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poly(maleic anhydride-alt-1-octadecene) into stable CsPbBr₃ perovskite emitters through intermediate heterostructures†

Transforming colloidal Cs₄PbBr₆ nanocrystals with

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The preparation of strongly emissive CsPbBr₃ perovskite nanocrystals with robust surface passivation is a challenge in the field of lead halide perovskite nanomaterials. We report an approach to prepare polymer-capped CsPbBr₃ perovskite nanocrystals by reacting oleylammonium/oleate-capped Cs₄PbBr₆ nanocrystals with poly(maleic anhydride-alt-1-octadecene) (PMAO). PMAO contains succinic anhydride units that are reactive towards the oleylamine species present on the Cs₄PbBr₆ nanocrystals' surface and produces polysuccinamic acid, which, in turn, triggers the Cs₄PbBr₆ to CsPbBr₃ conversion. The transformation occurs through the formation of Cs₄PbBr₆–CsPbBr₃ heterostructures as intermediates, which are captured because of the mild reactivity of PMAO and are investigated by high-resolution electron microscopy. The Cs₄PbBr₆–CsPbBr₃ heterostructures demonstrate a dual emission at cryogenic temperature with an indication of the energy transfer from Cs₄PbBr₆ to CsPbBr₃. The fully-transformed CsPbBr₃ NCs have high photoluminescence quantum yield and enhanced colloidal stability, which we attribute to the adhesion of polysuccinamic acid to the NC surface through its multiple functional groups in place of oleate and alkylammonium ligands. The PMAO-induced transformation of Cs₄PbBr₆ NCs opens up a strategy for the chemical modification of metal halide NCs initially passivated with nucleophilic amines.

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Introduction

Nanocrystals (NCs) of cesium lead halides have recently emerged as a class of semiconductor materials promising for light-emitting applications. The chemical reactivity of these NCs and the interconversion between the NCs of the two most studied bromides in this class, Cs_4PbBr_6 and $CsPbBr_3$ perovskite, have been of interest since these NCs were first synthesized in the colloidal form. The $Cs_4PbBr_6 \rightarrow CsPbBr_3$ conversion, which can be triggered using various reagents (for example, Prussian blue, olici acid, PbBr₂, and water) conversion, which can be triggered using various reagents (for example, Prussian blue, olici acid, or PbBr₂, and water) conversion, which can be triggered using various reagents (for example, Prussian blue, olici acid, or PbBr₂, and water) conversion, which can be triggered using various reagents (for example, Prussian blue, olici acid, or PbBr₂, or PbBr₃, NCs. For

example, Yin's group exploited heterogeneous water-mediated CsBr extraction from Cs_4PbBr_6 NCs in hexane as a method for making luminescent $CsPbBr_3/SiO_2$ or $CsPbBr_3/Ta_2O_5$ Janus-type heterostructures, ¹³ and branched $CsPbBr_3$ dodecapods. ¹⁵ Despite several reports on $Cs_4PbBr_6 \rightarrow CsPbBr_3$ transformation at the nanoscale, the nanocrystal intermediates of this reaction and the surface passivation and stability of the resulting $CsPbBr_3$ NCs have not been investigated.

Designing the $Cs_4PbBr_6 \rightarrow CsPbBr_3$ NC transformation in such a way that it delivers encapsulated $CsPbBr_3$ NCs with an enhanced stability is a promising approach for exploiting the Cs_4PbBr_6 NC reactivity, as shown by the above mentioned studies of Yin's group.¹³ The use of an organic polymer instead

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[†] Electronic supplementary information (ESI) available: Experimental details and procedures, EDS-STEM data, ¹H and ¹H-¹³C HSQC NMR spectra and discussion, annotated XRD patterns, PLQY spectra, FTIR and NIR absorbance spectra, tests of PMAO reactivity with powders of bulk Cs₄PbBr₆ and amine-free Cs₄PbBr₆ NCs, stability tests of CsPbBr₃/PMAO NCs, HRTEM images of Cs₄PbBr₆-CsPbBr₃ heterostructures, low-resolution TEM size analysis, PL maps and spectra of Cs₄PbBr₆ NCs at 27 K, and time-resolved PL, micro-PL, and Raman spectra for the NC-PMAO blend (PDF). A video showing transformation of non-luminescent Cs₄PbBr₆ NCs into green-emitting CsPbBr₃ NCs after addition of PMAO (MP4). See DOI: 10.1039/d0sc00738b.

