## Blue Light Driven C–C Bond Formation Reaction via $\alpha$ -Thiomethyl Radicals Derived from Thioanisole Derivatives

(Graduate School of Science and Engineering, Doshisha University) O Pijush Kanti Roy, Masahito Kodera, Yutaka Hitomi

**Keywords**: C–C Bond Formation; Thioanisole; Charge Transfer Complex; Titanium Dioxide; Oxidative Cyclization

Photochemical C–H activation of thioethers to  $\alpha$ -thioalkyl radical is an attractive strategy for subsequent C–C bond formation; in 2020, Alfonzo and Hande reported that thioethers' C–H activation, as shown in Scheme 1, produces  $\alpha$ -thioalkyl radicals, which afford alkylated products with electron-deficient olefins in the presence of photoredox and weak Brønsted base catalysis [1].

We found that the reactions between thioanisole derivatives and benzylmalononitrile, one of the electron-deficient olefins, proceed by irradiating their charge transfer complexes with blue light even without a photosensitizer.

However, the reactions between thioanisole derivatives and *N*-alkyl maleimide derivatives do not proceed under the same conditions, except



Scheme 1 Strategy for formation of thioalkyl radicals and subsequent carbon-carbon bond formation

for the reaction using 4-nitrothioanisole. However, to our delight, the reactions were promoted in the presence of titanium dioxide under blue light irradiation. In our previous work, TiO<sub>2</sub> can selectively transform toluene to benzaldehyde under blue light irradiation in the presence of dioxygen [2]. Therefore, we propose that an interfacial charge transfer occurs from thioanisole derivatives to the conduction band of TiO<sub>2</sub> under blue light irradiation, resulting in  $\pi$ -cation radical formation and deprotonation (Scheme 1).

1) E. Alfonzo and S. M. Hande ACS Catal. 2020, 10, 12590. 2) K. Aitsuki, D. Fukushima, H. Nakahara, K. Yo, M. Kodera, S. Okunaka, H. Tokudome, T. Koitaya, Y. Hitomi, New J. Chem. 2022, 46, 9010.