

Bulk Assembly of Multicomponent Zero-Dimensional Metal Halides with Dual Emission

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ABSTRACT: Bulk assemblies of zero-dimensional (0D) metal halides with exceptional structural versatility have enabled the development of a number of highly efficient emitters with tunable photophysical properties. Here we report a novel single crystalline bulk assembly of distinct multicomponent 0D metal halides, (bmpy)₉[SbCl₅]₂[Pb₃Cl₁₁] (bmpy = 1-butyl-1-methylpyrrolidinium), which exhibits dual emissions from distinct metal halide species. Excitation dependent warm white light emissions with high photoluminescence quantum efficiencies of > 70% can be obtained by combining the green emission from Pb₃Cl₁₁⁵⁻ and orange emission from SbCl₅²⁻. Due to complete site isolation by wide bandgap organic moieties and little-to-no spectral overlaps, no energy transfer occurs between the two distinct emitting species, allowing for precise color control by manipulating the excitation wavelengths. Our discovery of dual emitting organic metal halide hybrid opens up a new way to develop precisely ordered single-crystalline multicomponent materials with multi-functionalities.

Multicomponent complexes composed of more than one functional species provide excellent platforms to design function-directed materials, which have useful applications in various fields, such as catalysis¹⁻³, molecular magnetism⁴⁻⁵, small-molecule activation⁶⁻⁷, and photoluminescence⁸⁻⁹. As far as photoluminescence is concerned, single-phase multicomponent complexes containing multiple emitting centers have been developed to exhibit white emissions.¹⁰⁻¹¹ This strategy of integrating multiple functional species into a single-phase system has also been successfully exercised to afford many coordination assemblies with white light emissions, such as metal-organic frameworks and metal-organic cages.⁸ However, most of multicomponent assemblies developed to date still suffer from relatively low photoluminescence quantum efficiencies (PLQEs) and many rely on rare earth elements.¹²⁻¹³ Some recent efforts have extended this strategy to organic metal halide hybrids with

both organic and metal halide species emitting different wavelengths.¹⁴⁻¹⁷

Organic metal halide hybrids have recently emerged as an important class of solid-state photoactive materials. Synthetic control of the topology of metal halides has enabled this class of materials to possess three- (3D), two- (2D), one- (1D), and zero-dimensional (0D) structures at the molecular level.¹⁸⁻²⁴ In 0D organic metal halide hybrids or bulk assemblies of 0D metal halides, individual metal halide molecular/cluster species are isolated from each other by wide bandgap (HOMO-LUMO) organic moieties to form a perfect “host-guest” structure.²⁵⁻²⁸ Since our discovery of 0D (C₄N₂H₁₄X)₄SnX₆ (X = Br or I), a number of bulk assemblies of 0D metal halides have been developed as highly efficient light emitters with PLQEs of up to near unity. 0D organic metal halide hybrid structures could also accommodate various types of metal halide species/clusters in a single crystal with periodically embedded metal halide species independent of each other. However, synthesizing single crystalline organic metal halide hybrids simultaneously containing multiple metal halide clusters is not trivial due to the lack of design rules for this class of materials. Using mixed metal halide reactants for the preparation of organic metal halide hybrids often result in phase separation and crystallization of various single component 0D organic metal halide hybrids. To date only a couple of bulk assemblies of distinct metal halide clusters have been reported that contain multiple metal halides for this class of 0D hybrids.¹⁶⁻¹⁷ In these bulk assemblies of 0D metal halide clusters, Pb₃Cl₁₁⁵⁻ clusters are responsible for the light emission, while MCl₄²⁻ (M = Pb or Zn) species act as an inert structural scaffold that assist the formation of single crystals. Little-to-no contribution to the photophysical properties of these scaffold moieties is observed. Very recently, Mn²⁺ emission was incorporated in metal halide clusters but with both emissions in green/yellow region.²⁹ These recent discoveries suggest that incorporating multiple emitting metal halide species into a single crystal bulk assembly of 0D metal halides to exhibit dual/multiple

emissions is possible, which however has not been established to date, according to the best of our knowledge.

