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Blue Emitting Single Crystalline Assembly of Metal Halide Clusters

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Supporting Information

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ABSTRACT: The rich chemistry of organic−inorganic metal halide hybrids has enabled the development of a variety of crystalline structures with controlled morphological and molecular dimensionalities. Here we report for the first time a single crystalline assembly of metal halide clusters, $(C_9NH_{20})_7(PbCl_4)Pb_3Cl_{11}$, in which lead chloride tetrahedrons ($PbCl_4^{2-}$) and face-sharing lead chloride trimer clusters ($Pb_3Cl_{11}^{5-}$) cocrystallize with organic cations ($C_9NH_{20}^+$) to form a periodical zero-dimensional (0D) structure at the molecular level. Blue light emission peaked at 470 nm with a photoluminescence quantum efficiency (PLQE) of around 83% was realized for this single crystalline hybrid material, which is attributed to the individual lead chloride clusters. Our discovery of single crystalline assembly of metal halide clusters paves a new path to functional cluster assemblies with highly tunable structures and remarkable properties.

Molecular clusters are material species with well-defined chemical composition and structure at the nanometer scale, which possess unique physical and chemical properties beyond those available from typical molecules and bulk solids.[1−3] Assembling molecular clusters, including fullerenes, inorganic clusters, and inorganic nanocrystals, into hierarchical structures leads to new functional materials with potential applications in a wide range of technologies.[4−9] As the properties of cluster-assembled materials often preserve those of the molecular cluster building blocks, controlling the size, composition, and intracluster interactions of clusters offer them exceptional property tunability. However, building up cluster-assembled materials is not trivial due to the lack of rational design rules of governing the assembly of clusters. It remains a grand scientific challenge to develop discrete cluster-assembled materials for high performance functional devices.

Organic−inorganic metal halide hybrids, made of a great variety of organic and metal halide anions, are an emerging class of functional materials with exceptional structural tunability.[10,11] By reacting appropriate organic salts and metal halides, hybrids with distinct crystal structures can be prepared, in which the inorganic metal halides form three-dimensional (3D) networks,[12−14] two-dimensional (2D) planar or corrugated layers,[15−17] one-dimensional (1D) chains or tubes,[18,19] and zero-dimensional (0D) structures.[20,21] The structural versatility of this class of materials suggests that there are tremendous opportunities to further explore novel crystal structures to exhibit properties obeying nonobvious trends.

Herein we report a single crystalline assembly of metal halide clusters with a chemical formula of $(C_9NH_{20})_7(PbCl_4)Pb_3Cl_{11}$, in which lead chloride tetrahedrons ($PbCl_4^{2-}$) and fused face-sharing lead chloride trimers ($Pb_3Cl_{11}^{5-}$) cocrystallize with organic cations ($C_9NH_{20}^+$) to form a long-range order 0D structure at the molecular level. The complete isolation of $Pb_3Cl_{11}^{5-}$ by wide band gap $PbCl_4^{2-}$ and $C_9NH_{20}^+$ moieties leads to no electronic coupling between $Pb_3Cl_{11}^{5-}$ clusters. This results in the single crystalline assembly retaining many of the intrinsic characteristics of $Pb_3Cl_{11}^{5-}$ clusters. Highly luminescent blue emission with PLQE exceeding 80% was realized for this lead chloride hybrid, due to the formation of localized excitons in individual molecular clusters. Our discovery is significantly different from what was reported in another bulk assembly of lead bromide clusters, which does not exhibit high efficiency emission to show the intrinsic properties of metal halide clusters.[22]

A facile wet chemistry method was used to grow $(C_9NH_{20})_7(PbCl_4)Pb_3Cl_{11}$ single crystals with a high yield of around 70%, which involved slowly diffusing a nonsolubilizing solvent acetone into a acetonitrile (CH_3CN) precursor solution containing lead chloride ($PbCl_2$) and 1-butyl-1-methylpyrrolidinium chloride ($C_9NH_{20}Cl$) at room temperature (see Supporting Information for the details of synthesis). The crystal structure of this hybrid material adopting a triclinic space group $P\bar{1}$ was determined using single crystal X-ray Diffraction (SCXRD) (Table S1). Figure 1A shows the view of the crystal structure with a perfect 0D structure at the molecular level. We can find that the metal halide anionic species, $PbCl_4^{2-}$ tetrahedrons and $Pb_3Cl_{11}^{5-}$ trimer clusters, are completely separated from one another and embedded periodically in the matrix of counter organic cations $C_9NH_{20}^+$. Organic solvent CH_3CN molecules also present in

