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Spotlights

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Spotlights on Recent *JACS* Publications

CONFORMATIONAL CHANGE CONTROLS RADICAL INTERMEDIATES

Vitamin B_{12}, or cobalamin, is a cobalt-containing organometallic compound responsible for normal functioning of the brain and nervous system, as well as construction of new blood cells. Adenosylcobalamin (AdoCbl) is a cofactor form of B_{12}, required for the biological activity of proteins dependent on this form of vitamin B_{12}. AdoCbl, considered the radical warehouse of the cell, works by creating and controlling reactive free radical intermediates, but the catalytic mechanism of these reactions is not well-understood.

Now Jiayun Pang, Michael J. Sutcliffe, and co-workers have used a combination of computational techniques to look at D-ornithine 4,5-aminomutase (OAM), a metabolic AdoCbl-dependent isomerase enzyme (DOI: 10.1021/ja210417k). In OAM catalysis, a cobalt−carbon bond is broken homolytically to generate the radical intermediates responsible for ornithine isomerization. The researchers studied how, triggered by substrate binding, two domains of OAM undergo a large-scale shift with respect to one another, thereby regulating Co−C bond cleavage.

This description of the motion of the two protein subunits helps explain how OAM controls the highly reactive radical intermediates critical to the enzyme's function. More generally, it suggests that large-scale conformational change may play a more important role in the biomolecular function of OAM and other enzymes than previously thought. **Leigh Krietsch Boerner, Ph.D.**

ALL-INORGANIC NANOCRYSTALS BOOST INFRARED EMISSION

Conventional methods for synthesizing nanocrystals call for capping the particles with long-chain organic molecules to control particle size, morphology, and stability. But molecular vibrations associated with those organic ligands tend to sap the particles' excitation energies, which reduces their IR emission efficiency and stability.

Maksym V. Kovalenko, Dmitri V. Talapin, and colleagues report a simple, low-temperature method that can be used to prepare thin films of highly luminescent, infrared-emitting nanocrystals in an IR-transparent solution-cast matrix (DOI: 10.1021/ja2087689). To sidestep the problems often associated with organic ligands on nanocrystals, the researchers devised a solution-phase method for making PbS/CdS core/shell nanocrystals in which oleate groups that are key to forming intermediate particles are replaced with AsS_3^{3-} groups. The all-inorganic particles are then combined with a soluble precursor for As_2S_3 and treated at 130 °C in a step that converts both the precursor and AsS_3^{3-} groups at the nanocrystal surface to an IR-transparent As_2S_3 matrix.

Thin films of the matrix-encapsulated particles exhibit stable IR luminescence in the telecommunications wavelength region. The study may lead to methods for making low-cost devices such as waveguides—structures that confine electromagnetic wave propagation to one dimension—that are central to telecommunications technology, the authors say. **Mitch Jacoby**, *C&EN*

DECIPHERING DEMETHYLASE

DNA contains a wealth of information in its helical structure. Methylation—the addition of methyl groups to a biomolecule such as DNA—adds complexity to an already intricate system. Methylation and demethylation are involved in controlling DNA transcription, chromosome stability, embryological development, and even proliferation of some cancers.

To get better insight into the protein structures and chemistries that could be involved in demethylation, Karen Allen and colleagues determined the structure and activity of stachydrine demethylase (Stc2), a member of a class of demethylase enzymes that contain an iron−sulfur cluster, using various crystallographic and spectroscopic analyses (DOI: 10.1021/ja2111898). Because the bond between carbon and nitrogen is so strong, it is difficult for Stc2 to remove methyl groups from a nitrogen atom, like in the quaternary ammonium compound stachydrine. Similar to other enzymes of its kind, Stc2 forms a trimer with two other copies of the protein to get the job done.

Crystallographic analyses of Stc2 both in its unbound state and bound to a substrate revealed some unique characteristics that separate the protein from its cohorts: a disulfide bond is close to the mononuclear iron site, and the substrate coordinates directly with the mononuclear iron site. Stc2 only catalyzes a single demethylation step with its substrate. This analysis of the structures and chemistries that support demethylation reactions is an important step toward finding new demethylating proteins for epigenetic and post-translational control. **KennethJ. Moore**

LIGANDS MAKE THE DIFFERENCE WITH TWO-METAL NANOPARTICLES

Previous research has shown that the structure of two-metal nanoparticles depends in large part on similarities between the two metals' crystal structures. If the structures are similar, the second metal usually evenly blankets the nanoparticle. Conversely, a second metal with a very different structure may form separate units on the nanoparticle's surface to minimize contact. Conventional wisdom dictated that these growth patterns were not interchangeable for a given set of metals.

Hongyu Chen and co-workers turned this paradigm on its head by incubating gold nanoparticles for various times with the ligand 2-mercaptobenzoimidazole-5-carboxylic acid (MBIA) (DOI: 10.1021/ja211086y). These ligand-modified nanoparticles formed a variety of structures with silver, a metal with a crystal structure that closely matches that of gold. The researcher observed the typical gold core surrounded by an even coating of silver, as well as nanoparticles with off-center gold cores, nanoparticles that looked like acorns, and two-metal dimers. The authors hypothesized that MBIA was embedded

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at the silver–gold interface, thus explaining the ability to continuously tune the interfacial energy therein.

The findings suggest that it is possible to tune how combination nanoparticles form by adding ligands to the mix. This ability is valuable because nanoparticles made of multiple materials offer not only the combined advantages of each separate component but often also new or enhanced properties that result from synergy between the materials—properties that researchers are still working to understand and eventually exploit for designing nanodevices. **Christen Brownlee**

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