Recent advances in luminescent zero-dimensional organic metal halide hybrids

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Abstract

Organic metal halide hybrids (OMHHs) have attracted great research attention owing to their exceptional structure and property tunability. Using appropriate organic and inorganic metal halide components, OMHHs with controlled dimensionalities at the molecular level, from three- (3D) to two- (2D), one- (1D), and zero-dimensional (0D) structures, can be obtained. In 0D OMHHs, anionic metal halide polyhedrons are surrounded and completely isolated by organic cations to form single crystalline "host-guest" structures. These ionically bonded organic-inorganic hybrid systems often exhibit the intrinsic properties of individual metal halide species, for instance, highly efficient Stokes-shifted broadband emissions. In this progress report, we discuss the recent advances in the development and study of luminescent 0D OMHHs, from synthetic structural control to fundamental understanding of the structure-property relationship and device integration.

1. Introduction

Metal halide perovskites and perovskite-related hybrid materials have attracted tremendous interests for their various applications in photovoltaic cells (PVs)^[1, 2], light emitting diodes (LEDs)^[3-5], photodetectors^[6, 7], lasers^[8-10], scintillators^[11, 12], etc. The rich functionality of these materials benefits from their tunable structures, chemical compositions, and

morphologies.^[13] The first metal halide perovskites were discovered in 1958 by Moller with a three-dimensional (3D) structure, ^[14] which have a general formula of ABX₃, where A is a monovalent cation, such as methylammonium (MA), formamidinium (FA), or Cs; B is a divalent cation, such as Pb and Sn; and X is a halide ion.^[15] Derived from 3D metal halide perovskites, low dimensionality can be obtained by means of morphological control or dimensionality control at the molecular level.^[16] By using appropriate combinations of organic and metal halides, the dimensionality of OMHHs can be synthetically controlled, ranging from 3D to 2D, 1D, and 0D (Figure 1).^[13] In 3D structure with the general formula of ABX₃, BX₆ octahedra connect with each other via corner-sharing in three dimensions. By slicing along (100) or (110) crystallographic planes, 2D layered structures with corner sharing metal halide octahedra can be derived from 3D structures.^{[17] [18]} 1D and 0D structures based on metal halide octahedra can be obtained by further slicing 2D layers into metal halide wires and individual octahedra.^[19-22] In addition to corner-sharing, metal halide building blocks could also be connected via edge-sharing and face-sharing. Moreover, metal halide polyhedrons other than octahedra could serve as building blocks for the formation of organicinorganic hybrids, which significantly expands the family of OMHHs beyond perovskites.



Figure 1. Metal halides from corner-sharing 3D to 2D, 1D, and 0D structures based on octahedra, as well as other 0D metal halide polyhedrons and clusters.

0D metal halide hybrids are featured with isolated anionic metal halide polyhedrons surrounded by organic or inorganic cations. Some earliest reports of 0D metal halide hybrids are on inorganic Cs₄PbBr₆, in which PbBr₆⁴⁻ octahedra are surrounded and separated by Cs⁺ cations.^[14, 23-25] However, no excitonic emission in the visible range was observed in pure Cs₄PbBr₆.^[26] By replacing Cs⁺ with large organic cations and expanding PbBr₆⁴⁻ to other metal halide polyhedrons, a large number of 0D OMHHs have been developed and studied during the last few years. It should be pointed out that before the concept of 0D OMHHs was well-defined, several hybrid materials have been reported with a 0D structure ^[27, 28] ^[29-31] and shown interesting luminescent properties.^[29, 32-34]

The recent emergence of 0D OMHHs started with highly luminescent SnX₆⁴⁻ based organicinorganic hybrids discovered by our group in 2017, ^[20, 22, 35] when the characterized features of these hybrids, i.e. strongly Stokes-shifted broadband emissions with long decay lifetimes and high photoluminescence quantum efficiencies (PLQEs) of up to unity, were revealed and systematically investigated. Due to the complete isolation of metal halide anions by bulky organic cations, these 0D OMHHs could exhibit the photophysical properties of individual metal halides, with certain similarity to metal halide ions in solution phase.^[36] Therefore, these materials can be considered as solid state "host-guest" hybrid systems with the photoactive metal halide species as "guest" periodically embedded in the organic "host" matrix. Beyond metal halide octahedra, many other types of metal halide polyhedrons, including pyramidal, tetrahedral, and seesaw metal halides, have been utilized for the assembly of 0D OMHHs, which significantly increase the structural diversity and property tunability.^[37, 38] For instance, 0D (C₉NH₂₀)₂SnBr₄ with deep red emission has one of the largest Stokes shifts, as a result of strong structural distortion in the excited state, ^[37] while 0D (C13H19N4)2PbBr4 exhibits blue emission with a relatively small Stokes shift due to the low chemical reactivity of Pb 6s² lone pairs and the rigid organic cationic matrix.^[39] In addition to mononuclear metal halide anions, multinuclear metal halide clusters could serve as building

blocks in 0D OMHHs.^[29] Two distinct bulk assemblies of metal halide clusters, 0D (C₉NH₂₀)₇(PbCl₄)Pb₃Cl₁₁ and (C₉NH₂₀)₉(ZnCl₄)₂Pb₃Cl₁₁, have been reported recently to exhibit highly efficient blue and green emissions, respectively.^[21, 40] More recently, multicomponent 0D OMHHs containing more than one emitting center have been developed. For example, 0D (bmpy)₉[SbCl₅]₂[Pb₃Cl₁₁] was reported to exhibit tunable warm white emissions by combining green emission from Pb₃Cl₁₁^{5–} and orange emission from SbCl₅^{2–,[41]} In another case, three distinct metal halide ions, i.e. PbBr4^{2–}, MnBr4^{2–}, and SnBr4^{2–}, are incorporated into a single crystalline 0D hybrid ((HMTA)₄PbMn_{0.69}Sn_{0.31}Br₈) to display highquality white emissions.^[42] The major milestones of the research progress in 0D OMHHs are highlighted in Figure 2.



Figure 2. The development of 0D OMHHs with representative work over the years. Reprinted with permission. ^[13] ^[22] ^[32, 33] ^[36] ^[37, 38] ^[39] ^[24] ^[41] ^[42] ^[43] Copyright 1992, American Chemical Society; Copyright 2015, Royal Society of Chemistry; Copyright 2017, Wiley-VCH; Copyright 2018, the Royal Society of Chemistry; Copyright 2018, American Chemical Society; Copyright 2018, American Chemical Society; Copyright 2018, American Chemical Society; Copyright 2019, American Chemical Society; Copyright 2020, American Chemical Society; Copyright 2020, American Chemical Society; Copyright 2020, Wiley-VCH

In this progress report, we first introduce the definition of 0D OMHHs with various metal halide anions as an emitting center, followed by the discussions on how metal halide ions can be tuned from individual mononuclear metal halide species to multinuclear clusters, and from single component systems to multicomponent systems. In addition to material development, our understanding of the mechanisms of characteristic broadband emissions in 0D OMHHs will be discussed. The progress on the applications of 0D OMHHs in various technological areas, including optically pumped LED, scintillators, thermometers, will also be covered. In the end, issues, challenges, as well as our prospects on the field, will be presented. The historical overviews, photoluminescence mechanisms of some relevant low dimensional metal halide perovskites and hybrids have been reviewed in several recent publications.^[13, 16, 44-46]

2. The emergence of 0D OMHHs

0D OMHHs or bulk assemblies of quantum confined metal halides with 0D structure at the molecular level feature individual metal halide polyhedrons completely surrounded and isolated by organic cations. While ionically bonded organic-inorganic hybrids have been studied for decades, most of them do not possess 0D structure at the molecular level with functional units (either organic or inorganic species) completely isolated from each other

without electronic couplings. In 2017, our group reported a series of 0D OMHHs, $(C_4N_2H_{14}X)_4SnX_6$ (X = Br or I), in which individual metal halide building blocks SnX₆⁴⁻ are completely surrounded and isolated by large organic cations C₄N₂H₁₄X⁺ with the distance between two metal centers of > 1 nm (Figure 3a).^[22] The complete site isolation of individual metal halide species is achieved due to the large size of the organic cations, as well as the high molar ratio between organic cations and metal halide anions (4:1), which inhibits the electronic band formation. Therefore, these 0D OMHHs can be considered to possess a perfect "host-guest" structure with photoactive metal halide species periodically embedded in an inert host matrix. This allows 0D OMHHs to exhibit the intrinsic properties of the individual metal halide species.^[47] Unlike morphological 0D perovskite quantum dots with narrow direct band emissions, 0D OMHHs exhibit highly efficient Stokes-shifted broadband emissions with PLQEs of up to near-unity (Figure 3b). Color tuning of this class of materials has also been demonstrated via halide substitutions.^[48] Taking advantage of their efficient broadband emissions with high PLQEs, 0D OMHHs show great promise as down conversion phosphors for optically pumped LEDs.^[49-51] Following our seminal work in 2017, 0D OMHHs containing a variety of metal halide octahedra have been developed. Zhou et al. reported a lead-free indium based 0D (C₄H₁₄N₂)₂In₂Br₁₀ single crystal, containing octahedral $[InBr_6]^{3-}$ and tetrahedral $[InBr_4]^{-}$, ^[52] which shows a largely Stokes shifted (> 300 nm) broadband orangish-red emission. Chen et al. synthesized 0D (PMA)₃InBr₆ [PMA⁺: $(C_6H_5CH_2NH_3)^+$ via cooling crystallization,^[53] which exhibits a broadband orange emission peaked at 610 nm with a high PLQE of ~35 %. Two other isostructural 0D (PMA)₃SbBr₆ and (PMA)₃BiBr₆ were recently reported,^[54] which have good stability under ambient conditions as well as high decomposition temperatures under N2 gas flow. Lin et al. prepared 0D H₃SbBr₆(L)₆ [L=2-(3-methyl-1*H*-imidazol-3-ium-1-yl)acetate] by solvothermal reaction, which exhibits a greenish-vellow broadband emission with a PLOE of 53 %.^[55] Considering the environmentally friendly and high stability features of tin(IV) [56, 57], 0D tin(IV)-based

OMHHs have been developed and studied. For instance, 0D (C₆N₂H₁₆Cl)₂SnCl₆ with a blue emission peaked at 450 nm was found to exhibit remarkable stability in air and at high temperature.^[58] Very recently, our group reported 0D [(PEA)₄SnBr₆][(PEA)Br]₂[CCl₂H₂]₂ with a strong emission peaked at 566 nm with a high PLQE of ~90 %,^[59] which is almost identical to that of the previously reported 0D (C₄N₂H₁₄Br)₄SnBr₆.^[22] However, 0D [(PEA)₄SnBr₆][(PEA)Br]₂[CCl₂H₂]₂ is not stable, as it can undergo solvent-induced structural transformation upon drying dichloromethane to form 2D (PEA)₂SnBr₄ (Figure 3c).



