BODNs as Biocompatible Brominating Reagents for Visible-Light Photocatalytic Tyrosine Modification

([1]*Institute for Catalysis, Hokkaido University*, [2]*Department of Chemistry, Faculty of Science, Kyusyu University*, [3]*List Sustainable Digital Transformation Catalyst Collaboration Research Platform, Institute for Chemical Reaction Design and Discovery (ICReDD List-PF), Hokkaido University*) ○Rakuto Yoshida,[1] Yuichiro Hori,[2] Daisuke Uraguchi,[1,3] Keisuke Asano[1]

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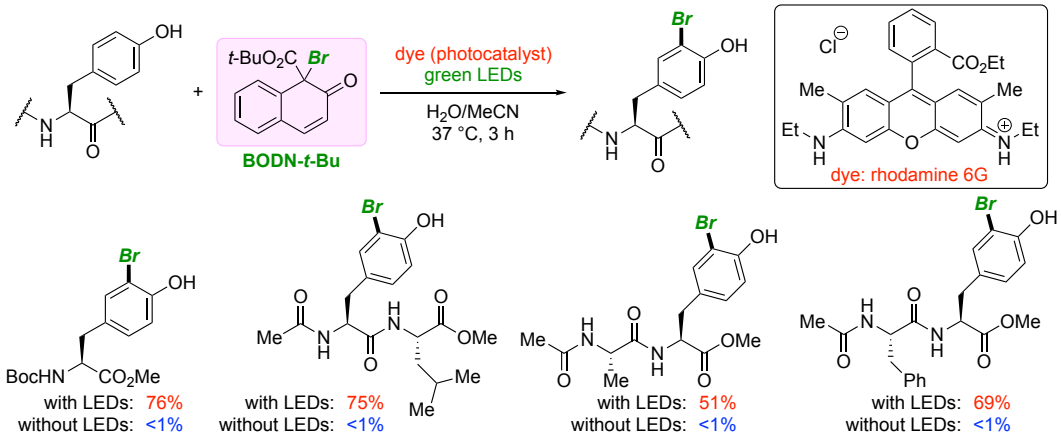
Photocatalytic labeling of amino acid side chains in proteins is crucial for understanding significant biomolecular communications. However, amino acid residues with limited surface exposure, such as tyrosine, exhibit lower reactivity, resulting in decreased sensitivity in mass analyses of labeled molecules despite their biological importance. The bromo group serves as a sensitive mass tag that is valuable for analyzing complex macromolecules due to the relative abundance of bromine isotopes. However, biocompatible methodologies for photocatalytic bromination remain underdeveloped due to the lack of a brominating reagent, reactions of which can be catalytically controlled under biocompatible conditions. In this study, we investigated the photochemical reactivity of 1-bromo-2-oxo-1,2-dihydronaphthalene-1-carboxylates (BODNs).[1] These compounds remain stable in the dark under physiological conditions but become activated as brominating reagents under visible light irradiation in the presence of a catalyst during tyrosine modification. Photocatalytic reactions offer advantages such as the use of less invasive light with a longer wavelength as compared to non-catalytic reactions and the spatiotemporal control of bromination. In our reaction system, the fluorescent dyes commonly utilized in bioimaging probes serve as photocatalysts. This characteristic facilitates the applications of BODNs as chemical biology tools enabling the installation of attractive labeling tags on tyrosine-containing peptides and proteins.



1) Yoshida, R.; Hori, Y.; Uraguchi, D.; Asano, K. *Chem. Commun.* **2024**, *60*, 12381.