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Spotlights

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Spotlights on Recent *JACS* Publications

PROTEIN SELECTIVELY REDUCES WHAT METAL CATALYSTS COULD NOT

Axially chiral molecules often serve as chirality tests in circular dichroism spectroscopy. One example, cyclohexane with a hydroxyl group across the ring from an exocyclic olefinic moiety, is also a useful precursor to enantiomerically pure liquid crystals. The question remains of how to build such a molecule. Transition metal catalysts fail in the enantioselective reduction of 4-alkylidene cyclohexanones because such molecules lack the required structural environment around the ketone function.

Now Manfred Reetz and co-workers have found an enzyme—a heat-stable alcohol dehydrogenase—to do the job (DOI: 10.1021/ja3092517). They mutate this bacterial protein using directed evolution to create enzymes that produce the *R*- and *S*-enantiomers of various olefin-substituted substrates with high selectivity.

The original enzyme from bacteria *Thermoethanolicus brockii* is heat-stable and tolerates organic solvents. Those properties make it and the evolved mutants potentially useful industrial biocatalysts. The chiral molecules produced by the new biocatalysts are also interesting synthetic building blocks. **Melissae Fellet, Ph.D.**

A STEP TOWARD THE RATIONAL DESIGN OF LIQUID CRYSTALLINE INTERLOCKED MOLECULES

A new study led by Stephen J. Loeb and S. Holger Eichhorn sheds light on the structure–property relationships of a class of mechanically interlocking molecules (MIMs) known as rotaxanes (DOI: 10.1021/ja309558p). Their findings may help lead to the rational design of MIMs with liquid crystalline properties for incorporation into materials that are responsive to chemical stimuli.

Liquid crystals, composed of self-organized molecules that contain a rigid moiety—or mesogen—flanked by flexible side chains, are mesomorphic, exhibiting properties of both conventional liquids and solid crystals. MIMs are candidates for inclusion into mesogens in liquid crystals because of their size, complex nature, and often ionic character. Yet although several examples of liquid crystalline materials made of MIMs exist in the literature, researchers are far from being able to rationally design and tune the properties of liquid crystalline interlocked materials.

The research team prepares two types of liquid crystalline rotaxane molecules and finds that sheltering the ionic core affects the material's thermal stability and mesomorphism. They also examine the effect of the nature of the side chains, size, and the number of charges in the ionic core. This study provides a general blueprint for the design of polyionic rotaxanes that form liquid crystal phases. **Christine Herman, Ph.D.**

NEWLY EQUIPPED NUCLEIC ACIDS

Nucleic acids can be exploited to act as receptors and catalysts with therapeutic and diagnostic applications through modification with synthetic functional groups. Current methods for modifying nucleic acids using DNA and RNA polymerases can bestow only relatively few functional groups—four in single-stranded DNA and eight in double-stranded DNA. The methods also require the functional groups' composition to be compatible with the active site of the polymerase.

Now David Liu and colleagues have found a way to increase the number and variety of functional groups that can be added to modify DNA or RNA (DOI: 10.1021/ja311331m). Inspired by the three-nucleotide coding system that translates messenger RNA to proteins in ribosomes, the researchers create trinucleotide substrates that each bear a different artificial functional group. Then they use T4 DNA ligase, an enzyme that joins together complementary strands of DNA, to polymerize these building blocks using a template DNA sequence. The method efficiently produces polymers 150 nucleotides in length bearing functional groups including a fluorinated thiourea, a metal chelator, and pyrene.

The method can be used to iteratively select and amplify these biopolymers at high throughput, the researchers show, indicating its promise for producing nucleic acids with novel applications. **Deirdre Lockwood**

UNDERSTANDING ENERGY TRANSFER IN π-CONJUGATED POLYMERS

The process of energy transfer within conjugated polymers is more dynamic than once believed. Researchers led by Jan Vogelsang use single-molecule spectroscopy to study energy transfer between chromophores in a π-conjugated polymer model system and find that even when chromophores are chemically identical, the excitation energy does not have a fixed path but rather travels randomly throughout a three-dimensional network of temporary "highways" (DOI: 10.1021/ja3108643).

Fluorescence resonance energy transfer, in which excitation energy migrates from the site of a fluorophore to a nearby quencher, depends on a process known as inter-chromophore coupling. The researchers prepare a pair of π-conjugated oligomer dimers to serve as a model system for larger, more complicated conjugated polymer systems. They examine the effect of geometry and conformation on the photon statistics, quantum yield, and energy-transfer dynamics.

The knowledge gained through this study may help researchers develop more efficient solar cells, improved organic light-emitting diodes for use in digital displays, and conjugated polymer materials for sensing applications. **Christine Herman, Ph.D.**

LEAD–ANTIMONY–TELLURIDE MATERIALS STABLE IN NANO, NOT BULK

When materials shrink toward the nanoscale, their physical properties change. This tunable nature from the variation of size, shape, and metal composition is why crystalline nanoparticles can be used for important technologies including biological imaging, optoelectronics, and photovoltaics. In the

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past, much of the research has focused on simple binary nanocrystals. However, materials that contain more metals are more complex and less understood. These ternary and quaternary nanocrystals may have unique new properties.

Now Mercouri Kanatzidis and co-workers have discovered a new solution-phase synthesis of rock-salt-type lead—antimony—telluride nanocrystals (DOI: 10.1021/ja309626q). These materials can be created on the nanoscale only and have no bulk scale analogues. The $Pb_mSb_{2n}Te_{m+3n}$ nanocrystals vary little in size and absorb in the middle of the infrared spectrum. Through pair distribution function analysis, the researchers find that the local structure is distorted with respect to the rock-salt structure, and that these deformations depend on the proportions of the Sb/Pb ratio. This represents a new class of nanomaterials, and lends credence to the practice of synthesizing materials that are unstable on the macroscale, the opposite of the accepted practice of creating nanoscale analogues of known bulk materials.

Leigh Krietsch Boerner, Ph.D.