

The Effect of the Alkylammonium Ligand's Length on Organic—Inorganic Perovskite Nanoparticles

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S Supporting Information

ABSTRACT: Here we investigated how the alkylammonium length influences the optical and physical properties of organicinorganic perovskite nanoparticles (NPs). The NPs were synthesized under ambient atmosphere. This synthesis led to the formation of luminescent, well-defined, cubic organic-inorganic perovskite NPs using different lengths of alkylammonium molecules. The optical and physical characterizations showed that when the alkylammonium length is increased, the size of the NPs increases as well. Both the experimental and computational results indicate that the length of the alkylammonium ligand regulates the dominance of the van der Waals interactions between the hydrocarbons at the surface of the NPs. These findings



Alkylammonium length $\uparrow \Rightarrow VDW$ interactions \uparrow

highlight the importance of studying the surface chemistry of hybrid organic-inorganic perovskite NPs, which will facilitate their implementation in optoelectronic applications.

rganic-inorganic perovskite (OIP) nanoparticles (NPs) are characterized by high photoluminescence quantum yields (PLQYs),¹ short radiative lifetimes,² and versatile optical properties^{3,4} that place them among the most attractive NPs to be implemented in optoelectronic applications.^{3,5}

Since the methylammonium lead bromide (MAPbBr₃) NPs were first synthesized in 2014, the PLQY of OIP NPs rose from ~20 to ~95%.^{1,6} The quick growth of PLQY in these NPs resulted from the development of an alternative synthetic route that uses a solvent/antisolvent combination as the trigger for forming the NPs.³ On the other hand, there are only a few reports concerning controlling the shape of these OIP NPs. Vybornyi et al. and Protesescu et al. reported the formation of methylammonium lead halide (MAPbX₃) and formamidinium lead bromide cubic nanocrystals using a hot-injection approach.^{7,8} This approach requires high temperature and an inert-gas atmosphere, which complicate its utilization. In addition, those MAPbX₃ NPs are unstable due to labile surface passivation, which allows fusion processes.

In another report, Liu et al. showed that when a highly concentrated dispersion of spherical MAPbBr₃ NPs is stored for 3 days, nanoplates (NPLs) of MAPbBr₃ are formed due to fusion processes among the spherical NPs.⁹ Moreover, because of the fusion processes, the length and the width of the NPLs cannot be controlled. Similarly, Teunis et al. reported the formation of MAPbBr₃ nanowires as a result of fusion processes

among spherical NPs.¹⁰ In our recent work, the synthesis of OIP nanorods (NRs) was reported.¹¹ The interaction between the octylammonium ligands and the antisolvent led to the formation of well-defined NRs. A rod shape was formed as a result of the optimized ligand ratio.

Aliphatic alkylammonium cations function as ligands in several synthetic routes of perovskite NPs.^{3,6,12} These cations stabilize the surface of the perovskite NPs due to the adsorption of their positively charged ammonium group, specifically upon the (00n) facets.¹³ These facets comprise the exposed, negatively charged halides that electrostatically attract the ammonium cations.¹⁴ Owing to the long tail of the aliphatic cation, which does not fit into the confined octahedral hole of the perovskite structure, the growth of the NPs is inhibited, whereas its surface is passivated. Importantly, the alkylammonium cation interacts with the crystalline structure of the perovskite NP and affects its electronic structure, in contrast to other common ligands, which stabilize NPs through interactions that are exterior to the electronic structure of the NPs.^{15,16}

Here we investigated how the length of the alkylammonium cation influences the optical and physical properties of OIP

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Figure 1. (a) Alkylammonium ligands that were used in this work: octylammonium (C8), dodecylamonium (C12), and octadecylammonium (C18). The gray spheres represent carbon, the blue spheres nitrogen, and the white spheres hydrogen. (b) Size of the NPs as a function of the alkylammonium length for both bromide-based NPs (green) and iodide-based NPs (brown). The average edge size of the C8-, C12-, and C18-based NPs was 3.3 ± 0.5 , 8 ± 2 , and 11 ± 4 nm for the bromide-based NPs, and 2.2 ± 0.4 (width), 5 ± 2 , and 13 ± 4 nm for the iodide-based NPs, respectively.



