

New sunlight-driven method to break tough C–F bonds useful for pharmaceutical and agrochemical industries

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Scientists have found a sunlight-driven method to break one of the toughest chemical bonds, the carbon–fluorine (C–F) bonds that needs severing for recycling, drug design, or transforming industrial chemicals.

Fluorinated organic compounds are widely used in research and industry due to their easy availability and well-established synthesis routes. However, activation of C–F is crucial for transforming poly- or perfluorinated compounds into more useful derivatives. However, it remains a significant challenge as the chemical bond is exceptionally strong. Traditionally, C–F bond cleavage has relied on harsh conditions, costly metal catalysts, and energy-intensive methods, which are often unsustainable and typically require homogeneous conditions. In contrast, heterogeneous photocatalysts offer a greener and more energy-efficient alternative under mild and recyclable conditions using sunlight.

Researchers at the S. N. Bose National Centre for Basic Sciences — an autonomous institute under the Department of Science and Technology (DST) — have explored a cutting-edge class of materials known as covalent organic frameworks (COFs), in an attempt to overcome the challenge of breaking the strong C–F bond. They developed a specially engineered COF that acts as a heterogeneous photocatalyst. COFs are crystalline, porous materials prized for their exceptional stability, large surface area and highly tunable structures. Their modular design enables scientists to easily modify their properties, making them highly attractive for catalytic applications.

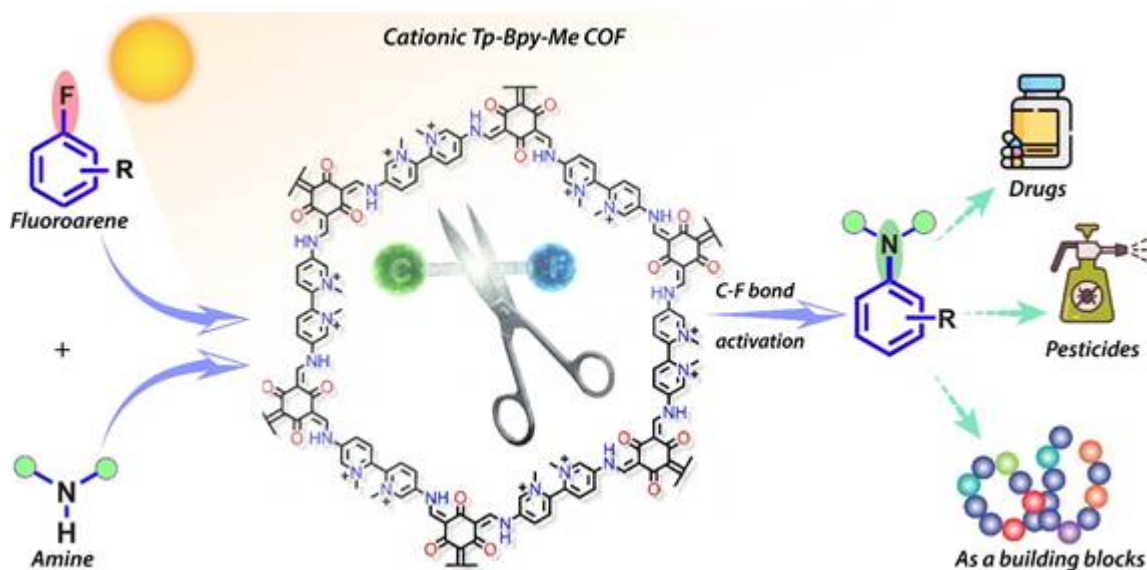


Fig: Sunlight-driven C–F bond activation of fluoroarenes over cationic Tp-Bpy-Me COF, leading to the formation of aminated products with potential applications across various sectors.

The team worked with a bipyridine-based COF (Tp-Bpy) and performed a simple post-synthetic modification by adding a methyl group, known as methylation. This single-step change produced a positively charged version of the COF, known as cationic Tp-Bpy-Me COF, while maintaining the original integrity of the framework. This seemingly small modification had a significant impact, making the COF more electron-deficient, improving its ability to absorb visible light and drive challenging photocatalytic reactions in an efficient manner.

When exposed to blue light, Tp-Bpy-Me COF successfully activated strong C–F bonds and promoted the formation of C–N bonds through the attack by amine nucleophile, an important step in building more complex organic molecules. Remarkably, the reaction could even proceed under natural sunlight, making the process not only efficient but also environmentally friendly.

This represents the demonstration of a COF-based photocatalyst capable of converting C–F bonds into C–N bonds. The resulting products hold significant potential for applications in the pharmaceutical and agrochemical industries, as well as serving as building blocks for various natural products.

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