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LETTER

Green Emitting Single-Crystalline Bulk Assembly of Metal Halide Clusters with Near-Unity Photoluminescence Quantum Efficiency

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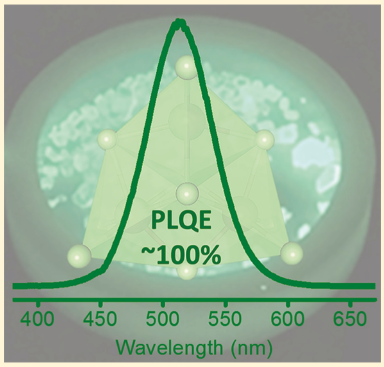
Supporting Information

ABSTRACT: **Organic metal halide hybrids with zero-dimensional (0D) structure at the molecular level, or single-crystalline bulk assemblies of metal halides, are an emerging class of light-emitting materials with high photoluminescence quantum efficiencies (PLQEs) and color tunability. Here we report the synthesis and characterization of a new single-crystalline bulk assembly of metal halide clusters, $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ (bmpy: 1-butyl-1-methylpyrrolidinium), which exhibits green emission peaked at 512 nm with a remarkable near-unity PLQE at room temperature. Detailed structural and photophysical studies suggest that there are two emitting states in $[Pb_3Cl_{11}]^{5-}$ clusters, whose populations are strongly dependent on the surrounding molecular environment that controls the excited-state structural distortion of $[Pb_3Cl_{11}]^{5-}$ clusters. High chemical- and photostability have also been demonstrated in this new material.**



Organic−inorganic metal halide hybrids have emerged as an important class of materials for a variety of optoelectronic applications, including light-emitting diodes,[1−3] photovoltaic solar cells,[4] optically pumped lasers,[5,6] etc. One significant scientific achievement in the field over the past few years is the synthetic control of dimensionality of this class of materials at the molecular level. By assembling appropriate organic and metal halide components, organic−inorganic metal halide hybrids with two- (2D), one- (1D), and zero-dimensional (0D) structures have been developed to exhibit properties significantly different from those of the extensively investigated three-dimensional (3D) ABX_3 metal halide perovskites.[7−12] Because of the spatial isolation of photoactive metal halide species by organic moieties, low-dimensional organic metal halide hybrids have exhibited higher stability than typical 3D perovskites.[13]

As far as 0D structures are concerned, a variety of metal halide species, including octahedral BX_6, pyramidal BX_5, and seesaw-shaped and tetrahedral BX_4, have been reported to form highly luminescent crystalline materials with photoluminescence quantum efficiencies (PLQEs) of up to near-unity.[14−16] In addition to individual molecular metal halide species, metal halide clusters have also been utilized as building blocks to form 0D structures with suitable organic

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cations.[17−22] Despite these recent achievements in the discovery of 0D metal halide hybrids, the capability of manipulating the structures and properties of this class of materials is still limited. For instance, achieving highly efficient narrow emissions with small Stokes shifts from 0D organic metal halide hybrids remains challenging, as strong structural distortion of metal halides often results in broadband emissions with a large Stokes shift. To date, efficient broadband yellow, red, and deep red emissions achieved in these materials have Stokes shifts of more than 200 nm.[16] To enable the application of this class of materials for full-color displays and solid-state lighting, short wavelength emissions, i.e., blue and green, are needed. However, reports on highly efficient blue and green emitting organic metal halide hybrids are very rare.[15,17,18]

Herein, we report a new single-crystalline bulk assembly of metal halide clusters, $(C_9NH_{20})_9[ZnCl_4]_2[Pb_3Cl_{11}]$, which exhibits green emission peaked at 512 nm with a remarkable near-unity PLQE at room temperature. This highly efficient green emission from $[Pb_3Cl_{11}]^{5-}$ clusters is significantly different from the blue emission peaked at 470 nm with a PLQE of ~83% of previously reported $(C_9NH_{20})_7[PbCl_4]$-$[Pb_3Cl_{11}]$, although both single-crystalline bulk assemblies contain $[Pb_3Cl_{11}]^{5-}$ clusters as the emitting centers. Detailed structural characterizations and photophysical studies were performed to reveal the pholuminescence mechanism for this new green emitting material. The results suggested that there are two emitting states in $[Pb_3Cl_{11}]^{5-}$ clusters, whose populations are strongly dependent on the surrounding molecular environment and temperature.

