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One-Color Reversible Control of Photochromic Reactions in a Diarylethene Derivative: Three-Photon Cyclization and Two-Photon Cycloreversion by a Near-Infrared Femtosecond Laser Pulse at 1.28 μm

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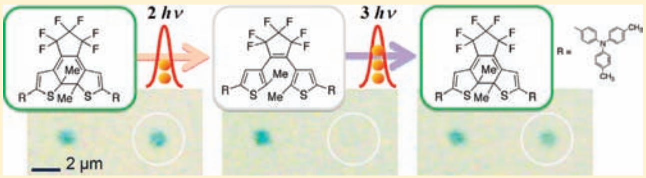
ABSTRACT: One-color control of colorization/decolorization reactions of diarylethene molecules was attained by using nonresonant high-order multiphoton absorption processes with a near-infrared (NIR) femtosecond laser pulse at 1.28 μm with 35 fs full width at half-maximum (fwhm). The intensity of a rather weak laser pulse (<1 nJ/pulse) can induce the simultaneous three-photon absorption leading to the colorization, while much weaker intensity induces two-photon absorption resulting in the decolorization. The spatial patterning concomitant with higher-order multiphoton absorption processes was also demonstrated.



INTRODUCTION

A photochromic compound can interconvert its molecular structure between two isomers having different properties such as color, refractive indices, dipole moments, oxidation/reduction potentials, and electro-conductivities.[1−4] These property changes accompanied with the photoinduced chemical reactions have been attracting much attention from the viewpoints of the application to various photonic devices with molecular level resolutions.[5,6] However, the switching through the photochromism usually requires two light sources with different colors, which does not allow simple device designing for the actual application.

A method based on multiphoton absorption processes seems quite effective to attain one-color reversible photochromic reactions. The transition probability of nonresonant simultaneous multiphoton (n photon) absorption processes[7−12] is dependent on the power of incident light intensity, I, as I^n. This power dependence proves that, in principle, the level of electronic states attained by the multiphoton absorption can be controlled by the light intensity. That is, the laser light with a rather weak intensity induces two-photon absorption to the energy level of $2h\nu$, while a higher-order multiphoton absorption process (to $n \geq 3$) becomes dominant with an increase in the light intensity. When near-infrared (NIR) laser light is employed, the energy level attained by the two-photon absorption corresponds to the visible region, while the three-photon absorption pumps a molecule into UV region.

The application of high-order multiphoton absorption in the NIR region to photochromic systems can lead not only to the control of the direction of reactions by the light intensity but also to several advantages in the utilization of photochromic molecules; tiny spots along the optical axis via multiphoton-gated reactions may benefit the increase in the memory density,[13,14] and the low scattering probability in the NIR region could contribute to the multilayer memory storage. Moreover, the control of the reaction by the NIR laser light around 1.3 μm in the light-wave communication frequency could provide the new application of molecular memory systems directly coupled with the communication light wave. Not only for the optical memory and imaging, a longer penetration depth of NIR light may also expand the applicability of photoswitchable molecules in the opaque materials such as biological tissues. Also for the spatial patterning, a combination of high-order multiphoton absorption processes could open a new maskless pattern formation by using photochromic material[15−17] because the order of the multiphoton absorption processes is dependent on the intensity profile of the laser beam. Although the multiphoton excitation is a luminous method to accomplish the versatile mode of excitation for the photoswitchable reactions, the difference in the absorption cross sections for different exponents is generally so large[11,12,18] that normal laser light sources cannot easily overcome this large difference in cross sections with different exponents,[19]

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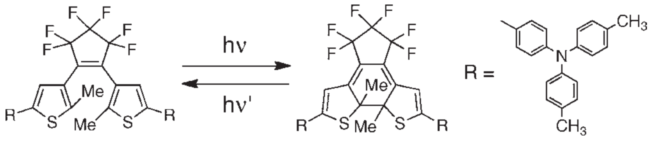
Scheme 1. Molecular Structure and Photochromic Reactions of 1,2-Bis(5-{4-[*N*,*N*-bis(4-methylphenyl) amino] phenyl}-2-methylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (APT)



