

Center for Hybrid Organic Inorganic Semiconductors for Energy (CHOISE)

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Lead Institution: NREL

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Mission Statement: “To demonstrate unprecedented control over spin, charge, phonon and light properties through synthesis and characterization of crystalline Hybrid Organic Inorganic Systems, their interfaces and heterostructures.”

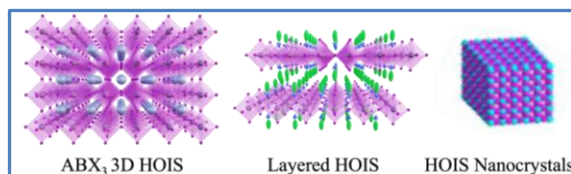
Hybrid organic-inorganic semiconductors (HOIS) exhibit unique physical phenomena resulting from synergistic interactions between organic and inorganic sub-components. The central hypothesis of CHOISE is: *HOIS offer unprecedented opportunities to control fundamental physical properties for the next generation of sustainable energy technologies.* CHOISE researchers are validating this hypothesis by addressing fundamental knowledge gaps of organic-inorganic interactions in this new class of ‘unconventional’ semiconductors. While *unprecedented* world-wide progress towards efficient HOIS PV systems argues for their unique physio-chemical properties, we have just scratched the surface of their full potential, and basic scientific understanding still lags far behind demonstrated results. CHOISE research aims to broaden HOIS by elucidating factors that control and define their exceptional properties. CHOISE proposes to focus on: precise synthetic pathways leading to well-defined heterostructures; understanding and controlling ion migration; controlling strain; chiral and other symmetry breaking motifs; magnetic ordering and quasi-2D magnetic systems; and impact of the soft lattice on defects, doping, and physio-chemical properties.

HOIS are unconventional semiconductors with properties that vary continuously from those associated with organic semiconductors having tightly bound Frenkel-type excitons characterized by large exciton binding energies, to those associated with inorganic semiconductors exhibiting delocalized Wannier-type excitons and free-charge carriers. However, the most intriguing aspects of HOIS are emergent properties, i.e., those that neither exist in organic or inorganic systems *but arise due to the interplay between the subcomponents.*

A prototypical HOIS has perovskite structure with ABX_3 stoichiometry where A is an organic cation such as methylammonium ($CH_3NH_3^+$), B is a metal cation such as Pb, and X is a halide anion. CHOISE efforts in 3D HOIS relate to understanding defects, strain, ion-migration, and controlling carrier dynamics. A broader class of hybrid compounds exist with HOIS in non-perovskite structures, low-dimensional structures, or with non-typical A/B/X species. Low-dimensional HOIS structures form when the organic cation is too large and/or an additional secondary organic molecule is added. HOIS nanocrystals (NCs) (e.g., quantum dots, nanoplates, nanorods, nanowires) provide unique opportunities via larger tolerance of A-site cations and influence from organic surface ligands.

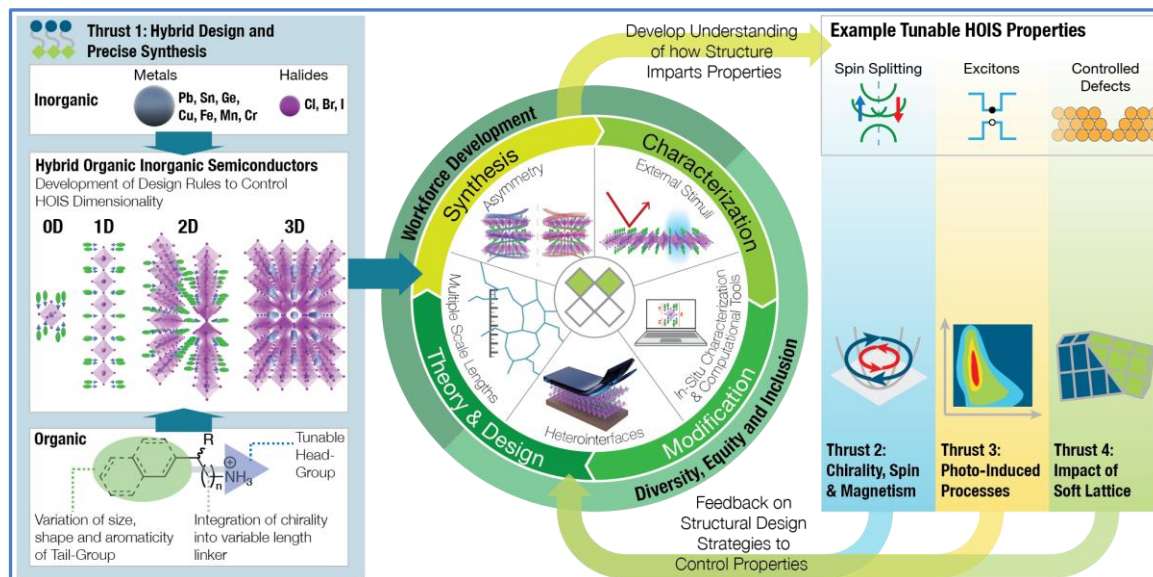
Spin-splitting occurs in the presence of spin-orbit coupling (SOC) and inversion asymmetry that locks the spin character to the linear momentum and creates unique spin textures. Incorporating chiral organic cations with the inorganic subsystem results in chiral-HOIS. Electrons transmitted through such oriented chiral systems become spin-polarized. This effect of chirality-induced spin selectivity (CISS) can impact a wide range of potential applications such as low-power electronics, chiral-light detectors and generators, electrochemical water splitting, enantiomer separations, and potentially many others not yet envisioned.

The soft nature is a distinguishing property setting HOIS apart from semiconductors like Si and GaAs. Softness reflects dynamic disorder, where ions undergo large and strongly coupled motions about their average lattice positions. The soft nature arises from weak noncovalent bonding and coupling between



lone pair *s* orbitals of the B cation and halide *p* orbitals. Weak bonds that are relatively easy to tilt, vibrate, and break significantly influence structural, electronic, optical, and defect properties, leading to dynamic behavior, ferroelasticity, ferroelectricity, electrostriction, hot-carriers, large polarons, broadband light emission, low recombination rate, and the challenge to extrinsically *n*- or *p*-type dope HOIS.

CHOISE goals are:



Inorganic/organic components form crystalline HOIS wherein the inorganic component may comprise 0D isolated anions, 1D chains, 2D/quasi-2D planes, or completely interconnected 3D network. CHOISE is uncovering the basic understanding and design rules to uncover unprecedented control over spin, light and charge.

- Develop precise synthetic methods allowing for atomic, micro-, and macro-level control over composition, structural dimensionality, symmetry breaking, phase instability, heterostructures, and defects.
- Uncover the mechanism(s) of spin-selectivity, develop control over spin-textures, and induce novel quasi-2D magnetic behavior by manipulating symmetry breaking motifs.
- Understand the interconversions between light, excitons, spins, and charge carriers, gaining control over photocatalytic transformations, hot-carrier utilization, spin-transfer, and polarized light absorption/emission.
- Uncover impacts of micro- and macro-scale strain, doping, lattice dynamics, ion migration, and defect distributions and feedback to enable synthesis of novel HOIS.

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