

Spotlights on Recent JACS Publications

■ EXCITING NEW INSIGHTS INTO PROTON-COUPLED ELECTRON TRANSFER REACTIONS

Chemists have long sought new ways to create energy-rich fuels—ideally via reactions powered by a renewable resource such as the sun. But scientists still have a lot to learn about solar-powered reactions, and a new study by Thomas Eisenhart and Jillian Dempsey sheds light on how they occur (DOI: 10.1021/ja505755k).

The proton-coupled electron transfer reaction (PCET) is a key light-driven step in the conversion of small molecules into energy-rich fuels. Although prior research has provided a basic understanding of PCET reactions between molecules in their ground states, much less is known about the reactions between electronically excited molecules.

Here, the team reports results from a mechanistic study of excited-state PCET reactions between two small molecules, acridine orange and tri-*tert*-butylphenol. The step-by-step process by which the reaction occurs has not been determined previously, but since each of the reaction components has a unique spectroscopic signature, the researchers can monitor each step with transient absorption spectroscopy. The results help explain the intimate coupling of light absorption with both proton and electron transfer, which the authors say will help pave the way for new avenues in solar fuel production.

Christine Herman, Ph.D.

■ STRETCHING THE ABSORPTION SPECTRUM FOR ORGANIC SOLAR CELLS

René A. J. Janssen and colleagues introduce semiconducting polymers that could extend the absorption spectrum of organic solar cells deeper into the near-infrared range than previously achieved (DOI: 10.1021/ja506265h).

Most current organic solar cells do not absorb near-infrared light, and as a result they miss the opportunity to harness power from a valuable portion of the sun's rays. Scientists have tried to bridge this gap by developing polymers that absorb light in the near-infrared part of the spectrum, which ranges from about 750 to 1400 nm. But so far researchers have not been able to make polymers that satisfactorily absorb and convert light over 900 nm.

Now Janssen and co-workers have designed semiconducting polymers whose absorption reaches up to 1200 nm. The polymers are made of alternating electron-rich pyrrole-based units and electron-deficient diketopyrrolopyrrole units. Solar cells built with these polymers and fullerenes tap into an unused part of the solar spectrum, and they reach power conversion efficiencies of 2.9–5.3%. The polymers could boost the power and efficiency of organic solar cells, including in multi-junction applications. They could also be used to make devices that detect near-infrared light.

Deirdre Lockwood, Ph.D.

■ NEW OXIDIZER FOR GREENER ROCKET PROPELLANTS

With gunpowder-powered prototypes dating back to as early as the 13th century, solid rockets today rely mainly on composite propellants consisting of highly energetic fuels and oxidizers. Ammonium perchlorate remains the chief choice of oxidizer in solid propellant formulations, although various concerns associated with its environmental impacts and health risks exist.

Now, tetranitroacetimidic acid, a novel high oxygen oxidizer discovered by Jean'ne M. Shreeve and co-workers, may be a greener replacement for the ubiquitous and notorious ammonium perchlorate (DOI: 10.1021/ja5074036). This new compound is shown to be an excellent rocket oxidizer, notably with a higher specific impulse—a measure used to evaluate the efficiency of rocket engines—than ammonium perchlorate.

In addition to its potential utility in rocket propellants, tetranitroacetimidic acid can be easily transformed into other energetic substances. Tetranitroacetimidic acid's synthesis and reactivity analysis will facilitate better understanding of the chemistry of trinitromethyl-containing materials as well.

Xin Su, Ph.D.

■ REDUCING THE CLUTTER IN MESSY NMR SPECTRA

Scientists hoping to study complex molecules with nuclear magnetic resonance (NMR) spectroscopy can run into significant challenges. The larger the molecule, the more signals there are competing for space in spectra. A perennial problem is spin–spin coupling—interactions between atoms that split signals into multiple peaks—exacerbating spectral crowding and cutting signal intensity. Signals then overlap, making chemical shift assignments and structure elucidation difficult or impossible.

Researchers have developed “pure shift” methods that reverse the effects of coupling, giving a single signal for each chemically distinct site, but only at a high cost in sensitivity. To preserve signal intensity while decluttering spectra, Gareth A. Morris and colleagues have developed an approach that combines Pure Shift Yielded by Chirp Excitation (PSYCHE) with two-dimensional total correlation spectroscopy (TOCSY) (DOI: 10.1021/ja507201t). The new technique suppresses the signal splittings but retains the coupling information, mapping out the network of couplings between spins.

The researchers test the method on estradiol, which has a notoriously crowded spectrum. The result is a high-quality, high-resolution map of singlet signals in two dimensions, validating this approach to simpler spectral analysis and structure elucidation.

Erika Gebel Berg, Ph.D.

Published: August 25, 2014