

The Role of Alkylammonium Bromides on the Surface Passivation of Stable Alcohol-Dispersed CsPbX₃ Nanocrystals and on the Stability Enhancement in Light-Emitting Applications

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The ligand passivation is considered an attractive strategy to prepare high-quality perovskite nanocrystals (PNCs) with improved photophysical features in polar media. However, the long-term stabilization of PNCs in these environments is still challenging, being pivotal to understanding the protection mechanism given by prominent surface ligands and avoiding material deterioration in polar solvents. In this work, how the nature of diverse alkylammonium bromides used during surface passivation influences the photophysical properties and quality of CsPbX₃ PNCs fully dispersed in alcohol environments, exhibiting stability up to 10 months are investigated. By adding didodecyldimethylammonium benzylododecyldimethylammonium and tetrabutylammonium bromides (DDAB, BDAB, and TBAB, respectively), DDAB and BDAB promote a suitable and partial surface coverage are observed, respectively, suppressing defect sites in the nanocrystals. Conversely, TBAB shows poor surface protection, decreasing the PL features of PNCs. The presence of DDAB and BDAB favors the fabrication of color converters, and efficient light-emitting diodes (LEDs) with external quantum efficiencies (EQE) of $\approx 23\%$. Interestingly, significant device stability with BDAB capping shows an LED half-life of 20-fold longer than for DDAB. This contribution offers a promising approach for preparing highly luminescent and stable alcohol-dispersed PNCs, useful for fabricating efficient optoelectronic devices.

1. Introduction

Perovskite nanocrystals (PNCs) have been recognized as the next generation of prominent colloidal semiconductors with mesmerizing defect-tolerant nature, modulable surface chemistry, and improved optical/electronic features, in addition to their low-cost and facile synthesis procedures.^[1] These characteristics have favored the preparation of nanoparticles (NPs) with high PL features and controllable band gap,^[2,3] guaranteeing the fabrication of light emitting diodes (LEDs) with external quantum efficiencies nearing 30%,^[4,5] and perovskite quantum dots-based solar cells with efficiencies close to 20%.^[6] Then, taking advantage of their UV-vis-NIR light absorption and carrier transport capabilities, PNCs are involved in photo(electro)chemical generation of H₂,^[7,8] CO₂ reduction for decarbonization processes,^[9,10] photocatalytic organic synthesis,^[11,12] and redox reactions to degrade toxic and recalcitrant organics.^[13–15]

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In this context, PNCs are useful in a wide range of applications. However, they exhibit a notable limitation due to their ionic structure, which can deteriorate in the presence of oxygen, moisture, and polar environments.^[16–18] In the absence of a protective coverage, the direct interaction between the NPs and the polar medium damages the crystalline structure of the material, emerging a high density of structural defects, and quenching rapidly the intrinsic properties of the perovskite.^[19,20]

With the purpose of extending the stability of the perovskite in polar media, interesting approaches have been studied such as polymer matrix encapsulation,^[21] to avoid the direct permeation of the polar molecules to reach the NPs surface. A stability record for PNCs systems has been reached by introducing methacrylate-based polymeric coverage for MAPbBr₃ PNCs, providing high resistance to organic, NaOH, and HCl aqueous solutions for almost 2 years (600 days), keeping a PL quantum yield (PLQY) $\approx 70\%$.^[22] In this scenario, the low density of H₂O molecules compensates for halide deficiency in the NPs, being adequate to improve the PL properties. The addition of micellar surfactants is also a prominent option for PNCs stabilization, as in the case of glycyrrhizic acid (GA).^[23] Considering the restrained desorption capability of GA surfactant from PNCs surface, the perovskite composite is stable in MeOH ambient, with a PLQY $\approx 85.3\%$ and 2 months stable in storage. Then, the addition of alternative ligands with higher binding capability to the NPs surface, as in the case of the (3-aminopropyl)triethoxysilane (APTES), controls the perovskite particle size and induces a gradual steric hindrance in the surface to block the polar molecules mobility.^[24] This effect can be easily reached by varying the APTES concentration, also avoiding the PNCs aggregation.^[25] Meanwhile, novel synthetic routes based on ligand ligand-assisted reprecipitation process (LARP) have been highlighted to mediate the PNCs growth from ethanol (EtOH) solution, in the presence of Bis(2,4,4-trimethylpentyl)-phosphinic acid (TMPPA).^[19] TMPPA can favor the emergence of polar Pb=O or Pb–OH moieties, promoting the formation of inter-ligand hydrogen bonds with EtOH and H₂O molecules. In this way, a barrier between the polar species and the PNCs core is produced, preserving the PL features of the PNCs. On the

other hand, CsPbBr₃ clusters (CNC) have been also obtained by adding polyvinylpyrrolidone (PVP) in the LARP procedure, making the final product stable in alcohol solvents such as EtOH, isopropanol, and organic acids for 30 days.^[26] The appearance of Pb–O coordination in the presence of PVP is the key factor for ligand passivation of the NPs, improving their dispersibility in the polar solvents for photocatalytic degradation of dyes.

Interestingly, laser ablation in EtOH medium has been employed for the synthesis of ligand-free CsPbBr₃ PNCs, through 2 different approaches: first one denominated 2-step synthesis where PbBr₂ compressed powder is irradiated with a Nd:YAG laser at 355 nm, and then reacted with CsBr precursor dispersed in same alcohol.^[27] Then, 1-step synthesis is based on a similar procedure to the 2-step synthetic route, but CsBr is already present in the alcohol solvent before the ablation process. NPs can reach a maximum PLQY of $\approx 16\%$, with long-term stability for 15 days. Although these alternatives offer an ecofriendly and sustainable way to grow PNCs from the polar environment, the absence of alkylammonium species suppresses the radiative recombination, deteriorates the structure of the perovskite, and decreases the quality of the final material. Neither actual modified synthetic procedures nor the use of robust ligands can fully avoid material deterioration in direct contact with polar medium.

Previously, we have explored the use of didodecyldimethylammonium bromide (DDAB) to stabilize PNCs in polar solvents.^[28] We have observed that DDAB can protect the CsPbX₃ PNCs from a methanol/butanol (MeOH/BuOH) environment, reaching 100% PLQY and long-term stability for up to 7 months (5040 h). DDAB mediates a ligand exchange with oleylammonium cations (OLA⁺), which interacts with the alcohols to form alkoxide groups.^[29–31] These species also contribute to the stabilization of polar solvents. Therefore, it is deducible that depending on the nature of the alkylammonium bromide (AlkylBr), different protection mechanisms would be achieved, impacting the surface chemistry, PL properties, and stability of the PNCs in a polar medium. In this work we show the influence of AlkylBr nature on the PL and electronic properties CsPbBr₃ PNCs fully dispersed in a MeOH/BuOH system, achieving long-term stability up to 10 months under ambient conditions. By adding the PNCs into diverse concentrations of DDAB, benzyldecylammonium bromide (BDAB), and tetrabutylammonium bromide (TBAB) (15, 85, and 200 mM) in BuOH, we infer that DDA⁺ structure is suitable to provide a more efficient coverage than BDA⁺ cation, where a partial passivation is promoted. Meanwhile, TBA⁺ cation is prone to exhibit a high degree of steric hindrance, offering a poor surface coverage. Therefore, the direct interaction between the alcohols and NPs is mediated, quenching faster their PL features. Thus, DDAB and BDAB were studied for PNCs processability to fabricate polymeric color converters with PL stability ≈ 4 h under a constant voltage, and active layers for green-LEDs with external quantum efficiencies (EQE) up to 23.2%. Interestingly the operational LED half lifetime (t_{50}) depends strongly on the AlkylBr nature of surface passivating agent. This work makes it possible to comprehend the passivation mechanism given by the type of AlkylBr and provides a novel strategy for less-defective PNCs processing in polar solvents, being useful for the fabrication of more efficient and stable LED devices.

