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Cycloreversion Reaction of a Diarylethene Derivative at Higher Excited States Attained by Two-Color, Two-Photon Femtosecond Pulsed Excitation

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S Supporting Information

ABSTRACT: Two-color, two-pulse femtosecond pulsed excitation was applied to the elucidation of the dynamics and mechanism of cycloreversion reaction of a diarylethene derivative in the higher excited states. Transient absorption spectroscopy under one-photon visible excitation revealed that the 1B state produced by the excitation undergoes the internal conversion into the 2A state with a time constant of 200 fs. Geometrical rearrangement of the 2A state takes place concomitantly with the vibrational cooling with a time constant of 3 ps. The resultant 2A state undergoes the transition into the conical intersection point in competition with nonradiative as well as radiative deactivation into the ground state with a time constant of 12 ps. The second pulse excitation of the 2A state,



especially the geometrically relaxed 2A state, led to the significant enhancement of the cycloreversion reaction through the large reaction quantum yield of ca. 50–90% in the higher excited state (S_n state), while the excitation of the 1B state, leading to the S_n' state, did not induce such enhancement. By integrating with the excitation wavelength dependence of the second pump laser pulse, we discussed the chemical reactivity of diarylethene derivatives in terms of the symmetry of the electronic states.

INTRODUCTION

For molecules consisting of more than 10-20 atoms, it is wellknown as Kasha's rule that electronically excited states higher than the lowest one rapidly undergo the internal conversion into lower excited states.¹ In the condensed phase, this rapid internal conversion, typically in a subps time range, is followed by the longitudinal vibrational relaxation in a several ps time range into the thermally equilibrated levels in the lowest electronically excited state.² These rapid relaxation processes lead to the loss of the photon energy in the case where the molecule is pumped up into highly excited states by absorption of light in the short wavelength region. Moreover, the rapid interconversion process of electronic states inhibits the utilization of the diversity in the property and reactivity of a molecule depending on the individual electronic state. Accordingly, most of the photoresponses and functions of molecules, especially for rather large molecules in the condensed phase, have been restricted by these processes; namely one-photon response of one-molecule in the lowest excited state.

Several processes beyond these restrictions, however, have been reported in these years.³ One of these phenomena is the

photoisomerization process in highly excited states of diarylethene, fulgide, and retinal derivatives. In these systems, isomerization reactions, such as cyclization/cycloreversion⁴⁻⁶ and trans-cis conversion,^{7,8} take place in highly excited states with reaction quantum yields much larger than those in the lowest excited state. For instance, it was reported for some of diarylethene derivatives that the yield of the cycloreversion (ring-opening) reactions in the highly electronic states excited by the stepwise two-photon absorption at 532 mm is a few thousand times larger than that in the lowest excited state.⁹ Although the sequential two-photon absorption of the closedring isomer leads to the marked enhancement of the ringopening reaction, the one-photon excitation by the UV light corresponding to the energy level of the two-photon excitation in the visible region does not show the large reaction yield.^{4b,10} These results strongly suggest that the specific electronic state accessible only by the two-photon transition is responsible for the marked enhancement of the cycloreversion reaction. This multiphoton cycloreversion reaction has been found in various

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diarylethene derivatives,^{4,9–11} which have different one-photon cycloreversion reaction yields (0.01–0.35), depending on the substituents at the terminal positions. Similar enhancement of the reaction was observed in fulgide derivatives,⁵ which are also 6π electron systems undergoing the pericyclic reaction. In these systems, two-photon absorption into the reactive higher excited state is partially allowed by UV one-photon excitation, due to lower symmetry of the molecular geometry, which results in increase of the one-photon reaction yield at shorter excitation wavelengths. This excitation wavelength dependence of the one-photon cycloreversion reaction yield was also reported especially in the UV region for typical diarylethene derivatives.¹² These findings indicate that several high-lying excited states are intimately involved in this multiphoton photochromic reaction.

This multiphoton-gated reaction can be applied to the advanced photofunctional molecular systems responding to the light intensity, such as optical molecular memories with two conflicting properties of photoreadable and photoerasable functions. Also from the basic viewpoints, the stepwise two-photon absorption can provide a method for the access to the electronic state unattainable by the usual one-photon absorption and/or vertical optical transitions, leading to the exploration of specific photoresponses through a cooperative interaction among multiple photons and molecules (photosynergetic effect),¹³ which is beyond the restriction of Kasha's rule.

