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Spotlights on Recent *JACS* Publications

MEASURING TWO POLARONS IN A POLYMER

Plastics or polymers are normally considered to be nonconducting, but conjugated or conducting polymers can carry current just like metal wires and can be used in devices such as solar cells and light emitting diodes. John R. Miller, Lori Zaikowski, and co-workers did experiments and calculations to describe how charge travels along conducting polymers (DOI: 10.1021/ja301494n).

Charges called polarons move through conducting polymers by hopping along and between polymer chains. To fully understand this movement, it is important to know if multiple charges exist as separate polarons on the same chain. The authors inject one or two electrons into conjugated fluorene polymers 1−10 monomers long, and they identify polarons based on the polymer's absorption of light. Long-chain polymers, 8 units and above, were found to carry two charges as side-by-side polarons, confirming what had previously been proposed to occur in long, oxidized sulfur-containing polymers.

These experiments strengthen scientists' understanding of how charges move through conducting polymer materials and may aid in the design and development of new functional materials. **Melissae Fellet**

EXPLAINING THE EFFECTS OF CATALYST LIGANDS ON CYCLOADDITION REACTIONS

(5 + 2) Cycloaddition of vinylcyclopropanes and various π-systems, such as alkynes, provides an effective method for producing seven-membered rings, which are otherwise challenging to synthesize. Seven-membered rings are part of many natural products, including some that are potential leads for cancer prevention, pain reduction, and HIV eradication. The groups of Paul A. Wender and K. N. Houk have a tradition of combining creative experiments from the Wender lab with computations from Houk's lab to understand interesting new phenomena in chemistry. This time they use DFT calculations to figure out how ligands used in Rh-catalyzed (5 + 2) cycloadditions could alter reactivities and change regioselectivities (DOI: 10.1021/ja3041724).

Experiments have demonstrated that the substituent on the π-system substrate and the type of ligand on the rhodium(I) catalyst can dramatically affect the reactivity and enhance or even reverse the regioselectivity of the cycloaddition. Calculations on intermolecular (5 + 2) cycloadditions of vinylcyclopropanes and a variety of substituted alkynes with three different Rh(I) catalysts supported and helped explain the earlier experimental results.

The researchers are able to correlate steric repulsions, electronic effects, and noncovalent dispersion effects with specific reactivity and regioselectivity. Thus, it could be possible to achieve highly regioselective and efficient cycloadditions by carefully choosing the ligand of the Rh(I) catalyst to complement the substituent of the alkyne. These studies will enable superior designs of new catalysts and increase the range and control of cycloadditions. **Yun Xie, Ph.D.**

CONTROLLING DNA HYBRIDIZATION WITH A LIGHT TUG

Double strands of DNA can bend into tweezers and coil into bricks that assemble into nanostructures. Controlling the motion and assembly of these DNA-based devices requires controlling hybridization of the two strands, often using a chemical input in the form of another control DNA strand that temporarily masks part of the nucleotide machine. Now, James Tucker and co-workers use light to trigger a structural change of the DNA backbone that in turn influences hybridization, thereby providing a potential alternative to the use of masking strands (DOI: 10.1021/ja304205m).

DNA hybridization can be controlled with light using photoactive tags built into the DNA backbone that, upon activation with light, disrupt the structure and inhibit duplex formation. In this work, the scientists incorporate two anthracene molecules into a single DNA strand. The two anthracenes snap together when light hits the strand, creating a loop of DNA above the newly formed junction. Larger loops prevent the complementary DNA strand from binding to the altered strand. Additionally, forming the DNA duplex before the light pulse prevents anthracene dimerization.

This ability to control both hybridization and dimerization could open new ways to easily regulate the activity of DNA-based, and possibly peptide-based, nanodevices. **Melissae Fellet**

VERSATILE COPPER-MEDIATED ARYL FLUORINATION

Patrick Fier and John Hartwig have discovered a simple and high-yielding way to synthesize fluorine-substituted aromatic rings, providing access to molecules that could impact biomedicine, agrochemistry, and other fields (DOI: 10.1021/ja304410x). Starting with iodine-substituted aryl rings, the researchers use a copper complex to effect the transformation. Sensitive functional groups, including esters and aldehydes, are stable under the reaction conditions, and this substitution works on a wide range of substrates, whether simple, substituted, or sterically hindered benzene rings, as well as some heterocyclic ring systems.

Molecules containing an aryl fluoride are very useful for agricultural or pharmaceutical chemistry applications because, as the authors point out, "the site containing fluorine is stable to degradation." In pharmaceuticals, introduction of fluorine may increase the bioavailability and lipophilicity as well as the metabolic stability of a molecule, resulting in improved biological activity. Additionally, ^{18}F-labeled compounds are used in positron emission tomography, or PET imaging. Hartwig and Fier's new route to a wide range of aryl fluorides may provide a straightforward way of synthesizing labeled molecules to be used in medical imaging. **Sonja Krane, Ph.D.**

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COMPUTER MODELING UNTANGLES PROTEIN CHAPERONE BIOLOGY

As growing polypeptide chains emerge from the ribosome inside cells, they spontaneously fold into their proper structure—something that very large proteins cannot always do easily in isolation in a test tube. Inside the cell, proteins called chaperones aid this process, but it is not always clear how. Now a new set of molecular simulations by Christopher Dobson and colleagues sheds light on the mechanisms used by one chaperone, the *E. coli* trigger factor (TF) (DOI: 10.1021/ja302305u).

Dobson's team develop a computational model of ribosomal translation in the presence and absence of TF and use it to probe the chaperone's impact on short and long peptide sequences. They find that TF has little effect on a 56-amino acid protein, but it slows folding of a 216-residue enzyme fragment via three distinct but interconnected "kinetic trapping" mechanisms. One mechanism slows down the new polypeptide's ability to randomly explore the folding space; another involves folding outside of the cradle formed by TF; and a final mechanism involves entangling the new polypeptide around the TF protein.

These mechanisms provide a biological rationale for earlier laboratory observations, the authors show, and may be generalizable to other large proteins, as well. "This approach can play an important role in identifying the molecular processes underlying experimental observations and suggest novel mechanisms by which chaperones such as TF can effect co-translational folding *in vivo*," they conclude. **Jeffrey M. Perkel**

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