

Spotlights on Recent JACS Publications

■ EXCITATION ENHANCES LEWIS ACIDITY OF METHYL VIOLOGEN

Molecules with acidic protons are known to be stronger acids upon photoexcitation. These so-called photoacids are used to probe dissociation dynamics, catalyze reactions, initiate protein folding, or trigger drug delivery. It was recently proposed that excitation may also increase the Lewis acidity of a molecule. In this case, molecules without an acidic proton can induce proton transfer within the solvent. Recent spectroscopic evidence supports the idea that methyl viologen has enhanced Lewis acidity in an excited state, but the underlying mechanism remains unclear.

To confirm its Lewis acidity and probe the mechanism, Edward Hohenstein has performed *ab initio* excited-state molecular dynamics studies on aqueous methyl viologen. He finds that the product of the photoreaction is an unexpected covalent addition of hydroxide ion to methyl viologen (DOI: [10.1021/jacs.5b08177](https://doi.org/10.1021/jacs.5b08177)). This adduct had been proposed, and dismissed, in the earlier spectroscopic work.

Hohenstein suggests further spectroscopic studies to look for the new covalent photoproduct. The observed mechanism also indicates that molecules with similar low-lying excited states and short fluorescence lifetimes in aqueous solution, like 4,4'-bipyridinium derivatives, could also exhibit similar enhanced Lewis acidity.

Melissae Fellet, Ph.D.

■ GETTING THE MOST OUT OF GRAPHENE

Graphene, a single layer of carbon atoms arranged like a honeycomb, has quite a few things going for it. It is strong, flexible, and transparent. Electrons move quickly through graphene, and it is highly tunable and easy to process. It would appear to be a perfect material for electrodes in photovoltaic devices, which generate electricity directly from sunlight, but after a decade of work, graphene-based electrodes still underperform those made with other materials. In this Perspective, Kian Ping Loh and colleagues assert that the strength of graphene is less its superiority and more its versatility, an asset thus far underutilized (DOI: [10.1021/jacs.5b10917](https://doi.org/10.1021/jacs.5b10917)).

To fully exploit graphene in a solar cell, the authors write, researchers should explore the material as cathode, anode, and a photoactive layer. Graphene-like molecules, which are arranged similarly but contain more than just carbon, can be converted into n-type semiconductors. Perhaps, they argue, graphene is better thought of as a performance enhancer for silicon-based photovoltaics than as their replacement. For real-world applications, researchers will need to further enhance graphene's light-harvesting capability while maintaining high electron mobility. The authors envision a flexible solar cell consisting of a graphene-like photoactive layer and charge transport layers made from solution-processed graphene, with all the components integrated onto one large graphene electrode.

Jenny Morber, Ph.D.

■ DIRECT HIT ON AN ELUSIVE ANTIBIOTIC TARGET

The rapid proliferation of drug-resistant bacteria has elicited calls for renewed research and development of antibiotics. One promising target is the bacterial cell wall, where penicillin drugs attack and stop bacteria. Here, David Sanders, David Palmer, and colleagues describe a novel inhibitor of dihydrodipicolinate synthase (DHDPS), an enzyme required for cell wall biosynthesis (DOI: [10.1021/jacs.5b12695](https://doi.org/10.1021/jacs.5b12695)).

DHDPS is a tetrameric enzyme that is allosterically controlled by lysine. Inspired by X-ray crystallography data of lysine bound to DHDPS, the team has developed "bislysine", essentially two molecules of the amino acid joined by a two-carbon linker. They find it to be a potent inhibitor, 300 times more effective than lysine itself. Bislysine acts as a mixed partial inhibitor and noncompetitive partial inhibitor with respect to the two substrates, the authors report, binding to all forms of the wild-type enzyme with a K_i near 200 nM for the wild-type enzyme.

Importantly, bislysine is also effective against a DHDPS mutant that is resistant to other inhibitors of wild-type enzyme with an IC_{50} of 400 nM, 5 orders of magnitude better than lysine. "By demonstrating that this enzyme is susceptible to potent inhibitors, we believe the [diaminopimelate] pathway remains a viable target for novel antibiotic research," the authors conclude.

