

Spotlights on Recent JACS Publications

■ POLYMER MANIPULATION WITH LIGHT AND METALS

Stimuli-responsive materials reversibly adapt to changes in their environment and have already been used in demonstrations of “smart” materials for controlled drug release, artificial muscles, and healable materials. Now, researchers led by Christopher Barner-Kowollik and Jean-Marie Lehn describe a multi-stimuli-responsive material that responds reversibly to both light and metals—the first material of its kind to simultaneously display optomechanical and ionomechanical properties (DOI: [10.1021/jacs.5b12198](https://doi.org/10.1021/jacs.5b12198)).

Although the majority of light-responsive polymers described thus far are made of azobenzene-based monomers, the team looks instead to monomers with simple imine groups, which are easier to synthesize and amenable to metal ion coordination. They synthesize a monomer containing internal α -bisimine units and perform metathesis polymerization to create polymers that undergo reversible changes in particle size and shape in response to both UV light and palladium ions.

This is the first reported metathesis-derived polymer material with the ability to react to both light and metal stimuli, which lays the groundwork for their application in advanced functional materials.

Christine Herman, Ph.D.

■ GETTING METHANE OVER THE FUEL CELL HUMP

Brent Gunnoe, Andrew Herring, Brian Trewyn, and their colleagues have developed a catalyst that oxidizes methane at low temperatures, suggesting that in the future we may extract methane’s energy from fuel cells instead of combustion (DOI: [10.1021/jacs.5b06392](https://doi.org/10.1021/jacs.5b06392)).

Methane, the primary component of natural gas, has a high per-mass energy content relative to other hydrocarbons and is declining in cost thanks to advances in drilling. Progress has been reported with methane in solid oxide fuel cells, but high operating temperatures reduce their benefits. In this article, the authors show that platinum organometallic molecules covalently anchored to porous carbon assist direct methane oxidation, without carbon monoxide poisoning, at temperatures as low as 80 °C. The porous carbon is an ideal support material, providing high surface area, uniform pore size, interconnected pores, high conductivity, and defect sites that covalently anchor catalysts, as the researchers show here.

The authors report extensive material characterization, which complements electrochemical studies of methane-oxidizing electrodes in fuel cell assemblies. Experiments also reveal relatively high current density in the devices, but much lower than would be expected from theoretical energy calculations or more conventional fuels such as hydrogen or methanol. Though slow methane adsorption and low platinum stability will need to be addressed, this work demonstrates a strong proof of concept for low-temperature direct methane fuel cells.

Jenny Morber, Ph.D.

■ MORE POROUS COVALENT ORGANIC FRAMEWORKS: THE HOLE STORY

Covalent organic frameworks (COFs)—extended crystalline structures in which organic building blocks are linked by strong covalent bonds—have attracted increasing attention because their porous structures and high surface areas may have potential applications in gas adsorption, catalysis, and energy storage. In a new study, Thomas Bein and co-workers have developed a way to substantially enhance both porosity and surface area by introducing modulating agents during synthesis (DOI: [10.1021/jacs.5b10708](https://doi.org/10.1021/jacs.5b10708)).

The researchers use the two-dimensional material COF-5. When phenylboronic acids are added they compete with other building blocks during synthesis, resulting in a significantly altered COF structure. The modified COF-5 is found to have significantly increased domain sizes reaching several hundreds of nanometers, as well as fully accessible pores with an internal surface area of over 2000 m² g⁻¹.

By using functionalized modulators as the starting point for subsequent reactions, the researchers are able to further functionalize external COF surfaces by attaching fluorescent dyes and hydrophilic polymers. The authors suggest that these enhanced characteristics, along with the option for outer surface functionalization, could benefit applications including gas separation, catalysis, super-resolution imaging, and optoelectronics.

Christen Brownlee

■ POLYELECTROLYTE COMPLEXES: ENTROPY MORE THAN ELECTROSTATICS

Many polymers and macromolecules, including DNA, carry charges along the polymer backbone. These charged sites often interact with sites of opposite charge on other macromolecules, which can play a role in folding and molecular recognition. Groups of macromolecules in water form dense polyelectrolyte complexes (PECs) or liquid-like phase separations known as coacervates, driven by electrostatic forces between the charges on the molecules—at least, this was the accepted model.

Jingcheng Fu and Joseph Schlenoff show with a series of experiments that this view may not be the complete picture (DOI: [10.1021/jacs.5b11878](https://doi.org/10.1021/jacs.5b11878)). Polyelectrolytes exist surrounded by a coat of counterions, ions with opposite charge that result in an electrically neutral species. The researchers surmise that when two polyelectrolyte molecules interact, they shed their counterion coats, allowing the charged sites on the polyelectrolytes to bind by ion exchange.

To demonstrate this hypothesis, the researchers study the interaction of two common polyelectrolytes in salt solutions. Using Raman scattering of water molecule vibrations, they show that solvation and the activity of counterions cause the respective enthalpic and entropic contributions to the binding of the two polymer species.

Alexander Helleman

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■ NEUROTROPHIC NATURAL PRODUCTS BY TOTAL SYNTHESIS

The loss of function caused by axon degeneration and neuronal atrophy in both chronic neurodegenerative disease and acute spinal cord injury has generally been thought to be irreversible. Therefore, agents able to promote regeneration and growth of injured neurons are of great interest across all areas of neuroscience research. A group of small-molecule natural products with interesting carbocyclic structures has been shown to possess potent neurotrophic properties, in addition to rectifying some of the shortcomings of earlier protein-based therapeutic agents.

Now, Xiayun Cheng and Glenn Micalizio report the total synthesis of (–)-jiadifenin and two analogues that are among the most potent members of the natural product class (DOI: [10.1021/jacs.5b12694](https://doi.org/10.1021/jacs.5b12694)). The researchers demonstrate the first application of a reaction developed in this laboratory—the alkoxide-directed, metallacycle-mediated, hydrindane-forming annulation reaction—in natural product synthesis.

The authors hope that this enantioselective pathway for the synthesis of several seco-prezizaanes might facilitate their goals of “further developing chemistry capable of producing neurotrophic agents inspired by the seco-prezizaanes”. Therapeutic applications may be enabled by the future discovery and development of less complex structures with scalable syntheses. **Sonja Krane, Ph.D.**

■ WATCHING MEMBRANE PROTEINS MOVE ON THE CELL SURFACE

Membrane proteins often function like light switches, turning on or off, based on a conformational change. Pulsed electron–electron double resonance (PELDOR) can track conformational changes in purified membrane proteins, but it has been unclear whether the proteins behave the same in a test tube as they do in their native environment: the membrane of a living cell. To answer that question, Benesh Joseph, Arthur Sikora, and David Cafiso have performed proof-of-principle PELDOR experiments on a membrane protein, cobalamin transporter BtuB, in intact *Escherichia coli* cells (DOI: [10.1021/jacs.5b13382](https://doi.org/10.1021/jacs.5b13382)).

As a first step, the researchers overexpress the transporter in a bacterial culture and add a nitroxide spin label to the transporter’s cysteine residues. At this point, biology lends a hand. The inside of cells is a reducing environment, which effectively turns off the spin label signals, leaving only the surface labels intact and making it much easier to interpret the data. Then, the researchers add ligands to the culture, triggering a conformational change in an extracellular loop region of BtuB. PELDOR experiments provide label-to-label distances, and thus high-resolution structural information about the conformational changes. These data verify conformations previously observed in crystal structures of purified protein.

Erika Gebel Berg, Ph.D.