

# Multiphoton-gated photochromic reaction of diarylethene derivatives in PMMA solid film

Senichi Ryo,<sup>1</sup> Yukihide Ishibashi,<sup>1</sup> Masataka Murakami,<sup>1</sup> Hiroshi Miyasaka,<sup>1\*</sup> Seiya Kobatake<sup>2</sup> and Masahiro Irie<sup>3\*\*</sup>

<sup>1</sup>Division of Frontier Materials Science, Graduate School of Engineering Science, and Center for Quantum Science and Technology Under Extreme Conditions, Osaka University, Toyonaka, Osaka 560-8531, Japan

<sup>2</sup>Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Sugimoto, Sumiyoshi, Osaka 558-8585, Japan

<sup>3</sup>Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan

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**ABSTRACT:** Cycloreversion (ring-opening) process of a photochromic diarylethene derivative in PMMA polymer solid film was investigated by means of picosecond laser photolysis. As was observed in our previous work in solution phase, the drastic enhancement of the cycloreversion reaction yield was observed under picosecond laser exposure. 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 with reaction yield of  $(50 \pm 10)\%$ . These results indicate that the multiphoton-gated reaction takes place also in the polymer solid and its efficiency was almost comparable with that in solution phase. Copyright © 2007 John Wiley & Sons, Ltd.

**KEYWORDS:** photochromism; diarylethene; picosecond dynamics; multiphoton process

## INTRODUCTION

Photochromism is a photoinduced reversible isomerization in a chemical species between two forms. The quick property change arising from the chemical-bond reconstruction via photoexcitation 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.<sup>1–13</sup> Among various photochromic molecules, diarylethenes with heterocyclic aryl rings have been developed as a new type of thermally stable and fatigue-resistant photochromic compounds.<sup>3–13</sup> Changes in various physical and chemical properties accompanied with the photochromic reactions<sup>8–13</sup> and the time-resolved detection of these processes<sup>14–25</sup> have been extensively investigated.

The photochromic systems for the actual application, however, require several conditions such as (a) thermal

stability of 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). Although some of diarylethene derivatives fulfill conditions (a)–(d), the non-destructive read-out capability is usually 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 multiphoton-induced enhancement of a cycloreversion reaction in photochromic systems in solution phase.<sup>21–25</sup> The detailed investigation of the excitation intensity dependence of the reaction profiles revealed that the successive two-photon absorption process via the  $S_1$  state opened the efficient cycloreversion process in higher excited states. For one of the diarylethene derivatives,<sup>23</sup> the cycloreversion reaction yield at the highly excited state was estimated to be  $(50 \pm 10)\%$ , while the cycloreversion quantum yield through the  $S_1$  state is only 1.3%. Moreover, it was also found that one-photon absorption directly pumped to

\*Correspondence to: H. Miyasaka, Division of Frontier Materials Science, Graduate School of Engineering Science, and Center for Quantum Science and Technology Under Extreme Conditions, Osaka University, Toyonaka, Osaka 560-8531, Japan.  
E-mail: miyasaka@chem.es.osaka-u.ac.jp

\*\*Correspondence to: M. Irie, Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan.  
E-mail: irie@cstf.kyushu-u.ac.jp

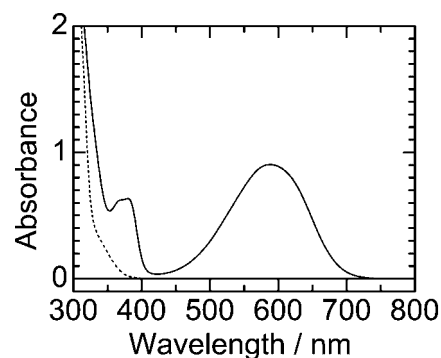
higher excited state did not lead to the efficient cycloreversion reaction. These results indicate not the energy of the excitation but the character of the electronic state takes an important role in the enhancement of the cycloreversion reaction. The selective excitation to a specific electronic state leading to the target reaction seems to provide a novel approach for the control of the photochemical reactions. Not only from the viewpoint of the basic photochemical reaction but also from the viewpoint of the application, this multiphoton-gated reaction may provide a new approach to erasable memory media with non-destructive readout capability. Along this line, we have studied the multiphoton reaction profiles of diarylethene derivatives in solid polymer films.

## EXPERIMENTAL

A picosecond laser photolysis system with a repetitive mode-locked Nd<sup>3+</sup>:YAG laser was used for transient absorption spectral measurements.<sup>26</sup> 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 light continuum generated by focusing a fundamental pulse into a 10 cm quartz cell containing D<sub>2</sub>O and H<sub>2</sub>O mixture (3:1) was employed as a monitoring light.

For the measurement of the dependence of the transient absorption spectra on the excitation intensity of the picosecond laser pulse, a pinhole with a diameter of 1.0 mm was placed before the sample. The intensity of the picosecond laser light was measured by a laser power meter (Gentec, ED-200).

