

Insights into the Role of Lead/Surfactants Ratio on Formation and Passivation of Cesium Lead Bromide Perovskite Nanocrystals

Roberto Grisorio^{,†}, Elisabetta Fanizza,^{‡,⊥} Ignazio Allegrretta,[#] Davide Altamura,[§] Marinella Striccoli,[⊥] Roberto Terzano,[#] Cinzia Giannini,[§] Viviana Vergaro,^{‡,§} Giuseppe Ciccarella,^{‡,§} Nicola Margiotta[‡] and Gian Paolo Suranna^{†,‡}*

[†]Dipartimento di Ingegneria Civile, Ambientale, del Territorio, Edile e di Chimica (DICATECh), Politecnico di Bari, Via Orabona 4, 70125 Bari, Italy

[‡]Dipartimento di Chimica, Università degli Studi di Bari "A. Moro", Via Orabona 4, 70126 Bari, Italy

[⊥]CNR–Istituto per i Processi Chimico Fisici, UOS Bari, Via Orabona 4, 70126 Bari, Italy

[#]Dipartimento di Scienze del Suolo, della Pianta e degli Alimenti, Università degli Studi di Bari "Aldo Moro", Via G. Amendola 165/A, 70126 Bari, Italy

[§]Institute of Crystallography, National Research Council, via Amendola 122/O, Bari 70126, Italy

^JDipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento & UdR
INSTM di Lecce, Campus Universitario, Via Monteroni 73100 Lecce, Italia.

[‡]CNR NANOTEC – Istituto di Nanotecnologia, Via Monteroni, 73100 Lecce, Italy

ABSTRACT. This study aims at rationalizing the effects of lead/surfactants ratio on the structural evolution of cesium lead-bromide perovskite nanocrystals (NCs), ascertaining how their shape and surface composition can be modulated by suitably adjusting the ligands amount (an equivolumetric mixture of oleic acid and oleyl amine) relatively to lead bromide. The tailoring of the reaction conditions allows the obtainment of blue-emitting CsPbBr₃ nanoplatelets in the presence of ligands excess, while green-emitting nanocubes are achieved in low-surfactant conditions. An insight into the NC's shape evolution dictated by the different reaction conditions suggests that the generation of CsPbBr₃ nanoplatelets is controlled by the dimensions of [(RNH₃)₂(PbBr₄)]_n layers formed before the injection of cesium oleate. The growth step promoted by preformed layers is concomitant to (but independent from) the nucleation process of lead-based species, leading to centrosymmetric nanocubes (prevalent in low-surfactant regimes) or Cs₄PbBr₆ NCs (prevalent in high-surfactant regimes). The proposed NC growth is supported by the analysis of the optical properties of non-purified samples, which reveal the selective presence of structures endowed with four cell unit average thickness accompanying larger emissive nanocubes. By combining nuclear magnetic resonance (NMR) and UV-Vis spectroscopies, it is ascertained that the lead/surfactants ratio also controls the relative proportion between lead-based species (PbBr₂, PbBr₃⁻, PbBr₄²⁻ and plausibly PbBr₅³⁻ or PbBr₆⁴⁻) formed before cesium injection, which regulate the size of [(RNH₃)₂(PbBr₄)]_n layers as well as the

formation of Cs_4PbBr_6 NCs during the nucleation stage. The surface chemistry of the differently structured perovskite NCs is investigated by correlating the elemental composition of the nanoparticles with specific NMR signals ascribable to the surface ligands. This level of investigation also sheds light on the stability of the time-dependent fluorescence exhibited by differently composed perovskite NCs before the loss of their colloidal integrity. Our findings can bring about a fine tuning of the synthetic methods currently employed for controlling shape and surface chemistry of perovskite NCs.

INTRODUCTION

Lead-halide perovskite nanocrystals (NCs) with generic formula APbX_3 (in which A represents methylammonium, formamidinium or cesium ions and $\text{X} = \text{Cl}, \text{Br}, \text{I}$ or a mixture thereof) have showcased their great potential as solution-processed materials for a wide range of photonic¹ and optoelectronic applications.^{2,3} The most important advantage of perovskite NCs resides in the easy modulation of their optical band gap by exchanging their individual components without compromising their high photoluminescence (PL) quantum yields.^{4,5} Due to their unusual tolerance to high defect levels,⁶ their PL is also characterized by narrow emission band widths throughout the whole visible range.⁷ In particular, all-inorganic CsPbX_3 perovskite nanoparticles offer an appealing alternative to prototypical metal chalcogenide NCs,⁸ thus allowing these materials to be considered a fundamental class of semiconductors with tunable emission in the visible spectrum.⁹ However, differently from metal chalcogenides, the crystal structure of CsPbX_3 NCs is characterized by a predominant ionic interaction between atoms, which confers a pronounced chemical and colloidal instability to this class of nanomaterials.¹⁰ To date, there

seems to be no general consensus on the role played by the individual components of the perovskite nanoparticles (comprising the organic shell protecting the inorganic framework) in their long-term stabilization, as well as on how to tune the reaction conditions towards this aim.^{11,12}

Two general synthetic strategies have been developed for the direct synthesis of metal-halide perovskite NCs. The first one is based on the ligand-assisted reprecipitation process, which is carried out at relatively low (up to 60 °C) temperature.^{13,14} Metal halide salts are previously dissolved in polar solvents and then slowly added to a nonpolar medium containing the surfactants. The scarce solubility of the metal-halide salts in the nonpolar solvent promotes their precipitation with the concomitant NC formation, but the solvent polarity can severely compromise the crystal structure of the CsPbX₃ NCs.¹⁵ Conversely, the second synthetic methodology is the hot injection (up to 200 °C) of a soluble cesium ion precursor (typically cesium oleate) to a mixture of an inorganic salt (*i.e.* PbX₂) in nonpolar solvents acting as both lead and halide source.¹⁶ In this case, the NC formation immediately follows the cesium addition and the reaction temperature as well as the ligand nature exert a crucial role on the nanoparticle morphology.¹⁷ Also the modulation of the acidity (or basicity) of the relevant reaction medium before the addition of cesium oleate influences the morphology of CsPbBr₃ NCs in hot-injection syntheses.¹⁸ A refinement of traditional hot-injection protocols envisages the dissolution of cesium and lead precursors in the presence of the appropriate combination of surfactants followed by the injection of the halide source,¹⁹ thus allowing to increase the halide/lead ratio which is crucial for the obtainment of highly luminescent perovskite NCs.^{20,21} With this approach, the synthesis of size tunable CsPbBr₃ nanocubes can be achieved by the introduction of controlled amounts of alkylammonium bromide salts at a fixed reaction temperature.²²

Furthermore, most syntheses of perovskite nanoparticles are carried out in the presence of aliphatic primary amines and carboxylic acids as passivating agents,^{23,24} which, in turn, provide them with a complex and dynamic ligand shell,²⁵ which is also influenced by the NC composition.²⁶ On the basis of recent studies on the rationalization of the surface chemistry of perovskite NCs,^{27,28} the modification of the nanoparticle organic shell has been also proposed aiming at improving stability^{29,30} and shape purity.^{31,32}

At the same time, the reciprocal interaction between the individual components of the reaction to achieve a full control over the nanoparticle generation as well as their properties and stability still remains elusive. To date, few studies have addressed the effects of the reaction conditions on the optical and morphological properties^{33,34} as well as on the surface chemistry of the resulting perovskite NC.^{35,36} Although synthetic methods based on the separation between the lead and halide sources warrant the suitable conditions for the obtainment of good quality and highly luminescent materials, the use of lead-halide salts as precursors remains the only approach for controlling the nanoparticle morphology in hot-injection recipes.

In this work, we gained insights into reaction mechanism leading to the obtainment of CsPbBr₃ NCs, employing readily accessible starting materials, such as PbBr₂, oleic acid (OLA) and oleyl amine (OAM) as the ligands. We ascertained that the lead/surfactants ratio is a crucial parameter for controlling shape, structure and surface of CsPbBr₃ NCs in hot-injection methods. An insight into the NC evolution guided by the different reaction conditions highlighted how the generation of two-dimensional layers before injecting cesium oleate constitutes the driving force for the obtainment of CsPbBr₃ nanoplatelets, which constitutes a pathway competing with the nucleation process of lead-based species. Being the fundamental studies of perovskite crystal growth in their

embryonic stage, this investigation could represent a further piece for fully understanding the formation of perovskite nanocrystals.

RESULTS AND DISCUSSION

Synthesis and characterization of CsPbBr₃ NCs. The solution of cesium oleate employed for the syntheses of lead halide perovskite NCs in this study was prepared by reacting the suitable amounts of cesium carbonate and oleic acid (OLA) in 1-octadecene (ODE). Before injection into the reaction mixture containing the lead precursor, the colorless solution of cesium oleate was kept at 140°C to warrant the complete solubility of the formed salt in the apolar solvent. It is important to remark that all syntheses of the perovskite nanoparticles in this study were carried out by using the same batch of cesium oleate solution, thus bypassing any complication related to the variability of results that might be ascribed to the preparation of cesium oleate itself.³⁷ The prototypical perovskite CsPbBr₃ NCs were obtained by dissolving PbBr₂ (0.38 mmol) at the chosen reaction temperature (140 °C) in a mixture composed of an equivolumetric amount of the two ligands (OAM and OLA) and ODE, the latter appropriately adjusted to maintain the same lead concentration (0.04 M) in all syntheses, as summarized in Table 1. After the lead salt was dissolved at the reaction temperature (10 minutes), the warm solution of the cesium source (0.09 mmol) was injected to obtain a yellow mixture, that was rapidly cooled (after 10 seconds) and centrifugated to isolate the nanoparticles. Hereafter, the perovskite nanoparticles obtained after the centrifugation will be referred to as "as-prepared" NCs.

The size and morphology of as-prepared CsPbBr₃ NCs synthesized with variable lead/surfactant ratios were investigated by transmission electron microscopy (TEM, Figure 1A-D). These

images clearly evidence that well-defined square shaped nanostructures ascribable to nanocubes were obtained only in the case of CsPbBr₃(1) and CsPbBr₃(2) syntheses, in which a low amount of both ligands is used. Conversely, the morphology of the other samples – *i.e.* CsPbBr₃(3) and CsPbBr₃(4) – can be described as nanoplatelets, because these nanoparticles tended to self-assemble into rod-like structures by "face-to-face" stacking.³⁸ The average sizes of CsPbBr₃(1-4) NCs are reported in Table 1, which clearly evidences a direct correlation between the amount of employed surfactants (OLA and OAM) and the lateral dimensions of the obtained nanoparticles, which passed from 8.1±0.8 nm in the case of CsPbBr₃(1) to 20.0±2.8 in the case of CsPbBr₃(4). At the same time, the lower contrast exhibited by TEM images of suggests that the dimension perpendicular to the grid is smaller than that of CsPbBr₃(3) NCs. In reality, CsPbBr₃(4) sample also contains Cs₄PbBr₆ impurities (see Figure S1 for a large area TEM image), which do not interfere with the optical properties of the material.¹⁸

