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Spotlights on Recent *JACS* Publications

ORGANIC STABLE RADICAL DEMONSTRATES "REMARKABLE" CHEMICAL STABILITY

Oxophlorins are the keto-tautomers of *meso*-hydroxyporphyrins, intermediates in the metabolic destruction of heme. Derivatives of oxophlorin have been studied as stable organic radicals. However, stable radicals such as these tend to be difficult to manipulate, making it challenging to alter their molecular structure for new applications. Now researchers have synthesized and characterized a triaryl-substituted oxophlorin, which can be easily handled and prepared on a large scale.

Ko Furukawa, Dongho Kim, Atsuhiro Osuka, and their colleagues prepare the new molecule both as a free base and with either a nickel or a zinc atom in the center of the porphryin (DOI: 10.1021/jacs.5b11223). The researchers characterize each molecule's structure using X-ray crystallography; they also study the molecules' optical, magnetic, electrochemical, and excited-state properties. The researchers find that they can manipulate these molecules as if they did not contain a radical, and they can also tune the properties by switching the metal atom inside the porphryin.

Organic stable radicals have been used for organic synthesis, polymer chemistry, magnetic materials, organic batteries, molecular spin memory, and bioimaging. These authors suggest that triaryl-substituted oxophlorins are promising building blocks for new types of functional materials, built from covalent or non-covalent oligomers.

Melissae Fellet, Ph.D.

BEE VENOM MOLECULE TURNED INTO AN ANTIBACTERIAL AGENT

The venom of the European honey bee contains a molecule called melittin, which belongs to a class of molecules called membrane-permeabilizing peptides that poke holes in membranes and cause cell leakage. Researchers are interested in these peptides because they can be exploited to, among other things, function as antibacterial, antifungal, and antiviral compounds. Unfortunately, melittin and similar peptides indiscriminately attack many types of membranes. Researchers want to find forms of the peptides that selectively attack only one particular membrane target.

Now William Wimley and colleagues have identified a form of melittin that selectively targets a particular type of membrane (DOI: 10.1021/jacs.5b10595). By screening a collection of peptides based on melittin, the investigators identify one peptide that has a single amino acid mutation. The change causes this peptide to take on a conformation that renders it incapable of forming pores in eukaryotic cell membranes. The peptide has no trouble forming pores in bacterial cell membranes.

This result makes the peptide a selective antibacterial agent that leaves eukaryotic cells unharmed. The investigators say that their approach "would be a useful strategy against cancer cells, pathogens, pathogen-infected cells or other target cells."

Rajendrani Mukhopadhyay, Ph.D.

ELECTROPHILE EFFICIENTLY OPENS A CRUCIAL SENSORY CHANNEL

If wasabi makes you sneeze, you can thank an important sensory channel protein—a receptor called TRPA1—which is activated by a spicy compound in this green condiment. Many other chemical irritants, some of which are electrophiles, stimulate the TRPA1 channel protein, which then opens to its active form to trigger pain, breathing changes, coughing, and even sneezing. Scientists think such agonists cause this effect when they covalently modify select cysteine residues in the protein. Researchers seek to further understand the receptor's chemistry so that it might be exploited to treat pain or other sensory responses.

By screening more than 1600 electrophilic molecules, Motanari Uesugi and co-workers have discovered a compound that opens the TRPA1 channel by covalently modifying a single cysteine residue (DOI: 10.1021/jacs.5b10162). The agonist could be used as a probe to advance future pharmacological studies of this target sensory channel, potentially yielding new approaches for reducing pain.

Deirdre Lockwood, Ph.D.

DYNAMICS OF PEROXO-DICOPPER MOLECULES REVEAL NEW REACTIVITY

The light-induced excitation of peroxodicopper(II) compounds has not been well studied, because such species are only stable at low temperatures. Kenneth Karlin, Gerald Meyer, Claudio Saracini, Shunichi Fukuzumi, and their colleagues have changed their instrument conditions so they can perform femtosecond laser-induced excited-state dynamics studies on three known peroxodicopper species at temperatures between −55 and −94 °C.

The researchers find that absorption of one photon of visible light generates a two-electron molecular oxidation, causing the release of dioxygen with around 10% efficiency (DOI: 10.1021/jacs.5b10177). All three molecules they have studied also pass through a previously unknown intermediate that contains both Cu(I) and Cu(II) along with a bound superoxide anion moiety.

Copper−dioxygen intermediates are important in biologically and chemically mediated oxidations, and the researchers write that it will be interesting to see if newly discovered copper water-splitting catalysts have similar photoreactivity. Splitting water into hydrogen and molecular oxygen requires two steps, each of which transfers two electrons: one transfer forms the peroxide bond, and the other releases molecular oxygen. Without the second transfer, the release of peroxide or superoxide could cause unwanted radical reactions.

Melissae Fellet, Ph.D.

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