

Spotlights on Recent JACS Publications

■ SOLVENT MATTERS! EFFECT OF ENVIRONMENT ON PHOTORELAXATION

Mario Barbatti shows, via molecular dynamics simulations, that the 7*H*-adenine in water cluster relaxes via a state intersection induced by electron transfer from water to the chromophore (DOI: 10.1021/ja505387c). More commonly, this type of radiationless relaxation occurs via distortions in the nuclear geometry of the chromophore itself and not involving surrounding water.

Diverse molecular properties, from luminescence to photostability, largely depend on relaxation of photoexcited chromophores. Studying excited-state deactivation of nucleobases could be of broad relevance in determining how DNA dissipates or can be damaged by incident light. The discovery of this previously unknown reaction pathway of electron transfer from water to the 7*H*-adenine chromophore “reinforces the idea that the solvent–chromophore electron transfer pathways need to be considered in the assignment of relaxation mechanisms of chromophores in polar solvents”, the author says.

Understanding the relaxation of photoexcited nucleic acid fragments such as adenine has specific implications for their photostability and possibly for processes such as mutagenesis and carcinogenesis. More broadly, internal conversion reduces the efficiency of photovoltaic devices, so understanding the different factors that impact this process can help design and improve organic electronic candidates for such devices.

Dalia Yablon, Ph.D.

■ EFFECTS OF TOPOLOGY ON INTERLOCKED MOLECULE STABILITY UNVEILED

While it is well-known that topology plays a crucial role in establishing the properties and functions of naturally occurring biomolecules, its role within synthetic compounds, such as mechanically interlocked molecules (MIMs), has been largely unexplored to date. Now, a new study led by J. Fraser Stoddart sheds some light on how topology controls the formation and stabilization of radical dimers within MIMs (DOI: 10.1021/ja504662a).

The researchers perform an experimental and theoretical investigation on MIMs that contain within their molecular framework a redox active motif known as tetrathiafulvalene (TTF). Given its unique electronic properties, such as its π -donating ability and the electrochemical switchability of its electronic states, researchers are interested in using TTF within artificial molecular switches. The team studies the redox-active behavior of the TTF radical dimers within each molecule, uncovering the role of molecular topology in modulating molecular recognition processes. In addition, these investigations reveal similarities between these synthetic constructs and natural biomolecules, such as the minimization of empty space and exploitation of noncovalent bonding interactions.

The results suggest that the properties of unnatural products can be tailored by controlling their topologies, laying the groundwork for the investigation of more complex chemical

processes that have yet to be explored.

Christine Herman, Ph.D.

■ ACIDITY SENSING PROBES GET A TUNE UP

A tiny particle rides along in a patient’s bloodstream. Suddenly it finds itself in a new environment. The particle is next to a tiny tumor, and the acidity has changed. Triggered by the pH fluctuation, the particle transforms. Blink, blink! It flashes its colored light. Such is the vision of researchers working to create cancer-sensing and -imaging nanoprobes.

Recent prototypes have shown great promise but could not respond sensitively to small changes in acidity. Jinming Gao, Baran Sumer, and co-workers have given their probes a tune-up (DOI: 10.1021/ja5053158). Improving on their previous work, the researchers have created a library of ten nanoprobes that fluoresce more brightly when activated, and respond to much finer pH increments. Changes in pH drive synthesis of ATP (cells’ energy currency), transport of compounds through vesicles, and viral entry into cells. Cancer cells display a “reversed” pH gradient that promotes metastasis, a change that may be a universal characteristic of all cancers.

The ability to distinguish cancer cells from healthy ones could help surgeons at the operating table, or guide treatments that focus drugs on diseased sites. Beyond biologists and clinicians, these tiny tools should also appeal to physical scientists, materials chemists, and anyone who could use a tiny, sensitive pH indicator.

Jenny Morber, Ph.D.

■ SIMPLE CALCULATION PREDICTS CATALYST ACTIVITY AND SELECTIVITY

When a new catalyst is created, its activity and selectivity are typically determined through a series of laboratory experiments—a process that can be time- and labor-intensive with no guarantee for good results. Now, researchers have a way to predict the success of a catalyst based on simple thermodynamic calculations, thanks to a new report from Kyoko Nozaki, Seiji Mori, and co-workers (DOI: 10.1021/ja5046814).

This study is the first where a diverse group of catalyst systems are compared, in contrast to previous mechanistic studies on catalysts for epoxide CO₂ copolymerization, which have been limited to a single catalyst family. The metal complex catalysts studied here do have a few traits in common: They all possess a planar tetradentate ligand and require cocatalysts in order to achieve optimum catalytic activities. The researchers perform density functional theory studies to predict the activity of catalysts for polycarbonate production. The studies are further extended to determine whether a monomer/catalyst system would produce (i) cyclic carbonate or polycarbonate and (ii) polycarbonate or polyether in the presence of carbon dioxide. A new class of iron catalyst has thus been invented.

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The findings hold promise for facilitating the design of new catalyst systems based on versatile metal complexes.

Christine Herman, Ph.D.