

# Exploring the Surface Chemistry of Cesium Lead Halide Perovskite Nanocrystals

*Roberto Grisorio,<sup>\*</sup> Milvia Elena Di Clemente,<sup>†</sup> Elisabetta Fanizza,<sup>†,‡</sup> Ignazio Allegretta,<sup>¶</sup> Davide Altamura,<sup>§</sup> Marinella Striccoli,<sup>‡</sup> Roberto Terzano,<sup>¶</sup> Cinzia Giannini,<sup>§</sup> Mihai Irimia-Vladu,<sup>#</sup> Gian Paolo Suranna<sup>||,⊥</sup>*

*<sup>||</sup>Dipartimento di Ingegneria Civile, Ambientale, del Territorio, Edile e di Chimica (DICATECh), Politecnico di Bari, Via Orabona 4, 70125 Bari, Italy*

*<sup>†</sup>Dipartimento di Chimica, Università degli Studi di Bari “A. Moro”, Via Orabona 4, 70126 Bari, Italy*

*<sup>‡</sup>CNR-Istituto per i Processi Chimico Fisici, UOS Bari, Via Orabona 4, 70126 Bari, Italy*

*<sup>¶</sup>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*

*<sup>§</sup>Institute of Crystallography, National Research Council, via Amendola 122/O, Bari 70126, Italy*

*<sup>#</sup>Joanneum Research MATERIALS - Institute for Surface Technologies and Photonics, Franz-Pichler Straße 30, Weiz A-8160, Austria*

*<sup>⊥</sup>CNR NANOTEC – Istituto di Nanotecnologia, Via Monteroni, 73100 Lecce, Italy*

## ABSTRACT

Colloidal nanocrystals (NCs) of cesium lead halide perovskites ( $\text{CsPbX}_3$ ,  $X = \text{Cl, Br or I}$ ) are emerging as an exciting class of optoelectronic materials, but the retention of their colloidal and structural integrity during isolation, purification and handling still represents a critical issue. The impelling questions concerning their intrinsic chemical instability are connected to the dynamic nature of the bonding between the inorganic surface and the long-chain capping ligands. However, the key aspects of  $\text{CsPbX}_3$  surface chemistry directly impacting on their stability remain elusive. In this contribution, we provide an in-depth investigation of the surface properties of differently composed  $\text{CsPbX}_3$  NCs, prepared by traditional hot-injection methods. The study, mainly relying on solution NMR spectroscopy, is backed up by elemental analysis as well as morphological, structural and optical investigations. We ascertained how the nature of ligand adsorption/desorption processes at the NC surface is dependent on its elemental composition, thus understanding the origin of the instability afflicting  $\text{CsPbI}_3$  NCs. We also evaluated the role of NC purification as well as of the degradation pathways involving the organic shell on the surface chemistry of  $\text{CsPbX}_3$  NCs. The rationalization of our findings discloses an important role of traditional capping ligands on the structural stability of  $\text{CsPbX}_3$  NCs, paving the way towards new synthetic, purification and post-functionalization strategies for this promising class of nanomaterials.

## INTRODUCTION

While semiconducting metal halide perovskites are strengthening their huge potential in photovoltaics<sup>1</sup> and light-emitting devices,<sup>2</sup> perovskite nanocrystals (NCs) have recently emerged as outstanding alternatives for optoelectronic applications.<sup>3</sup> In particular, all-inorganic cesium lead halide perovskite NCs<sup>4</sup> (with formula  $\text{CsPbX}_3$  in which X can be Cl, Br, or I) displayed excellent photophysical properties associated to quantum confinement<sup>5</sup> comprising high photoluminescence (PL) quantum yields and narrow emission peak widths.<sup>6</sup> By adjusting their dimensions as well as halide composition,<sup>7</sup> the emission of these materials can potentially span from the ultraviolet to the near-infrared region.<sup>8</sup>

Unfortunately, in spite of their promises, the chemical and colloidal instability of  $\text{CsPbX}_3$  NCs when exposed to polar solvents or moisture *de facto* precludes their vast utilization. With respect to the widely known chalcogenide quantum dots,<sup>9</sup> the crystal structure of  $\text{CsPbX}_3$  NCs exhibits a more predominant ionic character, which consequently dominates the interactions with the organic shell, making labile the ligand-NC bonds responsible for the passivation of the inorganic framework.<sup>10</sup> This peculiarity of  $\text{CsPbX}_3$  affects their colloidal stability and, in some cases, their structural integrity, mainly when the perovskite NCs get in touch with polar solvents tentatively added to isolate and/or purify the nanoparticles.<sup>11</sup> The poor structural stability is particularly evident in the case of  $\text{CsPbI}_3$  NCs, in which the degradation process leads to the phase transformation into a non-perovskite material.<sup>12</sup> Several approaches have been conceived for the stabilization of  $\text{CsPbI}_3$  cubic phase,<sup>13</sup> such as the substitution of cesium cations with formamidinium ones<sup>14</sup> and the use of alkyl phosphonic acids,<sup>15</sup> phosphines<sup>16</sup> or benzoyl iodide<sup>17</sup> during the synthesis without post-synthesis treatments. Based on these findings, it can be suspected that the phase instability of  $\text{CsPbI}_3$  NCs (and generally of  $\text{CsPbX}_3$  nanoparticles) is related to surface chemistry of the nanoparticle. However, understanding the structure of nanoscale interfaces requires an elaborate mix of concepts and techniques borrowed from surface science and coordination chemistry.

The principal actors generating a NC surface are the ligands, *i.e.* molecules that bind to the surface, which, as critical components of NC synthesis, not only influence the nucleation process preventing inter-particle aggregation, but also determine the physical and chemical behaviour of the resulting nanomaterials. Conventionally, oleic acid (OLA) and oleylamine (OLAm) ligands are used in the preparation of CsPbX<sub>3</sub> NCs. It has been suggested that oleylammonium halides are the main surface passivating agents of CsPbX<sub>3</sub> NCs,<sup>18,19</sup> while the role in passivation by OLA is still under debate. However, recent investigations are elucidating the crucial function exerted by OLA<sup>20</sup> and OLAm<sup>21</sup> on the transformations of perovskite NCs with degradation of their structural and optical properties. Since perovskite NCs are commonly synthesized by employing a ligand excess, the absence of a purification step able to remove the superfluous amount of ligands could be held responsible for the scarce long-term colloidal stability of the relevant nanomaterials. Furthermore, common capping ligands act as electrically insulating layers on the NC surface, which significantly hinder charge carrier injection and transport at the interface in optoelectronic devices.<sup>22</sup> All these observations point to a comprehensive investigation of CsPbX<sub>3</sub> surface chemistry to plan effective functionalization and to evaluate its effects on NC surface and stability.

Nuclear magnetic resonance (NMR) spectroscopy constitutes an ideal technique to study the details of the NC organic-inorganic interface unraveling the ligand shell composition and suggesting its binding motifs.<sup>23</sup> The combination of <sup>1</sup>H-NMR, nuclear Overhauser effect spectroscopy (NOESY) and diffusion ordered spectroscopy (DOSY) allows to clearly discriminate the dynamics of the adsorption/desorption processes involving the passivating agents.<sup>24</sup> Sharp resonances with negative nuclear Overhauser effect (nOe) cross peaks and fast diffusion coefficients are actually produced by weakly bound ligands resulting from a fast adsorption/desorption process at NC surface. Conversely, broadened resonances with negative nOe peaks and slow diffusion coefficients are due to tightly bound ligands not (or slowly) exchanging with free species.<sup>25</sup>

Here, we focus on inorganic CsPbX<sub>3</sub> NCs synthesized by the traditional hot-injection approaches to deeply investigate the impact of a different halide composition on their surface chemistry *via* solution <sup>1</sup>H-NMR techniques. Our studies indicate that, although with different contributions, both aliphatic carboxylic acids and amines used for the nanoparticle synthesis participate to the surface passivation of as-prepared perovskite NCs. However, the equilibria involved in the passivation process were found to be dependent on the NC composition and solvent, thus explaining the differences in stability observed for CsPbX<sub>3</sub> nanoparticles. We are also confident that the details on the degradation mechanism involving the common NC organic shell could inspire efforts for surface modifications required for the optoelectronic applications of these exciting nanomaterials.

## RESULTS AND DISCUSSION

**Synthesis and characterization of CsPbX<sub>3</sub> NCs.** As specified in the Experimental Section, perovskite CsPbX<sub>3</sub> NCs (X = Cl, Br, I, and mixed Br/Cl, I/Br) were prepared by following the synthetic procedure reported by Protesescu *et al.*<sup>8</sup> In brief, the relevant lead-halides (0.38 mmol) were dissolved in 7.5 mL of octadecene (ODE) containing 1.0 mL of each ligand (OIAm and OA). After the PbX<sub>2</sub> was dissolved at the chosen reaction temperature (160 °C), a warm Cs-oleate (0.09 mmol) solution was injected. The obtained mixture was rapidly cooled (< 10 sec) with an ice bath and centrifugated for the product isolation. The mixed-halide perovskite NCs were synthesized by mixing an equimolar ratio of the suitable lead halides under the same reaction conditions and their formal composition, based on the molar feed ratio is reported in Table 1. In all cases, it can be assumed that the centrifugation allows to recover most of the perovskite NCs as precipitate, as testified by the observation that the supernatant liquid after centrifugation is barely colored and not fluorescent. At this stage, the isolated perovskite nanoparticles probably include an indefinite amount of remnant synthetic precursors and solvent. While the purification by multiple precipitation/redispersion steps using polar solvents (such as ethanol, methanol, acetone, or ethyl acetate) is common practice in the

course of NC preparation, the isolation of the CsPbX<sub>3</sub> NCs in polar media often compromises their colloidal stability. These effects are related to the peculiar processes at the basis of CsPbX<sub>3</sub> surface passivation, which determine the drastic alteration of NC surface composition, when the nanoparticle interacts with the polar solvents better solvating the surface ligands. We decided to gain insights into the effects of purification on the NC surface chemistry by using solution NMR spectroscopy (*vide infra*).

The products collected from the first centrifugation were dispersed in hexane (1.2 mL), precipitated with acetone (1.2 mL) and recovered by a further centrifugation. The addition of 50 μL of both ligands prior to precipitation with acetone was proved crucial to maintain the colloidal stability of our CsPbX<sub>3</sub> NCs, except for CsPbI<sub>3</sub>, for which the contact with the polar solvent immediately caused its phase deterioration leading to an insoluble material.

