

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

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Diarylethene derivatives have been attracting much attention due to their excellent thermal stability, high fatigue resistance and fast response, which leads to realization of advanced photofunctions in the field of materials science. Their fundamental molecular framework is *cis*-stilbene and its two phenyl groups are replaced with heterorings such as thiophene and furan moieties. With respect to the orientation of the two heterorings, diarylethene derivatives can be categorized into two groups, normal type and inverse type. Previous studies have suggested that the cyclization and cycloreversion reaction yields of the inverse derivatives are higher than those of the corresponding normal derivatives, due to the absence of substantial energy barrier in the excited states.^{1,2} In this sense, the inverse derivatives have a great advantage for designing highly photoresponsive materials. Not only from the applications but also from the fundamental viewpoint, it is crucially important to elucidate the correlation between the chemical reactivity and topology of the potential energy surface in the excited states. In the present study, we have investigated the photocyclization reaction dynamics of a typical inverse derivative, **iDAE** in Figure 1a using time-resolved absorption and fluorescence spectroscopies. **iDAE** shows intriguing multi-color fluorescence in crystals and nanoparticles, and the elucidation of the reaction mechanism at the molecular level is the first step to create photoresponses and photofunctions in molecular aggregates, in which cooperative interactions between photons and molecules (“photosynergetic” effects) are a key process. Figure 1b,c present transient absorption spectra of **iDAE(o)** in *n*-hexane solution excited at 400 nm. Upon the photoexcitation, transient bands appear with absorption maxima at 570 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 and 710 nm independently. Concomitantly with this fast decay, positive and negative bands appear at 430 and 500 nm, respectively. The negative absorption around 500 nm could be due to the stimulated emission of the S₁ state. In the late time stage, these spectral features decay and broad absorption remains around 430 and 540 nm. The 540 nm band is ascribable to absorption of the triplet state from nanosecond laser photolysis, while the 430 nm band is attributed to the closed-ring isomer.

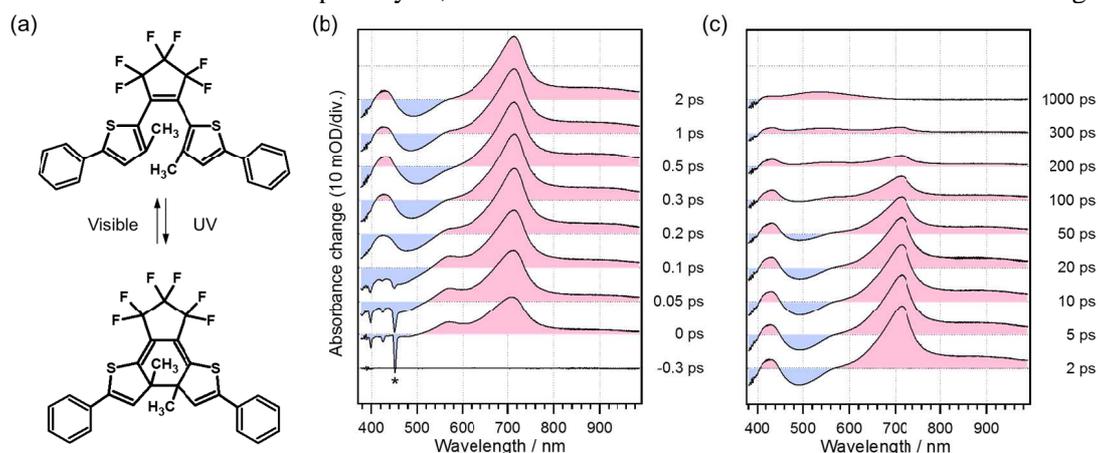


Figure 1. (a) Chemical structures of a typical inverse diarylethene derivative, **iDAE**. (b,c) Transient absorption spectra of **iDAE(o)** in *n*-hexane solution excited with a femtosecond laser pulse at 400 nm in the early and late time stages.

[1] S. Nakamura et al., *J. Phys. Org. Chem.* **2007**, *20*, 821.

[2] K. Uchida et al., *Tetrahedron* **2001**, *57*, 4559.