

Organic-Inorganic Perovskites: Structural Versatility for Functional Materials Design

Bayrammurad Saparov, David B. Mitzi*

Department of Mechanical Engineering and Materials Science, and Department of Chemistry,

Duke University, Box 90300 Hudson Hall, Durham, NC 27708-0300, USA

E-mail: david.mitzi@duke.edu

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Abstract: Although known since the late 19th century, organic-inorganic perovskites have recently received extraordinary research community attention because of their unique physical properties, which make them promising candidates for application in photovoltaic (PV) and related opto-electronic devices. This review will explore beyond the current focus on three-dimensional (3-D) lead(II) halide perovskites, to highlight the great chemical flexibility and outstanding potential of the broader class of 3-D and lower dimensional organic-based perovskite family for electronic, optical and energy-based applications as well as fundamental research. The concept of a multifunctional organic-inorganic hybrid, in which the organic and inorganic structural components provide intentional, unique and hopefully synergistic features to the compound, represents an important contemporary target.

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1. INTRODUCTION

Perovskite materials, most notably $\text{CH}_3\text{NH}_3(\text{Pb},\text{Sn})(\text{I},\text{Br})_3$, have recently taken a dominant position within the portfolio of compounds offering promise for future high performance and ultra-low-cost-per-watt photovoltaic operation.¹⁻⁶ This promise derives from the confluence of several factors, including extremely high optical absorption, small effective masses for electrons and holes, dominant point defects that only generate shallow levels and grain boundaries that are essentially benign.⁷ The methylammonium cation itself may also play a role in the special suitability of the hybrid materials for photovoltaic (PV) application, through a low barrier to reorientation within the structure and contributions to the dielectric/ferroelectric properties.⁸ While the three-dimensional (3-D) lead- and tin-based organic-inorganic perovskites hold great promise for PV, this remarkable class of compounds presents a vast array of other interesting structural possibilities.^{9,10} In the current review we focus beyond the highly-studied $\text{CH}_3\text{NH}_3(\text{Pb},\text{Sn})(\text{I},\text{Br})_3$ systems and explore the unusual degree of structure-property flexibility afforded by the hybrid perovskites.

We note that there have been a number of previous reviews on structures and properties in the halide-based perovskites.⁹⁻¹³ The current review seeks to examine recent developments and also consider the coupling between new structural concepts and potential applications or fundamental new concepts. As one overarching goal for the broader structural family, we highlight the idea of a multifunctional organic-inorganic hybrid (**Figure 1**) in which unique functionality is afforded to the composite from both the organic and inorganic structural components, to create a material that ideally has greater functionality than either of the components on their own.^{9,11,14,15} We envision that such materials will hold promise for a variety of applications including micro- and nanoelectronics, battery and energy storage, photocatalysis and photovoltaics.

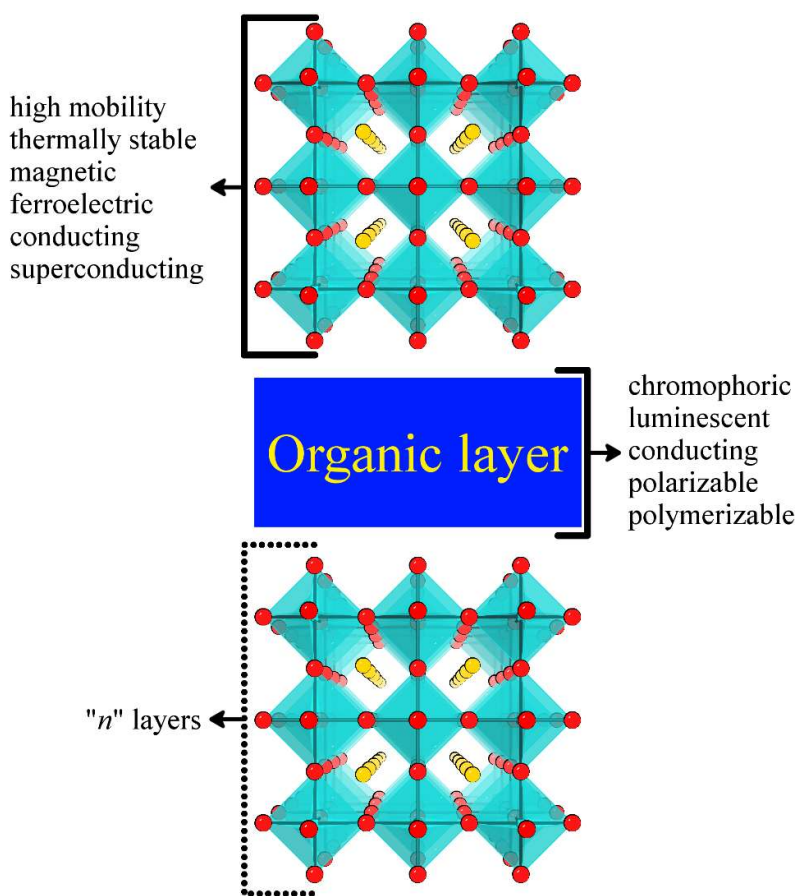


Figure 1. Concept of the multifunctional organic-inorganic hybrid in which unique attributes of organic and inorganic compounds are combined within a single material. It is envisioned that new properties could also arise as a result of the synergistic combination of the two components.¹¹

2. THREE-DIMENSIONAL (3-D) ORGANIC-INORGANIC PEROVSKITES

Perovskite refers to the mineral CaTiO_3 and any structure adopting the same ABX_3 three-dimensional (3-D) structural framework (**Figure 2**). In the case of organic-inorganic hybrid perovskites, at least one of the “A”, “B”, or “X” ions are organic; typically, the “A” cation is organic, while “B” is a metal and “X” is a halogen (Cl, Br or I)—e.g., $\text{CH}_3\text{NH}_3\text{PbI}_3$ or $\text{CH}(\text{NH}_2)_2\text{SnI}_3$, which employ the methylammonium and formamidinium “A” cations,

respectively.¹⁶⁻²⁰ Space filling ionic size constraints dictate whether a certain set of “A”, “B”, or “X” ions may adopt the perovskite framework, which involves a corner-sharing network of BX_6 octahedra (i.e., BX_3), with the “A” cations occupying 12-fold coordinated holes within the structure and counterbalancing the charge of the BX_3 extended anion. Treating all ions as rigid spheres and considering close packing yields the Goldschmidt’s Tolerance Factor concept,^{9,10,21} namely $(R_A + R_X) = t\sqrt{2} (R_B + R_X)$, where R_A , R_B , and R_X are the ionic radii for the corresponding ions and the tolerance factor must satisfy $t \approx 1$ —i.e., empirically it is found that $0.8 \leq t \leq 1.0$ for most 3-D perovskites.

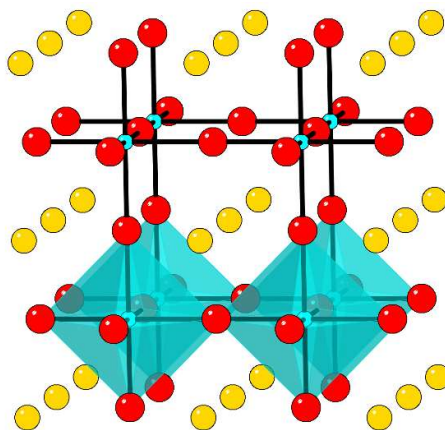


Figure 2. Combined ball-and-stick or skeletal (top) and shaded polyhedral (bottom) representations of the 3-D cubic ABX_3 perovskite structure. The structure is built upon corner-sharing BX_6 octahedra, which are emphasized by cyan-shaded polyhedra, and A cations filling the 12-fold cuboctahedral voids. A, B and X atoms are shown as gold, cyan and red spheres, respectively.

While it is relatively straightforward to assign ionic radii for elemental inorganic ions, non-spherically-symmetric organic cations and charged complexes pose a greater challenge. With the assumption of the molecule being free to rotate about its center of mass, it becomes

possible to assign effective radii for organic cations as shown in **Table 1**.²² Using $t = 1$ and essentially the largest values for R_M and R_X (i.e. Shannon ionic radii $R_{Pb} = 1.19 \text{ \AA}$ and $R_I = 2.20 \text{ \AA}$),²³ the limit on R_A is found to be approximately $2.6 \text{ \AA}$ for traditional BX_3^- frameworks with $B =$ divalent metal and $X =$ halogen.¹⁰ Referring to **Table 1**, we would expect that methylammonium and formamidinium would enable a 3-D perovskite with the PbI_3^- or the SnI_3^- framework, whereas ethylammonium would not. Recently, Kieslich et al. calculated the tolerance factor for over 2500 prospective organic cation/metal halide-based anion ABX_3 compounds and determined that >700 have a consistent tolerance factor with the perovskite structure, with more than 600 of these being unknown hypothetical compounds.²⁴ It is important to note that the concept of tolerance factor for ionic radii represents a necessary condition for the perovskite structure, and it has had significant success in predicting new perovskite structures; however, other space-filling considerations also need to be considered and more refined models for stability have been proposed.²⁵

Table 1. Effective radii of molecular cations and anions (Adapted from ref 22 with permission from The Royal Society of Chemistry)²²

Cation	Effective radius $r_{A, \text{eff}}$ (pm)
Ammonium $[NH_4]^+$	146
Hydroxylammonium $[H_3NOH]^+$	216
Methylammonium $[(CH_3)NH_3]^+$	217
Hydrazinium $[H_3N-NH_2]^+$	217
Azetidinium $[(CH_2)_3NH_2]^+$	250
Formamidinium $[NH_2(CH)NH_2]^+$	253
Imidazolium $[C_3N_2H_5]^+$	258

Dimethylammonium $[(\text{CH}_3)_2\text{NH}_2]^+$	272
3-pyrollinium $[\text{NC}_4\text{H}_8]^+$	272
Ethylammonium $[(\text{C}_2\text{H}_5)\text{NH}_3]^+$	274
Guanidinium $[\text{C}(\text{NH}_2)_3]^+$	278
Tetramethylammonium $[(\text{CH}_3)_4\text{N}]^+$	292
Thiazolium $[\text{C}_3\text{H}_4\text{NS}]^+$	320
Piperazinium $[\text{C}_4\text{H}_{12}\text{N}_2]^{2+}$	322 ^a
Tropylium $[\text{C}_7\text{H}_7]^+$	333
Dabconium $[\text{C}_6\text{H}_{14}\text{N}_2]^{2+}$	339 ^a

Anion	Effective radius $r_{\text{X, eff}}$ (pm)
Fluoride	129
Chloride	181
Bromide	196
Iodide I^-	220
Formate HCOO^-	136

^a Radii calculated from the single crystal X-ray data.²⁶

Besides ionic radii constraints, charge balance must also be achieved—i.e., if the “A” cation is monovalent, then the “B” cation must be divalent if “X” is a halogen and all sites are fully occupied. While typical examples of divalent “B” cations include Ge^{2+} , Sn^{2+} and Pb^{2+} , divalent alkaline-earth and rare-earth ions such as Ca^{2+} , Eu^{2+} and Yb^{2+} can also be employed.²⁷⁻²⁹ However, this valence assignment rule can be stretched with the realization

that the +2 charge on the “B” cation can be achieved by employing equal numbers of +1 and +3 cations (on average yielding a +2 overall charge on this site), as is the case for the semiconducting *inorganic* halide perovskite CsAuI₃, wherein the Au disproportionates into +1 and +3 states—i.e., the compound can more specifically be expressed as Cs₂Au(I)Au(III)I₆.^{30,31} Interest in the mixed-valent metal halide perovskites further follows from the theoretical prediction³² of superconductivity in CsTlX₃, which features Tl⁺ (6s²) and Tl³⁺ (6s⁰) ions that are isoelectronic to Bi³⁺ and Bi⁵⁺ in BaBiO₃. In a recent experimental work,³³ CsTlF₃ was prepared as a light brown powder that adopts a double cubic perovskite *Fm-3m* structure, whereas orange crystals of CsTlCl₃ were obtained in two different polymorphs, a tetragonal *I4/m* and a cubic *Fm-3m* phase. In all of these phases, charge ordering between Tl⁺ and Tl³⁺ was confirmed to exist. Although resistivity was found to decrease under pressure, no evidence of a phase transition to a Tl²⁺ (i.e., delocalized charge) state, which would be required for obtaining a superconducting phase, has been observed so far. In comparison to these inorganic systems, there are only a few known organic-inorganic mixed-valent perovskites, all featuring lower-dimensional or 3-D defect crystal structures (see section 3).

In addition to size and charge, there are also the details of the bonding/coordination preferences for the metal ions involved, which can impact the structural chemistry. For example, in the related inorganic Cs₂Au(I)Au(III)I₆ the primary bonding around Au(I) and Au(III) can perhaps more accurately be described as square planar for Au³⁺ and linear for Au⁺, with long Au⋯I contacts nominally completing octahedral coordination.³¹ In another example, the lone pair s² electrons on B = Tl⁺, Ge²⁺, Sn²⁺, Pb²⁺, Sb³⁺, Bi³⁺ may sterically interfere with BX₆ octahedral coordination, leading to structural distortions of the perovskite framework.^{22,34-37} In the perovskite structure, a stereochemically active lone pair (or s-orbital hybridization) generally gives rise to a shift of the metal atom away from the crystallographic

center of the metal halide octahedra, resulting in alternating long and short B-X bonds and the prospects of ferroelectricity.^{34,36,38} For organic-inorganic perovskites, the directional hydrogen bonding of the organic cation can also couple through intervening halogens to the stereochemically active s^2 electron pair, giving rise to a coordinated structural distortion, as has been discussed for the low temperature phase of $\text{CH}_3\text{NH}_3\text{SnBr}_3$.³⁶ On the other hand, a number of transition metal ions are also impacted by Jahn-Teller and related distortions—e.g., AMnO_3 (A = Pr, Nd, Dy, Tb, Ho, Er, Y),³⁹ $\text{Cs}_2\text{Au}_2\text{Br}_6$,⁴⁰ and KCuF_3 .^{41,42} Given the substantial size, charge and chemistry constraints, there are only a limited number of “A”, “B” and “X” chemical combinations that can yield a 3-D organic-inorganic perovskite.

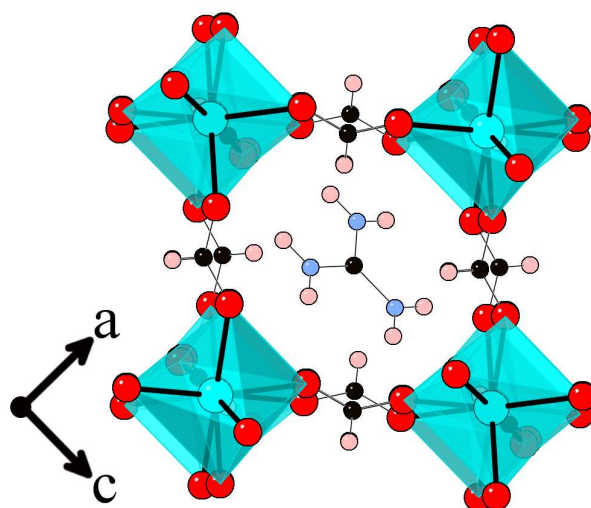


Figure 3. Metal-organic framework (MOF) structure of $[\text{C}(\text{NH}_2)_3]\text{Mn}(\text{HCOO})_3$.⁴³ In order to show the relationship with the halide perovskites, the oxygen atoms are drawn as red spheres in this figure; C, N, H and Mn are black, sky blue, light pink and cyan spheres, respectively.

Note that the perovskites based on metal halide frameworks and organic cations are often referred to as “organometal” perovskites – a terminology that is misleading, since there are no metal-carbon bonds or direct linkages between metals and organic ligands. These

structures can more accurately be referred to as “organic-inorganic” or “hybrid” perovskites. However, organic-inorganic perovskites with direct bonding between a metal and an organic ligand do exist,⁴³⁻⁴⁵ with prototypical examples including $[\text{C}(\text{NH}_2)_3]\text{M}(\text{HCOO})_3$, where $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$ and Zn .⁴³ In this example (**Figure 3**) the guanidinium cation occupies the “A⁺” site in the ABX_3 perovskite framework and the formate anion takes the role of the X^- anion (this time an organic anion). Examples of analogous structures with the guanidinium cation replaced with other organic amines are also known.^{44,45} This family of compounds provides a direct link between the traditional organic-inorganic perovskites based on metal halides and metal-organic frameworks or “MOFs”, a widely expanding class of compounds with potential application in catalysis, gas storage, purification and separation.^{46,47}

3. LOWER-DIMENSIONAL ORGANIC-INORGANIC PEROVSKITES

While the ABX_3 structure described above has fairly rigid structural constraints, one can explore within a broader extended family of lower-dimensional perovskites, which then allows for a remarkable structural tunability—i.e., from the parent 3-D structure, based upon corner-shared BX_6 octahedra, all the way down to isolated, zero-dimensional (0-D) BX_6 octahedral clusters.^{9,10} Note that the dimensionality discussed here refers to the connectivity of the corner-sharing BX_6 octahedra in the crystal structure, as conceptually excised from the 3-D parent compound (**Figure 4**). As the perovskite structure is cut into slices, the size restrictions, as outlined by the tolerance factor for the 3-D structures, are gradually lifted. For example, in two-dimensional (2-D) layered derivatives of the perovskite structure, there are no known restrictions for the interlayer “A” cation length and, in the 0-D derivatives, size restrictions are not applicable altogether as MX_6 octahedra are isolated and can readily shift in relative position. This structural flexibility and tunability of the dimensionality provides a rich

and fertile “playground” for the preparation of interesting crystal structures with varying physical properties.

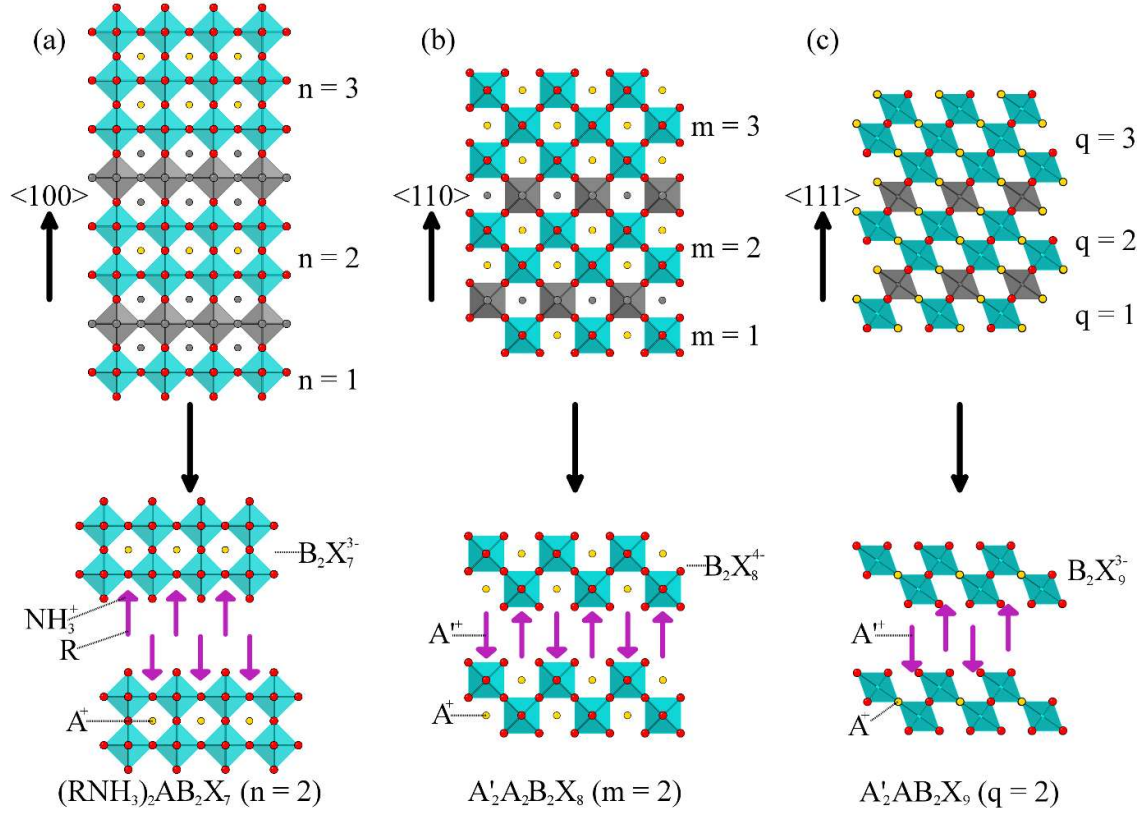


Figure 4. Schematic representation of the derivation of the lower dimensional organic-inorganic perovskites (lower sections) from different cuts of the 3-D perovskite structure (top sections). (a) The family of $\langle 100 \rangle$ -oriented layered perovskites with a general formula of $(\text{RNH}_3)_2\text{A}_{n-1}\text{B}_n\text{X}_{3n+1}$ are obtained by taking n layers from along the $\langle 100 \rangle$ direction of the parent structure. (b) Cuts along the $\langle 110 \rangle$ direction of the 3-D perovskite structure provide the $\langle 110 \rangle$ -oriented family, $\text{A}'_2\text{A}_m\text{B}_m\text{X}_{3m+2}$, which includes 1-D chain ($m = 1$) and 2-D layered ($m > 1$) members. (c) The $\langle 111 \rangle$ -oriented family, $\text{A}'_2\text{A}_{q-1}\text{B}_q\text{X}_{3q+3}$, is formed by excising along the $\langle 111 \rangle$ direction of the 3-D parent, and features 0-D isolated cluster ($q = 1$) and 2-D layered ($q > 1$) members. In each of these layered structures, the inorganic perovskite framework is separated by a layer of larger organic cations.

While the size restrictions may be relaxed for the lower dimensional perovskites, there are still other important parameters to consider for the successful design and synthesis of a targeted perovskite-derived structure.¹⁰ The organic cation “A” must contain terminal functional groups that can ionically interact with the anionic inorganic substructure, but without the rest of the organic molecule interfering with the inorganic components “B” and “X”. Most of the known layered (2-D) perovskite derivatives feature mono- or diammonium cations, yielding the general formulas of $(\text{RNH}_3)_2\text{BX}_4$ or $(\text{NH}_3\text{RNH}_3)\text{BX}_4$, where here “R” represents an organic functional group. The presence of ammonium cations leads to various hydrogen bonding schemes with the anionic substructure, which are important for determining the orientation and conformation of the interlayer organic cations (see ref. 10 for details). Depending on the choice of metal, the inorganic framework can be more or less rigid, which also influences the hydrogen bonding schemes. For example, perovskites containing Jahn-Teller ions such as Cu^{2+} feature highly distorted CuX_6 octahedra that enables greater flexibility for the interaction with interlayer organic cations.

For the diverse family of 2-D perovskite frameworks, although there is no definitive restriction for the length of the interlayer organic cations, there is a restriction for the width, which must fit into an area defined by the terminal halides from four adjacent corner-sharing octahedra. This is important both from the perspective of hydrogen bonding and electron counting schemes. The charge balance requirement dictates the presence of a certain concentration of cations, and organic molecules that are too large (in terms of their width) may cause steric hindrance with adjacent organic molecules, which in turn would render impossible fitting this number of cations into the targeted perovskite framework. However, if they are too narrow—i.e., much smaller than the area provided by the inorganic substructure—the structure can accommodate by allowing organic molecules to tilt. In

summary, both the organic cations and the anionic inorganic framework have templating influence on each other, allowing a certain degree of control over the final structures and properties.

As mentioned above, lower-dimensional derivatives of the perovskite structure can be obtained by making slices along different crystallographic directions in the parent compounds. The choice of the organic cation(s) and the reaction stoichiometry are among the most influential parameters on the orientation of the resultant inorganic frameworks. It is important to note that the dimensional reduction discussed here has significant impact on the physical properties of the compounds. For example, the band gap of the compounds typically increases as the dimensionality of the structure is lowered. This is best illustrated by the example of $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Sn}_n\text{I}_{3n+1}$ compounds, for which the parent 3-D perovskite ($n \rightarrow \infty$) $\text{CH}_3\text{NH}_3\text{SnI}_3$ is a dopable small band gap semiconductor (even yielding semi-metallic character), whereas the $n = 1$ compound $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{SnI}_4$ is a large band gap semiconductor.⁴⁸ In simple terms, this can be rationalized by the fact that the dimensionality of the inorganic framework is reduced by removing the metal “B”, which results in an increase in purely ionic interactions between “A” and “X”, two components with a very different set of electronegativities and, consequently, leading to a larger band gap. In the following sub-sections, we will review some of the recent reports on lower-dimensional perovskite derivatives that feature different cuts from the 3-D structure, including the well-known $\langle 100 \rangle$ -, $\langle 110 \rangle$ - and $\langle 111 \rangle$ -oriented families as well as more exotic possibilities.

3.1. $\langle 100 \rangle$ -Oriented Perovskites

The $\langle 100 \rangle$ -oriented perovskites are obtained by the ordered removal of the B-component from the inorganic framework along $\langle 100 \rangle$ in the ABX_3 structure. Alternatively, they can be thought of as intergrowth compounds with a general formula of $(\text{RNH}_3)_2\text{A}_n$.

$1B_nX_{3n+1}$, formed from the two end members—i.e., the 3-D-parent ABX_3 and 2-D-layered $(RNH_3)_2BX_4$. The $\langle 100 \rangle$ -oriented perovskites represent the richest subgroup of the perovskite derivative family, likely in part because the coordination of the interlayer RNH_3^+ cations is most readily accommodated in these structures. The interactions between organic cations and the inorganic substructure in general, and the hydrogen bonding schemes in particular, are important in the perovskite-derivative structures. The majority of known hybrid perovskites feature primary mono- or diammonium cations. An interesting example involves long chain alkyl “R” groups (**Figure 5**). Subject to the constraint of lateral restrictions imposed by the metal halide layers, these can provide a useful model system for the study of lipid bilayers.⁴⁹⁻

⁵¹ The advantageous feature of the hybrid perovskites is that, unlike free lipid bilayers, since the organic cations are anchored to the inorganic perovskite lattice, the phase transitions are solid-to-solid, which allows investigations of these transitions through a variety of spectroscopic techniques. Depending on the length of the organic chain and the nature of the B-metal cation, the temperature and the order of the phase transitions observed in hybrid perovskites can be different.⁴⁹ In addition to the regular dynamic rotational disordering of the ammonium functional group, the hybrid perovskites containing long chain organic cations undergo “melting transitions” as a function of temperature, which are characterized by an increased conformational disorder of the methylene units of the alkyl groups.⁵⁰ This large increase in gauche conformational disorder results in the non-uniform distribution of the orientation of the chains, and consequently, in the increase of the interlayer lattice parameter.⁵¹ Raman spectra of $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12, 16$ and 18) above the melting transition are noted to be similar to that of n -alkanes in the molten state. These spectra support the idea that, above the melting transition, the alkyl chains of the bilayers are liquid-like in two dimensions between adjacent inorganic layers.⁵⁰ Molecular dynamics (MD) simulations were used to successfully reproduce the experimental data, except for the detailed transition

temperatures, for $(C_nH_{2n+1}NH_3)_2PbI_4$ ($n = 12, 14, 16$ and 18).⁵¹ Snapshots of the simulated structures above and below the melting transition for $(C_{18}H_{37}NH_3)_2PbI_4$ are provided in **Figure 5**.

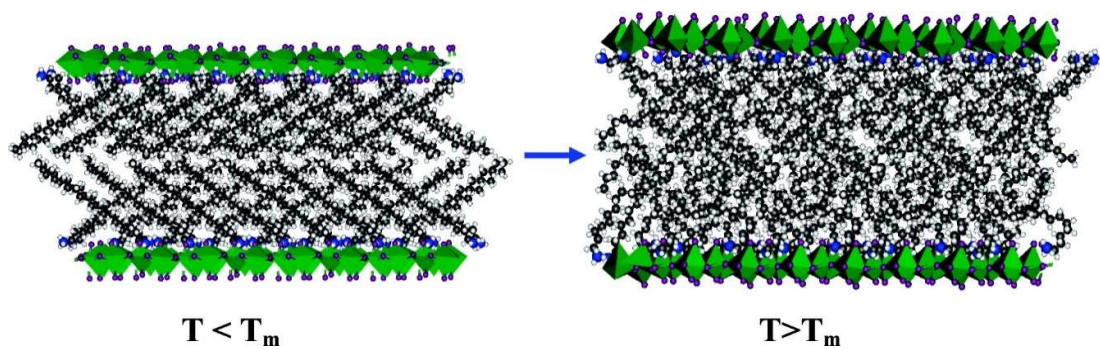


Figure 5. Structures of the organic cation bilayers in $(C_{18}H_{37}NH_3)_2PbI_4$, obtained using molecular dynamics simulations, below ($142\text{ }^{\circ}\text{C}$) and above ($272\text{ }^{\circ}\text{C}$) the melting transition of $T_m = 182\text{ }^{\circ}\text{C}$.⁵¹ Reprinted with permission from ref 51. Copyright 2010 American Chemical Society.

Recently, several examples of perovskites containing non-primary ammonium cations have also been prepared. In $(C_6H_8N_4)BI_4$ ($B = Pb, Sn$),⁵² for example, the inorganic $[BI_4]^{2-}$ sheets are separated by a monolayer of aromatic biimidazolium $(C_6H_8N_4)^{2+}$ dications (**Figure 6**). The biimidazolium dications are sandwiched within the two adjacent inorganic sheets, forming a very close approach between the iodide anions of the inorganic layers and the aromatic rings. Layered perovskite derivatives featuring primary ammonium cations tend to have distorted layers with the B-X-B angles ranging from 140 to 160° (compared to 180° for undistorted layers) due to the interactions between the halides of the inorganic layers and hydrogens of the ammonium functional groups.⁵³ In contrast, the inorganic layers are remarkably flat in $(C_6H_8N_4)PbI_4$ and $(C_6H_8N_4)SnI_4$, as indicated by the reported B-I-B angles of 174 and 172° , respectively. The flatness of the layers in $(C_6H_8N_4)BI_4$ has been attributed to

the non-primary nature of the biimidazolium dications;⁵² however, several structural parameters play a role in determining the degree of distortion. The B-X-B angles (β , **Figure 6**), commonly used to indicate the degree of distortion of the inorganic framework, can have out-of-plane and in-plane components. The former, in turn, could be due to cation-anion interactions or stereochemical activity of metal cation lone pairs, which is also reflected in the I-B-I bond angles within a given BI_6 octahedron. If the distorting influence of a lone pair is assumed negligible—i.e. for regular BI_6 octahedra—the deviation (**Figure 6**) of the axial B-I bonds from the normal to the plane of B atoms (α) can be used as a parameter to evaluate the out-of-plane distortions in the structure.⁵⁴ In $(\text{C}_6\text{H}_8\text{N}_4)\text{PbI}_4$, the PbI_6 octahedra are almost regular as shown by the I-Pb-I angles of $87.70\text{--}94.83^\circ$, and the Pb-I-Pb angle is $\beta = 174^\circ$, with the out-of-plane component measuring $\alpha = 2^\circ$.

