Low Dimensional Metal Halide Perovskites and Hybrids: From Synthetic Control to Device Integration

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Outline

- Metal Halide Perovskites
  - Molecular View of Metal Halide Perovskites
  - Perovskite Solar Cells
  - Electrically Driven LEDs

- Organic Metal Halide Hybrids Beyond Perovskites
  - From 3D to 2D, 1D, and 0D
  - From Single-Component to Multi-Component Systems
  - Applications of Organic Metal Halide Hybrids

- Conclusions

- Acknowledgement
Metal Halide Perovskites

$\text{ABX}_3$

A = Cs, CH$_3$NH$_3$, etc.

B = Pb, Sn, etc.

X = Cl, Br, I
Metal Halide Perovskites

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Metal Halide Perovskites

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- $A = \text{Cs, CH}_3\text{NH}_3$
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- **Solution Processable Semiconductors**
  - Low-cost, earth-abundant
  - Facile synthesis and preparation
  - Highly tunable band gaps
  - Exceptional charge transport
  - High absorption coefficients
  - Narrow emissions with high color purity

- **Issues and Challenges**
  - Low stability of materials and devices
  - Eco-friendly lead-free
  - Processing and patterning

Perovskite Solar Cells

Surface Passivation:
Suppress charge recombination at the interfaces between halide perovskite and charge transport layers for high device efficiency and prevent the penetration of degrading agents into the perovskite layer for high device stability. Various materials have been employed to passivate perovskite thin films, including low-dimensional metal halides, alkaline and organic halides, polymers, inorganic compounds, and so on.

*ACS Applied Materials and Interfaces, 2020, 12, 1159-1168*

*Journal of Materials Chemistry A, 2020, 8, 2039-2046*

*Angewandte Chemie, 2020, 60, 2485-2492*
Color Tuning and Perovskite LEDs

- Composition control, Quasi-2D, and Hollow nanostructures

Compositional Modulation

![Graph showing emission wavelengths and chemical formulas](image)

Quantum Size Effects

![Diagram illustrating bandgap and size effects](image)

*Nano Materials Science 2019, 1, 268–287*

*Topics in Current Chemistry 2016, 374, 58*
Color Tuning and Perovskite LEDs

- Composition control, Quasi-2D, and Hollow nanostructures
- Perovskite LEDs via Bottom-up & Top-down approaches

- JPCL, 2019, 10, 5836–5840
- Science Advances, 2020, 6, eaaz5961
- Advanced Materials 2016, 28, 305-311
- Advanced Energy Materials, 2022, 2201605
- Chemical Communications, 2016, 52, 3887-3890
- Advanced Materials, 2018, 30, 1707093
- Small Science, 2021, 1, 2000072
Metal Halide Perovskites
- Molecular View of Metal Halide Perovskites
- Perovskite Solar Cells
- Electrically Driven LEDs

Organic Metal Halide Hybrids Beyond Perovskites
- From 3D to 2D, 1D, and 0D
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Beyond Halide Perovskites

\[ \text{ABX}_3 \]
\( A = \text{Cs, CH}_3\text{NH}_3, \text{etc.} \)
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Beyond Halide Perovskites

\[ ABX_3 \]

A = Cs, CH\(_3\)NH\(_3\), etc.

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\[ BX_6^{4-} \]
By choosing appropriate organic cations and metal halides, can the crystallographic structures of organic metal halide hybrids be finely controlled to exhibit different dimensionalities at the molecular level, with the metal halide octahedra forming zero- (0D), one- (1D), two- (2D), and three-dimensional (3D) structures?
Low Dimensional Structures

- Morphological Low Dimensional Metal Halide Perovskites (Still 3D ABX₃)
- Molecular Level Low Dimensional Organic Metal Halide Hybrids

Single Crystalline Bulk Assemblies of Quantum Confined Materials
1D Organic Lead Bromide Hybrid

\[
\text{H}_3\text{C} - \text{NH} \rightarrow \text{HN} - \text{CH}_3 + 2\text{HBr} + \text{PbBr}_2 \rightarrow \text{C}_4\text{N}_2\text{H}_{14}\text{PbBr}_4
\]

PLQE: \(\sim 20\%\)

*Nature Communications, 2017, 8, 14051*
1D Organic Lead Bromide Hybrid

Nature Communications, 2017, 8, 14051

PLQE: ~ 20 %

Bulk Crystals
Microscale Crystals

Normalized PL intensity (a.u.)
Wavelength (nm)

PL intensity (a.u.)
Power density (W/cm²)

$R^2 = 0.996$

PL counts
Time (ns)

PL counts
Time (ns)

PL counts
Time (ns)

$T_c(K)$
Exciton Self-Trapping

In cases of strong coupling of electrons or holes to the crystal lattice, a carrier may be self-trapped as a small polaron in its own lattice distortion field. A bound electron-hole pair involving such a carrier is generally described as a **self-trapped exciton**, and it may dramatically influence luminescence, energy transport, and lattice defect formation in the crystal. The phenomenon of exciton self-trapping is particularly common in metal halide and rare-gas crystals, where **the strong exciton-lattice coupling** can usually be ascribed to the possibility of covalent bond formation in the excited state of a crystal which does not admit such bonding in its ground state.

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Other 1D Structures?