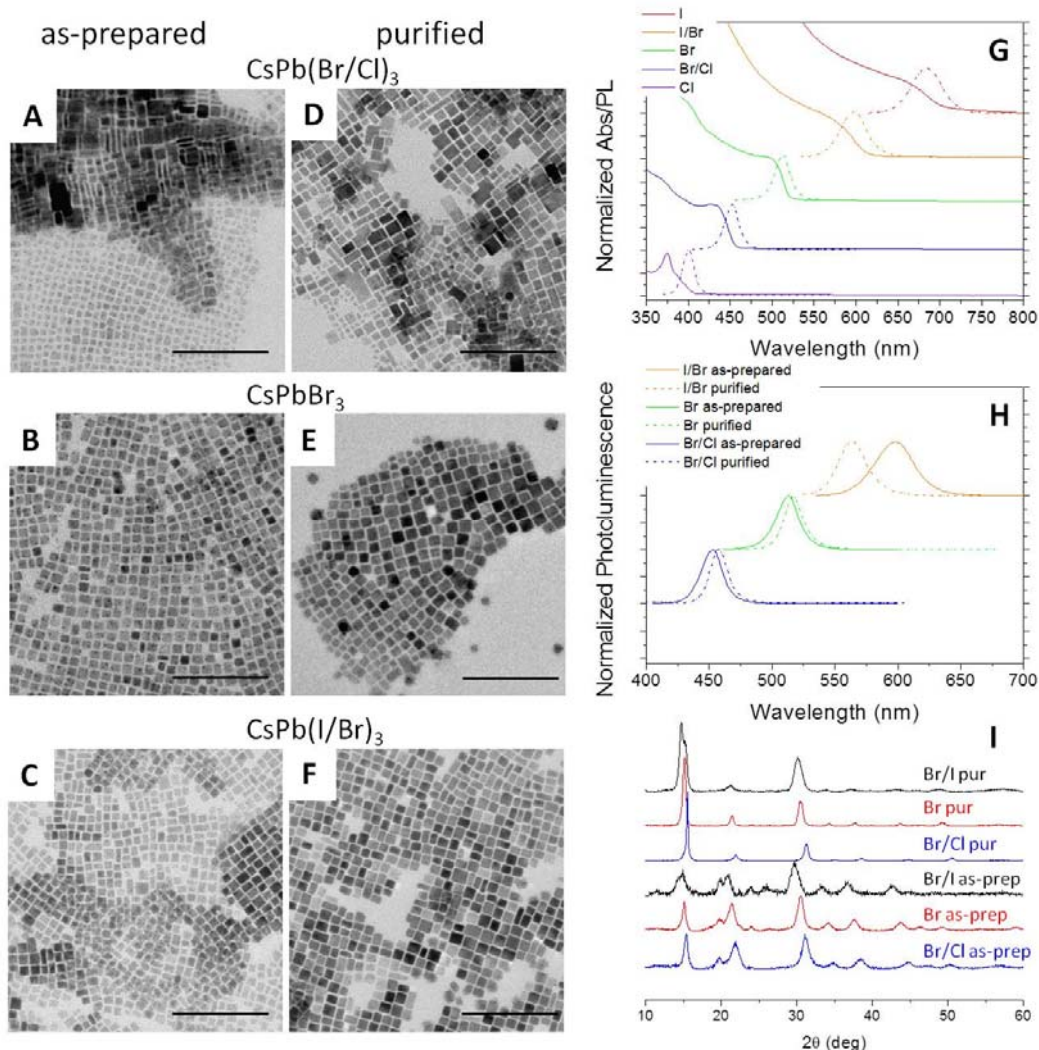
Molar feed ratio	Sample	Elemental composition	Dimension (nm)	UV-Vis onset (nm)	λ <sub>em</sub> (nm)	FWHM (nm)	PLQY (%)
CsPbCl <sub>3</sub>	as-prep	Cs <sub>1.1</sub> PbCl <sub>3.1</sub>	9.3±1.8	386	401	14	0.3
CsPbCl <sub>1.5</sub> Br <sub>1.5</sub>	as-prep	Cs <sub>1.1</sub> PbCl <sub>1.6</sub> Br <sub>1.4</sub>	7.1±0.9	437	452	20	5
CsPbCl <sub>1.5</sub> Br <sub>1.5</sub>	pur	Cs <sub>1.3</sub> PbCl <sub>1.5</sub> Br <sub>1.4</sub>	7.6±1.3	441	455	17	2
CsPbBr <sub>3</sub>	as-prep	Cs <sub>1.2</sub> PbBr <sub>2.8</sub>	9.0±0.8	502	513	21	74
CsPbBr <sub>3</sub>	pur	Cs <sub>1.3</sub> Pb Br <sub>2.8</sub>	10.9±1.1	501	516	16	74
CsPbBr <sub>1.5</sub> I <sub>1.5</sub>	as-prep	Cs <sub>1.4</sub> PbBr <sub>2</sub> I <sub>1.4</sub>	9.7±1.5	547	576	35	39
CsPbBr <sub>1.5</sub> I <sub>1.5</sub>	pur	Cs <sub>1.3</sub> PbBr <sub>2.6</sub> I <sub>0.6</sub>	11.3±1.4	523	533	27	32
CsPbI <sub>3</sub>	as-prep	Cs <sub>1.3</sub> PbI <sub>3.7</sub>	8.0±1.3	651	669	39	53

**Table 1.** Summary of the elemental composition, morphological (TEM) and optical properties (cyclohexane) of CsPbX<sub>3</sub> NCs.

The success of this purification protocol motivated us to attempt a further washing step using the same procedure on CsPbBr<sub>3</sub> NCs. Unfortunately, the colloidal stability of the resulting material resulted to be severely compromised. Probably, desorption of the protective ligand shell upon drastic purification leads to the loss of NC structural integrity, *i.e.* aggregation of NCs into bulk polycrystalline materials. Hence, the application of a single purification step is sufficient to remove excess ligand and impurities, preserving, at the same time, colloidal stability and improving stability of the resulting NCs (*vide infra*).

The size and morphology of as-prepared CsPbX<sub>3</sub> NCs were investigated by transmission electron microscopy (TEM), which clearly evidences predominant fraction of well defined square shaped nanostructures, ascribable to nanocubes for our perovskite nanomaterials (Figure 1A-F and Figure S1). Their average sizes are reported in Table 1. It can be observed that the purification step preserves the NCs morphology, while slightly increasing their average sizes, which suggests a sort of reorganization of the nanomaterials, as also confirmed by the structural analysis. The optical response of the obtained CsPbX<sub>3</sub> NCs was quantified by absorption measurements; their PL emission wavelength spanned the entire visible range (from 401 to 684 nm) by adjusting the halide composition (Figure 1G).<sup>26</sup> Since previous studies assessed that the precipitation with an antisolvent has a large impact on optical properties of the resulting NCs,<sup>27</sup> we compared the emission properties of the as-prepared products with those of the relevant purified samples in the case of CsPb(Br/Cl)<sub>3</sub>, CsPbBr<sub>3</sub> and CsPb(I/Br)<sub>3</sub> nanoparticles. As a general consideration, both as-prepared and purified CsPbX<sub>3</sub> solutions exhibits relatively narrow (FWHM of 14÷39 nm) and single-peak PL emission with small Stokes shifts, as evidenced in Table 1. While these observations point to a single halide composition for mixed-halide perovskite NCs, it can be noted that the purification procedure heavily affects only the PL behaviour of the mixed-halide CsPb(I/Br)<sub>3</sub> nanomaterial. The purification method preserves the CsPb(I/Br)<sub>3</sub> shape integrity, as confirmed by TEM investigations, but both absorption and emission maxima result remarkably blue-shifted by the treatment with the polar solvent (Figure 1H

and Table 1). In the case of the other perovskite NCs submitted to a single purification step – *i.e.* CsPb(Br/Cl)<sub>3</sub> and CsPbBr<sub>3</sub> – we observed that the optical properties (absorption, emission and quantum yield) remained almost unaltered upon purification. The slight red-shift of the emission in purified samples is due to the fact that the smallest NCs are apparently removed in the washing procedure, as supported by the observation that the centrifugation supernatant of CsPbBr<sub>3</sub> NCs (opportunistically diluted in cyclohexane) shows an intense and blue-shifted emission ( $\lambda_{em} = 498$  nm) with respect to that of as-prepared samples (Figure S2). As a consequence, the full-width at half maximum (FWHM) of the emission bands results to be smaller in the case of purified samples. Moreover, all samples exhibit high PL quantum yields, differently from what observed for chlorine-containing NCs (Table 1).





**Figure 1.** TEM micrographs of as-prepared CsPb(Br/Cl)<sub>3</sub> (A), CsPbBr<sub>3</sub> (B), CsPb(I/Br)<sub>3</sub> (C) NCs and the relevant purified samples (D-F). Scale bar = 100 nm. (G) UV/Vis absorption and PL spectra of as-prepared CsPbCl<sub>3</sub>, CsPb(Br/Cl)<sub>3</sub>, CsPbBr<sub>3</sub>, CsPb(I/Br)<sub>3</sub> and CsPbI<sub>3</sub> NCs obtained by hot injection at 160 °C. (H) Comparison between PL spectra of as-prepared and purified NCs shown in TEM images and (I) XRD patterns of the same samples. UV-Vis and PL have been recorded in cyclohexane.

From the structural point of view, the XRD patterns (detector scan) reported in Fig. 1I clearly show the effect of purification, as all purified and as-prepared samples feature similar patterns, respectively. In particular, Le Bail-based whole pattern analysis with EXPO<sup>28</sup> revealed a CsPbX<sub>3</sub> single phase with a distorted cubic symmetry in the purified samples, which is also present in the as-prepared ones along with an additional crystalline phase giving rise to extra peaks. The main peaks at about  $2\theta = 15^\circ$  and  $31^\circ$  would be the first and second diffraction orders of the *100* reflections in the cubic system according to the ICSD #201285 powder diffraction file. However, because of peak broadening due to the small NC size, it is hard to unambiguously discriminate among other possible crystal phases, such as monoclinic or orthorhombic, with similar cell parameters. Moreover, relative intensities are likely affected by NC preferred orientation, which in the case of cube shaped particles can be expected to be face on. Compared to the more surface sensitive detector scans (fixed  $0.5^\circ$  incidence angle) reported in Fig. 1I, the coupled sample-detector ( $\theta/2\theta$ ) scans reported in Figure S3 provide thus more reliable relative intensities for the *100* peaks (as they are collected from the very same lattice planes), besides a better angular resolution. Purified CsPbBr<sub>3</sub> and CsPb(Br/Cl)<sub>3</sub> samples show a clear single phase pattern: the former being compatible with the monoclinic or orthorhombic phases (JCPDS #18-0364 and ICDD #01-072-7929, respectively), both featuring a doublet at  $2\theta = 30.4^\circ / 30.7^\circ$ ; the latter, featuring a single peak at  $2\theta = 31.4^\circ$ , being compatible with the cubic phase. The ratio between the integrated areas under the two main peaks is (1.2) closer to that of the monoclinic phase (1.1 in JCPDS

#18-0364) in the as-prepared CsPbBr<sub>3</sub> sample (not shown), between the monoclinic and the orthorhombic phase value (1.8 in ICDD #01-072-7929) in the purified CsPbBr<sub>3</sub> sample, closer to the cubic phase (expected ratio 1.3 - JCPDS #18-0464 to 2.3 - ICDD # 01-072-7930 and JCPDS # 75-0412) in the purified CsPb(Br/Cl)<sub>3</sub> samples (1.7). On the other hand, purified CsPb(I/Br)<sub>3</sub> samples show further diffraction contributions convoluted with the first main peak, indicating a possible non-complete phase purification.

