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# Picosecond and femtosecond laser photolysis studies of a photochromic diarylethene derivative: multiphoton gated reaction

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## Abstract

Cycloreversion (ring-opening) process of one of the photochromic diarylethene derivatives, 1,2-bis(2-methyl-3-benzothienyl)perfluorocyclopentene (BPFC), was investigated by means of picosecond and femtosecond laser photolysis methods. The drastic enhancement of the reaction yield was observed by the picosecond laser exposure. On the other hand, the cycloreversion reaction yield under femtosecond laser exposure was consistent with the steady-state light irradiation. The excitation intensity effect of the reaction profiles revealed that the successive multiphoton absorption process leading to higher excited states opened the efficient cycloreversion process.

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## 1. Introduction

Photochromism is a photoinduced reversible isomerization in a chemical species between two forms. The instant property change arising from the chemical-bond reconstruction via photoexci-

tation has been attracting much attention not only from the viewpoint of the fundamental chemical reaction processes but also from the viewpoint of the application to optoelectronic devices such as rewritable optical memory and switches [1–10].

Among various photochromic molecules, diarylethenes with heterocyclic rings have been developed as a new type of thermally stable and fatigue-resistant photochromic compounds. Some of these molecules have no thermochromicity even at 150 °C, the colored-forms are estimated to be stable for more than 1900 years at 30 °C, and the

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cyclization and cycloreversion cycles can be repeated more than  $10^4$  times while keeping adequate photochromic performance [3–10]. In addition, the photochromic reaction can take place even in the crystalline phase [5,10]. Direct detection of the reaction dynamics [11–20] revealed that most of these photochromic reactions take place in the time region  $\leq 10$  ps.

The photochromic systems for the actual application, in general, require several conditions such as (a) thermal stability of both isomers, (b) low fatigue, (c) rapid response, (d) high sensitivity, and (e) non-destructive 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). On the other hand, the non-destructive read-out capability is in conflict with the above properties fulfilling conditions (b)–(d). Hence, the introduction of gated-function is required for the photochromic systems with non-destructive capability while reading-out by the absorption of the light. Recently, we reported laser-induced enhancement (more than 50 times) of cycloreversion reaction in a photochromic diarylethene derivative with a low reaction yield under the steady-state light irradiation [20]. The excitation intensity and pulse duration effects of the reaction profiles revealed that higher excited states attained by multiphoton absorption could open the effective photochromic reaction channel. This multiphoton-gated reaction may provide a new approach to erasable memory media with non-destructive readout capability. Not only from the viewpoint of the application but also from the basic viewpoints of photochemistry, the selective excitation to a specific electronic state leading to the target reaction seems to provide a novel approach for the control of the photochemical reactions.

To explore the applicability of the multiphoton-gated reaction, we have applied this method to the photochromic diarylethene derivative with high durability under steady-state light irradiation [21,22]. On the basis of the results depending on

the pulse duration of the pump laser light sources and the excitation intensity effects of the photochromic reactions, the laser-induced reactivity of the cycloreversion process will be discussed in the following.

## 2. Experimental

Picosecond laser photolysis system with a repetitive mode-locked  $\text{Nd}^{3+}$ :YAG laser was used for transient absorption spectral measurements [24,25]. The second harmonic (532 nm) with 15 ps fwhm and 0.5–1 mJ was used for excitation. The excitation pulse was focused into a spot with a diameter of ca. 1.5 mm. Picosecond white continuum generated by focusing a fundamental pulse into a 10 cm quartz cell containing  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  mixture (3:1) was employed as a monitoring light. A sample cell with 2 mm optical length cell was used for the 532 nm excitation. The sample solution was circulated during the measurement under the repetition rate  $< 0.1$  Hz and the data was obtained only with one-shot laser exposure for each spectrum.