Being related to their morphology, the optical response of CsPbBr₃(1-4) NCs also resulted to be dependent on the reaction conditions, as clearly evident by the comparison of their absorption spectra shown in Figure 1E. More specifically, in the case of cubic-shaped CsPbBr₃(1) NCs, the UV-Vis absorption spectrum is mainly constituted by a well-defined band-edge exciton transition peak at 504 nm accompanied by other resolved higher-energy transitions the presence of which is consequence of the small nanoparticle dimensions.³⁹ Structured absorption profiles are also exhibited by CsPbBr₃(2-4) NCs, in which the main absorption peak located at 475 nm is accompanied by a low-energy band, which is progressively blue-shifted directly following the increase of the surfactants employed for the corresponding NC synthesis. In parallel, the PL spectra of as-prepared CsPbBr₃(1-4) NCs (Figure 1F) also showed different emission contributions in relation with the variation of the lead/surfactant combination employed for NC

synthesis. In detail, the PL maximum of CsPbBr₃(1) is located at 511 nm as typically observed for lead-bromide perovskite nanocubes of comparable sizes,⁴⁰ while in the case of CsPbBr₃(2-4) NCs, the emission maxima passed from 507 nm to 478 nm, the latter emission recorded for nanoplatelets of four cell unit average thickness.⁴¹

Sample	OA/OAM/ODE (mL)	Elemental composition	Lateral dimension (nm)	λ_{abs} (nm)	λ_{em} (nm)	FWHM (nm)	PLQY (%)
CsPbBr ₃ (1)	0.25/0.25/9.0	Cs _{1.1} PbBr _{2.9}	8.1±0.8	504	511	20	58
CsPbBr ₃ (1) purified ^a	0.25/0.25/9.0	Cs _{1.3} PbBr _{2.9}	8.0±0.7	504	508	17	57
CsPbBr ₃ (2)	0.50/0.50/8.5	Cs _{1.3} PbBr _{3.0}	9.7±1.5	474	507	20	68
CsPbBr ₃ (3)	1.0/1.0/7.5	Cs _{1.4} PbBr _{3.0}	13.6±2.2	476	491	28	71
CsPbBr ₃ (4)	1.5/1.5/6.5	Cs _{2.8} PbBr _{3.9}	20.0±2.8	475	478	23	80
CsPbBr ₃ (4) purified ^a	1.5/1.5/6.5	Cs _{1.8} PbBr _{3.4}	19.6±2.7	475	483	20	82

Table 1. Summary of the experimental details, elemental composition, morphological and optical properties of as-prepared CsPbBr₃ NCs. ^aSample obtained as centrifugation precipitate after treatment with acetone.

Although as-prepared NCs exhibited relatively narrow emission widths (FWHM of 20÷28 nm) of the main PL peak (Table 1), PL spectra of CsPbBr₃(1-3) NCs are contaminated by a residual emission peaked at 478 nm typical of perovskite structures endowed with four cell unit average thickness.⁴¹ The analysis of the emission profiles of as-prepared samples could be fundamental for investigating the crystal growth during the nanoparticle formation. In fact, the emission

spectra of $\text{CsPbBr}_3(1-3)$ NCs are remarkably different with respect to those typically containing a systematic distribution of nanoplatelets, which are characterized by several fluorescence peaks, each for a determined platelet thickness.⁴² This peculiarity hints that the NCs growth is not a regularly controlled process, but could involve two independent pathways. At the same time, the main emission peak of $\text{CsPbBr}_3(4)$ NCs centered at 478 nm is "fouled" by a longer wavelength fluorescence tail. Remarkably, all materials displayed high PLQYs ($58 \div 80\%$, Table 1), which, in the case of $\text{CsPbBr}_3(4)$ are surprising, since one would expect that the high surface to volume ratio inherent to the platelet morphology should render the NCs exceptionally sensitive to surface defects and consequently prone to exhibit low PLQY.

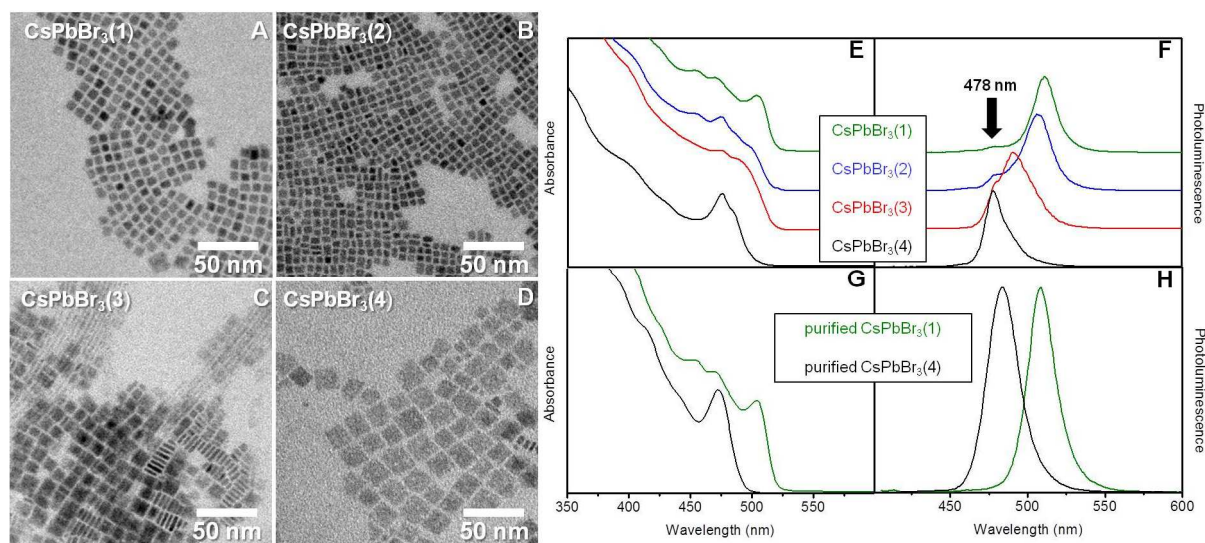


Figure 1. TEM images of as-prepared $\text{CsPbBr}_3(1-4)$. UV-Vis absorption and normalized PL spectra of as-prepared $\text{CsPbBr}_3(1-4)$ NCs (E-F); the traces are vertically shifted for clarity. Comparison between UV-Vis absorption (G) and PL spectra (H) of purified $\text{CsPbBr}_3(1)$ and $\text{CsPbBr}_3(4)$ NCs. UV-Vis and PL spectra were recorded in cyclohexane.

Next, we investigated the effects of the purification procedure on CsPbBr₃(1-4) NCs aiming at improving the emission quality of the relevant nanoparticles. We previously ascertained that the adoption of a purification methodology assisted by a small equivolumetric amount of the ligands preserves the elemental and morphological composition of CsPbBr₃ NCs.²⁶ While the purification did not remarkably affect the absorption and emission properties of CsPbBr₃(2) and CsPbBr₃(3) samples, the precipitation with acetone completely removes the residual high-energy emission in CsPbBr₃(1), thus affording a pure green fluorescence (λ_{em} = 508 nm, FWHM = 17 nm), as reported in Figure 1G-H. At the same time, the same procedure (exemplified in Figure 2) carried out on CsPbBr₃(4) allowed to isolate a product emitting at 483 nm with a narrow fluorescence band (FWHM = 20 nm). TEM investigations permitted to conclude that both the morphology and the dimensions (8.0±0.7 nm) of purified CsPbBr₃(1) NCs were not modified by the purification (Figure 2C). In the case of purified CsPbBr₃(4) NCs, TEM analyses revealed that the narrow fluorescence profile is due to the removal of thicker nanoplatelets as well as to Cs₄PbBr₆ impurities (Figure 2D-E), which contaminated the original sample. Remarkably, the PLQYs of the purified nanoparticles resulted to be nearly identical to those of the corresponding as-prepared NCs (Table 1). Hence, we demonstrated that it is possible to synthesize highly emissive blue- or green-emitting CsPbBr₃ NCs by varying the lead/surfactants ratio.

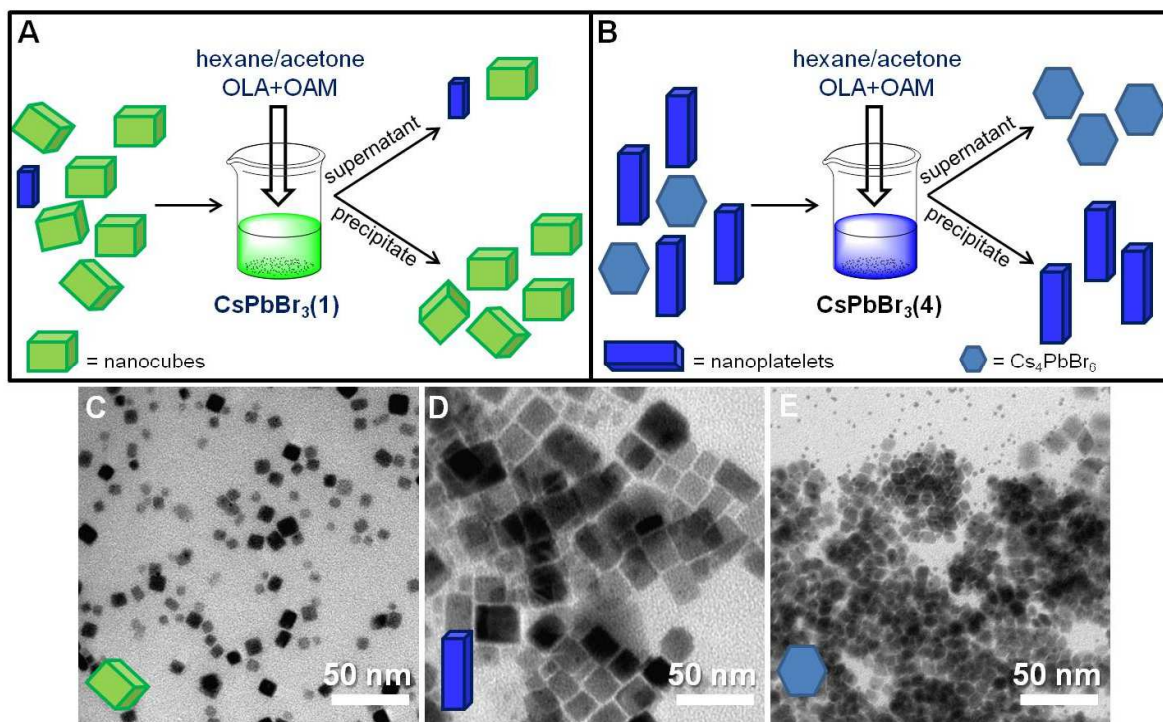


Figure 2. Representation of the purification procedure consisting in a precipitation with acetone of the original samples fractioned in precipitate and supernatant after centrifugation in the case of $\text{CsPbBr}_3(1)$ (A) and $\text{CsPbBr}_3(4)$ (B) nanoparticles. TEM images of relevant purified nanocrystals: (C) $\text{CsPbBr}_3(1)$ = precipitate; (D) $\text{CsPbBr}_3(4)$ = precipitate; (E) $\text{CsPbBr}_3(4)$ = supernatant.