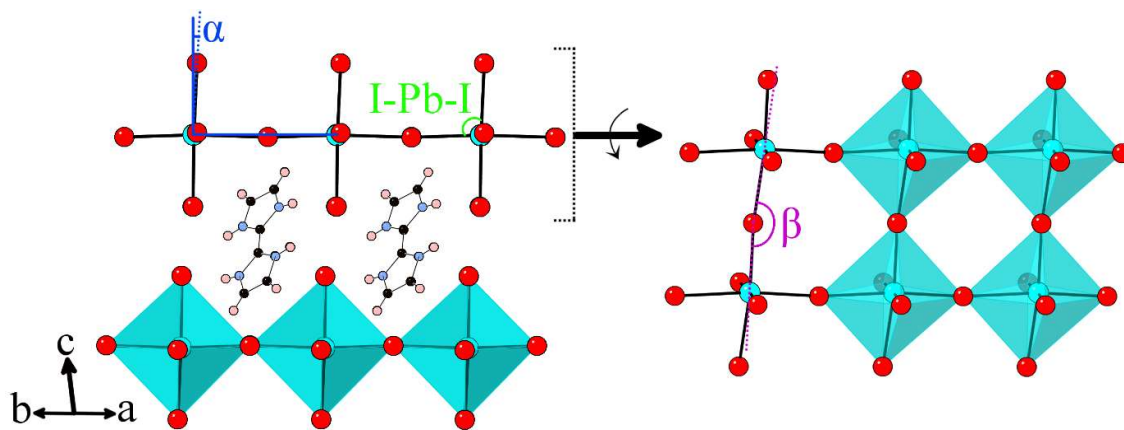


Figure 6. Combined skeletal (top) and polyhedral (bottom, shaded) representation of the crystal structure of $(\text{C}_6\text{H}_8\text{N}_4)\text{PbI}_4$, which features $[\text{PbI}_4]^{2-}$ sheets that are separated by a monolayer of aromatic biimidazolium $(\text{C}_6\text{H}_8\text{N}_4)^{2+}$ dications.⁵² The inorganic layers are remarkably flat, with a Pb-I-Pb angle of $\beta = 174^\circ$, and contain regular PbI_6 octahedra with the I-Pb-I angles of $87.70\text{--}94.83^\circ$, and the out-of-plane distortion of $\alpha = 2^\circ$.

In addition to a lower number of H atoms available, biimidazolium dications have steric hindrance with respect to hydrogen bonding to the BX_6 octahedra. Layered $\langle 100 \rangle$ -oriented perovskites $(C_5H_{11}N_3)PbX_4$ ($X = Br, Cl$) feature histaminium cations, which contain both primary ammonium and imidazolium heads.⁵⁵ As expected, the imidazolium group of the organic cation has steric hindrance to hydrogen bonding; however, when compared to the biimidazolium dications, histaminium cations with their primary ammonium groups strongly interact with the inorganic layers and distort them, with the corresponding distinct Pb-Br-Pb angles of 174.84° and 153.66° for $(C_5H_{11}N_3)PbBr_4$. $[(CH_3)_3NCH_2CH_2NH_3]SnI_4$ is another compound that contains a primary and non-primary (quaternary) ammonium dication, for which the bridging Sn-I-Sn bond angles of 162.3° and 171.5° are observed.⁵⁶ Here, the weaker hydrogen bonding characteristic of the quaternary ammonium group does not prevent the corrugation of the inorganic sheet.

Table 2. Electronic and structural parameters for (RNH₃)₂SnI₄ hybrid perovskite semiconductors (Adapted with permission from ref 54.

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amine (RNH₂)	exciton energy (eV, nm)	Sn-I-Sn bond angle (°)^a	in-/out-of-plane distortion (°)^a	eq/ax Sn-I bond length (Å)^a	distortion of SnI₆ octahedron^b
4-Chlorophenethylamine ^c	2.02, 615	157.0	22.9/<1	3.139/3.176	0.017
Phenethylamine	2.04, 609	156.5	23.5/<1	3.136/3.161	0.012
4-Fluorophenethylamine	2.04, 609	156.4	23.7/<1	3.135/3.181	0.020
2-Naphthaleneethylamine ^c	2.06, 602	156.6	23.4/<1	3.152/3.204	0.023
3-Fluorophenethylamine	2.07, 599	154.2	25.8/<1	3.136/3.207	0.033
2-Fluorophenethylamine	2.11, 588	153.3	26.7/<1	3.149/3.178	0.013
2-Chlorophenethylamine	2.12, 586	154.8	25.2/<1	3.169/3.156	0.006
Pentafluorophenethylamine ^c	2.17, 572	152.4	27.6/<1	3.169/3.173	0.041
2-Bromophenethylamine	2.23, 557	148.7	25.1/11.3	3.145/3.155	0.005
2-Trifluoromethylphenethylamine ^c	2.23, 556	149.6	23.2/12.3	3.147/3.162	0.007

1-Pyreneethylamine ^c	2.28, 545	144.1	28.5/12.3	3.124/3.170	0.020
<i>n</i> -Butylamine	2.04, 607	159.6	19.4/6.4	3.136/3.160	0.011
<i>n</i> -Dodecylamine	2.14, 580	155.7	16.7/11.2	3.138/3.152	0.007
2-Trimethylammonioethylamine	1.97, 630	166.9	0.8/11.8	3.162/3.127	0.015

^a Values represent averages for each structure. ^b Bond length distortion is defined as $\sum \text{abs}(d_i - \langle d \rangle) / 6$, where d_i is the summation over the six Sn-I distances and $\langle d \rangle$ represents the average bond length. ^c Unpublished crystal structures.

The buckling of the inorganic layers and B-I-B bond angles are important not only from the fundamental chemical bonding and crystallography points of view, but also because they correlate with the band gaps of the materials. Generally, larger B-I-B bond angles are observed for the narrower band gap hybrid perovskites.^{56,57} Theoretical studies⁵⁴ suggest that the in-plane Sn-I-Sn bond angle has the greatest influence on the band gap of compounds containing a SnI_4^{2-} framework (up to 1 eV tunability), with the equatorial Sn-I bond distances also having a significant influence (e.g., see **Table 2**). The degrees of in- and out-of-plane distortions were found to be determined by the relative charge density and steric requirements of the organic cations. It is important to note that, in this theoretical analysis,⁵⁴ structural parameters such as the in-plane (β) and out-of-plane angles (α) and bond lengths were considered, but the octahedral coordination around Sn^{2+} in the SnI_4^{2-} sheets was fixed. In fact, the distortions of SnI_6 also have a major impact on the band structure. For example, a recent theoretical work⁵⁸ on a family of A_2SnI_4 salts reports that, through variation of organic cations and associated structural distortions, the band gaps can be changed from 1.43 to 4.09 eV (>2.5 eV tunability). In this work, the band structure calculations were carried out using the atomic coordinates of Sn and I determined by X-ray diffraction—i.e., considered compounds have all sets of possible structural distortions including in-plane and out-of-plane distortions, varying bond lengths, and distortions of the SnI_6 octahedra. Comparing the structures of two members in the A_2SnI_4 family, Sn-I-Sn bond angles are 155.10 and 169.03° for compounds containing A = pentyl diammonium (C5di) and 3-Iodopyridinium (IPy) cations, respectively.⁵⁸ Based on these Sn-I-Sn bond angles alone, one would expect (C5di) SnI_4 to have larger band gap than that of (IPy) $_2\text{SnI}_4$; however, the band gaps were calculated to be 1.43 eV for the former, and 4.09 eV for the latter.⁵⁸ These findings are supported by the measured room-temperature resistivities of 20 Ω cm for (C5di) SnI_4 and 10⁷ Ω cm for (IPy) $_2\text{SnI}_4$.⁵⁸ In these two compounds, while the two axial Sn-I bonds are similar, the four equatorial Sn-I bonds are

notably different. In (C5di)SnI₄, the equatorial Sn-I bonds are nearly equal and range from 3.14 to 3.19 Å, whereas in (IPy)₂SnI₄, there are two shorter (~2.95 Å) and two much longer (3.47 and 3.66 Å) equatorial Sn-I contacts.⁵⁸ In fact, the Sn-I distance of 3.66 Å is ~17% longer than the sum of ionic radii of the two elements (Shannon ionic radii $R_{\text{Sn}^{2+}}$ (estimated)^{59,60} = 0.9-0.94 Å, R_{I^-} = 2.20 Å).²³ Six other members of the A₂SnI₄ family were also considered, and the observed band gap values follow the above-outlined trend in the Sn-I distances and the severe equatorial distortions of SnI₆ octahedra.⁵⁸ These results further highlight the important impact that equatorial Sn-I distances and SnI₆ octahedra distortion can have on electronic structure (in addition to Sn-I-Sn bond angle).

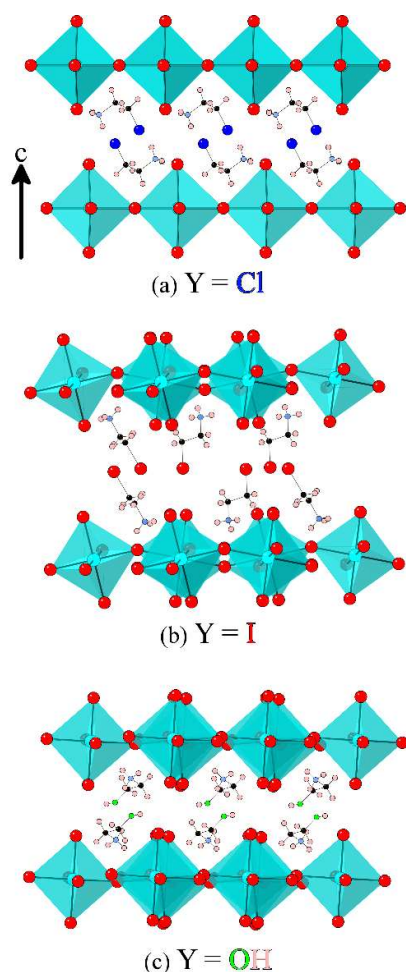


Figure 7. Crystal structures of (Y-(CH₂)₂NH₃)₂PbI₄, where Y = Cl, I and OH.^{61,62} The inorganic layers are relatively undistorted in (a) Y = Cl, presumably because the ammonium

functional groups lie outside of the perovskite layer. In (b) $Y = I$, the ammonium heads reside in the perovskite layer leading to stronger hydrogen bonding interactions and more highly distorted layers. In (c) $Y = OH$, the ammonium and ethyl parts are both located in the inorganic sheets leading to an intermediate case between $Y = Cl$ and $Y = I$.

A convenient way of controlling the in- and out-of-plane distortions is by employing bifunctional organoammonium cations such as $Y(CH_2)_2NH_3^+$ ($Y = OH, Cl, Br, I, CN$) in $(Y-(CH_2)_2NH_3)_2PbI_4$ (**Figure 7**).¹³ A large $I(CH_2)_2NH_3^+$ cation yields highly distorted perovskite layers with an in-plane Pb–I–Pb angle of $\beta = 147.4^\circ$ in $(I-(CH_2)_2NH_3)_2PbI_4$, but $Y = Cl$ and Br give relatively undistorted layers in the $(Y-(CH_2)_2NH_3)_2PbI_4$ series with $\beta \sim 178^\circ$.⁶¹ The main difference between the structures lies in the position of the ammonium cation heads, which are out of the perovskite layers in $Y = Cl$ and Br and, instead, the ethyl parts are located in the perovskite layers, leading to a much weaker hydrogen bonding interaction. In comparison, the ammonium functional group resides in the perovskite layer for the $Y = I$ compound, whereas the ethyl parts are located out of the inorganic framework, leading to stronger hydrogen bonding. As a result of the difference in the hydrogen bonding and distortions of the inorganic layers, the relatively undistorted $(Y-(CH_2)_2NH_3)_2PbI_4$ ($Y = Cl$ and Br) have band gaps of 2.2 eV and have a distinctly more disperse HOMO band compared to the highly distorted $(I-(CH_2)_2NH_3)_2PbI_4$, which has a larger band gap of 2.45 eV,⁶¹ thereby further highlighting the critical templating influence that the organic cations have on the electronic properties of the inorganic framework. Another interesting finding is that, upon heating $(Br-(CH_2)_2NH_3)_2PbI_4$ at 50-150 °C, halogen exchange between the organic and inorganic frameworks occurs yielding $(Br-(CH_2)_2NH_3)_{2-x}(I-(CH_2)_2NH_3)_xPbBr_xI_{4-x}$ with $x_{max} \sim 1.85$.⁶³

In $(\text{HO}(\text{CH}_2)_2\text{NH}_3)_2\text{PbI}_4$ ($Y = \text{OH}$), the $\text{CH}_2\text{CH}_2\text{NH}_3$ fragment lies within the inorganic layers, with the $-\text{OH}$ functional group also playing an active role in hydrogen bonding and with both the inorganic framework and the adjacent organic cation forming supramolecular dimers.⁶² Consequently, the inorganic sheets are less distorted compared to $Y = \text{I}$ and many other PbX_4^{2-} -based layered perovskites, with $\beta = 159.8^\circ$, but more distorted compared to $Y = \text{Cl}$ and Br and, accordingly, the band gap was measured to be 2.31 eV for this compound. Hydrogen bonding between the cyano and ammonium groups in $(\text{CN}(\text{CH}_2)_2\text{NH}_3)_2\text{PbI}_4$ ($Y = \text{CN}$) also leads to the formation of supramolecular dimers of organic cations. However, in this case, ethyl fragments are located in the inorganic layers, giving larger Pb-I-Pb angles of $\beta = 174.64^\circ$ and 177.59° .¹³ Looking at the β angle alone, one might expect a band gap value of ~ 2.2 eV, similar to that observed for $Y = \text{Cl}$ and Br ; however, the measured UV-VIS data suggest a 2.34 eV band gap for $(\text{CN}(\text{CH}_2)_2\text{NH}_3)_2\text{PbI}_4$. The difference has been attributed to the stereoactivity of the ns^2 lone pair, which manifests itself as a distortion of the BX_6 octahedra and originates from the mixing of the frontier HOMO (highest occupied molecular orbital)-LUMO (lowest unoccupied molecular orbital) orbitals known as a second-order Jahn-Teller (SOJT) effect.^{38,64}

The SOJT effects are observed for d^0 and $ns^2 d^0$ cations and, according to this theory, the distortions of the metal centered BX_6 octahedra lead to a stabilization of the HOMO and destabilization of the LUMO, which increases the band gap. As a result, the HOMO of compounds containing ns^2 metal cations feature contributions from the s orbitals, and the HOMO-LUMO mixing leads to the stereoactivity of the lone ns^2 pairs. The PbI_6 octahedra are distorted in $(\text{CN}(\text{CH}_2)_2\text{NH}_3)_2\text{PbI}_4$ with $\text{I}_{\text{eq}} - \text{Pb} - \text{I}_{\text{eq}}$ bond angles of 82.69 - 100.90° and $\text{Pb}-\text{I}_{\text{eq}}$ bond lengths ranging from 3.165 to 3.369 Å. In comparison, almost regular octahedra are found in $(\text{Br}(\text{CH}_2)_2\text{NH}_3)_2\text{PbI}_4$, for example, with the $\text{I}_{\text{eq}} - \text{Pb} - \text{I}_{\text{eq}}$ angles of 88.318 - 91.764° and $\text{Pb}-\text{I}_{\text{eq}}$ lengths of 3.1799–3.2799 Å,¹³ which could explain the lower band gap value for

this compound. Together with the variation of the functional groups in the bifunctional ammonium cations, one can also change the length of the organic chains and, as the chain length increases in $(\text{HO}(\text{CH}_2)_3\text{NH}_3)_2\text{PbI}_4$ and $[(\text{IC}_m\text{H}_{2m}\text{NH}_3)_2\text{PbI}_4]$ ($m = 2-6$), less in-plane distortion in the inorganic layer is observed.⁶⁵

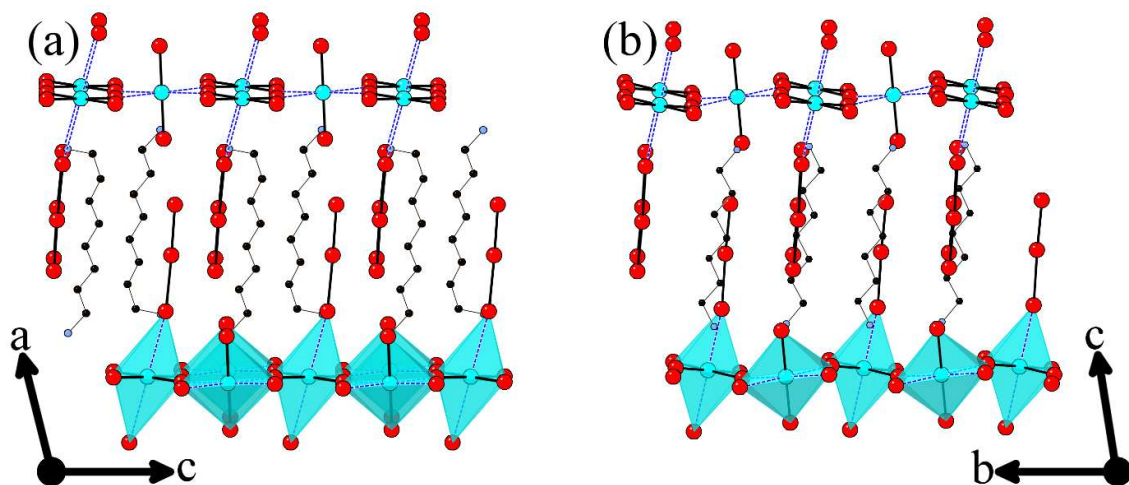


Figure 8. Combined skeletal (top) and polyhedral (bottom, shaded) view of the crystal structures of $\langle 100 \rangle$ -oriented derivatives (a) $[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_2[(\text{Au}^{\text{I}}\text{I}_2)(\text{Au}^{\text{III}}\text{I}_4)(\text{I}_3)_2]$ and (b) $[\text{NH}_3(\text{CH}_2)_7\text{NH}_3]_2[(\text{Au}^{\text{I}}\text{I}_2)(\text{Au}^{\text{III}}\text{I}_4)(\text{I}_3)_2]$, which feature strongly distorted AuI_6 octahedra (nominal) induced by the presence of mixed-valent $\text{Au}^{\text{I/III}}$ cations.⁶⁶ In fact, each layer is made of alternating linear $[\text{Au}^{\text{I}}\text{I}_2]^-$ and square planar $[\text{Au}^{\text{III}}\text{I}_4]^-$ units. Iodide ions that complete the elongated octahedra around the square planar $[\text{Au}^{\text{III}}\text{I}_4]^-$ become a part of I_3^- ions sandwiched between the inorganic layers. For clarity, hydrogen atoms are omitted, and the elongated Au-I contacts that complete octahedra are shown as blue dashed lines.

In addition to the organic cation-inorganic framework interactions, the presence of Jahn-Teller active metal cations and stereoactive lone pairs, another source of structural distortions in the perovskites is the presence of mixed-valent metal cations in the inorganic framework. Hybrid organic-inorganic perovskites containing mixed-valent metal cations are

underexplored—i.e., $\langle 100 \rangle$ -oriented derivatives $[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_2[(\text{Au}^{\text{I}}\text{I}_2)(\text{Au}^{\text{III}}\text{I}_4)(\text{I}_3)_2]$ and $[\text{NH}_3(\text{CH}_2)_7\text{NH}_3]_2[(\text{Au}^{\text{I}}\text{I}_2)(\text{Au}^{\text{III}}\text{I}_4)(\text{I}_3)_2]$ ⁶⁶ are rare examples of such systems (**Figure 8**). Both structures feature layers of corner-shared AuI_6 octahedra (nominal) separated by organic cations with interlayer distances of ~ 15.5 Å. Mixed-valent $\text{Au}^{\text{I/III}}$ alternate in each layer as linear $[\text{Au}^{\text{I}}\text{I}_2]^-$ and square planar $[\text{Au}^{\text{III}}\text{I}_4]^-$ units. Iodide ions that complete the elongated octahedra around the square planar $[\text{Au}^{\text{III}}\text{I}_4]^-$ become a part of I_3^- ions sandwiched between the inorganic layers. The structures of these two compounds are largely similar owing to the different conformations of the organic cations—i.e., $(\text{NH}_3(\text{CH}_2)_8\text{NH}_3)^{2+}$ dications adopt a gauche conformation, and $(\text{NH}_3(\text{CH}_2)_7\text{NH}_3)^{2+}$ are in a staggered anti conformation. This conformational difference between the cations results in the similar cation lengths of 10.13 Å and 10.04 Å, respectively. The organic cation length seems to be important in the formation of these compounds, as layered derivatives with other diamine homologues could not be prepared. Different conformations are also important, as $[\text{NH}_3(\text{CH}_2)_7\text{NH}_3]_2[(\text{Au}^{\text{I}}\text{I}_2)(\text{Au}^{\text{III}}\text{I}_4)(\text{I}_3)_2]$ forms a denser organic cation- I_3^- layer, which in turn leads to a greater corrugation of the inorganic layer. The optical band gaps of $[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_2[(\text{Au}^{\text{I}}\text{I}_2)(\text{Au}^{\text{III}}\text{I}_4)(\text{I}_3)_2]$ and $[\text{NH}_3(\text{CH}_2)_7\text{NH}_3]_2[(\text{Au}^{\text{I}}\text{I}_2)(\text{Au}^{\text{III}}\text{I}_4)(\text{I}_3)_2]$ were measured to be 1.14 and 0.95 eV, respectively, lower than the reported value of 1.31 eV for $\text{Cs}_2\text{Au}^{\text{I}}\text{Au}^{\text{III}}\text{I}_6$ (or CsAuI_3). This is unusual given that normally, as the dimensionality of a perovskite is reduced, the band gap increases, and the $\text{Cs}_2\text{Au}_2\text{I}_6$ structure is clearly structurally more 3-D compared to the hybrid mixed-valent compounds. Note that, for the hybrid perovskites, the formulas can be written as $\text{A}_2\text{Au}_2\text{I}_6(\text{I}_3)_2$; therefore, in addition to the large interlayer separation in the hybrid perovskites, the major difference between $\text{A}_2\text{Au}_2\text{I}_6(\text{I}_3)_2$ and $\text{Cs}_2\text{Au}_2\text{I}_6$ is the presence of I_3^- ions in the former. Interestingly, theoretical calculations⁶⁷ suggest that the linear I_3^- and $[\text{Au}^{\text{I}}\text{I}_2]^-$ ions are closely related and exchangeable. This has been demonstrated by the synthesis of $((\text{CH}_3)_3\text{S})_2[\text{AuI}_4][\text{I}_3]$, which features a structure similar to

that of $\text{Cs}_2\text{Au}_2\text{I}_6$ (**Figure 9**), i.e., linear $[\text{Au}^{\text{I}}\text{I}_2]^-$ in $\text{Cs}_2[\text{AuI}_4][\text{AuI}_2]$ is replaced by the I_3^- ions.⁶⁷ Another interesting finding, the iodide confined in the I_3^- structure can be extracted, as has been shown for $[\text{NH}_3(\text{CH}_2)_7\text{NH}_3]_2[(\text{Au}^{\text{I}}\text{I}_2)(\text{Au}^{\text{III}}\text{I}_4)(\text{I}_3)_2]$ by heating the compound to 85 °C, which resulted in $[\text{NH}_3(\text{CH}_2)_7\text{NH}_3]_2[(\text{Au}^{\text{I}}\text{I}_2)(\text{Au}^{\text{III}}\text{I}_4)(\text{I}_3)(\text{I})]$. The nominally interchangeable nature of $[\text{Au}^{\text{I}}\text{I}_2]^-$ and I_3^- ions, and $[\text{Au}^{\text{III}}\text{I}_4]^-$ and I_5^- ions,⁶⁷ and the unexpected changes these substitutions bring into the electronic structures of the compounds provides another layer of flexibility and complexity in designing molecular structures with desired properties.

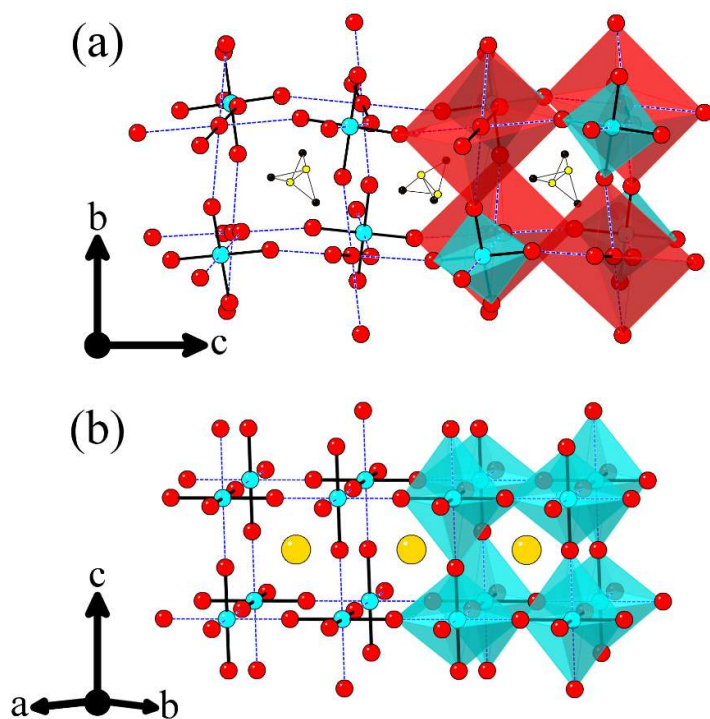


Figure 9. Combined ball-and-stick (left) and polyhedral (right, shaded) view of the crystal structures of (a) $((\text{CH}_3)_3\text{S})_2[\text{Au}^{\text{III}}\text{I}_4][\text{I}_3]$ and (b) $\text{Cs}_2\text{Au}_2\text{I}_6$, i.e., $\text{Cs}_2[\text{Au}^{\text{III}}\text{I}_4][\text{Au}^{\text{I}}\text{I}_2]$.^{67,68} The similarity between the two structures confirms the close relation and exchangeability of linear I_3^- and $[\text{Au}^{\text{I}}\text{I}_2]^-$ ions suggested by the theoretical calculations.⁶⁷ The elongated Au-I contacts that complete octahedra are shown as blue dashed lines, with the I-centered distorted octahedra formed by I_3^- ions being shown in red.

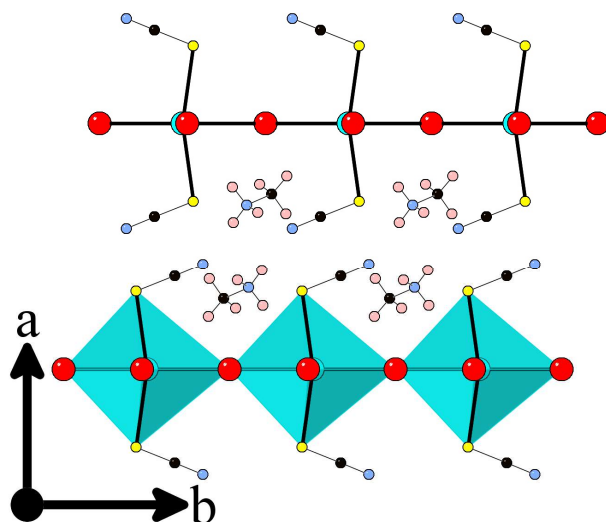


Figure 10. Combined skeletal (top) and polyhedral (bottom, shaded) view of the crystal structure of $(\text{CH}_3\text{NH}_3)_2\text{Pb}(\text{SCN})_2\text{I}_2$, featuring SCN^- anions on axial and I^- anions on equatorial positions.⁶⁹

Recently, another linear ion, the thiocyanate SCN^- anion, has been attracting the interest of photovoltaics (PV) and solid state chemistry communities.⁶⁹⁻⁷² It was found that incorporation of a small amount of $\text{Pb}(\text{SCN})_2$ (5 wt%) into the regular two-step solution deposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films resulted in better film qualities with larger grain sizes, which resulted in improved power conversion efficiencies (PCE).⁷¹ A small ~ 80 meV increase of the optical band gap and a noticeable enhancement in the photoluminescence emission quantum yield have been reported upon larger incorporation of SCN^- into $\text{CH}_3\text{NH}_3\text{PbI}_3$ using $\text{Pb}(\text{SCN})_2:\text{CH}_3\text{NH}_3\text{I}$ ratios ranging from 1:1 to 1:5.⁷⁰ Finally, solar cells with a targeted $\text{CH}_3\text{NH}_3\text{Pb}(\text{SCN})_2\text{I}$ composition showed similar PCE values to the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films, but the films containing thiocyanate ions were reported to provide enhanced stability under moist air.⁷² In all of these studies, the authors assumed that the incorporation of SCN^- ion takes

place through a direct substitution of I⁻ ion—hence, the “pseudohalide ion” term used for the thiocyanate ion in these publications. Unlike the linear I₃⁻ ion, however, SCN⁻ is asymmetric, which raises a question regarding the exact bonding pattern and orientation of the thiocyanate ion in the 3-D perovskite structure. In fact, one possible scenario is that the targeted 3-D perovskite CH₃NH₃Pb(SCN)₂I phase does not exist and, instead, crystals of a (100)-oriented layered compound (CH₃NH₃)₂Pb(SCN)₂I₂ form (**Figure 10**), as recently confirmed by repeating the previously reported reaction conditions.^{69,73,74}

In (CH₃NH₃)₂Pb(SCN)₂I₂, SCN⁻ ions coordinate to the inorganic layer through Pb-S contacts and occupy axial positions in the Pb-centered octahedra, extending out in a bent fashion with the corresponding Pb-S-CN angle of 103.5°. The Pb-centered octahedra are distorted with the I-Pb-I and I-Pb-S angles ranging from 81.63° to 98.49°. The in-plane distortions are modest but apparent with Pb-I-Pb angles of 169.84° and 173.30°. Remarkably, despite such distortions, the reported band gap values of 1.53-1.65 eV^{69,70,72,74} for (CH₃NH₃)₂Pb(SCN)₂I₂ are low for a single inorganic sheet hybrid perovskite. For comparison, the above-mentioned (Y-(CH₂)₂NH₃)₂PbI₄ (Y = Cl and Br), which feature relatively undistorted inorganic layers with Pb-I-Pb angle of ~ 178°, have lowest band gap value of 2.2 eV in this series;⁶¹ yet, these values are still much larger than the reported values for (CH₃NH₃)₂Pb(SCN)₂I₂. In addition, early theoretical work on (CH₃NH₃)₂Pb(SCN)₂I₂ indicated that the valence and conduction bands remain fully dispersive along all three dimensions,⁷³ a surprising finding given the layered nature of its crystal structure. A more recent combined theoretical and experimental evaluation⁷⁵ of (CH₃NH₃)₂Pb(SCN)₂I₂ suggests that there is almost no dispersion for the states near the conduction band minimum (CBM) and valence band maximum (VBM) along the interlayer direction (i.e., T-R direction in the electronic band structure) and that the band gap value of the material is actually closer to 2 eV, a more consistent value with the reported red coloration of the crystals and films.^{69,74,75}

Despite the ongoing uncertainty regarding the properties of $(\text{CH}_3\text{NH}_3)_2\text{Pb}(\text{SCN})_2\text{I}_2$, preparation of a low band gap layered hybrid perovskite material is an important target for potential electro-optical applications (e.g. in solar cells, transistors), because of the likely simpler deposition of high quality films of layered materials, and the added flexibility that the layered structure provides for further chemical and crystallographic manipulation.

