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Multicomponent Organic Metal Halide Hybrid with White Emissions

Liang-Jin Xu,[a] Sujin Lee,[a] Xingsong Lin,[a] Logan Ledbetter,[b] Michael Worku,[c] Haoran Lin,[a] Chenkun Zhou,[a] He Liu,[a] Anna Plaviak[a] and Biwu Ma* [a, c]

Abstract: Multicomponent single crystals have received great research attention for their capability of realizing multifunctionalities in a single phase material. Zero-dimensional (0D) organic metal halide hybrids are an emerging class of ionically bonded crystalline materials, in which organic and metal halide ions co-crystallize to form neutral species. The rich choices of organic and metal halide components make 0D organic metal halide hybrids a highly promising platform for the development of multifunctional crystalline materials, which however are very much unexplored to date. Here we report the design, synthesis, and characterization of a ternary 0D organic metal halide hybrid, $(HMTA)_4PbMn_{0.69}Sn_{0.31}Br_8$, in which an organic cation $HMTA^+$ ($HMTA^+$: N-benzyl hexamethylenetetramium, $C_{13}H_{19}N_4^+$) co-crystallizes with multiple metal halide anions, i.e. $PbBr_4^{2-}$, $MnBr_4^{2-}$, and $SnBr_4^{2-}$. The wide bandgap of the organic cation and distinct optical characteristics of three metal bromide anions enable a single crystalline "host-guest" system to exhibit emissions from multiple "guest" metal halide species simultaneously. The combination of these emissions could lead to a near-perfect white emission, with Commission Internationale d'Eclairage (CIE) of (0.32, 0.33), Color Rendering Index (CRI) of 95, and photoluminescence quantum efficiency (PLQE) of around 73%. Due to distinct excitations of three metal halide species, warm to cool white emissions with Correlated Colour Temperature (CCT) varying from 3237 K to 12730 K could be realized by controlling the excitation wavelength.

Organic-inorganic metal halide hybrids have recently emerged as an important class of crystalline materials with unique optical and electronic properties for various applications.[1] Besides 3D ABX_3 metal halide perovskites, organic metal halide hybrids with low dimensional 2D, corrugated-2D, 1D, and 0D structures have been developed using appropriate organic and metal halides.[1c, 1g, 2] In 0D organic metal halide hybrids, anionic metal halide molecular species or clusters are separate from each other and co-crystallize with cationic organic species to form periodical structures. The complete site isolation enables 0D organic metal halide hybrids to exhibit the intrinsic properties of metal halide molecular species or clusters, when wide bandgap organic cations are used. To date, various combinations of organic and metal halides have been used to synthesize 0D organic metal halide hybrids, which could exhibit highly efficient emissions with tunable colors covering the whole visible spectrum.[2a, 3] Other remarkable properties and applications, such as thermometry,[1f] scintillation,[4] and ferroelectric,[5] have also been observed in these materials.

0D organic metal halide hybrids provide an excellent platform for the development of multifunctional single crystalline materials, in which multiple metal halide species can be integrated into a single phase system. With proper synthetic control, several binary organic metal halide hybrids have been developed recently. Our group reported a series of highly luminescent binary metal halide hybrids containing MCl_x^{2-} (M = Pb, Zn or Sb, and x = 4 or 5) and $Pb_3Cl_{15}^-$ clusters.[3a, 3b],[3f] Xia group synthesized binary hybrids with dual-emissions by integrating $MnBr_4^{2-}$ and $Pb_3Br_{15}^-$ species.[1d] Despite these recent developments, design and synthesis of ternary or higher component organic metal halide hybrids remain challenging. 0D organic metal halide hybrids containing three or more distinct metal halide species have not been reported to date. One reason is that single component or binary single crystals, instead of multicomponent single crystals, would form preferentially, when several components are involved in the crystallization process. Here we refer 0D organic metal halide hybrids containing one kind of metal halide species as single component single crystals, and two kinds of metal halide species as binary single crystals. It is of great interest to develop ternary or higher component organic metal halide hybrids, which could provide a new avenue for preparation of multifunctional materials, e.g. integrating ternary components with blue, green, and red emissions to achieve white emissions, assembling strong X-ray absorption and visible light emitting species for X-ray scintillation, incorporating synergetic catalysts for catalysis, and so on.

