

Spotlights on Recent JACS Publications

■ A NEW WAY TO CAPTURE HIGHLY REACTIVE INTERMEDIATES

Chemical reactions usually involve one or more reactive intermediates before a final product is formed. These reactive intermediates are important tools in understanding the elementary steps of a chemical reaction and predicting the reaction course. Carbenium ions are among the most important reactive intermediates, and the highly reactive benzhydryl cation is a prototype of strongly electrophilic carbenium ions. The benzhydryl cation can only be thermodynamically stabilized for spectroscopic characterization in superacidic, highly ionic solvents. Wolfram Sander, Elsa Sanchez-Garcia, and co-workers report a new way to isolate and stabilize the highly reactive benzhydryl cation in a neutral environment (DOI: 10.1021/ja507894x).

The authors investigate the reactions of diphenylcarbene (DPC) either with single water molecules embedded in an argon matrix or in amorphous water ice at cryogenic temperatures. They find that, with water in an isolated matrix, benzhydryl alcohol forms even at 3 K, while in amorphous water ice, DPC is protonated to benzhydryl cation and is stable up to 50 K. This innovative technique may facilitate the synthesis and detailed spectroscopic characterization of other important reactive intermediates.

Hui Jin, Ph.D.

■ FLUORINATION PROVIDES AN EFFICIENCY BOOST TO POLYMER SOLAR CELLS

When it comes to renewable energy technology, one promising avenue is the development of organic solar cells, which have the potential to be a low-cost energy conversion technology. The key to their success strongly depends on their ability to efficiently harvest light from the sun, and chemists have a role to play in developing new materials and device architectures that provide the necessary efficiency boost.

But first, researchers need a better understanding of the relationship between chemical structures and photovoltaic properties, which can be difficult to attain since myriad parameters influence device performance. In a new study, Wei You, Harald Ade, Dieter Neher, and co-workers create a series of five copolymers with varying degrees of fluorination and find that increasing the fluorine content results in improved hole mobility—a desirable property for solar cells (DOI: 10.1021/ja5067724).

The team reports the boost in power conversion efficiency is likely the result of increased π - π stacking of the conjugated polymer backbones and a preferential face-on orientation of these stacks. Since the polymers in this study have similar molecular weights, morphologies, and molecular orientations, the researchers confidently attribute the enhanced performance to the degree of fluorination. The knowledge of this simple correlation could help researchers maximize the efficiency of future polymer solar cells.

Christine Herman, Ph.D.

■ MELANIN NANOPARTICLES AS THREE-WAY IMAGING AGENTS

Many detection reagents exist for magnetic resonance imaging (MRI), positron emission tomography (PET), and other clinical imaging techniques, but they generally only work for one method at a time. Multimodal imaging reagents allow greater flexibility, for instance to guide physicians during surgery, yet few are available or easily synthesized. Now, Zhen Cheng and colleagues describe an organic trimodal imaging reagent built from the skin pigment melanin (DOI: 10.1021/ja505412p).

Cheng's team takes melanin, a water-insoluble biopolymer that is detectable using photoacoustic imaging (PAI), and disperses it into 4.5 nm, water-soluble nanoparticles by first dissolving it in sodium hydroxide solution and then neutralizing while simultaneously sonicating. They coat the particles with polyethylene glycol and a tumor-targeting peptide, RGD, and exploit melanin's metal-chelating capabilities to incorporate Fe^{3+} (for MRI) or $^{64}\text{Cu}^{2+}$ (PET). The resulting material is active in tumor-containing mice, homing to exogenous tumors and generating signals detectable via PAI, MRI, and PET.

Further modification of the melanin nanoparticle is possible, the authors note, for instance as a drug-delivery vehicle. "We expect this work will stimulate further studies of multifunctional endogenous material as nanoplatforams for potential imaging and therapeutic applications," they write.

Jeffrey M. Perkel

■ AN INSIDE JOB SANS ACCOMPLICE

β -Chloride elimination is a well-known problem in the coordination–insertion polymerization of chloroolefins. The elimination reaction deactivates catalysts by forming inert chloride-coordinated species. It has been speculated that, for instance, in square-planar group 10 metal complexes, this process may be preceded by ligand dissociation, taking place via T-shaped intermediates with one open coordination site.

However, Joshua S. Figueroa and colleagues have recently found new evidence in the decomposition of a pentachloroethyl nickel complex, suggesting a different mechanism that does not necessitate ligand dissociation (DOI: 10.1021/ja508956q). On the basis of its crystal structure and decomposition kinetic studies, the authors propose that the elimination proceeds through direct transfer of chloride to the apical site of the nickel coordination sphere in a unimolecular pathway.

This new discovery has significant implications for the principles of developing late-transition metal catalysts for polymerization of vinyl chlorides. Because β -chloride elimination is independent of ligand dissociation, the design of new catalysts should completely obviate the formation of β -chloroalkyl ligands, instead of simply increasing olefin binding rates.

Xin Su, Ph.D.