of an inorganic oxide (e.g. SiO₂ or Ta₂O₅) shell would yield a NCpolymer blend which can be drop-cast, spin-coated or electrospun, widening the range of available applications.16 More generally, polymer encapsulation of CsPbX₃ perovskite NCs (X = Cl, Br, I, and their mixtures) is promising because it has been shown to enhance the shelf-time of NCs by providing enhanced stability against moisture and photodegradation.¹⁷ Interestingly, stability enhancement has been reported irrespective of whether polymer chains preserve the native CsPbX₃ NC surface ligands as in the case of polystyrene¹⁷⁻¹⁹ and poly(styreneethylene-butylene-styrene),17 or whether the polymer adheres to the surface of CsPbX3 NCs as in the case of ammonium bromide-terminated polystyrene²⁰ or poly(n-butyl methacrylate)modified with zwitterionic sulfobetaine or phosphorylcholine functional groups.21 Arguably, an ideal NC transformation of Cs₄PbBr₆ → CsPbBr₃ in this context could be caused by a polymer which acts both as a reactant and a macromolecular surfactant,20 minimizing the number of reagents and preparatory steps involved in the process.

In this work, we demonstrate that poly(maleic anhydride-1alt-octadecene) (PMAO) can simultaneously trigger the Cs₄PbBr₆ → CsPbBr₃ NC transformation and provide enhanced surface passivation to the resulting CsPbBr3 NCs. PMAO is a widely available co-polymer of 1-octadecene and maleic anhydride and has been extensively used for the surface functionalization of NCs.22-24 In our experiments, upon mixing PMAO with oleylammonium/oleate-capped Cs₄PbBr₆ NCs, the cyclic anhydride groups of PMAO react with oleylamine species, forming polysuccinamic acid (Fig. 1). Polysuccinamic acid destabilizes the NC surface by displacing both the amine and the oleate ligands and acidifies the reaction environment, thus triggering the formation of CsPbBr₃ NCs (Fig. 1). The core chemistry of the NC transformation is summarized by the following chemical equation: Cs₄PbBr₆ + nRNH₂ $(-R'(CHCO)_2O-)_n \rightarrow CsPbBr_3 + (-R'(CHCOOH)(CHCONHR)-)_n +$ $3Cs^{+}_{(solvated)} + 3Br^{-}_{(solvated)}$, where R = oleyl, R' = octadecenyl,

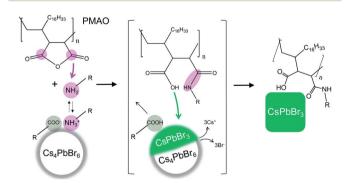


Fig. 1 Schematic representation of the Cs₄PbBr₆ → CsPbBr₃ NC transformation induced by PMAO. Oleylamine species from the NC surface react with the cyclic anhydride rings of PMAO, forming polysuccinamic acid. The removal of oleylamine-based and oleate ligands destabilizes the NC surface, and the formation of polysuccinamic acid increases the acidity of the medium, triggering the Cs4PbBr₆ \rightarrow CsPbBr₃ transformation (see the text for the chemical equation). The resulting CsPbBr3 NCs are stabilized by the polysuccinamic acid in place of the original ligands.

and the ratio between oleylamine molecules and anhydride units is assumed to be 1:1 for simplicity. The extent of the transformation is tunable by varying the amount of added PMAO, enabling the investigation of the transformation intermediates, which consist of Cs₄PbBr₆-CsPbBr₃ heterostructures. The fully-transformed CsPbBr3 NCs are bright emitters and retain their green emission for four weeks of storage under ambient conditions in air, even after one washing cycle with ethyl acetate (a solvent which typically causes the degradation of oleylammonium/oleate-capped CsPbBr3 NCs within hours or days). The increase in the stability of CsPbBr₃ NCs synthesized from Cs₄PbBr₆ and PMAO is attributed to the adhesion of polysuccinamic acid to the NC surface through its multiple functional groups.

Results and discussion

Cs₄PbBr₆ NCs and their transformation with PMAO in solution

The synthesis of the initial Cs₄PbBr₆ NCs was performed in air, via the hot injection of cesium oleate into the solution of lead(II) bromide dissolved in a mixture of oleylamine and oleic acid in 1-octadecene,7 as detailed in Section S1 of the ESI.† The synthesis is similar to that of CsPbBr3 NCs,5 except that it is performed at a higher concentration of oleylamine and oleic acid with respect to lead ([oleylamine] : [oleic acid] : [PbBr₂] \sim 0.63 : 0.31 : 0.027 M). Such reaction conditions favor the formation of a Pb-poor Cs₄PbBr₆ phase over the CsPbBr₃ phase, as detailed previously.25 The synthesis delivers batches of Csrich rhombohedral Cs₄PbBr₆ NCs with a narrow size distribution and an average diameter in the range from 10 to 16 nm (Fig. 2a, b, and S1-S5†). ¹H and ¹H-¹³C heteronuclear single quantum coherence (HSQC) nuclear magnetic resonance (NMR) experiments established that Cs₄PbBr₆ NCs are passivated by a mixture of oleylammonium oleate and neutral oleylamine with a ligand ratio of $\sim 3:2$ between (oleylamine + oleylammonium): oleate species (see Section S3 and Fig. S6-S9 of the ESI for details†).