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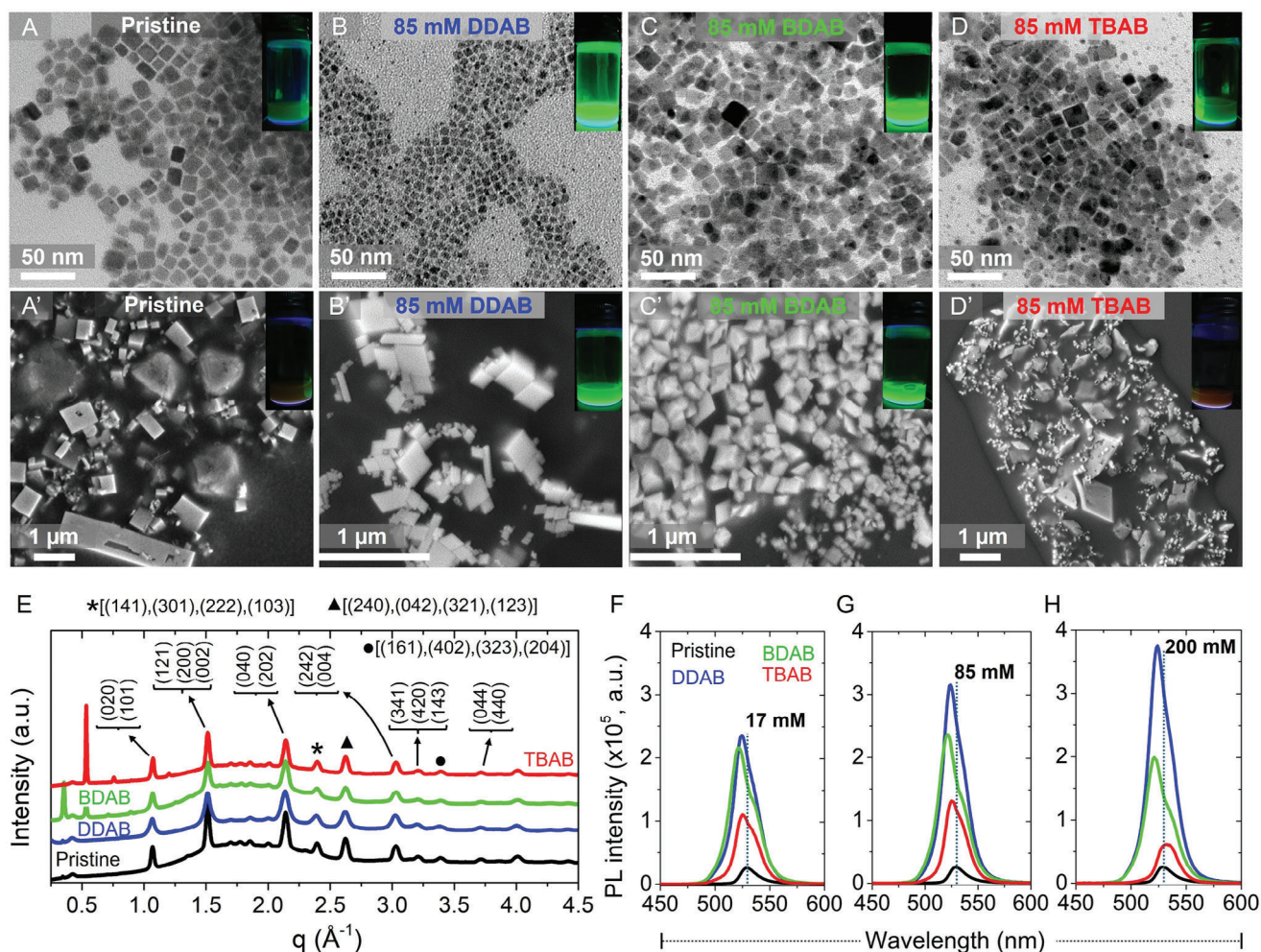


Figure 1. Typical A–D) TEM images of CsPbBr₃ PNCs dispersed in MeOH/BuOH polar environment at 0 h, and corresponding (A'–D') SEM images of the samples after 7300 h aging in the alcohol medium, in (A,A') absence and presence of the AlkylBr ligands: (B,B') DDAB, (C,C') BDAB and (D,D') TBAB. The inset of Figures (A–D) and (A'–D') shows the luminescence of as-prepared and aged nanocrystals, respectively. E) 1D line cuts from azimuthally integrated 2D GIWAXS patterns of CsPbBr₃ PNCs in the polar environment in the presence and absence of AlkylBr ligands. PL spectra of PNCs dispersions by varying the concentration of the AlkylBr ligands: F) 17 mM, G) 85 mM, and H) 200 mM.

2. Results and Discussion

With the aim to analyze the effect of the AlkylBr nature on the stabilization capability of CsPbBr₃ PNCs dispersed in an alcohol environment over time, we conducted transmission electron microscopy (TEM) and scanning electron microscopy (SEM) measurements. 500 μL of the colloidal PNCs dispersed in hexane (50 mg mL⁻¹) was added to a 2 mL of 85 mM DDAB, BDAB and TBAB ligands solutions in BuOH, and the resulting samples were studied under the following conditions: i) MeOH (500 μL) + BuOH system at 0 h (as-prepared material) and ii) MeOH (500 μL) + BuOH after 7300 h of aging. The molecular structure of each ligand is shown in Scheme S1 (Supporting Information). **Figure 1A–D** shows the typical TEM images of the as-prepared PNCs dispersed in the MeOH/BuOH medium (hereafter named as PNCs-C_xOH) in the absence and presence of the different AlkylBr ligands, where a nanocube shape is noted in all the samples. Nevertheless, the particle size and their corre-

sponding distribution, see Figure S1A–D (Supporting Information), is determined by the ligand nature. For pristine CsPbBr₃ PNCs, particle size is $\approx 11.6 \pm 2.7$ nm, while DDAB-, BDAB- and TBAB-modified PNCs-C_xOH exhibited particle sizes $\approx 6.8 \pm 0.8$, 9.7 ± 1.0 , and 14.1 ± 3.2 nm, respectively. The detachment of oleic acid (OA) and oleylamine (OLA) from nanocrystals surface by the presence of the alcohol molecules generate aggregation to compensate for the appearance of defect sites.^[32] This is the reason for evidence of big and nonuniform nanoparticles. On the contrary, the formation of smaller PNCs into the polar dispersion with high monodispersity in the presence of DDAB is caused by partial exfoliation of surface [PbBr₆]⁴⁻ octahedra units, restraining the perovskite growth.^[33,34] Low agglomeration is evidenced in this sample, corroborating the effective protection provided by this ligand in the alcohol medium.

On the contrary, bigger PNCs were obtained by introducing BDAB in the PNCs-C_xOH dispersion, suggesting a lower protection ability from this ligand to avoid the permeation of

MeOH/BuOH molecules to reach the nanocrystals. Taking into account the existence of a benzyl group in BDA⁺ cation unlike the linear dodecyl chain found in DDA⁺, we suggest that the aromatic functionality mediates some steric hindrance in the PNCs surface to hinder the BDAB ligand passivation,^[35] producing partial ligand-covered NPs and generating coalescence. However, a higher monodispersity and smaller particle size are estimated for this material (compared to pristine PNCs), indicating that BDAB can also restrain both the perovskite growth (exfoliation process) and the damage to its structural integrity. Conversely, in the case of adding TBAB, both higher average particle size and larger size distribution were obtained. We can deduce that poor ligand protection is established in the PNCs surface after the ligand exchange process, making more likely the interaction between the alcohol molecules and the perovskite. This can also be noticed by the presence of spherical shapes in the TEM image of TBAB-PNCs-C_xOH dispersion, see Figure 1D, associated with the emergence of a different crystalline phase in the perovskite.^[36] Through selected area electron diffraction (SAED) patterns, see Figure S2A–D (Supporting Information), we corroborate the co-existence of the orthorhombic phase (ICSD 97 851)^[37] and 0D Cs₄PbBr₆ phase (ICSD 162 158)^[38] in the TBAB-PNCs-C_xOH dispersion, while the orthorhombic phase was only kept for the pristine, DDAB- and BDAB-PNCs-C_xOH. We conclude that both bulky DDAB and BDAB can prevent the fast alcohol diffusion from interacting with the as-prepared PNCs than TBAB, where closer contact with the polar molecules would be promoted.

