JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Spotlights on Recent *JACS* Publications

CHEMOSENSOR LIGHTS UP WITH CARBON DIOXIDE DETECTION

In order to minimize the accumulation of harmful greenhouse gases, such as carbon dioxide, in the atmosphere, gas streams that may contain high levels of CO_2 must be analyzed prior to their release from industrial facilities. The ideal CO_2 detection method is one that is selective, quantitative, affordable, tolerant of interferents, and capable of real-time measurements.

Taking a step toward this goal, researchers led by Jin Yong Lee, Christopher Bielawski, Jonathan Sessler, and Juyoung Yoon synthesized a benzobisimidazolium salt that can be activated by a fluoride ion to create a complex that fluoresces upon reaction with CO_2 (DOI: 10.1021/ja306891c). The compound enables researchers to visualize and detect CO_2 to levels as low as 30 ppm.

Compared to common methods for CO_2 detection, such as GC-MS and IR spectroscopy, the developed optical gas sensor does not rely on bulky instrumentation and is simply constructed, inexpensive, and highly sensitive. Plus, the chemosensor, which is based on a benzobisimidazolium salt, does not require dry, air-free conditions, making it potentially more useful as a sensor in less rigorously controlled environments. **Christine Herman, Ph.D.**

ON THE SUNNY SIDE OF INORGANIC NANOTUBES

Inorganic nanotubes share the same structure with more familiar carbon nanotubes, but they tend to be easier to synthesize and, depending on the metal used, have more readily tunable electrical and thermal properties than their organic counterparts. In an effort to simplify the synthesis of inorganic nanotubes and to broaden the range of possible applications, researchers are exploring the impact of using different metals to make these materials. Now, a group led by pioneers in the field of inorganic nanotube synthesis, Reshef Tenne and Jeffrey Gordon, has developed a new way of synthesizing molybdenum and tungsten nanotubes using highly concentrated sunlight through a technique called solar ablation (DOI: 10.1021/ja307043w).

The researchers formed several different types of metal chalcogenide nanotubes, including MoS_2, $MoSe_2$, WS_2, and WSe_2, by utilizing a lead catalyst in a lengthy and high-temperature annealing process. This inorganic synthesis procedure has the potential to also work well for other metal chalcogenides that have similar layered crystal structures but have not been realized in nanotube form. In addition, the solar ablation mechanism is an inexpensive and easy way to make inorganic nanotubes and represents a clean, green way to synthesize these materials. **Leigh Krietsch Boerner, Ph.D.**

CHEAP AND EASY SURFACE PLASMONS

Localized surface plasmon resonance, the intense amplification of light waves at the exterior of a conductor, holds promise for next-generation biosensors, solar cells, and photothermal medicines. Although this phenomenon is most commonly seen in silver and gold nanoparticles, it is sometimes difficult to integrate those materials into working devices. In contrast, silicon is a practically ubiquitous material that already serves as the basis for a variety of technologies. The addition of impurities—a process called doping—provides a straightforward method to tune silicon's properties, and the raw materials are relatively inexpensive and easy to obtain. The technology to build nanoscale silicon objects with different sizes and shapes is also well established.

Now Michael Filler, Li-Wei Chou, and co-workers have synthesized phosphorus-doped silicon nanowires that absorb at mid-infrared wavelengths (DOI: 10.1021/ja3075902). The resonant frequency is tunable based on both the doping concentration and the length of the silicon nanowires. The work represents the first example of localized surface plasmon resonance in silicon nanowires and promises to streamline their integration into functioning devices. **Leigh Krietsch Boerner, Ph.D.**

RESEARCHERS STUDY HOW CROWDED ENVIRONMENTS AFFECT PROTEIN STABILITY

The stability of a protein is determined, in part, by how crowded its surrounding environment is. In the cell, any particular protein coexists with thousands of others, and macromolecules can reach concentrations as high as 300 g/L. Macromolecular crowding can have both positive and negative effects on protein stability: hard-core repulsion between a protein and other solutes leads to stabilization because the protein is less prone to unfold for entropic reasons, whereas nonspecific attractive chemical interactions can be destabilizing, leading to increased surface exposure and unfolding. Previous studies on protein stability have primarily focused on the effect of hard-core repulsions without considering chemical interactions.

Researchers led by Gary J. Pielak set out to better understand how both of these factors combine to influence protein stability (DOI: 10.1021/ja305300m). Using ^{15}N NMR, they detected amide proton exchange between a test protein, ubiquitin, and both synthetic and protein crowding agents. The team found that chemical interactions played a surprisingly large role in determining protein stability, in some cases even dominating hard-core repulsions. This study helps explain several previously confusing biophysical observations, such as why a crowded cellular environment sometimes fails to stabilize, or even destabilizes, proteins. **Christine Herman, Ph.D.**

RADICAL PROMOTES SENSITIVITY IN SOLID-STATE NMR

Solid-state nuclear magnetic resonance spectroscopy can provide a wealth of structural information, but the method is plagued by inherently low sensitivity. The problem is exacerbated when detecting NMR-active nuclei with a low natural abundance like ^{13}C, which makes up just 1.1% of the total carbon in molecules. Studying rigid molecules such as

Published: October 23, 2012

dx.doi.org/10.1021/ja310108x | *J. Am. Chem. Soc.* 2012, 134, 17840−17841

glucose and sulfathiazole is particularly difficult because they typically have long T_1 relaxation times, which further decreases sensitivity in NMR experiments.

To boost sensitivity, Lyndon Emsley and colleagues applied dynamic nuclear polarization (DNP) to solid-state NMR experiments of microcrystals (DOI: 10.1021/ja308135r). The strength of a molecule's NMR signal is related to how polarized its nuclei are in a magnetic field. With DNP, researchers can transfer polarization from unpaired electrons to nearby nuclei, enhancing the NMR signal. The researchers impregnated powdered glucose and sulfathiazole into a nonsolvent liquid containing a biradical—a molecule with two unpaired electrons—and then performed a series of DNP ^{13}C NMR experiments on the samples. Compared to typical NMR spectra of microcrystalline glucose and sulfathiazole, adding the biradical enhanced sensitivity by 2 orders of magnitude. Such an increase in sensitivity drastically reduces the amount of time it takes to do solid-state NMR experiments on natural abundance samples. **Erika Gebel, Ph.D.**

■ SPECTROSCOPY TELLS A TELOMERE TALE

Telomeres, repetitive sequences of DNA that reside at the ends of chromosomes, protect chromosomal DNA from damage during cell division. Telomeres have been implicated in various processes, including aging and cancer, leading to much interest in their structure, function, and regulation. Unlike the double-stranded, helical nature of most chromosomal DNA, the ends of telomeres do not undergo typical base-pairing and can adopt a variety of complex architectures made up of four-stranded structures called quadruplexes. To help characterize these structures, Jonathan Chaires and co-workers probe the energetic factors that guide the transition of a quadruplex from a folded to an unfolded state (DOI: 10.1021/ja307543z).

The authors use three spectroscopic methods, called circular dichroism, fluorescence emission, and fluorescence resonance energy transfer, to explore the structural transitions experienced by a model telomere fragment composed of 22 DNA bases. They demonstrate that quadruplex unfolding is a sequential process and provide the first experimental evidence of a three-stranded intermediate, a structure that had been previously predicted by computational models. This approach provides intriguing insight into telomere structure that could ultimately impact the design of drugs targeting cancer and aging-associated disorders. **Eva J. Gordon, Ph.D.**

dx.doi.org/10.1021/ja310108x | J. Am. Chem. Soc. 2012, 134, 17840−17841