


Spotlights on Recent JACS Publications

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■ CHEMISTRY AT THE SURFACES OF TOUCHING INSULATORS: THE ROLE OF EXCHANGED CHARGE CARRIERS

The phenomenon of surface electrification upon contact was first described by the Greek philosopher Thales of Miletus around 600 BC. He observed that when amber was rubbed it would attract feathers. Today when we step out of a car in dry weather we often experience electric shocks. It is now understood that two non-conductive materials brought into contact build up electric charges caused by the exchange of electrons and ions from the surface of one material to the other. However, the understanding of how this exchange of charge carriers influences chemical reactions between the two materials, a research area called triboelectrochemistry, remained elusive for a long time.

Jinyang Zhang, Michelle Coote, and Simone Ciampi present a comprehensive overview of how research over the past two decades has improved substantially the understanding of reaction mechanisms at the base of triboelectrochemistry (DOI: [10.1021/jacs.0c11006](https://doi.org/10.1021/jacs.0c11006)). They report advances in the understanding of how the exchange of electrons and ions at the touching surfaces controls the nature of reactions and of reactivity. Their Perspective hints at how a better understanding of these mechanisms can lead to the optimization of electrochemical processes currently used in certain areas of nanotechnology and in semiconductor and photoconductor technologies.

Alexander Helleman

■ THE KEY TO KEEPING THE (AMPHIPHILIC) BALANCE OF THE FORCE

Eukaryotic cells produce a broad spectrum of antimicrobial peptides (AMPs) to keep single-cell organisms like bacteria at bay. These AMPs have inspired scientists to manufacture polymers with similar properties since they are cheaper to synthesize compared to sequence-specific peptides. However, manufacturing an antimicrobial polymer is no easy feat—a polymer too hydrophobic tends to be a weaker antimicrobial, but if it is too hydrophilic it can be toxic to eukaryotic cells. Having an amphiphilic balance is crucial when designing these polymers, but what other factors can affect the biological activity profile?

Edwin Chapman, Samuel Gellman, and colleagues evaluate how the stereochemistry of polymers affects the biological activity profile when the amphiphilic balance is kept constant (DOI: [10.1021/jacs.0c12731](https://doi.org/10.1021/jacs.0c12731)). The group synthesized nylon-3 polymers with ethyl chains in the *cis* and *trans* subunits and observed that it did not improve microbial activity. However,

the synthesized polymers were less disruptive toward eukaryotic cells. The difference in activity suggests that there are other factors in addition to amphiphilic balance to keep in mind when synthesizing the polymers in efforts to improve their specificity and efficacy.

Attabey Rodríguez Benítez

■ NEW PROCESSES TO MAKE GOOD ON THE PROMISE OF HYDROGEN

Hydrogen has long been held up as a cleaner, greener fuel. The potential is chemically obvious: hydrogen combustion produces only water, and hydrogen gas would largely eliminate the negative environmental effects of fuel leaks and incomplete combustion. But hydrogen also brings challenges that have so far kept it from widespread fuel use. Its light weight and easy diffusion make it difficult to store and transport. Less obviously, the industrial production of hydrogen currently involves the steam reforming of natural gas, so that a shift to hydrogen fuel would simply move CO₂ production from automobiles to factories.

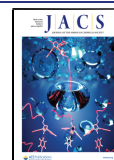
Masahiro Murakami, Naoki Ishida, and co-workers introduce a novel method for reacting H₂ extracted from ethanol with organic substrates by exploiting solar energy (DOI: [10.1021/jacs.0c13332](https://doi.org/10.1021/jacs.0c13332)). Specifically, a bis(azaxanthone) diol that is synthesized from ethanol and an aryl ketone by simple irradiation with sunlight on a rooftop is employed as the H₂ carrier. The resulting sterically hindered vicinal diol then transfers two hydrogen atoms, for example, onto an alkene to form an alkane. The reactions are highly efficient, and the intermediate diol can be stored as a solid at room temperature, opening up possibilities for storage and transfer. From a simple synthesis using a plastic bag on a rooftop, the authors have discovered an expedient and tractable alternative to using H₂ directly in complex hydrogenation reactions.

Kimberly Bolduc

■ CLUES TO CONTROLLING A CATALYTIC INTERMEDIATE'S REACTIVITY

Carbenes are among the most versatile intermediates in homogeneous and heterogeneous catalytic processes. In order

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to be effective, carbene reactivity can be “tamed” by formation of a transition metal carbene complex or by binding to a surface. Chemists led by Elsa Sanchez-Garcia, Wolfram Sander, and Karina Morgenstern have directly imaged a highly reactive carbene on a metal surface for the first time using scanning tunneling microscopy (STM), offering an understanding of pathways to modulate carbene reactivity (DOI: [10.1021/jacs.0c12995](https://doi.org/10.1021/jacs.0c12995)).

They image the chemisorption of a simple aromatic carbene, fluorenylidene (FY), on a Ag(111) surface using low-temperature, ultra-high-vacuum STM. FY exhibits a very strong interaction with the Ag surface that occurs through a partial electron transfer from the surface to the carbene center. This reduces the carbene’s electrophilicity and thus its reactivity. The results suggest that carbene reactivity can be tuned by selecting different metal surfaces with different carbene bond strengths in addition to changing carbene center substituents. These insights into the interplay of the metal surface and carbene present opportunities for the development of new classes of surface metal carbene-based catalytic systems.
Dalia Yablon Ph.D.

■ TOTAL SYNTHESIS OF CEPHANOLIDES A–D THROUGH CHEMICAL NETWORK ANALYSIS

The total synthesis of natural products has played a crucial role in chemical synthesis, providing ground for new methodologies, synthetic strategies, and even new ways of thinking. At the same time, it allows for the evaluation of physical organic theories while demystifying new areas of biology and providing promising candidates for drug discovery. Strategic disconnections are among the most important aspects when developing the total synthesis of an intrinsically intricate molecule. Chemical network analysis is able to provide convenient guidelines for tactfully identifying the most important bonds for this purpose.

Now, Richmond Sarpong and co-workers have developed concise total syntheses of cephanolides A–D from a commercially available indanone, utilizing retrosynthesis guided by chemical network analysis, which was successfully able to identify important and strategic bonds (DOI: [10.1021/jacs.1c00293](https://doi.org/10.1021/jacs.1c00293)). The approach also allows for the rapid construction of the cephanolide skeletal framework by employing a simple cross-coupling followed by an intramolecular inverse-demand Diels–Alder cycloaddition. The researchers were also able to display late-stage oxygenation which allowed for structural diversification, setting the stage for the preparation of other structurally similar natural products.
Aisha N. Bismillah Ph.D.