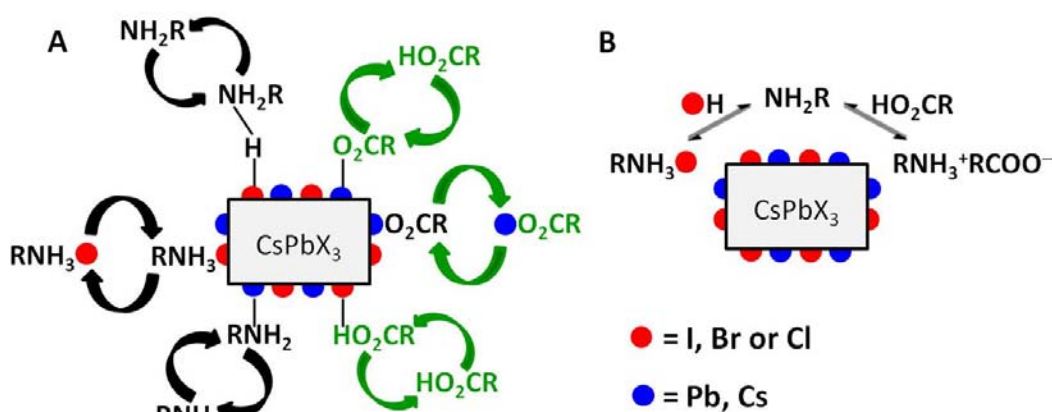
At the same time, it should be emphasized that our purified CsPbBr<sub>3</sub> and the corresponding mixed-halide NCs exhibit an excellent stability when exposed at ambient conditions, also after solvent evaporation. After being stored for three weeks in ambient conditions, the as-prepared CsPbBr<sub>3</sub> NCs appeared as a yellow solid, while the purified ones maintained their colloidal integrity (Figure S4). To explain this behaviour, an insight was needed into the surface chemistry of lead halide-based perovskite NCs, which is well known to play a crucial role in determining not only their optical performance,<sup>29</sup> but also their stability in air.<sup>30</sup>

To deepen this aspect, we firstly analyzed the composition of both as-prepared and purified samples *via* energy dispersive X-ray spectroscopy (EDX) coupled with field emission gun scanning electron microscopy (FEG-SEM). The relevant results in terms of the NC elemental composition are listed in Table 1 (see also Table S1 and Figure S5). All our CsPbX<sub>3</sub> NCs show an excess cesium with respect to lead, supporting the hypothesis that these nanoparticles exhibit Cs-exposed surfaces, despite the fact that the NC syntheses were carried out using a formal excess of lead precursors (see Experimental Section). It has been ascertained that part of the surface cesium atoms can be replaced by oleylammonium ions after the NC assembly,<sup>31</sup> thereby explaining most of the results on CsPbX<sub>3</sub> composition exhibiting a near equimolar Cs/Pb ratio.<sup>32</sup> Hence, considering the relatively mild synthetic conditions preserving the thermodynamically favored oxidation state of the relevant precursors, CsPbX<sub>3</sub> nanocubes with the elemental composition obtained by our EDX data would expose oleylammonium ions, Cs<sup>+</sup> and halides at the surface.<sup>33</sup> The eventual excess of positive charge

would be neutralized by oleate ions. Concerning as-prepared mixed-halide NCs, the halide composition of CsPb(I/Br)<sub>3</sub> NCs reported in Table 1 suggests that the larger volume of iodide ions hinders their incorporation within the NC structure, when they are competing with bromide ions for the perovskite crystalline structures synthesized by hot-injection methods. This behaviour was found to be remarkably different from that of CsPb(Br/Cl)<sub>3</sub> NCs, where bromide and chloride ions are incorporated within the nanomaterial in an equimolar ratio. Moreover, the elemental composition of our NCs seems to be marginally affected by the purification step, with the exception of CsPb(I/Br)<sub>3</sub> NCs, for which the Br/I molar ratio increases from 1.4 in as-prepared samples to 4.3 in purified samples, suggesting that iodide ions are removed in the course of purification.<sup>34</sup> In order to rationalize these observations, we explored the surface chemistry of perovskite CsPbX<sub>3</sub> NCs.

**The surface chemistry of CsPbBr<sub>3</sub> NCs.** Before elucidating the surface chemistry of CsPbX<sub>3</sub> NCs *via* solution NMR investigations, it is firstly convenient to report (Figure 2A) a pictorial description of all plausible equilibria involving the organic shell of the nanoparticles, based on the structural information drawn from nanomaterial characterization. Considering that our investigations have mainly been carried out on perovskite NCs which have not undergone post-synthetic purification steps, these equilibria could involve the excess ligands (OLA and OLAm) or unreacted synthetic precursors (cesium oleate). In parallel, the ionic structure of perovskite NCs could promote adsorption/desorption processes of weakly bound species at the nanoparticle surface. The organic cations (oleylammonium) are kept on the surface of the inorganic framework by ionic interaction or hydrogen bonding, but their dynamic surface passivation would necessarily engage neutral species, as oleylammonium halides or OLAm, to minimize the required energy for the process. The affinity of the NC surface anions toward protons could explain the catalytic activity shown by the nanoparticles for the amide formation from carboxylic acids and aliphatic amines (*vide infra*),<sup>35</sup> but the interaction of the nanoparticle with protons cannot be completely supported by NMR

investigations, since the possible presence of acidic protons on the NC surface is undetectable due to their fast  $T_2$  relaxation. The superficial electron-withdrawing halide atoms could also promote the formation of hydrogen bonds with OLA, while the nitrogen lone pair of OLAm could also passivate eventual undercoordinated metal atoms at the NC surface.<sup>36</sup> Furthermore, since elemental analyses supported the presence of cationic excess on the surface, ligand displacement involving excess OLA could be promoted by proton transfer, in analogy to what observed for chalcogenide quantum dots.<sup>37</sup> As a matter of fact, the passivation process is further complicated by the acid-base equilibrium of the same ligands, on which the NC surface itself can have an influence (Figure 2B).



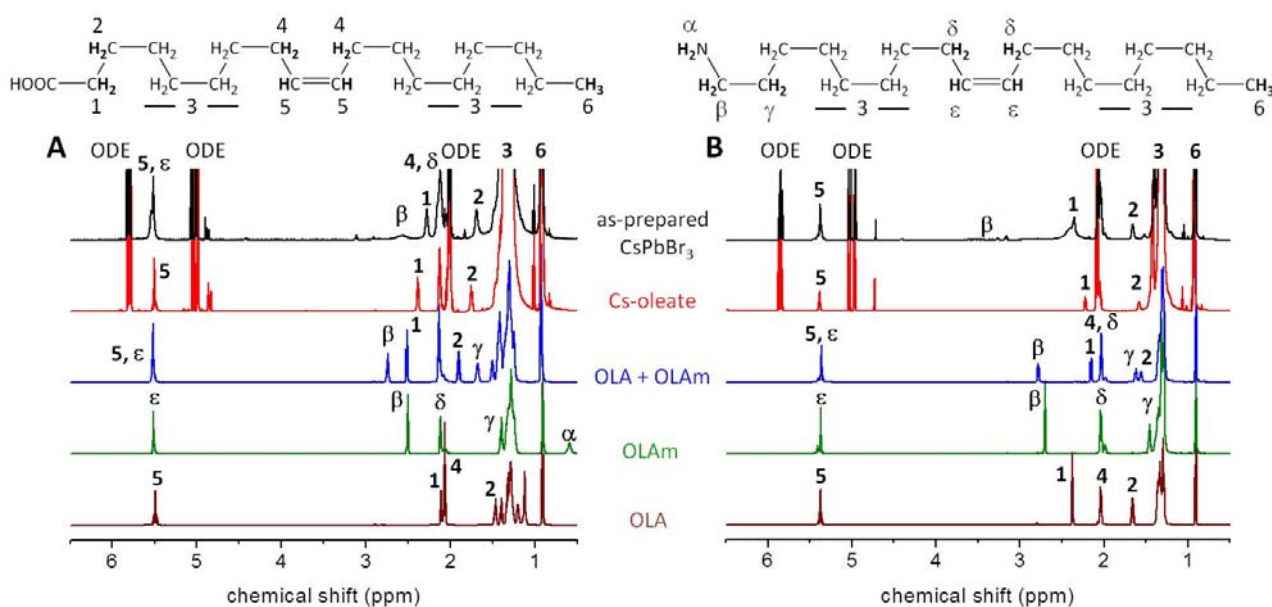
**Figure 2.** (A) Schematic representation of the equilibria involving aliphatic amines and carboxylic acids as the ligands for the passivation of perovskite NC surfaces. (B) Schematic representation of the equilibria involving the ligands while engaged in the passivation process.

On these bases, we compared the  $^1\text{H-NMR}$  spectra of as-prepared CsPbBr<sub>3</sub> NCs with those of the species employed for the nanomaterial synthesis: OLA, OLAm, an equivolumetric mixture of both, and Cs-oleate directly sampled from the solution used for the NC synthesis (Figure 3). The spectra were recorded in two solvents characterized by different viscosity and polarity, namely C<sub>6</sub>D<sub>6</sub> and CDCl<sub>3</sub>. As a first consideration, it is evident that, independently of the solvent polarity, some resonances of the nanomaterial appear significantly broadened with respect to those of free OLA and

OLAm, reflecting their nature of organic species more or less interacting with the NC surface.<sup>38</sup> The broadening of the NMR ligand signals could arise from multiple effects in NCs passivated by organic species, including slow tumbling of the large NCs, decreased spin-spin relaxation time ( $T_2$ ), heterogeneity of the NCs in size, shape and surface properties. The ligand behaviour in solution can properly be scrutinized by focusing on the resonances of methylene protons adjacent to the ligand binding group, which are labeled as **1** and  $\beta$  for OLA and OLAm, respectively (Figure 3). Importantly, the  $^1\text{H-NMR}$  spectrum of OLA recorded in  $\text{C}_6\text{D}_6$  is different with respect to that recorded in  $\text{CDCl}_3$ , being the signal of **1** remarkably downfield shifted in the polar medium. This peculiarity observed for OLA, which is also reflected in the corresponding spectrum of as-prepared  $\text{CsPbBr}_3$ , is likely due to the different solvation degree of the carboxylic acid moiety, which should be more prominent in the case of the more polar solvent. By contrast, the  $^1\text{H-NMR}$  spectra of OLAm are very similar and not affected by solvent polarity, but the spectrum of an equimolar mixture of OLA and OLAm (a mixture employed for the NC synthesis) reveals a downfield shift of the  $\beta$  resonance both in  $\text{C}_6\text{D}_6$  and in  $\text{CDCl}_3$ , as a consequence of the nitrogen protonation. In the case of OLA, deprotonation causes a downfield shift of the **1** resonance in  $\text{C}_6\text{D}_6$ , while an upfield shift is observed in  $\text{CDCl}_3$ . This trend was also confirmed by inspecting the **1** resonance of cesium oleate solution in ODE which is employed for the NC synthesis, as a reference species for the carboxylate moiety.

Concerning as-prepared  $\text{CsPbBr}_3$  NCs, the  $^1\text{H-NMR}$  spectrum features prominent resonances related to OLA and OLAm: the vinylene protons at  $\delta = 5.70\div 5.50$  ppm (**5** and  $\epsilon$ ), the methylene protons next to the vinylene protons at  $\delta = \sim 2.10$  ppm (**4** and  $\delta$ ), 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, as sketched in Figure 3. The intensity of these protons away from the NC surface gain benefit from internal molecular motional freedom. Notwithstanding the NMR broadening is particularly severe for protons close to the NC surface, in the case of as-prepared  $\text{CsPbBr}_3$  NCs we can observe the signals of the peculiar protons ascribable to the ligands (*i.e.* **1** and  $\beta$  for OLA and OLAm, respectively) needed for

ascertaining their behaviour in the passivation process. Since their chemical shifts are influenced by the acid-base equilibrium,<sup>39</sup> we can state that in the apolar solvent OLAm of as-prepared CsPbBr<sub>3</sub> NCs is partially protonated, while OLA is partially deprotonated. However, it is apparent how the signals associated to OLA (in particular **1** and **2**) are sharper and more intense with respect to the corresponding signals of OLAm, hinting a higher degree of solvation for the acid species. The same situation crops up from the analysis of the <sup>1</sup>H-NMR spectrum of as-prepared CsPbBr<sub>3</sub> NCs in CDCl<sub>3</sub>, in which the β signal is very broadened. In this case, however, the downfield shifted β resonance suggests that OLAm is completely protonated, while the characteristic resonances **1** and **2** of OLA appear at the same chemical shifts of the reference, but slightly broadened and upfield shifted. These insights point to a ligand absorption on the NC surface regulated by the solvent polarity and/or viscosity, which promote different passivation mechanisms. A more detailed description of the organic shell protecting the NC surface could emerge from the analysis of the surface chemistry of CsPbBr<sub>3</sub> NCs upon purification and from observations on their stability.

