

**Molecular Design of 2D Hybrid Halide
Perovskites:
Chirality, Intercalation and Doping**

विद्या वाचस्पति की
उपाधि की अपेक्षाओं की आंशिक पूर्ति में प्रस्तुत
शोध प्रबंध

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degree of Doctor of Philosophy

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पुणे

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This thesis is dedicated to my parents and sister

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CERTIFICATE

Certified that the work incorporated in the thesis entitled **“Molecular Design of 2D Hybrid Halide Perovskites: Chirality, Intercalation and Doping”** Submitted by Ms. Taniya Dutta was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other University or institution.

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.

List of Abbreviations

3D: Three dimensional

2D: Two dimensional

CBM: Conduction band minimum

FA: Formamidinium

FESEM: Field emission scanning electron microscopy

CD: Circular dichroism

FWHM: Full width at half maximum

HOMO: Highest occupied molecular orbital

ICP-OES: Inductively coupled plasma optical emission spectroscopy

IRF: Instrument response function

LED: Light-emitting diode

LUMO: Lowest unoccupied molecular orbital

MA: Methylammonium

PL: Photoluminescence

PLE: Photoluminescence excitation

PLQY: Photoluminescence quantum yield

PXRD: Powder X-ray diffraction

List of Abbreviations

STE: Self-trapped exciton

TCSPC: Time-correlated single-photon counting

TGA: Thermogravimetric analysis

DSC: Differential scanning calorimetry

VBM: Valance band maximum

UV: Ultraviolet

NIR: Near infrared

This thesis focuses on layered hybrid 2D lead and tin halide perovskites with generic formula A_2MX_4 , where A: organic ammonium ion; M: Pb, Sn; and X: I, Br. These materials have interesting optoelectronic properties because of their repeating quantum well structure comprising atomically thin semiconducting inorganic sublattice and insulating organic (A) sublattice. Primarily, the electron, hole and exciton reside in the inorganic sublattice exhibiting the optoelectronic properties. A large part of this thesis will show that a rational design of the organic sublattice can significantly change the structure and optical properties of the inorganic sublattice, in terms of chirality, band gap tuning and luminescence. The primary objective of the thesis is to explore novel strategies to design the organic-inorganic interface at a molecular level. The organic-inorganic interface interacts through various non-covalent interactions electrostatics, hydrogen and halogen bonding, along with π - π interactions. Single crystals and films of such 2D layered hybrid perovskites were prepared, and structural and optical properties were investigated in a wide range of temperatures 6-300 K. Chapter-wise descriptions of the thesis content are provided below.

Chapter 1: Introduction:

This chapter provides a comprehensive introduction to the field of perovskite semiconductors, along with defining the scope of the present thesis work. It starts with basics of metals-semiconductors-insulators, followed by a more detailed discussions of different aspects of traditional semiconductors like Si and GaAs. In this backdrop, the emergence of halide perovskite materials as a versatile class of semiconductors have been discussed. The discussion progresses to size-dependent quantum confinement in perovskites nanocrystals, and then crystal structure induced quantization in layered hybrid halide perovskites that are termed as 2D perovskites. The 2D perovskites shows a strong quantum well structures, irrespective of the size of the crystals. These 2D perovskites can be considered assembly of nanoscale organic-inorganic interfaces. Special attention is given to the role of interfaces in determining optoelectronic properties. Finally, the scope of the thesis is discussed, where molecular design of the interfaces leads to interesting optoelectronic properties.

Chapter 2: Conformer-Mediated Helical Chirality in 2D Layered Hybrid Perovskites:

2D chiral organic-inorganic hybrid lead halide perovskites combine structural asymmetry, semiconducting charge transport and strong spin-orbit coupling paving the way for unique chiral optoelectronic and spin-based properties. Here we introduce a new idea to design chiral perovskites by using different conformers of chiral organic ammonium ions. The gauche- and

anti-conformers of 1-iodopropane-2-ammonium (IdPA) are alternatively arranged in the chiral 2D perovskites (R-/S-IdPA)₂PbI₄. The anti-conformer of IdPA⁺ ion have significantly stronger electrostatic, hydrogen bonding, and halogen bonding interactions with the inorganic [PbI₄]²⁻ sublattice, compared to the gauche-conformer. This periodic asymmetry in non-covalent interactions caused by the alternative arrangement of gauche- and anti-conformers, induces chirality within the inorganic sublattice. Consequently, (R-IdPA)₂PbI₄ and (S-IdPA)₂PbI₄ crystallize in the helical enantiomorphic space groups P₄₃2₁2 and P₄₁2₁2 with four-fold screw axes, which is very rare in the literature of hybrid perovskites. The two chiral enantiomers (R-/S-IdPA)₂PbI₄ show mirror-image like circular dichroism spectra for excitonic absorption. The structure remains thermally stable in a wide temperature range of 15 K to 403 K, yielding interesting temperature-dependent photoluminescence properties. This conformer-mediated approach expands the structural diversity and chiral optoelectronic functionality of hybrid perovskites.

Chapter 3: Temperature-Dependent Photoluminescence of Hexafluorobenzene Intercalated Phenethylammonium Tin Iodide 2D Perovskite

2D layer hybrid tin halide perovskites also promise interesting optical and optoelectronic properties, similar to their Pb-halide counterparts. Some of these properties can be controlled by intercalation (non-covalent insertion) of molecules between the perovskite layers. Here we intercalate hexafluorobenzene in 2D layered phenethylammonium tin iodide [(PEA)₂SnI₄], and studied the luminescence properties in a temperature range of 6 K to 300 K. Hexafluorobenzene intercalation is found to increase the bandgap. Below 150 K, pristine [(PEA)₂SnI₄] shows luminescence quenching because of the presence of non-emissive states with slightly lower energy compared to emitting excitonic states. Hexafluorobenzene intercalation suppresses the non-emissive states, enhancing the luminescence intensity at cryogenic temperatures. Tuning electronic and optical properties of layered hybrid perovskites just by simple molecular intercalation highlights the newer approaches of controlling structure-property relationships in hybrid perovskites.

Chapter 4: Edge versus Interior Mn²⁺-Doping in 2D Layered Butylammonium Lead Bromide Perovskite Single Crystal

The exciton (electron-hole pair) in 2D layered hybrid perovskites like butylammonium lead bromide [(BA)₂PbBr₄] remains strongly confined within an atomically thin Pb-Br layer. Therefore, doping Mn²⁺ into (BA)₂PbBr₄ is expected to yield strong exciton-Mn²⁺ interactions

leading to interesting optical, optoelectronic and magneto-optic properties. But the exciton- Mn^{2+} interaction has not been found to be as strong as expected from a strongly quantum confined system. Is there a spatial separation between Mn^{2+} ions and excitons reducing the energy transfer efficiency? To address this question, we prepared single crystals of Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$ studied their photoluminescence (PL) properties. In this single crystals, the PL originating from excitons located in the interior vs. edge of layers can be distinguished. Therefore, we can distinguish the interaction of Mn^{2+} dopants with interior-excitons and edge-excitons. Our results show that, compared to interior-exciton, it is the edge-exciton that interact significantly more with the Mn^{2+} ions. Energy transfer from edge-excitons sensitizes the Mn^{2+} ions, leading to the characteristic Mn^{2+} d -electron emission at 2.05 eV. The Mn^{2+} doping is found to be preferred at the layer edges. Therefore, Mn^{2+} dopants are not in close proximity of the interior-excitons, that reduces their interactions, in spite of the strong quantum confinement.

Chapter 5: Thesis Summary and Future Outlook

In this section, we summarized the work presented in this thesis and highlight the major findings. Based on our findings and current literature a future research outlook is also provided.

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Chapter 1

Introduction

1.1 Conductor-semiconductor-insulator:

Solid materials can be classified into three groups based on their electrical conductivity: metals or conductors, semiconductors, and insulators. Figure 1.1 illustrates the range of conductivity values corresponding to these different material categories. Insulators, such as quartz and glass, demonstrate very low electrical conductivity, typically around 10^{-18} to 10^{-8} S/cm.¹ In contrast, conductors like copper and iron exhibit high electrical conductivities, generally ranging from 10^4 to 10^6 S/cm.¹ Semiconductors fall between the conductivity levels of conductors and insulators. Interestingly, the electrical conductivity of semiconductors can be modulated over many orders of magnitudes by applying different perturbations such as doping, temperature, illumination, electrical bias voltage, and magnetic fields. The sharp modulation of electrical conductivity with external perturbation makes semiconductors the active materials for various electronic, optoelectronic and spin-based applications.

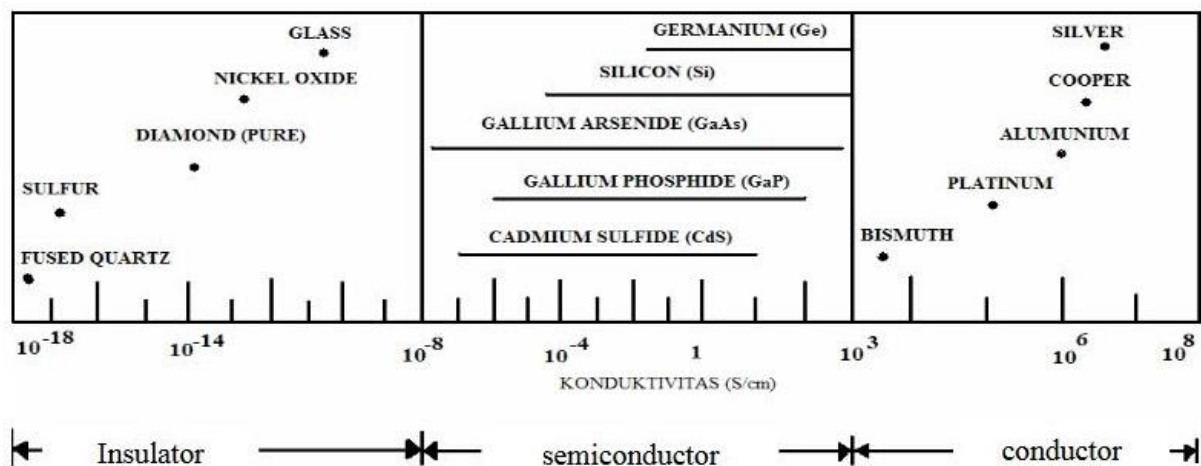


Figure 1.1: Typical range of conductivities for insulators, semiconductors, and conductors. The figure is reprinted from reference² with permission Copyright ©2008, Indonesian Journal of Physics.

1.2 Traditional semiconductor:

In 1950s and 1960s, germanium and silicon emerged as materials showing interesting semiconducting properties. Silicon shows a high electrical conductivity of approximately 10^2 S/cm and a significant diffusion length ranging from 100 to 300 μm , making it particularly suitable for electronic applications.¹ Its electrical conductivity, combined with its ample availability in the Earth's crust, positions silicon as a cost-effective semiconducting material. For applications such as solar cells, silicon has achieved an efficiency of 29% for a single-junction cell, which is notably close to the Shockley-Queisser limit of 33.16%.³ However,

silicon is an indirect band gap material. Consequently, and it has a low absorption cross-section on the order of 250 cm^{-1} .⁴ indicating poor absorptivity. Therefore, very thick silicon is required for solar cell. So light-weight and flexible solar cell and other optoelectronic devices are difficult to achieve using silicon. The indirect band gap also means that silicon cannot emit light and are not a preferred choice for light-emitting diode (LED) applications.

The issue of indirect band gap of silicon can be addressed by gallium arsenide (GaAs), that has a direct band gap. Efficient and thinner solar cells and LEDs are well reported with GaAs. There are other compound semiconductors like indium arsenide (InAs), indium phosphide (InP), gallium nitride (GaN), cadmium telluride (CdTe), and lead sulfide (PbS), covering a wide range of band gap. For example, GaAs with a band gap of 1.52 eV,^{5,6} yields near-infrared (NIR) LED, whereas, GaN, with a band gap of 3.4 eV,⁶ leads to fabrication of ultraviolet (UV) LEDs.

However, many of compound semiconductors like GaAs and GaN are grown by different epitaxial growth, making it expensive along with a challenge for large scale production. Consequently, there have been continued research to explore new solution processed organic, inorganic, and organic-inorganic hybrid semiconductors since 1980s. Colloidal quantum dots and hybrid metal halides are such important solution processed and cost-effective semiconductors that has emerged in recent times. Importantly, these new classes of semiconductors exhibit newer properties beyond the scopes of traditional semiconductors like Si, GaAs, InP etc.

1.3 Perovskite semiconductors:

The name "perovskite" is derived from the Russian mineralogist L. A. Perovski.⁷ Perovskite is a crystal structure that was assigned CaTiO_3 .⁸⁻¹¹ Subsequently, a large variety of materials were found to possess the same perovskite structure. Typically, the oxide materials with perovskite structure possess a wide band gap, and are not good semiconductor. But then emerged some halide perovskite materials showing interesting semiconducting properties.¹²⁻²² The cesium plumohalide, grouped lead halide perovskite structure was first reported by Moller in 1958.²³ Semiconducting properties Pb- and Sn- based metal halides were explored in 1990s. Kojima et al. in 2009, reported the first perovskite solar cell using methyl ammonium lead iodide perovskite as the light absorbing material.²⁴ The photo conversion efficiency in that first report was 3.8%.²⁴ But in subsequent reports, the efficiency jumped rapidly, with a present value of 27.3 %.²⁵ This success in solar cell efficiency has led to intense research on different

optoelectronic properties of 3D halide perovskites. Lead halide based perovskites such as CsPbBr_3 exhibit remarkably high optical absorption coefficient of nearly 10^5 cm^{-1} at 355 nm.²⁶ Long diffusion lengths ($\sim 0.1 \mu\text{m}$) is also observed for $(\text{CH}_3\text{NH}_3)\text{PbI}_3$ perovskites thin films along with efficient photoluminescence efficiency with narrow ($\sim 36 \text{ meV}$) emission line widths, making them promising materials for various optoelectronics applications.²⁸⁻³⁴

1.4 ABX_3 3D perovskite structure:

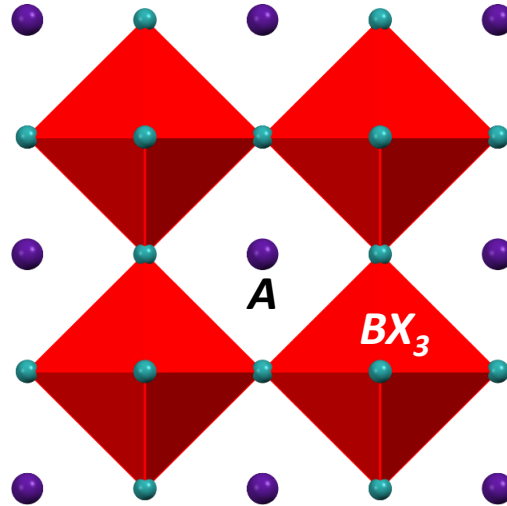


Figure 1.2: Schematic of 3D perovskite structure having formula ABX_3 . The Violet sphere is A site cation, and the red octahedral with sky-blue ball forms BX_3 octahedra.

Perovskites are represented by a generic formula ABX_3 , as illustrated in Figure 1.2.³⁵ In this structure, A and B represent positively charged cations, while X denotes a negatively charged anion. In the case of lead and tin halide perovskites, the cations occupying the A site include Cs^+ , MA^+ (methyl ammonium), and FA^+ (formamidinium), while the B site cations are Pb^{2+} and Sn^{2+} . The anions at the X site are Cl^- , Br^- , and I^- . The BX_3 framework forms an octahedral configuration, with these octahedra creating void spaces between them. It is within these voids that the A site cation resides, resulting in the formation of the ABX_3 structure.

Victor Moritz Goldschmidt examined various perovskite systems and observed that the formation of the perovskite structure is influenced by the ionic radii of the constituent ions.³⁶ Goldschmidt tolerance factor (t) is defined as:

$$\text{Goldschmidt tolerance factor (t)} = \frac{r_A + r_X}{\sqrt{2} (r_B + r_X)} \quad (1)$$

where, r_A = radius of A-site cation, r_B = radius of B site cation, r_X = radius of X-site cation.

This Goldschmidt tolerance factor is typically between 0.80 to 1 for a stable perovskite structure.³⁵ The structure factor value is applicable to 3D perovskite structures such as CsPbI₃ and MAPbI₃.

1.5 Perovskite nanocrystals:

When a 3D perovskite semiconductor is illuminated by light, electrons in the valence band move to the conduction band, resulting in the creation of holes in the valence band.³⁷⁻³⁹ This process generates an electron-hole pair, which is referred to as an exciton. Excitons are quasi-particles that maintain an equilibrium distance known as the Bohr exciton radius. When the size of a semiconductor crystal in any direction approach or become smaller than the Bohr exciton radius, the exciton experiences a reduced spatial environment compared to its equilibrium position. In this case, the scenario resembles a particle-in-a-box problem, where the length L is equivalent to the diameter of the crystal. According to the principles of the particle-in-a-box model

$$\Delta E \propto \frac{1}{L^2}$$

As L , the crystallite size decreases, the ΔE , the band gap increases. This phenomenon is known as size-dependent quantum confinement effect. Therefore, we achieve confinement by manipulating the crystallite size. Colloidal nanocrystal of different chemical compositions of ABX₃ perovskites have been prepared and their optoelectronic properties have been studied.

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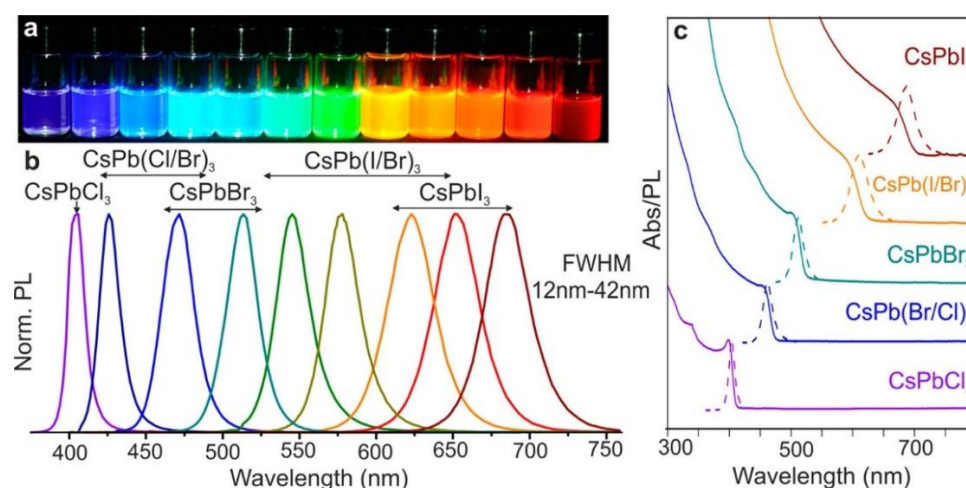


Figure 1.3: Colloidal CsPbX₃ (X = Cl, Br, I) perovskite nanocrystals exhibit size- and composition-tunable bandgap energies covering the entire visible spectral region with narrow and bright emission: (a) colloidal solutions in toluene under UV lamp ($\lambda = 365$ nm); (b) representative PL spectra ($\lambda_{\text{exc}} = 400$ nm for all but 350 nm for CsPbCl₃ samples); (c) typical optical absorption and PL spectra. The figures are reprinted from reference⁴⁰ with permission. Copyright ©2015, American Chemical Society.

Apart from the size-effect, there is another pathway to tune the band gap and the excitonic emission of CsPbX_3 nanocrystals is by anion exchange. The iodide counterpart typically emits in the red range, while the bromide counterpart emits in the green range, and the chloride counterpart shows color in the blue and ultraviolet range.⁴⁰ All these photoluminescence properties are excitonic and can be tuned across the entire visible spectrum by changing the anion from I^- to Br^- to Cl^- (see Figure 1.3).⁴⁰ The emitted colors are bright enough to be detected by the human eye.^{40, 41}

1.6 2D hybrid halide perovskites:

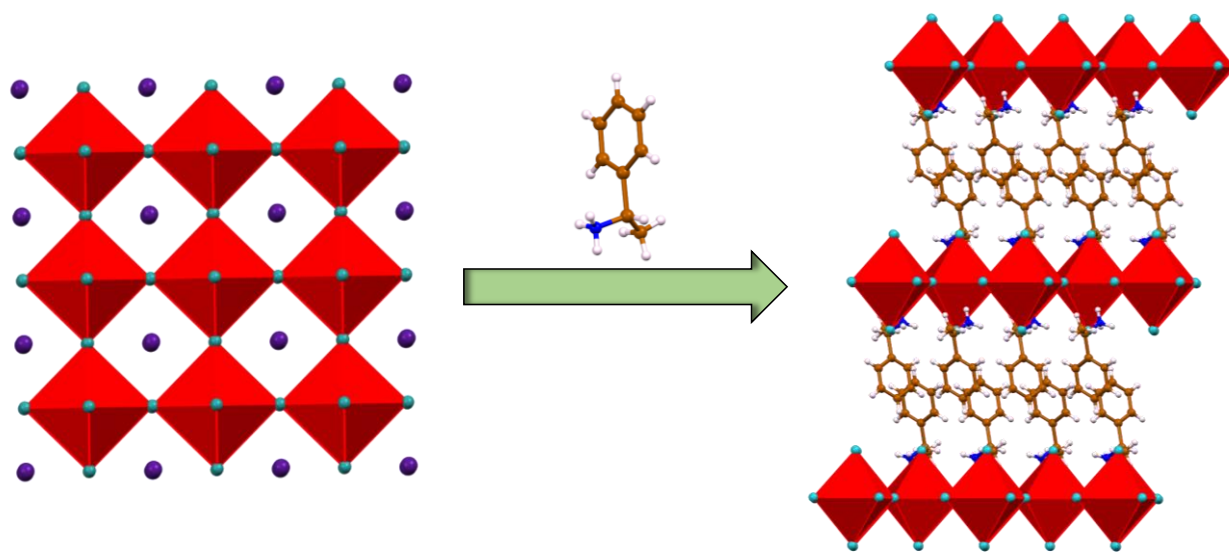


Figure 1.4: Left-hand side structure is 3D perovskites CsPbI_3 . The right-hand side structure is 2D hybrid perovskites $[(\text{S-MBA})_2\text{PbI}_4]$.

3D perovskite is a three-dimensional framework where octahedra are interconnected in all three dimensions, allowing carriers to move through each direction. If a larger A site cation is used instead of a smaller A site cation, the larger cation may not fit into the void, disrupting the connection of BX_3 octahedra in one direction (Figure 1.4),⁴²⁻⁴⁵ leading to either A_2PbX_4 or $\text{A}'\text{PbX}_4$ structures. The A cation is a monovalent ammonium ion, while A' is a divalent ammonium ion, and PbX_4^{2-} constitutes the octahedral sheet extending in two directions.

Rupturing of inorganic sublattice can occur along different crystallographic directions like $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$, as shown in Figure 1.5.⁴² When an organic cation interacts with the inorganic octahedra along the (100) plane, the inorganic octahedra will be separated by a distance along the "a" direction, corresponding to the (100) plane. The interplanar distance refers to the distance between two inorganic layers, which is designated by the (100) plane.

Most of the two-dimensional (2D) perovskites are found to belong to this category, specifically those characterized by the (100) plane.

Slicing along the (100) plane occurs due to the disruption of electrostatic interactions and hydrogen bonding interactions between the ammonium head and the inorganic octahedra. The amine group $-\text{NH}_2$ becomes protonated, transforming into $-\text{NH}_3^+$. This $-\text{NH}_3^+$ head forms electrostatic and hydrogen bonding-like non-covalent interactions with the inorganic cage. The ammonium ions situated between the two inorganic layers can be categorized into two types, as previously mentioned: (i) monovalent ammonium cations, which have one ammonium group at one end, and (ii) divalent ammonium cations, possessing two ammonium groups at different ends.

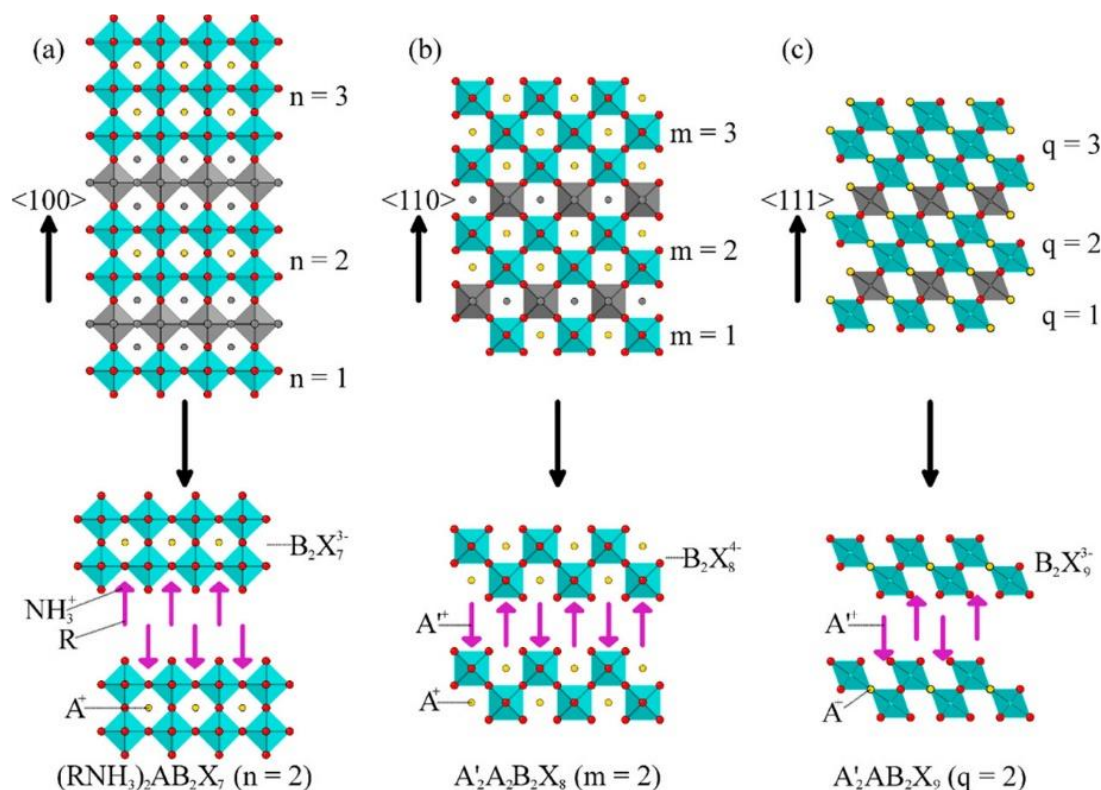


Figure 1.5: Schematic showing the slicing of a 3D perovskite into 2D layered perovskites along the different crystallographic directions: (a) $\langle 100 \rangle$, (b) $\langle 110 \rangle$, and (c) $\langle 111 \rangle$. “ n ” is the number of octahedral layers directly connected in (100) layered perovskites. The analogous of “ n ” in (110) and (111) layered perovskites are “ m ” and “ q ”, respectively. The figure is reprinted from reference ⁴² with permission. Copyright ©2016, American Chemical Society.

Cations can arrange themselves in specific patterns. In an ABAB-type pattern, two cations are positioned such that the octahedra from one layer are shifted to the $(0, 1/2)$ coordinate of the layer beneath,⁴⁶ resulting in a structure known as Ruddlesden-Popper (RP) perovskites (Figure 1.6), represented by the formula A_2PbI_4 . In contrast, when a divalent cation crystallizes in a 2D

hybrid perovskite structure, the inorganic octahedra from consecutive layers align directly on top of each other with a (0,0) coordinate shift, forming an AAAA arrangement.⁴⁷ This structure is referred to as Dion-Jacobson (DJ) perovskites and can be represented by the formula $A'\text{PbI}_4$. The presence of a single amine linked through the inorganic octahedra contributes to the greater rigidity of the DJ phase compared to the RP phase. However, it is noted that tuning various properties is generally easier in the RP phase than in the DJ phase.

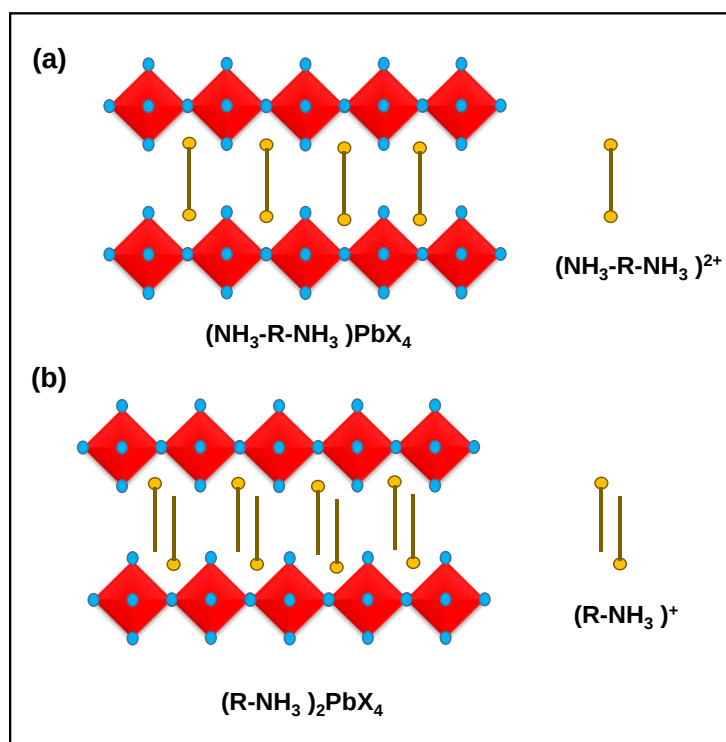


Figure 1.6: (a) Dion-Jacobson and (b) Ruddlesden-Popper type layered 2D hybrid perovskites.

1.7 Quantum well structure in 2D hybrid perovskite:

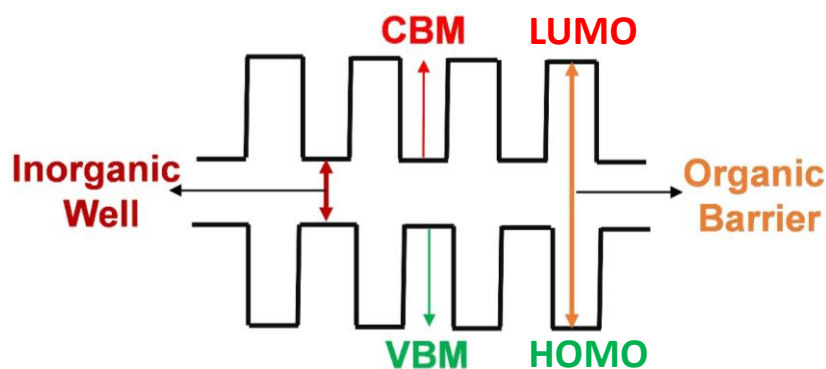


Figure 1.7: Schematic representations of the quantum well structure of 2D layered hybrid perovskites. The red arrow is the band gap, and the orange arrow is the energy gap between the LUMO and HOMO levels of the organic cations.

In 2D perovskites, thin inorganic octahedra possess semiconducting properties and are isolated by an insulating organic sub-lattice, creating a quantum well structure similar to Figure 1.7.⁴⁸⁻

⁵¹ The inorganic octahedra, acting as the inorganic well, define the conduction band minimum (CBM) and valence band maximum (VBM), while the organic sub-lattices serve as the organic barrier, contributing to higher energy levels in the band structure (Figure 1.7).