Along this line, we have investigated the dynamics and mechanism of multiphoton-gated cycloreversion reactions in a diarylethene derivative with various reaction quantum yields in the visible one-photon excitation. Because the stepwise twophoton absorption occurs through the intermediate state produced by the first one-photon absorption, the time interval between the first and second pulse selects the species during the temporal evolution in the intermediate state. In the present case of the closed-ring isomer of diarylethene derivatives, it has been predicted from the experimental and theoretical studies^{14–27} that the internal conversion from the 1B state to the 2A one takes place after the one-photon absorption from the ground state. Accordingly, the time interval between the two pump pulses can select the initial state of the second photon absorption. In addition, the wavelength of the second pulse can select the final state in the highly excited levels. Moreover, in the case where geometrical rearrangements in the intermediate state take place on the potential surface, the stepwise excitation may lead to the high excited state which cannot be attained by the vertical transition from the ground state. In the following, we discuss the mechanism of the twophoton-gated reaction by introducing the experimental results on the time interval and wavelength of the double pulse excitation.

EXPERIMENTAL SECTION

Bis(2-methyl-5-phenylthiophen-3-yl)perfluorocyclopentene, **DAE**, was synthesized and purified.²⁸ This molecule undergoes the photochromic reactions between the open-ring isomer, **DAE**(\mathbf{o}), and closedring one, **DAE**(\mathbf{c}). *n*-Hexane (Wako, infinity pure grade) was used without further purification.

Transient absorption spectra were measured using a home-built setup based on dual optical parametric amplifiers (OPA).²¹ The light source for OPA was provided by a Ti:sapphire regenerative amplifier (Spitfire, Spectra-Physics, 802 nm, 100 fs, 1 W, 1 kHz) seeded by a Ti:sapphire oscillator (Tsunami, Spectra-Physics, 802 nm, 100 fs, 820 mW, 80 MHz). The output of the amplifier was divided into two portions and used for generation of excitation and probe pulses. One portion was converted into the excitation pulse centered at 600 nm using a noncollinear OPA (TOPAS-White, Light-Conversion) and used for the excitation of the sample. The remaining portion drove a collinear OPA (TOPAS-Prime, Light-Conversion), which was tuned at 1180 nm. This near-infrared (NIR) output was focused into a 2 mm CaF₂ plate after passing through an optical delay stage for generating femtosecond white light probe pulse. The part of the white light was used as a reference signal for the calibration of intensity fluctuation of the probe pulse. The main probe pulse was guided into the sample and then both pulses, the main probe and the reference, were detected by a pair of multichannel photodiode arrays (PMA-10, Hamamatsu). Polarization of the excitation pulse was set to the magic angle with respect to that of the probe pulse. The excitation pulse was characterized by frequency-resolved optical gating, and the pulse duration was evaluated as 50 fs. The chirping of the white light probe pulse was corrected on the basis of optical Kerr signals of carbon tetrachloride. The fwhm of the cross correlation between the excitation and probe pulses was estimated to be ca. 80 fs. The excitation intensity was typically 50 nJ/pulse in front of the sample. The sample solution was set in a rotation cell with a 2 mm optical length and circulated during the measurements.

Reaction amounts induced by stepwise two-photon excitation were measured using three laser pulses: two are excitation pulses and the other is a probe pulse, which were generated from the same OPAs as transient absorption spectroscopy. The center wavelength of one OPA was tuned at 600 nm. Its output was further divided into two portions, and these were used for the first excitation (pump1) and probe pulses. The other OPA produced the second excitation (pump2) pulse. Its wavelength was varied from 530 to 880 nm with an interval of 50 nm. The two sequential excitation pulses were irradiated to the sample with a time interval of Δt_i , and the resultant bleaching signal was monitored with the probe pulse 400 ps after the irradiation of the pump1 pulse. The probe pulses were detected with photodiodes (Model 818-UV, Newport). At this delay time, all the transient species vanished, and the probe pulse detected only the permanent bleaching, which corresponds to the reaction amount. The polarization between the two excitation pulses was in parallel with each other, while the relative polarization of the probe pulse was set to the magic angle with respect to that of the excitation pulses. The typical intensities of the pump1 and pump2 pulses were, respectively, 200 nJ and 600 nJ. The width of the three pulses were ca. 100 fs. Thus, the correlation traces of the two-photon reaction amount was obtained as a function of Δt . During the measurements, continuous-wave (cw) ultraviolet light at 330 nm (bandwidth 10 nm fwhm) was irradiated to the sample solution so as to keep concentration of the closed-ring isomer constant. The measurements were initiated after the sample system led to the photostationary state, which was attained by the irradiation of the two excitation pulses and cw ultraviolet light. Steady-state absorption spectra were recorded before and after the data acquisition and photoinduced change in absorbance was <5%, confirming that the photodegradation of the sample was negligibly small.

