Organic–inorganic metal halide hybrids beyond perovskites

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ABSTRACT

Organic–inorganic metal halide hybrids have emerged as new generation functional materials with exceptional structure and property tunability for a variety of applications. Besides the most investigated ABX\textsubscript{3} metal halide perovskites, a variety of hybrids consisting of a wide range of organic cations and metal halide anions have been developed and studied recently. Here, we provide an overview of these new materials possessing various crystallographic structures, including double perovskites, low dimensional hybrids, and other perovskite-related materials. We discuss their syntheses, functional properties, and optoelectronic applications. Challenges and opportunities are then laid out for these hybrid materials beyond perovskites.

IMPACT STATEMENT

By choosing appropriate organic cations and metal halide anions, single crystalline ionically bonded hybrid materials can be assembled to possess various structures beyond the well-known ABX\textsubscript{3} perovskite. These hybrid materials exhibit exciting new properties with potential applications in a variety of areas.

1. Introduction

Organic–inorganic metal halide hybrids are a class of materials consist of organic cations and metal halide anions. Metal halide perovskites are the most common ones containing metal halide octahedra as the fundamental building blocks. Early report of three-dimensional (3D) metal halide perovskites dates back to 1950s, when the crystal structure and photoconductivity of CsPbX\textsubscript{3} (X = Cl, Br, I) were discovered [1]. In 1990s, Mitzi et al. discovered a series of two-dimensional (2D) organic inorganic hybrids containing \textless110\textgreater metal halide layers [2]. Later, the use of these 2D perovskites as semiconducting channels was explored by Kagan et al. [3]. And fabrication of light emitting diodes (LEDs) using these materials was also attempted [4].

The research attention in metal halide perovskites has grown exponentially since 2009, when the use of organometal halide perovskites as visible-light sensitizers for photovoltaic (PV) cells was reported by Miyasaka and co-workers with power conversion efficiencies (PCEs) of up to 3.8\% [5]. In 2014, the first room temperature electroluminescent devices based on organometal halide perovskites were reported [6]. In recent years, structure control of organic–inorganic metal halide hybrids has been explored to lower the dimensionality from 3D to 2D, 1D, and 0D at both morphological and molecular levels. Tyagi et al. reported the colloidal perovskite nanplatelets exhibiting quantum confinement effects [7]. Yang group reported an atomically thin 2D (C\textsubscript{4}H\textsubscript{9}NH\textsubscript{3})\textsubscript{2}PbBr\textsubscript{4}, which exhibits efficient photoluminescence and unusual...
The development of organic-inorganic metal halide hybrids over the years. From the discovery of 2D structure containing $<100>$ or $<110>$ layers to the synthesis of colloidal nanoparticles, nanowires, chalcogenide, and double perovskites, the metal halide hybrids show promise in a variety of optoelectronic applications, e.g. photovoltaic solar cells, light emitting diodes. By choosing appropriate organic cations, the dimensionality can be tuned from 3D to 2D, corrugated-2D, quasi-2D, 1D, and 0D. Besides, Mn ions were doped to metal halide hybrids with different dimensionalities to achieve efficient energy transfer with red emission. Reproduced from Ref. [2,3,5–15,19–21].

In 2016, highly uniform single crystalline ultrathin CsPbX$_3$ nanowires were synthesized by the same group with high photoluminescence quantum efficiencies (PLQEs) [9]. The stable colloidal solutions of CH$_3$NH$_3$PbX$_3$ nanoparticles with size below 10 nm were first reported in 2014 [10], which stimulated tremendous research interest in perovskite quantum dots. By controlling the number of metal halide layers, quasi-2D structures can be obtained with tunable band gaps and photoluminescence [11]. The corrugated-2D structures to produce white-light broadband emissions, first reported in 2014, were found to have large structure distortion and strong exciton-lattice coupling with efficient exciton self-trapping [12]. Lowering the dimensionality further to 1D at the molecular level, stronger quantum confinement and exciton-lattice interaction were observed with broadband emissions [13]. In an extreme case, when the metal halides are completely isolated by the organic moieties, 0D structure at the molecular level can be obtained to display the intrinsic properties of individual metal halide species [14]. In addition to structure control, doping Mn ions to this class of materials to achieve efficient red emission has been realized in different hybrids [15–18]. Replacing Pb$^{2+}$ by nontoxic trivalent and monovalent metals can yield double perovskites (A$_2$B$^1$B$^{III}$X$_6$), which provides a new route to fabricate lead-free PVs and other optoelectronic devices [19]. To address the materials stability and toxicity issues, chalcogenide ABX$_3$ compounds were also studied for PV applications [20]. Overall, the research in perovskites and perovskite-related materials has been highly active for years. Figure 1 highlights a few major milestones in the development of organic–inorganic metal halide hybrids.

In this overview, we briefly introduce the development and study of organic–inorganic metal halide hybrids, including metal halide perovskite materials with ABX$_3$ structure and hybrids beyond perovskites. We also provide our prospects for this class of materials with distinct structures and properties.

2. **3D metal halide hybrids**

2.1. **Bulk ABX$_3$ metal halide perovskites**

3D metal halide perovskites are a class of materials with a chemical formula of ABX$_3$, in which A stands for a monovalent cation that could be either organic or inorganic, B stands for a bivalent metal cation, and X represents halide anions. As shown in Figure 2(a), the crystal structure of
the ABX₃ could be regarded as a metal halide framework constructed by corner-sharing BX₆ octahedra with larger cations A filling into each cuboctahedra cavity formed by eight adjacent octahedra which is also referred by the term ‘perovskite structure’. The crystallographic stability of this ABX₃ structure could be estimated by the Goldschmidt tolerance factor \( t = (r_A + r_B)/(\sqrt{2}(r_B + r_X)) \) and octahedral factor \( \mu = r_B/r_X \) where \( r_A, r_B \) and \( r_X \) are the ionic radii of the corresponding ions [22]. Perovskite structure is likely to form when \( t \) falls in the approximate range of 0.8–1.1 and \( \mu \) in the range of 0.4–0.9 [2,23–25]. With these restrictions, only several inorganic cations such as Cs⁺ or Rb⁺ and organic cations such as methylammonium (MA⁺), ethylammonium (EA⁺), formamidinium (FA⁺) meet the requirement as A⁺. Similarly, B²⁺ in most cases is Pb²⁺ or Sn²⁺.

The current intense research on metal halide perovskites is prompted by the success of perovskite solar cells, after the report of using MAPbBr₃ and MAPbI₃ as light harvesters in 2009 [5]. With extensive research efforts [26–30], the PCEs of perovskite solar cells (Figure 2(b)) have been improved from 3.8% [5] to more than 22% [31]. For the exceptional optical and electronic properties, 3D metal halide perovskites have also found applications in other optoelectronic devices, e.g. LEDs (Figure 2(c)), optically pumped lasers (Figure 2(d)), etc [32–34]. To address the toxicity issue of Pb, 3D tin halide perovskites have been developed [35–39]. However, bivalent Sn²⁺ could be easily oxidized to Sn⁴⁺, resulting in the instability of the material itself and morphological change into other species [40]. Germanium in the same Group IV was also reported to form 3D perovskite structures with MA⁺, FA⁺ and Cs⁺ [41,42]. With higher tolerance factor \( t \), Ge based metal halide perovskites have higher structural stability but still suffer from its high reactivity with oxidants [43,44]. There are a number of review articles available for 3D metal halide perovskites, their properties, and applications in optoelectronic devices [45,46]. Here we will not get into the details of 3D metal halide perovskites.

