Colloidal CsPbX₃ (X = Cl, Br, I) Nanocrystals 2.0: Zwitterionic Capping Ligands for Improved Durability and Stability

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ABSTRACT: Colloidal lead halide perovskite nanocrystals (NCs) have recently emerged as versatile photonic sources. Their processing and optoelectronic applications are hampered by the loss of colloidal stability and structural integrity due to the facile desorption of surface coating molecules during isolation and purification. To address this issue, herein, we propose a new ligand capping strategy utilizing common and inexpensive long-chain zwitterionic molecules such as 3-(N,N-dimethylctadecylamonio)-propanesulfonate, resulting in much improved chemical durability. In particular, this class of ligands allows for the isolation of clean NCs with high photoluminescence quantum yields (PL QYs) of above 90% after four rounds of precipitation/redispersion along with much higher overall reaction yields of uniform and colloidal dispersible NCs. Densely packed films of these NCs exhibit high PL QY values and effective charge transport. Consequently, they exhibit photocconductivity and low thresholds for amplified spontaneous emission of 2 μJ cm⁻² under femtosecond optical excitation and are suited for efficient light-emitting diodes.

Semiconducting lead halides with perovskite crystal structure, recently known as photovoltaic materials showing power conversion efficiencies exceeding 22%,‡ also hold great promise as versatile photonic sources in the form of colloidal nanocrystals (NCs). Fully inorganic CsPbX₃ (X = Cl, Br, or I, or a mixture thereof) have become popular choices owing to their chemical stability and broadly tunable photoluminescence (PL, 400–700 nm), small PL full width at half-maxima (fwhm, 12–40 nm for blue-to-red), and high PL quantum yields (QYs = 50–90%).†,‡ Their intrinsic defect tolerance,‡,†,‡ i.e., the rather benign nature of surfaces with respect to PL efficiency, is a particularly important asset for employing these NCs in displays,‡ light-emitting diodes,§–‡ and potentially lasers.‡,†,‡,‡,‡,‡,‡,‡,‡,‡,‡,‡,‡

A highly pressing challenge related to organic–inorganic interfaces was identified in the early days of CsPbX₃ NCs. Highly dynamic binding exists between the surface capping ligands, typically a pair consisting of an anion (Br⁻ or olate, OA⁻) and a cation (oleylammonium, OLAH⁺), and the oppositely charged NC surface ions (Scheme 1a).‡,†,‡ Together with a mutual equilibrium between the ionized and molecular forms of these ligands (OA⁻ + OLAH⁺ ⇌ OLA + OAH or OLAH⁺ + Br⁻ ⇌ OLA + HBr, Scheme 1a), these dynamics cause rapid desorption of the protective ligand shell upon isolation and purification of colloids, which is practically observed as a loss of colloidal stability and a rapid decrease in PL QY. This eventually also leads to the loss of structural integrity, i.e., sintering of NCs into bulk polycrystalline materials. Thus far, the strategies to address such problems...
Scheme 1. (a) Depiction of Conventional Ligand Capping of Perovskite NCs Using Long-Chain Molecules with Single Head Groups, In the Ionized Form (OA\textsuperscript{−} or Br\textsuperscript{−}, OLAH\textsuperscript{+})\textsuperscript{a} and (b) a Novel Strategy wherein Cationic and Anionic Groups Are Combined in a Single Zwitterionic Molecule\textsuperscript{b}

\textsuperscript{a} The net effect of two possible sets of equilibria is facile ligand desorption during purification. \textsuperscript{b} Examples of long-chain sulfobetaines, phosphocholines, and \(\gamma\)-amino acids tested in this work are depicted left to right (\(n = 1\)): 3-(N,N-dimethyloctadecylammonio)-propanesulfonate, N-hexadecylphosphocholine, and N,N-dimethyldecylammoniumbutyrate.

