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Synthesis and Spectral Characterization of a Rotaxane of β-Cyclodextrin Threaded by a 4,4'-Diaminostilbene

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A rotaxane, in which a stilbene moiety threads the cavity of β-cyclodextrin (β-CyD), has been synthesized. The rotaxane structure has been proved by uv-visible and induced circular dichlorism (CD) spectra.

Rotaxanes[1-9] are compounds that a ring is threaded by a chain having bulky terminal cap groups that the chain cannot be extruded from the ring and are considerable attention has been focused recently on these compounds from the viewpoints of the synthesis of unknown organic compounds and their potential applica-

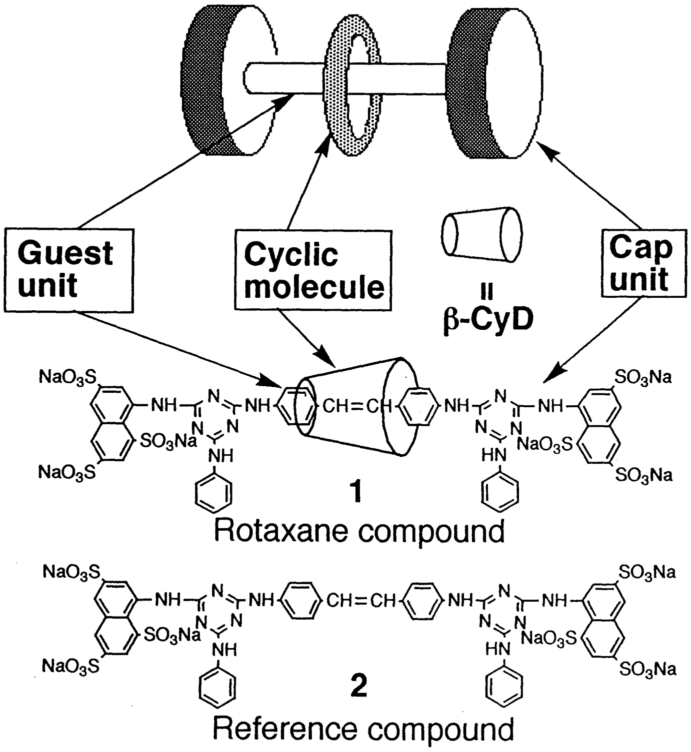

Fig. 1. Rotaxane **1** and reference compound **2**.

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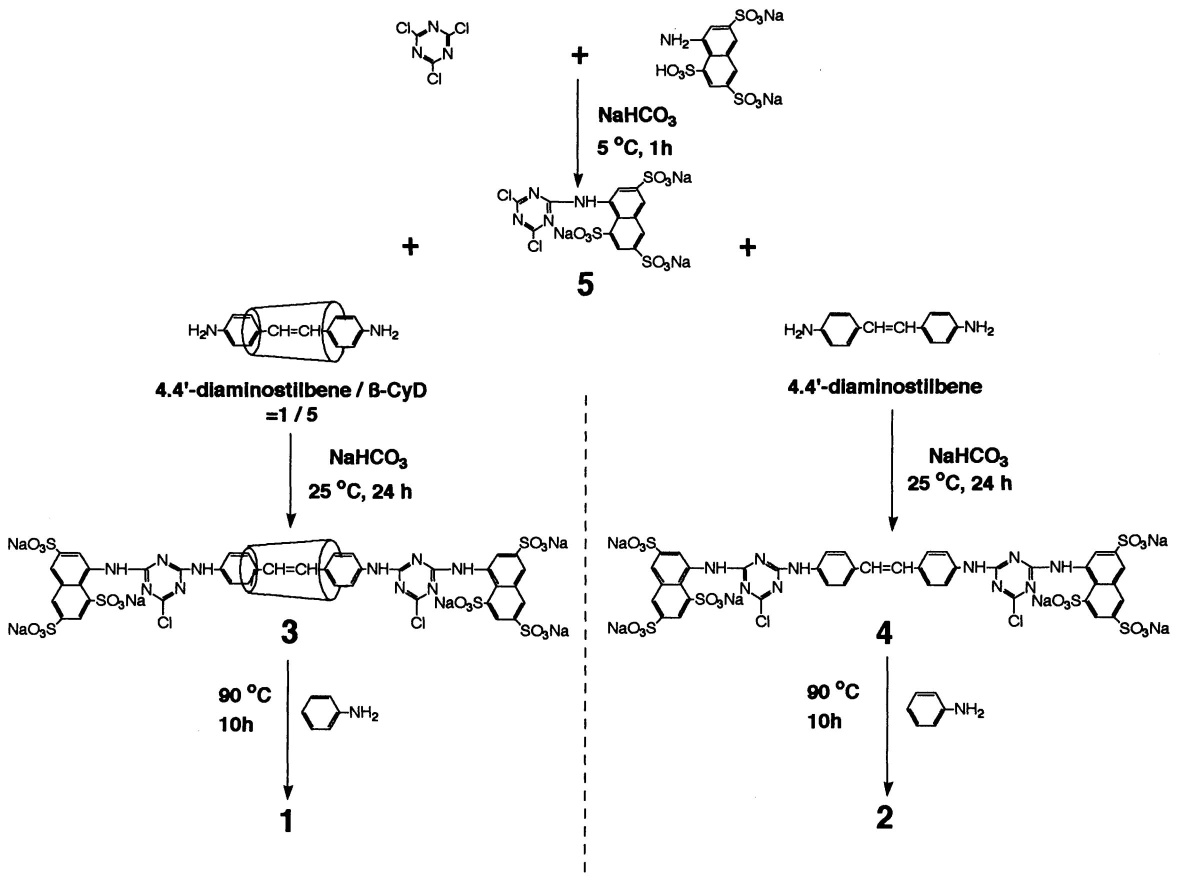