These Cs₄PbBr₆ NCs can react with PMAO in toluene, fully or partially transforming into CsPbBr₃ NCs, depending on the amount of the added polymer (Fig. 2c). The reaction of Cs₄PbBr₆ NCs with PMAO typically starts within a few minutes after the addition of PMAO at room temperature (Movie S1 and Fig. S10†) and can be accelerated by mild heating of the reaction mixture (up to 80 °C). It is important to highlight here that heating up the NCs alone to 80 °C without the addition of PMAO does not trigger any transformation (Fig. S11†). The fully-transformed CsPbBr₃ NCs have a narrow size distribution, as inferred from their self-organization into ordered close-packed monolayers on a carbon-coated TEM copper grid (Fig. 2a). The XRD patterns of the initial NCs, partially- and completely-transformed samples are shown in Fig. 2b. Following the transformation, the XRD reflections of the rhombohedral Cs₄PbBr₆ crystal structure gradually disappeared, and peaks characteristic of the orthorhombic CsPbBr3 perovskite phase emerged (Fig. 2b, see Fig. S12† for peak assignment). The progression of the reaction was monitored by steady-state UV-Vis absorption spectroscopy

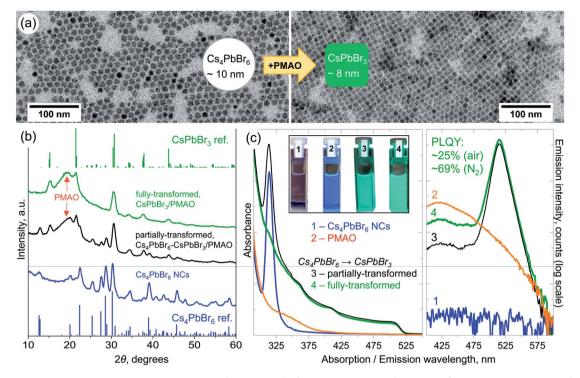


Fig. 2 (a) Low-magnification TEM images of the initial Cs₄PbBr₆ NCs (average diameter 10 ± 1.5 nm) and fully-transformed CsPbBr₃ NCs (average edge length 8 ± 0.4 nm) after their reaction with PMAO in toluene. (b) XRD patterns of the initial Cs_4 PbBr $_6$ NCs and of the partially- and fully-transformed ones. Top and bottom stick patterns are those of the reference bulk compounds: rhombohedral Cs_4PbBr_6 (pattern ID 04-015-9683, ICSD code 162158)²⁷ and orthorhombic CsPbBr₃ (pattern ID 96-451-0746, COD code 4510745).²⁸ The broad peak at ~20° is due to PMAO. (c) Optical absorption (left panel) and emission (right panel) spectra of toluene solutions of initial Cs₄PbBr₆ NCs (blue curve), PMAO (orange curve), and partially- (black curve), and fully-transformed (green curve) NCs. The inset in the left panel shows photographs of the samples under excitation with a 365 nm lamp demonstrating visible green PL of partially- and fully-transformed NC samples.

(Fig. 2c, left panel, Fig. S10†) in which the disappearance of the \sim 314 nm peak characteristic of Cs₄PbBr₆⁷ and the appearance of the ~510 nm band edge absorption of CsPbBr₃ are evident. The transformation was also tracked by steady-state photoluminescence (PL) spectroscopy, through the appearance of a cyan emission ($\lambda_{max} \sim 475-480$ nm) in the early stages of the reaction (Fig. S10†). The absolute PL quantum yield (PLQY) of the samples transformed in air was measured to be \sim 19% (partially transformed), and \sim 25% (fully transformed). On the other hand, when the transformation was performed under an inert atmosphere, the sample had a 69% PLQY (Fig. S13-S15†). Such a value is comparable to those reported for other Cs₄PbBr₆ \rightarrow CsPbBr₃ chemical transformations of NCs: 47% (ref. 7) and 62% (ref. 11) via the addition of solid PbBr2 at elevated temperatures, and 75% (ref. 12) upon reaction with H₂O. The lower PLQY of the samples transformed in air is attributed to the presence of electron traps formed as a result of sample exposure to atmospheric O2. Similar results have been reported by Rodà et al. who observed PL dimming in oxygen-exposed CsPbBr₃ nanocubes.²⁶

