

Spotlights on Recent JACS Publications

■ HOW BONDS BREAK IN SINGLE-MOLECULE JUNCTIONS

The breakdown of molecular electronics is often the result of current-induced rupture of chemical bonds. Researchers are interested in improving and controlling the stability of molecular electronics by better understanding how bonds break in molecular junctions, with the ultimate goal of preventing device failure. A new report by Michael Steigerwald, Colin Nuckolls, Pierre Darancet, James Leighton, Latha Venkataraman, and co-workers sheds lights on the mechanism underlying the rupture of silicon–silicon bonds in single-molecule junctions (DOI: [10.1021/jacs.6b10700](https://doi.org/10.1021/jacs.6b10700)).

The team chooses to investigate silicon since it is a vital component of electronics, serving as the active material in fiber optics, transistors, and integrated circuits. They apply a voltage to single-molecule junctions containing two different Si–Si backbones: one has an additional conducting naphthyl group present parallel to the Si–Si bond, and the other has no alternate conductive pathway. The researchers find that the two different junctions have different transport properties when they rupture under the electric field. Theoretical calculations and molecular dynamics simulations reveal that the excitation of vibrational modes in the molecular junction causes bond rupture. This study enhances our understanding of the mechanical and electrical characteristics of silicon–silicon bonds, which may help with future developments in silicon-based molecular devices.

Christine Herman, Ph.D.

■ NEW INSIGHTS INTO THE HYDRATION BEHAVIOR OF POLYMERS

Researchers interested in mimicking the crowded cellular environment *in vitro* commonly utilize aqueous solutions with a high concentration of polyethylene glycol (PEG). As the quintessential “crowder” molecule used for such studies, PEG is one of the most intensively studied synthetic polymers. It is believed to function by being well-hydrated and by being excluded from proteins and other colloids. But in a new study, Minhaeng Cho and colleagues report that even at high PEG concentrations, not all the surrounding water appears to be strongly affected by its presence (DOI: [10.1021/jacs.6b10164](https://doi.org/10.1021/jacs.6b10164)).

The researchers use an analytical technique known as femtosecond mid-IR pump–probe spectroscopy to yield information on water structure and dynamics in the macromolecular crowding environment. The results suggest that there are two distinct subpopulations of water molecules: those that interact with PEG as part of the polymer’s hydration shell and those that interact with other water molecules. Despite significant perturbation of the hydrogen-bonding network of water molecules by the highly crowded environment, the latter group appears to remain “bulk-like”. These results are likely to prompt further investigation into the underlying mechanism of the crowding effect and, more broadly, the hydration behavior of polymers in solution.

Christine Herman, Ph.D.

■ BUILDING THE “LADDER” TO UNDERSTAND LADDERANE LIPIDS

Ladderanes, as the name suggests, have consecutively fused cyclobutane backbones that resemble a ladder, and their lipid forms are produced by anammox bacteria, microbes that can convert nitrite and ammonium to nitrogen. Ladderane lipids may impart a wealth of information regarding membrane composition in anammox, but the study of these lipids has been hampered by a lack of access to pure material.

To circumvent this hurdle, Alejandro Gonzalez-Martinez, Steven Boxer, Noah Burns, and co-workers report the concise total syntheses of [5]-ladderanoic acid and [3]-ladderanol, two lipid tails, as well as their conversion into a full natural ladderane phospholipid (DOI: [10.1021/jacs.6b10706](https://doi.org/10.1021/jacs.6b10706)). Noteworthy in the synthetic strategy is the [2+2] photocycloaddition for quickly assembling the ladderane skeletons with high stereoselectivity. By preparing both enantiomers of [3]-ladderanol, the authors have also determined the absolute configuration of natural [3]-ladderane.

For the first time, a class of highly unusual and structurally complex, naturally occurring membrane hydrocarbons is made accessible via chemical synthesis, enabling further understanding of the biophysical function of ladderane lipid membranes in anammox bacteria.

Xin Su, Ph.D.

■ ODD BINDING MODE OF GOLD(I)

Gold catalysis has gained much popularity in the past decade, and it is widely used for many organic transformations. Catalytically relevant organogold complexes, such as gold hydrides, can help elucidate the unique reactivity of gold catalysts.

Daniela Bezuidenhout and collaborators discover a new class of gold(I)-pincer complexes, in which gold(I) is coordinated in T-shaped geometry to a ligand–heteroligand-type pincer compound consisting of a carbazole core and two side mesoionic carbenes (DOI: [10.1021/jacs.6b11359](https://doi.org/10.1021/jacs.6b11359)). Unlike other known gold(I) complexes, these unusually coordinated gold(I) species are nucleophilic, and can undergo protonation and alkylation with sterically directed chemoselectivity between the metal center and ligand. Interestingly, while the protonation product is characterized as gold(III) hydride, it exhibits protic instead of hydridic reactivity.

These findings make important contributions to understanding organogold chemistry, especially the interconversion between gold(I) and gold(III) oxidation states. The ligand-mediated oxidation of gold(I) to gold(III) can be harnessed to develop new gold-catalyzed reactions, further enriching the scope of gold catalysis.

Xin Su, Ph.D.

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