論　文　の　要　旨

題　目　　Development of Two-photon Responsive Photocatalysts and Their Application
(二光子応答性光触媒の開発とその応用)

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Conventional photocatalysts typically rely on one-photon (1P) absorption to achieve the excited state, and subsequently catalyze reactions via intermolecular electron transfer. However, this approach has limitations, as only high energy light in the ultraviolet or visible range can be utilized, resulting in low penetration and competing absorption with substrates. To overcome these limitations, two-photon (2P) responsive photosensitizers can be used. These utilize light in the near-infrared (NIR) region to undergo two-photon excitation processes. 2P responsive photocatalysts offer several advantages over 1P responsive photocatalysts, such as being less substrate competitive absorption, having high three-dimensional spatial resolution, deep penetration, and low scattering.

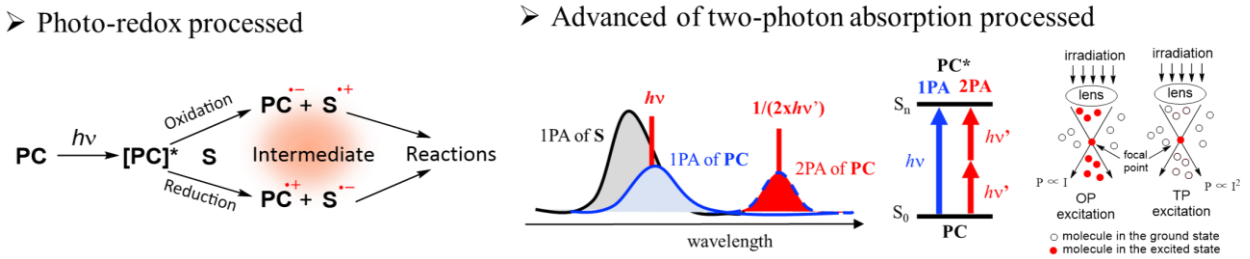

Figure 1. Photo-redox processed and different of 1P and 2P excitation

For above reason, my research focuses the design and synthesis of a new series of 2P responsive photocatalysts. In this study, new coumarin derivatives were designed using two combined approaches. One strategy involved replacing the alkylamines with aromatic groups such as carbazole or diphenylamine (Figure 2a). This substitution expanded the conjugation system, thereby improving the two-photon absorption (2PA) capability. Another approach entailed substituting the quadrupolar system with an octupolar system, a widely employed method to enhance 2PA characteristic.