Rationalization of the observed reactivity between PMAO and Cs₄PbBr₆ NCs

PMAO is a copolymer of octadecene-1 and maleic anhydride, and it consists of repeating units composed of a saturated hydrocarbon chain and a cyclic succinic anhydride ring (Fig. 1). PMAO has a negligible reactivity towards inorganic salts such as Cs₄PbBr₆, as confirmed in a control experiment on finely ground powder of bulk Cs₄PbBr₆ (Fig. S16 and S17†). However, the succinic anhydride rings of PMAO feature acyl groups that are reactive towards nucleophilic reagents such as water and primary amines (yielding, in the latter case, either succinamic acid at room temperature23,29-31 or cyclic imides at high temperatures31-33). The presence of a significant amount of water as a potential reactant towards PMAO in the Cs₄PbBr₆ NC samples was ruled out based on FTIR and NIR characterization (Fig. S18 and S19†). On the other hand, the ligand shell of Cs₄PbBr₆ NCs contains partially-protonated oleylamine (Section S3 and Fig. S6-S9†). In analogy with the widely studied oleylammonium/oleate-capped CsPbBr₃ NCs, 25,34-36 the ligands on the surface of Cs₄PbBr₆ NCs are likely to exist in a dynamic equilibrium between neutral and protonated species (oleylamine and oleylammonium, respectively). Thus neutral oleylamine is always available in the NC solution. Neutral oleylamine is a nucleophile with a documented reactivity towards linear and cyclic anhydrides,37,38 and polymaleic anhydride derivatives. 39,40 The reaction between neutral oleylamine and PMAO in the absence of NCs causes broadening of the vinyl hydrogen resonance of the oleyl chain in the ¹H NMR spectrum due to the attachment of small oleylamine molecules to PMAO

macromolecules (the specified $M_{\rm w}$ of PMAO is \sim 30 000–50 000 g mol^{-1} , which roughly corresponds to \sim 80-150 succinic anhydride-octadecene subunits) (Fig. S20-S22†). The addition of neutral oleylamine to cyclic anhydride produces a succinamic acid derivative, as was confirmed by ¹H and ¹H-¹³C HSQC NMR in a control reaction (Fig. S23†). Therefore, the formation of polysuccinamic acid (Fig. 1) is expected upon mixing of PMAO with oleylammonium/oleate capped Cs₄PbBr₆ NCs. The key role of oleylamine species in the Cs₄PbBr₆ → CsPbBr₃ NC transformation was further verified by a control reaction between PMAO and oleylamine-free Cs₄PbBr₆ NCs (synthesized with trin-octylphosphine oxide (TOPO) and oleic acid41). The Cs₄PbBr₆ NCs synthesized with TOPO and oleic acid were found to be unreactive towards PMAO (Fig. S27 and S28†).

In summary, the removal of oleylamine from the surface of Cs₄PbBr₆ NCs destabilizes them, while polysuccinamic acid acidifies the reaction environment. Surface destabilization and acidic environments are both general conditions that are known to cause the $Cs_4PbBr_6 \rightarrow CsPbBr_3$ transformation. The stoichiometry of the transformation is balanced by a nominal removal of 3 equivalents of CsBr from 1 equivalent of Cs₄PbBr₆, yet we have not experimentally detected crystalline CsBr by XRD or high-resolution TEM (HRTEM). This discrepancy is tentatively rationalized by solvation of Cs⁺ and Br⁻ ions by oleate and polysuccinamic acid species, similar to the previously reported dissociation of CsBr in dimethylformamide in the presence of the polyacrylic acid co-polymer. 43 Eventually, our ¹H NMR analysis also revealed that the final NCs were capped solely by polysuccinamic acid, indicating the displacement of both the oleate and amine/ammonium ligands from the NC surface upon transformation (see the discussion in Section S9 and Fig. S20-S26†).