Fluorescence lifetimes were measured using a time-correlated single-photon-counting (TCSPC) system with a Ti:sapphire oscillator (Tsunami, Spectra-Physics, 760 nm, 100 fs, 80 MHz) as a pulsed light source. Experimental setup of the measurement system was reported elsewhere.²⁹ Briefly, the fundamental output at 760 nm was frequencydoubled with a 1 mm β barium borate crystal. The second harmonics at 380 nm was used for the excitation of the sample. The repetition rate was reduced to 8 MHz by using an electro-optic modulator (Model 350, Conoptics). Typical excitation power was 16 μ W. Relative polarization of the excitation pulses was set to the magic angle with respect to that of the fluorescence detection using a film polarizer and Babinet-Soleil compensator. Fluorescence signals were detected using a photomultiplier tube (R3809U-50, Hamamatsu Photonics) with a preamplifier (C5594, Hamamatsu Photonics) and a TCSPC module (PicoHarp 300, PicoQuant) after the spectral selection with a monochromator (Princeton Instruments, Acton SP-2150). Sample solution was set in a 1 cm quartz cell. The instrumental response function (IRF) of the system was obtained from the fluorescence rise

of Rhodamine B ($\tau_{flu} = 1.7 \text{ ns}$) in water monitored at the same wavelength (700 nm) as the sample, which enables us to suppress the color effect of the photomultiplier tube. The fluorescence lifetime of the sample were extracted from the curve fitting analysis considering the IRF thus obtained.

Steady-state absorption and emission spectra were respectively recorded on Hitachi U-3500 spectrophotometer and Hitachi F-4500 fluorometer, by using a quartz cell with a 1 cm optical length. All the measurements were performed under O_2 free condition.

RESULTS AND DISCUSSION

Steady-State Absorption and Emission Spectra. Figure 1 shows steady-state absorption spectra of DAE in *n*-hexane



Figure 1. Steady-state absorption and fluorescence spectra of **DAE** in *n*-hexane solution. The dash-dotted red line is the absorption spectrum of the open-ring isomer, **DAE(o)**, and the solid black line is that under the photostationary (PSS) state upon the irradiation at 330 nm. More than 90% is in the closed-ring isomer, **DAE(c)**, in the PSS state. The dotted blue line is the fluorescence spectrum of **DAE(c)** excited at 580 nm.

solution. The open-ring isomer, DAE(o), has absorption bands only in the UV region, while the closed-ring isomer, DAE(c), has absorption bands both in UV and visible regions. The absorption maximum wavelength of DAE(c) in the visible region is 575 nm, and the absorption tail is observed up to ca. 700 nm. The cyclization reaction yield of the open-ring isomer, DAE(o), upon the excitation at 280 nm is 0.59 in *n*-hexane at 295 K. However, the cycloreversion yield of the closed-ring isomer, DAE(c), is very small, 0.013, under the irradiation at 492 nm.²⁸ The dotted line in Figure 1 is the emission spectrum of DAE(c) in *n*-hexane excited at 580 nm, showing a mirror image of the absorption band. Rather large Stokes shift, 4200 cm⁻¹, in nonpolar *n*-hexane solution suggests that the molecular structure in the fluorescent state is largely different from that in the ground state. Large Stokes shift of the closed-ring isomer was also observed for a derivative with benzothienyl moieties.^{21c} Its Stokes shift was 3600 cm⁻¹ in *n*-hexane, the value of which is slightly smaller than that of the present DAE(c). This difference is probably due to larger flexibility of aryl groups in DAE(c). That is, relative geometry of the phenyl group and thienyl one can change in DAE(c) while the derivative with benzothienyl moieties has rather rigid molecular framework.