Bis(2-methyl-5-phenylthiophen-3-yl)perfluorocyclopentene, **PT1**, was synthesized and purified.<sup>13d</sup> This molecule undergoes the photochromic reactions between the open-isomer and the closed-isomer as shown in Scheme 1. PMMA (Aldrich,  $M_w = 12\,000$ ) was purified by precipitation from toluene solution with methanol. Solid films with *ca.* 0.2 mm thickness were prepared from the chloroform solution of **PT1** by casting onto the quartz plate. The specimen was air-dried in dark room at room temperature for 2 h, followed by further drying in vacuum for more than 12 h. The laser exposure spot was replaced



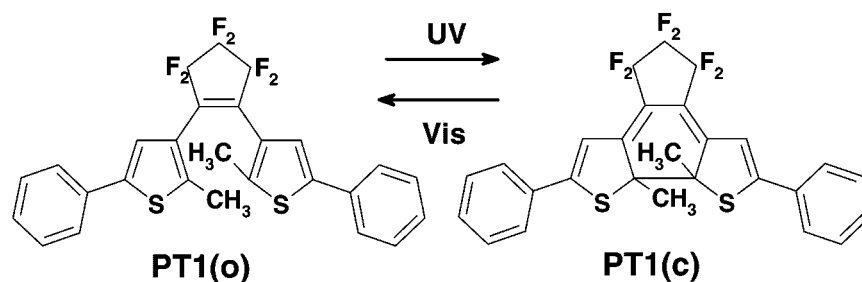
**Figure 1.** Steady-state absorption spectra of **PT1** in PMMA solid film. Closed-ring isomer of **PT1**, **PT1(c)**, (smooth line) and open-ring isomer, **PT1(o)**, (dotted line)

with unirradiated new position and the data was obtained only with one-shot laser exposure for each spectrum. The absorbance at the absorption maximum was *ca.* 1. All the measurements were performed under O<sub>2</sub> free condition at  $22 \pm 2$  °C.

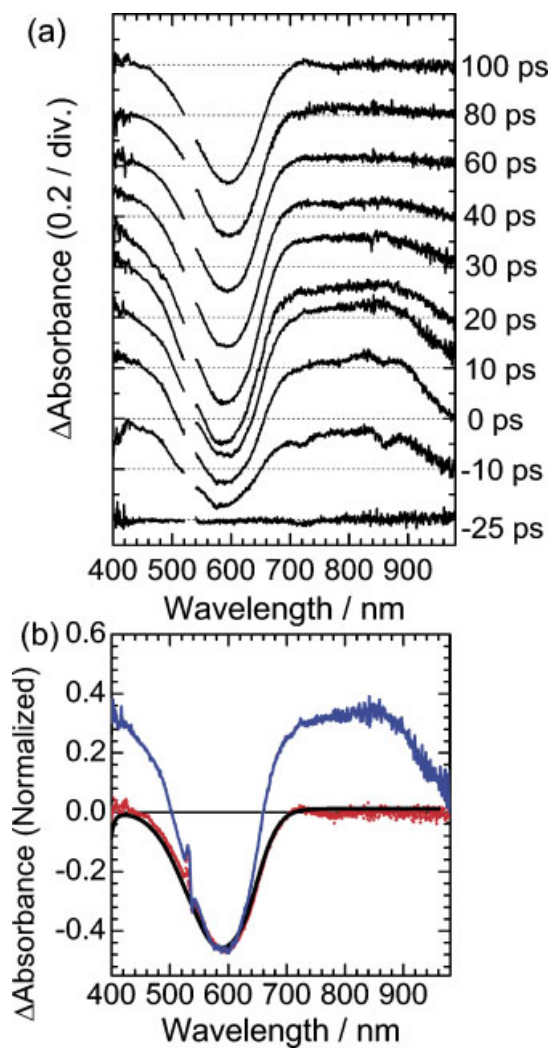
## RESULTS AND DISCUSSION

Figure 1 shows steady-state absorption spectra of **PT1** in PMMA solid film. The closed-form of **PT1**, **PT1(c)** has the absorption maximum at 590 nm in the visible region, together with peaks at 305 and 380 nm in the UV region. On the other hand, the open-form of **PT1**, **PT1(o)**, has the absorption only in the UV region. The absorption maxima and spectral band shapes of both spectra were respectively almost the same with those in *n*-hexane solution. The cycloreversion yield in *n*-hexane solution was reported<sup>13d</sup> to be 0.013, while that in PMMA matrix was estimated to be  $\leq 0.01$ . The cycloreversion reaction yield in PMMA solid film is slightly smaller or almost the same with that in *n*-hexane solution.

