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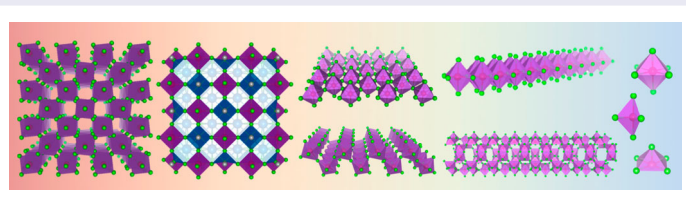
Organic–inorganic metal halide hybrids beyond perovskites

Chenkun Zhou^a, Haoran Lin^a, Sujin Lee^a, Maya Chaaban^b and Biwu Ma^{a,b,c}

^aDepartment of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, FL, USA; ^bDepartment of Chemistry and Biochemistry, Florida State University, Tallahassee, FL, USA; ^cMaterials Science and Engineering Program, Florida State University, Tallahassee, FL, USA

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 ABX₃ 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 ABX₃ perovskite. These hybrid materials exhibit exciting new properties with potential applications in a variety of areas.

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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 CsPbX₃ (X = Cl, Br, I) were discovered [1]. In 1990s, Mitzi et al. discovered a series of two-dimensional (2D) organic inorganic hybrids containing < 110 > 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 nanoplatelets exhibiting quantum confinement effects [7]. Yang group reported an atomically thin 2D (C₄H₉NH₃)₂PbBr₄, which exhibits efficient photoluminescence and unusual

CONTACT Biwu Ma bma@fsu.edu Department of Chemical and Biomedical Engineering, FAMU-FSU College of Engineering, Tallahassee, FL, 32310, USA; Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL, 32306, USA; Materials Science and Engineering Program, Florida State University, Tallahassee, FL, 32306, USA

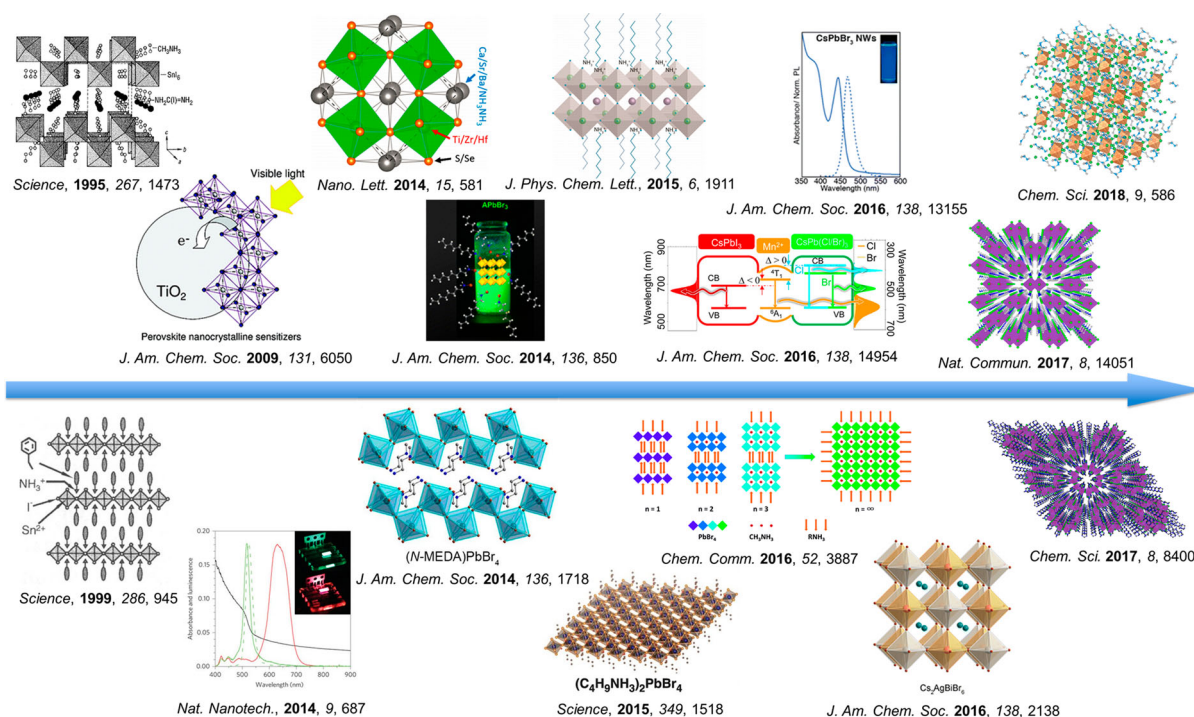


Figure 1. The development of organic-inorganic metal halide hybrids over the years. From the discovery of 2D structure containing $< 100 >$ or $< 110 >$ layers to the synthesis of colloidal nanoparticles, nanoplatelets, nanowires, chalcogenide, and double perovskites, the metal halide hybrids show promise 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].

structure relaxation [8]. 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 $\text{CH}_3\text{NH}_3\text{PbX}_3$ 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 ($\text{A}_2\text{B}^{\text{I}}\text{B}^{\text{III}}\text{X}_6$), 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

