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Spotlights on Recent *JACS* Publications

CHEMICAL CONTROL OVER PEROVSKITE EXPANSION AND CONTRACTION

Most materials expand when they are heated, but a few do the opposite as a result of certain kinds of atomic vibrations. One use for these so-called negative thermal expansion (NTE) materials is in compensating for positive expansion within mechanically stable hybrids. Thermo-mechanical stability can be important in applications such as tooth fillings and high-precision optical and electronic components. Ideally, researchers would like to be able to precisely dial-in the material's thermal response, but in these complex systems fine control has been elusive.

Mark Senn and colleagues demonstrate that a perovskite crystalline material can switch from positive to negative thermal expansion as a function of the relative amounts of its calcium and strontium atoms (DOI: 10.1021/jacs.5b13192). The researchers' experiments and analyses reveal that this switching results from two competing crystallographic phases with different symmetries. The result confirms that it is possible to switch on, switch off, or tune a material's NTE by controlling competing phases.

The work points to unprecedented chemical control over mechanical response to heat in the perovskite discussed here and other NTE compounds. Looking ahead, the authors predict that researchers will be able to use chemical control to design and dial-in thermo-mechanical and other related properties in a host of hybrid materials.

Jenny Morber, Ph.D.

BACTERIA MANIPULATE THEIR PREDATORS THROUGH CHEMISTRY

A few years ago researchers discovered that when the single-celled choanoflagellate *Salpingoeca rosetta* detects a particular sulfanolipid produced by the bacteria *Algoriphagus machipongonensis*, *S. rosetta* begins an incomplete type of cell division and forms multicellular rosettes (http://elifesciences.org/content/1/e00013). The researchers, led by Nicole King and Jon Clardy, hypothesized that *S. rosetta* uses the sulfonolipid as a signal of sufficient bacterial density that justifies transformation into a multicellular life stage.

Choanoflagellates are eukaryotic and are considered the nearest living relative of animals, so researchers use them to explore questions of how animals evolved and how they interact with single-cell life. After searching the bacteria for other potential signaling molecules, the King and Clardy team now reports that the bacteria are not just passive victims: *A. machipongonensis* produces another sulfonolipid that inhibits rosette formation, perhaps protecting the bacteria from the more voracious predation by the rosette form of *S. rosetta* (DOI: 10.1021/jacs.6b01190).

The researchers have also synthesized the molecule and some inactive isomers, which they argue could be useful for conducting experiments that require promoting or inhibiting rosette formation.

Lucas Laursen

HEAT AND DISORDER OF PROTEIN–LIPID BINDING

Many life processes are governed by interactions between proteins and ligands, which are in turn ruled by thermodynamics. Scientists routinely assess binding thermodynamics of protein systems—the free energy, entropy, and enthalpy that drive a binding reaction—but experimental limitations have left the thermodynamics of protein–lipid interactions in cellular membranes poorly understood. To address these limitations, researchers led by Arthur Laganowsky have developed an approach to thermodynamic analysis using native mass spectrometry, which, unlike conventional mass spectrometry, leaves non-covalent interactions, like many of those between membrane proteins and their neighboring lipids, intact (DOI: 10.1021/jacs.6b01771).

The researchers first establish that their native mass spectrometry method works by measuring thermodynamic quantities in three well-characterized protein–ligand systems and comparing these values against those obtained using more conventional thermodynamics methods. Reassured by the similar results, the researchers next tackle a particularly intractable system: the binding of a bacterial ammonia channel with membrane lipids. In a series of native mass spectrometry experiments, they mix the channel with different lipids, varying headgroup and chain length. Each lipid–channel combination produces a distinct thermodynamic signature. For example, lipids with longer chain lengths have decreased binding enthalpy. The researchers also mutate a specific lipid-binding site within the channel, which generates a distinct thermodynamic signature as well, offering the possibility of mapping key binding residues.

Erika Gebel Berg, Ph.D.

SPOTTING SINGLE-NUCLEOTIDE DIFFERENCES IN RNA AND DNA

Nucleic acids are composed of subunits called nucleotides, and a single nucleotide alteration between two otherwise identical nucleic acid strands can have dramatic effects. Single-point differences exist naturally in living organisms, but researchers often grapple with the problem of detecting these single-site mutations.

Now Sherry Xi Chen and Georg Seelig have devised a system to find those single-site differences (DOI: 10.1021/jacs.6b00277). The system builds on a well-established sensing method that uses DNA complexes modified with a fluorophore, which is active when fully complementary strands pair, and a quencher, which blocks the signal when single nucleotide variations are present. In addition to this specificity, the new system is also highly sensitive because it incorporates a catalytic amplification mechanism. This amplification further increases the specificity as well.

Chen and Seelig test their system on an important group of human nucleic acids, the let-7 microRNA family. They

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demonstrate that their system can distinguish among three members of the let-7 family that differ from each other by a single nucleotide. The authors say that their system will help measurably advance biotechnology applications.
Rajendrani Mukhopadhyay, Ph.D.

DIFLUORINATION OF UNACTIVATED ALKENES TACKLED WITH COMMERCIAL CATALYSTS

The polarization of a carbon−fluorine bond, coupled with the small atomic radius of fluorine, produces electronic and steric effects that influence a molecule's conformation. Hence, adding fluorine to a molecule is one way to control the structure of new catalysts, materials, and tools for chemical biology.

Many ways have been developed to insert fluorine into a molecule, but addition of fluorine across an unactivated alkene in a catalytic process has not yet been achieved. Now, two groups have concurrently tackled and report solutions to this challenge. István Gábor Molnár and Ryan Gilmour use *para*-iodotoluene as a catalyst with commercially available Selectfluor as the fluorine source (DOI: 10.1021/jacs.6b01183). Eric Jacobsen and colleagues address the problem using the same and alternative iodoarene catalysts together with pyridine·9HF as the nucleophilic fluoride source (DOI: 10.1021/jacs.6b02391). In both cases, the room temperature reactions tolerate a variety of functional groups on the alkene-containing substrates. And when the researchers utilize a chiral catalyst, the reactions yield products with moderate to good enantioselectivity.

In view of the importance of fluorine in medicinal chemistry, this strategy to introduce two neighboring fluorine atoms in a single step is exciting. The possibility for enantioselective difluorination using these new reactions is unique.
Melissae Fellet, Ph.D.

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