### 2.2. Double halide perovskites

A close derivative of ABX₃ metal halide perovskites is the double perovskite, which has switched to a quaternary \( A^{1+}_2B^{II}X_6 \) formula, with both monovalent and trivalent metal ions coexist in the same crystal. Figure 3(a)
Figure 3. (a) Illustration of cations transmutation strategy (by converting $2\text{Pb}^{2+}$ to pair of $[\text{B}^{2+} + \text{C}^{3+}]$) to design Pb-free halide double perovskites. (b) X-ray structure of the ordered double perovskite $\text{Cs}_2\text{AgBiBr}_6$. Orange, gray, turquoise, and brown spheres represent Bi, Ag, Cs, and Br atoms, respectively. (c) Photograph of a single crystal of $\text{Cs}_2\text{AgBiBr}_6$. (d) The $\text{Bi}^{3+}$ face-centered-cubic sublattice in $\text{Cs}_2\text{AgBiBr}_6$, consisting of edge-sharing tetrahedra. Reproduced from Ref. [19, 55].

shows the crystal structure of a typical double perovskite, in which each metal halide octahedra $\text{B}^\text{III}X_6$ or $\text{B}^\text{II}X_6$ shares corners with six adjacent octahedra containing different metal ions to form a 3D network. It could also be regarded as the $\text{B}^{2+}$ in an $\text{ABX}_3$ perovskite being periodically substituted by two distinct ions. The abundant elementary combinations provide vast choices for desired properties. In 1970s, the preparation of a few double perovskites with formula of $\text{Cs}_2\text{NaM}^\text{III}\text{Cl}_6$ were reported [48]. Recently, research on double perovskites has become active again, for their potential as stable and non-toxic light-absorbers in perovskite solar cells. All-inorganic $\text{Cs}_2\text{AgBiCl}_6$ and $\text{Cs}_2\text{AgBiBr}_6$ were synthesized and found to have indirect band structures with large band gaps of over 2 eV (Figure 3(b–d)) [19, 49]. Organic hybrid double perovskite (MA)$_2\text{KBiCl}_6$ was also discovered with a large indirect bandgap of 3.0 eV. Supported by theoretical studies [50, 51], (MA)$_2\text{TIBiBr}_6$ and $\text{Cs}_2\text{InAgCl}_6$ were designed and developed to have direct band structures [52, 53]. More theoretical and experimental studies are driven by the goal to employ less toxic elements, such as Cu, to establish double perovskites with desired properties [54, 55]. Nevertheless, double perovskites have not achieved comparable performance in optoelectronic devices as Pb based 3D perovskites yet, and further investigations are needed.

2.3. Oxide and chalcogenide perovskites

Another family of materials that adopt the 3D $\text{ABX}_3$ structure are oxide and chalcogenide perovskites, in which $\text{A}$ is a bivalent cation and $\text{B}$ is a tetravalent cation, $\text{X}$ is a VIA group element, i.e. O for oxide perovskites, and S or Se for chalcogenide perovskites. The oxide perovskites usually have larger band gaps due to the large electronegativity of the $\text{O}^{2-}$ and highly localized orbitals. Chalcogenide perovskites by contrast exhibit lower band gaps and usually highly distorted crystal phases [20]. These materials have been extensively studied before, but are often recognized as materials for capacitors, superconductors, memories mediums, etc [56–59]. There has not been much success in using these materials for optoelectronic devices, such as PVs and LEDs.

2.4. Morphological low dimensional metal halide perovskites

Before proceeding to introduce low-dimensional organic metal halide hybrids, it is necessary to clarify the
Figure 4. TEM images of lead halide perovskite (a) nanocubes, (b) nanowires, and (c) nanoplatelets, (d) Effect of capping agent on the morphology of CsPbX₃ nanoparticles. Reproduced from Ref. [63,79–81].

3. 2D and quasi-2D metal halide hybrids

2D and quasi-2D organometal halide perovskites can be considered as layers torn from 3D perovskites structures in a certain crystallographic direction. The general chemical formula is $A_{n-1}A'_{2}B_{n}X_{3n+1}$ where $A$ is a small
cation, $A'$ is a long chain organic cation, $B$ is a divalent metal, and $X$ is a halide. $n$ refers to the number of metal halide layers between the long chain organic cation layers. The value of $n$ can range from 1 to infinity, where the two extremely case with $n = \infty$ and $n = 1$ refer to 3D metal halide perovskites and layered-2D perovskites, respectively. Reducing number of layers leads to an increase in band gap due to the stronger quantum confinement [82–84] and the increase of the exciton binding energy [85]. Recently, 2D and quasi-2D metal halide perovskites received great research attention for their higher stability than their 3D counterparts [86].

Several approaches, including mechanical exfoliation [87,88], chemical vapor deposition [89], solution-processing [8,90,91], and colloidal methods [92] have been developed to prepare 2D perovskites. As compared to mechanical exfoliation and chemical vapor deposition techniques, solution-processing approach was

**Figure 5.** (a) Crystal packing diagram for (CyBMA)PbBr$_4$ showing propagation of [PbBr$_6$]$^{4-}$ octahedra along the ac-plane. (b) Crystal structure of (H$_2$Aepz)$_3$Pb$_4$I$_{14}$ with larger organic cations incorporated within the perovskite-like PbI layered structure. View of the unit cells of the (GAI)_(MA)$_n$Pb$_3$I$_{3n+1}$ ($n = 1–3$) perovskites along (c) the crystallographic b-axis and (d) the crystallographic a-axis highlighting the ordered crystal packing of the GA and MA cations between the perovskite layers. (e) The crystal structure of the (top) Ruddlesden–Popper (BA)$_2$(MA)$_3$Pb$_4$I$_{13}$ and (bottom) (BA)$_2$(MA)$_4$Pb$_5$I$_{16}$ layered perovskites. (f) PXRD of (BA)$_2$(MA)$_3$Pb$_4$I$_{13}$ and (BA)$_2$(MA)$_4$Pb$_5$I$_{16}$ (BA = butylammonium) powder indicating equally spaced (0k0) peaks at low angle, which are the signature for pure phase of synthesized materials. (g) Demonstration of tunable EL with well-defined $n$ units in the pure phase Ruddlesden-Popper perovskites. Reproduced from Ref. [95,96,99,104].
more effective to achieve high-quality crystals [93]. For instance, L. Dou et al. synthesized blue emitting 2D sheets with an unusual structural relaxation and photoluminescence shift [8]. Z. Yuan et al. developed a facile one-pot synthesis method to synthesize layered lead(II) bromide perovskite microdisks that exhibited deep blue emissions with PLQEs of up to 53% [94]. Neogi et al. reported a 2D perovskite (CyBMA)PbBr₄ (CyBMA: cis-1,3-bis(me-thylamino)cyclohexane) with a broadband emission due to exciton self-trapping (Figure 5(a)) [95]. Que et al. synthesized a novel layered lead iodide, (H₂Aepz)₃Pb₄I₁₄, where larger organic cations, bis-protonated 2-(2-aminoethyl)pyrazole (Aepz), were not only sandwiched between the inorganic layers, but also incorporated within the perovskite-like lead iodide layered structure (Figure 5(b)) [96]. Quasi-2D perovskites containing multiple inorganic metal halide layers have been extensively explored to display distinct photophysical properties. For instance, a series of nanoscale quasi-2D lead (II) bromide perovskites were obtained by a one-pot synthesis to exhibit tunable emissions from deep blue to bright green [11]. A strategy to obtain crosslinked 2D/3D structure Ava(MAPbBr₃)ₙ (Ava = 5-aminovaleric acid) with tunable emission was also reported, serving as a promising approach for in situ deposition of lead halide perovskite films [97]. Bulk quasi-2D perovskites containing lead iodide double layers and large organic cations (bis-protonated 2-(2-aminoethyl)-pyrazole) were developed to show promising PV performance [96]. Quasi-2D perovskite EA₄Pb₃Br₁₀-₄Cl₈ (EA: ethylammonium) was prepared to exhibit tunable white emissions, due to a high distortion level in their inorganic structures [98]. Besides Ruddlesden-Popper type, various 2D/quasi-2D structure, e.g. Dion-Jacobson structure feature divalent (2+) interlayer spacers, the halide perovskite containing alternating cation (guanidinium (GA) and methylammonium) in the interlayer space (Figure 5(c,d)), have also been studied to show lower band gap because of a less distorted inorganic framework [99,100].