Here we report the design, synthesis, and characterization of a ternary organic metal halide hybrid, by co-crystallizing delicately chosen organic and metal halides. Following the design strategy applied for the preparation of organic cocrystals,[6] $HMTA^+$ was employed as the organic cation for its bulk steric hindrance; and $PbBr_4^{2-}$, $MnBr_4^{2-}$ and $SnBr_4^{2-}$ were chosen for their same charges and similar sizes, but distinct emissions covering different regions of the visible spectrum. It was found that these metal halide species can co-crystallize with $HMTA^+$ to form a single phase system, $(HMTA)_4PbMn_{0.69}Sn_{0.31}Br_8$, which possess integrated properties from individual metal halide species. By combining blue emission from $PbBr_4^{2-}$, green emission from $MnBr_4^{2-}$, and red emission from $SnBr_4^{2-}$ in an appropriate ratio, efficient white emission could be achieved with CIE of (0.32, 0.33), CRI of 95, and PLQE of around 73 %. As three metal halide species have distinct excitations, the white emission can be tuned from warm to cool white with Correlated Color Temperature (CCT) in the range of 3237 to 12730 K using different excitation wavelengths. UV-pumped white LEDs have been fabricated by using this material as down conversion phosphor, which exhibited maximum brightness of 6570 cd/m2 at 3.5 V and luminous efficiency of 6.2 lm/w.

Binary 0D organic metal halide hybrids have been synthesized by selecting appropriate organic cations to enable two inorganic metal

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[a] Dr.L.-J. Xu, Dr. X Lin, Dr. Q. He, Prof. B. Ma
Department of Chemistry and Biochemistry, Florida State University
Tallahassee, FL 32306 (USA)
E-mail: bma@fsu.edu
[b] L. Ledbetter
Department of Chemistry and Physics, Troy University, Troy, AL
36082 (USA)
[c] M. Worku, Prof. B. Ma
Materials Science and Engineering Program, Florida State
University
Tallahassee, FL 32306 (USA)

Supporting information (Details of materials and synthesis, characterization methods, structural and photophysical properties of materials, cif file for the crystal structure of $(HMTA)_4PbMn_{0.69}Sn_{0.31}Br_8$.

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halide species to co-crystallize with each other. Simply introducing a third metal halide species into binary metal halide hybrid precursors may not lead to the formation of ternary single crystals, as the formation of single component or binary single crystals could dominate the crystallization process. To synthesize ternary organic metal halide single crystals, many parameters, such as geometry and solubility of metal halides, need to be considered carefully to suspense the formation of single component or binary single crystals, while making ternary single crystals as preferred products. A strategy similar to that used for the synthesis of organic cocrystals was therefore proposed, as shown in Figure 1. A, B, and C represent unit cells of single component organic metal halide crystals with the same organic cation. Binary single crystals cannot be obtained for the combination of A and B, as packed structures could not form as easy as single component crystals. However, by introducing a third building block C, ternary single crystals could form with a structure more packed than those of single component crystals. After screening organic cations and metal halides used to date for the preparation of single component 0D organic metal halide hybrids, we came up with the combination of $HMTA_2PbBr_4$ (A), $HMTA_2MnBr_4$ (B), and $HMTA_2SnBr_4$ (C), considering that they have similar structures containing the same organic ligand HMTA, but different sizes. (See their structural information in Figure S1 and Table S1) Moreover, they have the emissions covering different regions of the visible spectrum, blue from $HMTA_2PbBr_4$, green from $HMTA_2MnBr_4$, and red from $HMTA_2SnBr_4$. These distinct optical properties would make it straightforward to characterize the multifunctionality of a ternary system, which also has the potential to achieve white emissions for various applications.