Figure 2 show transient absorption spectra of **PT1(c)** in PMMA film, excited with a picosecond 532 nm laser pulse with an excitation intensity of 1.8 mJ/mm<sup>2</sup>. A negative absorption band with a maximum at 590 nm and positive absorption bands in the wavelength regions longer than 650 nm and shorter than 450 nm appear



**Scheme 1**

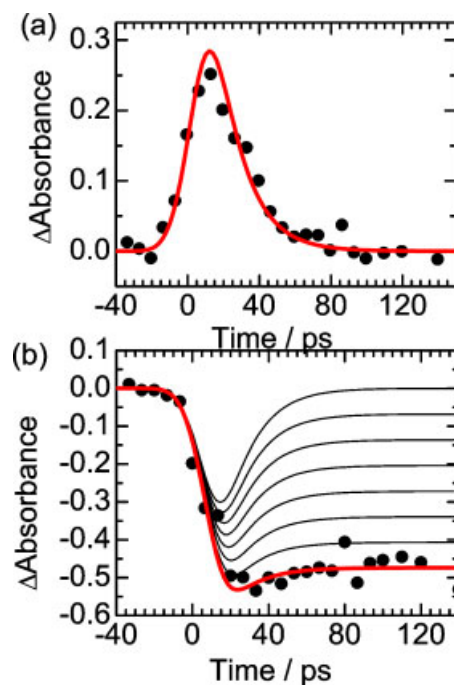


**Figure 2.** (a) Time-resolved transient absorption spectra of PT1(c) in PMMA solid film, excited with a 15 ps FWHM 532 nm laser pulse with  $1.8 \text{ mJ/mm}^2$  output power. (b) Transient absorption spectra of PT1(c) in PMMA solid film, normalized at 590 nm, observed at 10 ps (blue line) and 100 ps (red line) after the excitation. The black solid line is a negative image of ground-state absorption of PT1(c). This figure is available in colour online at [www.interscience.wiley.com/journal/poc](http://www.interscience.wiley.com/journal/poc)

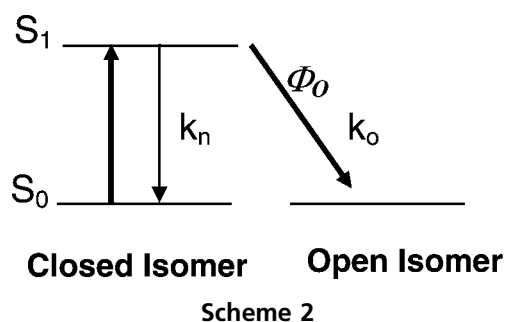
immediately after the excitation. The former negative absorption can be safely ascribed to the bleaching signal of the ground state PT1(c). On the other hand, the positive absorption bands are assigned to the excited state of PT1(c) because the decay time constant was in agreement with that for the recovery of the former bleaching signal as will be shown in later. At and after 100 ps following the excitation, almost all positive absorption signals disappeared and constant negative absorption remained. As shown in Fig. 2(b), the transient absorption spectrum at 100 ps after the excitation was identical with the negative image of the ground-state absorption spectrum, although the spectrum at 10 ps shows the absorption signal due to the excited state. In addition, this negative absorption spectrum as observed at 100 ps did not disappear even at

several hours after the excitation. Since the UV light irradiation at the spot irradiated by the picosecond 532 nm laser pulse perfectly recovered the absorbance of PT1(c), the negative absorption signal as observed in the transient absorption spectra at and after 100 ps following the excitation was assigned to the cycloreversion reaction from PT1(c) to PT1(o).

Figure 3 shows the time profiles of PT1(c) in PMMA solid film monitored at several wavelength points following the picosecond 532 nm laser excitation. The time profile at 800 nm shows the rapid appearance of the positive absorbance followed by the decay in several tens of picoseconds time region. The solid lines in Figure 3 are curves calculated on the basis of the pulse widths of the exciting and monitoring pulses and the decay time constant. In this calculation, the mono-phasic decay with a time constant of 15 ps was assumed. As shown in this figure, the calculated curves reproduce the experimental results well. On the other hand, the time profile at 590 nm shows that the negative transient absorbance appearing within the response of the apparatus recovers slightly in several tens of picosecond time region, followed by the



**Figure 3.** Time profiles of the transient absorbance of PT1(c) in PMMA solid film, excited with a 15 ps FWHM, 532 nm laser pulse with  $1.8 \text{ mJ/mm}^2$  output power, and observed at 800 nm, (a), and at 590 nm, (b). Solid lines are convolution curves calculated on the basis of the pulse widths of pump and probe pulse (15 ps) and a time constant (15 ps). The lines in (b) are the results calculated with the reaction yield as a parameter. From the top, the reaction yields of 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, and 0.7 were respectively set for the calculation with the pulse width of 15 ps and the time constant of 15 ps. The bold line with the reaction yield of 0.7 best reproduces the experimental result in (b). (see text) This figure is available in colour online at [www.interscience.wiley.com/journal/poc](http://www.interscience.wiley.com/journal/poc)