Note that, to this point in this section, we have primarily been discussing how the organic cation or choice of halogen (or pseudo-halogen in the “X” site) can impact or template the distortion of the inorganic metal halide framework. However, the templating influence of the organic cation can also enable the demonstration of layered perovskites with a broader range of “B” cations than would otherwise be possible, as has been demonstrated for the $(\text{H}_2\text{AEQT})\text{B}_{2/3}\text{I}_4$ (AEQT = 5,5'-bis(aminoethyl)-2,2':5',2'':5'',2'''-quaterthiophene; $\text{M} = \text{Bi}^{3+}$ or Sb^{3+}) compounds.⁷⁶ In these particular compounds, the inorganic perovskite sheets feature a random distribution of B-metal cations over available sites, which have occupancy of 2/3 due to the charge balance requirements following $(\text{H}_2\text{AEQT}^{2+})(\text{B}^{3+})_{2/3}(\text{I}^-)_4$. Given the vacancies, the perovskite structure has to compete against other non-perovskite structures with no vacancies and, in fact, Bi-based halides with simple ammonium cations often prefer non-perovskite alternatives.¹³ In $(\text{H}_2\text{AEQT})\text{B}_{2/3}\text{I}_4$, the perovskite structure is stabilized through the rigid, rod-like nature of the $\text{H}_2\text{AEQT}^{2+}$ cations and edge-to-face aromatic interactions among these quaterthiophene moieties (further discussion of oligothiophene-based perovskites can be found in Section 4).⁷⁶

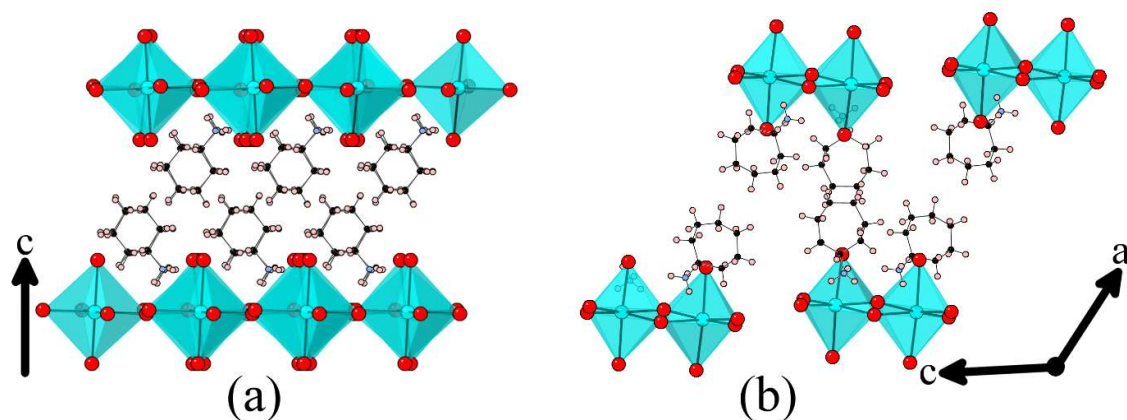


Figure 11. Crystal structures of $(\text{RNH}_3)_2\text{PbI}_4$ compounds, where (a) $\text{R} =$ cyclohexylammonium, and (b) $\text{R} =$ cycloheptylammonium.^{77,78} The $\langle 100 \rangle$ -oriented layered perovskites are obtained if small ring organic cations from $r = 3$ (cyclopropylammonium) to $r = 6$ (cyclohexylammonium) are used, whereas $r = 7$ (cycloheptylammonium) features inorganic 1-D chains of corner-sharing octahedra. Only a fraction of cycloalkylammonium cations are shown for clarity.

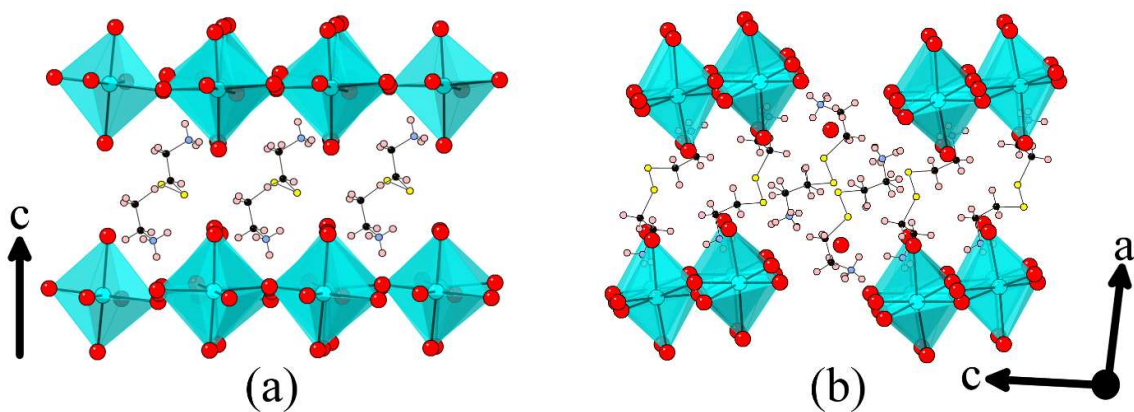


Figure 12. Crystal structures of the (a) 2-D layered $\alpha\text{-}[(\text{NH}_3(\text{CH}_2)_2\text{SS}(\text{CH}_2)_2\text{NH}_3)\text{PbI}_4]$ and (b) 1-D chain $[(\text{NH}_3(\text{CH}_2)_2\text{SS}(\text{CH}_2)_2\text{NH}_3)_2\text{PbI}_5 \cdot \text{I}]$ compounds, a mixture of which is obtained from the same reaction.⁶⁵

In the regular definition of $\langle 100 \rangle$ -oriented perovskite derivatives, this group includes only 2-D-layered compounds with the single sheet $(\text{RNH}_3)_2\text{BX}_4$ as the end member; however, $(\text{RNH}_3)_2\text{BX}_4$ can also be further cut into 1-D chain segments and isolated octahedral 0-D clusters (note that these 0-D and 1-D compounds can also be considered end-members of $\langle 111 \rangle$ - and $\langle 110 \rangle$ -oriented perovskite families, respectively, as will be discussed in the following sections). This can occur when the width (cross-sectional area) of the organic cation is too large ($> 40 \text{ \AA}^2$), as shown in the series of $(\text{RNH}_3)_2\text{PbX}_4$ ($\text{R} = \text{cycloalkylammonium}$; $\text{X} = \text{Cl, Br, I}$) (**Figure 11**).^{77,78} The $\langle 100 \rangle$ -oriented layered $(\text{RNH}_3)_2\text{PbX}_4$ perovskites are obtained if small ring organic cations, from $r = 3$ (cyclopropylammonium) to $r = 6$ (cyclohexylammonium), are used; however, $r = 7$ (cycloheptylammonium) gives 1-D chains of corner-sharing octahedra in $(\text{C}_7\text{H}_{13}\text{NH}_3)_3\text{PbI}_5$ and $(\text{C}_7\text{H}_{13}\text{NH}_3)_3\text{PbBr}_5 \cdot \text{H}_2\text{O}$.^{77,78} It should be noted that large cross-sectional area organic cations or a geometry that provides steric hindrance are not essential for obtaining 1-D compounds. An uncontrolled reaction can give a mixture of compounds with differing dimensionality for the same cation, such as in the case of 2-D layered α - $[(\text{NH}_3(\text{CH}_2)_2\text{SS}(\text{CH}_2)_2\text{NH}_3)\text{PbI}_4]$ and 1-D chain $[(\text{NH}_3(\text{CH}_2)_2\text{SS}(\text{CH}_2)_2\text{NH}_3)_2\text{PbI}_5 \cdot \text{I}]$ compounds (**Figure 12**).⁶⁵ These compounds were serendipitously obtained using $\text{HSC}_2\text{H}_4\text{NH}_2 \cdot \text{HCl}$ as a reactant, with the diprotonated cystamine cation $(\text{NH}_3(\text{CH}_2)_2\text{SS}(\text{CH}_2)_2\text{NH}_3)^{2+}$ forming in-situ. Interestingly, the obtained structures are very similar to the structures of 2-D layered $(\text{cyclohexylammonium})_2\text{PbI}_4$ and 1-D chain $(\text{cycloheptylammonium})_2\text{PbI}_4$ compounds (**Figure 11**); however, 2-D layered α - $[(\text{NH}_3(\text{CH}_2)_2\text{SS}(\text{CH}_2)_2\text{NH}_3)\text{PbI}_4]$ and 1-D chain $[(\text{NH}_3(\text{CH}_2)_2\text{SS}(\text{CH}_2)_2\text{NH}_3)_2\text{PbI}_5 \cdot \text{I}]$ feature identical cations. The difference can presumably be attributed to the incorporation of large iodine anions in the 1-D chain $[(\text{NH}_3(\text{CH}_2)_2\text{SS}(\text{CH}_2)_2\text{NH}_3)_2\text{PbI}_5 \cdot \text{I}]$ compound, and the subsequent fragmentation of the layers into chains. By heating at 150°C , 2-D layered α - $[(\text{NH}_3(\text{CH}_2)_2\text{SS}(\text{CH}_2)_2\text{NH}_3)\text{PbI}_4]$ can further be transformed into its β -polymorph, which is

retained down to 40 °C, indicating a large window of coexistence for these polymorphs.⁷⁹ The β -polymorph features disordered diprotonated cystamine cations in the structure.⁷⁹

3.2. $\langle 110 \rangle$ -Oriented Perovskites

The $\langle 110 \rangle$ -oriented perovskites, $A'_2A_mB_mX_{3m+2}$, are less common compared to the $\langle 100 \rangle$ -oriented perovskites, and have been mostly limited to compounds obtained using the structure-directing iodoformamidinium cation. The special role of the iodoformamidinium cation in the $[\text{NH}_2\text{C}(\text{I})=\text{NH}_2]_2(\text{CH}_3\text{NH}_3)_m\text{Sn}_m\text{I}_{3m+2}$ series⁸⁰ includes formation of hydrogen bonds down the channels of the $\langle 110 \rangle$ -oriented perovskite layers, and the fact that the iodine atoms of the iodoformamidinium cation complete the 12-fold coordination environment around the methylammonium cation. The known $m = 1$ -4 members of the $[\text{NH}_2\text{C}(\text{I})=\text{NH}_2]_2(\text{CH}_3\text{NH}_3)_m\text{Sn}_m\text{I}_{3m+2}$ series include the $m = 1$, 1-D-chain structures $[\text{NH}_2\text{C}(\text{I})=\text{NH}_2]_2\text{ASnI}_5$ ($A = \text{NH}_2\text{C}(\text{I})=\text{NH}_2^+$ or $\text{NH}_2\text{CH}=\text{NH}_2^+$), and the $m = 2$, 2-D-layered structure $[\text{NH}_2\text{C}(\text{I})=\text{NH}_2]_2(\text{CH}_3\text{NH}_3)_2\text{Sn}_2\text{I}_8$.^{10,80} As m is increased further, the thickness of the perovskite layers also increases, with $m = \infty$ corresponding to the 3-D parent perovskite structure. Therefore, this $\langle 110 \rangle$ -oriented family allows tuning of the dimensionality of the perovskite structure from the 3-D parent structure to various-thickness 2-D layers in the $m = 2$ -4 members, and to 1-D chains in the $m = 1$ member.

The Pb-analogs of the $m = 1$ members have been synthesized as well, and this demonstrates that the $\langle 110 \rangle$ -oriented compounds can also be prepared using other metal cations.⁸¹ In addition, another $m = 1$ compound, $[\text{CH}_3\text{SC}(=\text{NH}_2)\text{NH}_2]_3\text{PbI}_5$, has been reported, showing that other organoammonium cations can template this structure.⁸² However, the highly distorted inorganic framework of this compound can also be described as an assembly of loosely-coupled 0-D clusters,¹⁰ as such, a genuine $\langle 110 \rangle$ -oriented perovskite with other organic cations has remained somewhat elusive. A breakthrough in this regard has been made

with the discovery of the $m = 2$ $\langle 110 \rangle$ -oriented perovskite diguanidinium tetraiodoplumbate, $[\text{C}(\text{NH}_2)_3]_2\text{PbI}_4$, which, interestingly, undergoes a ferroelastic phase transition at 307 K.^{83,84} At higher temperatures, cationic disordering and the deformation of the inorganic sublattice are coupled in this compound. The authors note that the organic cation's size, shape and symmetry are all influential in the observed physical properties in $[\text{C}(\text{NH}_2)_3]_2\text{PbI}_4$.⁸³ Another example of the $m = 2$ $\langle 110 \rangle$ -oriented perovskite is $(\text{C}_6\text{H}_{13}\text{N}_3)\text{PbBr}_4$ (or $(\text{C}_6\text{H}_{13}\text{N}_3)_2\text{Pb}_2\text{Br}_8$), which is stabilized by a *N*-(3-aminopropyl)imidazolium (API) cation (**Figure 13**).⁸⁵ API, as a substituted imidazole derivative, is an optically active material featuring a primary amine as a functional group attached to the imidazole heterocyclic ring. The resultant dication features a propylammonium head, which is capable of templating a perovskite structure, and a ternary ammonium cation in the ring, which asserts steric hindrance for the formation of a perovskite framework. Without this combination of somewhat conflicting characteristics, the more symmetric biimidazolium $(\text{C}_6\text{H}_8\text{N}_4)^{2+}$ dications give the common $\langle 100 \rangle$ -oriented structures in $(\text{C}_6\text{H}_8\text{N}_4)\text{PbI}_4$ and $(\text{C}_6\text{H}_8\text{N}_4)\text{SnI}_4$ (see Section 3.1). The substitution position on the heterocyclic ring and the length of the alkylammonium chain is also important, as $(\text{C}_5\text{H}_{11}\text{N}_3)\text{PbBr}_4$ and $(\text{C}_5\text{H}_{11}\text{N}_3)\text{PbCl}_4$ featuring histaminium cations also adopt the $\langle 100 \rangle$ -oriented perovskite structures (see Section 3.1). The fact that subtle differences in the organic cations in $(\text{C}_5\text{H}_{11}\text{N}_3)\text{PbBr}_4$ and $(\text{C}_6\text{H}_{13}\text{N}_3)\text{PbBr}_4$ lead to the $\langle 100 \rangle$ -oriented and the $\langle 110 \rangle$ -oriented inorganic perovskite frameworks, respectively, underlines the importance of fine details in the structural preferences exhibited among the oriented perovskite derivatives.

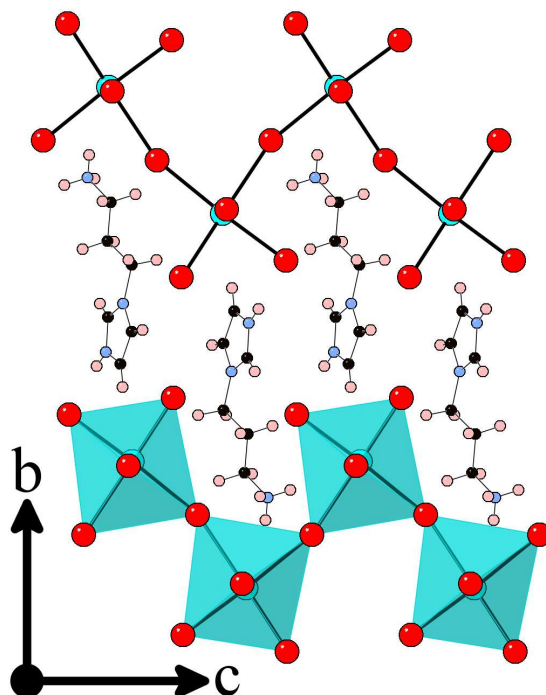


Figure 13. Combined skeletal (top) and polyhedral (bottom, shaded) view of the crystal structure of $(\text{C}_6\text{H}_{13}\text{N}_3)\text{PbBr}_4$ viewed down the a -axis.⁸⁵ The $\langle 110 \rangle$ -oriented perovskite layers are separated by the N -(3-aminopropyl)imidazolium (API) dications, which feature a propylammonium head and a ternary ammonium cation in the ring.

In $(\text{C}_6\text{H}_{13}\text{N}_3)\text{PbBr}_4$, the presence of the API dication simplifies the structure and composition compared to the previously known $m = 2$ members such as $[\text{NH}_2\text{C}(\text{I})=\text{NH}_2]_2(\text{CH}_3\text{NH}_3)_2\text{Sn}_2\text{I}_8$, which features 2 distinct cation sites, a smaller intralayer CH_3NH_3^+ cation site and the larger interlayer $\text{NH}_2\text{C}(\text{I})=\text{NH}_2^+$ site. Here, in addition to carrying +2 charge, API accepts dual functionality, combining the roles of CH_3NH_3^+ and $\text{NH}_2\text{C}(\text{I})=\text{NH}_2^+$ cations. The $[\text{PbBr}_4]^-$ layers in $(\text{C}_6\text{H}_{13}\text{N}_3)\text{PbBr}_4$ are corrugated, with the Pb-Br-Pb angles of 162.68 and 171.85°, and the PbBr_6 octahedra are distorted with Br-Pb-Br angles ranging from 86.35 to 96.42°. The latter suggests that the Pb lone ns pair is relatively stereochemically active in this compound. As a final thought for this section, the stabilization

of multiple $m = 2$ members of the $\langle 110 \rangle$ -oriented perovskites demonstrates that this family is accessible with organic cations other than the iodoformamidinium cation. For example, $(\text{C}_3\text{H}_{11}\text{SN}_3)\text{PbBr}_4$ is stabilized by diprotonated 2-(aminoethyl)isothiurea.⁸⁶ In this case, the organic cation combines a primary ammonium and a formamidinium head on the two opposite ends of the molecule. The use of such organic cations leads to contorted inorganic layers with Pb-Br-Pb angles of as low as 144.23° in $(\text{C}_3\text{H}_{11}\text{SN}_3)\text{PbBr}_4$. The family of $\langle 110 \rangle$ -oriented perovskites has been further expanded by the recent synthesis of several new $m = 2$ members with a potential for application in solid-state lighting applications (see section 7, **Figure 33**).^{87,88}

3.3. $\langle 111 \rangle$ -Oriented Perovskites

The cyclohexylammonium cation appears to be the largest ring cycloalkylammonium cation that allows formation of the $\langle 100 \rangle$ -oriented 2-D-layered $(\text{RNH}_3)_2\text{PbX}_4$ perovskites (see section 3.1, **Figure 11**). Interestingly, six-membered rings seem to carry similar influence for the compounds formed using aromatic heterocyclic cations. By changing the position of the aminomethyl group on the six-membered pyridine ring, Li et al. synthesized 2-(aminomethyl)pyridinium ($\text{H}_2\text{2-AMP}$)²⁺, 3-(aminomethyl)pyridinium ($\text{H}_2\text{3-AMP}$)²⁺ and 4-(aminomethyl)pyridinium ($\text{H}_2\text{4-AMP}$)²⁺ cations, which were subsequently used to obtain perovskite structures of different dimensionality under similar experimental conditions.⁸⁹ The resultant compounds $(\text{H}_2\text{2-AMP})\text{PbBr}_4$, $(\text{H}_2\text{3-AMP})_2\text{PbBr}_6$ and $(\text{H}_2\text{4-AMP})\text{PbBr}_4$ feature $\langle 100 \rangle$ -oriented 2-D layers, $\langle 111 \rangle$ -oriented 0-D clusters and 1-D-chains formed by edge-sharing octahedra, respectively (**Figure 14**). Although the substituted pyridinium dication used for these compounds are isomers, the subtle differences in the structures of the cations are sufficient to induce large differences in their steric hindrance and hydrogen bonding capabilities. It is somewhat unexpected that the $\langle 100 \rangle$ -oriented layered $(\text{H}_2\text{2-AMP})\text{PbBr}_4$ and

$\langle 111 \rangle$ -oriented 0-D cluster compound $(\text{H}_23\text{-AMP})_2\text{PbBr}_6$ have similar band gap values of ~ 2.8 eV. One normally would expect a larger band gap value for the metal poor isolated 0-D compound; however, one of the reasons for the close band gap values may be due to the SOJT effect (or stereochemical activity of the Pb lone pair states). The Br-Pb-Br angles range from 88.73 to 97.63° in the layered $(\text{H}_22\text{-AMP})\text{PbBr}_4$, and from 86.62 to $93.38(2)^\circ$ in $(\text{H}_23\text{-AMP})_2\text{PbBr}_6$, indicating the presence of the more distorted PbBr_6 octahedra in the former, which should lead to an increased band gap.

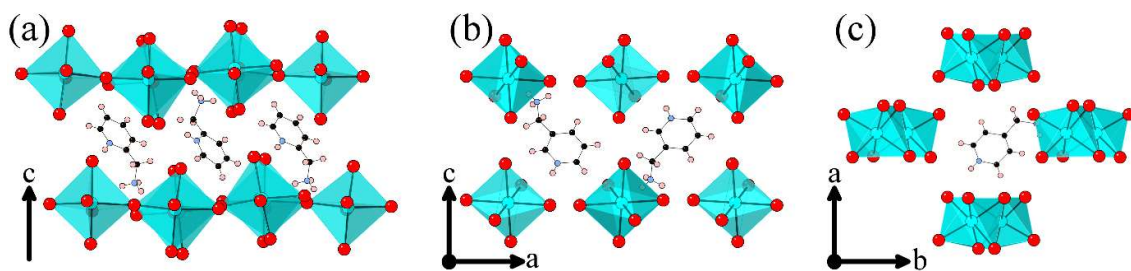


Figure 14. (a) Crystal structure of $(\text{H}_22\text{-AMP})\text{PbBr}_4$ features $\langle 100 \rangle$ -oriented inorganic 2-D-sheets and 2-(aminomethyl)pyridinium $(\text{H}_22\text{-AMP})^{2+}$ cations sandwiched in between the layers. In contrast, 3-(aminomethyl)pyridinium $(\text{H}_23\text{-AMP})^{2+}$ and 4-(aminomethyl)pyridinium $(\text{H}_24\text{-AMP})^{2+}$ cations give (b) $\langle 111 \rangle$ -oriented 0-D-clusters and (c) 1-D-chains formed by edge-sharing octahedra in $(\text{H}_23\text{-AMP})_2\text{PbBr}_6$ and $(\text{H}_24\text{-AMP})\text{PbBr}_4$, respectively.⁸⁹ For clarity, only a fraction of organic cations are shown.

The compositions of the $\langle 111 \rangle$ -oriented perovskites are given by the $\text{A}'_2\text{A}_{q-1}\text{B}_q\text{X}_{3q+3}$ formula, where A' and A are interlayer and intralayer organic cations. $(\text{H}_23\text{-AMP})_2\text{PbBr}_6$ provides an example of the most common $q = 1$ member of the $\langle 111 \rangle$ -oriented perovskites, which belong to the cubic K_2PtCl_6 -type structure with a great many known members. The K_2PtCl_6 -type structure is adopted, for example, by Cs_2SnI_6 , which has recently been used as a hole conductor in a solar cell device,⁹⁰ and A_2TeX_6 ($\text{A} = \text{NH}_4^+$, K^+ , Rb^+ , Cs^+ , TI^+ ; $\text{X} = \text{Cl}^-$, Br^- ,

I-),^{91,92} featuring Te^{4+} , which is isoelectronic to for example Sn^{2+} and Pb^{2+} . Since the extended inorganic framework is absent in this structure, no clear organic cation size restrictions can be outlined for $q = 1$ members, and the structure should, in principle, be able to accept a wide range of components as long as the charge balance is preserved. However, the majority of the known $q = 1$ members feature only relatively small cations. In addition to the above-mentioned $(\text{H}_2\text{3-AMP})_2\text{PbBr}_6$, mixed-valent $[\text{N}(\text{CH}_3)_4]_2\text{Sb}^{\text{III}}_{0.5}\text{Sb}^{\text{V}}_{0.5}\text{Cl}_6$ and $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{Sb}^{\text{III}}_{0.5}\text{Sb}^{\text{V}}_{0.5}\text{Cl}_6$ may be rare examples of $q = 1$ members with larger organic cations; however, no detailed structural data are available for these compounds.⁹³

Similarly, the known $q = 2$ members including $(\text{NH}_4)_3\text{Sb}_2\text{I}_9$, $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{Br}_9$, $[\text{NH}_2(\text{CH}_3)_2]_3\text{Sb}_2\text{Cl}_9$, $[\text{NH}(\text{CH}_3)_3]_3\text{Sb}_2\text{Cl}_9$ and $(\text{CH}_3\text{NH}_3)_3\text{Sb}_2\text{I}_9$, to name a few, also feature small organic cations.⁹⁴⁻⁹⁸ The inorganic $q = 2$ compounds, which crystallize in the $\alpha\text{-Cs}_3\text{Sb}_2\text{Cl}_9$ structure type, feature Cs^+ and Rb^+ cations.^{91,98} Recently, $\text{Cs}_3\text{Sb}_2\text{I}_9$ has been examined as a prospective Pb-free perovskite for use in PV devices.⁹⁹ In addition to strong absorption for wavelengths above the band gap, due to the p-like character of both the valence band and conduction band edges, and relatively small effective masses for both electrons and holes, one interesting feature of the band structure of this material is that the bands appear to be reasonably dispersive both parallel and perpendicular to the plane of the perovskite layers, indicating that the layered nature of these systems may not handicap them too much for use in 3-D PV devices. Although initial device performance has been low for $\text{Cs}_3\text{Sb}_2\text{I}_9$, this early device result shows the possibility of using these $\langle 111 \rangle$ -oriented layered perovskites in functional electronic devices.

Two interesting features are common in all of the known $q = 2$ members so far: 1) the metal cations are trivalent pnictogens, and 2) there is only little difference between the thickness of the single inorganic sheet and the interlayer distance. The former is due to the simple fact that, for a structure with monovalent A^+ cations, in order to balance the charges, B

must be trivalent in the $(A^+)_3(B^{3+})_2(X^-)_9$ composition. The small interlayer distance is due to the small sizes of the interlayer organic and inorganic cations and, as such, these compositions could have also adopted Sb(Bi)-deficient 3-D perovskite structures with a random distribution of vacancies. This conjecture is supported by the fact that cations such as $CH_3NH_3^+$ can be incorporated into the 3-D perovskite structure, as evidenced by the well-known photovoltaic material $CH_3NH_3PbI_3$. Another supporting evidence is that the Sb- and Bi-vacancies can also be disordered in the $\langle 100 \rangle$ -oriented layered perovskite framework, as demonstrated by the above-mentioned $(H_2AEQT)B_{2/3}I_4$ compounds⁷⁶ that feature random distributions of Sb- and Bi-vacancies in the perovskite layers. The preference for forming the $q = 2$ member of the $\langle 111 \rangle$ -oriented $A_3B_2X_9$ perovskites with a small A^+ cation (as opposed to a disordered 3-D perovskite), therefore, could be attributed to a greater stability of this structure (i.e., thermodynamic sink) in the energy landscape of the perovskite compounds.