These 2D and quasi-2D hybrids have shown promises for a variety of optoelectronic applications. The use of 2D perovskites in PVs was first reported in 2014 by Smith et al., which showed better chemical stability than 3D perovskites [101]. However, PCEs of 2D perovskite based PVs are still relatively low, partially because of the poor charge transport due to the insulating organic spacers. H. Tsai et al. overcame this problem by using hot-casting technique to fabricate 2D perovskite thin films with near single-crystalline quality, in which the charge transport was facilitated by the strongly preferential out-of-plane alignment of the inorganic layers with respect to electrodes [102]. Besides PVs, several reports have focused on using these materials in LEDs. Wang et al. demonstrated 2D perovskite-based LEDs with high external quantum efficiencies of up to 11.7%, along with good stability [103]. Vertically oriented thin films of phase pure 2D perovskites were reported to have efficient charge injection and transport, and stable efficient EL with ultralow turn-on voltage (Figure 5(e–g)) [104]. Furthermore, 2D halide perovskites were also employed to fabricate micro-ring laser arrays that showed high quality factor, high gain, and low threshold [105]. While great progress has been made in using 2D perovskites for optoelectronic devices, their performance is still largely lagging behind 3D perovskites. Moreover, the interactions between the inorganic metal halide layers and organic moieties with different electronic structures remain to be explored.

### 4. Corrugated-2D organic metal halide hybrids

Besides 2D perovskites containing (100) flat sheets of metal halide octahedra, corrugated-2D organic–inorganic metal halide hybrids can also be obtained by slicing along (110) crystallographic planes of the 3D cubic lattice [106]. (110)-perovskites have distinct in-plane a₀ × √2a₀ lattice parameters, where a₀ is the lattice parameter of cubic 3D perovskites [107]. Mitzi et al. reported the first corrugated-2D perovskite [NH₂₂(C(I) = NH₂]₂(CH₃NH₃)₃Sn₃SnI₃m+2 (m = 2) in 1990s. [2] Later, Li et al. reported a novel corrugated-2D hybrid stabilized by N-(3-aminopropyl)-imidazolium moieties [108]. The Stokes-shifted emission was attributed to the energy transfer from the inorganic components to the organic molecules. In 2014, intrinsic, broadband white-light emission was observed from the corrugated-2D lead-halide perovskites (N-MEDA)PbBr₄ and (EDBE)PbX₄ (N-MEDA = N₃-methylethane-1,2-diammonium; EDBE = 2,2’-(ethylenedioxy)bis(ethy-lammonium); X = Cl and Br) (Figure 6(a)). In addition to ‘2 × 2’ corrugated 2D structure, this family has been extended to ‘3 × 3’ [109] (Figure 6(b)) and ‘4 × 4’ [110] types. More recently, corrugated-2D perovskites have been used to stabilize the α-CsPbI₃ phase and achieve a record PCE of 11.8% by connecting α-CsPbI₃ crystallites for effective electron transfer and passivating the surface defects [111].

One of the most intriguing properties of corrugated-2D hybrids is their broadband white emission, which makes them promising single component phosphors for optically pumped white LEDs [112]. EDBEPbBr₄ exhibits a warm white light with a CRI value of 85. Recently, a high CRI of 93 was achieved for a corrugated-2D hybrid with N-(3-aminopropyl)imidazole as organic cation [113]. However, the PLQEs of these corrugated-2D hybrids are
still relatively low. \((N\text{-MEDA})\text{PbBr}_{4-x}\text{Cl}_x\) \((x = 0–1.2)\) shows the maximum PLQE of 1.5%. The most efficient white light emitting corrugated-2D hybrid, EDBEPbBr_4, with a CIE coordinate of \((0.30, 0.42)\) and a correlated color temperature (CCT) of 6519 K, has a PLQE of 9% in bulk single crystal form and 18% in microscale crystal form (Figure 6(c)) [114]. To make these phosphors practically attractive for solid-state lighting, further improving the PLQE is required.

The strongly Stokes-shifted broadband emissions from corrugated-2D hybrids are attributed to the radiative decays of self-trapped excitons (STEs), a mechanism well-accepted by the community [115,116]. Intrinsic self-trapping can cause a transient lattice distortion, thus does not need to have permanent defects. Karunadasa and coworkers described this phenomenon as a hard ball (electron/hole/exciton) dropping on a pliable rubber sheet (a deformable lattice) [115]. The sheet could distort or recover with the ball trapped or de-trapped, which is different from dropping a ball into an indentation in the sheet (a permanent defect) (Figure 6(d)). The model can be depicted as Figure 6(e), considering both the inhomogeneous nature of the STE states and their radiative and nonradiative decay [117]. In this model, a distribution of STE states with different self-trapping depths arises from free excitons through strong electron–phonon interactions. A recent review article by Smith and Karunadasa provides great insights into white-light emission from layered halide perovskites [115].

5. 1D metal halide hybrids

The first report of 1D metal halide hybrid could date back to 1990s, when Mitzi et al. extended \(< 110 >\)-oriented conducting halide perovskites, \([\text{NH}_2\text{C(I)=NH}_2\text{]}_2(\text{CH}_3\text{NH}_3)_m\text{Sn}_m\text{I}_3m\text{+}\), to \([\text{NH}_2\text{C(I)=NH}_2\text{]}_2(\text{CH}_3\text{NH}_3)\text{Sn}_1\text{I}_5\) with \(m = 1\), in which metal halide octahedra connect to form 1D chains via corner-sharing [117,118]. Theoretically, metal halide octahedra can also connect with each other via other ways, such as edge- and face-sharing, to form 1D structures to show unique properties. Unlike 3D and 2D structures that have been extensively investigated, 1D metal halide hybrids are still largely underexplored until recent years [119,120].

In 2017, our group reported an organic lead bromide hybrid, \(\text{C}_4\text{N}_2\text{H}_{14}\text{PbBr}_4\), in which the edge-sharing octahedral lead bromide chains \([\text{PbBr}_4]_2^–\) are surrounded by the organic cations \(\text{C}_4\text{N}_2\text{H}_{14}^+\) to form the bulk assembly of core–shell quantum wires (Figure 7(a)) [13]. The unique 1D structure leads to a strong quantum confinement with the formation of self-trapped exited
states. Broadband bluish white light emissions peaked at 475 nm with a large full width at half maximum of around 157 nm have been obtained with PLQEs of up to 20% (Figure 7(b,c)). Interestingly, its 1D Sn-based counterpart, C$_4$N$_2$H$_{14}$SnBr$_4$, with the same core–shell structure is non-emissive under UV light [121]. Instead,
photoinduced structural transformation from 1D to 0D tin bromide perovskites upon UV excitation was observed. This finding suggests that the metal halide bond breaking can happen upon photoexcitation followed by structural reorganization, and individual metal halide octahedra could be more thermodynamically stable than connected ones in this case.

Besides Group IVA elements, such as Pb(II) and Sn(II), non-toxic metal Bi(III) also has the capability to form 1D structure. Pasquier and co-workers reported a 1D bismuth chloride hybrid, (MV) [BiI3Cl2] (MV2+ = methylviologen), which exhibits remarkable ferroelectric properties at room temperature [122]. This room-temperature hybrid ferroelectric displays a clear electrical hysteresis loop with a very large spontaneous room-temperature dipole moment (MV2+ in which the metal halides form covalent bonds with the semiconductor organic τ-aggregates (Figure 7(j))). After photoinduced electron transfer, this 1D semiconducting material yields a long-lived charge-separated state with a broad absorption band covering the 200–900 nm region while increasing its conductance and photoconductance [129].

