

**Center for Hybrid Organic Inorganic Semiconductors for Energy (CHOISE)**

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**Lead Institution: National Renewable Energy Laboratory**

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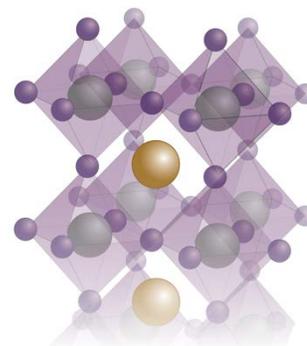
**Mission Statement:** *To enable unprecedented synthetic control over the emergent phenomena of spin, charge, and light-matter interactions, in tailored organic-inorganic perovskite-inspired systems for energy science.*

*Hybrid organic/inorganic semiconductors (HOIS) offer tremendous opportunities to control fundamental properties that underpin energy technologies. While currently there are enormous worldwide efforts exploring, exploiting and improving a narrow class of HOIS (lead-halide perovskites, such as methylammonium lead iodide (MAPbI<sub>3</sub>)), primarily for photovoltaic (PV) applications, an opportunity exists to transcend this initial focus on PV research and seek deeper understanding and control of their fundamental properties. Inherent in these unique hybrid systems is the dichotomy between organic/molecular moieties (quantum chemistry) and inorganic/extended systems (solid-state physics). As a result, they exhibit properties that are not solely a juxtaposition of the inorganic and organic sub-units, but are instead truly emergent phenomena, with the concomitant ability to control and design new properties by judicious choice of inorganic and organic components.*

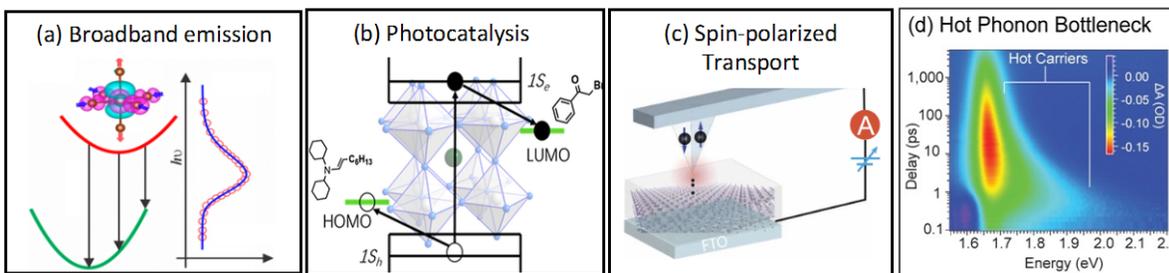
While emergent physical phenomena in HOIS result from their unique hybrid nature, *rules for rationally designing HOIS systems and the precise underlying chemical/physical mechanisms underlying the emergent properties remain under investigation.* Semiconductor physics has revolutionized our world in the past century due to investments in fundamental studies of quantum mechanics and solid-state physics. Unfortunately, this knowledge is insufficient to completely describe HOIS. Complex coupling among inorganic and organic components drive unprecedented (and often collective) dynamic phenomena involving light, matter, and energetic species such as spins, charge carriers, and phonons. Thus, we have a *unique* opportunity to develop the foundational knowledge of this new paradigm in energy sciences.

The prototypical HOIS has a perovskite structure with ABX<sub>3</sub> (Fig. 1) stoichiometry where A is the organic cation, such as methyl ammonium (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>), B is the metal cation, such as Pb, and X is a halide anion. Many opportunities exist for HOIS in non-perovskite structures or with use of non-typical A, B, and X species, which can tune structure-property characteristics.

The **Soft Nature** is one distinguishing property that sets HOIS apart from conventional semiconductors, such as Si and GaAs. Softness corresponds to dynamical disorder within the lattice, whereby ions undergo large and reportedly strongly coupled motions (vibrations) about their average lattice positions. In 3D HOIS, the soft nature arises from weak noncovalent bonding, due to the large/anisotropic organic ion and the confluence of ionic bonding and anti-bonding coupling between lone pair *s* orbitals of the B cation and the halide *p* orbitals. The weak bonds are relatively easy to tilt, vibrate, and break,



**Figure 1(a)** ABX<sub>3</sub>. A (gold sphere) site is the organic component, B site is the center of the octahedra, X site are tips of the octahedra.



**Figure 2.** (a) Broadband emission. (b) Photocatalysis. (c) Spin transport in Chiral systems (d) A hot phonon bottleneck dramatically slows carrier cooling.

significantly influencing the structural, electronic, optical, and defect properties, and leading to emergent properties (Fig.2) that include: dynamic behavior, ferroelasticity, ferroelectricity, electrostriction, photostriction, long lived hot-carriers, large polarons, broadband light emission, and low recombination rates. The presence of strong spin-orbit coupling (SOC) and breaking of inversion symmetry lead to other unique effects in HOIS, based on the effect known as **Rashba Splitting**. Rashba-Splitting should have important impacts on key phenomena underpinning energy technologies, including: long spin-coherence times, low recombination rates, high photoluminescence yields and spin-to-charge conversion, among others.

Goals for CHOISE are:

- Uncover *design rules dictated by the distinct requirements of organic/inorganic chemistry*, which allow for high-precision control over composition, structural dimensionality, defect density, orientation, and conformation of organic molecules within HOIS.
- Control SOC and Rashba-splitting, so as to uncover and exploit the unique roles of the inorganic and organic sub-components in the presence of large SOC enabling *unprecedented control over the energetics, coherent transport, and dynamics of spin populations*.
- Elucidate and exploit structure/function relationships, both within the bulk and at HOIS surfaces and interfaces, that enable energy-efficient interconversions between light, excitons, spins, and charge carriers.
- Control the degree of ‘softness’ to discover how *charges couple to static and dynamic lattice properties*, enabling emergent phenomena such as ferroelasticity, ferro- and piezoelectricity, giant electrostriction, slow hot-carrier cooling, and controlled doping.

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