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Photoresponsive Formation of Pseudo[2]rotaxane with Cyclodextrin Derivatives

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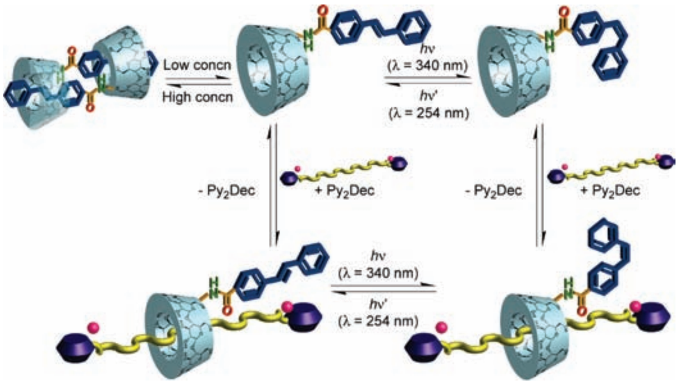
ABSTRACT



The two isomers of 6-stilbene-amide-α-CD (6-StiNH-α-CD) exhibit different inclusion behaviors upon complexation with an alkyl chain bearing pyridinium end caps. Photoisomerization of the stilbene moiety of the CD derivative affects threading due to complexation between the axle and *trans*- or *cis*-6-StiNH-α-CD.

Biological molecular motors can be roughly divided into linear molecular motors (e.g., myosin, kinesin, dynein, etc.[1−4]) and rotary motors (e.g., F_oF_1-ATP synthase, F_1-ATPase, etc.[5,6]). Rotaxanes consisting of mechanically interlocked macrocycles and dumbbell-shaped components have been studied as an example of controlled molecular movements for both artificial linear and rotary molecular motors. Recently, controlled synthetic linear[7,8] and rotary molecular motors using rotaxane building

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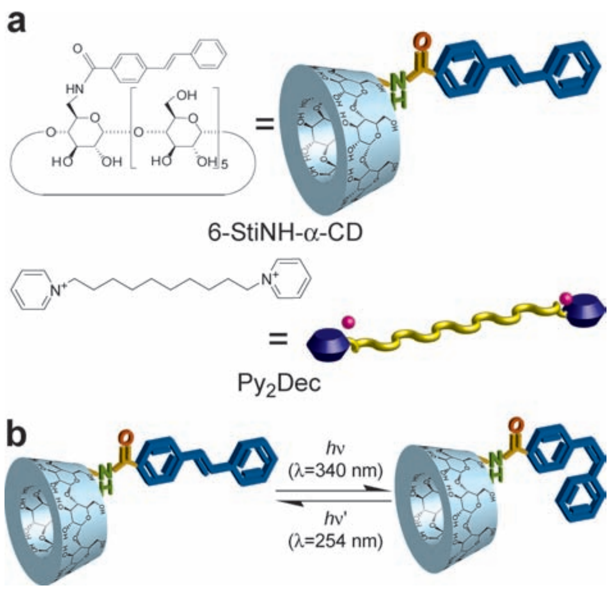

Figure 1. (a) Chemical structures of 6-StiNH-α-CD and Py_2Dec as an axis molecule. (b) Photoisomerization of 6-StiNH-α-CD.

blocks have been achieved by controlling the rotary movement.[9–12] We have previously reported that the direction of the faces of α-CD by the terminal group of the axle molecule controls the linear movement of α-cyclodextrin (α-CD) on *pseudo*[2]rotaxane with dicationic axle molecules.[13a,b] Upon complexation of modified α-CDs as host molecules for guest molecules consisting of an alkyl chain with pyridinium end caps, we have controlled complex formation and dissociation by pH responses of the functional groups on modified α-CDs.[13c] Although numerous types of CD-based *pseudo*-rotaxanes and rotaxanes have been prepared in the past two decades,[14] there are few reports on the threading–dethreading of CD-based *pseudo*-rotaxanes.[15] Moreover, *pseudo*-rotaxanes formed by CD derivatives with substituents sensitive to light or heat have yet to be reported. Herein we report *pseudo*-rotaxanes formed by 6-stilbene-amide-α-CD (6-StiNH-α-CD) and an alkyl chain with pyridinium end caps (Figure 1) where threading of the axle into the cavity of 6-StiNH-α-CD is controlled by light.

