

Spotlights on Recent JACS Publications

■ DEHYDROGENATION FOR THE CREATION OF NEW CARBON NANOSTRUCTURES

Dehydrogenation of is one of the most effective strategies for the synthesis of fullerenes, nanographenes, and nanoribbons. It is flexible and versatile, thanks to the broad range of available precursors. The pathway for molecular dissociation has been determined for small aromatic molecules, but it remains unexplored for larger molecules like the 24-carbon coronene. The pathway becomes more complex with increasing molecular size, degrees of freedom for molecular motion, and competition with other surface processes, such as desorption.

By combining density functional theory calculations with various experimental techniques, Alessandro Baraldi and co-workers have found that coronene molecules adsorbed on iridium single-crystal surfaces undergo major conformational changes during surface-assisted dissociation (DOI: [10.1021/jacs.5b12504](https://doi.org/10.1021/jacs.5b12504)): they first tilt upward, retaining their planar configuration, then they undergo a rotation, and finally they settle to form dome-shaped nanographene flakes.

The researchers suggest that this novel and complex breakup mechanism could be applied to the creation of new nanostructures with different functionalities. For example, by encapsulating magnetic atoms below the carbon dome, new applications in spintronic devices, such as molecular memories or sensors, become available.

Alexander Hellemans, Ph.D.

■ CRYSTAL CLEAR: COVALENT BONDS FOR METAL AND COVALENT ORGANIC FRAMEWORKS

Covalent chemistry involving organic and inorganic molecules is at the heart of many important advances in science, including pharmaceuticals, industrial chemicals, polymers, and more. Yet covalent bonds are useful for more than creating molecules. In their new Perspective, Omar Yaghi and colleagues explain how covalent bonds can be used to create extended structures, linking together molecular building blocks to create three-dimensional porous, crystalline materials, known as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) (DOI: [10.1021/jacs.5b10666](https://doi.org/10.1021/jacs.5b10666)).

The team describes how various strategies in covalent chemistry can make it possible for scientists to control the structure and porosity of the resulting crystalline material, introduce chemical linkers, and even encapsulate nanoparticles. The strength of the covalent bonds renders structures with robustness and permanent porosity, enabling chemists to perform post-synthetic modifications to introduce additional functionalities.

Looking into the future, the authors say that the ability to achieve multiple, complex functions will be possible through the introduction and organization of molecular motifs into MOFs and COFs, which should enable researchers in the field to build complex, multi-functional structures that are inspired by nature.

Christine Herman, Ph.D.

■ IONS MOVE IN, IONS MOVE OUT, INTERCALATION VISUALIZATION REDUCES DOUBT

Atomic-level visualization of ion intercalation of layered materials, such as metal chalcogenides, is extremely important in the development of high-performing, long-lasting batteries.

Kingo Itaya and colleagues describe an improved method for observing dynamic lithium ion intercalation into atomically flat molybdenum disulfide (MoS_2), a flaky material often used for catalysis, batteries, and solid lubricants (DOI: [10.1021/jacs.5b11849](https://doi.org/10.1021/jacs.5b11849)). The researchers have developed a combined microscopy technique that acquires information quickly enough to capture dynamic processes at atomic-level resolution with minimal sample disturbance. The work represents the first complete visualization of this intercalation/de-intercalation cycle, revealing distinct phase separation and layer-by-layer intercalation as lithium ions create channels in the material.

Such dynamic yet detailed visualization of intercalation in layered materials helps researchers understand the charge/discharge process, knowledge critical for developing robust high-performance battery electrodes. The authors note that, in addition to MoS_2 , this technique should also work well for imaging graphite, another popular battery electrode material.

Jenny Morber, Ph.D.

■ CATCHING UP WITH SUPER-FAST PROTEIN FOLDING REACTIONS

Many chemical reactions are faster than the blink of an eye. Protein folding, for example, can occur exceedingly quickly, making it difficult for researchers to fully elucidate the folding reaction.

