

Spotlights on Recent JACS Publications

■ “DOUBLE-SHOT” DIENES FOR CASCADE CYCLOADDITIONS

Cycloadditions, particularly well-choreographed consecutive cycloadditions, are straightforward and valuable synthetic tools for creating multiple carbon–carbon bonds as well as complex molecular frameworks with high synthetic economy. These reaction cascades are accessible through reagents that enable back-to-back cycloadditions.

Tetramethyleneethane diradical (TME) has been envisioned to play such a role in making [4.4.0]bicycles—a common structural feature in natural products, materials, and imaging agents—but TME is unstable and difficult to make. Now, Paul Wender and co-workers design and prepare a simple and stable TME equivalent (DOI: 10.1021/jacs.5b04091). 2,3-Dimethylene-4-trimethylsilylbutan-1-ol (DMTB) can couple with diverse dienophiles via a first Diels–Alder or metal-catalyzed [4+2] cycloaddition; the key that unlocks the cascading reaction pathway is the subsequent in situ generation of a new diene that undergoes a second cycloaddition.

Using this new strategy, the authors synthesize an anthralimide-based high-performance solvatochromic dye in three steps in good overall yield, where the [4.4.0]bicyclic scaffold is assembled in one flask without intermediate purification. This reaction provides a one-step solution for the synthesis of natural products and pharmaceutical compounds featuring such bicyclic or polycyclic ring systems. Its future scope can be vastly expanded by introducing heterodienophiles and integrating with other cascade reactions.

Xin Su, Ph.D.

■ PROTON–ELECTRON TRANSFER: A KEY TO UNDERSTANDING COMPLEX REACTION MECHANISMS

The coupled movement of protons and electrons—so-called “proton-coupled electron transfer” (PCET)—is an important mechanism in a large number of chemical and biochemical reactions. Such PCET reactions play essential roles in biological processes, such as photosynthesis and respiration, and in solar cells, hydrogen production, and other energy devices.

Sharon Hammes-Schiffer, in her recent *JACS* Perspective, illustrates the fundamental theoretical concepts and physical principles of PCET (DOI: 10.1021/jacs.5b04087). She also describes examples of more complex PCET reactions for which theoretical calculations and computer simulations applying these concepts and principles, combined with experimental approaches, have led to a better understanding of the mechanisms.

In many cases, these calculations and simulations have assisted in the interpretation and understanding of experimental results and have provided experimentally testable predictions. Examples include the catalytic action of the enzyme soybean lipoxygenase, electrochemical processes involving molecular electrocatalysts, the behavior of biomimetic catalysts, and the dynamics of photoinduced PCET reactions that are relevant to solar cells. Challenges still exist, however, and further fine-tuning of theories, simulations, and experiments will help to advance researchers’

understanding of PCET in important chemical and biochemical systems.

Alexander Hellemans

■ GREEN SYNTHESIS OF ARYL IODIDES

Researchers in Canada have designed a light-induced reaction for the efficient synthesis of aryl iodides. Aryl iodides are common building blocks for organometallic and aromatic cross-coupling reactions in organic synthesis. These molecules, when they carry radioactive iodides, are also used in medical imaging. Despite their utility, aryl iodides are hard to produce in high yields. Their synthesis can also involve stoichiometric amounts of metal reactants that are environmentally undesirable, although important progress has been made to use transition metals to catalyze such transformations.

A classic metal-free reaction produces alkyl iodides from a heated mixture of sodium iodide and alkyl chlorides or bromides. Inspired by this reaction, Zetian Mi, Chao-Jun Li, and their colleagues mix aryl chlorides or bromides with sodium iodide at room temperature and then shine ultraviolet light on the reaction (DOI: 10.1021/jacs.5b03220). Depending on the substitution of the aryl halide, the iodination reaction gives yields of 56–93%.

This reaction is a mild, green, and practical way to generate building blocks for organic and medicinal chemistry, the researchers write.

Melissae Fellet, Ph.D.

■ PROTECTIVE COATING GIVES LI BATTERIES A BOOST

Yi Cui and co-workers present a clever scalable solution that addresses the large irreversible capacity loss that lithium-ion batteries can suffer in their first charging cycle when a passivation film called solid electrolyte interphase (SEI) forms on the anode’s electrode/electrolyte interface. (DOI: 10.1021/jacs.5b04526).

Lithium-ion batteries are the rechargeable energy source of choice for portable electronics because of their high energy density, resistance to the decline in capacity known as “battery memory”, and slow charge loss when not in use. These batteries also have applications in electric cars, but in order for consumers to embrace this technology, the maximum driving range must be increased by boosting the battery’s energy density.

Here, the researchers react lithium and silicon (Li_xSi) nanoparticles with an organic compound that creates an “artificial” SEI, and this engineered coating serves as a protective passivation layer. Lithium-ion batteries that incorporate this layer show excellent cycling performance and very high energy density. In experiments with common electrodes tin, silicon, and graphite, the artificial-layer-protected Li_xSi nanoparticles eliminates irreversible first-cycle capacity loss. This protective SEI represents another step toward higher-density lithium ion batteries that can power a consumer vehicle with fewer stops to charge.

Jenny Morber, Ph.D.

Published: July 15, 2015