While 1D organic metal halide hybrids have attracted more attentions than before, with various 1D structures developed in recent years, most of the systems are based on metal halide octahedra as the building blocks. It will be of great interest to fabricate 1D structures using other metal halide building blocks, such as tetrahalide and bidentate pyramidal, to show distinct optical and electrical properties. Moreover, precise control of the size of metal halide wires and tubes at the molecular level has yet been realized. It would be of great interest to develop quasi-1D crystals, which can help us better understand the structure–property relationships from quantum confined wires to bulk materials.

6. 0D metal halide hybrids

0D metal halide hybrids are materials containing individual metal halide species isolated from each other. Cs4PbBr6 is perhaps the most known material containing disconnected metal halide octahedra, which is often called a ‘0D perovskite’. Controversial results on the physical properties of Cs4PbBr6 have been reported recently, with some claiming that it has intrinsic green emission, and others believing it is non-emissive in the visible wavelength. A recent perspective by Manna et al. has provided detailed discussions on the contrasting opinions on the properties, and suggested that defect-free Cs4PbBr6 has an intrinsic large band gap of > 3.2 eV and the green emission of those Cs4PbBr6 materials is likely from contamination by CsPbBr3 nanocrystal-like impurities [131]. To our point of view, Cs4PbBr6 cannot be considered as 'true' 0D structure, because the Cs+ cations are too small to have individual metal halide octahedra completely isolated from each other without electronic band formation.

Recently, our group has developed a series of ‘true’ 0D organic metal halide hybrids, in which metal halide species are completely isolated from each other and surrounded by large band gap organic cations. The complete isolation leads to no interaction between the photoactive metal halide species or electronic band formation. These single crystalline bulk assemblies of 0D materials can be considered as perfect host–guest systems, in which the photoactive metal halide species are periodically embedded in an inert host matrix (Figure 8(a–c)) [14]. Therefore, the potential energy diagram for these bulk assemblies of 0D materials can be described as
in Figure 8(d), suggesting that the bulk materials can exhibit the intrinsic properties of the individual metal halide species. Indeed, highly luminescent broadband emissions under UV irradiation were observed for 0D tin halide perovskites with PLQEs of up to near unity (Figure 8(e)). The excited state processes for these 0D organic metal halide hybrids can be depicted in the configuration coordinate diagram given in Figure 8(f). Upon photon absorption, the metal halide species are excited to the high energy excited states, which undergo ultrafast excited state structural reorganization to the lower energy excited states, to generate strongly Stokes shifted broadband emissions with lifetimes of microseconds.

In addition to metal halide octahedra, different metal halide polyhedrons, such as pyramid and tetrahedra, have also been explored as building blocks to assemble 0D organic metal halide hybrids. Highly luminescent 0D Sb halide hybrids, such as [Bmim]2SbCl5 [132] and (C9NH20)2SbCl5 [14], have been reported, which contain isolated pyramidal SbCl5 species. Recently, a facile synthetic approach was established to prepare 0D (Ph4P)2SbCl5 by taking advantage of the easy crystallization of tetraphenylphosphonium salts (Figure 8(g)).
With the same organic cation, a green emitting 0D hybrid containing tetrahedral MnBr₄ species was developed by Xu et al., which was used as solution processable emitter in OLEDs. (Figure 8(h,i)) [134]. The strongly Stokes-shifted emission with microsecond lifetime suggests its origin from spin-forbidden d-d $^4T_{1} \rightarrow ^6A_{1}$ transition of the Mn ions in d⁵ configuration with a tetrahedral coordination geometry. In addition to tetrahedral structure, a rare seesaw-shaped SnBr₄ based 0D hybrid was recently developed to exhibit a deep red emission with extremely large Stokes shift [135]. Other than molecular metal halide species, metal halide clusters containing multiple metal atoms can also serve as the building block to assemble 0D metal halide hybrids. For example, (CH₃NH₃)₃Bi₂I₉ was first reported by Kawai et al. in 1990s [136] and has recently emerged as a possible candidate as light absorber [137–139]. Smith et al. reported the synthesis of a family of sulfonium-based lead bromide hybrids consisting of Pb₃Br₁₂₆⁻ trimers [140]. From hexa- to penta-, tetra-, and even clustered metal halides, there is a vast space to explore novel structures with new and useful properties. These

Figure 9. (a) The optical properties of undoped (top) and Mn-doped (bottom) CsPbCl₃ NCs. (b) The energy level diagram of Mn:CsPbCl₃ NCs. $k_{\text{eh}}$: band edge electron-hole recombination $k_{\text{Mn}}$: deactivation of the Mn²⁺-based d-d transition; forward ($k_{\text{ET}}$) and back ($k_{\text{BET}}$) energy transfer between the NC and the impurity. (c) The diagram shows efficient energy transfer in 2D perovskites. (d) Photoluminescence of Mn²⁺-doped and undoped 2D perovskite. (e) Photoluminescence of Mn²⁺-doped 1D lead bromide perovskite. (f) Proposed energy diagram and excited state dynamics of Mn-doped 1D lead bromide perovskites: the straight and curved arrows represent optical and energy relaxation/transfer transitions, respectively. Reproduced from Ref. [15,17,18].
0D materials offer the opportunity to study molecular properties on the bulk crystal platform, and allow us relating molecular science to crystal physics.

7. Mn-doped metal halide hybrids

Doping impurity ions into semiconductor crystals has been well established as an effective approach to introducing novel functionalities and tuning the properties of the host materials [141–145]. Electronic and optical properties of semiconductors can be efficiently manipulated by doping different metal ions, such as Mn$^{2+}$ [15,16], Sn$^{2+}$, Cd$^{2+}$, Zn$^{2+}$ [146], Bi$^{3+}$ [147], Au$^{3+}$ [148], and various lanthanide ions (Ce$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, Er$^{3+}$, and Yb$^{3+}$) [149]. Among all these doped metal ions, Mn$^{2+}$ has attracted the most research attention, owing to the intriguing properties of Mn-doped metal halide hybrids, e.g., facile control of the doping concentration, highly luminescent red emission, efficient energy transfer. Since 2016, doping Mn$^{2+}$ ions into all inorganic perovskite CsPbX$_3$ NCs has been extensively explored [15,16,61,150–152]. In these CsPbCl$_3$ and CsPb(Cl/Br)$_3$ nanocrystals, strong sensitized luminescence from d-d transition of Mn$^{2+}$ was observed due to the strong exchange coupling between the charge carriers of the host and dopant d electrons mediating the energy transfer (Figure 9(a,b)). As a result, a spin-forbidden $^4T_1$-$^6A_1$ Mn d-electron emission with a long lifetime of a few microsecond was observed and the PLQEs of Mn-doped NCs were dramatically increased. Despite the high Mn substitution ratio of up to 46%, the crystal structure of the host remained mostly unchanged [153]. Besides doped all inorganic perovskite materials, Im et al. demonstrated that the flexible organic cation network (CH$_3$NH$_3^+$) can facilitate the replacement of Pb$_2^+$ by Mn$^{2+}$ to achieve a high Mn solubility limit of 90% and further decrease the toxicity of the red-emitting 3D materials [154].

Doping Mn$^{2+}$ ions into low dimensional organic metal halide hybrids has also attracted considerable research interest. Kundu et al. reported a simple and scalable synthesis of Mn$^{2+}$-doped 2D layered perovskites (C$_4$H$_9$NH$_3$)$_2$PbBr$_4$ (Figure 9(c)) [17]. Enhanced energy transfer from strongly bounded excitons of the host material to the d electrons of Mn$^{2+}$ ions was observed in 2D materials, resulting in its intense orange-yellow emission with a quantum yield of $\sim$ 37% (Figure 9(d)). Unlike Mn-doped 3D and 2D materials showing dual emission from free exciton and Mn ions, Mn-doped 1D materials was also investigated to show a combined emission from both self-trapped excited states and the doped Mn$^{2+}$ ions (Figure 9(e)) [18]. Due to the indirect nature of the self-trapped excited state, there is little-to-no energy transfer from these states to the Mn$^{2+}$ ions, resulting in an efficient broadband white emission (Figure 9(f)).

