

Spotlights on Recent JACS Publications

■ REDOX-ACTIVATED MOLECULAR SWITCHES WITH A TWIST

Owing to their unique spectral, optical, and structural features, helicenes—helically shaped, fused polycyclic aromatic compounds—have gained the attention of chemists in search of promising new candidates for light-responsive molecular machines. Helicenes are well-known for their large chiroptical signals, meaning they respond to optical spectroscopic techniques that are used to investigate chiral substances.

In a new report, researchers led by Lubomír Pospíšil, Lucie Bednářová, and Filip Teplý demonstrate a new level of control over the chiroptical properties of helicene-based systems, known as helquats (DOI 10.1021/ja500220j). By simply altering the molecules' redox states, they find that enantiopure helquats, while retaining their overall shape, undergo a profound change in their electronic state and thus sizable changes in their electronic circular dichroism spectra at certain wavelengths, which is unique for a chiroptical switch. This unprecedented example of a "chiro-switch" may lead to the development of new classes of optical switches and light modulators and contribute to the emerging field of chiral organic conducting systems.

Christine Herman, Ph.D.

■ MOLECULAR MOTOR MODIFICATIONS COULD HELP TUNE THEIR PERFORMANCE

Synthetic molecular motors are simpler and more robust versions of biological proteins involved in locomotion or intracellular transport. These moving molecules could one day power nanomachines.

Molecular motors are often activated by light, starting when the molecules absorb a photon to generate an excited state. Excited molecules then undergo a structural change that causes motion. Ben Feringa and his colleagues developed molecular motors that rotate due to a light-induced isomerization of a double bond. By designing molecules that easily rotate in one direction around the double bond, the researchers created motors that spun around millions of times a second.

Now Feringa, Stephen Meech, and their colleagues have used ultrafast spectroscopy to study how the structure of the molecular motor affects properties of its excited state. The researchers find that electron-withdrawing substituents like cyanide extend the lifetime of a nonlight-emitting excited state connected to the molecule's structural rearrangement and motion (DOI: 10.1021/ja5041368).

The observations suggest that intentional structural modifications might be a way to optimize the efficiency of molecular motors.

Melissae Fellet, Ph.D.

■ STUCK ON YOU: PREDICTING ADSORPTION ENERGIES ON TRANSITION METALS

A simple equation to predict adsorption energies of adsorbates bonding to a surface is developed by Matthew Montemore and J. Will Medlin in a theoretical study relevant to heterogeneous

catalysis (DOI: 10.1021/ja504193w). Heterogeneous catalysis is at the heart of many industrially important reactions, ranging from production of margarine and polyolefins to ammonia synthesis and petroleum processing. Typically adsorption on the solid catalyst is the first step in such processes, and so effective catalyst design requires an understanding of the thermodynamics of adsorption of the molecular species onto catalyst surfaces.

Using density functional theory, the authors study trends in adsorption energies of molecules onto a variety of transition-metal surfaces. They find two groupings with consistent trends in adsorption within each group: carbon and hydrogen fall into in one group, while oxygen, nitrogen, sulfur, and fluorine are in a second group, and these differences can be explained by the molecule's electronic properties.

The ability to accurately predict adsorption strengths can improve prospects for the development of catalysts for biomass conversion, fuel cells, industrial chemical processes, and much more.

Dalia Yablon, Ph.D.

■ COLOR-TUNABLE POLYMER FILMS WITH SWITCHABLE PROPERTIES

Chiral optoelectronic materials selectively reflect right- or left-handed circular polarized light (CPL), a property that is appealing to researchers looking to develop new materials for electronic displays and other devices.

Now, researchers led by Michinori Sugimoto report a new class of rigid-rod helical polymers (DOI: 10.1021/ja504808r). The researchers synthesize the molecules—known as poly-(quinoxaline-2,3-diryl)s (PQXs)—with a variety of side chains and use them to create thin polymer films. When annealed in chloroform vapor, the team observes the resulting dry films selectively reflect right-handed visible CPL. The color—or the reflection wavelength—can be switched by changing the composition of the side chains. However, if 1,2-dichloroethane is used instead, the films reflect left-handed CPL. Whether a film reflects right- or left-handed light can be reversibly switched by exposing the solid film to vapors containing mixtures of the two annealing solvents.

Researchers can switch the handedness of a film and also tune the wavelength of light that is selectively reflected just by changing the mixing ratio of the two annealing solvents without changing the polymer composition. This new class of chirality-switchable materials could lead to the development of vibrantly colored films for displays or decoration as well as new devices for sensing low-threshold lasing.

Christine Herman, Ph.D.

■ SETTING LASER SIGHTS ON MICROSECOND REACTIONS WITH NMR

Scientists can learn a great deal about reaction mechanisms by observing chemical reactions as they proceed, and nuclear

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magnetic resonance (NMR) spectroscopy has the ability to monitor the progress of a reaction over time, identifying newly formed molecules as they emerge. However, chemical transitions and intermediates or products present at low concentrations often elude detection because NMR's sensitivity is typically too low to give accurate measurements. Now, Simon B. Duckett, Robin Perutz, and colleagues follow hydrogen addition reactions on a microsecond time scale by using *para*-hydrogen (*para*-H₂), a magnetically altered state of hydrogen that increases NMR signals by orders-of-magnitude (DOI: 10.1021/ja504732u).

The researchers use a two-step process in their NMR experiment. First, they set up mirrors to shine a laser at a photoreactive NMR sample—transition-metal dihydride complexes in C₆D₆ solution—while it sits inside the spectrometer. The laser triggers the removal of a hydrogen molecule from the metal dihydride, which is quickly replaced by *para*-H₂. By varying the timing between the NMR pulses and the laser, the researchers enable the collection of a series of high-resolution spectra that are not only diagnostic of the nanomolar reaction products but include unusual magnetic oscillations that are unique to these chemical systems. This *para*-H₂ based NMR method has the potential to quantify chemical kinetics while simultaneously providing structural information.

Erika Gebel Berg, Ph.D.