論　文　の　要　旨

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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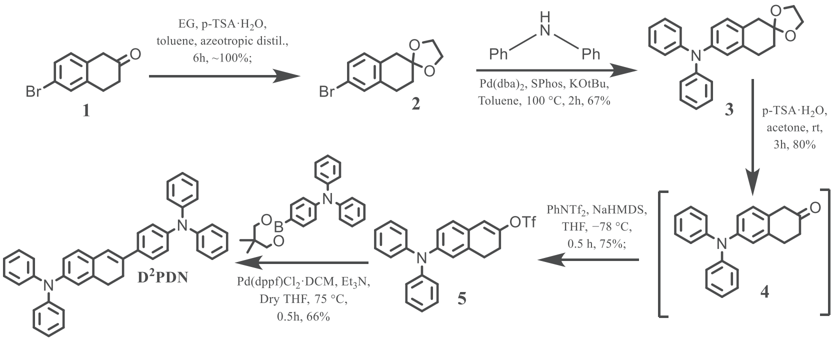
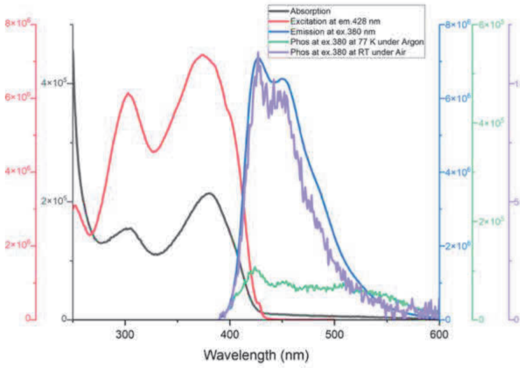
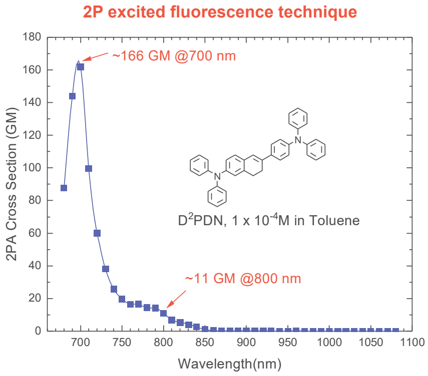
Compounds with two-photon (2P) absorption in the near-infrared region have attracted much interest since the beginning of the 2000s for research in micrometer-sized materials processing, multiphoton excitation luminescence materials, and the elucidation of biological phenomena in deep area of living tissues. For the physiological experiments that require 2P excitation using the biological window of 650 – 1050 nm light, relatively small π conjugated chromophores with high two-photon absorption ability is required due to the water solubility. Thus, we have focused on the stilbene skeleton, which has a small π-electron system but has relatively high two-photon absorption character. The design, synthesis, and application of stilbene derivatives have been done for the research of caged compounds that can release biologically active substances by light irradiation. In the course of study, we have found that D^{2}PDN, 6-(4-(diphenylamino)phenyl)-*N*,*N*-diphenyl-7,8-dihydronaphthalen-2-amine, in which a diphenylamine moiety having strong electron-donating ability and increasing the π-conjugation system is introduced into the cyclic stilbene skeleton, has an extremely high fluorescence efficiency (Φ_f = 0.89 under air and 0.99 under argon) and a relatively high two-photon absorption (~170 GM at 700 nm) in the biological window. The new cyclic stilbene derivative, D^{2}PDN, can be used not only as an imaging material because of its high quantum yield of luminescence, but can also be used as a photoredox catalyst, whose research area has been dramatically developed recently. In this study, the synthesis, characterization, and application of D^{2}PDN as a photoredox catalyst has been investigated.



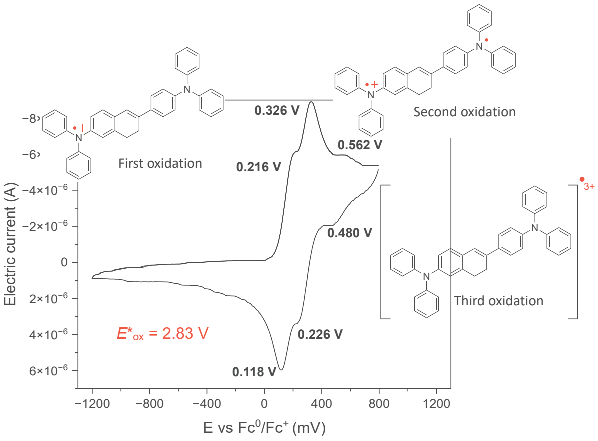


The cyclic stilbene D^{2}PDN was synthesized in 5 steps from the commercially available compound, 6-bromo-2-tetralone. After the protection of the ketone group, the C–N coupling reaction was performed to afford compound **2**. After the preparation of triflate **4**, Suzuki-Miyaura cross-coupling of **4** with 4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-*N*,*N*-diphenylaniline gave D^{2}PDN.