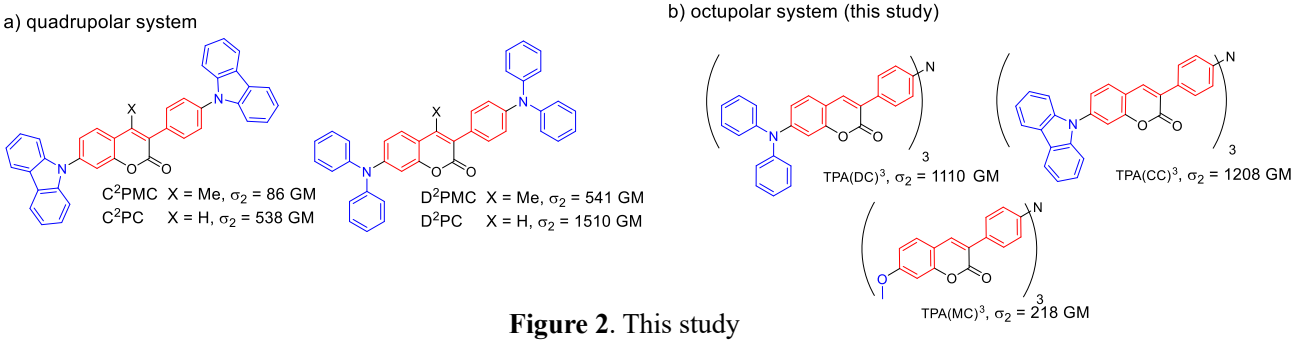

Figure 2. This study

Among the quadrupolar compounds, the introduction of a methyl group at the 4-position and the use of a carbazole group as the donor group led to high oxidation potential. However, these compounds exhibited hypsochromic shifts in absorption and emission maxima, along with reduced 2P characteristics compared to those without a methyl group and featuring a strong donor group such as diphenylamine instead of carbazole. The octupolar compounds demonstrated much higher maximum molar extinction coefficients compared to the quadrupolar compounds. Furthermore, octupolar compounds showed notable bathochromic shifts compared to their quadrupolar counterparts. For instance, TPA(CC)^3 displayed higher 2PA cross-section values than C^{2}PC (538 GM, at 680 nm). Other compounds such as C^{2}PMC (86 GM, at 680 nm), D^{2}PMC (541 GM, at 720 nm), D^{2}PC (1510 GM, at 740 nm), TPA(MC)^3 (218 GM, at 680 nm), and TPA(DC)^3 (1110 GM, at 740 nm) also showed strong 2PA characteristics. The enhancement in 2PA capacity was achieved by incorporating strong electron-donating groups or forming octupolar systems. These 2PA-responsive chromophores also hold potential applications in uncaging reactions of bioactive compounds and photosynthesis processes under 2PA conditions.

Quadrupolar compounds have already been applied as photocatalysts for borylation and C-C coupling reaction under LED light (1P absorption reaction) or a Ti-sapphire femtosecond laser (2PA reaction).

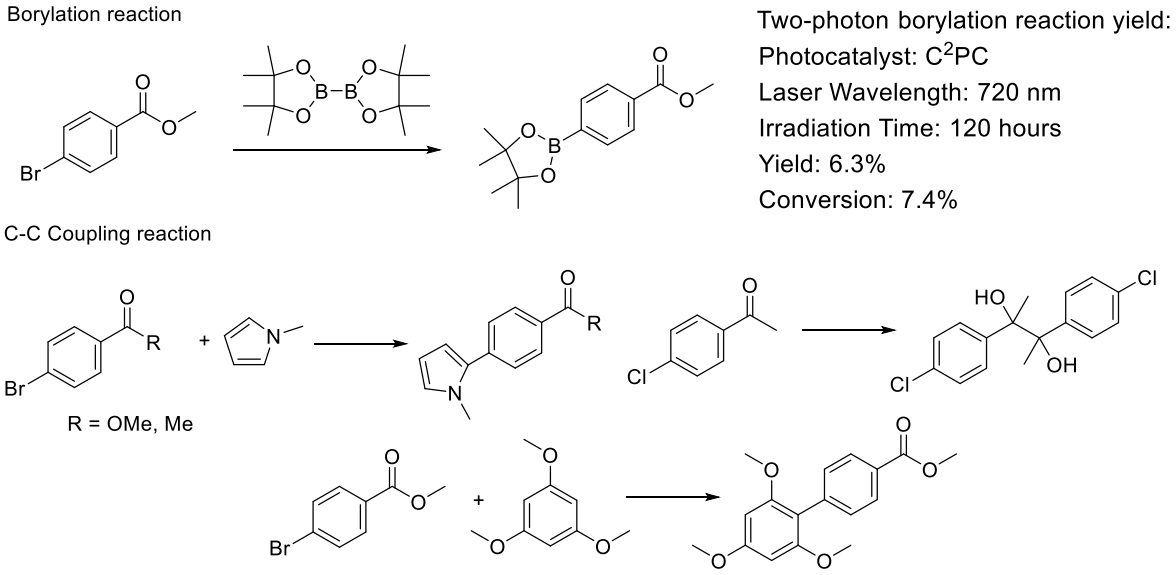

Figure 3. Photoreaction

1. L. T. B. Nguyen, M. Abe, Bull. Chem. Soc. Jpn. 2023, 96 (9), 899–906.
2. E. B Santiko, S. B Babu, F. Zhang, CL. Wu; TC. Lin, M. Abe, Chem Lett. 2023, 52(11), 846-849