

A Light-Driven Molecular Shuttle Based on a Rotaxane

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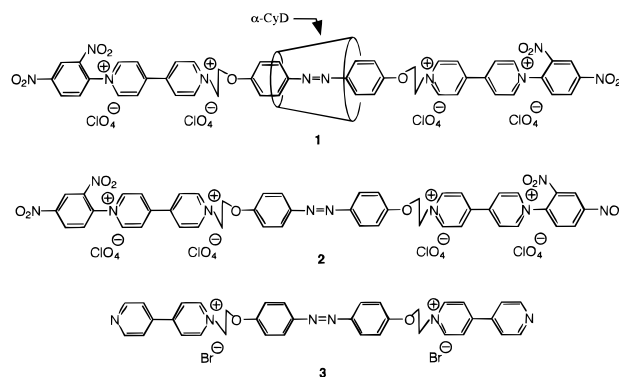
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We report here for the first time the design, synthesis, and characterization of a rotaxane **1** (Chart 1), which functions as a light-driven molecular shuttle. The chemistry of topological supramolecules such as catenanes, rotaxanes, and knots is of considerable interest in recent years.¹ The construction of stimuli-responsive molecular devices and molecular machines is a great challenge. The construction of molecular shuttles in which a ring moves back and forth like a shuttle between two or more “stations” in response to external stimuli is one such target.^{1,2} Rotaxanes³ are compounds in which a ring is threaded by a linear chain bearing bulky end units. Recently, Stoddart and co-workers described temperature-controlled (–140 to 50 °C) molecular shuttles using rotaxanes.² However, there is no report, so far, on a light-driven molecular shuttle based on rotaxanes.⁴

Cyclodextrins (CyDs)⁵ are known to form inclusion complexes with a variety of aromatic compounds in water. We have described a high-yield synthesis of a rotaxane using the host–guest interaction between a stilbene derivative and β -CyD.⁶ Here we designed and synthesized a photoswitchable rotaxane **1** where a ring, a threading chain molecule, and bulky terminal caps are α -CyD, azobenzene, and 2,4-dinitrobenzene moieties, respectively. UV–visible, circular dichroism (CD), and Nuclear Overhauser Effect (NOE) differential spectroscopies revealed that compound **1** has functioned as a light-driven molecular shuttle.

The syntheses of compounds **1**,⁷ **2** (a reference compound of **1**), and **3** (see ref 12) are described in ref 8. If the threading chain exists in the cavity of α -CyD was confirmed by ¹H NMR spectroscopy (JEOL JNM-GX400 NMR). The ¹H NMR spectra of **1** in D₂O over a temperature range of 5–80 °C and in DMSO-*d*₆ at room temperature showed a set of signals with equal intensity⁹ (typical data are shown in Figure 1a), which is in sharp contrast with that of **2**¹⁰ (Figure 1b), where chemically equivalent protons of the threading chain are located in the same

Chart 1



electromagnetic environment. This result supports the formation of rotaxane structure in **1**. That is, the respective protons in **2** are chemically equivalent for the C₂ symmetry axis on the azo group vs those of **1**, which loses the symmetry in the presence of α -CyD. The peaks at 7.86 and 7.16 ppm assigned to the aromatic protons of the azobenzene are separated more widely than other peaks because of the anisotropy produced by α -CyD, suggesting that α -CyD stays at the azobenzene moiety.

Both compounds **1** and **2** show photoisomerization. A typical result is shown in Figure 2a. UV light (360 nm)¹¹ irradiation onto the aqueous solution of **1** caused the photoisomerization from the *trans* to the *cis* configuration of the azobenzene unit in **1**, which reverts to the *trans* configuration on irradiation at 430 nm¹¹ with isosbestic points at 239, 322, and 418 nm. Both reactions reached the photostationary states within 15 and 11 min for **1** and **2**, respectively. The percentages of the *cis* isomers of **1** and **2** were respectively 67 and 80% at 5 °C, 46 and 58% at 30 °C. The rate order constants for the thermal isomerization of **1** in the dark at 5 and 30 °C were 1.5×10^{-5} (half-life time, 13 h) and $2.3 \times 10^{-4} \text{ s}^{-1}$ (half-life time, 50 min). The CD spectra of **1** after UV and visible light irradiation were recorded at 5 °C, where the thermal isomerization during the measurement is negligible.