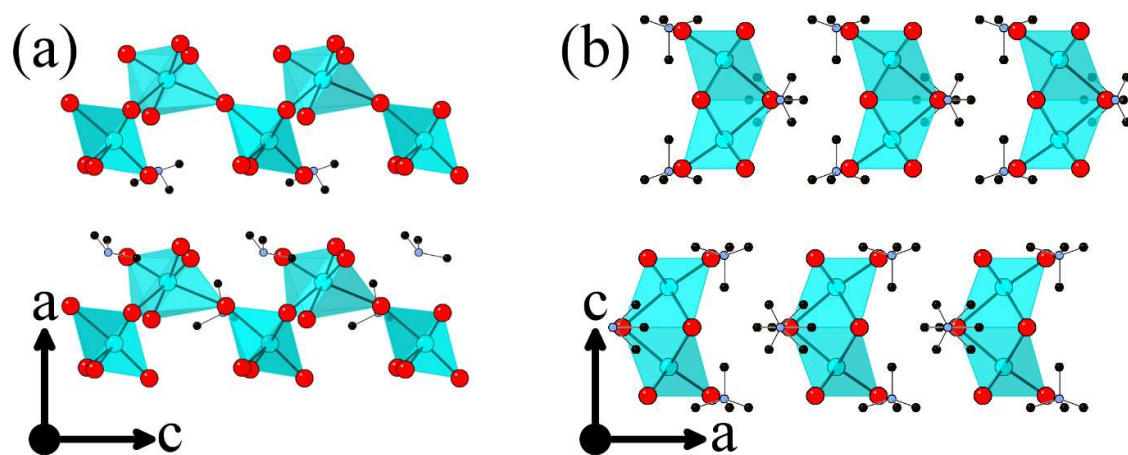


Figure 15. (a) Crystal structure of the $\langle 111 \rangle$ -oriented layered perovskite $[NH(CH_3)_3]_3Sb_2Cl_9$ viewed down the b -axis.⁹⁷ Use of larger organic cations leads to a further fragmentation of the layers into 0-D clusters. (b) Crystal structure of $[N(CH_3)_4]_3Sb_2Cl_9$ features $Sb_2Cl_9^{3-}$ dimers made of two $SbCl_6$ face-sharing octahedra.⁹⁵

In principle, there should be no constraints for the interlayer A' cation length for the $q = 2$ members of the $\langle 111 \rangle$ -oriented perovskites, if the intralayer "A" site is populated with smaller cations. However, no $q = 2$ members with two very different cations have been reported to date. The $q = 2$ perovskite structure collapses when the size of the organic cation is too big. For example, $[\text{NH}(\text{CH}_3)_3]_3\text{Sb}_2\text{Cl}_9$ adopts the layered $\langle 111 \rangle$ -oriented perovskite structure,⁹⁷ while $[\text{N}(\text{CH}_3)_4]_3\text{Sb}_2\text{Cl}_9$ features $\text{Sb}_2\text{Cl}_9^{3-}$ dimers made of two SbCl_6 face-sharing octahedra (**Figure 15**).⁹⁵ In this particular example, the hydrogen bonding abilities of $[\text{NH}(\text{CH}_3)_3]^+$ and $[\text{N}(\text{CH}_3)_4]^+$ cations are quite different, which may also contribute to the difference in the observed structural preference. Notwithstanding this fact, we observe that the dimer structure is a competing phase for many of the $q = 2$ members and, for compounds such as $\text{Cs}_3\text{Sb}_2\text{I}_9$ and $\text{CH}_3\text{NH}_3\text{Sb}_2\text{I}_9$, this polymorph is obtained from solution, whereas the layered modification may be obtained from solid state or gas phase reactions.^{98,99} This is an important observation, as solution synthesis has been the most common method for the preparation of the perovskite derivatives. The very high stability of the dimer and the $\langle 111 \rangle$ -oriented $q = 2$ $\text{A}_3\text{B}_2\text{X}_9$ structures with small A^+ cations, is therefore a stumbling block for the preparation of the $q = 2$ members with two cations of different sizes (A'^+ and A^+) and higher order $q > 2$ members of the $\langle 111 \rangle$ -oriented series $\text{A}'_2\text{A}_{q-1}\text{B}_q\text{X}_{3q+3}$. Note that, assuming A' and A are monovalent organic cations, the $\text{A}'_2\text{A}_{q-1}\text{B}_q\text{X}_{3q+3}$ formula of the $\langle 111 \rangle$ -oriented perovskites requires different metal B cation oxidation state for each q member (in contrast to the $\langle 100 \rangle$ and $\langle 110 \rangle$ families). In the $q = 1$ member A_2BX_6 and $q = 2$ member $\text{A}_3\text{B}_2\text{X}_9$ (A – monovalent cation; X – halide), B is tetravalent and trivalent, respectively, and the parent $q = \infty$ member ABX_3 features divalent M. This complicates the synthesis of the $\infty > q > 2$ members, because, unless a mixture of organic ammonium and diammonium cations were to be used, the oxidation state on the B cation must be fractional, i.e. between +2 and +3, and a mixture of two or more B-cations (or oxidation states for a single B-cation) is necessary.

3.4. More Exotic Frameworks

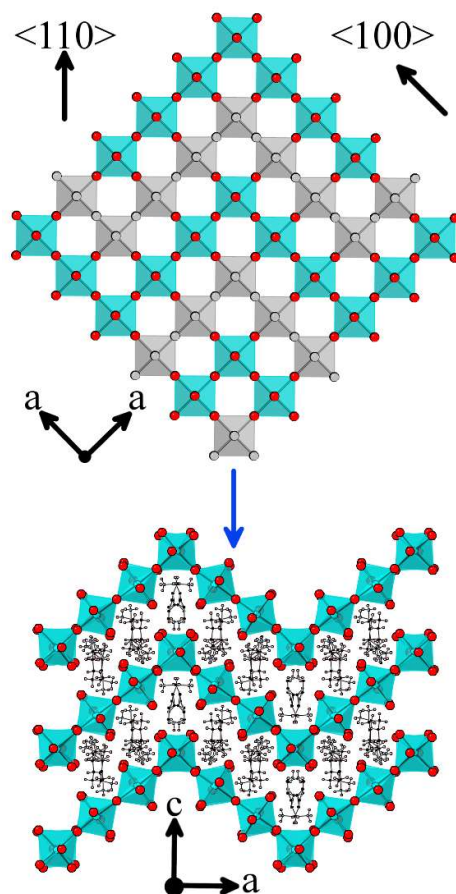


Figure 16. In the crystal structure of α -[NH₃(CH₂)₅NH₃]SnI₄,¹⁰⁰ the inorganic layers are composed of 4-octahedra long $\langle 100 \rangle$ -oriented layer fragments that are interconnected at 45° angles. The resultant zigzag perovskite layers are a combination of the $\langle 100 \rangle$ -and the $\langle 110 \rangle$ -oriented fragments that are separated by 1,5-pentanediammonium cations.

Owing to its flexibility and ease of manipulations, the perovskite structure offers endless possibilities. Although much has been accomplished in terms of syntheses and characterization of perovskite derivatives, there are a lot of questions remaining unanswered. The role of “spectator” ions (i.e., species that are added to the reaction medium but do not

feature in the final compound in a measureable concentration), for example, remains under-explored. The fact that foreign chemical species can have an important role can be illustrated with the example of α -[NH₃(CH₂)₅NH₃][SnI₄], which features zigzag perovskite layers that are separated by 1,5-pentanediammonium cations (**Figure 16**). Under regular synthetic conditions, the β -phase containing $\langle 100 \rangle$ -oriented SnI₄²⁻ layers is formed, whereas the α -phase is obtained when CH₃NH₃I is added to the reaction medium.¹⁰⁰ The zigzag perovskite layers of the α -phase, which feature *trans*- and *cis*-shared SnI₆ octahedra, can be seen as a combination of the $\langle 100 \rangle$ - and the $\langle 110 \rangle$ -oriented layers. In an alternative description of the α -[NH₃(CH₂)₅NH₃][SnI₄] structure, the layers are composed of 4-octahedra long $\langle 100 \rangle$ -oriented layer fragments that are interconnected at 45° angles to form a zigzag morphology. Although, the crucial role of a CH₃NH₃⁺ cation in the preferential formation of the α -phase was attributed to a possible formation of CH₃NH₃SnI₃ perovskite and subsequent more irregular fragmentation of the 3-D structure, the detailed formation mechanism still needs to be resolved.

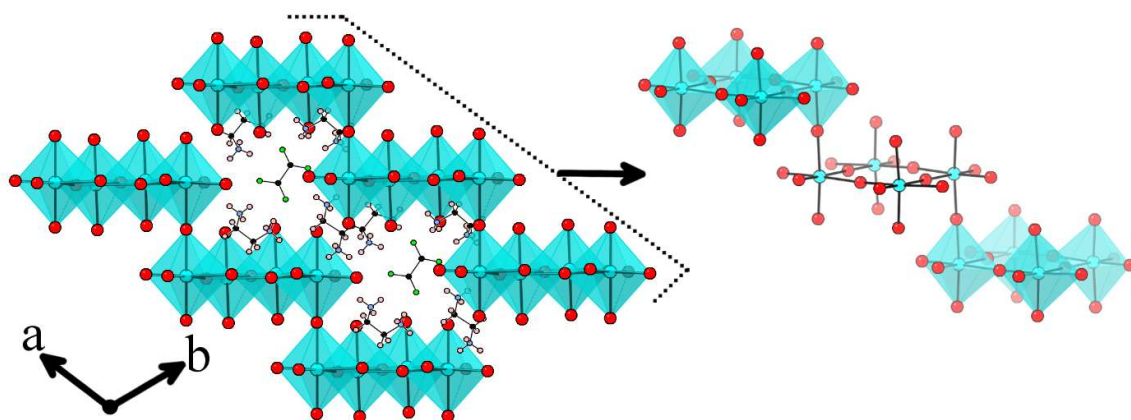


Figure 17. Crystal structure of [(H₂en)₇(C₂O₄)₂][Pb₄I₁₈] $\cdot$ 4H₂O features staircase [Pb₄I₁₈]¹⁰⁻ layers built upon corner-sharing tetrameric Pb₄I₂₀ units (right).¹⁰¹ Water molecules are not shown for clarity.

The fact that the reaction conditions in general, and the addition of uncommon reactants in particular, can influence the way in which the perovskite structure is fragmented can also be exemplified by the 2-D staircase $[\text{Pb}_4\text{I}_{18}]^{10-}$ sheets in $[(\text{H}_2\text{en})_7(\text{C}_2\text{O}_4)_2][\text{Pb}_4\text{I}_{18}]\cdot 4\text{H}_2\text{O}$, where en = ethylenediamine (**Figure 17**).¹⁰¹ This compound is obtained by a solvothermal reaction of PbI_2 , $\text{K}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$ and en in a concentrated HI and ethanol solution. The authors note the importance of reaction conditions, including $\text{pH} \sim 1$ and the $\text{K}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$ reactant, which cannot be replaced by $\text{H}_2\text{C}_2\text{O}_4$. The $\text{C}_2\text{O}_4^{2-}$ anions play a pivotal role in the formation of the structure, as they are incorporated with organic cations $(\text{H}_2\text{en})^{2+}$ forming supramolecular assemblies of distinct shapes. The resultant nominal cationic layer $[(\text{H}_2\text{en})_7(\text{C}_2\text{O}_4)_2]^{10+}$ plays, not only a co-templating role, but also necessitates an unprecedented charge of -10 in the inorganic $[\text{Pb}_4\text{I}_{18}]^{10-}$ sheets. Four PbI_6 octahedra share corners to form tetrameric Pb_4I_{20} building blocks, and these tetramers further share corners in a staircase fashion to form the anionic $[\text{Pb}_4\text{I}_{18}]^{10-}$ layers in the structure. The Pb-I-Pb bond angles of 176.04° and 180.0° are among the highest in the lead iodide based perovskites, indicating only negligible in-plane distortions in the structure. The ammonium functional groups are pointing out of the inorganic layers, toward the $\text{C}_2\text{O}_4^{2-}$ anions and, therefore, with only ethyl groups in the inorganic sheets, the hydrogen-bonding interactions are weak in this compound. $[(\text{H}_2\text{en})_7(\text{C}_2\text{O}_4)_2][\text{Pb}_4\text{I}_{18}]\cdot 4\text{H}_2\text{O}$ is reported as a direct band gap semiconductor with an optical band gap of 2.47 eV.

4. FUNCTIONAL ORGANIC CATIONS

Besides basic structural flexibility, organic-inorganic hybrids enable the combination of useful properties from both the organic and inorganic chemical palette within a single molecular-scale composite (e.g., as seen in **Figure 1**). While in the above discussion in

Sections 2 and 3, for the most part, the organic cation is playing solely a structural role in determining the properties of the full compound, there are now numerous examples wherein the organic cation is more functional (e.g., larger degree of conjugation provides a smaller HOMO-LUMO separation), therefore enabling a more active role in the optoelectronic properties of the solid.

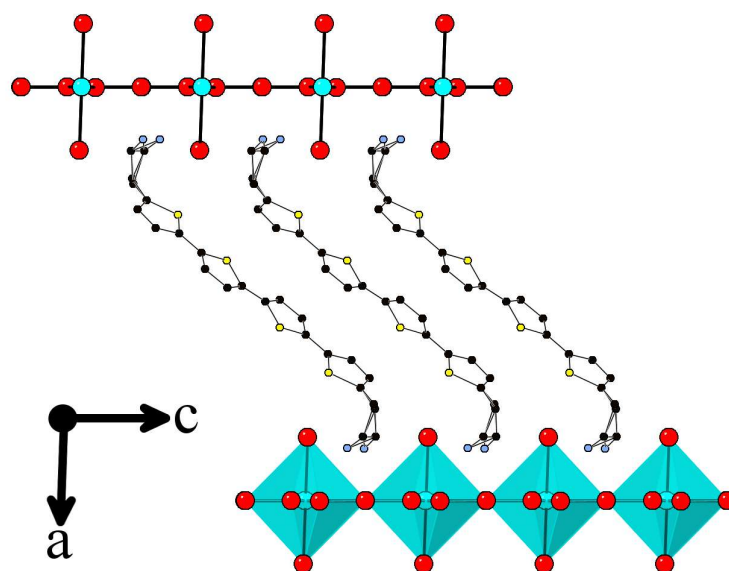


Figure 18. Combined skeletal (top) and polyhedral (bottom, shaded) view of the crystal structure of AEQTPbBr₄, where AEQT = 5,5'''-bis(aminoethyl)-2,2':5',2'':5'',2'''-quaterthiophene, consisting of self-assembling and ordered organic and inorganic layers.¹⁰²

A prototypical example, and one of the first in which the crystal structure and optoelectronic properties of the compound were analyzed, involved the design and incorporation of 5,5'''-bis(aminoethyl)-2,2':5',2'':5'',2'''-quaterthiophene (AEQT) into a $\langle 100 \rangle$ -oriented layered lead(II) halide perovskite framework (**Figure 18**).¹⁰² Oligothiophenes are particularly useful for electronic structure engineering studies because the HOMO-LUMO separation can readily be tailored relative to the band gap of the inorganic component of the

structure by changing the length of the thiophene chain—i.e., with “ n ” representing the number of α -linked thiophene rings within the chain, the absorption peak associated with the HOMO-LUMO separation varies from between approximately 302 nm (4.1 eV) for $n = 2$ to 432 nm (2.9 eV) for $n = 6$.¹⁰³ The quaterthiophene ($n = 4$) molecule, with its ~ 3.2 eV HOMO-LUMO separation, perfectly intersects the band gap range offered for the lead(II) halide perovskite sheet, as often monitored by the associated exciton absorption peak – i.e., approximately 330 nm (3.8 eV) for $X = \text{Cl}$, 400 nm (3.1 eV) for $X = \text{Br}$ and 500 nm (2.5 eV) for $X = \text{I}$. Strong photoluminescence from the AEQT molecule in the $X = \text{Cl}$ structure and quenching of this luminescence for $X = \text{I}$ suggests that interaction between the organic and inorganic structural components occurs in the hybrid.^{102,104} One model for the photoluminescence quenching observed for AEQTPbX₄ as X transitions to higher atomic number metal halides may be viewed in light of energy or charge transfer between components of the structure (**Figure 19**).¹⁰²

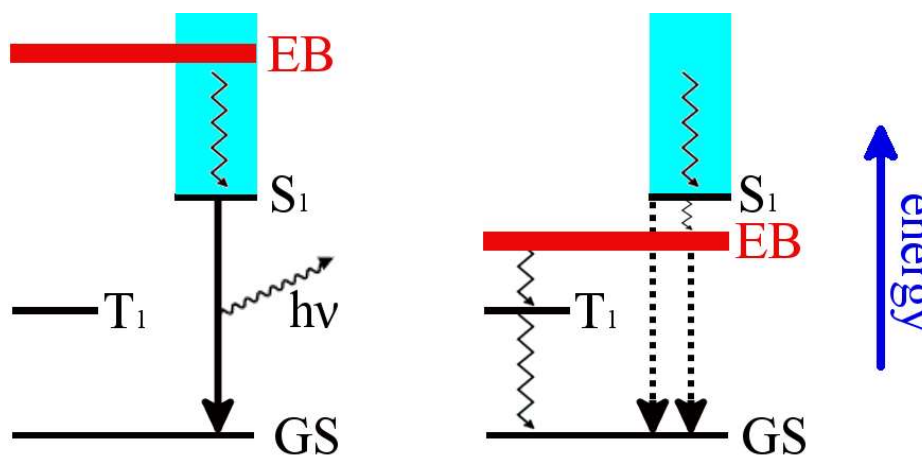


Figure 19. Prospective schematic energy level diagrams for the (AEQT)PbX₄ system with (a) $X = \text{Cl}$ and (b) $X = \text{I}$, as determined from the absorption data and literature values for the triplet state (T_1).¹⁰⁵ The relevant energy levels include the singlet (S_1) and T_1 states for the organic molecule (note that the cyan box above the S_1 state corresponds to the vibronic

progression and higher lying states for the organic molecule) and the exciton band (EB) for the inorganic framework. GS refers to the ground state for each of the transitions. The transitions in (b) that are indicated with the dotted lines are either not observed ($EB \rightarrow GS$) or only weakly observed ($S_1 \rightarrow GS$). The zigzag lines correspond to possible non-radiative transitions. The conduction and valence bands for the lead (II) halide framework have not been included in the diagram for the sake of clarity. Note that the spacing between energy levels has not been drawn to scale.¹⁰²

Efficient Förster resonant energy transfer between more extended Wannier-type excitons from inorganic semiconductor quantum wells and optically-active organic molecules in a nearby medium (i.e., conversion of Wannier to molecular excitations or Frenkel excitons) has been predicted^{106,107} and observed,¹⁰⁸ when there is strong spectral overlap between donor emission and acceptor absorption spectra. While Förster resonant energy transfer involves energy transfer through non-radiative dipole-dipole coupling and is inversely proportional to the sixth power of the distance between the donor and acceptor, Dexter charge transfer processes involve the non-radiative transfer of an excited electron from one species to the other and has a stronger exponential decay with separation. Ema et al. have demonstrated near perfect Dexter-type triplet-triplet energy transfer between the Wannier excitons in inorganic $PbBr_4^{2-}$ perovskite layers and naphthalene molecules in the organic layer, with demonstrated exponential dependence on separation distance, as controlled by the length of the tethering alkylammonium group linking the naphthalene moiety to the inorganic layers.¹⁰⁹ A number of other examples in which energy/charge transfer between organic and inorganic components of the perovskite structure have been explored include naphthalene and pyrene derivatives within lead(II) halide frameworks,¹¹⁰⁻¹¹² 3-2-(aminoethyl) indole ($C_8NH_6-CH_2CH_2NH_2$) incorporated in a $CuCl_4^{2-}$ framework,¹¹³ azobenzene associated with $CdBr_4^{2-}$,¹¹⁴ mixtures of organic cations

(chromophore and non-chromophore) within a PbBr_4^{2-} framework,¹¹⁵ and $\langle 110 \rangle$ -oriented structures stabilized by *n*-(3-aminopropyl)imidazole.⁸⁵ Such studies involving quaterthiophene, naphthalene and related aromatic organic components display the unique flexibility of the organic-inorganic perovskites to allow electronic tunability of both organic and inorganic species to create a cooperative response. Optical properties of such complex systems and the properties of excitons in these structures will be further explored in Section 7.

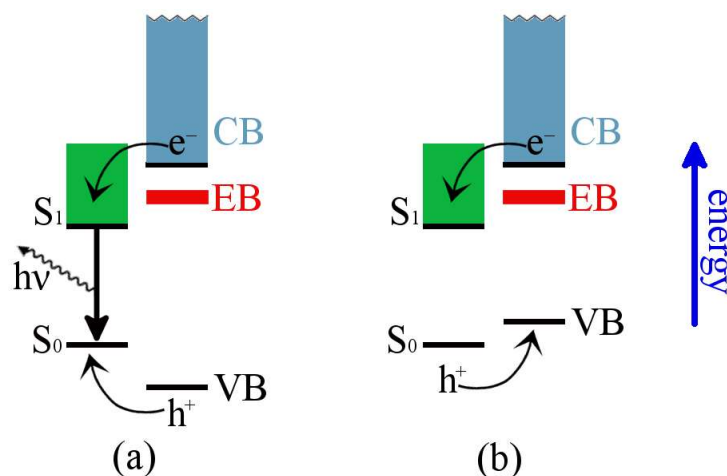


Figure 20. A proposed energy level scheme to describe the energy level configuration of the (a) AEQTPbCl₄ and (b) AEQTPbI₄ compounds. The relevant energy levels include the singlet S_0 and S_1 states for the chromophore and the valence band (VB), conduction band (CB) and exciton band (EB) states for the lead (II) halide sheets. For clarity, the triplet level (T_1) has not been included in the chromophore energy level scheme. Note also that, to draw this diagram, we have arbitrarily chosen an offset energy between the chromophore S_1 edge and the inorganic conduction band edge (CB).¹⁰²

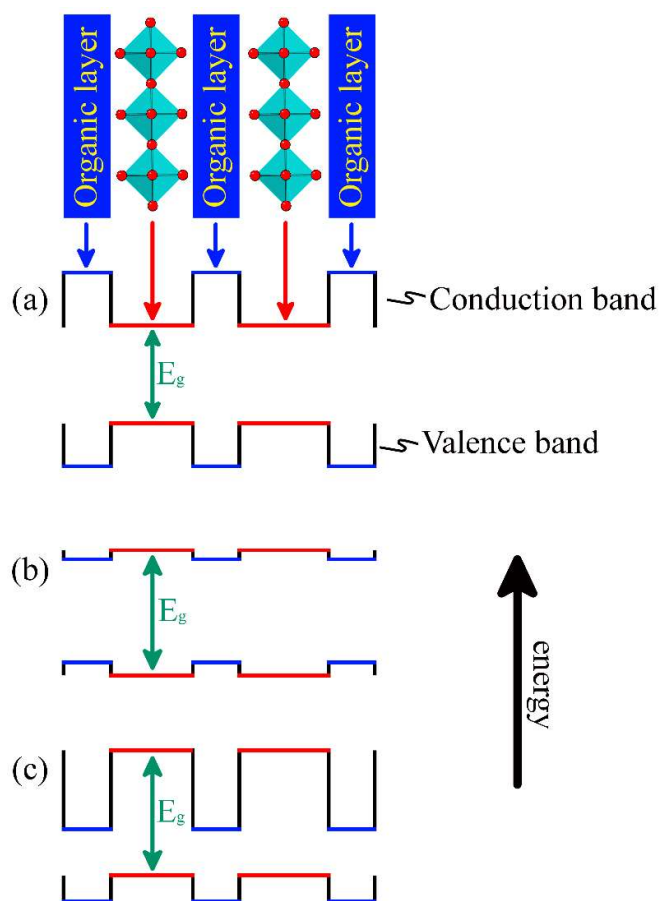


Figure 21. Several possible energy level schemes for the alternating organic-inorganic perovskite structure, highlighting the prospective analogy (still to be confirmed) with multilayer quantum-well (QW) structures. The structures represent (a) type I QW structures in which the organic layer has a much wider HOMO-LUMO separation than the corresponding band gap for the inorganic layer, (b) type I QW structure in which the roles of the organic and inorganic layers are reversed, and (c) type II QW structure.¹¹

An alternate vision for this type of structure can be found in **Figure 20**.¹¹ Namely, if we view the organic-inorganic perovskite structure as a self-assembling multi-layer quantum well (QW), then perhaps the organic and inorganic components can be selected such that they will enable tuning between a type I quantum well system and type II. Indeed, for the

AEQTPbX₄ hybrid discussed earlier, for X = Cl wherein the band gap is significantly larger than the HOMO-LUMO separation of the organic molecule, the lowest energy state for both electrons and holes may be on the organic cation layer. In contrast, as the halide is shifted from X = Cl to Br and I, the valence band is expected to shift up¹¹⁶ and the lowest energy state for electrons and holes may then be on different components of the structure.

Photoluminescence quenching of the AEQT molecule in the X = I structure is consistent with this model. An important area for further exploration involves understanding the extent to which this analogy to organic-inorganic QW structures (**Figure 21**) can be taken, given the combination of highly disparate organic and inorganic moieties and the short length-scales involved. Even et al. show that, for ultrathin layers, the effective mass model may fail due to the absence of superlattice coupling and importance of non-parabolicity, and they propose an alternative model based on concepts from composite materials.^{117,118}

Inclusion of more complex and larger organic moieties has also been attempted with other motivations in mind. One example involves the incorporation of metal-containing clusters as part of the organic cation. In [Cu(O₂C-(CH₂)₃-NH₃)₂]₂PbBr₄, incorporation of Cu₂(CO₂)₄ “paddle-wheel” clusters, can be accomplished using amino carboxylic acid zwitterionic molecules, with the anionic part of the molecule complexing to the metal and the cationic part serving to tether onto the PbBr₄²⁻ sheets.¹¹⁹ The coordinated metal clusters constitute “secondary building units” (SBUs) and have been used to design porous metal-organic frameworks (MOFs).¹²⁰ One special structural feature is that the terminal ligands of the Cu₂(CO₂)₄ moiety are coordinated by apical bromines from the PbBr₄²⁻ sheets, thereby creating Br-Cu-Cu-Br covalent linkages between nearest-neighbor perovskite layers (**Figure 22**) and increasing the effective dimensionality of the material (at least from a structural point of view). Use of such SBUs may provide a structured approach to modified electrical transport and optical response, although this still remains to be demonstrated practically.

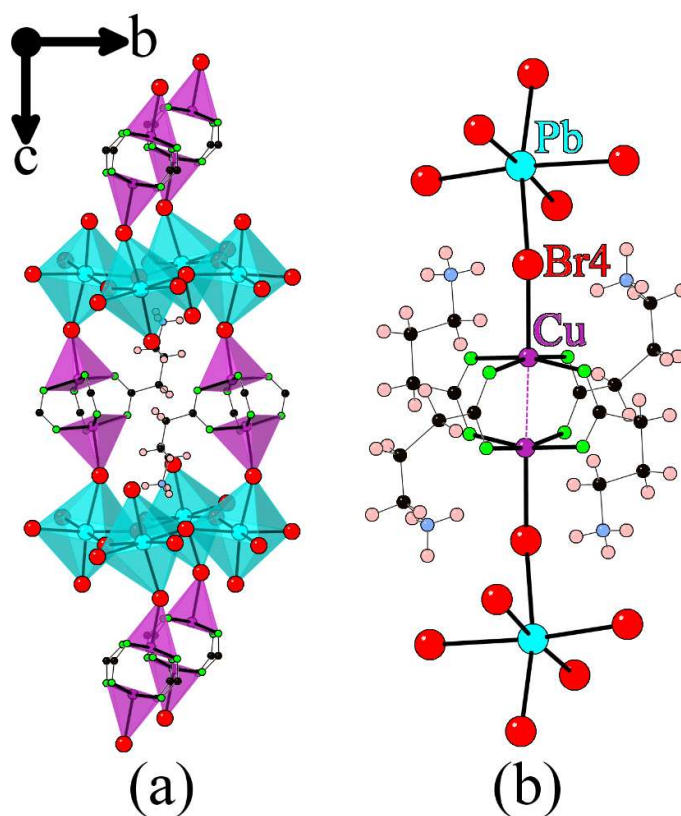


Figure 22. (a) Polyhedral representation of the $[\text{Cu}(\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3)_2]\text{PbBr}_4$ structure showing the connection of copper clusters to adjacent PbBr_6 octahedra. Except for two $-\text{O}_2\text{C}-(\text{CH}_2)_3-\text{NH}_3^+$ molecules, the propylammonium units have been removed for clarity.¹¹⁹ (b) Enlarged view of the copper cluster connected to two lead bromide octahedra via apical bromine atoms of the PbBr_4^{2-} sheets (Cu–Br4 and Cu–Cu distances are 2.643(1) Å and 2.649(2) Å, respectively).

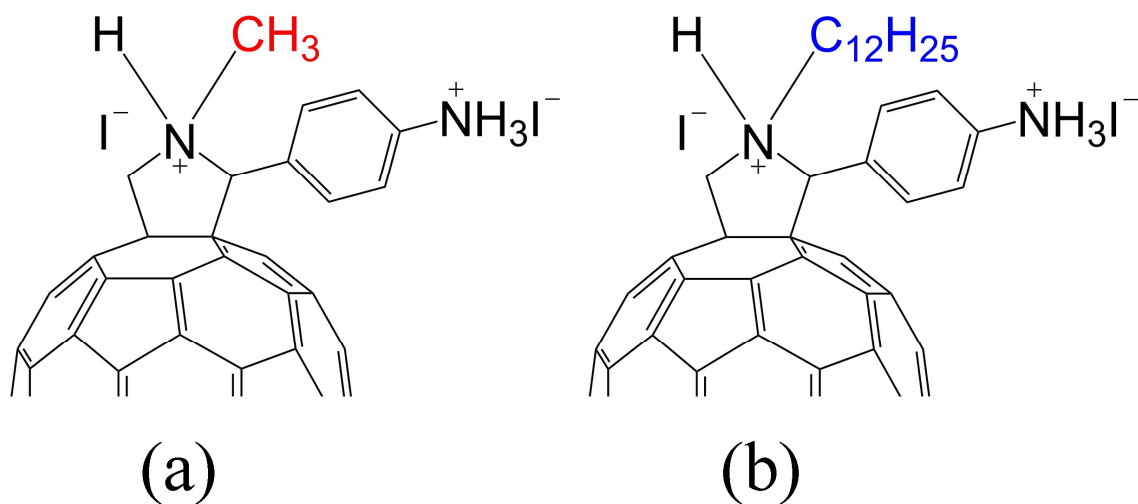


Figure 23. Structures of fullerene-derived molecules (a) AmPF-I₂ and (b) C12AmPF-I₂.¹²¹

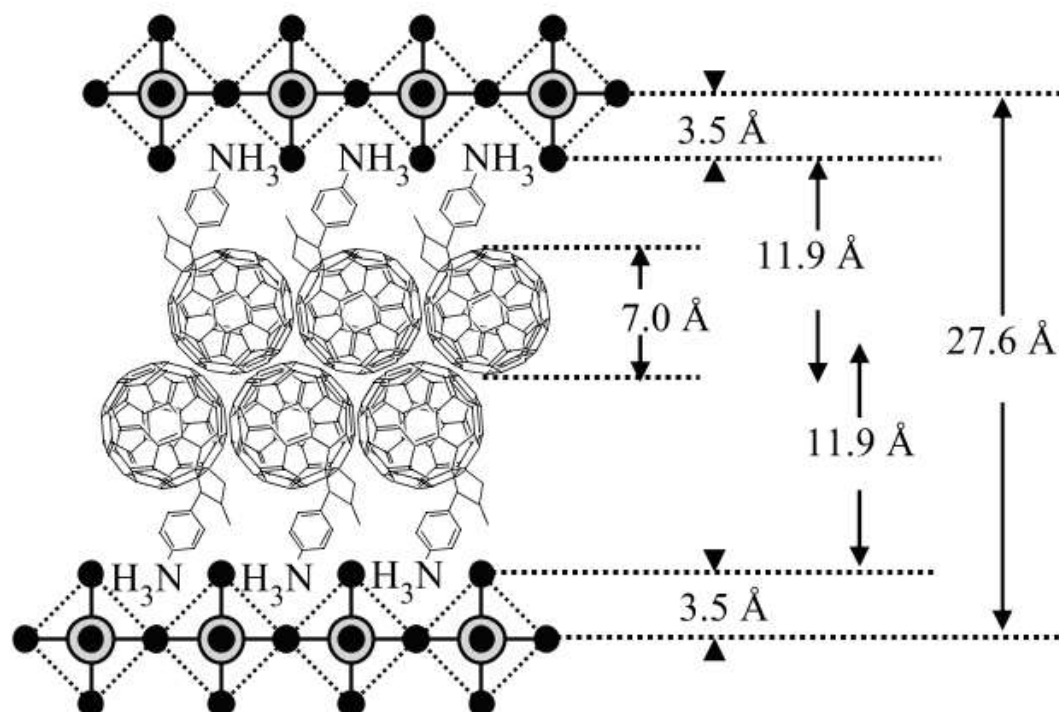


Figure 24. Picture showing four nearest neighbor PbI₆ octahedra sharing corners and the distance between cavities for the organic cation.¹²² This proposed structure remains to be confirmed with the fullerene-based cations. Reprinted with permission from ref 122.

