

Spotlights on Recent JACS Publications

■ CRYSTAL CONTORTIONISTS: MAKING FLEXIBLE ORGANIC CRYSTALS

Organic crystals have a variety of useful characteristics that confer advantages over their inorganic counterparts for applications such as transistors, solar cells, photonics, and bioelectronics. However, the brittle nature of these organic materials significantly limits their use in any device that requires flexibility. C. Malla Reddy and colleagues report a way to engineer organic crystals to make them extremely bendable to the extent that they are able to contort into different letters of the alphabet (DOI: [10.1021/jacs.6b05118](https://doi.org/10.1021/jacs.6b05118)).

The researchers accomplish this logical design by introducing slip planes as artificial layers in the crystal structure. These slip planes are composed of van der Waals functional groups that assemble via shape complementarity, which are supported in other directions by aromatic π -stack groups. This setup of functional groups allows molecular motions with minimal friction between molecular sheets, thus offering impressive mechanical flexibility. Mechanical tests of crystals show that they can bend up to 360° without breaking and could even be molded to the shape of letters of the alphabet. This design principle potentially has broad implication for materials chemistry, especially the concept of using weak van der Waals interactions to achieve flexibility in materials.

Christen Brownlee

■ TAMING RADICALS FOR INNOVATIVE ORGANIC SYNTHESIS

Free radicals are highly reactive species due to their unpaired valence electrons and are therefore less exploited in organic synthesis than their better-behaved ionic counterparts. However, over the past several decades, chemists have started harnessing the power of radicals to develop meaningful and useful reactions. In a recently published Perspective, Phil Baran and co-authors provide an overview of the historical and contemporary contexts of radicals as reactive intermediates for constructing common building blocks and accessing structural complexity (DOI: [10.1021/jacs.6b08856](https://doi.org/10.1021/jacs.6b08856)).

Numerous successful examples of radical chemistry, especially the more recently developed selective and scalable reactions, demonstrate a wealth of synthetic capability. Some of their unique advantages, such as compatibility with reactive functional groups and insensitivity to steric effects, enable radicals to solve conventionally challenging or unworkable problems with ease. With an excellent track record offering efficient solutions for pharmaceuticals, agrochemicals, and organic materials, among others, radical chemistry has gone far beyond complementing ionic chemistry. It not only enriches synthetic methodologies and strategies but also expands known chemical space.

Xin Su, Ph.D.

■ NEW WAY TO TRACK METABOLITES IN LIVING CELLS

Metabolism is a bit of a mystery, due to challenges associated with tracking minute quantities of metabolites in living cells. In vivo magnetic resonance spectroscopy can detect molecules in organisms, but is limited by low sensitivity. One way to bump up the signal is dissolution dynamic nuclear polarization (dDNP), a technique that involves transferring the hefty spin polarization from electrons to neighboring nuclei at low temperatures, boosting signal by a factor of 10,000 to 100,000. Most dDNP studies so far have focused on detecting long-lived nuclear spin species such as ^{13}C or ^{15}N to combat the relaxation issue in this technique. However, ^1H -based detection has great advantages, such as superior resolution in some cases.

Lucio Frydman and colleagues have developed a method to transfer hyperpolarization from ^{13}C to nearby hydrogen atoms, allowing the researchers to monitor metabolic pathways in living cells by ^1H detection (DOI: [10.1021/jacs.6b07483](https://doi.org/10.1021/jacs.6b07483)). They demonstrate the method in both bacteria and yeast cells, following the enzymatic conversions of pyruvate to acetaldehyde and formate. By detecting the hydrogen signal, the researchers can differentiate the starting pyruvate precursor from the carbonyl resonances in the resulting products, a distinction that was not possible with ^{13}C detection.

Erika Gebel Berg, Ph.D.

