

Spotlights on Recent JACS Publications

■ LOW- κ MATERIALS: TESTING RESISTANCE TO ELECTRICAL BREAKDOWN

In the semiconductor industry, silicon dioxide (SiO_2) is currently the most widely used insulating material. Low- κ materials, that is, those with a dielectric constant, κ , lower than that of SiO_2 , are advantageous because they permit the use of thinner insulation layers, increasing the packing density of semiconductor components on a chip. However, a lower dielectric constant comes at a price: such materials are more susceptible to breakdown under an electric field.

Latha Venkataraman, Colin Nuckolls, Michael Steigerwald, and co-workers report a new approach to measure the susceptibility to breakdown of low- κ materials by studying the rupture of single molecular junctions when subjected to an electric field (DOI: 10.1021/ja512523r). Using a scanning tunneling microscope with two gold electrodes, they investigate the probability of the breakdown of molecules carrying gold-binding groups at both ends and incorporating Si-C, Si-Si, Ge-Ge, C-C, or Si-O bonds.

They show that covalent bonds to the gold electrodes (Au-S) are much more stable under large electric fields than donor-acceptor bonds. Comparing bonds that occur in low- κ materials, they find that Si-C bonds are more likely to sustain large fields than either Si-Si or Si-O bonds. The work provides a new way to assess the reliability of molecular electronic devices.

Alexander Hellemans

■ NEW POLYMER EXHIBITS HIGH CONDUCTIVITY AND IMPRESSIVE ELECTRODE KINETICS

Organic π -conjugated polymers have come into the spotlight in recent years in the quest to replace the costly, energy-intensive, and sometimes toxic metal-based compounds used in energy applications today. Researchers know that semiconducting polymers with redox activity and electronic conductivity would be excellent candidates for use in energy storage devices, but the creation of devices made entirely from organic materials has lagged since most polymer materials suffer from limitations in electron transport.

Now, Antonio Facchetti, Yan Yao, and colleagues demonstrate that π -conjugated redox polymers exhibit high dopability, high stability, and electronic conductivity (DOI: 10.1021/jacs.5b02290). The team envisions that the polymer P-(NDI2OD-T2), an excellent n-type semiconductor, will combine the high redox activity of non-conjugated redox polymers with the high electronic conductivity of π -conjugated polymers. The researchers evaluate the new material as an organic electrode for rechargeable Li batteries and observe unprecedented electrode kinetics: the fastest charge-discharge capability reported for organic electrode materials for batteries to date. They attribute the polymer's impressive performance to its high electronic conductivity and suggest that π -conjugated redox polymers, when coupled with rational molecular design, may lead to the development of more sustainable energy-related devices, including batteries, supercapacitors, and thermoelectrics.

Christine Herman, Ph.D.

■ DESII REACTION MECHANISM PROBED WITH FLUORINATED ANALOGUES

DesII catalyzes a key step in the synthesis of macrolide antibiotics. The enzyme consumes *S*-adenosyl-L-methionine (SAM) in a deamination reaction required for the formation of TDP-D-desosamine, an unusual sugar that is required to glycosylate the antibiotics. But how this enzyme functions is unclear.

At least two reaction mechanisms have been proposed for DesII, a "1,2-migration" mechanism that mirrors B12-dependent ethanolamine ammonia lyase, and "direct elimination". To differentiate them, Geng-Min Lin and Sei-Hyun Choi in Hung-wen Liu's group have synthesized DesII substrate analogues containing fluorine and deuterium on the C3 carbon—a position that previously has been implicated in the reaction mechanism—and use HPLC and ESI-MS to monitor the fate of these analogues when supplied to DesII (DOI: 10.1021/jacs.5b02545).

The fluorine analogues are not consumed in the resulting reactions, but radical intermediates are formed, as indicated by deuterium exchange between the substrates and SAM. "These results imply that the C3 hydroxyl plays a key role in both reactions—thereby arguing against a 1,2-migration mechanism of deamination—and that homolysis of SAM concomitant with H atom abstraction from the substrate is readily reversible when forward partitioning is inhibited," the authors conclude.

Jeffrey M. Perkel

■ AN UNEXPECTED FINDING ABOUT HIGHLY ORDERED SUPRAMOLECULAR ASSEMBLIES

When it comes to creating supramolecular assemblies—complex chemical structures composed of molecules arranged in a highly organized manner—it seems logical to expect more well-ordered molecular building blocks to yield more highly ordered 3D structures. But researchers led by Virgil Percec have found the opposite to be true (DOI: 10.1021/jacs.5b02147).

In a recent comparative study, the team finds that for at least one class of building blocks, known as dendronized perylene bisimides (PBI), less ordered, twisted, and flexible molecules fare better than more ordered, planar, and rigid ones in the creation of supramolecular structures. The researchers use a variety of analytical techniques, including differential scanning calorimetry, X-ray diffraction, and solid-state NMR, to characterize the structures.

They find the sharpest, most well-resolved signals arise from crystals composed of PBI molecules functionalized with chlorine atoms—a modification that leads to a desirable increase in the molecule's ability to accept electrons, as well as a decrease in rigidity, which the researchers were pleasantly surprised to find is beneficial for creating ordered 3D structures. The new series of structures is of interest for organic electronics, photovoltaics, and other technological applications, the researchers say.

Christine Herman, Ph.D.

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