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Another interesting prospective example involves the incorporation of the fullerene derivatives N-methyl-2-(4-ammoniumphenyl)-fulleropyrrolidine iodide (AmPF-I₂) and N-(n-dodecyl)-2-(4-ammoniumphenyl)-fulleropyrrolidine iodide (C12AmPF-I₂) (**Figure 23**) in a lead(II) iodide framework.¹²¹ While evidence of layered structure formation from X-ray diffraction was taken as an indication that the perovskite structure is being formed with this combination, the fullerene molecule itself has a diameter of ~ 7.1 nm,¹²³ rendering it a very tight prospective fit within the layered perovskite structure (**Figure 24**). On the other hand, there may be the possibility of diluting it with long-chain alkylammonium cations to improve the fit.¹²² Also, the organic cation is doubly protonated, and the organic cation may therefore be, from a charge balance point of view, accommodated in the space allotted for two cations from the proto-typical (R-NH₃)₂PbI₄ structure, in which the cations are mono-protonated. It will be of great interest when the crystal structures of the proposed (AmPF-I₂)PbI₄ hybrids become available to confirm the structure type. In the meantime, it is important to realize that observation of a layered structure is not, in itself, convincing evidence of the perovskite framework (as an example, (n-C₁₂H₂₅NH₃)₂ZnCl₄ comprises a distinctly layered structure, but with layers of isolated ZnCl₄⁻² tetrahedral clusters rather than the extended perovskite sheets).¹²⁴ Observation of characteristic exciton features in the absorption spectrum is a valuable confirmation for systems containing Ge(II), Sn(II) or Pb(II) halide perovskite layers (for the 100% fullerene-incorporated systems, these features are absent).

Recently, another example of larger organic cation, in this case based on cationic propylammonium-functionalized polyhedral oligomeric silsesquioxane (POSS) interlayers, has been synthesized and structural studies are underway.¹²⁵ Organic functionalized POSSs themselves are recognized as an interesting class of hybrid materials with the POSS fragment providing mechanical, thermal and chemical stability, and rigidity. Insertion of functionalized

POSS cations into the perovskite framework would enable preparation of materials that are positioned in between all-inorganic perovskites and hybrid organic-based perovskites and, as such, it promises a great number of interesting properties and potential applications.

Successful preparation of $[\text{Si}_8\text{O}_{12}(\text{C}_3\text{H}_6\text{NH}_3)_8][\text{CuCl}_4]_4$ (CuPOSS) has been reported, along with the analogous derivatives PdPOSS, PbPOSS and MnPOSS; however, the structural characterization is incomplete, and the exact compositions and the intricacies of the crystal structures are not yet available. In earlier publications,^{126,127} preparation of layered perovskites containing silica networks as cationic layers were reported. For this purpose, the authors used 3-aminopropyltrimethoxysilane $\text{NH}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ (APS), and the successful formation of Si-O-Si networks was evidenced from FT-IR and ^{29}Si solid-state NMR data. Although no single crystal X-ray diffraction data were reported, suggestive (00*l*) peaks of the prospective perovskite sheets are observed in the powder X-ray diffraction patterns of $(\text{APS})_2\text{PbCl}_4$ and $(\text{APS})_2\text{PbI}_4$ films. In UV-Vis spectra, two absorption peaks at 256 and 332 nm for $(\text{APS})_2\text{PbCl}_4$, and at 382 and 507 nm for $(\text{APS})_2\text{PbI}_4$ are observed, apparently arising from the band-gap absorption and excitonic bands, respectively.^{126,127} The optical band gap values calculated using these data yield 4.84 eV for $(\text{APS})_2\text{PbCl}_4$ and 3.25 eV for $(\text{APS})_2\text{PbI}_4$, which are (if confirmed) among the highest reported band gap values for hybrid lead halide perovskites. For a more systematic characterization of the perovskites containing Si-based cations, a series of compounds with well-characterized crystal structures would be helpful to understand structure-property relationship.

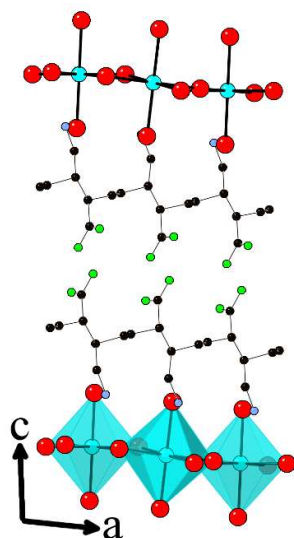


Figure 25. Combined skeletal (top) and polyhedral (bottom, shaded) view of the layered structure of the polymerized perovskite $(\text{HOOC-CH=CH-CH=CH-CH}_2\text{NH}_3)_2\text{CdCl}_4$ viewed down the b -axis.¹²⁸

While incorporating targeted relatively complex monomeric cations represents one method to generating functional hybrids, another approach involves incorporation of smaller but polymerizable moieties, so that the end product after polymerization can impart useful properties.¹²⁸⁻¹³¹ Polymerization under UV light or γ irradiation of the diene functional group within $[\text{HOOC-CH=CH-CH=CH-CH}_2\text{NH}_3]_2\text{CdCl}_4$ (6-amino-2,4-trans,trans-hexadienoic acid organic component), for example, results in ordered formation of the 1,4-trans-polybutadiene (**Figure 25**).^{128,129} The impact of the inorganic lattice in this process, in terms of holding the organic cations in an appropriate orientation for polymerization to occur, is evident in the fact that the analogous copper(II) chloride framework, with its associated anti-ferrodistortive Jahn-Teller distortion, does not enable polymerization.¹²⁹

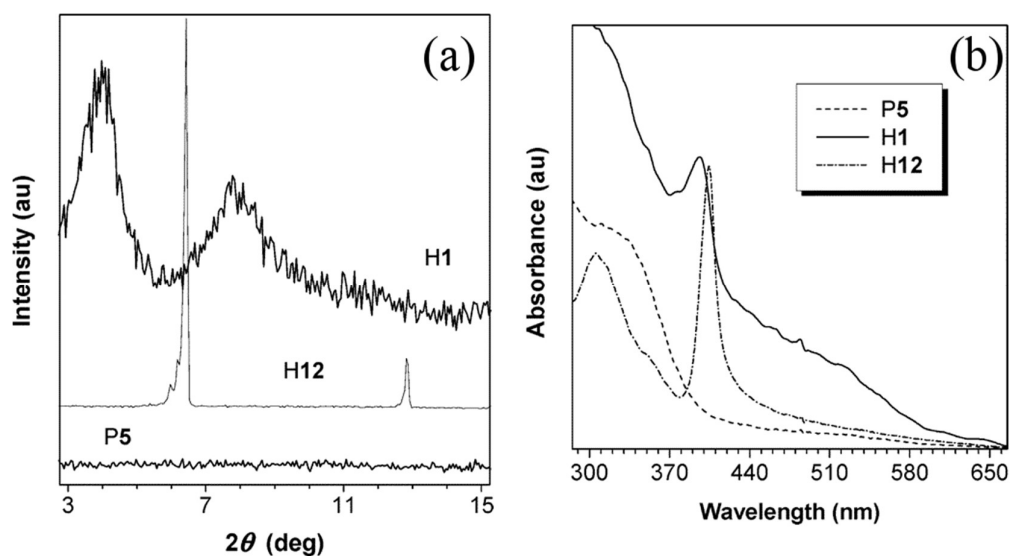


Figure 26. (a) X-ray diffraction patterns of the spin-coated films of poly(11-phenyl-10-undecyn-1-ammonium bromide) and hybrid poly(1-phenyl-1-undecyne) ammonium lead bromide labeled as P5 and H1, respectively. XRD pattern of the bulk powder of hybrid perovskite *n*-butylammonium lead bromide (H12) is shown for comparison.¹³¹ (b) Absorption spectrum of H1 has a characteristic peak at ~400 nm observed for hybrids containing lead(II) bromide perovskite sheets. Absorption spectra of model hybrid compound H12 and polymer P5 are also provided.¹³¹ Reprinted with permission from ref 131. Copyright 2006 American Chemical Society.

An alternatively approach has also been pursued for incorporating polymeric elements into the structure, which involves first creating polymer chains with tethering ammonium groups and then subsequently incorporating these polymeric moieties into the metal halide framework. One example targeting this approach involves dipping a film of the hydrogen bromide salt of poly(3-aminododecylthiophene) in an aqueous solution of lead(II) bromide, yielding a composite film that exhibits characteristic exciton absorption from the PbBr_4^{2-} layers.¹³² Another example of this involves combining preformed polyacetylene derivatives within a lead bromide framework.^{130,131} Although the X-ray diffraction pattern for these

compounds exhibit broad reflections, indicating relatively poor crystallinity or partial ordering, the long d-spacing from the lowest angle diffraction peak and additional observation of an absorption peak at ~400 nm, which is characteristic of the lead(II) bromide perovskite sheets (**Figure 26**), suggests that indeed these materials self-assemble into the layered perovskite framework (or a closely aligned structural type). The photoluminescence (PL) from the polyacetylene component of the hybrid structure is substantially improved (PL quantum efficiencies of as high as 62% are reported) compared with the polyacetylene component on its own, presumably because the interaction among polymer chains is reduced in the hybrid as a result of being sheathed in the lead(II) bromide layers.

One apparent practical application of perovskites containing polymerized units is the enhanced air- and moisture- stability provided by the protective polymer layers. For example, addition of small amounts of polyethylenimine hydrogen iodide (PEI·HI) into the regular solution deposition procedure for methylammonium lead iodide yields films that are stable up to 400 hours under ambient conditions with a relative humidity of ~50 %.¹³³ For this purpose, the authors first spin-coated a mixture of PbI_2 and PEI·HI, followed by a coating of a $\text{CH}_3\text{NH}_3\text{I}$ layer with targeted compositions of $(\text{CH}_3\text{NH}_3\text{PbI}_3)_{1-x}[(\text{PEI})_2\text{PbI}_4]_x$ ($0 \leq x \leq 0.04$). Incorporation of a small amount of 2-D perovskite $(\text{PEI})_2\text{PbI}_4$ ($x = 2\%$) improves surface roughness and grain size (up to 1 μm), resulting in smooth and pore-free films. Higher polymeric cation content of $x = 4\%$ gives films with reduced grain size of less than 100 nm, although their surface coverage is still better than the pristine $\text{CH}_3\text{NH}_3\text{PbI}_3$ films.¹³³ The beneficial impact of the polymeric protective layer to the stability of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was also shown by spin-coating a PEI solution (0.1 mg/ml in toluene) onto a perovskite layer.¹³⁴ Remarkably, devices with PEI coating maintain 85% of their initial performance after 14 days of exposure to 85% relative humidity.¹³⁴ Under these synthetic conditions, however, it is unclear if the 2-D perovskites form or an unreacted PEI layer acts as a blocking layer. For this

and other systems that involve incorporation of complex organic cations in hybrid perovskite structures, growth of single crystals suitable for single crystal X-ray diffraction measurements and/or detailed structural analysis of well-characterized thin films remains an important practical challenge.

5. INTERCALATION SYSTEMS

Another degree of engineering freedom enabled by the lower-dimensional perovskite structures involves intercalation. In the case of layered 2-D perovskites, the tail-to-tail arrangement of organic R-groups within the $(\text{R-NH}_3)_2\text{BX}_4$ structure should, depending upon the degree of inter-digitation, provide a van der Waals gallery or gap into which potentially functional molecules may intercalate. Intercalated structures are important, for example, in the fields of ionic conductivity and battery development,¹³⁵ tailoring of photofunctionality (photocatalysis, photoinduced charge separation, photoluminescence, photochromism and non-linear optics)¹³⁶ and superconductivity.¹³⁷ Early work on intercalation into 2-D organic-inorganic perovskites was described by Dolzhenko et al.,¹³⁸ where the weakly interacting molecules, 1-chloronaphthalene, *o*-dichlorobenzene and hexane were explored within perovskites comprised of long-chain aliphatic cations. However, the weak van der Waals type interaction between the proposed intercalation species and the organic cations made explicit structural characterization of the intercalated structure (e.g., by single crystal structure refinement) problematic, due to the instability of the composite.

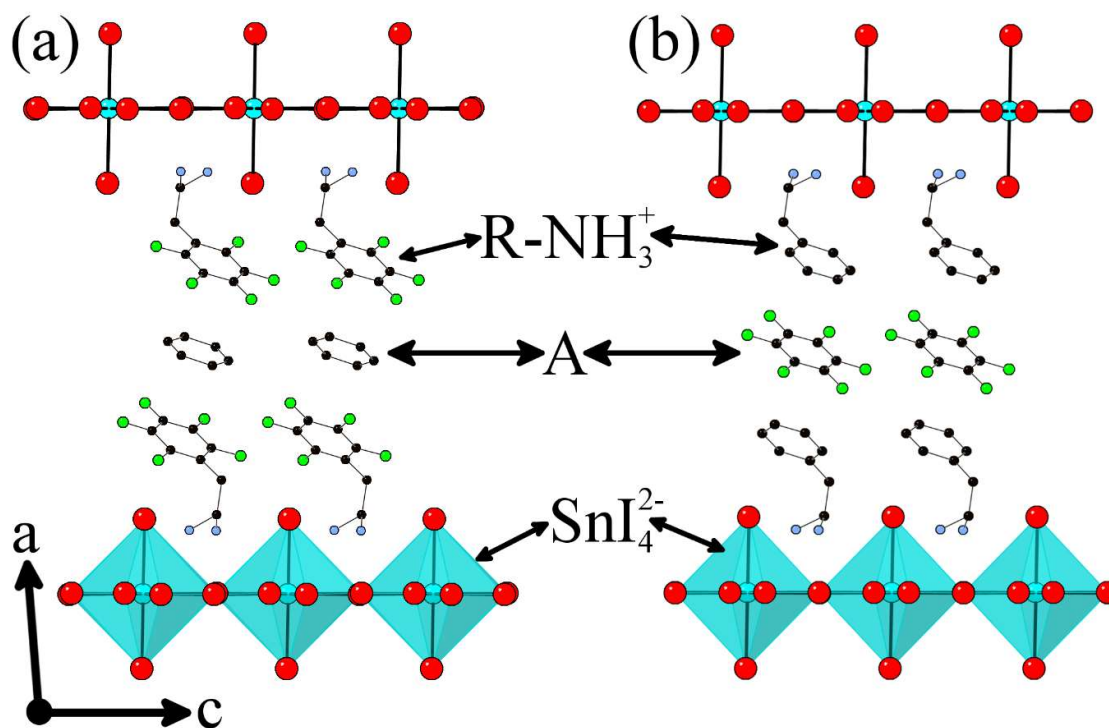


Figure 27. Combined skeletal (top) and polyhedral (bottom, shaded) views of the crystal structures of (a) $(\text{C}_6\text{F}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{SnI}_4 \cdot (\text{C}_6\text{H}_6)$ and (b) $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{SnI}_4 \cdot (\text{C}_6\text{F}_6)$ along the b -axis, showing the details of the stacking of the intercalated molecules within the perovskite framework. For clarity, the fluorine atoms are colored green and hydrogen atoms are omitted.¹³⁹

The first system where intercalation was unambiguously demonstrated involved molecular species that were structurally stabilized through non-covalent fluoroaryl-aryl interaction, which primarily arises from the relatively large but opposite in sign quadrupole moments for molecules based on C_6H_6 and C_6F_6 (or other analogous aromatic non-fluorinated and fluorinated molecules).¹³⁹ Films of $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{SnI}_4$ (where $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3^+ =$ phenethylammonium) deposited from methanol solutions yielded a crystal structure with interlayer separation (distance between the SnI_4^- perovskite sheets) of 16.3 Å. However, when

these films were dipped into a solution containing hexafluorobenzene, the interlayer separation, as deduced from the ($2h$, 0, 0) X-ray diffraction peaks, stretched to 20.6 Å (no long axis structure was achieved if films were dipped into benzene). Likewise, films of $(\text{C}_6\text{F}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{SnI}_4$ (where $\text{C}_6\text{F}_5\text{C}_2\text{H}_4\text{NH}_3^+$ = pentafluorophenethylammonium) deposited from methanol yielded interlayer separation of 17.5 Å, whereas these same films dipped in a solution containing benzene yielded interlayer separation of 20.7 Å (no long axis structure was observed for films dipped into hexafluorobenzene). Single crystal structure determination of the longer-axis structures (**Figure 27**) demonstrated offset face-to-face interaction between the intercalated molecules and the initial perovskite organic cations. This offset face-to-face interaction is structurally similar to that observed in the 1:1 benzene-hexafluorobenzene complex, a prototypical fluoroaryl-aryl compound. Gently heating the intercalated systems ($\sim 150^\circ\text{C}$) deintercalates the molecular species and leads to recovery of the parent layered perovskite. Interestingly, the inorganic framework can be used to control whether molecules will intercalate or not into the hybrid structure. While the tin(II)-based systems show facile and stable intercalation, $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{CuCl}_4$ crystals were not successfully intercalated, presumably because of the less favorable orientation of the phenyl ring in the copper(II) chloride structure for prospective interaction with fluorinated aromatic molecules.¹³⁹

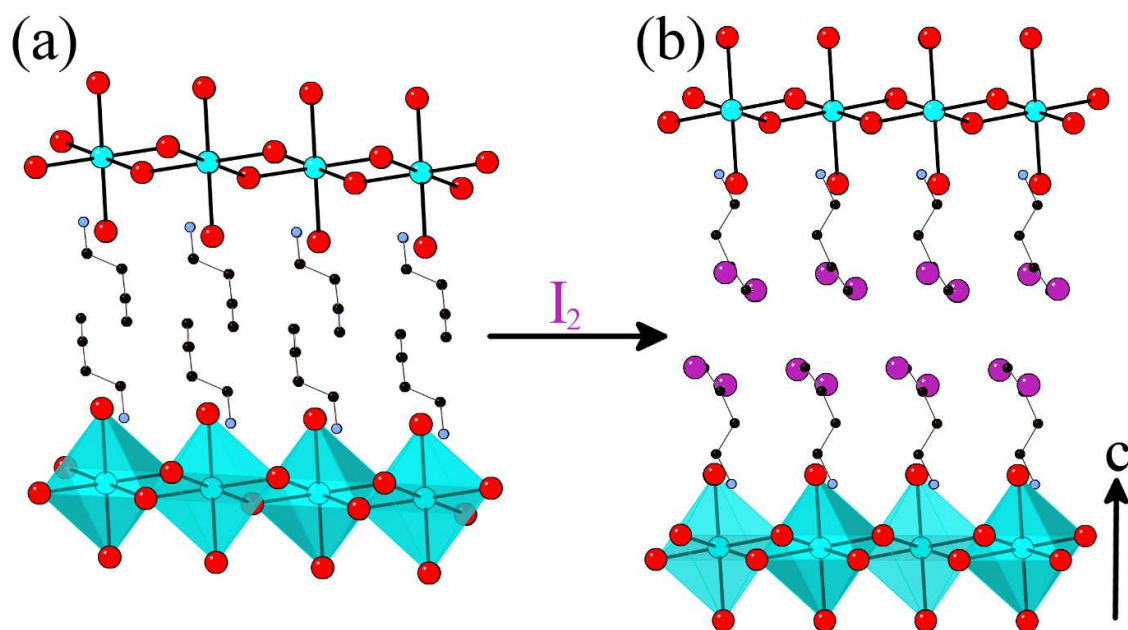


Figure 28. Combined skeletal (top) and polyhedral (bottom, shaded) view of the (a) $(\text{BYA})_2\text{PbBr}_4$ and (b) $(\text{BYA-I}_2)_2\text{PbBr}_4$ structures (BYA = but-3-yn-1-ammonium) showing the addition of the I_2 molecule to the BYA molecule. For clarity, the iodine atoms are colored purple, and the hydrogen atoms are omitted.¹⁴⁰

Intercalation can also be combined with chemical reactivity, as is the case for iodine-incorporated $(\text{R-NH}_3)_2\text{PbBr}_4$, where R-NH_3 comprises an organic cation with a terminal alkyne or alkene – e.g., but-3-yn-1-ammonium (BYA), but-3-en-1-ammonium (BEA), and prop-2-en-1-ammonium (PEA).¹⁴⁰ Using a lead(II) bromide framework, the parent layered perovskite undergoes topotactic transformation in the presence of iodine vapor, with iodine covalently bonding to the unsaturated hydrocarbons (**Figure 28**). In the case of PEA, the reaction $\text{PEA} \leftrightarrow \text{PEA-I}_2$ can be cycled, with addition/removal of two iodine atoms, showing the reversibility of the chemisorption process. For the alkyne-based cation (i.e., for $\text{BYA} \rightarrow \text{BYA-I}_2$), the reaction with iodine vapor appears to be irreversible. In each case the chemisorption of iodine leads to significant expansion of the structure, particularly

perpendicular to the perovskite layers—e.g., for $\text{BYA}_2\text{PbBr}_4$ the c-axis lattice parameter expands by 38% during the reaction, and the gravimetric and volumetric iodine capacities in the non-porous perovskite frameworks are comparable to what can be achieved with more typical porous frameworks used for gas capture (e.g., with gravimetric capacity of 0.43g I_2 per gram for the $\text{BYA}_2\text{PbBr}_4$ perovskite).¹⁴⁰ Given the higher stability of the iodine bonding to the alkyne-based derivative, the perovskite hybrids containing the BYA cations are proposed for use as thermally stable compounds for iodine capture (e.g., for radioactive iodine). As for the intercalation processes involving fluoroaryl-aryl interaction, the ability to conduct the iodine storage reaction depends on the inorganic framework—e.g., in $\text{PEA}_2\text{CuCl}_4$, no reactivity arises in an iodine-saturated vapor and the unsaturated hydrocarbon cations are therefore presumably held within an unsuitable configuration for the intercalation/reaction to occur.

The van der Waals gallery can also provide a means to facilitate thin-film deposition and fabrication approaches starting from the metal halide. In the two-step dip processing approach,¹⁴¹ for example, a film of PbI_2 may be dipped into a solution of $\text{R-NH}_2\cdot\text{HI}$ and, if the “R” group is selected so that a layered perovskite will form (e.g., butylammonium), then the reaction to form the layered perovskite structure will proceed in a matter of seconds to minutes (**Figure 29**). On the other hand, if the organic cation leads to the formation of the 3-D perovskite (e.g., methylammonium), then the reaction may take hours (unless conducted on a mesoporous framework that can significantly increase the surface area for the reaction).^{141,142} Evidently, when the layered perovskite forms, the organic cations and iodide species can readily diffuse through the van der Waals gap formed in the reacted material to reach the unreacted lead(II) iodide starting materials underneath. If the 3-D perovskite forms, then there is no van der Waals pathway and the diffusion of the reacting species proceeds much slower. In summary, as can be seen from each of the above examples, the particular structural/chemical details of the organic cation within the perovskite (as also templated by

the inorganic framework) may control the ability to intercalate molecules and the reactivity of these species with the underlying parent compound, as well as facilitate molecular transport during the perovskite film formation.

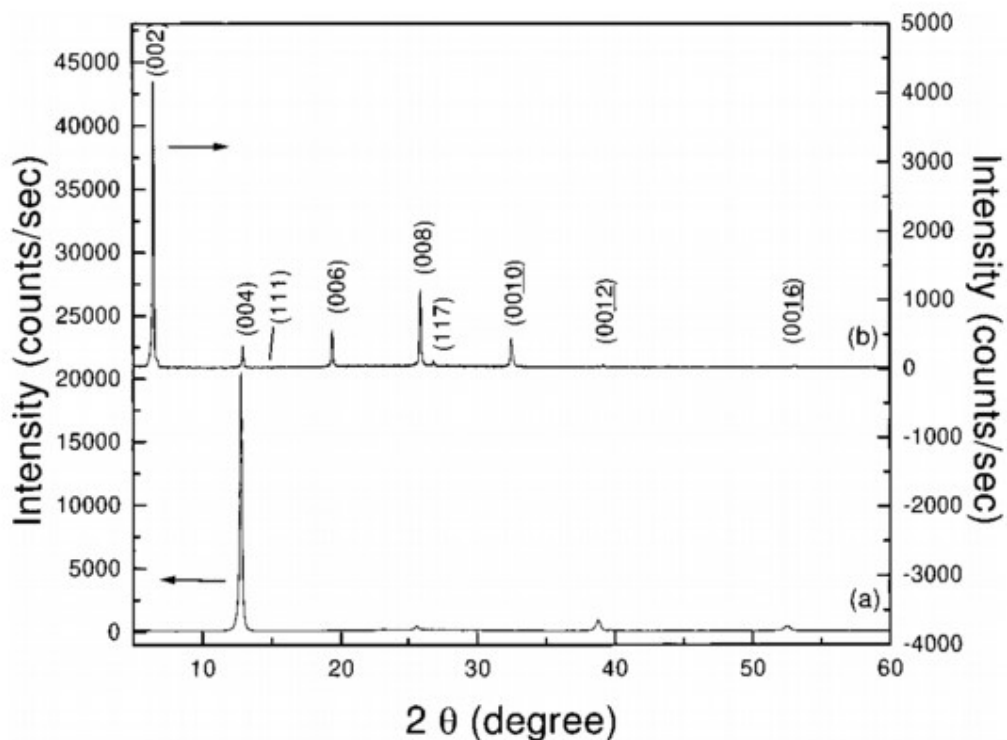


Figure 29. X-ray diffraction patterns for (a) vacuum-deposited PbI_2 thin film and (b) a $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ thin film, prepared by dipping the PbI_2 film into a 38 mM butylammonium iodide 2-propanol/toluene solution for 1 min.¹⁴¹ Reprinted with permission from ref 141.