Figure 3. a) Views of two [SnBr₆]⁴⁻ octahedra surrounded by (C₄N₂H₁₄Br)⁺ organic cations. b) (left) Images of 0D metal halide hybrids under ambient light (top) and 365 nm UV irradiation (bottom). (right) Stokes-shifted emission and excitation spectra of 0D metal halide hybrids at room temperature. c) (i) Images of phase transformation between 0D and 2D under UV irradiation. (ii) Absorption and emission changes of each state. (iii) PXRD patterns based on each state. d) View of the structure of (Ph₄P)₂SbCl₅ and an individual [SbCl₅]²⁻ pyramidal structure surrounded by Ph₄P⁺ cations and schematic synthetic approaches for growing (Ph₄P)₂SbCl₅ single crystals. e) Crystal structure of (C₉NH₂₀)₂SnBr₄ and the configuration coordinate diagram for the excited-state structural-deformation-induced large Stokes shift. Reproduced with permission. ^[22, 37, 38, 59] Copyright 2017, Royal Society of Chemistry; Copyright 2020, American Chemical Society; Copyright 2018, American Chemical Society; Copyright 2018, Wiley-VCH

Besides metal halide octahedra, 0D OMHHs containing other types of metal halide polyhedrons, such as pyramidal, tetrahedral, and seesaw structured metal halides, have been discovered. In 2017, highly luminescent 0D (Ph₄P)₂SbCl₅ containing pyramidal [SbCl₅]²⁻ was first studied in detail by our group ^[38]. Interestingly, (Ph₄P)₂SbCl₅ could be prepared by two facile synthetic approaches as shown in Figure 3d. One is slow solvent interdiffusion method, which could produce a thermodynamically stable material with red emission. The other is rapid crystal growth method via antisolvent injection precipitation, which yields a highly emissive metastable product with yellow emission followed by spontaneous transformation. In the last couple of years, a number of 0D organic antimony halide hybrids based on SbX5²⁻ have been developed ^[32, 38, 60]. Wang et al. reported 0D [Bzmim]₂SbCl₅ and [Bzmim]₃SbCl₆ [Bzmim=1-benzyl-3-methylimidazolium], which were prepared via unprecedented coolingmethod-dependent crystal processes.^[61] Upon UV irradiation, [Bzmim]₂SbCl₅ exhibits tunable dual-emissions at different excitation wavelengths with combined emissions from both [Bzmim]⁺ and [SbCl₅]²⁻, while [Bzmim]₃SbCl₆ exhibited a single broadband green emission peaked at 525 nm from [SbCl6]³⁻. An interesting transformation between [SbCl5]²⁻ and [SbCl₆]³⁻ was observed in these 0D hybrids, resulting in thermal and moisture-induced triplemode reversible PL switching (Figure 3e). More recently, Morad et al. reported their efforts in controlling the geometry of antimony halide building blocks SbX5²⁻ and SbX6³⁻, by adopting host-guest complexation of alkali and alkaline metal cations (Cs⁺, Rb⁺, Ba²⁺, etc.) with crown ethers to foster the formation of 0D hybrids.^[62] OMHHs containing tetrahedral metal halides have been investigated extensively. Xu et al. reported an efficient phosphorescent green emitting 0D (Ph₄P)₂[MnBr₄] containing a tetrahedral MnBr₄²⁻ surrounded by Ph₄P⁺ cations $^{[33]}$. The intense green emission of this material originates from the metal-centered d-d $^{4}T_{1}$ - $^{6}A_{1}$ transition in d⁵ configuration with a tetrahedral coordination geometry. Recently, systematic studies of MnX₄²⁻ based 0D hybrids have been conducted by a few research groups.^[43, 63, 64] It was found that longer Mn-Mn average distances afford higher PLQEs due to the reduction of

energy transfer between Mn²⁺ emitting centers. Other metal halide tetrahedra have also been used for the construction of 0D OMHHs. Yangui et al. reported 0D (C5H7N2)2HgBr4·H2O and (C₅H₇N₂)₂ZnBr₄, which exhibit dual-band emissions with high CRI of 87 and 96, respectively. ^[65] In these materials, emissions are from excitons localized in both organic cations and isolated metal halide tetrahedra. Seesaw-shaped metal halides are another type of metal halide polyhedrons. Our group reported the first 0D OMHH containing seesaw-shaped metal halides. (C9NH20)2SnBr4, which exhibits a strongly Stokes-shifted broadband deep-red emission peaked at 695 nm with a PLQE of 46 % (Figure 3e).^[37] Computational studies suggested that SnBr4²⁻ could undergo deformation from a seesaw structure to a flattened tetrahedron structure in the excited state, resulting in the extremely large Stokes shift. Recently, Morad et al. reported isostructural halide complexes of Ge(II), Sn(II), and Pb(II) with a large organic cation 1-butyl-1-methylpiperidinium (Bmpip), which exhibit bright emissions in blue to red and near-infrared spectral regions.^[43] Meanwhile, our group reported a blue emitting 0D $(C_{13}H_{19}N_{4})_{2}PbBr_{4}$ with a peak emission of 460 nm and a higher PLQE of ~ 40 %.^[39] The much smaller Stokes shift, as compared to those of other 0D hybrids, is due to the low chemical reactivity of Pb 6s² lone pairs and the rigid organic cationic matrix.

3. From individual polyhedrons to metal halide clusters

In addition to mononuclear metal halide species, multinuclear metal halide clusters can also be used to assemble 0D OMHHs. Back in 1996, (CH₃NH₃)₃Bi₂I₉ containing dioctahedral (Bi₂I₉)³⁻ clusters were reported with strong exciton-phonon interaction.^[66] After that, a few hybrid materials based on bismuth iodide clusters have emerged as light absorber for PVs.^{[67, ^{68]} In 2018, our group reported a single crystalline assembly of metal halide clusters, (C₉NH₂₀)₇(PbCl₄)Pb₃Cl₁₁, which exhibits blue light emission peaked at 470 nm with a high PLQE of around 83 %.^[21] The lead chloride tetrahedrons (PbCl₄²⁻) and face-sharing lead chloride trimer clusters (Pb₃Cl₁₁⁵⁻) co-crystallize with organic cation (C₉NH₂₀⁺) to form a 0D}

structure at the molecular level, as shown in Figure 4a. The $Pb_3Cl_{11}^{5-}$ clusters are completely isolated by wide-bandgap $PbCl_{4^{2-}}$ and $C_9NH_{20^{+}}$, which allow single crystals to exhibit the photophysical properties of individual lead chloride clusters. Upon UV irradiation, Pb₃Cl₁₁⁵⁻ trimer clusters are excited to the higher energy excited state and then undergo ultrafast structural reorganization and intersystem crossing from the singlet state to the triplet states due to the heavy atom effect (Figure 4b). Also containing Pb₃Cl₁₁⁵⁻ trimer clusters, another 0D OMHH (C₉NH₂₀)₉[ZnCl₄]₂[Pb₃Cl₁₁] was recently developed by our group.^[40] Unlike 0D (C₉NH₂₀)₇(PbCl₄)Pb₃Cl₁₁ with blue emission, (C₉NH₂₀)₉[ZnCl₄]₂[Pb₃Cl₁₁] exhibits green emission peaked at 512 nm with a remarkable near-unity PLQE at room temperature. It was found that 0D (C₉NH₂₀)₉[ZnCl₄]₂[Pb₃Cl₁₁] has a much less compact crystal structure than that of 0D (C₉NH₂₀)₇(PbCl₄)Pb₃Cl₁₁. Detailed structural and photophysical studies suggested two emitting excited-state structures of Pb₃Cl₁₁⁵⁻ clusters. Following these discoveries, Li et al. reported a series of 0D metal halide clusters, (C9NH20)9[Pb3X11](MX4)2 (X=Br, Cl; M=Mn, Fe, Co, Ni, Cu, Zn) featuring two distinct anionic building blocks of $[Pb_3X_{11}]^{5-}$ and $[MX_4]^{2-}$.^[69, 70] The different absorption of $[MX_4]^{2-}$ leads to the distinct colors of each single crystals, while $[Pb_3X_{11}]^{5-}$ clusters lead to the halogen dependent yellow/ green broadband emission (Figure 4c).^[70] Besides triangular trimer clusters, linear trimer clusters could also be formed in 0D hybrids. In 2019, topologic control of metal halide trimer clusters in two 0D hybrids, (C₉NH₂₀)₆[Pb₃Br₁₂] and (C₉NH₂₀)₉[ZnBr₄]₂[Pb₃Br₁₁], was realized by finely controlling the synthetic conditions.^[71] As shown in Figure 4d, Pb₃Br₁₁⁵⁻ clusters in (C₉NH₂₀)₉[ZnBr₄]₂[Pb₃Br₁₁] are triangular, while Pb₃Br₁₂⁶⁻ trimer clusters in (C9NH20)6[Pb3Br12] are linear. Detailed structural and photophysical studies found that their optical properties are highly dependent on the geometry of metal halide clusters. Meanwhile, by systematically varying templating N-alkylpyridinium cations, Febrainsyah and coworkers have developed distinct trimeric bromoplumbate architectures (Figure 4e).^[72] Detail studies of the optical properties were performed on (benzyl)6[Pb3Br12] and it was found that

(benzyl)₆[Pb₃Br₁₂] exhibits a large Stokes shifted broadband emission, which is more efficient than those of its 1D analogs. Despite these recent achievements on 0D organic-inorganic hybrids containing metal halide clusters, fundamental understanding of the structural-property relationships for this class of materials is still limited, and rational synthetic control of the size and geometry of metal halide clusters has not yet been well established.