Here we report a novel bulk assembly of multicomponent 0D metal halides with a formula of $(\text{bmpy})_9[\text{SbCl}_5]_2[\text{Pb}_3\text{Cl}_{11}]$ (bmpy = 1-butyl-1-methylpyrrolidinium), in which two different light emitting metal halide species $\text{Pb}_3\text{Cl}_{11}^{5-}$ and SbCl_5^{2-} co-crystallized with organic moieties bmpy^+ to form a 0D structure at the molecular level. Benefiting from the unique 0D structure with two “guests” ($\text{Pb}_3\text{Cl}_{11}^{5-}$ and SbCl_5^{2-}) periodically embedded in one wide bandgap “host” (bmpy^+), no electronic coupling is apparent between individual $\text{Pb}_3\text{Cl}_{11}^{5-}$ and SbCl_5^{2-} , allowing this multicomponent single crystalline material to combine properties from both metal halide species. Excitation dependent dual emissions with high PLQEs of > 70% were observed in this organic metal halide hybrid. With a good balance between the green emission from $\text{Pb}_3\text{Cl}_{11}^{5-}$ and orange emission from SbCl_5^{2-} by tuning suitable excitation wavelengths, good quality warm white light emissions are achieved.

$(\text{bmpy})_9[\text{SbCl}_5]_2[\text{Pb}_3\text{Cl}_{11}]$ single crystals were prepared by slowly diffusing acetone in the Dimethylformamide (DMF) precursor solution containing bmpyCl , antimony chloride

(SbCl_3) and lead chloride (PbCl_2) at room temperature. The crystal structure was determined using single-crystal X-Ray diffraction, adopting a monoclinic space group $P2_1$. Details can be found in Supporting Information (Table S1, S2). As shown in Figure 1A, a perfect 0D structure at molecule level was obtained, which is analogous to our previously reported green-emitting bulk assembly of metal halide clusters $(\text{bmpy})_9[\text{ZnCl}_4]_2[\text{Pb}_3\text{Cl}_{11}]$. View of the crystal structure from different angles can be found in Figure S1. Unlike wide-bandgap ZnCl_4^{2-} serving as an inert structural scaffold, SbCl_5^{2-} (Figure 1B) was chosen considering its efficient orange to red emission upon ultraviolet excitation observed in 0D organic metal halide hybrids.^{25, 28, 30} In this case, SbCl_5^{2-} pyramids could act as another emission center, in addition to the metal halide clusters $\text{Pb}_3\text{Cl}_{11}^{5-}$. The scheme of this newly designed 0D structure with two emitting “guests” periodically embedded in one wide-bandgap “host” is shown in Figure 1C. The composition and structural uniformity of prepared single crystals were further confirmed by elemental analysis and powder XRD with results presented in the Supplementary Information (Figure S2). Thermal gravimetric analysis suggests a good thermo-stability of $(\text{bmpy})_9[\text{SbCl}_5]_2[\text{Pb}_3\text{Cl}_{11}]$ single crystals without decomposition up to 200 °C (Figure S3).