This new single-crystalline bulk assembly of lead chloride clusters, $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$, was prepared using a solution diffusion crystal growth method, as illustrated in Figure 1A, in which acetone diffused into a DMF precursor solution containing $PbCl_2$, $ZnCl_2$, and (bmpy)Cl. The presence of $ZnCl_2$ was found to play a crucial role in the formation of this new bulk assembly of metal halide clusters and effectively improve the crystalline stability. Without $ZnCl_2$, blue emitting $(bmpy)_7[PbCl_4][Pb_3Cl_{11}]$ was the product. The crystal structure $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ was determined using single-crystal X-ray diffraction, which revealed a hexagonal (space group $P6_3$) structure. More details of the analysis of the crystal structure can be found in the Supporting Information. The view of the crystal structure is shown in Figure 1B, in which $[Pb_3Cl_{11}]^{5-}$ clusters cocrystallize with $[ZnCl_4]^{2-}$ tetrahedra to form a 0D structure at the molecular level. $[Pb_3Cl_{11}]^{5-}$ clusters have an average Pb−Cl bond length of ~2.84 Å and an ideal D_{3h} structure with three symmetric fused octahedrons. The symmetry of $[Pb_3Cl_{11}]^{5-}$ clusters was further confirmed by solid-state ^{207}Pb NMR spectrum with a single peak at −675.2 ppm, which suggests a similar molecular environment of three Pb(II) atoms in the $[Pb_3Cl_{11}]^{5-}$ cluster (Figure S2). $[ZnCl_4]^{2-}$ was reported to have a wide band gap (λ < 200 nm), which makes it function solely as an anionic spacer that stabilizes the crystal structure, without contributions to the optical properties.[23] Figure 1C clearly shows that the neighboring $[Pb_3Cl_{11}]^{5-}$ clusters are separated from each other with the shortest distance of more than 1 nm. As shown in Figure S1, the closest $[Pb_3Cl_{11}]^{5-}$ clusters along the *c*-axis are further apart from each other with two $[ZnCl_4]^{2-}$ tetrahedra sitting in between. The complete isolation of $[Pb_3Cl_{11}]^{5-}$ prevents the electronic band formation between the clusters. The powder XRD pattern is consistent with the simulated XRD pattern, suggesting the uniformity and purity of the as-prepared crystals (Figure S3). The molecular formula was further confirmed by elemental analysis (see details in the Supporting Information). The density of $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ was calculated to be 1.609 g/cm^3, much lower than that of the previously reported blue emitting $(bmpy)_7[PbCl_4][Pb_3Cl_{11}]$ at 1.751 g/cm^3, suggesting a less compact crystal structure. In other words, the molecular environments for $[Pb_3Cl_{11}]^{5-}$ clusters are different in $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ and $(bmpy)_7[PbCl_4][Pb_3Cl_{11}]$, which could affect their photophysical properties. Thermogravimetric analysis was also performed, showing that single crystals would not decompose until 210 °C (Figure S4).

This single-crystalline bulk assembly of $[Pb_3Cl_{11}]^{5-}$ clusters is colorless under ambient light, suggesting little-to-no absorption in the visible light range, as confirmed by the absorption spectrum (Figure S5). Upon UV (365 nm) excitation at room temperature, $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ single crystals display highly bright green emission, as shown in Figure 2A. The photophysical properties were further characterized. As shown in Figure 2B, the emission spectrum of $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ peaked at 512 nm with a full-width at half-maximum (fwhm) of 61 nm and a Stokes shift of 164 nm at room temperature. It should be emphasized that the PLQE of this green emission is near-unity (Figure S6), which is, to the best of our knowledge, the most efficient single-crystal-based green emitter ever reported. The excitation spectrum has a maximum of 348 nm, which is consistent with the absorption spectrum as shown in Figure S5, indicating that the green emission is not from the defects or impurities, but from the intrinsic property of the bulk assembly of metal halide clusters. The emission decay lifetime was measured to be 0.54 μs at room temperature, with a radiative decay rate of around 1.9×10^6 s^{-1}, suggesting the same phosphorescence nature as those of other 0D organic metal halide hybrids.[14,16,24] The photophysical properties were also characterized at low temperature. At 77 K, the emission shows an unusually large

