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Time-resolved spectroscopy of a multi-component supramolecular system

(Molecular Spectroscopy Lab., RIKEN) Matthew M. Sartin, Masahisa Osawa, Tahei Tahara

Introduction

We present the time-resolved spectroscopy of a supramolecular system, in order to better understand the influence of the motion of one component on another. The study of such systems can bridge our understanding of the dynamics of small molecules to those of larger, more complex systems, such as proteins or artificial molecular machines. While it is possible to observe the initial and final states of switchable supramolecular systems, a detailed study of the molecular motions of such systems is much more difficult, since the lack of chromophores

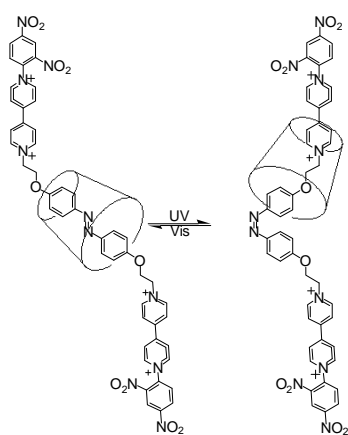


Figure 1. Rotaxane isomerization. The cone represents cyclodextrin.

often makes their dynamics inaccessible to ultrafast methods. In order to examine these dynamics, a model system that undergoes a photo-induced process followed by a measurable secondary process is needed.

For this purpose, we have chosen a system from the literature,¹ in which α -cyclodextrin is sterically trapped on a substituted azobenzene (Figure 1). In the *trans* state, the cyclodextrin remains on the azobenzene moiety, but upon photoisomerization, it is pushed out onto the substituents. We can indirectly study the motion of the cyclodextrin by its effect on the dynamics of the azobenzene moiety.

Experimental

The rotaxane was synthesized using a modified literature procedure.¹ The starting material for our method, 4,4'-dihydroxyazobenzene (DHAB), was prepared as described elsewhere,² and dibromoethoxyazobenzene was synthesized directly by reacting DHAB with CH_2Br_2 in acetone with added K_2CO_3 . For femtosecond transient absorption, the sample was excited at 350 nm and probed using a white light continuum.

Results

Exciting the $\pi^* \leftarrow \pi$ transition at ~ 350 nm causes *trans-cis* isomerization of the azobenzene moiety. This change can be monitored by a decrease in the 350 nm absorption band and a relatively small increase in the absorption at longer wavelength. The movement of

the cyclodextrin is separately observable by comparing the NMR or circular dichroism spectra before and after irradiation.

Femtosecond transient absorption experiments were used to compare the dynamics of the excited state processes of the rotaxane to those of unsubstituted azobenzene. The transient

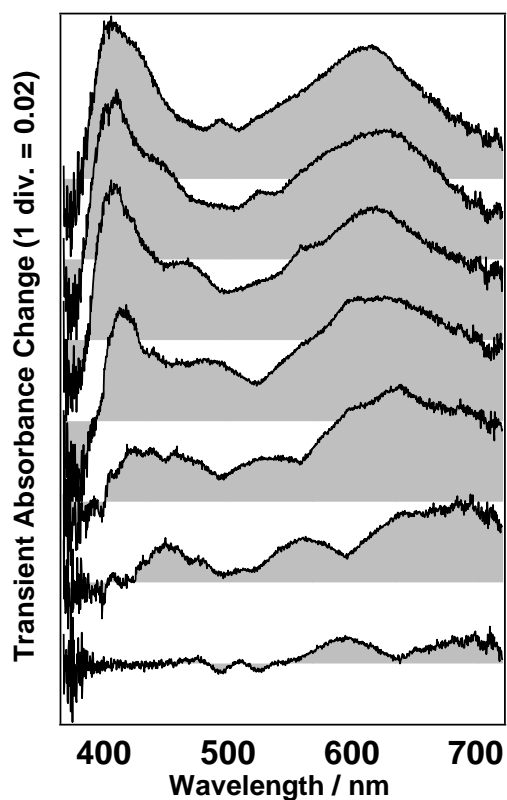


Figure 2. Transient absorption spectra of rotaxane in water from -0.2 to 0.2 ps.

absorption spectrum of unsubstituted azobenzene is broad and exhibits three observable decay processes. A small, short-lived peak around 650 nm is attributed to the $S_n \leftarrow S_2$ absorption, which decays within 0.5 ps. Another peak, at 405 nm, exhibits a two-exponential decay, with one component assigned to the $S_n \leftarrow S_1$ transition (1 ps in hexane), and the other assigned to vibrational cooling in the ground state (16 ps in hexane).³ The transient absorption spectra of the rotaxane exhibit both features (Figure 2), but the long-wavelength feature at 650 nm is more prominent than in azobenzene, and it hypsochromically shifts to 625 nm during its 1 ps decay. At 405 nm, the major component of the rotaxane decays with a time constant of 6 ps, which is considerably slower than that observed for unsubstituted azobenzene.

Conclusions

We have shown the electronic aspects of the time-resolved behavior of a rotaxane consisting of a cyclodextrin hosting a substituted azobenzene. The potential to correlate the differences in the spectroscopic behavior of these molecules to their structural dynamics could lead to better understanding of how such supramolecular systems operate at the molecular level.

¹ Murakami, H.; Kawabuchi, A.; Matsumoto, R.; Ido, T.; Nakashima, N. *J. Am. Chem. Soc.* **2005**, *127*, 15891.

² Shunhua L.; Yuefeng Z.; Chunwei Y.; Feiran C.; Jingou X. *New J. Chem.* **2009**, *33*, 1462.

³ Fujino, T.; Arzhantsev, S. Y.; Tahara, T. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1031.