Figure 4. a) View of metal halide clusters (Pb₃Cl₁₁⁵⁻) completely separated from each other by PbCl₄²⁻ and C₉NH₂₀⁺. b) Schematic mechanism of the photophysical processes in metal halide clusters. c) (top) Images of single crystals of (C₉NH₂₀)₉[Pb₃X₁₁](MX₄)₂ (X=Br, Cl; M=Mn, Fe, Co, Ni, Cu, Zn) under ambient light. (bottom) Emission and excitation of (C₉NH₂₀)₉[Pb₃X₁₁](MX₄)₂ (X=Br, Cl; M=Mn, Fe, Co, Ni, Cu, Zn) at room temperature. d) (top) View of single crystal structures of (C₉NH₂₀)[Pb₃Br₁₂] and the individual chain-shaped metal halide clusters [Pb₃Br₁₂]⁶⁻. (bottom) View of single crystal structures of (C₉NH₂₀)₉[ZnBr₄]₂[Pb₃Br₁₁] and the individual triangle-shaped metal halide clusters [Pb₃Br₁₁]⁵⁻. e) (top) A series of N-alkylpyridinium salts. (bottom) View of single crystal structure.

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4. From single component systems to multicomponent systems

0D OMHHs provide an excellent platform for metal halide molecular species or clusters to exhibit their intrinsic properties. By reacting various organic and metal halides, 0D OMHHs containing one type of photoactive metal halide species, or single component 0D OMHHs, have been developed extensively to exhibit tunable emissions covering the whole visible spectrum.^[13, 16, 22, 33, 37-39, 58, 59, 65, 71, 73] On the other hand, the photophysical properties of 0D OMHHs could be tuned by achieving multicomponent systems via doping metal ions, integrating multiple metal halides into a single-phase system, and compositional mixing of halogens.

Doping photoactive metal ions, such as Mn^{2+} , has been demonstrated as an effective way to modulate the photophysical properties of hosts without changing their crystal structures in many perovskite nanocrystals. This approach has been adopted to tune the photoluminescence and enhance the PLQEs of 0D OMHHs.^[64, 74, 75] Xia et al reported a trivalent antimony doped 0D (C₉NH₂₀)₉[Pb₃Cl₁₁](ZnCl₄)₂:Sb³⁺, which exhibit dual emission from Pb₃Cl₁₁⁵⁻ clusters and Sb³⁺. By controlling the concentration of Sb³⁺, the emission colors of those 0D hybrids could be well-tuned from green to yellow and orange as shown in Figure 5a-c.^[74] Integrating distinct metal halides into one single crystal provides another avenue to realize multi-functionalities in a single-phase material as individual metal halides could exhibit their properties simultaneously. Our group reported a series of binary 0D OMHHs containing Pb₃Cl₁₁⁵⁻ clusters and MClx²⁻ (M = Pb, Zn or Sb, and x = 4 or 5) by diffusing anti-solvent into mixture of C₉NH₂₀Cl, zinc chloride (ZnCl₂)/antimony chloride (SbCl₃) and lead chloride (PbCl₂) dissolved in DMF.^[21, 40, 41] In 0D (C₉NH₂₀)₉[SbCl₅]₂[Pb₃Cl₁₁], the combination of green and orange emissions from Pb₃Cl₁₁⁵⁻ and SbCl₅²⁻ results in excitation dependent dual

emissions with PLQEs of >70%, correlated color temperatures (CCTs) varying from 3599 to 1272 K, and color rendering indexes (CRIs) of up to 90 (Figure 5d, e). This is a result of complete site isolation of metal halide species by organic moieties and no spectral overlaps between the emission of $Pb_3Cl_{11}^{5-}$ and absorption of $SbCl_5^{2-}$. Xia group reported a similar binary 0D OMHH containing Pb₃Br₁₅⁻ with emission peaked at 565 nm and MnBr₄²⁻ with emission peaked at 528 nm (Figure 5f).^[69] Interestingly, the photoluminescence was governed by not only the excitation wavelength but also the environment temperature (Figure 5g). The back energy transfer (BET) process between two emitting center [Pb₃Br₁₁] and [MnBr₄] was found to be dependent on the temperature. At low temperature, Mn intra-atomic transitions is dominated as the BET from [MnBr4] to [Pb₃Br₁₁] is not activated. At high temperature, the Mn ⁴D excitation band disappear while Pb₃Br₁₁ excitation/emission band appears due to the activation of the BET from [MnBr₄] to [Pb₃Br₁₁]. Synthesizing ternary or higher component OMHHs is more challenging, as single component or binary single crystals, instead of multicomponent single crystals, would form preferentially, when several components are involved in the crystallization process. Therefore, delicately choosing appropriate organic and metal halides that could co-crystalize is of great importance. Recently our group reported for the first time a ternary 0D OMHH, (HMTA)₄PbMn_{0.69}Sn_{0.31}Br₈, in which a rigid organic cation HMTA⁺ (HMTA⁺: N-benzyl hexamethylenetetramium, C₁₃H₁₉N₄⁺) cocrystallized with blue emitting PbBr₄²⁻, green emitting MnBr₄²⁻, and red emitting SnBr₄²⁻ (Figure 5h). The wide bandgap of the organic cation and distinct optical properties of the three metal bromide anions enabled the single crystalline system to exhibit emissions from multiple metal halide species simultaneously with different decay lifetimes (Figure 5i). The combination of these emissions led to near-perfect white emission with a PLQE of around 73 %. Because three metal halides have different excitations, warm to cool white emissions could be generated by controlling the excitation wavelength.^[42]

Halogen substitution has been well established for bandgap control and color tuning of metal halide perovskites, as well as low dimensional OMHHs.^[48, 75, 76] In 2017, our group reported a highly efficient broadband yellow light emitter based on 0D (C₄N₂H₁₄Br)₄SnBr_xI_{6-x} (x = 3). The emission band of this mixed-halide 0D hybrid is broader than those of its pure halide counterparts, due to the multi-excited-states created by the structural reorganization of the metal mixed-halide octahedrons.^[22, 48] Xia's group developed a series of mixed halide 0D (C₉NH₂₀)₉Pb₃Zn₂Br₁₉(1-*x*)Cl_{19x} (*x* = 0–1),^[76] which exhibit tunable emissions by controlling the halogen contents. It was found that increasing Cl content from *x* = 0 to 1 would result in a significant blue shift of emission peaks from 565 nm to 516 nm, accompanied by strikingly increasing PLQEs from 8% to 91%, as shown in Figure 5j-l. Major photophysical properties of representative 0D OMHHs have been summarized in Table 1.



Figure 5. (a) Diagram of structural model and doping mechanism of (C₉NH₂₀)₉[Pb₃Cl₁₁](ZnCl₄)₂:Sb³⁺. (b) Schematic diagram of luminescence process for Sb₃₊ in (C₉NH₂₀)₉[Pb₃Cl₁₁](ZnCl₄)₂:Sb³⁺. (c) Room-temperature PL and PLE spectra of (C₉NH₂₀)₉[Pb₃Cl₁₁](ZnCl₄)₂:Sb³ under different Sb³⁺concentrations excited at 365 nm and 330 nm. (d) A Pb chloride cluster $[Pb_3Cl_{11}]^{5-}$, a Sb chloride pyramid $[Pb_3Cl_{11}]^{5-}$, and an organic cation $bmpy^+$ in the ball-and-stick model. (e) Excitation dependent photoluminescence spectra at room temperature (excitation wavelength = from 320 to 380 nm with a step of 10nm). (f) Luminescence model diagram of different illuminating centres at room temperature (g) Diagram of luminescence processes in $(C_9NH_{20})_9[Pb_3Br_{11}](MnBr_4)_2$ at room temperature. (h) View of the single crystal structure of (HMTA)₄PbMn_{0.69}Sn_{0.31}Br₈. (i) Absorption, excitation and emission spectra of (HMTA)₄PbMn_{0.69}Sn_{0.31}Br₈. (j) The schematic diagram of the evolution process from (C₉NH₂₀)₉[Pb₃Br₁₁](ZnBr₄)₂ to (C₉NH₂₀)₉[Pb₃Cl₁₁](ZnCl₄)₂ (**k**) Roomtemperature photoluminescence (PL; solid line) and photoluminescence excitation (PLE) spectra (dotted line) of (C9NH20)9Pb3Zn2Br19(1-x)Cl19x monitored at corresponding optimum wavelengths. (I) Variations of the PLQY of (C₉NH₂₀)₉Pb₃Zn₂Br_{19(1-x)}Cl_{19x} crystals with different excitation wavelength (365, 359, 355, 343, 333, and 327 nm, respectively). Reprinted with permission. ^[74] ^[41] ^[69] ^[42] ^[70] Copyright 2020, the Royal Society of Chemistry; Copyright 2020, American Chemical Society; Copyright 2019, Wiley-VCH; Copyright 2020, Wiley-VCH; Copyright 2020, Wiley-VCH.