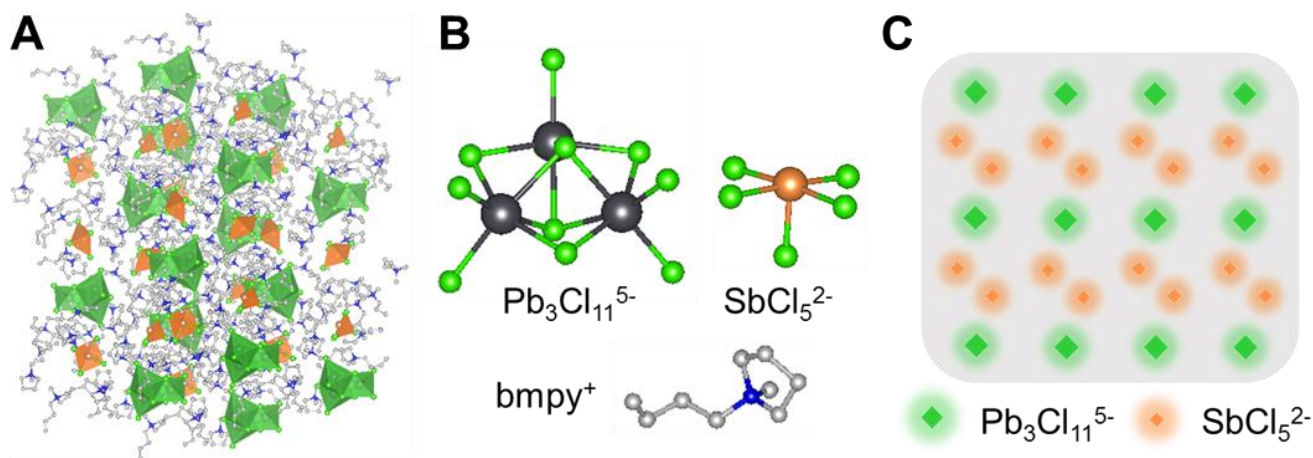


Figure 1. Crystal structure and the scheme of multicomponent metal halide hybrids. (A) View of the single-crystal structure of $(\text{bmpy})_9[\text{SbCl}_5]_2[\text{Pb}_3\text{Cl}_{11}]$ (color scheme: $[\text{Pb}_3\text{Cl}_{11}]^{5-}$, green polyhedrons; $[\text{SbCl}_5]^{2-}$, orange pyramids; N, blue atoms; C, gray atoms; hydrogen atoms are hidden for clarity). (B) A Pb chloride cluster $[\text{Pb}_3\text{Cl}_{11}]^{5-}$, a Sb chloride pyramid $[\text{SbCl}_5]^{2-}$, and an organic cation bmpy^+ in the ball-and-stick model. (C) Scheme of 0D “host-guest” structure with multiple metal halide species.

$(\text{bmpy})_9[\text{SbCl}_5]_2[\text{Pb}_3\text{Cl}_{11}]$ bulk crystals are pale yellow under ambient lighting, indicating a small amount of absorption in the visible light range, which is confirmed by absorption spectrum shown in Figure S4. The photophysical properties of $(\text{bmpy})_9[\text{SbCl}_5]_2[\text{Pb}_3\text{Cl}_{11}]$ at different conditions were further investigated. As shown in Figure 2A, a broadband dual emission peaked at 516 nm (Em I) and 673 nm (Em II) was recorded under 350 nm excitation. Interestingly, the excitation spectra of two emission peaks are completely different from each other, suggesting the distinct origins of two emission peaks. By fitting the emission spectra with two Gaussian-shaped peaks (Figure S5), the high energy peak shares many similarities with the emission of $(\text{bmpy})_9[\text{ZnCl}_4]_2[\text{Pb}_3\text{Cl}_{11}]$. For example, their emission peaks and fullwidth at half-maximum (fwhm) are 517 nm and 71 nm for $(\text{bmpy})_9[\text{SbCl}_5]_2[\text{Pb}_3\text{Cl}_{11}]$, and 512 nm and 61 nm for $(\text{bmpy})_9[\text{ZnCl}_4]_2[\text{Pb}_3\text{Cl}_{11}]$, which are very close to each other. Additionally, the emission decay lifetime of high energy Em I was measured to be 0.51 μs (Figure

2B), which compares well to that of $(\text{bmpy})_9[\text{ZnCl}_4]_2[\text{Pb}_3\text{Cl}_{11}]$ at 0.54 μs . Considering the similar crystal structure and chemical environment for $\text{Pb}_3\text{Cl}_{11}^{5-}$ in these two materials, it is reasonable to assign this high energy emission to the $\text{Pb}_3\text{Cl}_{11}^{5-}$ metal halide clusters. In addition to Em I, an emission with lower energy (Em II) peaked at 673 nm was observed, with a Stokes shift of 128 nm (0.43 eV) and a decay lifetime of 4.3 μs . These features can be attributed to SbCl_5^{2-} units, which have been reported with similar properties in other 0D organic antimony chlorides, such as $(\text{bmpy})_2\text{SbCl}_5$ and $(\text{Ph}_4\text{P})_2\text{SbCl}_5$, with a decay lifetime of 4.2 μs and 4.6 μs , respectively.^{25, 28}

