Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Kuwabara, Tetsuo , Nakamura, Asao , Ikeda, Tsukasa , Ikeda, Hiroshi , Ueno, Akihiko and Toda, Fujio(1996) 'Supramolecular assembly of dye-modified cyclodextrin formed by inclusion of its dye-part in native cyclodextrin', Supramolecular Chemistry, 7: 3, 235 — 238

To link to this Article: DOI: 10.1080/10610279608027522

URL: http://dx.doi.org/10.1080/10610279608027522

SUPRAMOLECULAR CHEMISTRY, 1996, Vol. 7, pp. 235–238
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Supramolecular assembly of dye-modified cyclodextrin formed by inclusion of its dye-part in native cyclodextrin.

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(Received December 8, 1995)

A dye-appended β-cyclodextrin (1) associates with α-cyclodextrin (α-CD) with color change, forming an asymmetric rotaxane-like structure containing two different cyclodextrins. The similar phenomenon was observed in the system of 1 and β-CD. The association constant of 1 for α-CD (198 M^{-1}) is larger than that for β-CD (43 M^{-1}), indicating that the pseudo-rotaxane is more stable when 1 associates with α-CD.

INTRODUCTION

Self-assemblies in biological systems are based on non-covalent interactions and form highly organized molecular arrays from relatively simple subunits. The resulting supramolecular entities exhibit a variety of integral functions operating as a result of the cooperative or synergistic effects of component molecules. In order to get insight into the action of such assembled molecules at the molecular level, several model systems have been studied.[1] In this report we show cyclodextrin (CD) units can be organized into a larger assembly by cooperation of two different CDs. The assembly consists of *p*-methyl-red-modified β-CD (**1**) and α-CD, the latter being threaded by the dye part of **1**.

RESULTS AND DISCUSSION

α-CD-Induced-Spectral Variations of 1 in Neutral Medium

Recently, we have prepared **1** as a guest responsive color change indicator.[2] Figure 1 shows the absorption spectra of **1** under various conditions. At pH 6.59, the solution of **1** shows a yellow color. The absorption maximum at 465 nm indicates that the dye moiety of **1** exists as the azo form.[3] A slight hyperchromic effect in the absorption spectrum of **1** was observed upon α-CD addition, suggesting a change in conformation of **1** and inclusion of the dye moiety in the cavity of α-CD.

This structural feature of **1** was confirmed by the induced circular dichroism spectra[4] (Figure 2) **1** exhibits a negative dichroism band around 410 nm and a positive one around 485 nm in neutral medium at pH 6.59, each associated with the π-π* and the n-π* transition of the dye moiety, respectively.[2] Since the transition moments of the π-π* and the n-π* bands of the *p*-methyl red moiety are parallel and perpendicular to the long axis of the dye part, respectively, the result obtained here indicates that **1** exists as an intramolecular complex, in which the dye moiety is included in its hydrophobic β-CD cavity with an orientation perpendicular to the CD axis. Upon the α-CD addition, the positive dichroism band decreased, and the negative band changed to the positive one with a peak around 420 nm. The α-CD-induced circular dichroism variation therefore implies that **1** converts into an intermolecular complex, in which the dye moiety is included axially in the cavity of α-CD (Scheme 1).

α-CD-Induced-Spectral Variations of 1 in Acidic Medium

At pH 1.00, the solution of **1** exhibits a red color. A strong peak around 510 nm suggests that the dye moiety of **1** exists as the azonium form, which is the form in which the azo group of the dye moiety is protonated