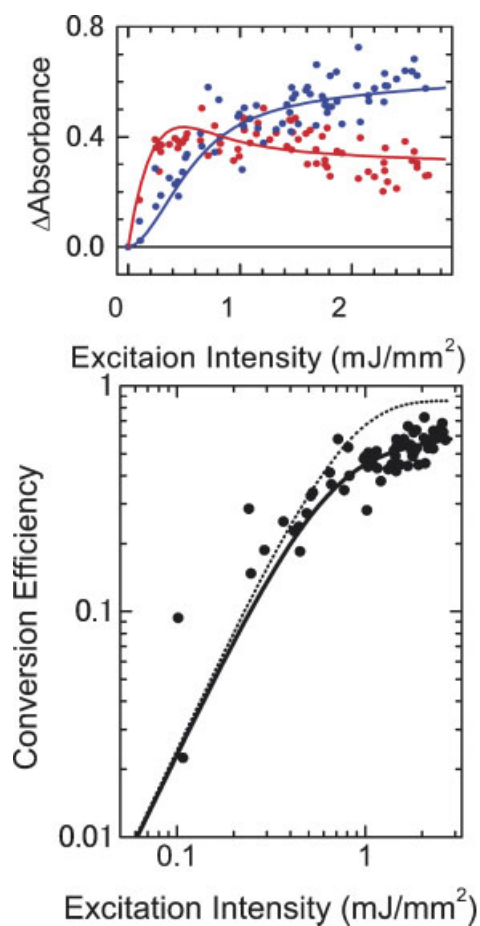


constant negative value due to the cycloreversion process from **PT1(c)** to **PT1(o)**.

For the analysis of the time profile at 590 nm, we tentatively assumed the simple reaction scheme that the excited state of **PT1(c)** undergoes the deactivation into the ground state in competition with the cycloreversion reaction leading to the **PT1(o)** production as shown in Scheme 2, where the reaction yield of the cycloreversion reaction,  $\Phi_o$ , is represented as  $k_o/(k_n + k_o)$ . Here,  $k_n$  and  $k_o$  are respectively the rate constant of the deactivation into the ground state and that of the cycloreversion reaction. In the analysis,  $1/(k_n + k_o)$ , was set to the decay time constant of the positive absorption signals of 15 ps. Solid lines in Fig. 3(b) are the curves calculated with various  $\Phi_o$  values. This figure indicates that the experimental result is well reproduced with  $\Phi_o = 70\%$  although the quantum yield of the **PT1(c)** to **PT1(o)** in PMMA solid film was obtained to be less than 1% under steady-state irradiation.

In order to elucidate the increase of the apparent reaction yield, the dependence of the apparent reaction yield on the picosecond 532 nm laser light was investigated. Fig. 4(a) shows the result at 20 ps after the excitation. The transient absorbance at 880 nm, due to the excited state of the closed-form, increased consistently with increasing excitation intensity in the region of low excitation intensity up to *ca.* 0.5 mJ/mm<sup>2</sup>. Although the data points are rather scattered and may be less reliable compared to those in solution phase,<sup>23</sup> further increase in the excitation intensity led to the slight decrease of the transient absorbance or almost constant. On the other hand, the bleaching signal monitored at 590 nm monotonously increased with increasing excitation intensity. This result clearly indicates that the decrease of the excited state in high excitation intensity was not attributable to the deactivation into the ground state.

Actually at 160 ps when the cycloreversion reaction was completely finished, the increase in the reaction yield with increasing excitation intensity was confirmed as shown in Fig. 4(b). In this figure, the ordinate is given as the conversion efficiency defined as  $-\Delta A_{590\text{ nm}}(160\text{ ps})/A_{590\text{ nm}}$ . Here,  $\Delta A_{590\text{ nm}}(160\text{ ps})$  and  $A_{590\text{ nm}}$  are the transient absorbance monitored at 160 ps after the excitation and the ground state absorbance at 590 nm, respectively. The slope of Fig. 4(b), 1.8–2.0, shows that



**Figure 4.** Excitation intensity dependence of transient absorbance of **PT1(c)** in PMMA solid film. (a) Observed at 590 nm (blue circles) and 880 nm (red circles) at 20 ps after the excitation with a 15 ps 532 nm laser pulse. (b) Observed at 590 nm at 160 ps after the excitation. Lines in figures are the calculated curves with the parameters (see text). This figure is available in colour online at [www.interscience.wiley.com/journal/poc](http://www.interscience.wiley.com/journal/poc)

the cycloreversion reaction is quadratically in proportion with the incident laser intensity in the region where the excitation intensity is not very high and indicates that the two-photon absorption process is responsible for the enhancement of the apparent cyclization reaction.