To investigate the dynamic behaviors under femtosecond laser light excitation, double OPA femtosecond laser system for kinetic transient absorption measurements was used. The block diagram of the optical system is shown in Fig. 1a. The output of a femtosecond Ti:Sapphire laser (Tsunami, Spectra-Physics) pumped by the SHG of a cw  $\text{Nd}^{3+}$ :YVO<sub>4</sub> laser (Millennia V, Spectra-Physics) was regeneratively amplified with 1 kHz repetition rate (Spitfire, Spectra-Physics). The amplified pulse (1 mJ/pulse energy and 85 fs fwhm) was divided into two pulses with the same energy (50%). These pulses are guided into two OPA systems (OPA-800, Spectra-Physics), respectively. OPA output pulses are converted to the SHG, THG, FHG, or sum frequency mixing with fundamental 800 nm pulse. These pulses can cover the wavelength region between 300 and 1200 nm with 1–10 mW output energy and ca. 120 fs fwhm. One of these two pulses was used as a pump light and the other one which is reduced to  $< 1/5000$  output power was utilized as a monitoring light. The pulse duration for the wavelength pair (640 and 670 nm) at the sample

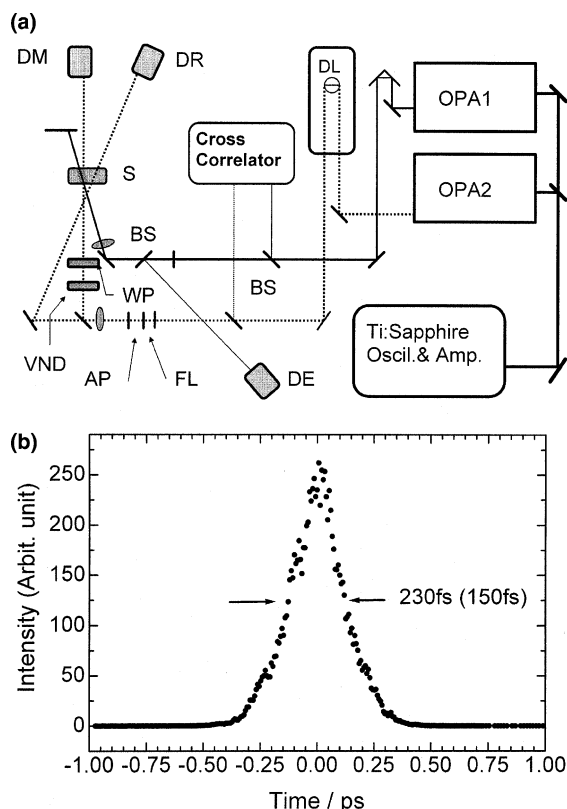


Fig. 1. (a) Schematic diagram of dual OPA femtosecond laser system. BS (beam sampler), AP (aperture), FL (ND filter), WP (polarization wave plate), VND (variable ND filter), DL (optical variable delay line with retro-reflector), DM (photodetector for the monitoring beam), DR (photodetector for the reference beam), and DE (photodetector beam for the probe beam intensity). (b) Typical example of the cross-correlation trace monitored at the sample position. The 640 nm pulse from OPA1 and the 670 nm pulse OPA2 were mixed by 1 mm BBO crystal.

position was estimated 150 fs from the cross-correlation trace at the same position (Fig. 1b). The intensities of the monitoring, reference, and the

pump beams were, respectively, detected by photodiode detectors and sent to the microcomputer for further analysis. In the present measurement, the repetition rate of the laser was reduced to 100 Hz. The sample cell with 2 mm optical length was used and the sample solution was circulated.

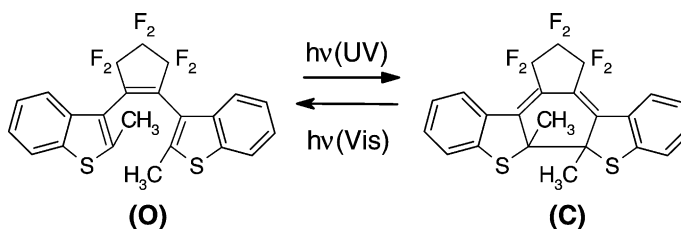
1,2-Bis(2-methyl-3-benzothienyl)perfluorocyclopentene (BPFC) was synthesized and purified [21–23]. *n*-Hexane (Wako, infinity pure grade) was used without further purification. All the measurements were performed under  $O_2$  free condition at  $22 \pm 2$  °C.