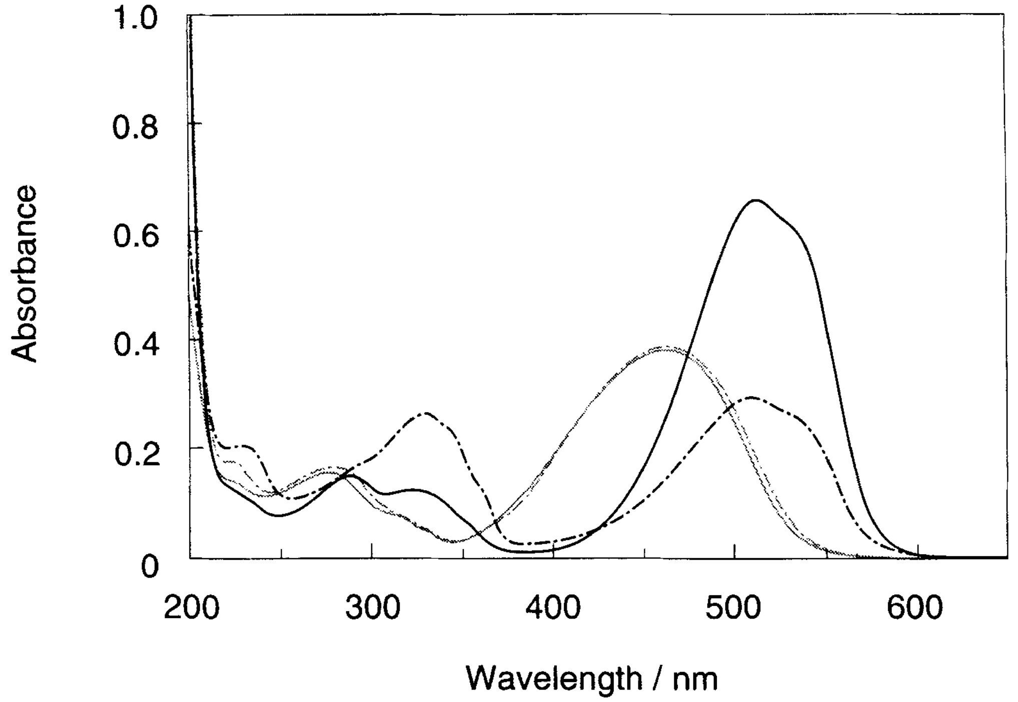


Figure 1 Absorption spectra of **1** (1.5×10^{-5} M) in a 10% ethylene glycol aqueous solution at various conditions: in the absence (··········) and presence (—·—·—) of α-CD (1.2×10^{-1} M) at pH 6.59, and in the absence (———) and presence (— - — - —) of α-CD at pH 1.00.

(Figure 1).[3] Upon addition of α-CD into this solution of **1**, the absorption intensity of **1** decreased around 510 nm and increased around 320 nm, respectively, resulting in the color change from red to colorless. This result suggests that there occurs a structural change of the dye moiety from the azonium form into the ammonium one, in which the terminal dimethylamino group in the dye moiety is protonated.[3] This can be explained by deep inclusion of the dye moiety of **1** into the cavity of α-CD (Scheme 1). Then the azo group of the dye moiety is

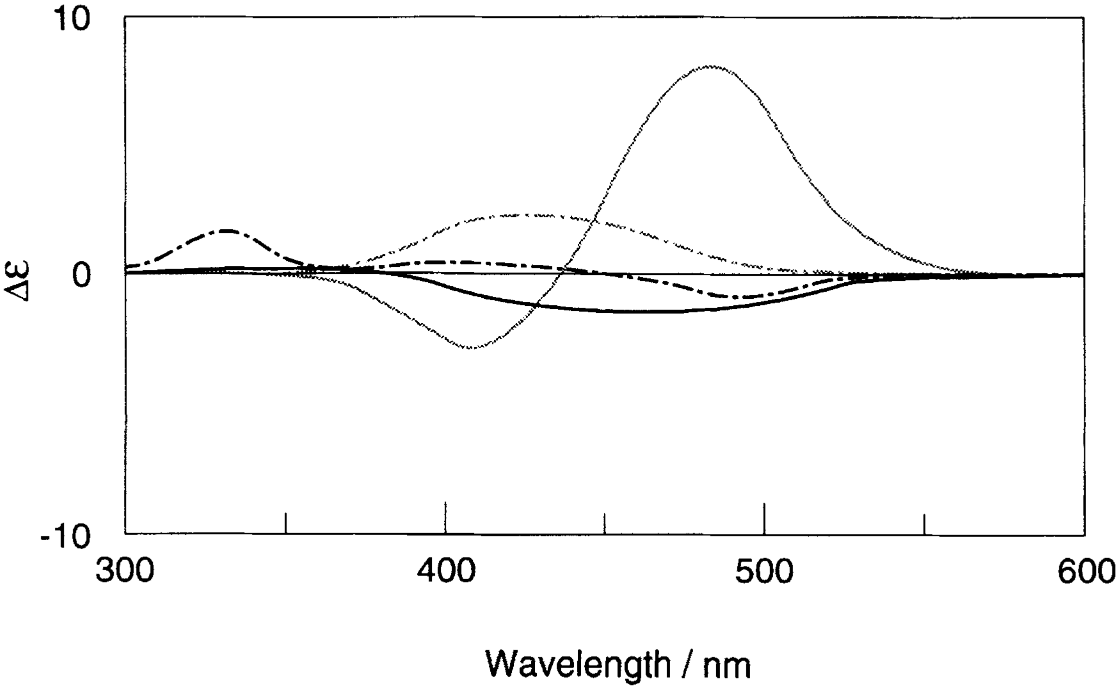
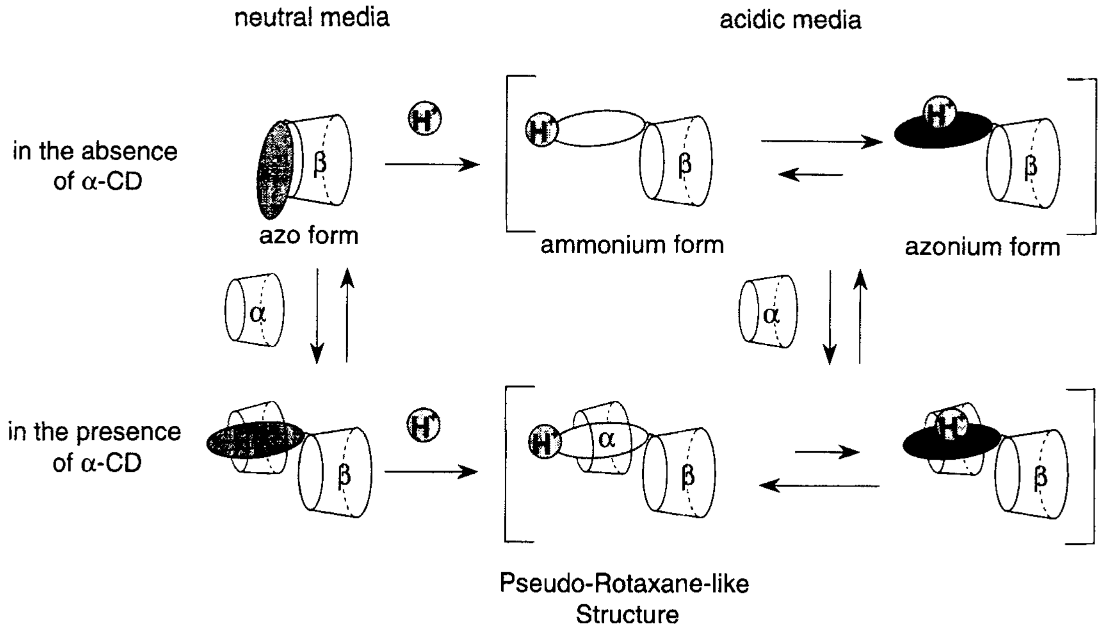