Usually, two-photon absorption processes are classified into two cases such as simultaneous absorption and stepwise absorption. In the former simultaneous absorption process, the ground state molecule is excited biphotonically even in the wavelength region where the molecule has no ground state absorption. The number of the molecules excited by the simultaneous two-photon absorption is represented by Eqn 1.

$$N_e = \delta \cdot N_g \cdot I^2 \quad (1)$$

Here,  $\delta$  and  $N_g$  are two-photon absorption cross-section and the number of the ground state molecules, respectively.  $I$  is the peak intensity of the excitation pulse with the dimension of the number of photon divided

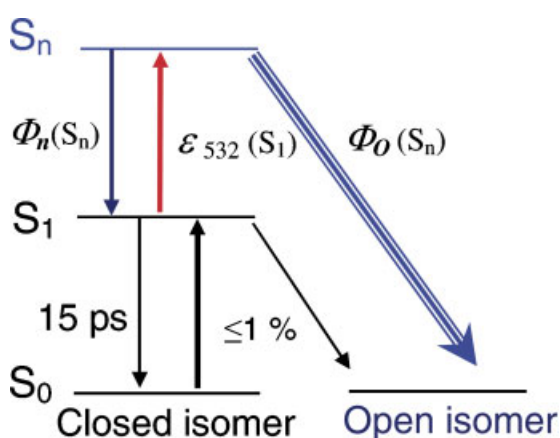


by the unit area size and the unit time. On the other hand, the latter stepwise two-photon absorption process takes place in such a manner that the transient species produced via the first one-photon absorption again absorbs the second photon resulting in the production of higher excited states. Since the second photon absorption by the transient species occurs in competition with the absorption by the ground state molecule, the number of photons in a laser pulse is an important factor for this stepwise two-photon absorption process.

The cross section<sup>27</sup> of the simultaneous two-photon absorption is typically in the order of  $10^{-50} \text{ cm}^4 \cdot \text{s} / \text{photon} \cdot \text{molecule}$ . The quantitative calculation with properties of the excitation laser pulse and the concentration of the ground state molecule estimates the number of molecules excited by the simultaneous two-photon absorption process at *ca.*  $10^{-9} \text{ M}$  in the present excitation condition.<sup>28</sup> On the other hand, the number of the open-form produced by the excitation of the picosecond laser pulse, as shown in Fig. 4, was  $10^{-5}$ – $10^{-4} \text{ M}$  and this number is  $10^4$ – $10^5$  larger than the estimated value. Hence, we can conclude that the simultaneous two-photon absorption did not largely contribute to the enhancement of the apparent reaction yield.

On the other hand, the decrease in the transient absorbance of  $S_1$  state in rather high excitation intensity in Fig. 4(a) directly supports the stepwise absorption process of the excited state. The reaction of  $S_1 + h\nu \rightarrow S_n \rightarrow \text{open-ring form}$  decreases the population of the  $S_1$  state in high excitation region, together with the decrease of the depopulation in the  $S_0$  state of **PT1(c)**. Summarizing above results and discussion, it can be concluded that the stepwise two-photon process via the actual intermediate  $S_1$  state, rather than the simultaneous two-photon process, was responsible for the enhancement of the cycloreversion process of **PT1(c)** under the picosecond laser excitation as shown in Scheme 3.

As stated in the Introduction, the drastic enhancement of the cycloreversion reaction via the stepwise two-



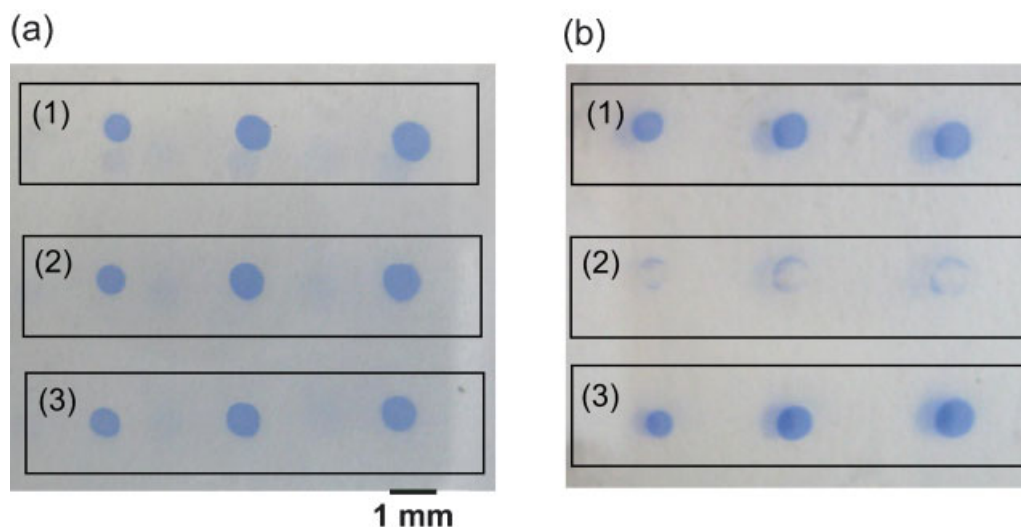
**Scheme 3.** This figure is available in colour online at [www.interscience.wiley.com/journal/poc](http://www.interscience.wiley.com/journal/poc)

photon absorption process with the picosecond laser pulsed excitation, as shown in Scheme 3, was observed in **PT1(c)** also in n-hexane solution.<sup>23</sup> From the numerical computer simulation, the cycloreversion reaction yield,  $\Phi$ , at the  $S_n$  state in n-hexane solution was estimated at  $0.5 \pm 0.1$ . In order to estimate the cycloreversion reaction yield also for the present polymer system, we have applied the same numerical simulation to the results in Fig. 4. Solid lines in Fig. 4 are the results thus calculated. The extinction coefficients of the  $S_0$  and  $S_1$  states of **PT1(c)**,  $11\,000$  and  $6000 \text{ M}^{-1} \text{ cm}^{-1}$ , were set to be the same as that used in the calculation of the solution phase<sup>23</sup> and the time constant of 15 ps for the lifetime of 15 ps was used for the calculation.