Figure 1A'–D' shows the typical SEM images of the samples after 7300 h in the MeOH/BuOH medium, observing the formation of microcrystals. Interestingly, there are some differences between the microcrystal size and shape depending on the AlkylBr ligand nature. DDAB and BDAB produce smaller cubes than pristine one ($0.5 \pm 0.3 \mu\text{m}$), with average sizes of 0.10 ± 0.09 and $0.10 \pm 0.03 \mu\text{m}$, respectively, see Figure S1A'–C' (Supporting Information). Mainly, DDAB-PNCs-C_xOH sample depicts smaller particles after aging in alcohol, considering that a double purification was conducted in this work, making that more external ligands can cover the NPs (instant capping effect).^[39] This fact suggests that both DDAB and BDAB ligands hinder the aggregation of PNCs exposed in the alcohol medium during the aging process, restraining the interaction with alcohol molecules. Meanwhile, rhombohedron-type microcrystals with a size of $0.4 \pm 0.4 \mu\text{m}$ and high polydispersity are formed in the presence of TBAB, as a result of the fast particle agglomeration, see Figure S1D' (Supporting Information). As discussed above, TBAB cannot provide effective ligand coverage in the PNCs, which can favor the coalescence of the NPs. Although some of the AlkylBr ligands can protect the CsPbBr₃ NPs from the polar environment, some of the alcohol molecules diffuse progressively through the organic coverage, generating the emergence of bigger particles.

Synchrotron-assisted grazing incidence wide-angle X-ray scattering (GIWAXS) was used in as-prepared PNCs films dried at ambient air, to resolve in-depth the crystalline structure of the samples, Figure 1E and Figure S3A–D (Supporting Information) depict the azimuthally integrated GIWAXS data (q) (q_{xy}) and the 2D circular integrated 1D patterns ($(q_{2\theta})$ vs q_z) of films in the absence and presence of AlkylBr ligands, detailing the typical

diffraction patterns at 1.07, 1.51, 2.15, 2.40, 2.62, 3.03, 3.21, and 3.72 \AA^{-1} corresponding to the [020; 101], [121; 200; 002], [040; 202], [141; 301; 222; 103], [240; 042; 321; 123], [242; 004], [341; 420; 143], [161; 402; 323; 204] and [044; 440] planes of the orthorhombic phase. No traces of 0D perovskite are detected. However, low-intense peaks were also found at smaller q values with certain periodicity in the 1D pattern for BDAB- and TBAB-PNCs, accompanied by the appearance of new signals into 2D GIWAXS pattern at low q . This fact is commonly attributed to the formation of 2D perovskites^[40] during surface exfoliation in the presence of BDAB and TBAB ligands. Therefore, we can establish that the presence of alcohol molecules can delay the octahedra exfoliation, preserving the 3D structure of the perovskite.

The optical features of the CsPbBr₃ PNCs were also influenced by the type of AlkylBr species used for the material stabilization. For this aim, we studied 3 diverse ligand concentrations in the MeOH/BuOH system: 17, 85, and 200 mM. As seen in Figure 1F–H, the absence of ligands generates a PL peak position at $\approx 529 \text{ nm}$, with a low emission intensity. This behavior is typical of aggregated particles, a product of ligand removal from their surface, which generates an eventual PL quenching.^[41] A PL quantum yield (PLQY) of 48% was achieved. However, the incorporation of DDAB and BDAB induces a slight blueshift in the PL of PNCs-C_xOH dispersions (at 523 and 521 nm, respectively), accompanied by a higher/slight decrease in the emission intensity, respectively at higher ligand concentrations, and the appearance of an emission shoulder at $\approx 535 \text{ nm}$. First, the displacement of PL emission to smaller wavelengths is attributed to a strong quantum confinement regime achieved by the $[\text{PbBr}_6]^{4-}$ exfoliation in the perovskite surface, which agrees with the blueshift of the absorption edge noted in the UV–Vis spectra of samples with DDAB and BDAB ligands,^[42] see Figure S4 (Supporting Information). Simultaneously, the above ligands can suppress surface defect sites in the PNCs (mainly halide vacancies), increasing the PL of the photomaterial. Therefore, a PLQY of 100% was reached in both cases.

However, the low degree of aggregation, homogeneous particle size, and small size distribution with DDAB as seen through TEM images, see Figure 1 and Figure S1 (Supporting Information), indicate a better surface protection and thereby, a lower intensity of the emission shoulder, unlike to the presence of BDAB, where a bigger particle size and larger size distribution were obtained. The partial surface passivation can induce some particle agglomeration, being more prominent in this PL signal, but this coverage is enough to avoid the PNCs-alcohol contact, as we have confirmed through PLQY. On the other hand, TBAB mediates a slight blueshift in the PL emission at 17 and 85 mM while a redshift was achieved in the PL at 200 mM with respect to DDAB and BDAB (also seen in the UV–Vis spectrum with the emergence of scattering, see Figure S4 (Supporting Information), with lower emission intensity than pristine one. At this point, the PL shoulder found in DDAB and BDAB cases, now is the characteristic PL of PNCs in the presence of TBAB at the highest concentration, indicating the highest degree of aggregation and the poorest effectiveness to enhance the radiative recombination. Thus, a PLQY of 58% was obtained, widely lower than those of its DDAB and BDAB analogous. Then, in terms of PL intensity of the PNCs-C_xOH dispersions, DDAB and BDAB favor the increase and slight diminution of this optical feature, respectively,

corroborating an efficient surface passivation in the polar solvent. Meanwhile, the lowered PL in PNCs with TBAB is ascribed to its possible strong steric hindrance produced on the PNCs surface, facilitating the diffusion of a high density of MeOH/BuOH molecules reaching the perovskite core.

Then, the stability of CsPbBr₃ PNCs was studied through their PL features along the aging time, in the function of the AlkylBr ligand added to the PNCs-C_xOH dispersions, see Figures S5 and S6 (Supporting Information). For this aim, PL measurements were initially performed on the PNCs dispersed in BuOH at 0 and 1 h in the absence of MeOH. Later, controlled volumes of MeOH were added to the corresponding dispersions at 3 and 7 h, (200 and 300 μ L MeOH, respectively), completing a total volume of 500 μ L. Lastly, the prepared PNCs-C_xOH dispersions were aged for a longer time to achieve a maximum time of 7300 h. At this point, the influence of the AlkylBr concentration on the green emission of the CsPbBr₃ PNCs was analyzed through changes in the relative PL intensity as seen in Figure S7 (Supporting Information). In the absence of AlkylBr ligands, the emission intensity of the NPs is redshifted and progressively quenched, see Figure S5 (Supporting Information). We attribute this behavior to the gradual detachment of OA/OLA ligands, facilitating the diffusion of the alcohol molecules, and compromising the integrity of the NPs.^[43] This direct interaction would mediate the appearance of diverse particle sizes, agreeing with the wide particle size distribution seen by TEM.

