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Spotlights

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# Spotlights on Recent *JACS* Publications

## CRYSTALLINE NANOWIRES AND POLYMER MOLECULES: SEPARATED AT BIRTH?

Ultrathin crystalline nanowires, less than 10 nm thick, display an unusual set of electrical, optical, and magnetic properties that differ significantly from those of thicker nanowires and bulk materials. Also, these materials have dimensions similar to those of linear polymer molecules, and recent studies have suggested that nanowires might grow in a similar fashion to polymers. Could crystallization and polymerization—the two most common processes to create synthetic materials—blur into each other at the nanoscale?

To investigate their commonalities, Geoffrey Ozin and co-workers use ultrathin $Bi_2S_3$ nanowires, which can withstand the same rigorous tools used to probe polymer molecules (DOI: 10.1021/ja301855z). Their experiments show that $Bi_2S_3$ nanowires grow using a combination of adding crystalline units akin to monomers to the ends of the nanowires (analogous to "living" polymer growth) and coupling nanowires end-to-end (analogous to "step-growth" polymerization). The rate at which these two types of growth occur is also similar to that of the equivalent polymer growth processes. Additionally, light scattering experiments show that the size and shape of these nanowires in solution is much like those of semiflexible polymer chains.

The authors suggest that this work demonstrates a physical analogy between the crystals and polymers and provides a useful model system to continue investigating commonalities between these two classes of materials and between polymerization and crystallization. **Christen Brownlee**

## CATALOGING THE COPPER-FREE CLICK CHEMISTRY OF BARAC

Kenneth Houk, Carolyn Bertozzi, and co-workers have developed a model that allows them to predict the reactivity of cyclooctyne analogues with azides in "copper-free click chemistry" (DOI: 10.1021/ja3000936). The researchers focus on a biarylazacyclooctynone structure they call BARAC, which reacts very rapidly and is synthesized in a manner that allows straightforward preparation of analogues.

The "click" reaction between alkynes and azides has far-reaching applications in the study of biological systems since there is no interference with the biomolecules critical to life. Cyclooctynes are exceptionally useful because the strain in the 8-membered ring makes them react quickly and without the cytotoxic copper catalyst required in other click reactions. Using calculations in combination with kinetic analysis, the group analyzed the relative effects of steric and electronic modifications to the BARAC core. They found that substituents that sterically hinder the transition state contribute significantly to slowing the overall reaction rate.

The authors conclude that the experimental trends they observed and verified computationally "may be used in the informed design of cyclooctynes with tailored reactivities." One example of the way in which these new reagents could be used is in selective protein labeling for imaging experiments. **Sonja Krane, Ph.D.**

## CONJUGATED POLYCYLIC COAT KEEPS BORON FLAT

Boron-containing conjugated systems have interesting electronic properties due to their ability to act as strong electron acceptors and Lewis acids. These materials can be used for electron transport, as light-emitting organic materials, or as chemosensors for anions. To protect these materials from water or air damage, scientists stabilize the boron by covering it with bulky groups or attaching heteroatoms like nitrogen or oxygen. But both approaches disrupt the valuable electronic properties of the materials.

Shohei Saito, Kyohei Matsuo, and Shigehiro Yamaguchi build the first conjugated polycyclic system with a planar boron at its center (DOI: 10.1021/ja3036042). The molecule is stable to water, air, and silica gel, requiring no glovebox for its synthesis. It absorbs light across the visible spectrum and fluoresces in the visible to near-infrared region of the spectrum.

A solution of the molecule containing the weak Lewis base pyridine changes color when cooled, due to the favorable formation of an adduct between the pyridine and boron at lower temperature. The interesting thermochromic and electronic properties could make this material useful for optoelectronic applications that convert electricity to light. **Melissae Fellet**

## NEW PROBE CAPTURES HISTIDINE KINASE ACTIVITY

There is no shortage of research tools for serine, threonine, and tyrosine kinases, enzymes used extensively to transmit signals and control complex processes in cells. But histidine kinases (HK) are a different story, due largely to the labile phosphohistidine P—N bond. Now Erin Carlson and colleagues have rectified that problem with an "activity-based probe" for HKs (DOI: 10.1021/ja3041702).

HKs represent one part of bacterial two-component systems, in which an extracellular signal induces a phosphorylation-based two-component signaling pathway to a "response regulator" (RR) protein, such as a transcription factor. To monitor this process, Carlson's team used a fluorescent ATP analogue (B-ATP$\gamma$S). When incubated with HK in vitro, B-ATP$\gamma$S transfers its fluorescent moiety to the kinase, and this protein can then be detected as a fluorescent signal on electrophoretic gels. The fluorescent HK complex, unlike normal phosphohistidine, is stable for hours. Yet it can still pass its fluorophore to an appropriate RR, albeit in an attenuated manner, an event that can also be monitored.

The result is a generalizable method for probing HK and two-component systems and, ultimately, testing potential inhibitors. "The delayed transfer of the thiophosphate to the RR makes B-ATP$\gamma$S an excellent tool to visualize the often

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fleeting phosphorylated HK species, while at the same time still enabling the examination of their cognate RR partners," the authors write. **Jeffrey M. Perkel**

## RESEARCHERS IDENTIFY HUNDREDS OF DENSITY STEP-GRADIENT SYSTEMS

The toolbox for density-based separations just got a lot bigger, thanks to a new study led by Charles Mace and George M. Whitesides (DOI: 10.1021/ja303183z). The research team identified more than 300 aqueous phase-separated systems, most of which were not previously known, in a systematic study on self-assembling density step-gradient systems.

Researchers who need to separate complex mixtures, for applications ranging from forensics to hematology, have traditionally relied on concentration gradients that are not ideal for separations because their density profiles change over time. Unlike concentration gradients, density step-gradients, made of insoluble phases of salts, polymers, and surfactants, spontaneously re-form after agitation and can be stored for long periods of time without changes in properties and composition. Prior to this study, only a handful of two- and three-phase aqueous systems had been reported.

To ensure broad applicability, the team limited their study to commercially available and inexpensive water-soluble polymers and surfactants. The researchers also demonstrated that the aqueous phases can be tailored for unique applications by incorporating water-miscible additives, such as deuterated water and cesium bromide. Since water is the common solvent, the method is likely to be suitable for separating complex biological mixtures. **Christine Herman, Ph.D.**