Enhanced stability of the CsPbBr₃/PMAO NCs

The fully-transformed CsPbBr3 NCs formed an optically clear solution in toluene. These CsPbBr₃ NCs possessed an enhanced stability compared to the polymer-free, ligand-capped CsPbBr₃ NCs directly synthesized by following the cesium oleate/lead(II) bromide route.5,25 Such enhanced stability was demonstrated by the fact that the NCs retained their green emission after four weeks of storage under ambient conditions in air (Fig. S29†), even after undergoing a washing cycle of precipitation/redispersion with ethyl acetate (Fig. S30 and S31†), while the polymer-free CsPbBr3 NCs aggregated within hours or days after undergoing a similar washing procedure. Another indicator of the increased stability is the observation that the CsPbBr₃/ PMAO NCs could be concentrated or diluted over \sim 5 orders of magnitude range of concentrations, from \sim 26 mg ml⁻¹ to \sim 1 \times 10⁻⁴ mg ml⁻¹, without any loss of optical transparency or PL emission (Fig. S32†). The increase in the stability of the fullytransformed CsPbBr₃/PMAO NCs is in agreement with prior reports on CsPbBr3 NCs blended with PMAO44,45 or with the dodecyl-grafted-poly(isobutylene-alt-maleic-anhydride).46 Our hypothesis is that the binding of polysuccinamic acid through its multiple functional groups to the NC surface, in place of the standard ligands used in the direct synthesis of CsPbBr₃ NCs (as discussed above and in Section S9, Fig. S20-S26†), is the origin of this enhancement. To test this hypothesis, we compared the solvodynamic diameters of PMAO and

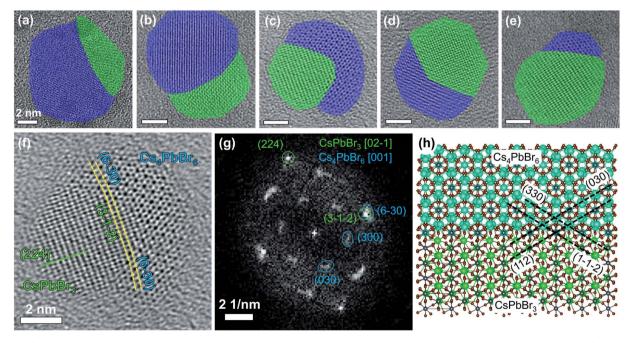


Fig. 3 (a-e) HRTEM images of Cs_4PbBr_6 – $CsPbBr_3$ heterostructures formed upon partial conversion of Cs_4PbBr_6 NCs with PMAO (scale bars are 2 nm). Cs_4 PbBr₆ domains are shaded in blue, and Cs_7 Bbr₃ domains are shaded in green; (f) a magnified view of (c) and (g) the corresponding FFT image; and (h) ball-and-stick atomic model of the epitaxial interface built using VESTA software (ver. 3.4.6, the atoms are depicted as spheres with radii corresponding to 40% of actual atomic radii). 47 Cs atoms in the model are colored in two different colors for clarity: in cyan for Cs_4PbBr_6 and green for CsPbBr3.

CsPbBr₃/PMAO NCs (washed once with ethyl acetate) determined by dynamic light scattering (\sim 1.7 \pm 1.2 nm and \sim 11.2 \pm 0.9 nm, respectively, Fig. S33 and S34†) with the sizes of the inorganic CsPbBr₃ cores from the TEM analysis of the same sample (\sim 7 nm edge length, Fig. S35†). The larger solvodynamic diameter of CsPbBr₃/PMAO NCs in solution compared to the CsPbBr₃ NC edge length from TEM is explained by the PMAO wrapping and NC tumbling in solution (the diagonal of a cube with a 7 nm edge length is \sim 12 nm). The lack of a substantial increase in the solvodynamic diameter of CsPbBr₃/PMAO NCs is interpreted as an indicator of PMAO wrapping around NCs, supporting the hypothesis about the origin of increased NC stability. In addition, the relatively small solvodynamic diameter of CsPbBr₃/PMAO NCs indicates that PMAO molecules do not bind multiple NCs together.