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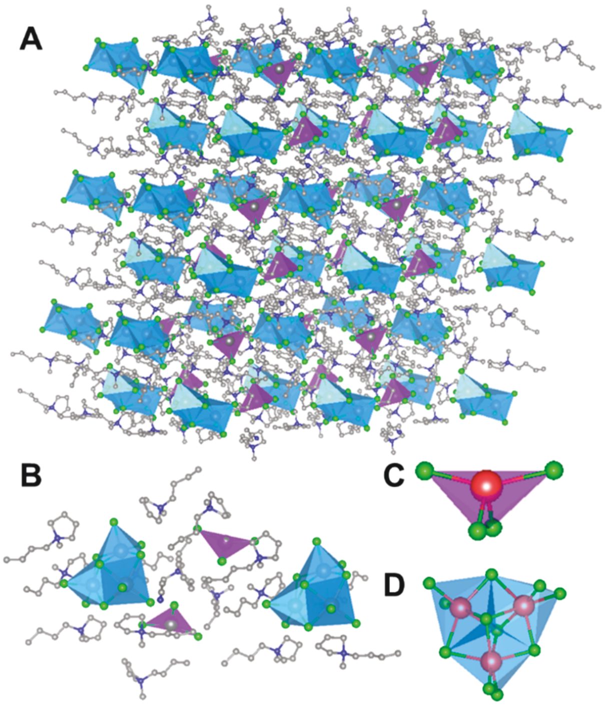

Figure 1. (A) View of the single crystal structure of $(C_9NH_{20})_7(PbCl_4)Pb_3Cl_{11}\cdot CH_3CN$ (red spheres, lead atoms; green spheres, chloride atoms; blue polyhedrons, lead chloride clusters; purple tetrahedrons, lead chloride tetrahedrons; hydrogen atoms were hidden for clarity). (B) View of two metal halide trimer clusters ($Pb_3Cl_{11}^{5-}$) completely separated from one another. (C) A metal halide tetrahedron ($PbCl_4^{2-}$) in a ball-and-stick model. (D) A metal halide trimer ($Pb_3Cl_{11}^{5-}$) in a ball-and-stick model.

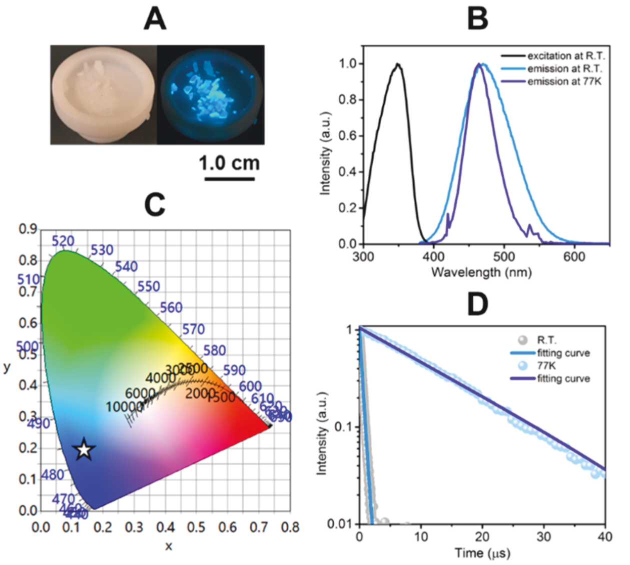

Figure 2. (A) Images of $(C_9NH_{20})_7(PbCl_4)Pb_3Cl_{11}\cdot CH_3CN$ single crystals under ambient light and 365 nm UV irradiation. (B) Excitation and emission spectra of the single crystals at room temperature and 77 K. (C) CIE chromaticity coordinates (0.14, 0.19) of the blue emission from the single crystals plotted on the CIE 1931 color space chromaticity chart. (D) The emission decay curves at room temperature and 77 K.

