Lead Halide Perovskites and Other Metal Halide Complexes As Inorganic Capping Ligands for Colloidal Nanocrystals

Dmitry N. Dirin,†,‡ Sébastien Dreyfuss,† Maryna I. Bodnarchuk,†,‡ Georgian Nedelcu,†,‡ Paris Papagiorgis,§ Grigoris Itskos,† and Maksym V. Kovalenko*,†,‡

†Institute of Inorganic Chemistry, Department of Chemistry and Applied Bioscience, ETH Zürich, CH-8093 Zürich, Switzerland
‡Laboratory for Thin Films and Photovoltaics, Empa – Swiss Federal Laboratories for Materials Science and Technology, CH-8600 Dübendorf, Switzerland
§Department of Physics, Experimental Condensed Matter Physics Laboratory, University of Cyprus, 1678 Nicosia, Cyprus

Supporting Information

ABSTRACT: Lead halide perovskites (CH3NH3PbX3, where X = I, Br) and other metal halide complexes (MXn, where M = Pb, Cd, In, Zn, Fe, Bi, Sb) have been studied as inorganic capping ligands for colloidal nanocrystals. We present the methodology for the surface functionalization via ligand-exchange reactions and the effect on the optical properties of IV–VI, II–VI, and III–V semiconductor nanocrystals. In particular, we show that the Lewis acid–base properties of the solvents, in addition to the solvent dielectric constant, must be properly adjusted for successful ligand exchange and colloidal stability. High luminescence quantum efficiencies of 20–30% for near-infrared emitting CH3NH3PbI3-functionalized PbS nanocrystals and 50–65% for red-emitting CH3NH3CdBr3- and (NH4)2ZnCl4-capped CdSe/CdS nanocrystals point to highly efficient electronic passivation of the nanocrystal surface.

Surface chemistry largely dictates the physical and chemical properties of individual nanocrystals (NCs) as well as electronic communication between the NCs in their densely packed solids.1 Since the early 1990s, organic capping ligands have enabled tremendous progress in the colloidal synthesis of monodisperse NCs of a wide variety of metals, semiconductors, and magnetic materials.1a,2 However, long-chain insulating organic ligands must be removed for the integration of NCs into solids with tunable electronic properties, as required for NC-based solar cells,3 light-emitting diodes,4 photodetectors,5 thermoelectrics,6 transistors,6,7 and integrated electronic circuits.8 Solution-phase exchange of organic ligands with smaller inorganic species has been recently demonstrated as a powerful methodology, as it preserves the integrity, size-tunable optical properties, and solution-processability of NCs, while greatly improving charge transport in NC solids. Common inorganic anions that have been successfully applied as inorganic capping ligands are metal chalcogenide complexes (MCCs, also known as chalcogenidometallates),9,10 o xo- and polyoxometallates,10 and metal-free ions (S2−, HS−, Se2−, OH−, SCN−, etc.).9,11 The strong adsorption of an anion combined with dissociation of cations in highly polar organic solvents leads to efficient colloidal stabilization. Here, we present metal halide complexes (halometallates) as capping ligands for a variety of colloidal inorganic NCs (Scheme 1). The factors governing successful ligand exchange and colloidal stability are discussed, and the results are compared to the previous work of some of us related to chalcogenidometallate capping.9,10 Importantly, we demonstrate the ability of halometallate ligands to efficiently passivate the surface of semiconductor NCs (PbS and CdSe/CdS), resulting in highly efficient excitonic photoluminescence (PL).

On their own halometallates represent a very important class of inorganic compounds. For instance, methylammonium lead iodides and bromides (MAPbI3, MAPbBr3, where MA = CH3NH3+), known as hybrid metal halide perovskites due to their perovskite crystal structure, have attracted enormous interest in recent years as low-cost, solution-deposited photovoltaic materials with record power conversion efficiencies of 10–15%.12 Also CsSnI3 has been recently used as a solid-state electrolyte in 12%-efficient dye sensitized solar cells.13 Hence the combination of the two attractive classes of semiconductors, NCs and metal halide perovskites, may open new and exciting opportunities. In particular, we find that MAPbI3 is the first example of inorganic capping ligands that is able to retain the highly efficient near-infrared PL of PbS NCs (quantum yield of 20–30%).