Although fully inorganic perovskite NCs show a remarkably bright fluorescence independently of the synthetic procedure and purification method, the observed sub-unity PLQY values of $\text{CsPbBr}_3(1-4)$ NCs suggest the presence of energy losses due to deleterious charge trapping and non-radiative recombination.⁴³ In order to investigate the origins of these energy loss processes, we analyzed the composition of as-prepared $\text{CsPbBr}_3(1-4)$ samples by using a field emission gun scanning electron microscopy (FEG-SEM) coupled with energy dispersive X-ray spectroscopy

(EDX). The relevant results in terms of the NC elemental composition are listed in Table 1 (see also Table S1 and Figure S2). Firstly, since their elemental composition shows a Cs/Pb ratio > 1.0, it can be deduced that our CsPbBr₃ NCs exhibit also cesium at their surface,⁴⁴ despite the fact that NC syntheses were carried out using a formal excess of lead precursors (see Experimental Section). At the same time, the highest Cs/Pb ratio in CsPbBr₃(4) sample should take into account the simultaneous formation of Cs₄PbBr₆ NCs, which alter the elemental composition of the final sample in the absence of a purification procedure. Another important information on the elemental composition of lead-halide perovskite nanoparticles can be deduced by the Br/Pb ratio, since deviations from the expected stoichiometry (Br/Pb = 3.0) can plausibly indicate the presence of point defects in the crystal lattice of the nanomaterial.⁴⁵ In our case, the Br/Pb ratio ranges from 2.9 for CsPbBr₃(1) to 3.9 for CsPbBr₃(4). Again, the contamination of CsPbBr₃(4) nanoplatelets explains the observed high bromine content in its elemental composition, while the lower Br/Pb ratio (2.9) in CsPbBr₃(1) should be consistent with bromide-poor synthetic conditions (related to the variable amount of surfactants) and the introduction of bromide vacancies in the NC lattice due to the extremely fast growth process.⁴⁶

Next, the effect of the purification on the elemental composition of the relevant samples was investigated. In the case of CsPbBr₃(1) NCs, the treatment with acetone does not alter the elemental composition of the sample, apart from a slight increase of the Cs/Pb ratio. Conversely, the purification drastically changed the composition of CsPbBr₃(4) NCs, as a consequence of Cs₄PbBr₆ removal from the sample (see also Table S2). In the absence of theoretical models for the surface description of perovskite nanoplatelets, we can reasonably argue that purified CsPbBr₃(4) NCs would expose cesium (partially substituted by oleylammonium ions) and bromide at the surface. The eventual excess of positive charge would be neutralized by oleate

ions. Remarkably, since a high cesium amount at the NC surface is typically associated with low emission intensities,³¹ A nice correlation can be evidenced between the PLQYs and the Br/Pb ratio of our samples which, in turn, as previously highlighted, can be modulated by acting on the reaction conditions.

XRD characterization of CsPbBr₃ NCs. The crystal nature and relevant crystalline phases of (as-synthesized or purified) CsPbBr₃(1-4) samples were revealed by the experimental XRD patterns (solid line) reported in Figure 3 and fitted through a Le Bail approach to refine unit cell parameters (see Figure S2). The XRD patterns were collected from the CsPbBr₃ NCs deposited as thin films by casting on silicon substrates. As expected and confirmed by previous observations,^{26,38} the flat substrate induces preferred orientations of the NCs, similarly to what observed on the TEM grid in Figure 1. The coupled sample/detector scan mode ($\theta/2\theta$) selects the main diffraction peaks around $2\theta = 15^\circ$ and $2\theta = 30^\circ$, as related precisely to the scattering vector (and hence the crystalline domain) perpendicular to the oriented facets of the NCs (as seen in the TEM micrographs of Figure 1), the other peaks being strongly suppressed due to the preferred NC orientation. The two main peaks indicate that all samples feature a main crystalline phase and at least a minority phase, which is almost invisible in all samples except CsPbBr₃(4). The preferred orientation of the NCs and size-induced broadening effects of diffraction peaks make hard the unambiguous assessment of the crystalline phase, among the commonly expected ones for CsPbBr₃ (*i.e.*, cubic, orthorhombic, monoclinic, tetragonal), only differing from each other basically for tiny distortions of the unit cell, while often keeping very similar periodicities of the crystal lattice.^{26,38} Moreover, in the presence of shape anisotropy, which implies different numbers of unit cells along different crystallographic directions in the crystal, peak intensity

ratios can further dramatically change, being for each reflection (diffraction “peak”) the integral intensity (area) proportional to the crystal volume and the maximum intensity proportional to the square of the number of unit cells in the crystalline domain along the direction of the scattering vector.⁴⁷ Therefore only the coupled sample/detector scan mode ($\theta/2\theta$), keeping the orientation of the scattering vector constant with respect to sample surface, allows to reliably compare the intensity ratio between different diffraction orders originated from the very same lattice planes (hence, for a given crystal orientation and from the same crystals as long as the beam illuminates the same sample region while changing the incidence angle), even in the case of crystals with different size/shape and non-random orientation (the intensity ratio will be also independent of crystal volume). The ratio between the areas under the two main peaks (A_2/A_1) was then calculated for each XRD profile and the result reported in the relevant panel of Figure 3. Finally, some variability in the Powder Diffraction Files from the crystallographic databases (for example the expected A_2/A_1 ratio for the cubic Pm-3m can range from 1.3 in JCPDS #18-0464 to 2.3 in ICSD #01072-7930) carries further uncertainty in the assessment of the crystalline phase, probably due to the intrinsic difficulty in obtaining stable CsPbBr₃ NCs featuring actually pure phases leading to unambiguous X-ray intensity ratios. Therefore, in our XRD data analysis on anisotropic and preferentially oriented NCs, we refer to the A_2/A_1 ratio as the most reliable experimental quantity to be related to crystallographic databases.

Based on the A_2/A_1 ratio, the purified CsPbBr₃(1) sample (Figure 3A-B) features an orthorhombic phase with Pbnm (or Pnma) space group (expected $A_2/A_1 = 1.8$, from the ICDD #01-072-7929 data sheet). Compared to CsPbBr₃(2) and CsPbBr₃(3) (Figure 3C-D), it can be deduced that CsPbBr₃(1), before and after the purification step, consists of smaller NCs leading to larger size-broadening of diffraction peaks that prevents the doublet at 30° to show up. In the

case of sample CsPbBr₃(2) the main peaks are definitely sharper (FWHM smaller by a factor of three), whereas the weak peak around 21° broadens, indicating larger crystalline domains highly oriented perpendicularly to the substrate. The splitting of the second order peak is still not visible, suggesting the presence of residual cubic crystal symmetry (Pm-3m), whereas the asymmetric peak shape and the value of the A_2/A_1 ratio indicate the presence of the orthorhombic symmetry (Pbnm), both supported by the result from the Le Bail fit (Figure S2).

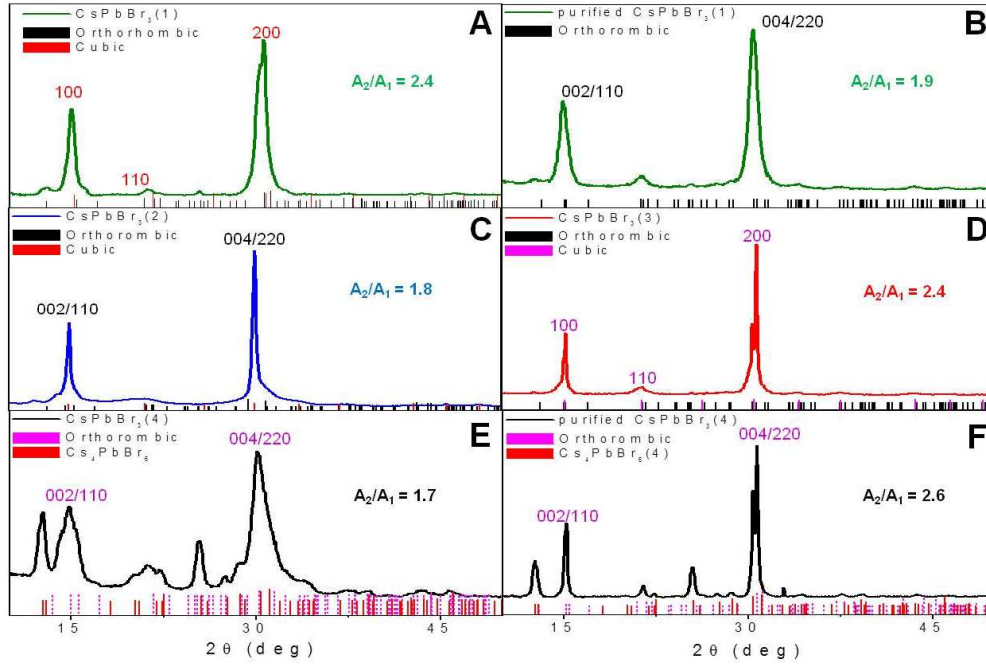


Figure 3. Experimental XRD patterns (solid line); expected peak positions (bars). The ratio (A_2/A_1) of the two main peak areas is reported in each panel, as well as the Miller indexes relevant to the main expected crystalline phase.

On the other hand, the as-prepared CsPbBr₃(1) and the CsPbBr₃(3) samples feature a larger A_2/A_1 ratio (2.4), intermediate between orthorhombic Pbnm (1.8) and cubic Pm-3m (1.3 in JCPDS #18-0464 to 2.3 in ICSD #01072-7930), tetragonal P4mm (3.3) or orthorhombic Pnma (9.4) phases, which would indicate the presence of at least two phases. The XRD profile of the as-prepared CsPbBr₃(1) shows more reflections relevant to the cubic symmetry, likely due to the lower preferred orientation of the NCs. The Le Bail fit of the experimental profiles (Figure S2) shows that the superposition of the cubic and the orthorhombic (Pnma) structures leads indeed to the best agreement with experiments, the cubic phase accounting for the larger A_2/A_1 ratio, and the orthorhombic accounting for the double peak around 30° (040 and 202 reflections) which becomes visible in the case of CsPbBr₃(3).

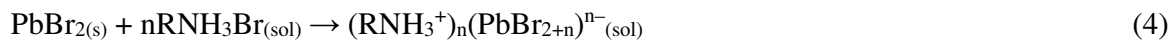
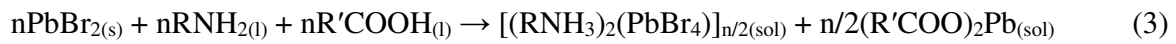
The high intensity of the double peak indicates a further increase of the crystalline domains, compatible with edge-on oriented platelets. Finally, the CsPbBr₃(4) sample clearly features an additional phase, characterized by extra peaks at 12.7° and 25.4° (Figure 3E). Based on Le Bail fitting of experimental data (Figure S2), a mixture of orthorhombic CsPbBr₃ and Cs₄PbBr₆ (trigonal, R-3c, COD number 4002857) can account for all peak positions in the experimental pattern. Although the separate evaluation of the A_2/A_1 ratio for the main peaks around $2\theta = 15^\circ$ and $2\theta = 30^\circ$ (their shape is clearly affected by the contribution of the extra phase) returned a value close to that expected for the orthorhombic as the main crystalline phase, the probably high size/shape polydispersity prevents a direct structure/morphology correlation. On the other hand, the XRD profile of the purified CsPbBr₃(4) sample, although still showing the residual Cs₄PbBr₆ crystalline phase, features the characteristic double peak at 30° associated to large oriented crystalline domains of orthorhombic CsPbBr₃ as well as a larger A_2/A_1 ratio than that expected for the orthorhombic symmetry (around 1.8) due to the intensity contribution of the Cs₄PbBr₆

doublet around 30°. As a result, the A_2/A_1 ratio is confirmed as a fast and reliable indication of the number and type of CsPbBr_3 phases, and as a guide for the whole profile fitting. On the other hand, due to the unreliability of peak intensity quantitative fitting in the Le Bail approach, no estimation is reported about the actual fraction of any phase in the mixture.

Concerning the presence of two phases in purified CsPbBr_3 (4), it can reasonably be supposed that the remaining Cs_4PbBr_6 crystalline phase (emerging only with XRD analyses) is probably due to the degradation of CsPbBr_3 NCs promoted by the simultaneous presence of ligands excess and residual polar acetone.³³ In fact, XRD analyses required long-time acquisitions (~ 1 day) under ambient conditions, while faster TEM and UV-Vis measurements (Figure S9) did not evidence the presence of the Cs_4PbBr_6 impurities.