Dynamics in Lower Excited States. Figure 2 shows timeresolved transient absorption spectra of DAE(c) in *n*-hexane solution, excited with a femtosecond laser pulse at 600 nm. Time evolution of the spectra following the excitation can be divided into three stages. In the time region immediately after the excitation (0-0.5 ps), the absorption band around 860 nm appears together with the negative signal due to the bleaching of the steady-state absorption. The intensity of the absorption band around 860 nm slightly decreases and that at 890 nm relatively increases, together with the appearance of the absorption around 700 nm in the initial 0.5 ps time range. The absorption around 860 nm is due to the initially formed 1B state, while the subsequently growing bands around 700 and 890 nm are attributable to the 2A state because precedent studies on the cycloreversion dynamics have reported that the molecules are first populated into the 1B state upon photoexcitation and then electronically relaxed into the 2A state within several hundreds femtoseconds.^{23,24,27,30} In the time region of 0.5-5 ps, the relative ratio of the transient absorbance at 890 and 700 nm vs that around 860 nm gradually increases. At and after ca. 5 ps following the excitation, the decay of the positive and negative absorption intensities to the baseline was observed with no remarkable evolution of the spectral band shape. The recovery of the transient absorbance to the baseline is attributable to the small cycloreversion reaction yield of DAE(c).

Figure 3 shows time profiles of the transient absorbance of DAE(c) in *n*-hexane solution excited with a femtosecond laser pulse centered at 600 nm and monitored at 840 and 700 nm.



Figure 2. Time-resolved transient absorption spectra of DAE(c) in n-hexane solution, excited with a femtosecond laser pulse at 600 nm.



Figure 3. Time profiles of the transient absorbance of DAE(c) in *n*-hexane solution excited with a femtosecond laser pulse centered at 600 nm. (a) Monitored at 840 and 700 nm. (b) Time profile of transient absorbance at 700 nm divided by that at 840 nm. The signals <1 ps are affected by the coherent oscillation. The monitoring wavelength at 840 nm was plotted, because the time profile at 840 nm contains the 200 fs and 3 ps components with higher amplitude than that at 860 nm.

Time profiles in Figure 3a are reproduced by a triple exponential function with time constants of 0.2, 3.0, and 12 ps. From theoretical and experimental investigations, the potential energy curves of the excited state 23,24,27,30 has been proposed for the closed-ring isomer of diarylethene derivatives as shown in Scheme 1. That is, the 1B state produced by the photoexcitation of the ground state undergoes the internal conversion to the local minimum of the 2A state (2A_C state) via

Scheme 1. Potential Energy Curves of the Ground State and Excited State of DAE^{a}



^{*a*}Time constants of 200 fs, 3 and 12 ps correspond to the internal conversion from the 1B state to the 2A state, vibrational cooling in the $2A_C$ state and transition from the $2A_C$ state into $2A_O$ state beyond the activation barrier ($2A_{TS}$).

the 1B/2A conical intersection (CI). The $2A_C$ state goes over the energy barrier, $2A_{TS}$, in competition with the direct nonradiative as well as radiative decay processes to the ground state. According to this scheme, the shortest time constant of 200 fs is attributed to the internal conversion from the 1B state to the $2A_C$ state, because the absorption band around 860 nm appears within the response of the apparatus and is accordingly attributable to the initial excited state directly pumped from the ground state (1A state). In addition, the bands at 700 and 890 nm are ascribable to the $2A_C$ state because the rise of these bands is accompanied by the decay of the 1B state.

To elucidate the origin of the 3 ps component, we plotted the time profile of the transient absorbance at 700 nm divided by that at 840 nm, of which result is shown in Figure 3b. Because the contribution of the rise component of the $2A_{C}$ state overlaps at 860 nm, we plotted the time profile at 840 nm instead. As clearly shown, the relative intensity rapidly increases within 1 ps and is followed by the gradual increase in a several ps time region. This time profile indicates that the rapid internal conversion yields the 2A_C state with the time constant of 200 fs and slow process in the 2A_C state leads to the spectral evolution. As was shown by the rather large Stokes shift of the fluorescence in Figure 1, this time constant may be attributed to the geometrical rearrangement in the excited state. Actually, recent time-resolved spectroscopic studies have reported that a phenylthiophene moiety undergoes molecular planarization in the S_1 state in a similar time scale (1.5 ps).³¹ In addition, because the present time constant of 3 ps is in the typical temporal scales of vibrational cooling processes in solutions, this geometrical rearrangement may be accompanied by the vibrational cooling.