### 3. Results and discussion

#### 3.1. Transient absorption spectroscopy with picosecond laser pulse

BPFC undergoes cyclization/cycloreversion between open- and closed-ring forms via the photoexcitation as shown in Scheme 1 [21,22]. The cyclization and cycloreversion quantum yields in *n*-hexane solution were, respectively, 0.35 and 0.35 [23].

Fig. 2a shows transient absorption spectra of the closed-ring form of BPFC (C) in *n*-hexane solution, excited by a 532 nm laser pulse with 15 ps pulse duration and the output energy of 0.7 mJ/mm<sup>2</sup>. In the early stage after the excitation, the sharp positive absorption at 710 nm and the negative signal at 490 nm appeared together with the broad absorption signals around 450 and 580 nm regions. With an increase in the delay time after the excitation, the negative absorption intensity increased and the maximum of the negative signal shifted from 490 to 510 nm, while the sharp absorption at 710 nm monotonously decreased with



Scheme 1.

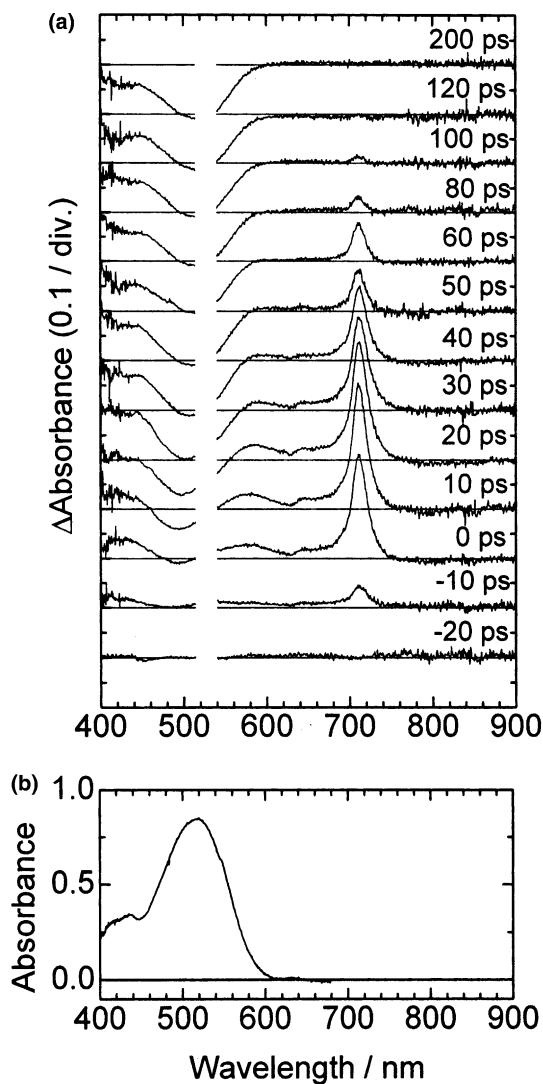


Fig. 2. (a) Transient absorption spectra of the closed-ring isomer of BPFC in *n*-hexane solution, excited with a picosecond 355 nm laser pulse. (b) Ground state absorption spectrum of the open-ring isomer of BPFC in *n*-hexane solution.

increasing delay time. As will be mentioned in later, the decay time constant of the positive absorption at 710 nm was identical with that of the recovery of the ground state closed-form. Hence, this sharp absorption at 710 nm can be assigned to the absorption due to the excited state. The transient spectra at and after 120 ps following the excitation were identical with a negative image of the ground state absorption of BPFC (C) as shown in

Fig. 2b, indicating that the photoinduced reaction completed in several tens of picosecond time region. This negative absorption was observed even at several seconds after the excitation without the circulation of the solution. By the UV light irradiation after the bleaching of the picosecond 532 nm laser pulse excitation, the perfect recovery of the closed-form was observed. Hence, this negative absorption observed at and after 120 ps following the excitation can be ascribed to the formation of the open-ring isomer of BPFC.