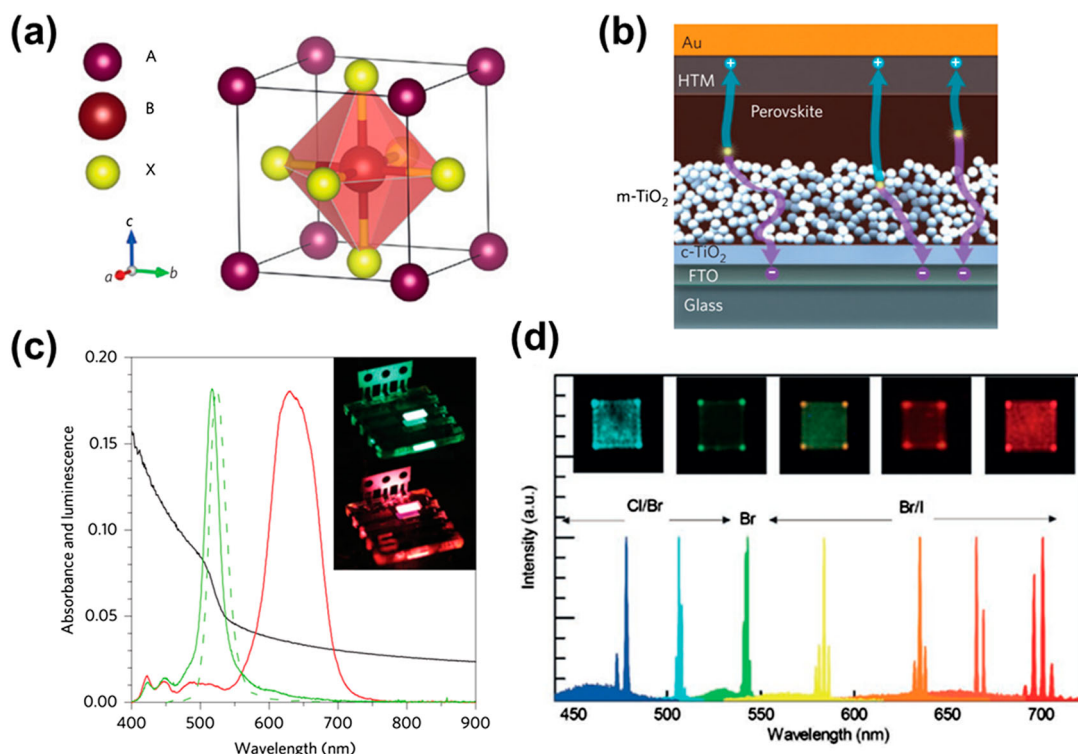


Figure 2. (a) ABX_3 perovskite crystal structure, in which $A = CH_3NH_3^+$ or Cs^+ , $B = Pb^{2+}$ or Sn^{2+} , and $X = I^-$, Br^- , Cl^- , or mixtures thereof. (b) Illustration of the charge generation processes in a ‘perovskite-sensitized’ solar cell. (c) Absorption (black), normalized electroluminescence (green, solid) and normalized photoluminescence (green, dashed) spectra of $CH_3NH_3PbBr_3$ perovskite. Normalized electroluminescence spectrum of $CH_3NH_3PbBr_2I$ mixed halide perovskite is shown in red. Inset image: Uniform green and red electroluminescence. (d) High-quality whispering-gallery-mode lasing from cesium lead halide perovskite nanoplatelets. Reproduced from Ref. [6,32,47].

the ABX_3 could be regarded as a metal halide framework constructed by corner-sharing BX_6 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 ABX_3 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 μ 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, B^{2+} in most cases is Pb^{2+} or Sn^{2+} .

The current intense research on metal halide perovskites is prompted by the success of perovskite solar cells, after the report of using $MAPbBr_3$ and $MAPbI_3$ 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 Sn^{2+} could be easily oxidized to Sn^{4+} , 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 ABX_3 metal halide perovskites is the double perovskite, which has switched to a quaternary $A^I_2B^IVB^{III}X_6$ formula, with both monovalent and trivalent metal ions coexist in the same crystal. Figure 3(a)