Table 1	. Photophysical	properties of re	epresentative 0D	OMHHs .
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	0D specie		Stokes		Ref.
Single crystal		$\lambda_{emission}$ (nm)	shift (nm)	PLQY (%)	
$(C_4 N_2 H_{14} Br)_4 SnBr_6$	$[\operatorname{SnBr}_6]^{4-}$	570	215	95±5	[22]
$(C_4N_2H_{14}I)_4SnI_6$	$[\operatorname{SnBr}_{6}]^{4-}$	620	210	75±4	[22]

$(C_4H_{14}N_2)_2In_2Br_{10}$	$[InBr_6]^3$, $[InBr_4]$	670	> 300	~ 3	[52, 58]
$(C_6H_5CH_2NH_3)_3InBr_6$	$[InBr_6]^{3-}$	610	245	~35	[53]
$(C_6H_5CH_2NH_3)_3SbBr_6$	$[SbBr_6]^{3}$	640	200	< 1	[54]
$(C_6H_5CH_2NH_3)_3BiBr_6$	$[\operatorname{BiBr}_6]^{3-}$	510	160	< 1	[54]
$(C_6H_8N_2O_2)_3SbBr_6$	$[SbBr_6]^{3-}$	530	170	55	[55]
$(C_6N_2H_{16}Cl)_2SnCl_6$	$[SnCl_6]^{4-}$	450	75	8.1	[58]
$[(C_{8}H_{12}N)_{4}SnBr_{6}][(C_{8}H_{12}N)Br]_{2}$ $[CCl_{2}H_{2}]_{2}$	$[\operatorname{SnBr}_6]^{4-}$	566	262	~90	[59]
$(C_{24}H_{20}P)_{2}SbCl_{5}$	$[SbCl_5]^{2-}$	648	273	87	[38]
$(C_{24}H_{20}P)_{2}MnBr_{4}$	$[MnBr_4]^{2}$	516	52	97	[33]
$(C_{11}H_{13}N_2)_2SbCl_5$	$[SbCl_5]^{2-}$	600	225	22.3	[61]
$(C_{11}H_{13}N_2)_3SbCl_6$	$[SbCl_6]^{3-}$	525	160	87.5	[61]
$(C_5H_7N_2)_2HgBr_4H_2O$	$[HgBr_4]^{2-}$	425	100	14.87	[65]
$(C_5H_7N_2)_2ZnBr_4$	$\left[ZnBr_{4}\right]^{2}$	438	118	19.18	[65]
$(C_9 NH_{20})_2 SnBr_4$	$\left[\mathrm{SnBr}_{4}\right]^{2}$	695	332	46	[37]
$(C_{10}H_{22}N)_{2}SnBr_{4}$	$\left[\mathrm{SnBr}_{4}\right]^{2}$	730	376	75	[43]
$(C_{10}H_{22}N)_{2}PbBr_{4}$	$\left[\text{PbBr}_{4}\right]^{2}$	470	123	24	[43]
$(C_{10}H_{22}N)_{2}GeBr_{4}$	$[\text{GeBr}_4]^2$	660	306	< 1	[43]
$(C_{13}H_{19}N_4)_2PbBr_4$	$\left[\text{PbBr}_{4}\right]^{2}$	460	111	~ 40	[39]

5. Luminescence Mechanisms

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It is widely accepted that self-trapped excitons (STEs) are responsible for most cases of the largely Stokes-shifted broadband emissions commonly observed in low-dimensional OMHHs.^[13, 77] The mechanism of self-trapped emissions can be described as follows: upon photoexcitation, bound electron and hole pairs referred to as "excitons" are generated, ^[47, 78] which can undergo either radiative decay to emit relatively small Stokes-shifted narrowband emissions with short lifetimes^[19, 79], or further interact with transient deformed crystal lattices to form localized self-trapped excitons.^[80, 81] Karunadasa et al. described this process as hardball (electron/hole/exciton) dropping on a pliable rubber sheet (a deformable lattice) and sinking into the potential minimum created by itself (Figure 6a).^[45] Because of the large degrees of structural distortions and multiple exciton-phonon interaction modes, self-trapped emissions from low dimensional OMHHs are usually broadband with large Stokes-shifts (Figure 6b).^[82, 83]



Figure 6. (a) Exciton self-trapping represented by a ball interacting with a rubber sheet (top). (b) Schematic of the adiabatic potential energy curves of the ground state (G), free-exciton state (FE), free-carrier state (FC), and various excited states (STEs) in configuration space. (c) Charge density maps of the hole (left) and the electron (right) in a relaxed exciton in (C4N₂H₁₄Br)₄SnBr₆. (d) Electronic band structure of (C4N₂H₁₄Br)₄SnBr₆ calculated by DFT. (e) Single coordinate diagram demonstrating the accessibility of both singlet and triplet bound excitonic states in Bmpip₂MBr₄ (M = Ge, Sn, Pb). LD, lattice distortion; ISC, intersystem crossing.(f) PL spectra of Bmpip₂MBr₄ at different excitation wavelengths, showing both singlet and triplet emission bands for Sn, Ge (RT), and Pb (inset, 10 K) cases. (g) Excitation

(dashed lines) and emission (solid lines) spectra of 0D OMHHs at room temperature. (h) Schematic diagram showing the energy adsorption, migration, and emission process of Mn(II) complex in a tetrahedral environment. (i) Density of states (DOS) of (C₄H₁₄N₂)₂In₂Br₁₀. (j) Schematic of the photophysical processes in [Pb₃Cl₁₁]^{5–}-based hybrids with two energy minima on the excited states. (k) The configuration coordinate diagram for the emission processes in Cs₃Cu₂Br₅. (a) and (b) show the ground-state and the relaxed excited-state of the Cu₂Br₅ cluster. (l) Schematic energy level diagram of (C₈NH₁₂)₄Bi_{0.57}Sb_{0.43}Br₇·H₂O. Reprinted with permission ^[45] [^{81]} [^{47]} [^{43]} [^{22]} [^{33]} [^{40]} [^{84]}. Copyright 2018, American Chemical Society; Copyright 2016, American Chemical Society; Copyright 2018, the Royal Society of Chemistry; Copyright 2017, Wiley-VCH; Copyright 2019, American Chemical Society; Copyright 2019, American Chemical Society.

In 0D OMHHs, metal halide species are spatially surrounded and separated by large-bandgap organic cations, which result in the strongly localized excitons on individual metal halide species upon excitation. The reasons account for this highly localized excitation are the dielectric confinement effect introduced by the organic cations with small dielectric constant and the quantum confinement effect due to minimum overlapping of the wavefunction of metal halide species.^[85, 86] The minimum overlap of the wavefunction of metal halide units can be confirmed by theoretical calculations. For instance, the flatness of the density functional theory (DFT) calculated conduction bands and valence bands of 0D (C4N2H14Br)4SnBr6 indicates that the electronic coupling between SnBr6⁴⁻ units is negligible (Figure 6c). The calculated valence band maximum and conduction band minimum associated charge density maps of (C4N2H14Br)4SnBr6 also show that the excitons are highly localized on individual SnBr6⁴⁻ anions (Figure 6d). Lin et. al. experimentally observed a photoluminescence quantum efficiency (PLQE) increase from (C6N2H16)SbCl5 to

(C₆N₂H₁₆)SbCl₅·H₂O due to the longer SbCl₅ distance and more localized excitons of the latter compound.^[87] Therefore, 0D OMHHs can indeed be considered as bulk assemblies of photoactive molecular/cluster species, which are similar in nature to a host-guest system with photo-/electro-active molecules/clusters orderly doped in an inert matrix. Since the excitation and relaxation processes occur on individual metal halides in 0D OMHHs, their photoluminescence mechanism resembles that of molecular systems. Therefore, the valence band maximum and conduction band minimum of these materials correspond to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of metal halide anions. The exciton-phonon interactions to form self-trapped excitons in 0D OMHHs are indeed excited state structural reorganization of metal halides to form the lowest excited states, resulting emissions with large Stokes-shifts, as depicted in Figure 6e. In certain cases, as-formed spin-singlet excitons could undergo a fast intersystem crossing to form spin-triplet excitons, accompanied by the structural reorganization. The relaxation from spin-singlet excitonic states and spin-triplet excitonic states generate fluorescence and phosphorescence with different decay lifetimes. Kovalenko et. al. experimentally observed coexistence of singlet and triplet emission of Bmpip2MBr4 (M = Ge, Sn, Pb) with the help of a streak camera (Figure 6f), $[^{43, 88]}$ while most 0D OMHHs containing ns² metal halides only give exclusive broad emissions from triplet excited states (Figure 6g).^[22]

It's worth mentioning that many factors, such as the rigidity of organic cations and the topology of metal halides, could have dramatic effects on the excited-state potential energy surface (PES) and subsequently photophysical properties, including Stokes-shift, emission peak width, and the number of emission peaks. For instance, 0D (C₉NH₂₀)₂SnBr₄, Bmpip₂PbBr₄, and (C₁₃H₁₉N₄)₂PbBr₄ all contain seesaw structured metal halides, but exhibit emissions with different Stokes shifts. 0D (C₁₃H₁₉N₄)₂PbBr₄ has the narrowest emission with smallest Stokes shift due to the low chemical reactivity of Pb 6s² lone pairs and the rigid

organic cationic matrix.^[39] In (C6N2H16Cl)2SnCl6, SnCl6 octahedra exhibit almost no structural distortion in the ground state as well as the excited state due to the absence of the stereochemically active lone pair electrons on the Sn⁴⁺ cations, resulting in much smaller Stokes shift and full width at half maxima (FWHM), as compared to those of $(C_4N_2H_{14}X)_4SnX_6$ (X = Br or I). While most of luminescent 0D OMHHs reported to date are based on ns² metal halides, in which the ns² lone pairs can be stabilized by structural distortion and s-p orbital mixing in the excited states responsible for the photoluminescence,^[89, 90] 0D OMHHs with different photophysical processes have also been investigated. For instance, the efficient green emission with microsecond lifetime from 0D [Ph₄P]₂[MnBr₄] is attributed to the spin-forbidden d–d transition from ⁴T₁ to ⁶A₁ of MnBr₄ with a tetrahedral coordination geometry (Figure 6h).^[33, 91] In another 0D hybrid $(C_4H_{14}N_2)_2In_2Br_{10}$, the emission center is the full shell metal based $InBr_6^{3-}$ octahedra, with HOMO mainly on Br 4p orbitals and LUMO on the mixed Br 4p and In 5s orbitals (Figure 6i).^[52] All 0D OMHHs containing metal halide clusters developed to date could still be regarded as molecular systems, as metal halide clusters compose too few atoms to merge the frontier orbitals into electronic bands. However, unlike mononuclear molecular metal halide species with one excited state energy well in the PES, metal halide clusters could have multiple excited state energy wells, resulting in various exciton localization sites and emission pathways. Dual emissions have been observed in several 0D OMHHs containing lead halide clusters due to coexistence of two exited state energy minima (Figure 6j).^[40, 71] The excitation of another [Cu₂X₅]³⁻ cluster-based material involves breakage of two Cu-halogen bonds (Figure 6k), suggesting that the extreme case of structural distortion in clusters could be breakage and formation of bonds.^[84] In another multicomponent 0D material (C₈NH₁₂)₄Bi_{0.57}Sb_{0.43}Br₇·H₂O, energy transfer occurs from BiBr₆³⁻ to SbBr₆³⁻, and the broadband emission is considered to be a combination of emissions from free excitons, spinsinglet excitons, and spin-triplet exciton (Figure 61).^[92]