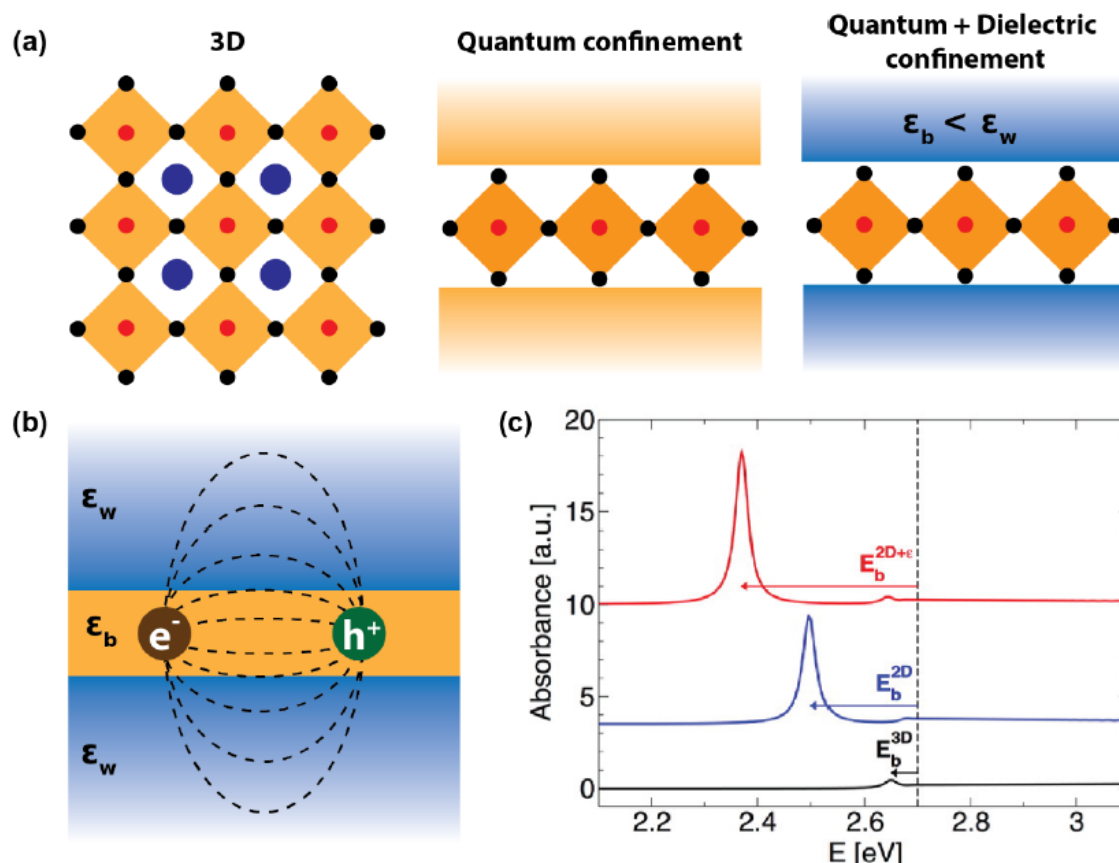


Figure 1.8: Quantum and dielectric confinement effects. (a) Origin of the confinement effects in the halide perovskite lattice. Here, ϵ_w and ϵ_b are the high-frequency dielectric constant of the well and barrier layers, respectively. (b) Schematic of the dielectric confinement in a quantum-well structure. The dashed lines indicate the attractive force acting between the electron and the hole. (c) Simulated effect of quantum and dielectric confinement on optical absorption due to 1s exciton. The band gap is set at 2.7 eV, indicated by the vertical dash-line. The black line is the absorbance spectra computed on a hypothetical 3D system having the same high-frequency dielectric constant as that of the well layer (ϵ_w). The small exciton binding energy, E_b^{3D} corresponds to the 3D exciton. Turning on the quantum confinement effect while keeping the dielectric constant homogeneous shifts the resonance peak at lower energy (blue line). Further incorporating the dielectric confinement results in an additional shift and an enhanced exciton resonance (red line). The figures are from reference⁵² and reprinted from reference⁷⁸ with permission. Copyright @2016, American Chemical Society.

The exciton primarily resides within the CBM and VBM, indicating that it is mainly confined to the inorganic octahedra (see Figure 1.8). Does this suggest that the organic barrier has no

effect? To answer this, we need to explore how the surrounding environment influences the exciton. An exciton is a quasi-particle, and its behavior is affected by the screening capacity of charge carriers (i.e., electron-hole pairs) in different media, which is defined by the dielectric constant of the medium. The dielectric constant of the organic barrier (sub-lattice) is lower than that of the inorganic well (octahedra).⁵²⁻⁵⁴ Although the exciton is confined within the few angstroms of the inorganic well, the electric fields created by the exciton extend through the barrier as well, since the Bohr radius is on the order of nanometers. This leads to decreased screening of the exciton's electric field, resulting in a higher Coulombic attraction between the electron and hole. Thus, it is evident that while the organic sub-lattices may not exhibit a direct effect on exciton photo-physics, such as in photoluminescence (PL), they do have an indirect impact. This raises a critical question: How does the interface chemistry of each sub-lattice in 2D hybrid perovskites affect exciton photo-physics in terms of their optical properties?

1.8 Interface of 2D hybrid halide perovskites:

The 2D hybrid structure consists of organic sub-lattices sandwiched between two inorganic sub-lattices. The semiconducting inorganic layer and the insulating organic layer create an interface held by hydrogen bonding and electrostatic interactions.⁵⁵⁻⁵⁸ These interactions enable communication between the layers, resulting in new physical and chemical properties such as new photoluminescence channels and chirality. Consequently, modulating the organic sublattice can also introduce new properties in 2D hybrid perovskite.

1.8.1 Chirality in 2D hybrid perovskites:

Chiral hybrid perovskites combine chiral ammonium ions with inorganic sub-lattices to create materials that exhibit unique properties. Organic semiconductors like polythienylenevinylene, as well as Chiral amines, while offering chirality, typically exhibit low charge transport capabilities, with electron mobility values ranging from 0.1 to 0.4 cm²/V·s.⁵⁹ In contrast, typical inorganic semiconductors like GaAs have much higher electron mobility, approximately 0.3×10^4 cm²/V·s.⁶⁰ However, GaAs lacks the chirality that chiral ammonium ions introduce. To bridge this gap, researchers have developed chiral hybrid perovskites that incorporate chiral ammonium ions alongside achiral inorganic sublattice. This combination aims to achieve a balance in electron mobility, providing enhanced performance for device applications while still utilizing the beneficial properties owed by chirality. This innovative approach allows for the design of materials that can potentially capitalize on both high mobility and chiral characteristics.

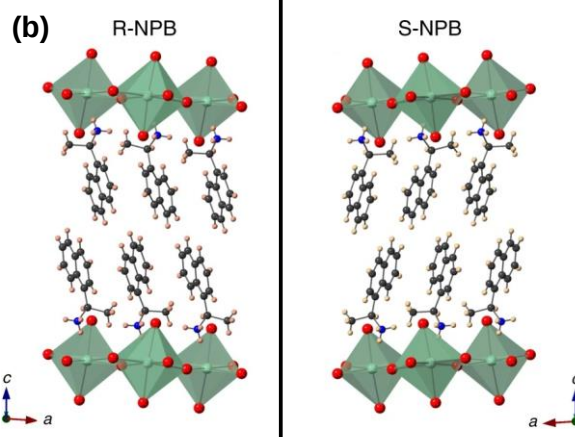
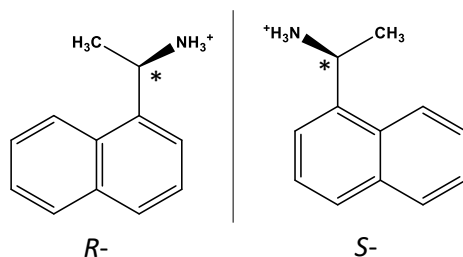
(a) NEA = 1-Naphthylethylammonium

Figure 1.9: (a) Mirror image structure of (R/S)- naphthylethylammonium (NEA). (b) Mirror image structure of *R*- and *S*-NPB. [NPB= (NEA)₂PbBr₄]. The figure is reprinted from reference⁵⁵ with permission. Copyright ©2020, Springer Nature.

Chiral organic ammonium cations, such as (R/S)-naphthylethylammonium, indeed exhibit a property known as handedness, which creates in the presence of *R*- and *S*-isomers—structural mirror images of each other (see Figure 1.9a). When these chiral ammonium ions are incorporated into hybrid perovskites, the resulting material retains the chirality characteristic of the original organic molecule (Figure 1.9b).^{55, 61} The ability of the hybrid perovskite to exhibit this mirror image relationship can be attributed to several factors, including noncovalent interactions and electrostatic forces.^{55, 62} Noncovalent interactions, such as hydrogen bonding, van der Waals forces, and ionic interactions, can play a crucial role in stabilizing the chiral arrangement within the perovskite structure.^{61, 63-65} These interactions help to maintain the overall chiral nature of the material. Electrostatic interactions between the charged ammonium ions and the inorganic sublattice can further influence the arrangement and orientation of the chiral ammonium within the hybrid structure.⁵⁵ This can lead to variations in how the chiral unit aligns with the inorganic components. This chirality characteristic leads to distinct interactions with different polarization states of light, as these isomers interact differently with left circularly polarized light (LCP) and right circularly polarized light (RCP), leading to circular dichroism (CD). Chiral ammonium ions usually exhibit circular dichroism in the ultraviolet (UV) or visible range.⁶¹ However, when these cations are incorporated into hybrid perovskites, they demonstrate distinct circular dichroism (CD) properties. These distinct circular dichroism properties are coming from the absorption maxima of the hybrid perovskites, which are associated with the inorganic octahedral (Figure 1.10). Therefore, circular dichroism signifies in favours of chirality induction.

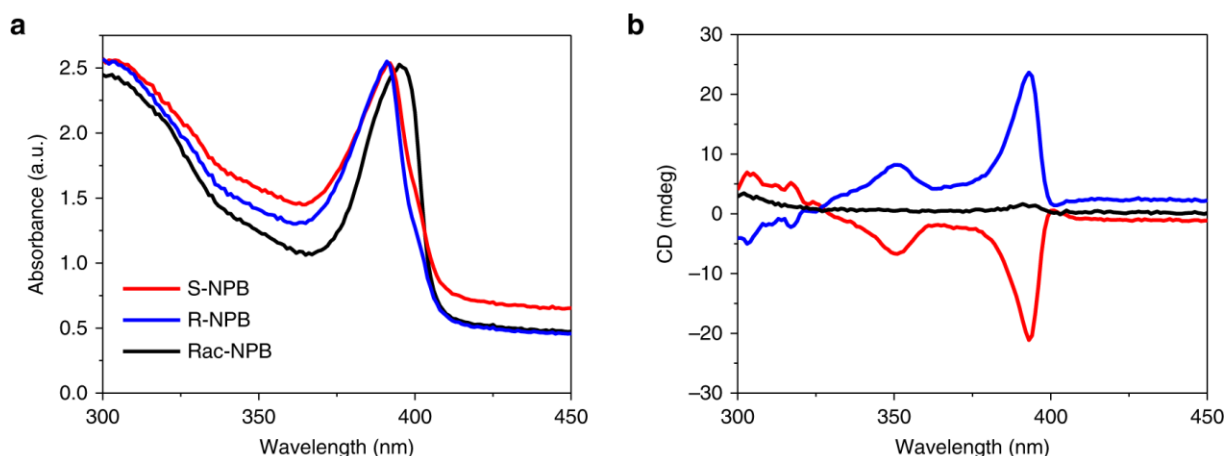


Figure 1.10: (a) UV–Vis linear absorption spectra and (b) circular dichroism (CD) spectra recorded at room temperature for thin films of racemic-, *R*- and *S*-NPB [NPB= (NEA)₂PbBr₄]. The figures are reprinted from reference⁵⁵ with permission. Copyright ©2020, Springer Nature

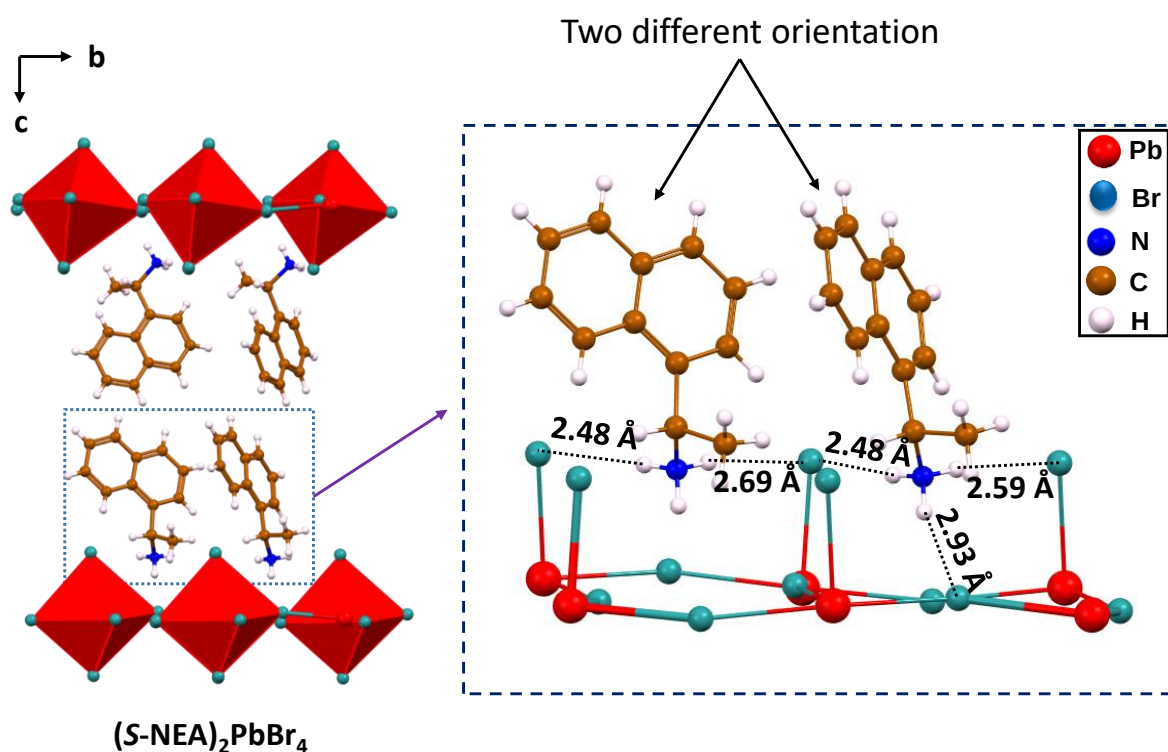


Figure 1.11: Crystal structure of (S-NEA)₂PbBr₄. A magnified view of a small portion of the interface has been given on the right-hand side.

The first question that arises in mind is how chirality is induced from the organic sub-lattices to the inorganic sub-lattices through non-covalent and electrostatic interactions. In most reported chiral hybrid perovskites, the chiral organic ions exist in two different orientations, a phenomenon known as the orientation effect.^{55, 56, 64, 66, 67} This orientation effect leads to asymmetric hydrogen bonding at the organic-inorganic interface (Figure 1.11). Consequently,

the chiral organic ammonium ions induce chirality through non-covalent and electrostatic interactions.

1.8.2 Intercalation in 2D hybrid perovskites:

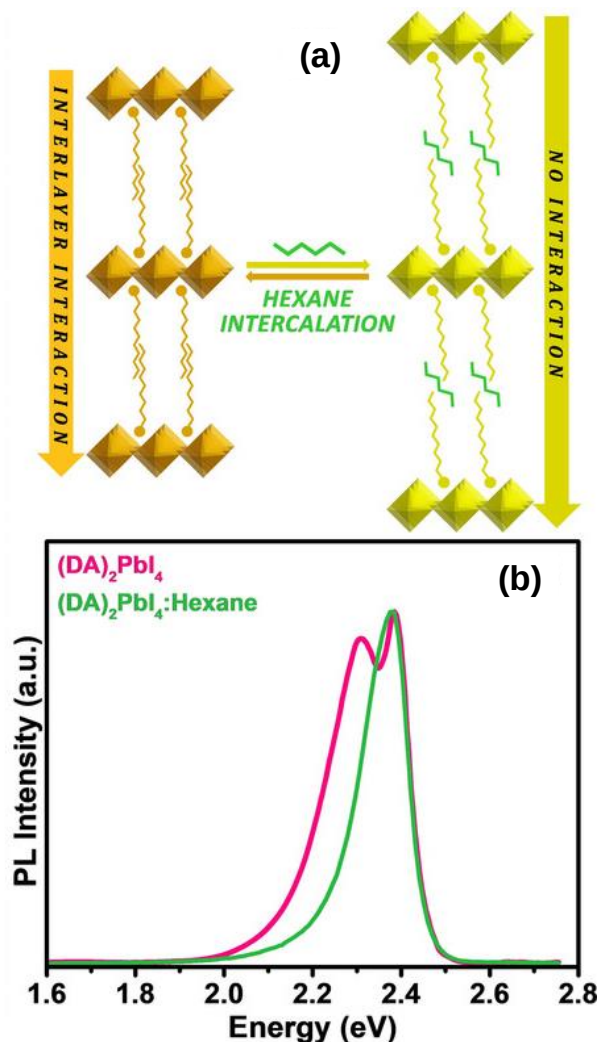


Figure 1.12: (a) Schematic representation of the reversible intercalation of molecular hexane in $(\text{DA})_2\text{PbI}_4$ single crystal. b) PL spectra of $(\text{DA})_2\text{PbI}_4$ single crystal before and after hexane intercalation. The figures are reprinted from reference⁵⁷ with permission. Copyright ©2020, John Wiley and Sons.

Some peculiar features of 2D hybrid halides have led researchers to explore intercalation.⁵⁷ For example, 2D hybrid perovskite structures, such as butylammonium lead iodide, exhibit two maxima in band-edge absorption and emission.⁶⁸ This suggests the presence of two distinct band gaps, which can be quite confusing. Many researchers have speculated that the unusual emission profiles arise from interactions between the inorganic sublattices.^{57, 68} It has been shown that intercalation in 2D hybrid perovskite-like structures, such as $(\text{BA})_2\text{PbI}_4$, $(\text{DA})_2\text{PbI}_4$ (where DA = decylamine), and $(\text{PEA})_2\text{SnI}_4$ (where PEA = phenylethylammonium),⁶⁹

eliminates the higher energy emission peak, likely linked to inorganic interlayer interactions.⁵⁷ The intercalating agents disrupt the hydrophobic tails of the organic sublattice. Sheikh et al. demonstrated that the photoluminescence (PL) spectra can reversibly switch from dual emission to single emission upon reversible intercalation (Figure 1.12).⁵⁷ Consequently, intercalation can also modulate exciton photo-physics, particularly in terms of photoluminescence.

1.9 Doping in 2D hybrid perovskites:

The incorporation of dopants such as Yb^{3+} and Mn^{2+} into a 3D perovskite structure like CsPbX_3 (where X can be Cl, Br, or I) has been shown to lead to remarkable optical, optoelectronic, and magneto-optic properties.⁷⁰⁻⁷⁵ Among these, the emission spectra from Yb^{3+} and Mn^{2+} , which occurs through energy transfer from the perovskite host to the dopant, is one of the most extensively studied phenomena.^{76, 77} In 3D perovskite quantum-confined nanocrystals, the energy transfer from excitons to dopants is significantly more efficient compared to bulk crystals.^{76, 77} This efficiency arises because the reduced dimensions of host crystallite size enhance the coupling between the excitons and the dopants, leading to improved emission characteristics. When transitioning to a 2D hybrid perovskite structure, the inorganic sublattices shrink to a few angstroms in thickness, resulting in a very confined excitonic system. This atomic thinness facilitates an efficient energy transfer to dopants due to the strong coupling in the layered structure. However, doping with Yb^{3+} , which carries a III charge, presents challenges, as its charge non-compatibility with the 2D structure, is limited. In contrast, Mn^{2+} ions, which exist in II oxidation state, can be easily incorporated into the 2D hybrid perovskite structures. This ability to integrate Mn^{2+} leads to the emergence of new emission channels within the material, highlighting the significant impact of dopant choice on the optical properties of hybrid perovskites. Consequently, researchers continue to explore the potential of 2D hybrid perovskites with Mn^{2+} doping to use for optoelectronic applications.

1.10 Scope of the thesis:

The broad objective the thesis is to rationally design the organic-inorganic interface of 2D hybrid halide perovskites to tailor the optoelectronic properties. Although excitons are confined within the inorganic sub-lattice, a thoughtful design of the organic sub-lattice can significantly change the excitonic photo-physics. Consequently, molecular design of the interface is explored here to introduce new optoelectronic functionalities of 2D hybrid perovskites. The organic and inorganic sub-lattices interact with each other through various non-covalent

interactions, such as electrostatic-, hydrogen-, and halogen-bonding interactions. Our molecular design mainly stems from controlling those non-covalent interactions, along with doping the inorganic sub-lattices.

In Chapter 2, we present a concept for designing chiral hybrid perovskites by utilizing different conformers of chiral A-site ions. Specifically, the gauche- and anti-conformers of 1-iodopropan-2-ammonium (IdPA) (see Figure 1.13) are alternately arranged in the structure (R-/S-IdPA)₂PbI₄. The anti-conformer of the IdPA ion exhibits significantly stronger electrostatic, hydrogen bonding, and halogen bonding interactions with the inorganic [PbI₄]²⁻ sub-lattices compared to the gauche-conformer. This periodic asymmetry in non-covalent interactions probably helps in inducing helical chirality in (R-/S-IdPA)₂PbI₄ 2D perovskite.

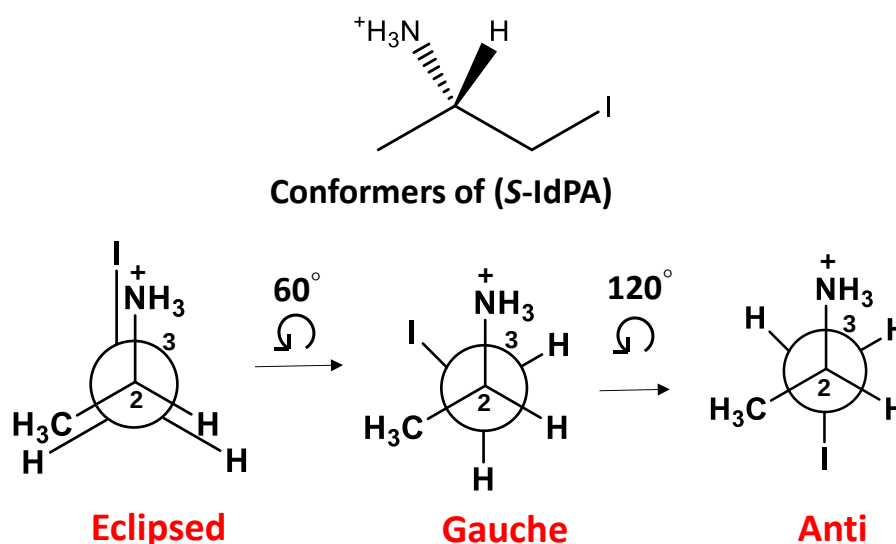


Figure 1.13: Three major conformers of S-IdPA that have been proposed to incorporate to synthesised (S-IdPA)₂PbI₄.

Another way to tailor the optoelectronic properties is by molecular intercalation through the labile organic sub-lattice. In chapter 3, We intercalated hexafluorobenzene (HFB) in phenethylammonium tin iodide [(PEA)₂SnI₄], as shown in Figure 1.14. The strong non-covalent π - π interactions between the HFB molecules and PEA ions lead to a stable intercalated structure. Importantly, the intercalation increases the bandgap and suppresses the non-emissive states at cryogenic temperatures. These findings show that the intercalation in organic sub-lattice alters the excitonic absorption and emission that is mainly originating from inorganic sub-lattice.

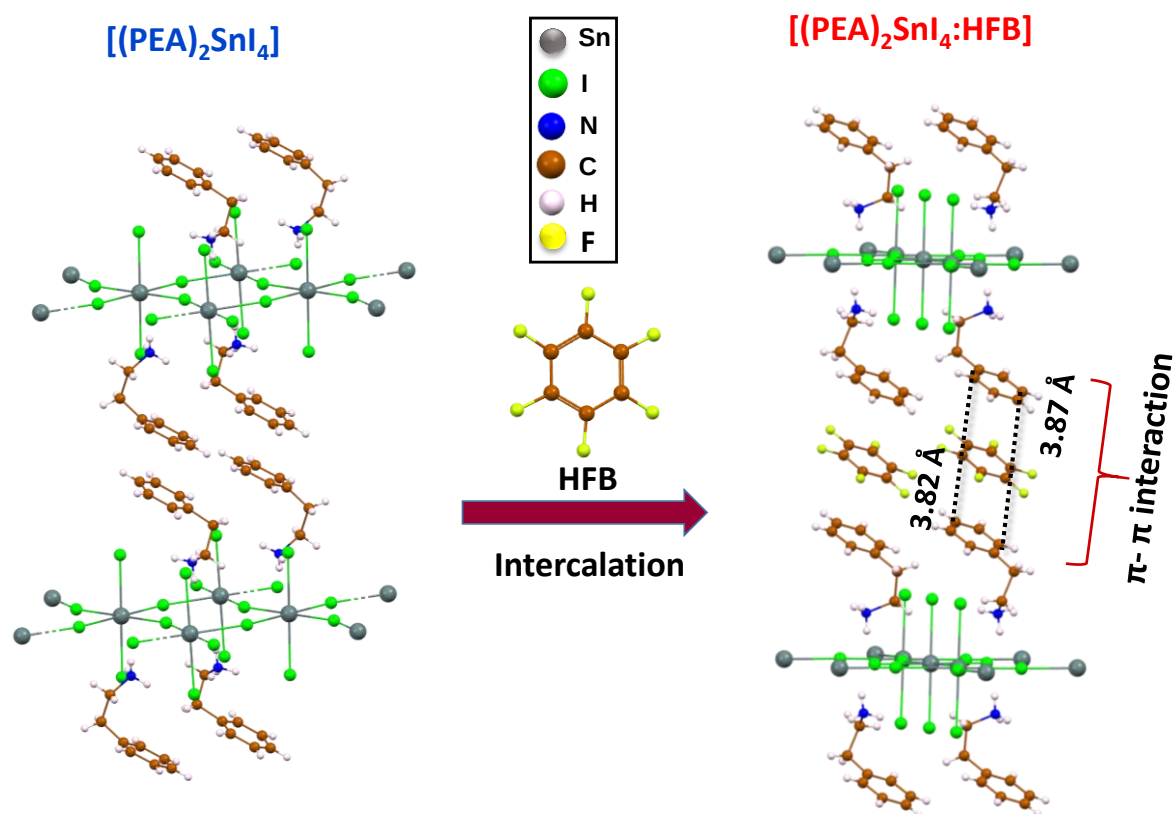


Figure 1.14: Intercalation of hexafluoroenzene (HFB) in phenethylammonium tin iodide $(\text{PEA})_2\text{SnI}_4$ 2D perovskite.

We also tailored the luminescence property by doping the inorganic sub-lattice. In Chapter 4, we doped Mn^{2+} ions in the single crystals of butyl ammonium lead bromide $[(\text{BA})_2\text{PbBr}_4]$. Figure 1.15 shows only one $(\text{BA})_2\text{PbBr}_4$ hybrid layer with Mn^{2+} dopant. The dopant site near the edge of the layer is marked as red sphere, and that at the interior of the layer is yellow sphere. Similarly, the red exciton is edge exciton and the yellow exciton is interior exciton.

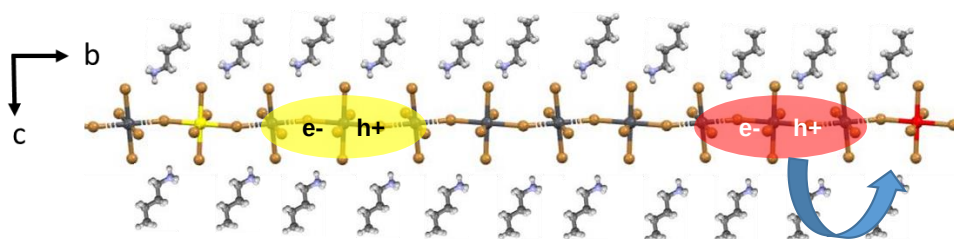


Figure 1.15: One hybrid layer of butylammonium lead bromide, where the inorganic layer has two kinds of doping sites, edge- and interior-site denoted by red and yellow colored spheres, respectively. The excitons ($e^- - h^+$ pair) located near the interior- and edge-sites are presented by yellow and red backgrounds.

The exciton marked in red will efficiently transfer energy to the red-dopant site, while the red dopant will experience minimal energy transfer from the yellow-colored exciton as energy

transfer from host exciton to dopant is distance dependent. Consequently, we can see edge exciton, facilitates efficient energy transfer to the dopant sites suggesting that the dopants are predominantly present at the near layer edges.

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Chapter 2

Conformer-Mediated Helical Chirality in 2D Layered Hybrid Perovskites

The work presented in this chapter is published in the following articles:

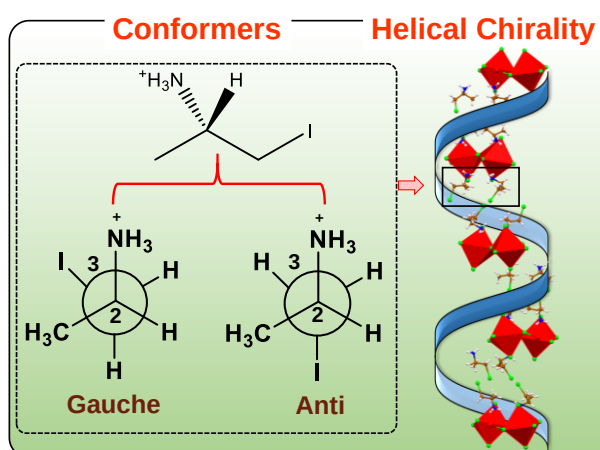
Dutta, T.; Swain, D.; Nag, A. Conformer-Mediated Helical Chirality in 2D Layered Hybrid Perovskites *Angew. Chem. Int. Ed.* **2025**, e202422550

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Declaration: Dr. Diptikanta Swain from Institute of Chemical Technology-Indian Oil Odisha campus, Bhubaneswar, has helped in the refinement of single crystal x-ray diffraction (XRD) data and profile fitting of powder XRD pattern.

Abstract:

Two-dimensional (2D) chiral hybrid perovskites A_2PbI_4 (A: chiral organic ion) enable chirality controlled optoelectronic and spin-based properties. A^+ organic sublattice induces chirality into the semiconducting $[PbI_4]^{2-}$ inorganic sublattice through non-covalent interactions at organic-inorganic interface. Often, the orientations of A^+ cations in the lattice have different orientations, leading to asymmetry in the non-covalent interactions. In a novel approach, we use different conformers of A^+ cations to create asymmetry in the non-covalent interactions, thereby, achieving chiral perovskites with rare helical enantiomorphic structures. We prepared $(R\text{-IdPA})_2PbI_4$ and $(S\text{-IdPA})_2PbI_4$ (IdPA: 1-iodopropan-2-ammonium) which crystallize in the helical enantiomorphic space groups $P4_32_12$ and $P4_12_12$, respectively. The gauche- and anti-conformers of IdPA^+ are arranged alternatively in the hybrid structure. Importantly, the anti-conformer of IdPA^+ ion have significantly stronger electrostatic, $\text{N-H}\cdots\text{I}$ hydrogen bonding, and $\text{I}\cdots\text{I}$ halogen bonding interactions with the $[PbI_4]^{2-}$ sublattice, compared to the gauche-conformer. This periodic asymmetry in non-covalent interactions caused by the alternative arrangement of gauche- and anti-conformers induces chirality in the inorganic sublattice with four-fold screw axes (4_3 and 4_1). The enantiomers $(R\text{-}/S\text{-IAP})_2PbI_4$ show mirror-image like circular dichroism from excitonic absorption of the inorganic sublattice. This conformer-based design of chiral hybrid perovskites in helical space groups broadens material choices for advanced optoelectronic applications.

Graphical Abstract:

2.1 Introduction:

Two dimensional (2D) chiral hybrid lead halide perovskites combines structural asymmetry, semiconducting charge transport and strong spin orbit coupling. Therefore, they promise to exhibit interesting chiral optoelectronic and spin-based properties. For example, circular dichroism (CD),¹⁻³ circularly polarized luminescence (CPL),⁴ circularly polarized photodetectors,⁵⁻⁶ chiral-induced spin selectivity (CISS),⁷⁻⁸ Rashba-Dresselhaus spin-splitting,⁹ ferroelectricity, circular photogalvanic effect (CPGE),¹⁰ and nonlinear optical properties¹¹ have already been observed from different chiral hybrid perovskites.¹²⁻¹³ However, the efficiency values of the observed properties are often limited for real-life applications.