8. Summary and perspective

Organic–inorganic metal halide hybrids are an important class of crystalline materials with exceptional structure and property tunability. By choosing appropriate organic and inorganic components, the connectivity of the metal halide polyhedrons can be tuned to form 3D, 2D, 1D, and 0D structures. The decreased dimensionality leads to the emergence of unique properties. Broadband photoluminescence with large Stokes shift has been realized in corrugated-2D, 1D, and 0D metal halide hybrids, as a result of exciton self-trapping or excited state structural reorganization. The versatility of this class of hybrid materials suggests that there is a vast parameter space to explore novel structures with new and useful properties. To advance the research in organic–inorganic metal halide hybrids, the following major issues and challenges need to be addressed:

(i) The general design principles to assemble organic–inorganic metal halide hybrids with controlled structure, composition and dimensionality need to be further developed. A better understanding on how the shape, size, and other characteristics of organic cations would affect the crystal structures of organic metal halide hybrids is needed. Besides metal halide octahedra, can other polyhedrons, such as tetrahedra and pyramid, be used as basic building blocks to assemble 1D, 2D and 3D structures through corner-, edge-, or face-sharing? Can metal halide clusters, such as fused octahedral metal halide dimers and trimers, be used to assemble new 1D, 2D, and 3D structures?

(ii) Comprehensive understanding of the photophysical processes and electronic properties of organic–inorganic metal halide hybrids is needed. Although the exciton self-trapping mechanism can well explain the strongly Stokes shifted broadband emissions from low dimensional organic metal halide hybrids, the excited state dynamics and kinetics are still not well understood. Moreover, the electronic properties of low dimensional organic metal halide hybrids have not been fully characterized. And it is still not clear how the topology of metal halide frameworks and their interactions with organic building blocks affect the charge transport and exciton diffusion. Organic–inorganic metal halide hybrids provide a perfect platform for fundamental studies of strongly coupled electronic and structural dynamics evolving on ultrafast timescales that arise...
from the localization and subsequent relaxation of charge carriers and excitons in materials with tunable dimensionalities and deformable lattices.

(iii) The photo and chemical stability of organic–inorganic metal halide hybrids are still relatively poor as compared to conventional organic and inorganic semiconductors. 3D perovskite materials are known to suffer from oxygen, moisture, light, and temperature. Low dimensional materials are reported to be more stable because of the protection of organic moieties, which make them promising candidates in a variety of applications. Nevertheless, there is a need to understand the fundamental mechanisms for the degradation of organic–inorganic metal halide hybrids under external stimuli such as O2, H2O, heat, light, and electric field stresses, and establish rules for designing materials with high stability.

Overall, the research in organic–inorganic metal halide hybrids is still in the early stage, although tremendous progress has been achieved in the past few years, especially for ABX3 type perovskite materials. The unlimited combinations of organic cations and inorganic metal halide anions offer tremendous opportunities for the development of new materials with novel physical and chemical properties that are not readily available in the existing materials. We hope this brief overview could provide some insights in developing organic–inorganic metal halide hybrids beyond perovskites, and stimulate more research efforts in this exciting field.

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References
[1] Møller CK. Crystal structure and photoconductivity of cesium plombohalides. Nature. 1958;182:1436–1436.
[2] Mitzi D, Wang S, Feild C, et al. Conducting layered organic-inorganic halides containing < 110 > - oriented perovskite sheets. Science. 1995;267:1473–1476.
[3] Kagan C, Mitzi D, Dimitrakopoulos C. Organic-inorganic hybrid materials as semiconducting channels in thin-film field-effect transistors. Science. 1999;286:945–947.
[4] Era M, Morimoto S, Tsutsui T, et al. Organic-inorganic heterostructure electroluminescent device using a layered perovskite semiconductor (C6H5H2C2H4NH3)2PbI4. Appl Phys Lett. 1994;65:676–678.
[5] Kojima A, Teshima K, Shirai Y, et al. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. J Am Chem Soc. 2009;131:6050–6051.
[6] Tan Z-K, Moghaddam RS, Lai ML, et al. Bright light-emitting diodes based on organometal halide perovskite. Nat Nanotechnol. 2014;9:687–692.
[7] Tyagi P, Arveson SM, Tisdale WA. Colloidal organohalide perovskite nanoplatelets exhibiting quantum confinement. J Phys Chem Lett. 2015;6:1911–1916.
[8] Dou LT, Wong AB, Yu Y, et al. Atomically thin two-dimensional organic-inorganic hybrid perovskites. Science. 2015;349:1518–1521.
[9] Zhang D, Yu Y, Bekenstein Y, et al. Ultrathin colloidal cesium lead halide perovskite nanowires. J Am Chem Soc. 2016;138:13155–13158.
[10] Schmidt LC, Perteégas A, González-Carrero S, et al. Nontemplate synthesis of CH3NH3PbBr3 perovskite nanoparticles. J Am Chem Soc. 2014;136:850–853.
[11] Yuan Z, Shu Y, Xin Y, et al. Highly luminescent nanoscale quasi-2D layered lead bromide perovskites with tunable emissions. Chem Commun. 2016;52:3887–3890.
[12] Dohner ER, Hoke ET, Karunadasa HI. Self-assembly of broadband white-light emitters. J Am Chem Soc. 2014;136:1718–1721.
[13] Yuan Z, Zhou C, Shu Y, et al. One-dimensional organic lead halide perovskites with efficient bluish white-light emission. Nat Commun. 2017;8:14051.
[14] Zhou C, Lin H, Tian Y, et al. Luminescent zero-dimensional organic metal halide hybrids with near-unity quantum efficiency. Chem Sci. 2018;9:586–593.
[15] Liu W, Lin Q, Li H, et al. Mn2+-doped lead halide perovskite nanocrystals with dual-color emission controlled by halide content. J Am Chem Soc. 2016;138:14954–14961.
[16] Parobek D, Roman BJ, Dong Y, et al. Exciton-to-dopant energy transfer in Mn-doped cesium lead halide perovskite nanocrystals. Nano Lett. 2016;16:7376–7380.
[17] Biswas A, Bakhatsalam R, Kundu J. Efficient exciton to dopant energy transfer in Mn2+-doped (C6H5NH3)2 PbBr4 two-dimensional (2D) layered perovskites. Chem Mater. 2017;29:7816–7825.
[18] Zhou C, Tian Y, Khabou O, et al. Manganese-doped one-dimensional organic lead bromide perovskites with bright white emissions. ACS Appl Mater Interfaces. 2017;9:40446–40451.
[19] Slavney AH, Hu T, Lindenberg AM, et al. A bismuth-halide double perovskite with long carrier recombination lifetime for photovoltaic applications. J Am Chem Soc. 2016;138:2138–2141.
[20] Sun Y-Y, Agiorgousis ML, Zhang P, et al. Chalcogenide perovskites for photovoltaics. Nano Lett. 2015;15:581–585.
[21] Lin H, Zhou C, Tian Y, et al. Bulk assembly of organic metal halide nanotubes. Chem Sci. 2017;8:8400–8404.
[22] Goldschmidt VM. Die gesetze der krystallochemie. Naturwissenschaften. 1926;14:477–485.
[23] Li C, Lu X, Ding W, et al. Formability of ABX$_3$ (X = F, Cl, Br, I) halide perovskites. Acta Crystallogr B. 2008;64:702–707.

[24] Kieslich G, Sun S, Cheetham AK. An extended tolerance factor approach for organic-inorganic perovskites. Chem Sci. 2015;6:3430–3433.

[25] Travis W, Glover ENK, Bronstein H, et al. On the application of the tolerance factor to inorganic and hybrid halide perovskites: a revised system. Chem Sci. 2016;7:4548–4556.