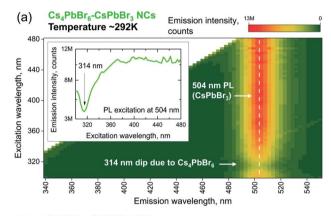
Cs₄PbBr₆-CsPbBr₃ heterostructures

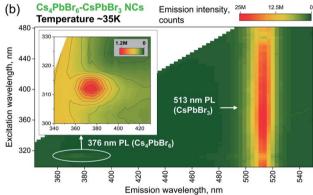
The Cs₄PbBr₆ → CsPbBr₃ NC transformation with PMAO is relatively slow at room temperature. This enabled the observation of NC intermediates consisting of Cs₄PbBr₆-CsPbBr₃ heterostructures (Fig. 3), which were investigated by HRTEM (Fig. 3a-e). In one of the partially-transformed samples we observed NCs with different degrees of conversion (Fig. 3a-e). The heterostructures displayed a variety of interfaces between Cs₄PbBr₆ and CsPbBr₃, some adopting an epitaxial relationship, some not (analysis of the cases is shown in Fig. S36†). For example, the heterostructure shown in Fig. 3c, analyzed in detail in Fig. 3f-h, is characterized by an epitaxial relationship adopted by the two domains, as indicated by the overlap of the spots from the planes of the two crystal structures in fast Fourier transform (FFT, Fig. 3g) of the real space image. The <5% mismatch between the atomic spacing of the two domains $[d(3\overline{12})_{CsPbBr_3} = 2.37 \text{ Å}, \ d(6\overline{30})_{Cs_4PbBr_6} = 2.29 \text{ Å}]$ a slight bending of the planes, as labeled by the dashed lines in Fig. 3f. This bending also indicates that the atomic planes of Cs₄PbBr₆ domains on the two sides of the CsPbBr₃ domain are rotated by a small angle. The rotation gives rise to extended diffraction spots in the FFT image, instead of single sharp spots that would otherwise appear for a single crystal. Considering an orthorhombic phase for CsPbBr₃ (ICSD: 97851, a = 8.207 Å, b =8.255 Å, c = 11.759 Å), the epitaxial relationship between the two domains can be described as follows: CsPbBr₃ [021]||Cs₄PbBr₆ [001], and $CsPbBr_3$ (112) $\|Cs_4PbBr_6$ (030) (see Fig. 3h).

The low-magnification TEM images of the two NC samples were analyzed to quantify changes in the NC dimensions before and after the transformation (Fig. S37–S42†). For example, a sample of 10.1 nm \pm 1.4 nm diameter Cs_4PbBr_6 NCs transformed into 8 nm \pm 0.4 nm edge length $CsPbBr_3$ NCs (Fig. 2a). The Scherrer analysis of the XRD patterns of the same sample before and after the transformation indicated a reduction in the crystallite size from 16.1 \pm 1.8 nm to 12.5 \pm 2.6 nm, in agreement with the TEM analysis (larger dimensions from XRD as compared to TEM are due to the differences between techniques and analyses). In another sample, 15.7 nm \pm 2.6 nm Cs_4PbBr_6 NCs transformed into 12 nm \pm 1.9 nm NCs (dimensions from TEM). If one assumes that such transformation does

not proceed by dissolution–recrystallization, but simply by the gradual removal of CsBr from each individual spherical NC of Cs_4PbBr_6 , converting it to a cube-shaped NC of $CsPbBr_3$, then by volume contraction the resulting $CsPbBr_3$ NCs should have an edge length of 6 nm in TEM (9.5 nm in the second sample), which is \sim 2 nm smaller than the obtained value (Table S1†). Hence, dissolution–recrystallization processes should also play an important role in this transformation. A similar mechanism has been previously invoked to rationalize the inverse NC transformation (from $CsPbBr_3$ to Cs_4PbBr_6).^{8,10}

The PL of the partially-converted sample containing Cs₄PbBr₆-CsPbBr₃ heterostructures was surveyed at room and





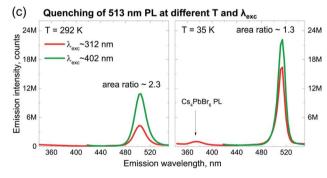


Fig. 4 PL maps of (a) partially-transformed $Cs_4PbBr_6-CsPbBr_3$ NCs at room temperature, and the inset shows the PL excitation spectrum at \sim 504 nm (indicated by a white dashed line in the PL map); (b) partially-transformed $Cs_4PbBr_6-CsPbBr_3$ NCs at \sim 35 K, and the inset shows the low intensity region around 376 nm; (c) PL spectra of $Cs_4PbBr_6-CsPbBr_3$ NCs at 292 K (left panel) and 35 K (right panel) collected under \sim 312 nm (red curve) and \sim 402 nm (green curve) excitation.

cryogenic temperatures (see Section S14 of the ESI† for experimental details) because their optical properties are unknown to date. The results are presented in Fig. 4a and b as excitationemission maps (PL maps). The room temperature ($T \sim 292$ K) PL map of the partially-converted sample contains a single emission peak of CsPbBr₃ at ~504 nm (Fig. 4a). The CsPbBr₃ emission has a broad PL excitation spectrum (inset in Fig. 4a) with a dip at ~314 nm characteristic of Cs₄PbBr₆ absorption. Upon cooling to $T\sim 35$ K, the PL map shows two emission peaks (Fig. 4b): an intense peak at \sim 513 nm and a weak peak at \sim 376 nm (inset in Fig. 4b). The \sim 513 nm peak is an emission feature of CsPbBr₃, red-shifted from ~504 nm as a result of cooling.^{48,49} The \sim 376 nm emission with narrow excitation at \sim 313 nm is assigned to Cs₄PbBr₆ because it matches with previously reported cryogenic PL spectra of bulk Cs₄PbBr₆ (ref. 50) and Cs₄PbBr₆ aggregates in CsBr.⁵¹ This assignment was further confirmed by collecting the PL map of the as-synthesized Cs_4PbBr_6 NCs at $T \sim 27$ K (Fig. S43†). At 27 K, the emission of the as-synthesized Cs₄PbBr₆ NCs is dominated by a peak at ~376 nm surrounded by weaker features due to various electronic transitions in Pb2+ ions.52-54 The as-synthesized Cs4PbBr6 NCs are not emissive at room temperature and, besides the discussed ~376 nm emission, are non-emissive up to the detection limit of 1600 nm when cooled (Fig. S44†).

