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Multiphoton Gated Photochromic Reaction in a Diarylethene Derivative

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Photochromism is a photoinduced reversible transformation in a chemical species between two forms. The instant property changes by photoirradiation have raised a possible application to high-density erasable optical data storage.[1−5] The photochromic systems for the application, however, require several conditions such as thermal stability of both isomers, low fatigue, rapid response, high sensitivity, and nondestructive readout capability. Since the reaction in the excited state generally takes place in competition with various processes in a finite lifetime, the large rate constant of the photochromic reaction (the quick response) is of crucial importance for an increase in the reaction yield (the high sensitivity) and a decrease in undesirable side reactions resulting in low durability (the low fatigue). Here, we present laser-induced enhancement (more than 50 times) of a cycloreversion reaction in a photochromic diarylethene derivative with a low reaction yield under steady-state light irradiation. The present result provides a new approach to erasable memory media with nondestructive readout capability.

Diarylethenes with heterocyclic rings have been developed as a new type of thermally irreversible and fatigue-resistant photochromic molecules.[4−10] Bis(2-methyl-5-phenylthiophen-3-yl)perfluorocyclopentene, **1**, is one of the diarylethene derivatives that undergoes cyclization/cycloreversion between open- and closed-ring forms via the photoexcitation as shown in Scheme 1.[10,11]

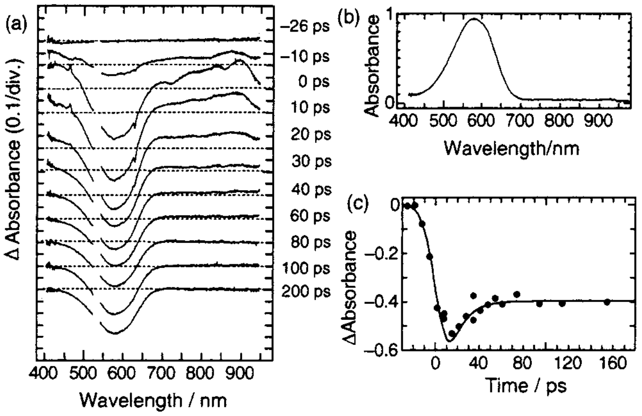

Figure 1. (a) Time-resolved transient absorption spectra of **1c** in O_2-free *n*-hexane solution, excited with a 15-ps fwhm laser pulse. (b) Ground-state absorption spectrum of **1c**. (c) Time profile of the transient absorbance at 590 -nm. The solid line was a convolution curve calculated on the basis of the pulse widths of pump and probe pulse (15 ps), time constant (10 ps), and the reaction yield (40%).

Scheme 1

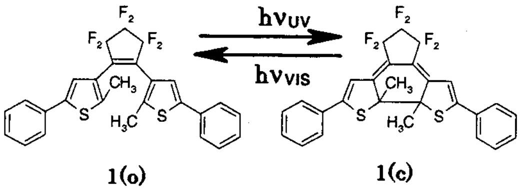

Figure 1 shows transient absorption spectra and time profiles of the closed-ring form of **1**, **1c**, in *n*-hexane solution, excited by a 532-nm laser pulse with 15-ps pulse duration and an output energy of 0.3 mJ/mm^2. The sample solution was circulated during the measurement under the repetition rate <0.1 Hz and the data were obtained only with one-shot laser exposure for each spectrum. The negative transient absorption centered at 590 nm, which is safely ascribable to the bleaching of the ground-state absorption of **1c** (Figure 1b), appears within the response of the apparatus. The negative absorption signal recovered with a time constant of 10 ps (Figure 1c) and was followed by the constant negative value that is due to the cycloreversion process from **1c** to **1o**.[12] On the other hand, the positive absorption signal in the wavelength region >650 nm observed in the early stage after the excitation can be ascribed to the excited state of **1c** since this positive absorption decreases with the time constant identical with that of the recovery of the ground-state absorption. The transient spectra at and after 80 ps following the excitation were identical with a negative image of the ground-state absorption of **1c**, indicating that the reaction completed in the several tens of picosecond region. The reaction yield from **1c** to **1o** in the present condition was estimated to be 40%, although the quantum yield of the **1c** to **1o** in *n*-hexane solution was obtained as 1.3% under steady-state irradiation.[10,11]

The time profiles of compound **1c** in *n*-hexane solution were also examined by using a 550-nm laser pulse with 150-fs fwhm and the output energy of 0.01 mJ/mm^2 as an excitation source. Figure 2 shows the time profile of the transient absorbance monitored at 590 nm. The quick appearance of the negative absorption signal due to the bleaching of the ground state of **1c** was followed by the recovery in the several tens of picosecond time region. This time profile was reproduced by a single-exponential function with the time constant of (9.6 ± 1.5) ps.

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(12) This negative absorption was observed even at several tens of seconds after the excitation without the circulation of the solution. By UV light irradiation after the bleaching of the picosecond 532 nm laser pulse excitation, the perfect recovery of the closed-form was observed.

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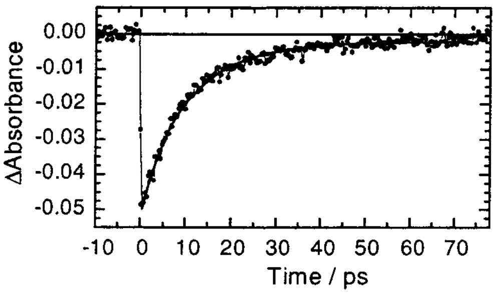


Figure 2. Time profile of the transient absorbance of **1c** in *n*-hexane, excited with a 150-fs fwhm laser pulse at 550 nm and monitored at 590 nm. These pulses were provided by a dual OPA lasers system driven by a 1 kHz Ti:Sapphire laser. During the measurements, the sample solution was circulated to avoid the effect of the permanent bleaching. The solid line was a calculated curve on the basis of the time constants (10 ps) and the reaction yield of 1.3%.