### 3.2. Reaction dynamics under femtosecond laser excitation

Prior to the discussion on the precise dynamic behaviors under picosecond laser excitation, we will show the reaction profiles under femtosecond laser light irradiation. Exhibited in Fig. 3 are the time profiles of the closed-ring form of BPFC (c) in *n*-hexane solution by using a 540 nm laser pulse with 150 fs fwhm and the output energy of 0.01 mJ/mm<sup>2</sup> as an excitation source. Fig. 3a shows the time profile of the transient absorbance monitored at 710 nm. The quick appearance of the positive absorption signal due to the excited state of BPFC (C) was followed by the decay in several tens of picosecond time regions. This time profile was reproduced by a double exponential function with the time constants of  $(4.8 \pm 1.5)$  and  $(22 \pm 2)$  ps. The pre-exponential factors for the faster and the slower component were, respectively,  $(28 \pm 2)\%$  and  $(72 \pm 2)\%$ .

To obtain the information on the biphasic decay, the time profile in the early stage after the excitation was investigated (Fig. 3b). The positive absorbance appeared within the response function of the apparatus and was followed by the decay accompanied with oscillatory modulation with the frequency of ca. 60 cm<sup>-1</sup>. Although it is rather difficult to derive a clear conclusion on this oscillatory motion, it is strongly suggested that rather large-amplitude motion is coupled with the modulation of the transient absorbance in the excited singlet state. In any how, the quick appearance of the absorption due to the excited state at 710 nm indicates that the excited state with the characteristic absorption at 710 nm has no precursor

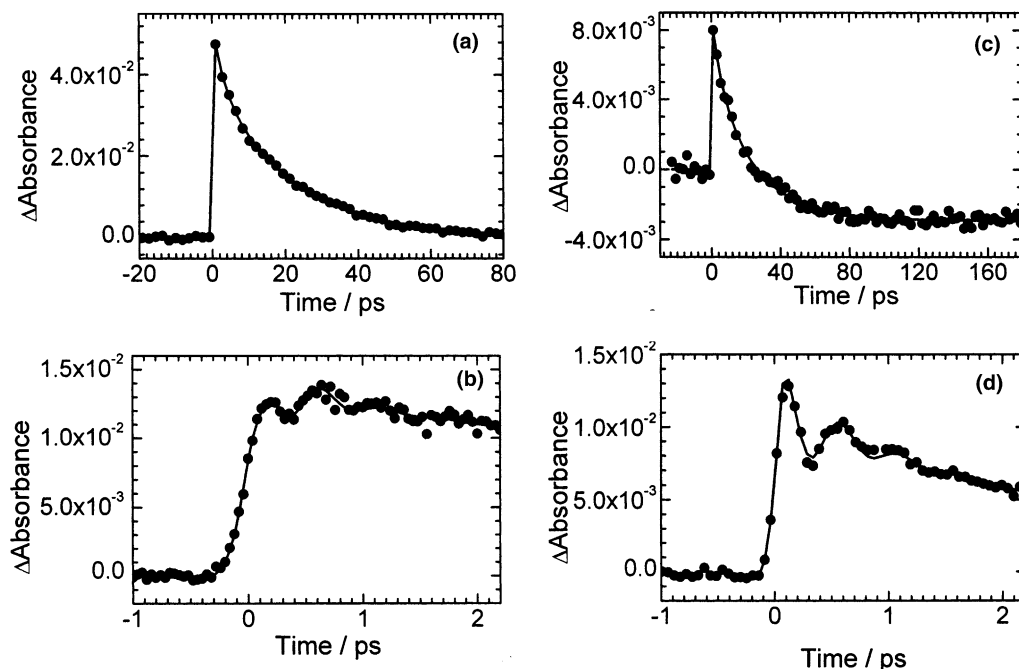


Fig. 3. Time profiles of transient absorbance of the closed-ring isomer of BPFC in *n*-hexane, excited with a 150 fs FWHM laser pulse at 540 nm: (a) and (b) monitored at 710 nm, and (c) and (d), monitored at 550 nm. Solid lines are the calculated curves by taking into account the pulse durations, the time constants, and the oscillation frequency (see text).

species with the lifetime detectable with our laser system ( $< \text{ca. } 50 \text{ fs}$ ).

