium bromide: Oleylammonium bromide was prepared by reacting HBr with the corresponding oleyl amines in ethanol at 0° C. Briefly, 50 mL of ethanol and 19 mmol of oleylamine were mixed in a 100 mL 2-neck flask and vigorously stirred. This mixture was cooled down in an ice-water bath, then 4.28 mL of HBr were added to it and the resulting mixture was allowed to react for 10 hours under N₂ flow. Then the solution was dried under vacuum and the solid product was purified by rinsing it with diethyl ether at least 3 times. The white precipitate was then dried overnight in vacuum oven at 40° C and stored in the glove box for further use.

Synthesis of CsCdₓPb₁₋ₓBr₃ NCs. Cs-oleate capped NCs were prepared following our previously reported secondary amine based synthesis. To synthesize CsCdₓPb₁₋ₓBr₃ NCs with various Cd²⁺ to Pb²⁺ ratios, lead acetate trihydrate (PbAc₂·3H₂O) was partially substituted with cadmium acetate dihydrate (CdAc₂·2H₂O) in a direct synthesis (see Table 1 for the details on feed ratios of cadmium and lead precursors). Briefly, 1.5 mmol of divalent cation precursors (CdAc₂·2H₂O + PbAc₂·3H₂O), 10 mg of cesium carbonate and 10 mL of octadecene were combined in a 25 mL 3-neck flask equipped with a thermocouple and a magnetic stirrer. The reaction mixture was degassed at room temperature for 5 minutes and under vacuum at 115°C for 30 min and then filled with N₂. Then, the ligand mixture containing 1 mL of pre-dried OA, 300 mg of didodecylamine dissolved in 1 mL of anhydrous toluene was rapidly injected. After the complete dissolution of the metal precursors, the temperature of the reaction mixture was decreased to 70 °C and 50 µL of a benzoyl bromide precursor diluted in 500 µL of anhydrous toluene was then injected into the mixture. After 45 s, the reaction mixture was cooled down to room temperature with an ice-water bath. Thereafter, 12 mL of anhydrous ethyl acetate was added into the crude solution and centrifuged at 12000 round per minute (r.p.m.) for 10 min. The precipitate was re-dispersed in 5 mL of toluene for further use.

Table 1. Reaction conditions for the synthesis of CsCdₓPb₁₋ₓBr₃ NCs (stoichiometries are estimated via SEM EDS)

| NC stoichiometry | Metal precursors (M⁺) used in the synthesis (mmol) | PL peak (nm) | PL line (nm) |
|-----------------|-----------------------------------------------|-------------|-------------|
| CsPbBr₃         | 0.025                                        | 507          | 16          |
| CsCdₐ₋ₓPb₁₋ₓBr₃ | 0.05                                         | 496          | 18          |
| CsCdₐ₋ₓPb₁₋ₓBr₃ | 0.075                                        | 484          | 20          |
| CsCdₐ₋ₓPb₁₋ₓBr₃ | 0.1                                          | 476          | 24          |
| CsCdBr₃ (main product) | 0.125                                    | Non- emissive |

Ligand Exchange. For the ligand exchange reactions, the crude solution of NC was divided into 6 parts (2 mL each). One fraction was purified as it is and was used as a reference (pristine samples). Each of the remaining fractions was mixed with a toluene solution containing the ligands (Cs-oleate, Cs-phenylacetae, oleylammonium bromide, phenethylammonium bromide, didodecylidimethylammonium bromide) 2 mL, 50 mM) and the resulting mixture was vigorously stirred for 2 min. Thereafter, the NCs were washed with ethyl acetate (10 mL) or methyl acetate and re-dispersed in 5 mL of anhydrous toluene. The toluene dispersion of the NCs was centrifuged once again (at 6000 rpm for 10 minutes), the colloidal unstable fraction was discarded and the supernatant was collected for further use.

X-ray diffraction (XRD) characterization. The XRD analysis was performed on a PANalytical Empyrean X-ray diffractometer, equipped with a 1.8 kW CuKα ceramic X-ray tube, operating at 45 kV and 40 mA, and a PIXcel® 2x2 area detector. To avoid preferred orientation effect, the concentrated dispersions of NCs were mixed with fumed silica powder prior to their deposition on zero-diffraction silicon substrate. All the diffraction patterns reported here were collected at room temperature under ambient conditions using parallel beam geometry and symmetric reflection mode. Post-acquisition XRD data analysis was carried out using the HighScore 4.1 software from PANalytical.

Transmission Electron Microscopy (TEM) characterization. Bright field TEM images of the NC samples were acquired with a JEOL-1100 transmission electron microscope operating at an acceleration voltage of 100 kV. Samples were prepared by drop casting diluted solutions of NCs onto carbon film-coated 200 mesh copper grids for low-resolution TEM.