Scheme 1.

tions for the construction of molecular devices.[4,5,7)

When a ring compound as a host coexists in the reaction solution with a threading molecule as a guest a rotaxane is formed. If there is a strong interaction between the host and the guest molecule, rotaxanes should be synthesized with high yield. Ogino[1)] reported the synthesis of a rotaxane with relatively high yield (7–19%) where hydrophobic interaction between α,w–diamino–alkanes and α–cyclodextrin (α–CyD) was available. Recently, Stoddart and co-workers[4,5)] have succeeded in the tactical synthesis of rotaxanes and catenanes based on the donor–acceptor interaction.

Our strategy for tactical rotaxane syntheses is to use host / guest interactions of aromatic compounds with β–CD followed by temperature dependent caping reactions. In this communication, we would like to report for the first time the synthesis of a rotaxane in which an aromatic chromophore (stilbene moiety) is threaded in the cavity of β–CD (see Fig.1) and its spectral properties. Lawrence et al.[10)] described very recently the synthesis of a rotaxane-like molecule which includes a biphenyl chromophore in the cavity of β–CD.

Scheme 1 shows synthetic routes of a rotaxane **1** and a reference compound **2**. A cap molecule **3** was synthesized by the reaction of 2,4,6–trichloro–s–triazine with 1–amino–3,6,8–naphthalene trisulfonic acid sodium salt at 5 °C.[11)] 4,4'–Diaminostilbene·2HCl (1.0 mmol) and β–CD (5.0 mmol)[12)] were dissolved in an 0.012 mol/dm^3 $NaHCO_3$ aqueous solution (400 cm^3) and then an aqueous solution of the cap compound **3** (2.2 mmol) was added. After reacted at 25 °C for 24 h, HCl was added to the solution until pH 1; resulted small amount precipitate was filtered off and $NaHCO_3$ was added to the solution until pH 8.(13) The solution was heated at 90 °C for 10 h after the addition of aniline (10 mmol). Salting–out with NaCl at −15 °C twice gave a precipitate which was identified as **1**.(14) Yield 1.04 g (28.1%). Synthesis of the reference compound **2** was conducted in a water/ acetone (3/2 v/v) mixed solvent (see Scheme 1). Experimental procedure is almost the same as in the synthesis of **1**. Yield of **2**(15) was 74.8%.

Compound **4** is assumed to be a rotaxane; however **4** and **5** were reacted with aniline for the following two reasons: (1) to lower water–solubility which is important in the purification by salting–out, (2) to take the reaction–active moiety of the cap away. Note that temperature dependent reactivity of three chloride groups of 2,4,6–trichloro–s–triazine was applied to the synthesis of **1** and **2**. Analysis of **1** and **2** were confirmed by elemental analysis(14,15) and HPLC.(16) Although **1** and **2** were found to include NaCl by elemental analysis and Beilstein test, they both gave single HPLC peak with retention times of 0.93 min and 1.61 min, respectively.

