

## Spotlights on Recent JACS Publications

### ■ CHIRAL AMINES FROM ASYMMETRIC HYDROGEN PINCHING

Frustrated Lewis pairs (FLPs)—reactive systems composed of sterically hindered Lewis acids and bases—have emerged as a metal-free alternative approach to organometallic hydrogenation catalysis due to their extraordinary H<sub>2</sub> activation capabilities. Asymmetric FLP catalysts are especially interesting, as they can be used to prepare chiral amines and alcohols, among other useful chiral building blocks.

Imre Pápai, Timo Repo, and colleagues have prepared a tweezer-like aminoborane-based chiral FLP, built on a binaphthyl skeleton with intrinsic axial chirality, that can activate H<sub>2</sub> both rapidly and reversibly (DOI: 10.1021/ja512658m). The FLP catalyst efficiently transforms enamines and unhindered imines into chiral amines through stereoselective hydrogenation, enabled by synergy between steric repulsion and non-covalent stabilization in the key hydride transfer process.

This new design avoids the formation of catalyst–product adduct in *N*-alkyl imine reduction, a common problem with FLP catalysts. Moreover, the successful asymmetric hydrogenation of enamines is an unprecedented feat in FLP catalysis. This simple yet powerful catalyst, constructed from a readily available platform via straightforward synthesis, is likely to gain a broader scope of chiral targets.

Xin Su, Ph.D.

### ■ ATOMISTIC STUDY OF DISLOCATIONS IN PEROVSKITE OXIDE

In perovskite oxides, many of which have broad applications in electrochemical devices, one-dimensional defects known as dislocations can significantly impact the properties of these materials. However, an atomic-level understanding and quantification of the effect of dislocations on the local electrical, chemical, and transport properties remain largely unknown. Now, Bilge Yildiz and colleagues use atomistic simulations to observe how edge dislocations in SrTiO<sub>3</sub>, a technologically relevant model perovskite oxide, impact the local defect chemistry and oxide ion transport, with implications for local electronic conductivity (DOI: 10.1021/ja513176u).

The authors report that SrTiO<sub>3</sub> can be more easily reduced at the dislocation core, with oxygen vacancy formation energy up to 2.0 eV lower than that of the bulk. Additionally, simulations and calculations of oxide ion diffusion in both low- and high-vacancy concentration regimes show no evidence of enhanced mobility, opposite to the diffusion of atoms along dislocations in metals.

The lower oxygen vacancy formation energy at the dislocation core can explain the electronic conductivity of these 1-D defects that serve as redox-based resistive switching sites in SrTiO<sub>3</sub>. Understanding the relationship between a perovskite oxide's electrical, chemical, and mechanical properties may facilitate the design of improved materials for information and energy technologies. "Reducibility and electronic transport at dislocations can also be quantitatively engineered into active materials for fuel cells, catalysis, and electronics," conclude the authors.

Hui Jin, Ph.D.

### ■ METAL-FREE MOLECULE RIVALS HIGH-PERFORMING METAL–ORGANIC DYES

A new organic compound could help pave the way to highly efficient dye-sensitized solar cells without the hefty price tag often associated with metal–organic dyes. A study by Peng Wang and co-workers is the first report of an organic molecule which, by itself, achieves a power conversion efficiency (PCE) that rivals those of the highest performing metal–organic dyes reported to date (DOI: 10.1021/jacs.5b01537).

The new compound consists of an electron-donating *N*-annulated indenoperylene unit that is conjugated with the electron acceptor benzothiadiazolylbenzoic acid. The team finds that the resulting metal-free donor–acceptor dye is capable of achieving a PCE of 12.5%. This is the closest an organic molecule has come to rivaling the 13% PCE achieved by a previously reported zinc porphyrin dye. Although other donor–acceptor organic dyes have been demonstrated with PCEs greater than 10%, those that have achieved a value greater than 11% have required coupling with photovoltage-enhancing co-adsorbates in order to attain the high efficiency values.

The researchers say their approach avoids many of the downsides of metal–organic dyes, like resource scarcity and heavy metal toxicity, and could lead to the development of low-cost, eco-friendly devices to convert solar energy to electricity.

Christine Herman, Ph.D.

### ■ ELECTRICALLY CONDUCTIVE G-QUADRUPLEX TRANSPORTS HOLES THROUGH GUANINE CORE

Scientists want to mimic the geometric precision of natural photosynthetic systems when they build molecules for organic electronics or photovoltaics. For example, researchers have built electronically conductive G-quadruplexes—self-assembled stacks of guanine tetramers—using guanines functionalized with electron acceptor domains along the periphery of the assembled structure. These domains also stabilize anionic charge between tetramer layers so that the quadruplex has a longer lifetime of charge separation than the monomer.

To determine how the core of the G-quadruplex is involved in charge transfer, Yi-Lin Wu, Michael Wasielewski, and their colleagues have built a monomer that contains a guanine-based electron donor connected to a chromophore and an electron acceptor that weakly stabilizes an anion between quadruplex layers (DOI: 10.1021/jacs.5b00977). They assemble the monomer into a G-quadruplex and use spectroscopy to track the charge location, structural changes, and spin state of the radical ion formed when the structure is excited by light.

The extended ion pair lifetime compared to that of the monomer, minimal structural changes in the excited state, and fast hole injection into the G-quadruplex suggest that the core can transport holes effectively. This rapid hole transport makes the G-quadruplex a useful design motif for molecules that transport charges over long distances, the researchers write.

Melissae Fellet, Ph.D.

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