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Blue light activates oxygen best - New catalyst system works with colors

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Photochemistry is increasingly proving to be the key to environmentally friendly chemical reactions. Under mild temperatures and normal pressure, photons - the energy of light - are expected to cause chemical reactions in the future. A team led by Esteban Mejía from the Leibniz Institute for Catalysis in Rostock, LIKAT, and Dengxu Wang from Shandong University in Jinan has now developed a modular system with which photocatalysts for processes in organic chemistry can be assembled almost at will, as if from a Lego construction kit.

The new catalyst is a silicone material to which the LIKAT chemists add different fluorescent dyes: yellow, green, red or blue. "Since each color belongs to a specific wavelength in the light spectrum, we can use it wonderfully to determine the energy range in which the catalyst should become active," explains Dr. Esteban Mejía, head of research for polymers and catalysis at LIKAT.

For the laboratory experiment, a reaction for C-H derivatization is irradiated with blue light.
Xuewen Guo/LIKAT

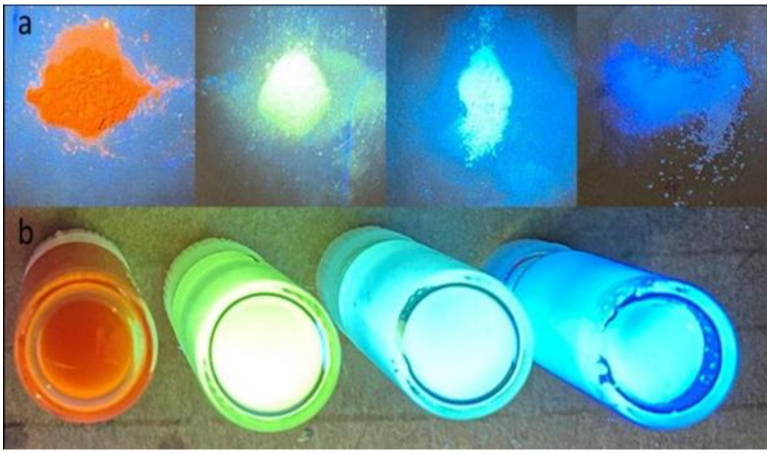
LIKAT

Metal-free and mild reaction conditions

"Becoming active" here means, above all, that the photocatalyst absorbs photons from the light, the energy of which it passes on to the reaction partners, precisely in the energy range of the particular color with which it has been mixed. In this way, chemists can activate starting materials so precisely that they form new chemical bonds with the desired reaction partners without exception. And hardly any by-products are generated.

Unlike conventional organic chemistry processes, the new catalyst system has decisive advantages. It operates at room temperature and atmospheric pressure, i.e. under unusually mild conditions, as Esteban Mejía says. "In addition, the catalyst contains no metals. And it can be easily recovered."

The catalyst is a silicone derivative (derivative) called POSS; it consists of organic and inorganic building blocks, which is why chemists call it "hybrid." Characteristic of the material is a kind of backbone of oxygen-silicon-oxygen bonds. Says Dr. Mejía, "This makes the catalyst thermally and chemically very stable, just like sand, which is, after all, mainly silicon." Oxygen and silicon are the two most common chemical elements in the Earth's crust.



Samples (top row) of the new hybrid photocatalysts spiked with different fluorene scene dyes. Bottom row: samples dispersed in ethanol.
Xuewen Guo/LIKAT
LIKAT

Pores as reaction space

POSS is highly porous, making it ideal for catalysis. "The pores provide suitable niches where excited starting materials come close enough to react with each other," says Esteban Mejía.

The catalyst also appeals aesthetically: When exposed to light, which is mandatory for photocatalysis, it begins to fluoresce in the particular colors that have been added to it.

The idea of using colored POSS as catalysts came to Esteban Mejía three years ago. At that time, Dengxu Wang, a former postdoctoral fellow, had developed sensors in his group to detect nitroaromatic explosives, metal ions and toxic gases, based on excited fluorescent polymers. Dengxu Wang added a dye to the polymers corresponding to the necessary wavelength for the pollutant being sought. As soon as the polymers detect molecules of this substance, they stop glowing.

Esteban Mejía suspected even then that molecules could not only be detected in this way, but also chemically activated. "With such a color-controlled modular function, we could develop a chemical Lego construction kit, so to speak, from which we could assemble catalysts."

Model reaction: C-H derivatization

The photocatalysts were then created in China, in the laboratory of Dengxu Wang, who has since been appointed to Shandong University. In Rostock, Esteban Mejía's doctoral student Xuewen Guo developed the model reaction for it, including tests and analyses. A process from organic synthesis served as the model. In organic compounds, carbon atoms (C) are usually bonded to hydrogen atoms (H). These C-H bonds are converted into carbon bonds (C-C) in intermediate and final stages for products in the pharmaceutical and agrochemical industries, for example.

An important step in this process is C-H derivatization to chemically activate the molecules, as Dr. Mejía explains. This is where the new process comes in. Usually, breaking the C-H bond requires a metal atom, which is provided by the catalyst. The new photocatalyst from LIKAT, however, does not contain any metal. Instead, the researchers relied on its highly porous structure. "We also knew that our material reacts well with oxygen." And that's what the reaction needs as an oxidant.

Photons as energy transmitters

In fact, the reaction works, and by now the chemists are also clear about the process. "The catalyst absorbs a photon from the light and transfers it to the oxygen," explains Dr. Mejía. "This forms a super-reactive oxygen particle." Chemists call it "singlet oxygen." This high-energy species manages to attack the molecules of the organic starting materials, thus activating them and preparing them for the next steps. In the laboratory, this process succeeded best when the samples were irradiated with blue light. A blue fluorescent dye was also added to the catalyst.

In the end, this approach saves a complete reaction step. In a sense, the work is done in one step: activating and derivatizing starting materials and adding special functions to the derivatives. This improves the ecological balance of such processes

The research team published its findings in the journal ACS APPLIED MATERIALS AND INTERFACES. It is a result of basic research, usable for all those involved in the generation of C-C bonds in organic chemistry.

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