On the excited states of the closed-ring isomer of diarylethene derivatives, it was reported from the *ab initio* MO calculation that a level of the dark excited state exists in the vicinity of the lowest excited state attainable from the ground state [26,27]. The biphasic decay process suggests that the fast decay with the time constant of  $(4.8 \pm 1.5) \text{ ps}$  is ascribable to the relaxation into the equilibrium between these two states, although further systematic investigation is necessary to derive a clear conclusion on this point.

On the other hand, the time profile monitored at 550 nm where the ground state absorption exists is exhibited in Fig. 3c. The positive absorption appears immediately after the excitation, followed by the decay in several tens of ps time region. The permanent negative absorbance at and after *ca.* 100 ps was due to the cycloreversion process, as was observed in Fig. 2. The decay process of the transient absorbance was biphasic with the faster time constant of  $(5.7 \pm 0.8) \text{ ps}$  and the slower one

of  $(23.5 \pm 0.5) \text{ ps}$ . The amplitude factors for the faster and the slower time constants were, respectively,  $(26 \pm 2)\%$  and  $(74 \pm 2)\%$ . These two time constants and the pre-exponential factors were almost the same with those obtained for the decay profile monitored at 710 nm. The time profile at 550 nm in the early stage after the excitation is shown in Fig. 3d. The positive transient absorbance appeared within the response of the apparatus and was followed by the decay with an oscillatory behavior. The frequency of this oscillation was obtained to be  $64 \text{ cm}^{-1}$ , of which value was in agreement with that obtained for the time profile at 710 nm within the experimental error. Since no ground state absorption exists at 710 nm and the frequency of the oscillation was almost the same with each other, the oscillatory behavior observed at 550 nm may be ascribed to the molecular vibration in the excited state. At any rate, the time profile at 550 nm indicates that the positive absorption due to the  $S_1$  state whose extinction coefficient was larger than that in the ground state appears within the response of the apparatus,

followed by the decay with the biphasic process. At and after ca. 100 ps following the excitation, the permanent bleaching due to the cycloreversion process was observed. In addition, the time profile at 550 nm was not affected by the excitation intensity in the range between 0.005 and 0.015 mJ/mm<sup>2</sup>, indicating that the multiphoton process was not involved for the cycloreversion reaction under femtosecond laser pulse exposure.

### 3.3. Difference in the reactivity between PS- and FS laser excitation conditions

Fig. 4 shows the time profiles of the transient absorption signals at several wavelength points by picosecond laser pulse excitation of which spectra were shown in Fig. 2. The positive absorption signal at 710 nm (Fig. 4a) appears within the response of the apparatus and decreases with increasing delay time after the excitation. The solid line is the result calculated by taking into account the durations of the excitation and monitoring laser pulses and time constants of absorbance changes. In this calculation, the time dependence of the transient absorbance was assumed to be biphasic decay, whose time constants and the amplitude factors were set to be identical with those obtained by the femtosecond photolysis as shown in Fig. 3. The solid line thus calculated reproduced the experimental fairly well as shown in Fig. 4a, indicating that the time profile at 710 nm by picosecond laser excitation was almost similar with that obtained by femtosecond laser excitation.

The time profile at 550 nm in Fig. 4b shows the positive absorbance around time origin and then the decrease of the absorbance follows. As in Fig. 4a, the dotted line is the result calculated on the basis of the durations of the excitation and monitoring laser pulses with parameters identical with those obtained by the femtosecond photolysis. In the calculation, it was assumed that only the slow component leads to the cycloreversion reaction. The calculated curve with parameters identical with those under the femtosecond laser excitation, however, did not reproduce the time profile obtained by the picosecond photolysis. In other word, the reaction yield by the picosecond laser exposure is much larger than that by the femto-

