

Stepwise Two-Photon-Gated Photochemical Reaction in Photochromic [2.2]Paracyclophane-Bridged Bis(imidazole dimer)

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S Supporting Information

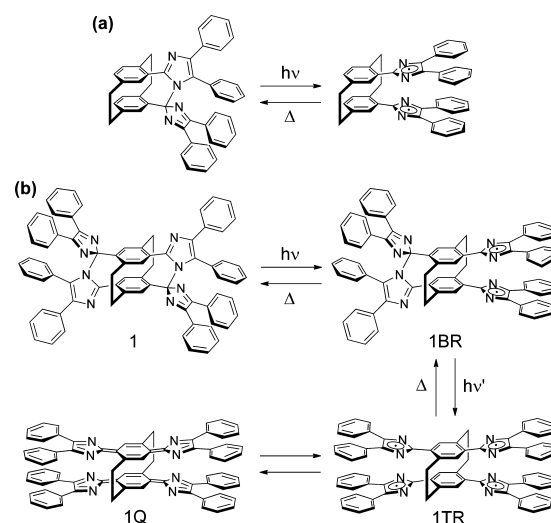
ABSTRACT: Stepwise two-photon processes not only have great potential for efficient light harvesting but also can provide valuable insights into novel photochemical sciences. Here we have designed a [2.2]paracyclophane-bridged bis(imidazole dimer), a molecule that is composed of two photochromic units and absorbs two photons in a stepwise manner. The absorption of the first photon leads to the formation of a short-lived biradical species (half-life = 88 ms at 298 K), while the absorption of the additional photon by the biradical species triggers a subsequent photochromic reaction to afford a long-lived quinoid species. The short-lived biradical species and the long-lived quinoid species display significantly different absorption spectra and rates of the thermal back-reaction. The stepwise two-photon excitation process in this photochromic system can be initiated even by incoherent continuous-wave light irradiation, indicating that this two-photon reaction is highly efficient. Our molecule based on the bridged bis(imidazole dimer) unit should be a good candidate for multiphoton-gated optical materials.

Molecules with multiphoton-induced optical properties have captured the interest of researchers for the underlying scientific principles and their potential in industrial applications such as two-photon microscopy.¹ While two-photon absorption through a virtual state can be induced only by a pulsed laser because of their high power thresholds ($\sim \text{MW}/\text{cm}^2$), two-photon absorption through long-lived transient species such as triplet states and electronic states of rare-earth compounds can be induced even by using incoherent continuous-wave (CW) light. One example of the latter process, the stepwise two-photon process, is a widely recognized fluorescence upconversion.² Stepwise two-photon processes have great potential and not only are interesting photochemical phenomena but also can be useful as efficient light harvesters. However, materials that undergo efficient stepwise two-photon processes are rare because of the stringent requirements on the transient species, i.e., they should be stable and long-lived and have large absorption coefficients.

Previous studies have reported on the stepwise reaction of photochromic compounds comprising two photochromic units.³ Efficient mutual interaction between the two chromophoric units enhances the overall photochromic property of the molecule. However, in many cases the electronic structure of the molecule

is merely the superposition of the two independent component chromophores. In addition, energy transfer between the colorless and colored chromophores can inhibit the photochromic reaction of the colorless photochromic chromophore.^{3a,b,f,4} Therefore, compounds that exhibit stepwise photochemical reactions are required for the development of efficient, functional photosensitive materials. The [2.2]paracyclophane ([2.2]PC)-bridged imidazole dimer is a T-type photochromic compound (Scheme 1a); UV-light-induced coloration rapidly fades in the

Scheme 1. Photochromic Reactions of [2.2]PC-Bridged Imidazole Dimer (a) and Bis(imidazole dimer) (1) (b)



dark (half-life ($\tau_{1/2}$) = 33 ms at 298 K in benzene).⁵ The colored form of the [2.2]PC-bridged imidazole dimer (biradical) does not undergo other photochemical reactions; rather, the absorbed photon energy is relaxed via a nonradiative relaxation pathway. The colored form of the [2.2]PC-bridged imidazole dimer can be considered as a metastable transient species, such as the long-lived excited state in triplet–triplet annihilation. The sufficiently long lifetime and the high fatigue resistance of the photo-generated biradical species allow for the induction of additional photochemical reactions. If the colored form of the [2.2]PC-

Received: March 21, 2015

Published: April 24, 2015

bridged imidazole dimer can undergo an additional photochemical reaction through the excited states, the [2.2]PC-bridged imidazole dimer can then undergo a novel stepwise two-photon process in which absorption of the first photon triggers a fast photoswitch and absorption of an additional photon triggers a second photochemical or photochromic reaction.

