

Spotlights on Recent JACS Publications

■ MULTITASKING NANOWORMS MADE EASY

Nanoworms look much like you might expect. They are tiny, soft, threadlike carbon-based structures that can move in and through an organism, evading its sentinels much more effectively than other shapes of similar materials. While nature's nanoworms are designed to infect and spread as viruses, researchers hope to use the synthetic variety for drug delivery, diagnostics, and tissue engineering. Now Michael Monteiro and his team have found a simple and versatile way to make them (DOI: 10.1021/ja500092m).

In a one-step process, the researchers exploit a temperature-driven shape change to morph functionalized nanospheres into functionalized nanoworms. A dip in the ultrasonicator breaks the worms into shorter nanorods, which do not stay in the body as long but are more palatable to cells. The whole process occurs in water, where the nanoworms can remain for months without disintegrating. Previously reported techniques require much more time and produce lower density batches. These nanoworms can support an array of linker molecules, making them a kind of multipurpose tool for biomedical applications. In experiments, the researchers have coupled four different molecular groups to the worms, and have used the linker groups to attach polymers, peptides, and fluorescent molecules. **Jenny Morber, Ph.D.**

■ "BUMP-HOLE" STRATEGY IDENTIFIES ADP-RIBOSYLATION SUBSTRATES

Seventeen human enzymes, called ARTDs, catalyze the ADP-ribosylation of protein targets in human cells. The reaction is a key component of energy metabolism, biosynthesis, and the cellular stress response, but working out which enzyme specifically targets which substrate is exceedingly complex. Now Michael Cohen and colleagues describe a strategy to simplify the problem (DOI: 10.1021/ja412897a).

Taking a page from research into non-natural amino acids, the researchers devise an artificial, orthogonal enzyme/substrate system—that is, one in which the modified substrate cannot be used by endogenous enzymes. Using a so-called "bump-hole" strategy, the team mutates a key, conserved lysine residue in the ARTD substrate-binding pocket to accept a C-5-ethyl-substituted nicotinamide adenine dinucleotide molecule, which is incompatible with wild-type ARTDs. The modified substrate also contains an alkyne group, meaning modified proteins could be biotinylated via click chemistry, isolated, and characterized using LC-MS/MS. Using that strategy, the authors identify 42 unique targets of ARTD1 and 301 for ARTD2.

"Given the difficulties in delineating the targeting specificities for this highly homologous enzyme class, our method provides a powerful new tool toward advancing our understanding of ARTD function in the cell," the authors conclude.

Jeffrey M. Perkel

■ SPACEY LATTICES HINT AT HOLES IN PACKING THEORY

Nanomaterials are not exciting to researchers just because they are small, but because their smallness causes them to behave in ways that are entirely unlike the substances we are used to. Size also can be an obstacle. How does one create a device from a material that cannot be easily handled? One method is called self-assembly, in which researchers entice nanomaterials to arrange themselves into desired patterns by providing ideal conditions.

Much work has been devoted to recipe-making for nanomaterial self-assembly, but now Dmitri Talapin and Michael Boles show that researchers still have much to learn (DOI: 10.1021/ja501596z). Though current theory is based on "dense packing"—the tendency of materials to fit themselves into the tightest possible arrangement—the team finds that their pyramid-shaped nanocrystals instead grouped themselves into low-density patterns. The authors propose that soft organic molecules within the solution line the faces of the pyramids and space them out. Interactions between these dangling molecules lead to unexpected arrangements.

The findings highlight a gap in the understanding of nanomaterial self-assembly. The authors suggest that molecular interactions such as these need to be incorporated into self-assembly theory to create a more powerful tool for materials design.

Jenny Morber, Ph.D.

■ METALLIC SWITCHEROO IN ORGANOMETALLIC MONOLAYER SHEETS

Changing up the constituents of a monolayer sheet can result in the creation of materials with unique chemical and physical properties. The process is analogous to melting another metallic component into a metal alloy, except it occurs on the nanoscale. One of the greatest challenges involves exchanging integral parts while keeping the monolayer intact.

Now, researchers led by Zhikun Zheng and A. Dieter Schlüter report the creation of organometallic monolayer sheets that are capable of swapping metals (DOI: 10.1021/ja501849y). The team demonstrates the site-to-site transmetalation can be performed either randomly or in a controlled fashion to yield predetermined patterns defined by photolithography. The latter process results in monolayer sheets that are analogous to 2D linear block copolymers.

Transmetalation modifies the sheet's internal network structure, which sets this method apart from the more common method of sheet modification and also from substitutional doping. This is the first demonstration of transmetalation at the level of single monolayer sheets, and it holds promise for applications in surface coating, molecular electronics, and nanoscale synthesis.

Christine Herman, Ph.D.

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■ A MORE EFFICIENT WAY TO THREAD A MOLECULAR MACHINE

In every cell, the ribosome is responsible for stringing together amino acids in a predetermined order to create proteins—this process is the foundation of life as we know it. Taking inspiration from this important biomolecule, researchers led by David Leigh sought to create an artificial molecular machine capable of performing a similar feat. They now report a new method for assembling an artificial molecular machine that can link together four amino acids in a way that, at a very basic level, mimics the ribosome (DOI: 10.1021/ja5022415).

The molecular machine is based on a class of molecules known as rotaxanes, which consist of a linear molecule that gets threaded through a macrocyclic molecule. In rotaxane-based molecular machines, the macrocycle travels along the linear strand and recruits reactive groups complementary to those present in the template.

The team reports a new strategy for assembling the rotaxane-based molecular machine that is more efficient than previously reported methods. Instead of creating the linear template and then threading the macrocycle as the final step, the team first assembles the rotaxane onto the initial portion of the template strand. This prethreaded ring is then attached to the remainder of the strand, which results in higher yields.

Christine Herman, Ph.D.