Later, the addition of AlkylBr capping agents in the PNCs-C_xOH dispersions hinders the fast deterioration of the PL properties of the NPs. As seen in Figures S6A–C and S7A (Supporting Information), the presence of DDAB avoids the decrease of the PL of the PNCs during the first couple of hours, and later the emission intensity is increased. As expected, the higher the DDAB concentrations, the better the PL intensity, indicating that the nonradiative recombination is suppressed by removing the A-site cation and X-site anion.^[28] In the case of BDAB, a similar behavior was found during the first 7 h of analysis, also observing the increase of emission intensity for a longer aging time, see Figures S6A'–C' and S7B (Supporting Information). However, this optical property was lower than DDAB by comparing the lowest concentration (17 mM), and eventually, the PL emission was slightly decreased at higher BDAB contents (85 and 200 mM). Accordingly, we suggest a partial coverage provided by BDAB, deducing that low concentrations of this ligand could favor surface passivation. Although the steric hindrance given by benzyl groups restrains the fact to introduce a high density of BDAB molecules, these functional moieties also would offer protection of nanocrystals against the harsh environment. This is in good agreement with the small particle size of BDAB-capped PNCs-C_xOH after 7300 h, avoiding material agglomeration as a result of the protective effect of BDAB. Lastly, although the main PL emission (and therefore the relative PL intensity) of PNCs-C_xOH is quenched during the first couple of hours (0–24 h), independently of the TBAB concentration, a new signal at \approx 460 nm emerges, making that the PL emission of CsPbBr₃ slightly increases at longer aging times (24–7300 h), see Figures S6A''–C'' and S7C (Supporting Information). This effect is more visible at the lowest ligand concentration (17 mM, see Figure S6A''). The new emission peak is attributed to the formation of 0D Cs₄PbBr₆ perovskite,^[44] which has been reported to act as a protective layer

to suppress the nonradiative recombination in CsPbBr₃.^[45] Nevertheless, by raising the TBAB concentration to 85 or 200 mM (Figure S6B'',C''), the appearance of 0D perovskite signal is hindered, inferring a better surface passivation (adequate ligand content to obtain the highest initial PL intensity), or the damage of the structural integrity of PNCs by a stronger steric hindrance of TBAB (excess of ligands), respectively. Despite observing the abovementioned scenarios in the function of TBAB concentration along the aging time, the surface protection provided by this ligand is not effective compared to DDAB and BDAB. At this point, we conclude that both DDAB and BDAB are prominent surface ligands to extend the stability of CsPbBr₃ PNCs for \approx 10 months, this value longer than the previous report addressed for the alcohol-stabilized CsPbX₃ PNCs in absence of any encapsulation.^[28]

To study the effect of the AlkylBr ligands on the chemical environment and composition of the CsPbBr₃ PNCs-C_xOH dispersions, X-ray photoelectron spectroscopy (XPS) analysis was performed. The concentration of all the ligands was fixed at 85 mM for comparative purposes. In all the samples, it was identified the co-existence of C, O, N, Cs, Pb, and Br elements, see the corresponding XPS survey spectra in Figure S8 (Supporting Information). Then, the composition of the NPs dispersions is summarized in Table S1 (Supporting Information). Figure 2A depicts the high-resolution (HR) XPS Cs 3d spectra of the PNCs-C_xOH dispersions in the absence and presence of DDAB, BDAB, and TBAB, observing a doublet at 724/738 eV. This signal is ascribed to Cs 3d_{5/2} and Cs 3d_{3/2} core levels, indicating the presence of Cs⁺ cations contained in the CsPbBr₃ nanocrystals.^[46] Meanwhile, Figure 2B shows the HR-XPS Br 3d spectra of the PNCs samples, where a doublet at 68/69 eV was associated with the Br 3d_{5/2} and Br 3d_{3/2} core levels. These signals indicate the formation of Pb-Br bonds coming from [PbBr₆]⁴⁻ octahedra in the PNCs.^[47] On the other hand, the HR-XPS N 1s spectra of pristine, DDAB, BDAB, and TBAB-capped PNCs show a signal located \approx 401 and 402 eV, associated with amine moiety and the alkylammonium species corresponding to each ligand,^[48] see Figure 2C. This allows us to infer that AlkylBr ligands promote the generation of free OLA, exhibiting a higher content for TBAB. Later, attending to Table S1 (Supporting Information), a Cs, Br, and N deficiency is noted in the pristine PNCs, corroborating the deterioration of the surface stoichiometry of the NPs in the polar solvent. However, the presence of the AlkylBr ligands increases the fraction of Br and N, deducing a better ligand coverage in the PNCs surface to compensate for the Cs⁺ and halide vacancies. This fact corroborates the passivation effect of the capping agents to protect the integrity of the PNCs against MeOH/BuOH environment.

Figure 2D depicts the HR-XPS Pb 4f spectra of pristine and AlkylBr-capped PNCs-C_xOH dispersions, observing the Pb 4f_{7/2} and Pb 4f_{5/2} core levels at 138/143 eV, respectively. These signals are attributed to the existence of Pb²⁺ coming from the [PbBr₆]⁴⁻ octahedra composing the perovskite structure. No undercoordinated Pb is seen in all the samples including the pristine one, indicating that the X-site positions into the octahedra building blocks are fully compensated either by adding carboxylate species from methyl acetate during washing process or/and ligand passivation from AlkylBr.^[28] On the other hand, the total oxygen-to-bromine and total oxygen-to-lead ratios [denoted as O_{total}/(Br+O_{total}) and O_{total}/(Pb+O_{total}), respectively] are higher in