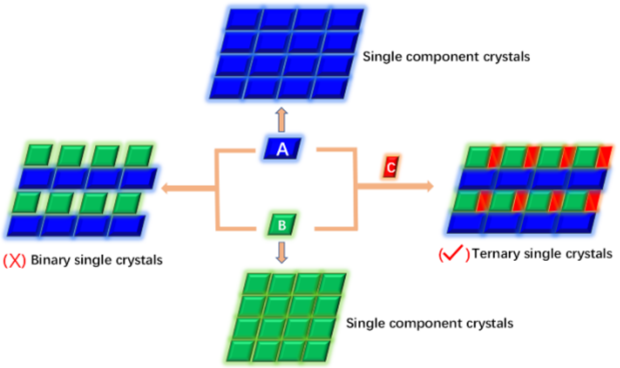

Figure 1. Scheme for the design of ternary single crystals based on organic metal halides hybrids. A, B, and C represent unit cells of single component organic metal halide crystals with the same organic cation.

Following the design strategy, we grew single crystals by slowly diffusing diethyl ether into a DMF precursor solution containing HMTA, $PbBr_2$, $MnBr_2$ and $SnBr_2$. (see Figure 2a and Scheme S1) By optimizing the ratio of different components (see supporting information on the experimental details), high-quality crystals were successfully prepared, which are white under ambient light and become strongly white emissive under UV light irradiation (Figure 2b). The crystal structure was solved by single crystal X-ray diffraction (SCXRD) (Figure 2c-d), which gave the material a chemical formula of $(HMTA)_4PbMn_{0.69}Sn_{0.31}Br_8$. The metal halide species are isolated from each other by $HMTA^+$ cations, among which $PbBr_4^{2-}$ polyhedron adopts a seesaw-shaped geometry with an average Pb-Br bond length of 2.87 Å, similar to that in previously reported 0D $HMTA_2PbBr_4$.[3g] Both $MnBr_4^{2-}$ and $SnBr_4^{2-}$ have distorted tetrahedral structures, which are positioned in the same lattice points with a occupancy of 69 % for $MnBr_4^{2-}$ and 31 % for $SnBr_4^{2-}$. The average bond lengths for Mn-Br and Sn-Br are 2.50 Å and 2.82 Å, respectively. (Details can be found in Table S2 and S3) The PXRD patterns of ground crystals are identical to the simulated results from the SCXRD data in Figure S2a, suggesting the purity and uniformity of as-synthesized single crystals. To further confirm the phase purity, PXRD patterns for single component hybrids, $HMTA_2PbBr_4$, $HMTA_2MnBr_4$, $HMTA_2SnBr_4$, were collected, which were compared to those of 0D $(HMTA)_4PbMn_{0.69}Sn_{0.31}Br_8$. It was found that the patterns of each single component hybrid and their mixtures are significantly different from those of the ternary hybrid. (Figure S2b) Energy dispersive X-ray fluorescence (EDXRF) was conducted to characterize the molar ratio of different elements, which suggested the ratio of Pb /Mn /Sn /Br at 1/0.67/0.35/7.77, agreeing well with the SCXRD result. (See more details in supporting information Figure S4 and Table S4) Thermal gravimetric analysis (TGA) was used to characterize the thermal stability of $(HMTA)_4PbMn_{0.69}Sn_{0.31}Br_8$, which exhibits good thermal stability without weight loss until $211\,^{o}C$ (Figure S3).

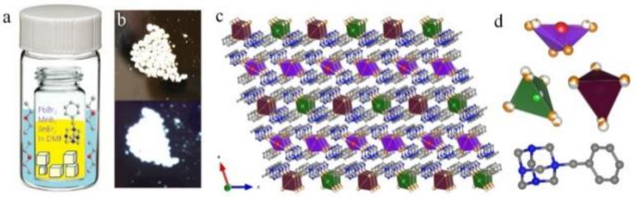

Figure 2. (a) The illustration of the crystal growing. (b) The images of $(HMTA)_4PbMn_{0.69}Sn_{0.31}Br_8$ single crystals under ambient light (up) and UV light (down). (c) View of the single crystal structure of $(HMTA)_4PbMn_{0.69}Sn_{0.31}Br_8$. (d) the building blocks ($PbBr_4^{2-}$ purple tetrahedrons, $MnBr_4^{2-}$ green tetrahedrons; $SnBr_4^{2-}$ brown tetrahedrons; and organic cation $HMTA^+$; Pb, red; Mn, green; Sn, brown; N, blue; C, gray; Hydrogen atoms are hidden for clarity).