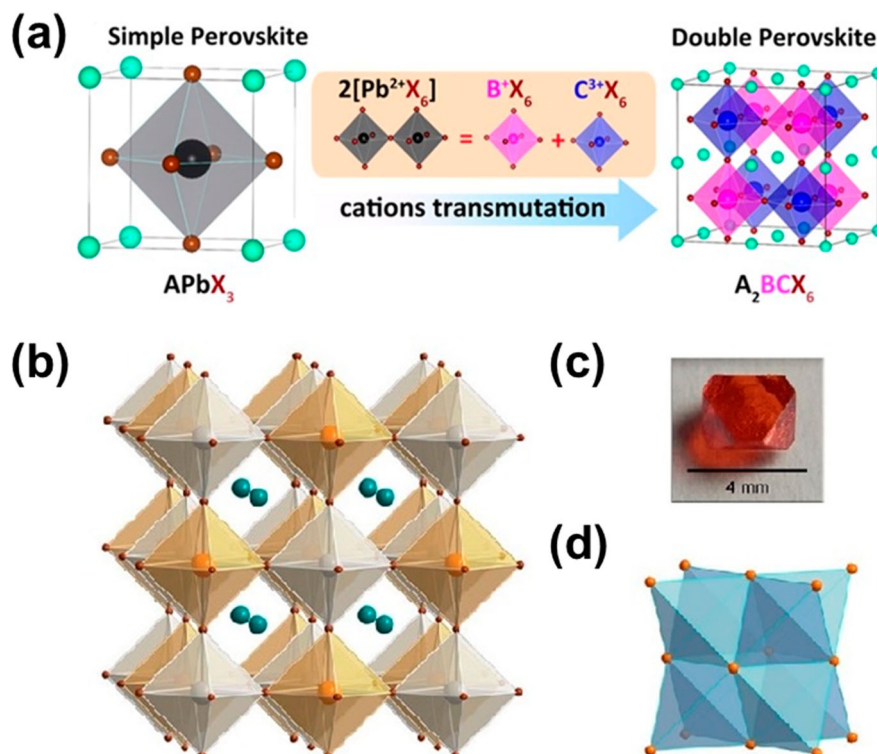


Figure 3. (a) Illustration of cations transmutation strategy (by converting $2Pb^{2+}$ to pair of $[B^+ + C^{3+}]$) to design Pb-free halide double perovskites. (b) X-ray structure of the ordered double perovskite $Cs_2AgBiBr_6$. Orange, gray, turquoise, and brown spheres represent Bi, Ag, Cs, and Br atoms, respectively. (c) Photograph of a single crystal of $Cs_2AgBiBr_6$. (d) The Bi^{3+} face-centered-cubic sublattice in $Cs_2AgBiBr_6$, 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 $B^I X_6$ or $B^{III} X_6$ shares corners with six adjacent octahedra containing different metal ions to form a 3D network. It could also be regarded as the B^{2+} in an 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 $Cs_2NaM^{III}Cl_6$ 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 $Cs_2AgBiCl_6$ and $Cs_2AgBiBr_6$ 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 $(MA)_2KBiCl_6$ was also discovered with a large indirect bandgap of 3.0 eV. Supported by theoretical studies [50,51], $(MA)_2TlBiBr_6$ and $Cs_2InAgCl_6$ 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 ABX_3 structure are oxide and chalcogenide perovskites, in which A is a bivalent cation and B is a tetravalent cation, 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 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

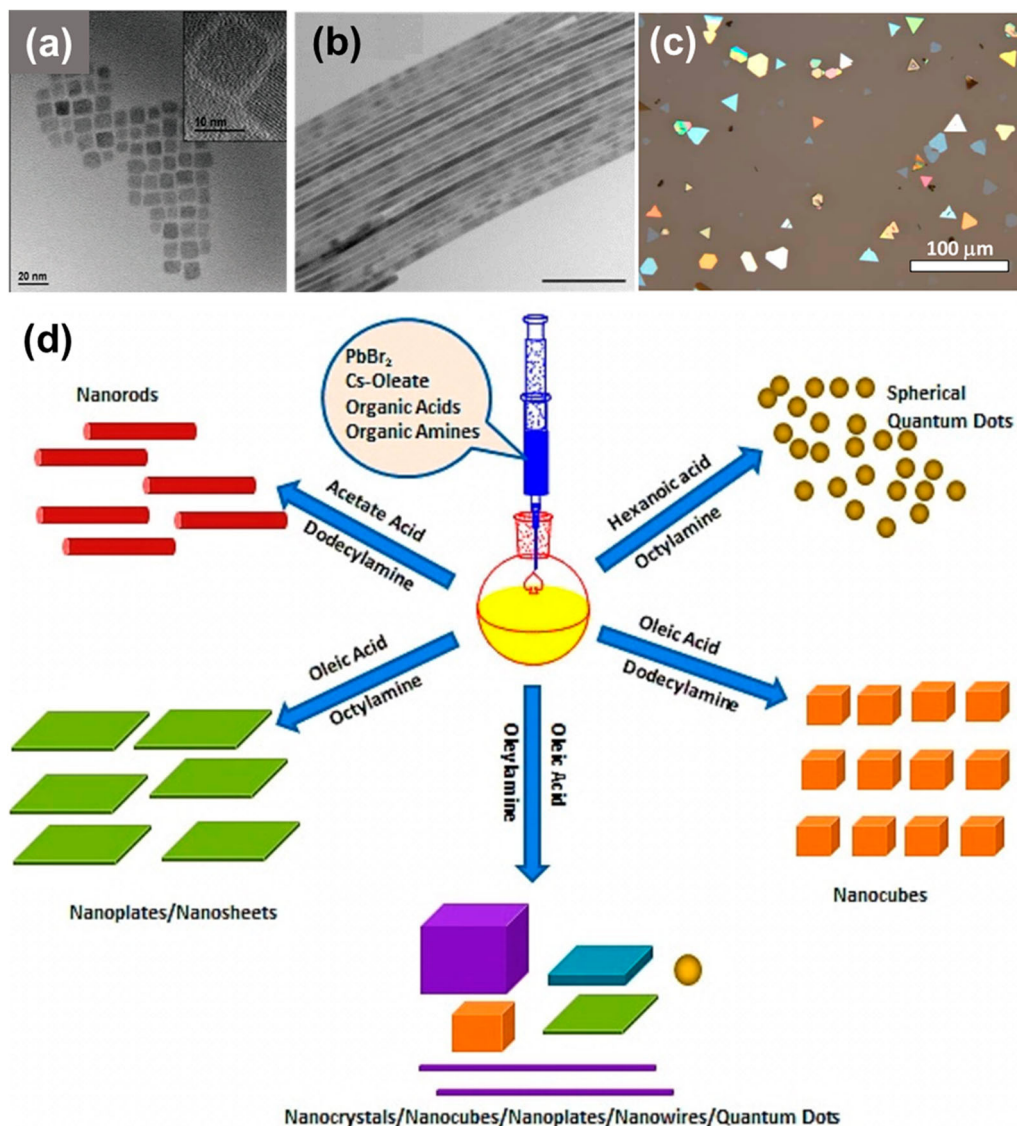


Figure 4. TEM images of lead halide perovskite (a) nanocubes, (b) nanowires, and (c) nanoplatelets, (d) Effect of capping agent on the morphology of CsPbX₃ nanoparticles. Reproduced from Ref. [63,79–81].

difference between ‘morphological’ and ‘molecular level’ low-dimensionalities. Morphological low-dimensional metal halide perovskites include ‘2D nanoplatelets’ [60–62], ‘1D nanowire or nanorods’ [63–66], ‘0D quantum dots’ [67,68], *etc.* These nanoscale materials might have quantum confinement in at least one direction. While intrinsically, they are still made of corner-sharing metal halide octahedra and their crystallographic structures inside are identical to that of bulk metal halide perovskites. Therefore, their chemical formulas are still expressed by ABX₃ and their properties are corresponding 3D ABX₃ perovskites with quantum confined effects. For instance, all-inorganic CsPbX₃ nanocrystals are found to have much higher stability than organic metal halide perovskites MAPbX₃, and exhibit narrow emissions with high PLQEs [69,70], which made them highly attractive for lasing and LEDs [34]. Tuning the

photoluminescence of cesium lead halide perovskites could be realized by both compositional control and quantum size engineering [71,72]. It was demonstrated that by changing the capping organic ligand, the morphology of CsPbX₃ could be effectively tuned from nanocubes to nanowires and nanoplatelets with different sizes (Figure 4) [73–75]. The synthesis, properties, and applications of morphological low dimensional metal halide perovskites have been well reviewed in several publications [45,46,65,76–78].

