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Spotlights

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Spotlights on Recent *JACS* Publications

PROBING BIMETALLIC BONDS OF FIRST-ROW TRANSITION METALS

Clusters of metals are often found in biological systems, and they play key roles in hydrogenases, nitrogenases, and carbon monoxide (CO) dehydrogenases, among others. One class of enzymes, Ic ribonucleotide reductases (RNRs), has evolved to use two different metals, iron and manganese, to catalyze the reduction of ribonucleotides to dexoynucleotides, which are the building blocks of DNA. However, scientists do not fully understand the roles of these two different metals—or other first-row transition metals—in this type of reaction.

Connie Lu, Eckhard Bill, Laura Gagliardi, and co-workers have studied this problem by synthesizing both homo- and heterometallic pairs of the first-row transition elements cobalt, manganese, and iron complexed with the multidentate ligand, *N,N,N*-tris(2-(2-pyridylamino)ethyl)amine (py_3tren) (DOI: 10.1021/ja409016w). The researchers find that, except for the iron−iron complex, the interactions between the metals are fairly weak. Further studies using density functional theory reveal that only the diiron compound has delocalized metal−metal bonding.

This study may help shed light on the chemical behavior of common metal-containing enzymes. In turn, this information can help scientists understand the function and mechanism of these enzymes within complex biochemical systems, such as the RNR-catalyzed formation of deoxyribonucleotides (used in DNA) from ribonucleotides (used in RNA).

Leigh Krietsch Boerner, Ph.D.

SEEING BEYOND THE SURFACE

Attaching biological receptors such as peptides and proteins to electrodes might make possible new biosensors. Many methods exist for studying structures in solution, yet most are not sensitive enough or do not provide enough detail to be useful for complex biological molecules on the inorganic surfaces of sensors.

One method, two-dimensional infrared (2D IR) spectroscopy, worked until now only when the structures were in solution. Now, a team led by Martin T. Zanni demonstrates that combining 2D IR spectroscopy with a surface sensitive spectroscopy called sum-frequency generation (SFG) spectroscopy can help characterize peptides and proteins on a surface (DOI: 10.1021/ja408682s).

By incorporating a series of shaped infrared pulses into the SFG spectrometer, the team is able to study the peptide structure by the way that it vibrates. They learn that the peptide stands perpendicular to the electrode surface and retains its in-solution helical shape, but has a disordered end, which is a feature that would not have been observed with standard SFG spectroscopy.

Lucas Laursen

OLEFINS' NEW GAME: REDUCTIVE COUPLING

Olefins are versatile building blocks for carbon−carbon bond formation, with particular significance in natural product synthesis and drug development. For example, as hidden radical donors, unactivated olefins can be coupled to carbon or heteroatom acceptors under reductive conditions, which can potentially be adapted for direct coupling between olefins.

Based on this premise, Julian Lo, Yuki Yabe, and Phil Baran have developed an Fe(III)-catalyzed reductive coupling reaction between unactivated and electron-deficient olefins (DOI: 10.1021/ja4117632). This reaction allows access to hindered bicyclic systems with adjacent quaternary centers—even including bicyclic cyclopropanes—in intramolecular settings, as well as to a wide variety of intermolecularly coupled compounds.

Using an inexpensive catalytic reductive system, this transformation proceeds quickly with excellent resistance to air and moisture, and it is feasible on gram scale. In addition to its practicality, it provides an easy approach to structural features that are otherwise challenging or impossible to construct, especially in terpene synthesis.

Xin Su, Ph.D.

PRINTING SCIENTIFIC INSTRUMENTS ON DEMAND

Three-dimensional (3D) printing creates solid objects by adding layer upon layer of material with a robotic printer. The method is quietly revolutionizing a variety of scientific and medical enterprises, and now the approach has proven itself in a new arena. Researchers led by Eduard Chekmenev have generated a 3D-printed device that can hyperpolarize xenon, which boosts signals—and can thereby improve diagnostic medical tests—in magnetic resonance imaging (MRI) (DOI: 10.1021/ja412093d).

The hyperpolarization of xenon gas typically requires a variety of components, including a polarized laser source, a static magnetic field, and a variable-temperature optical-pumping cell. Cobbling together these components presents a challenge, as they must be properly aligned for optimal performance. In this study, the researchers seamlessly integrate the components by using a 3D printer to build the hyperpolarization device, a process that ends up being faster and cheaper than conventional approaches.

In one test run, the researchers achieve a 129Xe nuclear spin polarization of nearly 75%, a record under the chosen experimental conditions. In addition, they successfully generate a low-field MRI image of the xenon gas after transferring it from the hyperpolarization device, demonstrating the method's applicability. Beyond hyperpolarization, the on-demand 3D printing approach may be used more generally to create a wide range of scientific instruments.

Erika Gebel Berg, Ph.D.

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