In a typical ligand-exchange procedure [for details, see the Supporting Information (SI)], a 0.05 M solution of a metal halide

Scheme 1. Schematics of the Ligand-Exchange Methodology for Obtaining Halometallate-Capped Colloidal Nanocrystals

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moisture-free techniques were needed, except for FeCl₂, SnX₂,
and redissolved in propylene carbonate (PC) or MFA. No air- or
transferred to the polar phase (Figure 1a). NCs were precipitated
in 1 mL) for several hours until the NCs were completely
stable solutions. Elemental analysis of purified halometallate-capped NCs in PC. (d, e) TEM images of PbS-
halometallate-capped NCs (CdS-SbCl₃, InP-InCl₃, CdSe-FeCl₂, Au-
stretching modes (2800 ~ 3500 cm⁻¹), C−H bending vibrations,
and carboxylic C =O and vinyl C=C stretching modes (600 ~
1500 cm⁻¹). Transmission electron microscopy (TEM) images
for PbS NCs capped with MAPbI₃ (Figure 1d) and PbI₂ (Figure
1e), as well as for other NC-ligand combinations (Figures S1 and S2 in SI), confirmed the integrity of the NCs and retention of their narrow size distribution. The true colloidal nature of halometallate-capped NCs, apart from the photographs (Figure 1a), was also confirmed by single-particle population in the measurements of dynamic light scattering (DLS, Figure S3). Colloidal solutions of PbS NCs stabilized with MAPbI₃ were stable for months without noticeable aggregation or precipitation. Pb and Cd chalcogenide NCs showed high affinity to nearly all studied ligands, whereas much fewer ligands formed stable colloidal solutions with metallic NCs (Table S1). Importantly, only in the case of CdSe NCs metal-free halide ions Γ⁺, Br⁻ (as salts with K⁺ and MA⁺ cations) can partially displace oleate ligands, yet without the formation of colloidalily stable solutions. Elemental analysis of purified halometallate-capped NCs confirmed the expected overall compositions (7~32 at% of ligand atoms for 3~5 nm NCs, Table S2). Halometallate-capped NCs are negatively charged, as seen from electrophoretic measurements providing ζ-potentials of at least −40 mV for MAPbI₃-stabilized PbS NCs (Figures 1c and S4; see Table S3 for other NC-ligand combinations). Highly negative ζ-potentials, caused by the surface-bound anions such as [PbI₃]⁻ or [PbBr₄]⁻, were measured for both preformed complexes (e.g., KpbI₃) and for neutral halide salts MXₖ (e.g., PbI₂). The latter can be attributed to the well-known self-ionization in polar solvents:¹⁴

\[
2MX_k \leftrightarrow [MX_{n+}]^- + [MX_{n-}]^+ \\
\Rightarrow [MX_{n+2}^-] + [MX_{n-2}^{2+}]
\]

We can emphasize the following factors governing efficient ligand exchange and colloidal stabilization. (i) The affinity of the incoming anionic ligands to the NC surface. Chalcogenido-
ketalate ions (Sn₂S₆²⁻, AsS₄³⁻, In₂Se₄°⁻) possess both X- and L-
type ligand functions, while halometallates can be viewed as almost purely L-type ligands. In other words, a halide ion cannot establish two σ-bonds (one with the central atom of the anion and the other with the metal on the NC surface), but a chalcogenide-based ligand can. Although the atomistic details of NC-ligand binding still have to be revealed for all known inorganic ligands, this simple consideration explains a much slower ligand-exchange reaction for halometallates compared to that for chalcogenometalates (hours vs minutes for CdSe-oleate NCs treated with MACdBr₃ and K₃AsS₄ as an example). (ii) The solvent dielectric constant, which allows electrolytic dissociation of cations, leading to the electrostatic mechanism of colloidal stabilization. Correspondingly, MFA and very similar N-methylacetamide are often the best solvents for performing ligand-exchange reactions due to very high static dielectric constants of 182 and 191, respectively. (iii) The solvation of anions. Once adsorbed, anions should stay on the surface. The Gibbs energy of anion adsorption on the solid/liquid interface changes with the solvent acidity due to the solvation of anions.¹⁵ A convenient parameter E_d (%) and its normalized version E_d/N for the evaluation of the solvent Lewis acidity were proposed by Dimroth and Reichardt.¹⁶ E_d/N indicates the ability of a given solvent to solvate anions and lies between 0 (tetramethylsilane) and 1 (water). In our case, PbS-MAPbI₃ NCs formed concentrated (25 mg/mL) solutions in MFA (a good Lewis acid with E_d/N = 0.722)¹⁷ but immediately precipitated upon dilution. At the same time, PbS-MAPbI₃ solutions in PC (weak Lewis acid, E_d/N = 0.472)¹⁷ were stable in a wide range of concentrations (0.1~50 mg/mL). This can be explained by the much stronger desorption of anions in MFA. (iv) The solvation of the cations. This factor is especially important for neutral metal halide salts because efficient solvation of complex cations such as [PbI₄]⁺ stabilizes the [PbI₃]⁻ anion as well (reaction 1). The ability of a given solvent to solvate cations strongly correlates with the solvent donor number (DN),¹⁷ which reflects the Lewis basicity of the solvent. PC (DN = 15.1) can solvate CH₃NH₃⁺ or K⁺. On the other hand, much less stable [PbI₄]⁺ cations formed by reaction 1 cannot be efficiently solvated by PC and thus PbS NCs stabilized with PbI₂ were not soluble in neat PC. At the same time, addition of a cosolvent (~1 wt %) with a high DN (dimethylformamide, DMF, DN = 26.6 or hexamethylphosphoramide, HMPA, DN = 38.8) immediately yields very stable colloids in PC.

