Molecular Intercalation and Electronic Two Dimensionality in Layered Hybrid Perovskites

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Abstract: In layered hybrid perovskites, such as (BA)2PbI4 (BA = C4H9NH3), electrons and holes are considered to be confined in atomically thin two dimensional (2D) Pb–I inorganic layers. These inorganic layers are electronically isolated from each other in the third dimension by the insulating organic layers. Herein we report our experimental findings that suggest the presence of electronic interaction between the inorganic layers in some parts of the single crystals. The extent of this interaction is reversibly tuned by intercalation of organic and inorganic molecules in the layered perovskite single crystals. Consequently, optical absorption and emission properties switch reversibly with intercalation. Furthermore, increasing the distance between inorganic layers by increasing the length of the organic spacer cations systematically decreases these electronic interactions. This finding that the parts of the layered hybrid perovskites are not strictly electronically 2D is critical for understanding the electronic, optical, and optoelectronic properties of these technologically important materials.

Introduction

Metal halide perovskites, including the layered hybrid perovskites, are now considered as technologically important optical and optoelectronic materials.[1] One of the simplest compositions of layered hybrid perovskites is (BA)2PbI4 (BA = C4H9NH3).[2] It is considered that the electron and hole are confined in atomically thin two dimensional (2D) Pb-I inorganic layers, which are electronically isolated from each other in the third dimension by the insulating organic layers.[3] A millimeter thick single crystal of (BA)2PbI4 contains millions of atomically thin Pb–I semiconducting layers (wells) in a periodic arrangement, separated by insulating organic layers (barriers), forming a repeating quantum well structure. Typical all-inorganic quantum wells, such as AlAs/GaAs/AlAs are well understood,[4] but the hybrid (BA)2PbI4 quantum well is distinctly different from the all-inorganic ones. In AlAs/GaAs, the electronic properties of individual components AlAs and GaAs are well understood, which are then extended to understand the interface between the components. But both the components of (BA)2PbI4, namely BA+ and (PbI)3– do not exist independently. Furthermore, the interaction between BA+ and (PbI)3– is ionic in nature, unlike the case of AlAs/GaAs interface. Another important difference is the huge dielectric contrast between the organic and inorganic parts, unlike the all-inorganic quantum wells. All these complexities make it difficult to understand the electronic and optical properties of the hybrid layered perovskites, demanding newer theoretical and experimental approaches to solve the problem.[5]

There are some peculiarities in the experimentally observed optical and electronic data of these layered perovskites. For example, a single crystal of (BA)2PbI4 and other layered hybrid perovskite systems exhibit two (band edge) excitonic absorption and emission features, as if the same crystal has two band gaps.[6] Furthermore, Wang et al. found that the edges of (BA)2PbI4 single crystals are significantly more electrically conducting than their terraces.[7] We hypothesize that some of these unusual experimental observations might arise from possible electronic interactions between the Pb–I layers. To verify such possibility, we intercalated insulating molecules in the single crystals of layered perovskites, such as (BA)2PbI4, (DA)2PbI4 (DA = decylamine), and (PEA)2SnI4 (PEA = phenylethylammonium). In addition to the increase in the distance between the Pb–I layers, the molecular intercalation disturbs the interaction between hydrocarbon tails of organic cations. The photoluminescence (PL) spectra in a layered perovskite single crystal switch reversibly from dual emission to single emission upon intercalation. These results, along with the spatially resolved PL spectra suggest that in parts of the single crystals, probably at the edges, Pb–I layers interact with each other. Further we tuned the strength of this electronic interaction systematically by changing the chain length of organic spacer cations.

Results and Discussion

We synthesize (BA)2PbI4 single crystals following a reported method (see Supporting Information for detailed methodology).[8] Intriguingly, PL spectrum of the as-synthesized single crystal shows two excitonic transitions (see Figure S1 in the Supporting Information) similar to our earlier report.[9] To verify whether the two emissions arise
from diverse spatial locations within a crystal, we performed energetically resolved PL imaging of (BA)$_2$PbI$_4$ single crystals using a home-built laser epi-fluorescence microscopy setup (see Supporting Information for details). Individual (BA)$_2$PbI$_4$ crystals can be easily visualized owing to intense greenish-yellow hue originating from both the excitonic emissions. The PL image (Figure 1 a) over both the emissions show that while the entire crystal is emissive, there is considerable spatial variation in the intensity. To selectively detect the spatial distribution of the lower energy emission, we collected the fluorescence image of the same crystal via a 540 nm (ca. 2.30 eV) long-pass filter (Figure S2). The energy-mapped intensity images (Figure 1b and Figure S2) suggested the dominance of the lower energy (yellow) emission near the crystal edges.

