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Spotlights

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Spotlights on Recent *JACS* Publications

FIRST NMR CHARACTERIZATION OF AN UNSTABLE COMPLEX

Anthony Hill, Graham Ball, and colleagues are the first to observe a tungsten alkane σ-complex by NMR spectroscopy, which can directly provide information about the hydrocarbon ligand (DOI: 10.1021/ja300281s). σ-Complexes have ligands that coordinate to a metal center by using the electrons in a single bond. Previously, only UV and IR spectroscopic methods had been used to observe or characterize group 6 alkane σ-complexes.

To create the tungsten alkane σ-complex, the researchers performed photolysis—light-induced chemical decomposition—on a tricarbonyl precursor compound. Photolysis causes the precursor to replace a carbonyl ligand with a carbon–hydrogen bond from pentane, preferring a terminal methyl group rather than an internal methylene group. This specificity is important to understand for future applications in site-directed C–H activation, and Ball and co-workers propose that the metal and ligand combination may dictate the site binding preference in alkanes.

Although transition metal alkane σ-complexes are short-lived and unstable and can be difficult to characterize, they can help scientists further understand and exploit C–H bond activation, reactions that result in the cleavage of C–H bonds and enable the conversion of alkanes into functionalized organic compounds. **Yun Xie, Ph.D.**

STACKING AND LAYER THICKNESS DETERMINE ELECTRON-TRANSFER RATE IN GRAPHENE

Patrick Unwin and co-workers have unraveled the electrochemical properties of graphene (DOI: 10.1021/ja3014902), a material comprising planar sheets of carbon with anywhere from a single monolayer to multiple layers. Using scanning electrochemical cell microscopy (SECCM), the researchers made thousands of electrochemical measurements across a graphene surface, with different numbers of layers and different stacking arrangements between the layers, and correlated the response with information from micro-Raman spectroscopy, optical microscopy, and atomic force microscopy.

With this multi-microscopy approach, the researchers were able to develop a comprehensive structure–activity picture. They found that increasing the number of graphene layers led to an increased rate of electron transfer, in essence that multilayer graphene (or thin graphite) promoted faster electron transfer than monolayer graphene. Additionally, the way the layers stacked was important—when the graphene in multilayers was loosely stacked, the electron-transfer characteristics were similar to those of monolayer graphene.

A thorough understanding of the electron transport properties of graphene, and how to tune graphene layers for desired performance, is essential to creating reliable electrochemical devices and technologies. SECCM provides a versatile means of making key underpinning measurements. **Polly Berseth, Ph.D.**

RARE-EARTH-BASED NANOCRYSTALS GO TWO-FOR-ONE

Nanocrystals that incorporate rare-earth elements have an unusual capacity to perform energy upconversion, in other words emitting light at a shorter wavelength and higher energy than that of photons used to excite these materials. This unique capability makes them natural fits for applications ranging from lighting to bioimaging. Though all the tripositive lanthanide and yttrium ions have been used to construct such nanomaterials that can perform energy upconversion, tripositive scandium (Sc^{3+})-containing nanocrystals of this type have not been reported.

Now, Ling Huang and co-workers have synthesized $Na_xScF_{(3+x)}$ nanocrystals as a host material for doping with different lanthanides (DOI: 10.1021/ja3016236). They varied the polarity of the reaction medium and found that the phase and morphology of the resulting nanocrystals changed as well, including the surprising finding that two phases can coexist within individual nanocrystals.

More significantly, a strong red upcoversion emission was observed, different from those of lanthanide- and yttrium-containing nanocrystals, which usually give strong green emission. The authors suggest that these series of new nanocrystals could broaden the range of applications previously suggested for rare-earth-based nanomaterials into areas such as telecommunications or disease diagnosis. **Christen Brownlee**

A MAGNET THAT STICKS TO A MOLECULAR TRAIL

Giuseppe Pileio and co-workers have figured out a way to lengthen the amount of time they can watch molecules by magnetic resonance imaging (MRI) (DOI: 10.1021/ja302814e), which could improve how doctors peer into the bodies of their patients noninvasively. MRI uses powerful magnets to track atomic nuclei in patients and has revolutionized medical imaging, but it has limitations. The MRI signal from molecules is short-lived, so researchers can typically only track individual molecules in the body for seconds to minutes.

The key to this group's method is detecting a signal that originates in a particular energy state, called a singlet order, not normally observable by magnet-based methods. This signal dissipates more slowly than a typical MRI signal. They tested their approach on pyruvate, a molecule central to cell metabolism. To enhance MRI signal intensity, the researchers coupled their long-living state with hyperpolarization. Using this method, intensity-enhanced pyruvate's MRI signal lasted twice as long as usual, and the researchers hope to extend the lifetime even further in future experiments.

A longer-lasting signal has the potential to provide novel insight into human biology and disease. For example, tracking other metabolites by MRI could reveal details about cancer cell metabolism. **Erika Gebel, Ph.D.**

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