Figure 2. TEM images of OIP NPs that were synthesized using different lengths of alkylammonium with bromide or iodide. The alkylammonium cations in each figure are the following: (a) C8–Br, (b) C12–Br, (c) C18–Br, (d) C8–I, (e) C12–I, and (f) C18–I.

NPs. Using facile synthesis under ambient atmosphere, we synthesized OIP NPs of a well-defined cubic shape using three alkylammonium cations (octyl, dodecyl, and octadecyl ammonium, C8, C12, and C18, respectively) that function as the ligands. The optical and physical properties were studied and compared to films of two-dimensional (2D) perovskite, where the same alkylammonium cations were used as barriers in these films. A clear dependence was observed between the length of the alkylammonium cations, the size of the NPs, and their optical properties.

In this work octylammonium (C8), dodecylammonium (C12), and octadecylammonium (C18, see Figure 1a) functioned as the ligands in the synthesis of OIP NPs. Both bromide- and iodide-based NPs were synthesized using each of the three linear alkylammonium cations.

The syntheses were carried out under ambient atmosphere based on our previous report,¹¹ including the following steps: (1) injection of lead halide (PbI₂ or PbBr₂) and methylammonium halide (MAI or MABr) solutions in dimethylformamide into a hot medium (80 °C) that contained octadecene, oleic acid (OAc), and alkylammonium halide (C8–I, C8–Br, C12–I, C12–Br, or C18–I, C18–Br) under vigorous stirring, (2) addition of chloroform, which triggered the formation of the NPs, and (3) centrifugation of the dispersions, which led to

sedimentation of bulky byproducts and the acquisition of clear dispersions. Considering the formation of both NPs and byproducts, the ratio between the alkylammonium (C8, C12, or C18) and the methylammonium is not the same as the ratio between the precursors that were introduced into the synthesis in the beginning.

The alkylammonium cations are defined as "ligands"; here the meaning of this term is different from the usual meaning in the colloidal synthesis of NPs. The common ligands stabilize the NPs by interacting with the surface orbitals of the atoms through chemical or physical bonds.¹⁶ In contrast, both the interaction of alkylammonium with the surface of the NPs and the interactions of methylammonium (inside of the core of the NP) with the inorganic octahedra are ionic because both methylammonium and alkylammonium form hydrogen bonds with the halogens that surround the metal cation.¹³ Consequently, the alkylammonium ligands affect the electronic structure of the NPs.^{4,11,15,17}

Figure 2 presents the transmission electron microscopy (TEM) images of the synthesized NPs. In all cases, clear and defined NPs (nanocubes or NRs) were observed. This observation is not trivial because these NPs were formed under ambient atmosphere. Other reports on OIP NPs prepared under ambient atmosphere indicated that they have



Figure 3. Absorbance spectra of (a) bromide- and (d) iodide-based OIP NPs that were synthesized using different lengths of alkyl ammonium ligands. PL spectra of (b) bromide- and (e) iodide-based OIP NPs that were synthesized using different lengths of alkyl ammonium ligands. Pictures of (c) bromide- and (f) iodide-based OIP NP dispersions (in chloroform) that were synthesized using different lengths of alkylammonium ligands under UV light and under white light (inset).

an imperfect spherical shape that did not assemble into the perovskite typical mosaic-like array.^{6,18,19} The TEM images in this work show the stability of the OIP NPs to the electron beam; therefore, clear shapes of the OIP NPs can be observed in Figure 2, i.e., nanocubes, NPLs, and NRs that were assembled in typical arrays (the NRs in Figure 2d were also assembled in a typical NR assembly^{20,21}). These shapes and arrays are typical for inorganic perovskite NPs, which have cubic or sheet-like shapes, as well as a mosaic-like assembly.^{22,23}

The size distribution of the NPs can be observed in the histograms in Figure S1 in the Supporting Information, SI. The length of the alkylammonium was found to affect the size of the NPs, as can be seen in Figures 1b and 2a-f. As the length of the alkylammonium increased, the average size of the NPs increased. The different shapes of the iodide–C8 NRs and the bromide–C8 NPs (NRs vs nanocubes) can result from different surface energies.⁶ The C8–I-based NRs had an average length of 10.6 ± 2.6 nm. This result is in agreement with the trend of the average size among the alkylammonium cations C8 to C12 to C18; thus, the aspect ratio (width/length) should be taken into account.

