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Structural Dimensionality Control of Organic-Inorganic Metal Halide Hybrids

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14. ABSTRACT
This project aims to develop and study novel organic-inorganic metal halide perovskites and hybrids with controlled compositions, structures, and dimensionalities. Its main thrust involves identification and understanding of phenomena and mechanisms associated with synthesis and processing of highly luminescent and stable metal halide perovskite nanocrystals, as well as organic metal halide hybrids containing various types of metal halide assemblies as the building blocks with three- (3D), two- (2D), one- (1D), and zero-dimensional (OD) structures at the molecular level, which can display unique optical/electronic properties with potential applications in a variety of optoelectronic devices. During the third year of this project, we have achieved tremendous research progresses in the development and study of low dimensional metal halide perovskite hybrids from material development to device integration, with major accomplishments summarized as bellow.

- Synthetic control has been achieved for the preparation of OD organic metal halide hybrids containing a variety of metal halide molecular species and clusters.
- Multicomponent OD organic metal halide hybrids have been developed via proper crystal engineering.
- Photophysical tuning of OD organic metal halide hybrids from efficient phosphorescence to ultralong afterglow has been achieved by controlling the metal halides.
- Efficient light emitting diodes and X-Ray scintillators have been demonstrated using OD organic metal halide hybrids. Several graduate students and postdoctoral researchers have participated in this project and received interdisciplinary research training. The research in the third year has produced ten publications in high profile peer reviewed journals.

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Structural Dimensionality Control of Organic-Inorganic Metal Halide Hybrids

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This project aims to develop and study novel organic-inorganic metal halide perovskites and hybrids with controlled compositions, structures, and dimensionalities. Its main thrust involves identification and understanding of phenomena and mechanisms associated with synthesis and processing of metal halide perovskite nanocrystals, as well as organic metal halide hybrids containing various types of metal halide assemblies as the building blocks with three- (3D), two- (2D), one- (1D), and zero-dimensional (0D) structures at the molecular level, which can display unique optical/electronic properties with potential applications in a variety of optoelectronic devices.

During the third (and final) year of this project, we have continued our development and study of organic metal halide hybrids and perovskites, and investigated their applications in PV, LEDs and X-ray scintillators. Of particular interest are multicomponent 0D organic metal halide hybrids containing various metal halide molecular species and clusters, as well as photoactive organic cations. A few representative results are highlighted as below.

1. Organic metal halide hybrids with exceptional structural versatility have enabled the development of a number of highly efficient emitters with tunable photophysical properties. In addition to organic metal halide hybrids containing homogenous metal halide species, we have explored multicomponent organic metal halide hybrids, in which various types of metal halide species are assembled together in a single crystal. For instance, we have developed a ternary 0D organic metal halide hybrid, $(\text{HMTA})_4\text{PbMn}_{0.69}\text{Sn}_{0.31}\text{Br}_8$, in which a rigid organic cation HMTA^+ (HMTA^+ : N-benzyl hexamethylenetetramium, $\text{C}_{13}\text{H}_{19}\text{N}_4^+$) co-crystallizes with blue emitting PbBr_4^{2-} , green emitting MnBr_4^{2-} , and red emitting SnBr_4^{2-} . The wide band gap 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. The combination of these emissions led to near perfect white emission with a photoluminescence quantum efficiency (PLQE) of around 73 %. Because three metal halides have different excitations, warm to cool white emissions could be generated by controlling the excitation wavelength. Our discovery of multicomponent organic metal halide hybrids opens up a new way to develop precisely ordered single-crystalline materials with multi-functionalities. This work has been published in the *Angewandte Chemie International Edition* (2020, 59, 14120-14123).
2. To date most of low dimensional organic metal halide hybrids 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 (either 1D metal halide wires or 0D metal halide molecules/clusters). Low dimensional organic metal halide hybrids 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 low dimensional organic metal halide hybrids to exhibit hidden properties of organic cations. In one of our recent studies, we discovered photophysical tuning of 0D organic metal halide hybrids from efficient phosphorescence to ultralong afterglow (persistent photoluminescence), by using various metal halides as counter anions to co-crystallize with tetraphenylphosphonium cations (TPP^+). It was found that the optical properties of 0D TPP metal halide hybrids were controlled by several factors, including the band structures of both TPP and metal halide species, as well as the molecular packing of TPP. When anionic metal halide species with lower emission energies than TPP^+ , such as SbCl_5^{3-} and MnCl_4^{2-} , are used, the optical properties of the hybrids are dominated by the photoluminescence of metal halide species. While for 0D TPP metal halide hybrids containing wide bandgap ZnX_4^{2-} ($\text{X} = \text{Cl}$,

Br, or Mixtures), efficient ultralong afterglow has been achieved, as a result of enhanced Pi-Pi stacking and intermolecular electronic coupling between TPP⁺ cations. The change of halide from Cl to Br introduced heavy atom effect that negatively affected the afterglow properties of TPP zinc halide hybrids. This work has been published in the *Angewandte Chemie International Edition* (2020, 59, 23067-23071).

3. As far as applications concerned, we have explored the application of highly luminescent 0D organic metal halide hybrids for X-ray scintillators. We have developed flexible x-ray scintillators based on ethylenebis-triphenylphosphonium manganese (II) bromide ((C₃₈H₃₄P₂)MnBr₄), which exhibits green emission peaked at 517 nm with a PLQE of ~95% . 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. X-ray imaging tests showed that scintillators based (C₃₈H₃₄P₂)MnBr₄ fine powders could provide a visualization tool for x-ray radiography, and high resolution flexible scintillators could be fabricated by blending (C₃₈H₃₄P₂)MnBr₄ powders with polydimethylsiloxane (PDMS). This work has been published in the *Nature Communications* (2020, 11, 4329).
4. For our contributions to the fields, we have been invited to write perspective and review articles for several prestigious scientific journals and two articles have been published during the past year, “Recent Advances in Luminescent Zero-Dimensional Organic Metal Halide Hybrids” in *Advanced Optical Materials* (2020, 2001766), in which we discussed the recent advances in the development and study of luminescent 0D organic metal halide hybrids from synthetic structural control to fundamental understanding of the structure–property relationship and device integration; and “The Past, Present, and Future of Metal Halide Perovskite Light-Emitting Diodes” in *Small Science* (2021, 2000072), in which we discussed the progresses of perovskite LEDs, the main issues and challenges in the field, and the prospects on addressing these issues and challenges.

Overall, we have achieved great successes in this project with more than two dozen of publications in high profile peer reviewed journals. Several patent applications have been filed based on the discoveries obtained in this program. The program has provided financial supports to a total of nine graduate students and postdoctoral researchers during the period of three years, who have participated in this program and received interdisciplinary research training.