High resolution High Angle Annular Dark Field Scanning Transmission Electron Microscopy characterization. High resolution HAADF-STEM images were acquired with a probe-corrected cubed FEI Titan Microscope operating at 300 kV with a probe semi-convergence angle of 20.5 mrad. Qualitative analyses of column intensities and column-to-column distances were performed using StatSTEM. The total scattered intensity and location of all atomic columns were determined by fitting Gaussian functions to these columns.
Scanning Electron Microscopy characterization (SEM). A JEOL JSM-7500FA microscope (Jeol, Tokyo, Japan) in high-vacuum mode, with an acceleration voltage of 5 kV and backscattered electrons was used for the EDS analysis.

UV-VIS absorption and PL measurements. The UV-Visible absorption spectra were recorded using a Varian Cary 300 UV-VIS absorption spectrophotometer. The PL spectra were measured on a Varian Cary Eclipse spectrophotometer using an excitation wavelength ($\lambda_{ex}$) of 390 nm for all the samples. Samples were prepared by diluting NC solutions in toluene, in quartz cuvettes with a path length of 1 cm.

PL Quantum Yields and time-resolved PL measurements. Absolute Photoluminescence quantum yields of NC samples were measured using an Edinburgh FLS900 fluorescence spectrometer equipped with a Xenon lamp, a monochromator for steady-state PL excitation, and a time-correlated single photon counting unit coupled with a pulsed laser diode ($\lambda_{ex} = 405$ nm, pulse width = 50 ps) for time-resolved PL. The PLQY was calculated using a calibrated integrating sphere ($\lambda_{ex} = 350$ nm for all CsCd$_3$Pb$_8$Br$_{16}$ nanocube samples). All NC dispersions were diluted to an optical density of 0.1 at the corresponding excitation wavelength in order to minimize the amount of fluorophore being reabsorbed.

NMR characterization. All the NMR spectra were acquired on Bruker Avance 400 MHz spectrometer, supplied with a BBI probe. NCs and free ligands were dispersed in 600 µL of deuterated toluene, transferred into 5 mm disposable tubes (Bruker) for the 1H NMR analyses which were performed at 300K as following: 64 scans were accumulated using 6536 data points, an inter-pulses delay of 30s, over a spectral width of 20.5ppm, with the offset positioned at 6.18ppm, and the receiver gain fixed (9). An exponential line broadening equivalent to 0.3 Hz, was applied to FIDs before the Fourier transform. The spectra, manually phased and automatically baseline corrected, were referred to the not deuterated residual toluene peak, calibrated at 7.09 ppm. For ligands shell composition analysis, the NCs dissolved in 300 µL of deuterated DMSO, were transferred into 3 mm disposable tubes (Bruker). The 90 degree pulse was optimized on each sample tube by an automatic pulse calculation routine and the q 1H-NMR was acquired with the previous acquisition parameters except for the number of transients and the receiver gain which were increased to 128 and to 64, respectively. Processing parameters were identical to the previous experiment. The spectrum was referred to the not deuterated residual DMSO peak, set at 2.50 ppm.

2D Nuclear Overhauser effect spectroscopy (3H-3H NOESY). The experiment (noesyphph, Bruker library), was acquired with 32 scans, a relaxation delay of 25, a mixing time of 300 ms, 2048 of digit points in the direct dimension and 256 increments.

X-ray Photoelectron Spectroscopy (XPS) characterization. Measurements were performed on a Kratos Axis Ultra DLD spectrometer, using a monochromatic Al Kα source (15kV, 20mA). The photoelectrons were detected at a take-off angle of $\phi = 0^\circ$ with respect to the surface normal. The pressure in the analysis chamber was kept below 7x10$^{-9}$ Torr for data acquisition. The data was converted to VAMAS format and processed using CasaXPS software, version 2.3.22. The binding energy (BE) scale was internally referenced to the C1’s peak (BE for C-C = 284.8 eV).