Investigation on the reaction mixtures before cesium injection. The use of inorganic salts (*i.e.* PbBr_2) as both lead and halide sources in nonpolar and non-coordinating solvents inevitably implicates the analysis of the processes involved in the dissolution of precursors. Although, as ascertained for phosphines,⁴⁸ **only the presence of OAM** could promote PbBr_2 solubilization,⁴⁹ as described in equation (1), due to the nitrogen coordination to lead atoms generating soluble species, the construction of perovskite crystalline frameworks necessitates the simultaneous presence of acids and bases. This restriction hints an early stage of the PbBr_2 reactivity before the introduction of the cesium precursor, which is probably consequent to the anion exchange between lead halide and OLA, supported by the intermediate scavenging of the stronger HBr acid (*vide infra*), with the formation of oleylammonium bromide, as reported in equation (2). Furthermore, metal ions endowed with an ns^2 electron configuration (such as Pb^{2+}) readily

undergo complexation by halide ions.⁵⁰ The consequent formation of plumbates not only promotes the dissolution of the lead atoms in nonpolar solvents, but also generates the effective precursors for the NC assembly, as schematized by equations (2-4):



It is reasonable to presume that the coordination states of lead-based species before the nucleation stage consequent to the cesium addition have a major influence on the crystal growth as well as on the introduction of structural defects in final perovskite NCs. In fact, according to equation (2), a high concentration of PbBr_4^{2-} species in solution determines the formation of a hybrid organic-inorganic two-dimensional structure with the formula $[(\text{RNH}_3)_2(\text{PbBr}_4)]_n$, in which RNH_3 represents the oleylammonium ion,⁵¹ before the inclusion of cesium precursor. At the same time, reaction conditions leading to a high concentration of oleylammonium bromide could promote the formation of high coordination states (up to six) for the lead-based species, as suggested by equation (4). This could explain the simultaneous formation of Cs_4PbBr_6 nanoparticles in high-surfactant regimes, as experimentally observed (*vide supra*). Therefore, although the formal Br/Pb ratio employed in our syntheses is related to that of the chosen inorganic salts (*i.e.* PbBr_2), the percentage of reactive metal and halide ions could be modified by

the ligands (*i.e.* OLA and OAM). Focusing on the nucleation process after the introduction of the cesium precursor, this scenario suggests that the high temperature should provide the necessary energy to rapidly drive off excess bromide and to induce the formation of the perovskite crystal lattice, while the same fast nucleation process probably interferes with the compensation of the missing bromide ions in the coordination sphere of lead-based precursors.⁵² This process can introduce bromide vacancies during the perovskite formation, which might explain the observation that halide-rich synthetic conditions usually resulted in the highest PLQYs for the corresponding nanoparticles.⁵³

In order to gain insights into the situation immediately before the nucleation process deriving from the introduction of cesium cations and to support the implications of equations (1-4), we analyzed by nuclear magnetic resonance (NMR) spectroscopy the mixture resulting from suitably mixing (see experimental part) ODE, PbBr₂, OLA and OAM previously kept at 140 °C for 10 minutes. NMR spectroscopy represents a powerful tool to explore not only the surface chemistry of perovskite NCs (*vide infra*), but also to scrutinize the interactions between the two ligands (*i.e.* OLA and OAM). In fact, the ¹H-NMR spectra of the ligands in C₆D₆ (reported in Figure 4A) show clear resonances related to their aliphatic chains, namely, the vinylene protons at $\delta \sim 5.50$ ppm (**5** and **ε**), the methylene protons next to the vinylene protons at $\delta \sim 2.10$ ppm (**4** and **δ**), an unresolved resonance at $\delta \sim 1.50$ ppm attributed to the methylene groups (**3**) and the methyl resonance (**6**) at $\delta \sim 0.90$ ppm. More importantly, peculiar information could be drawn by the signals of the protons adjacent to the functional groups of the ligands (*i.e.* **1** and **β** for OLA and OAM, respectively), since their chemical shifts ($\delta = 2.07$ and 2.51 ppm for **1** and **β**, respectively) are particularly susceptible to the acid-base equilibrium. In fact, an equivolumetric mixture of the two ligands evidences a remarkable downfield shift of both **1** and **β** resonances

(along with those of the **2** and γ protons) consequent to partial deprotonation of the carboxylic acid and partial protonation of the amine group, respectively. The entity of the downfield shift observed for these peculiar ^1H -NMR signals is related to the degree of proton transfer between the two ligands.²⁵

The presence of signals downfield shifted as a consequence of the acid-base equilibrium involving the surfactants was also ascertained by sampling the reaction mixtures comprised of PbBr_2 and the two ligands after the solubilization of the lead source at 140 °C. In these cases, however, it is apparent how the presence of the lead-halide species induces a more pronounced downfield shift for the OAM signals, while the **1** resonance of OLA results to be upfield shifted with respect to the signals recorded for the equivolumetric mixture of the two ligands (Figure 4B). In other words, the downfield shifted β resonance suggests that OAM is more protonated, while the characteristic resonances **1** and **2** of OLA appear slightly broadened and upfield shifted with respect to the reference, hinting that OLA is less deprotonated with respect to the situation recorded in the equivolumetric ligand mixture. This means that the acid-base equilibrium involving the two ligands is perturbed by a stronger acid (*i.e.* HBr) produced by the reaction between the PbBr_2 and the surfactant, according to equation (5). This observation also explains the presence of bromide ions for complexation with the lead-based species.



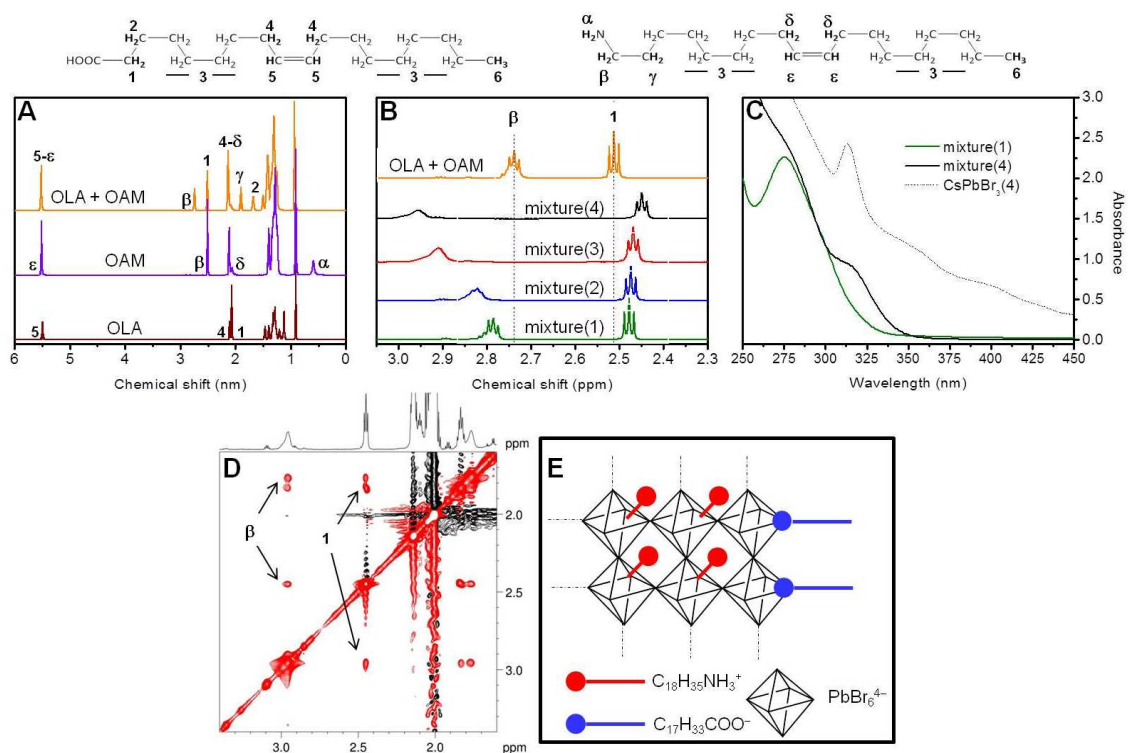


Figure 4. (A) ¹H-NMR spectra (C₆D₆) of OLA (0.02 M), OAM (0.02 M), a mixture of OLA and OAM (1/1 vol/vol, ~0.04 M). (B) Comparison between the ¹H-NMR spectra (C₆D₆) of the reaction mixtures (~0.04 M) before the introduction of the cesium ion source. (C) Comparison between the absorption spectra of mixture(1), mixture(4) and as-prepared CsPbBr₃(4) NCs in cyclohexane. (D) NOESY spectrum of the reaction mixture leading to CsPbBr₃(4). (E) Representation of the two-dimensional bromoplumbate scaffold passivated by organic ligands.

The protonation degree of the two ligands in the reaction mixture before injecting cesium oleate results to be correlated with lead/surfactants ratio, as clearly suggested by the resonances of **β** and **1** protons in Figure 4B. This behaviour is due to fact that higher quantities of the two surfactants promote a larger production of hydrobromic acid, according to eq. (5). The fate of the

bromide ions generated by the above-mentioned process was investigated by dissolving in cyclohexane small aliquots of the reaction mixtures before injecting cesium oleate. Their absorption spectra are reported in Figure 4C and compared with the absorption profile of as-prepared CsPbBr₃(4) NCs, which contain also Cs₄PbBr₆ impurities. The reaction mixture leading to CsPbBr₃(1) NCs – mixture(1) – showed an absorbance peak at 275 nm with a tail up to 325 nm. The optical characterization of mixture(1) is consistent with the prominent presence of PbBr₂ and PbBr₃⁻ species.⁵⁴ The absorption at longer wavelength is more pronounced in the case of the reaction mixture leading to CsPbBr₃(4) NCs – mixture(4) – suggesting the plausible formation of highly coordinated bromoplumbate species (PbBr₅³⁻ and PbBr₆⁴⁻). This explanation is in agreement with the larger formation of large amounts of hydrobromic acid in the presence of ligands excess and is also supported by the comparison with the UV-Vis characterization of CsPbBr₃(4) NCs, evidencing a strong absorption at 313 nm (Figure 4C) associated with the isolated PbBr₆ octahedra of the 0D trigonal phase impurity (Cs₄PbBr₆).⁵⁵

At the same time, the nuclear Overhauser effect spectroscopy (NOESY) evidenced the presence of negative (red) cross-peaks for the resonances ascribable to the two ligands (*i.e.* **1** and **β**) in the case of mixture(4) (Figure 4D). The negative nOe cross peaks are observable in species with long correlation times that diffuse more slowly in solution with respect to typical small molecules, thus suggesting the generation of a large two-dimensional structure. The same behaviour was observed in the case of mixture(1) (see Figure S4). As schematized in Figure 4E, the two-dimensional bromoplumbate scaffold is stabilized by the electrostatic interactions with oleyl ammonium cations, while the oleate moieties partially replaced the bromide ions contributing to preserve the colloidal stability of these structures.

