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Light unlocks fragrance in laboratory

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In Anna Gudmundsdottir's laboratory at the University of Cincinnati, dedicated researchers endeavor to tame the extremely reactive chemicals known as radicals.

Highly reactive radicals are atoms, molecules or ions frantically trying to become something else. Their lifetimes are measured in fractions of seconds and typically occur in the middle of a chain of chemical reactions. They are also known as reactive intermediates. Much of Gudmundsdottir's work has focused on a family of radicals known as triplet nitrenes.

"Triplet nitrenes are reactive intermediates with high spin," Gudmundsdottir said. "You have a nitrogen molecule that has two unpaired electrons on it. We discovered they were actually very stable for intermediates. They live for milliseconds and that's when we got into this idea can we make them stable enough for various investigations."

The potential uses of relatively stable radicals have excited interest from industry. The high spin Gudmundsdottir describes suggests that triplet nitrenes, for example, might be ideal candidates for creating organic magnets that are lighter, more flexible and energy-intensive than conventional metal or ceramic magnets. Gudmundsdottir's research suggests that radicals, including triplet nitrenes, may show a pathway to materials with many magnetic, electrical and optical properties.

"I talk a lot about radicals," Gudmundsdottir said. "Nitrenes are radicals. We study the excited state of the precursors to the nitrenes. We are looking at how you use the excited state of molecules to form specific radicals."

One line of inquiry, presented by Gudmundsdottir to a recent Gordon Research Conference, described how her team used radicals to create a specific trap for a fragrance, which is then slowly released when exposed to light.

"The question was, can you actually tether a fragrance to something so that it will release slowly?" Gudmundsdottir said. "It turned out that a precursor similar to the ones we used to form the nitrenes could be used it as a photoremovable protecting group."

The "photoprotectant" acts as a sort of cap, containing the fragrance until the cap is pried off by a photon of light. For this particular purpose, Gudmundsdottir said it was important to design a photoprotectant "cap" that was somewhat difficult to pry off. For household products, such as a scented cleaning fluid, consumers want fragrance to be released slowly over a long period of time. That requires what is known as a low "quantum yield." In other words, how much fragrance gets released by how many photons.

The difficulty, Gudmundsdottir said, is that different applications need different rates of release. For medical uses, doctors might want a higher quantum yield, by which a little bit of light releases a lot of medicine.

"There are all kinds of applications for photoreactions," she said, "from household goods, perfumes, sun-protection, drug delivery and a variety of biologically reactive molecules. So we just decided, OK, we are very fundamental chemists, we'll design different systems and see if we can manipulate the rate of release."

Gudmundsdottir's research group studies the release mechanism, locates where there are limitations, and tries to determine what controls the rate. They also consider environmental factors, including how the delivery systems react with oxygen.

"We do very fundamental work to get the knowledge here before can take it into specific directions," she said. "If we don't understand it, we can't design where to take it next."

Much of this understanding develops from watching how radicals form and decay. Gudmundsdottir's group uses a laser flash photolysis system to fire a laser into a sample and to track the spectrum of radiated light as the radicals decay.

"What I like about transient spectroscopy is actually seeing the intermediates we work with on nanosecond, microsecond and millisecond timescales," she said.

The team also uses computer modeling, but the chemical operations of these short-lived and rapidly reacting chemicals are difficult to model, so Gudmundsdottir has tapped into the resources of the Ohio Supercomputer Center.

"Calculating excited states takes up quite a bit of computer resources and that's why we use the supercomputer," she said. "That's a really nice resource to have available. I can sit anywhere or my students can sit anywhere and we can do the calculations to model reactions."

Gudmundsdottir said the questions raised by applications leads to helpful fundamental questions that can be tackled through basic research.

"Going forward, we probably want to do more applied study with our photo protective groups, to collaborate with someone to see them in some other applications," she said. "I'm interested in how they act inside cells."

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