The rapid change of the electronic state from the 1B state to the 2A state could be more apparently observed in the time profile of the transient absorbance in the NIR region in Figure 4a, where the temporal evolution of transient absorption spectra in the NIR region is shown for DAE(c) in *n*-hexane solution excited with a femtosecond laser pulse at 600 nm. As shown in Figure 4a, positive absorption immediately after the excitation in the wavelength region of 950-1600 nm is replaced with the negative transient signal in 1000–1400 nm region with an increase in the delay time after the excitation. Because DAE(c) in the ground state has no absorption in the NIR region as was shown in Figure 1, this negative signal could be ascribed to the stimulated emission. This negative signal decreases with the time constant of 12 ps, indicating that the time constant of this signal is due to the decay of the fluorescent state.

Figure 4b shows time evolution of the transient absorbance at 1065 nm, which is close to the minimum wavelength of the negative band corresponding to the stimulated emission. Time profiles at other wavelengths are shown in the Supporting Information (SI Figure S2). The time evolution at 1065 nm shows that the positive signal immediately after the excitation decays rapidly and the negative signal remains. The large change of the transient absorption signal also indicates the evolution of the electronic state. It should be noted that an oscillatory modulation of the transient absorbance is clearly observed in the time profile, which is due to the coherent nuclear wavepacket motion initiated by the pulsed excitation. This wavepacket motion could be safely assigned to a vibrational mode in the excited state, because the oscillatory feature was observed in the region of 1000-1400 nm, where the stimulated emission is dominant. The frequency of this



Figure 4. (a) Time-resolved transient absorption spectra of DAE(c) in *n*-hexane solution, excited with a femtosecond laser pulse at 600 nm and monitored in the near-infrared region. (b) Time profile of the transient absorbance monitored at 1065 nm.

vibrational mode is ca. 140 cm⁻¹. This low frequency could be attributed to the molecular vibration with large amplitude, which is involved in the dynamic motion of overall molecular framework. A further investigation of the contribution of the nuclear wavepacket motion to the cycloreversion reaction is now ongoing experimentally and theoretically. Accordingly, we concentrate our discussion in the time constants of time profiles. The time constant of the fast decay of the positive absorbance is 200 fs, of which value is the same with that observed in Figure 3. In the long time region, this negative signal decreases with constants of 3 and 12 ps, as observed for the time profile of the transient absorbance in the visible region in Figure 3.

The longest time constant of 12 ps is ascribable to the lifetime of the 2A state, because the recovery of the transient bleaching of the ground state DAE(c) and the decay of the positive transient absorbance have the same time constant of 12 ps. To more directly confirm the origin of this decay, we examined temperature dependence of the decay of the transient absorption and that detected by the time-resolved fluorescence measurements. Time profiles of the transient absorption and fluorescence decays at 193-333 K are shown in the SI (Figure S3). In both measurements, the longest decay time constant (12 ps component at 295 K) becomes longer with a decrease in temperature. The time constants obtained by both measurements were plotted against the inverse of temperature in Figure 5, indicating that the time constant of the transient absorption decay is almost identical to the fluorescence lifetime. It should be noted that the decay of the fluorescence is slightly faster



Figure 5. Temperature dependence of the excited state lifetime of DAE(c) in *n*-hexane solution obtained from transient absorption and fluorescence decays.

than that of the transient absorption. This is due to the analysis of the fluorescence time profiles. For the analysis of the decay of the fluorescence, we assumed monophasic decay owing to the time resolution of the measurement, although the decay of the stimulated emission in NIR region was biphasic as shown in Figure 4. The agreement of these two time constants in this context in Figure 5 indicates that the $2A_C$ state was detected in both measurements, because the $2A_O$ state in Scheme 1 is not likely to emit fluorescence due to small energy gap between the 2A and 1A potentials. According to Scheme 1, it is concluded that the $2A_C$ state evolve into the $2A_O$ state beyond the energy barrier ($2A_{TS}$) with the time constant of 12 ps at room temperature and finally lead to the photoproduct (DAE(o)) via the 2A/1A CI in competition with the deactivation to the closed-ring isomer in the ground state.