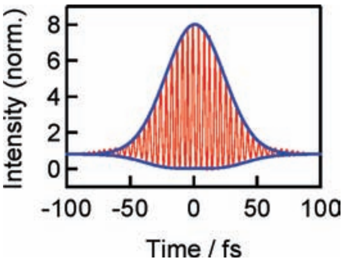


Figure 1. Autocorrelation signal of the femtosecond NIR laser pulse centered at 1.28 μm under the objective obtained by the interferometric second harmonic generation (SHG) with BBO crystal. The SHG signal at ca. 640 nm was detected by a photodiode (model 2031, New Focus). Envelopes as shown by solid lines were calculated on the basis of the pulse duration (fwhm) of 35 fs.

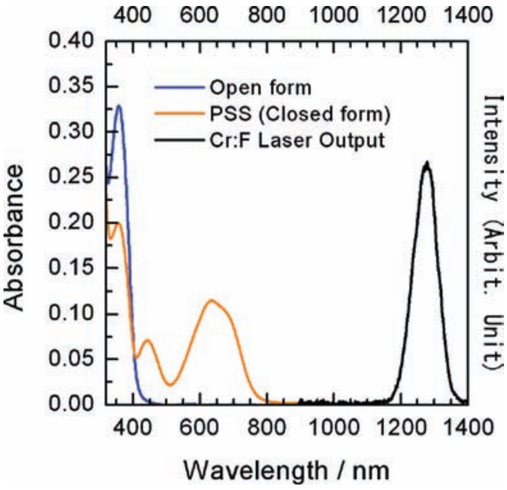


Figure 2. Steady-state absorption spectra of the APT amorphous film. The spectrum of Cr:F laser is also plotted as a black solid line.

and excellent chemical techniques such as up-converting nanoparticles[20] have been proposed as alternative methods.

In the present work, we have applied a NIR femtosecond laser microscope[21] to the one-color reversible control of photochromic reactions of a diarylethene derivative in the amorphous solid state. The laser microscope employed in the present study can provide the pulse duration of 35 fs for the femtosecond Cr: Forsterite (Cr:F) laser[22] at 1.28 μm under an objective (100×, NA 0.95). This short pulse width and the tight focusing by the objective can attain a high peak intensity of ca. $10^{31}-10^{32}$ photons cm^{-2} s^{-1}, even though the output energy of the laser is quite weak (typically, <1 nJ/pulse). That is, the high-order multiphoton process can be induced without large laser systems. In the following, we discuss the reversible control of photochromic reactions in a diarylethene derivative by using the femtosecond laser with the intensity less than one nJ/pulse.

EXPERIMENTAL SECTION

1,2-Bis(5-{4-[*N*,*N*-bis(4-methylphenyl)amino-]phenyl}-2-methylthiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene, APT, was synthesized and purified.[23] Photochromic reactions of APT through the cyclization and cycloreversion are shown in Scheme 1. An amorphous film of APT on the glass plate was prepared by spin coating of the toluene solution of the APT closed-isomer at 3000 rpm. The absorbance of the APT closed-isomer film at 633 nm was ca. 1.2. The thickness of the amorphous film was measured by AFM. The amorphous film of the APT open isomer was obtained by the steady-state irradiation of the visible light.

Details of the home-built femtosecond laser microscope were described elsewhere.[21] In brief, a home-built cavity dumped Cr:F laser[22] was used as a light source, whose output wavelength was centered at 1.28 μm with ca. 80 nm bandwidth, and the typical output was <1 nJ/pulse at a 100 kHz repetition rate. The output of the Cr:F laser was guided into an optical microscope (IX 71, Olympus) with an objective (MPlan 100× IR, Olympus, NA 0.95) after passing through a prism pair for the optimal compensation of the pulse duration at the sample position. The pulse duration at the sample position was 35 fs (fwhm) as shown in Figure 1, where the autocorrelation signal by interferometric second harmonic generation with BBO crystal was exhibited.