Figure 2 Induced circular dichroism spectra of **1** (1.5×10^{-5} M) in a 10% ethylene glycol aqueous solution at various conditions: in the absence (··········) and presence (—·—·—) of α-CD (1.2×10^{-1} M) at pH 6.59, and in the absence (———) and presence (— - — - —) of α-CD at pH 1.00.



Scheme 1 Schematic representation of the supramolecular assembly of **1** and α-CD.

located in the hydrophobic environment inside the α-CD cavity, while the terminal dimethylamino group projecting from the α-CD cavity is exposed to bulk water, being protonated. Since it is clear that β-CD cannot be included in the α-CD cavity, the β-CD unit is also exposed in bulk water. Thus, this supramolecular species exists as an asymmetric pseudo-rotaxane-like structure in which the α-CD ring is threaded by the dye moiety. The pseudo-rotaxane has two different end units, with a protonated dimethylamino group as a charged unit at one end and a β-CD unit as a bulky unit at the other end. The organization of **1**, its dye moiety, and α-CD in the acidic medium is reflected in the color change.

Such a rotaxane-like structure is also supported by the induced circular dichroism spectra of **1**. The small negative dichroism band of **1** around 500 nm disappeared upon addition of α-CD and the positive ones appeared around 420 nm and 320 nm. This result suggests that the dye moiety, which is hardly included in the β-CD cavity of **1**, is included in α-CD cavity with an orientation parallel to the α-CD axis. All the above results indicate that the dye moiety of **1** is included in the cavity of α-CD, rather than that of β-CD in the presence of α-CD, under both acidic and neutral conditions.

Furthermore, we have previously demonstrated that the pKa for **1** in the absence and presence of the guest is estimated to be 2.08 and 2.58, respectively, and these pKa values indicate that the dye moiety of **1** is accommondated partly in the hydrophobic environment inside the β-CD cavity with an orientation perpendicular to the CD axis in the absence of the guest, while located in the bulk water environment outside of the CD cavity in the presence of the guest, respectively.[2] The pKa estimated here for **1** in the presence of α-CD (1.2×10^{-1} M) is 2.05, and, consequently, this result suggests that the dye moiety of **1** is located in the hydrophobic environment of the α-CD in the presence of α-CD.