The photophysical properties of $(HMTA)_4PbMn_{0.69}Sn_{0.31}Br_8$ were investigated using UV-Vis absorption, steady state photoluminescence spectroscopy, as well as time-resolved photoluminescence spectroscopy. As illustrated in Figure 3a, the solid-state UV–Vis spectrum (purple solid line) shows an a very intense maximum absorption centered at 292 nm and a shoulder peak at 350 nm. Upon irradiation at λ_{ex} = 296 nm, white light emission with distinguishable peaks at 460 nm, 550 nm and 645 nm, can be observed with PLQE of around 73%, CRI of 95, and CIE of (0.32, 0.33). The excitation spectra (Figure 3a) and emission decay lifetimes were recorded for three emission peaks at 460 nm, 550 nm and 645nm, which show completely different characteristics (Figure 3b). PL decay lifetimes for three emission peaks were measured at 85 ns, 426.7 µs, and 3.4 µs, respectively. Based on the photophysical properties of single component 0D organic metal halide hybrids (Figure S5), we can attribute the blue emission at 460 nm to $PbBr_4^{2-}$ species,[3g] the green emission at 550nm to $MnBr_4^{2-}$ species,[1h] and the red emission at 645 nm to $SnBr_4^{2-}$ species.[3c] The similar photophysical properties of individual metal halide species in this ternary single crystal ($(HMTA)_4PbMn_{0.69}Sn_{0.31}Br_8$) and their single component crystals ($HMTA_2PbBr_4$, $HMTA_2MnBr_4$ and $HMTA_2SnBr_4$) suggest little-to-no interactions among three metal halide species. This is not surprising as three metal halide species are completely separate from each other and there is no overlap between their emissions and absorptions, resulting in no energy transfer. Overall, this ternary orgainc metal halide hybrid, a multifunctional single phase system, exhibits combined optical properties from individual building blocks. The stability of $(HMTA)_4PbMn_{0.69}Sn_{0.31}Br_8$ against moisture was characterized, which exhibited little-to-no change of PLQE after exposure in ambient atmosphere for two months. (Figure S6)

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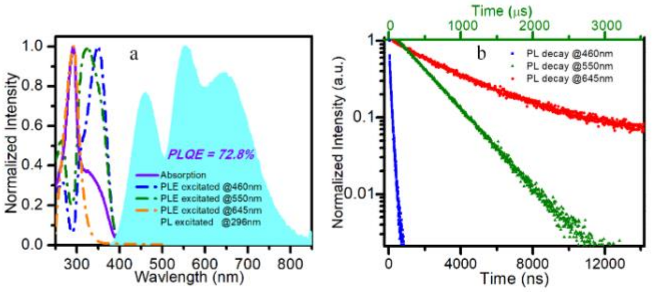

Figure 3. Optical properties of (HMTA)$_4$PbMn$_{0.69}$Sn$_{0.31}$Br$_8$ at room temperature. (a) Absorption, excitation and emission spectra of (HMTA)$_4$PbMn$_{0.69}$Sn$_{0.31}$Br$_8$. (b) Emission decay curves of (HMTA)$_4$PbMn$_{0.69}$Sn$_{0.31}$Br$_8$ monitored at 460 nm, 550 nm, and 645 nm, respectively.