Prior to the discussion on the simulation, it should be noted that the relaxation from the  $S_n$  state in n-hexane solution included the internal conversion leading to the specific electronic state, in addition to two deactivation pathways of the  $S_n$  state (cycloreversion reaction and the internal conversion to the  $S_1$  state). The energy level of this specific electronic state, as indicated as  $S_1'$  hereafter, was estimated to be close to the  $S_1$  state and the higher excited state produced by the absorption of  $S_1'$  state did not undergo the effective cycloreversion reaction.<sup>23</sup> This  $S_1'$  state is optically forbidden state from the  $S_0$  state, while  $S_1$  state can be produced via optically allowed absorption from the  $S_0$  state. The dotted line in Fig. 4(b) is the result calculated without taking into account the contribution of this  $S_1'$  state, while the solid line shows the result with this contribution. The experimental result in Fig. 4(b) is well reproduced by both calculated curves with  $\Phi_n$  of 0.5 in rather low excitation intensity region, while large deviation was observed in the curve without this additional contribution. On the other hand, the solid line in Fig. 4(b) is the curve calculated with the contribution of the  $S_1'$  state. As clearly shown in this figure, the experimental results in the entire region of the excitation intensity are well reproduced by this calculated curve. The iterative simulation estimated the reaction yield in the higher excited state was estimated at  $0.5 \pm 0.1$ .

The same numerical calculation was applied also to the analysis of the experimental results at 20 ps after the excitation (Fig. 4(a)). Although the experimental results are scattered, the calculated curves with the same parameters reproduce the experimental results. Summarizing above results and discussion, it can be concluded that the dynamic behaviors and the cycloreversion reaction yield of **PT1(c)** are almost the same with those in n-hexane solution.

For more direct confirmation of the two-photon gated reaction by picosecond pulsed excitation, we have investigated the difference of the cycloreversion reaction depending on the mode of the excitation. Fig. 5 shows the photographs of PT1 in the PMMA solid film. By the steady-state UV light irradiation through a photo-mask with *ca.* 0.1 mm diameter, the cyclization reaction took



**Figure 5.** Photographs of **PT1** in PMMA solid polymer films before and after the visible light irradiation. Blue spots in (a) were positions initially irradiated by the UV light leading to the formation of **PT1(c)**. Area (1) in (b) was not irradiated by the visible light (reference area). Area (2) was irradiated with one picosecond laser pulse at 532 nm with an intensity of  $6.1 \text{ mJ/mm}^2$ . Area (3) was irradiated with a steady-state 532 nm light with an intensity of  $0.04 \text{ mW}$  for 3 min ( $9.2 \text{ mJ/mm}^2$ ). (See text). This figure is available in colour online at [www.interscience.wiley.com/journal/poc](http://www.interscience.wiley.com/journal/poc)

place at nine colored spots in Fig. 5(a). The top three spots in Fig. 5(b) were reference marks, which were not irradiated with steady-state light or picosecond laser pulse at 532 nm. The one-pulse excitation with picosecond laser pulse with the intensity of  $6.4 \text{ mJ/mm}^2$  completely diminished the color of the irradiated area of each spot as shown in the middle three spots in Fig. 5(b). On the other hand, the bottom three spots were irradiated with steady-state light at 532 nm with  $0.04 \text{ mW}$  for 3 min. The total photon energy for these spots was  $9.2 \text{ mJ/mm}^2$ . As clearly shown in this figure, the color of each spot was almost the same with the reference spots, indicating that the picosecond pulsed excitation actually demonstrated the effective cycloreversion reaction.

Finally, it is worth noting here that the excitation intensity of  $6 \text{ mJ/mm}^2$  corresponds to  $6 \text{ nJ}/\mu\text{m}^2$ . In the actual application of the two-photon gated reaction in the memory media, it is not necessary to apply such large energy as  $\text{mJ/mm}^2$ . We anticipate the present method can be utilized for the construction of the photochromic memory system that can achieve the non-destructive read-out capability and the photo-erasability at the same time.

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### APPENDIX

The output of  $1 \text{ mJ/mm}^2$  of the picosecond laser pulse at 532 nm with 15 ps fwhm corresponds to  $I$  of  $1.79 \times 10^{28}$  photons/( $\text{cm}^2 \text{ s}$ ). The value of  $N_g$  is  $6.02 \times 10^{16}$  molecules/ $\text{cm}^3$  for  $1 \times 10^{-4} \text{ M}$  concentration. By using the typical value of the two-photon absorption cross-section (ref. 27),  $10^{-50} \text{ cm}^4 \text{ s}/(\text{photon molecule})$ , the number of the excited state produced by the above  $I$  value is estimated to be  $2.87 \times 10^{12}$  molecules/ $\text{cm}^3$  or  $4.78 \times 10^{-9} \text{ M}$ .