Transmittance images were measured by charge-coupled device (CCD) cameras (DSE330-A, Olympus or Cascade 512B, Roper). For the measurement of space-resolved absorbance, the latter CCD camera was employed. By using the transmittance light intensity at the uncolored position as a reference, the absorbance of the colored area at 633 nm was calculated. One pixel size was 66 nm × 66 nm.

RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra of the amorphous film of APT. In this figure, the spectrum of the Cr:F laser output is also exhibited. The closed-ring isomer has absorption bands in the visible region (green−blue color) with the peak at 630 nm. On the other hand, the open-ring isomer has absorption only in the wavelength region, <450 nm (pale yellow). The band shapes and absorption maxima are similar to those in solution phase.[23] This figure clearly demonstrates that three-photon absorption is, at least, necessary for the excitation of the open form. On the other hand, two-photon absorption could lead to the excitation of the closed form.

Figure 3a shows optical transmittance images of the amorphous film of the open-isomer APT (ca. 200 nm thickness), irradiated by the femtosecond Cr:F laser pulse at 1.28 μm. Two blue−green colored spots correspond to positions irradiated by the Cr:F laser light with the intensity of 0.7 nJ/pulse (100 kHz) for 50 ms. Then, the spot in the right-hand side was irradiated by the same colored laser light with the intensity of 48 pJ/pulse (100 kHz) for 180 s, showing that the color perfectly disappeared. Irradiation of the same uncolored spot with the intensity of 0.7 nJ/pulse (100 kHz) for 50 ms again induced the colorization. The decolorization of the green−blue spot could be again induced by the irradiation of the weaker intensity. This colorization and decolorization cycle could be repeated at least 5−10 times.

Figure 3b shows the absorption spectrum of the colored area after the irradiation with the Cr:F laser light. For the measurements of the spectrum, we irradiated the uncolored APT film of the open form by the NIR femtosecond laser light with the

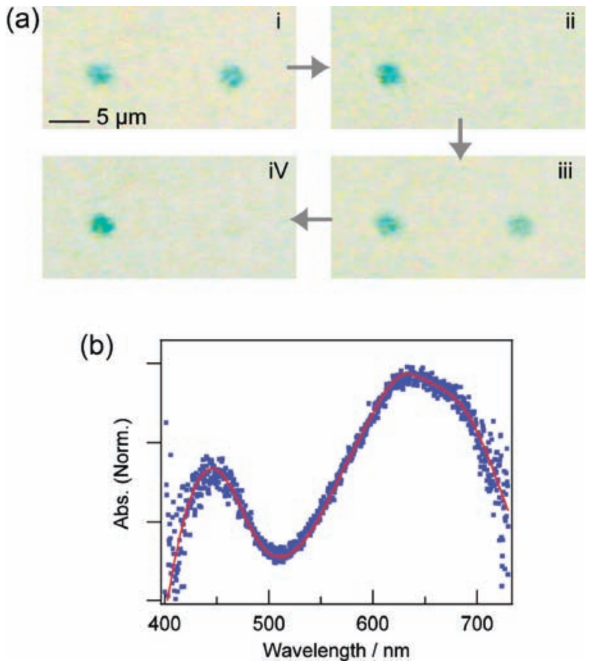


Figure 3. (a) Transmittance images of APT amorphous film, excited with a Cr:F laser centered at 1.28 μm. Irradiation of the NIR laser with the intensity of 0.7 nJ/pulse for 50 ms (100 kHz) induces the colorization (a-i), and the exposure with the weaker intensity of 48 pJ/pulse (100 kHz) for 180 s leads to decolorization (a-ii). This colorization and decolorization can be repeated (a-iii and a-iv). (b) Absorption spectrum of the colored area irradiated with Cr:F laser (blue dotted line). The smooth red line is the steady-state difference spectrum between closed and open forms of APT.