Long alkylic moieties undergo stronger attractive van der Waals (VDW) interactions with each other than do the short ones (as discussed in detail next). Considering this effect, the tails of the alkylammonium ligands prefer to increase the reciprocal VDW interactions among themselves. Thus, the surface energy (γ) of the NPs changes with the length of the ligand, i.e., $\gamma_{C_{18}} > \gamma_{C_{12}} > \gamma_{C_8}$. When the surface energy is high, the NPs prefer to have a small surface-to-volume ratio; therefore, a long alkylammonium forms larger NPs than does a short alkylammonium.

Figure 3a,d presents the absorbance spectra of the NPs that were synthesized using different alkylammonium lengths. Figure 3b,e presents the PL spectra, and Figure 3c,f shows the emission of the NPs under ultraviolet (UV) light ($\lambda = 254$ nm).

The difference between the bromide-based and the iodidebased NPs is reflected by the absorbance and the PL spectra of the samples. The different p orbitals of the halides (4p of bromide vs 5p of iodide) explain this difference.²⁴ Moreover, the absorbance onset and the PL maxima were shifted to higher energies than those of the corresponding bulk material.²⁴ The reason for that is the confinement that takes place in these NPs.^{4,11,15,17} As described earlier, the alkylammonium ligands strongly affect the electronic structure of the OIP NPs due to the strong ionic interaction between the ammonium group and the inorganic octahedra. The transition of the perovskite to low dimensions suppresses metal-halide interactions and increases the cation-halogen interactions. Importantly, the difference between the dielectric constants of the inorganic part (lead iodide/lead bromide octahedra) and the organic part (alkylammonium) is predominant; thus, the band gap energy of the perovskite increases.¹³

Another prominent observation is that the absorbance onset and the PL maximum varied when varying the alkylammonium length (the absorbance onset of the samples appeared at \sim 467, ~485, and ~525 nm for the C8, C12, and C18 bromide-based NPs, respectively, and at ~652, ~708, and ~740 nm for the C8, C12, and C18 iodide-based NPs, respectively). The optical properties of the OIP NPs can vary as a result of the length of the ligands due to several factors: (1) the variation of the ligands' dielectric constant, (2) the angle between the ligand and the perovskite surface, which defines the level of the crystalline structure's distortion, and (3) the dominance of VDW interactions between adjacent alkylammonium ligands at the surface of the NP. The dielectric constants of C8, C12, and C18 are similar (see Figure S2 in the SI); thus, this factor cannot explain the significant shift that was observed in the optical measurements.^{13,25} In addition, it was reported that the bonding angle between the alkylammonium and the perovskite surface is independent of the alkylammonium length. Therefore, the shift in the optical properties is probably not the result



Figure 4. Powder-XRD diffractograms of 2D perovskite layers of the formula $(RNH_3)_2(MA)_{n-1}Pb_nX_{3n+1}$, where R = C8, C12, or C18, n = 1 (black) or 3 (red), and X = Br⁻ or I⁻: (a) C8–Br, (b) C12–Br, (c) C18–Br, (d) C8–I, (e) C12–I, (f) C18–I.



Figure 5. (a) PLQYs of various NPs as a function of the alkylammonium length. (b) Elementary unit cells used for calculating the dispersion energies of the 2D perovskite; the uncovered top surface (α), the half-covered top surface (β), and the fully covered top surface (γ). (c) Subtractions that were calculated in order to evaluate the dispersion energies that were gained by surface passivation.

of variation in the angles between the ligand and the perovskite surface.²⁶ On the basis of this, the main factor that affects the optical properties of the NPs due to the different lengths of alkylammonium is the strength of the VDW interactions among the alkylammonium ligands.

