

Efficient cycloreversion reaction of diarylethene derivatives via higher excited states attained by non-resonant simultaneous two-photon absorption

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1. Introduction

Diarylethene derivatives are one of photochromic materials that undergo the cyclization (ring-closing) and cycloreversion (ring-opening) reactions between the open- and closed-ring isomers in the excited state. Excellent properties of these derivatives such as thermal stability of both the isomers and high fatigue resistance have been attracting much attention [1]. These derivatives undergo the effective cycloreversion reaction in higher excited states attained by the stepwise two-photon absorption of the visible light [2], while the electronic state prepared by the one-photon excitation corresponding to the two-photon energy does not lead to such an efficient reaction. This result indicates that higher excited states prepared by the one-photon forbidden excitation play an important role in the efficient cycloreversion reaction. In the present study, to get more detailed information on the efficient cycloreversion reaction and its relation with a one-photon forbidden electric state, non-resonant simultaneous two-photon excitation was applied to the ring-opening reaction of diarylethene derivatives. From the femtosecond transient absorption spectroscopy, it was revealed that the larger cycloreversion reaction yield was obtained in the simultaneous two-photon absorption than that by the one-photon excitation at the wavelength corresponding to the two-photon energy. We will discuss the mechanism of the reaction enhancement from the viewpoints of the specific electronic state inaccessible from the optically allowed one-photon absorption.

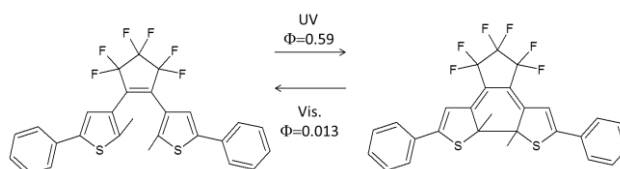


Fig. 1. Scheme of photochromic reaction of a diarylethene derivative, PT

2. Results and Discussion

Figure 1 shows the transient absorption spectra of the closed-ring isomer of PT in *n*-hexane excited with a femtosecond laser pulse at 730 nm and, 365 nm. The excitation at 730 nm is completely non-resonant with the absorption of PT, while the excitation at 365 nm

is resonant with the transition into the higher excited state via one-photon absorption. Under the 730-nm excitation, a transient absorption band at 585 nm appears immediately after the photoexcitation, concomitantly with stimulated Raman scattering of solvent. A similar absorption peak was also observed in the case of the 365-nm excitation. This band is assignable to the higher excited state, since it was not observed under the visible one-photon excitation at 600 nm, which is resonant with the S_1 - S_0 transition. In the sub-picosecond time region, this band rapidly decreases and another band gradually appears in 700-900 nm. It is worth noting that the resultant spectral shape is distinctly different between the 730- and the 365-nm excitation conditions. This result indicates that different intermediates are produced from the higher excited states in each case. These characteristic bands diminish in the timescale of 10-20 ps and are followed by the permanent bleaching due to the cycloreversion reaction remaining at and after 100 ps following the excitation. This bleaching signal is larger under the 730-nm excitation, compared with that by the 365-nm excitation, indicating that the efficient cycloreversion reaction takes place by the two-photon excitation at 730 nm. The quantum yield of this cycloreversion reaction was estimated to be ca. 20-30% for the 730-nm excitation. By integrating these results with the excitation wavelength dependence of the one-photon cycloreversion reaction yield, we can conclude that PT undergoes the efficient cycloreversion reaction in higher excited state which is accessible from non-resonant simultaneous two-photon excitation. At the conference site, we will discuss the detailed reaction scheme of the efficient cycloreversion reaction by introducing results on other systems.

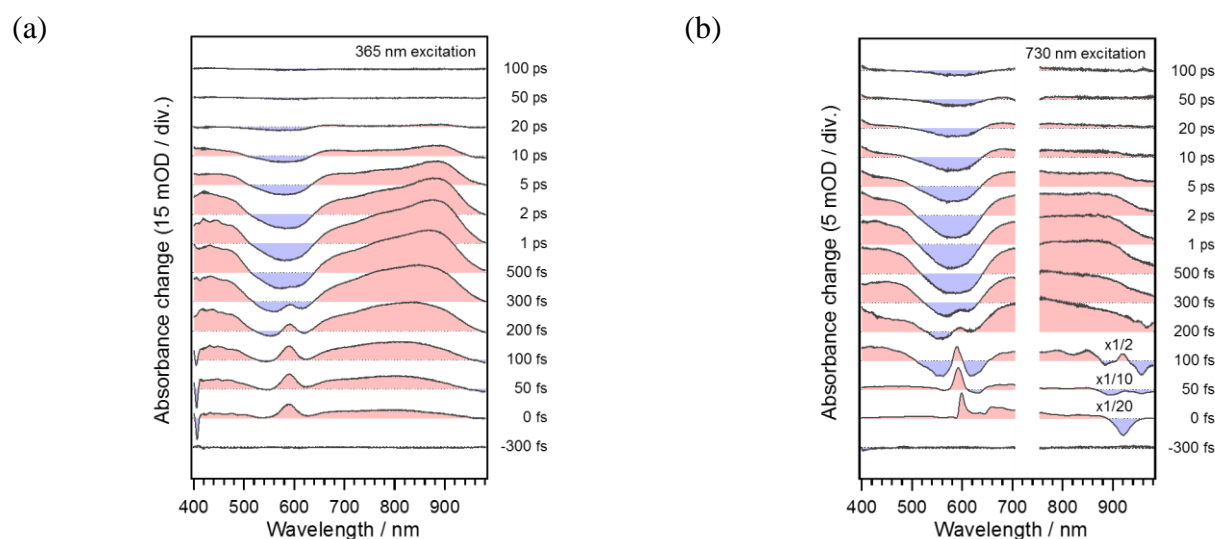


Fig. 2. Transient absorption spectra of PT in *n*-hexane excited with a femtosecond laser pulse at three distinct wavelengths, (a) 365 nm, (b) 730 nm. The excitation intensities were set to 0.17 mW and 0.74 mW at 365 nm and 730 nm, respectively. In the case of the 730-nm excitation, the spectra around the time origin were contaminated by stimulated Raman scattering due to solvent and the other coherent artifact.

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References:

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