

# 学位論文要約

## 題目 **Synthesis, Characterization, and Utilization of the Metal-Free Two-Photon Responsive Photoredox Catalyst**

(金属を含まない二光子応答性光レドックス触媒の設計、合成、特性評価および利用)

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Study of synthesis, characterization and utilization of new metal-free two-photon photoredox catalyst was carried out. A new cyclic stilbene derivative, 6-(4-(diphenylamino)phenyl)-*N,N*-diphenyl-7,8-dihydronaphthalen-2-amine (D<sup>2</sup>PDN), featuring quadrupolar system having electron-donating substituents (NPh<sub>2</sub>), was synthesized and characterized in this study. The fluorescence quantum yield was 89% (under air) and 99% (under argon) in toluene. The two-photon (2P) cross-section was determined to be 166 GM at 700 nm using 2P-excitation fluorescence method. The 2P-responsive chromophore in near-infrared region has reversible oxidation signals at 0.17, 0.28, and 0.53 V vs Fc<sup>0</sup>/Fc<sup>+</sup>. Compound D<sup>2</sup>PDN,  $E^*_{\text{ox}} = -2.83$  V, was found to be used as a simultaneous 2P-responsive photoredox catalyst. The simple reduction reaction of aryl halide was selected as a model reaction. The photoinduced reduction of methyl 4-bromobenzoate (MBB, 94 mM) and methyl 10-bromo-9-anthracenecarboxylate (MBA, 94 mM) were conducted at room temperature for 120 or 9 hours under a nitrogen atmosphere by 2P excitation at 700 nm using Ti-Sapphire laser or 405 nm-LED (band width = 20 nm), respectively, in the presence of D<sup>2</sup>PDN (5 mol%) and triethylamine (TEA) (11.6 equiv.) in dry dimethylformamide. The reduction product, methyl benzoate (MB) and methyl 9-anthracenecarboxylate (MA), were obtained in the 2P photolysis and 1P-photolysis: for MB 8.4% yields at 9.8% conversion and 95.9% yields at 96.5% conversion, respectively. Higher product selectivity of 9-anthracenecarboxylate (MA) obtained in 2P than 1P. No significant amount of MB and MA were detected in the 2P excitation reaction in the absence of D<sup>2</sup>PDN. In the present study, a new 2P-responsive stilbene, D<sup>2</sup>PDN, 6-(4-(diphenylamino)phenyl)-*N,N*-diphenyl-7,8-dihydronaphthalen-2-amine, was prepared in five steps from the commercially available compound. The new D- $\pi$ -D stilbene derivative featuring the cyclic structure and quadrupolar system showed the increase of the fluorescence quantum yield and 2P cross section, compared to the non-cyclic similar compound, (E)-4,4'-(ethene-1,2-diyl)bis(*N,N*-diphenylaniline). The 2P-responsive chromophore was found to be utilized for photoredox reactions as a photo-oxidation catalyst.