PL spectral profiles recorded from several locations of the crystal (Figure 1 c) reveal a remarkable spatial variation in the relative intensities of the two transitions. We find that the relative intensity of the lower energy (2.25 eV) emission is much higher near the edges compared to the interior regions. On the contrary, the high energy (2.39 eV) emission is typically much more pronounced far away from the crystal boundaries. Such spatial heterogeneity in PL characteristics is clearly visible in the spectrally resolved PL image (Figure 1d) obtained for a narrow strip at the bottom of the crystal. Spectral images (such as Figure 1d) additionally reveal a rather gradual variation in the relative intensity of the two excitonic transitions upon progression from the interior regions to the boundary zones. It is a relevant note that step-like edges are present throughout the surface of the single crystal, as evident from field emission scanning electron microscopy (FESEM) image (Figure 1e) and shown systematically in Figure 1f. It is likely that all these step-like edges contribute significantly to the lower energy transition, and consequently, the yellow emission is spread over the entire crystal, even at locations far from the crystal boundaries.

It is to be noted here that the edge-state emission from our (BA)$_2$PbI$_4$ is different than the previously reported$^{[7,10]}$ edge-state emission from (C$_4$H$_9$NH$_3$)$_3$(CH$_3$NH$_3$)$_n$Pb$_{3n}$I$_{10}$ and (C$_4$H$_9$NH$_3$)$_2$(C$_2$H$_5$NH$_2$)$_n$Pb$_{3n}$I$_{10}$ with $(n \geq 2)$. For samples with $n \geq 2$, the small A-site cations CH$_3$NH$_3^+$ leads to the formation of 3D perovskite compositions at the edges. Therefore, for $n \geq 2$, formation of 3D perovskite edge-states gives lower energy emission with peak energy similar to that of a pure 3D perovskite.$^{[6,10]}$ In our (BA)$_2$PbI$_4$ ($n = 1$), neither smaller A-site cations are present, nor the emission energy of edge states match with 3D perovskites.

To explore the origin of two excitonic emissions, we exposed the (BA)$_2$PbI$_4$ single crystals to the iodine (I$_2$) vapors, leading to insertion (intercalation) of molecular I$_2$ into the layered perovskites. I$_2$ is selected here based on the prior report of successful intercalation of I$_2$ into similar layered perovskite systems.$^{[10]}$ The intercalated I$_2$ slowly comes out (de-intercalate) from the perovskite crystals, upon removing the I$_2$ atmosphere. This reversibility of the I$_2$ intercalation process is schematically depicted in Figure 2a. The intercalation of I$_2$ is expected to increase the distance between Pb–I layers. Indeed, the powder X-ray diffraction (PXRD) patterns of (BA)$_2$PbI$_4$ single crystal (Figure 2b) show a shift in the peak position towards the lower angles ($2\theta$ values) upon I$_2$ insertion, which indicates an increase in the interlayer distance.$^{[6,11]}$ Subsequent de-intercalation process reverts the PXRD peaks to the original 2$\theta$ values.

The PL spectrum of (BA)$_2$PbI$_4$ single crystal (Figure 2c) shows dual emission peaks as discussed above.$^{[6,11]}$ Interestingly, after I$_2$ intercalation, the lower energy (2.21 eV) emission completely disappears without affecting the higher energy (2.38 eV) emission. Spatially resolved PL spectroscopy performed after I$_2$ intercalation validate that only the higher energy (green) emission emanates from entire crystals, and the lower energy emission is non-existent even at the crystal boundaries (Figure S3). Subsequently, during the de-intercalation process, the lower energy emission reappears within an hour, as shown in Figure 2d. Upon the progressive release of I$_2$, from the (BA)$_2$PbI$_4$ lattice, we observed a systematic increase in the intensity of lower energy emission with (de-intercalation) time. The intercalation of I$_2$ increases the distance between the inorganic layers, and further it is
expected to disrupt the interactions between the hydrocarbon tails of BA⁺ ions (see Figure 2a) thereby reducing the structural rigidity across the Pb–I layers. Therefore, the reversible disappearance and reappearance of the lower energy emission at 2.21 eV with intercalation and de-intercalation of I₂ respectively, suggests that the lower energy emission originates from some electronic interaction between the Pb–I layers.

