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Spotlights on Recent *JACS* Publications

A REDOX-CONTROLLED MOLECULAR MERRY-GO-ROUND

Rotational motion is essential for many macroscopic and microscopic processes, such as the rotation of gears to move the hands of a clock and the rotary motions of ATP synthase to provide energy for mammalian cells. For applications in nanotechnology, rotational motion must happen on a scale of 100 nm or less. Chemists have employed small molecules like ferrocene, an organometallic compound with two cyclopentadienyl (Cp) ligands linked by an iron center, to perform rotations on the nanometer scale.

Christophe Bucher and co-workers created a redox-responsive molecular carousel based on ferrocene, by attaching a bis-cationic bipyridinium to each of the two Cp's through a linker (DOI: 10.1021/ja209766e). The researchers report that when rigid linkers are used, the two Cp's reversibly pivot from an open position (with the bipyridiniums opposite one another in "charge-repelled" conformers) to a closed position (with the bipyridiniums stacked one on top of the other in the form of intramolecular π-dimers).

Electron transfers centered on the π-dimerizable bipyridiniums trigger the rotation, which overcomes the bipyridiniums' tetra-cationic charge repulsion. The researchers demonstrate that the properties of bipyridinium groups could make them useful components for the development of molecular switches or drivers for molecular motors. **Yun Xie, Ph.D.**

SINGLE-MOLECULE CONDUCTANCE EXPLORED, EXPERIMENT AND THEORY

Researchers are interested in creating electronic devices that are built from the bottom up (small molecules), rather than the top down (etching bulk silicon and other elements), with the goal of creating very small scale components to further miniaturize electronic devices. Single molecules that can join metal electrodes in a reproducible manner are of particular interest because the development of these single-molecule junctions is necessary to create devices based on molecules.

It is technically challenging to measure the conductance of one molecule. At the length scale of a few nanometers quantum effects must be taken into account, and the atomic surface of electrodes can change from one measurement to the next. A group led by Colin J. Lambert, Martin R. Bryce, and Thomas Wandlowski studied single-molecule junctions made from diaryl molecules with a variety of anchoring groups (DOI: 10.1021/ja209844r). The researchers used two different methods to create the junctions and expanded on their experimental conductance measurements by using density functional theory type model calculations and molecular dynamic simulations to explore structural and mechanistic details. A dipyridyl molecule was best able to form junctions reproducibly and with high conductance.

Understanding the fundamental details of how the anchoring group influences the structure and the electronic conductance through a single-molecule junction is a critical step toward creating electronic devices based on molecules. **Polly Berseth, Ph.D.**

HOW NANOTUBES GET COLOR

The colors of nanomaterials commonly vary depending on size, but basic electronic properties usually explain the differences. For instance, the color of metallic gold nanoparticles depends on the wavelength at which their free electrons collectively oscillate, known as the plasma resonance frequency. Semiconducting nanoparticles, or quantum dots, have the colors they do because their size changes the energy gap between their key molecular orbitals.

The colors of highly conducting armchair carbon nanotubes are determined by factors different from those that color other nanomaterials, researchers report. Erik H. Hároz and Junichiro Kono and their colleagues sorted sets of armchair nanotubes and obtained their absorption and Raman spectra (DOI: 10.1021/ja209333m). They learned that although the nanotubes are metallic, their colors do not depend on their plasma resonance, which occurs in the far-infrared, nor on band gaps, which are zero in armchairs. Instead, the color depends on how light is absorbed by electron–hole pairs called excitons, which differs depending on the diameter of the tubes.

The unique coloration mechanism of these gapless one-dimensional metals depends on the absorption bands of these carbon nanotubes and opens the door for further spectroscopic study of these materials, the authors suggest. **Carmen Drahl, Ph.D.,** *C&EN*

AN OLD ENZYME WITH A NEW TRICK

Plants and microorganisms use a variety of enzymes to synthesize natural products, many of which are of great therapeutic importance. In a method called chemoenzymatic synthesis, chemists have taken to combining the use of such enzymes with traditional organic synthesis methods to create interesting new compounds. The Picket–Spenglerase strictosidine synthase (STR1) is an enzyme involved in the biosynthesis of a family of natural products called indole alkaloids. One class of indole alkaloids, called piperazino indoles, are of significant interest biologically but are not commonly found in nature and are challenging to synthesize in the laboratory.

Now, Joachim Stöckigt, Hongbin Zou, and co-workers uncover a new activity of STR1 that enables the chemoenzymatic synthesis of the elusive piperazino indole scaffold (DOI: 10.1021/ja211524d). Insight into how STR1 is capable of catalyzing the synthesis of this unique structure was gained using methods such as X-ray crystallography and molecular modeling.

This study presents the first synthesis of an intriguing novel class of piperazino indoles that have never been reported synthetically or naturally. The newly discovered capability of STR1 illuminated in this report can be exploited for the generation of additional piperazino indoles, potentially leading to compounds with therapeutic utility. **Eva J. Gordon, Ph.D.**

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