In this study, we designed a [2.2]PC-bridged bis(imidazole dimer) (**1**) (Scheme 1b) in which two photochromic units are linked via the [2.2]PC moiety. Upon UV irradiation, C–N bonds in **1** are likely to be cleaved, leading to the formation of two colored species: a biradical species (**1BR**) and a quinoid species (**1Q**). Because **1Q**, which is generated by stepwise absorption of two photons, has a 1,4-bis(4,5-diphenylimidazol-2-ylidene)-cyclohexa-2,5-diene (BDPI-2Y)^{6a} motif, interactions between the imidazolyl radicals substituted at the 1,4-positions of the central phenylene ring are expected to influence the electronic structure of the molecule. Meanwhile, the electronic structure of **1BR**, generated by one-photon absorption, is influenced by the face-to-face interaction of the imidazolyl radicals. Thus, **1BR** and **1Q** likely will exhibit significantly different absorption spectra and thermal back-reaction rates. In this system, the color and rate of the photochromic reaction can be controlled by the power of the excitation source.

Compound **1** is synthesized as depicted in Scheme S1 in the Supporting Information (SI). Oxidation of the precursor lophine (**4**) gives a crude mixture of **1a** and **1b**, in which the 6 π - and 4 π -imidazole rings (Im 1 and Im 2, respectively) are connected via the [2.2]PC moiety in the anti and syn configurations, respectively. The molecular structures of **1a**, **1b**, and **4** were clarified by X-ray crystallographic analysis (Figure 1 and Figure

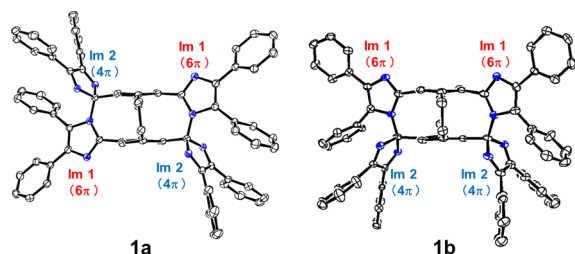


Figure 1. ORTEP representations of the molecular structures of **1a** and **1b** (thermal ellipsoids at 50% probability; N atoms shown in blue; H atoms and solvent molecules omitted for clarity).

S9 in the SI). The [2.2]PC moiety in **4** is distorted as a result of the steric repulsion between the faces of the two imidazole substituents; however, the formation of the C–N bond between the two imidazole rings in **1a** and **1b** reduces the associated strain. The lengths of the C–N bonds in **1a** (1.491 Å) and **1b** (1.487 Å) are nearly identical to that in the [2.2]PC-bridged imidazole dimer (1.489 Å).⁵ Henceforth, only the photochromic properties of **1a** are described, as photochromic reactions of either isomer lead to the formation of a mixture of **1a** and **1b** through photoisomerization via the photogenerated **1BR** or **1Q**.

Both **1a** and **1b** display absorption bands in the UV region only (Figure S10). Figure 2a shows the transient absorption spectra of **1a** recorded in benzene after irradiation with a 355 nm laser pulse (pulse width = 5 ns and pulse energy = 3 mJ). A sharp absorption band at 400 nm and broad absorption bands in the visible region (500–900 nm) are observed. This absorption profile is similar to that of the biradical species generated from the [2.2]PC-bridged imidazole dimer (Figure S11); therefore, the transient species generated upon UV irradiation is designated as **1BR**. The

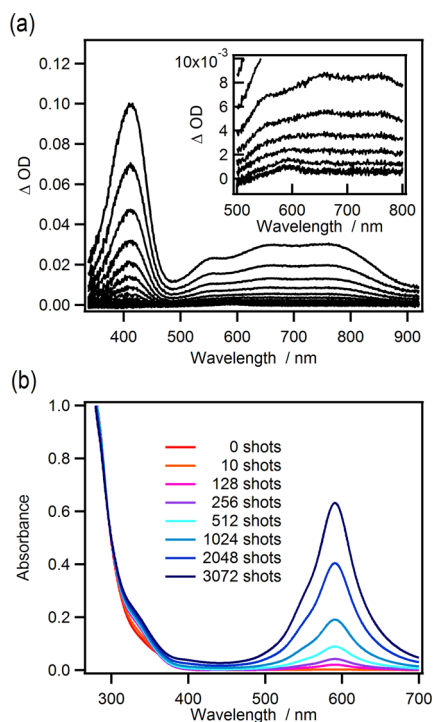


Figure 2. (a) Transient vis–NIR absorption spectra of **1a** in degassed benzene (2.1×10^{-5} M; $\lambda_{\text{ex}} = 355$ nm, pulse width = 5 ns, pulse energy = 3 mJ). The spectra were recorded at 50 ms intervals. (b) UV–vis absorption spectra for the degassed benzene solution of **1a** (298 K, 2.1×10^{-5} M) measured after repetitive irradiation with 355 nm laser pulses.