Rapid mixing is critical for capturing folding in the act, allowing scientists to observe the protein's transformation step-by-step starting at its earliest stages. To monitor ultrafast reactions, Daniel Mortensen and Evan Williams have combined a theta-glass emitter, which facilitates rapid mixing, with mass spectrometry (DOI: [10.1021/jacs.5b13081](https://doi.org/10.1021/jacs.5b13081)). The theta-glass emitter is a capillary divided into two sections, one containing an acid-denatured protein and the other an alkaline buffer. The capillary extrudes the two solutions into droplets when electrospray ionization is initiated, mixing the unfolded protein with the alkaline buffer and thereby raising the pH to induce protein folding. This mixture in the electrospray nanodrops is quickly fed into the mass spectrometer for analysis. Unfolded proteins have a higher charge than their folded counterparts, so as the folding reaction proceeds, the mass spectrometry data show a shift toward molecules with fewer charges.

Using this approach, the researchers measure folding reaction times as fast as $1 \mu\text{s}$, while conventional mixing approaches are limited to around $10 \mu\text{s}$. Furthermore, the theta-glass emitter's tiny droplets use less protein than conventional mixing approaches, which may be important for studying samples that are difficult to produce.

Erika Gebel Berg, Ph.D.

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■ PROGRESS TOWARD A STIMULUS-RESPONSIVE MOLECULAR MULTI-ROTOR

The sophisticated structures of biomolecular machines, such as enzyme assemblies, have inspired chemists to create synthetic supramolecular systems that integrate multiple functions. So far, the functions of such machines have been largely limited to simple tasks, such as unidirectional motion, on/off switching by external stimuli, and transmission of energy through coupled motions. And while several reports of molecular gearing systems have been made, velocity adjustment in this manner has not previously been investigated. Now, Miksuhiko Shionoya and colleagues report the synthesis of a self-assembling molecular four-gear system whose rotational rate can be dynamically altered via ligand exchange (DOI: [10.1021/jacs.5b13515](https://doi.org/10.1021/jacs.5b13515)).

The lantern-type structure contains dirhodium coupled to four triptycene-based ligands that behave like meshed gears, plus two axial ligands that control of the rotation rate of the molecular gear system. The team demonstrates dynamic control the rotation rate via a ligand exchange process. The researchers find that swapping out the ligands also impacts other characteristics of the system—such as the electronics and color—in a manner dependent on the bulkiness of the substituents and the type of coordination atoms present. These findings, the authors write, will provide a “useful design guide” for stimulus-responsive metal-based molecular rotors that undergo rotational motions caused by ligand exchange.

Christine Herman, Ph.D.

■ PEPTIDES FORM ASYMMETRIC FUNCTIONAL BILAYERS

Phospholipid bilayers, the primary membrane components of cells and subcellular organelles, are inherently symmetric leaflets maintained functionally asymmetric with proteins. Now a team of chemists and physicists, working across multiple departments and institutes, has created asymmetrically charged bilayer peptide membranes within spontaneously assembling nanotubes (DOI: [10.1021/jacs.6b00977](https://doi.org/10.1021/jacs.6b00977)).

The researchers use two amphiphilic heptapeptides that differ only in their N-terminal residue: one with a positively charged lysine (K) and the other with negatively charged phosphotyrosine (pY). These peptides co-assemble as anti-parallel β -sheets, maintaining charge neutrality at the leaflet interface, and give hollow nanotubes that are negatively charged on the outside and positively charged on the inside.

Electrostatic force microscopy and ^{13}C – ^{15}N NMR distance measurements reveal that the two limiting solutions to generate charge separation across the nanotube wall are both populated within single tubes. The authors show also that nanotube fragments of one type can “seed” these structures, for instance by mixing K seeds with pY peptides, to generate lateral asymmetry along the nanotube. Such nanotubes, the authors suggest, may now function as scaffolds for the designed organization and arrangement of “electrically and optically functional materials” through extended enzyme, metal, and synthetic catalyst arrays.

Jeffrey M. Perkel