### REFERENCES

- (a) Dürr H, Bouas-Laurent H. *Photochromism Molecules and Systems*. Elsevier: Amsterdam, 1990; 1–1068; (b) Brown CH. *Photochromism*. Wiley-Interscience: New York, 1971; 1–853.
- (a) *Molecular Switches*, Feringa B L (ed.). Wiley-VCH: Weinheim, 2001; 1–454; (b) Thematic issue on "Photochromism: Memories and Switches". *Chem. Rev.* 2000; **100**: 1063–1890; (c) *Photo-reactive Materials for Ultra-high Density Optical Memory*, Irie M (ed). Elsevier: Amsterdam, 1994; 1–248; (d) Kobatake S, Irie M. *Annu. Rep. Prog. Chem. C* 2003; **99**: 277.
- (a) Irie M. *Chem. Rev.* 2000; **100**: 1685; (b) Irie M, Uchida K. *Bull. Chem. Soc. Jpn.* 1998; **71**: 985; (c) Hanazawa M, Sumiya R, Horikawa Y, Irie M. *J. Chem. Soc. Chem. Commun.* 1992; 206; (d) Irie M, Mohri M. *J. Org. Chem.* 1988; **53**: 803; (e) Kobatake S, Irie M. *Bull. Chem. Soc. Jpn.* 2004; **77**: 195.
- (a) Fernandez-Acebes A, Lehn J-M. *Chem. Eur. J.* 1999; **5**: 3285; (b) Tsvigoulis GM, Lehn J-M. *Angew. Chem. Int. Ed. Engl.* 1995; **34**: 1119; (c) Gilat SL, Kawai SH, Lehn J-M. *J. Chem. Soc. Chem. Commun.* 1993; 1439.
- (a) Lucas LN, de Jong JJD, van Esch JH, Kellogg RM, Feringa BL. *Eur. J. Org. Chem.* 2003; **2003**: 155; (b) Feringa BL, Jager WF, Delange B. *Tetrahedron* 1993; **49**: 8267.
- (a) Peters A, Branda NR. *J. Am. Chem. Soc.* 2003; **125**: 3404; (b) Myles AJ, Branda NR. *Adv. Funct. Mater.* 2002; **12**: 167; (c)