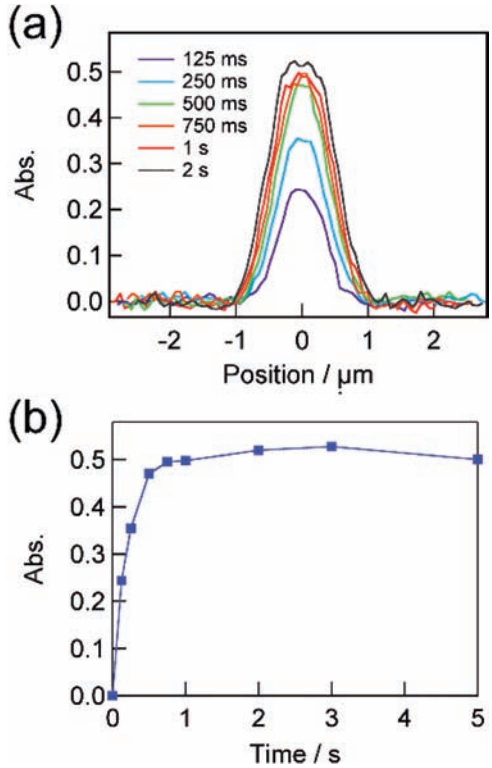


Figure 4. (a) Spatial profile of the absorbance at 633 nm in the APT amorphous film, under the irradiation with a Cr:F laser at 1.28 μm (the intensity of 0.24 nJ/pulse (100 kHz)). (b) Time profile of the absorbance at 633 nm of APT film under the irradiation of a Cr:F laser with 0.24 nJ/pulse (100 kHz).

output energy of 0.7 nJ/pulse (100 kHz) and the scan speed of 100 μm/s to obtain a widely colored region (ca. 0.1 mm × 0.1 mm). Absorption maxima and the band shape of the irradiated area in Figure 3b are in good agreement with those of the difference spectrum between the closed and open isomers, which was obtained by the steady-state UV light irradiation (smooth red line). This result indicates that the NIR femtosecond irradiation leads to the cyclization reaction. In addition, the repeated colorization and decolorization cycles indicate that the cycloreversion could be also induced by the same laser pulse.

To elucidate the details of the multiphoton absorption processes, we measured the time evolution of the closed isomer at the irradiated spot as a function of the exposure time. Figure 4a shows the space-resolved absorption of the closed isomer. As shown in Figure 4b, the absorbance at 633 nm due to the closed isomer increases with an increase in the irradiation time in the early stage in the irradiation time and reaches the plateau value, indicating that the photostationary state (PSS) is attained. In other excitation intensity conditions, similar behaviors were observed.

Time dependencies of the open and closed isomers at the PSS can be represented by the following equations. That is, the apparent temporal evolution between two isomers is canceled.

$$-\frac{\partial N_{\mathrm{O}}}{\partial t} = N_{\mathrm{O}} I^{n} \delta^{(n)} \Phi_{\mathrm{O}\rightarrow\mathrm{C}} - N_{\mathrm{C}} I^{m} \delta^{(m)} \Phi_{\mathrm{C}\rightarrow\mathrm{O}} = 0 \quad (1)$$

$$-\frac{\partial N_{\mathrm{C}}}{\partial t} = N_{\mathrm{C}} I^{m} \delta^{(m)} \Phi_{\mathrm{C}\rightarrow\mathrm{O}} - N_{\mathrm{O}} I^{n} \delta^{(n)} \Phi_{\mathrm{O}\rightarrow\mathrm{C}} = 0 \quad (2)$$

Here, N_{O} and N_{C} are respectively the number of open isomers and that of the closed isomer. I is the intensity of the laser pulse. $\delta^{(n)}$ and $\delta^{(m)}$ are the n- and m-photon absorption cross sections for the open- and the closed-isomer, respectively. $\Phi_{\mathrm{O}\rightarrow\mathrm{C}}$ and $\Phi_{\mathrm{C}\rightarrow\mathrm{O}}$ are the cyclization and cycloreversion quantum yields. From eqs 1 and 2 and the relation $N_{\mathrm{O}} + N_{\mathrm{C}} = N_{\mathrm{total}}$, we can obtain eq 3.

$$\frac{N_{\mathrm{C}}}{N_{\mathrm{O}}} = \frac{N_{\mathrm{C}}}{N_{\mathrm{total}} - N_{\mathrm{C}}} = \frac{\Phi_{\mathrm{O}\rightarrow\mathrm{C}}}{\Phi_{\mathrm{C}\rightarrow\mathrm{O}}} \times \frac{\delta^{(n)}}{\delta^{(m)}} \times I^{(n-m)} \quad (3)$$