the single crystalline assembly, which is not surprising if considering that the single crystal growth procedure involves CH_3CN. The complete isolation of $Pb_3Cl_{11}^{5-}$ by $PbCl_4^{2-}$ and $C_9NH_{20}^{+}$ with the closest distances between two $Pb_3Cl_{11}^{5-}$ of more than 1 nm, as shown in Figure 1B, eliminates interaction between $Pb_3Cl_{11}^{5-}$ moieties. Such a 0D structure at the molecular level would allow the bulk crystal to possess the properties of individual lead chloride clusters. Note that the $PbCl_4^{2-}$ tetrahedron (Figure 1C) has an extremely large band gap (~4.22 eV), which can be considered as an insert structural scaffold that does not affect the photophysical properties in the visible range of the single crystals.[23] Figure 1D shows an individual lead chloride cluster ($Pb_3Cl_{11}^{5-}$) in a ball-and-stick model, in which three lead chloride octahedrons are fused together to form a symmetric trimer with two shared faces of each octahedron. The metal halide octahedrons that form the trimer clusters are more distorted, as compared to those found in typical 3D and 2D metal halide perovskites.[24,25] The composition of the prepared single crystals was further confirmed by elemental analysis with results presented in the Supporting Information.

The $(C_9NH_{20})_7(PbCl_4)Pb_3Cl_{11}\cdot CH_3CN$ single crystals are colorless and transparent under ambient light (Figure 2A), suggesting little-to-no absorption in the visible region with a wide band gap. Under UV irradiation (365 nm), the crystals shine extremely bright blue light. The emission and excitation spectra were recorded as shown in Figure 2B. The blue emission peaked at 470 nm at room temperature has a Stokes shift of 122 nm (0.925 eV) and a full width at half-maximum (fwhm) of 84 nm. It is worth pointing out that broad-band emissions with large Stokes shifts are very common for 0D organic metal halide hybrids, due to the formation of highly localized excitons.[20] A remarkable PLQE of 83 ± 1% is achieved for this blue emitting organic metal halide hybrid (Figure S1), which is among the highest values reported to date for single crystalline blue light emitters (see Table S3 for other blue emitters). The molecular level 0D structure of this organic metal halide hybrid suggests that the bright blue emission comes from the individual metal halide species, either $PbCl_4^{2-}$ tetrahedrons or $Pb_3Cl_{11}^{5-}$ clusters, or both. Considering the excitation being at around 3.56 eV, much lower than the band gap of $PbCl_4^{2-}$ tetrahedrons (~4.22 eV), the blue emission is unlikely from the $PbCl_4^{2-}$ tetrahedrons, but attributed to the $Pb_3Cl_{11}^{5-}$ clusters. The Commission Internationale de l'Eclairage (CIE) chromaticity coordinate (Figure 2C) for this blue emission is calculated to be (0.14, 0.19). The luminescent decay of this blue emitter at room temperature is shown in Figure 2D, giving a long lifetime of approximately 418 ns by monoexponential fitting. This is consistent with what has been observed in other 0D organic metal halide hybrids with emissions from the excitons localized in individual metal halide species. At 77 K, the emission spectrum becomes narrower and shifts somewhat to the high energy region (Figure 2B), because of reduced thermally populated vibrational states at low temperature,[20] and the luminescent lifetime increases to approximately 12.4 μs by monoexponential fitting (Figure 2D). The decay lifetimes in hundreds of nanoseconds at room temperature and microseconds at 77 K suggest that these are phosphorescent emissions. The major photophysical properties are summarized in Table 1.