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6. MOLECULAR PEROVSKITES

In the preceding sections, we have considered a perovskite family that comprises a 3-D or lower-dimensional (2-D or 1-D) metal halide framework, with organic cations counterbalancing the anionic charge from the framework. In these structures, the extended metal halide anion is held together with covalent/ionic bonding and the organic cations interact via ionic and hydrogen bonding (i.e., charge-assisted hydrogen bonding). However,

metals are not a requirement for the “B” site within the ABX_3 perovskite structure. The molecular perovskite $C_4H_{12}N_2 \cdot NH_4Cl_3 \cdot H_2O$, for example, consists of a non-metal-containing 3-D corner-sharing network of $(NH_4)Cl_6$ octahedra, in a structure held together with charge-assisted hydrogen bonding, interspersed with the divalent piperazinium cations and water molecules (**Figure 30**).¹⁴³ One unusual feature of this ABX_3 perovskite is that the +2 ionic charge on the “A” cation is larger than the +1 charge on the “B” cation, in contrast to previously-discussed examples of organic-based metal-containing perovskites, in which the charge ordering is reversed. In addition, the structure contains water and can be considered a perovskite hydrate. The family has been further extended to include $(C_6H_{14}N_2)(NH_4)[BF_4]_3$ ($C_6H_{14}N_2^{2+}$ = 1,4-diazoniabicyclo[2.2.2]octane or the “dabconium” dication), which consists of a 3-D network of corner-sharing $(NH_4)[BF_4]_6$ octahedral units, in this case without water.¹⁴⁴ In each of these structures, hydrogen bonding plays a central role in establishing the global framework and covalent interactions play little role in the perovskite structure assembly (of course they do play a role within the constituent molecules themselves). Note that structures have also been reported in which the ammonium cation in the above frameworks has been replaced by alkali metals—i.e. $C_4H_{12}N_2 \cdot KCl_3 \cdot H_2O$, $C_4H_{12}N_2 \cdot RbCl_3 \cdot H_2O$, $C_4H_{12}N_2 \cdot CsCl_3 \cdot H_2O$, $C_6H_{14}N_2 \cdot RbCl_3$, and $C_6H_{14}N_2 \cdot CsCl_3$, thereby providing a link between the molecular-based perovskites and the main family of metal-containing organic-based perovskites.²⁶

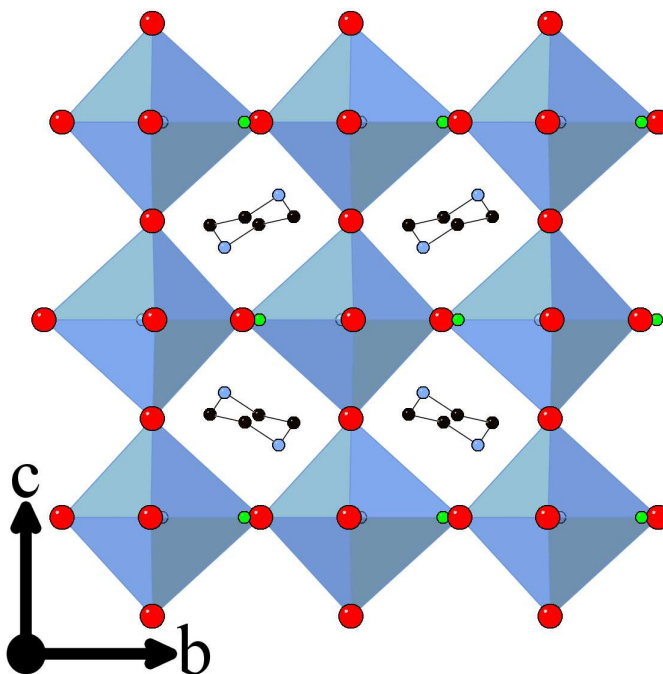


Figure 30. The crystal structure of $\text{C}_4\text{N}_2\text{H}_{12}\cdot\text{NH}_4\text{Cl}_3\cdot\text{H}_2\text{O}$ viewed down the a -axis. The 3-D anionic network of corner-sharing NH_4Cl_6 octahedra (blue) is interspersed with piperizinium dications and water molecules. H atoms are omitted for clarity; O atoms are shown as green spheres.¹⁴³

Although, given the lack of covalent character, the extended BX_3 frameworks in the above molecular compounds are insulating, they may help to template or stabilize non-centrosymmetric and even chiral structures, and systems with ferroelectric properties. The structures are also interesting since they provide examples of divalent organic cations that can behave as organic “A” cations in an ABX_3 framework (of course longer doubly charged diammonium cations are regularly used within a layered perovskite framework, as discussed in Section 3). These add to the collection of monovalent cations such as methylammonium, CH_3NH_3^+ , and formamidinium, $\text{H}_2\text{NCHNH}_2^+$, that can fit within the 12-coordinate holes provided by the extended BX_3 framework. Note that generally, in figuring out the largest effective radius of a cation occupying the “A” site in a 3-D perovskite, we have used the PbI_3^-

framework to deduce the value 2.6 Å.¹⁰ In the above examples, since we see that monovalent “B” ions can also be placed into the structure, when given the possibility of divalent organic cations, then the CsI₃²⁻ framework (Shannon ionic radii R_{Cs^+} (octahedral) = 1.67 Å and R_{I^-} = 2.20 Å)²³ represents a more reasonable largest practical metal-containing framework, thereby extending the organic cation size to as large as 3.27 Å (i.e., for $t = 1$) to fit within the “A” site of metal-containing organic-inorganic perovskites. Of course, even larger BX₃ⁿ⁻ frameworks and “A” cations are possible when considering molecular complexes for the “B” and “X” moieties. Note that, using the cubic perovskite crystal structures described above, we can deduce effective ionic radii for the piperazinium and dabconium cations of ~3.2 Å and ~3.4 Å (**Table 1**), which are slightly larger values (at least for dabconium) than the above-calculated largest possible size of 3.27 Å for $t = 1$. The discrepancy may perhaps be attributed to the less exact nature of the ionic size calculation method used for polyatomic ions²²—i.e., for example to uncertainty with regards to the radius of 1.77 Å used for C.²⁴ An area for further exploration involves elucidating and expanding the true limits to the collection of divalent and monovalent organic cations that fit within the 3-D perovskites, thereby providing a larger set of building blocks with which to put together functional organic-inorganic hybrids.

7. EXCEPTIONAL PROPERTIES AND DEVICE APPLICATION

Intense current interest in organic-inorganic perovskites has centered primarily on one set of materials—i.e., those based on APb_{1-x}Sn_xI₃, where “A” is a small organic cation such as methylammonium or formamidinium—and on their use in photovoltaic devices. The unprecedented jump in performance to >20% PCE (power conversion efficiency) levels in less than five years has been enabled by the unusual confluence of ideal semiconductor characteristics within a single material including: 1) a tunable direct band gap, E_g , where the value of the E_g can be tailored within the ideal range for terrestrial PV by the choice of metal

or halogen comprising the perovskite, 2) substantially higher optical absorption than conventional thin-film solar cell absorbers due to the specific orbital make-up of the valence and conduction band edges (i.e., high joint density of states due to band edge states that have high p -orbital character), 3) significant s - p anti-bonding coupling in the absorber leading to strongly dispersing conduction and valence bands and relatively small effective masses for both electrons and holes, 4) dominant point defects that are shallow (i.e., close to the band edge and therefore not effective as recombination centers) and 5) intrinsically benign grain boundaries with respect to recombination.⁷ Several reviews already outline the outstanding potential for organic-inorganic perovskites used for thin-film PV.¹⁻⁶ This contribution seeks to highlight the numerous other extraordinary properties and application possibilities for the broader family of organic-inorganic perovskites, given the high degree of structural/electronic flexibility described in previous sections.

7.1 Magnetic and Dielectric Properties and Application

7.1.1. Magnetic Interactions in Hybrid Perovskites. Early interest in properties of organic-inorganic perovskites focused on their magnetic properties.¹⁴⁵⁻¹⁴⁹ With incorporation of Cu (II), Fe (II), Cr (II) and Mn (II) as the metal, long-range magnetic ordering has been observed within the layered perovskite structures.^{145,146,148-152} Notably, the hybrid Cu (II) halides provided the first examples of 2-D ferromagnetic insulators.^{149,153} Since there are no direct metal-metal contacts in the hybrid perovskites, magnetic superexchange interactions, J , through the B-X-B linkages, usually determine the magnetism of these compounds. The primary factors influencing the magnetic exchange are the structural parameters, including the bond distances and angles.¹⁵⁴ In addition, the presence of Jahn-Teller active metal cations influence the structures and magnetism of the hybrid compounds. Note that the Goodenough-Kanamori (or Goodenough-Kanamori-Anderson) rules,^{155,156} which were originally developed

and are widely used for rationalizing the magnetism of oxide perovskites, also apply for hybrid halide perovskites. Briefly, the Goodenough-Kanamori rules predict a strong antiferromagnetism when the magnetic orbitals on adjacent B atoms are oriented at $\sim 180^\circ$ and B has partially filled *d* shells, and a weak ferromagnetism arises when the magnetic orbitals are at $\sim 90^\circ$.¹⁵⁷ For example, in the layered A_2CuX_4 salts, due to their antiferrodistortive structures, the magnetic interactions within the layers occur through $Cu-X\cdots Cu$ linkages where $X\cdots Cu$ represents the Jahn-Teller elongated copper-halide bond.¹⁵⁸ *Intralayer* coupling for the A_2CuX_4 salts is ferromagnetic because the bridging $Cu-X\cdots Cu$ angles are in the 160 - 170° range and the magnetic orbitals on adjacent Cu atoms are nearly orthogonal, i.e., there is essentially no magnetic orbital overlap.^{9,158} The magnitude of this intralayer exchange interaction in A_2CuX_4 is determined by the orbital overlap between the magnetic orbitals on two adjacent Cu atoms, which in turn strongly depends on the Jahn-Teller elongated $X\cdots Cu$ contacts. The magnetic exchange interaction *J* decreases rapidly with increasing $X\cdots Cu$ distance. Note that Cr (II) layered perovskite analogs are also ferromagnetic due to the cooperative Jahn-Teller effect, and the resulting structural distortions are similar to those observed for the Cu (II) salts.¹⁵¹ On the other hand, most layered perovskites featuring Mn (II) and Fe (II) do not exhibit Jahn-Teller distortion, and are antiferromagnetic.⁹ In these compounds, symmetrical B–X–B linkages are nearly linear, and consequently, following the Goodenough-Kanamori rules, the linear superexchange of two magnetic ions with partially filled *d* orbitals is strongly antiferromagnetic.

The *interlayer* coupling, *J'*, is strongly-dependent on the interlayer $X\cdots X$ distance, the geometry of the $B-X\cdots X-B$ linkage, and the halide X^- ion. As expected, the interlayer coupling increases rapidly with decreasing interlayer $X\cdots X$ distance. From the chemical design perspective, since the magnetic interactions generally arise in the inorganic perovskite layers, varying the length of the organic cation provides a knob to vary the effective

dimensionality of the magnetic interaction, from more 3-D to more 2-D with increasing organic cation length, as seen within the $(C_nH_{2n+1}NH_3)_2CuCl_4$ and $(C_nH_{2n+1}NH_3)_2MnCl_4$ families.¹⁴⁹ Structural symmetry also plays an important role in the magnetism of hybrid compounds. For instance, the $(C_nH_{2n+1}NH_3)_2MnCl_4$ ($n = 1, 2, 3 \dots$) series, members of which adopt the tetragonal K_2NiF_4 -type structure, has been considered to comprise the “best” 2-D antiferromagnets—i.e. those with the smallest possible ratio of interlayer to intralayer coupling $|J'/J|$.^{147,149} The rationale behind this designation follows from the fact that the magnetic 2-D character in the K_2NiF_4 structure mainly originates from the tetragonal symmetry, which in the case of an antiferromagnetic alignment within the NiF_2 sheets leads to a cancellation of the interaction between the adjacent layers.¹⁵⁹ In the $(C_nH_{2n+1}NH_3)_2MnCl_4$ compounds, the tetragonal K_2NiF_4 -type structure combines with the tunable interlayer distance (through varying n), leading to $|J'/J|$ values that can be much smaller compared to those in strictly inorganic K_2NiF_4 structures. Supporting this conjecture, even for the $n = 1$ compound $(CH_3NH_3)_2MnCl_4$, a superexchange interlayer coupling value of $J' = 10^{-10} J$ is reported, with J' occurring through two $CH_3NH_3^+$ cations and two Cl^- anions.^{147,149}

In addition to varying organic cation length and structural symmetry, varying the halogen from iodide down to fluoride allows for changing the exchange interaction among the magnetic ions both in and between the layers, providing further tunability of the magnetic interaction.^{151,152,160} It has been shown that both intralayer and interlayer couplings are weaker in the Cu (II) and Cr (II) chlorides compared to the corresponding bromides.^{151,158} The larger ferromagnetic intralayer couplings in the Cu (II) and Cr (II) bromides are attributed to the larger extension of the bromide valence electron shell.^{151,161} Unlike chlorides, it is reported that for some bromides, e.g., (ethylenediammonium) $CuBr_4$, the interlayer coupling is larger than the intralayer coupling, indicating that the dominant exchange pathway is between the layers.¹⁵⁸ The $|J'/J|$ ratio has a central role in the determination of the 3-D magnetic phase

transition temperature, T_c .¹⁵¹ Higher T_c of the Cr (II) bromides compared to chlorides is ascribed to a greater overlap and polarizability of the bromide ion, which results in a more efficient Cr–Br···Br–Cr exchange and, consequently, a stronger interlayer coupling.¹⁵¹ A small XY-like anisotropy is reported for the chlorides, whereas for bromides the small anisotropic component of the exchange is Ising-like.¹⁶¹ The relaxation properties, as measured by the electron paramagnetic resonance (EPR) spectroscopy linewidths, are very different, with an order of magnitude larger linewidths for the Cu- and Mn-based bromides compared to the chlorides.^{161,162} The temperature and angular dependence of the linewidths are also dissimilar.

7.1.2. Magnetic and Multiferroic Materials. Recently, an unusually high magnetic hardness, which could enable use as a data storage material (although with operating temperatures of 77 – 99 K), has been demonstrated for $(C_2H_5NH_3)_2[FeCl_4]$.¹⁶³ This compound undergoes four structural transitions associated with tilting and rotation of the octahedra and $C_2H_5NH_3^+$ cations. $(C_2H_5NH_3)_2[FeCl_4]$ is a 2-D-paramagnet above 100 K, and a canted antiferromagnet below 100 K, with a canting angle of 0.6° toward the c -axis. The related $(CH_3NH_3)_2[FeCl_4]$ also exhibits canted antiferromagnetism in a field above 200 Oe.^{150,164} However, unlike $(C_2H_5NH_3)_2[FeCl_4]$, which also demonstrates both ferroelectricity and ferroelasticity, $(CH_3NH_3)_2[FeCl_4]$ does not.^{163,165} Generally, longer alkyl chains (e.g., ethylammonium vs methylammonium) allow more degrees of freedom, subsequently resulting in more structural phase transitions. Ferroelectric transitions have also been reported for Cu(II)-based hybrid perovskites featuring longer alkyl chains.^{166,167}

Multiferroic materials combine ferroelectricity with ferromagnetism and reports of multiferroic behavior in the layered 2-D and 3-D perovskites have begun to appear.^{166,168} As an example, ferroelectric and ferromagnetic ordering co-exist in $(C_6H_5CH_2CH_2NH_3)_2CuCl_4$ at temperatures below 13 K.¹⁶⁶ Multiferroic materials provide interesting possibilities for

materials design because they enable direct control of the magnetism with an electric field, due to coupling between order parameters. Such coupling can enable data to be written in a storage media electrically and then read magnetically, which combines beneficial characteristics of ferroelectric random access memory (FeRAM) and magnetic data storage.¹⁶⁹ Other potential applications of multiferroics include electric field controlled magnetic sensors, spin filters or “spintronic” devices for data storage and spatial light modulators for optical switching.^{167,169-171} A grand challenge, however, is how to tailor materials design in such a way that the ferroelectric and ferromagnetic order parameters are strong at room temperature.^{172,173}

The high degree of tunability within the perovskite framework may help to facilitate achieving this goal in a material that can be readily and cheaply processed. In fact, $(\text{C}(\text{NH}_2)_3)\text{Cu}(\text{HCOO})_3$,¹⁷⁴ $(\text{C}(\text{NH}_2)_3)\text{Cr}(\text{HCOO})_3$,¹⁷⁵ and $(\text{CH}_3\text{CH}_2\text{NH}_3)\text{Mn}(\text{HCOO})_3$ ¹⁷⁶ (see **Figure 3**) have recently been theoretically predicted to be multiferroic materials. In $(\text{C}(\text{NH}_2)_3)\text{Cr}(\text{HCOO})_3$,¹⁷⁵ for example, according to theory, the lattice instability is responsible for both ferroelectricity and the appearance of the weak ferromagnetic ordering with $T_c \sim 40$ K. Experimental demonstration of multiferroic behavior in the related $[(\text{CH}_3)_2\text{NH}_2]\text{M}(\text{HCOO})_3$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{and Ni}$) has also been reported.¹⁷⁷ These compounds undergo paraelectric-to-antiferroelectric phase transitions below 160 – 185 K. Hydrogen bonding plays an important role in the associated structural transitions from disordered paraelectric to more ordered antiferroelectric phases, which coexist with canted weak ferromagnetism below 40 K. Study of chemical bonding characteristics of a related ferroelectric material, $(\text{NH}_3\text{NH}_2)\text{Zn}(\text{HCOO})_3$, showed that lone pairs located on oxygen are involved in salt bridge-like interactions with the ammonium group of NH_3NH_2^+ , similar to those in proteins and polymers.¹⁷⁸ Both ionic and hydrogen bonding interactions are present in $(\text{NH}_3\text{NH}_2)\text{Zn}(\text{HCOO})_3$, resulting in strong cation-metal formate interactions and,

consequently, a relatively stiff lattice with elastic moduli of $E_{001} = 26.5$ GPa and $E_{110} = 24.6$ GPa and a bulk modulus of $K = 19$ GPa.

For $(\text{CH}_3\text{NH}_3)\text{Co}(\text{HCOO})_3$, multiferroic behavior is induced by magnetic ordering (type II multiferroic behavior).¹⁷⁹ Due to hydrogen bonding interactions, the metal formate inorganic framework is distorted, providing grounds for anisotropic magnetic and electric behavior and coupling between them. The compound displays canted antiferromagnet behavior below 15.9 K, as confirmed by magnetization measurements.¹⁷⁹ When a pulsed magnetic field is applied along [101], a clear change in the electric polarization is detected. At a critical magnetic field, a spin rearrangement occurs that induces a change in the electric polarization along [101] and [10-1].¹⁷⁹ For another hybrid perovskite with confirmed multiferroic behavior, $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$, ferroelectricity sets in at a higher temperature of 247 K, and the dominant ferromagnetic interactions emerge below 20 K.¹⁶⁷ These examples clearly demonstrate that the hybrid perovskites are a promising class of materials for studying multiferroicity. However, the experimental challenge remains for the preparation of hybrid perovskites with small distances between magnetic ions, which would lead to strong exchange coupling and higher magnetic ordering temperatures, combined with a significant coupling among strain, electric polarization and magnetism.¹⁷⁶

7.1.3. Dielectric Properties. Dielectric properties of organic-inorganic hybrid perovskites can also be promising for technological applications. The inorganic framework in hybrid perovskites may facilitate high dielectric constants and, in the 3-D perovskites such as $\text{CH}_3\text{NH}_3\text{PbI}_3$, high dielectric constant provides an environment where defects are more effectively screened. For $\text{CH}_3\text{NH}_3\text{PbI}_3$, a high frequency dielectric constant value of $\epsilon = 6.5$ has been reported in the optical energy region.^{180,181} A more recent study of the dielectric properties of high-quality $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films over a large frequency range showed that the real part of the static dielectric constant is $\epsilon'_{\text{static}} \sim 70$, much higher than previously

thought.¹⁸² The authors attribute such a high static value to a $1/f$ behavior of the imaginary part of the dielectric constant, ϵ'' , which is known as “Jonscher’s Law”, and to the highly ionic character of the compound. Such a high dielectric constant can yield a very low excitonic binding energy value of 2 meV, in comparison to the binding energy value of 38 meV calculated assuming $\epsilon = 6.5$. This study, therefore, suggests that the $\text{CH}_3\text{NH}_3\text{PbI}_3$ system is mostly non-excitonic at ambient temperatures, and that the advantageous benign defect properties of $\text{CH}_3\text{NH}_3\text{PbI}_3$ -based solar cells are at least in part due to the associated high dielectric constant.¹⁸² For 3-D chloride perovskites such as the strictly inorganic CsPbCl_3 , the dielectric constant increases to values $\epsilon > 10$ (approaching 20), as expected from the trends in electronegativity and ionicity of halides.^{183,184} It should be noted that careful characterization of dielectric constants is necessary to study the trends, as film or crystal quality or even illumination can influence the results of such measurements.¹⁸⁵ Based on the available data, it can be concluded that, in addition to the advantageous semiconductor defect properties useful in PV applications, such high dielectric constant values also point to a potential application of hybrid perovskites in other electronic devices (e.g., gate insulators in field-effect transistors).

7.2. Electrical Transport Properties and Application

7.2.1. Band Structures and Tunable Electrical Properties. While metal halides are predominantly insulating in electrical character, the layered perovskites based on group IV metals Ge, Sn and Pb exhibit conductivity, with decreasing band gaps as the thickness of the perovskite layers is increased.^{11,48,58,186-188} One of the first examples of this behavior was found in the family of $\langle 100 \rangle$ -oriented perovskites $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Sn}_n\text{I}_{3n+1}$, which consists of “n” layers of $\text{CH}_3\text{NH}_3\text{SnI}_3$ perovskite, separated by bilayers of butylammonium cations.⁴⁸ The $n = 1$ compound $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{SnI}_4$ is a semiconductor with a band gap of ~ 1.98 eV,¹⁸⁹ whereas the band gap progressively decreases for higher order structures and the $n = \infty$

compound $\text{CH}_3\text{NH}_3\text{SnI}_3$ has a band gap in the range of 1.2-1.4 eV and can be easily doped to yield semi-metallic behavior.^{19,48,60,190} Demonstrating remarkable tunability of its electrical properties, $\text{CH}_3\text{NH}_3\text{SnI}_3$ normally exhibits a heavily-doped p-type semiconducting behavior^{19,48} presumably due to self-doping via the oxidation of Sn^{2+} to Sn^{4+} ;¹⁹⁰ however, targeted chemical manipulations may result in decreased doping levels, and ultimately, n-type semiconductors.⁶⁰ In the parent $\text{CH}_3\text{NH}_3\text{SnI}_3$, the top of the valence band is composed of Sn 5s and I 5p states, whereas the main contribution to the conduction band comes from Sn 5p states.¹⁹⁰⁻¹⁹² The mixing of the Sn lone pair 5s orbital with the I 5p orbital via an antibonding *s-p* coupling in the valence band maximum (VBM) results in several advantageous optoelectronic properties.⁷ First, since the divalent B-metal *s* orbitals are occupied, there is a direct gap *p-p* optical transition, which is the main reason for the strong optical absorption properties of these compounds.⁷ Furthermore, the band dispersion in the valence band is strongly enhanced due to the presence of the B-metal *s* states and the antibonding *s-p* coupling in the VBM, resulting in relatively small effective masses for holes in this system.⁷ It is clear that the organic cation, CH_3NH_3^+ , has no direct contribution to the states around the Fermi level, as expected from simple chemical trends. In these pseudo-ternary systems, the organic cations (or alternative inorganic cations such as Cs^+) mainly act as electron donors since their electronegativities are much lower compared to B-metals such as Sn/Pb and halogens. Therefore, the states around the Fermi level are dominated by the inorganic framework, which also applies to the band structures of lower dimensional perovskites (at least for those containing organic cations with large HOMO-LUMO separation).

Although they do not contribute to the states around the Fermi level, organic cations convey indirect influence (see Section 3 for specific examples) on the electronic structure of the $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Sn}_n\text{I}_{3n+1}$ ($n = 1, 2, 3$, etc) and related materials through crystal structure effects (e.g., dimensional reduction, induced tilting and deformations of the

inorganic framework, cation size changes, and hydrogen bonding).^{54,58,192} As mentioned above, in $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Sn}_n\text{I}_{3n+1}$ and related layered perovskite series, the band gap values increase when going from the 3-D parent compound $\text{CH}_3\text{NH}_3\text{SnI}_3$ to the low-dimensional 2-D layered derivatives, in part because of reduction in the valence/conduction band width.^{58,188,193,194} The observed bandwidth narrowing can be attributed to the lack of band dispersion in the direction perpendicular to the inorganic layer (i.e., decrease in dimensionality), as well as to structural distortions (e.g., induced by organic cations or the Jahn-Teller effect).¹⁹³ For example, the band dispersions in the directions perpendicular to the inorganic layers are close to zero in $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$. Additionally, a comparison of band structures of ideal (i.e., undistorted) and actual (i.e., distorted) $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ clearly indicates that the valence and conduction bands of the actual $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ are narrower and shifted to lower energies.¹⁹³ A significant valence bandwidth narrowing by up to 1.95 eV has also been calculated for the A_2SnI_4 family, where replacement of organic cations results in severe in-plane distortions of the SnI_4^{2-} inorganic sheets.^{54,58} This is an important finding, as the bandwidth narrowing also generally results in larger charge carrier effective masses and exciton binding energies in the 2-D crystals.^{118,193,194} From the application standpoint, the exciting aspect of the band gap progression in the series $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Sn}_n\text{I}_{3n+1}$ (or related layered Ge, Sn and Pb perovskites) is the achievement of a highly tunable semiconductor that can be simply (e.g., solution) processed for electronic and energy applications.^{11,58,195}

7.2.2. Application of Sn-based Conducting Hybrids. The first example of application of the tunable semiconducting character was use of spin-coated $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{SnI}_4$ films (based on the phenethylammonium cation) as channel layers in thin-film transistors (TFTs).¹⁹⁶ The layered hybrid perovskite forms a *p*-channel transistor, giving relatively high field-effect mobilities of 0.55-0.62 $\text{cm}^2/\text{V}\cdot\text{s}$ and current modulations

greater than 10^4 . Further improvements to the performance of the hybrid tin (II) based perovskite transistors have been made through melt processing of the films, yielding mobilities of as high as $2.6 \text{ cm}^2/\text{V}\cdot\text{s}$ in the saturation regime and $1.7 \text{ cm}^2/\text{V}\cdot\text{s}$ in the linear regime.¹⁹⁷ More recently, there have also been examples of hybrid TFTs prepared using vacuum-based deposition of the perovskites.^{198,199} In one example, $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{SnI}_4$ films were grown on boron-doped silicon (gate) / silicon dioxide (gate insulator) substrates kept at 60°C through dual-source vapor deposition of SnI_2 and $\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3\text{I}$.¹⁹⁸ These films were used as p-channel semiconductors in field-effect transistors (FET), which showed a hole mobility of $0.78 \text{ cm}^2/\text{V}\cdot\text{s}$ in the saturation regime, a threshold voltage of -1.7 V , and a drain current on/off ratio of 4.2×10^5 .¹⁹⁸ In the second example, using a similar deposition technique—i.e. dual-source evaporation of SnI_2 and $\text{CH}_3\text{NH}_3\text{I}$ on substrates at 50°C —a 50-nm-thick $\text{CH}_3\text{NH}_3\text{SnI}_3$ film was deposited.¹⁹⁹ The resultant film exhibited a low electrical resistivity of $8.7 \times 10^{-5} \Omega \text{ cm}$. The $\text{CH}_3\text{NH}_3\text{SnI}_3$ film was used as the source-drain electrodes on top of a vacuum-deposited pentacene layer, which acted as the semiconductor channel. The reported parameters for this FET are a saturation-regime hole mobility value of $0.004 \text{ cm}^2/\text{V}\cdot\text{s}$, current modulation value of 1.2×10^3 , and threshold voltage of -7.2 V .¹⁹⁹ Note that, in each of these examples, devices were made and measured under rigorously inert atmosphere conditions. One issue with the Sn(II)-based hybrid materials is the severe sensitivity to air/moisture and therefore the need to keep them encapsulated or isolated from the environment.

7.2.3. Pb- and Ge-based Semiconductors. While most of the examples covered in this section so far are focused on Sn-based compositions, hybrid perovskites featuring Pb^{2+} and Ge^{2+} also exhibit semiconducting behavior, including the now famous $\text{CH}_3\text{NH}_3\text{PbI}_3$. The band structures of such compounds are similar to those of the Sn-based analogs (see above) owing to the fact that all of these cations are isoelectronic. The normal chemical trends apply

in this family; however, since the differences in electronegativities between these elements is small,²⁰⁰ the influence of the electronegativities is secondary to structural factors. For example, the measured band gap values for $\text{CH}_3\text{NH}_3\text{SnI}_3$ are in the range of 1.2-1.4 eV, whereas the band gap values of $\text{CH}_3\text{NH}_3\text{PbI}_3$ are reported as 1.5-1.6 eV.^{60,201} This trend is expected given the fact that Sn (1.96) has a higher Pauling electronegativity compared to Pb (1.87),²⁰² and as such, the Sn states should be located lower in the band structure, leading to a smaller separation between the I 5*p* states in the valence band and the Sn 5*p* states in the conduction band. In other words, Pb is more metallic compared to Sn and therefore, based on chemical trends, Pb-I bonds should be more ionic compared to Sn-I bonds, leading to the larger band gap of $\text{CH}_3\text{NH}_3\text{PbI}_3$. These simple ideas are also confirmed by the results of ultraviolet photoelectron spectroscopy (UPS) measurements, which put the conduction band edges of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{SnI}_3$ at -3.90 eV and -4.17 eV, respectively—i.e. Sn states are located lower in the band structure of $\text{CH}_3\text{NH}_3\text{SnI}_3$.²⁰³ This comparison is purely based on the electronegativity difference between Sn and Pb, and ignores the influence of the detailed crystal structures and distortions (as discussed in section 3.1).

The dominant influence of detailed structural effects for the 3-D perovskites is exemplified by the case of $\text{CH}_3\text{NH}_3\text{GeI}_3$, featuring the smaller Ge^{2+} cation compared to Sn^{2+} and Pb^{2+} . Following the observed trends in electronegativities for Pb (1.87), Sn (1.96) and Ge (2.01),²⁰² one would expect a lower band gap for the $\text{CH}_3\text{NH}_3\text{GeI}_3$ member. However, the reported band gap for $\text{CH}_3\text{NH}_3\text{GeI}_3$ is 1.9 eV, much larger compared to that of Sn- and Pb-analogs.²⁰⁴ The larger band gap of the Ge-analog can be tied to its substantially different quasi-3-D hexagonal structure,²³ which contains GeI_6 octahedra comprised of three short and three long Ge-I bonds (see below for further discussion, **Figure 34**) due to a second-order Jahn-Teller (SOJT) effect.^{35,204} Although the compositions of the frontier states around the Fermi level are analogous to the Sn and Pb cases (i.e., the valence band being composed of

Ge 4s and I 5p states, and the conduction band arising from predominantly Ge 4p states), the stereochemical activity of the Ge 4s² electrons and the significant *sp*-hybridization of the Ge and I orbitals originating from the SOJT effect yield the large band gap of 1.9 eV for CH₃NH₃GeI₃.²⁰⁴

7.2.4. Sb- and Bi-based Semiconductors. Hybrid perovskites based on trivalent Sb and Bi are also expected to exhibit semiconducting behavior and very similar band structures to those of divalent Sn- and Pb-based compounds. This is because Sb³⁺ and Bi³⁺ ions are isoelectronic to Sn²⁺ and Pb²⁺, and electronegativities and ionic radii of these elements are close in value.^{23,202} Among the few known hybrid perovskites featuring trivalent Sb and Bi cations are the semiconducting *q* = 2 members of the ⟨111⟩-oriented A₃B₂X₉ perovskites. The layered modification of purely inorganic Cs₃Sb₂I₉, for example, has a band gap of 2.05 eV, and dispersive bands around the Fermi level, mainly composed of Sb 5s and I 5p states in the valence band and Sb 5p states in the conduction band, resulting in relatively low effective masses of charge carriers ($m_{h,e}^* = 0.34 - 0.91 m_0$).⁹⁹ The bromide analogs Cs₃Sb₂Br₉, Cs₃Bi₂Br₉, and Rb₃Sb₂Br₉ have larger band gaps of 2.30 eV, 2.50 eV, and 2.48 eV, respectively.⁹¹ Another example of a Bi-based perovskite is the compound (AEQT)Bi_{3/2}I₄, where AEQT = 5,5'''-bis(aminoethyl)-2,2':5',2'':5'',2'''-quaterthiophene. In this example, metal deficient layers of bismuth iodide octahedra alternate with layers of AEQT molecules, with the possibility of tuning the energy levels of both organic cations and inorganic framework, as mentioned in section 4.⁷⁶ Although there are clear advantages in replacing the toxic Pb²⁺ and unstable Sn²⁺ with the isoelectronic Sb³⁺ and Bi³⁺ in hybrid perovskite semiconductors, systematic work targeting synthesis and characterization of the semiconducting Sb- and Bi-containing perovskites is currently just beginning to be a center of focus.