Association Constants of 1 for CDs

The curve-fitting analysis of the α-CD-induced spectral variations of **1** performed by using a Benedi-Hildebrand type equation gave association constants of 198 and 305 M^{-1} for **1** in acidic (pH 1.00) and neutral (pH 6.59) media, respectively.[4] These values are much smaller than that of the complexation of α-CD and methyl orange (925 M^{-1} at pH 1.0 and 6300 M^{-1} at pH 11),[5] the latter having a similar structure as *p*-methyl red, although the carboxyl group for *p*-methyl red is replaced by a sulfonyl group for methyl orange. The smaller binding ability of **1** for α-CD suggests that there exists a steric hindrance preventing the two bulky CD units from a close approach.

On the other hand, similar spectral behavior of **1** was obtained in the system of **1** and β-CD. However, the β-CD-induced spectral variations of **1** were smaller than those by the α-CD-induced ones. The association constant of **1** for β-CD is estimated to be 43 M^{-1} at pH 1.00. These results indicate that the dye moiety of **1** fits better into the α-CD cavity than into the β-CD cavity, being consistent with the fact that the association constant of methyl orange for α-CD is larger than that for β-CD.[5] It is noted that Ueno *et al.* observed a similar association phenomenon in the system of naphthalene-appended γ-CD and β-CD.[6] The present study demonstrates the supramolecular assembly is associated with the structural change of the dye moiety, resulting in the color change, and the resulting assembly exists as a pseudo-rotaxane-like structure, particularly in acidic medium. Other supramolecular assemblies of this type will be constructed on the same basis.

EXPERIMENTAL

Materials

1 was prepared by the method reported previously. α-CD was a kind gift from Nihon Shokuhin Kako Co. Ltd., and was recrystallized from water.

Measurements

Absorption spectra and induced circular dichroism spectra were measured on a Shimadzu UV-3100 spectrophotopmeter and a JASCO J-600 spectropolarimeter. All spectroscopic measurements were made at 25 °C in a 10% ethylene glycol aqueous solution. The pH of the solution was measured on a TOA pH meter HM-60S, which has been calibrated with pH standard solutions of pH 4.01 and 6.86. Hydrochroric acid was used to set the pH.

Determination of the pKa of 1

The pKa of **1** was estimated by the following equation:

$$\Delta I = \frac{Ka \cdot \Delta I\,\mathrm{max} \cdot 10^{-\mathrm{pH}}}{1 + Ka \cdot 10^{-\mathrm{pH}}}$$

where *Ka* is the acid-base dissociation constant of the unprotonated and protonated form of **1**. It can be assumed that **1** exists almost totally as the azo form in neutral medium, and ΔI is the difference between the absorption intensity at 510 nm of **1** in neutral medium and that at a certain pH. When all **1** are protonated, ΔI is equated with ΔImax.

Determination of Association Constant

The association constants of **1** with α- or β-CD were determined by the following equation which holds under the conditions of large excess of α- or β-CD and 1:1 host-guest stoichiometry

$$\Delta I = \frac{K \cdot CD \cdot \Delta I\,\mathrm{max}}{1 + K \cdot CD}$$

where K is the association constant of **1** for α- or β-CD. CD represents the initial concentration of α- or β-CD. In acidic medium at pH 1.00, ΔI expresses the α- or β-CD-induced absorption variation of **1** at 510 nm, while in neutral medium at pH 6.00, ΔI expresses the α-CD-induced dichroism variation of **1** at 420 nm.

REFERENCES

1 (a) J. L. Atwood, G. W. Orr, F. Hamada, S. G. Bott and K. D. Robinson *Supramol. Chem.* **1992**, *1*, 15. (b) R. S. Wylie and D. H. Macartney *J. Am. Chem. Soc.*, **1992**, *114*, 3136. (c) A. Harada, J. Li, and M. Kamachi *Nature*, **1992**, *356*, 326. (d) R. Isnin and A. E. Kaifer *J. Am. Chem. Soc.*, **1991**, *113*, 8188.

2 (a) T. Kuwabara, A. Nakamura, A. Ueno and F. Toda *J. Phys. Chem.* **1994**, *98*, 6297. (b) A. Ueno, T. Kuwabara, A. Nakamura, and F. Toda *Nature*, **1992**, *356*, 136.

3 S. Yamamoto, N. Nishimura and N. Hasegawa *Bull. Chem. Soc. Jpn.* **1973**, *46*, 194.

4 (a) H. Shimizu, A. Kaito, M. Hatano *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2678. (b) M. Kodaka *J. Am. Chem. Soc.*, **1993**, *115*, 3702.

5 (a) Á. Buvári and L. Barcza *J. Inclusion Phenom.* **1989**, *7*, 313.

6 A. Ueno, Y. Tomita and T. Osa *J. Chem. Soc., Chem. Commun.* **1983**, 1515.