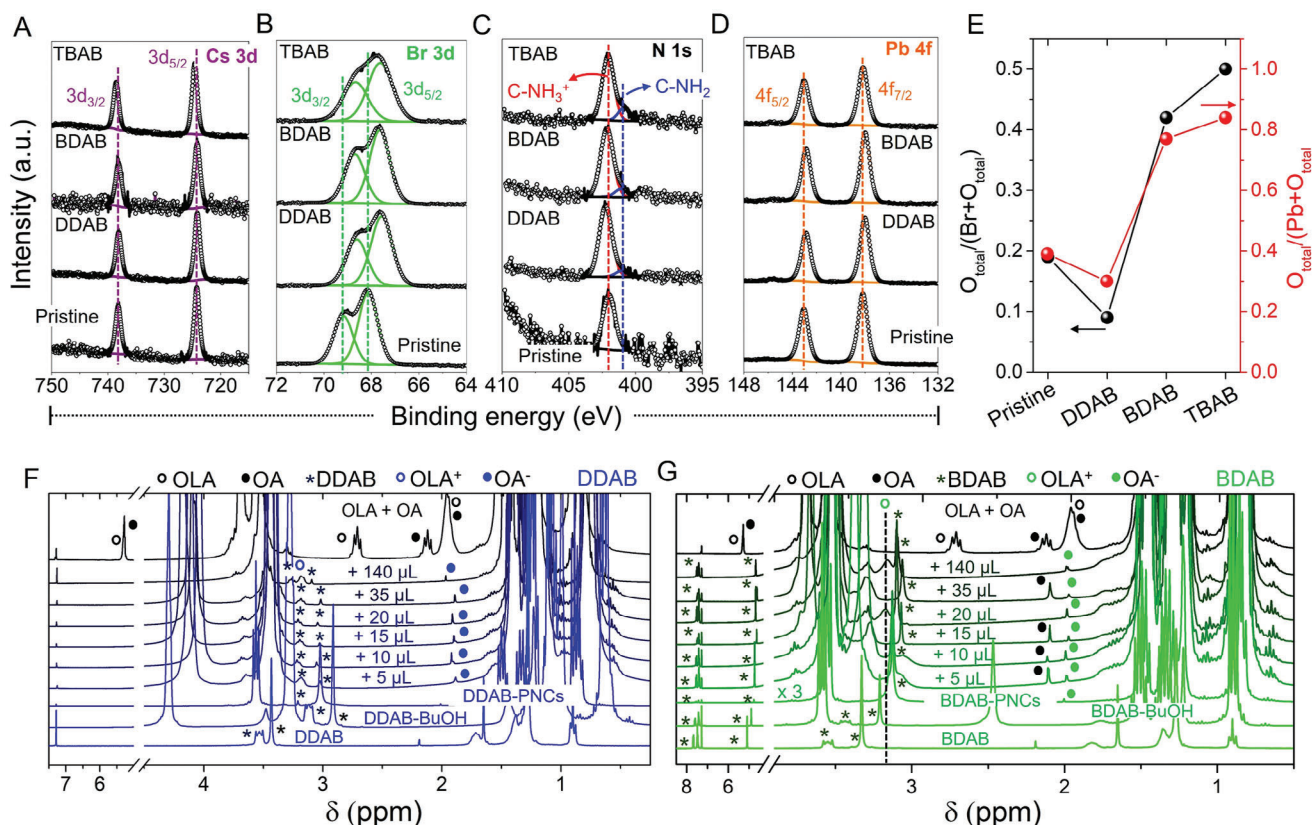


Figure 2. High-resolution XPS A) Cs 3d, B) Br 3d, C) N 1s, D) Pb 4f, and E) estimated total oxygen-to-halide/total oxygen-to-total lead ratios, for the CsPbBr₃ PNCs in the presence and absence of the AlkylBr ligands. 1H (300 MHz, CDCl₃, 298 K) NMR spectra of CsPbBr₃ PNCs in the absence and presence of F) DDAB (blue spectra) and G) BDAB (green spectra), dispersed in protic BuOH and titrated with different volume (μL) of deuterated methanol (MeOD). The concentration of ligands in the BuOH solvent was 85 mM. The corresponding NMR spectra of (OA+OLA)/BuOH and AlkylBr/BuOH samples without perovskite were obtained for comparative purposes.

the following order: DDAB < BDAB < TBAB, see Figure 2E. This behavior indicates that DDAB blocks the diffusion of a high density of MeOH/BuOH molecules to reach the NPs more efficiently, decreasing the oxygen content in the perovskite surface. Later, a lower N content is found in the presence of BDAB, reinforcing the hypothesis that the steric hindrance given by benzyl groups avoids the attachment of BDA⁺ cations. On the contrary, a higher N content in the samples is obtained in the presence of TBAB, an indication of a high density of TBA⁺ species surrounding the material surface. Although both the BDAB- and TBAB-capped PNCs-C_xOH samples exhibit close $O_{total}/(Br+O_{total})$ and $O_{total}/(Pb+O_{total})$ ratios, BDAB preserves the PL properties and extends the stability of the PNCs, while the optical properties of the perovskite are quickly quenched with TBAB ligand. Simultaneously, the above fractions for BDAB are higher than the pristine sample, indicating the possibility of a higher density of R-O⁻ species on the perovskite surface. In this context, while BDAB can stabilize the structure of the PNCs even though some alcohol molecules permeate through the ligand coverage, TBAB offers poorer protection, making that NPs experience a change of crystalline phase, taking into account the release of free OLA. We believe that both the change of the surface stoichiometry by introducing TBAB and the direct interaction with a higher density of alcohol molecules are the reasons to facilitate the formation

of Cs₄PbBr₆ perovskite. The formation of a secondary crystalline structure during the surface passivation given by a particular type of AlkylBr ligand in polar media will be focused on future works related to this research topic. Accordingly, we conclude that the addition of DDAB and BDAB is crucial to maintain the structural integrity and intrinsic properties of the PNCs in the alcohol environment, where a different passivation mechanism is carried out by these capping agents.

We have already reported that DDAB mediates a partial ligand exchange with native OA⁻ and OLA⁺ ligands covering initially the PNCs surface, generating free OA and OLA through the acid-base reaction equilibrium.^[28] Later, after the addition of MeOH to the perovskite dispersion, OLA is able to ionize a fraction of the alcohol species forming the corresponding alkoxide (R-O⁻) anions, which together with Br⁻ species from the alkylammonium capping agents, stabilize the final product by filling halide vacancies.^[28] To understand the protection mechanism given by the AlkylBr ligands in the MeOH/BuOH system, Nuclear Magnetic Resonance (NMR) spectroscopy measurements were performed. To distinguish the corresponding NMR resonances, the analysis was carried out on AlkylBr ligands (85 mM) with and without the presence of the CsPbBr₃ PNCs for comparative purposes. In this way, the corresponding description of NMR resonances of the OLA/OA system in the absence and presence of

PNCs, see Figure S9A (Supporting Information), is discussed in supporting information.

Attending the typical NMR resonances of the individual DDAB ligand seen at $\delta = 3.53$ and 3.43 ppm, see Figure 2F, associated with the methylene and methyl groups linked to quaternary N from the -NR_3^+ moiety,^[49] these signals were considerably shifted to lower chemical displacement in the presence of the polar solvent (BuOH) and/or PNCs. Simultaneously, the NMR resonance of OLA^+ cations is absent, and a signal at $\delta = 1.90$ ppm is attributed to free OA, see Figure 2F. These results, together with the changes in the signals from DDAB, are evidence of the ligand exchange between the AlkylBr ligand and OLA^+/OA^- species in the NPs surface, replaced by DDA^+/Br^- ions, respectively. By adding deuterated methanol (MeOD) in the DDAB-capped PNCs dispersed in BuOH to reach progressively a total volume of 35 μL , it is noticeable that the methyl and methylene resonances of DDAB and free OA are unprotected, being still absent the resonance of OLA^+ . After adding 140 μL , a low-intense signal at 3.22 ppm appears, ascribed to free OLA. From these results, we can establish that a high density of OLA^+ produced by the interaction between OLA (obtained after ligand exchange) and alcohol species is linked to the defective PNCs surface, providing an efficient ligand coverage. This is one of the pivotal explanations for the material stabilization in alcohol environments.

To analyze the NMR spectra of BDAB-capped PNCs samples, we first identified the typical resonances of methylene (from the hydrocarbon chain) and methyl protons from individual BDAB, appearing at $\delta = 3.55$ and 3.33 ppm, respectively, see Figure 2G. Compared to DDAB, additional signals are detailed at $\delta = 7.68$ –7.49 and 5.11 ppm, ascribed to protons from the aromatic ring and methylene from the benzyl group, close to the ammonium moiety, respectively. In the presence of the polar solvent and perovskite, all BDAB resonances exhibit a shift in the chemical displacement to lower values, indicating the direct interaction between the ligand and the material surface. It is worth noting the existence of OLA^+ in the sample, since the emergence of a shoulder at $\delta = 3.06$ ppm, accompanied by the resonance of the olefinic region of OA^- and free OA species, at $\delta = 2.09$ and 1.98 ppm, respectively. As expected, the OLA^+ resonance becomes more visible and shielded by dosing the NPs dispersion with MeOD, indicating that more OLA^+ is produced after alcohol ionization, see Figure 2G. However, after adding a higher MeOD volume up to 15 μL , the -CH_2 resonances from the hydrocarbon chain and benzyl group are more resolved and shifted to lower chemical displacements, disappearing the OLA^+ signal. Here, we infer the presence of free BDAB species. Furthermore, as seen in Figure S9B (Supporting Information), the NMR signal associated with alcohol species (in this case BuOH) in the presence of BDAB is highly shielded compared to other AlkylBr ligands ($\delta = 3.14$ ppm), suggesting a stronger interaction between BDAB and the alcohol molecule.