7.2.5. Cu-based Semiconductors. Replacement of Sn^{2+} and Pb^{2+} with first row transition metal cations such as Cu^{2+} has much more dramatic consequences to the band structures, since the $3d^9 4s^0$ electronic configuration of Cu^{2+} is very different than for the main group metal cations with lone pair electrons. Several groups have considered copper halide perovskites as alternative semiconductor absorbers to $\text{CH}_3\text{NH}_3\text{PbI}_3$ for use in solar cell devices.²⁰⁵ For example, $(p\text{-F-C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{CuBr}_4$ and $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2\text{CuBr}_4$ are reported to have optical band gaps of 1.74 eV and 1.76 eV, respectively, from the absorption data.²⁰⁵ The devices fabricated using FTO/ TiO_2 /Cu-halide perovskites/spiro-MeOTAD/Ag structures showed open-circuit voltages (V_{oc}) 0.87-0.88 V, short-circuit photocurrent densities (J_{sc}) of 1.46-1.78 mA cm^{-2} , and a fill factor (FF) of ~ 0.40 , giving PCE (power conversion efficiency) values of 0.51-0.63 %.²⁰⁵ The authors attributed poor performances of the devices to the low conductivities of the layered copper halides, which in turn derives from the modification of the band structure induced by the replacement of Pb^{2+} with Cu^{2+} . As discussed in section 7.1, Cu (II) halide perovskites are magnetic, which clearly indicates that Cu $3d$ orbitals have important contributions to the states around the Fermi level.^{149,206} The presence of the localized Cu $3d$ orbitals in the vicinity of the Fermi level is expected to result in higher effective masses of charge carriers, and hence, lower mobilities. In addition, $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{CuBr}_4$ and $(\text{CH}_3(\text{CH}_2)_3\text{NH}_3)_2\text{CuBr}_4$ are layered compounds, and therefore bandwidth narrowing due to the confinement of the inorganic framework also applies,^{188,193} making the bands more flat and further reducing the mobilities, all of which could contribute to the very low J_{sc} values observed for devices based on layered copper halide perovskites. These ideas are indirectly confirmed by the recent work on $(\text{CH}_3\text{NH}_3)_2\text{CuCl}_x\text{Br}_{4-x}$ perovskites,²⁰⁷ which feature band gaps in the 1.8-2.48 eV range and exhibit very high effective masses. In these materials, the DFT calculated effective mass along the Γ -Z

direction, for example, is infinity for holes as a result of the flat bands in the electronic structure.²⁰⁷

7.3. Optical Properties and Optoelectronic Applications

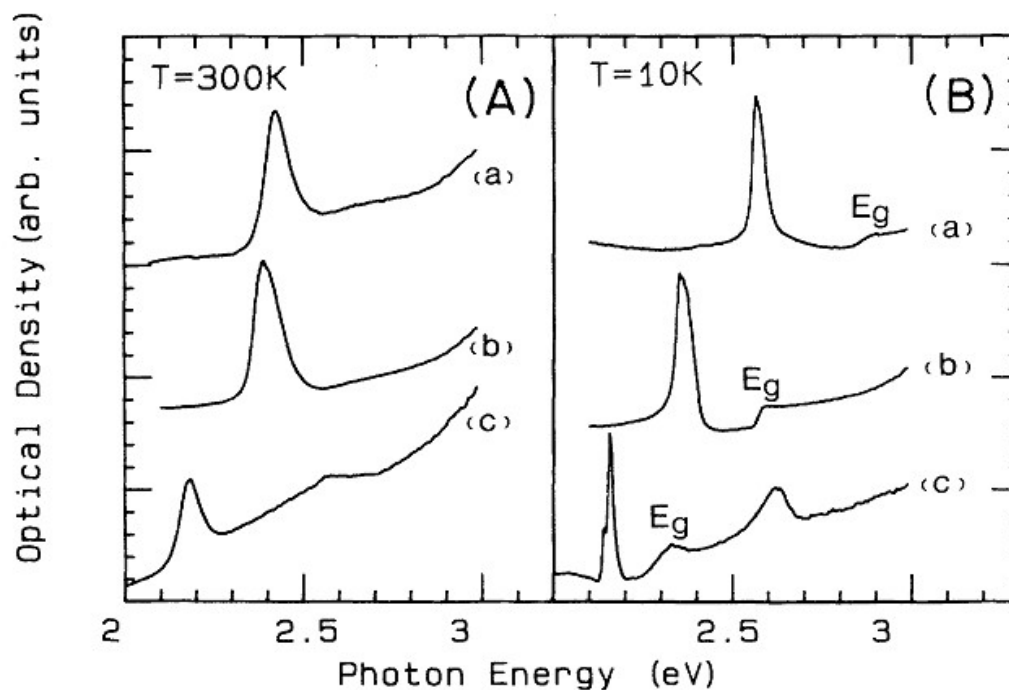


Figure 31. Absorption spectra for (a) $(C_{10}H_{21}NH_3)PbI_4$, (b) $(C_6H_5C_2H_4NH_3)PbI_4$, and (c) $(C_6H_5C_2H_4NH_3)_2(CH_3NH_3)Pb_2I_7$ taken at (A) 300 K and (B) 10 K. A tunable exciton peak is observed both at low temperature as well as at room temperature.²⁰⁸ Reprinted with permission from ref 208. Copyright 1992 American Physical Society.

7.3.1. Quantum and Dielectric Confinement Effects and Excitonic Properties.

Interest in optical properties and potential application of metal-halide-based perovskites can be traced to as early as the publication of a 1958 *Nature* article, in which the tunable photoconductive properties of $CsPbX_3$ were noted, with a peak photoconductive response that could be tailored by changing the halogen, from violet for $CsPbCl_3$ to red for $CsPbI_3$.²⁰⁹

Interestingly, a second, rather unique feature of the layered hybrid perovskites based on germanium (II), tin (II) and lead (II) halide sheets (in addition to the tunable semiconducting electrical properties discussed in the last section), is the sharp and intense exciton resonances in the optical absorption spectra (**Figure 31**).²⁰⁸ The strength of the exciton features at room temperature arises because of the quantum (i.e., dimensional reduction) and dielectric confinement effects. To evaluate individual contribution of each of these effects, for a model system with no dielectric mismatch between organic and inorganic layers, the binding energy would be expected to increase from 29 meV to 116 meV (4 times enhancement) in going from 3-D to 2-D excitons in a lead(II) iodide structure.²¹⁰ Dielectric mismatch leads to a dielectric confinement effect, also known as the “image charge effect.”^{211,212} In simple terms, due to a much lower dielectric constant in the organic cation layer, the effective Coulomb interaction between the electrons and holes in the inorganic well layer increases, which leads to a larger exciton binding energy.²¹³ The relative contribution of the dielectric confinement effect depends on several factors, including the dielectric constants of the inorganic well and organic barrier layers, and the thicknesses of these layers. For $[\text{C}_5\text{H}_{11}\text{NH}_3]\text{Pb}_2\text{I}_5$, which is a perovskite-related bilayer compound featuring edge- and corner-sharing PbI_6 octahedra, it was estimated that 146.4 meV of the exciton binding energy originates from the dielectric confinement effect, and this constitutes ~ 64 % of the total exciton binding energy of 230 meV for this compound.²¹⁰ This report is in agreement with the earlier findings that the enhancement of the exciton binding energies in lead iodide-based perovskite hybrids predominantly arise due to the dielectric confinement effects.²⁰⁸

As seen from the example above, the exciton binding energy can be as large as several hundred meV, much larger than k_bT at room temperature (~26 meV). The highest reported exciton binding energies for bulk hybrid perovskites are generally in the 300-400 meV range,^{210,213-215} including, for example, 320 meV for $(\text{C}_{10}\text{H}_{21}\text{NH}_3)_2\text{PbI}_4$.²⁰⁸ Note that the

organic cation contains a long alkyl chain for this system, which reinforces the idea that better isolation of the inorganic well layer enhances the exciton binding energy. The separation can be further improved through mechanical exfoliation of the bulk crystals into ultrathin crystalline layers. In nanosheets of $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ crystals prepared this way, the exciton binding energy of 490 meV has been measured.²¹⁶ For comparison, measurements on the bulk $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbI}_4$ crystals give an exciton binding energy value of 360 meV.²¹⁴ To the best of our knowledge, the largest exciton binding energy reported for the organic-inorganic hybrid perovskites so far is 540 meV for bulk $(4\text{-FC}_6\text{H}_4\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$,²¹⁷ a value that represents a more than 2-fold increase in the exciton binding energy by simple substitution of a fluorine into the phenyl ring (i.e., the exciton binding energy for $(\text{C}_6\text{H}_4\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$ is reported as 220 meV).²¹⁸ If confirmed, this dramatic binding energy increase would be another indication of the wide tunability of excitonic features in the layered perovskites.

Excitons, which correspond to a bound state of one electron and one hole, are conventionally classified into the small-radius (comparable to the unit cell dimension) Frenkel excitons, large-radius (larger than the unit cell size) Wannier (or Wannier-Mott) excitons and charge-transfer excitons typical for interfaces.²¹⁹ Wannier excitons are typical of inorganic semiconductors and possess radii on the order of 30-100 Å and binding energies of ~10-30 meV, whereas Frenkel excitons are typical of organic materials and exhibit radii of ~5 Å and binding energies of ~0.5-1 eV.^{219,220} Excitons in the 3-D parent hybrid perovskites are Wannier excitons—e.g., exciton binding energies of up to 50 meV and exciton Bohr radii of 22-38 Å are generally reported for $\text{CH}_3\text{NH}_3\text{PbI}_3$.^{180,181,188,221} However, a clear assignment of excitons to either Wannier- or Frenkel-types in the layered hybrid perovskites has been difficult due to the above-discussed quantum and dielectric confinement effects. Depending on the organic cations (e.g., length of alkyl chain, presence of functional groups) and inorganic layers (e.g., thicknesses, elemental composition), a large variation in the observed

exciton binding energies (60-540 meV) and radii (22.9-6.2 Å) have been reported.¹⁸⁸ (C₁₀H₂₁NH₃)₂PbI₄, for example, has an exciton binding energy of 320 meV and exciton Bohr radius of less than 7 Å.²²¹ The exact nature of excitons in 2-D hybrid perovskites, therefore, has been under debate, with various research groups proposing that the excitons are of Wannier type but with a small radius²²² and others, conversely, pointing to the fact that the observed magneto-optical properties, such as the anisotropic Zeeman splittings, are better explained using the Frenkel-exciton model.²²³

Recent work in this area suggests that, for appropriately tailored organic cations and inorganic frameworks (as discussed in Section 4) and as confirmed by electroabsorption and two-photon-absorption spectroscopy, two-dimensional (2-D) Wannier excitons may be formed in the inorganic layers,^{213,224,225} along with Frenkel excitons in the organic substructure.^{109,219} In fact, these different types of excitons can couple, forming “Frenkel-Wannier hybrid excitons” that have features derived from both the large radius and nonlinearity of the Wannier excitons and the large oscillator strength of the Frenkel excitons.^{109,219} Hybrid excitons are expected to exhibit unusual properties, including a strong enhancement of the optical resonance nonlinearity. The optical nonlinearity is limited in materials featuring either Wannier or Frenkel excitons; however, materials with hybrid excitons can demonstrate an increased (by 2 orders of magnitude) nonlinearity.²¹⁹ An efficient energy transfer between the organic and inorganic substructures is necessary for the formation of hybrid excitons. As previously referred to in Section 4, practical demonstration of nearly perfect (> 99%) triplet-triplet Dexter-type energy transfer from Wannier excitons in PbBr₄²⁻ layers to naphthalene has already been shown for (1-Naphthyl-C_nH_{2n}NH₃)₂PbBr₄.¹⁰⁹ Other examples of resonant coupling between Frenkel and Wannier excitons include studies involving (C₆H₅CH₂NH₃)₂PbCl_xBr_{4-x}^{111,226} and (C₁₀H₇CH₂NH₃)₂PbBr_xI_{4-x}.²²⁷

If the interaction between excitons is attractive, biexcitons can form²¹⁹ and, in the case of layered hybrid perovskites, the binding energy can be unusually high. In typical semiconductors, binding energies of biexcitons are small (<10 meV); however, binding energies of as large as 65 meV have been reported for $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$.^{228,229} For the hybrid bilayer compound $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)\text{Pb}_2\text{Br}_7$, since the confinement effect is weaker, the biexciton binding energy is twice smaller, 26 meV (still on the order of k_bT at room temperature).²³⁰ Such enhanced binding energies in hybrid perovskite systems are useful for studying the excitonic properties of semiconductors, in particular biexciton formation and relaxation, which are important in nonlinear optical processes. In addition to the fundamental interest, biexciton lasing has been demonstrated at temperatures of up to 40 K from a spin-coated 200-nm-thick $(\text{C}_6\text{H}_{13}\text{NH}_3)_2\text{PbI}_4$ film formed on a Ti-containing glass substrate.²³¹ A lasing threshold of 20 kW/cm² at 16 K and a maximum pump intensity of 600 kW/cm² are reported for this device.²³¹

In addition to Wannier, Frenkel and hybrid excitons, as well as biexcitons, bosonic quasiparticles known as polaritons can form through a strong exciton-photon coupling.²¹⁹ In fact, under the strong coupling regime, polaritons determine the optical properties of solids.²¹⁹ From a practical standpoint, the interest in this area is fueled by the promise of new nonlinear photonic devices and phenomena, including optical transistors, switching devices, polariton condensation,^{232,233} and a new kind of coherent light source, the polariton laser, which could have lower thresholds than conventional lasers.^{234,235} By spin-coating $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$ on a corrugated quartz substrate with a period of ~ 0.7 μm , Fujita et al. fabricated a distributed feedback microcavity that shows well-separated tunable polariton absorption in transmission measurements at room temperature.²¹⁸ Due to the large oscillator strength of excitons in $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$, a polariton mode splitting (*i.e.*, Rabi splitting) of as high as 100 meV at room temperature has been recorded.²¹⁸ A Fabry-Pérot microcavity containing

$(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$ between dielectric and metallic mirrors has also been fabricated, and shows anticrossing of 140-190 meV between the cavity and excitonic modes.^{236,237} In comparison, III-V and II-VI semiconductor quantum wells in Fabry-Pérot microcavities show polariton splitting energies of only 9-18 meV,²¹⁸ though a recent work using a hexagonal GaN/InGaN core-shell wire reports Rabi splitting energies of as large as ~ 180 meV.²³²

The maximum polariton splitting is limited by the oscillator strength of excitons in the material and not by the microcavity effect,²¹⁸ and therefore, further improvements are possible through careful tailoring of the hybrid perovskite excitonic properties. The spectral position of the excitonic transition can be tuned, for example, through substitution on the halide ion site, with UV polaritonic emission (~ 3.5 eV) being observed from a $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbCl}_4$ -based one-dimensional Fabry-Pérot microcavity.²³⁸ The Rabi splitting value of 230 meV for this system is also among the highest reported. As an added layer of complexity, hybrid polaritons can be created in a microcavity containing two different semiconductors that are both coupled to the same photon mode.²²⁰ In one example, $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4$ was used as the inorganic semiconductor with Wannier excitons and zinc tetraphenyl-porphrin (ZnTPP) was employed as the organic dye with Frenkel excitons.^{219,220} Reflectivity measurements were used to demonstrate the formation of hybrid exciton polaritons comprised of the cavity photon and the excitons in the organic and inorganic parts. The authors suggest that the hybrid polaritons can undergo radiative emission, and that these polaritons can act as an intermediate state between excitons in the organic and inorganic components.²²⁰

7.3.2. Optoelectronic Applications for $\text{CH}_3\text{NH}_3\text{PbX}_3$. In recent years, following the discovery of the PV properties of $\text{APb}_{1-x}\text{Sn}_x\text{I}_3$, interest in hybrid perovskites as photodetectors,^{239,240} LED emitters,^{241,242} lasers²⁴³ and thin-film transistors²⁴⁴ has been rekindled.¹¹ Many of these devices employ $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($X = \text{Cl}, \text{Br}$ and I) as the active materials and, given the focus of this review being targeted beyond $\text{CH}_3\text{NH}_3\text{PbX}_3$, we will

only cover a few examples to demonstrate the potential of the hybrid 3-D perovskites in this regards. In one example, photodetectors based on hybrid lead halide perovskites, with the ability to detect weak signals (approaching 10^{14} Jones), a linear dynamic range of over 100 decibels (dB) and a fast photoresponse with 3-dB bandwidth of up to 3 MHz were recently fabricated, employing a ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ /PCBM/Hole blocking layer (BCP and PFN)/Al structure.²³⁹ The authors note that the performance of this perovskite-based photodetector is significantly better than for most of the organic, quantum dot and hybrid detectors, and is comparable to inorganic semiconductor-based devices.

One important advantage of organic-inorganic hybrid perovskites for use as low-cost light-emitting diode (LED) emitters is their very high color purity, with full width at half maximum of ~ 20 nm for the electroluminescence spectral peaks.^{242,245} Unlike conventional inorganic nanomaterials, due to their intrinsic quantum-well structure, the high color purity is preserved irrespective of the crystal size.^{241,242} Therefore, hybrid perovskites can overcome some of the disadvantages of organic LEDs (OLEDs) and inorganic quantum dot LEDs, including issues with complex synthesis, high cost, poor color purity (OLEDs) and high ionization energy (quantum dot LEDs).²⁴⁵ To show the potential of perovskite-based LEDs, a thin (15-20 nm) layer of $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) was used to demonstrate electroluminescence in the near-infrared, green and red by tuning the halide composition.²⁴¹ For the infrared LED, the perovskite emitter was sandwiched between two larger band gap semiconductors, TiO_2 and poly(9,9'-dioctylfluorene) (F8) layers, in order to confine electrons and holes in the lower gap $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite layer for effective radiative recombination in the ITO/ TiO_2 / $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ /F8/ MoO_3 /Ag structure. The infrared radiance for such devices was found to be $13.2 \text{ W}/(\text{sr}\cdot\text{m}^2)$ at a current density of $363 \text{ mA}/\text{cm}^2$, with highest external (EQE) and internal quantum efficiencies (IQE) of 0.76% and 3.4%, respectively. The green LED with an ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbBr}_3$ /F8/Ca/Ag structure

gave a luminance of 364 cd/m² at a current density of 123 mA/cm², yielding EQE and IQE of 0.1% and 0.4%, respectively. In this device, PEDOT:PSS and Ca were employed as Ohmic hole and electron injectors, respectively, and the F8 polymer was used as a spacer layer for electron transport and to prevent emission quenching near the Ca interface.

Recently, a major improvement has been achieved through the demonstration of a green CH₃NH₃PbBr₃ perovskite LED with EQE of 8.53%.²⁴⁵ Minimizing the presence of metallic Pb impurity, which was achieved by using a slight 2-7% CH₃NH₃Br excess, was proposed as being central to improving the efficiency of the device. A second key factor was the fine control over grain size (with the average grain diameter of 99.7 nm), uniformity and coverage of the CH₃NH₃PbBr₃ films. The authors note that, for LED applications, smaller grains are preferred because smaller grains limit the exciton diffusion length, which in turn reduces the possibility of exciton dissociation before recombination.²⁴⁵ These manipulations result in the achievement of a current efficiency (CE) of 42.9 cd A⁻¹, which is comparable to that of phosphorescent OLEDs.²⁴⁵

The beneficial impact of the reduced crystal size of CH₃NH₃PbX₃ (X = Cl, Br, I) on the luminescence efficiency has also been shown in a separate work.²⁴⁶ In this work, the control over crystal size and shape has been achieved through mixing octylammonium (OA) cations into the reaction medium. Naturally, the presence of lower-dimensional hybrid perovskites is suspected in this scenario; however, a clear identification of lower-dimensional perovskites has not been carried out. The authors of this work note that photoluminescence quantum efficiency (PLQE) values increase with the increase of OA:MA (MA = methylammonium) ratio up to 0.6:0.4; however, higher OA content leads to the formation of platelets, which have lower PLQE.²⁴⁶ The reported average PLQE values are 20, 30, 36 and 18% for 1.0 MA:0.0 OA, 0.7 MA:0.3 OA, 0.4 MA:0.6 OA, and 0.1 MA:0.9 OA, respectively.

Excellent coherent light emission and the balanced ambipolar charge transport properties of $\text{CH}_3\text{NH}_3\text{PbX}_3$ may allow their use in electrically driven lasing.²⁴³ Measurements on a 65-nm thick $\text{CH}_3\text{NH}_3\text{PbI}_3$ film spin-coated on a quartz substrate show that there is a broad spontaneous emission (SE) with a full width at half maximum (FWHM) of ~ 50 nm, which narrows to a sharp peak with FWHM of < 10 nm with increasing pump fluence, and transitions to an amplified spontaneous emission (ASE). Concurrently, the average transient photoluminescence lifetimes also decrease and, above the threshold fluence of $12 \mu\text{J cm}^{-2}$, a superlinear increase in the emission intensity is observed with photoluminescence lifetime experiencing a sudden shortening. The stable ASE observed for this material is attributed to the large absorption coefficient, low bulk defect densities and slow Auger recombination.²⁴³ By manipulating the halide content, the authors were able to demonstrate visible spectral tunability between 390 and 790 nm. Following these findings, the authors note that organic-inorganic hybrid perovskites are a promising class of low-temperature solution-processable materials that show optical gain.²⁴³

ASE and lasing behavior from $\text{CH}_3\text{NH}_3\text{PbX}_3$ films have been reported from both cavity and non-cavity modes by several groups.^{243,247,248} The great potential of hybrid perovskites for application in solid-state electrical-pump lasers is further underlined by the reports of lasing from planar and spherical optical cavities.^{247,248} In addition, a recent report²⁴⁹ suggests that hybrid perovskites can also be used in semiconductor nanowire lasers, which are attractive due to their potential applications in nanoscale optoelectronic devices.

Semiconductor nanowire lasers notoriously suffer from the high threshold carrier density required for lasing. Interestingly,²⁴⁹ single crystal nanowire lasers based on $\text{CH}_3\text{NH}_3\text{PbX}_3$ perovskites demonstrate low lasing thresholds (220 nJ cm^{-2}) and high quality factors ($Q \sim 3,600$).²⁴⁹ This very low lasing threshold corresponds to carrier densities of as low as $1.5 \times 10^{16} \text{ cm}^{-3}$. Other remarkable findings include very low charge carrier trapping in the $\text{CH}_3\text{NH}_3\text{PbX}_3$

nanowires, and estimated lasing quantum yields approaching 100 %. The wavelength tunability provided by mixing of the halide content, the solution processability, and high lasing performance of the $\text{CH}_3\text{NH}_3\text{PbX}_3$ nanowires make these materials excellent candidates for a wide range of optoelectronic applications.²⁴⁹

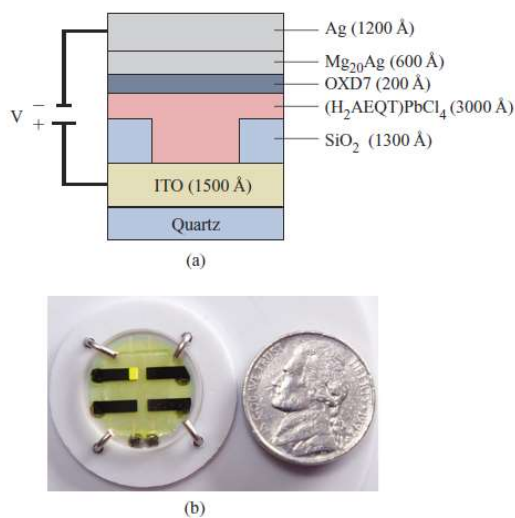


Figure 32. (a) Cross section of an OILED (Organic-Inorganic Light-Emitting Diode) device structure based on $(\text{H}_2\text{AEQT})\text{PbCl}_4$ as the emitter. (b) A picture of the top view of an operational device with the nickel on the right providing a scale for size comparison.¹¹ Adapted with permission from ref 11. Copyright 2001 *IBM Journal of Research and Development*.

7.3.3. Optoelectronic Applications for Layered Perovskites. Interest in light-emission from layered hybrid perovskites predates the current work focused on use of 3-D $\text{APb}_{1-x}\text{Sn}_x\text{I}_3$ perovskites as solar cell absorbers.¹¹ Thus, in the early 1990s, orange electroluminescence (EL) was observed for $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2(\text{CH}_3\text{NH}_3)\text{Pb}_2\text{I}_7$ below 200 K by applying a 10 kV/cm electric field.²⁵⁰ Initial devices²⁵⁰⁻²⁵² suffered from a dramatic reduction in EL efficiency near room temperature due to thermal quenching of excitons. In an attempt to

obtain room-temperature EL from hybrids, functional organic dye molecules were incorporated between the perovskite layers in (H₂AEQT)PbCl₄ (AEQT = 5,5''-bis(aminoethyl)-2,2':5',2'':5'',2'''-quaterthiophene).²⁵³ EL devices based on 300 nm-thick (H₂AEQT)PbCl₄ light-emitting layers produce bright green-yellow light ($\lambda_{\text{max}} \approx 530$ nm) under ambient conditions (**Figure 32**). For these devices, low turn on voltages of ~ 5.5 V were observed, and the I-V and EL-V curves were found to be similar, suggesting a balanced electron and hole injection.²⁵³ The observed electroluminescence spectrum is in agreement with the photoluminescence spectra of both (H₂AEQT)PbCl₄ and the dye salt AEQT·2HCl. This spectral agreement indicates that the electroluminescence originates from the quaterthiophene moiety. The maximum efficiency of 0.1 lm/W at 8 V and 0.24 mA (power conversion efficiency of 0.11%) was recorded.

More recently, lower-dimensional hybrid lead halides have been attracting renewed interest for solid-state lighting applications. Broadband white light emission has been observed for (N-MEDA)[PbBr₄] (where N-MEDA = N¹-methylethane-1,2-diammonium) under ultra-violet excitation (**Figure 33**).⁸⁷ (N-MEDA)[PbBr₄] belongs to the family of <110>-oriented layered perovskites, featuring a corrugated perovskite sheet in its structure and a band gap of 3.8 eV. (N-MEDA)[PbBr₄] shows a broad emission that spans the entire visible spectrum upon 380 nm excitation, resulting in a “warm” white light with chromaticity coordinates (CIE) of (0.36, 0.41) and a correlated color temperature (CCT) of 4669 K. The chromaticity of the emission can be tuned through halide substitution in (N-MEDA)[PbBr_{4-x}Cl_x] ($x = 0-1.2$). As expected, the emission spectra of the halogen-substituted perovskites demonstrate a systematic blue shift with increasing chloride content. The $x = 0.5$ member possesses CIE coordinates of (0.31, 0.36) and a CCT of 6502 K, giving a “cold” white light. It is reported that the chloride substitution improves color rendering index (CRI), which is a measure of how accurately colors are reproduced in comparison to a blackbody light source.

CRI values of 82 and 85 are reported for (N-MEDA)[PbBr₄] and (N-MEDA)[PbBr_{3.5}Cl_{0.5}], respectively. These values are remarkable for single phase materials, as they are higher than the values for basic fluorescent light sources (CRI ~ 65), and are close to the values for mixed-phosphor light sources (CRI > 90). Finally, the photoluminescence quantum efficiency (PLQE) of (N-MEDA)[PbBr₄] was measured to be ~ 0.5%. For mixed halide members, the PLQE is improved up to 1.5% for (N-MEDA)[PbBr_{2.8}Cl_{1.2}]. The PLQE values compare well with the reported values of 2-3% for white-light emitting CdSe nanocrystals in suspensions.⁸⁷

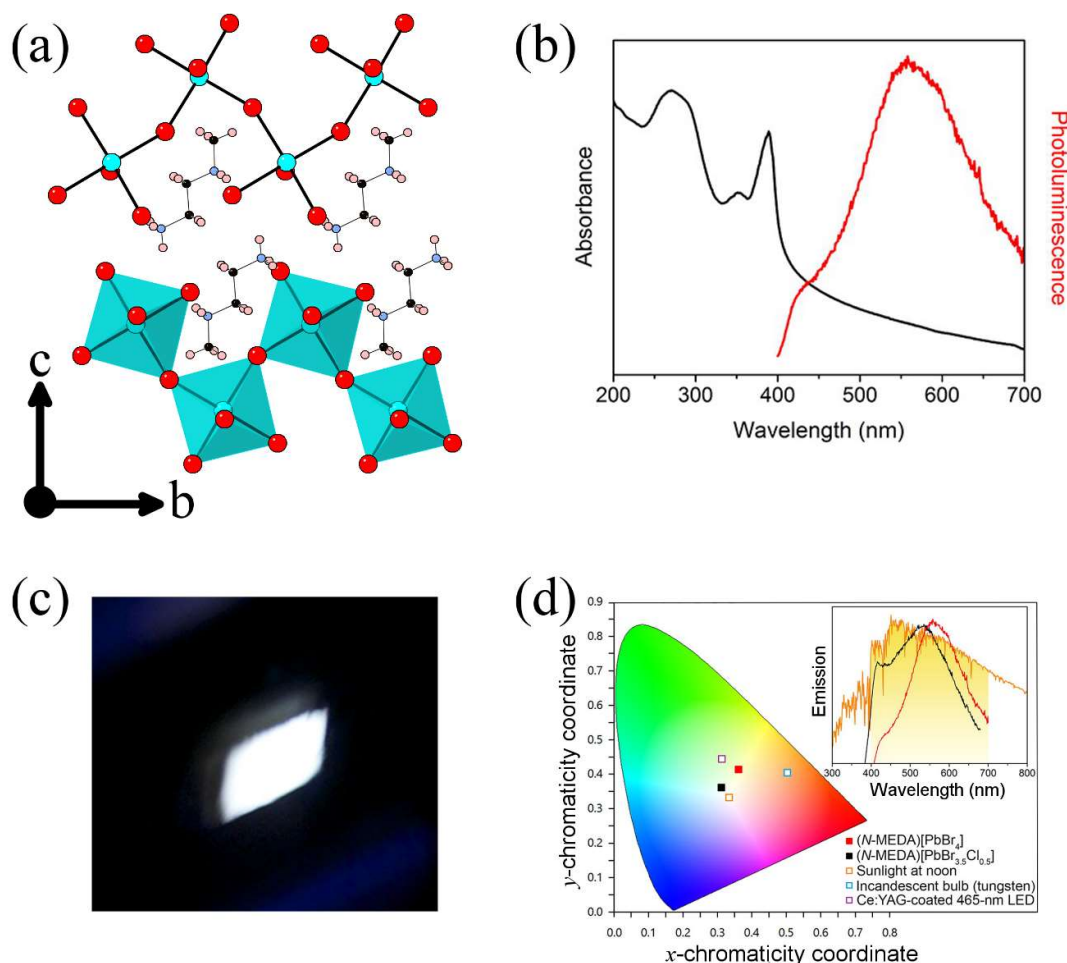


Figure 33. (a) Combined skeletal (top) and polyhedral (bottom, shaded) view of the $\langle 110 \rangle$ -oriented layered structure of (N-MEDA)[PbBr₄] (where N-MEDA = N¹-methylethane-1,2-diammonium). (b) Absorption (black) and emission (red, excitation at $\lambda_{\text{ex}} = 380$ nm)

spectra for (N-MEDA)[PbBr₄]. (c) Luminescence from a powder sample of (N-MEDA)[PbBr₄] under 380 nm irradiation. (d) Chromaticity coordinates (CIE) of white-light emitting (N-MEDA)[PbBr_{4-x}Cl_x] ($x = 0-1.2$) samples. Inset shows overlay of solar spectrum (orange) with the visible region shaded in yellow and emission spectra of (N-MEDA)[PbBr₄] (red, $\lambda_{\text{ex}} = 380$ nm) and (N-MEDA)[PbBr_{3.5}Cl_{0.5}] (black, $\lambda_{\text{ex}} = 360$ nm).⁸⁷ Adapted with permission from ref 87. Copyright 2014 American Chemical Society.

