JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Spotlights

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# Spotlights on Recent *JACS* Publications

## SUCCESS AT THE SURFACE: ETHANOL PRODUCTION VIA COPPER CATALYSIS

Ethanol, an important commercial product, is primarily produced by the fermentation of crops such as sugar cane, potatoes, and corn. Conversion of biomass to ethanol has gained popularity recently; however, there is still a long way to go before the technique is anywhere near being commercially viable. An alternative way to produce ethanol is using a mixture of carbon monoxide and hydrogen called synthesis gas, or syngas. But the catalysis of this reaction is sluggish and low-yielding.

Xinbin Ma and co-workers have found a way to speed up the process and increase the production of ethanol from syngas by using a copper/silica catalyst (DOI: 10.1021/ja3034153). Two surface copper species, Cu(0) and Cu(I), are found essential for the high reactivity of the catalyst, but Cu(0) is the main player in the reaction. Additionally, ethanol or ethylene glycol can be selectively synthesized by simply changing the reaction temperature. This use of inexpensive copper-based catalysts under mild reaction conditions has potential to make more sustainable production of ethanol a commercial reality. **Leigh Krietsch Boerner, Ph.D.**

## INTERNAL ACID COULD STRENGTHEN A SQUASHED POLYMER

Damaged polymers may be mended using heat or light. Alternatively, "healing agents"—reactive molecules stored in microcapsules—can be dispersed throughout the material to provide self-repairing function. When the material breaks or cracks, these capsules split open, mix, and solidify, thereby rebonding the cracks. One application is that unseen cracks in bridge beams coated with self-healing paints could be fixed without the need for a worker to first find the damage during an inspection.

Jeffrey Moore and co-workers have designed a polymer that would release an acid when the material is compressed (DOI: 10.1021/ja305645x). Toward new self-healing capabilities, the acid could catalyze a reaction that connects more polymer strands at the damaged site, potentially reinforcing the weakened material. The acid comes from a specially designed molecule used as a cross-linker in the polymer chain. This so-called mechanophore contains a strained three-membered ring—a cyclopropane with two chlorine atoms at its tip. Squashing the polymer strains and then opens the ring, releasing protons that could initiate the formation of additional covalent cross-linkages.

This new molecule extends the ways scientists can build self-healing materials. The researchers say the next step will be to streamline the mechanophore's synthesis and increase its stability before it is ready for practical applications. **Melissae Fellet**

## TWEEZING UNDERSTANDING OUT OF CHIRAL CONVERSIONS

Over 150 years ago, Louis Pasteur used tweezers to isolate grains of two mirror-image crystal forms. Even today, separating molecules by chirality can be incredibly difficult. Homochirality—when units of a molecule have the same chirality or handedness—is something that biological molecules such as amino acids and sugars require to function correctly. Homochirality is also an important characteristic of drug function, such as in the anticoagulant Plavix.

A new method to convert molecules of one handedness to the other by a process called attrition-enhanced deracemization has recently been reported, but the mechanism behind this process remains a subject of much debate. Donna Blackmond and co-workers have examined this phenomenon and come away with an improved understanding of how it works (DOI: 10.1021/ja303566g). The scientists unravel some of the physical and chemical processes that make it possible to convert molecules of one handedness to the other. They demonstrate that the process may be explained simply by the effect of crystal size on solubility of the enantiomers. Isotopic labeling helps determine each atom's origin and final destination when the molecules change from one chirality to the other.

The work provides new insights into the separation of chiral mixtures for the biopharmaceutical industry and gives a possible peek at the evolution of biological homochirality. **Leigh Krietsch Boerner, Ph.D.**

## TOWARD SPLITTING WATER ON A WIRE

Using the sun to split water into oxygen and hydrogen, which could be used for fuel, remains elusive. However, a new study by Dunwei Wang and co-workers brings this goal tantalizingly closer by crafting silicon nanowires coated with hematite ($\alpha$-$Fe_2O_3$) that work synergistically to collect photons from different areas of the solar spectrum for conversion into electricity (DOI: 10.1021/ja3051734).

Such sun-powered water splitting, also known as photoelectrochemical (PEC) water splitting, would be an efficient way to collect solar energy and use it in the form of hydrogen fuel. The choice of the photoelectrode—the component that collects solar energy and converts it into electricity—is especially important because it determines the water-splitting device's performance over time. The ideal photoelectrode would absorb light broadly, be inexpensive, and resist photocorrosion. Hematite fits some of these characteristics, but alone, it does not perform well enough for consideration.

To improve hematite's performance, the researchers grow crystals of this iron oxide on silicon nanowires, a material that absorbs light that is transparent to hematite. Together, the two materials absorb light from a much larger portion of the solar spectrum and efficiently convert that energy into electricity. The fact that the photoelectrode's active materials are

**Published:** August 15, 2012

"primarily composed of three of the four most abundant elements in Earth's crust (O, Si, and Fe) offers promise that renewable energy harvesting by PEC water splitting remains an achievable goal", the authors conclude. **Christen Brownlee**

## ■ ZIGZAGGING TOWARD THE ELUSIVE ZIGZAG CARBON NANOTUBE

Single-walled carbon nanotubes (SWNTs) come in three types—helical, armchair, and zigzag—named for their differing placement of fused hexagonal carbon rings. While synthetic methods have been able to reproduce the individual bands of joined carbon rings that make up helical and armchair SWNTs, zigzag nanotube synthesis has not yet been accomplished. In a current study, Hiroyuki Isobe and co-workers synthesize zigzag carbon nanotubes by taking a new approach (DOI: 10.1021/ja305723j).

Most previous synthetic attempts have focused on making cyclacene, a belt-shaped molecule composed of aligned carbon rings that typify the unit structure of a zigzag SWNT. However, the cyclacene molecule continues to elude synthesis. Researchers in the new study instead use chrysene, a molecule composed of four fused benzene rings, as their starting material. A series of reactions leads to cycloarylenes, belts of carbon rings with the desired zigzag structure, confirmed by nuclear magnetic resonance, high-performance liquid chromatography, and X-ray crystallography analyses. The authors conclude that this finding completes the trio of synthesized basic bands for each SWNT type. **Christen Brownlee**

## ■ SAFER MEERWEIN ARYLATIONS GO WITH THE FLOW

Monoarylated acetaldehydes may serve as building blocks for some pharmaceutically important molecules and natural products. Unfortunately these precursor molecules cannot be constructed via palladium-catalyzed arylation of acetaldehyde due to their sensitivity toward basic reaction conditions. The Meerwein arylation allows these compounds to be made in one step under relatively mild reaction conditions. This long-established radical reaction uses inexpensive and readily available anilines as the aryl group donors; however, this process has not found wide application due to the use of highly reactive aryldiazonium salts, which raises significant safety concerns, particularly at large scales.

Stephen Buchwald and Natalia Chernyak address the issue of safety by developing a continuous-flow version of this process (DOI: 10.1021/ja305660a). The aryldiazonium salt is prepared from the corresponding aniline in one reactor, followed by the ferrocene-catalyzed Meerwein arylation in a second reactor. The use of relatively mild conditions and low temperature allows for this reaction to proceed with wide functional group compatibility.

To demonstrate the utility of products, unpurified monoarylated acetaldehydes were transformed into common pharmaceutical skeletons, like indoles, benzofurans, and $\beta$-phenethylamines. Overall, the method allows for the efficient generation and handling of unstable aryldiazonium salts that should be adaptable to the large-scale synthesis of arylacetaldehydes and other pharmaceutically important molecules. Chemists who once avoided the Meerwein arylation may add the reaction back to their toolboxes. **Melissae Fellet**