In light of the present results and considering the existence of free BDAB (mediated by steric hindrance of benzyl groups on the material surface), we propose that a fraction of BDA^+ can interact with exchanged OA^- ions released after ligand exchange to form BDA^+OA^- species. In this context, the lower the density of free OA^- , the lower the density of released OLA^+ to form available OLA, hindering the subsequent alcohol ionization. At this point, it is also feasible for the interaction between BDA^+ and some R-

O^- species, to be able to replace OLA^+ and OA^- linked to the NPs. This behavior can explain the cyclic behavior of OLA^+ and OA^- resonances (emergence/absence) by adding more MeOD (20–140 μL). In this cyclic process, some alcohol molecules can also mediate the ligand detachment, causing some deterioration of the perovskite.

Lastly, in the case of TBAB, see Figure S9C (Supporting Information), a typical triplet is observed for the individual ligand at $\delta = 3.41$ ppm, attributed to the methylene directly linked to the nitrogen atom into the -NR_3^+ group, being this resonance shifted to lower values after the incorporation of the PNCs/BuOH. Then, by dosing the samples with MeOD, a broader and shielded NMR signal at $\delta = 3.09$ –3.03 ppm is observed, associated with released OLA^+ cations. Moreover, the OA^- resonance is also detailed in all the NMR spectra by increasing the MeOD volume. We deduce that the alcohol molecule mediates the detachment of OLA^+/OA^- from the material surface, even in the presence of the ligand, which agrees with the high density of free OLA found by XPS, Table S1 (Supporting Information). According to the fast lowering of the PL features in TBAB-capped PNCs- C_xOH dispersions, the coverage offered by this ligand is not enough to avoid the percolation of polar molecules to reach the material, inducing poor surface passivation. Thus, the formation of alkoxide species through free OLA^+ is a pivotal passivation mechanism to stabilize the PNCs dispersions in alcohol environments.

To validate the capability of the different AlkylBr capping to trigger the ligand exchange on PNCs surface, density functional theory (DFT) calculations were performed. Details for the DFT setup are described in supporting information. Based on the experience of determining the feasibility of replacing surface OLA^+/OA^- species by the presence of DDAB,^[28] we also analyze the introduction of BDAB and TBAB, both in the presence of MeOH molecules. First, we prepared the initial system in the absence of any AlkylBr ligands, which consisted of a CsPbBr_3 slab with 2 Cs^+ defects and 4 Br^- vacancies. While the Cs^+ deficiency is compensated with OLA^+ species, 2 Br^- defects are filled with OA^- ions, leaving 2 free Br^- vacancies, see Figure S10A (Supporting Information). By introducing the AlkylBr and MeOH species, 2 alkylammonium cations from the corresponding ligands can exchange with the 2 OLA^+ sites, while MeO^- anions replace the 2 OA^- positions. Subsequently, Br^- coming from the ligands compensates the remaining 2 Br^- vacancies. In this process, free OA is generated, while OLA^+ cations are linked to surface Br^- species, see Figure S10B–D (Supporting Information).

Then, we calculated the energy difference (ΔE) between initial and AlkylBr-modified systems (E_i and E_{LM} , respectively) taking values of -0.86 and 1.16 eV in the presence of BDAB and TBAB, respectively. Surprisingly, the more negative ΔE provided in BDAB-capped PNCs versus DDAB one (-0.49 eV, previously reported)^[28] implies that the surface passivation is thermodynamically more favorable by the addition of BDAB. This fact would be likely since the BDA^+ cation (according to Lewis's theory) is a stronger acid than DDA^+ due to the aromatic ring containing the benzyl group offering a negative inductive effect on the adjacent methylene close to nitrogen. Therefore, the electron donation ability toward nitrogen decreases, increasing the acidity of the -NR_3^+ moiety and thereby, making its binding to perovskite stronger. However, the fact that the PL properties are more prone to quench in the alcohol medium, and the N content is the lowest

found in the material surface, see Table S1 (Supporting Information), allows us to consider that a low density of this ligand is not linked to the perovskite surface, due a small degree of space occupied by the benzyl group. In the case of TBAB, the entire ligand structure is prone to cover a considerable part of the perovskite surface, generating a higher degree of steric hindrance. This could explain the highest content of amine moiety found by XPS, as a result of free OLA, indicating the detachment of a high density of OLA^+/OA^- from PNCs surface. At this point, it is expected to achieve poor surface protection given by TBAB, favoring the degradation of the PNCs in the polar solvent. Hence, we conclude that DDAB and BDAB are suitable AlkylBr ligands to protect the NPs surface, stabilizing their PL features against the interaction with alcohol molecules.

For further insight into how the AlkylBr ligands influence the carrier recombination kinetics of PNCs- C_xOH samples, time-resolved PL measurements were performed. As seen in Figure S11 (Supporting Information), bi-exponential PL decays were measured in all cases. We believe, however, that the longer component is not characteristic of the different carrier recombination rates but appears because of the PL decay lengthening due to an optical effect, more exactly, light scattering resulting in longer PL light passing inside the solution and therefore more efficient re-absorption/re-emission effect retarding the PL intensity decay.^[50] In such a case, we characterize the PL decay kinetics only by the faster decay components, which are 8.80, 12.9, 13.6, and 8.05 ns for pristine, DDAB, BDAB, and TBAB samples, respectively. Note that the highest PLQY values correspond to longer lifetimes, and ≈ 2 -fold lifetime shortening for pristine and TBAB samples correlates with the corresponding PLQY decrease. A longer lifetime with a 100% PLQY obtained for DDAB and BDAB corroborates the suppression of nonradiative channels by action of these ligands, indicating an efficient surface passivation by the introduction of Br^- and R-O^- species to fill halide defect sites.^[30,51]

After detailing the final photophysical features of the DDAB- and BDAB-capped PNCs- C_xOH dispersions, we investigated these materials for light emitting applications: i) down-converting systems and ii) LEDs. For the first kind of system for the on-chip application, we have embedded the corresponding PNCs dispersions into a commercial acrylate-based polymeric resin, perovskite: resin volume ratio = 4:1, and deposited the blend on a blue emitting LED chip, 3 W and wavelength: 445–450 nm, see supporting information for further details. Under the operation of the LED chips, part of the blue emission is transmitted, while the rest of the light is absorbed by the AlkylBr-modified PNCs, converting it into green emission. Then, we proceed to analyze the stability of green-LED chips by varying i) the applied voltage to modulate the PL emission intensity and later ii) the change of the operation time to study the retention of the initial luminescence.

As seen in Figure 3A,A', the PL of the color-converting DDAB- and BDAB-PNCs layer, with a PL peak position at 521 nm in both cases, is increased as the blue-light intensity from the LED chip raised by applying a voltage up to 3.5 V. Later, a lower decrease in PL was achieved at higher energy (4.0 V). This behavior is typical for an efficient blue-to-green light conversion from the modified PNCs.^[52] At this point, a better light conversion is achieved for the DDAB-LED system, indicating a favored radiative recombination into the perovskite layer. However, by analyzing the sta-

bility of the PL emission of the AlkylBr-LEDs under continuous irradiation at 3.0 V in the blue-LED chip for 4 h, we evidenced a longer PL stability in the BDAB-LED compared to DDAB-LED, see Figure 3B,B' and Figure S12A (Supporting Information). Inset of Figure 3B,B' shows the respective green LEDs under operation. The detachment of some ligands from the surface at prolonged irradiation flux is the common reason to mediate the decrease of the PL from the active layer.^[53] This is reasonable for DDA^+ since this capping shows a lower binding ability to PNCs surface than BDA^+ , as we have established from DFT calculations.

