

Spotlights on Recent JACS Publications

■ RIGHT ON CUE: NEW “SMART” MATERIALS RESPOND TO MULTIPLE STIMULI

Smart materials respond to changes in their environment in a predictable way, which allows researchers to control their physical properties for applications in biomaterials and bioengineering. Hai-Bo Yang and colleagues report a new class of building blocks for multiple stimuli-responsive materials, known as hexakis-pillar[5]arene metallocycles (DOI: 10.1021/ja413047r).

The team creates two types of the well-defined hexagonal metallocycles, which combine with ditopic guest molecules to form cross-linked supramolecular polymers via host–guest and metal–ligand interactions. By boosting the concentration, the team coaxes the molecular cocktail into forming polymer gels, which in the presence of various stimuli, such as a change in temperature, halide compound, or competitive guest, undergo reversible sol–gel transitions. The team creates the metallocycles in a quantitative yield through a relatively straightforward synthesis, eliminating the need for purification.

This work is one of very few examples of multiple stimuli-responsive supramolecular polymer gels made from multiple pillar[*n*]arene derivatives, and represents a new method for preparing “smart” soft materials.

Christine Herman, Ph.D.

■ A NEW STRUCTURE FOR ORGANIC PHOTOSWITCHES

Molecular switches change color, volume, or solubility when exposed to ultraviolet light. Incorporating these switches into drugs or polymers allows medicine activation or material assembly to be quickly and precisely initiated with light. Azobenzenes, spiropyrans, and diarylethenes are common scaffolds for these switches; however, these molecules require high-energy UV light for activation.

To minimize damage to cells or materials, the common scaffolds are modified so they can be activated by visible light. Now Javier Read de Alaniz, Craig Hawker, and colleagues have designed a new class of organic photoswitches that become colorless, compact, and hydrophilic when activated by visible light (DOI: 10.1021/ja503016b). The researchers find that switch structure can be easily modified because the molecule is built modularly, and the simple synthesis could allow nonexperts to synthesize this switch for biosensors or targeted delivery. Moreover, the starting material for the synthesis is furfural, a commodity chemical derived from renewable nonedible plant material.

To test the new switch’s ability to influence a larger system, the researchers add a switch to a poly(ethylene glycol) polymer. The polymer forms micelles in the presence of a red fluorescent dye. When the researchers shine visible light on the micelles, the intensity of red fluorescence decreases, indicating the switch disrupts the micelle structure enough to release the hydrophobic dye inside.

Melissae Fellet, Ph.D.

■ ORGANIC SPIN CROSSOVER COMPOUNDS: TO PAIR OR NOT TO PAIR

Spin crossover compounds, which can be induced to flip their magnetic state by light, physical pressure, or temperature, have important applications as switches or magnetic storage devices. Many examples exist of transition-metal-containing spin crossover compounds, but organic materials that can similarly flip their magnetic state have been less explored. The latter materials must be able to switch between stable high-spin radical and low-spin dimer forms. However, designing such systems to easily separate into discrete radicals instead of sticking together remains a challenge.

To examine this issue, Richard Oakley, Michael Shatruk, and co-workers have prepared and characterized the heterocyclic bisdithiazolyl radical in the solid state, both experimentally and computationally (DOI: 10.1021/ja502753t). The compound is unusual, as the radicals form a dimer through a configurational crossover and a four-center six-electron bond rather than a simple coupling of orbitals. In the solid state, the dimer can be broken apart by heat, pressure, or light at low temperature. In addition, the radicals photogenerated at low temperature can be trapped up to 242 K before reforming the dimer, showing unprecedented thermal stability.

This work etches a window into the fundamental understanding of organic crossover compounds and reveals why some of these compounds might make effective switchable magnetic materials while others would not. These results may lead to more abundant and flexible electronic and magnetic devices in the future.

Leigh Krietsch Boerner, Ph.D.

■ CHARGING TOWARD A MORE FLEXIBLE LITHIUM ION BATTERY

The rigidity of lithium ion batteries stands in the way of smaller wearable electronics. One way forward is the development of thin-film lithium ion batteries that use a solid polymer electrolyte instead of traditional liquid or ceramic electrolytes. However, the performance of lithium ion polymer batteries lags behind the standard varieties, preempting commercial success. Iain McKenzie and colleagues hope to improve thin-film batteries through a better understanding of lithium diffusion, a key property in battery performance, within solid polymer electrolytes (DOI: 10.1021/ja503066a).

To study the diffusion of lithium ions within a thin-film polymer, the researchers apply an exotic form of nuclear magnetic resonance (NMR) spectroscopy called β -NMR. For this method, the researchers polarize a beam of radioactive ^8Li ions, inject them into a thin film of poly(ethylene oxide), a popular solid polymer electrolyte, and then observe electron ejection (β decay) from the material. The time dependence of the β decay asymmetry is used to determine nuclear spin relaxation rates, which in turn relates to lithium diffusion. The researchers conclude that microscopic lithium ion diffusion is

Published: June 18, 2014

an activated process, while macroscopic diffusion is dominated by the segmental motion of the polymer chain. With these insights they may be able to design better flexible batteries.

Erika Gebel Berg, Ph.D.