The residual signal (1−2%) at and after several tens of picosecond following the excitation is ascribed to the conversion of **1c** to **1o**. Actually, the residual signal did not decrease in the time window available in this measurement (ca. 3 ns) and the yield was almost identical with the cycloreversion quantum yield of **1c** obtained by steady-state irradiation.[10,11] The time profile monitored for the excited state of **1c** decreased with the time constants of (10.6 ± 2.0) ps, which was in agreement with that for the recovery of the ground state.

Although the time constant obtained by the picosecond laser excitation was the same as that by the femtosecond laser excitation within the experimental error, the residual signals due to the ring-opening process at and after several tens of picosecond following the excitation was quite different. That is, the quantum yield from **1c** to **1o** under femtosecond excitation conditions was consistent with the result from steady-state light irradiation, while the drastic enhancement was obtained by picosecond laser light exposure.

To get an insight into this enhancement of the reaction efficiency, we explored the excitation intensity effect of the picosecond 532-nm laser light on the reaction profiles. Figure 3a shows the result at 20 ps after excitation. The transient absorbance at 880 nm, due to the excited state of **1c**, increased consistently with the excitation intensity in the region where N_{photon} (the number of the photon at 532-nm) is smaller than N_{mole} (the number of ground-state molecules of **1c**), while further increase of the excitation intensity led to the decrease of the transient absorbance in the region with $N_{\mathrm{photon}} > N_{\mathrm{mole}}$. The turning point of this change was estimated around $N_{\mathrm{photon}} = N_{\mathrm{mole}}$. Since the ground state bleaching monitored at 580 nm monotonically increased with increasing excitation intensity, the decrease of the excited state in high excitation intensity was not attributable to the deactivation to the ground state but to the cycloreversion reaction. Actually at 160 ps at which the cycloreversion reaction was finished, the increase in the reaction efficiency with increasing excitation intensity was confirmed as shown in Figure 3b. Here, the ordinate is given as the conversion yield.[13]

In the region where the excitation intensity was low, the slope of the reaction efficiency in Figure 3b is ca. 1.8. Since a less efficient nonlinear ring-opening process was observed under the femtosecond excitation, the stepwise two-photon process via the actual intermediate S_1 state, rather than the simultaneous two-photon process, was responsible for the cyclorevresion process. Under the condition that most of the ground state was pumped up to the S_1 state in high excitation intensity region, the production of the S_n state via the absorption of the second photon was considered as a one-photon process and hence the slope in Figure 3b was close to unity. The conversion yield of the ring-opening reaction in the present condition reached 70%, which is more than 50 times larger than the quantum yield under steady-state irradiation.

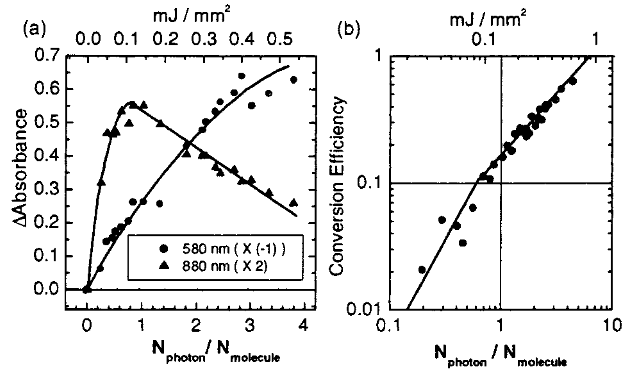
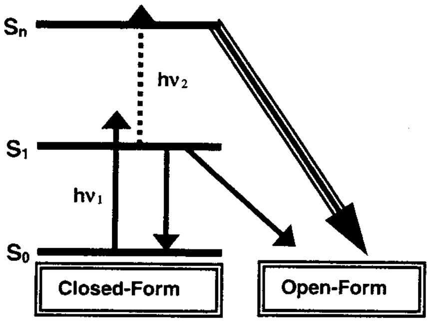


Figure 3. (a) Excitation intensity dependence of the transient absorbance of **1c** in *n*-hexane, observed 20 ps after the excitation with a 15-ps, 532-nm laser pulse. (b) Excitation intensity dependence of the conversion yield of **1c** in *n*-hexane, observed 160 ps after the excitation with a 15-ps, 532-nm laser pulse. Lines are to guide the eye.

Scheme 2



The above result leads to the conclusion that the excitation with the leading part of the picosecond laser pulse prepares the excited state, which is again excited by the trailing part of the pulse resulting in the efficient reaction, such as $S_0 + h\nu \rightarrow S_1$ and $S_1 + h\nu \rightarrow S_n \rightarrow$ open-ring form as shown in Scheme 2. We anticipate that the present result will provide a new approach for one-color light control of the gated photochromic system, which can be utilized to the erasable memory system with nondestructive readout capability. In relation to this, we are now investigating multiphoton-induced reactions of diarylethene derivatives with low one-photon reaction yield in the solid phase, the result of which will be published in the future.

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(13) The conversion yield is defined as the absorbance at 590 nm at 160 ps divided by the ground-state absorbance. This "conversion yield" is the minimum estimate of the cycloreversion quantum yield in the present condition.