Figure 2b shows the CD spectra of an aqueous solution of **1**. Before photoirradiation, a positive induced CD (ICD) band at 360 nm and a negative ICD band at 430 nm, which are assigned to π – π^* and n – π^* transitions, respectively, are observed. It is known theoretically and experimentally that the sign of the ICD of the long-axis polarized transitions of arene guests parallel to

(8) 4,4'-Bis(2-bromoethoxy)azobenzene (2.0 g, 4.7 mmol) and 4,4'-bipyridine (4.0 g, 21.7 mmol) were reacted in DMF (40 mL) at 85 °C for 24 h. A precipitate produced was filtered and washed with DMF and then diethyl ether to yield 2.0 g of 4,4'-bis[4-(4'-pyridyl)pyridinium-2-ethoxy]-azobenzene dibromide **3**, (57.3%) as an orange solid (mp 261–263 °C). Compound **3** (1.0 g, 1.3 mmol) and 2,4-dinitrofluorobenzene (2.4 g, 13.0 mmol) were reacted in water containing α -CyD (6.3 g, 6.5 mmol) at 25 °C for 48 h. After the extraction of unreacted 2,4-dinitrofluorobenzene with chloroform, an aqueous solution (30 mL) of ammonium hexafluorophosphate (31.0 mmol) was added to the aqueous layer. After the evaporation of the solvent, the residue was extracted with acetonitrile. The addition of the excess amount of tetraethylammonium chloride to the solution caused a precipitate, which was collected and then dissolved in water containing sodium perchlorate (5.0 g). After the solvent was evaporated, the residue was washed with acetone to yield 0.9 g of pure **1** (30.3%) as an orange solid (dec 194–196 °C). Anal. Calcd for C₈₄H₉₈O₅₆N₁₀Cl₄ + 1.5H₂O: C, 43.62; H, 4.40; N, 6.06. Found: C, 43.57; H, 4.69; N, 6.11. The synthesis of the reference compound **2** was carried out in the absence of α -CyD; the procedure was almost the same as in **1**. Compound **2** was obtained as a yellowish solid (dec 228–230 °C). The yield was 28%. Anal. Calcd for C₃₈H₄₈O₂₆N₁₀Cl₄ + 0.5H₂O: C, 43.61; H, 2.97; N, 10.60. Found: C, 43.79; H, 2.94; N, 10.40.

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(10) The measurement was conducted in DMSO-*d*₆ because the solubility of **2** in D₂O was not enough.

(11) A spectrofluorometer (JASCO FP-770; light source, 150 W xenon lamp) was used; the slit width used in the experiment was 20 nm.

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(7) In this study, the tetracationic compound was designed for the ease in the synthesis and for the enhanced solubility in water.

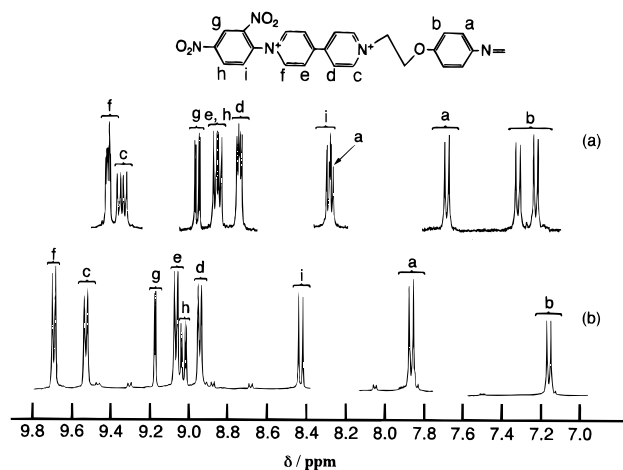


Figure 1. ^1H NMR spectra of (a) **1** in D_2O at $30\text{ }^\circ\text{C}$ and (b) **2** in $\text{DMSO}-d_6$ at $30\text{ }^\circ\text{C}$.

