



# A new strategy for PFAS decomposition and transformation using photocatalysis and Lewis acid activation

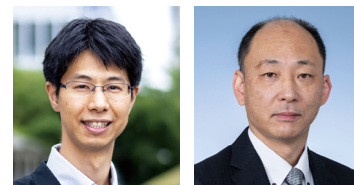
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## Abstract

In this study, we developed a new chemical transformation method to selectively cleave and replace the strong carbon–fluorine bonds of difluoromethylene (CF<sub>2</sub>) units in perfluoroalkyl compounds by combining light and Lewis acid activation. First, visible-light photocatalysis selectively removes one fluorine atom and introduces an organic radical. Subsequently, the remaining fluorine is replaced with other functional groups through Lewis acid-mediated substitution, enabling the formation of various useful compounds. This stepwise and mild transformation allows precise control over the robust C–F bonds, paving the way for both PFAS degradation and the creation of new functional materials.

## Background & Results

Per- and polyfluoroalkyl substances (PFAS) are highly persistent in the environment and have become a global pollution issue. In this work, we achieved the stepwise cleavage and conversion of the strong C–F bonds in the CF<sub>2</sub> core structure under mild conditions using a synergistic combination of photocatalysis and Lewis acid activation. This result demonstrates the possibility of transforming PFAS from “persistent pollutants” into “valuable chemical resources.” Looking forward, this approach may be applied to environmental PFAS remediation, resource-recycling chemical processes, and the development of general strategies for transforming other inert chemical bonds.

## Significance of the research and Future perspective

Organofluorine compounds are widely used in pharmaceuticals and advanced materials but are also known as persistent environmental pollutants (PFAS) due to their resistance to natural degradation. Among their structures, the difluoromethylene (CF<sub>2</sub>) unit poses a particular challenge because its C–F bonds are extremely strong. Conventional methods often require harsh conditions and lead to limited control, typically installing identical substituents on both fluorine atoms.

To address this, we designed a stepwise reaction sequence under mild conditions, combining light-induced and acid-mediated processes. First, visible-light photocatalysis with a phenothiazine-based catalyst enabled selective defluoroaminooxylation of one fluorine atom using TEMPO radicals. Next, Lewis acid activation with AlCl<sub>3</sub> allowed replacement of the remaining fluorine with various organosilicon reagents, yielding functionalized perfluoroalkyl alcohols.

A key to this success was the development of a novel phenothiazine catalyst bearing methyl substituents, which accelerated catalyst regeneration and improved overall efficiency. Time-resolved transient absorption spectroscopy and DFT calculations clarified the mechanism at the molecular level, showing that minimized structural deformation upon electron transfer leads to fast turnover. This method proved effective for a broad range of substrates with different electronic properties.

These results not only demonstrate selective transformation of strong C–F bonds under mild conditions but also highlight a promising pathway for converting persistent PFAS into useful chemical resources. This approach represents a new strategy in green and sustainable chemistry for controlling otherwise inert bonds.

## A new strategy for PFAS decomposition and transformation



## Mechanistic Study

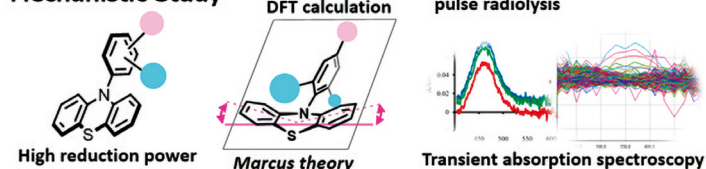


Fig. 1



Fig. 2

### Patent

### Treatise

Sugihara, Naoki; Nishimoto, Yoshihiro; Yasuda, Makoto et al. Sequential C–F bond transformation of the difluoromethylene unit in perfluoroalkyl groups: A combination of fine-tuned phenothiazine photoredox catalyst and Lewis acid. *Angew. Chem. Int. Ed.* 2024, 63, e202401117. doi: 10.1002/anie.202401117

### URL

<http://www.chem.eng.osaka-u.ac.jp/~yasuda-lab/e/>

### Keyword

photocatalysis, Lewis acid, PFAS degradation and transformation, C–F bond activation