

Spotlights on Recent JACS Publications

■ COMPLEX ZEOLITE FORMATION UNTANGLED

Zeolites are microporous, crystalline aluminosilicate frameworks widely used as industrial adsorbents, ion exchangers, and catalysts. Despite their widespread use and the large diversity of structures formed, scientists have yet to fully understand the mechanism by which these structures nucleate and grow. Some researchers believe that small, discrete secondary building units found in the final zeolite structure start the growth process. However, this belief is controversial, and chemists have not completely deciphered the complicated nucleation process.

Using the charge density mismatch approach designed to foster structure-directing agent cooperation, Suk Bong Hong and co-workers discern the crystallization mechanism of UZM-9LS, a high-silica version of the commercial Zeolite-A (LTA) (DOI: 10.1021/ja309831e). They find that the largest cages, called *lta*, are formed first, before aluminosilicate species from solution add to form the smaller *sod* and then *d4r*-type cages. By following the incorporation of tetraethylammonium (TEA⁺), tetramethylammonium (TMA⁺), and sodium ions into product, they find that Na⁺ and TMA⁺ guide the preliminary condensation and nucleation before TEA⁺ and increasing silicon content are integrated into the zeolite. This study offers valuable and exceptional insights into the mechanisms behind the formation of this and other industrially important zeolite structures. **Leigh Krietsch Boerner, Ph.D.**

■ BIEXCITON DECAY MEASUREMENTS CHALLENGE ASSUMPTIONS

When a semiconductor absorbs light, an electron enters an energetic state called an exciton. When two excitons are created within a single nanoparticle (a biexciton), the two excitons overlap strongly, and one of the excitons is rapidly annihilated. The short lifetime of a biexciton is a limitation in many optoelectronic applications. However, biexciton decay is difficult to measure because of interference from other species created by the light.

Mark A. Berg and colleagues use a technique called multiple population-period transient spectroscopy, or MUPPETS, to measure biexciton decays in CdSe/ZnS core-shell nanoparticles, free from these interferences (DOI: 10.1021/ja3112109). In traditional measurements, one light pulse creates excitons, biexcitons, and other species, and a second, later pulse measures the surviving species. MUPPETS uses a sequence of six light pulses that causes the signal from the biexciton to become negative. Subtracting the MUPPETS and two-pulse measurements cancels the interfering signals but leaves the biexciton signal. Although generally accepted mechanisms assume a single biexciton decay rate, here a range of rates is found. These measurements lay a foundation for future discoveries using MUPPETS with semiconductors, conjugated polymers, and other exciton-forming materials, and they challenge currently accepted ideas on how biexcitons decay. **Jenny Morber, Ph.D.**

■ ORGANIC ALLOY SOLAR CELLS ARE VOLTAGE CHAMELEONS

In solar cells, the open-circuit voltage is an important property, because it represents the maximum amount of voltage a solar cell can provide to power an external device. Therefore, being able to control this voltage allows chemists to synthesize a variety of solar cells for different purposes. Inorganic alloy solar cells have been known to change their open-circuit voltage depending on the respective composition of the alloy components. However, this characteristic has only been seen in the more expensive metal-based alloys and not cheaper, readily available materials.

Now Barry Thompson and co-workers replicate this result with organic solar cells containing a combination of polythiophene electron donors and fullerene acceptors (DOI: 10.1021/ja3112143). When they shine light on their cells, the researchers find that the HOMO and LUMO levels change based on the composition of the organic alloy. However, the light energy these solar cells absorb remains constant, based on the individual molecular components, and does not change with the ratio of the components within the cell. Substituting carbon-based materials will effectively bring the price of future solar cells down, while simultaneously making them more efficient. This work represents a solid step toward realistic alternative energy devices. **Leigh Krietsch Boerner, Ph.D.**

■ SCIENTISTS CLOCK THE SPEED OF FLOPPY PROTEINS

Most of what scientists know about proteins comes from studying classic folded proteins, but the recently recognized intrinsically disordered proteins (IDPs) may follow a different set of rules. These dynamic proteins are widespread and frequently act as signaling molecules. For example, the p53 upregulated modulator of apoptosis (PUMA) is an unstructured protein that promotes cell death upon binding to folded members of the Bcl-2 family, such as Mcl-1. Researchers are developing novel chemotherapies with peptides that mimic a disordered region of PUMA and bind Bcl-2 proteins, promoting apoptosis in cancer cells.

Understanding the kinetics of binding is critical for optimizing the efficacy and duration of action for drug candidates, but little is known about the kinetics of IDP binding. Jan Clarke and colleagues at the University of Cambridge measure the kinetics of binding between PUMA and Mcl-1 with standard stopped-flow techniques, varying solvent conditions and temperature, and determine the association rate constants (DOI: 10.1021/ja309527h). They find that the reaction between PUMA and Mcl-1 is not "diffusion-limited", meaning it does not proceed at the maximum possible rate. The researchers conclude that some standard kinetic tests may not be appropriate for IDPs and that the reaction does not necessarily proceed through an induced fit mechanism, whereby the disordered chains fold upon

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contact with a binding partner. More research is needed to determine the mechanism of binding. **Erika Gebel, Ph.D.**

■ MICROPARTICLES GATHER AND DISPERSE ON COMMAND

A new microparticle system, developed by Ayusman Sen and co-workers, is capable of responding collectively and reversibly to external stimuli, representing the first example of micromotors based on a nonredox chemical equilibrium shift (DOI: 10.1021/ja3120357).

Researchers are interested in using micro- and nanomotors capable of behaving collectively and cooperatively for applications in the fields of drug delivery, chemical sensing, particle assembly, and micro-robotics. The team finds the Ag_3PO_4 microparticles can be coaxed into reversibly clustering or dispersing by the removal or addition of NH_3 . Hierarchical particle clustering is observed when other inert particles are also present. Upon the addition of NH_3 , large Ag_3PO_4 microparticles function as pumps, pushing away inert particles from their vicinity. The authors also find that the transition from dispersion to clustering can be halted with UV light. By combining the two external stimuli, they demonstrate that micromotors can be used as logic gates, which suggests their potential for applications in computations.

While there are many examples in the literature of micro- and nanomotors that respond individually to various stimuli, this study is one of the few to demonstrate synthetic motors that respond collectively, presenting new principles for micromotor design. **Christine Herman, Ph.D.**