



Title	Development of Copper Photoredox Catalysis for Defluorinative Carbon–Heteroatom Coupling Reactions
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Degree Grantor	北海道大学
Degree Name	博士(総合化学)
Dissertation Number	甲第16629号
Issue Date	2025-09-25
DOI	https://doi.org/10.14943/doctoral.k16629
Doc URL	https://hdl.handle.net/2115/98239
Type	doctoral thesis
File Information	Priya_Saha_abstract.pdf, 論文内容の要旨 https://creativecommons.org/licenses/by/4.0/



学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（総合化学） 氏名 SAHA PRIYA

学 位 論 文 題 名

Development of Copper Photoredox Catalysis for Defluorinative Carbon–Heteroatom

Coupling Reactions

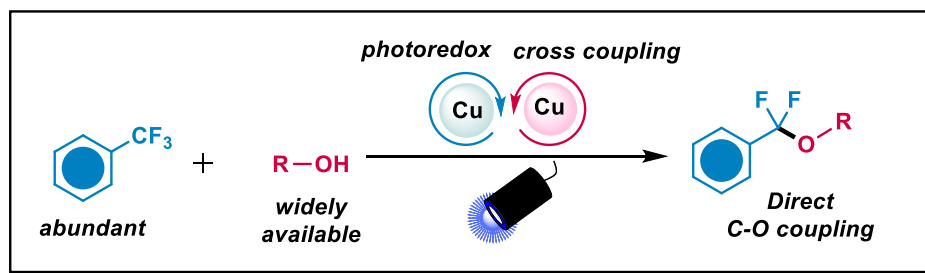
(脱フッ素型炭素-ヘテロ原子カップリング反応のための銅光酸化還元触媒の開発)

Fluorinated organic molecules continue to play a pivotal role in the development of functional materials and pharmaceuticals, with structural innovation serving as a key driver for unlocking novel properties. Among these, Difluoroalkylether ($R^1\text{--CF}_2\text{O--R}^2$) units are unique class of fluorinated molecule, found in liquid crystals and anticancer drug candidates. Traditional synthesis involves multi-step fluorination of carbonyl derivatives, which limits efficiency. In contrast, direct defluorinative C–O coupling between trifluoromethyl compounds and alcohols offers a more convergent and step-economical route.

In parallel, the field of photoredox catalysis has experienced rapid growth through the integration of earth-abundant base metals, particularly copper. Compared to traditional iridium-, ruthenium-, or organic-based photocatalysts, copper offers notable advantages, including cost efficiency, environmental sustainability, and broad tunability. The use of tailored ligands enables precise modulation of the copper center's photophysical and stereoelectronic properties, granting access to multiple oxidation states ($\text{Cu}^{\text{I/II/III}}$). These features have significantly expanded the utility of copper photocatalysts in organic synthesis.

Defluorinative C–O Coupling between Trifluoromethylarenes and Alcohols via Copper Photoredox Catalysis

Copper-catalyzed, photoinduced defluorinative C–O bond formation between trifluoromethylarenes and alcohols, affording access to a broad range of difluorobenzyl ethers (ArCF_2OR). By fine-tuning the reaction conditions we can selectively generate ArCF_2I compounds. Mechanistic studies revealed that ArCF_2I species can act as latent precursors for the generation of difluorobenzyl radicals ($\text{ArCF}_2\cdot$), which serve as key intermediates in the transformation. Experimental evidence supports a dual-catalytic mechanism involving two distinct copper(I) complexes: a homoleptic CuP_4 complex functioning as the light-absorbing photocatalyst for C–F bond activation, and a CuP_2 complex facilitating the C–O bond-forming step. The synergistic roles of LiI and $\text{Zn}(\text{OAc})_2$ as crucial additives were elucidated, highlighting their importance in maintaining the redox balance and catalytic efficiency. This dual-function copper system exemplifies the potential of base metal photoredox catalysis to coordinate complex bond activations and constructions within a unified catalytic framework.



Homoleptic copper(I)-bisphosphine complexes as photoredox catalysts

Copper-based photoredox catalysis has become a valuable tool in modern organic synthesis, with tetracoordinate copper complexes serving as key catalytic species. Among these, homoleptic CuN_4 complexes featuring two bisimine ligands and heteroleptic CuN_2P_2 complexes containing one bisimine and one bisphosphine ligand have been most extensively investigated due to their favorable catalytic performance. In contrast, homoleptic bisphosphine-ligated copper complexes (CuP_4) have remained relatively understudied, despite emerging evidence of their potential in facilitating novel photochemical transformations.

We did a comprehensive investigation of CuP_4 complexes as a distinct class of copper-based photocatalysts. A series of representative CuP_4 complexes were synthesized and subjected to detailed photophysical and electrochemical characterization. Their catalytic performance was evaluated in model photocatalytic coupling reactions, demonstrating their competence as an active species. The findings offer valuable insights into the structure–property relationships of CuP_4 systems and establish a foundation for the rational design of next-generation copper photocatalysts with enhanced reactivity and selectivity.