In order to realize the full potential of chiral hybrid perovskites, a better understanding of the chirality induced structure-property relationship is required. For example, it has been shown that though the overall crystal structure of 2D *R/S*-1-methyl benzylammonium lead iodide ((*R/S*-MBA)₂PbI₄) is chiral, the [PbI₄]²⁻ inorganic sublattice remains centrosymmetric (achiral).⁹ The organic chiral cations can induce the chiro-optic properties like CD and CPL, but did not induce structural chirality in the semiconducting inorganic lattice. In difference, *R*-(+)- or *S*-(-)-1-(1-naphthyl)ethylammonium lead bromide ((*R/S*-NEA)₂PbBr₄) show structural chirality in the inorganic [PbBr₄]²⁻ sublattice, and this symmetry-breaking lead to a substantial Rashba-Dresselhaus spin-splitting with opposite spin textures between *R*- and *S*-hybrids.⁹ The induction of chirality in the inorganic sublattice of (*R/S*-NEA)₂PbBr₄ was attributed to the strong asymmetric hydrogen bonding between the organic and inorganic sublattice. But (*R/S*-NEA)₂PbBr₄ with space group of *P*2₁, does not possess the helical right- or left-handed enantiomorphic structural chirality. Perhaps, most of the reported chiral hybrid perovskites crystallizes in the non-enantiomorphic space groups without having the helical structure.¹⁴⁻¹⁶ The first report of the helical chiral hybrid perovskite was *R*-1-(4-bromophenyl)ethylammonium lead iodide and *S*-1-(4-bromophenyl)ethylammonium lead iodide with enantiomorphic space groups *P*4₃2₁2 and *P*4₁2₁2.¹⁰

It is evident that the nature of the chiral organic sublattice mainly controls the nature of chirality of the inorganic sublattice, but the mechanistic insights behind the control parameters are unclear. In a typical chiral hybrid perovskites like (*R*-MBA)₂PbI₄ or (*R*-NEA)₂PbBr₄, the orientations of the adjacent organic ammonium ions are different, meaning that the adjacent organic cations are rotated with respect to each other.^{2, 9-10, 17-18} Probably such change in orientation helps enhancing the asymmetry in non-covalent interactions at organic-inorganic

interface. Another interesting aspect is that the organic ammonium ions can have different conformers, where the ion has different spatial arrangements due to rotations of a single (C-C) bond. But how such conformers of organic cation influence the chirality of hybrid perovskites? Here we address this question with the example of chiral organic ammonium ions (*R/S*) 1-iodopropan-2-ammonium (*R*-IdPA or *S*-IdPA), as shown in Figure 2.1a. Importantly, the rotation of C₂-C₃ bond can give rise to different conformers like eclipsed or gauche or anti, as shown in Figure 2.1b. The target is to achieve more than one conformers of the (*R/S*)-IdPA in the hybrid 2D perovskite (*R*-IdPA)₂PbI₄ and (*S*-IdPA)₂PbI₄, and subsequently explore the role of organic conformers in inducing structural chirality in the inorganic sublattice.

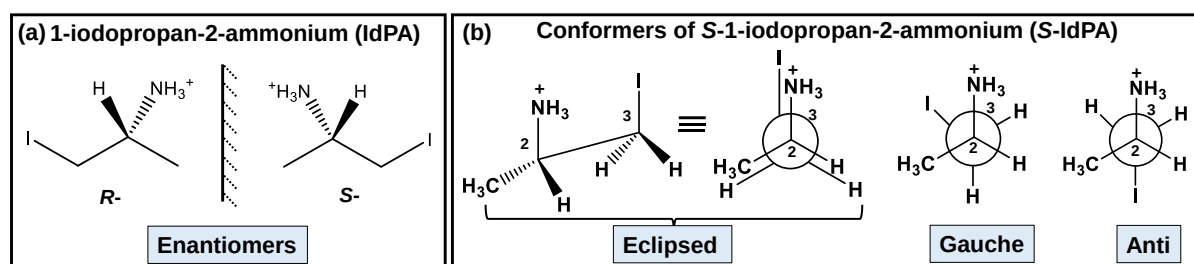


Figure 2.1: (a) Schematics representation of *R*- and *S*- enantiomers of 1-iodopropan-2-ammonium ions (*R*-IdPA and *S*-IdPA). (b) Newman projection of different conformers (eclipsed, gauche and anti) of *S*-IdPA. The correlation between sawhorse and Newman projection has been shown only for the eclipsed conformer.

Here, we could rationally design chiral 2D hybrid perovskites (*R/S*-IdPA)₂PbI₄ containing both the gauche- and anti-conformers of *R/S*-IdPA. Interestingly, the (*R*-IdPA)₂PbI₄ and (*S*-IdPA)₂PbI₄ crystallizes in the helical enantiomorphic space groups *P*4₃2₁2 and *P*4₁2₁2, respectively. The gauche- and anti-conformers are arranged alternatively in the periodic organic sublattice. Importantly the nature of non-covalent interactions, namely, electrostatic, hydrogen-bonding and halogen-bonding (I⋯I) interactions, at the organic-inorganic interface are found to be very different for the gauche- and anti-conformers. This asymmetry in non-covalent interaction probably induced the structural helicity in the inorganic sublattice. Owing to the chiral structure, the (*R/S*-IdPA)₂PbI₄ show mirror-image like CD spectra. The structure remains stable in wide temperature range of 15-403 K, allowing us to explore temperature dependent photoluminescence (PL) properties of (*R/S*-IdPA)₂PbI₄.

2.2 Experimental Section:

2.2.1 Chemicals: Lead oxide (Sigma Aldrich, PbO, 99.9%), hydroiodic acid (HI, Sigma Aldrich, 57% w/w in water), hypophosphorous acid (H₃PO₂, Avra chemicals, 50% w/w in water), (*R*)-(-)-2-amino-1-propanol (Sigma Aldrich, 98%), (*S*)-(+)-2-amino-1-propanol (Sigma

Aldrich, 98%), acetonitrile (Sigma Aldrich, HPLC, gradient grade $\geq 99.9\%$), diethyl ether (Rankem, Analytical grade, $\geq 99.5\%$), acetone (Rankem, 99.7%), isopropanol (Rankem, 99%).

2.2.2 Synthesis of $(R/S\text{-IdPA})_2\text{PbI}_4$ [IdPA = $\text{I}-(\text{CH}_2)_2-(\text{CH}_3)(\text{NH}_3)$, or 1-iodopropane-2-ammonium] single crystals: The single crystals of $(R/S\text{-IdPA})_2\text{PbI}_4$ were synthesized using acid precipitation method. 1 mmol PbO was dissolved in 2.5 mL HI and 0.2 mL hypophosphorus acid at 70°C under magnetic stirring. After that 2 mmol of (R/S) -2-amino-1-propanol has been added to the reaction mixture. The solution was stirred at 110°C for 1 hour. The $-\text{OH}$ of R - or S -2-amino-1-propanol got replaced with $-\text{I}$ of HI, along with ionization, forming R - or S -IdPA, similar to prior reports. The stirring was stopped and the solution was cooled down to room temperature. Then the solution was kept undisturbed for a day, yielding orange colored plate-like crystals. The supernatant was decanted and the crystals were washed with diethyl ether through suction filtration. The crystals were stored in vacuum desiccator and used for further study.

2.2.3 Film deposition of $(R/S\text{-IdPA})_2\text{PbI}_4$: Substrates (quartz or sapphire) were cleaned in soap water, acetone, isopropanol in a stepwise manner via ultrasound sonication. Then the substrates were dried in nitrogen flow. Then the substrates were treated with UV-ozone for 15 minute and were used for spin coating. Around 10 mg of $(R/S)\text{-(IdPA)}_2\text{PbI}_4$ crystals was dissolved in 100 μL acetonitrile via ultrasound sonication. The solution was then spin coated on the quartz or sapphire substrates at 2500 rpm for 30 s. The obtained films were annealed at 50°C for 10 min.

2.2.4 Structural characterization: Single crystal X-ray diffraction (XRD) data of both the crystals [$(R/S)\text{-(IdPA)}_2\text{PbI}_4$] were collected through Bruker Smart Apex Duo Diffractometer at two different temperatures 150 K and 296 K using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The single crystals were selected under an optical microscope and mounted on glass tip holder. For 150 K data, the crystals were kept under constant liquid nitrogen flow during the experiment. The frames have been integrated with the Bruker SAINT software package. The structures have been solved by the direct method using SHELXS and refined by full-matrix least-squares on F^2 using the SHELXL, as implemented in WinGX. Symmetry analysis of all structures were also performed using PLATON's ADDSYM tool on both the inorganic framework and the hybrid structure. The CIF files, containing the anisotropic displacement parameters, and the atomic positions obtained from the refinement, are available via CCDC with codes 2402785, 2402788, 2402792, 2402794.

Powder X-ray diffraction (PXRD) measurements at room temperature were performed using a Bruker D8 Advance X-ray diffractometer, employing Cu K α radiation in Bragg–Brentano geometry. For low temperature measurements, the powder XRD patterns were collected in a wide temperature range of 15 to 300 K using Malvern Panalytical Empyrean Series-III X-ray diffractometer equipped with Cu K α radiation and a 1Der strip detector.

Thermal stability of the sample was checked by thermogravimetric analysis (TGA) measurements carried out on powder samples under nitrogen atmosphere, with a Mettler Toledo system. Differential scanning calorimetry (DSC) measurements were also performed on powdered samples using a Mettler Toledo DSC823 system. About 2 mg of a powder sample and a reference were heated from 123 K to 493 K in a nitrogen atmosphere at a rate of 10 °C per minute.

2.2.5 Optical properties: UV-visible absorption spectra were recorded using Agilent Technologies Cary Series UV-Vis spectrophotometer. The spectra were recorded in the transmittance mode for films of (*R*-/*S*-IdPA)₂PbI₄ and solutions of *R*- or *S*-2-amino-1-propanol. Steady-state photoluminescence (PL) spectra were recorded using the FLS 980 spectrophotometer (Edinburgh Instruments). A 375 nm (3.31 eV) picosecond pulsed diode laser was the excitation source for recording the PL. Temperature-dependent PL measurements were carried out in the same Edinburgh instrument coupled with a cryostat. Films of (*R*-/*S*-IdPA)₂PbI₄ on sapphire substrate were fitted in gold-coated holders. The samples were then inserted in a closed cycle helium cryostat from Advanced Research Systems, which was attached with a Lake Shore 335 temperature controller to achieve the desired temperatures in the range of 6 K to 300 K.

Circular Dichroism (CD) measurements were performed using a Jasco J-815 spectropolarimeter. The CD spectra were acquired at a scan speed of 50 nm per minute, with 1 nm resolution, response time of 2 seconds, and 4 accumulations. The CD spectra were also recorded in transmittance mode using films of (*R*-/*S*-IdPA)₂PbI₄ and solutions of *R*- or *S*-2-amino-1-propanol.

2.3 Results and Discussion:

2.3.1 Synthesis and crystal structure of (*R*-/*S*-IdPA)₂PbI₄ with two conformers of IdPA:

The synthesis of (*R*-/*S*-IdPA)₂PbI₄ was carried out by using a modified acid precipitation method.¹⁹ Stoichiometric amount of PbO (1 mmol) and *R*- or *S*-2-amino-1-propanol (2 mmol)

are mixed in 2.5 mL HI and 0.2 mL of H_3PO_2 acid with magnetic stirring, forming a clear solution at 70 °C. The temperature of the reaction mixture was then raised to 110 °C, and maintained at that temperature for 1 hour. In the process, we expect the replacement of $-\text{OH}$ of *R*- or *S*-2-amino-1-propanol with $-\text{I}$ of HI, along with ionization, forming *R*- or *S*-IdPA.²⁰⁻²¹ The solution was cooled down to room temperature and kept undisturbed. Orange colored flake-like crystals appeared after one day. The crystals were washed with diethyl ether, dried, and stored in a vacuum desiccator. After characterization, the crystals were found to be 2D hybrid perovskite enantiomers $(R/S\text{-IdPA})_2\text{PbI}_4$.

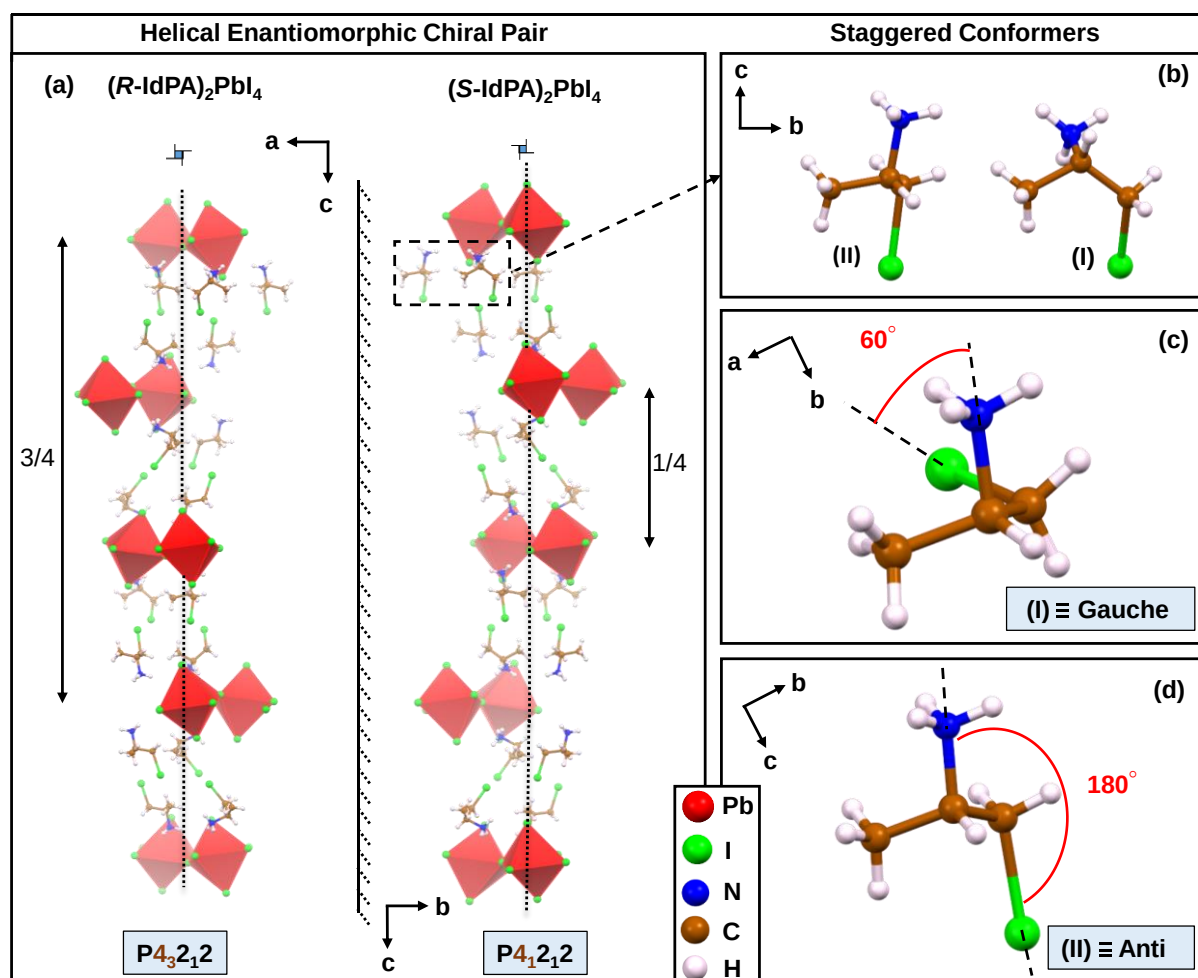


Figure 2.2: Crystal structure and conformers of chiral cation in $(R/S\text{-IdPA})_2\text{PbI}_4$ obtained from single crystal XRD data measured at 296 K. (a) Packing of $(R\text{-IdPA})_2\text{PbI}_4$ and $(S\text{-IdPA})_2\text{PbI}_4$. Non-superimposable mirror image symmetry is there between the two structures, as they are enantiomorphic pair. The 4_3 and 4_1 screw axes are shown by vertical dotted lines, which represent the helical chirality in the structure. (b) Magnified view of two adjacent *S*-IdPA cations marked as (I) and (II) present in the crystal structure of $(S\text{-IdPA})_2\text{PbI}_4$. When viewed from different directions, then (c) the conformer (I) is found to be gauche-conformer, and (d) the conformer (II) is found to be anti-conformer of *S*-IdPA in the crystal of $(S\text{-IdPA})_2\text{PbI}_4$.

Single crystal X-ray diffraction (XRD) data show the formation of 2D layered hybrid perovskites with space group for $(R\text{-IdPA})_2\text{PbI}_4$ is $P4_32_12$, while that for $(S\text{-IdPA})_2\text{PbI}_4$ is $P4_12_12$ at 296 K. The structure is shown in both Figure 2.2a and Figure 2.3. Crystallographic details are provided in Table 2.1 and 2.2. The obtained space groups $P4_32_12$ (left handed) and $P4_12_12$ (right handed) are non-superimposable enantiomorphic pair showing helical chirality (see Figure 2.2a), which is rare in the material class of chiral hybrid perovskites. Both samples crystallize in a primitive tetragonal unit cell having eight formula units per unit cell ($Z = 8$). Both structures display an unusually long c-axis for a chiral hybrid perovskite structure, likely to accommodate the 4_3 and 4_1 screw axes. It is to be noted that the majority of the reported chiral hybrid perovskites show only two-fold rotation/screw axes, unlike the present case of four-fold 4_3 and 4_1 screw axes, which in principle is expected to enhance Rashba-like effects in the electronic band structure.²²⁻²³

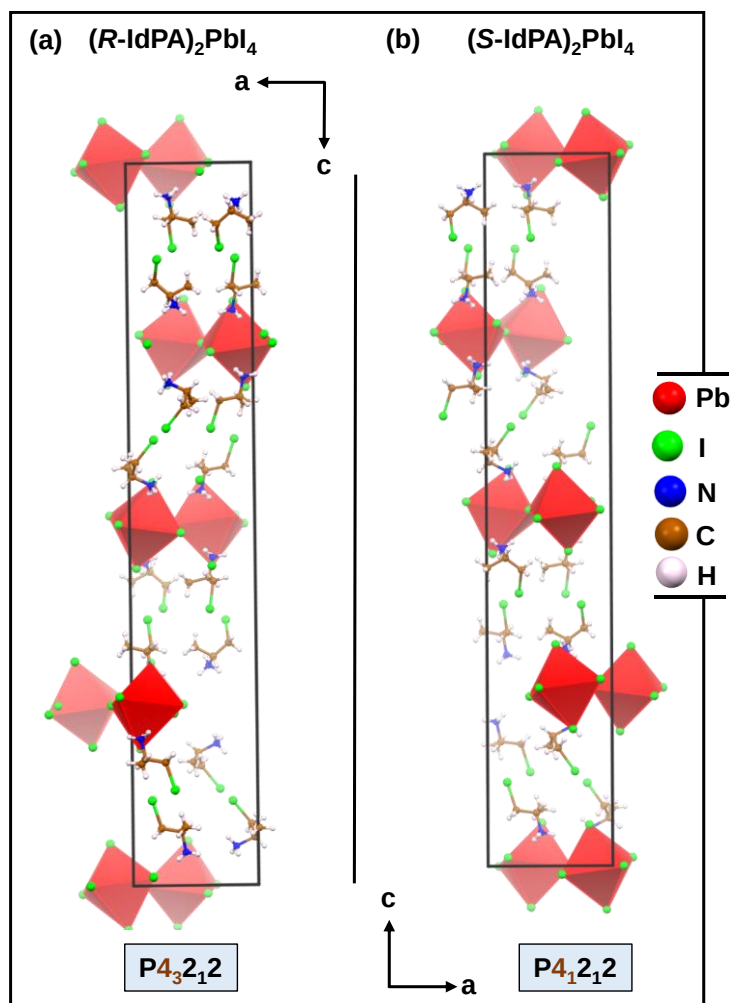


Figure 2.3: Packing in a unit cell (a) $(R\text{-IdPA})_2\text{PbI}_4$, and (b) $(S\text{-IdPA})_2\text{PbI}_4$ obtained from single crystal XRD data measured at 296 K.

Table 2.1: Crystallographic data for (S-IdPA)₂PbI₄ obtained from single crystal XRD data collected at 296 and 150 K.

	(S-IdPA) ₂ PbI ₄	
Temperature (K)	296(2)	150(2)
Empirical formula	(C ₃ H ₆ INH ₃) ₂ PbI ₄	(C ₃ H ₆ INH ₃) ₂ PbI ₄
Formula weight (g/mol)	1086.81	1086.81
Wavelength (Å)	0.71073	0.71073
Crystal System	Tetragonal	Tetragonal
Space group	<i>P</i> 4 ₁ 2 ₁ 2	<i>P</i> 4 ₁ 2 ₁ 2
Unit cell dimensions (Å)	a= b =9.0240(7), c=51.751(4)	a= b =8.9790(11), c=51.091(9)
Volume (Å ³)	4214.2(7)	4119.1(12)
Z	8	8
Calculated density (g/cm ³)	3.426	3.505
F(000)	3744	3744
Crystal size (mm ³)	0.18× 0.15× 0.12	0.18× 0.15× 0.12
θ _{min,max}	2.291, 25.688	2.303, 25.780
h _{min,max}	-10, 11	-10, 7
k _{min,max}	-11, 10	-9, 10
l _{min,max}	-48, 63	-58, 62
Absorption coefficient (mm ⁻¹)	16.781	17.169
Unique reflections/ No. parameters	3997/103	3952/104
Goodness-of-fit	1.089	1.068
Final R indices (I>2σ (I))	R _{obs} =0.0684 wR _{obs} =0.1465	R _{obs} =0.0717 wR _{obs} =0.1742
CCDC Number	2402785	2402788

Table 2.2: Crystallographic data for (R-IdPA)₂PbI₄ obtained from single crystal XRD data collected at 296 K and 150 K.

	(R-IdPA) ₂ PbI ₄	
Temperature (K)	296(2)	150(2)
Empirical formula	(C ₃ H ₆ INH ₃) ₂ PbI ₄	(C ₃ H ₆ INH ₃) ₂ PbI ₄
Formula weight (g/mol)	1086.81	1086.81
Wavelength (Å)	0.71073	0.71073
Crystal System	Tetragonal	Tetragonal
Space group	P4 ₃ 2 ₁ 2	P4 ₃ 2 ₁ 2
Unit cell dimensions (Å)	a = b = 8.9846(8), c = 52.164(5)	a = b = 8.9870(6), c = 51.155(6)
Volume (Å ³)	4210.8(9)	4131.6(7)
Z	8	8
Calculated density (g/cm ³)	3.429	3.494
F(000)	3744	3744
Crystal size(mm ³)	0.29× 0.26× 0.21	0.29× 0.26× 0.21
θ _{min,max}	2.300, 25.464	2.301, 25.689
h _{min,max}	-10, 10	-8, 10
k _{min,max}	-10, 10	-10, 10
l _{min,max}	-62, 61	-62, 61
Absorption coefficient (mm ⁻¹)	16.795	17.117
Unique reflections/ No. parameters	3907/103	3923/104
Goodness-of-fit	1.098	1.106
Final R indices (I>2σ (I))	R _{obs} = 0.0765, wR _{obs} = 0.1564	R _{obs} = 0.0741 wR _{obs} = 0.1624
CCDC Number	2402792	2402794

The asymmetric units of both crystals comprise two chiral organic cations and one PbI_4^{2-} inorganic anion, as shown in Figure 2.4. Interestingly, the two chiral cations are conformers of each other. To better understand this structural aspect, we discuss the sample $(S\text{-IdPA})_2\text{PbI}_4$ in detail. The magnified view of the adjacent organic cations is shown in Figure 2.2b. They appear to be two different conformers, marked as (I) and (II). The same two conformers are shown from different viewpoints, in Figure 2.2c and 2.2d. Figure 2.2c shows that the conformer (I), with angle between $-\text{NH}_3^+$ head and $-\text{I}$ tail is 60° , is the gauche conformer. This gauche-conformer of $S\text{-IdPA}$ (Figure 2.2c) obtained from the crystal structure of $(S\text{-IdPA})_2\text{PbI}_4$ matches well with the schematic of gauche-conformer defined in Figure 2.1b. In difference, Figure 2.2d shows that the bond between C_2 and C_3 is rotated by 120° for conformer (II), as compared to conformer (I). Consequently, the conformer (II) has 180° angle between $-\text{NH}_3^+$ head and $-\text{I}$ tail group, forming an anti-conformer (refer to schematics in Figure 2.1b). Our finding shows that the two adjacent chiral organic cations in the crystal of $(S\text{-IdPA})_2\text{PbI}_4$ are two different staggered conformers, namely gauche and anti. The same structural arrangement is true for $(R\text{-IdPA})_2\text{PbI}_4$ as well. This finding of two conformers is not observed in typical chiral hybrid perovskites. Instead, the adjacent organic cations in typical chiral hybrid perovskites have different orientations.

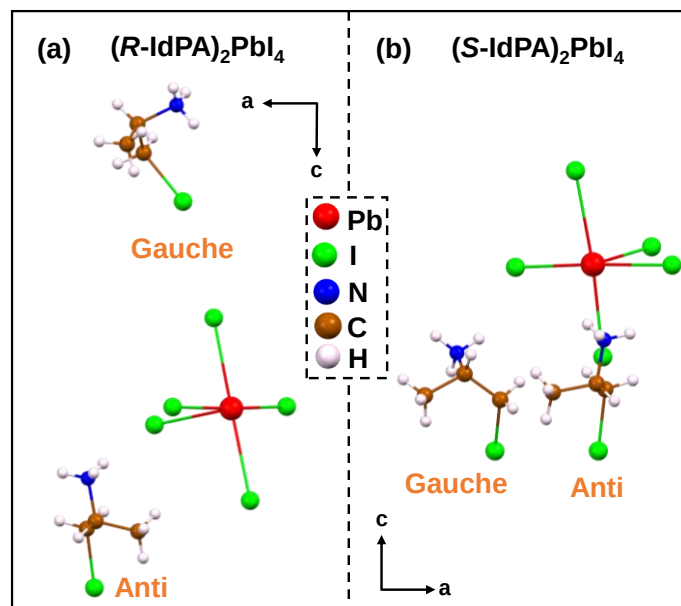


Figure 2.4: Asymmetric unit of (a) $(R\text{-IdPA})_2\text{PbI}_4$ and (b) $(S\text{-IdPA})_2\text{PbI}_4$ at 296 K.

2.3.2 Conformer-mediated asymmetric non-covalent interactions at the organic-inorganic interface: Now we discuss about how the two chiral organic conformers influence the non-covalent interactions at the organic-inorganic interface. Figure 2.5a shows that the

penetration depth of $-\text{NH}_3^+$ head of *S*-IdPA in the $[\text{PbI}_4]^{2-}$ inorganic sublattice is very different for the two adjacent *S*-IdPA conformers. The gauche (I) and anti (II) conformers penetrate by 0.27 Å and 0.63 Å, respectively. Therefore, the electrostatic interactions between the anti conformer of *S*-IdPA cation with $[\text{PbI}_4]^{2-}$ is more than that of the gauche conformer. The higher penetration depth in anti-conformer is also expected to enhance the $\text{N-H}\cdots\text{I}$ hydrogen bonds within the van der Waals limit for $\text{H}\cdots\text{I}$, approximately 3.15 Å. Indeed, the single crystal XRD data in Figure 2.5b suggest three strong hydrogen bonds between $-\text{NH}_3^+$ head of *S*-IdPA with iodine of $[\text{PbI}_4]^{2-}$ for the anti (II) conformer. In difference, the gauche (I) conformer of *S*-IdPA form two weaker hydrogen bonds. The related structural parameters for the hydrogen bonding interactions are listed in Table 2.3.

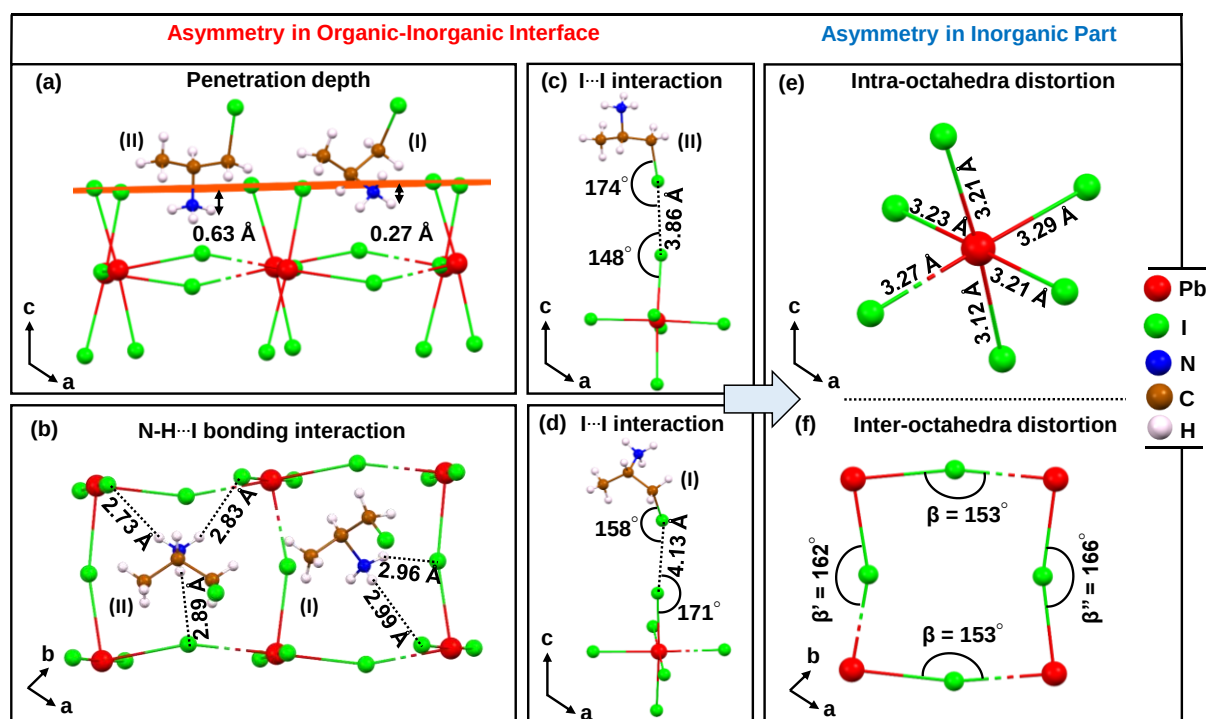


Figure 2.5: Role of chiral conformer cations on the asymmetry in non-covalent interactions at the organic-inorganic interface (a-d) of $(\text{S-IdPA})_2\text{PbI}_4$, leading to asymmetry in inorganic sublattice (e-f). (a) Different penetration depths of $-\text{NH}_3^+$ group in the inorganic anionic sublattice for anti (II) and gauche (I) conformers, leading to different extent of electrostatic interactions between the ammonium ions and $[\text{PbI}_4]^{2-}$ units. (b) Hydrogen-bonding and (c-d) $\text{I}\cdots\text{I}$ halogen-bonding interactions of the two conformers with the inorganic sublattice are also very different. The asymmetry in the interactions at the organic-inorganic interface leads to asymmetry in the inorganic sublattice. (e) Asymmetry in Pb-I bond lengths highlighting the distortion within the PbI_6 octahedra (intra-octahedra distortion). (f) The PbI_6 octahedra are tilted yielding different Pb-I-Pb bond angles signifying inter-octahedra distortion. All the plots are obtained from the single crystal XRD data of $(\text{S-IdPA})_2\text{PbI}_4$ measured at 296 K.

Table 2.3: N-H $\cdots$ I hydrogen bonds of (S-IdPA) $_2$ PbI $_4$ at 296, 150 K.

296 K				150 K		
Sl. No.	D-H $\cdots$ A	H $\cdots$ A (Å)	$\angle$ D - H $\cdots$ A ($^\circ$)	D-H $\cdots$ A	H $\cdots$ A (Å)	$\angle$ D-H $\cdots$ A ($^\circ$)
1	N4-H4A $\cdots$ I4	2.730	153	N4-H4C $\cdots$ I4	2.630	154
2	N4-H4B $\cdots$ I2	2.830	144	N4-H4A $\cdots$ I2	2.770	145
3	N4-H4C $\cdots$ I1	2.890	170	N4-H4B $\cdots$ I1	2.880	168
4	N8-H8A $\cdots$ I3	2.960	150	N8-H8A $\cdots$ I3	2.960	146
5	N8-H8B $\cdots$ I2	2.990	132	N8-H8B $\cdots$ I2	2.910	126

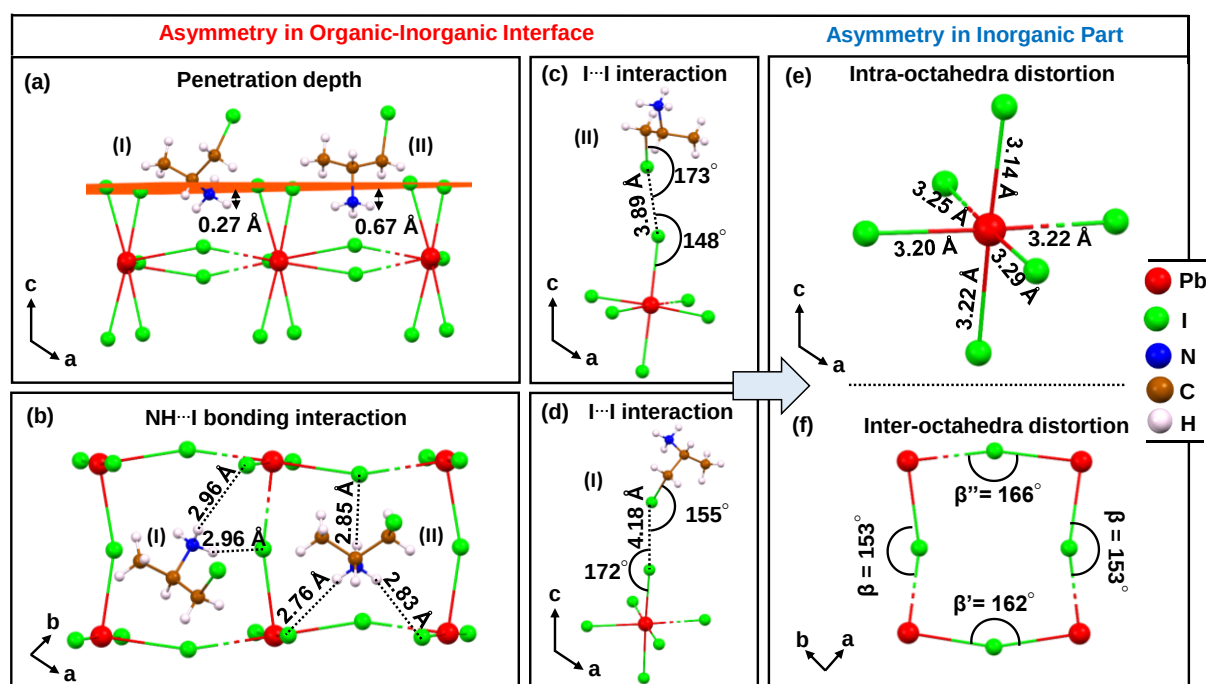


Figure 2.6: Role of chiral conformer cations on the asymmetry in non-covalent interactions at the organic-inorganic interface (a-d) of (R-IdPA) $_2$ PbI $_4$, leading to asymmetry in inorganic sublattice (e-f). (a) Different penetration depths of -NH_3^+ group in the inorganic anionic sublattice for anti (II) and gauche (I) conformers, leading to different extent of electrostatic interactions by the two conformers. (b) Hydrogen-bonding and (c-d) I $\cdots$ I halogen-bonding interactions of the two conformers with the inorganic sublattice are also very different. The asymmetry in the interactions at the organic-inorganic interface leads to asymmetry in the inorganic sublattice. (e) Asymmetry in Pb-I bond lengths highlighting the distortion within the PbI $_6$ octahedra (intra-octahedra distortion). (f) The PbI $_6$ octahedra are tilted yielding different Pb-I-Pb bond angles signifying inter-octahedra distortion. All the plots are obtained from the single crystal XRD data of (R-IdPA) $_2$ PbI $_4$ measured at 296 K.