Device Fabrication and Characterization. Glass slides with patterned ITO were cleaned via immersion in acetone for 30 minutes, rinsed with isopropanol and exposure to O$_2$ plasma. Device fabrication started with spin-coating of the PEDOT:PSS in air at 4000 rpm followed by annealing in air at 120 °C for 30 minutes. Afterward, the substrates were transferred into a N$_2$ filled glove-box where the hole-transport layer was prepared as following: spin-coating of poly-TPD solution (2mg/ml) in chlorobenzene at 2000 rpm for 40 sec. The obtained poly-TPD film was then annealed at 110°C for 20 min inside the glove-box and the PVK film was prepared on top via spin-coating of a Chlorobenzene solution (4mg/ml) at 2000 rpm. The NC active layer was then prepared via spin-coating of a toluene solution on top of the PVK at 2000 rpm. The substrates were then transferred to a thermal evaporator inside the glovebox where TPbi/LiF/Al were deposited. The obtained LEDs were finally encapsulated using a cover-slip and an epoxy resin. The current-voltage-luminance characteristics were measured using a Keithley 2636 source-measure unit coupled to a calibrated PDA 100A Si switchable gain detector from Thorlabs. The system was controlled via a LabView interface. The output of the Si detector was converted into power (photon flux) using the responsivity of the detector. The EQE was calculated as the ratio of the photon flux and the driving current of the device. The EL spectra were collected using an Ocean optics HR4000 spectrometer.

Computational Modelling. Band structure calculations were performed at the density functional theory level using the PBE exchange-correlation functional as implemented in the VASP 6.1 package. We employed a k mesh grid of $4 \times 4 \times 4$ for the Brillouin zone integration and a kinetic energy cutoff of 400 eV. The atomic positions and the lattice parameters were both relaxed until the forces were smaller than 0.001 Hartree/Å. The pure bulk CsPbBr$_3$ system we employed a 1x1x1 orthorhombic (Pnma symmetry) unit cell, whereas for the alloyed bulk CsCd$_{0.25}$Pb$_{0.75}$Br$_3$ we started from a cubic (Pm 3m symmetry) $2 \times 2 \times 2$ unit cell, where 2 out of 8 Pb ions were replaced with 2 Cd ions. Spin-orbit effect were also included in the band structure calculations. The geometries and electronic structures of the alloyed CsCd$_{0.25}$Pb$_{0.75}$Br$_3$ nanoclusters were computed on charge-balanced NCs of about 3nm in size. These atomistic simulations were carried out also at the DFT/PBE level of theory but with the CP2K 6.1 package. Here, we included a double-$\zeta$ basis set plus polarization functions on all atoms with effective-core potential for the inner electrons. Further details on the model systems employed are provided in the main text.

RESULTS AND DISCUSSION
In this work, we used a modified version of our previously reported synthesis which employs oleic acid and a secondary amine as surfactants. To prepare CsCd\(_2\)Pb\(_3\)Br\(_5\) NCs, benzyl bromide was injected into a solution containing cesium, cadmium and lead oleates in the presence of didodecylamine. As discussed in our earlier work,\(^3\) the NCs prepared with this method are exclusively coated with Cs-oleate ligands, with didodecylamine acting only as regulator of the overall growth kinetics. Henceforth, the NCs purified directly after the synthesis with ethyl acetate will be referred to as “pristine”, and the reader should recall that they are coated with Cs-oleate. For the ligand exchange reaction, the crude solution of NCs was mixed with a toluene solution of Cs-carboxylates or ammonium salts. Thereafter, ethyl acetate was added to the crude solution, the NCs were separated by centrifugation and redispersed in toluene (see the Experimental Section for details). We prepared several batches of CsCd\(_2\)Pb\(_3\)Br\(_5\) NCs by systematically varying the feed ratios of cadmium and lead ions in the synthesis while all the other reaction conditions were kept constant. We observed the formation of regularly cubic shaped NCs in all mixed-cation compositions, as revealed in the TEM images of Figure 1a-d. Based on the compositional analysis by SEM-EDX, the Cd/Pb ratio in the NCs was correlated with the molar Cd/Pb feed ratio in the synthesis. We observed that the maximum extent of substitution of Pb\(^{2+}\) with Cd\(^{2+}\) ions was 25 ± 2 % (obtained for a Cd/Pb feed ratio of 2:1), whereas working at higher Cd/Pb feed ratios led to the formation of non-luminescent CsCdBr\(_3\) NCs as a main product, see Figure S1 of the Supporting Information (SI). UV-Vis optical absorption and photoluminescence (PL) spectra recorded on the colloidal dispersions of CsCd\(_2\)Pb\(_3\)Br\(_5\) NCs immediately after the synthesis evidenced a progressive blue shift in their absorbance and PL spectra at increasing substitution of Pb\(^{2+}\) with Cd\(^{2+}\) ions (i.e. x ranging from 0 to 0.25). In particular, the PL peak position shifted from 507 to 476 nm, see Figure 1e-f. However, we found that the emission color of the sample was not stable over time and turned green upon ageing.

![Figure 1](image.png)

Figure 1. (a-d) TEM images evidencing size and shape uniformity of CsCd\(_2\)Pb\(_3\)Br\(_5\) NCs prepared by varying the feed ratios of cadmium and lead ions in the synthesis, while all the other reaction conditions were kept constant, see Experimental Section and Table 1 for details (scale bars are 100 nm).

