

Probing structural evolution and product formation in the cycloreversion reaction of a diarylethene derivative using time- and frequency-domain vibrational spectroscopies

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Photochromic reactions of diarylethene (DAE) derivatives serve as a suitable model for studying the mechanism of ultrafast formation and cleavage of chemical bonds. To date, we have investigated the cycloreversion (ring-opening) dynamics of DAE derivatives using transient absorption spectroscopy in the visible region, and revealed that the cycloreversion reaction is complete within a few tens of picoseconds after photoexcitation. In the previous work, however, the reaction dynamics was discussed on the basis of population change of photoexcited closed-ring isomer (reactant). This is because the open-ring isomer (photoproduct) does not have any absorption band in the observation window of the visible region. In the present study, we have employed time-resolved absorption spectroscopy in the mid-infrared region where the open-ring isomer has a number of vibrational peaks with less overlap with those of the closed-ring isomer. Figure 1 shows transient absorption spectra of **BT(c)** in *n*-hexane solution. The spectrum at the time zero is characterized by positive and negative bands, which are respectively ascribable to the excited state absorption and ground state bleaching. These spectral features decrease in a few tens of ps, and on a similar timescale a new positive band grows up at 1274 cm⁻¹, at which the open-ring isomer has the stretching mode of C-C of the fluorinated five-membered ring. This result clearly shows that the open-ring isomer in the ground state is directly produced from the energy minimum in the excited state of the closed-ring isomer.

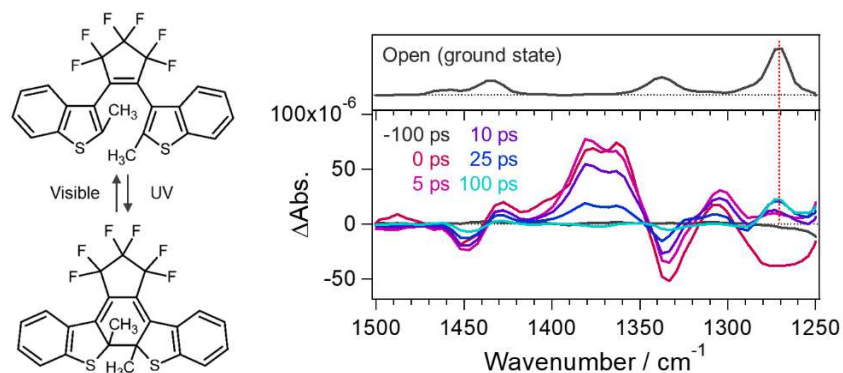


Figure 1. Chemical structures and mid-infrared transient absorption spectra of **BT(c)** in *n*-hexane.