In order to elucidate the effect of the alkylammonium length on the optical properties of the NPs, films of 2D perovskite having the formula $(RNH_3)_2(MA)_{n-1}Pb_nX_{3n+1}$ (where n = 1, 2,or 3, R is an aliphatic chain of the lengths C8, C12, or C18, and X is bromide or iodide) were fabricated. Importantly, several publications already reported^{26–28} the optical and structural characterizations of some of the above 2D perovskites; however, a clear relation to OIP NPs with the corresponding alkylammoinum ligands has never been reported. The absorbance spectra of the 2D films are presented in Figure S3. The absorbance of the layers of a specific *n* value varied among the different alkylammonium lengths. These results suggest that the length of the alkylammonium affects the assembly process of the perovskite layers.

Figure 4 presents the powder X-ray diffraction (PXRD) patterns of 2D perovskite films. Theoretically, the d_{001} value expands as the length of alkylammonium increases (see Figure S4a). Thus, the angle of the (001) diffraction peak is shifted toward low angles.²⁷ Indeed, this dependence was observed, as can be seen in Figure 4a-f. Another reason for the shift in the (001) peak is the increased *n* values (the number of inorganic layers between the aliphatic barriers), which increases d_{001} (see Figure S4b).²⁸ The results agree with this trend; for example, Figure 4a shows that the peaks of n = 1 and 3 layers of C8–Br appeared at different angles. The first peak of the n = 1 layer appeared at 4.2°, which indicates that $d_{001} = 21.02$ Å, whereas the n = 3 layer exhibited two peaks, the first at 2.7° ($d_{001} = 32.2$ Å) and the second at 3.4° (\hat{d}_{001} = 26.26 Å). Importantly, the layers of n > 1 exhibited weak 3D perovskite peaks that appear at 14-15 and 28-29° because the periodic inorganic parts also reflect the X-ray photons.²⁸ These 3D perovskite peaks can be observed in the diffractograms of the n = 3 2D perovskites (see the red diffractograms in Figure 4a-f).

In the diffractogram of pure 2D perovskite, a single set of (00n) peaks indicates the formation of a single 2D perovskite crystalline structure (this set of peaks appears due to the reflection of X-rays from the multiplicities of the (001) plane by integers). In contrast, it can be seen in Figure 4a—f that, instead of a single set of peaks, a few sets of peaks appeared for n > 1 (see the few peaks at angles below 5° in the red curves in Figure 4a—f). This observation is valid for both halides (Br⁻ and I⁻) and for all lengths of alkylammonium (C8, C12, and C18). Notably, the intensity of these peaks is more pronounced in the short alkylammonium than in the long alkylammonium. The appearance of these additional sets of peaks derives from the presence of a few n > 1 perovskite crystals.

Remarkably, Figure 4a–f shows that the similarity between the diffractograms of the n = 1 and 3 perovskite films increased as the alkylammonium ligand elongated. This means that when using long alkylammonium cations the n = 1 perovskite structure tends to be formed, whereas the formation of the n > 1 perovskite structures becomes undesirable.²⁸

These results show that long alkylammonium cations direct the crystalline organization toward lower n values. The reason for this is the VDW interactions among adjacent hydrocarbons. These interactions become more dominant as the alkylammonium length increases. This insight is in agreement with the conclusion from the TEM images of the NPs; both implied that a long alkylammonium cation generates strong VDW interactions.

These findings also shed light on the absorbance results of the NPs. Short ligands form NPs that have large surface-tovolume ratios because the VDW interactions among adjacent ligands are moderate. Accordingly, the numerous alkylammonium—halide interactions strongly affect the electronic structure and lead to band gap widening. Therefore, the absorbance onset of small NPs is shifted toward shorter wavelengths.