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'B_nX_{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 extreme cases 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

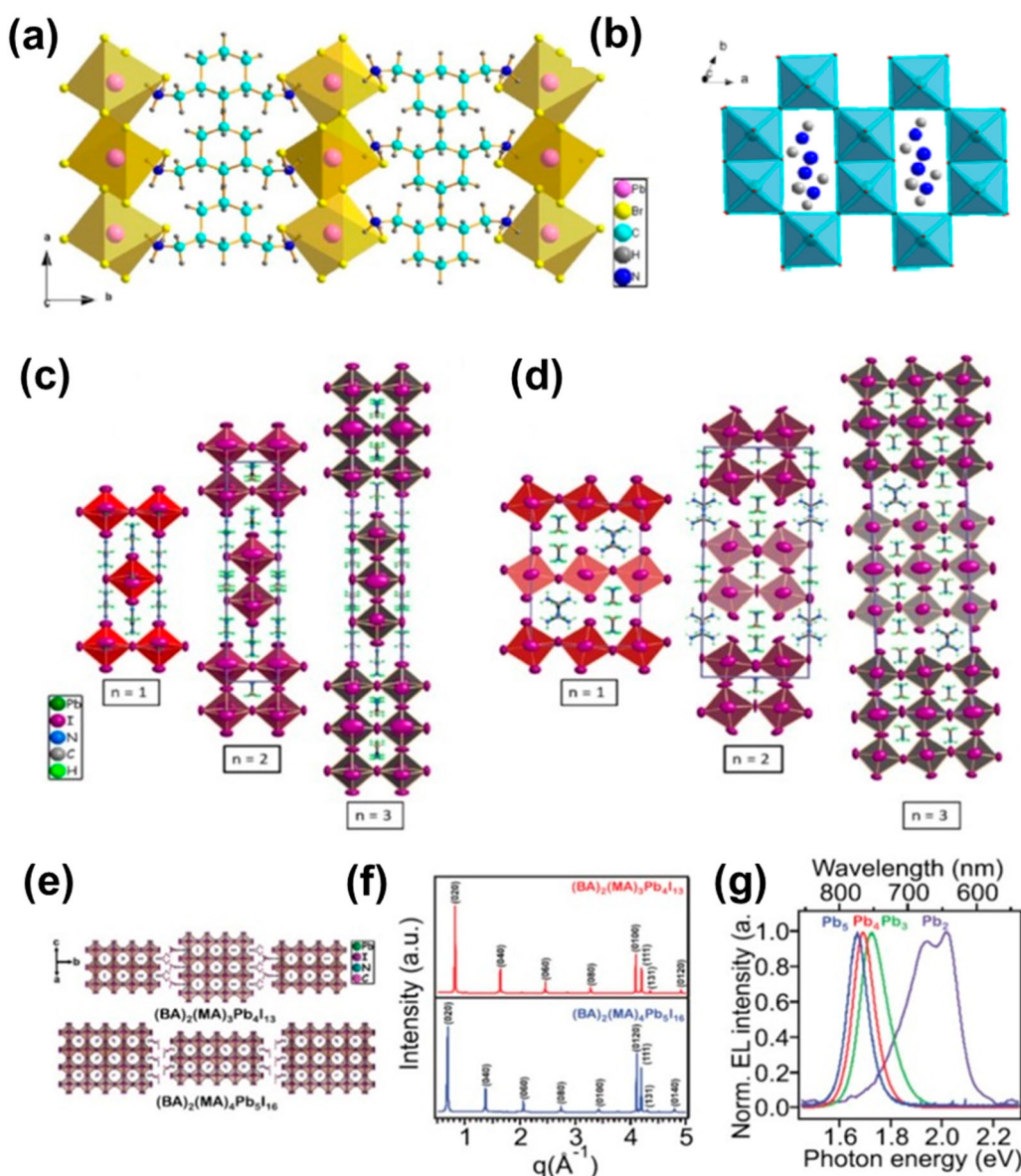


Figure 5. (a) Crystal packing diagram for (CyBMA)PbBr₄ showing propagation of [PbBr₆]⁴⁻ octahedra along the ac-plane. (b) Crystal structure of (H₂Aepz)₃Pb₄I₁₄ with larger organic cations incorporated within the perovskite-like PbI layered structure. View of the unit cells of the (GA)(MA)_nPb_nI_{3n+1} ($n = 1-3$) 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)₃Pb₄I₁₃ and (bottom) (BA)₂(MA)₄Pb₅I₁₆ layered perovskites. (f) PXRD of (BA)₂(MA)₃Pb₄I₁₃ and (BA)₂(MA)₄Pb₅I₁₆ (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 EA₄Pb₃Br_{10-x}Cl_x (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 $a_p \times \sqrt{2}a_p$ lattice parameters, where a_p is the lattice parameter of cubic 3D perovskites [107]. Mitzi et al. reported the first corrugated-2D perovskite [NH₂C(I) = NH₂]₂(CH₃NH₃)_mSn_mI_{3m+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 = *N*¹-methylethane-1,2-diammonium; EDBE = 2,2'-(ethylenedioxy)bis(ethylammonium); 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

