

## Spotlights on Recent JACS Publications

### ■ SIMPLE AROMATICS ASSEMBLE INTO “DECORATED” NANOGRAFENE

Nanographene molecules, also known as large polycyclic aromatic hydrocarbons, have unique electronic properties and the potential for supramolecular assembly. Researchers led by Junfa Wei present a bottom-up approach to the synthesis of highly substituted nanographene molecules from simple aromatic precursors (DOI: 10.1021/ja413018f). The team performs the two-step synthesis of the molecules, which contain the core molecule hexa-*cata*-hexabenzocoronene, with the help of a novel FeCl<sub>3</sub> catalyst. The protocol reported here for access to nanographenes avoids the preparation of corresponding oligophenylene precursors. For the starting material, they use simple aromatic compounds that arrange themselves into three-fold symmetrical nanographene structures, which are confirmed by X-ray crystallographic analysis.

The team “decorates” the molecules to present a variety of chemical functionalities. They envision these decorated nanographene molecules will enable the construction of larger, more complex  $\pi$ -conjugated molecules, which may lead to the creation of supramolecular architectures with interesting electronic and structural properties. This simple strategy for synthesis of large aromatic architectures with controllable size and shape is of interest to both chemists and material scientists. **Christine Herman**, Ph.D.

### ■ CRACKING THE CODE OF A SUN TO FUEL SYSTEM

Harvesting solar power has become one of the most common forms of renewable energy. A sun to fuel system allows solar energy to be stored, transferred, and used as needed, even in the absence of sunlight. To model sun to fuel systems, semiconductor nanorods can be coupled with hydrogenase, a remarkable enzyme catalyst. After photoexcitation, nanorods transfer an electron to the hydrogenase, and subsequently the redox hydrogenase system produces hydrogen as the fuel. Understanding the electron-transfer kinetics is essential to improving such a system. Gordana Dukovic and colleagues have described the electron-transfer kinetics in complexes of CdS nanorods and [FeFe]-hydrogenase I from *Clostridium acetobutylicum* (CaI) for the first time (DOI: 10.1021/ja413001p).

The researchers measure the rates and efficiencies of electron transfer in complexes of CdS nanorods and CaI hydrogenase using transient absorption spectroscopy. They find that the electron-transfer rate constant and the electron-relaxation rate in the CdS nanorods are comparable. This result suggests the gains in efficiencies of hydrogen production could be achieved by increasing the electron-transfer rate and/or decreasing the electron-relaxation rate through structural modifications of the nanorods. These results provide a first glimpse into the intricate kinetics of photochemical hydrogen generation in nanocrystal-enzyme biohybrids as next generation of solar materials, the authors conclude.

**Hui Jin**, Ph.D.

### ■ SQUARE KITE-LIKE PARTICLES MAKE GREAT CATALYSTS

Platinum is among the rarest earth elements. Its scarcity makes the metal a symbol of prestige in society, but a costly material in industry, as platinum is also a workhorse catalyst. To lower cost without sacrificing performance, researchers can substitute some platinum atoms with other elements, or they can increase the number of atoms in each particle that actively contribute to catalysis. The latter is done by increasing the available platinum at the surface—a quantity called surface area.

With their unusually shaped platinum and copper (PtCu<sub>3</sub>) nanocrystals, Yaqi Jiang, Zhaoxiong Xie, and colleagues marry both strategies to create high surface area catalysts that can do the job with less platinum (DOI: 10.1021/ja413209q). Previous research has shown that catalysts made with the copper and platinum alloy PtCu<sub>3</sub> could work even better than pure platinum. To create the nanocrystals' unusual concave star shape, the researchers use molecules that interfere with normal crystalline growth processes, so that higher energy crystal faces grow instead. Experiments show that the nanocrystals are excellent and long-lasting aids to electrochemical reactions and that both the copper substitution and the unusual geometry contribute to their good performance. The particles are an efficient and effective catalytic material and can increase utility in industrial settings.

**Jenny Morber**, Ph.D.

### ■ YET ANOTHER ADVANCE FOR THE DIELS–ALDER REACTION

The Diels–Alder reaction is by far the most well-known organic “named reaction” due to its ability to conveniently construct structural complexity and diversity in organic synthesis. Of particular interest are its catalytic asymmetric variations for building complicated yet stereochemically well-defined molecular architectures, especially when combined with additional transformations.

Now, Daniel Romo and colleagues have developed a catalytic Diels–Alder/lactonization organocascade reaction by taking advantage of the unique reactivity of  $\alpha,\beta$ -unsaturated acylammonium salts (DOI: 10.1021/ja501005g). A chiral isothioureia catalyzes the annulation between *in situ* generated acylammoniums and appropriate dienes, yielding bicyclic  $\gamma$ - and  $\delta$ -lactones in a highly stereoselective manner. A model that rationalizes the stereoselectivity was derived from the results of quantum chemical calculations, and this model reveals the importance of an S...O interaction in organizing the preferred transition-state assembly.

This approach allows up to four contiguous stereocenters in a single step and is stereodivergent as well, where racemic dienes are converted into easily separable diastereometric bi- and tricyclic lactones. The authors also demonstrate the prowess of this new method by concise access to the fused core of the natural product glaciolide and other bioactive

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compounds sharing similar structural features.

Xin Su, Ph.D.

#### ■ PIECING TOGETHER AN ENZYMATIC MECHANISM

John P. Richard and co-workers use mutation analysis and kinetics experiments to investigate the mechanism of triosephosphate isomerase (TIM), a key enzyme in the glycolytic pathway and whose deficiency is associated with a severe neurological disorder (DOI: 10.1021/ja501103b).

TIM is a highly efficient enzyme that catalyzes the reversible conversion of dihydroxyacetone phosphate to glyceraldehyde 3-phosphate. This reaction is an early step in glycolysis, a universal metabolic pathway for cellular energy production. The authors compare the energetics of this reaction using either TIM or strategically designed TIM mutants, with the natural substrate glyceraldehyde 3-phosphate and the compound split into two pieces, glycolaldehyde and phosphite dianion. They find that the reactions of the whole substrate and of its pieces proceed through remarkably similar transition states, stabilized by similar interactions with the enzyme.

These results provide compelling evidence that TIM employs its dianion binding domain to stabilize a catalytically active conformation and to facilitate reaction at a catalytic domain. These findings are relevant to the mechanism for activation of many enzymes that utilize phosphodianion binding energy in catalysis of decarboxylation and proton, hydride, and phosphoryl transfer reactions. The analysis suggests strategies for the development of therapeutic agents to inhibit enzymes, which employ catalytic and phosphodianion activating domains.

Eva J. Gordon, Ph.D.