In this work, we present a general approach for the efficient surface ligand capping of CsPbX\textsubscript{3} NCs using zwitterionic long-chain molecules, which are readily available commercially (i.e., sulfobetaines, phosphocholines, \(\gamma\)-amino acids, etc., Scheme 1b). For instance, 3-(N,N-dimethyloctadecylammonio)-propanesulfonate is a long-chain sulfobetaine, broadly used as a low-cost detergent in, for example, shower gels, protein isolation, and antibacterial coatings. There are two major structural differences with respect to conventional carboxylate and ammonium capping ligands (e.g., OLA\textsuperscript{+}OAH), both favoring stronger adhesion to the NC surface. First, the cationic and anionic groups have no possibility of mutual or external neutralization by Brønsted acid–base equilibria. Second, the binding to the NC surface is kinetically stabilized by the chelate effect.\textsuperscript{30} In agreement with this argument, one can explain also the effective bicarboxylate binding reported recently by Bakr et al. for CsPbI\textsubscript{3} NCs.\textsuperscript{29}

In the proof-of-principle experiment, we fully replaced the OAH and OLA by a zwitterionic ligand (Figure 1 a; b; see detailed methods in the Supporting Information and related Figures S1–S7). In a typical synthesis of 10 nm CsPbBr\textsubscript{3} NCs, cesium 2-ethylhexanoate (0.2 mmol), lead(II) 2-ethylhexanoate (0.24 mmol), and 3-(N,N-dimethyloctadecylammonio)-propanesulfonate (0.1 mmol, ligand) were combined in dried mesitylene (~6 mL) and heated to 130 °C under inert gas. At this point, a trioctylphosphine-Br\textsubscript{2} adduct (TOP-Br\textsubscript{2}, 0.3 mmol) dissolved in toluene (0.5 mL) was injected into the reaction mixture, which was then immediately cooled. The crude solution was centrifuged to remove insolubles (if any) and mixed with ethyl acetate (12 mL) to precipitate NCs. The NCs were isolated by centrifuging, redispersed in toluene (3 mL), and centrifuged again to remove a fraction of larger NCs (below 10% by weight; if any). Afterward, higher purity could be attained without the loss of structural integrity and a high PL QY could be retained by repeatedly (i.e., up to 3 more times) adding a nonsolvent (e.g., 6 mL of ethyl acetate, 3 mL of acetone, or 1 mL of acetonitrile), centrifuging the mixture, and redispersing the precipitate in toluene (3 mL). In contrast, conventional OA/OLA-capped CsPbBr\textsubscript{3} NCs fully transform into poorly luminescent bulk material upon analogous washing. Zwitterionic-ligand-capped CsPbBr\textsubscript{3} NCs can form much more concentrated colloids (up to 50–100 mg/mL) than their OA/OLA-capped counterparts. Furthermore, the typical synthesis yield of clean dispersible CsPbBr\textsubscript{3} NCs is ca. 80% compared to only 10–20% for rather impure NCs prepared with the conventional OA/OLA capping. The obtained CsPbBr\textsubscript{3} NCs showed a phase-pure orthorhombic crystal structure, identical to NCs received by OA/OLA synthesis\textsuperscript{3,31,32} (Pnma space group; see powder X-ray diffraction patterns in Figure S4). The

Figure 1. Synthesis of zwitterionic-capped CsPbX\textsubscript{3} NCs, exemplified for CsPbBr\textsubscript{3}: (a) reaction equation, (b) typical TEM images of CsPbBr\textsubscript{3} NCs, (c) absorbance and emission spectra, (d) QY of NCs covered with the 3-(N,N-dimethyloctadecylammonio)propanesulfonate and OA/OLA after two steps of purification on day 1 and after storage for 28 days.
mass fraction of organic ligands was estimated to be ca. 11% using thermogravimetric analysis (Figure S5), corresponding to a ligand density of ca. 1.7 nm$^{-2}$ (for 11 nm NCs).