The absorption and fluorescence spectra of D^2PDN are shown in Figure of the right-hand side. The two absorption bands were observed at 303 and 383 nm in toluene. The strong fluorescence signal was observed in ~400–550 nm with the quantum yield (Φ_f) of 99% under argon and 91% under air both in toluene and DMF. The fluorescence lifetime was determined to be 1.36 ns using time-correlated single photon counting (TCSPC) method. The decrease of the fluorescence quantum yield under air suggests the existence of thermally activated delayed fluorescence (TADF). Indeed, under oxygen atmosphere, the fluoresce intensity decreased by 40% of that under argon. The singlet excited state energy (E_S) was determined to be 68.9 kcal mol^{-1} in toluene from the crossing point between the absorption and fluorescence spectra. A very weak phosphoresce (delay time, 50 μs) was detected at 77 K with the concomitant observation with the fluorescence signal, suggesting the triplet energy (E_T) of D^2PDN is very close to the singlet excited state energy. The 2P absorption spectrum of D^2PDN in toluene determined by the 2P excited fluorescence (2PEF) technique showed a 2P absorption maximum at ~700 nm with 2P cross section (σ_2) of 166 GM (Figure 2). The 2P signal peak was blue-shifted compared to the double wavelength (766 nm) of 1P absorption maximum (383 nm), which is a typical phenomenon for quadrupole system. The fluorescence quantum yield and 2P cross section value were higher than those of acyclic stilbene derivative, $\Phi_f = 0.78$ under air and σ_2= 75 GM at 720 nm in tetrahydrofuran (THF).



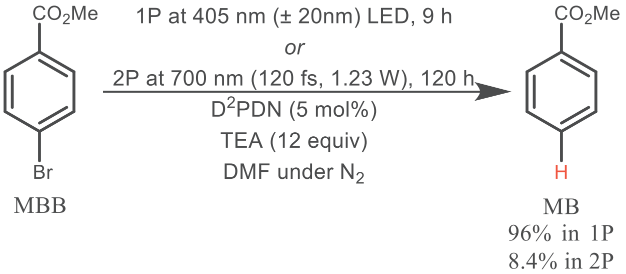
The sub-nanosecond time-resolved transient absorption (TA) spectroscopy was conducted at 355 nm (pulse-width 200 ps) for D^2PDN using randomly-interleaved-pulse-train (RIPT) method at 295 K in toluene. The strong TA signal at ~700 nm was observed with the lifetime of 1.56 ns under argon and 1.41 ns under air, which are near consistent with the fluorescence lifetimes measured by the TCSPS method. The recovering process of D^2PDN with the similar rate constant was observed at ~450 nm, suggesting that the signal at ~700 nm is derived from the electronic excitation from S_1 to S_n state. After disappearing the singlet-excited signal, the weak and broad signal at ~550 nm was observed, whose lifetime was 3.1 μs under argon and 128 ns under air. The significant quenching in the presence of oxygen clearly indicates that the signal is from the triplet state of D^2PDN. The observation of the triplet signal supports the TADF phenomenon of D^2PDN.



The redox property of D^2PDN was a nalyzed using cyclic voltammetry in dichloromethane. The three oxidation signals were observed at 0.17, 0.28, and 0.53 V vs Fc^0/Fc^+. Thus, the oxidation potential of the singlet-excited state D^2PDN was determined to be –2.83 V vs Fc^0/Fc^+. The formation of monocation $[D^2PDN]^{\cdot+}$ and dication $[D^2PDN]^{2+}$ were observed at ~1400 nm and ~800 nm in the reaction with 1 equivalent of $AgSbF_6$ and 18.8 equivalent of $AgSbF_6$ in dichloromethane. The absorption spectra were well reproduced by the time-dependent density functional theory (TD-DFT) calculations for the radical cation and singlet state of dication-diradical at the

UB3LYP/6-31G(d) level of theory. The generation of monocation species was also confirmed by the electron paramagnetic resonance (EPR) spectroscopy.

Since the relatively high oxidation ability of singlet excited state of D^2PDN was uncovered by this study, $E^*_{ox} = -2.82$ V, D^2PDN was applied to use as a photoredox catalyst. The simple reduction reaction of aryl halide was selected as a model reaction (equation 1). The photoinduced reduction of methyl 4-bromobenzoate (94 mM) was conducted at room temperature for 9 hours under nitrogen atmosphere using 405 nm-LED (band width = 20 nm) in the presence of D^2PDN (5 mol%) and triethyl amine (11.6 equiv) in dry dimethyl formamide (DMF). The reduction product methyl benzoate was obtained in 97% using 1P and 87% using 2P, suggesting that D^2PDN can be used as a photoredox catalysis.



Equation 1. Photoredox reaction of MBB to MB by D^2PDN

In the present study, a new 2P-responsive stilbene, D^2PDN, 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–π–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 chromatophore was found to be utilized for photoredox reactions as a photo-oxidation catalyst.

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