6. Applications

6.1. Optically pumped and electrically driven LEDs

During the last couple of years, a number of 0D OMHHs have been developed to exhibit highly efficient emissions with tunable colors covering the entire visible spectrum, from blue to green, yellow, orange, and red. The remarkable photophysical properties with high PLQEs, negligible self-absorption, and good thermal/photostability make them highly promising down conversion phosphors for optically pumped white LEDs (WLEDs). UV-pumped WLEDs fabricated using the blends of yellow emitting 0D (C4N2H14Br)4SnBr3I3 and blue phosphor BaMgAl₁₀O₁₇:Eu²⁺ in polydimethylsiloxane (PDMS) matrix can exhibit high color rendering indexes (CRIs) of up to 85 (Figure 7a). White lights ranging from "cold" to "warm" have been achieved by simply varying the ratio of yellow and blue phosphors as shown in Figure 7b and 7c.^[48] By using a series of 0D OMHHs with broadband emissions, (PPh₄)₂SbCl₅, (C4N2H14)4SnBr6), and (PPh4)2MnBr4, together with BaMgAl10O17:Eu2, we have demonstrated WLEDs with light outputs mimicking sunlight at different times of day with correlated color temperatures (CCTs) ranging from 3000 to 6000 K and CRI as high as 99 (Figure 7d and 7e).^[49] Recently, multicomponent 0D OMHHs with white emissions have also been utilized as single phase down-conversion phosphors for WLEDs.^[41, 42, 69, 92] For instance, (bmpy)9[SbCl5]2[Pb3Cl11] enables tunable warm white emissions with CCTs) varying from 3599 to 1272 K and color CRIs of up to 90 (Figure 7f).^[41] The use of 0D (HMTA)₄PbMn_{0.69}Sn_{0.31}Br₈ as single down conversion phosphor afforded a UV (360 nm) pumped WLED with CIE of (0.32, 0.33) and CRI of 95.^[42] A maximum brightness of 6570 cd m⁻² at 3.5 V and luminous power efficiency of 6.2 lm w⁻¹ were achieved (Figure 7g). The relatively low power efficiency is due to the use of a UV LED with low efficiency and mismatching of the excitation wavelength (deep UV excitation sources in the range 290-310 nm are not readily available), a single device architecture, and only front emission being

counted in measurement. This UV-pumped LED exhibited spectra stability at various driving current as show in Figure 7h. Making electric-driven LEDs based on 0D OMHHs is more challenging, as most of these materials have large direct band gaps with extremely low conductivity and charge carrier mobility due to insolating organic cations. To date, only Mn-based 0D OMHH (PPh₄)₂(MnBr₄) has successfully been used for electrically driven LEDs with EQEs of up to 10 % as shown in Figure 7i.^[33, 93]



Figure 7. (a) Images of blue and yellow phosphors with different weight ratios (from left to right, 1:0, 4:1, 2:1, 1:1 and 0:1) embedded in PDMS under ambient light and UV light. (b) The emission spectra of UV pumped LEDs with different weight ratios. (c) CIE coordinates and CCTs for the UV pumped LEDs plotted on the CIE1931 color space chromaticity chart. (d) CRI comparison between the champion 4000 K device and a YAG:Ce³⁺-based commercial white LED. (e) CIE 1931 diagram showing the chromaticity points of prototype devices; inset, CIE coordinates of devices lie on or close to the Planckian locus; (f) CIE coordinates for the excitation dependent photoluminescence of (C₉NH₂₀)₉[SbCl₅]₂[Pb₃Cl₁₁]: excited by 320 (blue), 330 (cyan), 340 (dark green), 350 (green), 360 (yellow), 370 (orange), and 380 nm (red). (g) voltage versus brightness and luminous efficiency of a UV-pumped LED (Inset shows the image of a UV pumped LED). (h) Emission spectra of a UV-pumped

LED at different driving currents. (i) The external quantum efficiency/current efficiency versus luminance for (Ph4P)₂[MnBr4] based OLEDs. Reprinted with permission. ^{[48] [49] [41] [42]} ^[33] Copyright 2020, the Royal Society of Chemistry; Copyright 2020, American Chemical Society; Copyright 2019,Wiley-VCH; Copyright 2020, Wiley-VCH.

6.2. X-ray Scintillators

X-ray scintillators, with the ability to convert high-energy X-ray into low-energy visible photons, have received great attention in recent years. 0D OMHHs are highly promising Xray scintillation materials, considering their characteristics matching well with the requirements of X-ray scintillators, including large X-ray stopping power of metals, little to no self-absorption, and high PLQEs of near-unity. Kovalenko et al. reported X-ray-excited luminescence (radioluminescence) of 0D Bmpip₂SnBr₄ and Bmpip₂PbBr₄ with brightness being commensurate with that of a commercial inorganic X-ray scintillator (NaI:Tl) (Figure 8a-e). [43] Recently our group reported the use of 0D (PPN)₂SbCl₅ as x-ray scintillation material with high light yield and exceptional environmental stability as shown in Figure 8f-i. (PPN)₂SbCl₅ single crystals prepared by solution growth exhibit visible PL with a PLQE of 98%. When excited by X-ray, (PPN)₂SbCl₅ single crystals exhibit red radioluminescence with a near-perfect linearity in a large range of X-ray dose rate, and a light yield (~49,000 photons/MeV) comparable with that of a commercial CsI(Tl) scintillator (~ 54,000 photons/MeV). A low detection limit of (PPN)₂SbCl₅ (191.4 nGy/s) was recorded, which is much lower than the required value for regular medical diagnostics $(5.5 \mu Gy/s)$. (PPN)₂SbCl₅ single crystals also display remarkable stability with little-to-no change of properties after storage in ambient conditions for two years.^[73] In another work, our group has developed flexible X-ray scintillators based on 0D (C₃₈H₃₄P₂)MnBr₄ (Figure 8j), which exhibits green emission peaked at 517 nm with a PLOE of ~ 95% (Figure 8k). By diffusing diethyl ether into a dichloromethane (DCM) precursor solution containing ethylenebis(triphenylphosphonium

bromide) (C₃₈H₃₄P₂) and MnBr₂ in a ratio of 1:1, inch-sized 0D (C₃₈H₃₄P₂)MnBr₄ single crystals could be prepared. The characterization of its X-ray scintillation found exceptional performance with an excellent linear response to X-ray dose rate, a high light yield of ~ 80,000 photons/MeV, and a very low detection limits of 72.8 nGy/s, which are superior to most of today's commercially available scintillators (Figure 81 and 8m). X-ray imaging tests showed that scintillators based (C₃₈H₃₄P₂)MnBr₄ fine powders could provide a visualization tool for X-ray radiography with as high spatial resolution of 0.322 mm. Flexible scintillators could be fabricated by blending (C₃₈H₃₄P₂)MnBr₄ powders with polydimethylsiloxane (PDMS), which show excellent flexibility and can be easily bent and stretched.^[94] To prepare high quality polymer/OMHH composite films, it is important to choose an appropriate polymer that is chemically inert to the OMHH. Also the particle size of OMHH should be small enough to achieve its uniform distribution in the polymer matrix. The investigations on the applications of flexible scintillators need further exploration.



Figure 8. (a) Crystal structure of Bmpip₂MBr₄, viewed along the [110] crystallographic

direction. (b) Disphenoidal coordination of lead, tin, and germanium, demonstrating a different degree of repulsion between axial bromide atoms and the lone pair, which occupies one of the equatorial positions. (c) RT spectra of PL (color-shaded) and PLE for Bmpip₂PbBr₄ (blue), Bmpip₂SnBr₄ (red), and Bmpip₂GeBr₄ (vellow) and (inset) a photograph of Bmpip₂PbBr₄ and Bmpip₂SnBr₄ under UV excitation. (d) X-ray fluorescence spectra under 50 kV Ag tube irradiation. (e) The normalized total amount of photons comparison with the same X-ray excitation source. NaI:Tl commercial scintillator, Bmpip₂PbBr₄ pellet, and Bmpip₂SnBr₄ pellet .(f) Crystal structure of (PPN)₂SbCl₅. (g) Excitation and emission spectra of (PPN)₂SbCl₅ single crystals. (h) RL spectra of (PPN)₂SbCl₅ and CsI(Tl) under 50 keV Xray excitation. The inset shows a digital photograph of the (PPN)₂SbCl₅ crystals under X-ray irradiation. (i) A linear relationship between the dose rate and RL intensity for (PPN)₂SbCl₅ and CsI(Tl) scintillators. The inset shows the data for (PPN)₂SbCl₅ measured at a low dose rate. (j) Crystal structure of (C₃₈H₃₄P₂)MnBr₄ (Mn green, Br orange, P blue, C gray; hydrogen atoms were hidden for clarity). (k) Absorption, excitation, and emission spectra of (C₃₈H₃₄P₂)MnBr₄. (I) Dose rate dependence of the RL intensity of standard reference Ce:LuAG and (C₃₈H₃₄P₂)MnBr₄. The inset shows the detection limit measurement under low X-ray dose for (C₃₈H₃₄P₂)MnBr₄. (m) Comparison of scintillator light yields of (C38H34P2)MnBr4. and previously reported and commercially available scintillators. Reprinted with permission. ^[43] ^[73] ^[94] Copyright 2019, American Chemical Society; Copyright 2020, American Chemical Society; Copyright 2020, Nature Publishing Group.