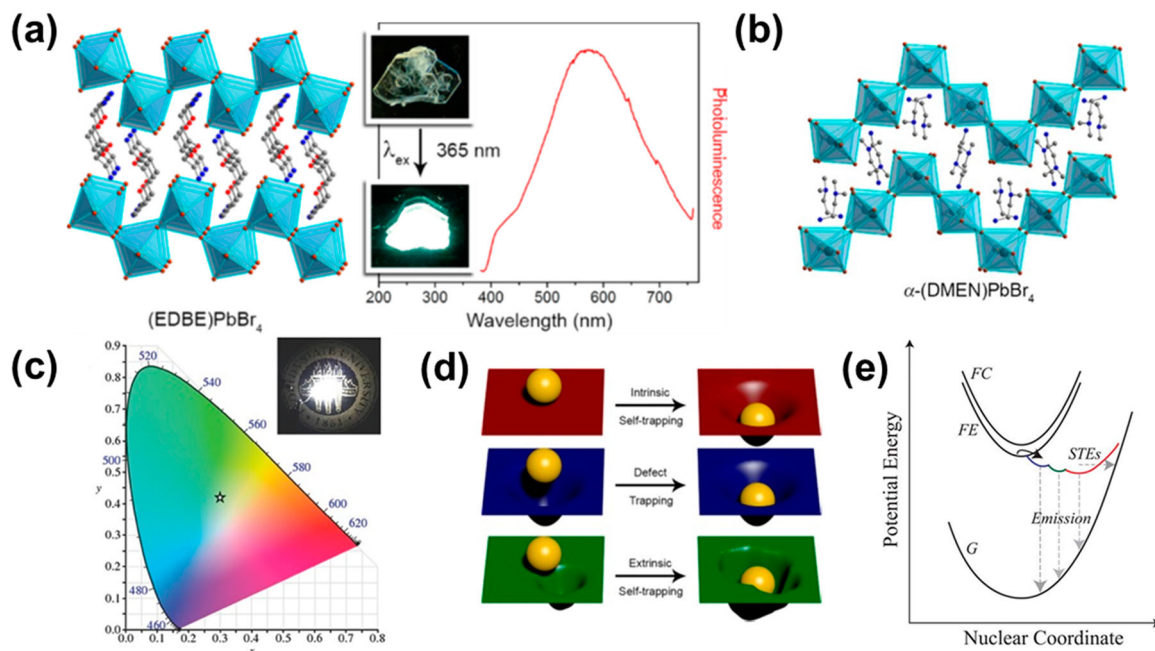


Figure 6. (a) X-ray crystal structure of the (110) perovskite (EDBE)PbBr₄ and its emission spectrum. Inset: Photographs of an (EDBE)PbBr₄ crystal. (b) Crystal Structure of white-emitting α -(DMEN)PbBr₄ with 3×3 structure (α -DMEN = N¹,N¹-dimethylethane-1,2-diammonium). (c) CIE coordinates for a white LED based on microscale EDBEPbBr₄ (inset) Image of a UV-pumped white LED (operated at 3.0 V). (d) Schematic of self-trapping, trapping at permanent defects, and self-trapping influenced by permanent defects represented by a ball interacting with a rubber sheet. (e) Schematic of the adiabatic potential energy curves of the ground state (GS), free-exciton state (FE), free-carrier state (FC), and various excited states (STEs) in a configuration space. The horizontal dashed line shows possible nonradiative decay processes of the STEs. Reproduced from Ref. [109,114–117].

still relatively low. (N-MEDA)PbBr_{4-x}Cl_x ($x = 0$ – 1.2) shows the maximum PLQE of 1.5%. The most efficient white light emitting corrugated-2D hybrid, EDBEPbBr₄, 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 PLQEs 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, $[\text{NH}_2\text{C}(\text{I}) = \text{NH}_2]_2(\text{CH}_3\text{NH}_3)_m\text{Sn}_m\text{I}_{3m+2}$, to $[\text{NH}_2\text{C}(\text{I}) = \text{NH}_2]_2(\text{CH}_3\text{NH}_3)\text{SnI}_5$ 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 $\text{C}_4\text{N}_2\text{H}_{14}^{2+}$ 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 excited