transient absorption spectra decay monotonically with first-order kinetics, and the $\tau_{1/2}$ of **1BR** is estimated to be 88 ms at 298 K in benzene (Figure S12). The rates of the thermal back-reaction at temperatures ranging from 278 to 313 K are summarized in Table S4 in the SI. The activation parameters estimated from Eyring plots (Figure S13) are $\Delta H^\ddagger = 61.8$ kJ mol⁻¹, $\Delta S^\ddagger = -20.4$ J mol⁻¹ K⁻¹, and $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger = 67.9$ kJ mol⁻¹ at 298 K. The values of these activation parameters are similar to those determined for the [2.2]PC-bridged imidazole dimer.⁵

While the properties of **1BR** are similar to those of the biradical species of the [2.2]PC-bridged imidazole dimer, another long-lived deep-blue-colored species was also observed upon nanosecond UV irradiation of **1a**. The transient absorption band of the deep-blue-colored species was weakly observed at ~600 nm with single-pulse excitation at 355 nm (Figure 2a inset). With repeated exposure to the laser pulses, the intensity of this band gradually increased (Figure 2b). This absorption spectrum (the band at ~600 nm) and the IR spectrum of the photogenerated species are nearly identical to those of the quinoid species of BDPI-2Y (Figure S14),⁶ indicating the formation of **1Q** from the photogenerated transient **1BR**. When stored in the dark at room temperature, the absorption band attributed to **1Q** gradually but completely disappeared in 4 days (Figure S15). This extreme deceleration of the thermal back-reaction, i.e., the decoloration leading to the formation of the colorless bis(imidazole dimer), indicates the stabilization of **1Q** by the delocalization of the π electrons over the framework of BDPI-2Y. The thermally excited **1Q**, which has a tetraradical character, reverts back to the initial imidazole dimer.^{6b,c} On the basis of these observations, a plausible reaction scheme for the photochromic reaction of **1** can be formulated. In the one-photon reaction, cleavage of the C–N bond in **1** leads to the

formation of **1BR**, which immediately reverts back to the initial **1** (Figure 2). Meanwhile, when the photogenerated **1BR** absorbs an additional photon (two-photon reaction) during the incidence of the laser pulse, another C–N bond of **1BR** is cleaved, resulting in the formation of **1Q** through the short-lived tetradical **1TR**. In other words, the proposed mechanism states that the formation of **1Q** is not dependent on the total number of irradiated photons but dependent only on the ability of the biradical species **1BR** to absorb an additional photon.

Two kinds of experiments were pursued to evaluate the proposed mechanism: (1) repetitive exposure of **1a** to femtosecond laser pulses and (2) double pulse nanosecond laser flash photolysis measurements. Previously reported femtosecond pump–probe experiments revealed that the formation of radicals in the bridged imidazole dimer and hexaarylbiimidazole (HABI) occur on the subpicosecond time scale.⁷ If the photocleavage of **1** occurs on a similar time scale, excitation with a femtosecond laser pulse (pulse width = 160 fs) does not prompt the stepwise two-photon reaction because the photocleavage reaction takes longer than the duration of the femtosecond laser pulse. Figure S16 shows the UV–vis absorption spectrum of **1** after repetitive exposures to the femtosecond laser pulses (365 nm, 7 $\mu\text{J}/\text{pulse}$). To discourage the residual **1BR** from absorbing any photons, the repetition rate of the femtosecond laser was set to 2.5 Hz, and the sample solution was irradiated with 50000 shots of the femtosecond laser. Alternatively, the solution was irradiated with CW UV light (365 nm, 110 mW) for 2 s. The total photon energies were 0.35 and 0.22 J for the femtosecond pulses and CW light, respectively. While the absorption band at ~ 600 nm did not appear upon irradiation with the femtosecond laser pulses, irradiation with the CW light produced **1Q** efficiently despite the fact that the photon density and total number of photons in the CW are much lower than those in the femtosecond laser pulse (movie S1 in the SI). This result indicates that **1Q** is formed when **1BR** absorbs the additional photon during the thermal back-reaction.