The PLQE value of the layered lead bromide perovskites has been improved up to 9% in another $\langle 110 \rangle$ -oriented layered perovskite (EDBE)[PbBr₄] (where EDBE = 2,2'-(ethylenedioxy)bis(ethylammonium)).⁸⁸ For (EDBE)[PbBr₄], CIE chromaticity coordinates of (0.39,0.42), a CCT of 3990 K, which correspond to a “warm” white light, and a CRI value of 84 are reported. Interestingly, a crystalline sample of (EDBE)[PbBr₄] enclosed in an evacuated quartz container showed stable emission over 3 months of continuous irradiation with a 4-W (720 $\mu\text{W}/\text{cm}^2$), 365 nm lamp. The authors note that the broad white-light emission is not likely due to deep traps at surface sites, as they observe similar emission and PLQEs from larger single crystals.⁸⁸ The broad emission has been attributed to excitons trapped through elastic lattice deformations and inhomogeneous broadening resulting from a distribution of trap states.

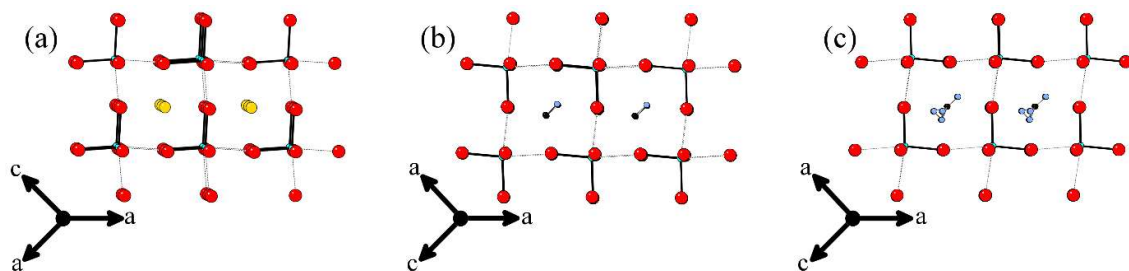


Figure 34. (a) Ball-and-stick representations of the crystal structures of a family of quasi 3-D AGeI₃ perovskites with A = (a) Cs⁺, (b) CH₃NH₃⁺, and (c) HC(NH₂)₂⁺. The

inorganic framework is made of pyramidal GeI_3^- units with three regular bonds (thick lines, $d_{\text{Ge-I}} = 2.733\text{-}2.772 \text{ \AA}$). Three additional elongated Ge-I contacts (dotted lines, $d_{\text{Ge-I}} = 3.256\text{-}3.577 \text{ \AA}$) from neighboring pyramidal GeI_3^- units complete the octahedral coordination around Ge^{2+} in the GeI_6^{4-} components.²⁰⁴

7.3.4. Non-linear Optical Applications. Compared to the Sn- and Pb-based hybrid perovskites, germanium-based hybrids are much less studied, presumably due to the instability of Ge^{2+} cations, with the divalent state being dictated by charge balance for the majority of perovskite compounds discussed here. A recent report on a family of quasi 3-D AGeI_3 perovskites ($\text{A} = \text{Cs}^+, \text{CH}_3\text{NH}_3^+, \text{HC}(\text{NH}_2)_2^+$)²⁰⁴ (**Figure 34**), however, suggests that these compounds may not be as unstable as previously thought. For these compounds, the first sign of oxidation was detected only after 12 hours in air, suggesting more stability than for the divalent tin based compounds.⁶⁰ We note, however, that comparisons of stability among different compounds require care, and it is important to take into account factors such as grain size and shape, as well as storage conditions—e.g., environmental humidity, in light or in dark—when comparing different systems. It was found that AGeI_3 compounds crystallize in polar space groups, and have direct band gaps of 1.6 eV for CsGeI_3 , 1.9 eV for $\text{CH}_3\text{NH}_3\text{GeI}_3$ and 2.2 eV for $\text{HC}(\text{NH}_2)_2\text{GeI}_3$, with band gaps increasing as the A^+ cation size increases.

The AGeI_3 family of perovskites demonstrate remarkably strong, type I phase-matchable second harmonic generation (SHG) response with high laser-induced damage thresholds of up to $\sim 3 \text{ GW/cm}^2$ (**Figure 35**). Interestingly, contrary to the expected decrease of the SHG coefficient ($\chi^{(2)}$) with increasing band gap, $\text{CH}_3\text{NH}_3\text{GeI}_3$ ($E_g = 1.9 \text{ eV}$) and $\text{HC}(\text{NH}_2)_2\text{GeI}_3$ ($E_g = 2.2 \text{ eV}$) exhibit much higher SHG efficiencies in their transparent regions compared to that of CsGeI_3 ($E_g = 1.6 \text{ eV}$). The second-order nonlinear susceptibility, $\chi^{(2)}$, was determined to be $125.3 \pm 10.5 \text{ pm/V}$ for CsGeI_3 , $161.0 \pm 14.5 \text{ pm/V}$ for $\text{CH}_3\text{NH}_3\text{GeI}_3$

and 143.0 ± 13.5 pm/V for $\text{HC}(\text{NH}_2)_2\text{GeI}_3$. These values are much higher than the reference material AgGaS_2 (36 pm/V), and similar to that for the record-holding (for band gaps > 1 eV) chalcogenides KPSe_6 (142.8 pm/V)²⁵⁴ and $\gamma\text{-NaAsSe}_2$ (337.9 pm/V).²⁵⁵ The observed trends in band gaps and SHG efficiencies are explained by the fact that larger A^+ cations result in stereochemically active lone pairs on Ge^{2+} , which in turn leads to a widening of the band gap (*sp*-hybridization of the Ge and I orbitals was confirmed by the results of DFT calculations). It is also suspected that the polar nature of the organic cations contributes to the increased SHG response.

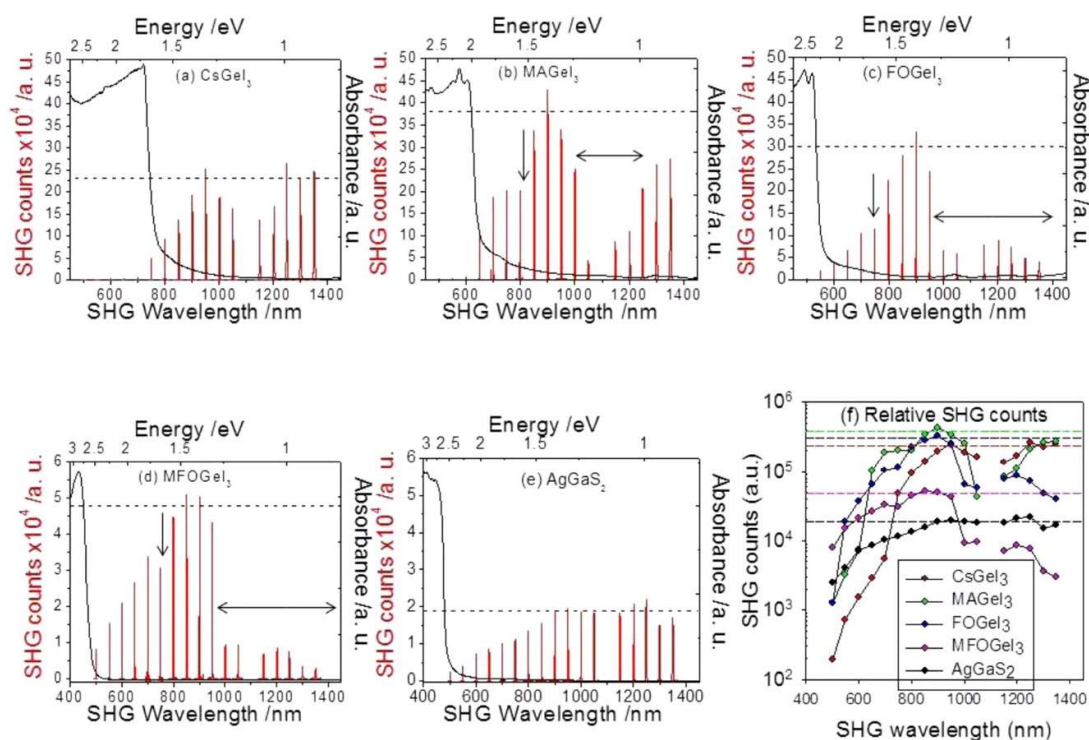


Figure 35. Wavelength-dependent second harmonic generation (SHG) scans for (a) CsGeI_3 , (b) $\text{CH}_3\text{NH}_3\text{GeI}_3$, (c) $\text{HC}(\text{NH}_2)_2\text{GeI}_3$, (d) $\text{CH}_3\text{C}(\text{NH}_2)_2\text{GeI}_3$, and (e) AgGaS_2 . The measurements were carried out between $\lambda = 1000 - 2700$ nm, and the corresponding SHG range is $\lambda/2 = 500 - 1350$ nm. The dashed lines indicate the predicted SHG counts in the static limit. The absorption edge is drawn as a black line for each compound for comparison. The

arrows shown in (b)-(d) indicate the spectral ranges in which linear absorption of the input beam results in significant decreases in the observed SHG counts. (f) Semilog plot of the relative SHG counts.²⁰⁴ Reprinted with permission from ref 204. Copyright 2015 American Chemical Society.

As opposed to the polarity caused by the inorganic framework in 3-D CsGeI₃, the use of chiral disulfide based cations, such as a diprotonated cystamine cation, could also result in crystals forming in a chiral space group in lower-dimensional systems. For example, α -[(NH₃(CH₂)₂SS(CH₂)₂NH₃)PbI₅] $\cdot$ H₃O crystallizes in the *P*2₁ space group and contains only one enantiomeric form of cystaminium cation. Note here that this compound features 1-D PbI₅ chains of corner-sharing octahedra similar to the chains in [(NH₃(CH₂)₂SS(CH₂)₂NH₃)₂PbI₅·I] (**Figure 12**). Upon heating, a reversible phase transition to a racemic β -phase occurs at 75 °C.²⁵⁶ Such conformational chirality, which can be controlled using temperature, provides a convenient route for preparation of switchable non-linear optical (NLO) materials, which has been successfully demonstrated for a related α -[(NH₃(CH₂)₂SS(CH₂)₂NH₃)BiI₅].²⁵⁷ The use of trivalent Bi³⁺ instead of divalent Pb²⁺ allows preparation of hydronium (H₃O⁺)-free crystals in the noncentrosymmetric space group *P*2₁*cn*. The reversible transition to a centric β -phase occurs at ~37 °C for this compound. The authors note that the material is easy to prepare in thin film form using the drop casting method, and that it demonstrates promising second (SHG) and third harmonic generation (THG) responses, which can be further fine-tuned.

Layered perovskite derivatives with non-centrosymmetric crystal structures can also be obtained, as shown by the *n* = 2 members of the $\langle 100 \rangle$ -oriented family (C₄H₉SCCH₂NH₃)₂(CH₃NH₃)Pb₂I₇²⁵⁸ and (HO₂C(CH₂)₃NH₃)₂(CH₃NH₃)Pb₂I₇.²⁵⁹ Interestingly, the related *n* = 1 members, (C₄H₉SCCH₂NH₃)₂PbI₄²⁵⁸ and (HO₂C(CH₂)₃NH₃)₂PbI₄,²⁵⁹

crystallize in the centric space group *Pbca*. The difference between the $n = 1$ and $n = 2$ members has been primarily attributed to the acentric nature of the $\text{Pb}_2\text{I}_7^{3-}$ inorganic bilayers, which in turn originates from the subtle shifts of the apical iodide atoms induced by the organic cation-inorganic framework interactions, leading to a loss of the center of symmetry.^{258,259} By extension, the authors note that while the $n = 3$ members such as $(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2\text{Sn}_3\text{I}_{10}$ are centrosymmetric, the $n = 4$ members could adopt non-centrosymmetric structures.²⁵⁸ Importantly, these findings demonstrate that non-centrosymmetric hybrid perovskite structures can be engineered by manipulating both the organic and inorganic structural fragments. A combination of suitable organic cations and inorganic perovskite frameworks, containing highly polarizable atoms such as iodide atoms, is therefore promising for second order non-linear optical applications.^{258,259}

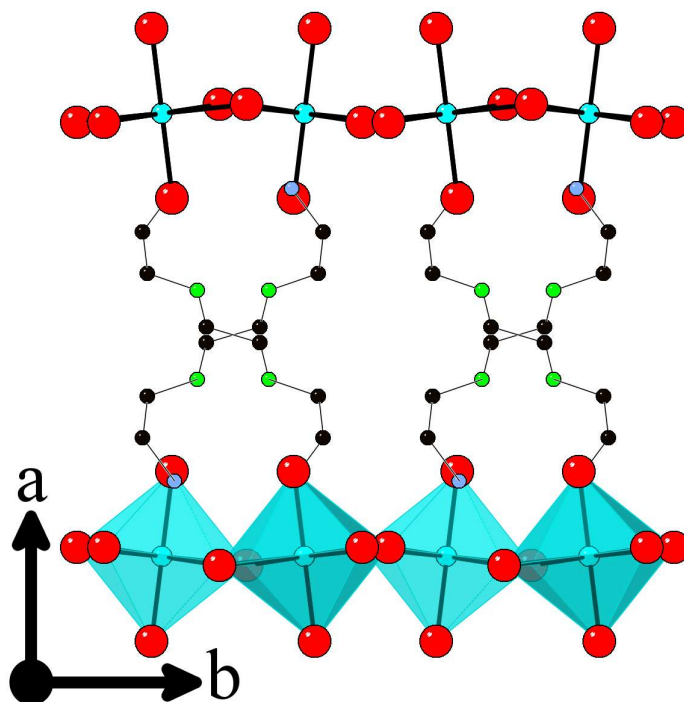


Figure 36. Combined skeletal (top) and polyhedral (bottom, shaded) view of the crystal structure of $(\text{EDBE})[\text{CuCl}_4]$, viewed down the c -axis. Cyan, red, green, sky blue and black spheres represent Cu, Cl, O, N, and C atoms, respectively. The channels present in the organic

component of the structure are suited to the intercalation of lithium ions for use in energy storage application.²⁶⁰

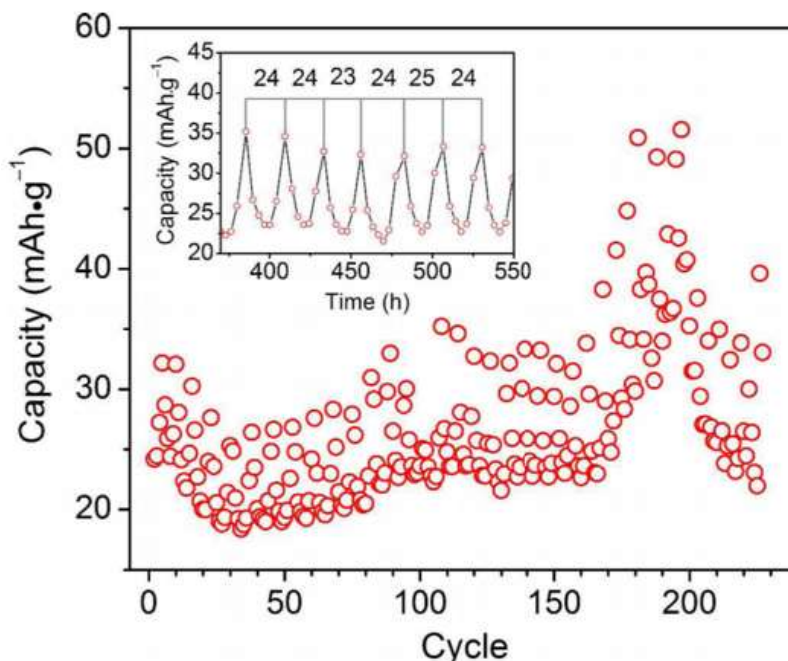


Figure 37. Capacity verses cycle number for a cell based on (EDBE)[CuCl₄] that is cycled between 2.1 V and 3.2 V vs Li^{+/0} at 28 mA g⁻¹. Inset: Capacity changes as the cell heats (from 22 to 40 °C) over a 24 hour period.²⁶⁰ Reprinted with permission from ref 260. Copyright 2014 American Chemical Society.

7.4. Charge Storage Properties and Applications

The layered perovskite structures, which enable facile and controllable intercalation (described in section 5), suggest possible application as battery cathodes. Recently, an organic-inorganic perovskite based on a copper(II) chloride framework and an appropriately selected organic cation, (EDBE)[CuCl₄] (**Figure 36**), was cycled over 200 times at a rate of 28 mA g⁻¹, as a lithium battery cathode with an open-circuit voltage of 3.2 V (**Figure 37**).²⁶⁰ In order to mimic the temperature fluctuations in large-scale battery installations, the authors

allowed their cell to heat by the sun over a 24-hour period. The measured average capacities over 225 cycles were 38(6) mA g⁻¹ at 40 °C and 26(4) mA g⁻¹ at 22 °C (**Figure 36**, inset).²⁶⁰ Impressively, capacity degradation was not observed during the cycling, however, the cell failed abruptly during the 227th cycle.²⁶⁰ The authors note that this is indicative of a failure through a short circuit and not material degradation and, therefore, this may be prevented by further optimizing the device structure.

(EDBE)[CuCl₄] consists of typical CuCl₄²⁻ sheets with Jahn-Teller distortion (antiferrodistortive arrangement) within the Cu d⁹ octahedra. The ether groups were selected to mimic the coordination environment of Li⁺ in ethereal solvents and, in the solid state structure, adjacent polyether chains cross to create 0.7 Å-diameter channels (**Figure 36**).²⁶⁰ These channels are likely involved in the process of lithium intercalation. Analogous structures with the specially-targeted polyether cation replaced by a simple alkylidiammonium group, with simply solid CuCl₂ or with stoichiometric (but unreacted) mixtures of CuCl₂ and EDBE, all exhibited lower capacities and unsuitability for cycling. Ultimately, this work shows the potential for the organic group in hybrid perovskites to be used to tailor designer materials for Li⁺ cycling in relatively non-toxic organic-inorganic metal halide electrodes, which can additionally be prepared with low-cost and abundant elements and using very simple and inexpensive fabrication approaches.²⁶⁰

8. CONCLUSION AND VISION FOR THE FUTURE

Over the >100 years that organic-inorganic perovskites have been known,²⁶¹ a number of highly interesting structural, magnetic, electrical and optical properties have arisen, primarily as a result of distinct properties of the organic or inorganic component of the structure. Most recently, solar cells based on lead halide perovskite absorbers have been attracting worldwide interest due to their remarkable light-harvesting properties and high

efficiencies above 20 %, achieved in an unprecedented short time period (~ 5 years) using simple low-temperature, low-cost processing. However, these materials suffer from the presence of the toxic heavy element Pb and from poor stability in moist air. Additionally, devices based on lead halide perovskites often exhibit hysteretic electrical behavior, the magnitude of which strongly depends on the device structure and fabrication procedure. Other combinations of metal halides may encounter similar challenges with regards to stability and hysteresis, given the “soft” nature of the materials. Manipulation of the highly versatile chemistry of hybrid organic-inorganic perovskites will likely play an important role in addressing these issues.

In part due to charge balance requirements, most studies on hybrid perovskites have focused on monovalent organic cations on the A-site, divalent metals on the B-site, and a halide ion on the X-site in 3-D ABX_3 and lower dimensional perovskite structures. A departure from these constraints might provide one viable path to stabilizing prospective non-toxic-element high-performance hybrid materials for electronic/optical and energy applications. For example, partial or full substitutions on the A-site (with organic cations in higher oxidation states of +2 or +3) and the X-site (with anions in more negative oxidation states of -2 or -3) represents one logical next step for consideration, and these in turn will allow necessary substitutions on the B-site.²⁶² Given the air-stability issues, which at least in part originate from the highly ionic nature of the hybrid halide perovskites, substitutions on the X-site leading to more covalent bonding character would be especially welcome. In fact, mixed-anion perovskites containing halide and chalcogenide ions on the X-site would bridge two of the richest classes of perovskites, one based on hybrid organic-inorganic halide perovskites and the other on all-inorganic chalcogenide/oxide perovskites.

Although rare, we note that several families of mixed-anion all-inorganic perovskites are known, including oxychloride $Sr_2CuO_2Cl_2$,^{263,264} oxynitrides AMo_2N and $RMON_2$ ($A =$

Ca, Sr, Ba; R = La, Pr; M = Ta, Nb, Ti)²⁶⁵⁻²⁶⁸, nitride-fluoride Ce₂MnN₃F₂₋₈,²⁶⁹ and oxyfluorides²⁷⁰ such as K₂NbO₃F,²⁷¹ Sr₂CoO₃F,²⁷² ASrNb₂O₆F²⁷³ and RbRTiNbO₆F²⁷⁴ (A = Li, Na, Rb; R = La, Pr, Nd), Sr₃Fe₂O₄F₄,²⁷⁵ Bi₂TiO₄F₂ and Bi₂NbO₅F,^{276,277} to name a few. These examples clearly demonstrate the wide array of substitutions possible in the mixed-anion compounds, suggesting that continued effort may enable the translation of the success in the preparation of mixed-anion all-inorganic perovskites into prospective hybrid organic-inorganic systems. When taking on this challenging task, however, as seen from examples within this review, one has to be mindful about important parameters such as tolerance factors, ionic radii, electronegativities and preferential coordination geometries as, under normal conditions, segregation of anions into distinct phases or separation into different structural segments in the same compound often dominates the materials formation behavior.^{262,278} The latter scenario is exemplified by the non-perovskite Sillén-type oxyhalides ABiO₂X (A = Ca, Sr, Ba, Cd; X = Cl, Br, I),²⁷⁹⁻²⁸¹ which despite a promising stoichiometry with regards to perovskite formation exhibit alternating layers of halide and oxide anions with metal cations sandwiched in between. In addition, the hybrid organic-inorganic perovskites exhibit low formation and decomposition energies;²⁸² therefore, harsh synthetic conditions, such as reactions at higher temperatures to induce mixing of anions, cannot be employed in most cases.

Beyond PV, the very high degree of structural flexibility, excellent optoelectronic properties and ease of fabrication could enable use of hybrid organic-inorganic perovskites in photodetectors, LEDs, batteries and solid-state lighting applications. In addition, there are several reports of exciting multiferroic and non-linear optical properties of hybrid perovskites. The full potential of the broad class of hybrid perovskites in these applications is just starting to be uncovered. In a broader context, however, for industrial scale implementation of hybrid perovskites, demonstration of stable working devices and materials, at least at near-ambient

temperatures, is necessary and, in fact, many of the challenges for applications beyond PV are largely similar to those described for perovskite PV. One of the often-cited and important advantages of hybrid perovskites is the simple low-temperature, low-cost processing, owing to their low formation energies. On the flip side, as mentioned above, the decomposition energies and hence decomposition temperatures are correspondingly low ($< 300\text{ }^{\circ}\text{C}$) and moisture/UV light can further accelerate the decomposition process.^{9,282-287} Better understanding of the stability limitations in the broader class of organic-inorganic perovskites and related halides is therefore an important further research target.

Continuing to look into the future, although there will still be great latitude and interest to develop new hybrid perovskites in which properties of either the organic or inorganic component are targeted, truly multifunctional organic-inorganic hybrids may be the next important frontier. Useful attributes of organic materials include luminescence and optical response, electrical transport, flexible processability and mechanical softness, whereas inorganic components can impart high electrical mobility, tunable conductivity, magnetic and dielectric responsiveness, and thermal/mechanical robustness. Each component has a wide range of structural and electronic tunability. Hybrid optoelectronic devices, for example, might benefit from having strongly absorbing/emitting organic molecules included in the structure to facilitate light absorption/emission, while leaving the long-range charge transporting function to the inorganic framework. Another possibility might be having transport of electrons and holes segregated to different layers within the structure, with the electronic nature of the interfaces targeted to avoid recombination. Thirdly, absorbing/emitting and charge transport might be confined to the inorganic layer and the organic component might be utilized to mechanically or chemically protect the active layers from degradation (e.g., using the strongly hydrophobic character of a larger organic cation to repel moisture from the structure, as has already been demonstrated to some extent).²⁸⁸⁻²⁹¹ In

implementing these and other scenarios, for many applications it may be necessary to appropriately tailor the energy levels of the different structural components and also control film growth so that the layers are nominally perpendicular to the substrate. Alternatively, applications or device structures will be targeted that favor lateral transport (relative to the substrate) rather than vertical, as for the most commonly-used device structure for organic-inorganic field-effect transistors.¹⁹⁶ The grand challenge remains to create a self-assembling organic-inorganic hybrid with properties substantially greater than the sum of its parts. One exciting aspect of the hybrid perovskites in this regards is that they can be prepared in single crystal form, and therefore, the expected rich structure-property relationships can be studied in great detail.

To further reflect on how multifunctionality might be imparted to complex organic-inorganic structures, exfoliation of (100)-oriented $(\text{RNH}_3)_2\text{A}_{n-1}\text{B}_n\text{X}_{3n+1}$ -type perovskites is facilitated by the fact that each organic (RNH_3) – inorganic $(\text{A}_{n-1}\text{B}_n\text{X}_{3n+1})$ – organic (RNH_3) sandwich is typically only bonded to nearest neighbors through weak van der Waals forces and can therefore be separated from its neighboring layers through ultrasonication in a suitable non-solvent. For example, recently $(\text{C}_6\text{H}_9\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$ and $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ materials have been exfoliated and the properties of the individual layers have been explored.^{292,293} The question then comes up, can distinct sets of individual functional perovskite sheets be reassembled to provide more complex functionality? Additionally, while organic-inorganic perovskites constitute a subclass of crystalline hybrid organic-inorganic compounds formed through corner sharing of metal-centered BX_6 octahedra, alternative connectivity of BX_6 octahedra based on edge- or face-sharing is also possible.²⁹⁴ Furthermore, organic-inorganic compounds based on other types of metal anion polyhedra including tetrahedral BX_4 units can also be envisioned (and perhaps merged with the perovskite structures using the exfoliation-reassembly idea discussed above). A systematic study of such

types of non-perovskite crystalline organic-inorganic hybrids is currently lacking; however, it is clear that these changes in the structures will lead to major changes in the properties. The possibility of alternative coordination polyhedra and connectivity scenarios not only adds another layer of complexity, but also provides even more structural flexibility and tunability that could potentially result in the emergence of many new useful applications. Preparative solid-state chemistry is renowned for a lack of predictability compared to organic synthesis; however, the continued study of structure-property relationship in hybrid organic-inorganic compounds is an important step for bringing reproducibility and predictability to this diverse and interdisciplinary field.

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Author Brief Biographies:

Bayrammurad Saparov: Bayrammurad Saparov is a Department of Energy (DOE) Energy Efficiency and Renewable Energy (EERE) SunShot Postdoctoral Fellow at Duke University. He received his Diploma in Chemistry from Lomonosov Moscow State University in 2006 and Ph.D. in Inorganic Solid State Chemistry from the University of Delaware in 2011. Before joining David Mitzi's group at Duke in 2014, Dr. Saparov was a postdoctoral researcher at Oak Ridge National Laboratory, focusing on the magnetism and superconductivity of transition metal pnictides and chalcogenides, as well as investigating permanent magnets with reduced rare-earth content. He is currently interested in materials design for energy applications including affordable chalcogenide and hybrid organic-inorganic perovskite solar cell absorbers.

David B. Mitzi: David Mitzi is the Simon Family Professor of Engineering at Duke University, with joint appointments to the Department of Mechanical Engineering and

Materials Science and the Department of Chemistry. He received his B.S. in Electrical Engineering and Engineering Physics from Princeton University in 1985 and his Ph.D. in Applied Physics from Stanford University in 1990. Prior to joining the faculty at Duke in 2014, Dr. Mitzi spent 23 years at IBM's T.J. Watson Research Center, where his focus was on the search for and application of new electronic materials, including organic-inorganic hybrids and inorganic materials for photovoltaic, LED, transistor and memory applications. For his final five years at IBM, he served as manager for the Photovoltaic Science and Technology Department, where he initiated and managed a multi-company program to develop a low-cost, high-throughput approach to deposit thin-film chalcogenide-based absorber layers for high-efficiency solar cells. Dr. Mitzi's current research interests are making emerging photovoltaic materials more effective, cost-efficient and competitive for the energy market. He holds a number of patents, and has authored or coauthored more than 190 papers and book chapters.

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