Formation pathways of CsPbBr₃ NCs. We were able to isolate two-dimensional bromoplumbate scaffold only in the case of the reaction leading to CsPbBr₃(4) NCs (see Figure 5 for TEM image), while in the other cases no white precipitate was formed before the introduction of cesium precursor. It can be deduced that the higher is the surfactant content in the reaction mixture, the greater is the size of bromoplumbate scaffold, which, in turn, is related to the concentration of PbBr₄²⁻ species, which, in turn, is governed by the lead/surfactants ratio. Nevertheless, in the cases of the absence of a white precipitate, NOESY spectrum (Figure 4S) of the reaction mixture before the injection of the cesium precursor confirms the formation of layered structures. Importantly, the dimensions of the bromoplumbate scaffold deducible by TEM images (19.4±2.9 nm) are comparable with those of the final sample – *i.e.* CsPbBr₃(4) –, although it has been reported that the dimensions of layered structures generated in different conditions are remarkably greater than those recorded in our sample.¹⁸

The basic knowledge of perovskite crystal growth is still in its embryonic phase and more investigations are undoubtedly necessary to fully comprehend the formation mechanism of these NCs. However, with these preliminary information in hand, we can infer that in the early stages of the NC formation, a growth pathway reasonably implicates the addition of lead-based species (monomers) to the previously generated two-dimensional seeds promoted by the intercalation of the introduced cesium ions (Figures 5). The size of these seeds related to the specific reaction conditions governs the final lateral dimensions of the nanoparticles. Very recently, the assumption that layered seeds might be the driving force for obtaining the CsPbBr₃ perovskite square platelets has been also formulated by Pradhan and coworkers.⁵⁶ The longitudinal perovskite growth proceeds until reaching the equilibrium with the monomers themselves.^{57,58} On the basis of the optical characterization carried out on as-prepared samples (*vide supra*), we

can reasonably suppose that, under our reaction conditions, the critical size coincides with four cell unit average thickness of the nanoplatelets (Figure 5C-D). The kinetic energy barrier for the NC growth depends on the surface energy of the crystal facets, which can be controlled by the concentration of surface passivating ligands present in the reaction mixture. The continuous supply of surface passivating ligands probably inhibits NC growth especially in the case of high surfactants concentration.

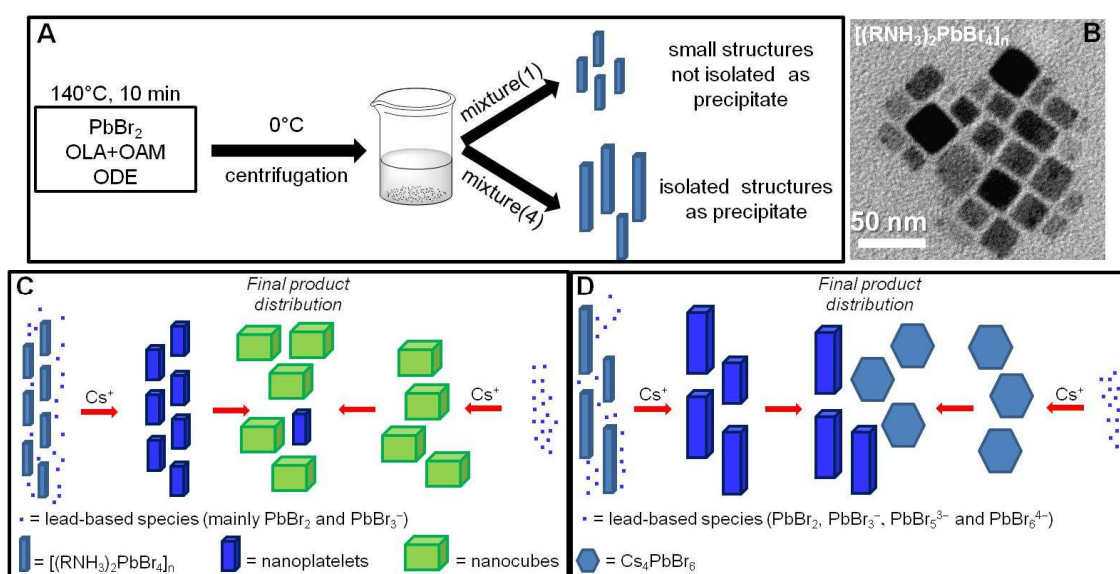


Figure 5. (A) Exemplification of the experimental procedure leading to the isolation of bromoplumbate layers. (B) TEM image of [(RNH₃)₂PbBr₄]_n layer before the addition of cesium in the case of CsPbBr₃(4) formation. Schematization of the nanocube (C) and nanoplasmid formation (D) for the two limit situations – i.e. CsPbBr₃(1) and CsPbBr₃(4). In the case of nanocubes formation (B), the mechanism **explains** the formation of thinner structures that are responsible for the emission at 478 nm. In the case of nanoplasmids formation (B), the mechanism **explains** the formation of Cs₄PbBr₆ NCs.

The above-mentioned reaction pathway is competitive with the nucleation mechanism involving lead-based species (Figure 5C-D), which generates the crystalline structures for the 3D growth. In the case of bromide-poor conditions, the plausible low concentration of templating $[(\text{RNH}_3)_2\text{PbBr}_4]_n$ layers determines the formation of the 3D orthorhombic phase as the main product of these reaction conditions. Conversely, in the case of bromide-rich conditions, the relatively high concentration of templating $[(\text{RNH}_3)_2\text{PbBr}_4]_n$ layers leads to a significant formation of nanoplatelets. However, the presence of highly coordinated lead species probably hampers the crystallization of the 3D phase in favour of the 0D trigonal phase.

The surface chemistry of differently composed CsPbBr₃ NCs. NMR spectroscopy constitutes one the most powerful technique to study the features of the organic-inorganic interface at the NC surface, both unraveling the organic shell composition and suggesting its binding motifs.⁵⁹ In the case of lead-bromide perovskite NCs, the number of ligands commonly exceeds the one required to fully passivate the surface sites of the nanoparticle. The combination of ¹H-NMR and nuclear Overhauser effect spectroscopy (NOESY) allows to clearly discriminate the dynamics of the passivation process involving the ligands.⁶⁰ In fact, sharp resonances with negative nuclear Overhauser effect (nOe) cross peaks are generated by weakly bound passivating agents resulting from a fast adsorption/desorption process at the NC surface. Conversely, broad resonances with negative nOe peaks are due to tightly bound ligands not (or slowly) exchanging with free species.⁶¹

In Figure 6A, the ¹H-NMR spectra of as-prepared CsPbBr₃(1-4) NCs are compared with that of the equivolumetric mixture of OLA and OAM in a nonpolar solvent (C₆D₆). It is clearly apparent

that the line width of the resonances attributable to the ligands results to be broadened by the interaction with the NC surface⁶² with respect to those of the free surfactants. As recently observed for metal-chalcogenides⁶³ and perovskite nanoparticles,²⁶ the line-broadening and chemical shift of NMR signals belonging to NC surface ligands are strongly influenced by the deuterated solvent, imparting peculiar surroundings or dynamic equilibria at the NC surface.⁶⁴

In perovskite NCs obtained in the presence of carboxylic acids and aliphatic primary amines as the passivating agents, their behaviour can be properly investigated by focusing the attention on the resonances of methylene protons adjacent to the binding group, especially the β signal of OAM. In the case of CsPbBr₃(1) and CsPbBr₃(2), the chemical shifts of the β resonances resemble the one of pure OAM, suggesting a low degree of protonation for the amine. This observation is in agreement with the plausible PbBr₂-terminated surface of CsPbBr₃(1) and CsPbBr₃(2) NCs previously ascertained by EDX analyses (*vide supra*) which suggest the presence of the undercoordinated lead sites prevalently passivated by OAM. The slight excess of cesium in the elemental composition of these perovskites (see Table 1) is explained by the surface passivation by cesium oleate, as confirmed by the presence of discernible resonances ascribable to deprotonated OLA (Figure 6A). Conversely, in the case of CsPbBr₃(3) and CsPbBr₃(4) the chemical shift of the β signal is remarkably downfield shifted ($\delta \sim 4.00$ ppm) hinting a higher degree of protonation for the amine in these samples.¹⁸ Since the interpretation of the EDX analyses points to a CsBr-terminated surface for these nanoparticles, cesium ions can be partially substituted by oleyl ammonium at the NC surface. The NMR response of these nanoparticles well correlates with their elemental composition, because the Cs/Br charge unbalance is due to oleate anions, which partially replaced surface bromides, as clearly ascertained by the presence of deprotonated OLA in the relevant NMR spectra (Figure 6A).

To explore the bonding nature of the species passivating the NC surface, the chemical shift and broadening of the distinct vinylene resonances (**5** and **ε**, $\delta = 5.40\text{-}5.70$ ppm) are particularly indicated, since, with respect to other discriminating signals, they gain intensity due to their sufficient distance from the NC surface. In this region, as-prepared CsPbBr₃(1) and CsPbBr₃(2) NCs exhibit an intense featureless resonance at a chemical shift resembling that of free surfactants, accompanied by weaker downfield shifted signals ascribable to bound ligands. The large difference in chemical shift for the vinylene resonances is due to the fact that the solvent does not penetrate the organic shell protecting the NC surface, modifying the environment of bound ligands with respect to that of fully solvated ones.⁶³ The attribution of the alkene signals in the ¹H-NMR spectrum of lead-bromide perovskite NCs can be straightforwardly achieved by modifying the composition of the organic shell.⁶⁵ Hence, the slightly perceptible resonance at $\delta = 5.72$ ppm is due to bound oleate, while the signal ascribable to the bound amine appears upfield shifted ($\delta = 5.60\text{-}5.55$ ppm). The NMR difference between the two ligands could originate from the faster adsorption/desorption dynamics involving the amine species in comparison with the exchange process concerning the carboxylic acid, requiring a slow proton transfer.⁶⁶ Therefore, the chemical shift of the amine signals are the result of the weighted average between the bound and free states of the ligand.