These results suggest that there are parts in a single crystal of (BA)₂PbI₄ showing the high-energy PL emission, where Pb–I layers do not interact with each other, as this emission is independent of the molecular intercalation. In some other parts, Pb–I layers interact with each other originating the lower energy PL emission. Spatially resolved PL spectra (Figure 1) suggest that the edges of the crystals have more contribution from the lower energy PL emission. Therefore, the edges of the crystals can be considered as those locations where the Pb–I layers interact predominantly, introducing the pseudo 2D nature in the system. These results agree with the recent report that showed edges could conduct electricity unlike other parts of (BA)₂PbI₄ single crystal. It is to be noted here that electron injection/extraction, required for any electronic and optoelectronic applications, occur through these edge states because the terraces of layered perovskites are insulating. Therefore, not only the optical properties but also the charge transfer or transport properties need to consider this pseudo 2D electronic nature of the edge states.

Unfortunately, there is an overlap in the optical absorption of intercalated I₂ with (BA)₂PbI₄ (see Figure S4), which complicates the comparison of the absorption spectra before and after the intercalation process. To compare both absorption and emission spectra before and after the intercalation process, we searched for a system where there is no overlap in the absorption of the intercalating molecules with that of the host perovskite. From the literature, we found that molecular hexane can be intercalated into layered perovskites. However, as hexane is larger than I₂, the chain length of organic cations in the hybrid perovskite also has to be longer to accommodate hexane. Consequently, (DA)₂PbI₄ (DA = decylamine) single crystals are synthesized and intercalated with hexane. Details of synthesis, characterization and intercalation methodologies are provided in the Supporting Information. Figure 2e depicts the reversible hexane intercalation in a (DA)₂PbI₄ single crystal. PXRD patterns (Figure S5) show an increase in interlayer distance after hexane intercalation, and the interlayer distance comes back to the original value after de-intercalation of hexane. PL spectra in Figure 2f switch from dual emission for pristine (DA)₂PbI₄ to a single emission for hexane intercalated (DA)₂PbI₄. The disappearance of the lower energy emission is also accompanied by a blue-shift in the absorption spectrum of (DA)₂PbI₄ after hexane intercalation, as shown in Figure S6. The switching of PL from dual to single emission is again reversible with intercalation/de-intercalation of hexane, as

Figure 2. a) Schematic representation of the reversible intercalation of molecular iodine into a (BA)₂PbI₄ single crystal. b) PXRD patterns and c) PL spectra of (BA)₂PbI₄ single crystal with and without I₂ intercalation. d) Evolution of PL peak during the de-intercalation process of (BA)₂PbI₄:I₂. e) Schematic representation of the reversible intercalation of molecular hexane in (DA)₂PbI₄ single crystal. f) PL spectra of (DA)₂PbI₄ single crystal before and after hexane intercalation.
shown in Figure S7. Overall, the reversible intercalation of I\textsubscript{2} and hexane into (BA)\textsubscript{2}PbI\textsubscript{4} and (DA)\textsubscript{2}PbI\textsubscript{4} single crystals, respectively, resulted in similar reversible changes in optical absorption and emission. In both cases, intercalations reduce (or eliminates) interactions between the Pb–I layers, eliminating the lower energy emission.

We preferred reversible intercalation in the previous cases for reliable correlation of intercalation with electronic dimensionality and optical properties. However, this reversible process has one demerit. Structural analysis of the intercalated crystals using single-crystal XRD is challenging, because of the de-intercalation process during the measurement. So, it remains unclear whether the intercalated molecules are ordered or disordered and how many molecules are present within the intercalating layers. To address this issue, we made irreversible intercalation of hexafluorobenzene (HFB) in phenylethylammonium tin iodide [(PEA)\textsubscript{2}SnI\textsubscript{4}], following the work of Mitzi et al.[13] The highly electron-deficient HFB strongly binds with the electron-rich phenyl rings of (PEA)\textsubscript{2}SnI\textsubscript{4}, providing stability to the intercalated system that can be termed as (PEA)\textsubscript{2}SnI\textsubscript{4}:HFB.

