

Spotlights on Recent JACS Publications

■ EVAPORATION TURNS TINY BLOCKS INTO CITY SKYLINE

Who says block building is just for children? Hiroaki Imai and colleagues use rectangular nanoblocks to build tiny lines, planar arrays, and three-dimensional stacks (DOI: 10.1021/ja410183q).

The researchers disperse tiny rectangular prisms of manganese oxide in a liquid solvent and then allow the liquid to evaporate. Because capillary forces string the blocks together as the liquid dries, the researchers only need to control the concentration of the nanoblocks to determine the type of structure that forms: lower concentrations form lines and high concentrations yield 3D arrays, with 2D planes at the midpoint. While nanoblocks dispersed in low-polarity solvents such as toluene and hexane form long, linear chains, evaporation of Mn_3O_4 nanoblocks in more polar ethanol leads to 3D builds. The polarity of the solvent also influences the crystallographic orientation of the nanoblock structures.

While building with nanocubes has been reported before, control over dimension and direction has been difficult without the application of an external field. This simple method should work with a variety of materials and could help researchers to more easily control nanoblock assembly for catalysts, electrode materials, magnetic materials, and rechargeable battery components.

Jenny Morber, Ph.D.

■ A HEAT SNAPSHOT OF FORMIC ACID ADSORPTION

There are many reasons to adsorb gases onto solids and catalysts—such as removing pollutants from car emissions—but few ways of measuring the exchange of energy involved. Part of the reason for this gap is that the reactions can involve multiple steps, leaving little time to measure the energy of each step. Multistep breakdowns also prevent researchers from reversing the reactions, a crucial step in conventional measurements. For this reason, researchers developed years ago an approach called single-crystal adsorption calorimetry (SCAC), which involves firing a well-measured beam of molecules at a single-crystal solid in a high-vacuum environment and taking a quick measurement of current generated in a pyroelectric ribbon attached to the solid.

Charles Campbell and colleagues have adapted the SCAC technique to study the adsorption of formic acid on platinum, a prototype for study of carboxylates bonded to surfaces, used for many technologies (DOI: 10.1021/ja412878u). The team first develops a new analysis method to account for changes in the heat signal's duration. Using the modified method, they generate the first estimate of the energy exchange of formic acid adsorption onto platinum, paving the way for heat measurements of other metal adsorption processes.

Lucas Laursen

■ ONE-POT SYNTHESIS OF REDOX-SWITCHABLE "DAISY CHAIN" STRUCTURES

Researchers are interested in molecular switches made from molecularly interlinked molecules (MIMs) because their interconnected nature offers control over the mechanical motion of their molecular components with respect to one another. The motion exhibited by MIMs is determined both by which molecular components comprise the MIMs and by how they are linked. Typically, the components in catenanes are limited to rotations, while those in rotaxanes can both rotate and move linearly. As more intricate architectures are developed, researchers hope MIMs will be capable of even more sophisticated motions.

The redox-switchable molecular compounds created in a one-pot synthesis by a team led by J. Fraser Stoddart belong to a class of structures known as molecular "daisy chains", since they are reminiscent of garlands children construct from flowers (DOI: 10.1021/ja500675y). The structures are composed of ring and rod components typical of MIMs, except that they are directly connected by covalent bonds to form ring-rod monomers that are self-complementary. The structures exhibit radical-mediated interconversion in solution and are promising candidates for nanomechanical switches.

Christine Herman, Ph.D.

■ UNDER THE MASK OF A CATALYST

Any chemistry student can explain that a catalyst increases the rate of a chemical reaction by lowering the activation energy required for the reaction to proceed. Therefore, the uncatalyzed counterpart of a catalytic reaction is supposed to proceed at a slower rate. During the study of catalytic enantioselective alkene carbosulfonylation, however, Scott Denmark and Hyung Min Chi observe a seeming contradiction, where the stoichiometric transformation is slightly faster in the absence of the catalyst (DOI: 10.1021/ja413270h).

Combining thorough kinetic and spectroscopic analyses, the researchers establish a detailed mechanism for the catalytic cycle. They reveal that, in the presence of catalyst, the byproducts generated along with the reactive intermediate significantly suppress the uncatalyzed racemic pathway. It thus becomes clear that the enantioselectivity of the catalysis is not compromised despite its slower observed rate.

This work elegantly demonstrates that the actual background reaction in a catalytic process cannot be evaluated by simply eliminating the catalyst and is likely to draw attention to secondary effects of catalysts in a broader context.

Xin Su, Ph.D.

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