(e-f) Optical absorption and PL spectra recorded in toluene dispersions for all the samples.

In an attempt to stabilize the emission color, especially for the bluest emitting NCs (CsCd\(_2\)Pb\(_3\)Br\(_5\)), we tried various post-synthesis surface treatments. To this aim, the crude NC solution obtained from the synthesis was treated with various ligands, such as Cs-oleate, Cs-phenylacetate (Cs-PhAce), oleylammonium bromide (OLABr), phenethylammonium bromide (PhEAbr) and didodecyl dimethylammonium bromide (DDABr) and then washed with ethyl acetate (or methyl acetate). The reader might be induced to think that the Cs-oleate treated NCs and the pristine NCs should have exactly the same surface chemistry, as Cs-oleate is indeed the ligand shell present after the synthesis. However, it is likely for the Cs-oleate treated NCs to have slightly more surface sites passivated by ligands than the pristine NCs, and indeed the two samples did not behave identically, as it will be shown later.

Based on TEM, the ligand exchange did not alter the shape and size distribution of the NCs except for the Cs-PhAce case (Figure S2a-f). The optical features of the freshly prepared and of the aged NC dispersions are compared in Figure 2a-c, Figure S2g-I and Figure S3a-l. The freshly ligand-exchanged NCs had essentially the same emission spectrum as the pristine NCs, with PL around 475-480 nm, except for the Cs-PhAce case (emission at 485 nm), see Figure 1a and Figure S2g-I. However, upon ageing, the emission spectrum of the pristine and Cs-carboxylate treated samples (both Cs-oleate and Cs-PhAce) began to shift considerably towards the green, with the PL peak moving to ~ 510 nm over 14 days of storage under air. Over the same time span, the emission from NCs coated with ammonium bromide ligands shifted much less (about 10 nm), and the one from the DDABr coated sample remained practically unchanged (Figure 2a, see also Figure S3a-I). The trends in PLQY are reported in Figure 2c and S3m-r. The freshly prepared pristine NCs (PL peak at 478 nm) were weakly emissive, with a PLQY of 5 ± 0.5 %, and the exchange with Cs-carboxylates did not improve their PLQY further. The increase in PLQY was much notable for the ammonium bromide exchanged samples, peaking at 40 ± 4 % for the DDABr case. Here again, the DDABr coated NCs were the best sample, retaining their initial emission efficiency over time, while all the other samples experienced a decrease in PLQY. A notable exception was the pristine NCs, for which an increase in the PLQY was measured over time, but this is also a sample that over time lost a considerable amount of Cd\(^{2+}\) ions (see later), hence approaching a quasi-pure CsPbBr\(_5\) composition. An overall picture of the different optical behaviors of the two extreme samples (namely, the pristine NCs and the DDABr exchanged ones) is given in Figure 2c (here spectra are normalized), their TEM images and PL lifetimes are reported in Figure S4-5 and Table S1. The absorption and the emission features of the pristine sample changed considerably over time, while the DDABr sample was much less affected, with the PL peak position and linewidth remaining practically unchanged. As the DDABr ligand exchange appeared to be the best strategy to preserve the emission characteristics,
we then extended this treatment to CsCd$_x$Pb$_{1-x}$Br$_3$ NCs with other compositions (from x=0 to 0.12). The PLQY of the freshly prepared DDABr treated CsCd$_x$Pb$_{1-x}$Br$_3$ NCs in col-

Figure 2. a) Evolution of PL spectra recorded in colloidal dispersions upon ageing for pristine and NCs treated with various ligands (optical absorption and PL spectra of the corresponding samples are reported in Figure S5) and the changes in PLQY upon ageing for the corresponding samples are reported in panel (b). c) Optical absorption and PL spectra of two representative samples (pristine and c) DDABr exchanged) recorded after the synthesis (fresh) and over storage in ambient air for 14 days. d) Liquid state $^1$H NMR spectra of d-toluene solutions of oleic acid (i), pristine CsCd$_{0.83}$Pb$_{0.17}$Br$_3$ NCs (ii), DDABr (iii) and NCs after DDABr treatment. e) XRD patterns of the pristine and DDABr exchanged sample fresh and after two weeks of ageing along with the bulk reference pattern for cubic and orthorhombic phases (CsPbBr$_3$).

