Sighting the golden cage

Clusters of 16, 17, or 18 gold atoms produced by laser vaporization of gold form hollow cage structures akin to fullerene molecules, new theoretical and experimental studies suggest (Proc. Natl. Acad. Sci. USA, published online, dx.doi.org/10.1073/pnas.0600637103). These anionic clusters are the first experimentally identified hollow cage structures made entirely of metal atoms, according to Lai-Sheng Wang of Washington State University, Richland, and Pacific Northwest National Laboratory and Xiao Cheng Zeng of the University of Nebraska, who jointly led the effort to identify the structures. Gold anion clusters of 13 atoms or fewer tend to be planar, while clusters of 20 atoms take on a pyramidal structure. Wang and Zeng’s group therefore speculated that gold clusters with 14 to 19 atoms would be the most likely to assume a hollow cage structure. Using photoelectron spectroscopy and theoretical calculations, they found that all but one of the lowest energy isomers of Au_{16}^{-} (shown), Au_{17}^{-}, and Au_{18}^{-} are hollow cages with an empty interior roughly 6 Å across.

Iododiacylenes may lead to ‘linear carbon’

Polydiacylenes are useful optoelectronic materials, but the conjugated polymers are tricky to make because they require bulky substituents to stabilize against explosive decomposition and to produce an ordered polymer structure. Thus, cocrystallizing the monomer with a spacer compound is a common synthetic route. In the latest twist on this approach, Aiwu Sun, Joseph W. Lauher, and Nancy S. Goroff at the State University of New York, Stony Brook, have synthesized a novel bis(nitrile) oxalamide spacer and used it to make poly(diiododiacetylene), or PIDA (shown), a conjugated carbon chain adorned only with iodine side groups (Science 2006, 312, 1030). The oxalamide groups, \(-\text{NHCOCONH}−\), form a hydrogen-bonded network, whereas the terminal nitriles, \((-\text{CH}_2)_{2}\text{CN}\), form weak Lewis acid-base pairs with the iodine atoms of the butadiyne monomer, \(\text{IC} = \text{CC} = \text{Cl}\). The resulting molecular scaffold aligns the monomers, prompting spontaneous polymerization. PIDA is a potential precursor to substituted polydiacylenes, and it could lead to carbyne, a long-sought hypotheti- cal linear sp-hybridized carbon allotrope, if the iodine atoms can be removed.

Laser breaks H–Si bonds selectively

The ability to control the breaking of chemical bonds by using lasers to selectively excite the bonds’ vibrational frequencies has been a long-standing but as-yet-unrealized goal. In most experiments, the initial vibrational excitation quickly distributes throughout molecules as thermal energy. Now, using a free-electron laser, Philip I. Cohen of the University of Minnesota and colleagues have selectively broken H–Si bonds on a silicon surface. In addition to being a scientific milestone, the work could also find utility in semiconductor research, such as nanostructure fabrication. The group bombarded a silicon surface covered with 15% H and 85% D atoms with a laser tuned to the same energy as the vibrational mode of the H–Si bond. H₂ was the primary molecule released, ruling out a thermal process, which would have generated large quantities of D₂ (Science 2006, 312, 1024). The mechanism remains unresolved, but the authors hypothesize that the bonds absorb multiple photons before breaking.

Genome-wide analysis of intractable proteins

A procedure has been devised for obtaining structures, potentially across entire genomes, of proteins that are intractable to crystallographic analysis (Proc. Natl. Acad. Sci. USA, published online May 11, dx.doi.org/10.1073/pnas.0602660103). In the technique, developed by Michael Strong, David Eisenberg, and coworkers at UCLA, computational genomic analysis is used to identify a protein likely to interact functionally with an intractable protein. The two partners are then coexpressed as a complex in bacteria, crystallized, and structurally analyzed. The idea is that complexes may be more easily expressed and more readily crystallized than their individual component proteins. The researchers demonstrated the technique by analyzing a complex (shown) of the proteins PE (red) and PPE (blue) from tuberculosis bacteria. “The predicted complex was readily expressed, purified, and crystallized, although we had previously failed in expressing individual PE and PPE proteins on their own,” the researchers note. “Our entire procedure for the identification, characterization, and structural determination of protein complexes can be scaled to a genome-wide level.”

Clue to thiamin assembly

Identification of an unusual metabolite bound to a protein implicated in thiamin biosynthesis has provided a key clue about how eukaryotes make this essential vitamin (J. Am. Chem. Soc., published online May 11, dx.doi.org/10.1021/ja061413o). Thiamin (shown) is stitched together from preassembled thiazole (red) and pyrimidine moieties. A team led by Steven E. Finkel and Tadgh P. Begley of Cornell University has now used a combination of NMR and mass spectrometry and crystallography to provide a more detailed picture of how the thiazole is put together. The researchers identified and characterized a metabolite tightly bound in the active site of the yeast enzyme thiazole synthase. The metabolite’s structure—a surprising adenylated version of the thia- zole—suggests that thiazole is derived from nicotinamide adenine dinucleotide, which typically functions as a redox cofactor, rather than a biosynthetic starting material.