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Spotlights on Recent *JACS* Publications

OXIDATION TAKES A TURN IN A RUTHENIUM-HELICENE CHIROPTICAL COMPOUND

Chiroptical materials are activated by changing their chirality, or handedness. Often these materials are triggered by light that only one of the mirror image molecules can absorb, setting off the flip. Helicenes—extended fused benzene rings that contain a helical turn—are often used in chiroptical materials due to their very large magnitude chiroptical effect. Past research has focused on improving their chiroptical properties through addition of more benzene rings, changing the pitch of the helical turn, or incorporating other atoms or metals into the framework.

Jeanne Crassous, Jochen Autschbach, Régis Réau, and co-workers have synthesized a helicene-based chiroptical switch that can be turned on by oxidation as well, by fusing a vinylruthenium fragment to the end of the molecule (DOI: 10.1021/ja304424t). The researchers thoroughly examine the compound, one of the few known to be redox activated, by a number of analytical techniques. In addition, through computational studies, they are able to show exactly the impact of the redox process on the helicene. It is encouraging that the chiroptical properties of a helicene can be adjusted by organometallic chemistry, without modifying the fused benzene ring system, which opens new pathways into the design of chiroptical devices for nonlinear optics, luminescent materials, and sensing technologies. **Leigh Krietsch Boerner, Ph.D.**

"DIMPLE MACHINE" PROBES SINGLE-MOLECULE REACTIONS

Most of what we know of biochemistry was worked out by studying bulk chemical reactions. Things are different in the cell, where tiny volumes yield relatively high local concentrations. Now Min Ju Shon and Adam Cohen describe an approach that may overcome shortcomings of earlier strategies for monitoring single-molecule dynamics in solution (DOI: 10.1021/ja3062425).

The pair devised a microfluidic "dimple machine", in which an array of attoliter-scale depressions are repeatedly filled with a mixture of two DNA strands, each labeled with a green or red fluorescent dye, sealed, measured, and emptied by means of a flow cell and vacuum-controlled reversible lid. They used this device to monitor the occupancy, kinetics, and thermodynamics of the resulting binding reactions, measuring the dynamics of DNA hybridization and observing effects not normally seen in studies of bulk materials.

If two strands were present in the same well and formed a DNA duplex, they would undergo fluorescence resonance energy transfer, such that excitation of the green fluorophore would yield red fluorescence; if not, only green fluorescence was observed. "The confinement effects reported here are likely to be significant whenever molecules are confined to nanoscale volumes," the authors conclude—for instance, in membrane vesicles or emulsions, where interactions of fluorescently labeled molecules could be measured without purification. **Jeffrey M. Perkel**

AROMATIC HYDROCARBON DERIVATIVES CAN HOLD THE BIRADICAL

Biradical polycyclic aromatic hydrocarbons (PAHs) are open-shell molecules that have potential for use in functional materials. Because their unpaired electrons sit in the π-space, the radicals can interact with each other, causing PAHs to be electrically conducting or ferromagnetic. One such molecule, a tetraphenyldixylene called Chichibabin's hydrocarbon, has been extensively studied due to its interesting physical properties. However, open-shell PAHs often decay at room temperature, forming polymers or decomposition products. Thus, being able to stabilize these molecules is paramount to their applicability.

Dongho Kim, Kuo-Wei Huang, Richard Webster, Juan Casado, Jishan Wu, and co-workers have created two stable derivatives of Chichibabin's hydrocarbon and studied the transitions between their open-shell and closed-shell resonance forms, both computationally and by numerous analytical techniques (DOI: 10.1021/ja3050579). Both structures have tetrabenzo units incorporated onto the dixylene frame; one compound (1-OS) has *tert*-butyl units added to the terminal phenyl rings, while the second (2-OS) is capped by fluorene moieties. They found that the ground state of 1-OS exists as a closed-shell compound, while 2-OS is the open-shell biradical, due to the added stability from the extended conjugation. In addition, 2-OS shows two photon absorption, suggesting that these molecules have potential applications not only as magnetic materials, but in optical devices as well. **Leigh Krietsch Boerner, Ph.D.**

ALKYNES PROTECT SEMICONDUCTING ACENES FROM OXYGEN DAMAGE

Acenes—oligomers of fused benzene rings—such as anthracenes (three rings), tetracenes (four rings), and pentacenes (five rings) are useful organic semiconductors and luminescent sensors. These materials are notorious for their high reactivity with oxygen, which can be essential to using them as luminous oxygen sensors; however, this same reaction also destroys their semiconducting properties.

Functionalizing portions of the acene can influence the molecule's reactivity toward oxygen. Werner Fudickar and Torsten Linker study how alkyne groups attached to different acenes help the materials resist oxygen damage (DOI: 10.1021/ja306056x). The researchers synthesized a range of alkynyl-substituted acenes and studied their reaction with molecular oxygen in its singlet state. Alkynyl-bearing acenes reacted more slowly with oxygen than aryl-substituted acenes or unsubstituted acenes. The researchers also reversed the oxidation—thus removing the oxygen—by heating the materials. Calculations of reaction energies, molecular orbitals, and radical

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stabilization energies help clarify the mechanism of oxygen addition and removal.

Understanding how alkynyl substituents protect acenes from oxidation could help researchers improve organic semiconductors, allowing such materials to be inexpensively produced for large, flexible devices. **Melissae Fellet**

MAGNETIC WINDOW INTO A BATTERY'S HEART

Longer-lasting and more powerful lithium batteries could be a boon for electric automobiles as well as personal electronic devices. One of the main drags on battery life is the loss of energy that occurs as lithium ions travel between electrodes. The choice of electrolyte—the solution that bathes the ions inside the battery—affects ion mobility. However, there are few methods available for detecting lithium ion movement while inside a live battery and so choosing the best electrolyte remains a challenge.

István Furó and colleagues have developed a new approach for monitoring lithium ions inside a battery using *in situ* ^{7}Li NMR imaging (DOI: 10.1021/ja305461j). For the experiment, the researchers use a custom-built battery cell, fitted inside an NMR sample tube. At first, the ions were roughly evenly distributed inside the battery electrolyte. Then the researchers switched on the power and scanned the sample periodically over the next 18 h. Over time, the intensity of the NMR signal increased near the battery's anode and decreased near the cathode, suggesting that the lithium ions had migrated to form a concentration gradient well in line with expectations from electrochemical models. The researchers hope that their approach will help battery developers investigate electrolyte behavior and create a better battery. **Erika Gebel, Ph.D.**

NUISANCE ELIMINATION REACTION BECOMES USEFUL SYNTHETIC TOOL

Gregory Fu and co-workers report a palladium-catalyzed elimination of HBr from an alkyl bromide to give a terminal C−C double bond (DOI: 10.1021/ja306323x). This reaction proceeds under mild conditions, at room temperature with the addition of an amine base.

The elimination of hydrogen and a leaving group like a halide, hydroxide, or sulfonate is a common transformation in organic synthesis. Previous methods only work with selected substrates, elevated temperatures, or large amounts of toxic reagents. This type of β-hydride elimination is often an undesired byproduct during palladium-catalyzed cross-coupling reactions involving alkyl bromides, like the Suzuki reaction. Here the researchers are able to push the metal catalyst toward a β-hydride elimination in very good yield.

The researchers found that the catalytic cycle for this elimination lacks the intermediate palladium complex thought to occur in Heck reactions. The elimination does not occur when the reaction is seeded with this expected complex. Understanding the organometallic intermediates in this elimination process might explain the poor performance of some Heck reactions. **Melissae Fellet**