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Spotlights on Recent *JACS* Publications

SWITCHING THE LUMINESCENCE OF AN EUROPIUM ION ON AND OFF WITH LIGHT

Photochromic molecules react to light by changing physical properties such as their structure or absorption spectrum. Yu Liu and co-workers report a luminescent supramolecular complex where the luminescence can be switched on or off by alternating UV and visible light irradiation (DOI: 10.1021/ja4018804).

The researchers combine a perfluorocyclopentene-based photochromic diarylethene derivative (DAE) with an europium complex linked to a dibenzo-24-crown-8. This large, macrocyclic crown moiety encircles a chain of the DAE, forming a pseudorotaxane. The ring in the photochromic molecule isomerizes from an open structure upon irradiation with visible light to a closed structure under UV light. Because the absorption band of the closed DAE matches the emission band of the europium complex, energy transfers from the metal complex to the DAE, thereby quenching the luminescent emission of the europium ion. The luminescence is restored upon irradiation with visible light.

A well-known example of this important class of photochromic molecules—switches that can alternate between two states by irradiation with light of different wavelengths—is sunglasses that darken when exposed to intense light. These types of molecular and supramolecular photochromic complexes have potential further applications in optoelectronics, smart materials, optical memory devices, logic gates, and molecular machines. **Alexander Hellemans**

THE TIES THAT BIND CARBOHYDRATES AND PROTEINS TOGETHER

Carbohydrate—protein interactions are essential for a variety of biological processes, including cellular recognition and immune function. Researchers are not sure which physical force dominates in bringing carbohydrates and proteins together: hydrogen bonding, the hydrophobic effect, or the attraction between CH bonds and aromatic rings. Jeffery Kelly and colleagues collect structural and energetic data on a series of molecules to tease out the relative contributions of the latter two forces to carbohydrate and protein binding (DOI: 10.1021/ja4040472).

The researchers synthesize 44 pairs of proteins—one protein with a carbohydrate moiety and the other without—that differ only at residue 16. While in a folded conformation, the protein's structure forces the carbohydrate to interact with the particular segment of the protein that includes residue 16. As they heat the proteins, the researchers monitor the energetics of unfolding using circular dichroism. They calculate the interaction energy between the carbohydrate and each of the variants by comparing the folding energy from the carbohydrate-linked protein to that of the corresponding carbohydrate-free version.

Using these energies and information about the chemical identity of residue 16 for each variant, the researchers ascertain that the hydrophobic effect makes a substantial contribution to carbohydrate−protein interaction energies and is supplemented by CH−π interactions when the carbohydrate interacts with aromatic amino acid side chains. Such information could help scientists engineer properties of glycoproteins and develop medications that mimic carbohydrates. **Erika Gebel, Ph.D.**

LET'S TALK: BUILDING BRIDGES BETWEEN CHEMISTRY SUBDISCIPLINES

Researchers in both natural products and materials chemistry have a lot to offer not only to researchers in other disciplines but also to each other. Yet, according to Horst Kunz and Klaus Müllen, authors of a recent Perspective, there is an ever-growing divide between the two chemistry subdisciplines. In particular, this divide is fueled by financial influence resulting in the overemphasis on specialization in one area of expertise that suppresses cross-talk between them (DOI: 10.1021/ja309186q).

Even as new interdisciplinary collaborative efforts continue to spring up between chemists and biologists or engineers, the stereotype persists that chemists simply provide compounds that other experts use in their experiments. In reality, the authors say, chemists' unique ability to investigate the relationship between a molecule's structure and its properties has led to crucial advances in fields ranging from medicine to electronics. This skill could also lead to fruitful collaborations among chemists in different subdisciplines, if only the bridges would be built to promote such efforts.

To encourage better collaboration between specialized chemists, the authors recommend several changes, including the stronger appreciation of interdisciplinary research by funding agencies and the training of young researchers to understand the value of crossing the borders of scientific subdivisions. **Christine Herman, Ph.D.**

CHEAP AND EASY C−F BONDS

Fluorinated aromatic compounds' unique chemical properties make them both highly valued and difficult to synthesize. They are used for everything from pharmaceuticals to agrochemicals to imaging materials, but their synthesis often requires high reaction temperatures and harsh conditions. In 2005, Olafs Daugulis and co-workers demonstrated they could use directing groups and palladium catalysis to regioselectively arylate C−H bonds (DOI: 10.1021/ja054549f). Now they couple this idea with a copper catalyst to create C−F bonds via C−H activation under mild conditions (DOI: 10.1021/ja4047125).

Using readily available copper(I) iodide as a catalyst and silver(I) fluoride as the nucleophilic fluoride source, the researchers are able to fluorinate the C−H bonds of benzoic acid and benzylamine derivatives. They use 8-aminoquinoline and picolinic acid as directing groups and dimethylfuran, pyridine, or dimethylpropyleneurea as solvent at reaction temperatures ranging from 80 to 125 °C. In the past, Cu-

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catalyzed C−F bond formation using C−H activation has only been used for fluorination of benzene at 550 °C.

In addition, this method allows the researchers to add a selected number of fluorines depending on how much catalyst or reagent is used, is highly tolerant to functional groups, and provides an easy and inexpensive way to prepare ortho-fluorinated benzoic acids. This important discovery could drive down the cost of many goods in the future, from foods to drugs and biomedical devices. **Leigh Krietsch Boerner, Ph.D.**