

Spotlights on Recent JACS Publications

■ CHIRAL ORGANOBORANES FROM B–H INSERTION BY CARBENES

Organoboron compounds are among the most widely used synthetic intermediates because their unique reactivity enables access to a broad range of functional groups as well as carbon backbone extension. While chiral organoboranes are ideal reaction partners in stereoselective synthesis, their application has been hindered by the lack of convenient preparation strategies.

In an extension of the well-established catalytic system for asymmetric C–C bond formation, Ming-Hua Xu and co-workers now use Rh(I)–carbenes with chiral olefin ligands to enantioselectively construct C–B bonds (DOI: 10.1021/jacs.5b00892). In the presence of a bicyclodiene ligand with C_1 symmetry, the researchers are able to transform a variety of α -diazoesters and ketones into corresponding α -boryl products in high chemical and stereochemical yields under exceptionally mild conditions.

This new method is practical and cost-effective, as it uses easily prepared ligands and readily available boryl sources. The successful adaptation of Rh(I)–carbene intermediates in asymmetric C–B bond formation showcases their versatility as synthetic tools, which also further expands the scope of metal–carbene insertion in constructing chiral carbon–heteroatom bonds.

Xin Su, Ph.D.

■ CONNECTING MOLECULAR DOTS BY VISUALIZING HIDDEN *J*-COUPLINGS

Nuclear magnetic resonance spectroscopy is one of only a few methods that can solve the structure of molecules, a critical aspect of understanding molecular function. A key NMR measurement is the *J*-coupling, which describes through-bond interactions between adjacent nuclei and provides information on bond distances, bond angles, and the connectivity between atoms. However, in many cases, NMR spectra are complex and overlapped, leading some *J*-couplings between nuclei to get lost in an NMR peak's line width.

To amplify the *J*-coupling for easier measurement, Simon Glanzer and Klaus Zangger have developed a new NMR method, called real-time *J*-upscaling, that stretches the recorded coupling patterns and minimizes inhomogeneities in the magnetic field that can cause signal broadening (DOI: 10.1021/jacs.5b01687). The result is spectra with improved resolution that display previously hidden *J*-couplings.

The researchers test *J*-upscaling on a variety of molecules, including propanol, cholic acid, and azithromycin, in both 1-D and 2-D NMR experiments. They tune the degree of upscaling, allowing for the visualization of elaborate coupled multiplets as well as smaller *J*-couplings. The approach also provides *J*-coupling constants in experiments with only limited acquisition time, such as the common HSQC experiment, a workhorse of structure determination.

Erika Gebel Berg, Ph.D.

■ CARGO-CARRYING NANOPARTICLE REALLY GETS AROUND

In recent decades, interest in both self-propelled nanomotors and cargo-carrying mesoporous silica nanoparticles (MSNPs) has grown. In a new study, Samuel Sanchez and co-workers bring together these disparate areas by developing Janus nanomotors with a MSNP base capable of transporting and releasing cargo (DOI: 10.1021/jacs.5b02700).

Janus nanoparticles are named after a Roman god with two faces, and those reported here are created by coating half of a spherical MSNP with a thin platinum layer. When placed into hydrogen peroxide, this platinum surface catalyzes a reaction that triggers the decomposition of H_2O_2 into O_2 and H_2O , propelling the particles by forming an asymmetric chemical gradient. Tests show that this self-propulsion can move the particles from one reservoir to another on a microchip through a channel with a width of 100 μm . Additionally, because the pores on the other side of the particles are left exposed, they can be filled with a variety of cargo.

As proof of principle, the researchers load the particles' pores with the dyes Rhodamine B and methylene blue. Experiments show that these dyes are continuously released over the next several hours. These experiments suggest that Janus nanomotors with a MSNP base could serve as vehicles for directed delivery of drugs and other agents.

Christen Brownlee

■ ORGANIC CRYSTALS GOBBLE UP NANOPARTICLES

Crystal growth has been studied for centuries, but it appears that there is still much to learn. Yang Liu, Xutang Tao, and colleagues have observed the crystallization and growth of a metal–organic compound in a solvent-free environment, with the help of optical, transmission electron, and atomic force microscopes equipped with heated stages (DOI: 10.1021/jacs.5b02637).

The researchers report a fascinating and unexpected mechanism: the metal–organic nanoparticles migrate together to form a crystalline fiber that grows by recruiting other nearby particles, orienting them, and adding them to the fiber's end. The behavior appears almost as if the crystal is “eating up” the particles around it. The nanoparticles travel distances far too long to be explained by conventional theories such as molecular diffusion, the authors attest. Because the organic portions of these nanoparticles are more molecularly complex and their bonds less stable than those of alternative non-carbon-based crystals, studying them is more challenging, and their crystallization is poorly understood.

These results demonstrate that Nature has developed a solution for crystal growth far different from the idealized models envisioned by many chemists. A richer understanding of such non-classical growth may help researchers to better engineer complex molecules such as molecular cages and pharmaceuticals.

Jenny Morber, Ph.D.

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