The assignment of the 12 ps time constant to the lifetime of the 2A_O state in Scheme 1 can be rationalized also with the time constant of the ring-closing (cyclization) reaction of DAE(o). Hania et al. reported¹⁷ that the cyclization reaction of DAE(o) is complete within 1 ps, while the cycloreversion reaction takes place with the time constant of 12 ps as shown above. In the case that the same CI as the cycloreversion reaction mediates the 2A and 1A potential energy surface as has been widely accepted in pericyclic reactions of 6π electron systems, ^{23,24,27,30} the difference in the reaction time scale clearly shows that staying time in the 2A_O state should be less than 1 ps. Inferring from the above results and discussion, dynamics around the lowest excited state of DAE(c) after the excitation at 600 nm can be summarized in the following manner. The 1B state produced by the excitation of the ground state DAE(c)undergoes the internal conversion into the 2A_C state with the time constant of 200 fs, which is followed by the geometrical rearrangement with the vibrational cooling. The resultant 2A_C state goes over the activation barrier into the 2A_O state with the time constant of 12 ps and finally leads to the open-ring isomer via the 2A/1A CI.

Dynamics under the Double Pulse Excitation. As mentioned in the Introduction, successive two-photon excitation of the closed-ring isomer of diarylethene derivatives generally induces the effective ring-opening reaction in higher excited states.^{4–6} In order to directly elucidate the mechanism of the nonlinear cycloreversion reaction, we employed two fs laser pulses for the excitation and investigated the amount of reacted molecules as a function of the time interval between these two pulses. Figure 6a shows the schematic illustration of the experimental setup, where one of the two fs laser pulses (Pump 2) for the sequential excitation was guided into the optical delay line to set the time interval, Δt , from the pump1



Figure 6. (a) Schematic illustration of the experimental setup for the stepwise two-photon cycloreversion reaction amount measurement. (b) Permanent bleaching formed via the stepwise two-photon cycloreversion reaction vs the time interval between the two excitation pulses, Δt . Wavelengths of the pump1 and pump2 pulses were set to 600 and 530 nm, respectively.

pulse. The amount of the cycloreversion reaction was monitored as transient absorbance at 600 nm, corresponding to the permanent bleaching of DAE(c) in the ground state, at 400 ps after the excitation of the second pulse. The monitoring time at 400 ps selectively probes the amount of the cycloreversion reaction, because the lifetime of the excited state of DAE(c) is 12 ps. This optical setup is almost the same with that employed for the ps double-pulse excitation.³² The angle between the optical paths of the two fs pump pulses was set to avoid the effect of the four-wave mixing.

Figure 6b shows one of the experimental results of the double-pulse excitation with fs lasers, where the first pulse at 600 nm and second one at 530 nm were employed. The amount of the cycloreversion reaction by the one-photon absorption at 600 and 530 nm excitation conditions were subtracted from the ordinate. The increase in the negative absorbance clearly indicates that the sequential two-photon absorption into higher excited states leads to the enhancement of the cycloreversion reaction. Interestingly, the Figure 6 indicates that the reaction amount increases in the region of Δt = 0 to ca. 5 ps and is followed by the decrease in a few tens of ps time region. The solid line is the curve calculated with a triple exponential function with time constants of 0.2, 3, and 12 ps. The time constant of 12 ps as a decay component is safely ascribed to the decay of the 2A_C state. However, the components of 0.2 and 3 ps are rise components, indicating that the excitation into higher electronic states from the state at and after a few ps following the absorption of the first pump pulse can more effectively induce the cycloreversion reaction. As discussed in previous sections, DAE(c) after the excitation at the visible wavelength undergoes the geometrical rearrangement coupled with the vibrational cooling in the $2A_{C}$ state with the time constant of 3 ps. By integrating the result on the twopulse excitation and that on the dynamics around the 2A_C state, it is concluded that the second photon absorption from the geometrically relaxed 2A_C state more effectively induces the cycloreversion reaction yield than the second photon

absorption from the 1B and $2A_C$ state prior to the geometrical rearrangement under the re-excitation of the intermediate state at 530 nm.