1D \(\text{C}_4\text{N}_2\text{H}_{14}\)\text{PbBr}_4

- **Size**
- **Shape**
- **Composition**
- **Structure**
1D Organic Metal Halide Hybrids

Metal Halide Nanoribbons

Graphene Nanoribbons

Graphene
1D Organic Metal Halide Nanoribbons

$1D \text{C}_8\text{H}_{28}\text{N}_5\text{Pb}_3\text{Cl}_{11}$

\begin{align*}
\text{Wavelength (nm)} & \quad \text{Intensity (a.u.)} \\
300 & \quad 0.0 \\
400 & \quad 0.2 \\
500 & \quad 0.4 \\
600 & \quad 0.6 \\
700 & \quad 0.8 \\
800 & \quad 1.0 \\
\end{align*}

Exc @ 420 nm Ems
Exc @ 540 nm Ems
Ems @ 360 nm exc

Chemical Communications, 2023, 59, 3711-3714
1D Organic Metal Halide Nanoribbons

Chemical Communications, 2023, 59, 3711-3714
Free and Self-Tapped Excitons

(A) Direct band formation with free excitons only resulting in narrow emission. (B) Thermally activated equilibrium between direct band free exciton excited state and self-trapped excited state resulting in emissions from both excited states: narrow high energy emission from free excitons and below-gap broadband emission from self-trapped excitons. (C) Spontaneous exciton self-trapping to form localized excitons with below-gap broadband emission.
From 3D to 2D, 1D, and 0D?

The isolation of the photoactive metal halide species by the wide band gap organic ligands leads to no interaction or electronic band formation between the metal halide species, allowing the bulk materials to exhibit the intrinsic properties of individual metal halide species. 0D organic metal halide hybrids can be considered as perfect host-guest systems, with metal halide species periodically doped in the organic matrix.
Luminescent 0D Sn halide hybrids with near-unity PLQE!

A General Concept

Octahedral \( \text{MX}_6 \)

Trigonal Prismatic \( \text{MX}_6 \)

Trigonal Bipyramidal \( \text{MX}_5 \)

Square Pyramidal \( \text{MX}_5 \)

Tetrahedral \( \text{MX}_4 \)

0D SnBr\(_6\)  0D SnI\(_6\)  0D SbCl\(_5\)  0D SnBr\(_4\)

Dimensionality Dependence

3D and 2D: With band formation and little structure distortion, have emissions from the direct excited states, narrow, small stokes shift, and short lifetimes.

Corrugated-2D and 1D: With band formation and structure distortion, have broadband emissions from both direct and self-trapped excited states.

0D: No interactions between metal halide octahedrons or band formation, have emissions from the distorted excited states only, broadband, large stokes shift, and long lifetimes.

Application I: UV Pumped White LEDs

Chemical Science, 2018, 9, 586-593; ACS Applied Materials and Interfaces, 2018, 10, 30051-30057; APL Materials, 2020, 8, 010902
Application II: X-Ray Scintillators

X-ray/Neutron

Scintillator
Visible Photons

CCD or sCMOS
Detector

X-ray dose rate: 20.8 µGy s⁻¹

Radio luminescence intensity (a.u.)

X-ray dose rate (µGy s⁻¹)

RL intensity (10⁸cps)

Ce:LuAG (C₃₈H₃₄P₂)MnBr₄
(Cu₄H₄P₄)MnBr₄

X-ray on 89.4 µGy s⁻¹

FWHM = 322 µm

pixel intensity (a.u.)

pixel position (µm)
Application II: X-Ray Scintillators
A highly luminescent 0D organic antimony bromide hybrid containing semiconducting organic cation is developed for the first time, with which electrically driven LEDs are fabricated to exhibit an EQE of 5.12%, a peak luminance of 5957 cd m\(^{-2}\), and a current efficiency of 14.2 cd A\(^{-1}\).
From Molecules to Clusters and Crystals: The Progress of Electronic Band Formation
Metal Halide Clusters

\[(C_9NH_2O)_7(PbCl_4)Pb_3Cl_{11}\]

*Journal of The American Chemical Society, 2018, 140, 13181-13184*
Perfect Host-Guest System

0D Organic Metal Halide Hybrids

Multicomponent Systems (I)

ACS Materials Letters, 2020, 2, 376-380
Recent Advances in Luminescent Zero-Dimensional Organic Metal Halide Hybrids

Applications
- Light Emitting Diodes
- Thermometers
- Scintillators
- Sensors

Properties
- Broadband Emissions
- Near-Unity PLQEs
- Localized Excitons

Multi-component
- Single-component
- Multinuclear Clusters
- Mononuclear Metal Halides

Structures

Advanced Optical Materials, 2021, 9, 2001766
Metal Halides as Regulator

\[ \text{M} = \text{Sb, Mn, Zn} \]
Tetraphenylphosphonium Metal Halides

TPPCl, TPP$_2$ZnCl$_4$, TPP$_2$ZnBr$_2$Cl$_2$, TPP$_2$ZnBr$_4$, TPP$_3$SbCl$_6$, TPP$_2$MnCl$_4$
Metal Halides as Sensitizer

Advanced Materials, 2023, 2301612
Conclusions

• Precise synthetic control has been achieved for the preparation of 1D and 0D organic metal halide hybrids.

• Understanding of the photoluminescence mechanisms has been achieved for organic metal halide hybrids with different dimensionalities at the molecular level.

• Multicomponent organic metal halide hybrids have been developed via proper crystal engineering.

• Photophysical tuning of 0D organic metal halide hybrids from phosphorescence to ultralong afterglow has been achieved by controlling the metal halides.

• Using metal halides and many other complex species as counter ions to co-crystallize with organic ions to form ionically bonded systems has remarkable potential to deliver new functional materials.
Perovskites and Beyond

Morphological Low Dimensionality

Other Polyhedral Building Blocks

Chalcogenide Perovskites
Double Perovskites
New 3D Structures

Molecular Level Low Dimensionality

Corrugated 2D
1D Tubes
0D Clusters

New Perovskite Structures
There is a vast space to explore organic-inorganic hybrids beyond perovskites, and we expect to see a lot of new science.
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