6.3.Sensors

The change of photophysical properties of 0D OMHHs under stimulations, e.g. heat, volatile organic solvents, and humidity, make them potential candidates for various types of sensors. Recently, Kovalenko's group developed a high-precision thermal sensor, by taking advantage of the temperature dependent photoluminescence lifetimes of 0D [C(NH₂)₃]₂SnBr₄, Cs₄SnBr₆

and (C₄N₂H₁₄I)₄SnI₆.^[95] The sensitive range could span from -100 to 110 °C with a thermometric precision down to 0.013 °C. A ToF fluorescence lifetime imaging (FLI) was demonstrated using Cs₄SnBr₆ powder with a much higher lateral thermographic resolution than that of a conventional bolometric thermogram (Figure 9a-d). Xia's group demonstrated a fast, switchable, and highly selective fluorescent sensor platform based on green emitting 0D (C₉NH₂₀)₂MnBr₄ for different organic solvents.^[96] It was found that the emission of (C₉NH₂₀)₂MnBr₄ could be quickly quenched in 10 s after exposure to acetone vapor, while no obvious fluorescence change was observed for many other solvents including ethanol, methanol, hexane and toluene (Figure 9e and 9f). Tang's group reported the use of PEA₂MnBr₄ could go through a luminescent humidity chromism from green emission at the water-desorption state to pink emission at the water-adsorption state (Figure 9g). Then they used this visible chromism to check the water content in toluene and obtain a low detection limit between 0.02 and 0.05 vol% as shown in Figure 9h.



Figure 9. (a) Temperature evolution of TRPL traces for Cs₄SnBr₆ excited at 355 nm. (b) PL lifetime temperature dependence for $[C(NH_2)_3]_2SnBr_4$ (blue curve), Cs₄SnBr₆ (green curve), $(C_4N_2H_{14}I)_4SnI_6$ (red curve). (c) Response of PL lifetime to a controlled temperature step of 0.05 °C. Repeated measurements yield a PL lifetime and temperature s.d. of ±0.04 ns and ±0.013 °C, respectively. (d) ToF-FLI thermogram of the sample under heating conditions (e)

Digital photos of (C₉NH₂₀)₂MnBr₄ upon exposure to various organic vapors for 10 min under 365 nm UV excitation. **(f)** Time-related emission spectra of (C₉NH₂₀)₂MnBr₄ toward acetone vapor. **(g)** Cycling durability (green PL intensity of dehydrated PEA₂MnBr₄) with repeated water adsorption and desorption. **(h)** Dehydrated PEA₂MnBr₄ in toluene solvent containing different amounts of water (0.01-0.1% v/v). Reprinted with permission. ^[95] ^[96] ^[97] Copyright 2019, Nature Publishing Group; Copyright 2019, American Chemical Society; Copyright 2020, the Royal Society of Chemistry.

6.4. Other Applications

In addition to diverse luminescent properties, photovoltaic and ferroelectric properties have been discovered on 0D OMHHs.^[98-100] For instance, by using mixed-anion halogenobismuthate(III) (CH₃-NH₃)₆BiI_{5.22}Cl_{3.78} (MBIC) with an optical indirect bandgap of 2.25 eV as light absorber, PVs were fabricated to exhibit a maximum power conversion efficiency of 0.18% and a high fill factor of almost 60% with a device structure of glass/ ITO/compact TiO₂/mesoporous TiO₂/MBIC /spiro-OMeTAD/Au.^[99] Gao et al, improved the PCE to1.09 % by employing a 0D (CH₃NH₃)₃[BiI₆]·3 CH₃NH₃Cl as absorber.^[98] For ferroelectric devices, Xiong's group demonstrated a molecular ferroelectrics by using [cyclopentylammonium]₂CdBr₄, which shows a moderate above-room-temperature Tc of 340.3 K.^[100] The order-disorder transition of both the organic cations and inorganic anions are responsible for the ferroelectric phase transition from *P*_{nam} to *P*_{na21}.

7. Summary and Outlook

Remarkable progress has been achieved in the development and study of 0D OMHHs based on numerous organic and metal halide building blocks during the last few years. From mononuclear molecular metal halide species to multinuclear metal halide clusters, from insulating organic moieties to semiconducting units, from a single component to multicomponent systems, the rich chemistry of this class of hybrid materials offer tremendous

opportunities to realize desired functionalities in single phase systems. One particular achievement is color tuning of their photoluminescence, covering the whole visible spectral region from blue to green, yellow, orange, red, and even white with PLQEs of up to nearunity. Detailed structural and photophysical studies together with DFT calculations have generated some fundamental understanding of the structure-property relationship for 0D OMHHs. For many 0D OMHHs containing site-isolated light-emitting metal halide species, their photophysical processes could be well described as molecular-type transitions, involving excited state structural reorganization and/or intersystem crossing. The remarkable optical properties of 0D OMHHs have enabled their applications in a variety of optoelectronic devices, including optically pumped and electrically driven LEDs, X-ray scintillators, fluorescent sensors, etc.

Despite these significant advances on 0D OMHHs, synthetic control of the crystallographic structures of this class of materials has not yet reached the same level as in conventional organic and inorganic materials. Moreover, the physical understanding of this class of hybrid materials is still very limited. For instance, photoluminescence remains the major functionality that has been extensively investigated to date, while other properties, such as electronic and magnetic properties, remain under-explored.^[101, 102] Investigations on the potential applications of this class of materials are also in a very early stage. To this end, there is a need to further pursue multidisciplinary research at a level beyond the current state-of-the-art to realize the potential of 0D OMHHs. The following are several issues and challenges to be addressed.

 Although 0D OMHHs containing various metal halide polyhedrons and clusters have been developed, the synthesis of this class of materials has mainly relied on the trial-and-error method and rational synthetic control has not yet been well established. One challenge to address is to control the distance between individual metal halides in 0D OMHHs and understand how the distance would affect their electronic couplings. Moreover, it would

be of great interest to achieve synthetic control of the composition and size of metal halide clusters with the formation of electronic band structures in individual metal halide clusters. From mononuclear metal halide molecular species to small metal halide clusters with molecular photophysical behaviors, and eventually large metal halide clusters as semiconductor quantum dots, 0D OMHHs could be a great platform to bridge molecules to clusters and crystals. The combinations of different metals and halides enable a large number of fundamental metal halide building blocks for the assembly of clusters with tunable electronic structures and bandgaps, which could be beneficial to the development of electronic devices based on 0D OMHHs.

- 2. Most 0D OMHHs developed to date exhibit optical properties controlled by the light emitting metal halide species, with organic cations serving as scaffolding components to achieve complete site isolation for individual metal halide species. 0D OMHHs with their optical properties dominated by the organic cations have not been well explored yet. As the molecular packing of organic cations could be significantly changed upon the interactions with metal halides, it is possible for 0D OMHHs to exhibit hidden properties of organic cations. Recently, we discovered photophysical tuning of 0D OMHHs from efficient phosphorescence to ultralong afterglow, by using various metal halides as counter anions to co-crystallized with tetraphenylphosphonium cations.^[103] This most recent advance in 0D OMHHs opens a new avenue for the development of functional materials, by using metal halides and many other complex species as counter ions to co-crystallized with organic ions to form functional ionically bonded hybrid systems.
- 3. While the number of publications on 0D OMHHs is soaring, challenges in understanding fundamental light-matter interactions in these condense hybrid materials with soft/deformable lattices remain. To date, most of the characterizations of this class of materials have been on the steady state photophysical properties, and the excited state dynamics and kinetics have not been well investigated. A number of questions, for

instance, how the topology of the metal halide frameworks, the rigidity of organic components, and the interactions between organic and metal halide moieties would affect the parameters of the ground state and excited states, remain unanswered. The exceptional tunability of this class of materials could be leveraged to control the softness of the lattice by changing the organic cations, allowing tuning the confinement to study exciton and charge carrier dynamics in the same photoactive metal halide structures. To understand the mechanisms of exciton delocalization, exciton localization and self-trapping, excitedstate structural reorganization, and decay of excited states in 0D OMHHs, detailed studies of the excited-state dynamics and kinetics using ultrafast spectroscopies, including timeresolved photoluminescence (TRPL) and transient absorption (TA) spectroscopies, are needed.

4. To date, various applications have been demonstrated for 0D OMHHs, in particular, those devices using them as light emitters. The most promising application established so far is perhaps X-ray scintillators, considering the low cost and high performance, although further research and development are needed to replace existing inorganic scintillators with 0D OMHHs in commercial products. To enable the use of 0D OMHHs for high-energy radiation detection, large single crystals or thick films are desired. While inchsized crystals could easily be prepared using anti-solvent diffusion or slow-cooling method, further investigation of crystal growth of 0D OMHHs is needed to deliver larger single crystals. For other device applications, the performance of 0D OMHHs based devices has not reached the level to meet the requirements for practical adaption. For instance, the large Stokes shifts of 0D OMHHs require the use of UV LED as optical pump source for WLEDs, which significantly reduce power efficiency. To address this issue, 0D OMHHs with small Stokes shifts are desired. Meanwhile, considering the exceptional structural and property tunability of 0D OMHHs, new functionalities and applications remain to be explored.

5. Despite the relatively good stability in ambient conditions arising from their "host-guest" structure, 0D OMHHs could suffer from moisture and other environmental conditions due to their ionic nature. In terms of long-term stability, strategies that can increase their moisture resistivity without negatively affecting their optoelectronic and photophysical properties are desired. Our current understanding suggests that organic moieties play an important role in stabilizing the hybrids. Also, the degradation pathways could be reduced by choosing resilient metal ions for OMHHs.

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References

[1] M. Saliba, T. Matsui, K. Domanski, J.-Y. Seo, A. Ummadisingu, S. M. Zakeeruddin, J.-P. Correa-Baena, W. R. Tress, A. Abate, A. Hagfeldt, Science 2016, 354, 206.

[2] M. Saliba, S. Orlandi, T. Matsui, S. Aghazada, M. Cavazzini, J. P. Correa-Baena, P. Gao, R. Scopelliti, E. Mosconi, K. H. Dahmen, F. De Angelis, A. Abate, A. Hagfeldt, G. Pozzi, M. Graetzel, M. K. Nazeeruddin, Nat. Energy 2016, 1, 15017.