The mechanism for the formation of **1Q** via the stepwise two-photon process was investigated using temporally delayed double pulse nanosecond laser flash photolysis experiments. Because we first confirmed that excitation of **1** with a laser pulse of 420 nm does not lead to any photochemical reaction, the excitation wavelength for the second laser pulse was set to 420 nm. The transient absorption spectra recorded after the double pulse excitation are shown in Figure 3a. It is clearly evident that the concentration of **1Q** increased upon excitation with 420 nm laser pulses provided after a 1 μs delay after the first excitation with 355 nm light. In contrast, **1Q** was not observed when the second excitation was attempted with a laser pulse at 550 or 650 nm (Figure S17), indicating that there is an energy threshold to cleave the C–N bond of **1BR**. In previous reports, density functional theory (DFT) calculations and electrochemistry studies suggested that the transition to the LUMO, where the C–N bond has antibonding character, is necessary for the photochromic reaction to occur in the [2.2]PC-bridged imidazole dimer.^{8,9} The $S_0 \rightarrow S_1$ transition of the [2.2]PC-bridged imidazole dimer, which is attributed to the HOMO \rightarrow LUMO transition, was calculated by time-dependent DFT to appear at 460 nm.⁹ However, because the [2.2]PC-bridged imidazole dimer has weaker absorption at 460 nm as a result of the low oscillator strength of the $S_0 \rightarrow S_1$ transition, the photochromic reaction occurs through transitions to highly excited states, which have higher oscillator strengths. The imidazole dimer unit of **1BR** would also have the optically

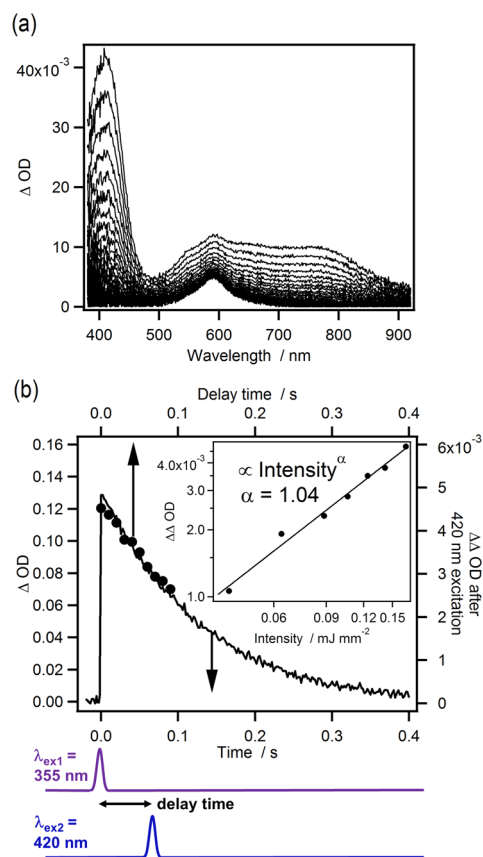


Figure 3. (a) Transient vis–NIR absorption spectra of **1a** in degassed benzene after the double pulse laser excitation (1.2×10^{-5} M; $\lambda_{\text{ex1}} = 355$ nm, pulse width = 5 ns, pulse energy = 1 mJ; $\lambda_{\text{ex2}} = 420$ nm, pulse energy = 5.5 mJ, delay time = 1 μs). The spectra were recorded at 20 ms intervals. (b) Decay profile of **1BR** monitored at 400 nm (line) and $\Delta\Delta\text{OD}$ values at 590 nm as a function of the delay time in degassed benzene (solid circles) (1.2×10^{-5} M; $\lambda_{\text{ex1}} = 355$ nm, pulse width = 5 ns, pulse energy = 1 mJ; $\lambda_{\text{ex2}} = 420$ nm, pulse energy = 5.5 mJ, delay time = 1 μs –90 ms). The inset shows the double logarithmic plot of $\Delta\Delta\text{OD}$ at 590 nm as a function of the intensity of the 420 nm laser pulse (1.2×10^{-5} M; $\lambda_{\text{ex1}} = 355$ nm; pulse width = 5 ns, pulse energy = 1 mJ; $\lambda_{\text{ex2}} = 420$ nm, pulse energy = 1.2–4.7 mJ, delay time = 1 μs).

inactive $S_0 \rightarrow S_1$ transition at around 460 nm, similar to that of the [2.2]PC-bridged imidazole dimer. The photocleavage reaction of the C–N bond of **1BR** can be considered as follows. The biradical unit of **1BR** acts as a light harvester to obtain the sufficient energy to cleave the C–N bond. The absorption of **1BR** at 420 nm would be dominated by the transition of the biradical unit because the spectral shape of **1BR** is very similar to that of the biradical of the [2.2]PC-bridged imidazole dimer (Figure 2a). Thus, the imidazole dimer unit of **1BR** could obtain enough energy to cleave the C–N bond from the excited biradical unit upon excitation at 420 nm.

