

Spotlights on Recent JACS Publications

■ SYNTHETIC PEPTIDE SCORES MORE PORES FOR DRUG DELIVERY

William Wimley and colleagues report a synthetic peptide that creates long-lived macromolecule-sized pores in a lipid bilayer membrane (DOI: 10.1021/ja500462s). The work could support a host of biotechnology applications, including drug delivery.

To deliver a large or polar drug into a cell, researchers need a way to breach the cell membrane. One promising approach is to introduce peptides that self-assemble into pores in the lipid bilayer membrane. But scientists have struggled to find or design peptides that potently form and maintain these pores for an extended period of time. Now Wimley and co-workers have synthetically evolved a peptide that fits the bill. They take a bee venom peptide that forms transient membrane pores and make modifications to several of its residues. Then they screen the ensuing variants for their pore-forming ability.

The team identifies a peptide that introduces multiple, long-lasting pores with very low concentrations of peptide. The pores are large enough for a macromolecule to pass through. The advance could be used as a platform for many applications in biotechnology, including drug delivery, targeted cancer and HIV therapies, and biosensor development.

Deirdre Lockwood, Ph.D.

■ PROTECTIVE ELECTROCHEMICAL N-FUNCTIONALIZATION OF IMIDAZOLES

When Michael Faraday established the foundation of electrochemistry nearly two centuries ago, he would probably have never imagined how widely used it would become. As an elegant example of electrochemical organic synthesis, Jun-ichi Yoshida and co-workers have recently developed a convenient approach to N-functionalized imidazoles by electrooxidative activation of aryl and benzylic compounds (DOI: 10.1021/ja501093m).

Activating unreactive C–H bonds is a highly sought-after target within the community of synthetic methodology, which electrochemical methods can rarely be harnessed to achieve. For instance, overoxidation presents an obstacle in the case of direct C–N coupling between imidazoles and aryl or benzylic compounds via anodic oxidation. However, the authors provide an ingenious solution to this problem by introducing a protecting group to imidazoles, which renders the products nonsusceptible to side reactions.

The versatile utility of this strategy is demonstrated by the easy syntheses of two bioactive N-substituted imidazole derivatives. Being chemoselective and metal-free, it dramatically simplifies the transformation that would otherwise require prefunctionalization and metal catalysts.

Xin Su, Ph.D.

■ ENHANCING SOLAR CELL EFFICIENCY WITH SINGLET FISSION IN PENTACENE

The maximum efficiency of single-junction solar cells is 33.7%, the so-called Shockley–Queisser limit. Singlet fission, a process

that generates two excitons from one excited singlet state after absorbing one photon, could be the key to push the efficiency beyond this limit. Tao Zeng, Roald Hoffmann, and Nandini Ananth present a detailed quantum chemistry study of pentacene monomer and dimer that serves to reconcile existing views of the singlet fission process and gives a clearer picture of the mechanism (DOI: 10.1021/ja500887a).

Using a computational method that can accurately handle both nondynamical and dynamical electron correlations, the team calculates the electronic states of pentacene monomer and dimer. The authors characterize the six low-lying singlet states of a pentacene dimer at geometries that approximate the unit cell structure of crystalline pentacene and elucidate the roles of these six states in singlet fission. Study of structural effects on singlet fission in the pentacene dimer suggests a significant dependence of the efficiency of singlet fission on intermonomer distance and orientation.

Hui Jin, Ph.D.

■ COLOR CODERS GET A BOOST

Biological researchers rely heavily on molecular tagging to determine where cells and molecules go and how they interact. Luminescent dots work well for tagging, but sometimes researchers need more options. So-called biological barcodes add a layer of complexity, incorporating multiple colors and patterns into a light-emitting tag. A biological barcode needs to be bright, distinct, abundant, versatile, and low-cost. Unfortunately, current choices rarely meet all these needs.

Xiaogang Liu and colleagues contribute a valuable addition to the toolbox with multicolor barcodes based on lanthanide crystal rods (DOI: 10.1021/ja5013646). Through a process called upconversion, lanthanide crystals can convert longer wavelength, lower energy light into higher energy, visible wavelengths. This property is ideal for observing delicate cells and tissues without causing damage.

The researchers vary the rods' composition from the center to the ends so that the rods emit different patterns of red, green, and blue light. The crystals are low-cost, bright, long-lasting, and size-flexible and can be created in large batches. In experiments the glowing rods were easily readable with a conventional optical microscope. In addition to cell tracking, these materials would make excellent optical barcodes for anticounterfeiting and security applications.

Jenny Morber, Ph.D.

■ ISOBUTANOL: A FURTHER STEP TOWARD MODELING ITS COMBUSTION

Donald Truhlar and co-workers have described, using several new developments in computational chemistry, essential parameters related to the combustion of isobutanol (DOI: 10.1021/ja5011288). Isobutanol, $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$, which can be obtained by the fermentation of carbohydrates, is of interest as a biofuel because it has combustion properties close

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to that of gasoline, and also because it can be blended with gasoline.

Modeling the combustion mechanism of isobutanol requires reliable values of the reaction rates for the abstraction reactions of a hydrogen atom from each of four distinguishable sites by hydroxyl radicals (OH). The four kinds of hydrogen atoms are attached to the carbon atom of one of the methyl groups, to the two remaining carbon atoms of the molecule, and to the oxygen atom of the hydroxyl group. However, experimental determinations of the reaction rates have remained inconclusive because of many secondary reactions as well as difficulties in detecting product radicals, while previous computations were affected by various kinds of errors.

Here, the researchers have determined the individual rate constants of each of the four abstraction reactions and the branching ratios by applying variational transition-state theory. Taking into account a large number of factors, including conformations of transition structures, barrier heights, tunneling transmission coefficients, anharmonicity in zero-point energy, and in torsional vibrational modes, they obtain values for the four reaction rate constants as a function of temperature. The results agree with available experiments for the sum of the rate constants over wide ranges of temperature, but also supply the experimentally missing branching ratios.

Alexander Hellemans