Taking advantage of the improved intrinsic properties of the AlkylBr-capped PNCs- C_xOH dispersions, we were interested in preparing mixed halide $\text{CsPbBr}_{3-x}\text{I}_x$ PNCs inks by combining these PNCs samples with a fixed volume of CsPbI_3 colloidal solution. In this context, we studied the optical features of sensitive iodide-based PNCs layers for down-converting luminescent optoelectronics. As seen in Figure 3C,C', the addition of 500 μL CsPbI_3 PNCs caused a redshift of the PL emission in both kinds of color-converting materials, but the degree of displacement was contrasting each other. In the case of DDAB-LEDs, a broad PL signal located at ≈ 588 nm was reached, covering the green-yellow-red region of the energy spectrum. Accordingly, white-light emission was noted in the device, see Inset of Figure 3C. Conversely, the BDAB-LED produces a narrower PL at longer wavelengths, with an emission peak position ≈ 632 nm. Here, a reddish light emission was detected from the LED chip, see Inset of Figure 3C'. This discrepancy can be explained in terms of the ability of the AlkylBr to facilitate the anion-exchange (A-E) process between iodide and bromide species in the NPs surface. As we highlighted in Figure S13 (Supporting Information), we have explored the combination of each DDAB- and BDAB-capped CsPbBr_3 PNCs dispersed in BuOH, with an iodide source as the case of potassium iodide (KI) dissolved in MeOH. By dosing the AlkylBr-PNCs with the iodide compounds, the PL of the initial materials was redshifted, depicting a more appreciable change in the presence of BDAB, even with a lower iodide dosage. We can deduce that DDAB provides a better compensation for Br deficiency, giving more content of this halide for the exchange dynamics, compared to BDAB, which can partially suppress the Br^- defects. Therefore, there would be more available halide vacancies to fill with external iodide (KI or CsPbI_3). Nevertheless, the stability of the A-E-AlkylBr-PNCs displays a more beneficial effect in the presence of BDAB, retaining the initial PL of the device for a longer time, see Figure S12B (Supporting Information). At this stage, the stronger ability of the BDA^+ cation to the PNCs surface confers a better resistance to the color converter, enhancing the operational stability of the LED.

For the second type of light emitting applications, LEDs, the AlkylBr-PNCs- C_xOH dispersions were centrifugated, recovering the respective NPs powder from supernatant, and concentrating at 10 mg mL^{-1} in hexane for further use. This concentration was prepared to avoid PNCs aggregation during the layer deposition. Then, the PNCs active layers were integrated into the following configuration: PEDOT:PSS/Poly-TPD/PNCs/POT2T/LiF/Al.^[54] In this context, the band alignment is displayed in Figure S14A (Supporting Information), guaranteeing the carrier mobility into the green LED devices. Additionally, we prepared diverse batches of LEDs to prevent

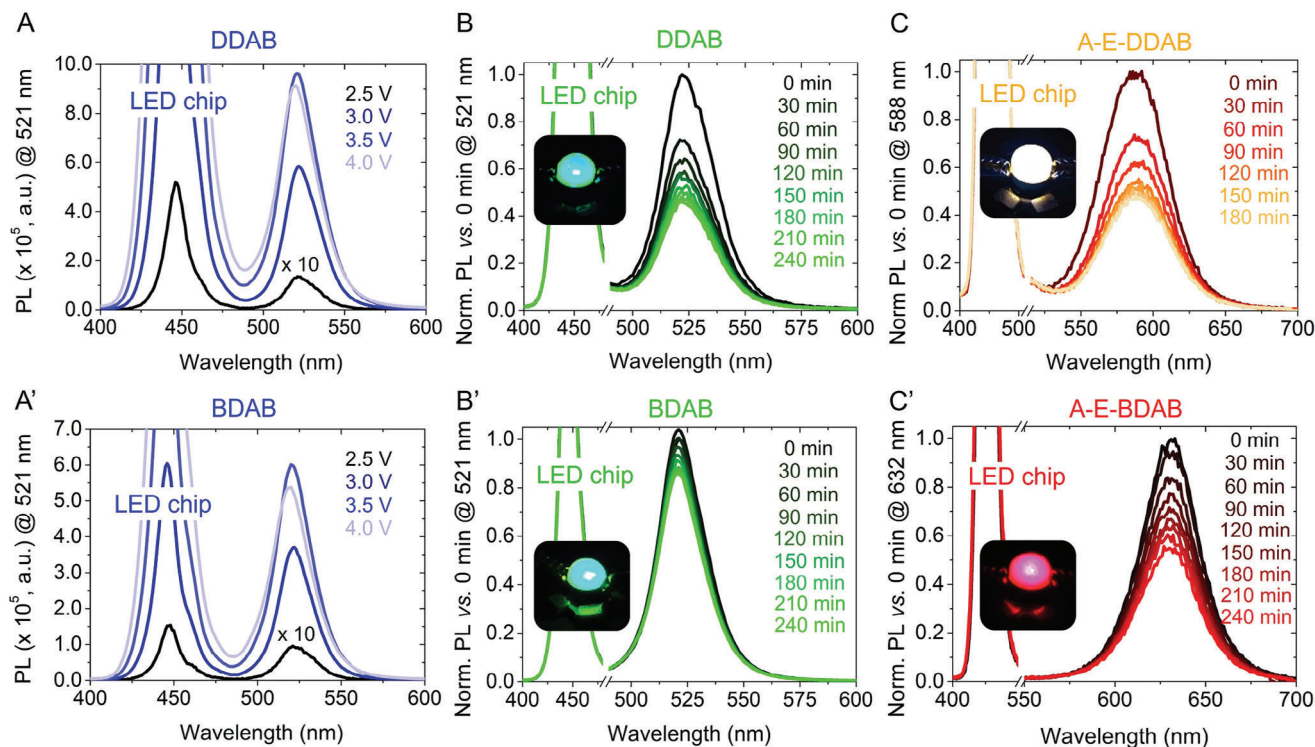


Figure 3. PL spectra of polymeric green-LEDs by using A–C) DDAB- and (A'–C') BDAB-color converters (A,A') by varying the applied voltage. (PL peak position at 521 nm). (B',B) Normalized PL emission stability (PL peak position at 521 nm) of the green-LED devices by applying a constant voltage of 3.0 V at different operational times. The inset of Figure 3B,B' exhibits the characteristic green luminescence of the respective color converter under LED operation. Normalized PL emission stability of (C) polymeric white- and (C') red-LEDs by using anion-exchanged (A-E) color converters by applying a constant voltage of 3.0 V at different operational times. The inset of Figure 3C shows the white luminescence of the A-E-DDAB color converter, measured at 588 nm, while the inset of Figure 3C' displays the red luminescence of the A-E-BDAB color converter measured at 632 nm. The peak at 446 nm is ascribed to the PL emission of the commercial blue LED chip.

the influence of the thickness of the active, hole, and electron-transporting layers. **Figure 4A,B** illustrates the maximum performance of PNCs-based LEDs in the presence of DDAB ($L = 10\,340\text{ cd m}^{-2}$, $J = 828\text{ mA cm}^{-2}$, and $\text{EQE} = 23.2\%$) and BDAB ligands ($L = 4363\text{ cd m}^{-2}$, $J = 1324\text{ mA cm}^{-2}$, and $\text{EQE} = 20.3\%$), both types of devices showed a turn-on voltage

(V_{ON}) of 2.5 V. The corresponding electroluminescence (EL) spectra of the green LEDs are shown in Figure S14B,C (Supporting Information). As we have thoroughly exposed in XPS analysis, DDAB favors sufficient surface passivation in the PNCs, producing a PNCs active layer containing a low content of halide defects. In consequence, the carrier injection into the DDAB-LED will be