The dual emission of partially-transformed NCs provides an opportunity to probe the energy transfer between Cs₄PbBr₆ and CsPbBr₃. Fig. 4c shows a comparison between pairs of emission spectra for the partially-converted sample collected at two different temperatures (292 K and 35 K) and two different excitation energies: one matching with Cs₄PbBr₆ absorption ($\lambda_{\rm exc} \sim$ 312 nm) and one below it ($\lambda_{\rm exc} \sim 402$ nm, only CsPbBr₃ absorbs). At 292 K (Fig. 4c, left panel), only CsPbBr3 emits, regardless of excitation energy, and its emission is quenched by a factor of \sim 2.3 after changing the excitation energy from \sim 402 nm to \sim 312 nm. This quenching is attributed to the attenuation of \sim 312 nm excitation due to absorption by Cs₄PbBr₆ and an excitation-

dependent PL efficiency.55 At 35 K, both materials emit, and the CsPbBr₃ emission is guenched by a smaller factor of \sim 1.3 (Fig. 4c, right panel). We can assign the lower quenching of CsPbBr₃ emission at 35 K to the energy transfer from Cs₄PbBr₆, which indeed is favored due to the overlap between the emission of the donor (Cs₄PbBr₆) and the absorption of the acceptor (CsPbBr₃). These initial observations make Cs₄PbBr₆-CsPbBr₃ NCs a promising platform for future spectroscopic studies of the energy flow between lead halide perovskites and related compounds.

Reactivity of Cs₄PbBr₆ NC samples with PMAO in drop-cast

The reaction described above can also proceed inside a polymer film (as was confirmed by in situ Raman spectroscopy, see Fig. S45†), which makes its investigation relevant for the emerging application of blends between PMAO and oleylammonium/oleate-capped perovskite NCs in light-emitting diodes.44,45 From this point of view, the Cs₄PbBr₆ to CsPbBr₃ transformation is an indicator of amine-anhydride reactivity, and its kinetics can be studied in situ by steady-state and timeresolved PL. Fig. 5 shows the results of the in situ PL measurements from a macroscopic area (\sim 2 mm excitation spot size) of the film made by quick drop-casting of a freshly prepared PMAO-Cs₄PbBr₆ NCs blend. Green PL develops within the first few minutes in the drop-cast film, and reaches a stable intensity and position (\sim 510 nm, full width at half maximum of 18 nm) after \sim 2 hours (Fig. 5a and b), indicating the timescale of the complete conversion. Both the PL intensity and the absorbance of the film (at 405 nm, the wavelength of the CW laser used for excitation) increase over the course of the transformation, with a characteristic time constant of about ~ 10 minutes (Fig. 5c). Similar kinetics were obtained by in situ micro-PL performed with a confocal fluorescence microscope (Fig. S46†), suggesting that the transformation proceeds uniformly across the blend. The PLQY in the film remains almost constant at \sim 20%

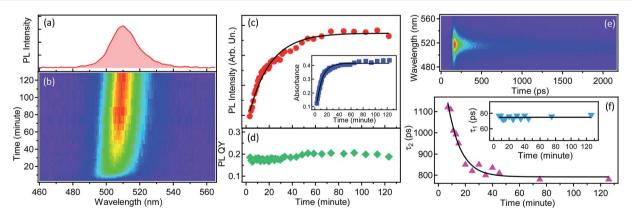


Fig. 5 Tracking the Cs₄PbBr₆ → CsPbBr₃ NC transformation in a drop-cast film by PL spectroscopy. (a) PL spectrum of the fully transformed CsPbBr₃ NCs, peaking at \sim 510 nm. (b) Spectrally-resolved temporal evolution of the PL spectrum on a minute scale, for \sim 120 minutes. (c) Time evolution of the integrated PL intensity fitted with first-order kinetics (solid black line, time ~10 min). The inset shows time-dependent absorbance at 405 nm over the course of the transformation. (d) Time-dependent PLQY of the drop-cast film. (e) PL intensity map showing the picosecond temporal behavior of the emission intensity of the drop-cast films. (f) Temporal evolution of the longer PL decay lifetime, τ_2 , over the NCs transformation. The continuous line is a fit to the data by first-order kinetics. The corresponding trend for the shorter component, τ_1 , is shown in the inset.

throughout the transformation, similar to the values measured in the solution (Fig. 5d).