Besides the hydrogen bonds, a type-II halogen bond ($I\cdots I$) is identified between the $-I$ tail of *S*-IdPA and iodine of $[PbI_4]^{2-}$, with an $I\cdots I$ distance of 3.86 Å and angles $\theta_1=174^\circ$ and $\theta_2=148^\circ$ for anti (II) conformer *S*-IdPA, as shown in Figure 2.5c. The iodine of the organic cation acts as halogen bond donor, and the iodide ion of $[PbI_4]^{2-}$ is the acceptor. In difference, $I\cdots I$ halogen bonding distance become 4.13 Å for the gauche (I) conformer as shown Figure 2.5d, indicating a significantly weaker halogen bonding for the gauche conformer.

Table 2.4: N-H $\cdots$ I hydrogen bond of $(R\text{-IdPA})_2PbI_4$ at 296, 150 K.

296 K				150 K		
Sl. No.	D-H $\cdots$ A	H $\cdots$ A (Å)	$\angle D - H \cdots A$ (°)	D-H $\cdots$ A	H $\cdots$ A (Å)	$\angle D - H \cdots A$ (°)
1	N4-H4A $\cdots$ I4	2.760	151.0	N4-H4A $\cdots$ I4	2.680	152.0
2	N4-H4B $\cdots$ I1	2.850	173.0	N4-H4B $\cdots$ I1	2.830	169.0
3	N4-H4C $\cdots$ I2	2.830	143.0	N4-H4C $\cdots$ I2	2.830	142.0
4	N8-H8A $\cdots$ I3	2.960	151.0	N8-H8A $\cdots$ I3	2.950	144.0
5	N8-H8C $\cdots$ I2	2.960	129.0	N8-H8C $\cdots$ I2	2.950	126.0

Clearly, all the non-covalent interactions, namely electrostatic, hydrogen bonding and halogen bonding interactions of the two conformers of *S*-IdPA with the inorganic sublattice $[PbI_4]^{2-}$ are different. And since the two conformers are arranged periodically one after another in the crystal of $(S\text{-IdPA})_2PbI_4$, a periodic asymmetry is introduced in the non-covalent interactions at the organic-inorganic interface. The same type of asymmetry in the crystal structure and noncovalent interaction is also observed for $(R\text{-IdPA})_2PbI_4$ enantiomorph pair, as shown in Figure 2.6 and Table 2.4. Consequently, chirality transfer might occur from the organic to inorganic sublattice through these asymmetric non-covalent interactions. Figure 2.5e shows that the Pb-I bond distances of $(S\text{-IdPA})_2PbI_4$ in the octahedral unit are very different from each other. Similar is the case for $(R\text{-IdPA})_2PbI_4$ as shown in Figure 2.6. The Pb-I bond distances vary in the range from 3.139-3.286 Å and 3.117-3.295 Å for the *R*- and *S*- crystals, respectively, (see Table 2.5 and 2.6). The 12 intra-octahedral angles (*cis* I-Pb-I bond angles) range from 86-95°, and the three *trans* bond angles (I-Pb-I) range from 176-178° for both crystals (see Table

2.7 and 2.8), indicating intra-octahedral distortion. Parameters such as bond length distortion (Δd_{oct}), bond angle variance (σ^2), and octahedral elongation (λ_{oct}) are calculated and shown in Table 2.5 and 2.6. We attribute this intra- octahedral distortion to the asymmetric non-covalent interactions (Figure 2.5a-d) at the organic-inorganic interface.

Table 2.5: PbI_6 octahedral bond distances and structural distortion parameters of $(S\text{-IdPA})_2\text{PbI}_4$ at 296 and 150 K

$(S\text{-IdPA})_2\text{PbI}_4$			
296 K		150 K	
Bond	Distance (Å)	Bond	Distance (Å)
Pb1-I4	3.117(3)	Pb1-I4	3.107(3)
Pb1-I2	3.208(3)	Pb1-I2	3.191(3)
Pb1-I5	3.211(1)	Pb1-I5	3.209(2)
Pb1-I3	3.234(1)	Pb1-I3	3.220(1)
Pb1-I1	3.266(2)	Pb1-I1	3.252(2)
Pb1-I1	3.295(2)	Pb1-I1	3.287(2)
Distortion parameters			
Bond distance distortion (Δd_{oct})	3.0×10^{-4}	Bond distance distortion (Δd_{oct})	3.03×10^{-4}
Bond angle variance (σ^2)	5.6987	Bond angle variance (σ^2)	8.4008
Quadratic elongation (λ_{oct})	1.0021	Quadratic elongation (λ_{oct})	1.0029

Table 2.6: PbI_6 octahedral bond distances and structural distortion parameters of $(R\text{-IdPA})_2\text{PbI}_4$ at 296 and 150 K.

$(R\text{-IdPA})_2\text{PbI}_4$			
296 K		150 K	
Bond	Distance ($\text{\AA}$)	Bond	Distance ($\text{\AA}$)
Pb1-I4	3.139(3)	Pb1-I4	3.110(3)
Pb1-I5	3.197(2)	Pb1-I2	3.191(3)
Pb1-I3	3.220(2)	Pb1-I5	3.212(2)
Pb1-I2	3.224(3)	Pb1-I3	3.224(1)
Pb1-I1	3.248(3)	Pb1-I1	3.254(2)
Pb1-I1	3.286(3)	Pb1-I1	3.290(3)
Distortion parameters			
Bond distance distortion (Δ_{oct})	1.9×10^{-4}	Bond distance distortion (Δ_{oct})	3.03×10^{-4}
Bond angle variance (σ^2)	5.30	Bond angle variance (σ^2)	8.20
Quadratic elongation (λ_{oct})	1.0018	Quadratic elongation (λ_{oct})	1.0028

Table 2.7: Intra-octahedral (I-Pb-I) and inter-octahedral (Pb-I-Pb) angles of $(S\text{-IdPA})_2\text{PbI}_4$ at 296 and 150 K.

296 K		150 K	
Angle	Value	Angle	Value
I4-Pb1-I3	86.52(6)	I4-Pb1-I3	85.85(6)
I2-Pb1-I1	86.86(7)	I2-Pb1-I1	86.85(7)
I4-Pb1-I1	87.88(7)	I4-Pb1-I1	88.23(7)
I3-Pb1-I1	88.92(8)	I3-Pb1-I1	88.16(9)
I5-Pb1-I1	89.32(10)	I5-Pb1-I1	87.75(11)
I4-Pb1-I1	89.97(7)	I4-Pb1-I1	89.17(7)
I3-Pb1-I1	90.45(8)	I3-Pb1-I1	91.06(9)
I2-Pb1-I3	90.52(6)	I2-Pb1-I3	90.38(7)
I4-Pb1-I5	91.06(6)	I4-Pb1-I5	90.83(7)
I5-Pb1-I1	91.21(10)	I5-Pb1-I1	92.88(11)
I2-Pb1-I5	91.99(7)	I2-Pb1-I5	93.21(7)
I2-Pb1-I1	95.25(7)	I2-Pb1-I1	95.70(7)
I4-Pb1-I2	175.65(9)	I4-Pb1-I2	174.47(10)
I5-Pb1-I3	177.06(10)	I5-Pb1-I3	174.81(12)
I1-Pb1-I1	177.80(4)	I1-Pb1-I1	177.33(4)
Pb1-I1-Pb1	153.21(8)	Pb1-I1-Pb1	152.43(7)
Pb1-I3-Pb1	166.23(14)	Pb1-I3-Pb1	167.26(17)
Pb1-I5-Pb1	161.97(18)	Pb1-I5-Pb1	158.1(2)

Table 2.8: Intra-octahedral (I-Pb-I) and inter-octahedral (Pb-I-Pb) angles of (R-IdPA)₂PbI₄ at 296 and 150 K

296 K		150 K	
Angle	Value	Angle	Value
I4-Pb1-I3	86.42(7)	I4-Pb1-I3	85.88(7)
I2-Pb1-I1	87.24(8)	I2-Pb1-I1	86.88(7)
I4-Pb1-I1	87.94(8)	I4-Pb1-I1	88.19(7)
I3-Pb1-I1	88.88(10)	I3 Pb1 I1	88.27(10)
I5-Pb1-I1	89.32(12)	I5-Pb1-I1	87.81(11)
I4-Pb1-I1	89.82(9)	I4-Pb1-I1	89.19(8)
I3-Pb1-I1	90.51(10)	I3-Pb1-I1	90.93(10)
I3-Pb1-I2	90.62(8)	I3-Pb1-I2	90.43(7)
I4-Pb1-I5	91.08(8)	I4 Pb1 I5	90.82(7)
I5-Pb1-I1	91.19(12)	I5-Pb1-I1	92.83(11)
I5-Pb1-I2	91.97(8)	I5-Pb1-I2	93.12(7)
I2-Pb1-I1	94.98(8)	I2-Pb1-I1	95.69(8)
I4-Pb1-I2	175.81(11)	I4-Pb1-I2	174.57(10)
I5-Pb1-I3	176.97(12)	I5-Pb1-I3	174.96(13)
I1-Pb1-I1	177.70(6)	I1-Pb1-I1	177.31(5)
Pb1-I1-Pb1	153.10(9)	Pb1-I1-Pb1	152.48(8)
Pb1-I3-Pb1	166.24(18)	Pb1-I3-Pb1	166.84(17)
Pb1-I5-Pb1	161.9(2)	Pb1-I5-Pb1	158.0(2)

Due to the influence of the chiral organic cations on the inorganic sublattice and the inversion asymmetry of the crystal structure, the inter-octahedral Pb-I-Pb bond angles (β) deviates significantly from the ideal value of 180° , indicating inter-octahedral tilting distortion. There are three inequivalent inter-octahedral angles in the equatorial plane of octahedral layers ($S\text{-IdPA}$)₂PbI₄, as shown in Figure 2.5f, namely $\beta = 153^\circ$, $\beta' = 162^\circ$, and $\beta'' = 166^\circ$, resulting in a disparity in adjacent β angles with $\Delta\beta \neq 0$. In our structures, there are two $\Delta\beta$ values: $\Delta\beta_1 = \beta - \beta' = 9^\circ$ and $\Delta\beta_2 = \beta - \beta'' = 13^\circ$. Generally, for inversion symmetric structures, the $\Delta\beta$ values are either zero or nearly zero. This large difference of inter-octahedral angles forces the inorganic layer to follow the inversion asymmetry, as confirmed through PLATON symmetry analysis.²⁴ The PLATON symmetry analysis is generally used to verify whether the isolated inorganic layers in a chiral organic-inorganic hybrid crystal follow the same inversion asymmetry as the overall crystal. The results, shown in Figure 2.7, indicate no change in the space group, confirming that the inorganic layers also follow the inversion asymmetry.

(R-IdPA)₂PbI₄

PLATON														
PLATON/ADDSYM for mo_SAP_298K_0m Ln P4(312)112														
ADDSYM Search on ALL NON-H Chem. Types (Treated EQUAL) (Max NonFlt 20 Perc)														
Criteria: 1.00 Deg (Metric), 0.25 Ang (Rad), 0.25 Ang (Inv), 0.25 Ang (Transl)														
Symm.	Input	Reduced	(Ang)	(Deg)	Perc	ArrDev.	(Ang)	Input Cell						
Elem	Cell_Row	Cell_Row	d	Type	Dot	Angle	Flt	MaxDev.	x	y	z			
4	1	0 0 1	1	0 0 1	52.16	4	1	0 100	0	Through	0	1/2	0	0
2	1	1 1 0	1	1 1 0	12.71	2	2	0 100	0	Screw	0	0	3/4	0
2	1	1 0 1	1	1 0 1	8.98	2	1	0 100	0	Through	1/2	1/2	0	0
2	1	1 0 0	1	1 0 0	8.98	2	1	0 100	0	Through	0	3/4	1/8	0
2	1	0 1 1	1	0 1 1	8.98	2	1	0 100	0	Screw	1/2	0	0	0
2	1	0 1 0	1	0 1 0	8.98	2	1	0 100	0	Through	1/4	0	3/8	0
2	1	1 1 1	1	1 1 1	12.71	2	2	0 100	0	Screw	0	1/2	0	0
2	1	1 1 0	1	1 1 0	12.71	2	2	0 100	0	Through	0	0	1/4	0
Reduced-to-Convent Input-to-Reduced T = Input-to-Convent: a' = T a														
(	1	0	0	1	(	1	0	0	1	(	1	0	0	1
(	0	1	0	1	x	(	0	-1	0	1	(	0	-1	0
(	0	0	1	1	(	0	0	-1	1	(	0	0	-1	1
Cell Lattice a b c Alpha Beta Gamma Volume Crystal System Laue														
Input	tP	8.985	8.985	52.164	90.00	90.00	90.00	4211	tetragonal	4/mmm				
Reduced	P	8.985	8.985	52.164	90.00	90.00	90.00	4211	tetragonal	4/mmm				
Convent	tP	8.985	8.985	52.164	90.00	90.00	90.00	4211	tetragonal	4/mmm				
:: Origin Shifted to: 0.000, 0.000, -0.250 after Cell Transformation														
:: SpaceGroup = P43212 - No Obvious Spacegroup Change Needed/Suggested														

(S-IdPA)₂PbI₄

PLATON																			
PLATON/ADDSYM for mo_SAP_298K_422.0m Ln P4(112)1																			
ADDSYM Search on ALL NON-H Chem. Types (Treated EQUAL) (Max NonFlt 20 Perc)																			
Criteria: 1.00 Deg (Metric), 0.25 Ang (Rad), 0.25 Ang (Inv), 0.25 Ang (Transl)																			
Symm.	Input	Reduced (Ang)	(Deg)	Perc	RvDev.	(Ang)	Input Cell	Cell_Row	Cell_Row	d	Type	Dot	Angle	Flt	MaxDev.	x	y	z	
4	[0 0 1]	[0 0 1]	51.75	4	1	0	100	0	Through	1/2	0	0	0	0	0	1/2	0	0	
2	[1 1 0]	[1 1 0]	12.76	2	2	0	100	0	Screw	0	0	0	1/4	0	0	1/4	0	0	
2	[1 1 0]	[1 1 0]	12.76	2	2	0	100	0	Through	1/2	1/2	1/2	1/2	0	0	1/2	1/2	0	
2	[1 0 1]	[1 0 1]	9.02	2	1	0	100	0	Through	0	3/4	7/8	7/8	0	0	3/4	7/8	0	
2	[1 0 1]	[1 0 1]	9.02	2	1	0	100	0	Screw	1/2	0	0	0	0	0	1/2	0	0	
2	[1 0 1]	[1 0 1]	9.02	2	1	0	100	0	Through	3/4	0	5/8	5/8	0	0	3/4	5/8	0	
2	[1 1 1]	[1 1 1]	12.76	2	2	0	100	0	Screw	0	1/2	0	0	0	0	1/2	0	0	
2	[1 1 1]	[1 1 1]	12.76	2	2	0	100	0	Through	0	0	3/4	3/4	0	0	0	3/4	3/4	
Reduced-to-Convent Input-to-Reduced T = Input-to-Convent: a' = T a																			
(	1	0	0	1	(	1	0	0	1	(	1	0	0	1	(	1	0	0	1
(	0	1	0	1	x	(	0	-1	0	1	(	0	-1	0	1	(	0	-1	0
(	0	0	1	1	(	0	0	-1	1	(	0	0	-1	1	(	0	0	-1	1
Cell Lattice a b c Alpha Beta Gamma Volume Crystal System Laue																			
Input	tP	9.024	9.024	51.751	90.00	90.00	90.00	4214	tetragonal	4/mmm									
Reduced	P	9.024	9.024	51.751	90.00	90.00	90.00	4214	tetragonal	4/mmm									
Convent	tP	9.024	9.024	51.751	90.00	90.00	90.00	4214	tetragonal	4/mmm									
:: Origin Shifted to: 0.500, 0.500, -0.250 after Cell Transformation																			
:: SpaceGroup = P41212 - No Obvious Spacegroup Change Needed/Suggested																			

Figure 2.7: PLATON analysis verifies that the inorganic sublattice exhibit inversion asymmetry and maintain the same space group as the hybrid chiral crystal (R-IdPA)₂PbI₄ and (S-IdPA)₂PbI₄

It is clear from the above discussion that the asymmetry in non-covalent interaction at the organic-inorganic interface, caused by the two different conformers of R/S-IdPA chiral ion, leads to the asymmetry in the inorganic sublattice. In the process, (R-IdPA)₂PbI₄ and (S-IdPA)₂PbI₄ forms helical enantiomorphous chiral pairs having four-fold screw axes 4₃ and 4₁, which is rare in the class of chiral hybrid perovskites. The direct correlation between the conformers and enantiomorphous structure is not yet clear. The prior literature does not discuss about the possible role of such conformers in the chiral structures of hybrid perovskite. By screening the published crystal structures, we found (R/S-MPEA)_{1.5}PbBr_{3.5}(DMSO)_{0.5} where MPEA is β -methylphenethylammonium,²⁵ and (R/-S-HP1A)₂PbBr₄ where HP1A is 2-

hydroxy-propyl-1-ammonium,²² have conformers of the organic ions in their crystal structure. $(R/S\text{-MPEA})_{1.5}\text{PbBr}_{3.5}(\text{DMSO})_{0.5}$ does not crystallize in the enantiomorphic space group. Interestingly, $(R/S\text{-HP1A})_2\text{PbBr}_4$ crystallizes in enantiomorphic space groups with four-fold screw axes having only conformer effect, similar to our work. These initial results indicate about the possible connection between conformer-mediated chirality with formation of the helical enantiomorphic structures of chiral hybrid perovskites, but such a possibility needs to be verified further. It is to be noted that the most (a few tens) of the 2D chiral hybrid perovskites reported so far do not have conformers of organic cations and show only two-fold rotation/screw axes without forming helical enantiomorphic structures.

To check the phase purity of the overall sample, we measured the XRD patterns from the powdered samples and performed profile refinements. Figure 2.8 shows the profile fitted powder XRD patterns of $(S\text{-IdPA})_2\text{PbI}_4$ and $(R\text{-IdPA})_2\text{PbI}_4$ confirming the single-phase nature of the respective materials.

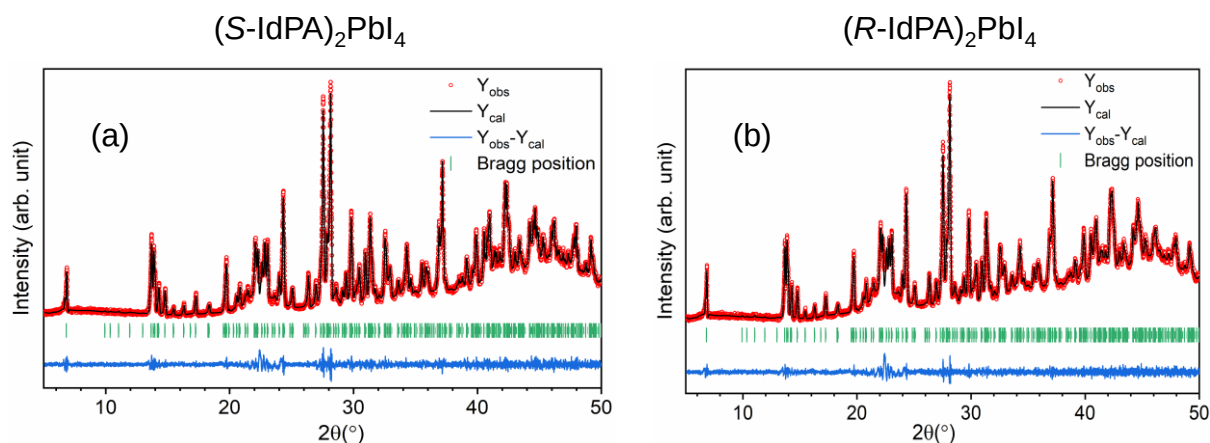


Figure 2.8: Profile fitted of powder XRD patterns of $(S\text{-IdPA})_2\text{PbI}_4$ and $(R\text{-IdPA})_2\text{PbI}_4$ powder measured at room temperature.

2.3.3 Optical absorption and CD Spectra: To measure the CD spectra of the samples, we prepared films of $(R/S\text{-IdPA})_2\text{PbI}_4$. The films were prepared by dissolving the respective crystals in acetonitrile followed by spin-coating the solution at 2500 rpm on quartz or sapphire substrate with subsequent annealing for 10 min at 50 °C, similar to methods reported earlier.²¹ The photographs of the films are shown in the insets of Figure 2.9. Powder XRD patterns (Figure 2.9) of the films are dominated by (00l) peaks suggesting oriented film growth, similar to prior reports of 2D layered hybrid perovskites.²⁵⁻²⁶

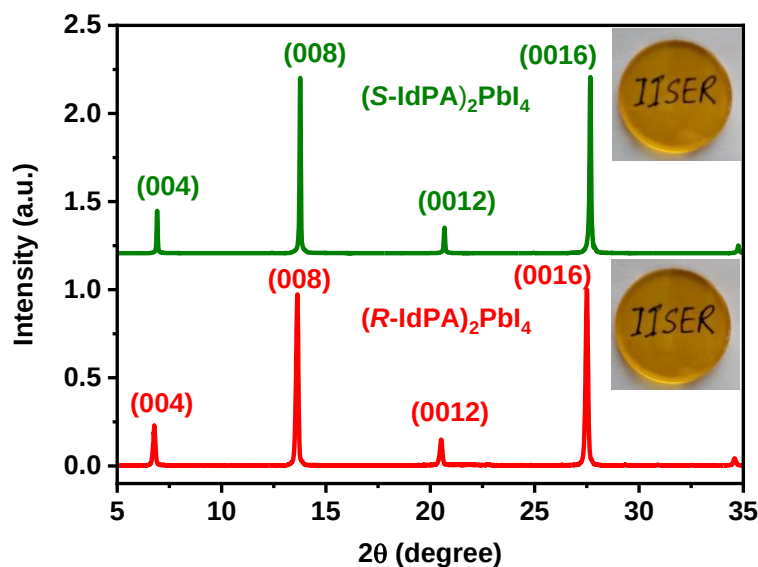


Figure 2.9: Powder XRD patterns of $(S\text{-IdPA})_2\text{PbI}_4$ and $(R\text{-IdPA})_2\text{PbI}_4$ films. Photographs of the films are shown in the inset.

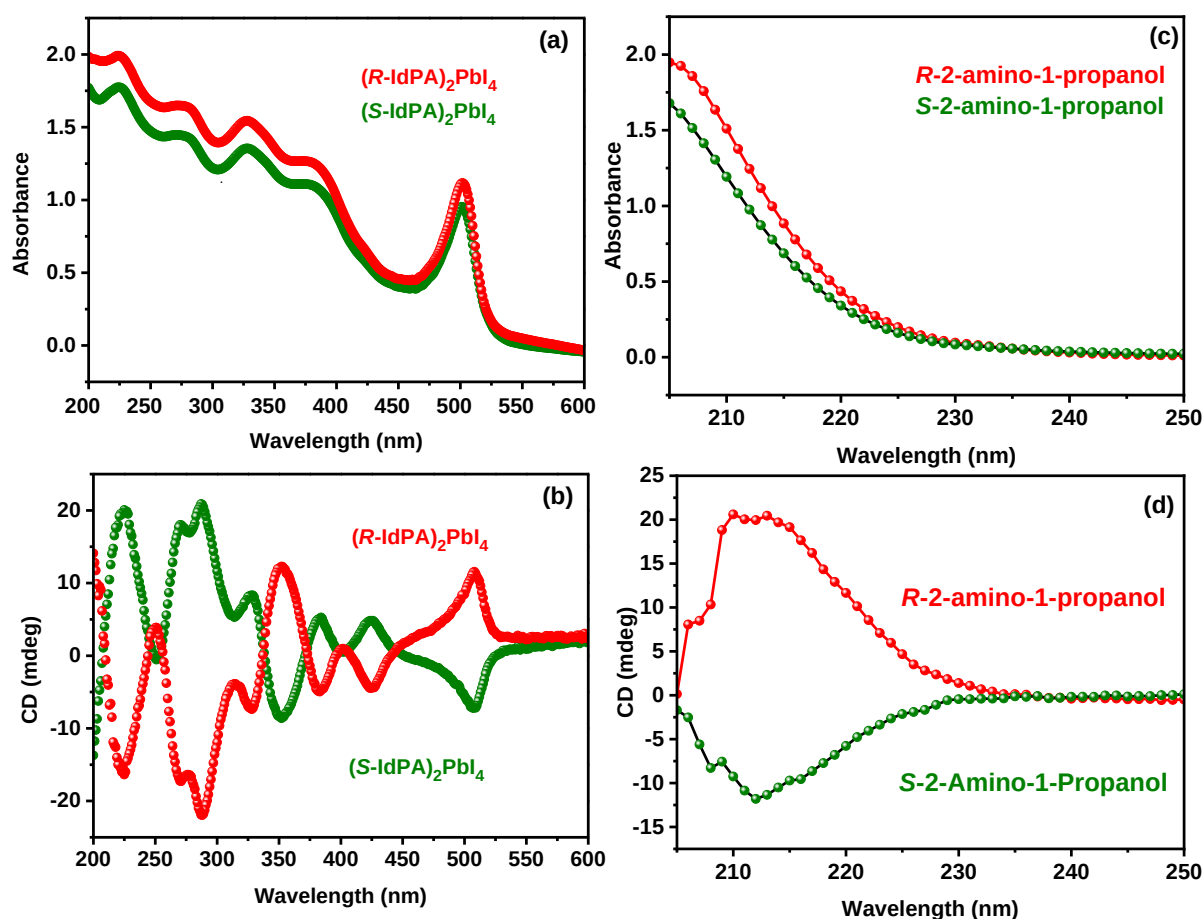


Figure 2.10: (a) UV-visible absorption, and (b) CD spectra of $(R\text{-}/S\text{-IdPA})_2\text{PbI}_4$ films at room temperature. (c) UV-visible absorption, and (d) CD spectra of $(R\text{-}/S\text{-})$ -2-amino-1-propanol solution in hexane, measured at room temperature.

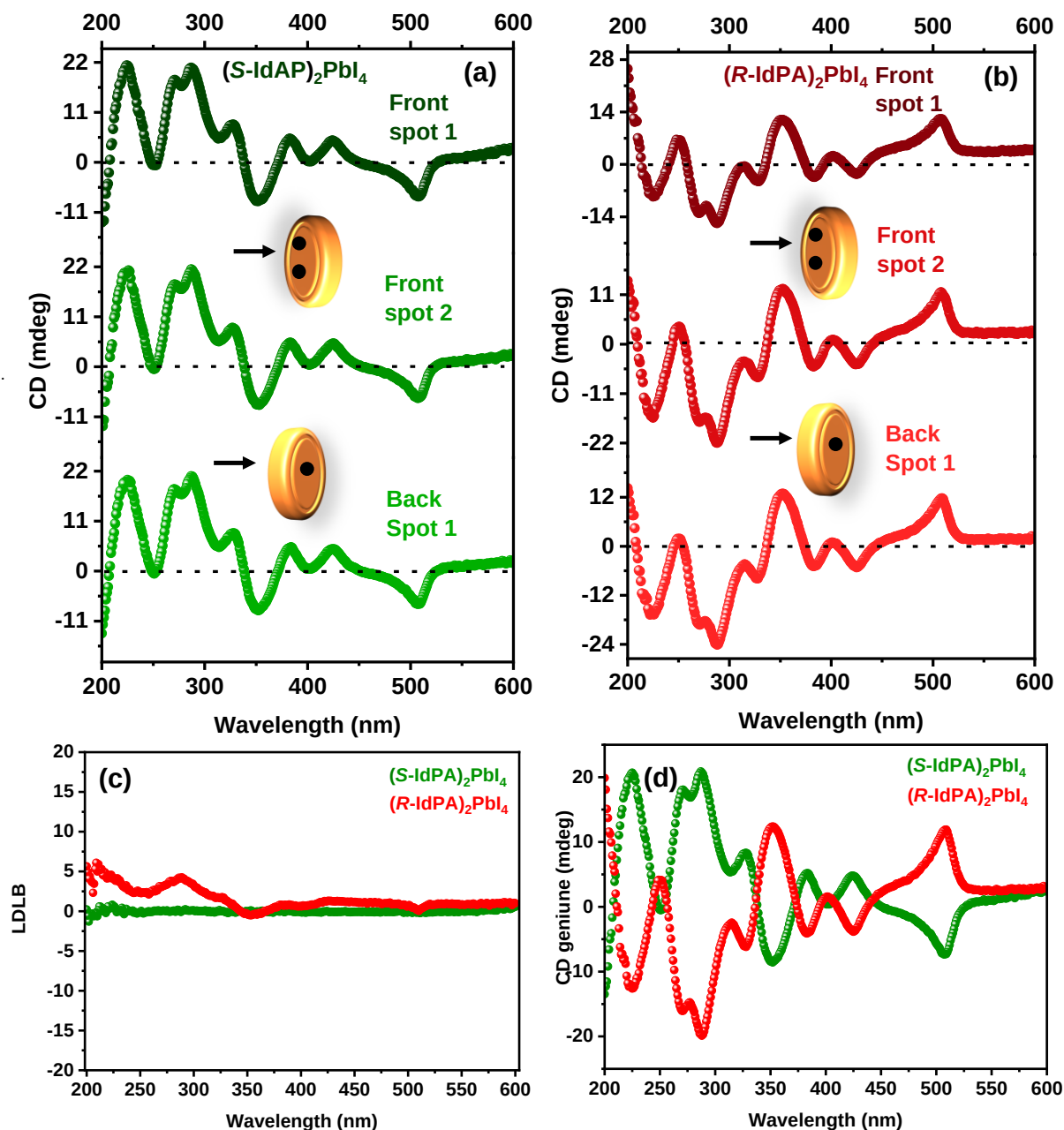


Figure 2.11: CD spectra at different positions of film of (a) $(S\text{-IdPA})_2\text{PbI}_4$ and (b) CD $(R\text{-IdPA})_2\text{PbI}_4$. (c) LDLB contribution of both $(S\text{-IdPA})_2\text{PbI}_4$ and $(R\text{-IdPA})_2\text{PbI}_4$. (d) CD genuine of $(S\text{-IdPA})_2\text{PbI}_4$ and $(R\text{-IdPA})_2\text{PbI}_4$. CD spectra were collected from the same film in two geometries, as shown in the inset of Figure (a-b). “Front”- means incident light passes through the film first then the substrate. “Back”- means the film is flipped such that the incident light first passes through the substrate and then through the film. CD spectra from the front (CD_{front}) the back (CD_{back}) side of the same film was used to obtain the LDLB and CD_{genuine} using the following equations²⁷⁻²⁸

$$LDLB = \frac{1}{2} \times (CD_{\text{front}} - CD_{\text{back}})$$

$$CD_{\text{genuine}} = \frac{1}{2} \times (CD_{\text{front}} + CD_{\text{back}})$$

UV-visible absorption spectra of the films of $(R/S\text{-IdPA})_2\text{PbI}_4$ are shown Figure 2.10a. The lowest energy excitonic peak is observed at 508 nm (2.44 eV). The 2D layered hybrid perovskite possesses a repeating quantum well structure with the excitons (electron-hole pairs) confined in the atomically thin inorganic layer, yielding a large excitonic binding energy and sharp excitonic absorption peak.²⁸⁻²⁹ Both the *R*- and *S*- enantiomeric pair show almost identical absorption of the linearly polarized light.

