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Spotlights on Recent *JACS* Publications

ESR MARKS THE SPOT IN SCANDIUM CLUSTERFULLERENES

Studies of clusterfullerenes—spherical carbon molecules that encapsulate clusters of metal complexes—are becoming more prevalent due to the molecules' interesting endohedral electrochemical properties. Endohedral electrochemistry focuses mainly on the so-called endohedral (*in cavea*) redox reactions, where an electron passes through the fullerene cage and only interacts with the metallocluster at the center, via an electron-transfer process. In past computational studies, the clusterfullerene $Sc_4O_2@C_{80}$ was shown to have a unique electronic structure, where localization of the frontier orbitals enabled an endohedral electron transfer through both oxidation and reduction. However, chemists have not been able to view this phenomenon experimentally.

Now Alexey Popov and co-workers have matched the computational results with experimental techniques and pinpointed this electron movement with electron spin resonance (ESR) spectroscopy (DOI: 10.1021/ja306728p). The researchers found that the endohedral electron transfer forms ion radicals with Sc_4O_2-localized spin density. In addition, two distinct types of scandium atoms were identified within the cluster. This study sets an example of using ESR spectroscopy as an experimental tool in the studies of clusterfullerenes and advances the understanding of endohedral chemistry, which may lead to technologies that employ this specialized property in the future. **Leigh Krietsch Boerner, Ph.D.**

CHEMOSENSORS ENABLE TWO-COLOR NUCLEOSIDE POLYPHOSPHATE DETECTION IN VIVO

Nucleoside polyphosphates (NPPs), particularly adenosine triphosphate, are key indicators of cell status, serving as both cellular energy and enzyme cofactors. Researchers study NPP concentration as a marker of cellular physiology, but quantifying nucleosides in vivo is not easy. Now Itaru Hamachi and colleagues report a pair of "turn-on" fluorescent chemosensors that can report NPP concentration specifically either at the cell membrane or within mitochondria (DOI: 10.1021/ja308754g).

The team designed two xanthene-based fluorescent chemosensors in which coordination on zinc ions quenches fluorescence, but subsequent NPP binding restores it. One sensor was coupled to a long hydrophobic tail, targeting it to the plasma membrane; the other used a positively charged pyronin ring to target the mitochondria. The different emission peaks enabled simultaneous two-color imaging, and fluorescence intensity varied with NPP concentration.

When added to cells, both sensors localized to their intended cellular compartments, and fluorescence changed upon NPP perturbation. Inducing necrosis, for instance, increased extracellular [NPP], while inhibiting oxidative phosphorylation lowered mitochondrial [NPP]. Now, the authors write, the goal is to develop sensors for other cellular compartments and sensors that are more selective for individual NPPs. **Jeffrey M. Perkel**

KEY TO CHALCOGENIDE NANOCRYSTALS IS CHOICE OF PRECURSOR

To be able to control the physical properties of nanomaterials, chemists have to be able to direct their dimensionality—that is, whether they are zero-dimensional like dots, or one-dimensional like nanorods or wires. There is growing interest in two-dimensional materials, such as layered transition-metal chalcogenide (TMC) nanocrystals. These materials have exceptional optical and electrical properties thanks to their d-orbital electrons. However, good methods to synthesize these materials are unusual and tend to be incomplete or not appropriate for many TMCs.

Jinwoo Cheon and co-workers have found that choosing the right chalcogen is a key step in successful synthesis of these TMCs (DOI: 10.1021/ja3089845). They synthesized a series of 2-D early transition-metal sulfide and selenide nanocrystals that have highly ordered crystallinity and distinctly layered structures. For these group IV and V transition metal structures, they found that CS_2 works best to make the metal sulfide materials, and elemental selenium is the best choice for the selenide congeners. This work is an important first step toward finding a general method for the synthesis of TMCs and may be used to create a wide variety of these 2-D layered nanocrystals in the future. **Leigh Krietsch Boerner, Ph.D.**

ENZYME TARGETS HARD-TO-OXIDIZE CHEMICAL BONDS

To help chemists oxidize and further functionalize certain carbon—hydrogen bonds in complex organic molecules, researchers led by Rudi Fasan have developed a strategy to evolve enzymes capable of adding hydroxyl groups at unreactive sites in the antimalarial drug artemisinin with high yield and regio- and stereoselectivity (DOI: 10.1021/ja3073462).

When chemists want to convert a molecule's C—H bonds into other chemical groups, they often turn to small organometallic catalysts that usually target the molecule's most reactive C—H bond. To target less reactive bonds, enzymes may be used; however, generating enzymes that target pre-defined C—H bonds with high site-selectivity is a very challenging and time-consuming process.

Fasan and his colleagues developed a faster, three-step approach to generate P450 enzymes that oxidize certain C—H bonds in artemisinin, replacing a hydrogen with a hydroxyl group. They narrowed a library of more than 100,000 P450 mutants using experiments and computations to identify three enzymes that selectively oxidized artemisinin at three distinct C—H sites. Medicinal chemists are interested in adding hydroxyl groups at specified positions so they can eventually convert them into other functional groups, such as fluorine

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substituents, to improve a drug's effectiveness.
Erika Gebel, Ph.D., *C&EN*

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