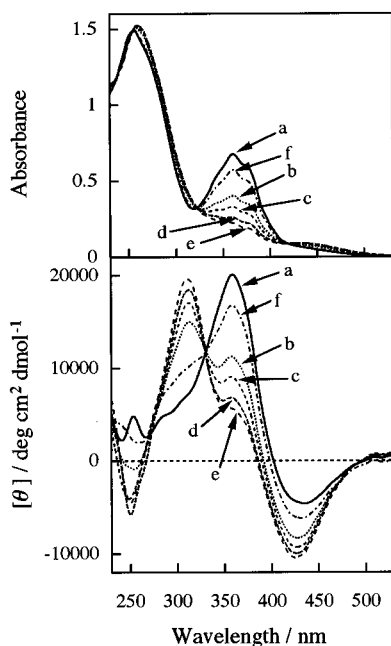


Figure 2. UV-visible absorption (top) and CD (bottom) spectra of aqueous solution of **1** ($2.0 \times 10^{-5}\text{ M}$) at $5\text{ }^\circ\text{C}$ after UV light (360 nm) irradiation for 0 (a), 2.0 (b), 4.0 (c), 8.0 (d), and 13.0 min (e) and after visible light (430 nm) irradiation for 14 min (f).

the axis of the CyD cavity is positive.¹² Therefore, the obtained result tells us that the azobenzene moiety is captured in the cavity of α -CyD. After irradiation with the UV light, the

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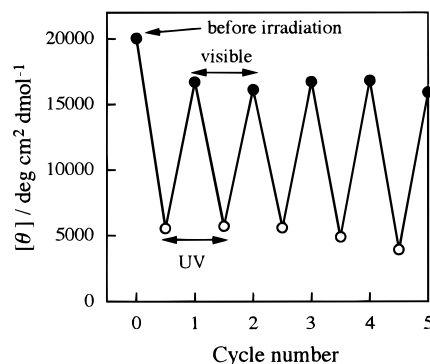


Figure 3. Cyclic responses of the $[\theta]$ values at 360 nm for aqueous solution of **1** on alternating irradiation of UV and visible light.

positive ICD sign at 360 nm decreased together with the increase in the positive ICD sign at 312 nm and the negative ICD sign at 430 nm assigned to $\pi-\pi^*$ and $n-\pi^*$ transitions, respectively.¹³ Upon irradiation with the visible light (430 nm), the spectrum of the photostationary state was reverted to that of the *trans* configuration with the isosbestic points at 269 and 330 nm . The plot of the molecular ellipticity $[\theta]$ at 360 nm as a function of the cycle numbers of alternating photoirradiation of the UV and visible light reveals that the photoswitching process is reversible (Figure 3).

Where is α -CyD in the chain when the azobenzene moiety in **1** is the *cis* configuration? After UV light irradiation, the NOE differential spectrum of **1**, in which the peak of the methylene spacer protons at 5.30 ppm was perturbed, showed a negative NOE peak¹⁴ at 3.65 ppm assigned to H-3 and/or H-5 protons of α -CyD, which are directed toward the inside of the cavity. There are no NOE peaks around 3.65 ppm when **1** is the *trans* isomer. These results suggest that after UV light irradiation, α -CyD exists at the methylene spacer moiety in **1**.

We can conclude that rotaxane **1** functions as a light-driven molecular shuttle in which α -CyD moves back and forth from/to the azobenzene moiety to/from the methylene spacer by alternating photoirradiation of UV and visible light. The present study would afford the opportunity to design and develop nanoscale switching devices based on light-driven molecular shuttles.

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(13) We also measured the CD spectrum of compound **3** ($4.0 \times 10^{-5}\text{ M}$ aqueous solution) in the presence of α -CyD ($4.0 \times 10^{-4}\text{ M}$) and found that the observed positive ICD sign at 360 nm ($[\theta]_{360} = 1.56 \times 10^4\text{ deg cm}^2\text{ dmol}^{-1}$) disappeared when the azobenzene moiety in **3** isomerized from *trans* to *cis* configuration via UV light irradiation, suggesting that the *cis* isomer is unable to be captured in the cavity of α -CyD.

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