Methodologies for synthesizing and intercalating (PEA)\textsubscript{2}SnI\textsubscript{4} single crystals are given in the Supporting Information. PXRD patterns provided in Figure S8 confirm the intercalation of HFB between the (PEA)\textsubscript{2}SnI\textsubscript{4} layers. Figure 3a shows the crystal structure of (PEA)\textsubscript{2}SnI\textsubscript{4} before and after intercalation, obtained by recording single-crystal XRD. Both (PEA)\textsubscript{2}SnI\textsubscript{4} and (PEA)\textsubscript{2}SnI\textsubscript{4}:HFB crystalize in a triclinic lattice with P(−1) space group. The lattice parameters of (PEA)\textsubscript{2}SnI\textsubscript{4} and (PEA)\textsubscript{2}SnI\textsubscript{4}:HFB are a = 8.6321(16) Å, b = 8.6344(16) Å, c = 16.358(3) Å, α = 94.696\(\pm\) (5)\(^{\circ}\), β = 100.426(5)\(^{\circ}\), γ = 90.450(5)\(^{\circ}\) and a = 8.5663(12) Å, b = 8.5699(12) Å, c = 20.485(3) Å, α = 98.638(4)\(^{\circ}\), β = 93.594(4)\(^{\circ}\), γ = 90.064(4)\(^{\circ}\) respectively (see Table S1). The HFB molecules are sandwiched between the phenyl rings of two phenylethylammonium ions of the adjacent layers in a regular pattern. Similar to the lead halide systems, (PEA)\textsubscript{2}SnI\textsubscript{4} single crystal also shows a dual emission with peak energies at 1.98 eV and 1.82 eV, as shown in Figure 3b. The energy difference between the two peaks is nearly similar to that observed in lead halide systems. These results rule out any significant role of spin-orbit splitting for the occurrence of dual emission since the spin-orbit coupling is significantly diminished in Sn-halides compared to Pb-halides. Interestingly, (PEA)\textsubscript{2}SnI\textsubscript{4}:HFB shows a single PL emission (Figure 3b).

Therefore, the switching of dual PL emissions to a single PL emission after intercalation is a generic observation for all the three systems, namely, I\textsubscript{2} in (BA)\textsubscript{2}PbI\textsubscript{4}, hexane in (DA)\textsubscript{2}PbI\textsubscript{4} and HFB in (PEA)\textsubscript{2}SnI\textsubscript{4}. These results confirm that in all the three pristine layered perovskite single crystals, the lower energy emission peaks come from the parts of crystals where Pb–I or Sn–I layers interact with each other. It is noteworthy here that the single emission peak in (PEA)\textsubscript{2}SnI\textsubscript{4}:HFB is slightly blue-shifted compared to the higher energy emission of (PEA)\textsubscript{2}SnI\textsubscript{4}. The absorption spectra (Figure S9) also show a blue-shift upon HFB insertion. This blue-shift in PL and absorbance is because of some minor structural difference between (PEA)\textsubscript{2}SnI\textsubscript{4} and (PEA)\textsubscript{2}SnI\textsubscript{4}:HFB (see Figure S10 and S11) similar to the prior report.[13] The average Sn–I–Sn bond angle decreases from around 155.9\(^{\circ}\) to 152.2\(^{\circ}\) and average Sn–I bond length increases from approximately 3.139 Å to 3.152 Å upon HFB intercalation in (PEA)\textsubscript{2}SnI\textsubscript{4}. Both the decreased bond angles and increased bond lengths support the observed blue-shift in the PL emission, upon HFB intercalation.[20]