Next, we performed a detailed investigation of the surface and structural composition of the pristine and DDABr exchanged samples, which correspond to the worst and best performing samples, respectively. Similarly to a previous work of ours, we performed liquid state $^1$H-NMR spectroscopy to assess their surface chemistry. Figure 2d shows the $^1$H-NMR spectra of the pristine (ii) and of the DDABr exchanged NCs (iv) along with free ligands, oleic acid (i) and DDABr (iii) recorded in d-toluene. $^1$H NMR analysis of the pristine sample indicated the presence of significantly broadened resonances around 5.47 ppm, as is expected for molecules bound to a NC. This was further confirmed by the 2D $^1$H NOESY (See figure S8) which features negative NOE signals (red, typical signature of ligands bound to the surface of NC with longer correlation time) rather than the positive NOE signal (blue), thus confirming that the as-purified NCs were exclusively coated with oleate molecules. Similarly for DDABr exchanged sample, the $^1$H NMR resonances around 4.0 and 3.6 ppm broadens and shifts downfield compared to the corresponding free ligands, a proof that the ligand exchange was successful and DDABr was bound to the surface of the NCs. The additional sharp and resolved signal at ca. 5.43 ppm arises from residual, free oleic acid molecules (see Figure S9). This was indeed supported by the 2D $^1$H NOESY featuring negative (red) NOE signal for DDA (didodecyldimethyl ammonium) ligands and the positive (blue) NOE signal for oleic acid, thereby corroborating the interaction of the former (DDA) only with the surface of NC (See figure S10). To determine the content of organic species in the DDABr exchanged sample, we dissolved the NCs in deuterated dimethyl sulfoxide (DMSO) and performed quantitative NMR ($^1$H-NMR) analysis (Figure S11). The ratio between the integrated peak intensities of vinyl protons of oleic acid and methyl moiety on nitrogen of DDABr, each normalized for the number of resonances generating the signals, revealed that 86% of ligands are didodecyldimethyl ammonium and 14% are oleate species. This is further supported by XPS analysis showing no signature of nitrogen (which we consider as a marker for the presence of ammonium species on the surface of NC) in the pristine sample, while the DDABr exchanged NCs evidence the presence of N, see Figure S12. Finally, the compositional analyses (by XPS, TEM-EDX and SEM-EDX) of both pristine and the DDABr exchanged samples are reported in Table S3 and Figure S13. According to both analyses, upon DDABr exchange, the Cs:(Cd+Pb) ratio decreased (from 1.24 to 1.05 (XPS) and from 1.13 to 1 (SEM-EDS)) and the Br:(Cd+Pb) ratio increased (from 2.68 to 2.89 (XPS) and from 2.85 to 3.21 (SEM-EDX)). These trends, overall, confirm the exchange of Cs-oleate with DDABr ligands on the surface of the NCs.
We also carried out XRPD analyses of the pristine and DDABr-exchanged NCs, for both the freshly prepared samples and the same samples aged for 14 days. The relevant data are seen in Figure 2e (the corresponding patterns without background subtraction of both fresh and aged samples are reported in Si4 and Si5 respectively). The XRPD patterns of the fresh samples both closely matched the cubic perovskite phase, in contrast with the orthorhombic phase of the pure CsPbBr3 NCs. The slight shift of the XRPD peaks to higher angles compared to the reference CsPbBr3 pattern (reference code: 98-018-1287) indicates a decrease in the cell volume, due to the partial substitution of lead with cadmium. Over ageing, the DDABr exchanged sample remained nearly unchanged while the pristine sample evidenced a shift of peaks towards lower angles confirming the expansion in cell volume, which we ascribed to the loss of Cd2+ ions (the details are discussed later in the electron microscopy section of aged NCs). Furthermore, the emergence of additional diffraction peaks upon ageing in the pristine sample around 24, 25 and 28 2-theta (conforming to the orthorhombic phase of CsPbBr3) suggests the change in crystal structure from cubic to orthorhombic (see the inset of pristine aged sample in figure 2e).

We then proceeded to investigate the crystal structures of the pristine NCs and of the corresponding NCs after the various ligand exchange procedures through quantitative high resolution HAADF-STEM imaging. We first discuss in detail the two cases of the pristine and of the DDABr exchanged samples (both freshly prepared and aged), as those two samples are the most diverging ones in terms of emission color stability, as discussed above. The corresponding analyses of the other samples are reported in the SI and are briefly discussed at the end of this section. Figure 3a shows a typical image of a pristine NC. Since the HAADF-STEM signal approximately scales with the square of the atomic number Z, three atomic columns types with different brightness could be distinguished outside the dashed white region (see inset of Figure 3a): type 1 corresponds to pure Cs columns (Z_Cs = 55), type 2 to Pb/Cd-Br columns (Z_Pb = 82, Z_Cd = 48, Z_Br = 35); and type 3 to Br columns. The type 3 columns are hardly visible due to their relatively lower atomic number Z. The Fourier Transform (FT) of this region (see Figure Si6) corresponds to a metal halide perovskite cubic structure imaged along the [100] zone axis. Unlike in standard CsPbBr3 NCs, we additionally observed several regions, e.g. inside the white dashed box indicated in Figure 3a (see also Figure Si7 and Si8 for additional examples). Here, the difference in intensity for the different atomic columns is smaller. Moreover, the intensities appear higher (lower) in comparison to the Type 1(2) columns for the CsPbBr3 cubic structure.

