

Spotlights on Recent JACS Publications

■ QUICK PEEK AT ONE-ELECTRON INTERMEDIATES

Solar-to-fuel generation technologies can use water as a fuel feedstock to convert light energy to fuel. An important step in this process is photoinitiated water oxidation, a heterogeneous catalytic reaction that is electrochemically controlled. The initial reaction step is charge localization into a one-electron intermediate at the surface, a process that had yet to be observed experimentally. Tanja Cuk and her team have now measured the time constant for formation of these radicals at the metal oxide/aqueous interface (DOI: [10.1021/jacs.6b09550](https://doi.org/10.1021/jacs.6b09550)).

Stabilization of the one-electron intermediates plays an important role in the catalyst's ability to facilitate bond formation. Using ultrafast optical spectroscopic techniques, the researchers measure a 1.3 ps time constant for solvation, a force that stabilizes the radical species at the interface. They further propose a kinetic mechanism for producing and stabilizing these radicals. While ground-state characterization of water oxidation catalysts is typically the focus of research, insights from this work on the one-electron intermediates and their surface distribution may facilitate future catalyst design as well.

Dalia Yablon, Ph.D.

■ ASYMMETRIC HYDROGENATION: A MIDAS TOUCH ON OLEFINS

The stereoselective hydrogenation of unfunctionalized olefins is a common and efficient strategy to generate chiral carbon centers in organic synthesis, which is particularly relevant in both industrial applications and academic research. Following a brief historic recount and mechanistic discussions, Cristiana Margarita and Pher Andersson in a recent Perspective review the latest key developments on this topic (DOI: [10.1021/jacs.6b10690](https://doi.org/10.1021/jacs.6b10690)). In addition to iridium-, rhodium-, and palladium-based catalysts with bidentate ligands featuring different binding modes, the authors focus on emerging catalytic systems that use non-precious early transition metals, such as cobalt and iron.

Following a summary of the state of the art in asymmetric olefin hydrogenation, the authors move on to catalogue a number of critical challenges in the field, including the expansion of the current substrate compatibility, the possibility to directly saturate aromatic rings, and regioselective hydrogenation of polyenes. Furthermore, most hydrogenation methods are not able to convert *E/Z* isomer mixtures into single enantiomers. Eventually, the field must evolve to rely on more cost-effective and environmentally friendly Earth-abundant metal-based catalysts.

Xin Su, Ph.D.

■ USING NATURE AS A STEPPING STONE FOR CATALYTIC C–H AMINATION

Cytochrome P450 enzymes, found in all kingdoms of life, have long captured the interest of chemists because of their ability to catalyze challenging C–H bond oxidations. Although protein

engineering has led to variants that catalyze C–H bond amination with high enantioselectivity, a capability largely beyond natural enzymes, these amination reactions suffer from poor chemoselectivity. They usually produce equal amounts of byproducts that result from competing reduction of substrate.

To improve chemoselectivity in engineered P450 enzymes, John Hartwig and co-workers try a new approach: replacing the enzyme's native heme cofactor (Fe-PIX) with an iridium porphyrin cofactor, Ir(Me)-PIX (DOI: [10.1021/jacs.6b11410](https://doi.org/10.1021/jacs.6b11410)). Their experiments show that Ir(Me)-PIX catalyzes the amination of C–H bond in various substrates with high chemoselectivity. As part of their directed evolution to develop variants of the P450 enzyme from an archaeon, the researchers streamline evaluation of these variants by using cell lysates instead of purified enzymes. Their efforts result in a series of artificial metalloenzymes that insert nitrenes into C–H bonds with yields up to 98%, high turnover numbers, and high enantioselectivity. These findings set the stage for the discovery of other enzymes that catalyze challenging aminations of C–H bonds.

Christen Brownlee

■ RHODOPSIN VARIANTS SHOW PROMISE AS NEAR-IR-ACTIVATED PROTON PUMPS

Rhodopsins are a family of light-activated membrane proteins. Their active site contains a photoreactive chromophore known as retinal. In nature, they enable cells to transport ions and sensory signals across their membranes. In the laboratory, scientists are interested in exploiting these transport properties for synthetic biology applications, such as membrane sensors and light-activated biotechnological and optogenetic tools.

In a new report, researchers led by Srividya Ganapathy and Willem de Grip describe a new approach that combines analogues of retinal with site-directed mutagenesis to generate novel rhodopsin proton-pump variants (DOI: [10.1021/jacs.6b11366](https://doi.org/10.1021/jacs.6b11366)). The team demonstrates that a novel retinal analogue can push the light absorption of rhodopsins into the deep red to near infra-red part of the spectrum modifications at specific sites in the protein near the retinal binding pocket and enable tuning the position of the major absorbance band. These novel analogue rhodopsins are the first of their kind to be activated with near-infrared light (>700 nm) and have the potential to open up new applications for light-driven proton pumps.

Christine Herman, Ph.D.

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