■ MATERIALS CHEMISTRY: A BIRADICAL BALANCING ACT

In a joint experimental and theoretical study, Michael Haley, Juan Casado, Marina Petrukhina, Masayoshi Nakano, and co-workers provide new insights into the oxidation and reduction states of the diindenoanthracene derivative known as diindeno- $[b,i]$ anthracene (DOI: [10.1021/jacs.6b07882](https://doi.org/10.1021/jacs.6b07882)). The team studies the molecule using various analytical instruments and finds that the structures of the radical cation/anion and dication/dianion states are similar. This feature is attractive for organic electronic applications, since it is known that when molecules undergo large structural reorganization, the change can often hamper electronic performance.

The researchers show that the molecule's quinoidal skeleton has a biradicaloid character that can stabilize both negative and positive charge, accepting and donating electrons reversibly. This quality allows the quinoidal skeleton to serve as the amphoteric redox unit. Understanding how this molecule carries out this biradical balancing act will be of broad interest to the materials chemistry community. The investigation "provides a clearer understanding of the nature of charge carriers in ambipolar organic field-effect transistors," the authors write, adding that future studies will focus on tuning the solid-state packing and device performance of the system.

Christine Herman, Ph.D.

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■ WATCHING A VIRUS GROW UP WITH SOLID-STATE NMR

After budding from infected host cells, HIV-1 must undergo a dramatic structural maturation before it can infect other cells. Scientists hope to halt HIV's spread by developing agents that trap the virus in a juvenile stage. However, the maturation process remains somewhat mysterious. In immature HIV-1, 5000 copies of a protein called Gag form a lattice that lines the viral membrane. During maturation, Gag is cleaved into multiple subunits, which then form a new lattice around the viral RNA. Some HIV-1 medications work by inhibiting the last step of Gag disassembly, an enzymatic cleavage near the junction between the capsid and peptide SP1 subunits (CA-SP1) of Gag.

To figure out how CA-SP1 cleavage jumpstarts maturation, Robert Tycko and colleagues study its structural features in immature and mature lattices with solid-state nuclear magnetic resonance spectroscopy (ssNMR) (DOI: [10.1021/jacs.6b07259](https://doi.org/10.1021/jacs.6b07259)). They find a 16-residue α -helix near the CA-SP1 cleavage site in the immature lattice. However, in the mature lattice, these same residues appear unstructured, according to earlier ssNMR studies by Tatyana Polenova and co-workers (DOI: [10.1021/ja406907h](https://doi.org/10.1021/ja406907h)). The evidence supports the idea that the α -helix acts as a structural linchpin that stabilizes the immature viral lattice. Once cleaved, the virus is free to mature. The findings highlight the utility of ssNMR in studies of viral maturation.

Erika Gebel Berg, Ph.D.

■ AMORPHOUS SILICON COMES TO THE RESCUE OF SOLID-STATE LITHIUM BATTERIES

Lithium-ion batteries power smartphones and laptops, and are being investigated as power sources for electric cars. However, recent lithium battery fires in airliners and smartphones have highlighted dangers associated with formation of lithium dendrites in highly combustible organic electrolytes. One solution to this problem is to replace the liquid electrolyte with a solid-state one, such as garnet, that is not flammable and is resistant enough to impede the formation of lithium dendrites. However, the garnet material does not form a good contact with the lithium anode, resulting in the poor conduction of lithium ions through the contact surface.

Liangbing Hu, Eric Wachsman, and co-workers report that by depositing an ultrathin, 10 nm thick coating of amorphous silicon on the garnet, they can improve conduction drastically (DOI: [10.1021/jacs.6b06777](https://doi.org/10.1021/jacs.6b06777)). Silicon reacts with the lithium surface, forming a silicon–lithium compound that interfaces well with the lithium anode as well as with the garnet, resulting in a 7-fold decrease of the interfacial resistance between the solid-state electrolyte and the lithium anode. Because the amorphous silicon layer can be created with plasma-enhanced chemical vapor deposition, a well-developed technique in the semiconductor industry, the future of all-solid-state and safe lithium batteries is promising.

Alexander Hellems