

Spotlights on Recent JACS Publications

■ BROAD-RANGE LIGHT-HARVESTING COMPLEXES

Artificial photosynthetic systems that split water into hydrogen and oxygen are of interest for the conversion and storage of solar energy. Researchers may examine existing photosynthetic systems in nature as a source of inspiration, and also to test ways to improve the efficiency of artificial systems.

Takehisa Dewa and colleagues report how they have extended the wavelength range of the photosynthetic bacterial light-harvesting complex LH2 by attaching the fluorescent chromophore Alexa Fluor 647 (A647) (DOI: [10.1021/jacs.5b08508](https://doi.org/10.1021/jacs.5b08508)). The native LH2 complex absorbs light in the visible and near-infrared regions; addition of A647 units extends the range of light absorbed by LH2 to shorter wavelengths covering the 620–750 nm region.

Further, LH2 bacteriochlorophyll molecules form assemblies B800 and B850 that absorb light at peak wavelengths of 800 and 850 nm, respectively. Energy absorbed by B800 is quickly transferred to B850 with a time constant of 700 fs. Femtosecond transient absorption spectroscopy shows that light energy absorbed by A647 is transferred with time constants varying between 440 fs and 23 ps to the chromophores B800 and B850 of LH2, using in part the bacteriochlorophyll's native pathway. This research illustrates an interesting method to increase the wavelength range and efficiency of artificial photosynthetic systems.

Alexander Hellemans

■ METAL–ORGANIC FRAMEWORKS WITH A NOSE FOR TOXIC VAPORS

Because volatile organic compounds, or VOCs, are often toxic and flammable, detecting VOCs in the environment can be important for health and safety. Mircea Dinca and colleagues demonstrate that planar arrays of porous extended materials called metal–organic frameworks (MOFs) can function as sensors that discriminate between different categories of VOCs (DOI: [10.1021/jacs.5b09600](https://doi.org/10.1021/jacs.5b09600)).

Until recently, MOFs conductive enough for quality chemical sensing did not exist. Here the team extends earlier work to develop a conductive MOF by testing its performance as a broad sensor array. By changing the metallic portion of the MOF while maintaining the organic framework, the team creates a device that can discriminate among alkanes, alcohols, ketones, ethers, amines, and aromatic hydrocarbons with 92% accuracy at relatively small perturbations. The result is remarkable for a device comprising only three different MOF materials, which were not designed for specific interactions with functional groups. Rather than a lock-and-key sensing mechanism, this cross-reactive sensor works much more like the human nose.

This work demonstrates the promise of MOF sensors as attractive alternatives to existing technologies based on carbon nanotubes and metal oxide composites. Tuning and development will likely further improve the accuracy and selectivity of these chemi-resistive sensors.

Jenny Morber, Ph.D.

■ PALLADIUM-CATALYZED AEROBIC OXIDATION UNTANGLED

Robert Waymouth, Richard Zare, and colleagues take a mechanistic peek at the fate of transient hydrogen peroxide in the aerobic oxidation of alcohols catalyzed by a common palladium acetate catalyst (DOI: [10.1021/jacs.5b08719](https://doi.org/10.1021/jacs.5b08719)). By examining a number of intermediates in a complex reaction network, the researchers identify a trinuclear palladium species involved in the catalytic pathways for simultaneous oxygen activation and hydrogen peroxide disproportionation.

In addition to standard kinetic techniques, this study heavily relies on *in situ* electrospray ionization mass spectrometry, a valuable and indispensable tool to obtain structural information on reaction intermediates. The method may also prove to be useful for interpreting other complicated catalytic transformations.

Although aerobic oxidation is well-known in organic chemistry, details on oxygen reduction in palladium catalysts for this reaction are largely unexplored. Now, the reaction's mechanistic landscape has been extended to illuminate this vast and hidden aspect. This bigger picture will not only help to develop oxidation catalysts with higher efficiency and better selectivity, but provide further unique insights into biomimetic oxygen binding and activation as well.

Xin Su, Ph.D.

■ ICE ICE, MAYBE

Angelos Michaelides and colleagues use computer simulations to answer what would seem to be a simple question: what makes an ideal ice-forming surface (DOI: [10.1021/jacs.5b08748](https://doi.org/10.1021/jacs.5b08748))?

Water into ice—the change is so familiar it seems there should be little room for mystery, but teasing out the complex interactions at play is tricky. Pure water can supercool as much as 40 degrees below normal freezing temperatures, but in nature ice forms much more easily, thanks to the presence of nucleation-aiding impurities. The process is so fast, and the length scales so small, that nucleation is difficult to quantify experimentally.

Atomistic simulations are a well-suited alternative. The researchers simulate a few thousand water molecules interacting with an idealized impurity, represented as four orientations of a face-centered cubic crystal. The simulation produces “heat maps” of nucleation likelihood across each surface as its atomic spacing changes. Together with other data, these show that optimal lattice mismatch—traditionally regarded as the most important parameter—is not a requirement. Instead, nucleation depends heavily on the formation and nature of surface water overlayers.

These results are first steps toward identifying what makes a good nucleator, and should support basic and applied science in diverse applications that include atmospheric models, ice-inhibiting technologies, and efforts to improve cryopreservation.

Jenny Morber, Ph.D.

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