To investigate this intensity difference in more detail, we measured the total scattered intensities of both types of columns in the NC using the StatSTEM software. During this analysis, the columns are modelled as a superposition of Gaussian functions. The unknown model parameters, including the location and total scattered intensity, are estimated for each atomic column. The results, shown in Figures 3b and 3c for the type 1 and 2 sub-lattice columns, respectively, confirm the intensity difference of the atomic columns within and outside the dashed white region (see also Figure Si8 for the same analysis of another NC). More precisely, columns corresponding purely to Cs in the CsPbBr3 cubic structure show an increase in intensity in the region between the dashed lines, whereas columns expected to correspond to the Pb/Cd-Br type show a reduction of intensity inside the dashed white region. These observations suggest different compositions of the atomic columns in the dashed white region in comparison to conventional perovskite phases. This is usually the signature of a Ruddlesden-Popper phase (RP). A RP phase consists of n cubic perovskite layers separated by a [CsBr] layer, where n is an integer. This leads to a drastic change of column compositions that mix both type 1 and 2 columns into one column. Our modelling of the corresponding RP and perovskite crystal lattices (see also the computations section later on) indicates that, if the Cd and Pb ions were homogeneously distributed throughout the NCs, there would be no difference in the lattice parameter between the RP domains and the other regions of the NCs, which adopt the cubic perovskite phase. However, the experimentally measured lattice parameter (i.e. the mean value of the column to column distance from the same sub-lattice) in these RP regions (5.83±0.012 Å) is significantly smaller than the mean value in the rest of the NC (5.86±0.005 Å), where the error bar corresponds to the standard deviation on the mean. This is also confirmed by a statistical Student’s t-test\(^{63}\) for the comparison of two mean values, see Figure 3d-f and Figure Si8. These results based on theoretical predictions (see later) suggest that the Cd/Pb ratio is higher here than in the rest of the NCs, suggesting that Cd\(^{2+}\) ions preferentially segregate in the RP regions leading to a lattice contraction. We then performed a similar quantitative analysis on the DDABr exchanged NCs. The relevant data are displayed in Figures 3 g-k. No RP phases were observed for these NCs. This was confirmed by the rather homogenous distribution over the whole NC of both type 1 and type 2 column sub-lattices, which are shown in Figures 3h and 3i, respectively, as the rather narrow distribution of the column-to-column distance of type 2, see Figure 3 j. The mean lattice parameter (MLP) measured for this NC equals 5.876 ± 0.005 Å (Figure 3k). Hence, it appears that the exchange with DDABr caused the transition of the RP domains to the cubic perovskite phase.
We then analyzed both samples after ageing. Figures 4a-d and 4e-h show the HAADF-STEM analysis of aged pristine and aged DDABr exchanged NCs, respectively. Remarkably, in the pristine sample aged for 6 days, the RP phases had disappeared (Figure 4a and figure S19), which is confirmed by the relatively homogenous distribution of column intensities of type 1 (figure 4c) and type 2 (figure 4d). Such structural evolution upon aging, also backed by the corresponding optical features of the fresh and aged samples, as previously discussed (Figure 2), appears to be a
direct consequence of the loss of Cd\(^{2+}\) ions from the NCs. In addition, the FT of the NC of Figure 4a, reported in Figure 4d, evidences the presence of specific planes corresponding to the orthorhombic phase of CsPbBr\(_3\), testifying a transition from cubic to orthorhombic structure accompanying the loss of Cd\(^{2+}\). This was further supported by STEM-EDX analysis of the aged pristine sample, which revealed a 7% content of Cd, down from 25% of the fresh pristine sample (Table S4). On the other hand, Figure 4e-h shows images of a DDABr exchanged NC after 10 days of ageing. No significant structural differences were observed when compared to the fresh DDABr exchanged NC sample (Figure 3g-k). The quantitative analyses of the column intensities of type 1 and 2, presented in Figure 4f-g are similar to the ones of the corresponding fresh sample, reported in Figure 3g-k. The lattice constant distribution (Figure S20) indicates a mean lattice of 5.888 ± 0.006 Å. According to the Student’s t-test, there is no significant difference in mean lattice distance between the fresh and aged DDABr exchanged NCs. This is a strong indication that in the DDABr exchanged NCs, the Cd\(^{2+}\) ions were retained in the NCs more efficiently than in the pristine NCs.