Solution nuclear magnetic resonance (NMR) spectra were acquired at various stages of the purification, confirming the formation of $R_xP(\text{OOCR})_3$ [trioctyl-$\lambda^3$-phosphaneoxy bis(2-ethylhexanoate), Figure S6] and the complete removal of the free zwitterionic ligand, reagents, and reagent byproducts (Figure S7). Solution NMR fails to accurately resolve the resonances attributed to surface-immobilized ligand molecules because the slow tumbling of NCs in solution results in significant signal broadening. Therefore, the purified NCs were decomposed to liberate the ligands by their complete ionic dissolution in deuterated dimethyl sulfoxide (DMSO-d$_6$). The NMR spectra of the resulting solution point to the zwitterionic ligand as the sole surface-bound species (Figure S7). Analogous findings on the preferential and exclusive binding of sulfobetaine and on colloidal durability were obtained when 2-ethylhexanoate was replaced with the oleate in the synthesis (Figure S8). We also tested halide sources such as oleyl ammonium bromide (OLAHBr) as alternatives to TOP-Br$_2$. The OLA was found as a co-ligand at the surface (Figure S9), presumably in the form of OLAHBr. The sulfobetaine-to-OLA ratio was ca. 1.5. Diffusion-ordered NMR spectroscopy (DOSY NMR, Table S2), which probes the diffusion speed of the detected molecules, estimated that the diffusion coefficients for the broad resonances obtained from the zwitterionic ligand were nearly identical to the value independently calculated using the Stokes–Einstein equation for the actual size of the NCs (i.e., $5.17 \times 10^{-11}$ m$^2$/s for the 11 nm NCs). The motion of a free ligand molecule, on the contrary, is 2 orders of magnitude faster (Table S2). The photophysical qualities (i.e., PL QYs, PL fwhm, and PL lifetimes) of the sulfobetaine-capped CsPbX$_3$ NCs were commensurate with those of standard OLA/OA-capped NCs (see Figure 1c for CsPbBr$_3$ NCs, Figure S10 for time-resolved PL, and Figures S11 and S12 for chlorides and iodides). The utility of other zwitterionic ligands—phosphocholines and $\gamma$-amino acids—is illustrated in Figure S13. The decisive role of zwitterionic surface capping for improving the chemical durability of perovskite NCs can be illustrated by a comprehensive study relating the optical characteristics, foremost the PL QYs, to the variation in the number of washing steps, solvents, and aging period; see Figures 1d, S14, and 15 and additional discussions and details in the Supporting Information. The retention of PL QYs above 60% for 28 days of CsPbBr$_3$ NCs was considered a benchmark for stability. Briefly, standard OLA/OA-capped NCs exhibited such PL QYs ($\sim$80%) only when the number of washing steps did not exceed two and only for one antisolvent: ethyl acetate. Even in this best case, the PL QY dropped to ca. 20% after 28 days of storage under ambient conditions. On the contrary, the sulfobetaine-capped CsPbBr$_3$ NCs, washed twice with ethyl acetate, acetone, or acetonitrile as antisolvents, retained PL QYs in the range of 70–90% for 28–50 days. These NCs could even moderately tolerate washing with alcohol (i.e., ethanol), showing a PL QY of 65% after two washings and ca. 40% after 28 days. The absorption and PL spectra as well as PL lifetimes of the zwitterionic-capped NCs remained largely unchanged during intense washing for up to four times (Figure S16).

By means of density functional theory (DFT), we analyzed the passivation of CsPbBr$_3$ NCs capped with OLAH'Br$^-$, OLAH'OA$^-$, and C$_3$-sulfobetaine (Figure 2). The details of the methodology employed are provided in the Supporting Information. All of the relaxed species comfortably fit the perovskite crystal structure, with the ammonium group in the OLAH$'Br^-$ and OLAH$'OA^-$ engaging in hydrogen bond interactions with the corresponding anion. Remarkably, the dimethylammonium group of the zwitterion, which can be expected as rather bulky, also can be easily accommodated in a cation site at the surface. For all species, the binding energy was computed to be ca. 40–45 kcal/mol, suggesting good affinity of all of the ion pairs to the surface. However, there is no substantial energetic difference between the conventional and zwitterionic passivation. This supports the theory proposed earlier in the introduction that the experimentally observed improvements are due to the chelate effect. We also analyzed the electronic structure to verify whether the different kinds of passivation could lead to the formation of localized surface states. For all cases, the bandgap of the perovskite remained intact and free of midgap states. The HOMO–LUMO levels of the ligands used were calculated and found to reside within the valence band and conduction band, respectively (Figure S17).

Interestingly, the spacing between the cationic and anionic head groups of the sulfobetaines, namely, three or four carbon atoms, has observable experimental effects. The C$_3$-sulfobetaines were better suited for the synthesis of the Cl- and Br-
containing perovskites, while their C₄ counterparts performed better for synthesizing the iodides, presumably owing to the larger cation–anion distances at the NC surface. This comparison held true for both the oleyl and octadecyl side chains; see the discussion in the Supporting Information and Figures S12 and 13.

