

Spotlights on Recent JACS Publications

■ FAR-REACHING EFFECTS OF INFRARED LIGHT EXCITATION

When infrared light shines on a molecule, its energy is absorbed. Release of this excess energy can change the molecule's conformation. This phenomenon, known as IR-induced conformational isomerization, has been observed numerous times since its discovery more than 50 years ago. In those demonstrations, however, interconversion between two conformational states results from excitation of a molecular fragment located nearby the so-called isomerization coordinate. Now, Igor Reva and colleagues report the first experimental observation of a conformational switching event induced by the excitation of a moiety located far away from the isomerizable group (DOI: [10.1021/jacs.5b08588](https://doi.org/10.1021/jacs.5b08588)).

The molecule, known as 6-methoxyindole, exists in two conformations, *syn* and *anti*, differing only in the orientation of the methoxy group. Excitation with near-IR light tuned to the NH bond stretching of a chosen conformer results in conformational switch. Essentially, activation of one end of the molecule results in a "reaction" at the other end—a phenomenon that could open up the possibility of manipulating the conformational distribution of a variety of molecular systems. This study helps expand the understanding of intramolecular vibrational energy transfer, which is important in the study of sunlight-driven atmospheric photochemistry.
Christine Herman, Ph.D.

■ ONE STEP CLOSER TO DNA-BASED SMART MATERIALS

One of the major goals of nanotechnology is to create smart materials based on nanoscale structures capable of performing tasks in response to external stimuli. Now, researchers led by Robert Häner have made progress toward this goal with the development of a new class of DNA-grafted supramolecular polymers (DOI: [10.1021/jacs.5b09889](https://doi.org/10.1021/jacs.5b09889)).

The team creates the supramolecular polymers by attaching DNA strands to pyrene-based helical polymers. In the presence of complementary DNA strands, these chimeric oligomers self-assemble into nanosized ribbons that further associate with one another to form an extended supramolecular network. The researchers use spectroscopic methods to monitor the stepwise formation of the network. First, aromatic stacking interactions among pyrene units drive the formation of helical nanoribbons, and then individual nanoribbons aggregate into the extended networks via coaxial stacking of terminal GC base pairs. They also demonstrate the ability to use external stimuli—heat or the addition of another DNA strand—to disassemble the network.

Supramolecular polymeric networks such as these may lead to the development of "DNA-based smart materials, such as stimuli-responsive carriers of biologically active agents," the researchers write.

Christine Herman, Ph.D.

■ EXCITED MOLECULE REVEALS FIRST STEPWISE MULTIPLE PROTON TRANSFER

Researchers have built a molecule that shows, for the first time, a distinct stepwise double proton transfer in the excited state (DOI: [10.1021/jacs.5b08562](https://doi.org/10.1021/jacs.5b08562)).

Proton transfer is common in biological systems. It often involves moving multiple protons in an excited molecule across hydrogen bond bridges in the structure. However, the mechanism of this movement—simultaneous proton transfer versus stepwise relocation—has been difficult to study because the structures of the hydrogen-bonded intermediates can be ill-defined, particularly when solvent molecules are also involved.

To understand multiple proton transfer more clearly, Pi-Tai Chou, Wei-Ping Hu, and their colleagues have built 1,8-dihydroxy-2-naphthaldehyde. Ultrafast optical spectroscopy in cyclohexane, along with computational models of this molecule, shows two distinct emission states corresponding to first and second isomers, indicating a stepwise mechanism of proton transfer.

The naphthaldehyde molecule provides new insight into transfer of multiple protons in biological systems, as previous attempts to study multiple proton transfers with specially designed molecules could not clearly identify the transfer mechanism.

Melissae Fellet, Ph.D.

■ NEW CLASS OF RUGGED, SHAPE-CHANGING THERMOSETS

When it comes to thermosetting polymers, mechanical strength usually comes at the expense of malleability, and vice versa. Yet for many applications, the ideal material is both strong and capable of reshaping or repair. Researchers led by William Dichtel have taken a significant step toward the development of such materials with the discovery of a new class of thermosetting networks that exhibits these seemingly paradoxical properties (DOI: [10.1021/jacs.5b08084](https://doi.org/10.1021/jacs.5b08084)).

The polymer network, composed of polyhydroxyurethanes (PHUs), belongs to a family of dynamic, cross-linked polymers known as vitrimers, which owe their properties to associative exchange processes that occur at elevated temperatures to enable broken bonds to be re-formed. This process is typically facilitated by catalysts that have been embedded into the polymer network. Combining experimental and theoretical tools, the researchers have found that even without the presence of an external catalyst, the PHU vitrimers can be molded into various shapes at high temperatures. After reprocessing, the materials recover roughly 75% of their original mechanical strength, making PHU vitrimers a promising new class of mechanically tough yet repairable polymer networks.

Christine Herman, Ph.D.

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