

Spotlights on Recent JACS Publications

■ X-BONDS: TOWARD STEREOSELECTIVE HALOGENATING AGENTS

Halogen bonds are similar to hydrogen bonds in that a central halogen atom acts as an electron acceptor in a non-covalent bond with an electron-rich donor. Halogens typically occupy spaces on the exterior faces of organic molecules, and hence they can strongly influence directional intermolecular interactions.

Máté Erdélyi and colleagues report a detailed combined experimental and computational study of bis(pyridine) halogen complexes that incorporate a halogen bond linking a halogen to two nitrogen atoms that are part of pyridine rings (DOI: [10.1021/jacs.6b03842](https://doi.org/10.1021/jacs.6b03842)). The electron-donating capability of the nitrogen atoms can be modulated by attaching electron-withdrawing or -donating substituents to the pyridine rings. By investigating the changes in N–I bond lengths using NMR techniques, X-ray diffraction, reaction kinetics, and computer modeling, the researchers find that the N–I bond lengths depend only slightly on changes in the electron population of the pyridine rings. In contrast, the bond energies vary to a greater extent.

“As [bis(pyridine)iodine]⁺ complexes are common synthetic reagents, this work may be of significance for the development of new, stereoselective halogenating agents in the future,” the authors conclude.

Alexander Hellemans

■ RUTHENIUM OXIDE: MORE THAN A CATALYST

The production of hydrogen by water splitting with sunlight continues to be intensively investigated as an environmentally friendly energy source. One approach to such photocatalytic reactions is based on the use of electrons liberated by photons at a semiconductor–water interface. The liberated electrons fuel the reaction splitting the water molecules and producing hydrogen atoms. Ruthenium oxide (RuO₂) has been investigated for several years as a promising cocatalyst, promoting the production of hydrogen using the photoelectrons from the semiconductor surface to perform redox reactions.

Michael Henderson, Roger Rousseau, and co-workers now report in a combined experimental and theoretical effort that RuO₂ itself displays photochemical activity (DOI: [10.1021/jacs.6b05083](https://doi.org/10.1021/jacs.6b05083)). They have shown that photon absorption by a thin RuO₂ film with a rutile structure promotes the split-off of adsorbed hydrogen molecules, a process called photodesorption.

The researchers investigate the desorption properties of RuO₂ by first allowing deuterium molecules to adsorb onto a thin RuO₂ film cooled to 40 K. Desorption via gradually heating the film suggests that visible light photons should have sufficient energy to dislodge the deuterium molecules. Irradiating the RuO₂ film with light pulses and observing the sample with a scanning tunneling microscope confirms that the layer of hydrogen molecules on the RuO₂ surface becomes largely depleted.

Alexander Hellemans

■ ON CLOUD NINE: ELUCIDATING THE STRUCTURE OF ATMOSPHERIC ICE

Ice plays an important role in Earth’s atmosphere and in clouds, where it can affect processes ranging from lightning to rain droplet creation to reactions with atmospheric aerosols. Through molecular simulation studies under conditions relevant to clouds, Arpa Hudait and Valeria Molinero have elucidated the structure of ice formed from vapor deposition (DOI: [10.1021/jacs.6b05227](https://doi.org/10.1021/jacs.6b05227)).

Ice grown from the liquid phase does not always assume the same geometry as ice grown from water vapor. In the relatively cold temperatures of Earth’s atmosphere, ice crystals nucleate from supercooled water and then continue to grow through vapor uptake; it is therefore important to understand ice formation from either phase.

The authors confirm an earlier hypothesis that stable hexagonal ice is in fact formed from vapor deposition in clouds, in contrast to the metastable cubic polymorph grown from the liquid phase. The preference for the hexagonal structure can be attributed to thermodynamics, and its formation is driven by entropy. Understanding the structure of ice grown under varying conditions will guide experimental studies of ice formation to further expand knowledge regarding atmospheric processes.

Dalia Yablon, Ph.D.

■ FOR THIOLATES ON GOLD NANOCRYSTALS, NanoSAM I AM

Self-assembled monolayers (SAMs) of thiolates on gold surfaces have found use in a variety of nanotechnology applications. Determining their atomic structures has been difficult on large and sometimes irregular gold surfaces, but with the development of atomically precise thiolate-protected metal clusters, researchers have a new tool for solving this mystery by taking advantage of their regular and predictable structures.

In a recent study, Rongcao Jin and co-workers use a gold nanocrystal they have developed to investigate the thiolate layer on its surface (DOI: [10.1021/jacs.6b04835](https://doi.org/10.1021/jacs.6b04835)). Au₉₂(SR)₄₄, where SR is the 4-*tert*-butylbenzenethiolate, has a highly regular, tetragonal structure with six flat, extended crystalline facets. Using these thiolate-covered facets as “nanoSAMs”, the researchers investigate the structure of the overlying monolayer. They find that thiolates bind to the nanocrystal’s planar surfaces with a simple bridge-like structure connecting each gold atom. The thiolate sulfur atoms align as do the hydrocarbon tails, forming an ordered, symmetrical overlayer. The authors suggest that these findings shed light on the potentially more complicated self-assembly behavior on bulk gold surfaces and thereby help to further the use of thiolate SAMs.

Christen Brownlee

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