- Murguly E, Norsten TB, Branda NR. *Angew. Chem. Int. Ed.* 2001; **40**: 1752.
7. (a) Luo Q, Chen B, Wang M, Tian H. *Adv. Funct. Mater.* 2003; **13**: 233; (b) Yokoyama Y, Shiraiishi H, Tani Y, Yokoyama Y, Yamaguchi Y. *J. Am. Chem. Soc.* 2003; **125**: 7194; (c) Uchida K, Saito M, Murakami A, Nakamura S, Irie M. *Chem. Phys. Chem.* 2003; **4**: 1124; (d) Bertarelli C, Gallazzi MC, Stellacci F, Zerbi G, Stagira S, Nisoli M, De Silvestri S. *Chem. Phys. Lett.* 2002; **359**: 278; (e) Cho H, Kim E. *Macromolecules* 2002; **35**: 8684.
8. (a) Irie M, Fukaminato T, Sasaki T, Tamai N, Kawai T. *Nature* 2002; **420**: 759; (b) Kawai T, Sasaki T, Irie M. *Chem. Commun.* 2001; 711; (c) Norsten TB, Branda NR. *J. Am. Chem. Soc.* 2001; **123**: 1784; (d) Takeshita M, Irie M. *Chem. Lett.* 1998; 1123; (e) Takeshita M, Soong C-F, Irie M. *Tetrahedron Lett.* 1998; **39**: 7717.
9. (a) Chauvin J, Kawai T, Irie M. *Jpn. J. Appl. Phys.* 2001; **40**: 2518; (b) Kawai T, Fukuda N, Gröschl D, Kobatake S, Irie M. *Jpn. J. Appl. Phys.* 1999; **38**: L1194.
10. (a) Gilat SL, Kawai SH, Lehn J-M. *Chem. Eur. J.* 1995; **1**: 275; (b) Kawai T, Kunitake T, Irie M. *Chem. Lett.* 1999; 905.
11. (a) Yamamoto S, Matsuda K, Irie M. *Angew. Chem. Int. Ed.* 2003; **42**: 1636; (b) Kodani T, Matsuda K, Yamada T, Kobatake S, Irie M. *J. Am. Chem. Soc.* 2000; **122**: 9631; (c) Yamaguchi T, Uchida K, Irie M. *J. Am. Chem. Soc.* 1997; **119**: 6066.
12. (a) Matsuda K, Matsuo M, Mizoguti S, Higashiguchi K, Irie M. *J. Phys. Chem. B* 2002; **106**: 11218; (b) Matsuda K, Irie M. *J. Am. Chem. Soc.* 2001; **123**: 9896; (c) Matsuda K, Irie M. *Chem. Eur. J.* 2001; **7**: 3466; (d) Matsuda K, Irie M. *J. Am. Chem. Soc.* 2000; **122**: 8309.
13. (a) Morimoto M, Kobatake S, Irie M. *Chem. Rec.* 2004; **4**: 23; (b) Kobatake S, Irie M. *Bull. Chem. Soc. Jpn.* 2004; **77**: 195; (c) Irie M, Kobatake S, Horichi M. *Science* 2001; **291**: 1769; (d) Irie M, Lifka T, Kobatake S, Kato N. *J. Am. Chem. Soc.* 2000; **122**: 4871; (e) Kobatake S, Yamada T, Uchida K, Kato N, Irie M. *J. Am. Chem. Soc.* 1999; **121**: 2380; (f) Kobatake S, Irie M. *Bull. Chem. Soc. Jpn.* 2004; **77**: 195.
14. Tamai NMiyasaka H. *Chem Rev* 2000; **100**: 1875.
15. (a) Miyasaka H, Araki S, Tabata A, Nobuto T, Mataga NN, Irie M. *Chem. Phys. Lett.* 1994; **230**: 249; (b) Miyasaka H, Nobuto T, Itaya A, Tamai N, Irie M. *Chem. Phys. Lett.* 1997; **269**: 281; (c) Miyasaka H, Nobuto T, Murakami M, Itaya A, Tamai N, Irie M. *J. Phys. Chem. A* 2002; **106**: 8096; (d) Kaieda T, Kobatake S, Miyasaka H, Murakami M, Iwai N, Nagata Y, Itaya A, Irie M. *J. Am. Chem. Soc.* 2002; **124**: 2015.
16. Tamai N, Saika T, Shimidzu T, Irie M. *J. Phys. Chem.* 1996; **100**: 4689.
17. (a) Ern J, Bens AT, Bock A, Martin H-D, Krysch C. *J. Luminesc.* 1998; **76&77**: 90; (b) Ern J, Bens AT, Martin H-D, Mukamel S, Schmid D, Tretiak S, Tsiper E, Krysch C. *Chem. Phys.* 1999; **246**: 115; (c) Ern J, Bens AT, Martin H-D, Mukamel S, Tretiak S, Tsyganenko K, Kuldova K, Trommsdorff HP, Krysch C. *J. Phys. Chem. A*. 2001; **105**: 1741; (d) Ern J, Bens AT, Martin H-D, Kuldova K, Trommsdorff HP, Krysch C. *J. Phys. Chem. A* 2002; **106**: 1654.
18. Hania PR, Telesca R, Lucas L.N, Pugzlys A, van Esch J, Feringa BL, Snijders JG, Duppen K. *J. Phys. Chem. A* 2002; **106**: 8498.
19. Okabe C, Nakabayashi T, Nishi N, Fukaminato T, kawai T, Irie M, Sekiya H. *J. Phys. Chem. A* 2003; **107**: 5384.
20. Shim S, Joo T, Bae SC, Kim KS, Kim E. *J. Phys. Chem. A* 2003; **107**: 8106.
21. Miyasaka H, Murakami M, Itaya A, Guillaumont D, Nakamura S, Irie M. *J. Am. Chem. Soc.* 2001; **123**: 753.
22. Miyasaka H, Murakami M, Okada T, Nagata Y, Itaya A, Kobatake S, Irie M. *Chem. Phys. Lett.* 2003; **371**: 40.
23. Murakami M, Miyasaka H, Okada T, Kobatake S, Irie M. *J. Am. Chem. Soc.* 2004; **126**: 14764.
24. Uchida K, Takata A, Ryo S, Saito M, Murakami M, Ishibashi Y, Miyasaka H, Irie M. *J. Mater. Chem.* 2005; **15**: 2128.
25. Ishibashi Y, Murakami M, Miyasaka H, Kobatake S, Irie M, Yokoyama Y. *J. Phys. Chem. C*. 2007; **111**: 2730.
26. (a) Miyasaka H, Moriyama T, Kotani S, Muneyasu R, Itaya A. *Chem. Phys. Lett.* 1994; **225**: 315; (b) Miyasaka H, Moriyama T, Itaya A. *J. Phys. Chem.* 1996; **100**: 12609.
27. (a) Sutherland RL. *Handbook of Nonlinear Optics* (2nd edn). Chap. 13, Marcel Dekker, Inc.: New York, 2003; 767–792; (b) Kershaw Stephan. “Two-photon Absorption” in *Characterization Techniques and Tabulations for Organic Nonlinear Optical Materials*, Mark G Kuzyk, Carl W Dirk (eds). Chap. 7. Marcel Dekker, Inc.: New York, 1998; 515–654.