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Spotlights

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Spotlights on Recent *JACS* Publications

MOLECULAR CAGE RELEASES CAPTIVES WITH A LITTLE LIGHT

Porous coordination polymers (PCPs), at least the three-dimensional variety, can be visualized as molecular cages with polymer bars that come together at metal atom junctions. Researchers use these materials like cages too, though the captive species is called a "guest". Because the structures can be engineered to trap specific small molecules, they are well-suited for storage, separation, catalysis, and sensing.

Until now, researchers had focused on how to get the guests to come in. Susumu Kitagawa, Shuhei Furukawa, and colleagues have designed a way to instead control their departure (DOI: 10.1021/ja403108x). The researchers deposit alumina onto gold nanorods and then convert the aluminum oxide into a crystalline coordination polymer. The end result resembles a gridded box with a tiny gold bar inside. The researchers dunk the PCP in a solution that contains a molecule of the right size—in this case anthracene—and the guest fills the spaces. Upon near-infrared light irradiation, the gold nanorod converts optical energy into heat, which jostles and drives the guest to rapid movement, resulting in a quick release.

The technique offers light-controlled molecular release that may be useful for catalysis and, when used with bioactive molecules, for the stimulation of living cells. **Jenny Morber,** Ph.D.

HOW TO BUILD A CRYSTAL

To a child, crystal formation must seem like magic. A "seed" planted in a jar of liquid in a few days transforms into jagged rock. Indeed, not all the pieces of the crystallography puzzle have been illuminated. Despite years of study, researchers still do not fully understand how molecules assemble into crystals. The problem lies in the inherent complexity of the process. The behavior of a molecule's functional group during crystallization depends on the nature and position of all other functional groups in the molecule. There are just too many variables.

Bridging crystallography and chemistry, the field of crystal engineering seeks to tease out the relationship between a molecule's structure and the crystal that it forms. In this Perspective, Gautam Desiraju takes the reader on a tour of crystal engineering: its history, its challenges, and its potential (DOI: 10.1021/ja403264c). Ultimately, crystal engineers seek the capability to design crystal structures for desired traits, much like today's molecular synthesis. Unsurprisingly, pharmaceutical companies are very interested in these technologies. Crystal engineers have responded to overwhelming complexity with a unit called the "synthon", which can be likened to a synthetic molecule. Desiraju discusses the synthon's continued popularity and how computational methods can assist more traditional experimental techniques. The Perspective radiates a combination of frustration and enthusiasm that likely mirrors researchers at the dawn of synthetic crystal engineering. **Jenny Morber,** Ph.D.

LANTHANIDE AND ACTINIDE OCTAHEDRAL COMPLEXES: CLOSING IN ON F ORBITALS

Certain lanthanides and actinides have similar ionic radii and are therefore difficult to separate in spent nuclear fuel. Lanthanides and actinides form octahedral complexes with halides, and the covalent bonding is stronger in the actinide complexes than in the lanthanide complexes. The difference is caused by the importance of f-orbitals in the bond, where 5f orbitals have a larger radial extend than 4f orbitals. The covalent bond in these complexes is under intensive study because it could lead to better separation techniques of radioactive isotopes.

In addition to halides, other ligands, such as alkyl, alkoxide, amide, and ketimide, show promise in this research. In 2012, Wayne Wendell Lukens and co-workers reported a detailed spectroscopic analysis of the importance of f orbitals in the covalent bonds in an octahedral uranium ketimide (DOI: 10.1021/ja211875s).

In a follow-up study, the group investigates the covalency and bonding strength of a number of octahedral f complexes (DOI: 10.1021/ja403815h). They use a new, more precise molecular orbital (MO) model including the effect of covalency on spin−orbit coupling and the effect of covalency on orbital reduction. When covalency is significant, it is found to be in better agreement with the experimental data than the existing MO developed by Thornley in 1966. The work represents a step forward in quantitative assessment of covalent interactions in f-element materials. **Alexander Hellemans**

LESSONS IN LABELING LANTHIPEPTIDES

Lanthipeptides—a large class of cyclic peptides characterized by thioether cross-links and unusual amino acids called lanthionine and methyllanthionine—exhibit diverse biological activities, including promising antimicrobial activity. To help explore the activity of these structurally and functionally intriguing natural products, Noah Bindman and Wilfred van der Donk develop a general method for labeling lanthipeptides with molecular probes such as fluorescent compounds and affinity tags (DOI: 10.1021/ja4010706).

The authors exploit the fact that a naturally occurring modification found in some lanthipeptides, an N-terminal ketone, is capable of selectively reacting with an aminooxy functional group. They incorporate N-terminal ketones into lanthipeptides and then label three lanthipeptides—lacticin 481, haloduracin α, and haloduracin β—with an aminooxy-containing fluorophore. The fluorescent lanthipeptides are used to visualize the distribution of the compounds in bacterial cells, offering insight into their cellular localization properties.

The strategy reported in this study presents a novel, versatile method for investigating lanthipeptide biology. In addition to creating fluorescent lanthipeptides for imaging studies, other aminooxy-conjugated molecular tags could be incorporated into lanthipeptides to enable exploration of additional aspects of

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their biology, such as their cellular targets, their mechanisms of action, and their therapeutic potential. **Eva J. Gordon,** Ph.D.