The strongly Stokes shifted blue emissions with long lifetimes on the order of microseconds at room temperature and 77 K suggest that this hybrid material behaves more like individual molecules than inorganic semiconductors or 3D metal halide perovskites, which often exhibit narrow emissions

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Table 1. Summary of Major Photophysical Properties of $(C_9NH_{20})_7(PbCl_4)Pb_3Cl_{11}{\cdot}CH_3CN$ Single Crystals

T (K)	λ_{exc} (nm)	λ_{em} (nm)	fwhm (nm)	ϕ (%)	τ_{av} (μs)
298	348	470	84	83 ± 1	0.418
77	N/A	464	49	N/A	12.4

with small Stokes shifts and short lifetimes in the order of nanoseconds.[26,27] It is not surprising that these metal halide clusters composed of very few atoms exhibit molecule-like transitions, as the density of states is not sufficient to merge the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) into the valence and conduction bands that occur in inorganic semiconductors and 3D perovskites.[28,29] Therefore, the photophysical processes for this hybrid material can be depicted as shown in Figure 3.

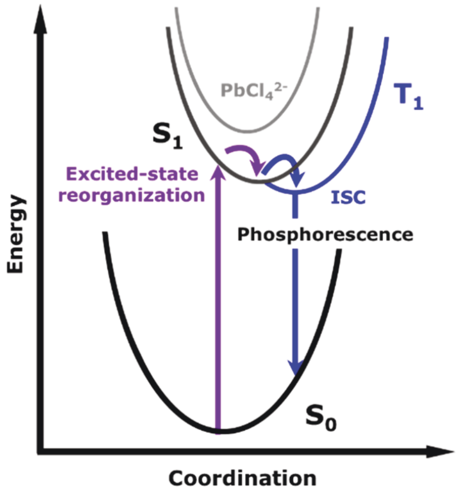

Figure 3. Schematic of the photophysical processes in a metal halide cluster.

Upon UV photoexcitation, only $Pb_3Cl_{11}^{5-}$ clusters are excited to the higher energy excited state, which can undergo ultrafast structure reorganization and intersystem crossing (ISC) from the singlet state (S_1) to the triplet states (T_1) due to the heavy atom effect.[30] The radiative decay from the lowest triplet states generates a highly efficient blue phosphorescence with a large Stokes shift.

To ensure that the cocrystallized solvent CH_3CN molecules have little-to-no effect on the photophysical properties, we have characterized the material after removing the CH_3CN molecules. By placing the fresh single crystals in vacuum overnight, the CH_3CN molecules could be successfully removed, which was confirmed by ^1H NMR spectra. As shown in Figure S2, a small peak at ~2.08 ppm vanished after overnight drying, suggesting that CH_3CN molecules have been removed from the bulk crystals. The removal of CH_3CN molecules could further be confirmed by TGA measurements. For the fresh crystals, an obvious weight loss of 1.7% at around 85 °C was observed, which is attributed to the loss of CH_3CN molecules (Figure S3), while no such weight loss was observed in the dry samples. Although we did not succeed in obtaining high quality diffraction data to solve the single crystal structure for the dry samples, due to the formation of an opaque surface layer during the drying process, we believe that the crystal structure remains largely the same, based on the powder XRD results in Figure S4. The emission, absorption, and decay profiles of dry samples are almost identical to those of the fresh crystals containing solvent CH_3CN molecules (Figure S5).

In summary, we have synthesized and characterized for the first time a single crystalline assembly of metal halide clusters with highly efficient blue emission. This single crystalline assembly of metal halide clusters expands the family of organic−inorganic metal halide hybrids, from connected 3D networks to 2D layers, 1D wires and tubes, 0D mononuclear molecules, and now 0D molecular clusters. Our finding once again shows the molecule nature of small metal halide species in the 0D structure and allows us to relate the emission from either structure reorganization or localized excitons in metal halides to molecular phosphorescence. Synthetic control of the size and shape of metal halide clusters in bulk assemblies is currently underway, as well as gaining a fundamental understanding of the luminescent mechanisms of these metal halide clusters using ultrafast spectroscopies and computational studies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b07731.

Crystallographic data for $(C_9NH_{20})_7(PbCl_4)Pb_3Cl_{11}{\cdot}CH_3CN$ (CIF)

Details of syntheses and characterizations of structural and optical properties (PDF)

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Notes

The authors declare no competing financial interest.

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