[3] B. Zhao, S. Bai, V. Kim, R. Lamboll, R. Shivanna, F. Auras, J. M. Richter, L. Yang, L. Dai, M. Alsari, X.-J. She, L. Liang, J. Zhang, S. Lilliu, P. Gao, H. J. Snaith, J. Wang, N. C. Greenham, R. H. Friend, D. Di, Nat. Photonics 2018, 12, 783.

[4] Y. Cao, N. Wang, H. Tian, J. Guo, Y. Wei, H. Chen, Y. Miao, W. Zou, K. Pan, Y. He, H. Cao, Y. Ke, M. Xu, Y. Wang, M. Yang, K. Du, Z. Fu, D. Kong, D. Dai, Y. Jin, G. Li, H. Li, Q. Peng, J. Wang, W. Huang, Nature 2018, 562, 249.

[5] S. D. Stranks, H. J. Snaith, Nat. Nanotechnol. 2015, 10, 391.

[6] M. Shoaib, X. H. Zhang, X. X. Wang, H. Zhou, T. Xu, X. Wang, X. L. Hu, H. W. Liu, X. P. Fan, W. H. Zheng, T. F. Yang, S. Z. Yang, Q. L. Zhang, X. L. Zhu, L. T. Sun, A. L. Pan, J. Am. Chem. Soc. 2017, 139, 15592.

[7] L. Dou, Y. Yang, J. You, Z. Hong, W.-H. Chang, G. Li, Y. Yang, Nat. Commun. 2014, 5, 5404.

[8] S. A. Veldhuis, P. P. Boix, N. Yantara, M. Li, T. C. Sum, N. Mathews, S. G. Mhaisalkar, Adv. Mater. 2016.

[9] H. Zhang, Q. Liao, Y. Wu, Z. Zhang, Q. Gao, P. Liu, M. Li, J. Yao, H. Fu, Adv. Mater. 2018, 30, 1706186.

[10] H. M. Zhu, Y. P. Fu, F. Meng, X. X. Wu, Z. Z. Gong, Q. Ding, M. V. Gustafsson, M. T. Trinh, S. Jin, X. Y. Zhu, Nat. Mater. 2015, 14, 636.

[11] Q. Chen, J. Wu, X. Ou, B. Huang, J. Almutlaq, A. A. Zhumekenov, X. Guan, S. Han, L. Liang, Z. Yi, Nature 2018, 561, 88.

[12] W. Zhu, W. Ma, Y. Su, Z. Chen, X. Chen, Y. Ma, L. Bai, W. Xiao, T. Liu, H. Zhu, Light Sci. Appl. 2020, 9, 1.

[13] C. Zhou, H. Lin, Q. He, L. Xu, M. Worku, M. Chaaban, S. Lee, X. Shi, M.-H. Du, B. Ma, Mat. Sci. Eng. R 2019, 137, 38.

- [14] C. K. MØLLER, Nature 1958, 182, 1436.
- [15] L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X.
- Yang, A. Walsh, M. V. Kovalenko, Nano Lett. 2015, 15, 3692.
- [16] H. R. Lin, C. K. Zhou, Y. Tian, T. Siegrist, B. W. Ma, ACS Energy Lett. 2018, 3, 54.

[17] I. C. Smith, E. T. Hoke, D. Solis-Ibarra, M. D. McGehee, H. I. Karunadasa, Angew. Chem. Int. Ed. 2014, 53, 11232.

[18] M. D. Smith, A. Jaffe, E. R. Dohner, A. M. Lindenberg, H. I. Karunadasa, Chem. Sci. 2017, 8, 4497.

[19] Z. Yuan, C. Zhou, Y. Shu, Y. Tian, J. Messier, J. Wang, L. Burgt, K. Kountouriotis, Y. Xin, E. Holt, K. S. Schanze, R. Clark, T. Siegrist, B. Ma, Nat. Commun. 2017, 8, 14051.

[20] C. Zhou, Y. Tian, M. Wang, A. Rose, T. Besara, N. K. Doyle, Z. Yuan, J. C. Wang, R. Clark, Y. Hu, T. Siegrist, S. Lin, B. Ma, Angew. Chem. Int. Ed. 2017, 56, 9018.

[21] C. Zhou, H. Lin, M. Worku, J. Neu, Y. Zhou, Y. Tian, S. Lee, P. I. Djurovich, T. Siegrist, B. Ma, J. Am. Chem. Soc. 2018, 140, 13181.

[22] C. Zhou, H. Lin, Y. Tian, Z. Yuan, R. Clark, B. Chen, L. J. van de Burgt, J. C. Wang, Y. Zhou, K. Hanson, Q. J. Meisner, J. Neu, T. Besara, T. Siegrist, E. Lambers, P. Djurovich, B. Ma, Chem. Sci. 2018, 9, 586.

[23] M. Nikl, E. Mihokova, K. Nitsch, F. Somma, C. Giampaolo, G. Pazzi, P. Fabeni, S. Zazubovich, Chem. Phys. Lett. 1999, 306, 280.

[24] H. L. Wells, American Journal of Science 1893, s3-46, 34.

[25] C. K. Møller, *On the structure of caesium hexahalogeno-plumbates (II)*, Vol. 32, Munksgaard Copenhagen, Denmark, 1960.

[26] Q. A. Akkerman, S. Park, E. Radicchi, F. Nunzi, E. Mosconi, F. De Angelis, R. Brescia, P. Rastogi, M. Prato, L. Manna, Nano Lett. 2017, 17, 1924.

- [27] H. Wells, H. Foote, American Journal of Science (1880-1910) 1897, 3, 461.
- [28] O. Lindqvist, G. Johansson, F. Sandberg, T. Norin, Acta Chem. Scand 1968, 22, 2943.
- [29] V. Schramm, Inorg. Chem. 1978, 17, 714.
- [30] B. Krebs, K. Büscher, Z. Anorg. Allg. Chem. 1980, 463, 56.
- [31] K. A. Jensen, Z. Anorg. Allg. Chem. 1937, 232, 193.

[32] Z.-P. Wang, J.-Y. Wang, J.-R. Li, M.-L. Feng, G.-D. Zou, X.-Y. Huang, Chem. Commun. 2015, 51, 3094.

- [33] L.-J. Xu, C.-Z. Sun, H. Xiao, Y. Wu, Z.-N. Chen, Adv. Mater. 2017, 29, 1605739.
- [34] T. V. Sedakova, A. G. Mirochnik, V. E. Karasev, Opt. Spectrosc. 2011, 110, 755.
- [35] C. Zhou, H. Lin, S. Lee, M. Chaaban, B. Ma, Mater. Res. Lett. 2018, 6, 552.
- [36] H. Nikol, A. Becht, A. Vogler, Inorg. Chem. 1992, 31, 3277.

[37] C. Zhou, H. Lin, H. Shi, Y. Tian, C. Pak, M. Shatruk, Y. Zhou, P. Djurovich, M.-H. Du, B. Ma, Angew. Chem. Int. Ed. 2018, 57, 1021.

[38] C. Zhou, M. Worku, J. Neu, H. Lin, Y. Tian, S. Lee, Y. Zhou, D. Han, S. Chen, A. Hao, P. I. Djurovich, T. Siegrist, M.-H. Du, B. Ma, Chem. Mater. 2018, 30, 2374.

[39] H. Lin, C. Zhou, M. Chaaban, L.-J. Xu, Y. Zhou, J. Neu, M. Worku, E. Berkwits, Q. He, S. Lee, X. Lin, T. Siegrist, M.-H. Du, B. Ma, ACS Mater. Lett. 2019, 1, 594.

[40] C. Zhou, H. Lin, J. Neu, Y. Zhou, M. Chaaban, S. Lee, M. Worku, B. Chen, R. Clark, W. Cheng, J. Guan, P. Djurovich, D. Zhang, X. Lü, J. Bullock, C. Pak, M. Shatruk, M.-H. Du,

T. Siegrist, B. Ma, ACS Energy Lett. 2019, 1579.

[41] C. Zhou, S. Lee, H. Lin, J. Neu, M. Chaaban, L.-J. Xu, A. Arcidiacono, Q. He, M. Worku, L. Ledbetter, X. Lin, J. A. Schlueter, T. Siegrist, B. Ma, ACS Mater. Lett. 2020, 376.

[42] L. J. Xu, S. Lee, X. Lin, L. Ledbetter, M. Worku, H. Lin, C. Zhou, H. Liu, A. Plaviak, B. Ma, Angew. Chem. Int. Ed. 2020, 59, 14120.

[43] V. Morad, Y. Shynkarenko, S. Yakunin, A. Brumberg, R. D. Schaller, M. V. Kovalenko, J. Am. Chem. Soc. 2019, 141, 9764.

[44] G. Zhou, B. Su, J. Huang, Q. Zhang, Z. Xia, Mat. Sci. Eng. R 2020, 141, 100548.

[45] M. D. Smith, H. I. Karunadasa, Acc. Chem. Res. 2018, 51, 619.

[46] Q. A. Akkerman, A. L. Abdelhady, L. Manna, The Journal of Physical Chemistry Letters 2018, 9, 2326.

[47] D. Han, H. Shi, W. Ming, C. Zhou, B. Ma, B. Saparov, Y.-Z. Ma, S. Chen, M.-H. Du, J. Mater. Chem. C 2018, 6, 6398.

[48] C. K. Zhou, Y. Tian, Z. Yuan, H. R. Lin, B. H. Chen, R. Clark, T. Dilbeck, Y. Zhou, J. Hurley, J. Neu, T. Besara, T. Siegrist, P. Djurovich, B. W. Ma, ACS Appl. Mater. Interfaces 2017, 9, 44579.

[49] M. Worku, Y. Tian, C. Zhou, S. Lee, Q. Meisner, Y. Zhou, B. Ma, ACS Appl. Mater. Interfaces 2018, 10, 30051.

[50] M. Worku, L.-J. Xu, M. Chaaban, A. Ben-Akacha, B. Ma, APL Mater. 2020, 8, 010902.

[51] P. Fu, M. Huang, Y. Shang, N. Yu, H.-L. Zhou, Y.-B. Zhang, S. Chen, J. Gong, Z. Ning, ACS Appl. Mater. Interfaces 2018, 10, 34363.

