Photo-induced Chiral Switching of a Stilbene-Binaphthyl Supramolecular System

Takenori Tose^{1,3} and Takashi Yamashita^{*1,2}

¹ Department of Pure and Applied Chemistry, Tokyo University of Science,
2641 Yamazaki, Noda, Chiba 270-8560, JAPAN

² School of Computer Science, Tokyo University of Technology,
1404-1 Katakura, Hachioji, Tokyo 192-0982, JAPAN

³RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198 JAPAN

e-mail: ¹ 7214660@ed.tus.ac.jp, ² yamashitaks@stf.teu.ac.jp

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1. Introduction

Photochemical reactions are one of the tools to control molecular structure and properties, as well as those of various supramolecules such as, rotaxanes and catenanes which can be manipulated by photochemical stimuli. These molecules are expected to be applied to molecular switches, optical memory, photo-mechanical materials, logic gates and so on [1].

We have reported novel light-driven chiral compounds containing azobenzene moiety as a photo responsive group and binaphthyl moiety as a chiral source in a single molecule, to have found that the chirality of the molecule can be reversibly switched by photoirradiation, because *trans-cis* photo-isomerization of azobenzene moiety changes the face angle of the binaphthyl group [2]. *Cis-trans* thermal backward isomerization of azobenzene moiety took place even at room temperature in the molecular system, however, resulting in the loss of the stored chiral information. In this paper we synthesized novel photo responsive chiral cyclic molecule containing stilbene instead of azobenzene moiety to increase the thermal stability, and then we evaluated the photo response and the chiral optical properties of the material [3].

2. Experimental

2.1 Material

4SES was synthesized by Williamson

reaction of (S)-(-)-1,1'-bi-2-naphthol and 1,2-dibromoethane-capped dihydroxy stilbene which was prepared by McMurry coupling of 4-hydroxybenzaldehyde (Fig. 1).

Fig.1 chemical structure of 4SES used in this study.

2.2 Measurement

Photo irradiation of 4SES in acetonitrile was performed by 254 nm light with a low pressure mercury lamp and by 365nm light with an ultrahigh pressure mercury lamp. Thermal isomerization of 4SES was measured in acetonitrile or toluene, which was heated up to 338 K and 373 K.

3. Results and Discussion

Photo-irradiation of 4SES in acetonitrile at 254 nm (250 $\mu\text{W}/\text{cm}^2$, 60 sec) induced *cis-trans* isomerization of the stilbene moiety with increase in absorption at 330 nm and decrease at 280 nm. On the other hand, Photo-irradiation at 365 nm (180 $\mu\text{W}/\text{cm}^2$, 60 sec) reproduced *cis*-isomer by reversible *trans-cis* isomerization with showing isosbestic point at 297 nm (Fig. 2).

Fig.2 UV-Vis spectra of 4SES in acetonitrile solution (black), after photoirradiation at 254 nm (red), and after photoirradiation at 365 nm (blue).

Fig 3 shows change in CD spectrum of 4SES in acetonitrile under photoirradiation. Circular dichroism ($\Delta\epsilon$) of 4SES decreased at 230nm and 250nm by the photoirradiation at 254nm, while the CD signal reversibly changed by photoirradiation at 365 nm, showing that the circular dichroism of binaphthyl moiety was induced by the isomerization of stilbene moiety in 4SES (Fig.3).

Fig. 3 CD spectra of 4SES in acetonitrile (black), after irradiation (red) at 254 nm, and after irradiation (blue) at 365 nm.

Fig. 4 Circular dichroism change during repetition cycle of 4SES at 280 nm (purple line) and 330 nm (green line) after photoirradiation at 254 nm (red region), and photoirradiation at 365 nm (blue region).

The CD signal change is reversibly reproduced by the photoirradiation at 254 nm and 365 nm, corresponding to the photoisomerization of stilbene moiety, shown in Fig. 4.

In order to estimate the thermal stability of *cis*-form of 4SES, an acetonitrile solution of 4SES was prepared, and then the spectral change was compared between *trans*-SES, *cis*-4SES, and *cis*-3RAA, heating up to 338 K. Absorption of *cis*-3RAA rapidly decreased with rate constant of $3.3 \times 10^6 \text{ s}^{-1}$ by *cis-trans* thermal back isomerization of stilbene moiety, while no change in absorption was observed for *trans*-4SES nor *cis*-4SES after heating for 2 hours (Fig 5). The difference is based on the thermal stability of *cis* form of stilbenes compared to that of azobenzene derivatives. In order to confirm the stability of the *cis*-4SES, absorption change of *cis*-4SES was measured at elevated temperature. Fig 6 shows the change in absorption of *cis*-4SES in toluene solution heated up to 100 °C for 2 hours, but no thermal backward reaction was observed at all.

4. Conclusion

Novel photoresponsive chiral supramolecule 4SES was prepared and its chiral switching and thermal stability were measured. 4SES shows reversible CD change up on photoirradiation, due to face angle change of binaphthyl group induced by *trans-cis* photoisomerization. The *cis* isomer of

Fig.5 Plots of $\ln(\text{Abs.}/\text{Abs}_0)$ of trans-4SES, cis-4SES, and cis-3RAA in CH_3CN at 338 K [2].

Fig.6 Absorption change of 4SES in toluene after photoirradiation to convert cis form, followed by heating at 373 K.

4SES has high thermal stability whose absorption does not change even by heating at 100 °C for 2 hours, which is quite contrast to the case of 3RAA. 4SES is expected as the potential materials for chiral optical data storage, asymmetric synthesis, and so on.

Reference

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