

Spotlights on Recent JACS Publications

RENEWABLE ENERGY: PHOTOCHEMICAL HYDROGEN PRODUCTION WITH LOW-COST CATALYSTS

Hydrogen is an ideal fuel as it does not produce greenhouse gases during combustion. However, the storage and transport of liquid hydrogen are problematic because of the need for heavy high-pressure tanks. Organic hydrates, as an alternative material for hydrogen production/storage, have received much attention recently. Here, the hydrogen is released via a hydrogen evolution reaction (HER), usually at high temperature, using costly, often platinum-based, metal catalysts.

Ho-Chol Chang, Masako Kato, and co-workers report a new approach toward the use of a low-cost catalyst for evolving hydrogen under light irradiation (DOI: 10.1021/ja4025116). They explore the photochemical production of hydrogen catalyzed by an iron-phenylenediamine complex (FeII-opda). Light stimulates the transfer of protons from the phenylenediamine ligands to the iron ion. Therefore this complex is an effective electron–proton pooler, and in a tetrahydrofuran solution it liberates hydrogen molecules when irradiated with light. Adding hydroquinone, an electron–proton donor, improves the evolution of hydrogen.

The researchers conclude that further research toward a better understanding of the reaction mechanism may lead to compounds suitable for hydrogen evolution with visible light. Cost-effective renewable energy could be realized by utilizing this plentiful natural resource in photochemical hydrogen production and storage. **Alexander Hellemans, Ph.D.**

THE BACKBONE OF PROTEIN STABILITY

Protein structure, conformation, and stability are intimately linked, and disruption of any of these properties can lead to conditions such as Parkinson's or Alzheimer's disease. Ron Raines and co-workers explore the electronic nature of the chemical bonds that hold proteins together, called backbone amide bonds, to help understand how they influence the stability of the proteins they comprise (DOI: 10.1021/ja4033583).

Using a combination of computational and experimental methods, the authors investigate a relatively understudied type of interaction between amide bonds called an $n \rightarrow \pi^*$ interaction. They are able to calculate an association energy that represents this interaction, and they also determine that the $n \rightarrow \pi^*$ association energy of an amide bond analogue called a thioamide is 3 times stronger than that of a regular amide bond.

Their findings have several implications for the study of protein conformation and stability. Because $n \rightarrow \pi^*$ interactions are more prevalent when peptides or proteins adopt certain conformations, such as α -helices, over others, like β -sheets, they may offer insight into the factors that govern protein conformation and its association with disease. Their findings may also provide clues about how to engineer more stable proteins, and argue for the inclusion of $n \rightarrow \pi^*$ interactions into computational models of protein structure and energetics. **Eva J. Gordon, Ph.D.**

ON THE ANTIOXIDANT ACTIVITY OF VITAMIN E

That vitamins are “good for you” is generally accepted. How they work, though, often is unclear. Now Thad Harroun and colleagues have probed the membrane properties and antioxidant activity of vitamin E (DOI: 10.1021/ja312665r).

Harroun's team incorporates alpha-tocopherol, or aToc—a form of vitamin E comprising a chromanol ring headgroup and a fully saturated 13-carbon tail—in different model lipid membranes. They then study the molecule's vertical position in those membranes using neutron diffraction and NMR, and its antioxidant activity with UV spectroscopy.

The data suggest vitamin E resides with its headgroup bobbing near the membrane surface (at a height determined by membrane composition) and its tail dangling into the bilayer. From there aToc engages aqueous reactive oxygen species at the membrane surface, as well as deep-membrane lipid radical chain reaction events that it encounters via “snorkeling” of the fatty acid's acyl chain.

What aToc does not do, the authors note, is “explore the hydrophilic center of the lipid bilayer”. The authors suggest that the diverse range of lipids in cell membranes will also affect aToc's lateral movement, which may have further implications for its activity. **Jeffrey M. Perkel**

ELECTRIC FIELD COAXES UNIFORM, SPHERICAL PARTICLES INTO CONTROLLED CLUSTERS

Colloidal molecules, or clusters of small particles assembled into predetermined arrangements, are important building blocks for next-generation functional materials such as photonic crystals or metamaterials—synthetic materials constructed to have properties not found naturally. A new approach developed by Ning Wu and co-workers may now make it easier to create and study colloidal molecules made from simple spherical particles (DOI: 10.1021/ja403172p).

Colloidal molecules are typically made from nonspherical particles or spherical particles with nonuniform interfacial properties. Mixtures of such particles can self-assemble into well-ordered aggregates, such as lock-and-key colloids that pair up on the basis of complementary geometries and surface interactions. Limitations of current approaches, however, often include polydispersity, or lack of uniform particle size, low throughput, and also the requirement for building blocks that can be difficult to make.

With the help of an alternating-current electric field, the research team finds they can coax spherical, isotropic particles with uniform surface properties into creating colloidal oligomers and never-before-seen macro-colloidal molecules. Since the approach does not rely on material-specific properties, it holds promise for being used to create colloidal molecules out of a broad range of particles with different chemical properties, which may be useful for creating functional materials or serving as model systems for probing complex molecular phenomena. **Christine Herman, Ph.D.**

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