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# Transforming colloidal Cs<sub>4</sub>PbBr<sub>6</sub> nanocrystals with poly(maleic anhydride-*alt*-1-octadecene) into stable CsPbBr<sub>3</sub> perovskite emitters through intermediate heterostructures†

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The preparation of strongly emissive CsPbBr<sub>3</sub> 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 CsPbBr<sub>3</sub> perovskite nanocrystals by reacting oleylammonium/oleate-capped Cs<sub>4</sub>PbBr<sub>6</sub> nanocrystals with poly(maleic anhydride-*alt*-1-octadecene) (PMAO). PMAO contains succinic anhydride units that are reactive towards the oleylamine species present on the Cs<sub>4</sub>PbBr<sub>6</sub> nanocrystals' surface and produces polysuccinamic acid, which, in turn, triggers the Cs<sub>4</sub>PbBr<sub>6</sub> to CsPbBr<sub>3</sub> conversion. The transformation occurs through the formation of Cs<sub>4</sub>PbBr<sub>6</sub>-CsPbBr<sub>3</sub> heterostructures as intermediates, which are captured because of the mild reactivity of PMAO and are investigated by high-resolution electron microscopy. The Cs<sub>4</sub>PbBr<sub>6</sub>-CsPbBr<sub>3</sub> heterostructures demonstrate a dual emission at cryogenic temperature with an indication of the energy transfer from Cs<sub>4</sub>PbBr<sub>6</sub> to CsPbBr<sub>3</sub>. The fully-transformed CsPbBr<sub>3</sub> 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 Cs<sub>4</sub>PbBr<sub>6</sub> 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.<sup>1–3</sup> The chemical reactivity of these NCs and the interconversion between the NCs of the two most studied bromides in this class, Cs<sub>4</sub>PbBr<sub>6</sub> and CsPbBr<sub>3</sub> perovskite, have been of interest since these NCs were first synthesized in the colloidal form.<sup>4–8</sup> The Cs<sub>4</sub>PbBr<sub>6</sub> → CsPbBr<sub>3</sub> conversion, which can be triggered using various reagents (for example, Prussian blue,<sup>9</sup> oleic acid,<sup>10</sup> PbBr<sub>2</sub>,<sup>7,11</sup> and water)<sup>12–14</sup> is an interesting approach to prepare emissive CsPbBr<sub>3</sub> NCs. For

example, Yin's group exploited heterogeneous water-mediated CsBr extraction from Cs<sub>4</sub>PbBr<sub>6</sub> NCs in hexane as a method for making luminescent CsPbBr<sub>3</sub>/SiO<sub>2</sub> or CsPbBr<sub>3</sub>/Ta<sub>2</sub>O<sub>5</sub> Janus-type heterostructures,<sup>13</sup> and branched CsPbBr<sub>3</sub> dodecapods.<sup>15</sup> Despite several reports on Cs<sub>4</sub>PbBr<sub>6</sub> → CsPbBr<sub>3</sub> transformation at the nanoscale, the nanocrystal intermediates of this reaction and the surface passivation and stability of the resulting CsPbBr<sub>3</sub> NCs have not been investigated.

Designing the Cs<sub>4</sub>PbBr<sub>6</sub> → CsPbBr<sub>3</sub> NC transformation in such a way that it delivers encapsulated CsPbBr<sub>3</sub> NCs with an enhanced stability is a promising approach for exploiting the Cs<sub>4</sub>PbBr<sub>6</sub> NC reactivity, as shown by the above mentioned studies of Yin's group.<sup>13</sup> The use of an organic polymer instead

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† Electronic supplementary information (ESI) available: Experimental details and procedures, EDS-STEM data, <sup>1</sup>H and <sup>1</sup>H-<sup>13</sup>C HSQC NMR spectra and discussion, annotated XRD patterns, PLQY spectra, FTIR and NIR absorbance spectra, tests of PMAO reactivity with powders of bulk Cs<sub>4</sub>PbBr<sub>6</sub> and amine-free Cs<sub>4</sub>PbBr<sub>6</sub> NCs, stability tests of CsPbBr<sub>3</sub>/PMAO NCs, HRTEM images of Cs<sub>4</sub>PbBr<sub>6</sub>-CsPbBr<sub>3</sub> heterostructures, low-resolution TEM size analysis, PL maps and spectra of Cs<sub>4</sub>PbBr<sub>6</sub> 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 Cs<sub>4</sub>PbBr<sub>6</sub> NCs into green-emitting CsPbBr<sub>3</sub> NCs after addition of PMAO (MP4). See DOI: 10.1039/d0sc00738b.









CsPbBr<sub>3</sub>/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 CsPbBr<sub>3</sub> cores from the TEM analysis of the same sample ( $\sim 7$  nm edge length, Fig. S35†). The larger solvodynamic diameter of CsPbBr<sub>3</sub>/PMAO NCs in solution compared to the CsPbBr<sub>3</sub> 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 CsPbBr<sub>3</sub>/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 CsPbBr<sub>3</sub>/PMAO NCs indicates that PMAO molecules do not bind multiple NCs together.

