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Spotlights on Recent *JACS* Publications

NANOPARTICLES GATHER AROUND OR GET IN LINE

When nanoparticles assemble into higher-order structures, known as supramolecular assemblies, they typically exhibit collective properties different from those of the individual particles or bulk samples of the same material. One of the major challenges in nanomaterials research is controlling the formation of these supramolecular structures, which is prerequisite to studying and exploiting their unique optical, electronic, and magnetic properties.

Now, researchers led by Yao Lin present a method for coaxing polypeptide-tagged inorganic nanoparticles to self-assemble into supramolecular structures (DOI: 10.1021/ja402757e). By controlling the size of the nanoparticles and the grafting density of the polypeptides, they find that they can influence the shape of the resulting nanoparticle assemblies, creating either globular or fibrous structures. The process mimics the nucleation−growth mechanism seen in biological processes, such as the formation of actin filaments and bacteria flagella. First, a nucleation center is formed, followed by additional particles gathering around to form clusters or getting in line to form fibers, depending on the experimental conditions.

The method makes it possible for researchers to systematically study these supramolecular structures, which have potential for applications in plasmonics and optoelectronics. **Christine Herman, Ph.D.**

MANIPULATING MAO

Many drugs and drug candidates contain a chemical entity called a chiral amine, which is composed of a nitrogen atom bound to three chemical groups in a precise 3D orientation. When compared with their more widely studied chiral carbon cousins, chiral amines are particularly challenging to synthesize and isolate from their mirror image structures, or enantiomers, due to their low-energy barrier for conversion to the enantiomeric compound. Nicholas Turner and co-workers (DOI: 10.1021/ja4051235) facilitate access to these important structures by manipulating the activity of an enzyme called monoamine oxidase (MAO).

MAO has the remarkable ability to convert certain amine-containing compounds to chiral amines, but the enzyme only reacts with a small subset of amines. By combining protein engineering and high-throughput screening methods, the authors generate modified enzymes capable of reacting with a more diverse set of amines. The utility of the engineered MAO enzymes is demonstrated through their use in the synthesis of several chiral amine-containing natural products as well as two important drugs, the antihistamine levocetirizine and the antispasmodic solefenacin.

The MAO variants described in this study facilitate chemical synthesis of the various chiral amines that are so prevalent in drug discovery efforts. Extension of this approach to additional enzyme families could enable access to other synthetically challenging structures for pharmaceutical and industrial applications. **Eva J. Gordon, Ph.D.**

CALMING DOWN EXCITED DNA

The aromatic bases of DNA strongly absorb ultraviolet light. The energy from the UV light pushes the bases into higher energy states from which the molecule then falls to lower energy states. During this process, the molecule gives off excess energy. Researchers have long sought to understand exactly how excess energy can be dissipated without harming DNA.

Now Bern Kohler and colleagues describe a falling process (DOI: 10.1021/ja4049459). The investigators make double-stranded DNA molecules with 10 pairs of A and T bases and cap either one or both ends of the DNA with a short polymer. The capping effectively constrains the bases in the DNA to adopt the ordered positions found in much longer DNA strands. Kohler and colleagues then analyze these molecules with a laser technique called deep UV femtosecond transient absorption spectroscopy.

The investigators discover two ways for excess energy to leave the DNA. In one way, excited states decay in less than 1 ps. The excess energy is ultimately transferred to vibrations of the surrounding water molecules at a rate that is nearly twice as slow in double-stranded DNA as in single-strands. The investigators suggest that the slower rate is because double-stranded DNA forms fewer hydrogen bonds with surrounding water molecules. For the second way, energy is retained in the double helix one hundred times longer, decaying in about 70 ps. This second and slower dissipation mechanism occurs even more slowly in single-stranded DNA, indicating that base pairing between A and T bases can accelerate energy dissipation. **Rajendrani Mukhopadhyay, Ph.D.**

HALOGENATION OF C−H BONDS: IODINE GOES IT ALONE

Aryl halides are common precursors to radiolabeled compounds, which can be used by pharmaceutical researchers to track a drug as it distributes itself through the body. Chemists can attach iodine to compounds in a variety of ways, with the help of metal catalysts, oxidants, and other reagents. But many previously reported methods are either limited in substrate scope, result in scrambled regioselectivity, or are impractical for other reasons.

Researchers led by Jin-Quan Yu report a more simple catalytic system for iodinating a wide variety of heterocycles (DOI: 10.1021/ja4055492). The palladium-catalyzed reaction uses the inexpensive and mild reagent molecular iodine (I_2), to iodinate a variety of heterocycles, including pyridines, oxazoles, and other heterocycles that had previously been found to inhibit directed C−H activation. This new simple and efficient method adds a new reaction to pharmaceutical researchers' toolbox for creating radiolabeled derivatives of drug leads for research and clinical purposes. The team's pharmaceutical industry collaborators are currently using the approach to create radioactive tritiated drug leads for *in vivo* studies on drug metabolism. **Christine Herman, Ph.D.**

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