The axle molecule (Py_2Dec) and *trans*-6-StiNH-α-CD were prepared according to the previously reported methods.[13a,16] Stilbene derivatives show photoinduced isomerization; irradiating with UV and visible light induces isomerization from *trans* to *cis* and from *cis* to *trans*, respectively.[17] After photoirradiation with visible light (λ = 340 nm), 92% of *trans*-6-StiNH-α-CD was isomerized to *cis*-6-StiNH-α-CD (*trans*/*cis* = 8:92). However, the *trans* form was recovered by irradiating at λ = 254 nm.

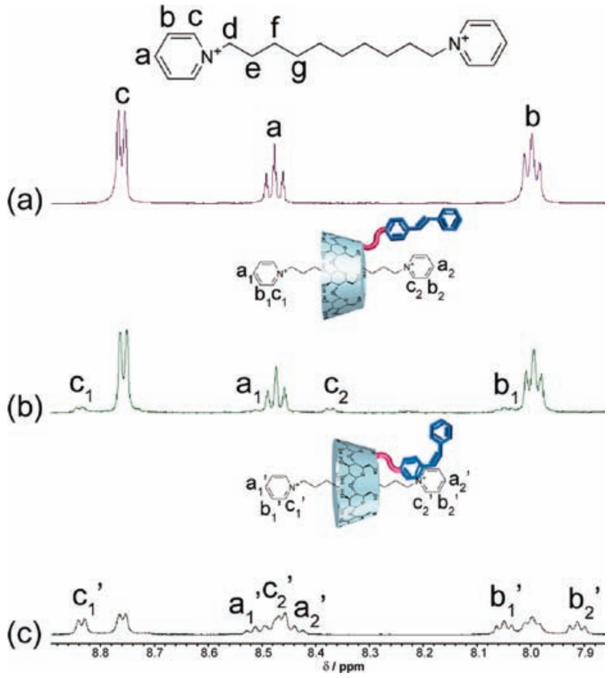

Figure 2. Partial ^{1}H NMR of Py_2Dec (4.0 mM) (a) in the absence of 6-StiNH-α-CD, (b) in the presence of *trans*-6-StiNH-α-CD (4.0 mM), and (c) in the presence of *cis*-6-StiNH-α-CD in D_2O (4.0 mM) at 30 °C.

Based on the isomerization of 6-StiNH-α-CD described above, Py_2Dec was mixed with *trans*-6-StiNH-α-CD or *cis*-6-StiNH-α-CD at room temperature. ^{1}H NMR spectroscopy in D_2O monitored the formation of *pseudo*-rotaxanes. These 6-StiNH-α-CDs were isolated by preparative reversed phase HPLC. Figure 2 shows the partial ^{1}H NMR spectra of Py_2Dec, Py_2Dec/*trans*-6-StiNH-α-CD, and Py_2Dec/*cis*-6-StiNH-α-CD. After 10 min, equilibrium of the complexation was reached. Mixing

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Table 1. Thermodynamic Parameters of Complexation between 6-StiNH-α-CD and Py_2Dec at 298 K

pseudo[2]rotaxane	$\Delta H°$/ kJ·mol^{-1}	$\Delta S°$/ J·mol^{-1}·K^{-1}	$\Delta G°$/ kJ·mol^{-1}	*K*/ M
Py_2Dec/*trans*-6-StiNH-α-CD	-31.5 ± 2.2	-57.7 ± 6.9	-14.3	320
Py_2Dec/*cis*-6-StiNH-α-CD	-33.9 ± 1.1	-55.6 ± 3.4	-17.4	1.1×10^3