Jeffrey M. Perkel

■ FINE-TUNING THE PROPERTIES OF POLYMERS

In the field of polymer synthesis, significant focus has been on creating and studying polymers with increasingly narrow molecular weight distributions. For some applications, however, researchers may desire polymers with weight distribution profiles that are broad, or polymers that have a distribution profile other than the typical Gaussian curve, but much remains unknown about how to control for these characteristics. Now, researchers led by Brett Fors report a new strategy for tuning the breadth and shape of the molecular weight distribution profile of polymers, while also retaining control over the average molecular weight (DOI: [10.1021/jacs.5b13565](https://doi.org/10.1021/jacs.5b13565)).

The team creates a series of polystyrene samples using nitroxide-mediated polymerization and characterizes the polymers with size exclusion chromatography to determine their molecular weight distribution. The researchers find that, when they change the rate at which the initiator is added to the reaction mixture, they can predictably tune the breadth of the molecular weight distribution and control the shape of the distribution profiles. This work may lead to a better understanding of the relationship between a polymer's properties and the shape of its molecular weight distribution profile, which may lead to the development of new, tunable materials for applications in nanolithography, photonics, filtration, and thermoplastic elastomers.

Christine Herman, Ph.D.

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■ PINNING DOWN NANOPARTICLE GEOMETRIES

For decades, the billiard ball theory of close-packed assemblies of equal-sized spheres has helped researchers visualize how atoms arrange themselves within materials. Unlike bulk materials, whose atoms layer upon each other in vast sheets, ligated nanomaterials are more like small clusters of balls pressed together in space. These clusters often pack themselves into ordered icosahedra, with some arrangements more stable than others.

One of the more stable configurations is the Mackay two-shell 55-atom icosahedron. Now, Larry Dahl and colleagues have successfully isolated a Mackay two-shell 55 palladium-atom icosahedron—a cluster with two concentric cages of atoms, similar to a Russian matryoshka nesting doll (DOI: [10.1021/jacs.5b13076](https://doi.org/10.1021/jacs.5b13076)).

The work involves a designed synthesis and characterization by X-ray diffractometry, IR/NMR spectroscopy, and DFT computations of the first example of this two-shell Mackay polyhedron. Its detailed architecture has enabled a structural/bonding comparison with interior two-shell icosahedral geometries that are formed in capped three-shell Pd₁₄₅, four-shell Pd₁₆₄, and the recently reported four-shell Au₁₃₃ nanoclusters. The research highlights the importance of this structure in studies of nanoparticles, intermetallic clusters, and quasi-crystals, with particular relevance to current studies of gold–palladium catalysts.

Jenny Morber, Ph.D.

■ FAST ELECTRONS IN FLAVOPROTEINS KEY TO A RANGE OF PROCESSES, INCLUDING ANIMAL NAVIGATION

Cryptochromes and photolyases are flavoproteins found in all living organisms including bacteria, plants, and animals. Charge-transfer processes in these flavoproteins (through a chain of tryptophan residues) play an important role in light signaling, circadian rhythms, and DNA repair, and may form the molecular basis for navigation systems in migratory animals. These processes are initiated by light-induced charge migrations that belong to the fastest known electron transfers in proteins.

Aurélien de la Lande and co-workers investigate electron transfer in a frog (6–4) photolyase—a protein closely related to the putative magnetosensitive animal cryptochromes—using state-of-the-art molecular dynamics simulations and density functional theory calculations (DOI: [10.1021/jacs.5b10938](https://doi.org/10.1021/jacs.5b10938)). They focus on two electron-transfer mechanisms: incoherent hopping, based on an existing (Marcus) theory, and coherent tunneling, based on the flickering resonance model. Incoherent hopping is determined to be the dominant mechanism and the recently discovered fourth tryptophan to be the terminal electron donor to the photoexcited flavin. The researchers conclude that further study of similar animal cryptochromes may lead to a better understanding of their sensitivity to magnetic fields and their role in animal orientation based on the perception of the Earth's magnetic field.

Alexander Hellemans