The evolution of PL during the transformation was also monitored by in situ spectrally-resolved transient PL. The temporal PL decay is sub-ns and contains two main components, the shorter (\sim 70 ps) and longer (950 ps) ones (Fig. 5e and S47†). The shorter decay component varies little over the course of the transformation while the longer decay component decreases from \sim 1.1 ns to \sim 800 ps with a time constant of \sim 10 minutes (Fig. 5f). The PL decay of the emitting NCs in the film is much shorter than that of the NCs in solution (\sim 4–5 ns), the polymer-free CsPbBr₃ NCs^{5,35,56-58} (~2-10 ns), and polymerencapsulated single CsPbBr₃ NCs (~6 ns).¹⁸ It is definitely much shorter than that of MAPbBr₃ NCs/polymer blends (>100 ns).⁵⁹ The fast PL decay of CsPbBr₃/PMAO NCs in the drop-cast film can be attributed to various possible causes, including: (i) the appearance of a new non-radiative carrier recombination channel, ascribable to oxygen molecules (as the samples were prepared in air) which act as traps for electrons;26 (ii) electron hopping between neighboring nanocrystals in the film;60 (iii) a more defective surface of NCs formed in films, due to reduced mobility of ions and molecules (preventing efficient passivation of surface sites in comparison to the solution case). The sub-ns PL decay of NCs in blends with PMAO, combined with a reasonable PLQY, should be of interest for applications in scintillators, where ultrafast and efficient emission is required for fast timing capability of imaging detectors. 61,62

Conclusions

Chemical transformation of colloidal Cs₄PbBr₆ NCs to perovskite CsPbBr₃ NCs induced by the organic co-polymer PMAO is presented as a promising strategy to prepare stable and bright CsPbBr3 NC emitters. The PMAO reactivity towards oleylammonium/oleate-capped Cs₄PbBr₆ NCs favors an addition reaction of oleylamine ligands from the NC surface to the succinic anhydride groups of the polymer. This destabilizes the NCs and acidifies the reaction environment through the formation of polysuccinamic acid, a PMAO-oleylamine adduct, which binds to the surface of the NCs in lieu of the original ligands. These two factors - ligand replacement and in situ acid formation - drive the Cs₄PbBr₆ to CsPbBr₃ NC transformation. The lower reactivity of PMAO, as compared to that of the previously reported reagents, enabled the investigation of Cs₄PbBr₆-CsPbBr₃ intermediate heterostructures by HRTEM. The heterostructures feature a variety of epitaxial and nonepitaxial relationships between the two structurally dissimilar domains. At cryogenic temperature, Cs₄PbBr₆-CsPbBr₃ NCs display dual emission at ~376 nm and 513 nm with evidence of energy transfer from Cs₄PbBr₆ to CsPbBr₃. The PMAO-induced transformation proceeds both in solutions and in drop-cast films, producing CsPbBr₃ NCs with a narrow size distribution and attractive photoluminescence properties (up to 69% PLQY in solution and a sub-ns PL lifetime in the drop-cast films). The resulting CsPbBr₃/PMAO NCs demonstrate enhanced stability by retaining their green emission for several weeks in air. The increased stability of CsPbBr₃/PMAO NCs is attributed to the

adhesion of polysuccinamic acid through its multiple functional groups to the NC surface. The PMAO-induced transformation of $\rm Cs_4PbBr_6$ NCs opens up a general strategy for chemical modification of inorganic NCs passivated with nucleophilic amines.

Author contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

Abbreviations

COD Crystallography open database EDS Energy dispersive X-ray spectroscopy

FFT Fast Fourier transform

FTIR Fourier transform infrared spectroscopy

HRTEM High resolution TEM

HSQC Heteronuclear single quantum coherence ICSD Inorganic crystal structure database

NIR Near infrared

NMR Nuclear magnetic resonance

NC Nanocrystal PL Photoluminescence

PMAO Poly(maleic anhydride-alt-1-octadecene)

QY Quantum yield STEM Scanning TEM

TEM Transmission electron microscopy

XRD X-ray diffraction

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