Because the open isomer has no absorption at 633 nm, the absorbance at 633 nm at PSS with the laser intensity of I, $A(I)$, is represented by eq 4.

$$\frac{N_{\mathrm{C}}}{N_{\mathrm{O}}} = \frac{A(I)}{A_{\mathrm{T}} - A(I)} = \frac{\Phi_{\mathrm{O}\rightarrow\mathrm{C}}}{\Phi_{\mathrm{C}\rightarrow\mathrm{O}}} \times \frac{\delta^{(n)}}{\delta^{(m)}} \times I^{(n-m)} \quad (4)$$

Here, A_{T} is the absorbance of the same film where all of the molecules are in the closed isomer.

Figure 5a shows the relation between $N_{\mathrm{C}}/N_{\mathrm{O}}$ and I, where both ordinate and abscissa are given as logarithmic scales. This figure clearly shows that the slope of the curve is unity, indicating that the value of $n - m$ corresponds to one. To determine n and m, we plotted the excitation intensity dependence of the colorization (cyclization) reaction in the beginning stage of the irradiation, because the contribution of the decolorization (cycloreversion) reaction could be ignored. The absorbance at 633 nm in each of the excitation intensities was normalized for the exposure time of 1 s. As shown in Figure 5b, the production of the closed-ring isomer is in proportion with the cube of the

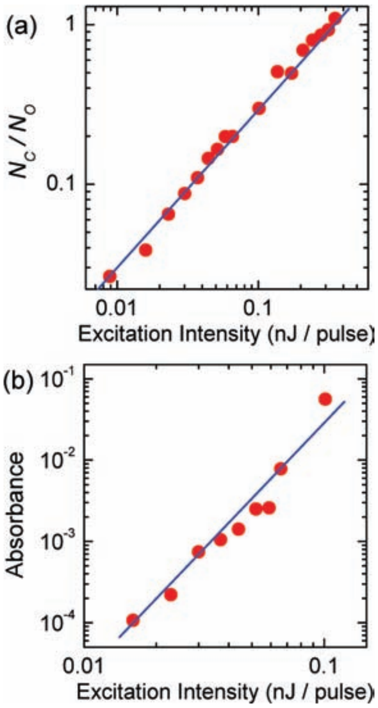


Figure 5. (a) Relation between N_C/N_O and the intensity of Cr:F laser at the photostationary state (closed circles). The solid line in the figure indicates the slope of unity, indicating that $n - m$ in eq 4 is unity (see text). (b) Excitation intensity dependence of the absorbance at 633 nm in the early stage of the irradiation. The absorbance at 633 nm in each of the excitation intensities was normalized for the exposure time of 1 s.

excitation intensity, indicating that the three-photon absorption process is responsible for the cyclization reaction. Integrating the result in Figure 5a,b, we could conclude that the three-photon absorption leading to the colorization and the two-photon absorption resulting in the decolorization take place in the present diarylethene derivative.

With $n = 3$ and $m = 2$ in eq 4, the ratio, $\delta^{(3)}\Phi_{O\rightarrow C}/\delta^{(2)}\Phi_{C\rightarrow O}$, was estimated from Figure 5a to be 6.7×10^{-32} cm^2·s/photons. In this estimation, it was assumed that the spot size of the laser beam is diffraction-limited. Reaction yields for APT in the amorphous film were reported[22] to be 0.33 for the cyclization by the steady-state UV light irradiation and 1×10^{-3} for the cycloreversion by the visible light irradiation. Provided that multiphoton reaction yields are almost the same with those in the one-photon processes, $\delta^{(3)}/\delta^{(2)}$ can be estimated to be 2×10^{-34} cm^2·s/photons. On the other hand, in the case that these two reaction yields are comparable with each other in the case of multiphoton processes, the ratio of $\delta^{(3)}/\delta^{(2)}$ is estimated to be 6.7×10^{-32} cm^2·s/photons. Cross sections for two- and three-photon absorption processes were reported for naphthalene and anthracene.[18] Ratios between the three- and the two-photon absorption processes were 10^{-32}–10^{-34} cm^2·s/photons for these two compounds. The present value for $\delta^{(3)}/\delta^{(2)}$ is almost similar to these values reported previously, supporting that the present excitation condition can induce the one-color control of photochromic reactions.