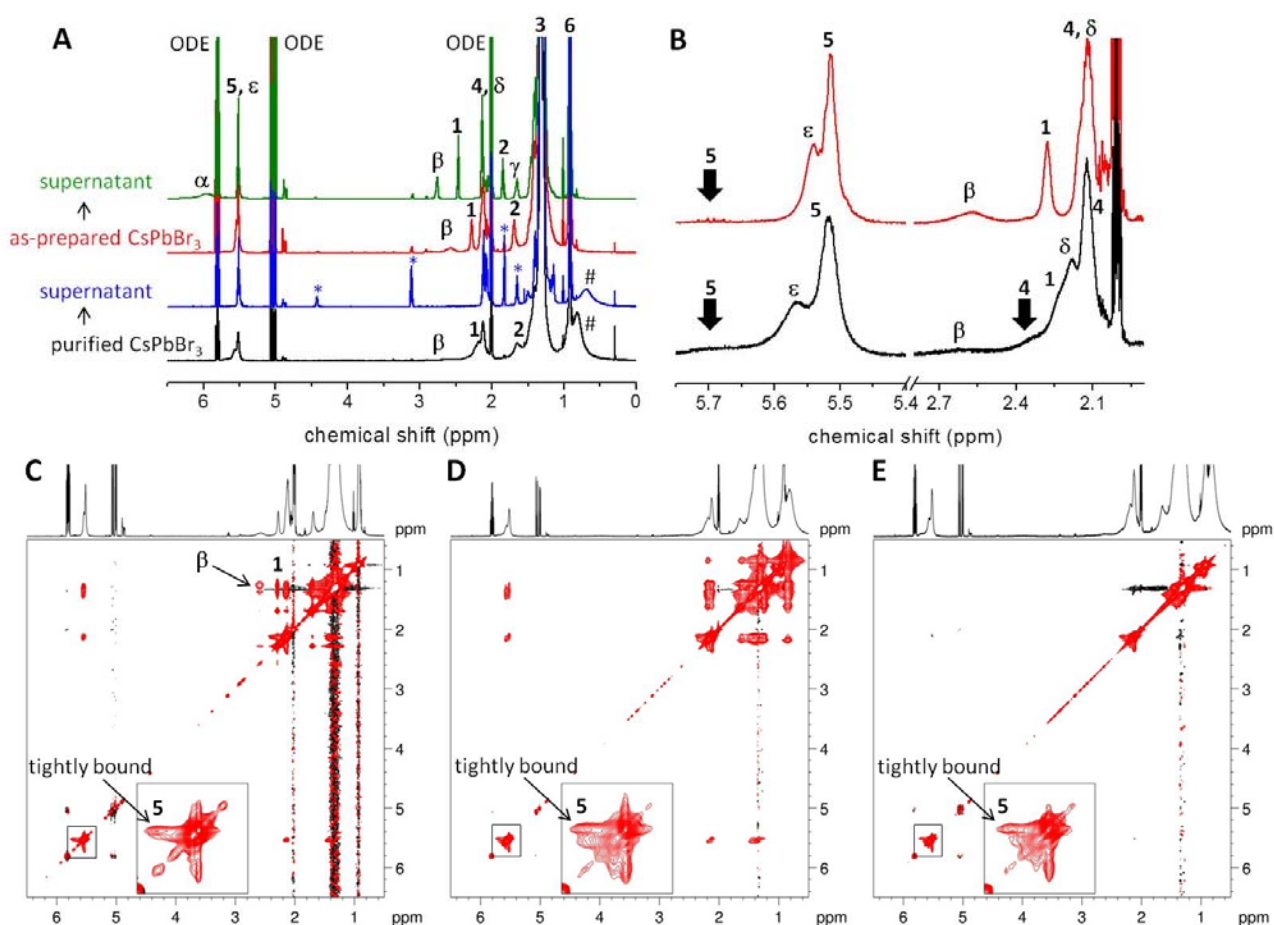


**Figure 3.** <sup>1</sup>H-NMR spectra of OLA, OLAm, a mixture of OLA and OLAm (1/1 vol/vol), cesium oleate and CsPbBr<sub>3</sub> NCs recorded in C<sub>6</sub>D<sub>6</sub> (A) and CDCl<sub>3</sub> (B). The sample of cesium oleate was obtained from the same solution used for the NC synthesis.

Figure 4A compares the  $^1\text{H}$ -NMR spectrum of as-prepared  $\text{CsPbBr}_3$  NCs in  $\text{C}_6\text{D}_6$  with those of purified sample as well as of the relevant supernatant solution obtained after the isolation procedure by centrifugation. It can be noted that, apart from the reaction solvent (ODE), the first centrifugation removes the ligands and traces of the amide byproduct deriving from condensation between OLA and OLAm. This species is characterized by the typical resonances at  $\delta = 4.42$  and  $3.11$  ppm, ascribable to  $-\text{NHCO}-$  and  $-\text{CH}_2\text{NHCO}-$  protons, respectively (supported by the HMBC spectrum in Figure S6). The purification by a single precipitation from hexane with an equivalent volume of acetone in the presence of ligands 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. However, the supernatant solution obtained after the centrifugation prevalently contains the amide itself, hinting that the perovskite surface catalyzes the amide formation in the presence of a polar solvent, but that this impurity can be completely removed. Hence, it can be concluded that due to this surface-catalyzed amide formation, passivating ligands are easily lost during the purification procedures, even when a small amount of both OLA and OLAm is added to preserve the NC integrity. Unfortunately, in the relevant  $^1\text{H}$  NMR spectrum, the presence of the characteristic resonances of ODE at  $4.94$  and  $5.8$  ppm suggests an unsatisfactory purification of the sample from the reaction solvent. By carrying out only a further purification cycle, high-quality  $\text{CsPbBr}_3$  NCs could be obtained, since  $^1\text{H}$ -NMR reveals that ODE contamination can be totally removed from the sample. However, the relevant NC stability and solubility result to be severely compromised by the progressive elimination of ligands. The NMR characterization of this twice-purified  $\text{CsPbBr}_3$  NCs sample is reported in Figure S7 along with the spectrum of the supernatant solution obtained from the isolation centrifugation.

The  $^1\text{H}$  NMR spectrum of as-prepared  $\text{CsPbBr}_3$  in  $\text{C}_6\text{D}_6$  shows relatively broad signals, including the distinct resonance of the vinylene protons of the aliphatic chains ( $\delta = 5.40\div 5.70$  ppm), but, with respect to other discriminating signals, these gain intensity due to their sufficient distance from the

NC surface. Hence, the chemical shift and broadening of the vinylene resonances are indicated to explore the bonding nature of the species passivating the NC surface. In fact, three contributions for the vinylene resonances can clearly be identified from inspection of Figure 4B, if one counts also the weak, slightly low-field shifted signal marked with an arrow at  $\delta = 5.70$  ppm. This observation implicates that solution NMR analysis can distinguish between three species interacting with the NC surface to a greater or lesser extent. By removing part of the organic shell, the first purification step does not alter the chemical composition of CsPbBr<sub>3</sub> NCs (as also confirmed by elemental analyses, *vide supra*) and the slight chemical shift variation of the main resonances (see Figure 4B) can be interpreted by the perturbation of the acid-base equilibrium due to the lower amount of the ligands engaged in passivation processes at the purified NC surface.





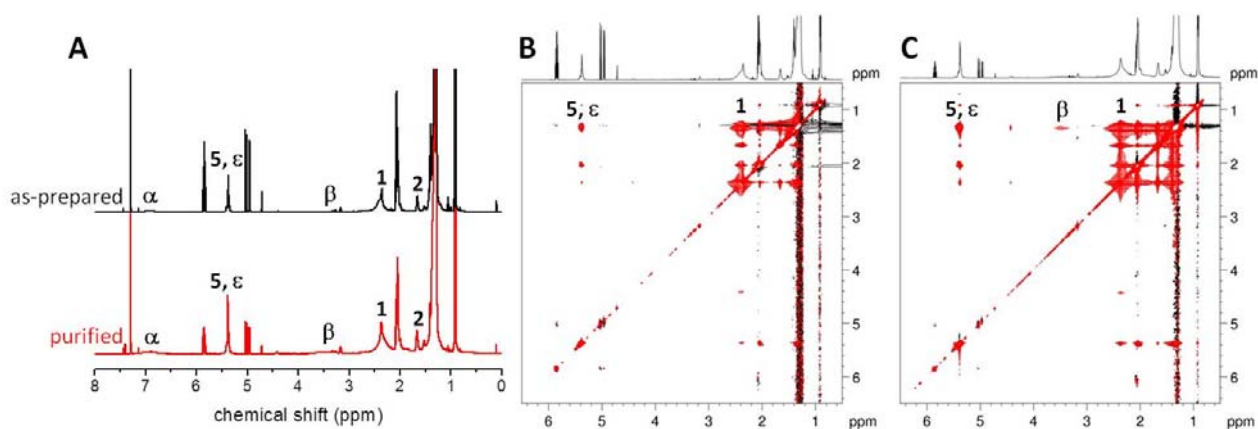
**Figure 4.** (A)  $^1\text{H-NMR}$  spectra of as-prepared and purified  $\text{CsPbBr}_3$  NCs compared with the relevant supernatant solutions deriving from the product isolation by centrifugation. The resonances denoted with \* correspond to the amide of OLA and OLAm, while that marked with # is due to water. (B) Expansions of the same  $^1\text{H-NMR}$  spectra of as-prepared and purified  $\text{CsPbBr}_3$  NCs evidencing their main resonances. 2D NOESY spectrum of as-prepared (C) and purified (D) sample; the inset shows an expansion of the vinylene region. (E) ROESY spectrum of purified  $\text{CsPbBr}_3$  NCs. All spectra are recorded in  $\text{C}_6\text{D}_6$ .

The NOESY spectrum of the as-prepared sample in  $\text{C}_6\text{D}_6$  (Figure 4C) confirms that ODE impurities are not bound to the  $\text{CsPbBr}_3$  NCs showing positive (black) cross peaks, owing to lack of interaction with the surface. Concerning the ligands, cross-peaks connect different proton species involving cross-relaxation at some point of the molecules. Differently from what observed in previous investigations,<sup>18</sup> the NOESY spectrum of freshly as-prepared  $\text{CsPbBr}_3$  NC indicates that OLA binds the surface in apolar solvent, as hinted by the appearance of negative (red in Figure 4C) cross-peaks attributable to the **1** resonance. Moreover, also the negative cross peaks observable between the OLAm resonances corroborate the interaction of the amine with the surface. Considering the previously described equilibria (Figure 2), we infer that in apolar solvents the surface passivation by the aliphatic amine mainly involves adsorption/desorption processes of OLAm rather than oleylammonium bromide. This is confirmed by the fact that part of the OLAm interacts with the carboxylic acid, giving downfield **1** resonances of OLA consequent to deprotonation (as actually observed in the NMR spectrum) while the HBr that would form by dissociation from oleylammonium bromide is significantly more acidic than the carboxylic acid. The nOe behaviour of the alkene resonances in as-prepared  $\text{CsPbBr}_3$  NC (inset in Figure 4C) reveals negative cross peaks for the weak and broad resonance at  $\delta = 5.70$  ppm, confirming its bound nature. We can anticipate that this broad resonance belongs to OLA bound fraction. Also, the sharper alkene resonances features negative nOe

cross peaks and there is a cross peak from the broad to the sharp alkene resonance. We can conclude that the broad resonance is due to tightly bound ligands, in slow exchange with weakly bound ligands, featuring sharp resonances.<sup>40,41</sup> In the case of as-prepared CsPbBr<sub>3</sub>, the cross-peak between the vinylene protons **5** derives from the connection between bound and free OLA species (inset of Figure 4C). The same interactions are also present in the case of the purified sample (Figure 4D), where a cross-peak between tightly bound **5** and  $\epsilon$  resonance of OLAm can additionally be noted. These interactions can either originate from intramolecular cross-relaxation between the vinylene protons of neighboring molecules or result from the simple exchange of molecules between the pool of bound and free OLA. While NOESY cannot distinguish cross-relaxation from chemical exchange, rotating-frame nuclear Overhauser effect spectroscopy (ROESY) spectrum of purified CsPbBr<sub>3</sub> NCs (Figure 4E) evidences negative cross-peaks between signals attributable to tightly and weakly bound OLA molecules. This means that this cross-peak mainly originates from chemical exchange of OLA molecules between the pools of tightly bound and excess OLA.

