

Spotlights on Recent JACS Publications

■ FACILE APPROACH TO ENANTIOPURE HELICENES OVERCOMES LONG-STANDING CHALLENGE

Helicity is used to describe chiral molecules with helical, propeller, or screw-shaped geometry in the structures. It plays an important role in various fields of science, including biology, catalysis, material science, and nanoscience. Helicenes—helically chiral polyaromatics with angularly fused, overcrowded benzene rings—are perfect examples of helicity. However, their exotic geometry makes them extremely difficult targets for stereoselective synthesis, which has been one of the most challenging problems of helicene chemistry for more than half a century since their first discovery.

Now, a team led by Irena G. Stará and Ivo Starý has discovered how to prepare helicenes with full stereocontrol instead of resorting to chiral chromatography (DOI: 10.1021/jacs.5b02794). Combining biocatalysis and transition metal catalysis, the researchers can make enantiopure aromatic helicenes from simple starting materials, through cycloisomerization of chiral triynes followed by asymmetric transformation controlled by 1,3-allylic-type strain. This “point-to-helical” chirality transfer strategy elegantly addresses the long-standing synthetic challenge. As a general and facile approach to enantiopure helicenes, it opens a range of opportunities for developing helicene-based catalysts and materials.

Xin Su, Ph.D.

■ NEW CHEMISTRY YIELDS SYNTHETIC POLYMERS WITH HIGHLY CONTROLLED SEQUENCES

Craig Hawker and Will Gutekunst describe a new approach to creating sequence-controlled synthetic polymers that brings together several recent important advances in the field (DOI: 10.1021/jacs.5b04940). Their new method combines a technique known as ring opening metathesis polymerization and a step-growth approach that yields periodic polymers from preformed sequences.

Over the years, numerous techniques have been developed for stringing together molecules in a controlled manner. But the job of creating large, elaborate polymers with well-defined sequences is easier said than done. Each synthetic approach has its limitations: Some are able to yield precisely sequenced polymers but are time-intensive, while others enable rapid generation of elaborate polymers but lack control over molecular weight distribution or sequence precision.

Here, the team has developed a small molecule “polymerization trigger” that can be incorporated into unstrained macrocyclic monomers. Once the trigger is activated, the macrocycles polymerize as the result of an intramolecular ring opening reaction. The researchers demonstrate the incorporation of a variety of functional groups without compromising control over molecular weight and molecular weight distribution. Next, they plan to further develop the technique toward the generation of new functional materials for applications in areas such as catalysis and drug delivery.

Christine Herman, Ph.D.

■ NEW METAL–ORGANIC FRAMEWORK PACKS A PROTON-CONDUCTING PUNCH

George K. H. Shimizu and colleagues have synthesized a metal–organic framework (MOF) with excellent proton conductivity and stability in water (DOI: 10.1021/jacs.5b04399). These properties could be exploited in the development of cheaper fuel cells.

To make fuel cells more cost competitive as an alternative energy technology, researchers are on the hunt for more efficient electrolyte materials. MOFs are a promising new electrolyte option: they can conduct protons and are easily tailored for specific applications. But few MOFs conduct protons efficiently enough to meet the benchmark of 10^{-2} S·cm⁻¹ that is thought to be required for translation into fuel cell components. Even those materials that meet this threshold often do not form robust enough hydrogen-bonding networks to ensure stability in water, which is required for operation below 100 °C.

Now Shimizu and co-workers have developed a magnesium carboxyphosphonate framework with a two-dimensional grid-like structure and very high proton conductivity of 3.55×10^{-2} S·cm⁻¹. Magnesium phosphonate bonding fosters a strong hydrogen-bonding network with water molecules, so that the framework retains its structure and resists swelling when immersed in water. This manuscript reports key advances, but to pioneer new fuel cell approaches critical developments still need to be made in terms of mechanical strength of the membrane and manufacture of optimal membrane electrode assemblies, the authors say.

Deirdre Lockwood, Ph.D.

■ A TRANSIENT WATER FINGER SLOWS ION TRANSFER THROUGH WATER–OIL INTERFACES

Nobuaki Kikkawa, Lingjian Wang, and Akihiro Morita have performed molecular dynamics simulations of ion transport through the interface between two immiscible electrolyte solutions—water and dichloromethane. Their approach reveals a hidden barrier to the passage of ions through the interface caused by the formation of a water finger that affects the rate of interfacial ion transfer (DOI: 10.1021/jacs.5b04375).

Experimental methods for studying the dynamics of liquid–liquid interfaces at a microscopic level are limited, and during the past two decades researchers have developed molecular dynamics simulations to study structural fluctuations at liquid–liquid interfaces associated with ion transfer. Using these simulations, Ilan Benjamin reported in 1993 the formation of a “water finger” by an ion passing through a water–oil interface (DOI: 10.1126/science.261.5128.1558). However, these approaches do not allow quantification of the “coordinate”, that is, a measure for the length, of the transient water finger trailed by the moving ion.

Using computations of the free energy surface during the passage of the ion from the water phase into the organic phase,

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the authors can now demonstrate the formation and breakage of a water finger. This finding explains why the observed rate of ion transfer differs from computations of this rate based on diffusion alone.

Alexander Hellemans

■ ORIGIN OF AQUEOUS MALONALDEHYDE'S ULTRAVIOLET ABSORPTION

Malonaldehyde (MA), the simplest β -diketo compound, has long been used to study and predict the chemical and photochemical properties of more complex β -diketos. MA predominantly exists in the enol rather than the keto form, and its conformational equilibrium in solution remains a topic of active research and intense debate.

Using a combined static and dynamical theoretical approach, Xuefei Xu, Jingjing Zheng, and Donald G. Truhlar calculate the solvent effect on conformational populations of neutral undeprotonated MA in water, as well as its ultraviolet (UV) absorption spectra (DOI: 10.1021/jacs.5b04845). Through conformational analysis with a solvation model, the authors find that two solvent-stabilized conformers are the dominant species as a result of more favored intermolecular hydrogen bonding with water. These two species account for the UV absorption spectrum of MA, rather than the anticipated internally hydrogen-bonded all-*cis* conformer.

In this study, the authors recognize the solvent effect on conformational equilibria as an important contributing factor to solvatochromism that has been overlooked in the current standard treatments. Furthermore, the work is an excellent example demonstrating the proficiency of quantum chemical analysis, where calculations provide otherwise unavailable details for proper interpretations of experimental data.

Xin Su, Ph.D.