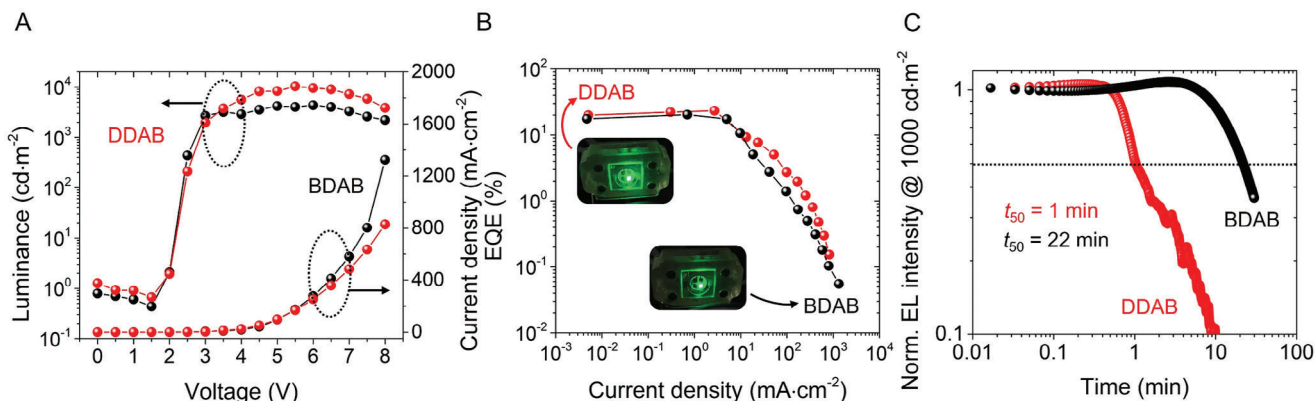


Figure 4. A) J–V–L characteristics and B) EQE versus J curves of layer-by-layer green-LEDs devices by using DDAB- (red curves) and BDAB-capped (black curves) CsPbBr_3 PNCs active layers. The inset of Figure 4B depicts the corresponding devices under operation. C) Operational stability for the DDAB- and BDAB-green-LEDs by measuring their EL at $L_0 = 1000\text{ cd m}^{-2}$.

facilitated, improving the radiative recombination by the emergence of a lower density of energy traps. In contrast, the fact that BDAB provides a partial surface coverage produces that certain NPs exhibit a higher density of non-radiative recombination centers, favoring the carrier trapping (electron accumulation) into the PNCs active layer, limiting the increase of L compared with DDAB. The electron trapping induced by the non-radiative channels can facilitate the current leakage, as a result of the unbalanced carrier injection toward the perovskite.^[55] This can explain the emergence of the roll-off effect at lower currents for the LED device with BDAB compared with DDAB, see Figure 4B, indicating a faster current leakage. Surprisingly, by measuring L of both AlkylBr-LEDs in the function of time at an initial luminance (L_0) = 1000 cd m⁻², see Figure 4C, it is noticeable that a more than one order better operational half lifetime (t_{50}) is obtained in the presence of the BDAB, t_{50} = 22 min, than that of DDAB ligand, t_{50} = 1 min. This behavior is similar to the achieved one for down-converting PNCs layers, confirming that the stronger surface binding ability of the BDA⁺ cation to PNCs delays the decrease of the efficiency in the green-LEDs. Other points contributing to the higher stability can be associated with the presence of the benzyl group contained in the BDAB and the lower surface capping coverage, facilitating the carrier transport through the LED along the time.

Lastly, we tried to fabricate efficient electrical-driven red-LEDs by passivating CsPbI₃ PNCs with both of the AlkylBr capping agents to produce a CsPbBr_{3-x}I_x mixed halide perovskite, but the co-existence of BDAB and MeOH restrains the material redispersion and thereby, avoiding the preparation of the PNCs active layer.^[56] NPs aggregation emerges, indicating the removal of a high content of surface ligands in the presence of alcohol. In this context, only DDAB-capped CsPbI₃ could be dispersed to obtain a suitable solution for LED fabrication, using the same device architecture for green LEDs. As seen in Figure S15A,B (Supporting Information), we were able to obtain a performance with L = 365 cd m⁻², J = 125 mA cm⁻², and EQE = 11.8%, with a V_{ON} = 2.5 V, and an EL peak position at 669 nm, see Figure S15C (Supporting Information). Attending to the fact that iodide-based PNCs are more prone to degrade in contact with polar solvents, a low performance can be reached. However, this is the first report of LEDs composed of alcohol-stable red-emitting CsPbBr_{3-x}I_x PNCs, offering new insight into the PNCs processing for future optoelectronics. In conclusion, the nature of bulky AlkylBr ligands provides a different surface passivation mechanism in alcohol environments, reaching the stabilization of the PL features in halide PNCs and the fabrication of optical down-converters or architecture-layer LED devices with high performance, being promising for liquid crystal display technologies.

3. Conclusion

In this work, we analyze the influence of different AlkylBr ligands such as DDAB, BDAB, and TBAB, on the photophysical properties, surface chemistry, and stabilization of CsPbBr₃ PNCs dispersed in alcohol environments. Depending on the alkylammonium cation nature composing the capping agent, a distinct ligand passivation mechanism was established. We deduce that DDAB provides an efficient compensation of structural defects on the PNCs surface, mainly Cs⁺ and Br⁻ sites, removing car-

rier traps and favoring radiative recombination. In the case of BDAB, a partial surface coverage is promoted, due to the presence of benzyl groups providing steric hindrance on the material surface. Accordingly, a lower density of this ligand can protect the PNCs against direct interaction with MeOH/BuOH molecules. However, considering that a higher density of free BDAB is available in the dispersion, this ligand can also induce the formation of R-O⁻ anions to replace surface OA⁻ linked to the PNCs. In both bases, we achieve a 100% PLQY and long-term stability for ≈10 months. Conversely, TBAB offers poor protection of the PNCs in the polar solvent, presenting a higher degree of steric hindrance through its structure. This feature makes the defect passivation, favoring the fast quenching of the PL features in the photomaterial. By using DDAB and BDAB, we prepare efficient green-color converters and LEDs, reaching a slightly higher optical performance for the DDAB-PNCs layers than for BDAB-PNCs. The ligand passivation given by DDAB favors the formation of an active layer with fewer defects, enhancing radiative recombination and facilitating carrier mobility into the devices. At this point, a maximum EQE of 23.2 and 20.3% was obtained by using DDAB and BDAB, respectively. Nevertheless, in terms of stability, BDAB-PNCs layers present a significantly better capability to resist continuous irradiation and extend the operational performance of the LED device 20-fold longer than DDAB, considering the stronger surface binding of BDAB to the perovskite surface. By extrapolating the surface passivation concept to another kind of PNCs systems, we also obtain efficient stable-alcohol CsPbBr_{3-x}I_x color-converters with typical PL features, and active layers for the fabrication of red-LEDs devices, depicting a EQE ≈11.8%. This contribution paves the way for a novel PNCs processing strategy to prepare alcohol-stable multi-color CsPbX₃ PNCs with enhanced stability for light-emitting applications, such as LEDs or LCD technologies.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

P. U.-V. and A. V.-A. contributed equally to this work. A.F.G.-R., I. O.-R., and J. M. designed the experiments. A.F.G.-R., A.V.-A., and O. S. synthesized and characterized the CsPbX₃ PNCs. P. U.-V. and C. S. prepared and characterized the alcohol dispersions. F. W., K. R. A., R. C., J. M., and O. S. T. designed and performed the NMR analysis. A.F.G.-R., M.E.F., and C. S. fabricated and characterized the CsPbX₃ color converters, respectively. A. V.-A. and O.S. fabricated and characterized the LEDs. B. P., C. S., M. P., and J. H performed and analyzed the synchrotron measurements. C. E.-A. developed theoretical calculations. M. E. F., S. D. A., S. M., and I. M.-S. contributed to the analysis of material characterization. J.R.-P. contributed to the XPS measurements and analysis. All authors contributed to writing the manuscript and the discussions.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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alcohol-stable nanocrystals, color converters, light-emitting diodes, surface passivation, steric hindrance

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