The <sup>1</sup>H-NMR spectra recorded in the polar solvent (CDCl<sub>3</sub>) of both as-prepared and purified CsPbBr<sub>3</sub> NCs are reported in Figure 5A, revealing the presence of a relatively broad resonance attributable to weakly bound OLA. The interaction of OLA with the surface is confirmed by the relevant NOESY spectra, which showcase negative cross-peaks for **1** and **2** protons both in as-prepared and purified sample (Figure 5B and C). On the other hand, the entity of the downfield-shift of the  $\beta$  protons resonance reasonably suggests that OLAm is fully protonated and exhibited a negative cross-peak (more evident in the case of purified sample) in the relevant NOESY spectra, suggesting that this species is interacting with the NC surface. Differently from what recorded in the apolar C<sub>6</sub>D<sub>6</sub>, no signals attributable to tightly bound OLA species could be observed. We can infer that also in the polar solvent the stabilization mechanism promoted by the aliphatic amine is highly dynamic, but the exchange process at the NC surface involving OLA is faster with respect to that observed in apolar

solvents. The dynamic stabilization in polar solvents promotes desorption of oleylammonium bromide with consequences on the surface chemistry and stability of the relevant purified NCs.



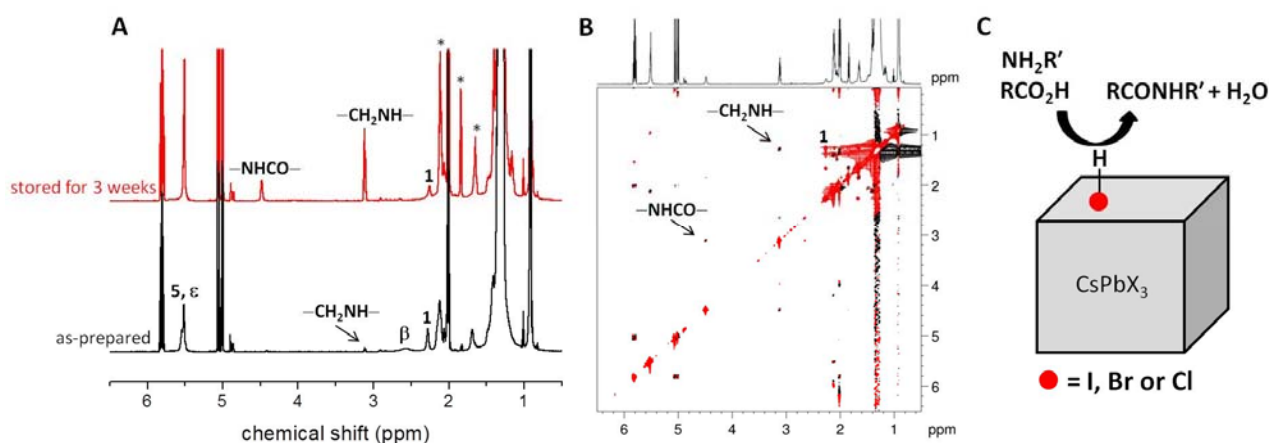
**Figure 5.** (A) Comparison between the  $^1\text{H-NMR}$  spectra of as-prepared and purified  $\text{CsPbBr}_3$  NCs in  $\text{CDCl}_3$ ; 2D NOESY spectrum of as-prepared (B) and purified (C) sample.

To support our findings, we measured DOSY spectra of purified  $\text{CsPbBr}_3$  NCs in the two aforementioned solvents ( $\text{C}_6\text{D}_6$  and  $\text{CDCl}_3$ ). By focusing on the vinylene resonances and using a biexponential fitting, we obtained two different diffusion coefficients ( $D = 5.7 \times 10^{-10} \text{ m}^2/\text{s}$  and  $8.1 \times 10^{-10} \text{ m}^2/\text{s}$  for OLAm and OLA, respectively) in  $\text{C}_6\text{D}_6$  effectively attributable to the ligands engaged in the passivation process. In fact, these values are smaller than those of the relevant free species ( $D \approx 1.0 \times 10^{-9} \text{ m}^2/\text{s}$ ), but remarkably higher than those evaluated from the TEM measurements ( $D = 5.1 \times 10^{-11} \text{ m}^2/\text{s}$ ).<sup>18</sup> This observation implies that OLAm is not tightly bound to the NC surface but is subject to a fast exchange between its bound and free state; as a consequence, an average diffusion coefficient between the two situations appears in the DOSY spectrum. Conversely, OLA slowly exchanges with bound ligands (suggested by the aforementioned broad resonances at  $\delta = 5.65 \text{ ppm}$ ) and its diffusion coefficient is near to that of free molecules. In the polar medium, we observed an analogous situation, since two species are evident with diffusion coefficients ( $D = 3.3 \times 10^{-10} \text{ m}^2/\text{s}$  and  $8.8 \times 10^{-10} \text{ m}^2/\text{s}$  for OLAm and OLA, respectively) incompatible with the average NC

dimensions. The slower diffusion for the amine species suggests that the interaction of oleylammonium bromide with the NC surface in  $\text{CDCl}_3$  is stronger than that of OLAm in the apolar solvent.

**Degradation pathway of the organic shell in  $\text{CsPbBr}_3$  NCs.** Concerning the crucial issue of perovskite NC stability, we analyzed the  $^1\text{H-NMR}$  spectrum of as-prepared  $\text{CsPbBr}_3$  NCs stored in  $\text{C}_6\text{D}_6$  solution at ambient conditions for three weeks (Figure 6A). Inspection of the solution after three weeks revealed the incipient formation of a yellow precipitate, strongly hinting transformations of the nanomaterial, which compromise its colloidal stability. It is reasonable to suppose that these transformations involve the NC surface favouring aggregation between nanoparticles. Actually, the appearance of new signals attributable to the amide formation from the condensation of OLA and OLAm is evident, while the disappearance of the amine resonances is probably related to the complete conversion into the amide (Figure 6A). Since the relevant NOESY spectrum exhibits positive (black) cross-peaks in Figure 6B for the amide, one can conclude that this species is not interacting with the NC surface and that this degradation pathway depauperates the surface of passivating agents lowering the NC colloidal stability. The same reactivity was observed in the case of the purification step (*vide supra*) when acetone was added to the NC solution. While engaging the passivation process, oleylammonium species can release protons to the NC surface, as suggested by the  $^1\text{H-NMR}$  analysis of the  $\text{CsPbBr}_3$  nanomaterial (*vide supra*). We suspect that the acid surface of the perovskite NCs is responsible for the amide evolution as schematized in Figure 6C, because the mixture of OLA and OLAm (in the absence of  $\text{CsPbBr}_3$  NCs) stored in the same conditions did not evidence the amide formation.<sup>42</sup> The catalytic effect of the nanomaterial is due to the affinity of both ligands toward its surface, promoting the spatial proximity necessary for the condensation. Concerning the degradation mechanism, it is reasonable to suppose that the interaction of the surface protons with the carboxylic groups approaching to the nanomaterial increases their electrophilicity, thus favouring the amine

attack and promoting the amide formation. At the same time, the amide evolution is noticeably slowed down in the case of purified CsPbBr<sub>3</sub> NCs stored at ambient conditions for three weeks (Figure S8), thus explaining their higher stability. On these bases, we can rationalize the impact of purification on the colloidal stability of the resulting NCs. As-prepared samples suffer from degradation of the organic shell compromising NC colloidal stability, probably due to adsorbed protons which catalyzes ligand condensation. The first purification step, carried out with acetone removes most of adsorbed protons from the NC surface, as the corresponding oleylammonium halide, thus inhibiting this degradation pathway in the purified material. Although the above-mentioned degradation pathway is extremely slow at room temperature, anyhow it is sufficient to induce the colloidal instability of the corresponding nanomaterial.



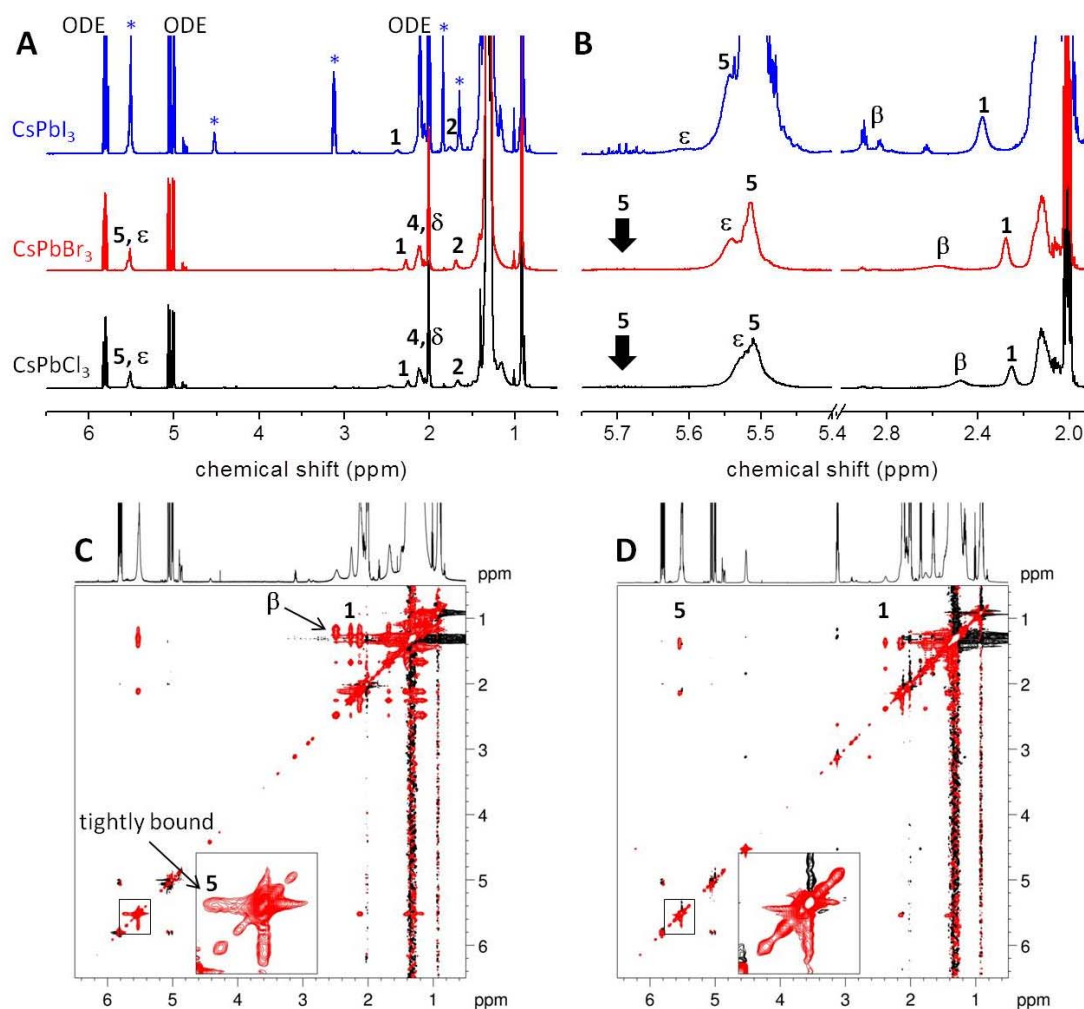
**Figure 6.** (A) Comparison between the <sup>1</sup>H-NMR spectra in C<sub>6</sub>D<sub>6</sub> of as-prepared CsPbBr<sub>3</sub> NCs and the same sample stored for three weeks under ambient conditions and room lighting. Along with the characteristic signals of -NHCO- and -CH<sub>2</sub>NHCO- protons, the resonances denoted with \* are fingerprints of the amide evolution. (B) 2D-NOESY spectrum of degraded sample. (C) Schematic representation of amide evolution catalyzed by adsorbed protons on the perovskite NC surface.

