

Spotlights on Recent JACS Publications

■ A MOVE TOWARD FUNCTIONAL DEVICES VIA CONTACT ENGINEERING

One of the biggest challenges when it comes to creating electronic devices with single-molecule junctions is determining how to properly wire the molecular junction into an electrical circuit. Typically, an atom or chemical moiety, known as an anchoring point, is added to the molecule to serve as the contact point with the adjoining metal. The properties of this metal–molecule contact can greatly influence both the mechanical stability and the electrical conductance of the resulting circuit, so it is important that it be engineered well.

A new study by Manabu Kiguchi, Kazunori Sugiyasu, Hisao Nakamura, and co-workers investigates the possibility of dynamically controlling the anchoring site of a single-molecule junction (DOI: 10.1021/ja413104g). Their findings suggest it may be possible to switch the anchoring point in a single molecule, and thus switch between various conductance states, without changing either the binding modes or the chemical structure of the contact point.

The team creates a molecular wire junction based on quaterthiophene (QT), a π -conjugated molecule, since previous studies suggest that a metal– π contact point could lead to greater electronic coupling than those created by standard molecular junctions. Additional work is needed to determine if QT-based molecular wire junctions can be successfully incorporated into functional electronic devices.

Christine Herman, Ph.D.

■ UPCYCLING CO₂

Right now, researchers, government leaders, and businesses are working to decrease carbon dioxide in the air and oceans. Suggested approaches for carbon capture include reforestation, sprinkling iron in the ocean, and storing waste CO₂ underground. Perhaps one of the most appealing strategies is to use the CO₂ to produce something else of value.

Once captured, CO₂ can be converted into formate or formic acid, carbon monoxide, or hydrocarbons. Formate and its acid are used in livestock feed, rubber production, hydrogen storage, and some fuel cells. Unfortunately, such conversion strategies are currently underutilized, in part, because of a lack of robust, efficient, environmentally friendly catalysts.

Thomas Meyer and his team show that carbon nanotubes doped with nitrogen and coated with an absorbent polymer layer work well to ease the CO₂-to-formate transition (DOI: 10.1021/ja5031529). Most previous studies on CO₂ reduction catalysis have focused on noble metals, but these materials can be expensive and can come with their own environmental costs. The researchers find that their metal-free electrodes perform on par with the best known metal-based electrocatalysts, and benefit from straightforward fabrication and inexpensive carbon-based materials.

Jenny Morber, Ph.D.

■ A SURPRISING ENCOUNTER WITH PHENOLS

Widely represented in natural products, the phenol functional group is also extensively used in organic and pharmaceutical syntheses. The highly reactive hydroxyl group enables easy O-functionalization of phenols, but the same group also confers limitations on direct activation of C–H bonds. Therefore, C-functionalization of phenols generally requires the installation of protective directing groups.

By taking advantage of the unique carbophilicity of gold, researchers led by Lu Liu and Junliang Zhang discover that α -aryl α -diazoacetates and diazooxindoles can be exclusively coupled to the aromatic ring of unprotected phenols with high regioselectivity in the presence of an organophosphite-based gold catalyst (DOI: 10.1021/ja503163k). The key step presumably involves the electrophilic addition of gold–carbene species to phenolic substrates.

As an unprecedented accomplishment in direct C–H activation of phenols, this new strategy successfully addresses the competing O–H insertion reaction. Moreover, its versatility, along with its robustness and the ease of scale-up to at least gram scale, makes it a promising synthetic tool for natural products and pharmaceuticals, especially in late-stage modification.

Xin Su, Ph.D.

■ COLD, SLOW SPECTROSCOPY IDENTIFIES STRUCTURES OF METAL OXIDE CLUSTERS

Titanium and zirconium oxides are widely used in pigments, ceramics, and catalysis, as well as other commercial and industrial applications. The reactivities of these materials in bulk are well understood, but the way in which point defects in the materials can be important, catalytically active sites is less clear. Transition metal oxide clusters may serve as models for such defects, and Daniel Neumark and co-workers now report the first high-resolution photoelectron spectra of stable gas-phase oxide isomers of anionic polynuclear transition metal oxides (DOI: 10.1021/ja502713v).

The researchers use slow electron velocity-map imaging (SEVI) spectroscopy, a supercooled variant of conventional anion photoelectron spectroscopy, to probe the structure of clusters Ti₂O₄ and Zr₂O₄. The SEVI technique yields a high-resolution map of the electronic and vibrational energy levels of the gas-phase clusters. By comparing the experimental spectra with simulations, the authors identify the C_{2v} and C_{3v} isomers as the ground states of Ti₂O₄ and Zr₂O₄ anions, respectively.

SEVI “allows for vibrational resolution of many more systems, resulting in more conclusive assignments of structures, energies, and vibrational frequencies,” the authors conclude. Additionally, this understanding of gas-phase metal oxide clusters may translate to explain how point defects in bulk materials function catalytically.

Hui Jin, Ph.D.

Published: May 21, 2014

■ CATALASE–PEROXIDASE REACTION MECHANISM DECIPHERED

When it comes to enzymes and hydrogen peroxide, there are catalases and peroxidases. The former degrade hydrogen peroxide; the latter use it to oxidize other molecules. The heme-containing catalase–peroxidases (KatG's) perform both activities, but as the enzymes' active sites tend to resemble peroxidases (which have poor catalase activity), it has never been clear how they work. Now Carme Rovira, Ignacio Fita, and colleagues describe a reaction mechanism that resolves this mystery (DOI: 10.1021/ja502794e).

Traditional catalases degrade hydrogen peroxide via a mechanism involving a heme group and proton transfer from a key histidine residue. Such transfer is not possible in KatG's, as their only active-site histidine has a different orientation. However, they do have a methionine–tryptophan–tyrosine (MWY) “covalent adduct” near the heme ring, as well as a critical arginine residue that alternates between “in” and “out” orientations. Using quantum mechanical/molecular mechanics calculations and X-ray crystallography of the active site, the authors propose an eight-step mechanism in which the MWY complex and mobile arginine act as an “electronic switch” that drives conversion of hydrogen peroxide to water and oxygen.

“The mechanism presented provides a consistent interpretation for all the relevant experimental and computational results available for the catalytic activity of KatG's,” the authors write.

Jeffrey M. Perkel