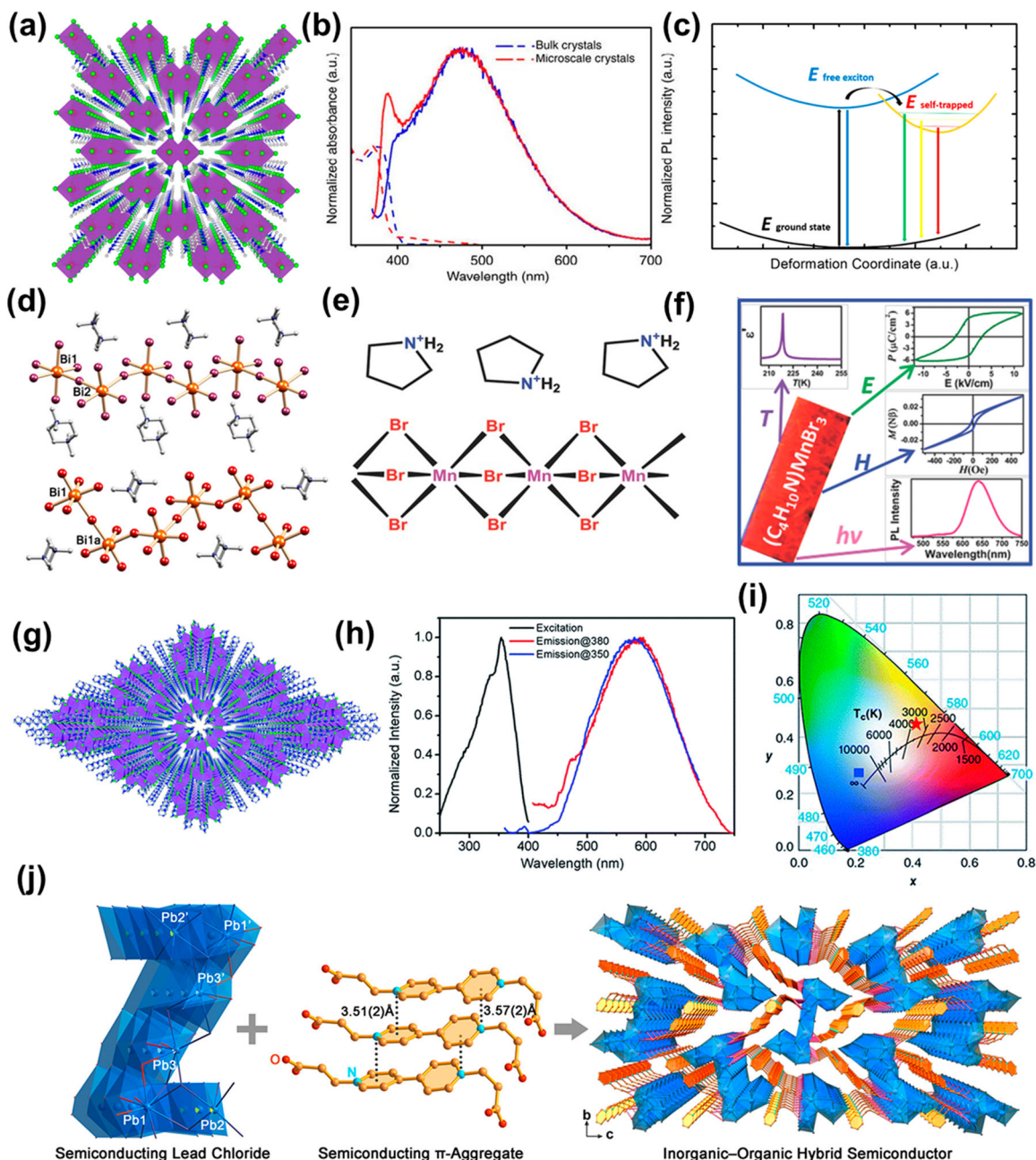


Figure 7. (a) Structure of 1D perovskite $C_4N_2H_{14}PbBr_4$ (red spheres: lead atoms; green spheres: bromine atoms; blue spheres: nitrogen atoms; gray spheres: carbon atoms; purple polyhedrons: $PbBr_6^{4-}$ octahedra; hydrogen atoms were hidden for clarity). (b) Absorption (dash lines) and emission (solid lines, excited at 360 nm) spectra of the bulk and microscale 1D perovskite $C_4N_2H_{14}PbBr_4$ at room temperature. (c) Configuration coordinate diagram for the coexisting of free and self-trapped excitons in 1D perovskites; the straight and curved arrows represent optical and relaxation transitions, respectively. (d) Crystal structure of 1D organic bismuth halide hybrids (e) The structure formula of (Pyrrolidinium) $MnBr_3$. (f) Multiferroic photoluminescence suitable for future applications in luminescence materials, photovoltaics, and magneto-optoelectronic devices. (g) View of the structure of $(HMTA)_3Pb_2Br_7$ (red: lead atoms; green: bromine atoms; blue: nitrogen atoms; gray: carbon atoms; purple polyhedrons: $PbBr_6$ octahedra and Pb_2Br_9 dimers; hydrogen atoms are hidden for clarity). (h) Excitation (black line, probed at 580 nm) and emission (red line, excited at 380 nm; blue line, excited at 350 nm) spectra of $(HMTA)_3Pb_2Br_7$ crystals at room temperature. (i) CIE chromaticity coordinates of the bulk assembly of 1D nanotubes $(HMTA)_3Pb_2Br_7$ (red star), and the bulk assembly of 1D nanowires $C_4N_2H_{14}PbBr_4$ (blue square). (j) Crystal structure of 1D semiconducting lead chloride nanoribbons. Reproduced from Ref. [13,21,127,129,130].

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, $C_4N_2H_{14}SnBr_4$, 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 polarization ($> 15 \mu\text{C cm}^{-2}$) in the field of hybrid ferroelectrics. Moreover, a light absorbing semiconductor with a narrow direct band gap of 2.02 eV, (C₆H₁₃N)₂BiI₅, was reported to have 1D perovskite-like zigzag chains through corner-sharing (Figure 7(d)) [123,124]. This environmentally friendly 1D metal halide hybrid has other features that make them highly attractive for optoelectronic applications, including moisture stability, a long room-temperature PL lifetime, and photoconductive behavior. 1D structures containing transition metal manganese (Mn) have also been studied recently [13,125–128]. These Mn-based 1D hybrids were reported to exhibit bright photoluminescence originating from the $(t_{2g})^3(e_g)^2-(t_{2g})^4(e_g)^1$ electronic transition of Mn²⁺ ions with a high quantum yield under UV excitation. The combination of ferroelectricity and luminescence within organic–inorganic hybrids would lead to a new type of luminescent ferroelectric multifunctional materials (Figure 7(e,f)) [127].

