JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Spotlights
pubs.acs.org/JACS

Spotlights on Recent *JACS* Publications

ELECTRIFYING NEW APPLICATION FOR METAL–ORGANIC FRAMEWORKS

Metal–organic frameworks (MOFs), a class of crystalline nanoporous materials composed of inorganic "nodes" linked together by organic "struts", have found myriad uses in gas storage, gas separation, and catalysis since their discovery several years ago. More recently, with the development of conductive MOFs, scientists have been pursuing the use of these materials in semiconducting applications. Although conductive MOFs' features—including long-range crystallinity, modulatable pathways for charge transport, tunable electronic band structure, and easy solution processability—make them an attractive component for field-effect transistors (FETs), such devices have yet to be demonstrated.

Jun He, Gang Xu, and co-workers report new FETs that use a MOF as the active channel (DOI: 10.1021/jacs.6b08511). The researchers prepare a high quality conductive MOF thin film, $Ni_3(HITP)_2$, with an air-liquid interfacial growth method, which is then transferred to a SiO_2/Si substrate to fabricate microporous FETs. These devices show high on/off ratios and charge mobilities that rival those of the best performing solution-processed organic or inorganic FETs. The authors suggest that this work could expand MOF applications to include FET-based sensors, voltage-gated ion channels, and microfluidic chips.

Christen Brownlee

β-CARBOLINE AMIDES SELF-DIRECT REMOTE C–H FUNCTIONALIZATION

Site-selective transition metal-catalyzed C–H functionalization reactions are powerful synthetic tools in modern organic chemistry. Selective activation of specific C–H bonds usually requires the introduction of removable directing groups, a disadvantage especially in complex synthetic applications.

Exploring instead the native directing capabilities of substrate functional groups could help to overcome this difficulty. Now, Richmond Sarpong and colleagues find that the β-carboline amide framework can act as an intrinsic directing group to mediate remote palladium-catalyzed C(sp^2)–H alkynylation at the δ-position under mild conditions (DOI: 10.1021/jacs.6b12569). The site-selective C–H activation proceeds via a favorable six-membered palladacycle intermediate, and shows broad substrate compatibility.

As one of only a handful of examples taking advantage of intrinsic directing groups, the reported strategy is highly versatile, capable of other types of δ-C–H functionalization, including alkenylation, arylation, and C–N bond formation. Moreover, β-carboline amides are widely present in natural products and drug candidates, making this new method attractive for natural product synthesis and modification, as well as drug development.

Xin Su, Ph.D.

MAKING A CASE FOR CONTROLLING PROTON TUNNELING DISTANCES IN CATALYSIS

Proton-coupled electron transfer (PCET) is a fundamental reaction involving concerted or stepwise transfer of electrons and protons to/from a substrate, and occurs in biomimetic, organometallic, and enzyme-driven catalysis. Protons tunnel over very short distances, less than 1 Å, and these transfers are difficult to observe or quantitate experimentally. Now, Sascha Ott, Leif Hammarström, and co-workers describe how PCET rate constants change as the proton tunneling distance is systematically varied while keeping other variables nearly constant (DOI: 10.1021/jacs.6b12531).

The authors use transient (time-resolved) optical spectroscopy to measure the kinetics of PCET reactions in a series of custom-designed molecules where the proton tunneling distance from the proton donor (a phenolic oxygen) to the proton acceptor (a quinoline nitrogen) ranges from 0.719 to 1.244 Å. Their results reveal that the PCET rates decrease substantially over the range of proton tunneling distances. Based on these results, proton transfer distance should be considered a criterion in the future design of more efficient catalysts that feature multiple PCET reactions such as water oxidation or proton reduction.

Dalia Yablon, Ph.D.

LEARNING THE TRICKS OF A TUNNELING ENZYME

Scientists have long dreamed of building enzymes that catalyze reactions of their choosing for pharmaceutical or industrial uses. But first, they need to learn the enzymes' tricks. Enzymes use a variety of clever means to speed up chemical reactions; one of the more enigmatic approaches involves quantum tunneling, the breach of a seemingly impassable energetic barrier. Lipoxygenase, for example, catalyzes the dioxygenation of fatty acids by activating the notoriously inert C–H bond via a hydrogen tunneling mechanism. The activation requires the proton donor and acceptor to be no more than 2.7 Å—any farther and tunneling would not be possible. However, due to unsuccessful efforts to crystallize the enzyme–substrate complex, structural details have remained speculative.

Fortunately, lipoxygenase has a metal at its active site, which offers alternate opportunities for structural characterization. Brian Hoffman, Judith Klinman, Sharon Hammes-Schiffer, and colleagues employ electron–nuclear double resonance (ENDOR) spectroscopy, which can detect distances between a paramagnetic metal center and nearby nuclei, to solve the three-dimensional structure of the enzyme's active site (DOI: 10.1021/jacs.6b11856). Using a protocol they developed, it is shown that the distance between the proton donor and acceptor is too far (3.1 Å) for tunneling. Thus, protein movements—or active site compression—must occur during catalysis to bring the proton-acceptor into closer proximity and facilitate hydrogen tunneling.

Erika Gebel Berg, Ph.D.

Published: February 1, 2017

DOI: 10.1021/jacs.7b00784
J. Am. Chem. Soc. 2017, 139, 1345–1345