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

Spotlights on Recent *JACS* Publications

RARE LIGAND-BASED RADICAL PALLADIUM COMPLEX CAPTURED

Redox-active ligands are useful compounds in catalysis, bond activation, and other metalloenzymatic transformations where they donate electrons to metal centers to which they are attached. However, ligands that can activate the substrate while leaving the metal unaffected are rare. This type of transformation could allow selective substrate activation through a controlled radical-type mechanism, combined with favorable metal−substrate coordination.

Now Jarl Ivar van der Vlugt and colleagues have synthesized such a ligand, and they present ligand-to-substrate single-electron transfer without metal redox changes (DOI: 10.1021/ja502164f). The ligand binds with palladium(II) to form a paramagnetic complex that bears a ligand-centered radical, as evidenced by both experimental and computational data. Once reduced, the complex creates a diamagnetic Pd−Co complex that can bind an organic azide. Activation by ligand-induced electron transfer leads to H-atom abstraction and cyclization of the resulting Pd-bound radical to produce pyrrolidine.

The reaction is rare in that it goes through a radical-type pathway with a metal that ordinarily goes through two-electron processes, and it also proceeds very cleanly. "This concept is likely more broadly applicable with group 8−10 metals, including for cooperative bond activation processes and catalysis," the authors say.

Leigh Krietsch Boerner, Ph.D.

NEW PIPET DISPENSES SINGLE CELLS

Though most biological studies average the properties of thousands or millions of cells, single-cell studies are becoming increasingly common. Researchers have several options for single-cell isolation, including fluorescence-activated cell sorting and micromanipulation. Now Lidong Qin and colleagues describe a simpler approach: a hand-held single-cell pipet (hSCP) (DOI: 10.1021/ja5053279).

The hSCP resembles a typical laboratory micropipet but with two knobs to control positive and negative pressure. The pipet tip comprises a two-channel microfluidic circuit built of polydimethylsiloxane, one channel of which sports a cell-sized hook. The tip is dipped into a cell suspension and negative pressure applied, causing cells to enter the main channel, where one is captured (or other defined numbers: the authors demonstrate tips with up to 10 hooks). After a wash step, the cell is ejected into a ~350 nL droplet and dispensed. The total procedure time is ~10 s.

A multiplexed integrated single-cell pipet (iSCP) is also described. A polymeric disk containing 50 cell-isolation circuits, the iSCP allows users to image and culture cells prior to releasing them, a feature the authors use to record the membrane protrusion lengths of 50 captured cells.

Jeffrey M. Perkel

NANO GUITAR PICK IS NEW SHAPE ON THE BLOCK

There are nanorods and nanopods, nanowires and nanospirals, and after over a decade of work and an explosion of interest, you might think that there are no new nano-sized shapes left to be discovered. But Choon Hwee Bernard Ng and Wai Yip Fan now add to the toolbox a tiny Reuleaux triangle (DOI: 10.1021/ja506625y).

Guitar picks are a familiar example of planar Reuleaux triangles. Here, the researchers create a rounded, 3D version out of basic bismuth nitrates, which are used today to kill bacteria that cause stomach ulcers. The Reuleaux triangle as a material crystal is very unusual: the shape has never been observed in nature. Knowing that, in the world of nano, function often follows form, these materials may display unique and useful properties.

The authors describe a non-classical mechanism to explain how the structures grow, which may help other researchers to make their own strange new materials or to understand how materials grow in other, similar systems. Furthermore, the preparation method is simple and reproducible, gives high yields, and makes single-crystal particles of similar size.

Jenny Morber, Ph.D.

NEW INFO ON HOW PEROVSKITE SOLAR CELLS WORK MAY SHIFT PARADIGM

Research into lead halide perovskite solar cells has become widespread in the past few years because the materials are highly efficient, cheap, and very flexible. They were originally developed from sensitized solar cells, but scientists now think that the working principle of perovskite cells may be different from that of the parent solar cells. So far, researchers have used the so-called exciton model to describe the behavior of photogenerated electrons and holes in these materials. New research by Yasuhiro Yamada, Yoshihiko Kanemitsu, and coworkers shows that these cells work by radiative recombination of free electrons and holes, and not by the exciton model as previously thought (DOI: 10.1021/ja506624n).

The researchers examine the photocarrier recombination and relaxation dynamics of $CH_3NH_3PbI_3$ perovskite thin films using time-resolved photoluminescence and transient absorption spectroscopy. They find that the perovskite semiconductors are unlike organic semiconductors for solar cells, whose recombination dynamics are typically controlled by excitons. Instead, the researchers discover that the radiative recombination rate of their lead halide materials was more like that of classic direct-gap semiconductors often used in optoelectronic devices. These findings provide great insight into how these devices work at the fundamental level and may lead to more efficient solar cells and halide perovskite semiconductors in the future.

Leigh Krietsch Boerner, Ph.D.

Published: August 20, 2014