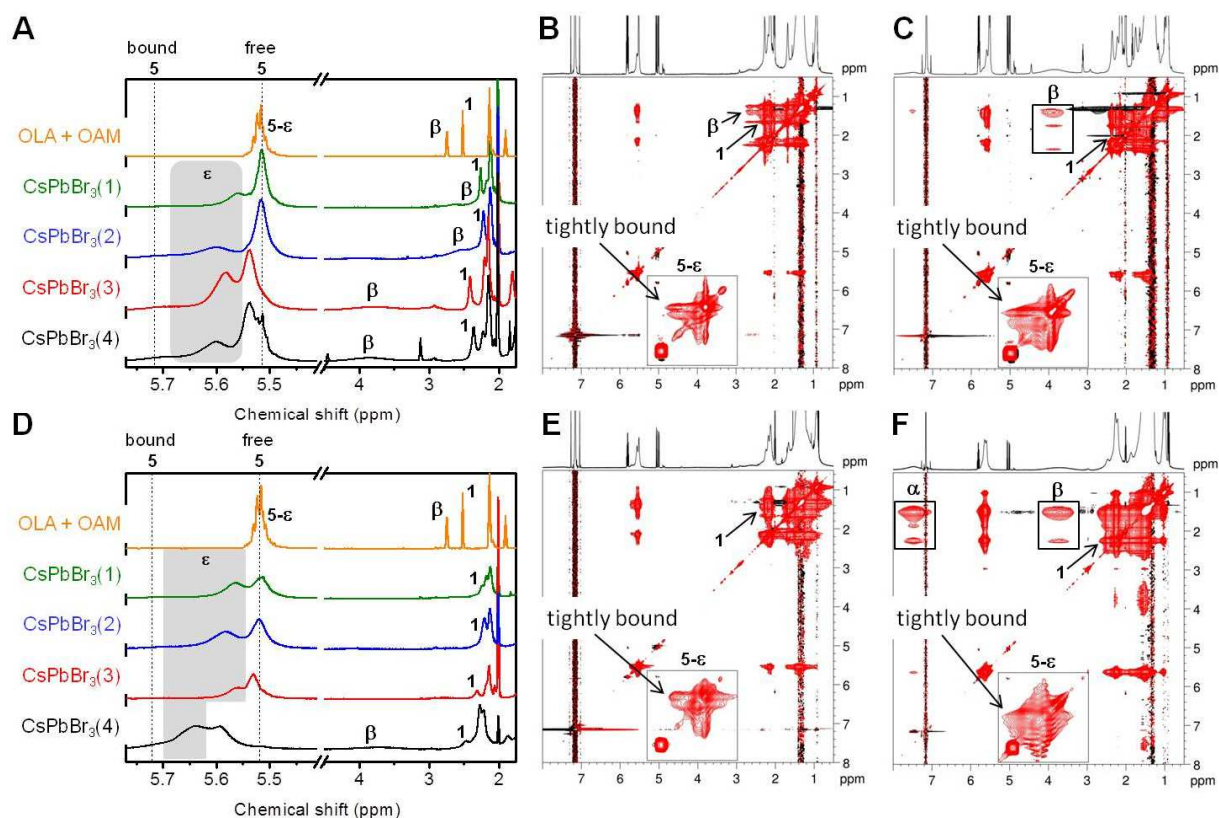


Figure 6. (A) ^1H -NMR spectra of as-prepared CsPbBr_3 NCs compared with the one recorded for the equimolar mixture of the relevant ligands (OLA and OAM). (B) 2D-NOESY spectrum of as-prepared $\text{CsPbBr}_3(1)$ NCs. (C) 2D-NOESY spectrum of as-prepared $\text{CsPbBr}_3(4)$ NCs. (D) ^1H -NMR spectra of purified CsPbBr_3 NCs compared with the one recorded for the equimolar mixture of the relevant ligands. (E) 2D-NOESY spectrum of purified $\text{CsPbBr}_3(1)$ NCs. (F) 2D-NOESY spectrum of purified $\text{CsPbBr}_3(4)$ NCs. The insets of the NOESY spectra show an expansion of the diagonal in the vinylene region. All spectra are recorded in C_6D_6 . The shaded areas in the ^1H NMR indicate the chemical shift range in which the ϵ resonance may fall.

The NOESY spectrum of as-prepared CsPbBr₃(1) NCs confirms that OLA binds the surface, owing to the appearance of negative (red) cross-peaks attributable to **1** resonance (Figure 6B). Also the negative cross peaks attributable to OAM resonances corroborate its interaction with the surface. The nOe behaviour of the alkene resonances in this sample (inset in Figure 6B) reveals negative cross peaks for the weak and broad resonance at $\delta = 5.72$ ppm, confirming its bound nature. The sharper alkene resonances feature negative nOe cross peaks and a cross peak correlating the broad to the sharp alkene resonance is also observable. From this analysis it can be concluded that the broad resonance is due to tightly bound ligands, in slow exchange with weakly bound ligands, featuring sharp resonances;⁶⁷ moreover, the third species ($\delta = 5.57$ ppm) attributable to the observed vinylene resonances corresponds to the amine species in fast exchange between bound and free states. A similar situation also emerges from the inspection of the NOESY spectra of CsPbBr₃(2) NCs (Figure S5).

Three contributions for the vinylene resonances can be clearly identified in CsPbBr₃(3) and CsPbBr₃(4) NCs, but in these cases it can be noted the absence of signals that could be ascribed to free surfactants (Figure 6A). Instead, the structured resonances observable in CsPbBr₃(4) NCs are ascribable to the amide impurity deriving from the condensation reaction between the two ligands.²⁶ The variation of the chemical shifts ascribable to "non-bound" OLA molecules can be explained by assuming the presence of physisorbed species in fast equilibrium with their free state at the organic-inorganic interface. The presence of physisorbed species was also proposed by Brutchey and coworkers.⁶⁸ The NMR response for these signals is the result of the weighted average between the physisorbed and free states of the ligand. Physisorption of OLA molecules can be rationalized in CsPbBr₃(3) and CsPbBr₃(4) NCs by the establishment of hydrogen bonds between the carboxylic acids and the bromide-rich surface of these nanoparticles. The absence of

negative cross-peaks for free ligands in the NOESY spectrum of CsPbBr₃(4) NCs (Figure 6C) strongly suggests that these resonances have to be ascribed to species (such as amide impurities formed) not interacting with the NC surface. Conversely, the clear cross-peak between **5** and **ε** resonance of tightly bound OAM originates from intramolecular cross-relaxation between the vinylene protons of neighboring molecules. A similar scenario can also be deduced from inspection of the NOESY spectrum of CsPbBr₃(3) NCs (Figure S6).

We decided to corroborate this interpretation by evaluating the NMR responses of perovskite NCs obtained by purification in the presence of a nonsolvent, such as acetone. The addition of a less viscous and polar solvent, in fact, facilitates the removal of excess surfactants and impurities. ¹H-NMR spectra of the relevant samples purified as described in the experimental part, are illustrated in Figure 6D. By removing a fraction of the organic shell, the signals of all NCs are generally broadened with respect to those of as-prepared samples, due to the lower amount of ligands engaged in passivation processes at the NC surface. In the case of purified CsPbBr₃(1) and CsPbBr₃(2) NCs, it can be observed a relative increase of the resonance intensity ascribable to bound **ε** protons, while the signal attributable to **β** protons completely disappeared. This behaviour is explained by the fact that broadening is more severe for protons closer to the surface, making them in some cases undetectable by ¹H-NMR spectroscopy.⁶⁹ The relevant NOESY spectrum for purified CsPbBr₃(1) NCs (Figure 6E) suggest that these ligand species are interacting with the NC surface. The purification led to the complete removal of the amide, as testified by the absence of signals attributable to such species in the spectrum of the purified product and confirming the absence of NMR-detectable free species in this sample. Furthermore, the removal of excess ligand causes a downfield shift of the resonances, while the **β** proton signals are clearly observable. Also in this case, NOESY spectrum highlights the presence of

bound oleate and oleyl ammonium species (Figure 6F). The NOESY spectra of purified CsPbBr₃(2) and CsPbBr₃(3) NCs are reported in Figures S7-8 and are in line with the aforementioned considerations.

Stability of CsPbBr₃ NCs. Once ascertained the aspects differentiating the surface chemistry of CsPbBr₃(1-4) NCs, we deemed it worthwhile to investigate the stability of the corresponding nanoparticles by measuring the PLQYs of their dispersions as a function of time. We submitted to the stability test only CsPbBr₃(1) and CsPbBr₃(4) NCs, which showed drastically different surface compositions. As shown in Figure 7, the PLQY behaviour of the nanoparticles was monitored over 10 days, during which the dispersions retained their colloidal stability. However, only CsPbBr₃(1) NCs substantially preserved the initial PLQY (50% after 10 days, Figure 7A). To explain this result, we should focus on the surface chemistry of CsPbBr₃(1), which, based on what ascertained by elemental analyses and NMR investigations, is prevalently passivated by cesium oleate and OAM (Figure 7B). The well-known dynamic surface of perovskite NCs can promote desorption of passivating agents only as neutral species (Figure 7C). Although the appearance of undercoordinated lead sites at the NC surface could compromise the long-term colloidal stability of the nanoparticles,²⁶ the nature of the organic species involved in these desorption processes marginally modifies the PbBr₂-terminated surface of CsPbBr₃(1) NCs.³¹ This peculiarity justifies the preservation of the relatively lower PLQYs in CsPbBr₃(1) NCs until the irreversible coalescence of the nanoparticles promoted by the depletion of the organic protecting shell. At the same time, the aged CsPbBr₃(1) sample exhibits a different PL profile after 10 days (Figure S10), plausibly as a consequence of the spontaneous coalescence of the smallest particles endowed with a high surface reactivity.

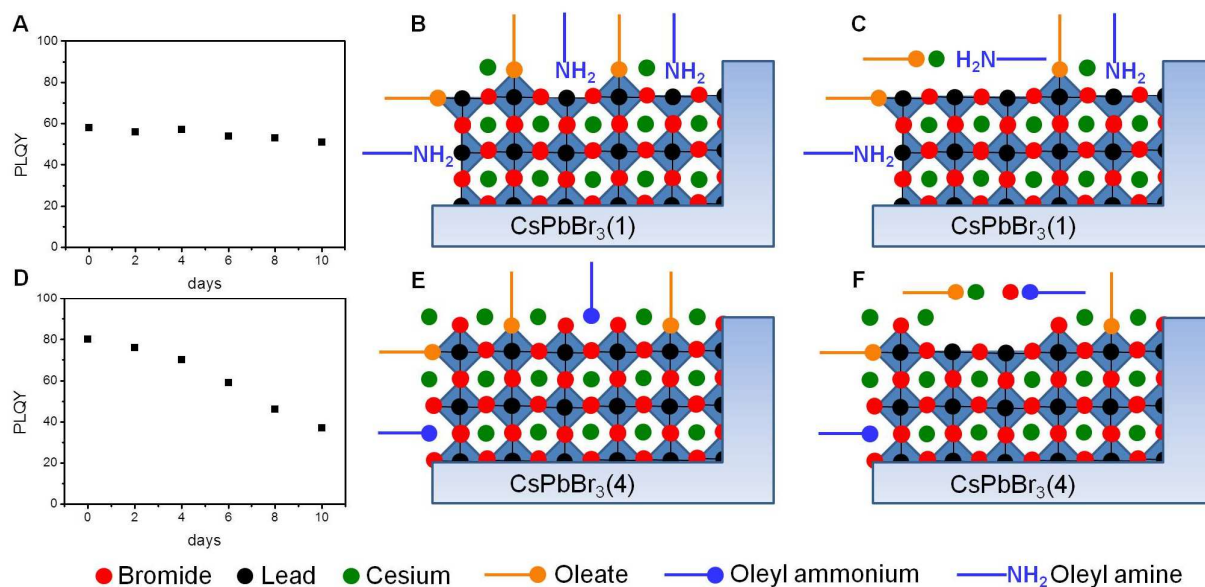
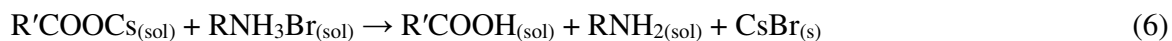


Figure 7. PLQY of as-prepared $\text{CsPbBr}_3(1)$ NCs over a period of 10 days (A). Schematic representation (B) of the surface chemistry of freshly prepared $\text{CsPbBr}_3(1)$ NCs and (C) of the effect of ligand desorption processes. PLQY behaviour of as-prepared $\text{CsPbBr}_3(4)$ NCs over a period of 10 days (D). Schematic representation (E) of the surface chemistry of freshly prepared $\text{CsPbBr}_3(4)$ NCs and (F) of the effect of ligand desorption processes.

Conversely, in the case of $\text{CsPbBr}_3(4)$ NCs, the PLQY drop with time is remarkable (Figure 7D). Considering the NC surface previously described, once that the solvent penetrates the protecting organic shell, desorption of the passivating components is possible. However, it is unfavorable for oleylammonium ions to dissociate as discrete solvated ions in low-polarity solvents such as cyclohexane (Figure 7E); therefore, they are most likely removed from the surface accompanied by a counterion (bromide) to preserve charge neutrality. The same motivations can be translated to oleate ions, which dissociate from NC surface as cesium oleate (Figure 7F). The

adsorption/desorption equilibria potentially leave undercoordinated lead sites on the NC surface. Moreover, along with the coordination chemistry between surface lead and passivating ligands to explain the coordination and dissociation of several species, their solubility may also play a role. In the case of CsPbBr₃(4), the direct interaction between desorbed ligands can promote the formation of CsBr, which is insoluble in nonpolar solvents, as described by equation (6).



The irreversible cleavage of CsBr from the organic-inorganic interface inevitably introduces bromide vacancies at the NC surface, which are responsible for the PLQY drop with time (37% after 10 days). However, the passivation of CsPbBr₃(4) surface prevents nanoparticle aggregation and consequently, the PL profile of the aged sample results unvaried after ten days (Figure S11).

