

Spotlights on Recent JACS Publications

■ AIR/LIQUID INTERFACE SELECTS STEREOCHEMICAL CONFORMATION

Nucleation and growth of aerosols—airborne particulates—are important for understanding weather and enabling climate predictions. Anthropogenic sulfur-based compounds are postulated to play a role in aerosol growth, but new reports show that nonpollutant oxygenated organic molecules are also important species in aerosol chemistry. Glyoxal is one such compound that is thought to catalyze aerosol growth through interfacial chemistry. Using electronic structure calculations and molecular dynamics simulations, Ivan Gladich, Joseph Francisco, and colleagues elucidate the stereochemistry of glyoxal at the liquid water interface (DOI: [10.1021/jacs.6b10208](https://doi.org/10.1021/jacs.6b10208)). Their studies reveal selective solvation of the glyoxal trans conformation resulting in an elevated concentration of the cis isomer at the interface.

With symmetry-breaking capabilities, surfaces and interfaces have long been known to play a role in favoring conformations of certain molecules. The isomerization of the organic compound glyoxal at the air–liquid interface serves as an elegant example of this phenomenon in a reaction important to aerosol chemistry, and the surprising effect of the liquid water interface on glyoxal’s reactivity is likely also applicable to larger molecular species. The influence of interfacial chemistry must be considered as aerosol reactions continue to be mapped for an improved understanding of atmospheric chemistry.

Dalia Yablon, Ph.D.

■ ALLYLBORONS: UPSTARTING SYNTHETIC ORGANIC REAGENTS

Kálmán Szabó and Colin Diner in their recent Perspective review the current status of the preparation and synthetic application of allylic boronates, a versatile family of reagents with increasingly broad scope, especially in the context of asymmetric transformations (DOI: [10.1021/jacs.6b10017](https://doi.org/10.1021/jacs.6b10017)). Compared to conventional organometallic reagents, organoboron species are more chemically stable and thus easier to handle. The authors focus on the catalytic preparation of both achiral linear and highly substituted chiral allylboronates, as well as their applications in chemo-, regio-, and stereoselective allylboration and cross-coupling reactions.

Although allylboronates have shown impressive utility in organic synthesis, and in particular asymmetric synthesis, the authors point out that the direct integration of other functionalities to allylboronates, which could lead to more convenient access to useful intermediates in drug discovery, still requires much attention. Equally important is the development of new catalytic stereoselective reactions involving achiral γ -substituted allylboronates and allylboronic acids to enable shortcuts from simple achiral reagents to densely functionalized synthetic targets with well-defined stereochemistry.

Xin Su, Ph.D.

■ AZOBENZENE MOLECULAR SWITCHES NOW FUELED BY ELECTRONS

Azobenzenes are a simple and widespread family of photochromic compounds that can serve as molecular switches, as they are capable of reversible $E \leftrightarrow Z$ isomerization. Usually, irradiation switches stable E isomers to metastable Z isomers that can thermally return to the E configuration.

In contrast to classic photoswitches, Stefan Hecht, Peter Saalfrank, and co-workers find that, upon electrochemical reduction, Z isomers of azobenzenes undergo significantly accelerated isomerization to E isomers, 13 orders of magnitude faster than normal $Z \rightarrow E$ thermal conversion (DOI: [10.1021/jacs.6b10822](https://doi.org/10.1021/jacs.6b10822)). More interestingly, when an iridium-based photoelectron transfer agent is used, the $Z \rightarrow E$ process becomes photoelectrocatalytic, in which the Z/E ratio at equilibrium under irradiation is dependent on the amount of the photocatalyst.

The researchers establish the general mechanism for electrochemical switching of Z azobenzenes and develop a photoelectrocatalytic strategy to achieve the transformation. Merging photochromism and photoredox catalysis, this platform enables an external and orthogonal control over the molecular system, a previously unattained accomplishment that may be applicable to other photochromic switches.

Xin Su, Ph.D.

■ MOLECULAR MACHINES: MICROMOTORS MADE OF METAL–ORGANIC FRAMEWORKS

The driving force behind years of research on molecular machines has been the desire to mimic the complex transport processes in living cells with synthetic molecules. A key component of a nano/micro-scale machine is the motor, which converts energy into mechanical motion. Among the limitations of previously demonstrated micromotors are the high cost and the lack of tunability for on-demand operations. Now, researchers led by Seth Cohen and Joseph Wang describe a metal–organic framework (MOF) material that can be transformed into a self-propelled, tunable micromotor (DOI: [10.1021/jacs.6b11899](https://doi.org/10.1021/jacs.6b11899)).

The transformation occurs through the incorporation of several different metal-based propulsion systems into the zirconium(IV)-based MOF scaffold, known as UiO-67. The team demonstrates that the propulsion of the micromotors can be tuned by the choice of metal ion, and the chemical “braking” system can be activated through the use of metal-chelating agents that sequester the essential metal ions. Further tunability of the braking system is achieved through the use of different chelators, which each have a unique deceleration capacity. The researchers say that progress in self-propelled micro/nano-machines will lead to advances in several fields, including catalysis, energy storage and conversion, and environmental decontamination.

Christine Herman, Ph.D.

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