

Review

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Optoelectronic Properties of Expanded Halide Perovskite Analogs Enriched by Molecular Diversity

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Abstract

Hybrid materials offer the potential of coupling the electronic properties of covalent organic molecules and ionic inorganic solids. In the family of hybrid halide perovskites, the diversity of organic molecules has not been observed in three-dimensional (3D) structures due to the small size of the cuboctahedral cage, whereas two-dimensional (2D) derivatives can hold aliphatic and aromatic molecules of a wide range of sizes between the inorganic sheets. Expanded 3D perovskite analogs are emerging materials that mitigate the limitation on the molecular variety in the 3D perovskite, where a single metal-halide octahedron in the perovskite is replaced by a dimer of edge-sharing octahedra. Unlike 3D perovskites, the expanded analogs can hold large molecular dications while maintaining a dispersed inorganic band structure. Flexible choices about organic cations allow us to tune the energy levels of molecular orbitals relative to the inorganic valence and conduction bands. The interplay between active molecular orbitals and inorganic bands affords intriguing optoelectronic properties.

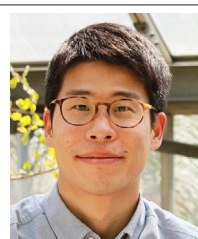
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1. Introduction

The diversity of organic molecules provides organic-inorganic hybrid materials with rich structural and electronic variety, which is one of the most attractive features of this class of materials.¹⁻⁴⁾ In the family of hybrid halide perovskites, two-dimensional (2D) structures can accommodate organic molecules of a wide range of sizes between the inorganic sheets.^{5,6)} The well-defined structure results in the quantum-well-like electronic structure of 2D hybrid perovskites, enabling the manipulation of the relative energy levels of the organic and inorganic components.⁷⁻⁹⁾ On the other hand, due to the small size of the cuboctahedral cage for organic cations, the molecular diversity in three-dimensional (3D) hybrid perovskites is severely limited. Indeed, the 3D hybrid perovskite A[PbI₃] is reported to accommodate only methylammonium (MA) and formamidinium (FA) cations as stoichiometric A-site

cations,^{10,11)} which limits the electronic diversity in 3D hybrid perovskites. In this regard, a general method to access the electronic diversity seen in 2D perovskites while preserving the 3D inorganic network and dispersed band structure has been desired.

Recently, we and others reported a method to expand the 3D lattice of perovskite, where the basic building unit of the inorganic lattice is replaced by the edge-sharing dimer of BX₆ octahedra (B = Pb²⁺, Sn²⁺; X = I⁻, Br⁻, Cl⁻).¹²⁻¹⁸⁾ The new building unit, B₂X₁₀, shares corners to form 3D inorganic structures in an analogous way perovskites' BX₆ does (**Fig. 1**). Because of the similarity in the connectivity of the basic building unit, these expanded structures are called “perovskite analogs” or “perovskitoids.” The expanded perovskite



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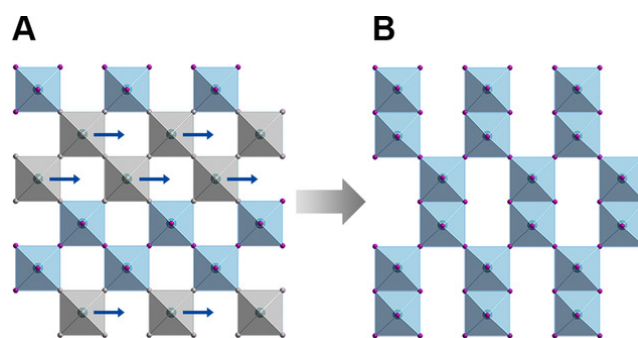


Fig. 1 Conceptual transformation of the inorganic sublattice from (A) a 3D perovskite to (B) its expanded analog, where the lead-halide octahedra in (A) are replaced with edge-sharing dimers of octahedra in (B). Reprinted from Ref. (14) with permission from Wiley-VCH.