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Spotlights on Recent *JACS* Publications

SHINING A LITTLE LIGHT ON GOLD NANOCLUSTERS

Thiols are organic molecules that contain a carbon-bonded sulfur group. Sulfur binds readily to gold, and researchers have exploited thiol−gold interactions for applications from fabrication of electronic devices to medical imaging.

Here, Peng Zhang, De-en Jiang, Jianping Xie, and colleagues explore the properties of tiny gold clusters to which are attached many trailing thiols, like snakes on the head of Medusa (DOI: 10.1021/ja411643u). In such a $Au_{22}(SR)_{18}$ cluster, which here contains only 22 gold atoms and 18 thiol "snakes", an atom added or subtracted can lead to remarkable property changes. Sometimes these properties include luminescence, but why some clusters emit light and others do not has puzzled researchers for a long time.

The team had previously discovered strong luminescence in a thiolated gold nanocluster, but an uncertain molecular formula limited the ability to probe structure/property relationships. This time the team creates and then determines the exact structure and molecular composition of a thiolated gold nanocluster that emits a bright red light. Interestingly, clusters very similar to $Au_{22}(SR)_{18}$—a few extra gold atoms or an extra thiol—luminesce only very weakly. The study bridges a knowledge gap that should help researchers to understand the origin of luminescence in these and other sulfur and gold complexes.

Jenny Morber, Ph.D.

SOLID-STATE NMR CAPTURES WIGGLE OF LIGHT-SENSING MEMBRANE PROTEIN

Membrane proteins are the cell's gatekeepers, sensing chemicals, binding partners, and even light, and then transmitting that information into a cell's interior. Structural analysis of membrane proteins remains a challenge, and more difficult still is determining their dynamics. Protein motions are often essential to function. In X-ray crystallography, mobility is a liability that inhibits protein crystallization. Nuclear magnetic resonance (NMR) spectroscopy is well-equipped to capture protein motions, but measuring site-specific dynamic information from proteins locked in a membrane has remained elusive.

Now, Vladimir Ladizhansky and colleagues report using solid-state NMR (ssNMR) to tease out site-specific molecular motions of a membrane protein within a lipid bilayer (DOI: 10.1021/ja411633w). The seven transmembrane helical protein detects light in a cyanobacterium and helps regulate photosynthesis. The protein's NMR structure had been solved previously.

For this study, the researchers collect relaxation rates and dipolar order measurements for specific residues along the protein chain. Using a simple model, they turn the ssNMR data into information about how quickly different parts of the membrane protein move. Notably, both the parts of the protein inside the membrane and the loop regions that extend into solution move with surprising rigidity. This result departs from the common notion that loop regions wave wildly while membrane segments hold still.

Erika Gebel Berg, Ph.D.

HIGH PRESSURE CREATES MORE THAN JUST DIAMONDS

Piezoelectric materials are odd. Squish them or pull them, and an electric charge appears on the material's surface. Deliver a charge, and the material mechanically responds. Piezoelectricity and other interesting behaviors that include ferroelectricity, pyroelectricity, and piezo-optics result from a lack of symmetry in a material's crystal structure. Such symmetry breaking means that positive and negative ions in the structure do not line up in neat rows, and one face of the crystal becomes polarized compared to its opposite. Structures that have this particular property are called noncentrosymmetric.

In the same way that precious stones are formed deep in the Earth's mantle, Yoshiyuki Inaguma and co-workers use high pressure to create a new noncentrosymmetric material, $ZnTiO_3$ (DOI: 10.1021/ja408931v). Calculations and experiments indicate that the material is a metastable phase formed in decompression, and crystal analysis suggests that it may be highly ferro- and piezoelectric. The researchers suggest that $ZnTiO_3$ should be well-suited as a thin film, and if this is the case, it could find use in tiny sensors and actuators, computer memory, and infrared cameras. $ZnTiO_3$ appears promising as a material of choice in applications that require structural polarity.

Jenny Morber, Ph.D.

MAKING UBIQUITIN UBIQUITOUS FOR BIOLOGICAL EXPLORATION

The protein ubiquitin, named for its ubiquitous presence in biological tissues, plays a key role in the removal of old or damaged proteins from cells, as well as in several other biological signals. The mechanism of ubiquitin is unique—multiple copies of the protein need to be attached to target proteins in order to signal for their demise. A challenge in investigating ubiquitin biology is gaining access to homogeneous forms of polyubiquitinated proteins. Now, Ashraf Brik and co-workers devise a novel approach to create proteins appended with multiple ubiquitin units (DOI: 10.1021/ja412594d).

The authors use the protein α-globin, a component of the blood protein hemoglobin, as a model system to test their approach. They install a chemical group called an acyl hydrazide at one end of ubiquitin, which can be converted to an electrophilic center, enabling conjugation of one or more ubiquitins onto α-globin via its cysteine residue. They demonstrate that these semisynthetic ubiquitin conjugates react as expected with ubiquitin-modifying enzymes and are able to mark target proteins for degradation.

The chemistry developed in this study enables the creation of homogeneous polyubiquitinated proteins for systematic investigation of mono- and polyubiquitinated proteins. This approach provides invaluable new biological tools for delineating ubiquitin biology, with potentially broad implications for our understanding of normal and disease-related cell processes.

Eva J. Gordon, Ph.D.

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