But the CD spectra of the two samples changes drastically for circularly polarized light. The CD spectra in Figure 2.10b shows mirror-image like spectra for the $(R\text{-IdPA})_2\text{PbI}_4$ and $(S\text{-IdPA})_2\text{PbI}_4$. This is because of the differential absorption of the left- and right- circularly polarized light by the two chiral enantiomer. Importantly, this optical activity is prominent at the excitonic absorption that originates mainly from the inorganic sublattice. Therefore, the CD spectra corroborate the structural aspects showing that the chirality is induced in the inorganic sublattice. For a comparison, we have also measured the UV-visible absorption and CD spectra of the organic molecule $(R/S)\text{-2-amino-1-propanol}$ as shown in Figure 2.10(c-d). The absorption and CD signal of the organic molecules are in the spectral range < 230 nm, suggesting that the CD spectra of $(R/S\text{-IdPA})_2\text{PbI}_4$ at longer wavelengths are dominated by the inorganic sublattice. Under certain circumstances, the CD spectra of films of chiral hybrid perovskites show large contributions from anisotropic linear dichroism (LD) and linear birefringence (LB).³⁰⁻³² Figure 2.11 and related discussion show negligible contributions from LDLB, and the observed CD spectra in Figure 2.11d are genuine CD signals. The values of absorption anisotropic factor (g_{CD}) are $\sim 3 \times 10^{-4}$ at 508 nm excitonic absorption for $(R/S\text{-IdPA})_2\text{PbI}_4$.

2.3.4 Temperature dependent structure and photoluminescence: Hybrid perovskites often undergo temperature-dependent structural phase transitions.³³⁻³⁴ Such phase transitions can alter nature of non-covalent interactions and chirality, in an undesired way. Therefore, another aspect of designing chiral organic cation *R/S*-IdPA is the thermal stability of the hybrid perovskite. It has been shown earlier that the $\text{I} \cdots \text{I}$ halogen bonding interaction can provide structural rigidity avoiding structural phase transition over a wide temperature range.²⁰ Interestingly, similar halogen bonding interactions is also present in our $(R/S\text{-IdPA})_2\text{PbI}_4$. Comparison of single crystal XRD data in Figure 2.12 shows that both $(R\text{-IdPA})_2\text{PbI}_4$ and $(S\text{-IdPA})_2\text{PbI}_4$ retain the enantiomeric chiral space groups $P4_32_12$ and $P4_12_12$, respectively, at both 296 K and 150 K. This absence of phase transition in $(R\text{-IdPA})_2\text{PbI}_4$ and $(S\text{-IdPA})_2\text{PbI}_4$ over a wider temperature range of 15 K to 300 K is also observed from the temperature-

dependent powder XRD patterns shown in Figure 2.13. The nature of powder XRD patterns do not change with temperature, other than a small contraction of the unit cell at lower temperatures (Figure 2.14). The profile fitting of the temperature dependent powder XRD patterns shown in Figure 2.15 also confirms that the crystal phase did not change throughout the temperature range.

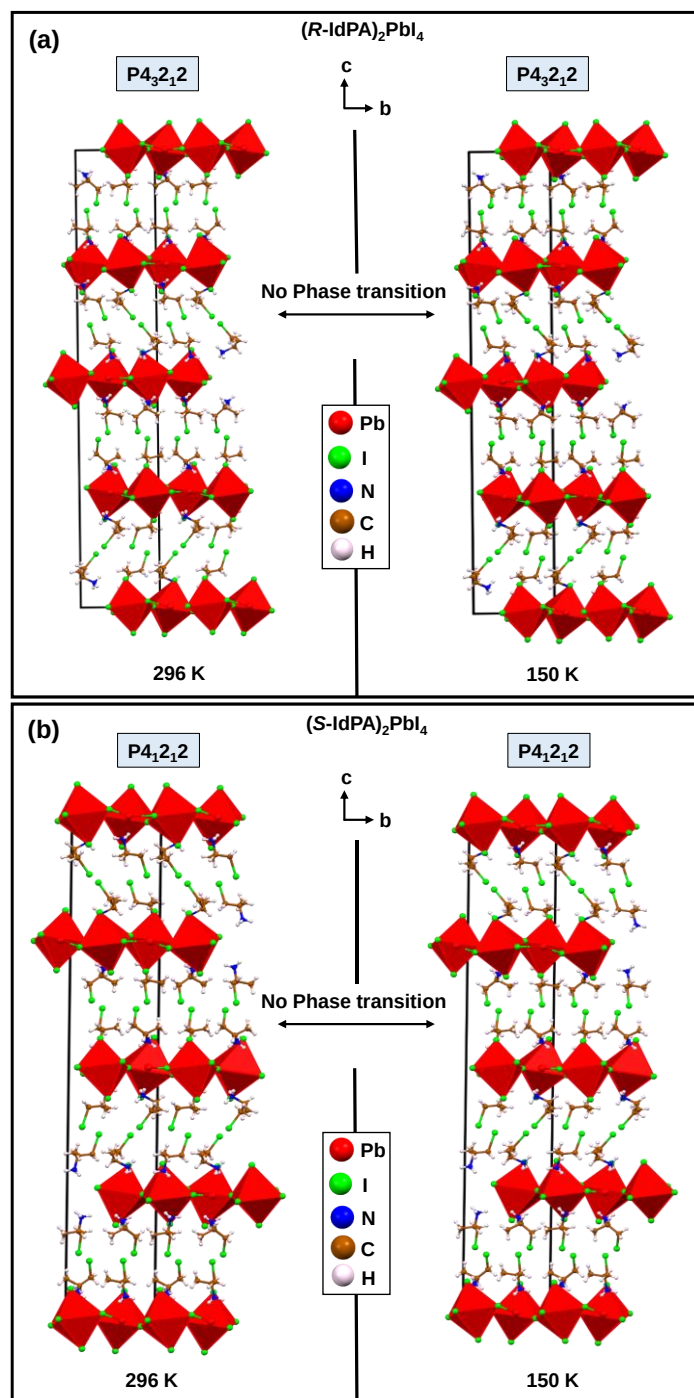


Figure 2.12: (a) Comparison of the single crystal structure of $(R\text{-IdPA})_2\text{PbI}_4$ measured at 296 K and 150 K. (b) Comparison of the single crystal structure of $(S\text{-IdPA})_2\text{PbI}_4$ measured at 296 K and 150 K.

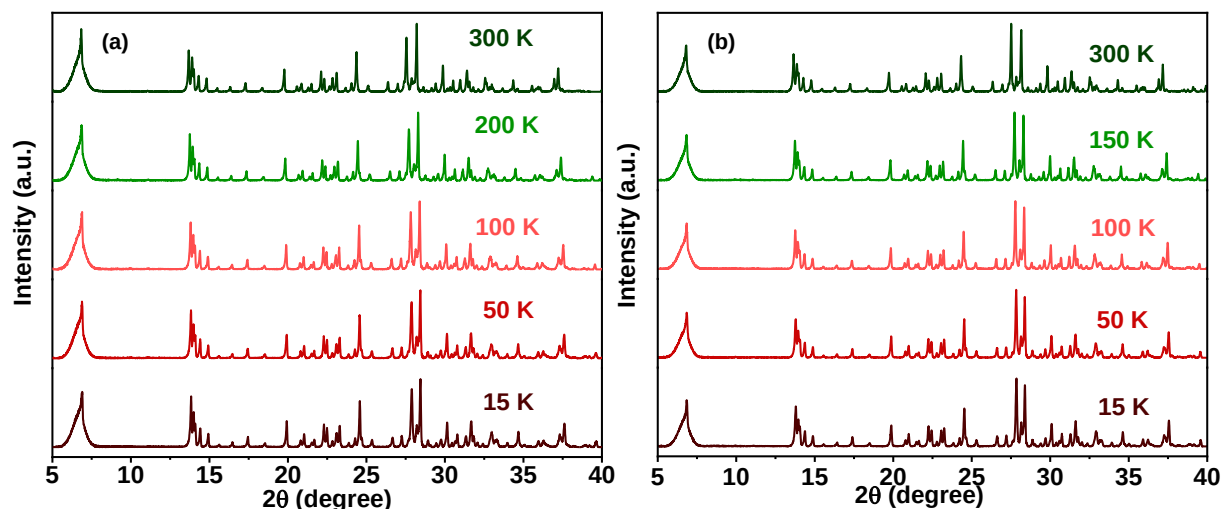


Figure 2.13: Temperature dependent structure properties of $(R/S\text{-IdPA})_2\text{PbI}_4$. Temperature-dependent powder XRD (300 K to 15 K) of (a) $(R\text{-IdPA})_2\text{PbI}_4$ and (b) $(S\text{-IdPA})_2\text{PbI}_4$.

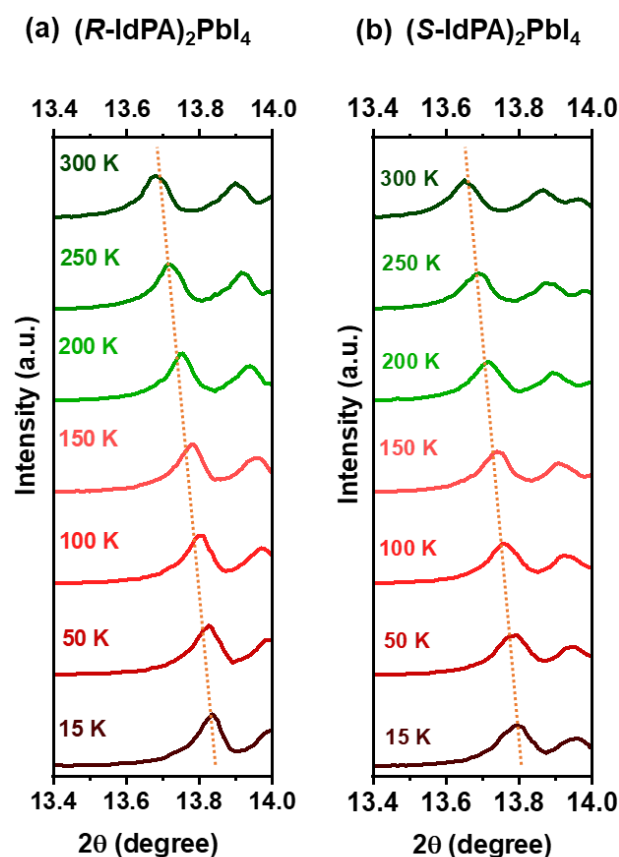


Figure 2.14: Powder XRD patterns in a zoom portion of $13.4^\circ\text{-}14.0^\circ$ 2θ for (a) $(R\text{-IdPA})_2\text{PbI}_4$, and (b) $(S\text{-IdPA})_2\text{PbI}_4$. The dotted arrows show a systematic shift of XRD peaks towards higher 2θ values with decreasing temperatures. This suggests lattice parameter contraction with decreasing temperature.

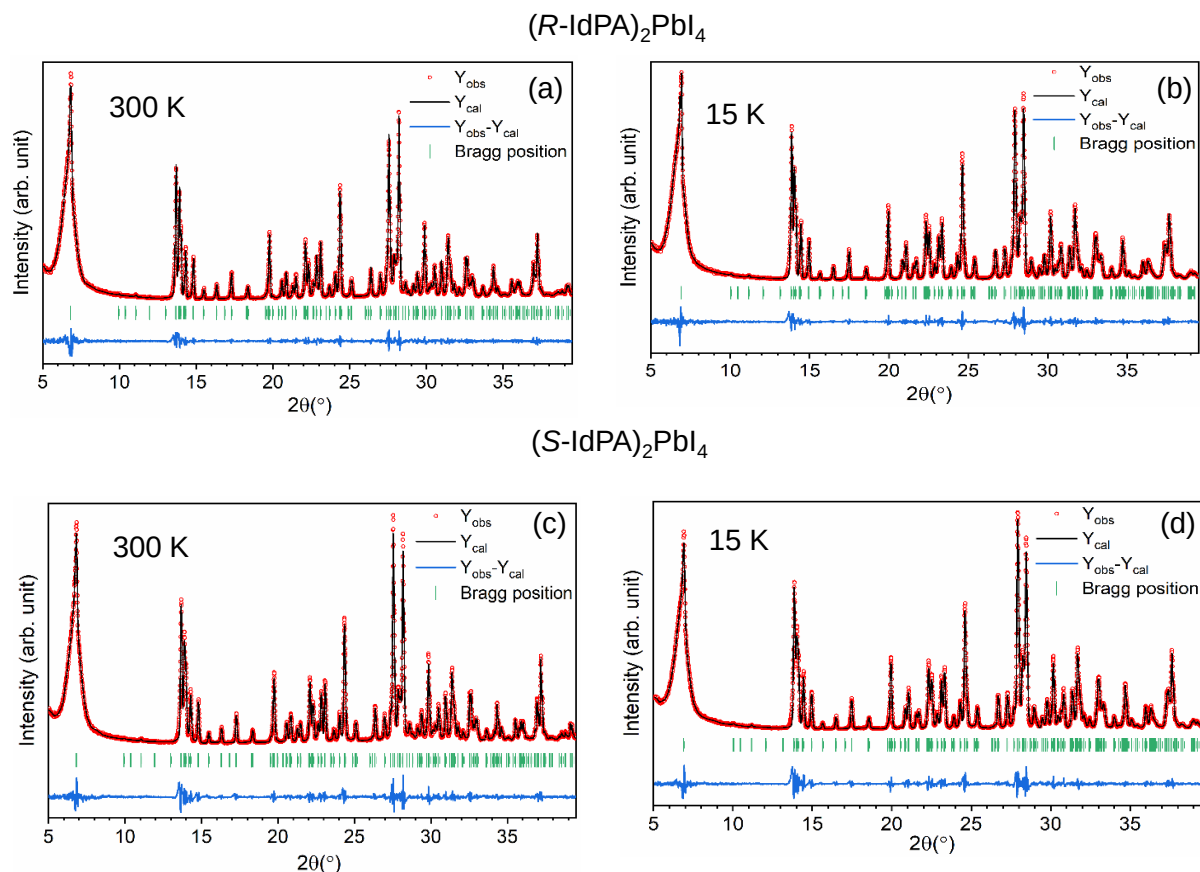


Figure 2.15: Profile fitted of powder XRD patterns of $(R-IdPA)_2PbI_4$ powder measured at (a) 300 K and (b) 15 K. Profile fitted of powder XRD patterns of $(S-IdPA)_2PbI_4$ powder measured at (c) 300 K and (d) 15 K.

Differential scanning calorimetric (DSC) data in Figure 2.16a also corroborate the absence of phase transition in the temperature range of 130 K to 403 K for $(R-IdPA)_2PbI_4$. Then a phase transition peak is observed at 432 K, indicated by T_s in Figure 2.16a. However, thermogravimetric analysis (TGA) plot does not show any weight loss at this temperature. The sample remains in the solid state just above the phase transition temperature 432 K, but the solid-to-solid phase transition at T_s leads to a color change of the sample from orange to yellow. The TGA data shows a weight loss at 476 K forming volatile species, accompanying a DSC peak at the similar temperature. Visualization of the sample suggest a melting and evaporation of the sample at similar temperatures around T_M shown in Figure 2.16a. Similar DSC and TGA data are also observed for $(S-IdPA)_2PbI_4$ as shown by Figure 2.16b. Overall, the powder XRD, single crystal XRD, and DSC data together confirm the thermal stability enantiomorphic chiral space groups of $(R/S-IdPA)_2PbI_4$ in a broad temperature range of 15 K to 403 K. This absence of phase transition might originate from rigidity of the organic sublattice because of the $I \cdots I$ halogen bonding interactions, similar to the prior report.²⁰

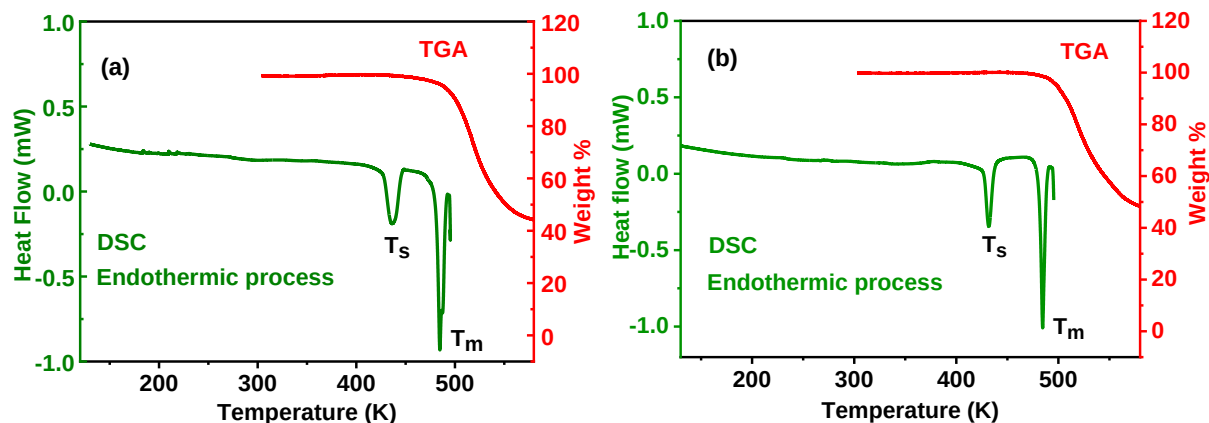


Figure 2.16: Temperature dependent structure properties of (R-/S-IdPA)₂PbI₄. TGA (300 K to 580 K), and DSC (123 K to 493 K) of (a) (R-IdPA)₂PbI₄ and (b) (S-IdPA)₂PbI₄ data suggest a stable enantiomorphous chiral structure in the temperature range of 15 K to 403 K.

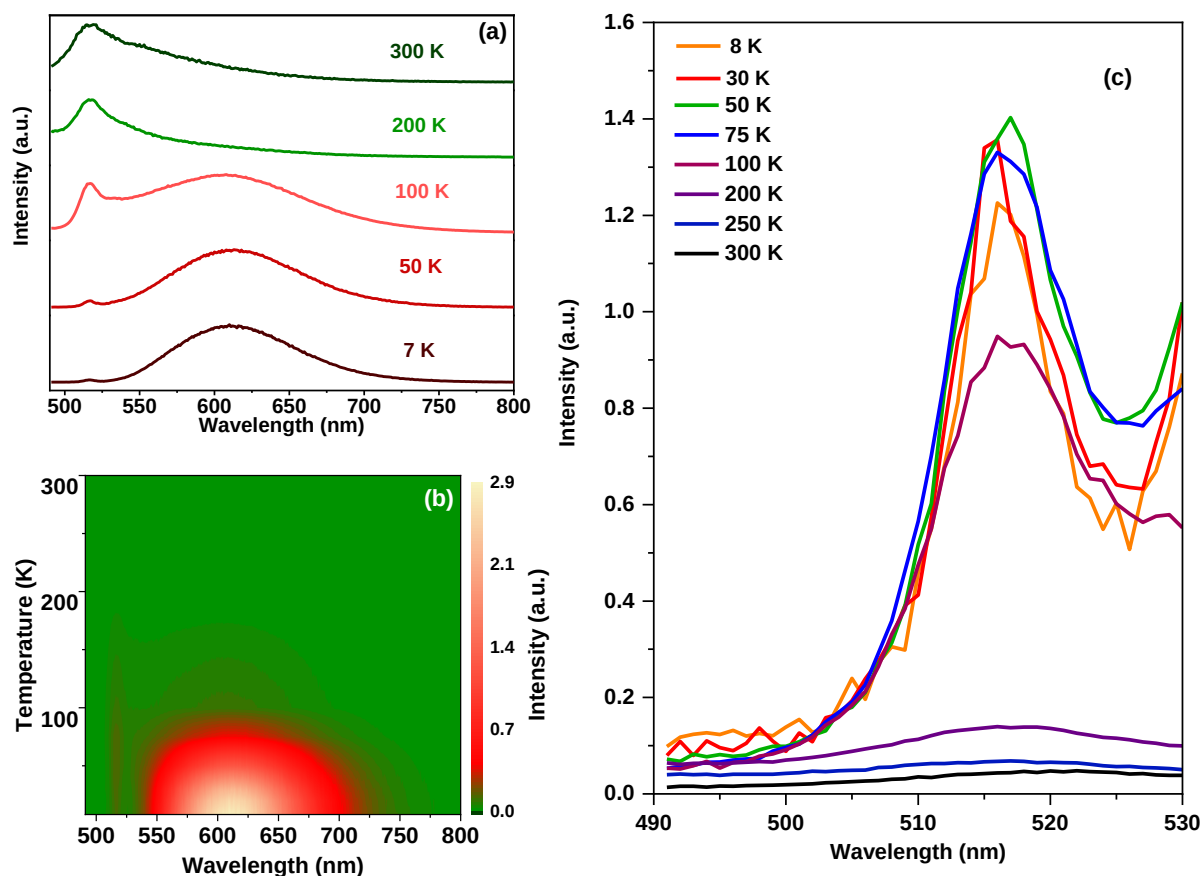


Figure 2.17: Temperature-dependent (a) PL spectra, and (b) their pseudo colormap of (R-IdPA)₂PbI₄ film in the range of 300 K to 7 K. (c) Excitonic emission of (R-IdPA)₂PbI₄ at different temperatures. All the measurements have been done with laser excitation at 375 nm.

Temperature-dependent photoluminescence (PL) emission spectra of (R-IdPA)₂PbI₄ film are shown in Figure 2.17(a-c). A weak emission signal is observed at 300 K under excitation with 375 nm laser diode. The PL emission peak at 516 nm might arise from the excitonic emission,

with 8 nm Stokes shift compared to the excitonic absorption peak 508 nm (Figure 2.10). But a broad emission tail at longer wavelengths are observed because defect or self-trapped exciton (STE) emission.³⁵ As the temperature decreases, the relative intensity of the broad emission with peak at 612 nm increases compared to the excitonic emission. The pseudo colormap in Figure 2.17b represents many more temperature dependent spectra comparing their actual

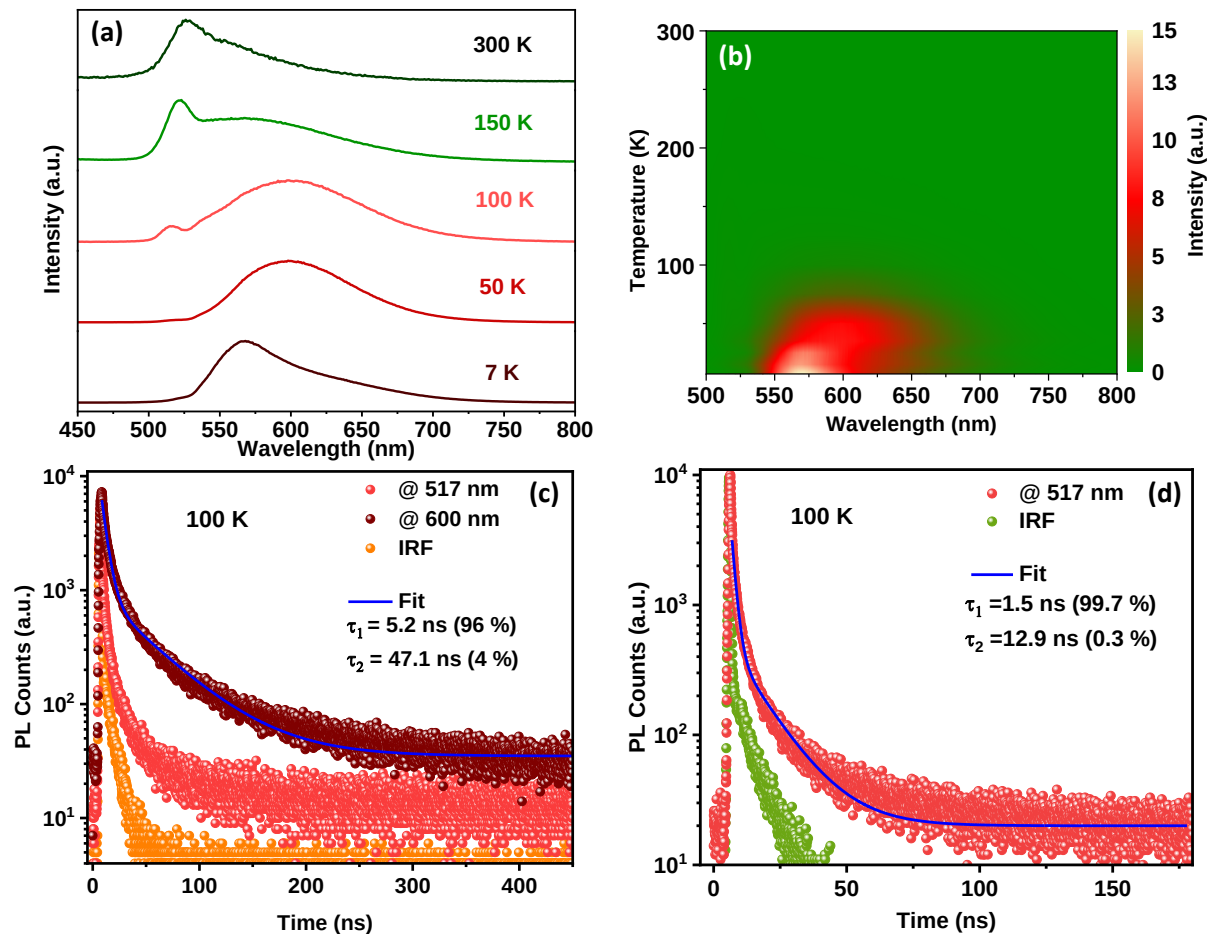


Figure 2.18: Temperature-dependent (a) PL spectra, and (b) their pseudo color map of (S-IdPA)₂PbI₄ film in the range of 300 K to 7 K. (c-d) PL decay dynamics of (S-IdPA)₂PbI₄ film at 100 K. (c) 500 ns time window for both 517 nm and 600 nm emission peaks, and (d) 200 ns time window for 517 nm peak. IRF stands for instrument response function in both the time windows. The decay at 600 nm emission is slower compared to the IRF for 500 ns time-window data, and therefore used for analysing the lifetimes (see Figure c). However, the decay at 517 nm emission is faster with significant overlap with IRF for 500 ns time-window data (Figure c). Consequently, the lifetime analysis of the 517 nm emission was carried out using the 200 ns time-window data (Figure d). The decay plots have been fitted with a bi-exponential decay equation $I = I_0 + A_1 \times \exp(-t/\tau_1) + A_2 \times \exp(-t/\tau_2)$, where I is the PL counts at any time t , I_0 is the offset, τ_1 and τ_2 are lifetimes with contributions A_1 and A_2 respectively. The average lifetime is obtained by using the equation by $\tau_{avg} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$ with $i = 1, 2$. All the decay measurements have been done with laser excitation at 375 nm.

intensity. The overall PL intensity increases significantly below 150 K. The intensity of the excitonic emission ~ 516 nm also increases with decreasing the temperature and saturates below 75 K (Figure 2.17c). Similar temperature dependent PL spectra are also obtained for (S-IdPA)₂PbI₄ films, as shown in Figure 2.18a-b. The excitonic emission has a fast PL decay with average lifetime 1.8 ns at 100 K, whereas, a longer lifetime is observed for the red-shifted broad emission (see Figure 2.18c-d).

2.4 Conclusion:

We have synthesized two new chiral 2D perovskite compounds (R-IdPA)₂PbI₄ and (S-IdPA)₂PbI₄. Single crystal XRD data show that the two adjacent IdPA⁺ ions in the lattice adopt distinct conformations- gauche and anti. Interestingly, the two IdPA⁺ conformers have very different non-covalent electrostatic, N-H $\cdots$ I hydrogen bonding, and I $\cdots$ I halogen bonding interactions with the [PbI₄]²⁻ sublattice. This alternative arrangement of gauche- and anti-conformers in the lattice, and subsequent asymmetry in the non-covalent interactions at the organic-inorganic interface, induces helical chirality in the inorganic sublattice with four-fold screw axes. Overall, the compounds (R-IdPA)₂PbI₄ and (S-IdPA)₂PbI₄ crystallizes in the helical enantiomorphic space groups P₄₃2₁2 and P₄₁2₁2, respectively. Such enantiomorphic space groups are rare in the case of chiral hybrid perovskites. The structures remain stable in a wide temperature range of 15 K to 403 K, probably because of the I $\cdots$ I interactions, yielding improved structure rigidity at the tail end of IdPA⁺. The quantum well nature of (R-/S-IdPA)₂PbI₄ shows sharp excitonic absorption at 508 nm. Interestingly, the CD shows mirror-image like signals for both the enantiomers. PL emissions is dominated by a broad STE emission along with excitonic emission, particularly at temperatures below 150 K. This work shows IdPA⁺ conformers containing chiral carbon-centers leads to helical chirality in hybrid perovskites. However, rational design of conformational chirality in the absence any chiral center still remains a challenge for hybrid halide perovskites, unlike the cases of some helical crystals of molecular or framework systems.³⁶

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Chapter 3

Temperature-Dependent Photoluminescence of Hexafluorobenzene Intercalated Phenethylammonium Tin Iodide 2D Perovskite

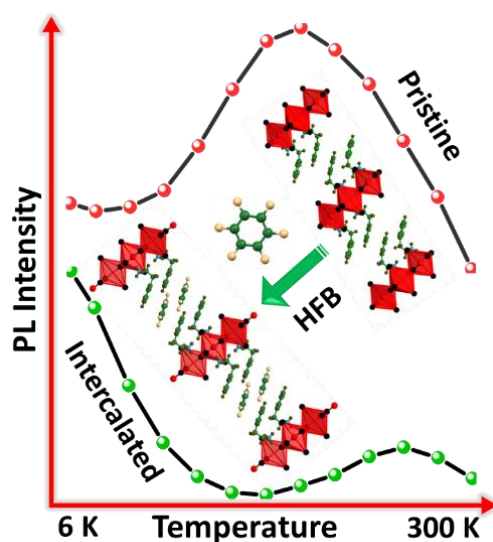
The work presented in this chapter is published in the following articles:

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Abstract: Tin halide perovskites are the potential alternatives of lead halide perovskites. However, the easy oxidation of Sn^{2+} to Sn^{4+} brings in a challenge. Recently, layered two-dimensional hybrid tin halide perovskites have been shown to partially resist the oxidation process because of the presence of hydrophobic organic molecules. Consequently, such layered hybrid perovskites are being explored for optoelectronic applications. The optical properties of layered tin halide perovskites depend on the interlayer separation and the dielectric mismatch between the organic and inorganic layers. Intercalation (insertion) of a molecular species between the layers modifies the interlayer interactions affecting the optical properties of layered hybrid perovskites. We investigated the effect of hexafluorobenzene (HFB) intercalation in phenethylammonium tin iodide $[(\text{PEA})_2\text{SnI}_4]$ using temperature-dependent (6 K to 300 K) photoluminescence (PL). HFB intercalation increases the bandgap. A strong PL quenching is observed in pristine $(\text{PEA})_2\text{SnI}_4$ below 150 K, probably because of the presence of non-emissive states. HFB intercalation suppresses the influence of such non-emissive states resulting in an increase in PL intensity at the cryogenic temperatures. Our results highlight that a simple molecular intercalation (non-covalent interaction) into layered hybrid perovskites can significantly tailor the electronic and optical properties.