We define $\Delta\Delta\text{OD} = \Delta\text{OD}_{420} - \Delta\text{OD}_{355}$ as the difference between the optical density difference (ΔOD) measured at 590 nm after the first laser excitation at 355 nm (ΔOD_{355}) and the ΔOD measured at 590 nm after the second laser excitation at 420 nm (ΔOD_{420}). The $\Delta\Delta\text{OD}$ value corresponds to the population of **1Q** generated as a result of excitation with the 420 nm laser pulse. Changing the time delay between the first and second excitation pulses allows the effect of the population of **1BR** on the photogeneration of **1Q** to be investigated (Figures S18 and S19). The variation in $\Delta\Delta\text{OD}$ as a function of the time delay between

the two laser pulses readily describes the decay kinetics of **IBR** excited with only the 355 nm laser irradiation (Figure 3b). In addition, the value of $\log(\Delta\Delta\text{OD})$ increases linearly (slope = 1.04; Figure 3b inset) with the increase in the logarithm of the intensity of the second laser pulse. The power threshold of the stepwise two-photon process was estimated by the 5 ns laser pulse excitation (repetition rate = 1 Hz) at 355 nm (Figure S20). The absorbance due to **IQ** showed a quadratic dependence on the excitation intensity. The power threshold to observe **IQ** through the stepwise two-photon reaction was estimated to be 0.1 mJ/mm^2 (10 mW/cm^2). Thus, the stepwise two-photon process is a plausible mechanism summarizing the photochromic reactions of **1**. This stepwise two-photon process can be initiated even by incoherent CW light. Irradiation with CW white light (420–700 nm, 500 mW) did not change the color of the solution of **1**. Irradiation with weak CW UV light (5 mW) marginally changed the color of the solution of **1** from colorless to pale blue. In contrast, a prominent change in color was observed when the solution of **1** was irradiated with both CW visible and CW UV light (Figures 4 and S21 and movie S2).

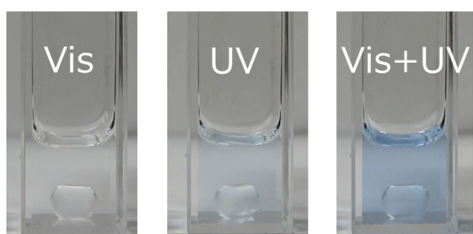


Figure 4. Color change of a benzene solution of **1a** (293 K , $9.4 \times 10^{-5} \text{ M}$) after CW light irradiation for 25 s (vis: $\lambda_{\text{ex}} = 420\text{--}700 \text{ nm}$, 500 mW; UV: $\lambda_{\text{ex}} = 365 \text{ nm}$, 5 mW). Also see movie S2.

In conclusion, we have developed [2.2]PC-bridged bis(imidazole dimer) **1**, which consists of two photochromic units. While the photogenerated biradical species **IBR** rapidly reverts back to its initial colorless form, much like that observed in case of the [2.2]PC-bridged imidazole dimer, further photochemical reaction of **IBR** leads to the formation of the long-lived colored species **IQ**. This highly efficient stepwise two-photon process can be also initiated with the incidence of incoherent CW light because the stepwise photochromic reaction of **1** is dependent on the re-excitation of the reversibly generated biradical species **IBR** (Figure 5). These experiments show that the bridged bis(imidazole dimer) is a viable candidate for use as a multiphoton-gated optical material and can be used for the development of new functional photochromic molecules.

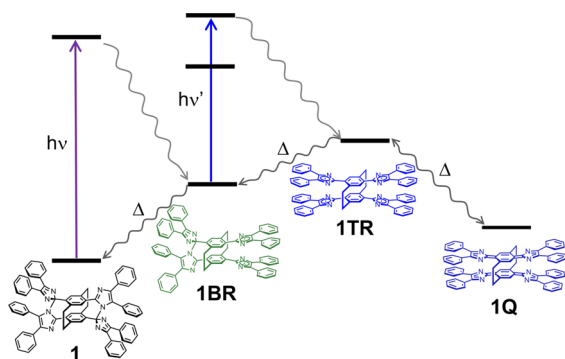


Figure 5. Schematic of the stepwise photochromic reaction of **1**.

■ ASSOCIATED CONTENT

Supporting Information

Synthesis, additional results, CIFs, and movies (AVI). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b02862.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by the CREST Program of the Japan Science and Technology Agency and a Grant-in-Aid for Scientific Research on Innovative Areas “Photosynergetics” (26107010) from MEXT, Japan.

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