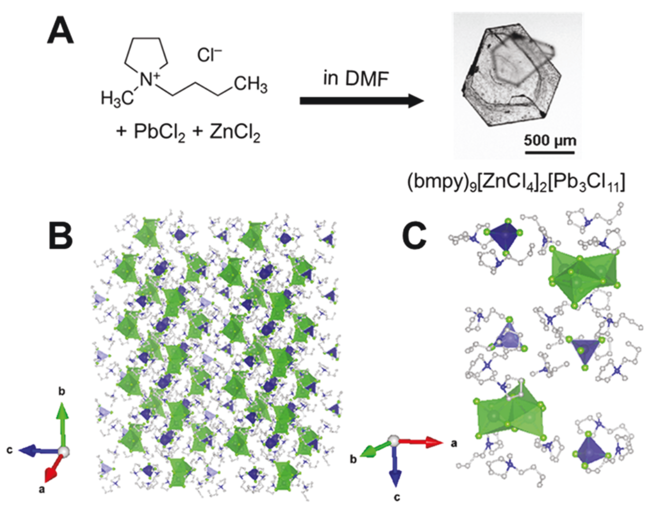

Figure 1. (A) Synthetic route and optical image of $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ single crystals. (B) View of the single-crystal structure of $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ from different angles (color scheme: $[Pb_3Cl_{11}]^{5-}$, green polyhedrons; $[ZnCl_4]^{2-}$, mazarine tetrahedrons; N, blue atoms; C, gray atoms; hydrogen atoms are hidden for clarity). (C) View of two neighboring metal halide trimer clusters $[Pb_3Cl_{11}]^{5-}$ completely separated from one another.

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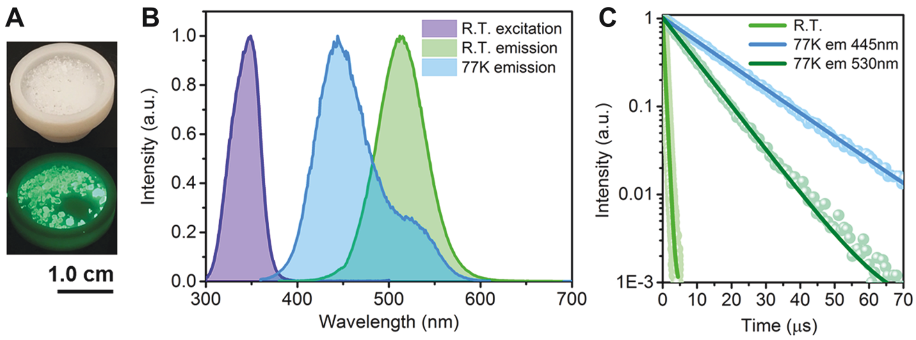

Figure 2. (A) Images of $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ single crystals under ambient light and UV irradiation (365 nm). (B) Excitation and emission spectra of $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ at room temperature and 77 K. (C) Emission decay curves of $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ at room temperature and 77 K.

blue-shift with the peak changing from 512 to 444 nm and appearance of a shoulder at around 530 nm. Interestingly, the emission decay lifetimes monitored at 445 and 530 nm are different, with one at 16.0 μs and the other at 8.7 μs, suggesting the presence of two nonequilibrium emitting states at low temperature. To better illustrate the photophysical properties of this bulk assembly of metal halide clusters, temperature-dependent photoluminescence was recorded between 80 and 260 K, with the normalized spectra at different temperatures shown in Figure 3A (see Figure S7 for the original spectra). It