Graphical Abstract:



3.1 Introduction:

Lead halide perovskites have emerged as a wonderful class of semiconducting material due to their exciting optoelectronic properties.¹⁻⁷ However, the inherent lead toxicity motivates researchers to look for environmentally benign alternatives.⁸⁻¹³ Tin halide perovskites became the first potential alternatives of lead halide perovskites. But the tin halide perovskites are prone to oxidation of Sn^{2+} to Sn^{4+} , disturbing the perovskite structure.¹⁴⁻¹⁶ Interestingly, the hybrid layered two-dimensional (2D) tin halide perovskites show resistance against the oxidation process. All thanks to the long-chain hydrophobic A-site organic cations, which prevent the interaction of tin halide perovskites with moisture, which is the major contributor to the oxidation process.¹⁷⁻²⁰ So, a number of layered tin halide perovskites were synthesized in the past few years and explored for applications, including solar cells to light-emitting diodes.²¹⁻²⁵

2D layered hybrid tin halide perovskites are represented by the general formula A_2SnX_4 , where A is a long-chain aliphatic or aromatic organic cation (like butylammonium ion, phenethylammonium ion, etc.), and X is the halide ion ($\text{X} = \text{Cl}, \text{Br}$ or I).²⁶⁻²⁸ The crystal structure consists of 2D semiconducting Sn-X octahedral layers, separated from each other by insulating organic cations.²⁹⁻³² Figure 3.1 (left panel) shows a schematic of the structure of phenethylammonium tin iodide $[(\text{PEA})_2\text{SnI}_4]$ that has been studied in this paper. The layered architecture of these inorganic and organic layers gives rise to a quantum well structure.³³⁻³⁴ The charge carriers created upon photoexcitation get confined to the semiconducting inorganic layers, giving rise to the quantum confinement effect, irrespective of the crystal size.³⁵ In addition to the quantum confinement, the layered tin halide perovskites also show dielectric confinement due to a large dielectric mismatch between the organic and inorganic layers. The 2D layers in layered perovskites are not completely isolated from each other, despite having the electrons and holes confined to the 2D inorganic layers.³⁶ The adjacent layers in layered perovskites interact electronically or magnetically with each other.³⁶⁻³⁷

One way to control the interaction between the inorganic layers is to intercalate neutral molecules in layered perovskites like $(\text{PEA})_2\text{SnI}_4$.³⁸⁻³⁹ Here, we have intercalated hexafluorobenzene (HFB) into $(\text{PEA})_2\text{SnI}_4$, as shown schematically in Figure 3.1 (right panel). HFB intercalation increases the separation between adjacent inorganic layers. Also, the intercalation is expected to modify the dielectric environment between the inorganic layers in $(\text{PEA})_2\text{SnI}_4$, thereby modifying its dielectric confinement. We study the effect of this molecular intercalation on the optical properties using temperature-dependent (6 K to 300 K)

photoluminescence (PL). HFB intercalation increases the bandgap blue-shifting both the UV-visible absorption and PL spectra. At cryogenic temperatures, PL properties of pristine $(\text{PEA})_2\text{SnI}_4$ differ significantly from HFB intercalated $(\text{PEA})_2\text{SnI}_4$. The pristine sample shows an aggressive quenching of PL intensity below 150 K, probably because of the presence of non-emissive states at slightly lower energy below the emissive excitonic states. In contrast, for HFB intercalated sample, the PL intensity increases sharply below 150 K without showing significant contribution from such non-emissive states. These results show that the HFB intercalation, though a physical process, can significantly tailor the optical properties of $(\text{PEA})_2\text{SnI}_4$.

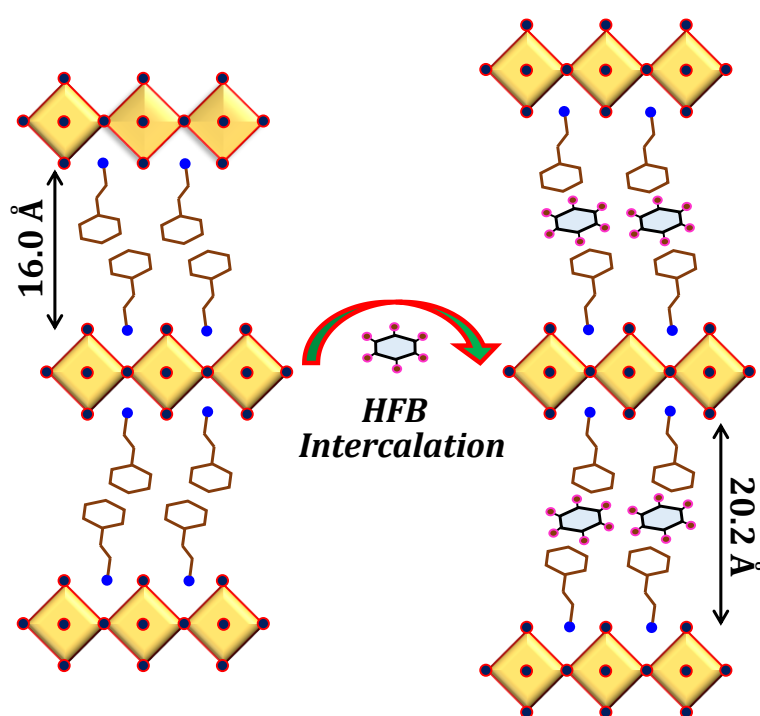


Figure 3.1: Schematic showing the intercalation of molecular HFB in $(\text{PEA})_2\text{SnI}_4$. The interlayer separation in $(\text{PEA})_2\text{SnI}_4$ increases upon the HFB intercalation.

3.2 Experimental section:

3.2.1 Chemicals: Tin(II) oxide (Sigma Aldrich, 97%), hydriodic acid (Sigma Aldrich, 57% w/w in H_2O , 99.9%), hypophosphorous acid (Avra, 50% w/w H_2O), phenethylamine (Sigma Aldrich, 99.9%) hexafluorobenzene (Sigma Aldrich, 99%).

3.2.2 Synthesis of $(\text{PEA})_2\text{SnI}_4$: $(\text{PEA})_2\text{SnI}_4$ single-crystals were synthesized by following a reported acid precipitation method.³⁶ In a nitrogen-filled glove box, 80 mg (0.6 mmol) tin(II) oxide was taken in a glass vial and sealed with a rubber septum. The sealed glass vial was taken out of the glove box, and 7 mL hydriodic acid and 4 mL hypophosphorous acid was injected

into it by a syringe. The reaction mixture was heated to 80 °C under constant stirring. Tin(II) oxide dissolved completely, giving rise to an orange-colored solution, to which 160 μ L (1.2 mmol) of phenethylamine were injected. The heating was stopped, and the solution was cooled to room temperature by decreasing the temperature manually, 5 °C after every 15 minutes. During the cooling process, dark brown crystals of (PEA)₂SnI₄ precipitated out. The crystals were filtered, dried and stored in the N₂ filled glove box for further use.

3.2.3 Intercalation of HFB in (PEA)₂SnI₄: HFB was inserted between the (PEA)₂SnI₄ perovskite layers by modifying a reported method.³⁸ 18 mg (PEA)₂SnI₄ were dissolved in a mixture of 1 mL methanol and 1 mL HFB. A quartz substrate was immersed in the solution. The solution was allowed to evaporate naturally under the inert atmosphere. During the evaporation process, HFB intercalated (PEA)₂SnI₄ got deposited on the quartz substrate.

3.2.4 Characterization: Powder X-ray diffraction (PXRD) patterns were collected using a Bruker D8 Advance X-ray diffractometer using Cu K α radiation (λ = 1.54178 Å). Field emission scanning electron microscopy (FESEM) images were collected using Zeiss Ultra Plus FESEM instrument. UV-Visible absorbance data were recorded using Cary Series UV-Vis Spectrophotometer (Agilent Technologies). Steady-state photoluminescence (PL) data were recorded on FLS 980 (Edinburgh Instruments). All the PL data presented in the manuscript were recorded in front side alignment, i.e., both the source and the detector were on the same side of the crystal and perpendicular to each other. Low-temperature PL measurements were performed in the FLS980 instrument. A 405 nm pulsed diode laser was used as an excitation source. The samples were packed in sapphire substrates and mounted to a gold-plated sample holder. The sample holder was attached to a closed-cycle He-cryostat (Advanced Research Systems), which was connected to a temperature controller (Lakeshore Cryotronics) to achieve the desired temperatures.

3.3 Results and Discussion:

3.3.1 Intercalation: (PEA)₂SnI₄ single crystals are synthesized by a reported aqueous acid precipitation method.³⁶ All the synthesis presented in this manuscript are carried under an controlled inert atmosphere. Detailed synthesis methodology is provided in the experimental section. The powder x-ray diffraction (PXRD) pattern (red pattern in Figure 3.2a) of (PEA)₂SnI₄ matches well with the reported one (green pattern), confirming the successful synthesis of phase pure layered perovskites system. PXRD peaks at regular intervals are

observed. This regular peak pattern is a characteristics of layered perovskite single crystals, and the observed peaks correspond to the interlayer spacing ($00l$ planes). The corresponding interlayer spacing, calculated from the 001 peaks, is 16 Å, which matches well with the reported interlayer spacing of $(\text{PEA})_2\text{SnI}_4$. The layered structure is also reflected in the field emission scanning electron microscopy (FESEM) image, shown in Figure 3.2b.

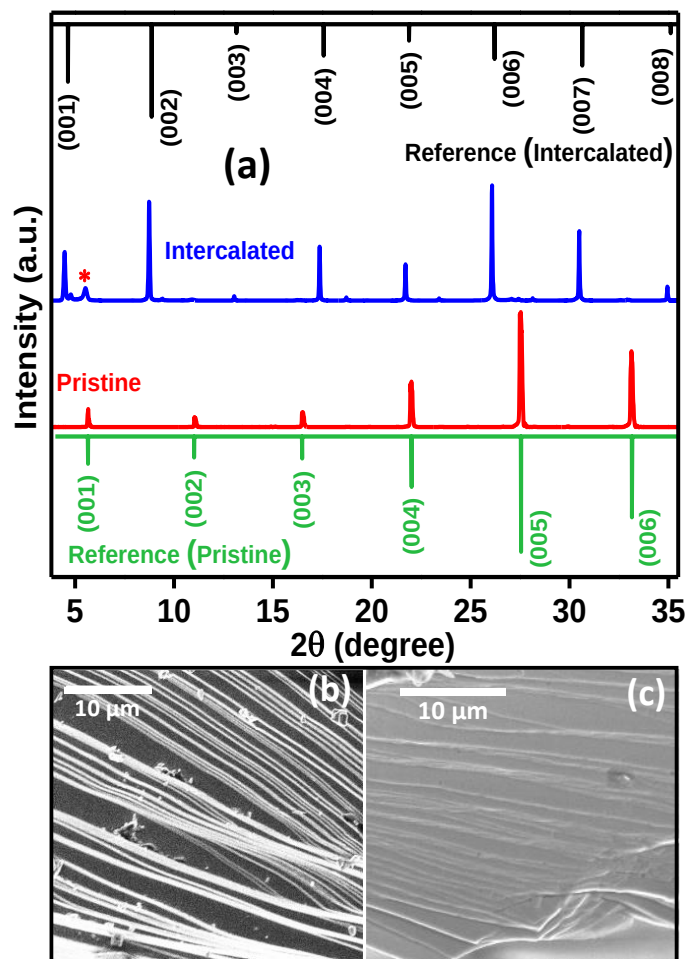


Figure 3.2: (a) PXRD patterns of pristine (red) and HFB intercalated (blue) $(\text{PEA})_2\text{SnI}_4$, showing the shifting of PXRD peaks towards the lower 2θ values upon HFB intercalation that increases the interlayer separation. The reference PXRD patterns of pristine (green) and HFB intercalated (black) $(\text{PEA})_2\text{SnI}_4$ are also provided. The peak highlighted by “*” in the PXRD pattern of HFB intercalated $(\text{PEA})_2\text{SnI}_4$ corresponds to the pristine $(\text{PEA})_2\text{SnI}_4$ formed by the de-intercalation of HFB. FESEM images of (b) pristine and (c) HFB intercalated $(\text{PEA})_2\text{SnI}_4$, showing a layered architecture.

After the successful synthesis of $(\text{PEA})_2\text{SnI}_4$, molecular HFB is intercalated between its layers. The detailed process of HFB intercalation in $(\text{PEA})_2\text{SnI}_4$ is discussed in the experimental section. Briefly, 18 mg $(\text{PEA})_2\text{SnI}_4$ is dissolved in a 1:1 mixture of methanol and HFB by stirring. After complete dissolution of $(\text{PEA})_2\text{SnI}_4$, the resultant solution is allowed to evaporate. During the evaporation, a crystalline film of HFB intercalated $(\text{PEA})_2\text{SnI}_4$ is

deposited on a quartz substrate placed in the solution. A shift of the PXRD peaks towards the lower 2θ values is observed after the HFB intercalation (blue pattern in Figure 3.2a). The shifting of the PXRD peaks towards the lower 2θ values indicates an increase in the interlayer separation and hence confirms the intercalation of HFB between the $(\text{PEA})_2\text{SnI}_4$ layers. A small impurity peak at 5.5° (marked by “*”) corresponding to the pristine $(\text{PEA})_2\text{SnI}_4$ is also observed in the PXRD pattern of HFB intercalated $(\text{PEA})_2\text{SnI}_4$. This impurity peak suggests either the incomplete intercalation of HFB or the possible de-intercalation of the HFB molecules during the measurement. Except the peak of pristine $(\text{PEA})_2\text{SnI}_4$, all the prominent peaks in the PXRD pattern of HFB intercalated $(\text{PEA})_2\text{SnI}_4$ match well with the reported PXRD pattern of phase pure HFB intercalated $(\text{PEA})_2\text{SnI}_4$ (Figure 3.2a). However, there are a few minor low-intensity peaks coming from unknown impurities. The FESEM image of HFB intercalated $(\text{PEA})_2\text{SnI}_4$ also shows a layered architecture (Figure 3.2c), where the white bright lines indicate the layer edges.

3.3.2 Optical properties at room temperature: Figure 3.3a shows the UV-visible absorption spectra of the pristine and HFB intercalated $(\text{PEA})_2\text{SnI}_4$. Both the samples show a strong absorbance in the visible region. Generally, two excitonic features are observed in the absorption spectra of the layered perovskites.⁴⁰ But, in the present case, the absorbance is recorded in the transmittance mode, and due to the high absorption cross-section and high thickness of the samples, the light with energy higher than the bandgap does not pass through. Consequently, the absorption spectra show only the lowest energy absorption edge, beyond which the spectra saturate. Nevertheless, Figure 3.3a clearly shows a blue shift in the lowest energy absorption edge of $(\text{PEA})_2\text{SnI}_4$ upon HFB intercalation, indicating an increase in the bandgap. This increase in the bandgap upon HFB intercalation is due to a minor structural change in the inorganic layer of $(\text{PEA})_2\text{SnI}_4$, as reported previously.³⁶ The room temperature PL spectrum of $(\text{PEA})_2\text{SnI}_4$ single crystals shows two emission features centered at ~ 1.97 eV (630 nm) and ~ 1.84 eV (674 nm), shown in Figure 3.3b. Such dual emission features are previously reported for layered lead and tin halide perovskite single crystals.³⁶ The higher energy peak (1.97 eV) arises from the excitonic recombination of the free excitons in the isolated inorganic layers, whereas the lower energy peak (1.84 eV) arises from the interaction between excitons in the adjacent 2D inorganic layers, mostly dominated at the layer edges of the crystal.

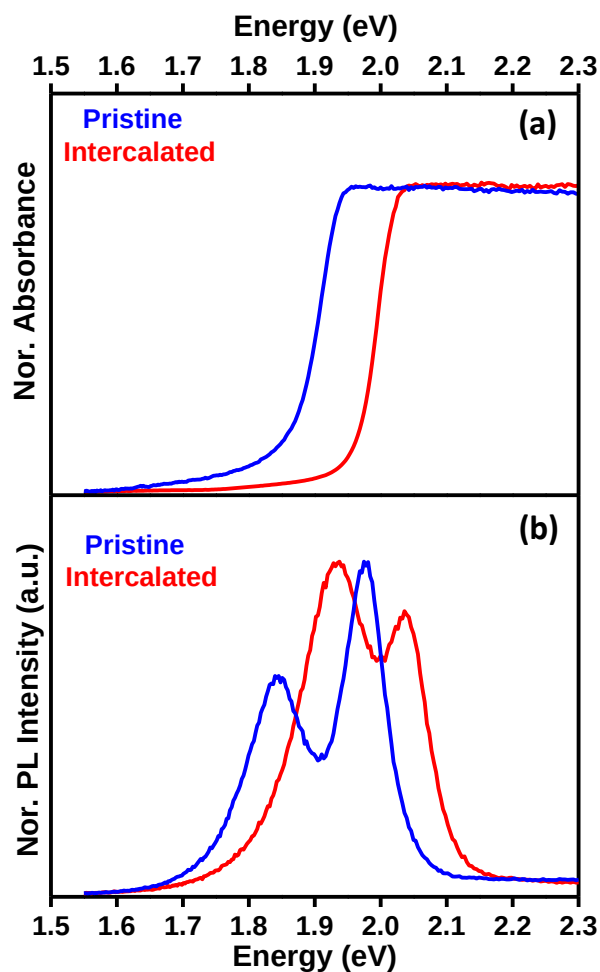


Figure 3.3: (a) UV-visible absorption (measured in transmission mode) and (b) PL spectra of pristine and HFB intercalated $(\text{PEA})_2\text{SnI}_4$. “Nor.” indicates normalized data by making the maximum absorbance or intensity values of both samples equal to one. HFB intercalation is accompanied by blue shifts in the absorption and PL spectra.

Similar to the absorbance, both the peaks in the PL spectrum of $(\text{PEA})_2\text{SnI}_4$ are blue-shifted upon HFB intercalation (Figure 3.3b). The blue shift in the higher energy emission is expected as this emission originates from the isolated inorganic layers, which have a slightly higher bandgap, due to a structural change, compared to the pristine $(\text{PEA})_2\text{SnI}_4$. In a previous report of HFB intercalated $(\text{PEA})_2\text{SnI}_4$ single crystal, the lower energy emission peak was reported to have almost vanished. However, for the present HFB intercalated $(\text{PEA})_2\text{SnI}_4$, we observed both the emission peak (Figure 3.3b). This difference is probably due to the difference in the two samples. In the present case, we observed the presence of some pristine $(\text{PEA})_2\text{SnI}_4$ impurity in HFB intercalated samples suggesting the possibility of either incomplete intercalation or partial de-intercalation. Since the lower energy emission mostly originates from the layer edges of the crystal, its presence in the HFB intercalated $(\text{PEA})_2\text{SnI}_4$ indicates significant absence of HFB from the layer edges of the crystal.

3.3.3 Temperature dependent photoluminescence: In order to explore the effect of HFB intercalation on the light emission properties more clearly, we recorded the temperature-dependent PL in both pristine and HFB intercalated $(\text{PEA})_2\text{SnI}_4$. Figure 3.4a shows the selective PL spectra of pristine $(\text{PEA})_2\text{SnI}_4$ recorded at different temperatures. Two emission peaks are observed throughout the temperature range of 300 to 6 K. The higher energy peak (P1) shows a gradual red-shift upon lowering down the temperature from 300 to 6 K, as is evident from the PL peak energy vs temperature plot also (Figure 3.4b). The red-shift in the PL peak energy of the higher energy peak (P1) indicates a decrease in the excitonic bandgap of $(\text{PEA})_2\text{SnI}_4$ upon decreasing the temperature. Similar temperature dependence of the bandgap has been observed in the thin films of pristine $(\text{PEA})_2\text{SnI}_4$, owing to the decrease in the Sn-I bond lengths due to the lattice compression with the decrease in the temperature.⁴¹ Contrarily, the lower energy peak (P2) initially shows a gradual blue-shift upon lowering the temperature from 300 to 100 K, below which it remains almost unchanged (Figure 3.4b). The reason for the blue shift of the lower energy peak (P2), in the temperature range 300 to 100 K, is not clear yet.

Figure 3.4c shows the PL spectra of HFB intercalated $(\text{PEA})_2\text{SnI}_4$ at selected temperatures. The PL spectral profile of HFB intercalated $(\text{PEA})_2\text{SnI}_4$ is different from the pristine $(\text{PEA})_2\text{SnI}_4$ at cryogenic temperatures. The higher energy peak (P1) in HFB intercalated $(\text{PEA})_2\text{SnI}_4$ shows a gradual red-shift upon decreasing the temperature, similar to the pristine sample (Figure 3.4d). Such similarity in the temperature dependence of the higher energy peak (P1) in pristine and HFB intercalated $(\text{PEA})_2\text{SnI}_4$ supports the assignment that P1 originates from the isolated 2D layers of the same Sn-I framework. The lower energy peak (P2) in HFB intercalated $(\text{PEA})_2\text{SnI}_4$ initially shows a gradual blue-shift, similar to that of the pristine $(\text{PEA})_2\text{SnI}_4$. However, the blue shift in this peak continues till 150 K only, unlike the pristine $(\text{PEA})_2\text{SnI}_4$ in which the low energy peak (P2) blue shifts till 100 K. Also, an additional emission peak (P3) appears in PL spectra of HFB intercalated $(\text{PEA})_2\text{SnI}_4$ below 150 K. This new emission peak probably arises from the pristine impurity present in the sample, as this peak (P3) almost overlaps with the lower energy peak (P2) of the pristine $(\text{PEA})_2\text{SnI}_4$, at 6K Figure 3.4a. At slightly higher temperatures (50 to 150 K), P3 overlaps with the tail of P2 for HFB intercalated $(\text{PEA})_2\text{SnI}_4$ sample. Such overlap might be a reason for a small increase in P3 peak energy from 50 K to 150 K, reported in Figure 3.4d.

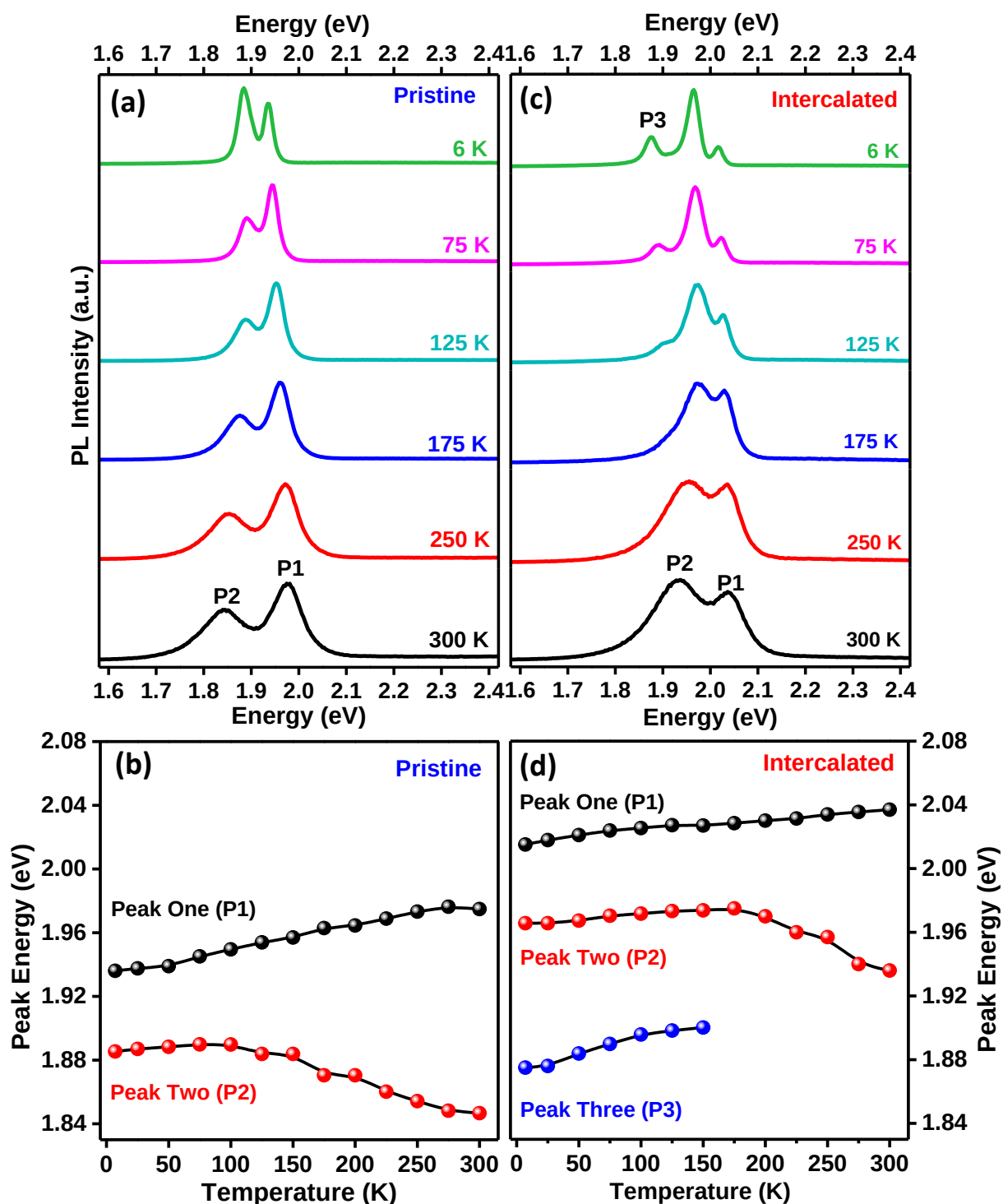


Figure 3.4: (a) Temperature-dependent PL spectra of (b) PL peak energies vs temperature plot of pristine $(\text{PEA})_2\text{SnI}_4$. (c) Temperature-dependent PL spectra of (d) PL peak energies vs temperature plot of HFB intercalated $(\text{PEA})_2\text{SnI}_4$. PL spectra in (a) and (c) are shifted vertically for clarity of presentation.

Figure 3.4 showed PL spectra only at a few temperatures. The spectra measured at a large number of temperature points can be plotted through the pseudo color maps. The peak energy vs temperature discussed in Figures 3.4b and 3.4d gets reflected in the color maps. In addition,

the color map gives information about the change in the intensity with temperature. Figures 3.5a and 3.5b show the PL-temperature pseudo color maps of the pristine and HFB intercalated $(\text{PEA})_2\text{SnI}_4$, respectively. The two emission features discussed above are clearly visible in the color map of the pristine $(\text{PEA})_2\text{SnI}_4$ throughout the temperature range. The combined integrated PL intensity of the two emission features increases with the decrease in temperature but reaches a maximum around 175 K, below which its intensity decreases (blue symbols in Figure 3.5c). From 300 K to 175 K, the integrated PL intensity increases due to the quenching of the non-radiative recombination pathways at lower temperatures. The decrease in the integrated PL intensity below 175 K is somewhat unusual but has been observed in a previous report on $(\text{PEA})_2\text{SnI}_4$ thin film. Such decrease was attributed to the presence of a non-emissive state with slightly lower energy compared to emissive excitonic states. Excited-state population transfer from the emissive excitonic state to the non-emissive state reduces the PL intensity. Above 175 K, the thermal energy is sufficient for the back transfer of the excited state population from the non-emissive to the emissive state. But below 175 K, the rate of back transfer decreases with decreasing temperatures, and therefore, decreasing the PL intensity.

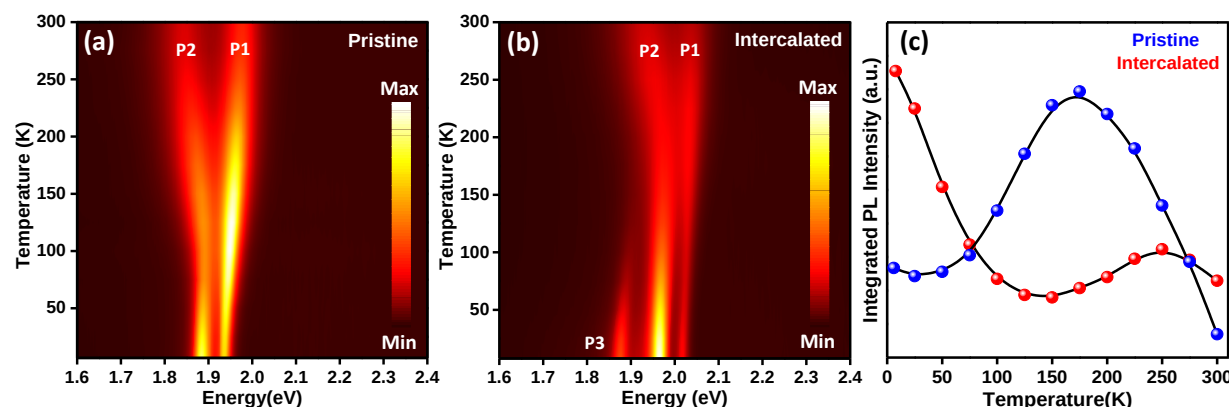


Figure 3.5: PL-temperature pseudo color maps of (a) pristine and (b) HFB intercalated $(\text{PEA})_2\text{SnI}_4$. (c) Variation of the integrated intensity over the entire energy range of PL emission for pristine (blue) and HFB intercalated (red) $(\text{PEA})_2\text{SnI}_4$ with temperature.

The PL-temperature pseudo-color map of HFB intercalated $(\text{PEA})_2\text{SnI}_4$ is different from the pristine $(\text{PEA})_2\text{SnI}_4$ (Figure 3.5b). Three emission features are observed in the HFB intercalated $(\text{PEA})_2\text{SnI}_4$ at the cryogenic temperatures, unlike the pristine $(\text{PEA})_2\text{SnI}_4$. As discussed above, this third emission feature (P3) probably arises from the pristine impurity present in the intercalated sample. The combined integrated PL intensity of the HFB intercalated $(\text{PEA})_2\text{SnI}_4$ is shown in Figure 3.5c (red symbols). Initially, the integrated PL intensity increases slightly with the decrease in temperature from 300 K to 250 K. Below 250 K, the integrated PL intensity decreases till 150 K, probably again because of the existence of a non-emissive state similar to

the pristine sample. But compared to the pristine sample (175 K), HFB intercalated (PEA)₂SnI₄ has an intensity maximum at a higher temperature (250 K), suggesting a higher barrier for back transfer of excited state population from non-emissive to emissive state. In other words, there is a possibility of an increased energy gap between emissive and non-emissive states after HFB intercalation. The increased energy gap will also suppress the non-radiative transfer of the population from an emissive excitonic state to a non-emissive state at lower energy. Consequently, the decrease in PL intensity from 250 K to 150 K is significantly smaller compared to the pristine sample that shows a drastic decrease in the intensity below the corresponding temperature of maximum intensity (Figure 3.5c). Further decrease in temperature below 150 K continues suppressing the state filling of the non-emissive state, along with suppression of other kinds of non-radiative losses. Consequently, PL intensity increases sharply below 150 K for the HFB intercalated (PEA)₂SnI₄.

3.4 Conclusion:

(PEA)₂SnI₄ and HFB intercalated (PEA)₂SnI₄ 2D layered hybrid perovskites are prepared. The HFB intercalation in (PEA)₂SnI₄ increases the interlayer separation. The HFB intercalation is also accompanied by a blue shift in the bandgap of the (PEA)₂SnI₄. This blue shift in the bandgap mainly arises from a minor structural change in the crystal structure of the Sn-I layers. To investigate the effect of HFB intercalation on the PL emission properties, we studied PL in the temperature range of 300 -6 K. The pristine (PEA)₂SnI₄ showed two excitonic PL peaks throughout the temperature of 300 to 5 K. The HFB intercalated (PEA)₂SnI₄, showed an additional third peak (P3) below 150 K, probably because of the presence of pristine sample as an impurity. The temperature-dependent intensity variation in (PEA)₂SnI₄ is significantly affected by the HFB intercalation. The integrated PL intensity of the HFB intercalated (PEA)₂SnI₄ showed a sharp rise below 150 K, whereas that of the pristine (PEA)₂SnI₄ decreases at the lower temperatures. The sharp increase in the integrated PL intensity in the HFB intercalated (PEA)₂SnI₄ at lower temperatures is probably due to the suppression of non-emissive state filling. So the HFB intercalation not only changes the bandgap of the (PEA)₂SnI₄ but also affects the abundance and energy level of non-emissive states, significantly influencing the PL intensity.

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Chapter 4

Edge versus Interior Mn²⁺-Doping in 2D Layered Butylammonium Lead Bromide Perovskite Single Crystals

The work presented in this chapter is published in the following article:

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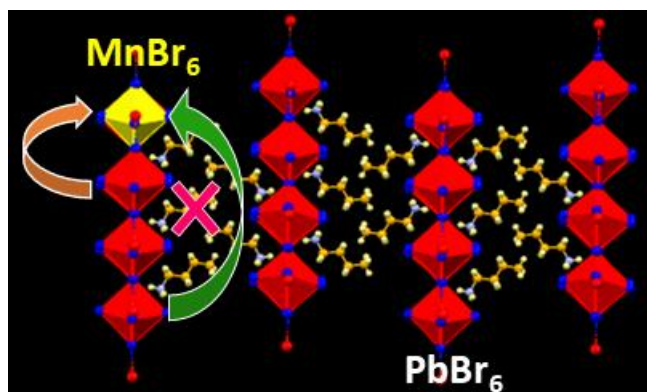
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Declaration: Dr. Somnath M. Kashid and Prof. Arindam Chowdhury, from Indian Institute of Technology Bombay, have recorded the spatially resolved fluorescence microscopy and spectroscopy data.

