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Spotlights on Recent *JACS* Publications

METAL–ORGANIC CAGES CAPTURE AND RELEASE MOLECULAR PRISONERS

There is a new tool in the chemist's toolbox for the creation of multifunctional materials that allow molecules to be captured and released in response to stimuli or over time. Researchers led by Jonathan Nitschke describe a new method for the creation of polymeric hydrogels that employ metal–organic cages to capture and release guest molecules in response to stimuli (DOI: 10.1021/jacs.5b05507).

The team creates a polymeric hydrogel capable of capturing molecules in two distinct ways: by binding them between cross-linked polymer threads or by firmly locking them away in the cavities of metal–organic cages that form cross-links between the threads. The researchers use droplet-based microfluidics to fabricate the hydrogels into microparticles and demonstrate their responsiveness to multiple stimuli for the triggered release of the molecular cargo.

Notably, the release profiles for the two modes of capture are distinct, as the loosely bound molecules can readily leach out of the gel matrix, while those held inside the molecular cages, which are formed via the metal-templated condensation of amine and aldehyde subcomponents, require a specific chemical stimulus to effect their release. "Metal–organic cage-cross-linked polymers therefore represent a platform for the development of new multifunctional materials," the authors conclude.

Christine Herman, Ph.D.

ORDER FROM CHAOS WITH BLUEPRINT FOR DNA-ASSISTED CRYSTALLIZATION

Recently, Marcus Weck, David Pine, and colleagues reported success in coaxing micrometer-sized spheres into uniform, crystalline arrangements with the help of selectively sticky DNA (http://dx.doi.org/10.1038/ncomms8253). The key was creating DNA-coated particles that could rearrange themselves and anneal like atoms in traditional, well-studied crystals. Such colloidal crystallization has been achieved before with nanoparticles, but larger spheres had proved much more challenging.

Here the researchers present a detailed blueprint for how to make these micrometer-sized DNA-coated particles (DOI: 10.1021/jacs.5b06607). The particles' chemical composition can vary—polymers, inorganic materials, and hybrids all work—but the sphere surface must be smooth and the DNA linkers must be dense. Colloids can be the same material or different, of similar size or not, and crystallization patterns can be programmed by using complementary DNA sequences.

This ability to mix and crystallize micrometer-sized particles of different materials is ideal for the fabrication of photonic crystals, which require ordered arrangements of high and low refractive index materials. Detailed studies of plasmonic and magnetic phenomena also require precisely engineered arrangements. The authors' careful and thoughtful explanations of experimental procedures make this paper a useful resource for those who seek to explore DNA-directed assembly, and the uniform arrangements of particles in the micro world.

Jenny Morber, Ph.D.

READY OR KNOT, HERE COME SYNTHETIC ANION-BINDING MOLECULES

Naturally occurring molecular knots, with mechanically interlocked architectures, have been found in both DNA and proteins. Although chemists have successfully created artificial molecular knots, previous reports have not shown any interesting or unusual chemical properties. In a new report, researchers led by David Leigh describe molecular knots and links that selectively bind anions with surprisingly strong affinities (DOI: 10.1021/jacs.5b06340).

The team has synthesized three molecules—a molecular pentafoil knot, and doubly and triply entwined [2]catenane molecules—which are all based on circular Fe(II) double helicate scaffolds. Using X-ray crystallography, the researchers find that the molecules' salts contain well-ordered anions associated with their central cavities. Solid-state and NMR analyses show the binding is facilitated by both hydrogen-bonding and long-range electrostatic interactions. One molecule exhibits an affinity of $(3.6 \pm 0.2) \times 10^{10}$ M^{-1} in acetonitrile solvent, and this unique property places it among the strongest synthetic noncovalent binders of halide anions found to date.

Christine Herman, Ph.D.

PROPER SUBSTITUENTS KEY TO CREATING ALTERNATING SEQUENCE POLYMERS

Synthetic polymers with controlled monomer sequences and microstructures are highly desirable for their ability to create high-order structures that mimic biological macromolecules possessing unique functions and properties. Established methods for synthesizing lengthy, well-defined polymers typically involve the use of solid supports and laborious protection–deprotection steps. Now, Benjamin Elling and Yan Xia report a new method for the creation of polymers with precisely alternating sequence and high microstructure regularity without these time-intensive steps (DOI: 10.1021/jacs.5b05497).

Using a technique known as living alternating ring-opening metathesis polymerization (AROMP), the researchers can combine two monomers together with a metal catalyst to create polymers with well-defined molecular weights and end groups and narrow molecular weight distribution. The polymers also have precisely alternating sequences, made possible by the use of monomer substituents that prevent homoaddition. In other words, the monomers do not react with themselves but instead take turns adding one at a time in an alternating fashion. The substituents in the judiciously designed monomers also help prevent undesirable side reactions known as secondary metatheses, which include both intermolecular chain transfer and intramolecular "backbiting". This chemistry advances our ability to control polymer sequences and microstructures in homogeneous polymerizations. Well-defined polymers such as these products could provide useful properties for a broad range of engineering applications.

Christine Herman, Ph.D.

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