Figure 5a provides the PLQYs of the reported NPs. The bromide-based NPs resulted in higher PLQYs compared with the iodide-based NPs. These results are in agreement with other reports that present similar trends.^{3,29} A reasonable explanation relates to the surface passivation, which was shown to be better when a bromide-based perovskite was used. The better surface passivation is attributed to the stronger hydrogen bonds between the alkylammonium and the bromide compared with the hydrogen bonds between the alkylammonium and the iodide because the iodide is less electronegative. In addition, the PLQY varied among NPs of different sizes and shapes. This effect can be explained by the differences in the aspect ratio and the crystal quality among the various NPs.^{30–32}

To support the experimental results, the dispersive interactions (i.e., the VDW interactions) among adjacent alkylammonium ligands on the surface of 2D perovskite crystals were calculated using the DFT + VDW method. A bromide-based 2D perovskite of n = 2 was chosen for the numerical simulations (see the elementary unit cells in Figure 5b); the length of the alkylammonium cations was varied among C8, C12, and C18. The ligand-to-ligand dispersion energies in the systems of the 2D perovskite with the different alkylammonium ligands were extracted from the total dispersive energies of the system.

The unit cells in Figure 5b display a fully covered bottom surface of the 2D perovskite by alkylammonium ligands,

whereas the degree of coverage of the top surface varied (uncovered (α), half-covered (β), or fully covered (γ)). Figure 5b,c presents schemes of the systems that were calculated, whereas the corresponding differential dispersion energies are presented in Table 1. The results show that elongation of the

Table 1. Energy Gained by the Adsorption of Ligands to the Top Surface of the n = 2 Bromide-Based 2D Perovskite Structure

	$\beta - 2\alpha$ (eV)	$2\gamma - \beta \;(\mathrm{eV})$	$2\gamma - 2\alpha$ (eV)
C8	-1.07	-0.91	-1.98
C12	-1.31	-1.41	-2.72
C18	-1.74	-1.96	-3.70

aliphatic chain of the alkylammonium from C8 to C18 stabilizes the whole structure, i.e., the dispersion energy is more negative; therefore, the total energy is lower. The subtraction $\beta - 2\alpha$ confirms the higher stability of the half-covered top surface relative to the uncovered top surface, $2\gamma - \beta$ confirms the higher stability of the fully covered top surface relative to the half-covered top surface, and $2\gamma - 2\alpha$ confirms the higher stability of the fully covered top surface relative to the uncovered top surface. The enhanced stability is a result of the VDW interactions among neighboring alkylammonium cations that support the experimental results. Furthermore, the results also show that the stability of the 2D perovskite increases with the length of the alkylammonium cation. Importantly, these results suggest that when using the C18 cation one can gain more energy due to the adsorption of the C18 alkylammonium cations than the energy gained during the crystal growth.

In this work, luminescent hybrid perovskite NPs of controlled size and shape were synthesized. Three lengths of alkylammonium ligands (C8, C12, and C18) governed the physical and optical properties of the NPs. The syntheses were performed in ambient atmosphere, and well-defined cubic NPs of hybrid perovskite were obtained. The optical and physical characterizations showed that as the length of the alkylammonium increases the band gap energy of the NPs decreases, whereas their size increases. The main factor that is related to these effects is the VDW interactions between adjacent alkylammonium ligands.

In order to elucidate the specific reason for the changes in the NP properties, films of two-dimensional perovskites of the formula $(C_m H_{2m+1} N H_3)_2 (MA)_{n-1} Pb_n X_{3n+1}$ (where m = 8/12/18, n = 1/2/3, and X = Br⁻/I⁻) were fabricated using the same alkylammonium ligands, and their optical and crystallographic properties were analyzed. It was found that the VDW interactions among the alkylammonium ligands are dominant; thus, they determine the crystalline structure and the optical properties of the two-dimensional perovskite films. DFT calculations showed that the dispersion energies among neighboring alkylammonium ligands influence the stability of the perovskite crystal and govern the structure. The VDW interactions among the different alkylammonium ligands are the main factor for the differences in the optical and physical properties of the synthesized OIP NPs. The PLOY of the NPs varied from 30 to 60%, depending on the halide and the alkylammonium ligand length. Understanding how the length of the alkylammonium affects the properties of the NPs is essential for future implementation of these NPs in optoelectronic applications.

EXPERIMENTAL SECTION

All of the experimental procedures are detailed in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergy-lett.8b00554.

Figures that support the hypotheses described in the article and experimental details regarding the synthesis and the charcterization of the discussed samples (PDF)

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Notes

The authors declare no competing financial interest.

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