

Excited State Dynamics in the Open-Ring Isomer of a Diarylethene Derivative: Approach to Efficient Photochromic Reaction

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Electrocyclic reactions take important roles in various photo-functions. It is important to elucidate their reaction dynamics and mechanism for the development of advanced systems. According to studies on the dynamics of 6π electron systems, the cyclization and cycloreversion reactions take place on the 2A potential energy surface (PES) and the same conical intersection (CI) mediates the 2A and 1A (ground state) PESs in both the reactions. We have recently reported that the excited state of the closed-ring isomer is directly produced in the cyclization reaction of a dithiazolylarylene derivative with a reaction yield of almost unity [1]. It is strongly suggested that this reaction behavior originates from the suppression of the molecular motion around 6π electron moiety due to intramolecular hydrogen bond and S-N interaction. In the present study, we have investigated the cyclization reaction dynamics of a typical diarylethene derivative (Figure 1a, **BT**) to explore the new efficient photochromic materials. Figure 1b and 1c show transient absorption spectra of **BT(c)** and **BT(o)** in *n*-hexane solution excited at 550 and 330 nm, respectively. An absorption band appeared around 710 nm, as shown in the spectra of **BT(c)**. This marked peak was also observed in the spectra of **BT(o)**. This result indicates that the cyclization and cycloreversion processes, at least in part, via the common intermediate as well as a dithiazolylarylene derivative. To more clearly confirm this reaction scheme, we measured transient absorption spectra of **BT(o)** nanoparticles, in which the molecular motion is suppressed due to the rigid environment in the nanoparticles. The absorption band around 710 nm showed up more prominently upon the photoexcitation of **BT(o)** nanoparticles. Furthermore, the fluorescence of **BT(o)** nanoparticles were detected in the similar wavelength region to that of **BT(c)**. These results indicate the geometrical restriction of **BT(o)** can be a key approach toward the efficient reactions.

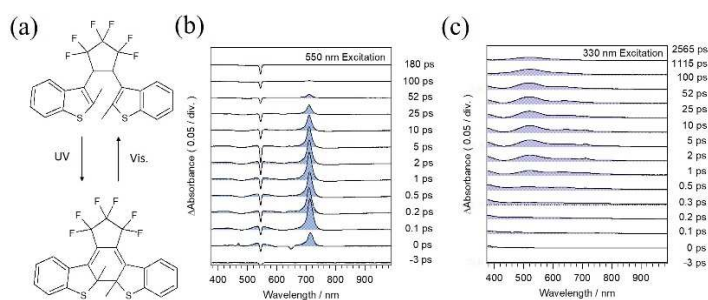


Figure 1. (a) Photochromic reaction of **BT**. (b,c) Transient absorption spectra of **BT(c)** and **BT(o)** in *n*-hexane solution excited at 550 and 330 nm, respectively.

[1] T. Nagasaka, H. Sotome, S. Morikawa, L. M. Uriarte, M. Sliwa, T. Kawai, H. Miyasaka, *RSC Adv.*, 2020, **10**, 20038-20045.