CONCLUSIONS

In this study, we explored the effects of lead/surfactants ratio on the structural evolution of cesium lead bromide perovskite NCs. The shape and surface composition of CsPbBr₃ NCs were modulated by adjusting the equivolumetric amount of the ligands (*i.e.*, oleic acid and oleyl amine) relatively to that of lead bromide. The tailoring of the synthetic conditions permitted to obtain blue-emitting CsPbBr₃ nanoplatelets in the presence of ligands excess, while green-

emitting nanocubes were generated in low-surfactant regimes. The photoluminescence quantum yields of nanoplatelets were found to be higher with respect to those of nanocubes consequent to the formation mechanism of the relevant NCs. An insight into the NC evolution consequent to the different reaction conditions suggested that preformed $(\text{RNH}_3)_2\text{PbBr}_4$ layers before the introduction of cesium precursor templates the formation of CsPbBr_3 nanoplatelets. The growth step promoted by these preformed layers is concomitant to (but independent from) the nucleation of lead-based species, leading to centrosymmetric nanocubes in low-surfactant regimes or Cs_4PbBr_6 NCs in high-surfactant regimes. The proposed scenario is supported by the analysis of the optical properties of non-purified samples, which reveal features that are compatible with the selective presence of structures endowed with four cell unit average thickness accompanying the emissive nanocubes. By combining nuclear magnetic resonance (NMR) and UV-Vis spectroscopies, it is ascertained that the lead/surfactants ratio also regulates the relative proportion between lead-based species (PbBr_2 , PbBr_3^- , PbBr_4^{2-} and plausibly PbBr_5^{3-} or PbBr_6^{4-}) formed before cesium injection, which are responsible for the size of $[(\text{RNH}_3)_2(\text{PbBr}_4)]_n$ layers (governing, in turn, the dimensions of the final nanoplatelets) as well as for the formation of Cs_4PbBr_6 NCs during the nucleation stage. A detailed investigation of the NC surface chemistry was achieved by comparing the NMR response of specific signals ascribable to the ligands belonging to the perovskite nanoparticles obtained under different lead/surfactant ratio. The consequent interpretation also provides a *vademecum* for the NMR-based description of the organic–inorganic interface in perovskite NCs. This research can furnish the sparkle for new ideas aimed at the shape control of perovskite NCs and support the description of the surface chemistry of these materials.

EXPERIMENTAL SECTION

Materials. Cesium carbonate (Cs_2CO_3 , 99.9% metals basis, Alfa Aesar), lead(II) bromide (PbBr_2 , 99.999% metals basis, Aldrich), oleylamine (OAM, technical grade 70%, Aldrich), oleic acid (OLA, technical grade 90%, Aldrich), 1-octadecene (ODE, technical grade 90%, Aldrich), acetone (ACS grade), cyclohexane (Aldrich, spectrophotometric grade). The procedures involving perovskite nanocrystal synthesis were performed under nitrogen flow using standard Schlenk techniques

Synthesis of as-prepared CsPbBr_3 NCs. Cs_2CO_3 (0.407 g, 1.25 mmol), OLA (1.55 mL, 4.91 mmol) and ODE (20 mL) were mixed in a 50 mL Schlenk tube and kept in vacuum for 1 hour at 120 °C. Subsequently, the tube was filled with nitrogen after the complete solubilization of the solid material, which leads to the formation of a clear solution of cesium oleate (Cs-oleate). As Cs-oleate precipitates out of ODE at room temperature, it was kept at 140 °C under N_2 atmosphere before injection. ODE (6.5-9.0 mL), PbBr_2 (0.138 g, 0.38 mmol), OLA (0.25-1.5 mL) and OAM (0.25-1.5 mL) were added to a 50 mL Schlenk tube and the mixture was heated at 140°C. After complete solubilization of the salt, temperature was kept for 10 minutes followed by injection of Cs-oleate solution (0.8 mL). After 10 sec, the reaction mixture was cooled in an ice bath. The crude solution was centrifuged at 4000 rpm for 40 min. The supernatant containing unreacted precursors was discarded and the obtained precipitate was eventually dispersed in cyclohexane and properly stored for subsequent characterization or measurements. The material obtained through this procedure is referred to as "as-prepared" CsPbBr_3 NCs.

Purification of CsPbX_3 NCs. When a purification procedure had to be adopted, acetone (9.5 mL) was added to the mixture obtained after the cooling. After centrifugation (4000 rpm for 10 min),

the supernatant was separated, and the precipitate was redispersed in cyclohexane and properly stored for subsequent characterization or measurements. The material obtained through this procedure is referred to as "purified" CsPbBr₃ NCs.

Nuclear Magnetic Resonance. ¹H-NMR spectra were recorded at 298.2 K on a Bruker Avance III 700 MHz spectrometer equipped with a Cryoprobe optimized for ¹H observation. All chemical shifts were referred to the non-deuterated benzene residue signal at 7.16 ppm. The NOESY spectra were acquired using standard pulse sequences; mixing time was set to 300 ms.

Optical characterization. UV–vis absorption spectra were collected using a Jasco V670 spectrometer in transmission mode. Steady-state PL spectra from solutions were acquired on a Varian Cary Eclipse instrument. The quantum yields were determined by using coumarin 343 as standard, according to typical procedures.⁷⁰

TEM characterization. Transmission electron microscopy (TEM) measurements were carried out using a JEOL JEM1011 microscope, operating at an accelerating voltage of 100 kV and equipped with a tungsten electron source, and a high-resolution CCD camera. Samples for TEM analysis were prepared by dipping the carbon-coated copper grid into the NC cyclohexane solution diluted with anhydrous hexane. Statistical size analysis (NC average size and standard deviation) for each sample was performed by using a freeware image analysis application, by measuring dimensions of not less than 200 nanoparticles for each sample.

FEG-SEM-EDX. Elemental analyses were performed using a field emission gun scanning electron microscope (FEG-SEM) Zeiss Sigma 300 VP (Zeiss Oberkochen, Germany) equipped with an energy dispersive spectrometer (EDX) C-MaxN SDD with an active area of 20 mm² (Oxford Instruments, Oxford, United Kingdom). NC solutions in cyclohexane were deposited on aluminum stubs covered with a pure graphite tape. Analysis were carried out at 15 kV using a

7.5 mm working distance at a 1000× magnification. Data accuracy was checked using standards by MAC (Micro-Analysis Consultants Ltd., United Kingdom).

X-Ray Diffraction. XRD data were collected in coupled sample-detector scan mode, by a Bruker D8 Discover equipped with a Cu source ($K\alpha$ line), a Göbel mirror, and a scintillation point detector. XRD patterns were fitted by QUANTO,⁷¹ a whole-pattern fitting program for quantitative phase analysis of polycrystalline mixtures. The diffraction patterns were described with the Le Bail approach, with the aim of better identifying concurrent crystalline phases.⁷²

ACKNOWLEDGMENT

The authors gratefully acknowledge Dr. Milvia Elena Di Clemente for technical assistance during the preparation of perovskite nanocrystals. Regione Puglia (INNOLABS project DEMETRA – COD. Y8V9H90-1) is gratefully acknowledged for funding.

AUTHOR CONTRIBUTION

R.G. and G.P.S. conceived and designed the experiments. R.G. and V.V. synthesized and purified the nanocrystals. R.G. and G.C. performed the optical characterization. R.G. and N.M. carried out NMR experiments. E.F. and M.S. conducted TEM measurements. I.A. and R.T. carried out SEM-EDX investigations. D.A. and C.G. performed XRD characterization. R.G. wrote the first draft of the paper. All the authors contributed to the writing of the paper and approved its submission.

REFERENCES

- ¹ B. R. Sutherland and E. H. Sargent, *Nat. Photonics*, 2016, **10**, 295–302.
- ² K. Lin, J. Xing, L. N. Quan, F. P. G. de Arquer, X. Gong, J. Lu, L. Xie, W. Zhao, D. Zhang, C. Yan, W. Li, X. Liu, Y. Lu, J. Kirman, E. H. Sargent, Q. Xiong and Z. Wei, *Nature*, 2018, **562**, 245–248.
- ³ W. S. Yang, B.-W. Park, E. H. Jung, N. J. Jeon, Y. C. Kim, D. U. Lee, S. S. Shin, J. Seo, E. K. Kim, J. H. Noh and S. I. Seok, *Science*, 2017, **356**, 1376–1379.
- ⁴ V. D’Innocenzo, A. R. Srimath Kandada, M. De Bastiani, M. Gandini and A. Petrozza, *J. Am. Chem. Soc.*, 2014, **136**, 17730–17733.
- ⁵ Q. A. Akkerman, V. D’Innocenzo, S. Accornero, A. Scarpellini, A. Petrozza, M. Prato and L. Manna, *J. Am. Chem. Soc.*, 2015, **137**, 10276–10281.
- ⁶ J. Kang and L.-W. Wang, *J. Phys. Chem. Lett.*, 2017, **8**, 489–493.
- ⁷ Y. Wu, X. Li and H. Zeng, *ACS Energy Lett.*, 2019, **4**, 673–681.
- ⁸ M. A. Boles, D. Ling, T. Hyeon and D. V. Talapin, *Nat. Mater.*, 2016, **15**, 141–153.
- ⁹ Z. Shi, Y. Li, Y. Zhang, Y. Chen, X. Li, D. Wu, T. Xu, C. Shan and G. Du, *Nano Lett.*, 2017, **17**, 313–321.
- ¹⁰ D. Yang, X. Li and H. Zeng, *Adv. Mater. Interfaces*, 2018, **5**, 1701662.
- ¹¹ A. Swarnkar, A. R. Marshall, E. M. Sanehira, B. D. Chernomordik, D. T. Moore, J. A. Christians, T. Chakrabarti and J. M. Luther, *Science*, 2016, **354**, 92–95.
- ¹² Y. Kim, E. Yassitepe, O. Voznyy, R. Comin, G. Walters, X. W. Gong, P. Kanjanaboos, A. F. Nogueira and E. H. Sargent, *ACS Appl. Mater. Interfaces*, 2015, **7**, 25007–25013.

- ¹³ S. Sun, D. Yuan, Y. Xu, A. Wang and Z. Deng, *ACS Nano*, 2016, **10**, 3648–3657.
- ¹⁴ M. C. Weidman, M. Seitz, S. D. Stranks and W. A. Tisdale, *ACS Nano*, 2016, **10**, 7830–7839.
- ¹⁵ K. Hoshi, T. Chiba, J. Sato, Y. Hayashi, Y. Takahashi, H. Ebe, S. Ohisa and J. Kido, *ACS Appl. Mater. Interfaces*, 2018, **10**, 24607–24612.
- ¹⁶ L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 3692–3696.
- ¹⁷ A. Pan, B. He, X. Fan, Z. Liu, J. J. Urban, A. P. Alivisatos, L. He and Y. Liu, *ACS Nano*, 2016, **10**, 7943–7954.
- ¹⁸ G. Almeida, L. Goldoni, Q. Akkerman, Z. Dang, A. H. Khan, S. Marras, I. Moreels, L. Manna, *ACS Nano*, 2018, **12**, 1704–1711.
- ¹⁹ S. Wei, Y. Yang, X. Kang, L. Wang, L. Huang and D. Pan, *Chem. Commun.*, 2016, **52**, 7265–7268.
- ²⁰ M. Imran, V. Caligiuri, M. Wang, L. Goldoni, M. Prato, R. Krahne, L. De Trizio and L. Manna, *J. Am. Chem. Soc.*, 2018, **140**, 2656–2664.
- ²¹ A. Dutta, R. K. Behera, P. Pal, S. Baitalik and N. Pradhan, *Angew. Chem. Int. Ed.*, 2019, **58**, 5552–5556.
- ²² A. Dutta, S. K. Dutta, S. D. Adhikari and N. Pradhan, *ACS Energy Lett.*, 2018, **3**, 329–334.
- ²³ J. Maes, L. Balcaen, E. Drijvers, Q. Zhao, J. De Roo, A. Vantomme, F. Vanhaecke, P. Geiregat and Z. Hens, *J. Phys. Chem. Lett.*, 2018, **9**, 3093–3097.
- ²⁴ G. Jiang, C. Guhrenz, A. Kirch, L. Sonntag, C. Bauer, X. Fan, J. Wang, S. Reineke, N. Gaponik and A. Eychmüller, *ACS Nano*, 2019, **13**, 10386–10396.

