

Photocyclization Reaction Dynamics of an Inverse Diarylethene Derivative as Revealed by Time-resolved Absorption and Fluorescence Spectroscopies

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Diarylethene derivatives undergo a reversible photochromic reaction between the closed- and open-ring isomers. A series of these compounds have been attracting much attention due to their excellent thermal stability, high fatigue resistance and fast response, leading to realization of the advanced photofunctions in the field of material science.^[1] Their fundamental molecular framework is *cis*-stilbene and its two phenyl substituents are replaced by heterorings such as thiophene and furan rings. With respect to the orientation of two heterorings, diarylethene derivatives can be categorized into two groups, *normal* type and *inverse* type, as shown in Figure 1a. Theoretical studies on the inverse derivative have suggested no substantial activation barrier on the S₁ potential energy surface in the cyclization and cycloreversion reaction pathways, while the normal derivatives have a barrier along the cycloreversion reaction coordinate, which more or less decreases the reaction yields.^[2] Actually, it was experimentally demonstrated that the reaction yield of the inverse derivatives is higher than that of the normal derivatives.^[3] In this sense, the inverse derivatives have a great advantage for designing photofunctional molecules with higher reactivity, compared with normal derivatives. In addition, from the fundamental viewpoint, it is crucially important to investigate ultrafast dynamics evolving on the barrierless potential surface toward the conical intersection, which is not described with the conventional state-to-state photochemistry. In the present study, we have investigated the photocyclization reaction of a typical inverse derivative, iDAE (Figure 1a, right) by means of ultrafast spectroscopy to elucidate the detailed reaction mechanism.

Figure 1b shows steady-state absorption and fluorescence spectra of iDAE in *n*-hexane solution. The open-ring isomer has an absorption peak at 370 nm while the closed-ring isomer exhibits absorption band peaked at 440 nm. It was reported that iDAE in the open-ring isomer has two conformers: reactive anti-parallel (AP) form and unreactive parallel (P) form as well as other normal derivatives.^[4]

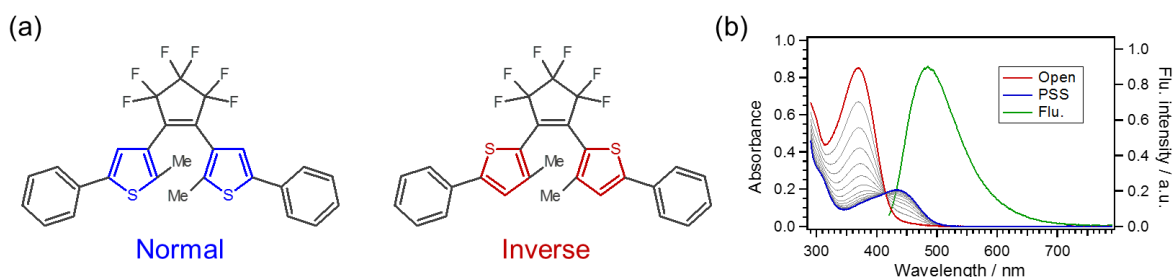


Figure 1. (a) Normal and inverse diarylethene derivatives. (b) Absorption and fluorescence spectra of iDAE in *n*-hexane solution.

Figure 2 presents transient absorption spectra of iDAE in *n*-hexane solution excited at 400 nm. Upon the photoexcitation, a broad transient band appears with absorption maxima at 570 nm and 710 nm. The 570-nm band rapidly decreases in the sub-picosecond time region while the 710-nm band keeps its intensity unchanged in this time region, indicating that different species show absorption bands at 570 nm and 710 nm independently. Together with this fast decay, positive and negative bands appear at 430 nm and 500 nm, respectively. The negative absorption around 500 nm could be due to the stimulated emission (SE) of the S_1 state. On the other hands, the 430-nm band is ascribable to absorption of the closed-ring isomer (photoproduct) generated through the cyclization reaction. These results can be interpreted as follows. Upon the photoexcitation, the AP form of the open-ring isomer is first pumped up to the Franck-Condon (FC) state in the S_1 state, which shows the 570-nm band. This FC state has two parallel relaxation channels: (1) cyclization reaction into the closed-ring isomer through the conical intersection and (2) relaxation into the fluorescent state showing the SE around 500 nm. On the other hand, the 710-nm band appearing immediately after the excitation is probably due to the unreactive P form. In the time region of 2 ps-1 ns, the 500-nm SE and 710-nm absorption band decreased and another band gradually grew up with the absorption maximum at 530 nm. This 530-nm band completely vanished at 100 ns under the O_2 purged condition although it persisted up to 1 μ s under the N_2 purge condition. This result clearly shows that the fluorescent state of the AP form and/or directly excited P form is relaxed into the triplet state. At the conference site, we will also discuss solvent viscosity effect on the cyclization reaction yield and its time scale.

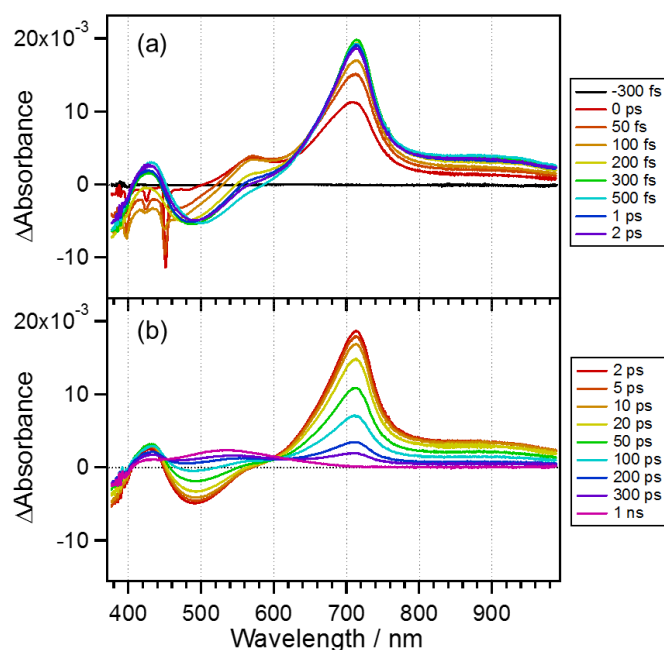


Figure 2. Transient absorption spectra of iDAE in *n*-hexane solution excited with a femtosecond laser pulse at 400 nm. (a) femtosecond-picosecond, (b) picosecond-nanosecond time region.

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