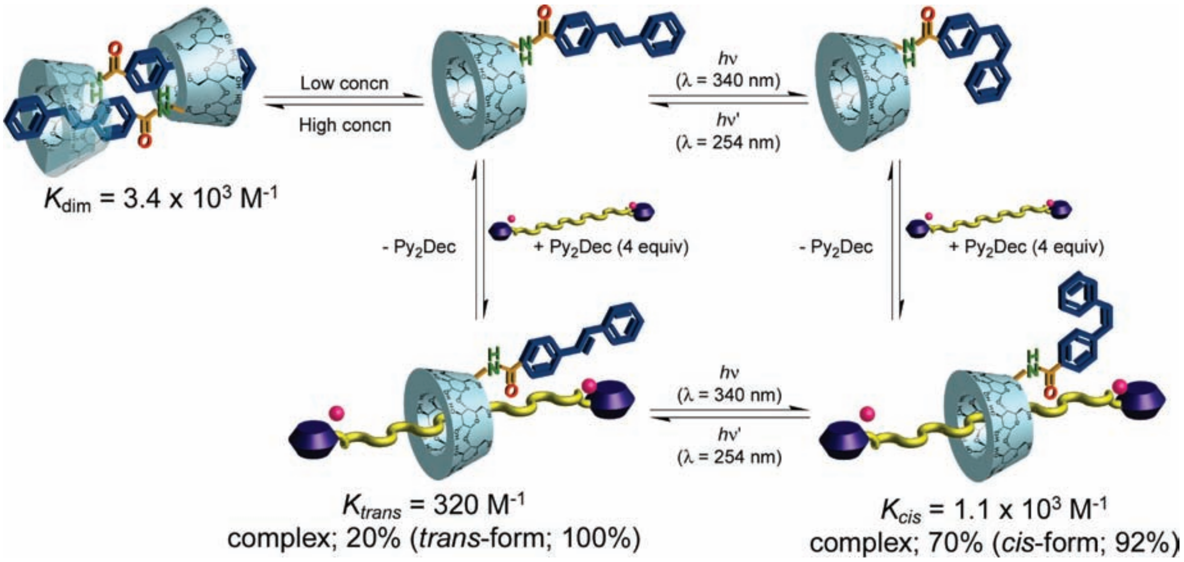

Figure 3. Schematic illustration of the formation of *pseudo*[2]rotaxane and the double threaded dimer with 6-StiNH-α-CDs. 6-StiNH-α-CD photoisomerizes between the *trans*- and *cis*-forms by irradiating with UV lights (λ = 340 and 254 nm).

trans-6-StiNH-α-CD with Py_2Dec caused the protons in the axis molecule to split in an aqueous solution (Figure 2b). This splitting was related to the formation of *pseudo*[2]rotaxane. 2D-ROESY NMR spectroscopy indicated that the inner protons of 6-*trans*-StiNH-α-CD and alkyl protons of Py_2Dec were correlated, suggesting the formation of *pseudo*[2]rotaxane (Figure S18).

The degree of complexation of Py_2Dec/*trans*-6-StiNH-α-CD, which was determined by the integrated intensity of the protons (such as proton c) for the complexed and uncomplexed axle Py_2Dec, reached 13%, which was lower than we initially envisioned. When the axle was mixed with *cis*-6-StiNH-α-CD in D_2O (equal molar), the protons of Py_2Dec split (Figure 2c). The degree of complexation reached 55%, which was calculated by the splitting of proton b. *Pseudo*[2]rotaxane with *cis*-6-StiNH-α-CD and Py_2Dec more easily formed than that with *trans*-6-StiNH-α-CD.