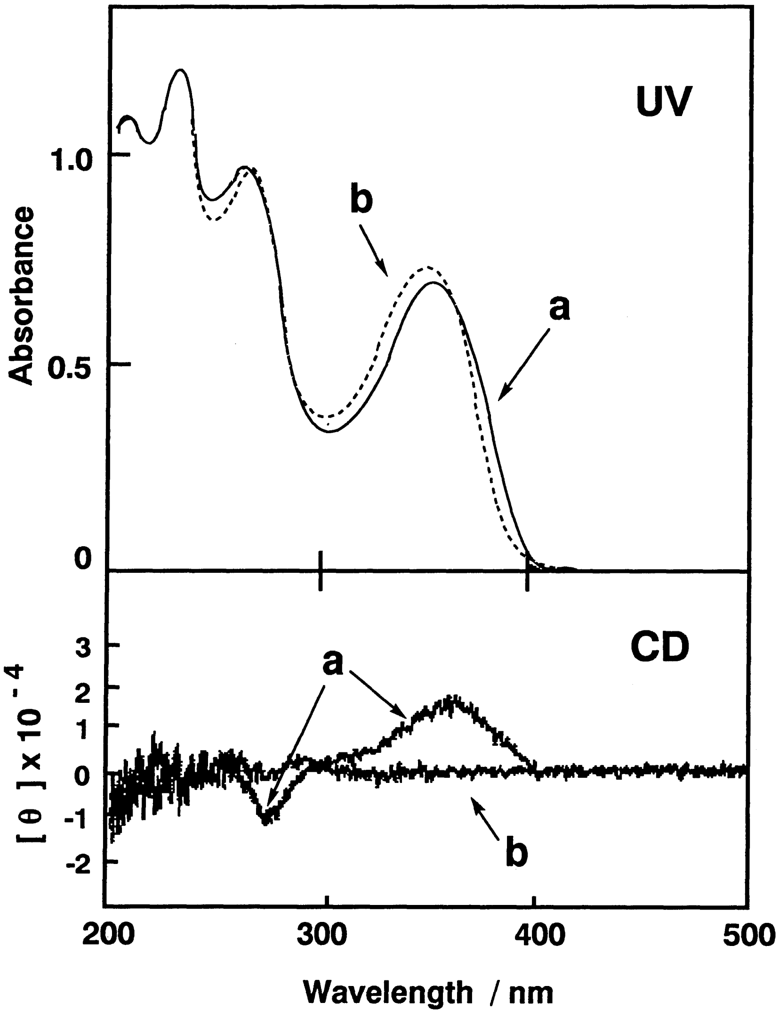

Fig. 2. UV–visible and CD absorption spectra of **1** and **2** in an aqueous solution at 25 °C: (a) **1** (8.0×10^{-6} mol/dm^3), (b) **2** (8.0×10^{-6} mol/dm^3) + β–CyD (8.0×10^{-4} mol/dm^3)

Spectroscopic properties of an aqueous solution of **1** were examined and compared with those of **2**. Figure 2 shows UV–visible and CD spectra of **1** and **2** plus excess β–CyD in aqueous solutions. A UV peak maximum (346 nm) of **1** was found to shift to 4 nm–longer wavelength compared to that of **2** and the absorbance was decreased by 6%. The absorption spectrum of 4,4'–diaminostilbene embedded in the host cavity of β–CyD (large excess) showed similar behavior (4nm–longer wavelength shift). The results are the proof that in molecule **1** stilbene moiety is incorporated in the cavity of β–CyD. CD experiment provides a further proof for the formation of the rotaxane structure; i.e. aqueous solution of **1** gave a distinct induced CD spectrum at 300–400nm region which corresponds to the absorption band of stilbene moiety. This means that π–π^* transition of stilbene chromophore is perturbed from the chiral environment of β–CD. No such ICD spectrum was observed for the compound **2** in the presence of large excess of β–CyD indicating that the compound is too bulky to form an inclusion complex with β–CyD.

In conclusion, we succeeded in the synthesis of the rotaxane in which the aromatic chromophore was embedded in the cavity of β–CyD. Further characterizations are currently under way in our laboratory.

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11) Anal. for **3**. Found: C,20.55; H,1.85; N,7.60%. Calcd for $C_{13}H_5N_4O_9S_3Na_3Cl_2$+4.5$H_2O$+1.4NaCl: C,20.53;H,1.86; N,7.37%.
12) This molar ratio was chosen because the binding constant between 4,4'–diaminostilbene and β–CyD obtained by the UV spectroscopic measurement was 2.6 x 10^3 M^{-1}.
13) Yield of **4** determined by HPLC was 75%.
14) Anal. Found: C,30.52; H,3.56; N,4.44%. Calcd for $C_{94}H_{104}N_{12}O_{53}S_6Na_6$+13$H_2O$+15NaCl: C,30.58; H,3.56; N,4.55%.
15) Anal. Found: C,34.61; H,3.00; N,9.35%.Calcd for $C_{52}H_{34}N_{12}O_{18}S_6Na_6$+10$H_2O$+3NaCl: C,34.68; H,3.03; N,9.33%.
16) HPLC measurement conditions are as follows: column, Inertsil ODS10 (150 mm length); eluent solvent, CH_3CN/methanol/H_2O=1/6.7/30.8(v/v/v%); Wavelengths of the UV detector, 260 and 350 nm.

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