We also performed similar analyses on the NCs exchanged with the other ligands (Cs-oleate, Cs-PhAce, OLABr, PhEABr) and noticed the almost complete absence of RP phase already in the freshly exchanged samples (See Figures S2a). This evidence suggests that any of ligand exchange procedures tested was harsh enough for the NCs to accelerate the transformation of the RP phases to cubic perovskite phases. However, when crossing these data with the various analyses discussed earlier, we conclude that no surface treatment was as efficient as the DDABr one in preventing the escape of Cd\(^{2+}\) ions from the NCs.

![Figure 4](image)

To understand with atomistic detail the structure and optoelectronic behavior of the CsCd,Pb\(_x\),Br\(_3\) NCs prepared and analyzed in this work, we also performed density functional theory (DFT) calculations. At first, we looked at the origin of the blue shift that the system with mixed Pb/Cd composition experiences compared to the pure CsPbBr\(_3\) NCs. To this aim, we computed the band structure for the orthorhombic (Pnma) CsPbBr\(_3\) NCs at the DFT/PBE+SOC (SOC stands for spin-orbit coupling) level of theory, as shown in Figure 5a. The bandgap is computed at 1.0 eV and is underestimated against the experiment, as is expected for the pure exchange-correlation functional such as PBE. Our goal, however, is to look at the effect of adding Cd to the lattice rather than in the absolute bandgap, an effect that is captured by this level of theory. We computed the band structure for a 2x2x2 cubic CsPbBr\(_3\) lattice, where one of the Pb atoms has been replaced by Cd, thus obtaining a 75%/25% Pb:Cd composition, in line with the experiments. The band structure in Figure 5a (right-side) shows that the gap widens to 1.44 eV and it becomes slightly indirect with the lowest transition occurring from a Gamma (G) to a R point. This indirect transition explains in part the worsening of the optoelectronic characteristics of the material in terms of PLQY. The opening of the gap is in line with what is observed in the experiments and is characterized by a less dispersive conduction band minimum at the G point, which is shifted higher in energy, followed by a strong stabilization of the band at the R point emerging from the
bonding orbital overlap of the empty 5s orbitals of Cd with the unoccupied 6p of Pb. Overall, both effects lead to a gap opening.

Figure 5. (a) Band structure of CsPbBr$_3$ (left) and alloyed CsCd$_{0.75}$Pb$_{0.25}$Br$_3$ (right) systems. The former was computed on a 1x1x1 unit cell, whereas the latter on a cubic 2x2x2 cell with one quarter of the metal atoms as Cd and the rest as Pb. (b) Cluster calculation of three types of stoichiometric alloyed NCs with a different distribution of the Cd ions (25% in total) inside the lattice. The numbers below each system are the relative energies in kcal/mol versus the uniform distribution that is taken as reference. (c) NC model of the alloyed CsCd$_{0.75}$Pb$_{0.25}$Br$_3$ exhibiting the RP phase from three different orientations. All calculations of (a), (b), (c) were computed at the DFT/PBE level of theory.

Besides this, we built and computed also explicit NC models of mixed CsCd$_{0.75}$Pb$_{0.25}$Br$_3$ NCs to understand how Cd and Pb are distributed inside the lattice. Since the number of possible combinations is enormous, we focused on three types of configurations: a uniform distribution of Cd$^{2+}$ and Pb$^{2+}$ ions inside the lattice; a cluster configuration where Cd$^{2+}$ ions are segregated at the surface and finally another cluster configuration where all the Cd$^{2+}$ ions are segregated at the core (Figure 5b). The main result is that a Cd clusterization in the core region of the NC is energetically very unfavorable, whereas the Cd$^{2+}$ ions appear either to be distributed uniformly across the NCs or to segregate at the surface. It is likely (although we have no further supporting ground for this hypothesis) that a surface segregation of Cd$^{2+}$ ions can favor the local formation of a RP phase bordering the surface of the NC and rarely entirely embedded in the NC, as revealed by our electron microscopy analysis. To better understand this aspect, we also computed the geometry and electronic structure of a NC model system that exhibits the RP phase. As shown in Figure 5c for the pure “perovskite-CsPbBr$_3$/RP-CsPbBr$_3$” NC, and in the SI for the “perovskite-CsCd,Pb$_{0.75}$Br$_3$/RP-CsCd,Pb$_{0.75}$Br$_3$” NC, the RP phases are stable from the computational point of view and their electronic structures are substantially similar to those of the pure perovskite phase, albeit with the additional presence of localized states at the interface possibly explaining the loss of PLQY of the native NCs compared to the pure CsPbBr$_3$ NCs. Even more interestingly, we noted that the presence of the RP phase by itself is not sufficient to explain the lattice contraction in the RP region observed in the TEM images. The analysis of the Pb-Pb bond distance in the DFT calculations indeed shows that this remains the same in both phases (see Figure S22). On the other hand, when we modeled a preferential accumulation of Cd in the RP phase and then analyzed the Cd-Cd distances, we noticed a contraction of the lattice in the RP region that is comparable to what was observed experimentally be electron microscopy.