Although the information on the initial state of the second photon absorption leading to the effective cycloreversion reaction was obtained, the information on the final state has not yet been elucidated. To precisely obtain the information on the final states, the dependence of the cycloreversion reaction yield on the wavelength of the second laser pulse was investigated, the result of which is shown in Figure 7. As was



Figure 7. Permanent bleaching signal observed via the stepwise twophoton cycloreversion reaction vs the time interval between the two excitation pulses, Δt . Dependence on the wavelength of the second laser pulse. Wavelength of the pump1 pulse is 600 nm.

done for Figure 6b, the contribution of the one-photon reaction was subtracted. As shown, the rise of the reaction amount within ca. 5 ps of Δt was confirmed for the second laser pulse in the wavelength region of 530–680 mm, while such behavior was not detected for the second pulse excitation at the wavelength longer than 680 nm. That is, the largest value of the enhancement of the cycloreversion reaction around $\Delta t = 0$ and was followed by the monophasic decrease with a time constant of 12 ps in the wavelength region.

To elucidate the difference in the behaviors depending on the wavelength of the second laser pulse, we plotted the yield of the cycloreversion reaction as a function of the wavelength of the second pump laser pulse. To obtain the reaction yield at higher excited states, we took into account the intensity of the laser pulse, the extinction coefficients, and the concentration of the molecules in the ground and excited states. The procedure of the estimation is almost the same as that employed for the analysis of the results by pulsed excitation with a picosecond laser^{4b} (details are shown in SI).

Figure 8 shows the relation between the wavelength of the second laser pulse and the reaction yield. As clearly shown, the cycloreversion reaction yield by the second laser pulse in the wavelength region shorter than 680 nm is ca. 50-70%. In the previous work by the multiple excitation of DAE(c) by a picosecond 532 nm laser pulse,^{4b} the cycloreversion reaction yield in higher excited states was estimated to be $50 \pm 20\%$. The present results are almost in the same order as the previous result. However, the reaction yield is much smaller, less than



Figure 8. Dependence of the reaction yields in the higher excited states on the wavelength of the second excitation pulse.

1%, in the wavelength region >680 nm. It is worth noting for the second pulse >680 nm that the amount of the cycloreversion reaction induced by the second photon absorption showed no selectivity depending on the initial electronic state or the geometry of the molecule for the second photon absorption (200 fs and 3 ps components), as shown in Figure 7. These results indicate that the marked increase of the cycloreversion reaction requires conditions not only of the initial state but also of the final state of the second photon absorption.

Lifetime of Higher Excited State. Prior to the discussion on the wavelength dependence of the second pump pulse as were shown in Figures 7 and 8, we show the dynamics of the higher excited state which was observed as time profiles of transient absorbance under the double-pulse excitation. In Figure 9a, time profile of the transient absorbance monitored at 600 nm after the excitation of DAE(c) in *n*-hexane solution with a femtosecond laser pulse at 600 nm. The difference



Figure 9. (a) Time profile of the transient absorbance monitored at 600 nm after the excitation of DAE(c) in *n*-hexane solution with a femtosecond laser pulse at 600 nm. (b) The difference between the transient absorption signals with and without the second pulsed excitation at 530 nm. The transient absorbance with the second laser pulse was subtracted from that without the second pulse. The second pulse was guided at 5 ps after the excitation by the first pulse.

between the transient absorption signals with and without the second pulsed excitation at 530 nm is shown in Figure 9b. where the transient absorbance with the second laser pulse was subtracted from that without the second pulse. The second pulse was introduced at 5.0 ps after the first pulse at 600 nm. The positive signal corresponds to the increase of the transient absorbance induced by the second pulsed excitation. Although the signal is rather scattered, the fast decay in a subps time region is followed by the gradual decay in a few tens ps time range. At and after a few tens of ps, a constant negative signal was observed. The solid line in Figure 9 is the curve calculated with a double exponential function with the shorter and longer time constants of 300 fs and 12 ps. The longer time constant corresponds to the lifetime of the S_1 (2A_C) state. In the case where the cycloreversion reaction takes place in the higher excited state produced by the second laser pulse at 530 nm, the population of the 2A_C state decreases by the introduction of the second laser pulse. Accordingly, the decay of the 2A_C state appears in the difference of the time profiles. However, the decay in the subps time region could be attributed to the higher excited state, because this signal appears immediately after the excitation of the second pulse. In addition, time constants in the subps time range are a typical lifetime of highly excited states of rather large molecules in the condensed phase. The result indicates that the cycloreversion reaction takes place via higher excited state in the very short lifetime of ca. 300 fs.