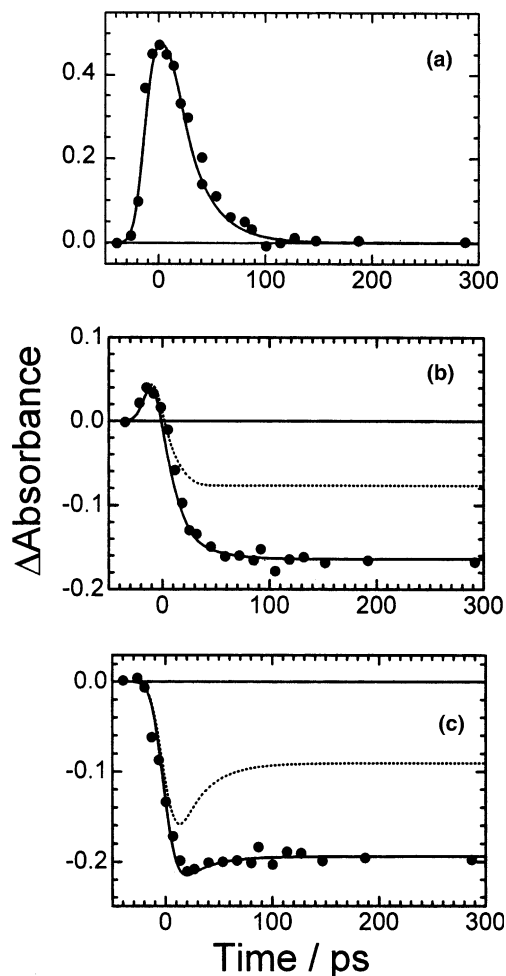


Fig. 4. Time profiles of transient absorbance of closed-ring isomer of BPFC, excited with a picosecond 532 nm laser pulse: (a) monitored at 710 nm, (b) at 550 nm, and (c) at 495 nm. Solid lines are convolution curves calculated on the basis of laser pulse durations and the time constants (see text).

second laser excitation. The solid line calculated with the reaction yield of 75% reproduces the experimental result fairly well, indicating that the reaction yield by the picosecond laser excitation is more than twice larger than that under steady-state light irradiation.

The enhancement of the cycloreversion reaction yield was confirmed also by the time profile at 495 nm shown in Fig. 4c. The negative absorption appeared with the response of the apparatus and slightly recovered in several tens of picosecond

time regions, followed by the constant negative value due to the cycloreversion process [28]. On the assumption that the excited state has no absorption at 495 nm and only the slow component leads to the cycloreversion reaction, the cycloreversion yield was estimated to be 75% in the present experimental condition (the solid line). On the other hand, the calculated curve with the reaction yield of 35% (the dotted line) does not reproduce the experimental result. Summarizing the above results and discussion, it is concluded that the reaction yield in the present condition of the picosecond excitation is ca. twice larger than that under steady-state light irradiation and the femtosecond laser excitation.

### 3.4. Excitation intensity effect of the picosecond 532 nm laser light on the reaction profiles

Although the time constants obtained by the picosecond laser excitation were almost the same with those by the femtosecond laser excitation, the residual signal due to the cycloreversion process at and after ca.120 ps following the excitation was quite different from each other. That is, the cycloreversion quantum yield under femtosecond excitation condition was consistent with the result by the steady-state light irradiation, while the drastic enhancement was obtained by the 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. Fig. 5a shows the result at 20 ps after the excitation. The transient absorbance at 710 nm, due to the excited state of the closed-form, increased consistently with increasing excitation intensity in the region of low excitation intensity, while further increase in the excitation intensity led to the decrease of the transient absorbance. Since the ground state bleaching monitored at 510 nm monotonously increased with increasing excitation intensity, the decrease of the excited state in high excitation intensity was not attributable to the deactivation into 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