To validate our hypothesis of the presence of the interactions between the Pb–I layers, we also adopted a different approach where we tuned the strength of interactions between Pb–I layers by changing the distance between the Pb–I layers. This can be achieved by changing the chain length of organic cations R–NH\textsubscript{3}\(^{+}\). As the length of organic cations is systematically increased from C\textsubscript{4} (C\textsubscript{4}H\textsubscript{9}NH\textsubscript{3}\(^{+}\)) to C\textsubscript{16} (C\textsubscript{16}H\textsubscript{33}NH\textsubscript{3}\(^{+}\)), including only even number of carbon atoms, the interlayer distance and barrier width increased systematically, as shown in Figure 4a. The systematic shift of PXRD peaks toward the lower 2\(\theta\) values, shown in Figure 4b, confirms the increased distance between Pb–I layers with increasing the C-chain lengths. Both high thickness and high absorption cross-section do not allow light with
energy above the band gap to pass through the single crystals. Consequently, when we measure the UV/Vis absorption spectra of these crystals in transmission mode (Figure 4c), only the lowest energy absorption edge is observed, beyond which the absorbance saturates for all the samples. Nevertheless, Figure 4c clearly shows a systematic blue-shift in the lowest energy absorption edge with increasing C-chain length. The absorption spectra recorded in the reflectance mode also show a similar trend (Figure S12). PL spectra in Figure 4d show two well-separated emissions for samples with C-chain lengths C4 to C12. The lower energy emission peak, similar to their absorption edges, systematically blue-shifts with increasing C-chain length. In contrast, the higher energy emission at 2.38 eV remains unchanged for all the samples. For a large enough interlayer distance in C14 system \([\text{C}_{14}\text{H}_{29}\text{NH}_{3}]_{2}\text{PbI}_{4}\), the lower energy emission overlaps with, the higher energy emission giving rise to a single but asymmetric and broader emission. With further increase in the interlayer spacing in C16 system \([\text{C}_{16}\text{H}_{33}\text{NH}_{3}]_{2}\text{PbI}_{4}\), a single emission peak with narrower spectral width is observed.

These results corroborate that the higher energy emission at 2.38 eV does not depend on barrier width, (i.e., the C-chain length), similar to the intercalation results in Figure 2. Therefore, this higher energy peak is attributed to individual 2D layers and is independent of interlayer interaction, whereas, the lower energy emission peak depends on barrier width. Lower the barrier width with shorter carbon chain, the stronger is the interlayer electronic interaction, and therefore,
more is the red-shift compared to the higher energy emission peak. For samples like C12, we still observe the signature of small interlayer interactions. The crystal structure suggests a distance of approximately 1.7 nm between Pb—I layers. This is a large distance for possible electronic interactions. However, one would expect a structural reorganization at the edges, probably reducing the Pb—I inter-layer distance facilitating the inter-layer electronic interactions. This could be a plausible reason behind the higher relative intensity of lower energy PL near the edges, as shown in Figure 1. Further theoretical and experimental studies are required to understand the structural and compositional characteristics of edges of these layered perovskites.

Conclusion

Two excitonic emissions from single crystals of layered hybrid lead and tin halide perovskites are puzzling. Spatially resolved fluorescence microscopy imaging of (BA)2PbI4 single crystals shows that the ratio of the two emission peaks change at different parts of the crystal, with the higher relative intensity of lower energy emission near the edges of the crystal. Interestingly, intercalation of iodine in (BA)2PbI4 and hexane in (DA)2PbI4 reversibly switches the PL from two emission peaks, by the disappearance of the lower energy PL peak. Similarly, insertion of HFB in (PEA)2SnI4 single crystal also eliminates the lower energy PL peak. Therefore, we assign the lower energy emission peak to Pb—I interlayer interaction. Furthermore, we decrease the strength of the interlayer interaction almost continuously by increasing the chain length (C4 to C16) of R-NH3+ spacer cations. Subsequently, the lower energy PL peak systematically blue-shift with increasing chain length from C4 to C16, and eventually merge with high energy peak for C14 and C16. All these results show that in parts (particularly edges) of the layered hybrid perovskites crystals, the Pb—I inorganic layers electronically interact with each other. This finding not only explains the unusual optical properties of these systems but will also be important to understand and design charge transfer and charge transport pathways in optoelectronic devices of layered perovskite.

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Conflict of interest

The authors declare no conflict of interest.

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Trial separation: 2D layered Pb- and Sn-halide perovskites show surprising optical properties, such as dual excitonic emissions. Such unusual properties are shown to arise through the interaction between the 2D inorganic layers. Separating the inorganic layers either by molecular intercalation or by increasing the length organic spacer ion reversibly switches the optical properties.