To apply this one-color reversible photochromic reaction to the space-resolved patterning, we irradiated the partially colored film with the Cr:F laser under the microscope. Figure 6a shows the transmittance images after the irradiation. Although the decolorization of boundary area of the spot was observed, the center of the spot stays colored. This result clearly indicates that the center of the beam with stronger intensity induces the three photon absorption, while the two-photon absorption is dominant in the boundary area with low intensity of the beam. The fwhm of the colored spot was ca. 600 nm, indicating that the submicrometer resolution can be easily attained by using one-color multiphoton colorization and decolorization reactions.

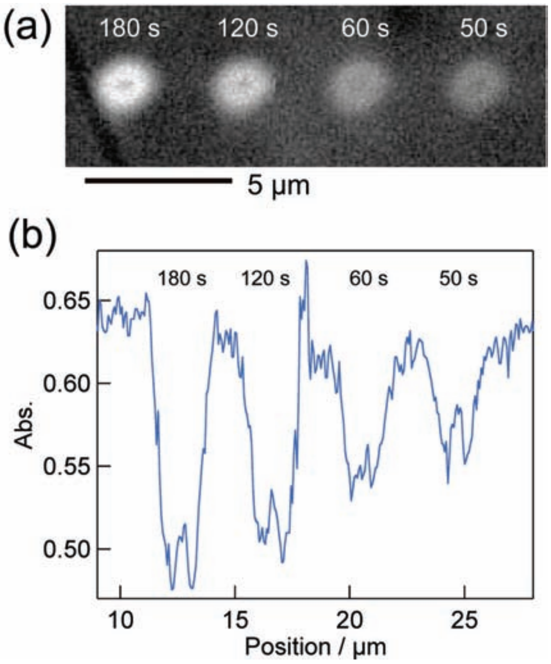


Figure 6. (a) Transmittance images of APT amorphous film at N_C/N_O = ca. 1, irradiated by Cr:F laser with the intensity of 66 pJ/pulse at 100 kHz. (b) Spatial profile of the absorbance at 633 nm in the APT film (see text).

CONCLUDING REMARKS

The present results clearly indicate that the nonresonant 1.28 μm multiphoton absorption can induce reversible colorization and decolorization of diarylethene molecules. In addition, the combination of higher-order multiphoton absorption can easily realize one-color spatial patterning with sub-micrometer spatial resolution. Because the cycloreversion reaction yield of the present derivative, APT, is small, a rather long irradiation time was necessary to induce the decolorization reaction via the two-photon absorption. The increase in the pulse duration, however, could reduce the irradiation time to perform the decolorization, owing to the suppression of the three-photon absorption process leading to the colorization via cyclization reaction even in the case that the pulse energy is larger. In other words, not only the intensity of the laser pulse but also the temporal width of the laser pulse could be utilized as important factors for the control of the direction of the reactions.

It is worth mentioning that the excited states attained by two-, three-, and four-photon excitation of the present Cr:F laser correspond to ca. 640, 430, and 320 nm, respectively. These modes of excitation can cover the absorption band from visible to ultraviolet. Compared to the multiphoton laser microscope with Ti:sapphire laser oscillating around 800 nm, the present femtosecond Cr:F laser microscope has a wider selectivity of compounds. Hence, the present NIR multiphoton excitation also could potentially provide the selective excitation of multichromophore systems where each molecule has different absorption bands by changing factors of the laser pulse such as intensity and pulse duration. This may lead to the control of the photofunctionality of molecular aggregates and to the utilization in the multicolor fluorescence imaging without introduction of multiple dichroic mirrors and multiple blocking filters. We are now studying this multicolor photochemistry by using the one-color NIR laser, results of which will be published.

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