A major and very typical issue for CsPbBr₃ NCs is facile room-temperature sintering, which quickly renders the material polycrystalline and nonluminescent. In contrast, zwitterionic-sulfobetaine-capped NCs, we used a device structure similar to that of Li et al. (Figure S18). Strong coupling between neighboring NCs facilitates exciton–exciton interactions, enabling multie exciton processes, which favor optical gain in the compact NC medium. When the optical pumping levels substantially exceed one exciton per NC, the population inversion of biexcitonic states is observed as emergence of an amplified spontaneous emission band (ASE, Figure 3a). The ASE threshold of 2 µJ/cm² (with 100 fs pulses, Figure 3b) is one of the lowest values reported for solution-processed NC films.

Dense NC packing and hence improved electronic coupling enable the observation of photoconductivity. In CsPbBr₃ NC films, the photoresponsivity spectrum closely resembles the optical absorption spectrum, with typical responsivities (R) of about 0.5 A/W (Figure 3c). Hence, a photoconductive gain close to unity can be estimated (from G = R·hν·e⁻, where hν and e are the photon energy and electron charge, respectively). This finding is corroborated by the observation of high PL QYs in these films. G > 1 can be expected only in the presence of secondary, i.e., trap-assisted, photocurrent. The photocurrent vs bias dependence shows saturation above 30–40 V (Figure 3d), indicating efficient charge collection. The apparently trap-free photoconductivity is also revealed in the linearity of the photocurrent vs incident light intensity plot (at least over 3 orders of magnitude in intensity) and in the relatively large bandwidth of about 90 Hz (Figure S19).

Efficient charge transport and high PL QYs are required characteristics for the eventual use of perovskite NC films in light-emitting diodes (LEDs). To assess the potential of the sulfobetaine-capped NCs, we used a device structure similar to that of Li et al. (Figure 3e).

The current density passing through the devices was rather high, limiting the peak external quantum efficiency (EQE) to 2.5% at 3.5 V (J = 21.7 mA/cm², L = 1641 cd/m², Figure 3f; see the statistics in Figure S20 and the plot of EQE/current efficiency vs voltage in Figure S21), trailing behind the most efficient CsPbBr₃ NC LEDs in terms of EQEs (8.73 and 6.27%). At the same time, the peak luminescence of such devices exceeded 24 000 cd/m² (Figure 3f), significantly brighter than the aforementioned efficient LEDS (1660 and 15 185 cd/m², respectively) but lagging behind the Cs/formamidinium mixed-cation bromide perovskite NC LED (55 005 cd/m²). The electroluminescence wavelength and fwhm were 516 and 16 nm, respectively (at 3.5 V; inset in Figure 3f). Despite sulfobetaine being a long-chain ligand, the charge transport is not severely impeded, seen as high photoconductivity and high current densities in the LEDs. The current densities in our LEDs (current density vs voltage characteristics, Figures 3f and S22) are higher than those reported in LEDs from Li et al. (EQE = 6.27%) but without concomitant increase in luminance, thus leading to a lower EQE (2.5%). This reduced efficiency may be due to imbalance between electrons and holes at higher current densities.

In conclusion, a novel class of capping ligands for perovskite NCs is proposed, wherein each ligand molecule is capable of coordinating simultaneously to the surface cations and anions. Colloidal perovskite NCs prepared with tightly bound ligands and without large quantities of excessive capping ligands will serve as an ideal platform for further engineering of these NCs.
This may include the development of core–shell NC morphologies with enhanced thermal and environmental stability, as critically needed for applications in displays and lighting, or even for rendering perovskite NCs water-compatible for biomedical applications.

**ASSOCIATED CONTENT**

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.8b00035.

Experimental methods and supplementary figures (PDF)

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#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This work was financially supported by the European Union through the FP7 (ERC Starting Grant NANOSOLID, GA No. 306733) and by the Swiss Federal Commission for Technology and Innovation (CTI-No. 18614.1 PFNM-NM). The authors thank ScopeM for use of the electron microscopes, the MoBiAS molecular and biomolecular analytical service of ETH Zurich for mass spectrometry measurements and elemental analysis and Prof. Manfred Fiebig and his research group for access to their femtosecond laser and for experimental assistance. Ms. Laura Piveteau is gratefully acknowledged for stimulating discussions. I.I. acknowledges The Netherlands Organization of Scientific Research (NWO) for financial support through the Innovational Research Incentive (Vidi) Scheme (Grant No. 723.013.002). The computational work was carried out on the Dutch national e-infrastructure with the support of the SURF Cooperative.

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