- ²⁵ J. De Roo, M. Ibáñez, P. Geiregat, G. Nedelcu, W. Walravens, J. Maes, J. C. Martins, I. Van Driessche, M. V. Kovalenko and Z. Hens, *ACS Nano*, 2016, **10**, 2071–2081.
- ²⁶ R. Grisorio, M. E. Di Clemente, E. Fanizza, I. Allegretta, D. Altamura, M. Striccoli, R. Terzano, C. Giannini, M. Irimia-Vladu and G. P. Suranna, *Nanoscale*, 2019, **11**, 986–999.
- ²⁷ M. I. Bodnarchuk, S. C. Boehme, S. ten Brinck, C. Bernasconi, Y. Shynkarenko, F. Krieg, R. Widmer, B. Aeschlimann, D. Günther, M. V. Kovalenko and I. Infante, *ACS Energy Lett.*, 2019, **4**, 63–74.
- ²⁸ D. P. Nenon, K. Pressler, J. Kang, B. A. Koscher, J. H. Olshansky, W. T. Osowiecki, M. A. Koc, L.-W. Wang and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2018, **140**, 17760–17772.
- ²⁹ J. Pan, Y. Shang, J. Yin, M. De Bastiani, W. Peng, I. Dursun, L. Sinatra, A. M. El-Zohry, M. N. Hedhili, A.-H. Emwas, O. F. Mohammed, Z. Ning and O. M. Bakr, *J. Am. Chem. Soc.*, 2018, **140**, 562–565.
- ³⁰ F. Krieg, S. T. Ochsenbein, S. Yakunin, S. ten Brinck, P. Aellen, A. Süess, B. Clerc, D. Guggisberg, O. Nazarenko, Shynkarenko, Y.; S. Kumar, C.-J. Shih, I. Infante and M. V. Kovalenko, *ACS Energy Lett.*, 2018, **3**, 641–646.
- ³¹ G. Almeida, O. J. Ashton, L. Goldoni, D. Maggioni, U. Petralanda, N. Mishra, Q. A. Akkerman, I. Infante, H. J. Snaith and L. Manna, *J. Am. Chem. Soc.*, 2018, **140**, 14878–14886.
- ³² M. Imran, P. Ijaz, D. Baranov, L. Goldoni, U. Petralanda, Q. Akkerman, A. L. Abdelhady, M. Prato, P. Bianchini, I. Infante and L. Manna, *Nano Lett.*, 2018, **18**, 7822–7831.
- ³³ T. Udayabhaskararao, M. Kazes, L. Houben, H. Lin and D. Oron, *Chem. Mater.*, 2017, **29**, 1302–1308.

- ³⁴ Y. Tong, B. J. Bohn, E. Bladt, K. Wang, P. Mueller-Buschbaum, S. Bals, A. S. Urban, L. Polavarapu and J. Feldmann, *Angew. Chem., Int. Ed.*, 2017, **56**, 13887–13892.
- ³⁵ Y. Li, H. Huang, Y. Xiong, S. V. Kershaw and A. L. Rogach, *Angew. Chem. Int. Ed.*, 2018, **57**, 5833–5837.
- ³⁶ L. Peng, A. Dutta, R. Xie, W. Yang and N. Pradhan, *ACS Energy Lett.*, 2018, **3**, 2014–2020.
- ³⁷ C. Lu, M. W. Wright, X. Ma, H. Li, D. S. Itanze, J. A. Carter, C. A. Hewitt, G. L. Donati, D. L. Carroll, P. M. Lundin and S. M. Geyer, *Chem. Mater.*, 2019, **31**, 62–67.
- ³⁸ E. Fanizza, F. Cascella, D. Altamura, C. Giannini, A. Panniello, L. Triggiani, F. Panzarea, N. Depalo, R. Grisorio, G. P. Suranna, A. Agostiano, M. L. Curri and M. Striccoli, *Nano Res.*, 2019, **12**, 1155–1166.
- ³⁹ Y. Dong, T. Qiao, D. Kim, D. Parobek, D. Rossi and D. H. Son, *Nano Lett.*, 2018, **18**, 3716–3722.
- ⁴⁰ A. Swarnkar, R. Chulliyil, V. K. Ravi, M. Irfanullah, A. Chowdhury and A. Nag, *Angew. Chem. Int. Ed.*, 2015, **54**, 15424–15428.
- ⁴¹ Y. Bekenstein, B. A. Koscher, S. W. Eaton, P. Yang and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2015, **137**, 16008–16011.
- ⁴² Y. Tong, E. Bladt, M. F. Aygler, A. Manzi, K. Z. Milowska, V. A. Hintermayr, P. Docampo, S. Bals, A. S. Urban, L. Polavarapu and J. Feldmann, *Angew. Chem. Int. Ed.*, **2016**, **55**, 13887.
- ⁴³ Y. Wu, X. Li and H. Zeng, *ACS Energy Lett.*, 2019, **4**, 673–681.
- ⁴⁴ S. ten Brinck and I. Infante, *ACS Energy Lett.*, 2016, **1**, 1266–1272.
- ⁴⁵ M. V. Kovalenko, L. Protesescu and M. I. Bodnarchuk, *Science*, 2017, **358**, 745–750.

- ⁴⁶ G. Nedelcu, L. Protesescu, S. Yakunin, M. I. Bodnarchuk, M. J. Grotevent and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 5635–5640.
- ⁴⁷ C. Giacovazzo, H. L. Monaco, D. Viterbo, F. Scordari, G. Gilli, G. Zanotti and M. Catti, *Fundamentals of Crystallography*. Oxford University Press Inc., New York, 1992, Reprinted 1995. Chap. 3, pag. 152, 163, 178.
- ⁴⁸ F. Liu, Y. Zhang, C. Ding, S. Kobayashi, T. Izuishi, N. Nakazawa, T. Toyoda, T. Ohta, S. Hayase, T. Minemoto, K. Yoshino, S. Dai and Q. Shen, *ACS Nano*, 2017, **11**, 10373–10383.
- ⁴⁹ D. Baranov, M. J. Lynch, A. C. Curtis, A. R. Carollo, C. R.; Douglass, A. M. Mateo-Tejada and D. M. Jonas, *Chem. Mater.*, 2019, **31**, 1223–1230.
- ⁵⁰ J. S. Manser, M. I. Saidaminov, J. A. Christians, O. M. Bakr and P. V. Kamat, *Acc. Chem. Res.*, 2016, **49**, 330–338.
- ⁵¹ M. P. U. Haris, R. Bakthavatsalam, S. Shaikh, B. P. Kore, D. Moghe, R. G. Gonnade, D. D. Sarma, D. Kabra and J. Kundu, *Inorg. Chem.*, 2018, **57**, 13443–13452.
- ⁵² S. Rahimnejad, A. Kovalenko, S. Martí Forés, C. Aranda and A. Guerrero, *ChemPhysChem*, 2016, **17**, 2795–2798.
- ⁵³ P. Liu, W. Chen, W. Wang, B. Xu, D. Wu, J. Hao, W. Cao, F. Fang, Y. Li, Y. Zeng, R. Pan, S. Chen, W. Cao, X. W. Sun and K. Wang, *Chem. Mater.*, **2017**, **29**, 5168–5173.
- ⁵⁴ S. J. Yoon, K. G. Stamplecoskie and P. V. Kamat, *J. Phys. Chem. Lett.*, **2016**, **7**, 1368–1373.
- ⁵⁵ Y. Zhang, M. I. Saidaminov, I. Dursun, H. Yang, B. Murali, E. Alarousu, E. Yengel, B. A. Alshankiti, O. M. Bakr and Mohammed, O. F., *J. Phys. Chem. Lett.*, 2017, **8**, 961–965.
- ⁵⁶ S. K. Mehetor, H. Ghosh and N. Pradhan, *J. Phys. Chem. Lett.*, 2019, **10**, 1300–1305.
- ⁵⁷ X. Peng, J. Wickham and A. P. Alivisatos, *J. Am. Chem. Soc.*, 1998, **120**, 5343–5344.

- ⁵⁸ M. B. Teunis, M. A. Johnson, B. B. Muhoberac, S. Seifert and R. Sardar, *Chem. Mater.*, 2017, **29**, 3526–3537.
- ⁵⁹ Z. Hens and J. C. A. Martins, *Chem. Mater.*, 2013, **25**, 1211–1221.
- ⁶⁰ I. Moreels, B. Fritzinger, J. C. Martins and Z. Hens, *J. Am. Chem. Soc.*, 2008, **130**, 15081–15086.
- ⁶¹ B. Fritzinger, I. Moreels, P. Lommens, R. Koole, Z. Hens and J. C. Martins, *J. Am. Chem. Soc.*, 2009, **131**, 3024–3032.
- ⁶² R. Grisorio, D. Debellis, G. P. Suranna, G. Gigli and C. Giansante, *Angew. Chem. Int. Ed.*, 2016, **55**, 6628–6633.
- ⁶³ J. De Roo, N. Yazdani, E. Drijvers, A. Lauria, J. Maes, J. S. Owen, I. Van Driessche, M. Niederberger, V. Wood, J. C. Martins, I. Infante and Z. Hens, *Chem. Mater.*, 2018, **30**, 5485–5492.
- ⁶⁴ R. Grisorio, D. Quarta, A. Fiore, L. Carbone, G. P. Suranna and C. Giansante, *Nanoscale Adv.*, 2019, **1**, 3639–3646.
- ⁶⁵ E. G. Ripka, C. R. Deschene, J. M. Franck, I.-T. Bae and M. M. Maye, *Langmuir*, 2018, **34**, 11139–11146.
- ⁶⁶ B. Fritzinger, R. K. Capek, K. Lambert, J. C. Martins and Z. Hens, *J. Am. Chem. Soc.*, 2010, **132**, 10195–10201.
- ⁶⁷ C. N. Valdez, A. M. Schimpf, D. R. Gamelin and J. M. Mayer, *ACS Nano*, 2014, **8**, 9463–9470.
- ⁶⁸ S. R. Smock, T. J. Williams and R. L. Brutchey, *Angew. Chem. Int. Ed.*, 2018, **57**, 11711–11715.

- ⁶⁹ J. De Roo, S. Coucke, H. Rijckaert, K. De Keukeleere, D. Sinnaeve, Z. Hens, J. C. Martins and I. Van Driessche, *Langmuir*, 2016, **32**, 1962–1970.
- ⁷⁰ M. Grabolle, M. Spieles, V. Lesnyak, N. Gaponik, A. Eychmüller and U. Resch-Genger, *Anal. Chem.*, 2009, **81**, 6285–6294.
- ⁷¹ A. Altomare, M. C. Burla, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Rizzi, *J. Appl. Cryst.*, 2001, **34**, 392–397.
- ⁷² A. Le Bail, H. Duroy and J. L. Fourquet, *Math. Res. Bull.*, 1988, **23**, 447–452.