[52] L. Zhou, J. F. Liao, Z. G. Huang, J. H. Wei, X. D. Wang, H. Y. Chen, D. B. Kuang, Angew. Chem. Int. Ed. 2019, 58, 15435.

[53] D. Chen, S. Hao, G. Zhou, C. Deng, Q. Liu, S. Ma, C. Wolverton, J. Zhao, Z. Xia, Inorg. Chem. 2019, 58, 15602.

[54] D. Chen, F. Dai, S. Hao, G. Zhou, Q. Liu, C. Wolverton, J. Zhao, Z. Xia, J. Mater. Chem. C 2020, 8, 7322.

[55] F. Lin, H. Wang, W. Liu, J. Li, J. Mater. Chem. C 2020, 8, 7300.

[56] T. Zhifang, L. Jinghui, Z. Cheng, L. Zha, H. Qingsong, X. Zewen, K. Toshio, H. Hideo, N. Guangda, L. Efrat, C. Yibing, T. Jiang, Adv. Funct. Mater., 0, 1801131.

[57] B. Lee, C. C. Stoumpos, N. Zhou, F. Hao, C. Malliakas, C. Y. Yeh, T. J. Marks, M. G. Kanatzidis, R. P. Chang, J. Am. Chem. Soc. 2014, 136, 15379.

[58] G. Song, M. Li, Y. Yang, F. Liang, Q. Huang, X. Liu, P. Gong, Z. Xia, Z. Lin, J. Phys. Chem. Lett. 2020, 11, 1808.

[59] L.-J. Xu, H. Lin, S. Lee, C. Zhou, M. Worku, M. Chaaban, Q. He, A. Plaviak, X. Lin, B. Chen, M.-H. Du, B. Ma, Chem. Mater. 2020, 32, 4692.

[60] Z. Li, Y. Li, P. Liang, T. Zhou, L. Wang, R.-J. Xie, Chem. Mater. 2019, 31, 9363.

[61] Z. Wang, Z. Zhang, L. Tao, N. Shen, B. Hu, L. Gong, J. Li, X. Chen, X. Huang, Angew. Chem. Int. Ed. 2019, 58, 9974.

[62] V. Morad, S. Yakunin, M. V. Kovalenko, ACS Mater. Lett. 2020, 2, 845.

[63] L. Mao, P. Guo, S. Wang, A. K. Cheetham, R. Seshadri, J. Am. Chem. Soc. 2020, 142, 13582.

[64] G. Zhou, Z. Liu, J. Huang, M. S. Molokeev, Z. Xiao, C. Ma, Z. Xia, J. Phys. Chem. Lett. 2020, 11, 5956.

[65] A. Yangui, R. Roccanova, T. M. McWhorter, Y. Wu, M.-H. Du, B. Saparov, Chem. Mater. 2019, 31, 2983.

[66] T. Kawai, A. Ishii, T. Kitamura, S. Shimanuki, M. Iwata, Y. Ishibashi, J. Phys. Soc. Jpn. 1996, 65, 1464.

[67] B. W. Park, B. Philippe, X. Zhang, H. Rensmo, G. Boschloo, E. M. Johansson, Adv. Mater. 2015, 27, 6806.

[68] R. L. Hoye, R. E. Brandt, A. Osherov, V. Stevanovic, S. D. Stranks, M. W. Wilson, H.

Kim, A. J. Akey, J. D. Perkins, R. C. Kurchin, J. R. Poindexter, E. N. Wang, M. G. Bawendi, V. Bulovic, T. Buonassisi, Chemistry 2016, 22, 2605.

[69] M. Li, J. Zhou, G. Zhou, M. S. Molokeev, J. Zhao, V. Morad, M. V. Kovalenko, Z. Xia, Angew. Chem. Int. Ed. 2019, 58, 18670.

[70] M. Li, M. S. Molokeev, J. Zhao, Z. Xia, Adv. Opt. Mater. 2020, 8.

[71] S. Lee, C. Zhou, J. Neu, D. Beery, A. Arcidiacono, M. Chaaban, H. Lin, A. Gaiser, B. Chen, T. E. Albrecht-Schmitt, T. Siegrist, B. Ma, Chem. Mater. 2019, 32, 374.

[72] B. Febriansyah, C. S. D. Neo, D. Giovanni, S. Srivastava, Y. Lekina, T. M. Koh, Y. Li,

Z. X. Shen, M. Asta, T. C. Sum, N. Mathews, J. England, Chem. Mater. 2020, 32, 4431.

[73] Q. He, C. Zhou, L. Xu, S. Lee, X. Lin, J. Neu, M. Worku, M. Chaaban, B. Ma, ACS Mater. Lett. 2020, 2, 633.

- [74] J. Zhou, M. Li, M. S. Molokeev, J. Sun, D. Xu, Z. Xia, J. Mater. Chem. C 2020, 8, 5058.
- [75] Y. Jing, Y. Liu, X. Jiang, M. S. Molokeev, Z. Lin, Z. Xia, Chem. Mater. 2020, 32, 5327.

[76] M. Li, Y. Li, M. S. Molokeev, J. Zhao, G. Na, L. Zhang, Z. Xia, Adv. Opt. Mater. 2020, 2000418.

[77] M. D. Smith, B. A. Connor, H. I. Karunadasa, Chem. Rev. 2019, 119, 3104.

[78] J. Frenkel, Phys. Rev. 1931, 37, 17.

[79] L. Mao, Y. Wu, C. C. Stoumpos, M. R. Wasielewski, M. G. Kanatzidis, J. Am. Chem. Soc. 2017, 139, 5210.

[80] A. Yangui, D. Garrot, J. S. Lauret, A. Lusson, G. Bouchez, E. Deleporte, S. Pillet, E. E. Bendeif, M. Castro, S. Triki, Y. Abid, K. Boukheddaden, J. Phys. Chem. C 2015, 119, 23638.

[81] T. Hu, M. D. Smith, E. R. Dohner, M. J. Sher, X. X. Wu, M. T. Trinh, A. Fisher, J.

Corbett, X. Y. Zhu, H. I. Karunadasa, A. M. Lindenberg, J. Phys. Chem. Lett. 2016, 7, 2258.

[82] D. Cortecchia, S. Neutzner, A. R. Srimath Kandada, E. Mosconi, D. Meggiolaro, F. De Angelis, C. Soci, A. Petrozza, J. Am. Chem. Soc. 2017, 139, 39.

[83] J. Yin, H. Li, D. Cortecchia, C. Soci, J.-L. Brédas, ACS Energy Lett. 2017, 2, 417.

[84] R. Roccanova, A. Yangui, H. Nhalil, H. Shi, M.-H. Du, B. Saparov, ACS Appl. Electron. Mater. 2019, 1, 269.

[85] D. B. Tran Thoai, R. Zimmermann, M. Grundmann, D. Bimberg, Phys. Rev. B 1990, 42, 5906.

[86] X. X. Wu, M. T. Trinh, X. Y. Zhu, J. Phys. Chem. C 2015, 119, 14714.

[87] G. Song, M. Li, S. Zhang, N. Wang, P. Gong, Z. Xia, Z. Lin, Adv. Funct. Mater. 2020, 30, 2002468.

- [88] P. W. M. Jacobs, J. Phys. Chem. Solids 1991, 52, 35.
- [89] W. C. de Gruijter, J. Solid State Chem. 1973, 6, 151.
- [90] A. Vogler, H. Nikol, Comments Inorg. Chem. 1993, 14, 245.
- [91] M. Wrighton, D. Ginley, Chem. Phys. 1974, 4, 295.

[92] R. Zhang, X. Mao, Y. Yang, S. Yang, W. Zhao, T. Wumaier, D. Wei, W. Deng, K. Han, Angew. Chem. Int. Ed. 2019, 58, 2725.

[93] T. Jun, K. Sim, S. Iimura, M. Sasase, H. Kamioka, J. Kim, H. Hosono, Adv. Mater. 2018, 30, 1804547.

[94] L.-J. Xu, X. Lin, Q. He, M. Worku, B. Ma, Nat. Commun. 2020, 11, 4329.

[95] S. Yakunin, B. M. Benin, Y. Shynkarenko, O. Nazarenko, M. I. Bodnarchuk, D. N. Dirin, C. Hofer, S. Cattaneo, M. V. Kovalenko, Nat. Mater. 2019, 18, 846.

[96] M. Li, J. Zhou, M. S. Molokeev, X. Jiang, Z. Lin, J. Zhao, Z. Xia, Inorg. Chem. 2019, 58, 13464.

[97] W. Gao, M. Leng, Z. Hu, J. Li, D. Li, H. Liu, L. Gao, G. Niu, J. Tang, Dalton T. 2020, 49, 5662.

[98] Y. Zhang, F. Fadaei Tirani, P. Pattison, K. Schenk-Joss, Z. Xiao, M. K. Nazeeruddin, P. Gao, Dalton T. 2020, 49, 5815.

[99] S. F. Hoefler, T. Rath, R. Fischer, C. Latal, D. Hippler, A. Koliogiorgos, I. Galanakis,

A. Bruno, A. Fian, T. Dimopoulos, G. Trimmel, Inorg. Chem. 2018, 57, 10576.

- [100] C. R. Huang, X. Luo, W. Q. Liao, Y. Y. Tang, R. G. Xiong, Inorg. Chem. 2020, 59, 829.
- [101] C. Bellitto, E. M. Bauer, G. Righini, Coord. Chem. Rev. 2015, 289, 123.
- [102] P. Vishnoi, J. L. Zuo, T. A. Strom, G. Wu, S. D. Wilson, R. Seshadri, A. K. Cheetham, Angew. Chem. Int. Ed. 2020, 59, 8974.

[103] L.-J. Xu, A. Plaviak, X. Lin, M. Worku, Q. He, M. Chaaban, B. J. Kim, B. Ma, Angew. Chem. Int. Ed. 2020.



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Zero-dimensional organic metal halide hybrids (0D OMHHs) have emerged as highly promising photoactive hybrid materials with unique properties and applications in a variety of areas. This progress report discusses the recent advances in the development and study of luminescent 0D OMHHs, from synthetic structural control to fundamental understanding of the structure-property relationship and device integration.

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Recent advances in luminescent zero-dimensional organic metal halide hybrids

