

# 1P031 ロタキサンの超高速初期過程の研究：シクロデキストリンに包摂されたアゾベンゼン誘導体の光異性化ダイナミクス

(理研・田原分子分光<sup>1</sup>、理研・光量子工学<sup>2</sup>)

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## Ultrafast initial motions of a rotaxane consisting of cyclodextrin threaded by an isomerizable guest

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**[Introduction]** Synthetic supramolecules make ideal model systems for studying dynamic intermolecular interactions. Their value lies in the possibility of synthesizing custom materials for studying individual intermolecular interactions. In this work, we prepared a previously reported Rotaxane, consisting of a long-chain-substituted azobenzene guest threading a cyclodextrin host.<sup>1</sup> Based on NOESY results,<sup>1</sup> the cyclodextrin initially resides over the azobenzene moiety, but following photoisomerization, the cyclodextrin ring translates to a

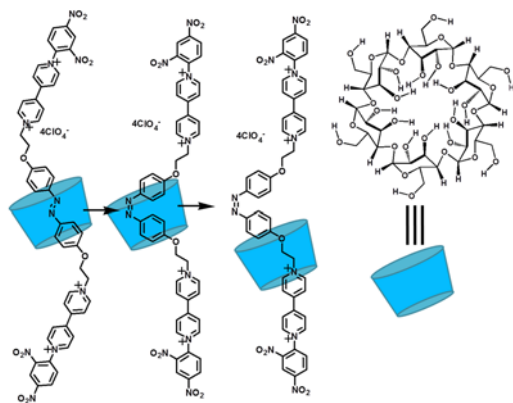


Fig. 1. Schematic of Rotaxane isomerization.

different position, as shown in Fig. 1. The isomerization of azobenzene is well-characterized,<sup>2</sup> and the rate can be obtained from the lifetime of its  $S_1$  state. Since isomerization causes the translation of the cyclodextrin, we measured the excited state dynamics of the azobenzene moiety to describe the initial step in the process.

**[Results]** Time-resolved fluorescence upconversion spectroscopy was used to describe the decay from the  $S_1$  state. First, the azobenzene moiety was excited into the  $S_2$  state. The

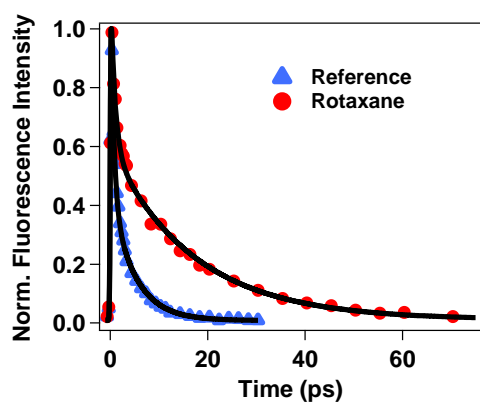
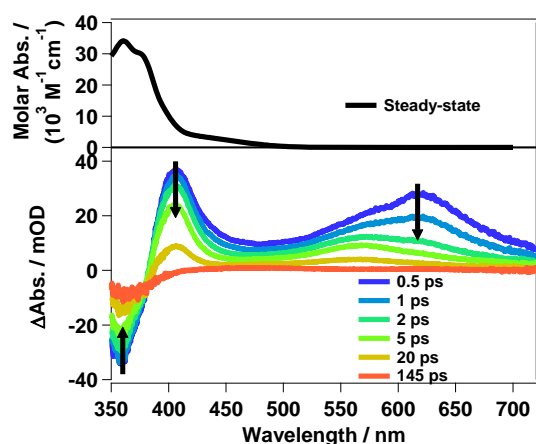


Fig. 2. Time-resolved fluorescence of Rotaxane and Reference in 1:1 water/acetonitrile at 610 nm, following excitation at 375 nm.

characteristic  $S_2$  emission at short wavelengths was found to decay within 400 fs, giving rise to the  $S_1$  state. The relaxation from  $S_1$  was then characterized using its time-resolved fluorescence, which exhibited a biexponential decay, with time constants of  $1.2 \pm 0.2$  and  $17 \pm 2$  ps for the two transients, TrA and TrB, respectively (Fig. 2). The  $S_1$  fluorescence of a Reference molecule prepared without a cyclodextrin ring decayed with time constants of  $0.6 \pm 0.1$  and  $4.8 \pm 0.5$  ps. The slower  $S_1$

decay of Rotaxane indicates that enclosure by cyclodextrin creates a steric barrier to isomerization.

Transient absorption spectroscopy was used to identify the processes corresponding to TrA and TrB. Selected transient absorption spectra obtained after relaxation from  $S_2$  are shown in Fig. 3. These exhibit two positive features at long wavelengths with decay times corresponding to TrA and TrB: 1 and 18 ps, respectively. Near 400 nm is an additional feature that decays with a 3 ps time constant. Based on its position at the red edge of the absorption band and its absence from the time-resolved fluorescence, this feature is attributed to vibrational relaxation in the ground state. In the region of the ground state bleach recovery ( $< 400$  nm), the



**Fig. 3.** Transient absorption spectra of Rotaxane in 1:1 water/acetonitrile. Excitation at 350 nm.

3 ps (vibrational cooling) and 18 ps (TrB) decay constants are sufficient to describe the repopulation of the ground state. Because the decay constant of TrA is not observed in the ground state recovery, TrA represents relaxation within the excited state. The small increase in the time constant of TrA on going from Reference to Rotaxane shows that cyclodextrin weakly affects this process. Therefore, it likely corresponds to a structural change preceding isomerization.

Conversely, the time constant of TrB is observed in the ground state repopulation, indicating that the corresponding process is not a relaxation within the excited state. It is also more sensitive than TrA to the presence of cyclodextrin, as would be expected for isomerization within a highly constrained environment. Therefore, the time constant of TrB corresponds to the actual isomerization. Successful isomerization likely requires coupling of an isomerization attempt with the motion of the cyclodextrin. Thus, this time constant represents the isomerization and the initial translation of the cyclodextrin.

## [References]

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