The experimental and theoretical data that we have presented above allows us to draw a solid hypothesis on the overall optical/structural stability of the NCs and their evolution depending on the type of surface passivation. We expect that mixing lead and cadmium precursors at the synthesis stage leads to the formation of the RP phases already during the nucleation and growth of the Cs-oleate capped NCs. Here, Cd is distributed homogenously inside the perovskite phase, albeit with a slight accumulation in the RP phase. Overall, the symmetry of the structure is closer to cubic than to the orthorhombic one, which is typical of the pure CsPbBr$_3$ composition, and the bandgap shifts to the blue region, as also evidenced by the DFT calculations. When left untreated, the Cs-oleate coated NCs evolve by expelling a considerable fraction of the Cd$^{2+}$ ions through a concomitant loss of loosely bound Cs(oleate) and Cd(oleate)$_2$ species, and a structural reorganization of the RP domains into perovskite ones. By doing so, the overall optical features of the NCs evolve towards those of the pure, green emissive CsPbBr$_3$ NCs. The various ligand exchange treatments, on the other hand, accelerate the RP to perovskite transition. This is understandable, as a configuration in which perovskite and RP domains are mixed in the same NC appears to be unstable, and a surface reaction is apparently enough to trigger the elimination of the RP phase. Also, following this transition, the Cd$^{2+}$ ions are homogenously re-distributed throughout the NC lattice. On the other hand, the various ligand exchange treatments have different efficacies in preventing the loss of Cd$^{2+}$ ions from the NCs: the treatments with Cs-carboxylate ligands are less successful in preventing such loss, while those with ammonium bromide ligands are more successful, especially the one with DDABr. Hence, we conclude that the latter ligands are the most efficient in saturating surface...
traps, which are most likely the channels through with Cd$^{2+}$ ions could escape from the NCs. In this case, the bandgap is retained in the blue, even after ageing, and the optimal surface passivation helps to preserve the PLQY at values around 40%. Yet, the indirect bandgap nature of the lowest energy transition however precludes a further enhancement of the PLQY to values typical of the pure CsPbBr$_3$ composition.

Finally, we fabricated light-emitting diodes (LEDs) to verify the stability in the electroluminescence (EL) of a film of DDABr exchanged CsCd$_{0.25}$Pb$_{0.75}$Br$_3$ NCs. Details on LED fabrication and device structure are reported in the Experimental Section and in Figure 6a, respectively. A typical LED, under constant applied bias (4 V, Figure 6b), featured an EL spectrum centered at 480 nm, i.e. slightly red-shifted from the PL of the colloidal dispersion (476 nm). The emission did not vary significantly under device operation over 3 minutes, again supporting the structural stability of the DDABr exchanged NCs. The luminescence-voltage-current density and the external quantum efficiency curves of a typical LED are reported in Figure S23 and S24.

Figure 6. (a) schematic illustration of the device structure used to fabricate LED, (b) electroluminescence spectra of DDABr exchanged NCs under voltage bias recorded at different time intervals, inset shows a photo of the blue LED.

CONCLUSIONS

In conclusion, we have shown that the structural and spectral stability of mixed cation perovskite NCs strongly depends on their surface passivation. Combined experimental and theoretical investigation reveals that Cs-oleate capped CsCd$_{0.25}$Pb$_{0.75}$Br$_3$ NCs are characterized by Cd segregated RP-phases in addition to the perovskite phase. The structural heterogeneity can be removed by treating the NCs with various ligands post-synthesis or by simply ageing, but in most cases their emission color remains unstable due to expulsion of Cd ions. Among the various post-synthesis ligand exchange strategies, we found that the ones with ammonium bromides, and especially with DDABr, suppressed the out-diffusion of Cd$^{2+}$ ions and the NCs tend to retain their blue emission over time, both in colloidal dispersions and in electroluminescent devices, as well as their cubic phase. This work highlights the critical role of surface passivation on the structural and optical properties of mixed cation halide perovskite NCs and should be generalized to study the effect of different types of ligand passivation on the stability of other halide perovskite alloy compositions.

ASSOCIATED CONTENT

Supporting Information. The detailed results of various surface treatments such as TEM images, optical absorption, PL, PLQY and PL lifetimes, XRD patterns, EDS compositional analysis, HR-TEM/STEM images, XPS, NMR spectra (‘H, and ‘H-NOESY) and computational analysis.

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