The photoluminescence of this single phase ternary hybrid also shows a strong dependence on the excitation, as the three emitting species, blue emitting PbBr$_4^{2-}$, green emitting MnBr$_4^{2-}$, and red emitting SnBr$_4^{2-}$, have distinct excitations. Figure 4a shows the excitation-dependent PLs with excitation shifting from 290 to 310 nm, with emission intensities at 460 nm and 550 nm increasing, while decreasing at 645nm. This excitation-dependence enables color tuning of the white emission from (HMTA)$_4$PbMn$_{0.69}$Sn$_{0.31}$Br$_8$, with CCT varying from 3237 (warm white) to 12730 K (cool white) upon excitation from 290 to 380 nm. Variant CIEs with high CRIs of up to 97 and PLQEs as high as 82% (exictated at 350 nm) could be achieved, as shown in Figure 4b, Figure S7 and Table S5. Considering its high stability and strong white emissions, (HMTA)$_4$PbMn$_{0.69}$Sn$_{0.31}$Br$_8$ could serve as down conversion phosphor for UV pumped white LEDs. A simple device was fabricated by embedding the grounded (HMTA)$_4$PbMn$_{0.69}$Sn$_{0.31}$Br$_8$ powders into polydimethylsiloxane (PDMS) polymer matrix. The resulting composite thin films were then attached to a commercial UV-LED (360 nm). As shown in Figure 4c, a UV pumped LED displays bright white emission with a maximum brightness of 6570 cd/m^2 at 3.5 V and luminous power efficiency of 6.2 lm/w. The relative low power efficiency is due to the use of a UV LED with low efficiency and mismatching of excitation wavelength (deep UV nm 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 excellent color stability at different driving currents, as shown in Figure 4d.

In summary, a ternary orgainc metal halide hybrid with excitation dependent white emissions has been prepared, by carefully choosing organic and metal halides with appropriate geometries and comprising emissions to cover blue, green, and red regions. This is by far the first single phase 0D organic metal halide hybrid containing three distinct metal halide species. With this multicomponent single crystal as down conversion phosphor, a UV pumped white LED was demonstrated. Our work enriches the family of multicomponent single crystals based on organic metal halide hybrids, and provides a versatile approach to design and prepare multifunctional materials based on ionically bonded systems.

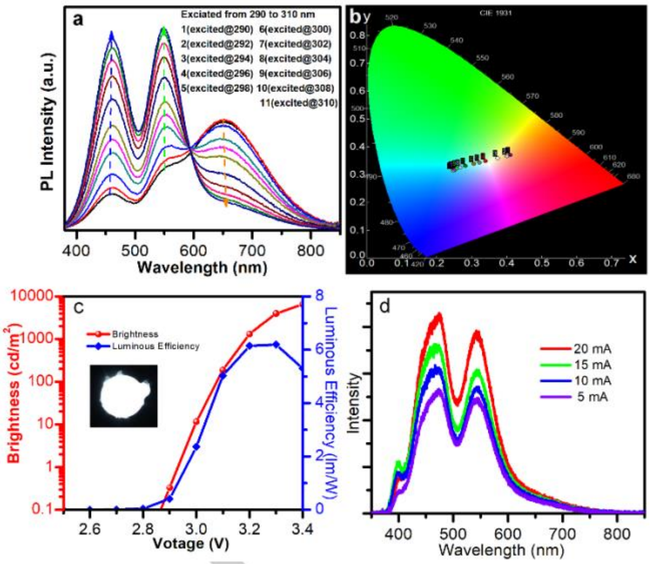

Figure 4. (a) The excitation-dependent PL with the excitation wavelength ranging from 290 to 380 nm. (b) CIE 1931 diagram showing the chromaticity points of emissions when the material was excited from 290 to 380 nm. (c) voltage versus brightness and luminous efficiency of a UV-pumped LED (Inset shows the image of a UV pumped LED) (d) Emission spectra of a UV-pumped LED at different driving currents.

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Keywords: multicomponent • organic metal halide hybrid • single crystal • white emission • light emitting diode

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COMMUNICATION

A ternary organic metal halide hybrid (HMTA)$_4$PbMn$_{0.69}$Sn$_{0.31}$Br$_8$ has been developed, which contains three distinct metal halide species with emissions covering blue, green, and red spectral regions. This multicomponent single crystalline material exhibits highly efficient excitation dependent emissions, with near-perfect white emissions obtained under appropriate excitation wavelengths.

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