### Cs<sub>4</sub>PbBr<sub>6</sub>-CsPbBr<sub>3</sub> heterostructures

The Cs<sub>4</sub>PbBr<sub>6</sub> → CsPbBr<sub>3</sub> NC transformation with PMAO is relatively slow at room temperature. This enabled the observation of NC intermediates consisting of Cs<sub>4</sub>PbBr<sub>6</sub>-CsPbBr<sub>3</sub> 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 Cs<sub>4</sub>PbBr<sub>6</sub> and CsPbBr<sub>3</sub>, 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 [ $d(3\bar{1}2)_{\text{CsPbBr}_3} = 2.37$  Å,  $d(6\bar{3}0)_{\text{Cs}_4\text{PbBr}_6} = 2.29$  Å] leads to a slight bending of the planes, as labeled by the dashed lines in Fig. 3f. This bending also indicates that the atomic planes of Cs<sub>4</sub>PbBr<sub>6</sub> domains on the two sides of the CsPbBr<sub>3</sub> 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 CsPbBr<sub>3</sub> (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: CsPbBr<sub>3</sub> [02 $\bar{1}$ ] || Cs<sub>4</sub>PbBr<sub>6</sub> [001], and CsPbBr<sub>3</sub> (112) || Cs<sub>4</sub>PbBr<sub>6</sub> (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  $10.1 \text{ nm} \pm 1.4$  nm diameter Cs<sub>4</sub>PbBr<sub>6</sub> NCs transformed into  $8 \text{ nm} \pm 0.4$  nm edge length CsPbBr<sub>3</sub> 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,  $15.7 \text{ nm} \pm 2.6$  nm Cs<sub>4</sub>PbBr<sub>6</sub> NCs transformed into  $12 \text{ nm} \pm 1.9$  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<sub>4</sub>PbBr<sub>6</sub>, converting it to a cube-shaped NC of CsPbBr<sub>3</sub>, then by volume contraction the resulting CsPbBr<sub>3</sub> 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<sub>3</sub> to Cs<sub>4</sub>PbBr<sub>6</sub>).<sup>8,10</sup>

The PL of the partially-converted sample containing Cs<sub>4</sub>PbBr<sub>6</sub>-CsPbBr<sub>3</sub> heterostructures was surveyed at room and



Fig. 4 PL maps of (a) partially-transformed Cs<sub>4</sub>PbBr<sub>6</sub>-CsPbBr<sub>3</sub> 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<sub>4</sub>PbBr<sub>6</sub>-CsPbBr<sub>3</sub> NCs at  $\sim 35$  K, and the inset shows the low intensity region around 376 nm; (c) PL spectra of Cs<sub>4</sub>PbBr<sub>6</sub>-CsPbBr<sub>3</sub> 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.





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<sup>†</sup>). 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 CsPbBr<sub>3</sub> NCs<sup>5,35,56–58</sup> ( $\sim 2$ – $10$  ns), and polymer-encapsulated single CsPbBr<sub>3</sub> NCs ( $\sim 6$  ns).<sup>18</sup> It is definitely much shorter than that of MAPbBr<sub>3</sub> NCs/polymer blends ( $>100$  ns).<sup>59</sup> The fast PL decay of CsPbBr<sub>3</sub>/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;<sup>26</sup> (ii) electron hopping between neighboring nanocrystals in the film;<sup>60</sup> (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.<sup>61,62</sup>

## Conclusions

Chemical transformation of colloidal Cs<sub>4</sub>PbBr<sub>6</sub> NCs to perovskite CsPbBr<sub>3</sub> NCs induced by the organic co-polymer PMAO is presented as a promising strategy to prepare stable and bright CsPbBr<sub>3</sub> NC emitters. The PMAO reactivity towards oleylammonium/oleate-capped Cs<sub>4</sub>PbBr<sub>6</sub> 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 Cs<sub>4</sub>PbBr<sub>6</sub> to CsPbBr<sub>3</sub> NC transformation. The lower reactivity of PMAO, as compared to that of the previously reported reagents, enabled the investigation of Cs<sub>4</sub>PbBr<sub>6</sub>–CsPbBr<sub>3</sub> intermediate heterostructures by HRTEM. The heterostructures feature a variety of epitaxial and non-epitaxial relationships between the two structurally dissimilar domains. At cryogenic temperature, Cs<sub>4</sub>PbBr<sub>6</sub>–CsPbBr<sub>3</sub> NCs display dual emission at  $\sim 376$  nm and 513 nm with evidence of energy transfer from Cs<sub>4</sub>PbBr<sub>6</sub> to CsPbBr<sub>3</sub>. The PMAO-induced transformation proceeds both in solutions and in drop-cast films, producing CsPbBr<sub>3</sub> 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 CsPbBr<sub>3</sub>/PMAO NCs demonstrate enhanced stability by retaining their green emission for several weeks in air. The increased stability of CsPbBr<sub>3</sub>/PMAO NCs is attributed to the

adhesion of polysuccinamic acid through its multiple functional groups to the NC surface. The PMAO-induced transformation of Cs<sub>4</sub>PbBr<sub>6</sub> 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- <i>alt</i> -1-octadecene)
QY	Quantum yield
STEM	Scanning TEM
TEM	Transmission electron microscopy
XRD	X-ray diffraction

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