General Discussion on the Selectivity of the Cycloreversion Reaction Depending on the Mode of the Excitation and the Initial Electronic State for the Second **Photon Absorption.** As was shown in previous sections, the enhancement of the cycloreversion reaction takes place in the case where the 2A_C state after the geometrical rearrangement absorbs the second photon in the wavelength range <680 nm. From experimental and theoretical studies on the reaction processes of diarylethene derivatives so far accumulated, it has been deduced that in the one-photon cycloreversion reaction, the vibrationally excited 2A_C state produced from the 1B state via the 1B/2A CI overcomes the activation barrier $(2A_{TS})$ and reaches 2A₀ state.³⁰ This 2A₀ state is electronically relaxed into the 1A state through the orthogonal 2A/1A CI, where the fate of the molecule, the open- or closed-ring isomers, is determined. The reaction yields of the cyclization and cycloreversion reactions are mainly determined by the branching ratio at the 2A/1A CI. The cyclization yield of DAE(o) is ca. 0.6 upon UV irradiation while the cycloreversion yield is ca. 0.01 in the visible light excitation. It should be noted that the open-ring isomer of diarylethene derivatives has at least two conformers, antiparallel, AP, and parallel, P, conformers. The cyclization reaction generally occurs only in the AP conformer, and the P conformer does not contribute to the cyclization reaction. Hence, the branching ratio to the closedring isomer from the AP conformer of the open-ring isomer can be estimated to be rather large (≥ 0.9), because the cyclization yield²⁸ of **DAE(o)** is 0.59, and the fraction of the AP conformer could be estimated to be ca. 0.6-0.7. Hence, the relaxation to this CI from higher excited states does not lead to the enhancement of the cycloreversion reaction such as >50%. Actually, as was shown in Figure 9a, the effective reaction could be induced during the very short lifetime of the higher excited state. These results strongly suggest that the character of the electronic state in higher levels takes a crucial role in the enhancement of the cycloreversion reaction, as summarized in Scheme 2(a).

Scheme 2. Mechanism of the Two-Photon Cycloreversion Reaction Induced by the Second Pulsed Excitation at Different Wavelengths^a



^{*a*}(a) $\lambda_{2nd ex.} < 680$ nm. (b) $\lambda_{2nd ex.} > 680$ nm.

In the simple model of the 1,3,5-hexatriene and cyclohexadiene, the phase of the molecular orbital between the C–C chemical bond between the two aryl rings is opposite in LUMO. Alternatively, the phase of it is the same in the ground state (1A). Accordingly, the optical allowed transition from the 1B state to higher excited state may have the same phase as shown in Scheme 3. On the other hand, the allowed transition

Scheme 3. Phase of MO in A and B States



from the 2A state may have the opposite phase, leading to the effective ring-opening. It should be noted that this explanation is quite simplified and detailed theoretical investigation is necessary. In addition, the 1B and 2A states are the extreme case for the description of the lowest excited state of diarylethene derivatives. That is, the actual electronic state involves both characters. The simple model in Scheme 3, however, provides a qualitative explanation for the present experimental results.

Alternatively, in the case where the wavelength of the second pump pulse is longer than 680 nm, large reaction enhancement was not observed, indicating that the higher excited states attained by the second-photon absorption in the wavelength region >680 nm do not lead to the marked enhancement of the cycloreversion reaction. In addition, Figure 7 showed that the slight increase of the cycloreversion reaction was independent of the initial sate of the second photon excitation (1B and $2A_{C}$ states) and the geometry of the molecule. These results strongly suggest that not the specific higher excited state but rather the vibrationally excited state in the lowest electronically excited state is responsible for the slight increase in the cycloreversion reaction. As shown in Scheme 2(b), the rapid internal conversion from the highly excited states pumped by second pulse excitation in the wavelength region >680 nm results in the production of the vibrationally hot states in lower

excited states, of which excess energy may assist the molecules in overcoming the activation barrier on the 2A potential energy surface, leading to the slight increase in the reaction yield of the cycloreversion reaction. Actually, the cycloreversion reaction yield of diarylethene derivatives generally increases with increasing temperature.³⁰ To more directly elucidate characters and reactivity of higher excited is underway using detailed theoretical treatments, the result of which result will be published soon.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b09763.

Supplementary steady-state and time-resolved spectroscopic data and detailed description of estimation of the cycloreversion quantum yield in the higher excited state (PDF)

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Notes

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