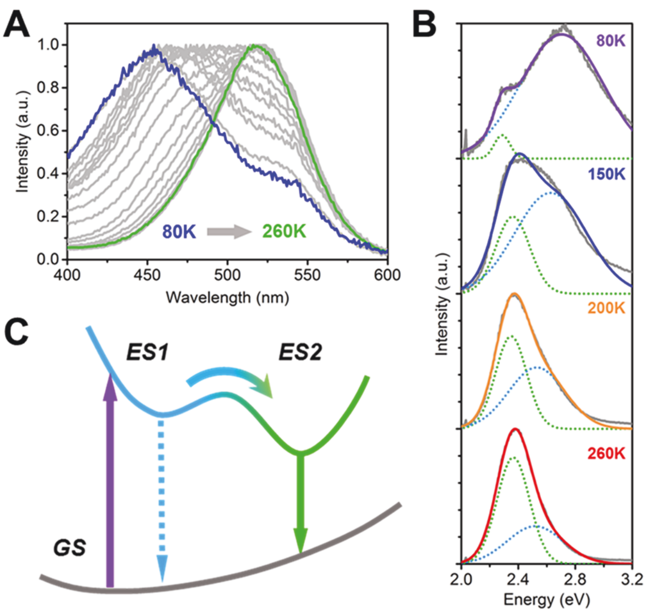

Figure 3. (A) Temperature-dependent photoluminescence spectra of $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ from 80 to 260 K and (B) their fitting by the combinations of blue and green emissions at different temperatures. (C) Schematic of the photophysical processes in $[Pb_3Cl_{11}]^{5-}$-based hybrids with two energy minima on the excited state.

was found that the emission spectra could be well fitted by the combination of Gaussian shaped blue and green emissions, as shown in Figure 3B (see fitting in Figure S8). Thus, the change of emission spectrum was not a simple gradual blue shift, but rather the combined variations of two emission bands, with the green emission decreasing and the blue emission increasing and blue-shifting upon the decreasing of temperature. It should be noted that there is no phase change occurring between 80 K and room temperature, as evident by the fact that similar cell parameters and volume were obtained at different temperatures (Figure S9).

Considering the similarity of this temperature-dependent dual emission of $[Pb_3Cl_{11}]^{5-}$ to those of platinum molecular butterfly complexes and low-dimensional metal halide hybrids with two emitting excited states,[25−28] we propose the presence of two triplet energy minima on the excited-state potential energy surface in this bulk assembly of $[Pb_3Cl_{11}]^{5-}$ clusters, as shown in Figure 3C. As the formation of two different emitting excited states likely involves structural distortion, a kinetic energy barrier between two emitting excited states with distinct distorted structures is expected.[25−27] The structural distortion of $[Pb_3Cl_{11}]^{5-}$ clusters on the excited state, on the other hand, could be affected by their molecular environment; that is, a less compact and soft matrix would lead to easier structural distortion. Therefore, the excited-state dynamics for $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ can be described as follows: At low temperature with rigid molecular environment for $[Pb_3Cl_{11}]^{5-}$ clusters and low thermal energy, the photogenerated excitons localized in the emitting state 1 (ES1) have difficulty overcoming the energy barrier to reach the emitting state 2 (ES2), resulting in mainly blue emission. While at room temperature with relatively soft molecular environment and high thermal energy, the excitons would easily overcome the energy barrier to reach the ES2, resulting in green emission. Overall, the effects of temperature increasing are twofold: reducing the rigidity of the molecular environment for $[Pb_3Cl_{11}]^{5-}$ clusters and increasing thermal energy, both facilitating overcoming the energy barrier between two emitting excited states.

In addition to its remarkable optical properties, the stability of $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ is worth mentioning. The emission spectrum and PLQE of $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ single crystals show little-to-no change after storage in ambient conditions (with humidity of >50%) for several weeks. High photostability has also been verified. As shown in Figure S10, the emission intensity at peak wavelength barely changes (maintains ∼99% intensity) after 1 h of continuous high-power mercury lamp (150 mW cm^{-2}) irradiation. The high chemical- and photostability along with the remarkable photophysical properties make this material a promising green light emitter for optoelectronic applications, for instance, a green down-conversion phosphor for UV-pumped white light-emitting diodes.

In summary, we have synthesized and characterized a green emitting single-crystalline bulk assembly of metal halide

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clusters $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ with a remarkable near-unity photoluminescence quantum efficiency. Detailed structural and photophysical studies suggested that the light-emitting $[Pb_3Cl_{11}]^{5-}$ clusters have two possible emitting excited-state structures, whose populations are strongly dependent on the surrounding molecular environment that controls the excited-state structural reorganization of $[Pb_3Cl_{11}]^{5-}$ clusters. Our work suggests that the molecular environment plays a critical role in determining the properties of metal halide clusters, and controlling the crystal structures represents an effective way to achieve tunable emissions in bulk assemblies of metal halide clusters. Detailed studies of the excited-state structural and photophysical processes of this class of bulk assemblies of metal halide clusters using ultrafast X-ray and optical spectroscopies are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.9b00991.

Syntheses and characterizations of the metal halide clusters and results (PDF)

Crystallographic information file for $(bmpy)_9[ZnCl_4]_2[Pb_3Cl_{11}]$ (CIF)

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Notes

The authors declare no competing financial interest.

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