

Spotlights on Recent JACS Publications

■ SAFER, EASIER HYDROGENATION

Catherine Cazin and co-workers have isolated and characterized a hydridoformatopalladium complex that can perform a catalytic hydrogenation reaction using stable and readily available formic acid as a hydrogen source (DOI: 10.1021/ja311087c).

Hydrogenation is one of the most commercially important chemical reactions currently used, with applications ranging from the transformation of liquid fats into solid spreads and shortenings to the liquefying of fuels. The hydrogen source most commonly used is H₂, which is both highly flammable and difficult to control under common reaction conditions. The mechanism of the alternative formic acid-mediated reaction is unclear, but the reaction is thought to go through a hydridoformatopalladium species.

Through NMR and X-ray diffraction, the researchers study palladium tricyclohexylphosphine N-heterocyclic carbene complexes, and they find that the catalysts play two important roles in the hydrogenation reaction. Both complexes dehydrogenate the formic acid to produce hydrogen *in situ*, and subsequently facilitate the reduction of double and triple C–C bonds. Cazin and co-workers also verify the mechanism through computational analysis, discovering that the reaction is stereo- and chemoselective for transformation of internal alkynes to *Z* alkenes. This mild reaction may make industrial hydrogenations easier, and lead to cheaper consumer goods in the long term. **Leigh Krietsch Boerner, Ph.D.**

■ RESEARCHERS CREATE MAGNETIC SUPERATOMS

Kit H. Bowen, Shiv N. Khanna, and colleagues provide evidence that magnetic superatoms exist and are more than just an enticing idea (DOI: 10.1021/ja400830z). The authors had previously predicted the existence of magnetic superatoms, but until now, no one knew how to create them, much less how to measure their magnetic moments.

The periodic table of elements helps to classify and describe the unique electronic and chemical behavior of atoms. Recently, researchers have found that stable clusters of metal atoms can form electron configurations that resemble atomic electron clouds. These so-called “superatoms” can mimic the behavior of elements.

The researchers ionize pure sodium and vanadium under vacuum to create bimetallic clusters. To get around the experimental limitations of measuring such small magnetic moments, the researchers use an indirect method that combines photoelectron spectroscopy and first-principles calculations. In experiments, neutral and anionic VNa₈ clusters demonstrate behaviors that match predictive calculations for magnetic superatoms. That is, the electron cloud around VNa₈ clusters mimics those of magnetic elements. The work opens the door for others to synthesize and study magnetic superatoms, and for potential applications that include multifunctional electronic devices and high-density digital memory. **Jenny Morber, Ph.D.**

■ DESIGNING A FLY SWATTER FOR CANCER CELLS

Chemotherapy has been compared to killing flies with a cannonball. Now Chulhun Kang, Jong Seung Kim, and their colleagues have designed and synthesized a so-called theranostic drug that could both target cancer cells directly and allow researchers to monitor uptake to assess optimal dosage (DOI: 10.1021/ja401350x). Theranostics anticancer drugs have the potential to increase the efficiency of chemotherapy and to allow dosages to be tailored to individual cancer patients.

Here, the researchers link the chemotherapeutic compound gemcitabine with biotin—a small molecule that targets many types of cancer cells—and the fluorescent reporter coumarin. The resulting conjugate specifically targets cancer cells with biotin receptors, the team finds. When the conjugate enters the cell, naturally present thiols cleave a disulfide bond between the drug and coumarin, serving the dual purpose of delivering the active form of the drug and increasing the fluorescence of coumarin.

This discovery could lead to personalized medicine that combines the targeted delivery of anticancer drugs with sensitive and noninvasive monitoring of their uptake. **Deirdre Lockwood**

■ STIMULUS-RESPONSIVE HYDROGELS TAKE SHAPE ON CUE

Inspired by the ability of plants to change shape in response to cues from their environment, researchers led by Eugenia Kumacheva present a new class of soft, stimulus-responsive biomaterials, which hold promise for the fields of tissue engineering, robotics, and biosensing (DOI: 10.1021/ja400518c).

The research team prepares the thin hydrogel sheets from multiple different polymers that respond to external cues, such as heat, acidity, and ionic strength, by swelling or shrinking. The researchers use light to cross-link the polymers within the planar hydrogel sheets in patterns such that the shrinking and swelling events cause them to transform into unique three-dimensional conformations. Currently, a single hydrogel sheet may contain up to three distinct polymers, each of which responds exclusively and reversibly to its cue, enabling the material to take on multiple shapes in response to different stimuli.

While previous reports have demonstrated self-shaping materials capable of taking on two stable shapes in the presence or absence of a single cue, this new approach enables the creation of a single material capable of undergoing multiple shape transformations in response to multiple different cues, adapting to its environment in a way that mimics nature. **Christine Herman, Ph.D.**

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