[26] Lee MM, Teuscher J, Miyasaka T, et al. Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. Science. 2012;338:643–647.

[27] Burschka J, Pellet N, Moon S-J, et al. Sequential deposition as a route to high-performance perovskite-sensitized solar cells. Nature. 2013;499:316–319.

[28] Buin A, Pietsch P, Xu J, et al. Materials processing routes to trap-free halide perovskites. Nano Lett. 2014;14:6281–6286.

[29] Yang WS, Noh JH, Jeon NJ, et al. High-performance photovoltaic perovskite layers fabricated through intramolecular exchange. Science. 2015;348:1234–1237.

[30] Saliba M, Orlandi S, Matsu T, et al. A molecularly engineered hole-transporting material for efficient perovskite solar cells. Nat Energy. 2016;1:15017.

[31] Wang A, Yan X, Zhang M, et al. Controlled synthesis and characterization of a Sn-deficient perovskite derivative Cs$_2$SnI$_6$. Chem Mater. 2016;28:1348–1354.

[32] Manser JS, Christians JA, Kamat PV. Intriguing optical properties of metal halide perovskites. Chem Mater. 2016;28:6968–6974.

[33] Stranks SD, Snaith HJ. Metal-halide perovskites for photovoltaic and light-emitting devices. Nat Nanotechnol. 2015;10:391–402.

[34] Wang Y, Sun HD. All-inorganic metal halide perovskite nanostructures: from photophysics to light-emitting applications. Small Methods. 2018;2:1700252.

[35] Dang Y, Zhong C, Zhang G, et al. Crystallographic investigations into properties of acentric hybrid perovskite single crystals NH(CH$_3$)$_3$SnX$_3$ (X = Cl, Br). Chem Mater. 2016;28:6968–6974.

[36] Saparov B, Sun J-P, Meng W, et al. Thin-film deposition and characterization of a Sn-deficient perovskite derivative Cs$_2$SnI$_6$. Chem Mater. 2016;28:2315–2322.

[37] Wang A, Yan X, Zhang M, et al. Controlled synthesis of lead-free and stable perovskite derivative Cs$_2$SnI$_6$ nanocrystals via a facile hot-injection process. Chem Mater. 2016;28:8132–8140.

[38] Yokoyama T, Cao DH, Stoumpos CC, et al. Overcoming short-circuit in lead-free CH$_3$NH$_3$SnI$_3$ perovskite solar cells via kinetically controlled gas-solid reaction film fabrication process. J Phys Chem Lett. 2016;7:776–782.

[39] Yokoyama T, Song T-B, Cao DH, et al. The origin of lower hole carrier concentration in methylammonium tin halide films grown by a vapor-assisted solution process. ACS Energy Lett. 2017;2:22–28.

[40] Jiang Y, Zhang H, Qiu X, et al. The air and thermal stabilities of lead-free perovskite variant Cs$_2$SnI$_6$ powder. Mater Lett. 2017;199:50–52.

[41] Seo DK, Gupta N, Whangbo MH, et al. Pressure-induced changes in the structure and band gap of CsGeX$_3$ (X = Cl, Br) studied by electronic band structure calculations. Inorg Chem. 1998;37:407–410.

[42] Li-Chuan T, Yia-Chung C, Jung-Yau H, et al. First principles calculations of linear and second-order optical responses in rhombohedrally distorted perovskite ternary halides, CsGeX$_3$ (X = Cl, Br, and I). JPN J Appl Phys. 2009;48:112402.

[43] Krishnamoorthy T, Ding H, Yan C, et al. Lead-free germanium iodide perovskite materials for photovoltaic applications. J Mater Chem A. 2015;3:23829–23832.

[44] Huang L-Y, Lambrecht WRL. Electronic band structure trends of perovskite halides: beyond Pb and Sn to Ge and Si. Phys Rev B. 2016;93:1109.

[45] Hong K, Le QV, Kim SY, et al. Low-dimensional halide perovskites: review and issues. J Mater Chem C. 2018;6:2189–2209.

[46] Chen P, Bai Y, Lyu M, et al. Progress and perspective in low-dimensional metal halide perovskites for optoelectronic applications. Solar Rrl. 2018;2:1700186.

[47] Zhang Q, Su R, Liu X, et al. High-quality whispering-gallery-mode lasing from cesium lead halide perovskite nanoplatelets. Adv Funct Mater. 2016;26:6238–6245.

[48] Morris LR, Siegal M, Stenger L, et al. Preparation of cubic chloro complex compounds of trivalent metals: Cs$_2$NaMCl$_6$. Inorg Chem. 1970;9:1771–1775.

[49] McClure ET, Ball MR, Windl W, et al. Cs$_2$AgBiX$_6$ (X = Br, Cl): new visible light absorbing, lead-free halide perovskite semiconductors. Chem Mater. 2016;28:1348–1354.

[50] Savory CN, Walsh A, Scanlon DO. Can Pb-free halide double perovskites support high-efficiency solar cells? ACS Energy Lett. 2016;1:949–955.

[51] Tran TT, Panelia JR, Chamorro JR, et al. Designing indirect–direct bandgap transitions in double perovskites. Mater Horiz. 2017;4:688–693.

[52] Wei F, Deng Z, Sun S, et al. The synthesis, structure and electronic properties of a lead-free hybrid inorganic-organic double perovskite (MA)$_2$KCl (MA = methylammonium). Mater Horiz. 2016;3:328–332.

[53] Volonakis G, Haghhiirad AA, Milot RL, et al. Cs$_2$InAgCl$_6$: a new lead-free halide double perovskite with direct band gap. J Phys Chem Lett. 2017;8:772–778.

[54] Xiao Z, Du KZ, Meng W, et al. Chemical origin of the stability difference between copper(1)- and silver(1)-based halide double perovskites. Angew Chem Int Ed. 2017;56:12107–12111.

[55] Zhao XG, Yang D, Sun Y, et al. Cu-In halide perovskite solar absorbers. J Am Chem Soc. 2017;139:6718–6725.

[56] Rosenbaum TF, Xu R, Husmann A, et al. Large magnetoresistance in non-magnetic silver chalcogenides. Nature. 1997;390:57–60.

[57] Yan B, Jansen M, Felser C. A large-energy-gap oxide topological insulator based on the superconductor BaBiO$_3$. Nat Phys. 2013;9:709–711.

[58] Hoefler SF, Trimmel G, Rath T. Progress on lead-free metal halide perovskites for photovoltaic applications: a overview. Monatsh Chem. 2017;148:1487–9826.

[59] Xiao Z, Zhou Y, Hosono H, et al. Bandgap optimization of perovskite semiconductors for photovoltaic applications. Chemistry. 2018;24:2305–2316.
Shamsi J, Dang Z, Bianchini P, et al. Colloidal synthesis of quantum confined single crystal CsPbBr$_3$ nanosheets with lateral size control up to the micrometer range. J Am Chem Soc. 2016;138:7240–7243.

Imran M, Di Stasio F, Dang Z, et al. Colloidal synthesis of strongly fluorescent CsPbBr$_3$ nanowires with width tunable down to the quantum confinement regime. Chem Mater. 2016;28:6450–6454.

Zhang YP, Liu JY, Wang ZY, et al. Synthesis, properties, and optical applications of low-dimensional perovskites. Chem Commun. 2016;52:13637–13655.

Min X, Pengchen Z, Gu S, et al. Research progress of low-dimensional perovskites: synthesis, properties and optoelectronic applications. J Semiconductors. 2017;38:19–27.

Misra RK, Cohen B-E, Iagher L, et al. Low-dimensional organic-inorganic halide perovskite: structure, properties, and applications. ChemSus Chem. 2017;10:3712–3721.

Koolyk M, Amgar D, Aharon S, et al. Kinetics of cesium lead halide perovskite nanoparticle growth; focusing and defocusing of size distribution. Nanoscale. 2016;8:6403–6409.

