

## Spotlights on Recent JACS Publications

### ■ STRATEGY FOR IMPROVING CHARGE CARRIER TRANSPORT OF CONJUGATED POLYMERS

Crystalline regions of conjugated polymers have a more regular arrangement than amorphous regions. Hence, they typically also have higher rates of charge carrier transport due to enhanced charge carrier delocalization. So it comes as a surprise to researchers led by Taiho Park to find that a random polymer exhibiting low crystallinity has superior field-effect mobility compared to a highly crystalline conjugated polymer (DOI: [10.1021/jacs.6b01046](https://doi.org/10.1021/jacs.6b01046)).

In an effort to improve charge carrier transport in low-crystalline conjugated polymers, the researchers form localized aggregates in amorphous regions of the polymer by introducing thiophene monomers without alkyl chains into the polymer. They find that the resulting increase in connectivity and backbone planarity within the amorphous regions give rise to enhanced intra- and inter-chain charge transport.

The study provides additional support for the notion that inter-chain interactions between engineered conjugated polymers play a key role in macroscopic charge carrier mobility. The long-term applications of low-crystallinity polymers may include soft electronics, for which high-crystallinity conjugated polymers have been found to be inadequate due to their poor mechanical resistance.

Christine Herman, Ph.D.

### ■ FREE ENERGY LANDSCAPE REVEALS MOLECULAR MECHANISM OF NUCLEOSOME DISASSEMBLY

Nucleosomes—DNA wrapped around octamers of histone protein—are the fundamental unit for packaging the genome. Expression, replication, and repair of eukaryotic genomes require the nucleosome to be unwrapped and disassembled to allow access to DNA binding sites. The detailed molecular mechanism of nucleosome disassembly is crucial for understanding transcription and gene regulation.

Bin Zhang, Weihua Zheng, Garegin Papoian, and Peter Wolynes investigate the conformational dynamics of single nucleosome disassembly by computing the free energy landscape using a predictive coarse-grained protein DNA model with transferable force fields (DOI: [10.1021/jacs.6b02893](https://doi.org/10.1021/jacs.6b02893)). The authors find that DNA unwinding is closely coupled with histone dissociation into tetramer and dimers, and also that DNA unwinds asymmetrically from the histone proteins.

This successful simulation theoretically supports histone octamer disruption that was suggested in previous experimental studies. The combined chemical accuracy and computational efficiency of the coarse-grained model can be applied more generally to provide important mechanistic understanding of the numerous nucleosome alterations that occur during DNA processing.

Hui Jin, Ph.D.

### ■ STEREOSELECTIVITY OF BINOL-BASED CATALYSTS NOW PREDICTABLE

Stereoselective catalytic reactions are a core component of modern organic synthesis and are therefore the focus of extensive research efforts. In practice, understanding of stereoselectivity builds largely on the accumulation of empirical evidence. Similarly, while computational modeling of key intermediates can account for the theoretical origin of stereoselectivity, it is not appreciably simpler.

In order to establish an accurate yet quick approach to predicting stereoselectivity, Jonathan Goodman and Jolene Reid examine the dependence of stereoselectivity on catalyst descriptors (DOI: [10.1021/jacs.6b02825](https://doi.org/10.1021/jacs.6b02825)). For chiral, BINOL-derived phosphoric acid-catalyzed imine hydrogenation, the researchers introduce two steric parameters that can quantify the selectivity-determining geometric profiles of the catalysts. They find that enantioselectivity correlates non-linearly to the size of the neighboring substituents.

Based on readily available steric parameters, this study provides a facile and powerful qualitative method to predict stereoselectivity of a class of widely used organocatalysts. These results will facilitate design of BINOL-based catalytic systems and may have useful implications for other catalyst families.

Xin Su, Ph.D.