The rich chemistry of metal halides allows the formation of other unique 1D structures. Tubular structure is another 1D structure that has been extensively explored in a number of material systems. Is it possible to use metal halide octahedra as building blocks to build 1D tubular structure? By using protonated hexamethylenetetramine (HMTA, C₆H₁₃N₄⁺) as cationic moieties, a bulk assembly of 1D metal halide nanotubes with a chemical formula of (C₆H₁₃N₄)₃Pb₂Br₇ was recently developed by our group (Figure 7(g)) [21]. This new material can display the intrinsic properties of individual nanotubes due to the complete isolation and strong quantum confinement by a bulky wide-band-gap organic moiety. A strongly Stokes shifted broadband yellow emission was observed, as a result of exciton self-trapping in the metal halide framework (Figure 7(h,i)). An organic metal halide hybrid containing lead-chloride nanoribbons is another 1D structure recently reported, in which the metal halides form covalent bonds with the

semiconducting organic π -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 tetrahedra and pyramid, 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 discusses 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

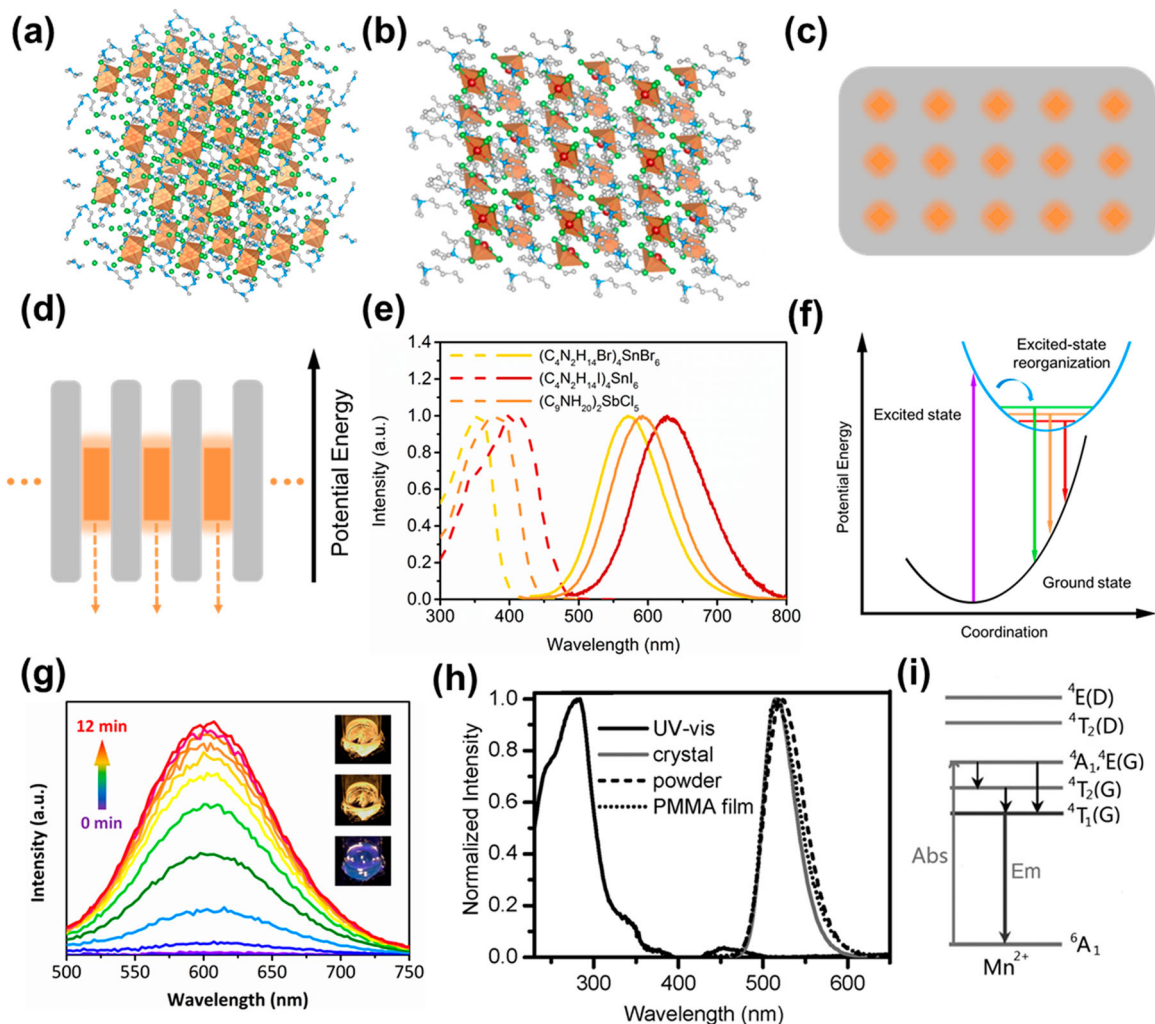


Figure 8. Views of the structures of $(\text{C}_4\text{N}_2\text{H}_{14}\text{Br})_4\text{SnBr}_6$ (a) and $(\text{C}_9\text{NH}_{20})_2\text{SbCl}_5$ (b) (red spheres: metal centers; green spheres: halide atoms; blue spheres: nitrogen atoms; gray spheres: carbon atoms; yellow polyhedrons: SnBr_6^{4-} octahedra and SbCl_5^{2-} quadrangular pyramids; hydrogen atoms were hidden for clarity). (c) Schematic drawing of a perfect host-guest system with the light emitting species periodically embedded in an inert matrix. (d) The potential energy diagram of the perfect host-guest system (e) Excitation (dashed lines) and emission (solid lines) spectra of 0D organic metal halide hybrids at room temperature. (f) The mechanism of excited state structural reorganization: the straight and curved arrows represent optical and relaxation transitions, respectively. (g) *In situ* photoluminescence spectra of bulk 0D Sb chloride crystals during rapid crystal growth. (h) The solid-state UV-vis absorption (black solid line) and emission spectra in crystals (gray solid line), powder (short dashed line), and PMMA film (dotted line) for $(\text{Ph}_4\text{P})_2[\text{MnBr}_4]$. (i) Schematic diagram showing the energy adsorption, migration, and emission process of Mn(II) complex in a tetrahedral environment. Reproduced from Ref. [14,133,134].