Zhang Q, Ha ST, Liu X, et al. Room-temperature near-infrared high-Q perovskite whispering-gallery planar nanolasers. Nano Lett. 2014;14:5995–6001.

Aamir M, Adhikari T, Sher M, et al. Cesium lead halide perovskite nanostructures: tunable morphology and halide composition. Chem Rev. 2017;117:1–10.

Saouma FO, Stoumpos CC, Song J, et al. Selective enhancement of optical nonlinearity in two-dimensional organic-inorganic lead iodide perovskites. Nat Commun. 2017;8:542.

Traore B, Pedesseau L, Assam L, et al. Composite nature of layered hybrid perovskites: assessment on quantum and dielectric confinements and band alignment. ACS Nano. 2018;12:3321–3332.

Stoumpos CC, Cao DH, Clark DJ, et al. Ruddlesden-Popper hybrid lead iodide perovskite 2D homologous semiconductors. Chem Mater. 2016;28:2852–2867.

Gelvez-Rueda MC, Hutter EM, Cao DH, et al. Interconversion between free charges and bound excitons in 2D hybrid lead halide perovskites. J Phys Chem C. 2017;121:26566–26574.

Huo C, Cai B, Yuan Z, et al. Two-dimensional metal halide perovskites: theory, synthesis, and optoelectronics. Small Methods. 2017;1:1600018.

Yaffe O, Chernikov A, Norman ZM, et al. Excitons in ultrathin organic-inorganic perovskite crystals. Phys Rev B. 2015;92:716.

Niu W, Eiden A, Vijaya Prakash G, et al. Exfoliation of self-assembled 2D organic-inorganic perovskite semiconductors. Appl Phys Lett. 2014;104:171111.

Chen J, Wang Y, Gan L, et al. Generalized self-doping engineering towards ultrathin and large-sized two-dimensional homologous perovskites. Angew Chem Int Ed. 2017;56:14893–14897.

Soe CMM, Nie W, Stoumpos CC, et al. Understanding film formation morphology and orientation in high member 2D Ruddlesden-Popper perovskites for high-efficiency solar cells. Adv Energy Mater. 2018;8:1700979.

Cao DH, Stoumpos CC, Farha OK, et al. 2D homologous perovskites as light-absorbing materials for solar cell applications. J Am Chem Soc. 2015;137:7843–7850.

Sichert JA, Tong Y, Mutz N, et al. Quantum size effect in organometal halide perovskite nanoplatelets. Nano Lett. 2015;15:6521–6527.

Shi E, Gao Y, Finkenauer BP, et al. Two-dimensional halide perovskite nanomaterials and heterostructures. Chem Soc Rev. 2018;47:1, doi:10.1039/C7CS00886D.

Yuan Z, Shu Y, Tian Y, et al. A facile one-pot synthesis of deep blue luminescent lead bromide perovskite microdisks. Chem Commun. 2015;51:16385–16388.
[95] Neogi I, Bruno A, Bahulayan D, et al. Broadband-emitting 2D hybrid organic-inorganic perovskite based on cyclohexane-bis(methylammonium) cation. ChemSus Chem. 2017;10:3759–3772.

[96] Que CJ, Mo CJ, Li ZQ, et al. Perovskite-like organic-inorganic hybrid lead iodide with a large organic cation incorporated within the layers. Inorg Chem. 2017;56:52467–4722.

[97] Zhang T, Xie L, Chen L, et al. In situ fabrication of highly luminescent bifunctional amino acid crosslinked 2D/3D NH3C4H9COO(CH3NH3PbBr3)n perovskite films. Adv Funct Mater. 2017;27:1603568.

[98] Mao L, Wu Y, Stoumpos CC, et al. Tunable white-light emission in single-cation-templated three-layered 2D perovskites (CH3(CH2)3NH3)4Pb3Br10−xClx. J Am Chem Soc. 2017;139:11956–11963.

[99] Soe CMM, Stoumpos CC, Kepenekian M, et al. New type of 2D organic–inorganic perovskite compound stabilized by N=N bonds and photovoltaic performance. J Am Chem Soc. 2017;139:16297–16309.

[100] Mao L, Ke W, Pedesseau L, et al. Hybrid Dion-Jacobson 2D lead iodide perovskites. J Am Chem Soc. 2018;140:3775–3783.

[101] Smith IC, Hoke ET, Solis-Ibarra D, et al. A layered hybrid perovskite solar-cell absorber with enhanced moisture stability. Angew Chem Int Ed. 2014;53:11232–11235.

[102] Tsai H, Nie W, Blancon JC, et al. High-efficiency two-dimensional Ruddlesden-Popper perovskite solar cells. Nature. 2016;536:312–316.

[103] Wang N, Cheng L, Ge R, et al. Perovskite light-emitting diodes based on solution-processed self-organized multiple quantum wells. Nat Photonics. 2016;10:699–704.

[104] Tsai H, Nie W, Blancon JC, et al. Stable light-emitting diodes using phase-pure Ruddlesden–Popper layered perovskites. Adv Mater. 2018;30:1704217.

[105] Zhang H, Liao Q, Wu Y, et al. 2D Ruddlesden-Popper perovskites microring laser array. Adv Mater. 2018;30:1706186.

[106] Saparov B, Mitzi DB. Organic-inorganic perovskites: structural versatility for functional materials design. Chem Rev. 2016;116:4558–4596.

[107] Mitzi DB. Templating and structural engineering in organic-inorganic perovskites. Dalton T. 2001:1–12.

[108] Li Y, Lin C, Zheng G, et al. Novel <110> oriented one-dimensional organic-inorganic perovskite compound stabilized by N,N-(3-Aminopropyl)imidazole with improved optical properties. Chem Mater. 2006;18:3463–3469.

[109] Mao L, Wu Y, Stoumpos CC, et al. White-light emission and structural distortion in new corrugated two-dimensional lead bromide perovskites. J Am Chem Soc. 2017;139:5210–5215.

[110] Guan J, Tang Z, Guloy AM. α-[NH3(CH3)2NH3]SnI3: a new layered perovskite structure. Chem Commun. 1999;0:1833–1834.

[111] Zhang T, Dar MI, Li G, et al. Bication lead iodide 2D perovskite component to stabilize inorganic α-CsPbI3 perovskite phase for high-efficiency solar cells. Sci Adv. 2017;3:e1700841.

[112] Ye S, Xiao F, Pan Y, et al. Phosphors in phosphor-converted white light-emitting diodes: recent advances in materials, techniques and properties. Mat Sci Eng R. 2010;71:1–34.

[113] Wu Z, Ji C, Sun Z, et al. Broadband white-light emission with a high color rendering index in a two-dimensional organic–inorganic hybrid perovskite. J Mater Chem C. 2018;6:1171–1175.

[114] Yuan Z, Zhou C, Messier J, et al. A microscale perovskite as single component broadband phosphor for down-conversion white-light-emitting devices. Adv Opt Mater. 2016;4:2009–2015.

[115] Smith MD, Karunadasa HI. White-light emission from layered halide perovskites. Acc Chem Res. 2018;51:619–627.

[116] Dohner ER, Jaffe A, Bradshaw LR, et al. Intrinsic white-light emission from layered hybrid perovskites. J Am Chem Soc. 2014;136:13154–13157.

[117] Hu T, Smith MD, Dohner ER, et al. Mechanism for broadband white-light emission from two-dimensional (110) hybrid perovskites. J Phys Chem Lett. 2016;7:2258–2263.

[118] Wang S, Mitzi DB, Feild CA, et al. Synthesis and characterization of [NH2C(I):NH2]3SnI5 (M = Sn, Pb): stereochemical activity in divalent tin and lead halides containing single <110> perovskite sheets. J Am Chem Soc. 1995;117:5297–5302.

