JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Spotlights
pubs.acs.org/JACS

Spotlights on Recent *JACS* Publications

METAL−METAL COOPERATIVITY REVIVES CATALYTIC PHOTOCHEMICAL C−H BORYLATION

Organoboron compounds are important reagents in organic synthesis. Current strategies for the synthesis of organoboron compounds usually involve C−H borylation utilizing noble metal catalysts that are toxic and expensive. Many efforts have been made recently to develop to nontoxic and inexpensive catalysts from more abundant base metals. However, catalytically viable two-electron redox processes are generally unavailable in base metal chemistry.

Neal Mankad and Thomas Mazzacano have now achieved great success in the photochemical C−H borylation of arenes, using Cu−Fe and Zn−Fe heterobimetallic catalysts (DOI: 10.1021/ja408861p).

Inspired by a previously reported stoichiometric C−H borylation with a single-site boryliron complex, the authors exploit the metal−metal cooperativity between Cu/Zn and Fe to achieve catalytic turnover, where two-electron oxidative addition and reductive elimination are made possible. Utilizing light as the energy source, this new method eradicates the need for noble metals, and opens new avenues for efficient and low-cost borylation.

Xin Su

A MAGNETIC EYE SPIES THE PROTEIN ELECTRIC FIELDS

Many of the most important phenomena in biology, such as catalysis and the binding of drugs to their targets, are influenced by the charged parts of molecules. Scientists use computational models to determine how the protein structures impact the electrostatic forces and energies within proteins. One input into these calculations is the protein dielectric constant—a measure of how proteins behave in an electric field—but researchers still debate what this value of this constant should be. Now, Jens Erik Nielsen and colleagues determine dielectric constants of proteins by measuring their electric fields with nuclear magnetic resonance spectroscopy (DOI: 10.1021/ja406995j).

To broadly characterize protein electric fields, the researchers measure chemical shifts from the hydrogen and nitrogen atoms of backbone amides in 14 proteins at varying pH values. The chemical shifts are sensitive to pH, and the researchers can use the magnitude of these chemical shift perturbations to calculate protein electric fields. Next, they plug a range of dielectric constants into two computational models that calculate electric fields in an attempt to reproduce the experimental electric fields. They identify optimal protein dielectric constants for each model, offering new opportunities to study how a protein's electrostatic properties determine its function.

Erika Gebel Berg, Ph.D.

EXCITON FISSION JUST GOT COOLER

In a textbook solar cell diagram, light hits a material, energizes an electron, and frees the electron to do its work. It sounds simple, but the process is fraught with inefficiencies. Sometimes the photon does not have enough energy to get an electron moving. Sometimes it has too much, and the excess energy is wasted.

In materials that undergo singlet electron fission, high-energy photons instead create two bound electron−hole pairs that travel through the material. This event essentially doubles the photocurrent and can boost the efficiency of a red-absorbing solar cell, which is why researchers have recently regained interest in a phenomenon originally studied in the 1960s.

Previous indirect measurements seemed to show that the process was thermally activated, but recent results have called this into question. Here, Mark Wilson, Richard Friend, and their team observe the process directly and find that singlet electron fission is temperature independent (DOI: 10.1021/ja408854u). This result contradicts the generally accepted mechanism, and emphasizes the need for careful exciton management in emerging fission-enhanced solar devices.

Jenny Morber, Ph.D.

CARBON AND GOLD MAKE VALUABLE BONDS

Research literature is awash with papers that examine the fruitful relationships between gold clusters and dangling molecules of phosphine or thiolate (phosphorus or sulfur)—and for good reason: these molecules have allowed researchers to modify gold particles and films for incredible new uses in medicine, electronics, and catalysis, to name a few.

Katsuaki Konishi and colleagues add another tool to the box—gold coordinated with triple-bonded carbon (DOI: 10.1021/ja4099092). The researchers find that when triple carbon bonds connect gold on one side, and benzene rings with a bit of nitrogen on the other, interesting optical properties result. Exposure to proton-laden acid causes the modified gold clusters to absorb and emit higher-wavelength light. Interestingly, the effect is completely reversible, which suggests that the clusters may work well as pH indicators.

The researchers show that the optical effects are likely due to a kind of electron resonance in which the center of the oval-shaped gold cluster is strongly affected by the molecules attached to its ends. Perhaps with a little engineering, these molecular modifiers could become a new class of functional gold accessory.

Jenny Morber, Ph.D.

Published: November 20, 2013