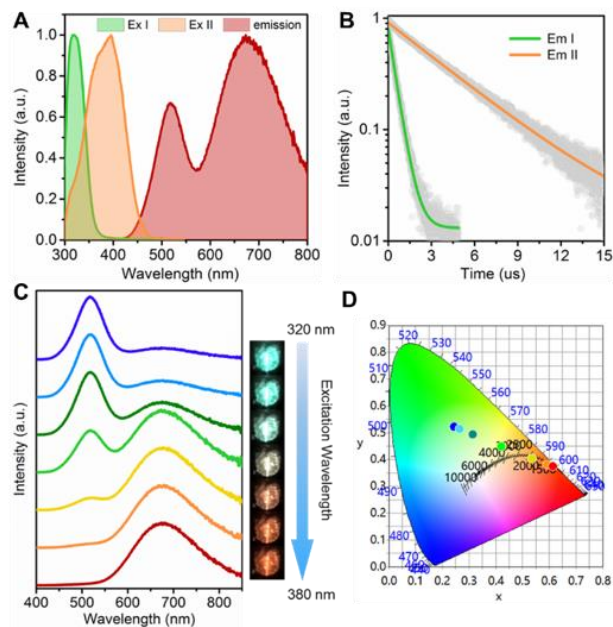


Figure 2. Optical properties of (bmpy)₉[SbCl₅]₂[Pb₃Cl₁₁] at room temperature. (A) Excitation and emission (excited at 350 nm) spectra of (bmpy)₉[SbCl₅]₂[Pb₃Cl₁₁] at room temperature. (B) Emission decay curves of (bmpy)₉[SbCl₅]₂[Pb₃Cl₁₁] monitored at 510 nm and 630 nm, respectively, at room temperature. (C) Excitation dependent photoluminescence spectra at room temperature (excitation wavelength: from 320 nm to 380 nm with a step of 10 nm). (D) CIE coordinates for the excitation dependent photoluminescence plotted on the CIE1931 color space chromaticity chart: excited by 320 nm (blue), 330 nm (cyan), 340 nm (dark green), 350 nm (green), 360 nm (yellow), 370 nm (orange), and 380 nm (red).

To further confirm the independent nature of dual emissions, excitation dependent emission spectra were recorded for the single crystals, as shown in Figure 2C. As the excitation shifts to longer wavelengths, the ratio of Em I to Em II becomes smaller due to the more red-shifted excitation spectrum of Em II than that of Em I, as shown in Figure 2C. Unlike previously reported multicomponent structures with efficient energy transfer between different emitting centers, there is little-to-no energy transfer between high energy Pb₃Cl₁₁⁵⁻ and low energy SbCl₅²⁻ species, due to (i) complete isolation by wide-bandgap organic moieties and (ii) minimum spectral overlap between the emission of Pb₃Cl₁₁⁵⁻ and absorption of SbCl₅²⁻. The excitation dependent luminescent properties offer a facile way to tune the emission color in this 0D organic metal halide hybrid, and high-quality broadband white emission can be achieved. The CIE coordinates of dual emissions under different excitations from 320 nm to 380 nm are shown in Figure 2D. Tunable warm white emissions can be obtained with correlated color temperatures (CCTs) varying from 3599 to 1272 K and color rendering index (CRI) of up to 90. Benefiting from the perfect “host-guest” structure, this bulk assembly of multicomponent 0D metal halides possesses high photoluminescence quantum efficiencies of >70% (Figure S6), which is one of the most efficient single-phase white emitters reported to date.³¹⁻³² To verify that these emissions are the intrinsic properties of (bmpy)₉[SbCl₅]₂[Pb₃Cl₁₁], we characterized the dependence of photoluminescence on the excitation power at room temperature. As shown in Figure S7, both Em I and Em II

exhibit linear dependence on the excitation power density, suggesting that both emissions do not originate from permanent defects or vacancies. It should be noted that this single-crystalline bulk assembly of multicomponent 0D metal halides is different from the heterogeneous mixture of multiple types of 0D organic metal halide hybrids containing single metal halide species each. Although mixing different 0D organic metal halide hybrids could afford dual emissions, the mixture is not a single phase with a periodic and uniform structure. Furthermore, preparing uniform mixtures of two or multiple 0D organic metal halide hybrids could easily introduce a great number of defects that can significantly impact the optical properties, for instance reducing PLQEs.

The photophysical properties of (bmpy)₉[SbCl₅]₂[Pb₃Cl₁₁] were also investigated at 77K. Owing to the complete isolation between Pb₃Cl₁₁⁵⁻ and SbCl₅²⁻ by organic moieties with the shortest distance exceeding 0.5 nm, individual metal halide species are believed not to interact with each other. Therefore, it is not surprising that excitation dependent dual emissions still display at 77K, as shown in Figure 3a. It was found that Em I showed a clear blue shift with temperature changing from room temperature to 77K, a similar behavior observed in green-emitting (bmpy)₉[ZnCl₄]₂[Pb₃Cl₁₁].¹⁷ This finding suggests that not only the optical properties but also other characteristic features (e.g. environment/temperature-dependent properties) of individual metal halide species can be reserved in bulk assemblies of multicomponent 0D metal halides. This environment-dependent property of Pb₃Cl₁₁⁵⁻ was further confirmed by recording the emission decay profiles at 77K. The emission decay lifetime of high energy emission I was increased to 12.1 μs, consistent with the change from emitting state 2 (ES2) to emitting state 1 (ES1) in (bmpy)₉[ZnCl₄]₂[Pb₃Cl₁₁] due to the insufficient thermal activation energy and more rigid environment at low temperature. In contrast, there was no obvious change on Em II in terms of peak position and decay lifetime, consistent with what has been observed in other 0D Sb chloride hybrids.^{25, 28}