**Surface chemistry of CsPbX<sub>3</sub> NCs.** The surface chemistry of as-synthesized CsPbCl<sub>3</sub> and CsPbI<sub>3</sub> was compared to that of CsPbBr<sub>3</sub> and the relevant <sup>1</sup>H-NMR spectra in C<sub>6</sub>D<sub>6</sub> are shown in Figure 7A. Apparently, the <sup>1</sup>H-NMR spectrum of CsPbCl<sub>3</sub> is very similar to that of CsPbBr<sub>3</sub>. Considering that all CsPbX<sub>3</sub> NCs of this study have been submitted to the same reaction condition and the same isolation procedures, the main aspect emerging from the comparison between the spectra of the three NCs is the presence of a large amount of amide contaminating the CsPbI<sub>3</sub> sample, which, by contrast, is negligible in the other two samples. We ascertained that the amide evolution is not occurring at the early stage of the reaction by sampling an aliquot of PbI<sub>2</sub>/OLA/OLAm mixture immediately before the addition of cesium-oleate solution (Figure S9). On the basis of the previously described correlation between amide formation and NC stability, the rapid amide evolution in CsPbI<sub>3</sub> NCs is a hint of an incipient degradation of the organic shell protecting these nanomaterials. Since the solution NMR spectrum was recorded immediately after the NC isolation it can be stated that a fast degradation occurs for this material. The rationale for this peculiar behavior observed for CsPbI<sub>3</sub> NCs might be found in the “soft” character of the iodine atoms that could favour the interaction of OLA molecules with the surface through secondary bond interactions with the COOH groups.<sup>43</sup> If OLA interacts more strongly with the NC surface, the catalytic condensation with OLAm yielding the corresponding amide would be reasonably favored.

Noticeably, the weak resonances ascribable to OLA and OLAm in CsPbI<sub>3</sub> (Figure 7B) are remarkably downfield shifted with respect to the corresponding resonances of CsPbCl<sub>3</sub> and CsPbBr<sub>3</sub> NCs. The position of the broad signal attributable to  $\beta$  resonance ( $\delta = \sim 2.85$  ppm) suggests the complete protonation of OLAm passivating the NC surface, while the chemical shift of **1** resonance ( $\delta = 2.38$  ppm) suggests that OLA is largely deprotonated if compared with the signals in CsPbCl<sub>3</sub> and CsPbBr<sub>3</sub> NCs. Indeed, the **1** resonance perfectly coincides with that of cesium-oleate both in C<sub>6</sub>D<sub>6</sub> and CDCl<sub>3</sub> (Figure S10). We can conclude that the surface passivation of CsPbI<sub>3</sub> NCs is due to the competition between oleylammonium iodide and cesium-oleate both in apolar and in polar solvents, which

effectively results extremely labile (see also the schematic picture of Figure 8C). Since most of the ligands are consumed in the formation of the inert amide, the NC surface is heavily exposed to structural decomposition induced by interaction with polar solvents or ambient moisture.

The NOESY spectrum of the as-prepared CsPbCl<sub>3</sub> NC reveals tightly bound species with negative cross peaks in analogy with the CsPbBr<sub>3</sub> counterpart. The sharper vinylene resonance also features negative nOe cross peaks and the spectrum displays also a cross peak from the broad to the sharp **5** resonance, most probably due to chemical exchange (see inset Figure 7C). By contrast, the tightly bound species are not detected in the case of CsPbI<sub>3</sub> NCs, while negative cross-peaks are evident for the resonances attributable to cesium-oleate indicating some interaction with the surface. Moreover, the amide byproduct gave positive cross-peaks confirming the absence of interaction with the surface as in the case of ODE. These results support the hypothesis that both in apolar and polar solvents cesium-oleate and oleylammonium iodide are the species engaged in surface passivation. Conversely, the stronger Pb–Cl and Pb–Br bonds hamper the dissociation of the corresponding ammonium salts in apolar solvents and, at the same time, offer the appropriate substrate for the interaction with cesium cations, which firmly bind oleate moieties.



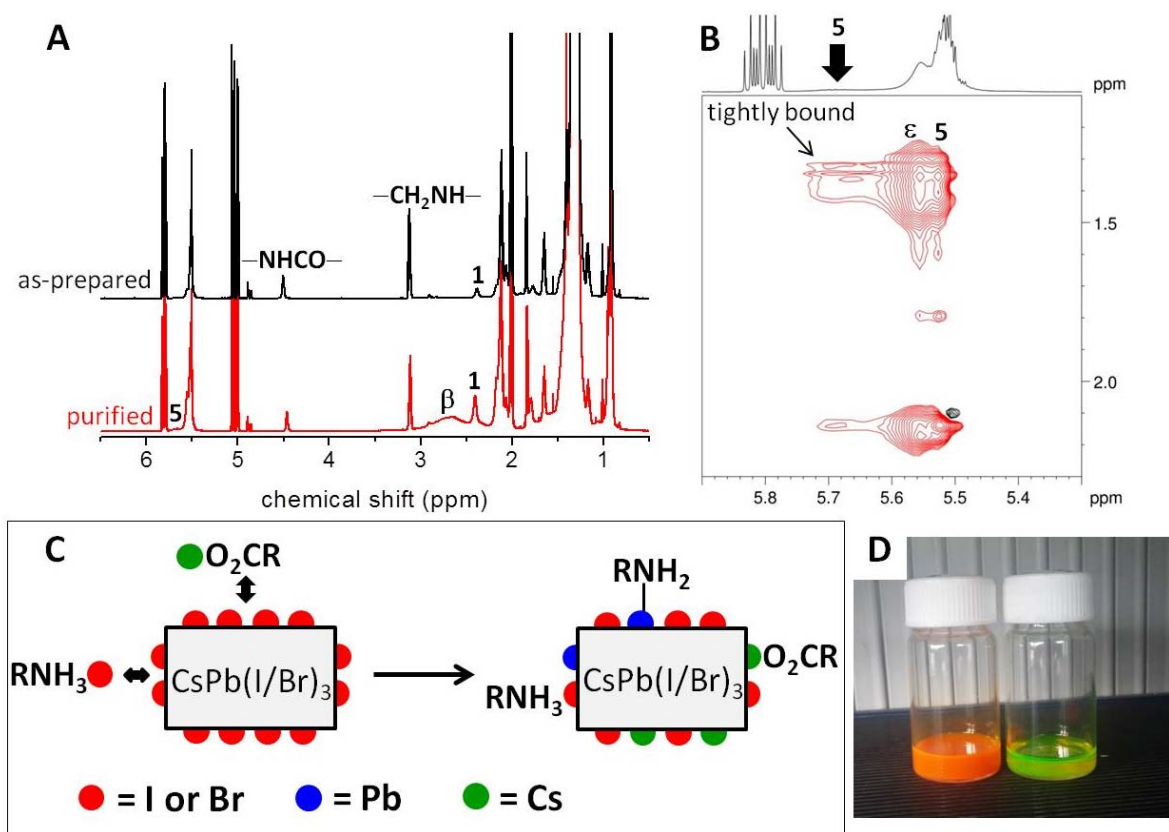
**Figure 7.** (A)  $^1\text{H-NMR}$  spectra of as-prepared  $\text{CsPbBr}_3$  NCs compared with  $\text{CsPbCl}_3$  and  $\text{CsPbI}_3$  NCs. The resonances denoted with \* correspond to the amide of OLA and OLAm. (B) Expansions of the same  $^1\text{H-NMR}$  spectra in the region of the main observable resonances. 2D NOESY spectrum of as-prepared  $\text{CsPbCl}_3$  (C) and  $\text{CsPbI}_3$  (D) NCs.

Since as-prepared  $\text{CsPb(I/Br)}_3$  NCs exhibited a halide composition (*vide supra*) far from the equimolar ratio of the precursor feed used for the synthesis (as obtained for example in  $\text{CsPb(Br/Cl)}_3$  NCs, Figure S11), we deemed it worthwhile to explore the surface chemistry of mixed-halide perovskite nanomaterials on the basis of the knowledge gained on the relevant single-halide materials. Starting from the element composition of  $\text{CsPb(I/Br)}_3$  NCs, the lower amount of iodine can tentatively



be explained by the competition between iodine and bromine ions for the incorporation in the crystal lattice, disfavoring the larger iodide ions. If this hypothesis is true, we would expect an excess iodine on the relevant mixed-halide NC surface. As a matter of fact, we observed that  $^1\text{H-NMR}$  spectrum of as-prepared  $\text{CsPb}(\text{I/Br})_3$  NCs is very similar to that of  $\text{CsPbI}_3$  NCs, suggesting that the mixed-halide material exposes a I-rich surface (Figure 8A). In fact, all the peculiarities of a I-rich surface are observed: a large quantity of formed amide, weak signals attributable to ligands, the simultaneous presence of oleylammonium and cesium-oleate, the absence of tightly bound oleate (Figure S12).

The purification changes on the compositional and optical properties of purified  $\text{CsPb}(\text{I/Br})_3$  NCs are reflected on their surface chemistry. Recalling that all syntheses and purifications were carried out by using the same amounts of reactants and solvents, the  $^1\text{H-NMR}$  spectrum of purified  $\text{CsPb}(\text{I/Br})_3$  NCs shows relatively intense signals attributable to the ligands, although the amide impurity was not completely removed by the purification. The inspection on the vinylene cross-peaks in 2D-NOESY spectrum of this sample evidences the presence of tightly bound oleate and weakly interacting passivating agents (Figure 8B). If dangling iodides are removed in the course of purification, the new surface now exposes strongly bound cesium and undercoordinated lead atoms, which are promptly passivated by OLAm and OLA (Figure 8C). The more efficient passivation is explicated by the higher colloidal stability of the resulting purified sample. Indeed, a solution of purified  $\text{CsPb}(\text{I/Br})_3$  NCs stored for 3 weeks in ambient conditions appears as clear, while a suspension is formed in the case of an unpurified sample (see Figure 8D).



**Figure 8.** (A)  $^1\text{H-NMR}$  spectrum of as-prepared  $\text{CsPb}(\text{I}/\text{Br})_3$  NCs compared with that of the relevant purified sample. (B) 2D NOESY spectrum of purified  $\text{CsPb}(\text{I}/\text{Br})_3$  NCs. (C) Schematic picture illustrating the NC surface modification upon purification. (D) Solutions of as-prepared (left) and purified (right)  $\text{CsPb}(\text{I}/\text{Br})_3$  NCs dissolved in cyclohexane and stored in ambient conditions for three weeks under room lighting conditions.