Abstract:

Butylammonium lead bromide $[(\text{BA})_2\text{PbBr}_4]$ has an atomically thin two dimensional quantum well structure. So if Mn^{2+} ions are doped into such crystals, then one would expect efficient energy transfer from the strongly confined exciton to the dopants. Perhaps, the energy transfer happens yielding Mn^{2+} emission with peak at 2.05 eV (605 nm). But significant excitonic emission is also observed suggesting that the energy transfer process is not that efficient. Is there a spatial separation between Mn^{2+} ions and excitons reducing the energy transfer efficiency? To address the question, here we study single crystals of Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$. The excitons located in the edge and interior of layers of $(\text{BA})_2\text{PbBr}_4$ show different exciton emissions. This difference allows us to separately probe the interaction of edge-excitons and interior-excitons with the Mn^{2+} ions, using temperature dependent (7 K to 300 K) photoluminescence (PL) spectroscopy and spatially resolved PL. We find that the edge-excitons mainly sensitize the Mn^{2+} ions, because the Mn^{2+} doping is preferred near the layer edges. Both the poor doping concentration (0.6% Mn^{2+}) and edge-doping lead to large spatial separation between the interior-excitons and dopant centers, reducing the energy transfer efficiency. These new insights will be helpful for the better design and application of luminescent Mn^{2+} -doped 2D layered hybrid perovskites.

Graphical Abstract:



4.1 Introduction:

Incorporation of Mn^{2+} as dopants into the lattice of quantum-confined semiconductors like ZnSe, CdSe, and CsPbX_3 ($X = \text{Cl}, \text{Br}$) nanocrystals leads to interesting optical, optoelectronic, and magneto-optic properties.¹⁻¹⁰ Energy transfer from the host exciton to the dopant, leading to Mn^{2+} d -electron emission, is one of the most studied properties in such samples. The increased overlap of the host exciton (or charge carriers) and the dopant in quantum-confined semiconductor significantly enhances the energy/charge transfer efficiency.¹¹⁻¹² Therefore, it is natural to dope Mn^{2+} in the two dimensional (2D) layered organic-inorganic hybrid lead halide perovskites like butylammonium lead bromide $[(\text{BA})_2\text{PbBr}_4]$, with quantum well structure.¹³⁻¹⁵ The excitons are confined within the atomically thin Pb-Br inorganic layers. Consequently, one would expect a very efficient energy transfer from the host exciton to the dopants in Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$. But photoluminescence shows peaks originated from both the host excitons and the Mn^{2+} ions, suggesting an inefficient energy transfer process. Why so?

To address the question, we look into the relationship between the host's structure and dopant's local structure. A single hybrid layer in $(\text{BA})_2\text{PbBr}_4$ is shown in Figure 4.1a. Such layers stack together (Figure 4.1b) through van der Waals interactions forming the extended layered crystal.¹⁶⁻¹⁹ In a typical Pb-Br inorganic layer, Mn^{2+} dopants can have two sites, namely, edge and interior as denoted by red and yellow colored spheres respectively, in Figure 4.1a. In the extended van der Waals solid, each of such inorganic layers provide the edge (red) and interior (yellow) doping sites for Mn^{2+} ions (see Figure 4.1b). It is expected to have breakages in the layers. Therefore, edge-doping sites are available deep inside the crystal as well. If Mn^{2+} ions are preferentially doped in the edge-sites, then it might increase the spatial separation between the host excitons and dopant ions, reducing the energy transfer efficiency.

To elucidate the nature of doping, i.e., edge- vs. interior-site doping, and the corresponding exciton-dopant interactions, we prepared single crystals of Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$, and studied temperature dependent (7 K – 300 K) photoluminescence (PL) spectroscopy and spatially resolved PL. Importantly, PL of single crystals can distinguish between the interior- and edge-excitons,²⁰ as shown by $e^- - h^+$ pairs shown with yellow and red background, respectively, in Figure 4.1b. And therefore, single crystals are used here to distinguish the energy transfer processes from the interior- and edge-excitons to the dopant centers. Our results suggest that the dopant concentration is small (0.6%), along with preferential edge-doping. Consequently, edge- at excitons predominantly sensitize the Mn^{2+} ions leading to Mn^{2+} d -

electron emission with peak 2.05 eV (605 nm). The interior-excitons, though highly quantum confined are spatially separated from Mn^{2+} ions, leading to inefficient energy transfer. Furthermore, low-temperature PL shows that the energy transfer is a thermally activated process.

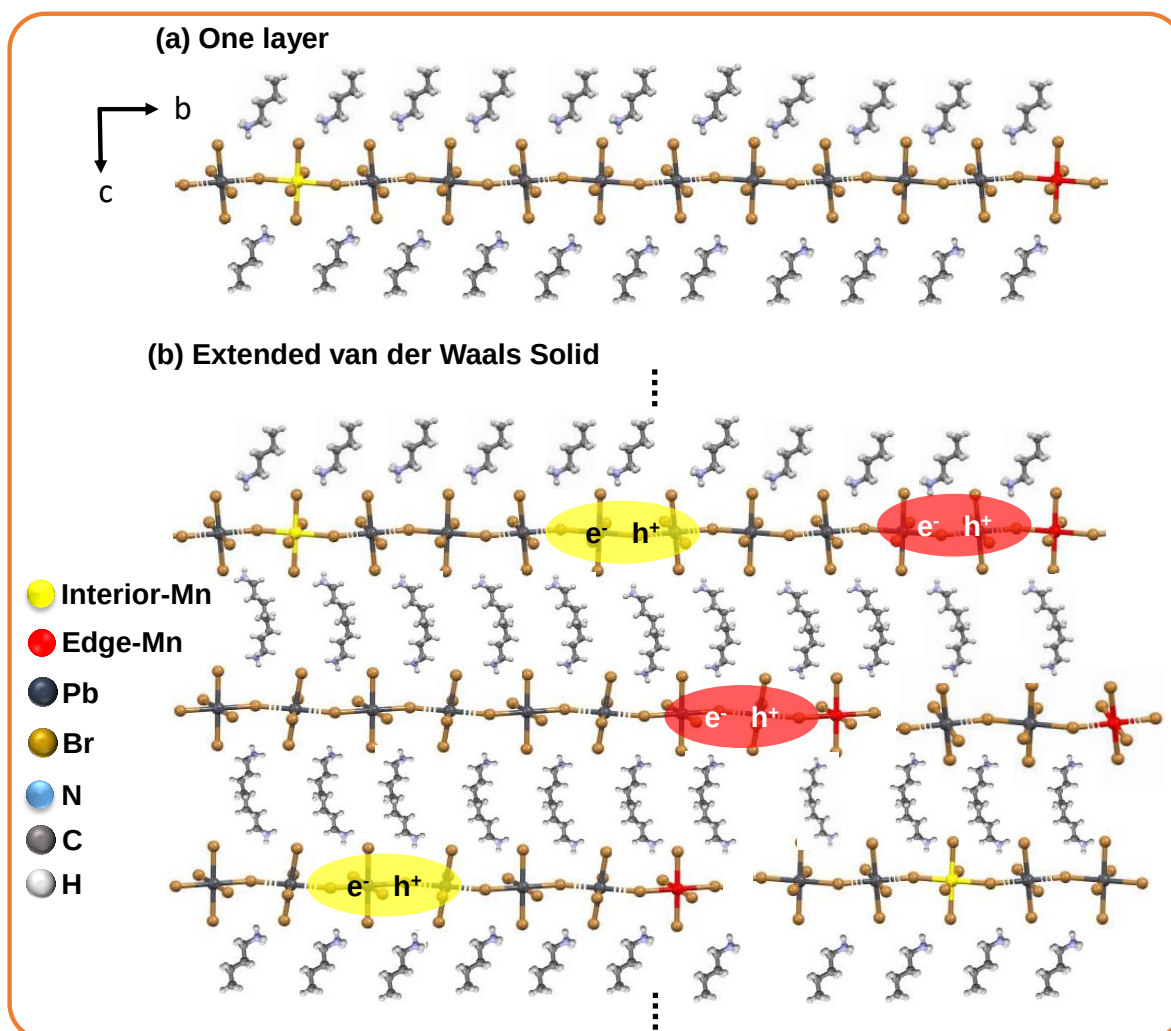


Figure 4.1: Schematic representation of 2D layered hybrid perovskite structure of Mn^{2+} -doped $(BA)_2PbBr_4$. (a) One hybrid layer where the inorganic layer has two kinds of doping sites, edge- and interior-site denoted by red and yellow colored spheres, respectively. (b) Infinite numbers (for simplicity only three layers are shown here) of hybrid layers stack/assemble forming an extended van der Waals solid. Each layer of the extended solid has both edge- and interior-sites. Some of the layers are expected to be broken generating the edge-sites deep inside the crystal as well. The excitons ($e^- - h^+$ pair) located near the interior- and edge-sites are presented by yellow and red backgrounds.

4.2 Experimental Section:

4.2.1 Chemicals: Lead oxide (Sigma Aldrich, PbO, 99.9%), butylamine (Sigma Aldrich, 99.5%), hydrobromic acid (Sigma Aldrich, 48% w/w aqueous, 99.9%), hypophosphorus acid

(Avra, 50% w/w H₂O), manganese bromide (Sigma Aldrich, 98%).

4.2.2 Synthesis of butylammonium bromide: Butylammonium bromide solution was prepared by mixing 468 μ L butylamine with 3 mL hydrobromic acid (48% w/w aqueous) in an ice bath after minor modifications of a reported method.¹⁴

4.2.3 Synthesis of Mn²⁺-doped (BA)₂PbBr₄ single crystals: Both the doped and undoped samples were prepared after minor modifications of the reported¹⁴ acid precipitation method. The only difference between the synthesis of undoped and doped sample is the addition Mn²⁺ precursor in the synthesis of doped sample. For a typical synthesis of Mn²⁺-doped (BA)₂PbBr₄, PbO (558 mg, 2.5 mmol) and MnBr₂ (2147.48 mg, 10 mmol) were added in 3.5 mL 48% w/w aqueous hydrobromic acid. The mixture was then heated at 80 °C to obtain a clear solution. Thereafter, a solution of 5 mmol butylammonium bromide in 2.5 mL 48% hydrobromic acid (48% w/w aqueous) was added to the above solution and heated at 100 °C for 10 min. The reaction temperature was then slowly (~10 °C per hour) decreased to room temperature to grow the flake-like single crystals with lateral sizes about 6 mm and thickness around 0.2 mm.

4.2.4 Characterization: Single crystal X-ray diffraction (XRD) data were recorded using a Bruker Smart Apex Duo diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). Bruker saint software package was used for integration by narrow-frame algorithm. Powder X-ray diffraction (PXRD) data were recorded using Bruker D8 Advance X-ray diffractometer equipped with Cu K α radiation (1.54 Å). Field emission scanning electron microscopy (FESEM) measurements were done using Zeiss ultra plus FESEM instrument. Inductively coupled plasma – optical emission spectroscopy (ICP-OES) measurements were performed using ARCOS M/s apparatus (Spectro, Germany).

4.2.5 Optical properties: All the spectra were recorded from single crystals. Shimadzu UV-3600 Plus UV–vis–NIR spectrophotometer is used to measure UV-visible diffuse-reflectance spectra. The reflectance data were then converted to absorbance spectra following the Kubelka–Munk transformation.²¹ Steady-state PL spectra and time-resolved PL decays were measured using an FLS 980 spectrometer (Edinburgh Instruments). To measure PL decays for exciton emissions, 340 nm and 405 nm laser were used as the excitation source. Whereas, decay of Mn²⁺ PL were measured after excitation with microsecond flash lamp. The PL decay for exciton and Mn²⁺ emissions were fitted by using bi-exponential and mono-exponential decay equations, respectively. For bi-exponential decay, the average lifetimes were calculated by

using $\tau_{av} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$ where, A_i is the weight average of lifetime τ_i . Low temperature PL data were collected using the same setup FLS 980 (Edinburgh Instruments), after connecting it with a closed-cycle He-cryostat (Advanced Research Systems) and a Lakeshore temperature controller. Single crystals were glued on sapphire by silver paste and mounted in the gold coated sample holder.

4.2.6 Spatially resolved PL microscopy and spectroscopy: PL imaging and spatially resolved spectroscopy measurements were carried out using a home built spectrally-resolved laser epifluorescence microscopic setup, details of which can be found elsewhere.²² In brief, the crystals were placed on a freshly cleaned coverslip and excited using a 405 nm laser (LaserGlow, LRD-0405PFR) via an oil immersive objective lens (Nikon TIRF 1.49NA 60X oil). The emission from samples were collected using same objective lens, passed through appropriate dichroic and band-pass filters and imaged using a sCMOS camera (Hamamatsu Orca flash4 V3). For spatially-resolved PL spectroscopy, the emitted light was passed through a slit and a transmission grating (70 g/mm) placed before the sCMOS detector, which allowed us to obtain spectrally-resolved images of a vertical strip along each crystal. All PL microscopy data were analysed using ImageJ and Origin 7.5.

4.3 Results and discussion:

4.3.1 Doping efficacy, structure and morphology: Mn^{2+} -doped $(BA)_2PbBr_4$ single crystals were synthesized by following the acid precipitation method reported earlier.¹⁴ Elemental analysis by ICP-OES finds out that only 0.6% Mn^{2+} (with respect to Pb^{2+}) is present in the product, in spite of using very high (400%) concentration of Mn^{2+} precursor in the reaction mixture. The poor doping affinity of Mn^{2+} into the lattice of $(BA)_2PbBr_4$ might be attributed to the significantly smaller ionic size of Mn^{2+} (0.83 Å) in octahedral coordination compared to that of Pb^{2+} (1.19 Å).²³ Consequently, a large compressive strain develops upon Mn^{2+} doping. It is relatively easier for the edge-sites to release such strain by structural reorganization, however, this process costs much more energy for the interior sites in this 2D crystal. The growth rate is slow for single crystals, and the lattice strain can be released by ejection of the dopants towards the layer-edges during the growth process. Therefore, relatively more doping density of Mn^{2+} is expected at the edge-site of $(BA)_2PbBr_4$ as compared to the interior sites. In general, the doping might become more difficult in the single crystals of structurally low-dimensional hybrid perovskites.

Table 4.1: Crystallographic data and structure refinement for undoped and Mn²⁺-doped (BA)₂PbBr₄ obtained by analysing single crystal XRD data collected at 298 K.

	(BA) ₂ PbBr ₄	0.6% Mn ²⁺ -doped (BA) ₂ PbBr ₄
CCDC number	2206192	2206193
Chemical formula	C ₈ H ₂₄ Br ₄ N ₂ Pb	C ₈ H ₂₄ Br ₄ N ₂ Pb
Formula weight	675.12 g/mol	675.12 g/mol
Temperature	298(2) K	298(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	orthorhombic	orthorhombic
Space group	P b c a	P b c a
Unit cell dimensions	a = 8.3137(12) Å α = 90°	a = 8.314(4) Å α = 90°
	b = 8.2117(12) Å β = 90°	b = 8.208(4) Å β = 90°
	c = 27.535(4) Å γ = 90°	c = 27.622(13) Å γ = 90°
Volume	1879.8(5) Å ³	1885.0(15) Å ³
Z	4	4
Density (calculated)	2.386 g/cm ³	2.379 g/cm ³
Absorption coefficient	17.459 mm ⁻¹	17.412 mm ⁻¹
F(000)	1232	1232
Theta range for data collection	2.86 to 25.00°	2.86 to 25.00°
Index ranges	-9 ≤ h ≤ 8, -9 ≤ k ≤ 9, -32 ≤ l ≤ 28	-9 ≤ h ≤ 9, -8 ≤ k ≤ 9, -32 ≤ l ≤ 32
Reflections collected	26784	16273
Independent reflections	1641 [R(int) = 0.0850]	1646 [R(int) = 0.0904]
Coverage of independent reflections	99.90%	99.90%
Absorption correction	Multi-Scan	Multi-Scan
Structure solution technique	direct methods	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	Σ w(F _o ² - F _c ²) ²	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	1641 / 12 / 73	1646 / 0 / 72
Goodness-of-fit on F ²	1.803	1.47
Final R indices; ; I > 2σ(I)	R1 = 0.0932, wR2 = 0.3983	R1 = 0.0616, wR2 = 0.2042
All data	R1 = 0.1147, wR2 = 0.4204	R1 = 0.0798, wR2 = 0.2155
Weighting scheme	w = 1/[σ ² (F _o ²) + (0.2000P) ²]	w = 1/[σ ² (F _o ²) + (0.1000P) ²]
	where P = (F _o ² + 2F _c ²)/3	where P = (F _o ² + 2F _c ²)/3
Largest diff. peak and hole	2.228 and -1.696 eÅ ⁻³	2.177 and -1.887 eÅ ⁻³
R.M.S. deviation from mean	0.381 eÅ ⁻³	0.232 eÅ ⁻³

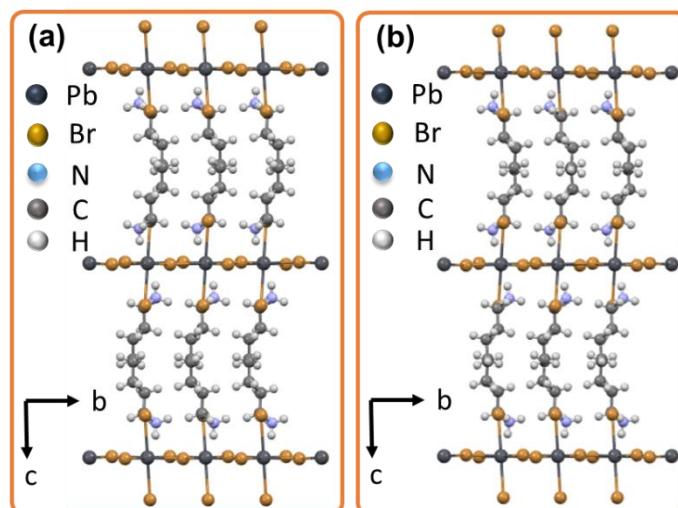


Figure 4.2: Layered crystal structure of (a) undoped $(\text{BA})_2\text{PbBr}_4$ and (b) doped $(\text{BA})_2\text{PbBr}_4$ obtained from single crystal XRD data.

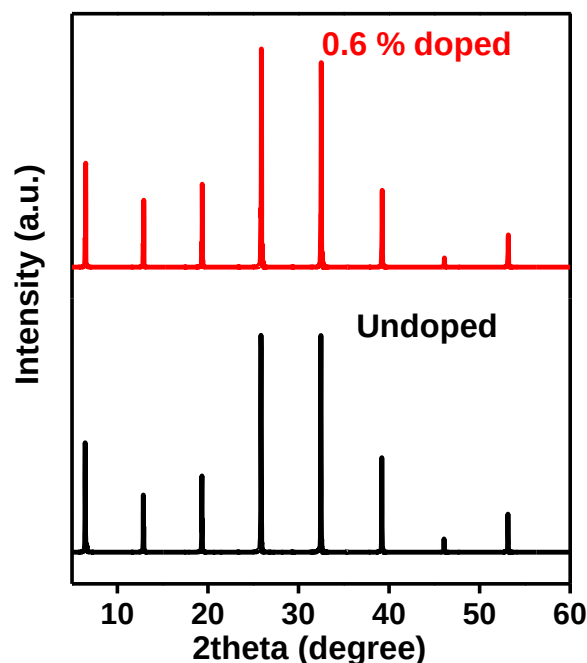


Figure 4.3: Powder XRD patterns of undoped $(\text{BA})_2\text{PbBr}_4$ and Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$ single crystals. The data are shifted vertically for a better presentation.

Single crystal XRD data for both undoped and doped samples were measured at 298 K. Refined structural parameters are shown in Table 4.1. The structures obtained from single crystal XRD data of undoped and Mn^{2+} -doped samples are shown in Figure 4.2a and Figure 4.2b, respectively. Both crystals possess orthorhombic structure with Pbca space group, similar to the earlier report¹⁴ of undoped $(\text{BA})_2\text{PbBr}_4$. Further, we find that the lattice parameters are nominally affected upon doping, consistent with the small (0.6%) Mn^{2+} doping obtained from

ICP-OES data. The powder XRD patterns of both the undoped and doped samples are compared in Figure 4.3. Both samples show similar (00l) planes in accordance with the periodic arrangement of hybrid layers in the crystal. The spacing between the two inorganic layers is estimated as 13.81 Å, which agrees with the single crystal XRD data of (BA)₂PbBr₄. The FESEM images of undoped (Figure 4.4a) and doped (Figure 4.4b) samples show the layered morphology attributed to their layered crystal structure.

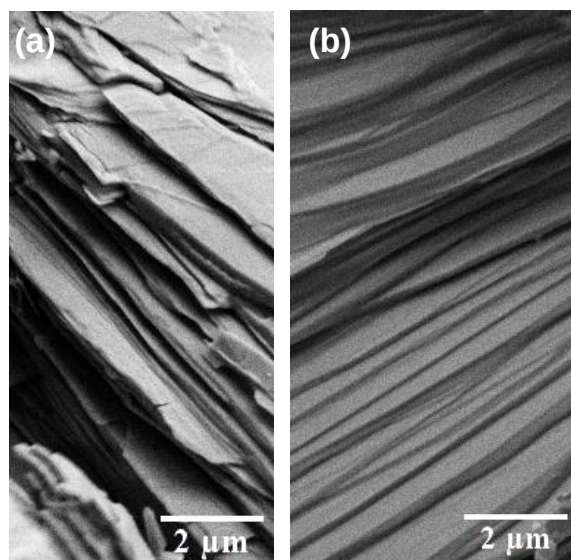


Figure 4.4: FESEM image of a part of (a) undoped (BA)₂PbBr₄ and (b) doped (BA)₂PbBr₄ crystal showing the layered morphology.

4.3.2 Room temperature PL probing interaction of edge- and interior-exciton with Mn²⁺ dopants:

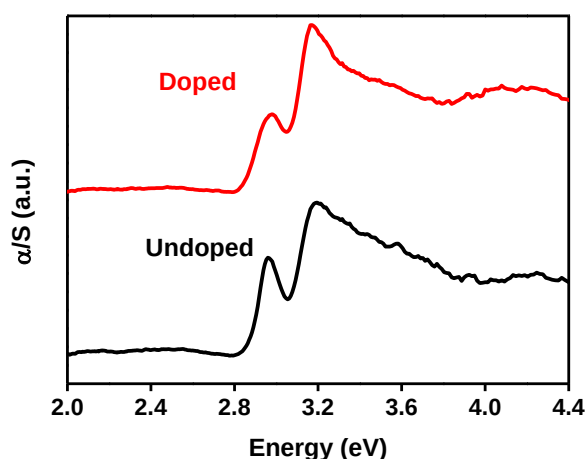


Figure 4.5: Optical absorption spectra obtained after converting the measured diffuse-reflectance data using the Kubelka–Munk transformation ($\alpha/S = (1 - R)^2 / 2R$) of undoped and Mn²⁺-doped (BA)₂PbBr₄, where α is the absorption coefficient, S is the scattering coefficient and R is the reflectance. The data are shifted vertically for a better representation.

Optical absorption of both samples are shown in Figure 4.5. Emission profiles for both samples have been shown in Figure 4.6a. The undoped sample shows two absorption and emission features, which has been attributed to excitonic transitions.^{20, 24} Based on prior literature, we assign the lower energy emission peak at 2.84 eV (437 nm) to edge-excitons, while the higher energy transition at 3.01 eV (412 nm) are designated to interior-excitons. Following Mn^{2+} doping, the excitonic transition energies (spectral peak positions) do not change, however, a new emission peak appears at 2.05 eV (605 nm), attributed to the spin-forbidden $^4\text{T}_{1g} \rightarrow ^6\text{A}_{1g}$ $d-d$ transition of Mn^{2+} ions. We note that the Mn^{2+} ions have octahedral coordination in a centrosymmetric crystal (space group Pbca), which lead us to use “g” in the molecular term symbols of Mn d -states. We do not observe the corresponding feature in the absorption spectra likely owing to the spin-forbidden nature of the $d-d$ transition. Therefore, it is reasonable to conclude that the Mn^{2+} ions get excited to the $^4\text{T}_{1g}$ via transferring the excitonic energy from the host,¹³ and consequently, a lower energy sensitized emission occurs from the dopant ions.

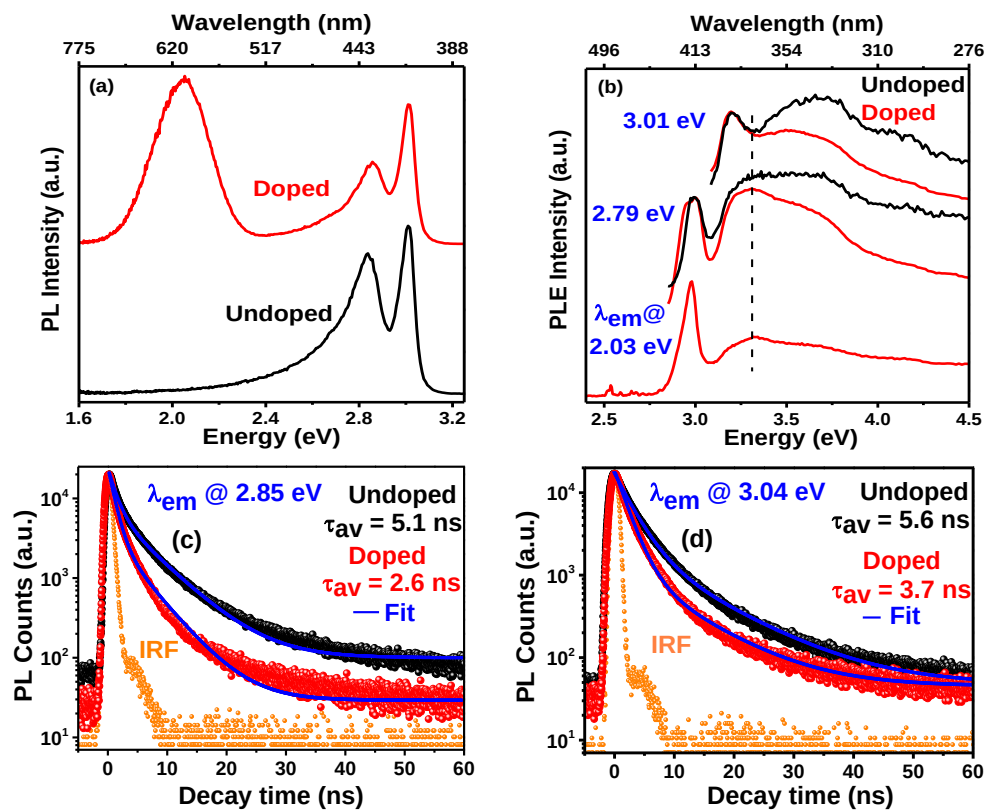


Figure 4.6: (a) Photoluminescence (PL) data of undoped and Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$ single crystals. (b) PL excitation (PLE) spectra of undoped and Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$ single crystals at three different emission energies corresponding interior-exciton (3.01 eV), edge-exciton (2.79 eV) and Mn^{2+} (2.03 eV) emissions. PL and PLE intensities in (a) and (b) are shifted vertically for a clear presentation. Time-resolved PL decay of (c) edge-exciton, and (d) interior-exciton for undoped and Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$ single crystals. IRF refers to instrument response function.

Subsequently, we collected PL excitation (PLE) spectra on the crystals to address whether both the edge- and interior-excitons have the same propensity to sensitize the Mn^{2+} dopants. The PLE spectra measured for the Mn^{2+} emission at 2.03 eV and for the edge-exciton emission at 2.79 eV, are found to be very similar (Figure 4.6b). This suggests that the excitation mechanism for both the emissions is likely to be analogous, i.e., originate from the same source. The edge-excitons are first created by light absorption, a proportion of which emit at 2.85 eV, while the remaining ones non-radiatively transfers excitation energy to the dopants, thereby leading to the characteristic Mn^{2+} emission with peak at 2.05 eV. Importantly, the PLE spectra corresponding to the interior-exciton emission (3.01 eV) is somewhat different from that of edge excitons and Mn^{2+} -emission. For example, at 3.32 eV, both the Mn^{2+} and edge-exciton emission has a broad feature, however, the interior-exciton emission has a clear trough, as shown using a vertical line in Figure 4.6b. The PLE spectra suggest that although the major pathway of energy transfer to the Mn^{2+} dopant is from the edge-excitons, some of the interior-excitons can also transfer excitation energy to the Mn^{2+} dopants.

To better understand the modes of excitation energy transfer from host to Mn^{2+} ions, time-resolved PL decay were recorded of both the excitonic emissions for the doped as well as undoped samples. It is evident from the PL decay data (Figure 4.6c-d) that both the excitonic emissions decay faster following Mn^{2+} doping. Interestingly, compared to interior-exciton emission (Figure 4.6d), doping impacts the radiative decay of edge-exciton emission more severely (Figure 4.6c). The biexponential fits to the PL decay profiles reveals that for the undoped sample, the edge-excitons (at 2.85 eV) have an average lifetime of 5.1 ns (Figure 4.6c), with the fast component of 1.3 ns (70 % contribution) and a slow component of 6.0 ns (30 %). Identical analyses on the Mn^{2+} -doped samples show that the average lifetime of the edge-excitons drastically reduces to 2.7 ns with faster and slower lifetimes of 1.1 ns (86%) and 4.8 ns (14%). The faster lifetime typically has contributions from non-radiative decay processes. Our observation that the contribution of faster lifetime increases significantly in the Mn^{2+} doped samples is consistent with additional energy transfer pathways from the edge-excitons to the Mn^{2+} ions. We find that the interior-excitons (λ_{em} @ 3.04 eV) in the undoped sample decays with average PL lifetime of 5.6 ns (Figure 4.6d), with fast and slow lifetime components of 2.8 ns (86%) and 10.4 ns (14%), respectively. Further, the average lifetime for these excitons in the doped samples decrease slightly to 3.7 ns, with corresponding fast and slow components of 2.0 ns (93 %) and 9.0 ns (7 %). This decrease in PL lifetime after Mn^{2+} doping can be rationalized either by direct sensitization of Mn^{2+} dopants from interior-excitons,

or via increased non-radiative energy transfer from the interior to edge excitons upon Mn^{2+} doping. Nonetheless, the overall decrease in average PL lifetime of interior-excitons upon Mn^{2+} doping is considerably less with respect to that for the edge-excitons. This suggests enhanced efficiency of excitation energy transfer from the edge-excitons to Mn^{2+} dopants as compared to that for the interior excitons.

4.3.3 Spatially resolved PL spectroscopy: To gain more insights, we employ spatially resolved PL imaging and spectroscopy using a home built wide-field epi-fluorescence microscopy setup.²² The PL image of a part of a single crystal of Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$ excited with a 405 nm (3.06 eV) laser is shown in Figure 4.7a. A clear heterogeneity in emission intensity at the edge and the interior regions of the crystal is observed. However, the emission from different locations of a single crystal needs to be spectrally resolved to interpret the origin of the observed heterogeneity. Large-sized layered crystal allows us to perform the spatially resolved spectroscopic measurements from multiple diffraction limited nano-domains (~ 250 nm FWHM) at the edge and the interior regions of the crystal. Emission spectra at three different locations, two from the interior and one at the edge (marked as 1, 2, and 3 in Figure 4.7a) of the crystal, are shown in Figure 4.7b. The Mn^{2+} emission peak around 605 nm could be clearly observed in all the three locations. Both the spectral shape and transition energy of Mn^{2+} emission remain similar for all dopant locations, indicating similar octahedral ligand field splitting for all the Mn^{2+} dopants. This similarity of $[\text{MnBr}_6]^{4-}$ octahedron in the interior and layer edge will also make it difficult to distinguish the two kinds of Mn^{2+} dopants using characterization techniques such as electron paramagnetic resonance spectroscopy.¹⁴

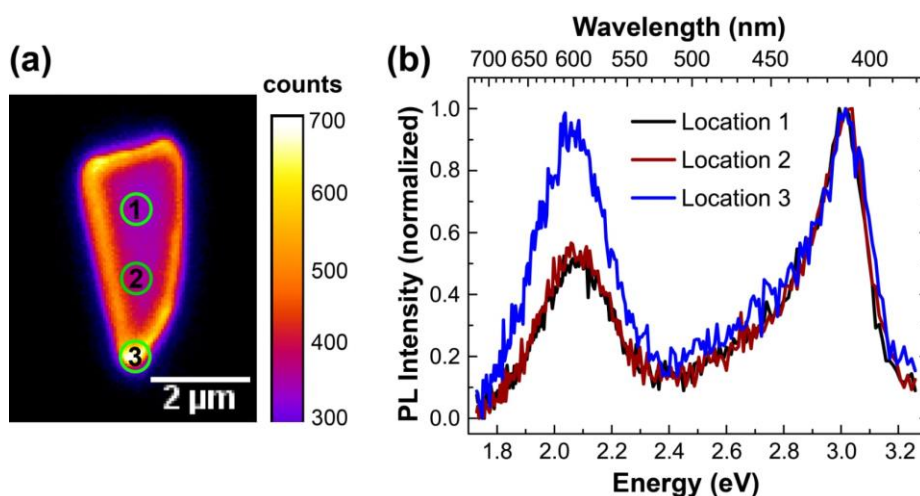


Figure 4.7: (a) Pseudo colored PL intensity image of a Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$ single crystal. (b) Spatially resolved PL emission spectra of the regions 1, 2, and 3. Locations (1, 2, and 3) are marked in the figure (a).