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 $[\text{Bmim}]_2\text{SbCl}_5$ [132] and $(\text{C}_9\text{NH}_{20})_2\text{SbCl}_5$ [14], have been reported, which contain isolated pyramidal SbCl_5 species. Recently, a facile synthetic approach was established to prepare 0D $(\text{Ph}_4\text{P})_2\text{SbCl}_5$ by taking advantage of the easy crystallization of tetraphenylphosphonium salts (Figure 8(g))

[133]. With the same organic cation, a green emitting 0D hybrid containing tetrahedral MnBr_4 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 d^5 configuration with a tetrahedral coordination geometry. In addition to tetrahedral structure, a rare seesaw-shaped SnBr_4 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, $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$ 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 $\text{Pb}_3\text{Br}_{12}^{6-}$ trimers [140]. From hexa- to penta-, tetra- coordinated, and even clustered metal halides, there is a vast space to explore novel structures with new and useful properties. These

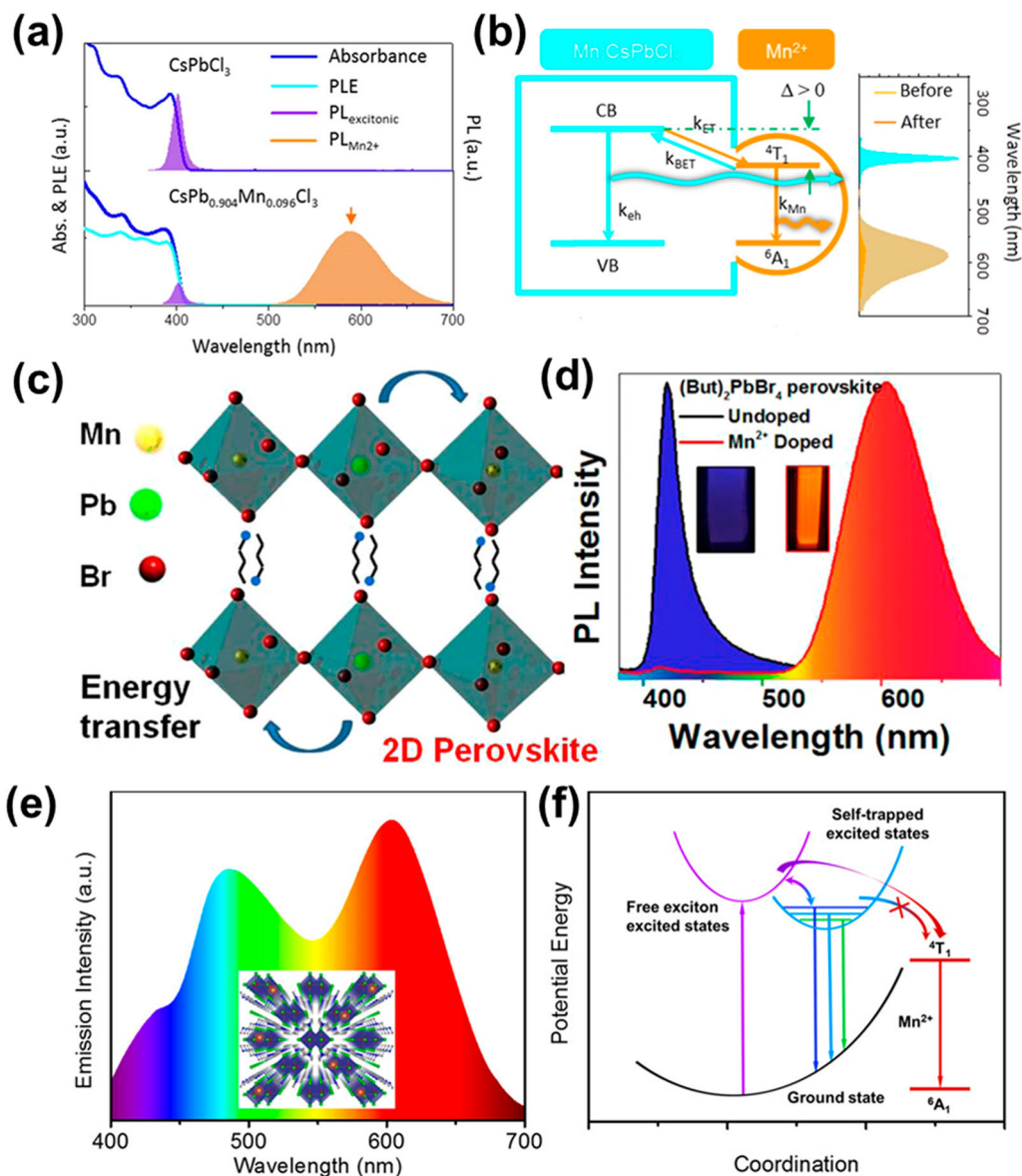


Figure 9. (a) The optical properties of undoped (top) and Mn-doped (bottom) CsPbCl_3 NCs. (b) The energy level diagram of $\text{Mn}:\text{CsPbCl}_3$ NCs. k_{eh} : band edge electron-hole recombination k_{Mn} : deactivation of the Mn^{2+} -based d-d transition; forward (k_{ET}) and back (k_{BET}) energy transfer between the NC and the impurity. (c) The diagram shows efficient energy transfer in 2D perovskites. (d) Photoluminescence of Mn^{2+} -doped and undoped 2D perovskites. (e) Photoluminescence of Mn^{2+} -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 $\text{CsPb}(\text{Cl}/\text{Br})_3$ 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 $^4\text{T}_1$ – $^6\text{A}_1$ 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_3NH_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 $(\text{C}_4\text{H}_9\text{NH}_3)_2\text{PbBr}_4$ (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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Disclosure statement

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