[119] Mousdis G A, Gionis V, Papavassiliou G C, et al. Preparation, structure and optical properties of [CH3SC(NH2)2NH2]3Pb3I10 and [CH3SC(NH2)2NH2]3Pb2Br8 and [CH3SC(NH2)2NH2]3PbCl3, CH3SC(NH2)2NH2Cl. J Mater Chem 1998:8:2259–2262.

[120] Mitzi DB, Liang K, Wang S. Synthesis and characterization of [NH2C(I):NH2]3AsSnI5 with A = iodoformamidinium or formamidinium: the chemistry of cyanamide and tin(II) iodide in concentrated aqueous hydriodic acid solutions. Inorg Chem. 1998;37:321–327.

[121] Zhou C, Tian Y, Wang M, et al. Low-dimensional organic tin bromide perovskites and their photoinduced structural transformation. Angew Chem Int Ed. 2017;56:9018–9022.

[122] Leblanc N, Mercier N, Zorina L, et al. Large spontaneous polarization and clear hysteresis loop of a room-temperature hybrid ferroelectric based on mixed-halide [BiI3Cl2] polar chains and methylviologen dication. J Am Chem Soc. 2011;133:14924–14927.

[123] Zhang W, Tao K, Ji C, et al. (C6H13N)2BiI5: a one-dimensional lead-free perovskite-derivative photoconductive light absorber. Inorg Chem. 2018;57:4239–4243.

[124] Trigui A, Abid H, Mlayah A, et al. Optical properties and vibrational studies of a new self assembled organic-inorganic nanowire crystal (Cs6H13N3)2Pb3I10. Synth Met. 2012;162:1731–1736.

[125] Sun X-F, Li P-F, Liao W-Q, et al. Notable broad dielectric relaxation and highly efficient red photoluminescence in a perovskite-type compound: (N-Methylpyrrolidinium)MnCl3. Inorg Chem. 2017;56:12193–12198.

[126] Ye H-Y, Zhou Q, Niu X, et al. High-temperature ferroelectricity and photoluminescence in a hybrid organic–inorganic compound: (3-Pyrrolinium)MnCl3. J Am Chem Soc. 2015;137:13148–13154.
[127] Zhang Y, Liao WQ, Fu DW, et al. The first organic-inorganic hybrid luminescent multiferroic: (pyrrologinium)MnBr3. Adv Mater. 2015;27:3942–3946.

[128] Zhang Y, Liao W-Q, Fu D-W, et al. Highly efficient red-light emission in an organic-inorganic hybrid ferroelectric: (Pyrrolidinium)MnCl3. J Mater Chem Soc. 2015;137:4928–4931.

[129] Sun C, Xu G, Jiang X-M, et al. Design strategy for improving optical and electrical properties and stability of lead-halide semiconductors. J Am Chem Soc. 2018;140:2805–2811.

[130] Li M-Q, Hu Y-Q, Bi L-Y, et al. Structure tunable organic–inorganic bismuth halides for an enhanced two-dimensional lead-free light-harvesting material. Chem Mater. 2017;29:5463–5467.

[131] Akkerman QA, Abdelhady AL, Manna L. Zero-dimensional cesium lead halides: history, properties and challenges. J Phys Chem Lett. 2018;9:2326–2337.

[132] Wang Z-P, Wang J-Y, Li J-R, et al. [Bmim]2SbCl5: a main group metal-containing liquid exhibiting tunable photoluminescence and white-light emission. Chem Commun. 2015;51:3094–3097.

[133] Zhou C, Worku M, Neu J, et al. Facile preparation of light emitting organic metal halide crystals with near-unity quantum efficiency. Chem Mater. 2018;30:2374–2378.

[134] Xu L-J, Sun C-Z, Xiao H, et al. Green-light-emitting diodes based on tetrabromide manganese(II) complex through solution process. Adv Mater. 2017;29:1605739.

[135] Zhou C, Lin H, Shi H, et al. A zero-dimensional organic seesaw-shaped tin bromide with highly efficient strongly Stokes-shifted deep-red emission. Angew Chem Int Ed. 2018;57:1021–1024.

[136] Kawai T, Ishii A, Kitamura T, et al. Optical absorption in band-edge region of (CH3NH3)3Bi2I9 single crystals. J Phys Soc Jpn. 1996;65:1464–1468.

[137] Park BW, Philippe B, Zhang X, et al. Bismuth based hybrid perovskites A3Bi2I9 (A: methylammonium or cesium) for solar cell application. Adv Mater. 2015;27:6806–6813.

[138] Hoye RL, Brandt RE, Osherov A, et al. Methylammonium bismuth iodide as a lead-free, stable hybrid organic-inorganic solar absorber. Chem-Eur J. 2016;22:2605–2610.

[139] Abulikemu M, Ould-Chikh S, Miao X, et al. Optoelectronic and photovoltaic properties of the air-stable organohalide semiconductor (CH3NH3)2Bi3I9. J Mater Chem A. 2016;4:12504–12515.

[140] Smith MD, Watson BL, Dauskardt RH, et al. Broadband emission with a massive Stokes shift from sulfonium PbBr hybrids. Chem Mater. 2017;29:7083–7087.

[141] Goede O, Heimbroidt W. Optical properties of (Zn, Mn) and (Cd, Mn) chalcogenide mixed crystals and superlattices. Phys Status Solidi B. 1988;146:11–62.

[142] Pradhan N, Goorskey D, Thessing J, et al. An alternative of CdSe nanocrystal emitters: pure and tunable impurity emissions in ZnSe nanocrystals. J Am Chem Soc. 2005;127:17586–17587.

[143] Bhargava RN, Gallagher D, Hong X, et al. Optical properties of manganese-doped nanocrystals of ZnS. Phys Rev Lett. 1994;72:416–419.

[144] Norris D, Yao N, Charnock FT, et al. High-quality manganese-doped ZnSe nanocrystals. Nano Lett. 2001;1:3–7.

[145] Bol AA, Meijerink A. Long-lived Mn2+ emission in nanocrystalline ZnS: Mn2+. Phys Rev B. 1998;58:R15997–R16000.

[146] van der Stam W, Geueches JJ, Altantzis T, et al. Highly emissive divalent-ion-doped colloidal CsPb1–xMxBr3 perovskite nanocrystals through cation exchange. J Am Chem Soc. 2017;139:4087–4097.

[147] Tan Z, Li J, Zhang C, et al. Highly efficient blue-emitting Bi-doped Cs2SnCl6 perovskite variant: photoluminescence induced by impurity doping. Adv Funct Mater. 2018;1801131.

[148] Balakrishnan SK, Kamat PV. Au-CsPbBr3 hybrid architecture: anchoring gold nanoparticles on cubic perovskite nanocrystals. ACS Energy Lett. 2017;2:88–93.

[149] Pan G, Bai X, Yang D, et al. Doping lanthanide into perovskite nanocrystals: highly improved and expanded optical properties. Nano Lett. 2017;17:8005–8011.

[149] Adhikari SD, Dutta SK, Dutta A, et al. Chemically tailoring the dopant emission in manganese-doped CsPbCl3 perovskite nanocrystals. Angew Chem Int Ed. 2015;56:8746–8750.

[150] He M, Cheng Y, Yuan R, et al. Mn-doped cesium lead halide perovskite nanocrystals with dual-color emission for WLED. Dyes Pigments. 2018;152:146–154.

[151] Lin CC, Xu KY, Wang D, et al. Luminescent manganese-doped CsPbCl3 perovskite quantum dots. Sci Rep. 2017;7:3.

[152] Liu HW, Wu ZN, Shao JR, et al. CsPb0.5Mnx1–xCl3 perovskite quantum dots with high Mn substitution ratio. ACS Nano. 2017;11:2239–2247.

[153] Arunkumar P, Gil KH, Won S, et al. Colloidal organolead halide perovskite with a high Mn solubility limit: a step toward Pb-free luminescent quantum dots. J Mater Chem Lett. 2017;8:4161–4166.