

## Spotlights on Recent JACS Publications

### ■ DINUCLEAR BIS-OXO-BRIDGED URANIUM COMPLEX SHOWS UNUSUAL MAGNETIC PROPERTIES

Wayne Lukens, Karsten Meyer, and co-workers report a rare series of dinuclear bisoxo uranium complexes with strong antiferromagnetic coupling between the uranium atoms, which before has only been seen in the solid state (DOI: 10.1021/ja504528n).

Uranium and its complexes are both interesting and important because uranium-235 is the only naturally occurring fissionable fuel. The uranyl unit, a linear dioxygen uranium compound, is well-known within uranium chemistry. However, very few terminal monooxo uranium complexes are known, and even fewer have a dinuclear motif.

Here, a series of three dinuclear uranium complexes bridged by two oxo ligands have been synthesized via multiple-bond metathesis of CO<sub>2</sub> with a uranium(V) imido complex. The researchers note that the oxidation state of the complex greatly affects the magnetic behavior displayed, and the main complex, the dinuclear bis( $\mu$ -oxo)-bridged U<sup>V</sup>/U<sup>V</sup> complex, shows very strong magnetic exchange within the diamond-shaped uranium core. By examining this structurally similar series of compounds, the researchers gain new insights into the role that electronic structures play in the reactivity of uranium oxo complexes, which in turn may increase the fundamental knowledge of the importance of the f orbitals part in uranium–ligand multiple bonding.

Leigh Krietsch Boerner, Ph.D.

### ■ HYDROGEN–DEUTERIUM SUBSTITUTION CAN HAVE DRAMATIC EFFECTS

In certain types of molecules, the addition of a single neutron to each of three hydrogen atoms in a large organic structure can have a surprisingly dramatic effect on the molecule's physical properties, and thanks to a new study led by Akira Ueda and Hatsumi Mori, we now better understand why this happens (DOI: 10.1021/ja507132m).

Given their ubiquity in biomolecules and their crucial role in (bio)chemical reactions, researchers have long been interested in studying the dynamics of the hydrogen atom in the context of the hydrogen bond. Here, the team studies the effect of swapping out hydrogen atoms for deuterium atoms in a hydrogen-bonded purely organic conductor crystal, known as  $\kappa$ -H<sub>3</sub>(Cat-EDT-TTF)<sub>2</sub> or  $\kappa$ -H, which has a unique structure composed of two equivalent components joined by a symmetric anionic hydrogen bond.

Although hydrogen and deuterium differ by only one neutron, the researchers find that replacing just three hydrogen atoms with deuterium atoms in  $\kappa$ -H causes the structure to transform from a paramagnetic semiconductor into a non-magnetic insulator. The authors explain this fascinating unprecedented phenomenon in terms of hydrogen-bonding equilibrium and dynamics and say they plan to next explore novel stimuli-responsive molecular materials and devices based

on chemical modifications of this system.

Christine Herman, Ph.D.

### ■ HYDRAZYL RADICAL REVEALS FIRST SPIN TRANSITION

Persistent radicals on organic molecules are promising materials for new electronic devices. The magnetic, optical, and electrical behavior of these materials can be altered in response to external stimuli such as heat, light, or pressure. Radicals, such as 1,3,2-dithiazolyl radicals, respond to those external cues by switching spin state. In persistent organic radicals, a spin transition is possible when it occurs between two structurally similar phases, and little heat is released or absorbed when radicals dimerize.

Now Panayiotis A. Koutentis and his colleagues have found the first example of a spin transition in a 1,2,4-benzotriazinyl, a subclass of hydrazyl radicals (DOI: 10.1021/ja5063746). The researchers examine the magnetic behavior of 1-phenyl-3-trifluoromethyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl. Upon heating the material, they notice a sharp transition from diamagnetism to paramagnetism around 58 K; the transition is complete within 5°.

Then the researchers use variable-temperature X-ray diffraction to connect the magnetic changes to structural changes between two types of stacked radicals in a crystal. This class of molecules is interesting, the researchers write, because it is one of the few air and moisture stable organic radicals that exhibit a first-order spin transition, particularly one that spans a small temperature range.

Melissae Fellet, Ph.D.

### ■ A NEW SAM: SELF-ASSEMBLED MONOLAYER ON GOLD MADE FROM ALKYNES

Self-assembled monolayers (SAMs) are an important class of substrates for a variety of analyses, ranging from bioanalytical to electrochemical, and they have a vital role in applications such as the control of wetting and adhesion, chemical resistance, and nanofabrication.

SAMs form from the spontaneous adsorption of molecules onto a surface, usually gold or silver, in a highly ordered fashion. The most common type of SAMs is that of alkanethiolates on metal surfaces. Chemists, however, are eager to expand the repertoire of SAMs based on different molecules so that they can explore the physical chemistries of other types of surfaces.

Now Piotr Cyganik and colleagues describe the formation of SAMs made from alkynes, which contain acetylene groups attached to gold via a strong gold–carbon bond (DOI: 10.1021/ja506647p). There are previous reports of alkyne-based SAMs, but the details surrounding their formation and structure were limited.

The researchers use microscopic, spectroscopic, and contact-angle measurements to demonstrate that SAMs built from

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alkynes on gold are highly sensitive to oxygen; trace amounts of oxygen can lead to disordered films with oxidized contaminants. The investigators demonstrate that under oxygen-free conditions, highly ordered alkyne-based SAMs can be formed and, upon analysis, find that alkyne-based SAMs have properties similar to SAMs of alkanethiolates. The ability to form high-quality SAMs having an acetylene anchoring group provides an alternative surface chemistry to the well-known alkanethiolates.

**Rajendrani Mukhopadhyay, Ph.D.**