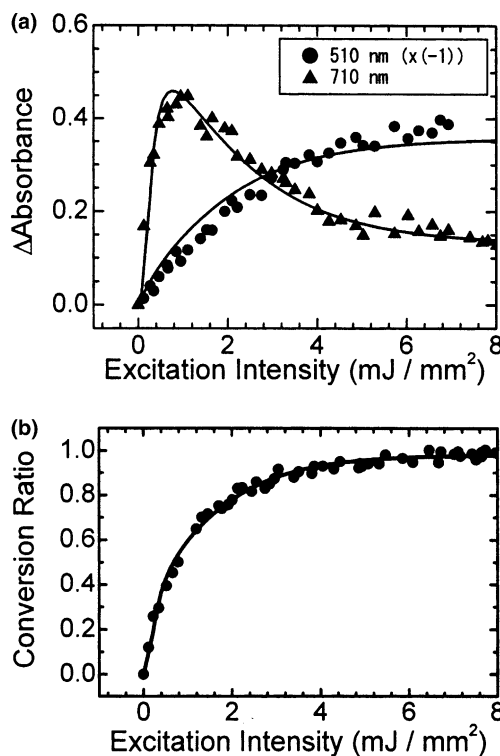


Fig. 5. (a) Excitation intensity dependence of transient absorbance of the closed-form of BPFC in *n*-hexane, observed at 20-ps after the excitation with a 15-ps 532-nm laser pulse. (b) Excitation intensity dependence of the conversion ratio of the closed-form of BPFC in *n*-hexane, observed at 160-ps after the excitation with a 15-ps 532-nm laser pulse. Lines are drawn to guide the eye.

increasing excitation intensity was confirmed as shown in Fig. 5b. Here, the ordinate is given as the conversion ratio defined as  $-\Delta A_{510}(160 \text{ ps})/A_{510}$ . Here,  $\Delta A_{510}(160 \text{ ps})$  and  $A_{510}$  are the transient absorbance at 510 nm monitored at 160 ps after the excitation and the ground state absorbance at 510 nm, respectively. The slope of Fig. 5b was almost linear in low excitation intensity and then saturated with increasing excitation intensity. This tendency may be interpreted in the following way. The number of the photon in the exposed volume at ca. 1  $\text{mJ} / \text{mm}^2$  was almost the same with the number of the ground state molecules. 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 consid-



ered as one-photon process and hence the slope in Fig. 5b was close to the unity in rather low excitation intensity. With further increase in the excitation, the number of the excited molecules also decreases and reaches the conversion ratio of the cycloreversion reaction of 100%. In any how, the above results indicate that the multiphoton absorption process is responsible for the enhancement of the cycloreversion process under the picosecond laser excitation.

The multiphoton absorption process is usually divided into two cases; the simultaneous absorption process and the stepwise absorption process. Since less efficient non-linear cycloreversion process was observed under the femtosecond excitation, the stepwise two-photon process via the actual intermediate  $S_1$  state, rather than the simultaneous process, was responsible for the cycloreversion process. 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. As mentioned in Section 1, we reported laser-induced enhancement (more than 50 times) of cycloreversion reaction in a photochromic diarylethene derivative with a low reaction yield under the steady-state light irradiation [20]. Also in the present case, the multiphoton gated reaction was confirmed for the diarylethene derivative. BPFC was known to have extremely

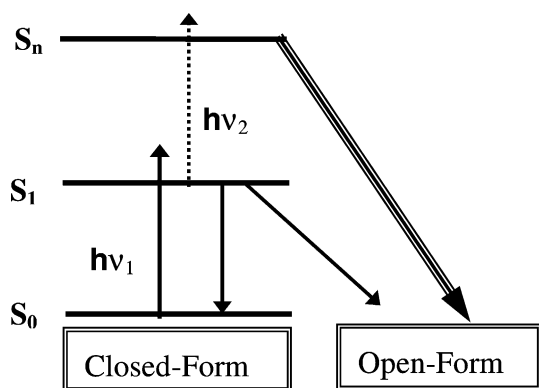
high durability; 90% of the performance remains after 14000 cycles of the cyclization and the cycloreversion [23]. In the present picosecond multiphoton excitation condition, we could not detect any bi-products other than the open-ring form after more than 1000 laser shots with ca. 3–5 mJ laser pulse into 2 ml sample solution of  $10^{-4}$  M. The present results indicate that the higher excited state attained by two-photon absorption has very small reaction pathways leading to the degradation. We are now going on the investigation of the multiphoton-gated reaction of diarylethene derivatives with high durability and low cycloreversion reaction yield under one-photon excitation together with the analysis of the reaction profiles by the computer simulation to estimate the reaction yield in higher excited state, result of which will be published soon.

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Scheme 2.

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