## CONCLUSIONS

This study aimed at unraveling the surface chemistry of  $\text{CsPbX}_3$  NCs pointing to disentangle the open issues regarding their instability and the necessity of a purification step after their preparation. The colloidal NCs under investigation were prepared by traditional hot-injection methods with a different halide composition and were systematically analyzed for their elemental composition, morphology, crystalline structure and optical properties. Concerning the need for a purification step, we ascertained

that addition of small amounts of oleic acid and oleylamine before precipitation with acetone preserves the colloidal integrity of the NCs, except for the case of CsPbI<sub>3</sub> NCs, which undergo a fast phase transition immediately after the contact with the polar solvent. We were pleased to ascertain a higher phase purity of the all other purified perovskite samples, which comes along with quantum yields substantially unaltered with respect to as-prepared samples. A further purification step did afford practically uncontaminated samples, but resulted to be deleterious for the long-term colloidal stability of the NCs. A thorough NMR investigation allowed us to establish the CsPbX<sub>3</sub> surface as governed by the following species and equilibria in apolar solvents:

- 1) strongly bound oleate species likely anchored to undercoordinated lead or cesium atoms;
- 2) formal oleylamine weakly bound through protons of the NC surface and undercoordinated lead atoms.
- 3) carboxylic acid exchanging with tightly bound oleate, a process favored by desorbed amine.

When the perovskite NCs were dissolved in polar solvents, we observed a modification of the equilibria at the basis of NC surface passivation in favor of the oleylammonium halide desorption from the surface. We gained insight into the origin of the long-term colloidal instability of CsPbX<sub>3</sub> NCs by ascertaining the evolution of the amide formed by condensation of carboxylic acid and aliphatic amine in the case of the as-prepared samples, which is catalyzed by the acid NC surface. The single purification step with a polar antisolvent removed adsorbed protons from the NC surface as the corresponding oleylammonium halide leading to a long-term stable nanomaterial. In the case of I-containing NCs, we observed their surface passivated by oleylammonium halide and cesium-oleate both in apolar and in polar solvents. The I-rich surface of these NCs favored the acid-catalyzed amide evolution which depauperates the nanomaterial of the organic passivating shell, thus explaining their pronounced instability in the presence with polar solvents. Although the structural stability of perovskite NCs is very likely a multifaceted problem involving not only the surface equilibria of the

organic ligands but also other factors, such as halide equilibrium,<sup>44</sup> in perspective, the insights reported in this study support the critical need for a NC passivation strategy with surface ligands that are also compatible with the charge transport requirements of optoelectronic applications.

## EXPERIMENTAL SECTION

*Materials.* Cesium carbonate ( $\text{Cs}_2\text{CO}_3$ , 99.9% metals basis, Alfa Aesar), lead(II) bromide ( $\text{PbBr}_2$ , 99.999% metals basis, Aldrich), lead(II) chloride ( $\text{PbCl}_2$ , 99.999% metals basis, Aldrich), lead(II) iodide ( $\text{PbI}_2$ , 99.999% metals basis, Aldrich), oleylamine (OLAm, technical grade 70%, Aldrich), oleic acid (OLA, technical grade 90%, Aldrich), 1-octadecene (ODE, technical grade 90%, Aldrich), acetone (ACS grade), hexane (VWR, LC-MS grade), cyclohexane (Aldrich, spectrophotometric grade).

*Synthesis of as-prepared  $\text{CsPbX}_3$  NCs.* All manipulations were performed under nitrogen flow using standard Schlenk techniques.  $\text{Cs}_2\text{CO}_3$  (0.407 g, 2.50 mmol), OLA (1.55 mL, 5.00 mmol) and ODE (20 mL) were mixed in a 50 mL Schlenk tube and kept in vacuum for 1 hour at 120 °C. Later the tube was filled with nitrogen for 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 120 °C under  $\text{N}_2$  atmosphere before injection. ODE (7.5 mL),  $\text{PbX}_2$  (0.38 mmol), OLA (1.0 mL) and OLAm (1.0 mL) were loaded in a 50 mL Schlenk tube and the mixture was heated at 160°C. After complete solubilization of the  $\text{PbX}_2$  salt, temperature was kept for 20 minutes followed by injection of Cs-oleate solution (0.8 mL). The reaction mixture was cooled in an ice-water bath after 5 s. The crude solution was centrifuged at 4000 rpm for 40 min. The supernatant containing unreacted precursors was discarded and obtained precipitate was finally dispersed in cyclohexane for measurements.

*Purified CsPbX<sub>3</sub> NCs.* In the case of purification, the precipitate obtained after the first centrifugation was dissolved in hexane (1.2 mL). Next, 50  $\mu$ l of OLA and OLAm were added to the suspension before the addition of acetone (not dried, 1.2 mL). After centrifugation (4000 rpm for 10 min), the supernatant was discarded, and the precipitate was redispersed in cyclohexane for subsequent characterization.

*Nuclear Magnetic Resonance.* <sup>1</sup>H-NMR spectra of samples dissolved in N<sub>2</sub>-saturated solution were recorded at 298.2 K on a Cryoprobe-equipped Bruker Avance III 700 MHz spectrometer equipped with a Cryoprobe optimized for <sup>1</sup>H observation. The NOESY and ROESY spectra were acquired using standard pulse sequences; NOESY and ROESY mixing times were set to 300 ms and 200 ms, respectively. The DOSY measurements were performed using standard pulse sequences. In order to keep a constant time of measurement throughout all the experiments, the diffusion time ( $\Delta$ ) and the diffusion gradient length ( $\delta$ ) were set to 100 ms and 5 ms, respectively and kept constant. The gradient strength was linearly increased in 16 steps and monitored by the attenuation (from 2% to 95%) of the first increment signal. The diffusion coefficients were obtained by fitting the appropriate Stejskal–Tanner equation to the signal intensity decay.<sup>45</sup>

*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 Varian Cary Eclipse instrument. The quantum yields were determined using appropriate dye references for blue, green and red spectral regions (coumarin 343, fluorescein, and rhodamine 6G, respectively) according to standard procedures.<sup>46</sup>

*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 CCD high resolution camera. Samples for TEM analysis were prepared by dipping the carbon-coated copper grid into the NC cyclohexane solution diluted with anhydrous hexane. Statistical analysis of the size (NC average size and standard deviation) of each

sample was performed by using a freeware image analysis program, by measuring more than 200 of nanoparticles.

*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 mm<sup>2</sup> (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 15kV using a 7.5 mm working distance at a magnification of 1000×. The data accuracy was checked using standards by MAC (Micro-Analysis Consultants Ltd., United Kingdom).

*X-Ray Diffraction.* XRD data were collected in detector scan mode or 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.

## ACKNOWLEDGMENTS

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## ASSOCIATED CONTENT

**Supporting Information.** Additional characterization and images of NCs.

**Notes.** The authors declare no competing financial interest.

## AUTHOR INFORMATION

### Corresponding author

E-mail: roberto.grisorio@poliba.it

## REFERENCES

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- <sup>1</sup> Jeon, N. J.; Noh, J. H.; Yang, W. S.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I. Compositional Engineering of Perovskite Materials for High-Performance Solar Cells. *Nature* **2015**, *517*, 476–481.
- <sup>2</sup> Tan, Z.-K.; Moghaddam, R. S.; Lai, M. L.; Docampo, P.; Higler, R.; Deschler, F.; Price, M.; Sadhanala, A.; Pazos, L. M.; Credginton, D.; Hanusch, F.; Bein, T.; Snaith, H. J.; Friend, R. H. Bright Light-Emitting Diodes Based on Organometal Halide Perovskite. *Nat. Nanotechnol.* **2014**, *9*, 687–691.
- <sup>3</sup> Akkerman, Q. A.; Rainò, G.; Kovalenko, M. V.; Manna, L. Genesis, challenges and opportunities for colloidal lead halide perovskite nanocrystals. *Nat. Mater.* **2018**, *17*, 394–405.
- <sup>4</sup> Zhang, Q.; Yin, Y. All-Inorganic Metal Halide Perovskite Nanocrystals: Opportunities and Challenges. *ACS Cent. Sci.* DOI: 10.1021/acscentsci.8b00201.
- <sup>5</sup> Butkus, J.; Vashishtha, P.; Chen, K.; Gallaher, J. K.; Prasad, S. K. K.; Metin, D. Z.; Laufersky, G.; Gaston, N.; Halpert, J. E.; Hodgkiss, J. M. The Evolution of Quantum Confinement in CsPbBr<sub>3</sub> Perovskite Nanocrystals. *Chem. Mater.* **2017**, *29*, 3644–3652.
- <sup>6</sup> Song, J. Z.; Li, J. H.; Li, X. M.; Xu, L. M.; Dong, Y. H.; Zeng, H. B. Quantum Dot Light-Emitting Diodes Based on Inorganic Perovskite Cesium Lead Halides (CsPbX<sub>3</sub>). *Adv. Mater.* **2015**, *27*, 7162–7167.

- 
- <sup>7</sup> Akkerman, Q. A.; D’Innocenzo, V.; Accornero, S.; Scarpellini, A.; Petrozza, A.; Prato, M.; Manna, L. Tuning the Optical Properties of Cesium Lead Halide Perovskite Nanocrystals by Anion Exchange Reactions *J. Am. Chem. Soc.* **2015**, *137*, 10276–10281.
- <sup>8</sup> Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX<sub>3</sub>, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, *15*, 3692–3696.
- <sup>9</sup> Boles, M. A.; Ling, D.; Hyeon, T.; Talapin, D. V. The surface science of nanocrystals. *Nat. Mater.* **2016**, *15*, 141–153.
- <sup>10</sup> Yang, D.; Li, X.; Zeng, H. Surface Chemistry of All Inorganic Halide Perovskite Nanocrystals: Passivation Mechanism and Stability. *Adv. Mater. Interfaces* **2018**, *5*, 1701662.
- <sup>11</sup> Swarnkar, A.; Marshall, A. R.; Sanhira, E. M.; Chernomordik, B. D.; Moore, D. T.; Christians, J. A.; Chakrabarti, T.; Luther, J. M. Quantum dot-induced phase stabilization of  $\alpha$ -CsPbI<sub>3</sub> perovskite for high-efficiency photovoltaics. *Science* **2016**, *354*, 92–95.
- <sup>12</sup> Trots, D. M.; Myagkota, S. V. High-temperature structural evolution of caesium and rubidium triiodoplumbates. *J. Phys. Chem. Solids* **2008**, *69*, 2520–2526.
- <sup>13</sup> Swarnkar, A.; Marshall, A. R.; Sanhira, E. M.; Chernomordik, B. D.; Moore, D. T.; Christians, J. A.; Chakrabarti, T.; Luther, J. M. Quantum dot-induced phase stabilization of  $\alpha$ -CsPbI<sub>3</sub> perovskite for high-efficiency photovoltaics. *Science* **2016**, *354*, 92–95.
- <sup>14</sup> Protesescu, L.; Yakunin, S.; Kumar, S.; Bär, J.; Bertolotti, F.; Masciocchi, N.; Guagliardi, A.; Grotevent, M.; Shorubalko, I.; Bodnarchuk, M. I.; Shih, C.-J.; Kovalenko, M. V. Dismantling the “Red Wall” of Colloidal Perovskites: Highly Luminescent Formamidinium and Formamidinium–Cesium Lead Iodide Nanocrystals. *ACS Nano* **2017**, *11*, 3119–3134.
- <sup>15</sup> Wang, C.; Chesman, A. S. R.; Jasieniak, J. J. Stabilizing the cubic perovskite phase of CsPbI<sub>3</sub> nanocrystals by using an alkyl phosphinic acid. *Chem. Commun.* **2017**, *53*, 232–235.