To investigate the stabilities of *pseudo*[2]rotaxanes, the thermodynamic parameters of the complexation were evaluated by a van't Hoff plot. Table 1 shows the results. Complexation between *cis*-6-StiNH-α-CD and Py_2Dec had more negative enthalpy changes ($\Delta H°$) than that between *trans*-6-StiNH-α-CD and Py_2Dec. The larger $\Delta H°$ is attributed to stronger van der Waals interactions. The association constants of *trans*-6-StiNH-α-CD with Py_2Dec exhibited K_{trans} = 320 M^{-1}, whereas that of *cis*-6-StiNH-α-CD with Py_2Dec exhibited $K_{cis} = 1.1 \times 10^3$ M^{-1}. These results indicate the *pseudo*[2]rotaxane formed by Py_2Dec/*cis*-6-StiNH-α-CD is more stable than that by Py_2Dec/*trans*-6-StiNH-α-CD due to the steric repulsion between the *trans*-stilbene group and Py_2Dec.

Next, we examined the influence of photoirradiation on the complex formation ratio of Py_2Dec/6-StiNH-α-CD. When a mixture of Py_2Dec and *trans*-6-StiNH-α-CD (4 molar excess) in D_2O was sequencially irradiated by UV light (λ = 350 nm) at room temperature, 92% of *trans*-6-StiNH-α-CD was converted into *cis*-6-StiNH-α-CD. The degree of complexation of *pseudo*[2]rotaxane increased from 20% to 70%. After irradiating the aforementioned solution at 254 nm, 62% of the *cis*-6-StiNH-α-CD returned to *trans*-6-StiNH-α-CD (*trans*/*cis* = 62:38).[18] The degree of complexation decreased from 70% to 46%.

Additionally, we investigated the formation of supramolecular complexes with 6-StiNH-α-CD and its influence on the formation of *pseudo*[2]rotaxane because our previous

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[18] The decline in the photoisomerization efficiency from cis to trans is attributed to the pyridinium group, which serves as an energy acceptor, and the steric hindrance between Py_2Dec and the stilbene group.

report indicated that *trans*-3-StiNH-α-CD in aqueous solutions forms a double-threaded dimer.[19] Circular dichroism spectra, 2D NMR spectra, and vapor pressure osmometry measurements of *trans*-6-StiNH-α-CD suggested the formation of a double-threaded dimer in aqueous solutions, but *cis*-6-StiNH-α-CD did not form supramolecular complexes (see Supporting Information). The association constant (K_{dim}) of *trans*-6-StiNH-α-CD for dimerization was 3.4×10^3 M^{-1}, which was higher than that (K_{trans}) for complexation between *trans*-6-StiNH-α-CD and Py_2Dec. These results indicate that mixing *trans*-6-StiNH-α-CD with Py_2Dec preferentially forms the double-threaded dimer over *pseudo*[2]rotaxane (Py_2Dec/*trans*-6-StiNH-α-CD).

In conclusion, we studied the threading/dethreading of Py_2Dec into/out of the cavity of 6-StiNH-α-CD by photoinduced isomerization of the stilbene moiety of the CD derivative (Figure 3). Although we hypothesized that *trans*-6-StiNH-α-CD would effectively form *pseudo*-[2]rotaxane, and *cis*-6-StiNH-α-CD would decompose *pseudo*[2]rotaxane after photoirradiation, our results are contrary to our expectations. The thermodynamic studies exhibited that *trans*-6-StiNH-α-CD shows a relatively low complex fomation ratio compared to *cis*-6-StiNH-α-CD due to the low stability. *Cis*-6-StiNH-α-CD formed *pseudo*[2]rotaxane with Py_2Dec. Regardless, complex formation of *pseudo*[2]rotaxane was observed upon irradiating with the appropriate wavelength. This threading–dethreading process might be applicable to light-powered molecular machines or logic gates based on CD derivatives.

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Supporting Information Available. Select NMR data (1D NMR and ROESY spectrum), determination of the diffusion coefficient, UV spectra, cd spectra, and turboion spray mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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