For PbS NCs, there is growing recognition that halide ions reduce the density of surface trapping states and therefore enhance the performance of solar cells based on PbS NCs,
reaching power conversion efficiencies of 6% and 7%.18 The authors of ref 18 used solid-state ligand exchange or partial halide passivation via solution-phase treatment of oleate-capped PbS NCs, maintaining most of the oleate capping for efficient colloidal stabilization in nonpolar solvents. Our present study shows the possibility of obtaining fully inorganic, halide-covered PbS NCs in the form of stable colloidal solutions. The integrity of PbS NC cores after the ligand exchange with MAPbI3 is evidenced by absorption spectra (Figure 2), which contain sharp excitonic features, slightly red-shifted with respect to the oleate-capped NCs. The extent of electronic passivation was monitored with steady-state and time-resolved PL measurements. Colloidal solutions of MAPbI3-PbS NCs exhibit PL quantum yields (QY) of 20−30%, comparable with the QYs of NCs capped with oleic acid before the ligand exchange and much higher than the QY of PbS NCs capped with [AsS4]3− (QY ≤ 1%). A similar perovskite compound, MAPbBr3, also preserved the efficient and stable PL properties of PbS NCs. Enhanced surface passivation, suggested by the high PL QY, is also evidenced by the retention of stable PL properties of PbS NCs. For the visible spectral region, we prepared two sizes of CdSe/CdS NCs (emission peaks at 608 and 640 nm, CdS shell thickness of 2.8−3 nm), according to the recent method of Bawendi et al.19 These NCs feature a high PL QY of ~72−75% in combination with a very narrow ensemble PL line width of ≤30 nm (≤90 meV). MACdBr3 and (NH4)2ZnCl4 ligands retain...
bright PL with a QY $\approx 50\text{–}65\%$ (higher for (NH$_4$)$_2$ZnCl$_4$, Figures 3A and 3E). In contrast, the capping with chalcogenido-metallate ligands such as K$_2$SnS$_6$ and K$_2$AsS$_4$ results in significantly quenched PL QYS of 10\text{–}15\%.

The generality of the halometallate-capping method can be further illustrated for CdSe, CdS, and InP NCs stabilized with various metal halides (Figure 3B), including magnetic transition metal ions (FeCl$_3$). Contrary to chalcogenido-metallates, halometallates are able in some cases to extract cations from the NCs due to the solubility of the corresponding metal halides.

This was clearly revealed for Cd-chalcogenides: treatment with (NH$_4$)$_2$ZnCl$_4$ converts CdSe NCs into PbSe NCs. Ligand exchange with isocationic halometallates such as K$_4$Sn$_2$S$_6$ and K$_3$AsS$_4$ results in K$_4$Sn$_2$S$_6$ and K$_3$AsS$_4$ retains the Cd-rich stoichiometry of CdSe NCs. Future work will involve functionalization of nanocrystals with metal halides such as PbI$_2$, which we have demonstrated, allowing electronic applications of NC solids composed of densely packed halometallate-capped NCs.

**ASSOCIATED CONTENT**

Supporting Information

Experimental details and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author

mkovalenko@ethz.ch

Notes

The authors declare no competing financial interest.

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