### ■ METAL CATALYSTS SYNERGIZE TO CARRY OUT ALKANE METATHESIS

The process of lengthening acyclic saturated hydrocarbons using metal catalysts is known as alkane metathesis. Researchers are interested in increasing the efficiency of the reaction for applications such as converting petroleum-derived short-chain alkanes into longer, diesel-grade alkanes. Numerous recent advances have been made in the synthesis of highly active catalysts for alkane conversion, with many of these advances centered on improving the turnover number (TON) of the catalysts to increase efficiency, yet there is still room for improvement. Dual tandem catalytic systems have also been explored, but they typically require high reaction temperatures. Low-reaction-temperature, dual-catalytic systems have been reported, but they typically suffer from low efficiency.

Now, researchers led by Jean-Marie Basset and Manoj Samantary report a silica-supported bimetallic precatalyst that may improve the efficiency of alkane metathesis while avoiding extremely high temperatures (DOI: [10.1021/jacs.6b04307](https://doi.org/10.1021/jacs.6b04307)). Using *n*-decane as a substrate, the team finds that the maximum TON can be improved from 350 to greater than 1000 using the synergistic two-metal system compared to its monometallic counterpart. This is the first demonstration of two chemically compatible organometallic complexes grafted onto a single surface resulting in a remarkable synergism effect.

Christine Herman, Ph.D.

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## ■ NIOBIUM OXIDES HAVE THE POWER, EVEN WITHOUT NANOSTRUCTURING

Modern electronic devices that require faster rate performance and higher charge storage capability than traditional battery materials can offer have spurred the need for new high-power, high-capacity energy storage materials. One route toward this goal is through nanostructuring materials currently used or under investigation for lithium-ion battery cathodes, which improves the ability for lithium to reach the electrode interior. However, disadvantages including safety concerns, increased side reaction inside the battery, toxicity, environmental concerns, high cost, and complex synthesis are significant obstacles preventing the use of nanoparticles in batteries.

In a new study, Clare Grey and co-workers circumvent these issues with a promising lithium-ion electrode material whose large particles demonstrate charge storage capacity and rate performance on par with the best nanostructured electrodes (DOI: [10.1021/jacs.6b04345](https://doi.org/10.1021/jacs.6b04345)). Two of the four forms of Nb<sub>2</sub>O<sub>5</sub> the researchers synthesize demonstrate fast rates, high lithium ion densities, good gravimetric capacities, and excellent capacity retention.

Further investigation shows that these favorable qualities stem from the unique “room-and-pillar” structure of these materials, providing an ideal environment for lithium intercalation. The authors suggest that Nb<sub>2</sub>O<sub>5</sub>'s excellent characteristics make it an interesting candidate for energy storage applications.

**Christen Brownlee**

## ■ FLUORINATED TYROSINES PRECISELY PLACED TO TRACK ENZYME REACTIONS

The amino acid tyrosine, or its oxidized form called a tyrosyl radical, can often play critical but distinct roles in enzyme-catalyzed reactions. For several decades, researchers have used fluorinated tyrosines to understand how this amino acid affects enzyme function, but site-selected replacement of a tyrosine with the fluorinated analogue as a probe in a protein of interest has remained a challenge.

Now JoAnne Stubbe and colleagues report a method to use fluorinated tyrosyl radicals to study the complex reaction catalyzed by the enzyme called class Ia ribonucleotide reductase, which relies on a tyrosyl radical to produce the building blocks for DNA (DOI: [10.1021/jacs.6b03605](https://doi.org/10.1021/jacs.6b03605)). Using biophysical techniques to track reaction progress, they are able to discern how the tyrosyl radical participates in class Ia ribonucleotide reductase's catalytic activity.

As tyrosyl radicals play important roles in many other enzyme-catalyzed pathways, including the oxygen-evolving complex in photosynthesis and an important enzyme in lipid biosynthesis, the investigators note that these fluorinated tyrosine radicals, described in detail spectroscopically, “may be useful in unraveling the mechanisms of these systems and other enzymes that have yet to be discovered.”

**Rajendrani Mukhopadhyay, Ph.D.**