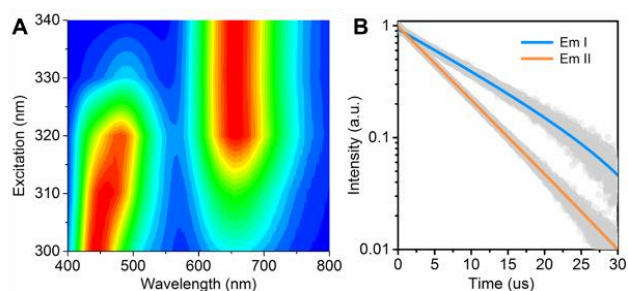


Figure 3. Optical properties of (bmpy)₉[SbCl₅]₂[Pb₃Cl₁₁] at 77K. (A) Excitation dependent photoluminescence spectra at 77K. (B) Emission decay curves of (bmpy)₉[SbCl₅]₂[Pb₃Cl₁₁] monitored at 440 nm and 630 nm, respectively, at 77K.

As the interactions between the light emitting species SbCl₅²⁻ and Pb₃Cl₁₁⁵⁻ are negligible, the photophysical processes for this novel organic metal halide hybrid can be depicted as shown in Figure 4. When illuminated with low energy light, SbCl₅²⁻ pyramids can be excited following ¹S₀→³P₁ transition and undergo structural reorganization in the excited state to exhibit Stokes-shifted broadband emission.³³ While upon high energy excitation, the Pb₃Cl₁₁⁵⁻ metal halide clusters are excited and undergo structural distortion to reach emitting state 2

(ES2) and emit light, behaving alike to the green-emitting (bmpy)₉[ZnCl₄]₂[Pb₃Cl₁₁].¹⁶⁻¹⁷ As the excitation energy changes, the ratio of Em I to Em II changes due to the varying distribution of the photo-generated excitons. At low temperature (77 K), the thermal energy is insufficient to enable photo-generated excitons to overcome the energy barrier between ES1 and ES2, blue emission peaked at around 450 nm was observed from emitting state 1 (ES1). Meanwhile, the emission peak from SbCl₅²⁻ merely become narrower due to the reduced thermally populated vibrational states at low temperature. These results clearly show that the multiple emitting metal halide species in single-crystalline bulk assemblies of multicomponent metal halides can preserve their intrinsic properties as displayed in 0D metal halide hybrids containing one type of metal halides clusters only.

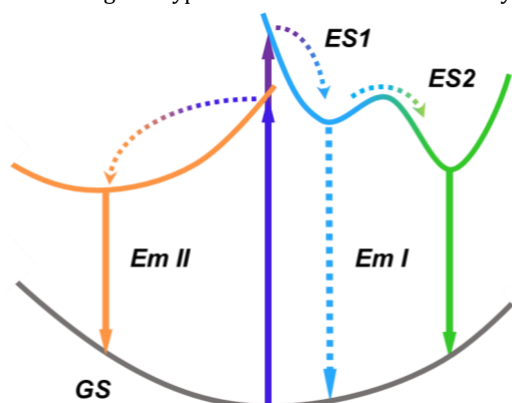


Figure 4. Mechanism of excited-state structural relaxation in multicomponent 0D metal halide hybrids.

In summary, we have synthesized and characterized a novel organic metal halide hybrid with 0D structure, (bmpy)₉[SbCl₅]₂[Pb₃Cl₁₁], in which two independent light-emitting metal halide species are integrated into a single crystalline phase. The complete site isolation by wide-bandgap organic moieties and little-to-no spectral overlaps between two metal halide species enable the single crystals to exhibit photophysical properties from both metal halide species. Excitation dependent dual emissions with tunable color temperatures and remarkable photoluminescence quantum efficiencies have been achieved in this material. Our work paves a new way to develop single-phase highly efficient light emitters containing multiple emitting species, and bulk assemblies of multicomponent 0D metal halides could become a highly promising material platform for the development of multifunctional materials.

ASSOCIATED CONTENT

Supporting Information

Details of syntheses and characterizations of structural and optical properties. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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