- 
- <sup>16</sup> Liu, F.; Zhang, Y.; Ding, C.; Kobayashi, S.; Izuishi, T.; Nakazawa, N.; Toyoda, T.; Ohta, T.; Hayase, S.; Minemoto, T.; Yoshino, K.; Dai, S.; Shen, Q. Highly Luminescent Phase-Stable CsPbI<sub>3</sub> Perovskite Quantum Dots Achieving Near 100% Absolute Photoluminescence Quantum Yield. *ACS Nano* **2017**, *11*, 10373–10383.
- <sup>17</sup> Imran, M.; Caligiuri, V.; Wang, M.; Goldoni, L.; Prato, M.; Krahne, R.; De Trizio, L.; Manna, L. Benzoyl Halides as Alternative Precursors for the Colloidal Synthesis of Lead-Based Halide Perovskite Nanocrystals. *J. Am. Chem. Soc.* **2018**, *140*, 2656–2664.
- <sup>18</sup> De Roo, J.; Ibáñez, M.; Geiregat, P.; Nedelcu, G.; Walravens, W.; Maes, J.; Martins, J. C.; Van Driessche, I.; Kovalenko, M. V.; Hens, Z. Highly Dynamic Ligand Binding and Light Absorption Coefficient of Cesium Lead Bromide Perovskite Nanocrystals. *ACS Nano* **2016**, *10*, 2071–2081.
- <sup>19</sup> Pan, A.; He, B.; Fan, X.; Liu, Z.; Urban, J. J.; Alivisatos, A. P.; He, L.; Liu, Y. Insight into the Ligand-Mediated Synthesis of Colloidal CsPbBr<sub>3</sub> Perovskite Nanocrystals: The Role of Organic Acid, Base, and Cesium Precursors. *ACS Nano* **2016**, *10*, 7943–7954.
- <sup>20</sup> Udayabhaskararao, T.; Houben, L.; Cohen, H.; Menahem, M.; Pinkas, I.; Avram, L.; Wolf, T.; Teitelboim, A.; Leskes, M.; Yaffe, O.; Oron, D.; Kazes, M. A Mechanistic Study of Phase Transformation in Perovskite Nanocrystals Driven by Ligand Passivation. *Chem. Mater.* **2018**, *30*, 84–93.
- <sup>21</sup> Liu, Z.; Bekenstein, Y.; Ye, X.; Nguyen, S. C.; Swabeck, J.; Zhang, D.; Lee, S.-T.; Yang, P.; Ma, W.; Alivisatos, A. P. Ligand Mediated Transformation of Cesium Lead Bromide Perovskite Nanocrystals to Lead Depleted Cs<sub>4</sub>PbBr<sub>6</sub> Nanocrystals. *J. Am. Chem. Soc.* **2017**, *139*, 5309–5312.
- <sup>22</sup> Pan, J.; Shang, Y.; Yin, J.; De Bastiani, M.; Peng, W.; Dursun, I.; Sinatra, L.; El-Zohry, A. M.; Hedhili, M. N.; Emwas, A.-H.; Mohammed, O. F.; Ning, Z.; Bakr, O. M. Bidentate Ligand-Passivated CsPbI<sub>3</sub> Perovskite Nanocrystals for Stable Near-Unity Photoluminescence Quantum Yield and Efficient Red Light-Emitting Diodes. *J. Am. Chem. Soc.* **2018**, *140*, 562–565.
- <sup>23</sup> Hens, Z.; Martins, J. C. A Solution NMR Toolbox for Characterizing the Surface Chemistry of Colloidal Nanocrystals. *Chem. Mater.* **2013**, *25*, 1211–1221.

- 
- <sup>24</sup> Moreels, I.; Fritzing, B.; Martins, J. C.; Hens, Z. Surface Chemistry of Colloidal PbSe Nanocrystals. *J. Am. Chem. Soc.* **2008**, *130*, 15081–15086.
- <sup>25</sup> Fritzing, B.; Moreels, I.; Lommens, P.; Koole, R.; Hens, Z.; Martins, J. C. In Situ Observation of Rapid Ligand Exchange in Colloidal Nanocrystal Suspensions Using Transfer NOE Nuclear Magnetic Resonance Spectroscopy. *J. Am. Chem. Soc.* **2009**, *131*, 3024–3032.
- <sup>26</sup> Liu, H.; Wu, Z.; Gao, H.; Shao, J.; Zou, H.; Yao, D.; Liu, Y.; Zhang, H.; Yang, B. One-Step Preparation of Cesium Lead Halide CsPbX<sub>3</sub> (X = Cl, Br, and I) Perovskite Nanocrystals by Microwave Irradiation. *ACS Appl. Mater. Interfaces* **2017**, *9*, 42919–42927.
- <sup>27</sup> Kim, Y.; Yassitepe, E.; Voznyy, O.; Comin, R.; Walters, G.; Gong, X. W.; Kanjanaboos, P.; Nogueira, A. F.; Sargent, E. H. Efficient Luminescence from Perovskite Quantum Dot Solids. *ACS Appl. Mater. Interfaces* **2015**, *7*, 25007–25013.
- <sup>28</sup> Altomare, A.; Cuocci, C.; Giacovazzo, C.; Moliterni, A.; Rizzi, R.; Corriero, N.; Falcicchio, A. EXPO2013: a kit of tools for phasing crystal structures from powder data. *J. Appl. Cryst.* **2013**, *46*, 1231–1235.
- <sup>29</sup> Koscher, B. A.; Swabeck, J. K.; Bronstein, N. D.; Alivisatos, A. P. Essentially Trap-Free CsPbBr<sub>3</sub> Colloidal Nanocrystals by Postsynthetic Thiocyanate Surface Treatment. *J. Am. Chem. Soc.* **2017**, *139*, 6566–6569.
- <sup>30</sup> Pan, J.; Sarmah, S. P.; Murali, B.; Dursun, I.; Peng, W.; Parida, M. R.; Liu, J.; Sinatra, L.; Alyami, N.; Zhao, C.; Alarousu, E.; Ng, T. K.; Ooi, B. S.; Bakr, O. M.; Mohammed, O. F. Air-Stable Surface-Passivated Perovskite Quantum Dots for Ultra-Robust, Single- and Two-Photon-Induced Amplified Spontaneous Emission. *J. Phys. Chem. Lett.* **2015**, *6*, 5027–5033.
- <sup>31</sup> Ravi, V. K.; Santra, P. K.; Joshi, N.; Chugh, J.; Singh, S. K.; Rensmo, H.; Ghosh, P.; Nag, A. Origin of the Substitution Mechanism for the Binding of Organic Ligands on the Surface of CsPbBr<sub>3</sub> Perovskite Nanocubes. *J. Phys. Chem. Lett.* **2017**, *8*, 4988–4994.

- 
- <sup>32</sup> Maes, J.; Balcaen, L.; Drijvers, E.; Zhao, Q.; De Roo, J.; Vantomme, A.; Vanhaecke, F.; Geiregat, P.; Hens, Z. Light Absorption Coefficient of CsPbBr<sub>3</sub> Perovskite Nanocrystals. *J. Phys. Chem. Lett.* **2018**, *9*, 3093–3097.
- <sup>33</sup> ten Brinck, S.; Infante, I. Surface Termination, Morphology, and Bright Photoluminescence of Cesium Lead Halide Perovskite Nanocrystals. *ACS Energy Lett.* **2016**, *1*, 1266–1272.
- <sup>34</sup> Jing, Q.; Zhang, .; Huang, X.; Ren, X.; Wang, P.; Lu, Z. Surface passivation of mixed-halide perovskite CsPb(Br<sub>x</sub>I<sub>1-x</sub>)<sub>3</sub> nanocrystals by selective etching for improved stability. *Nanoscale* **2017**, *9*, 7391–7396.
- <sup>35</sup> De Roo, J.; Van Driessche, I.; Martins, J. C.; Hens, Z. Colloidal metal oxide nanocrystal catalysis by sustained chemically driven ligand displacement. *Nat. Mater.* **2016**, *15*, 517–522.
- <sup>36</sup> Pan, J.; Quan, L. N.; Zhao, Y.; Peng, W.; Murali, B.; Sarmah, S. P.; Yuan, M.; Sinatra, L.; Alyami, N. M.; Liu, J.; Yassitepe, E.; Yang, Z.; Voznyy, O.; Comin, R.; Hedhili, M. N.; Mohammed, O. F.; Lu, Z. H.; Kim, D. H.; Sargent, E. H.; Bakr, O. M. Highly Efficient Perovskite-Quantum-Dot Light-Emitting Diodes by Surface Engineering. *Adv. Mater.* **2016**, *28*, 8718–8725.
- <sup>37</sup> Anderson, N. C.; Hendricks, M. P.; Choi, J. J.; Owen, J. S. Ligand Exchange and the Stoichiometry of Metal Chalcogenide Nanocrystals: Spectroscopic Observation of Facile Metal-Carboxylate Displacement and Binding. *J. Am. Chem. Soc.* **2013**, *135*, 18536–18548.
- <sup>38</sup> Grisorio, R.; Debellis, D.; Suranna, G. P.; Gigli, G.; Giansante, C. The Dynamic Organic/Inorganic Interface of Colloidal PbS Quantum Dots. *Angew. Chem. Int. Ed.* **2016**, *55*, 6628–6633.
- <sup>39</sup> Almeida, G.; Goldoni, L.; Akkerman, Q.; Dang, Z.; Khan, A. H.; Marras, S.; Moreels, I.; Manna, L. Role of Acid–Base Equilibria in the Size, Shape, and Phase Control of Cesium Lead Bromide Nanocrystals. *ACS Nano* **2018**, *12*, 1704–1711.
- <sup>40</sup> Fritzinger, B.; Capek, R. K.; Lambert, K.; Martins, J. C.; Hens, Z. Utilizing Self-Exchange To Address the Binding of Carboxylic Acid Ligands to CdSe Quantum Dots. *J. Am. Chem. Soc.* **2010**, *132*, 10195–10201.

- 
- <sup>41</sup> Valdez, C. N.; Schimpf, A. M.; Gamelin, D. R.; Mayer, J. M. Low Capping Group Surface Density on Zinc Oxide Nanocrystals. *ACS Nano* **2014**, *8*, 9463–9470.
- <sup>42</sup> De Roo, J.; Baquero, E. A.; Coppel, Y.; De Keukeleere, K.; Van Driessche, I.; Nayral, C.; Hens, Z.; Delpech, F. Insights into the Ligand Shell, Coordination Mode, and Reactivity of Carboxylic Acid Capped Metal Oxide Nanocrystals. *ChemPlusChem* **2016**, *81*, 1216–1223.
- <sup>43</sup> González-Pedro, V.; Veldhuis, S. A.; Begum, R.; Bañuls, M. J.; Bruno, A.; Mathews, N.; Mhaisalkar, S.; Maquieira, A. Recovery of Shallow Charge-Trapping Defects in CsPbX<sub>3</sub> Nanocrystals through Specific Binding and Encapsulation with Amino-Functionalized Silanes. *ACS Energy Lett.* **2018**, *3*, 1409–1414.
- <sup>44</sup> Dong, Y.; Qiao, T.; Kim, D.; Parobek, D.; Rossi, D.; Son, D. H. Precise Control of Quantum Confinement in Cesium Lead Halide Perovskite Quantum Dots via Thermodynamic Equilibrium. *Nano Lett.* **2018**, *18*, 3716–3722.
- <sup>45</sup> Stejskal, E. O.; Tanner, J. E. Spin Diffusion Measurements: Spin Echoes in the Presence of a Time-Dependent Field Gradient. *J. Chem. Phys.* **1965**, *42*, 288–292.
- <sup>46</sup> Grabolle, M.; Spieles, M.; Lesnyak, V.; Gaponik, N.; Eychmüller, A.; Resch-Genger, U. Determination of the Fluorescence Quantum Yield of Quantum Dots: Suitable Procedures and Achievable Uncertainties. *Anal. Chem.* **2009**, *81*, 6285–6294.