We note that the blue edge of the excitonic peak from the host is partially obscured owing to the scattering of the 405 nm laser excitation by the large crystal. The peak at 3.02 eV (410 nm) observed in Figure 4.7b has a large contribution from the scattered excitation light, which partially overlaps with excitonic emissions. We were able to minimize the scattering by using an emission filter and decreasing the laser excitation power resulting in minimal change in scattering intensity at different locations. In order to compare the relative intensity of Mn^{2+} emission at the edge and interior of the crystal, we normalized the emission spectra with the scattering peak intensity at 3.02 eV (410 nm). To ensure that such normalization does not affect the Mn^{2+} emission, PL spectroscopic measurements were performed on both Mn^{2+} -doped and undoped $(\text{BA})_2\text{PbBr}_4$ single crystals which revealed similar scattering intensity ratio between the interior and edges for both (see Figure 4.8). Interestingly, for more than 20 doped crystals investigated, we consistently find that the Mn^{2+} PL centered around 605 nm has more dominant emissivity at the edges compared to the interior regions. Thus, the spatially resolved PL spectra further supports our inference that Mn^{2+} emission preferentially originates from layer/crystal edges of Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$ single crystals.

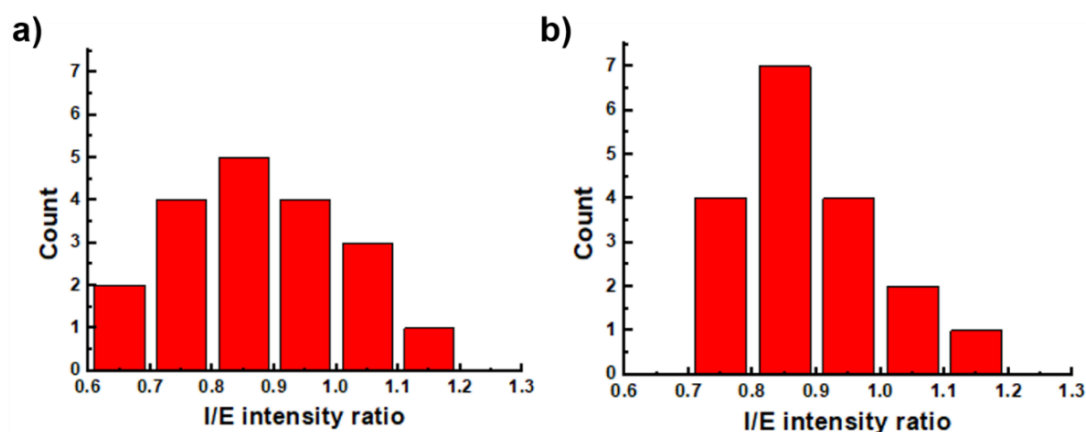


Figure 4.8: Distribution of scattering intensity ratio (intensity at the interior (I)/edge(E)) for (a) undoped and (b) Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$ crystals.

PLE (Figure 4.6b), PL decay (Figure 4.6c-d) and spatially resolved PL (Figure 4.7) data suggest that the Mn^{2+} emission originates preferentially from the Mn^{2+} dopants located near the layer edges. These findings, along with poor 0.6% doping (in spite of adding 400% Mn^{2+} precursor in the reaction mixture), indicate that the doping preferentially happens near the layer edges. The efficiency of energy transfer process from the exciton to dopant decreases sharply with increasing distance between them.¹¹ Therefore, the energy transfer efficiency from the interior-exciton (yellow background of Figure 4.1b) to Mn^{2+} ions is lesser compared to the edge-exciton

(red background of Figure 4.1b). However, the presence of a smaller fraction of dopants in the interior cannot be ruled out, and efficient energy transfer is possible from interior-excitons located near the interior-dopant ions as well. Further, we note that the exciton diffusion length is quite large (~ 40 nm) for similar 2D layered perovskites.²⁵⁻²⁶ So, there is a possibility of interior-exciton diffuse through the layer to reach closer to an Mn^{2+} ions near layer edges, leading to the energy transfer and subsequent Mn^{2+} emission. Overall, our results suggest that, in spite of high quantum confinement of exciton (Bohr radius ~ 1 nm)²⁷ in such 2D layered hybrid perovskites, the exciton-dopant distance is large because of the small dopant concentration and inhomogeneous doping. Consequently, the energy transfer efficiency (particularly from interior excitons) is nominal, yielding a significant exciton emissivity in the PL spectrum of Mn^{2+} -doped samples. We note here that recent reports suggest that doping lanthanide ions in such layered 2D perovskites is also very difficult along with inefficient host-to-dopant energy transfer.²⁸⁻²⁹

4.3.4 Low temperature PL: To gain further insights about the energy transfer processes, we performed temperature dependent PL measurements in the range of 7 K to 300 K. The single crystal XRD data of $(BA)_2PbBr_4$ measured at 100 K (see Table 4.2) shows that the crystal structure remains unchanged compared to the data that measured at room temperature (298 K). The temperature dependent PL spectra of $(BA)_2PbBr_4$ shown in Figure 4.9a, and the corresponding pseudocolor map in Figure 4.9b also do not show any sudden change, indicating absence of a temperature dependent structural phase transition. Similar changes in the excitonic emission with temperature have been reported earlier for such 2D layered perovskites, and is therefore not discussed here in detail.³⁰⁻³¹ Instead, we mainly focus on the excitation and emission processes of Mn^{2+} d -electrons in Mn^{2+} -doped $(BA)_2PbBr_4$. While there are a few recent reports of low-temperature PL study of Mn^{2+} -doped in 2D layered perovskites down to 77 K,³²⁻³³ there are no reports on PL spectral and PL lifetime measurements on such systems down to 7 K. More importantly, we emphasize that the Mn^{2+} dopants near the layer edges predominantly contribute to the observed Mn^{2+} -emission, and therefore we probe the temperature dependence of Mn^{2+} -emission arising from such edge-dopant sites.

Mn^{2+} -doped $(BA)_2PbBr_4$ show the additional Mn^{2+} emission peak around 2.0 eV in the entire temperature range (7 K to 300 K), as evident from the pseudocolor map shown in Figure 4.10a. The corresponding PL spectra at a few representative temperatures between 7 and 300 K are shown in Figure 4.10b. We find that the Mn^{2+} emission peak systematically red-shift with decreasing temperature (2.05 eV at 300 K to 1.99 eV at 7 K). The red-shift of Mn^{2+} PL with

decreasing temperature is consistent with the previous reports, and is attributed to an increase in crystal field splitting of $^4T_{1g}$ state due to compression of host lattice at lower temperatures, and may also be a consequence of depopulation of vibronic hot band.³⁴⁻³⁶ Figure 4.11 reveals that the spectral width of the Mn^{2+} emission decreases with the lowering of temperature owing to suppression of lattice vibrations.

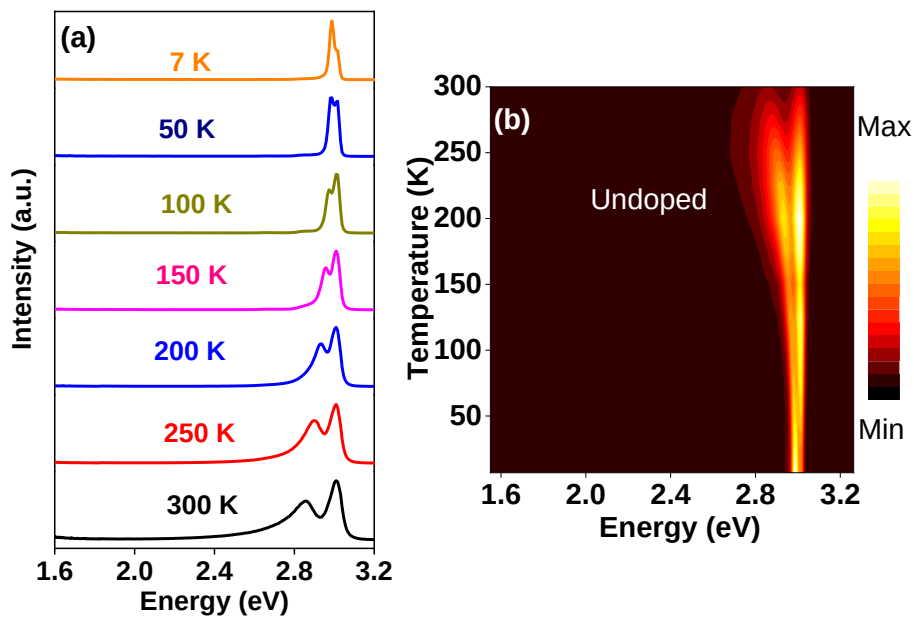


Figure 4.9: (a) Temperature dependent PL spectra of undoped $(BA)_2PbBr_4$ single crystals. (b) Pseudocolor emission intensity map of undoped $(BA)_2PbBr_4$ single crystals.

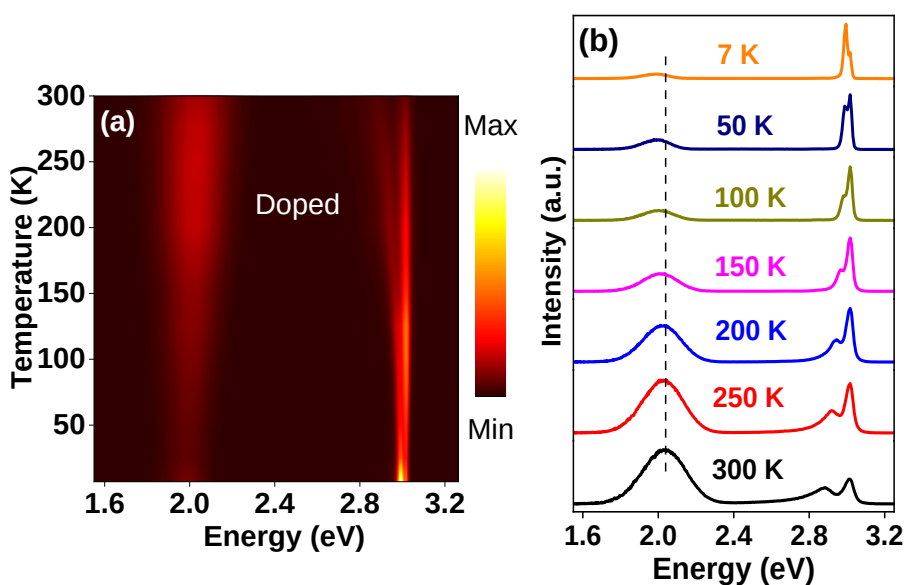


Figure 4.10: (a) Temperature dependent PL spectra of Mn^{2+} -doped $(BA)_2PbBr_4$ single crystals. (b) Pseudocolor emission intensity map of Mn^{2+} -doped $(BA)_2PbBr_4$ single crystals.

Table 4.2: Crystallographic data and structure refinement for undoped and Mn²⁺-doped (BA)₂PbBr₄ obtained by analysing single crystal XRD data collected at 100 K.

	(BA) ₂ PbBr ₄	0.6% Mn ²⁺ -doped (BA) ₂ PbBr ₄
CCDC number	2206190	2206191
Chemical formula	C ₈ H ₂₄ Br ₄ N ₂ Pb	C ₈ H ₂₄ Br ₄ N ₂ Pb
Formula weight	675.12 g/mol	675.12 g/mol
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	orthorhombic	orthorhombic
Space group	P b c a	P b c a
Unit cell dimensions	a = 8.2800(15) Å $\alpha=90^\circ$	a = 8.2391(16) Å $\alpha = 90^\circ$
	b = 8.1615(14) Å $\beta=90^\circ$	b = 8.1223(16) Å $\beta = 90^\circ$
	c = 27.499(5) Å $\gamma=90^\circ$	c = 27.427(6) Å $\gamma = 90^\circ$
Volume	1858.3(6) Å ³	1835.4(6) Å ³
Z	4	4
Density (calculated)	2.413 g/cm ³	2.443 g/cm ³
Absorption coefficient	17.661 mm ⁻¹	17.881 mm ⁻¹
F(000)	1232	1232
Theta range for data collection	4.15 to 25.35°	2.88 to 28.40°
Index ranges	-9<= <i>h</i> <=9, -9<= <i>k</i> <=9, -33<= <i>l</i> <=33	-8<= <i>h</i> <=11, -10<= <i>k</i> <=10, -36<= <i>l</i> <=36
Reflections collected	32397	29821
Independent reflections	1684 [R(int) = 0.0649]	2293 [R(int) = 0.0563]
Coverage of independent reflections	99.60%	99.40%
Absorption correction	Multi-Scan	Multi-Scan
Structure solution technique	direct methods	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	1684 / 0 / 75	2293 / 0 / 74
Goodness-of-fit on F2	1.372	0.874
Final R indices; ; I>2 σ (I)	R1 = 0.0576, wR2 = 0.1377	R1 = 0.0589, wR2 = 0.1784
All data	R1 = 0.0629, wR2 = 0.1398	R1 = 0.0658, wR2 = 0.1845
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0200P)^2+10.0000P]$	$w=1/[\sigma^2(F_o^2)+(0.1000P)^2+20.0000P]$
	where $P=(F_o^2+2F_c^2)/3$	where $P=(F_o^2+2F_c^2)/3$
Largest diff.peak and hole	0.967 and -0.996 eÅ ⁻³	0.582 and -0.994 eÅ ⁻³
R.M.S. deviation from mean	0.126 eÅ ⁻³	0.143 eÅ ⁻³

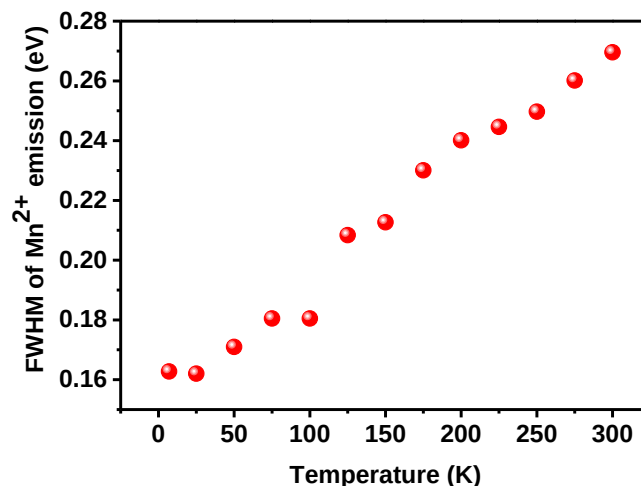


Figure 4.11: Full width at half maximum (FWHM) of Mn^{2+} emission in the temperature range of 7 K to 300 K.

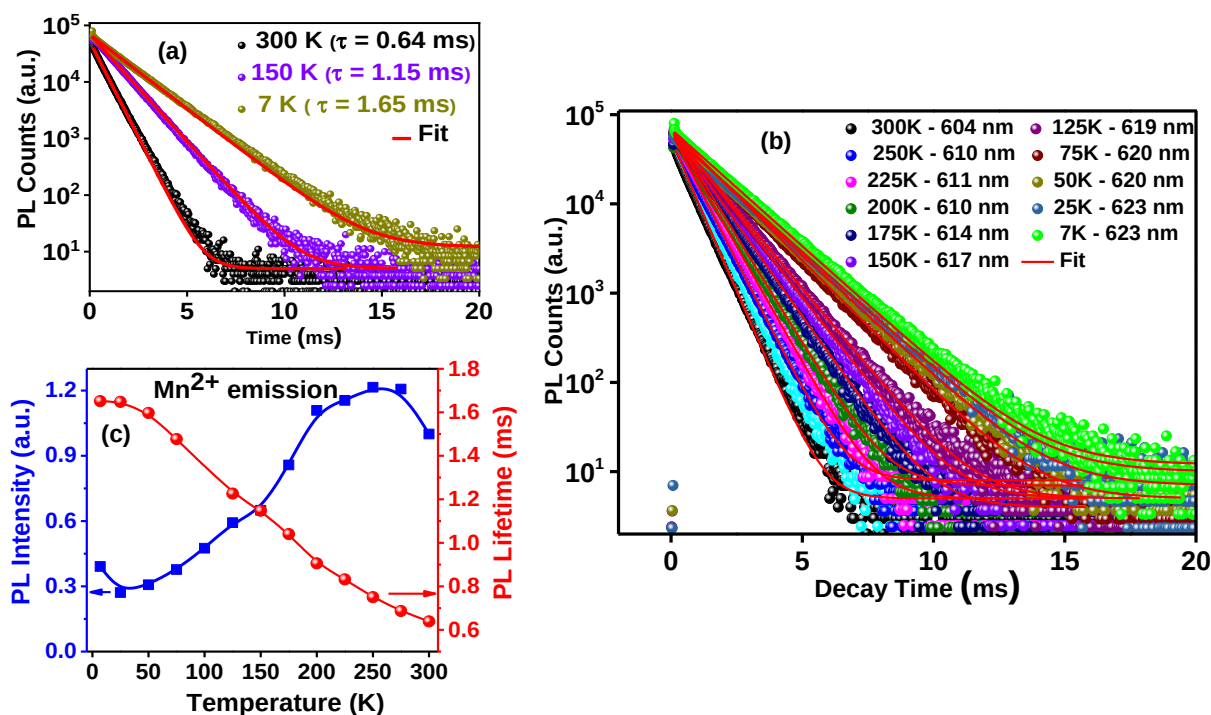


Figure 4.12: (a) PL decay dynamics (emission at 2.05 eV) of Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$ measured at three different temperatures. (b) PL decay dynamics (emission at 2.05 eV) of Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$ measured at different temperatures. Excitation at 3.44 eV (360 nm). (c) Temperature dependent integrated PL intensity and lifetime of Mn^{2+} emission arising from Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$ single crystals.

Figure 4.12a and Figure 4.12b show the lifetimes of Mn^{2+} emission at different temperatures, which are all quasi-single exponential in nature. At 300 K, the lifetime for Mn^{2+} emission is found to be 0.639 ms; such a long lifetime is attributed to the spin- and parity-forbidden ${}^4\text{T}_{1g} \rightarrow {}^6\text{A}_{1g}$ $d-d$ transition of Mn^{2+} ions. Upon lowering of the temperature, the PL lifetime

systematically increases from ~ 0.64 ms (at 300 K) to ~ 1.65 ms at 7 K (Figure 4.12a). Such increase in PL lifetimes likely owes to the suppression of non-radiative relaxation processes as the temperature is lowered, which should therefore be associated with an increase in emission intensity. While we do observe an increase in the emissivity from 300 K to 250 K, intriguingly, upon further lowering of temperature, we find Mn^{2+} -emission intensity decreases continuously down to ~ 25 K and then increases slightly at 7 K (Figure 4.12c). This unusual trend illustrated that correlation of the dopant emission intensity with its lifetime is not straightforward, and perhaps, some other processes are operational within the range of 25-250 K. We note that the PL lifetime is solely governed by the relaxation process of $^4\text{T}_{1g}$ state, while the emission intensity depends both on the excitation processes populating the $^4\text{T}_{1g}$ state, as well as on subsequent relaxation processes. Therefore, it is reasonable to infer that the decrease in emission intensity below 250 K owes to a suppression of the excitation process which populates the $^4\text{T}_{1g}$ (Mn^{2+}) state.

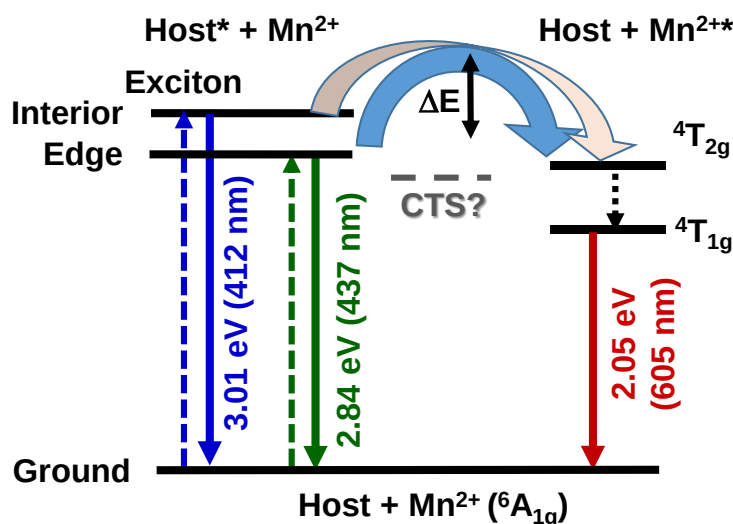


Figure 4.13: Schematics of excitation and emission processes in Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$ single crystals. Ground state represents the total energy of the host and Mn^{2+} in $^6\text{A}_{1g}$.³⁷ Excited states ($\text{host}^* + \text{Mn}^{2+}$) represent host with an exciton (either interior or edge) and Mn^{2+} in $^6\text{A}_{1g}$. Another set of excited states ($\text{host} + \text{Mn}^{2+*}$) represent host along with Mn^{2+} in $^4\text{T}_{1g}$ or $^4\text{T}_{2g}$. Both the interior-exciton (blue arrows) and edge-excitons (green arrows) are responsible for light absorption (upward arrow) and emission (downward arrow). Energy transfer from edge-excitons to Mn^{2+} ions is more efficient, and therefore, indicated by the thicker blue colored curved arrow. Whereas the lower efficacy of energy transfer process from interior-exciton is shown by a thinner curved arrow. “ ΔE ” indicates the thermal activation energy required for the energy transfer. The excited state of Mn^{2+} ion then relaxes back to the ground state by emitting 2.05 eV light (red colored downward arrow). Black colored broken arrow indicate possible non-radiative relaxation processes from $^4\text{T}_{2g}$ to $^4\text{T}_{1g}$. Transient charge transfer states (CTS) like Mn^{3+} (or other trap states) might mediate the energy transfer process.

The decrease in PL intensity below 250 K further suggests that the energy transfer from host excitons to Mn^{2+} dopant ions is a thermally activated process. Figure 4.13 schematically depicts the excitation and emission processes of Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$. The host absorbs the incident photons generating both interior- and edge-excitons. A sub-population of those excitons radiatively recombine at slightly different energies, and the remaining ones transfer their energy to sensitize Mn^{2+} dopants which eventually emit at 2.05 eV (605 nm). Our results depicted in Figure 4.6-4.7 suggest that the edge-exciton is relatively more efficient in transferring the energy to Mn^{2+} ions as compared to the interior-excitons. Further, the low-temperature PL data (Figure 4.9-4.12) suggest that the energy transfer is a thermally activated process, as indicated by the energy barrier “ ΔE ” depicted in Figure 4.13. Prior reports suggest that the energy transfer process in Mn^{2+} II-VI semiconductor nanocrystals and Mn^{2+} doped in CsPbX_3 (X: Cl, Br) perovskite nanocrystals and bulk samples proceed via transient charge transfer states (CTS) like Mn^{3+} or shallow traps. Such a situation might occur in our samples as well, however, at this stage we do not have sufficient experimental evidence to conclusively comment whether transient CTS and/or traps mediate the host to dopant energy transfer process.³⁸⁻⁴¹ However, it is likely that the energy transfer process involves excitation of higher energy levels of Mn^{2+} ions (such as $^4\text{T}_{2g}$) eventually yielding PL emission owing to $^4\text{T}_{1g}$ to $^6\text{A}_{1g}$ transition.

4.4 Conclusion:

We prepared single crystals of Mn^{2+} -doped $(\text{BA})_2\text{PbBr}_4$ 2D layered hybrid perovskites. In spite of using 400% Mn^{2+} in the reaction mixture with respect to Pb^{2+} ions, doping is found to be difficult, yielding only 0.6% Mn^{2+} in the product. Single crystal XRD data of the undoped and Mn^{2+} -doped samples are very similar without any noticeable change in the lattice parameters. The single crystals show two kinds of excitonic PL emissions with transitions at 2.84 eV and 3.01 eV, characteristic of edge-excitons and interior-excitons, respectively. PL excitation spectra, time-resolve PL decay and spatially resolved PL spectral measurements reveal that, the edge-excitons more efficiently sensitize the Mn^{2+} dopants as compared to the interior-excitons, resulting in Mn^{2+} emission at 2.05 eV. Our results suggest that the doping in the interior of the 2D inorganic layers is rather challenging; instead, the Mn^{2+} ions are preferentially located near the layer edges. Owing to lack of proximity between the interior-exciton and Mn^{2+} ions, the efficacy of host-to-dopant energy transfer process is low. Perhaps, smaller ($\sim$ a few tens of nanometers) crystals of 2D hybrid perovskite can enhance the

proximity between excitons and Mn²⁺ ions without altering the excitonic confinement (Bohr radius ~ 1 nm), and can thereby facilitate efficient energy transfer from hosts to dopants. Furthermore, the temperature (7 K to 300 K) dependent PL data show that the energy transfer is a thermally activated process, and might involve shallow traps or charge transfer states. The insights provided here on Mn²⁺ doping in the interior- vs. edge- sites of 2D hybrid perovskite, and the corresponding host-to-dopant energy processes, should aid future development of this class of material as functional luminescent and optoelectronic material.

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Chapter 5

Thesis Summary and Future Outlook

5.1 Thesis summary:

Two-dimensional (2D) layered hybrid perovskites with generic formula A_2MX_4 , where A: organic ammonium ion; M: Pb, Sn; and X: I, Br exhibit interesting quantum well structure.¹⁻² The atomically thin inorganic M-X layers act as a semiconducting well and insulating organic (A) layers act as barrier. The electron, hole and exciton remain confined in the inorganic layer. Consequently, the inorganic part predominantly determines the optoelectronic properties. In difference, the present thesis is focused on developing in new optoelectronic properties by rationally designing the organic sublattice. Though the quantum well structure is still retained with exciton in the inorganic layer, still a smart choice of organic cation can induce interesting changes in the optoelectronic properties.

Essentially, the main focus of the thesis remained in molecular design of organic-inorganic interface, by controlling different non-covalent interactions at the interface. Single crystal X-ray diffraction measurements at different temperatures provides insights on different structural aspects including the non-covalent interactions at the interface. Complementary spectroscopic techniques, such as temperature-dependent photoluminescence (PL), optical absorption, and circular dichroism (CD), are employed to investigate the influence of interface design on optical properties. The chemical composition-structure-property correlation is studied in this thesis emphasizing how molecular engineering of the organic sublattice can drive emergent optoelectronic properties in 2D hybrid perovskites.

Chapter 2, we explored chirality induction in the inorganic sublattice through interface engineering by employing (R/S)-1-iodopropan-2-ammonium (IdPA), a chiral ammonium ion. We designed two new chiral 2D hybrid perovskites that exhibit a unique helical or handedness property. The 2D chiral hybrid ((R/S)-IdPA)₂PbI₄ consists of two conformers of (R/S)-IdPA in both gauche- and anti-conformer forms. These conformers interact with the inorganic sublattice through asymmetric electrostatic interactions, asymmetric hydrogen bonding interactions, and asymmetric non-covalent halogen bonding interactions. Notably, these interactions are stronger for the anti-conformer than for the gauche-conformer. As a result, the repetitive arrangement of anti- and gauche- conformers induces helical chirality in the system. We have observed a connection between the conformers and the helical chirality, suggesting that the conformers may play a role in inducing the helical chirality by tuning the organic-inorganic interface.

In Chapter 3, we have modified the interface through intercalation by inserting organic molecules in the organic sublattice. We intercalated hexafluorobenzene (HFB) into phenethylammonium tin iodide [(PEA)₂SnI₄]. The HFB molecules fit between the two phenyl rings, resulting in stable π - π stacking.³ This π - π stacking leads to a stable intercalated product. Following intercalation, the band gap shifts to a higher energy compared to the pristine sample. Additionally, the non-emissive state is suppressed in the intercalated product, which influences the emission properties by modifying the organic part of the interface.

In Chapter 4, we doped with Mn²⁺ ions in butylammonium lead bromide [(BA)₂PbBr₄] 2D hybrid perovskites and probed the nature of spatially resolved exciton-dopant interactions. In this kind of 2D hybrid perovskite single crystals, there are two types of excitons with respect to their spatial distribution: edge excitons and interior excitons.⁴ The energy transfer from excitons to the dopant site is dependent on the distance between them. Consequently, the location of the dopant affects the photo-physics of nearby excitons. This allows us to infer the position of the dopant by monitoring the photo-physical properties of the host excitons. Our findings suggest that the Mn²⁺ ions are preferentially located at the edges of the crystal. Consequently, edge excitons can easily transfer their energy to the dopant site compared to the interior excitons. The 2D hybrid structure and the large size mismatch between the Mn²⁺ ion (0.89 Å) and Pb²⁺ ion (1.19 Å)⁵ are the probable reasons for this preferential edge doping.

5.2 Future outlook:

5.2.1 Origin of helical chirality of 2D hybrid perovskites:

We have observed that different orientation of ammonium ion leads to asymmetric hydrogen bonding in organic-inorganic interfaces in chapter 2.⁶⁻⁷ In this thesis, we have taken a different approach in chapter 2 to achieve the same asymmetric hydrogen bonding by utilizing the conformers of ammonium ion instead of different orientations. Consequently, we have found that the conformers induce helical chirality in the 2D chiral hybrid perovskite system. We aim to explore how different conformers induce this helical chirality. Chiral induction from organic to inorganic structures occurs through various well-known mechanisms. One such mechanism is the discrete dipole approximation.⁸ In this approximation, the polarizability of a chiral molecule interacts with the polarizability of an achiral molecule, resulting in a net dipole that combines both the dipoles (induced by polarizability) of the chiral and achiral molecules. Therefore, the dipolar interaction between the chiral and achiral dipoles is responsible for chirality induction. An increase in the dipolar interaction between the chiral organic and achiral

inorganic components leads to a shift in the bandgap toward higher energy levels. Additionally, as the dipole interaction increases, the dielectric confinement also increases. This increased screening of the dipole enhances exciton confinement, which ultimately raises the bandgap.

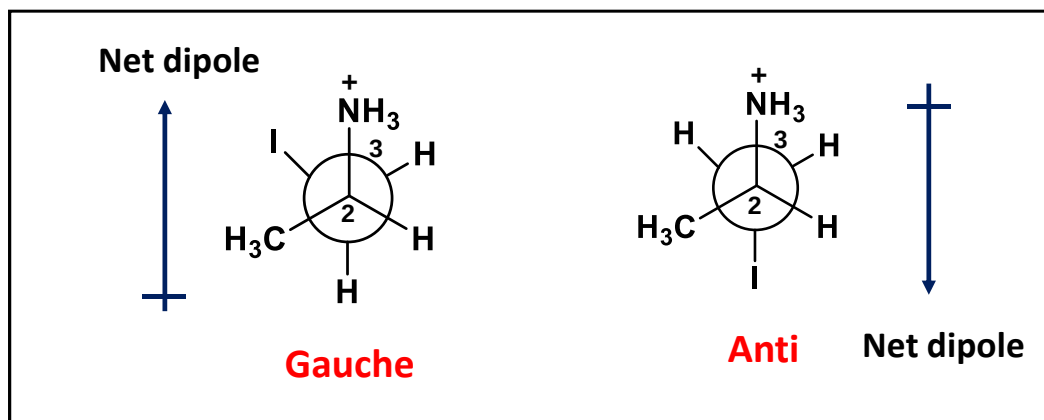


Figure 5.1: schematic of anti and gauche conformers of (R/S)-IdPA cation. The net dipole moment direction has been given besides each molecule.

We have previously reported an example of helical chirality in the compound $((\text{R/S})\text{-IdPA})_2\text{PbI}_4$. In this hybrid system, the arrangements of the anti and gauche conformers of (R/S)-IdPA induce a rare form of helical chirality. The periodic arrangement of the dipoles associated with these conformers must be considered in relation to the (R/S)-IdPA arrangement. The net dipole moment of the gauche conformers points towards the inorganic component along the $-\text{NH}_3$ direction, while the net dipole moment of the anti-conformer points along the $-\text{I}$ bond, which is oriented in the opposite direction relative to the inorganic sublattices (see Figure 5.1). Consequently, the alternating arrangements of the gauche and anti-conformers create a pattern of reverse dipoles. Without the influence of the conformers, this reversal of the dipole moment does not occur, which may result in a non-helical structure.

To demonstrate that the dipole reflects chirality, we need to add one extra carbon chain to the IdPA molecule to create its perovskite structure. If this modification leads to the formation of a 2D chiral hybrid perovskite without any conformer effects, we would not expect any changes in the band gap due to the additional carbon chain. However, if we observe an increase in the band gap solely due to orientation effects, it suggests that the reversal of the dipole moment in the organic moiety may play a crucial role in inducing helical chirality. We predict this because an increase in dipolar interactions is likely to result in an increased band gap.

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Included in thesis:

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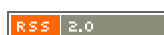
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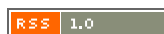
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Author: Laurent Pedesseau, Daniel Sapori, Boubacar Traore, et al

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