

EXCITON COUPLING, EXCIMER EMISSION AND UNIQUE BINDING BEHAVIOR OF  
γ-CYCLODEXTRIN SUBSTITUTED BY TWO NAPHTHYL RESIDUES

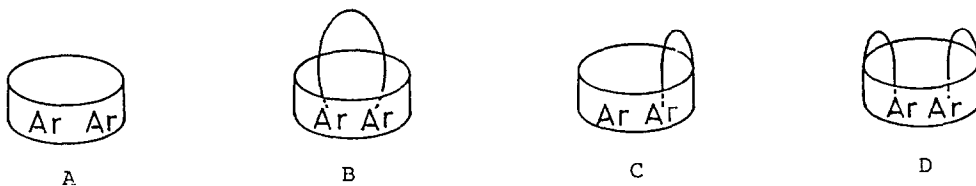
Akihiko Ueno,\*<sup>a</sup> Fumio Moriwaki,<sup>a</sup> Tetsuo Osa\*<sup>a</sup>,  
Fumio Hamada,<sup>b</sup> and Koichi Murai<sup>b</sup>

<sup>a</sup> Pharmaceutical Institute, Tohoku University, Aobayama,  
Sendai 980, Japan

<sup>b</sup> Department of Fuel Chemistry, Mining College, Akita  
University, Gakuen-cho, Tegata, Akita 010, Japan

Abstract: A modified γ-cyclodextrin substituted by two naphthyl residues,  
which exhibits exciton coupling band and excimer emission, binds various  
guests by changing the location of the naphthyl residues.

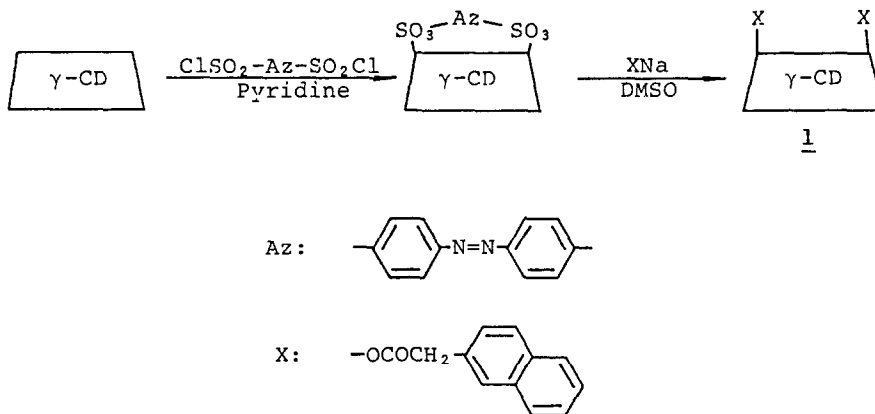
γ-Cyclodextrin (γ-CD) has recently excited much attention because of its  
ability to bind two guest molecules in its large cavity.<sup>1-3</sup> The excimer  
emission promoted by γ-CD is direct evidence for inclusion of two aromatic  
residues in the γ-CD cavity.<sup>1a</sup> Heretofore, three γ-CD systems in which two  
aromatic units are not covalently bound (A),<sup>1</sup> linked at both ends of a chain  
(B)<sup>2</sup> and joined together as guest and a part of host (C)<sup>3</sup> have been reported  
to show excimer emission. When the aromatic unit is naphthalene, no exciton  
coupling band has been observed in circular dichroism (c.d.) spectra for any  
case of these systems, contrasting the observed exciton coupling band for a  
mixture of pyrene and γ-CD.<sup>1b</sup> We report here that exciton coupling band of  
naphthalene as well as excimer emission can be observed in the fourth system  
where two naphthyl moieties are covalently bound to γ-CD (D).



Another feature of this communication is that this is the first report for  
binding behavior of modified cyclodextrins substituted by two aromatic  
residues.

Compound 1 was prepared according to the following scheme.

Scheme I



Purification of the crude product of 1 has been performed by Sephadex G-15 column chromatography (yield from azobenzene capped  $\gamma$ -CD, ca. 20%). The purified product was identified by elemental analysis, n.m.r., u.v. (277 nm ( $\epsilon$  7900), water, dimethyl sulfoxide 9:1 by volume), and t.l.c. ( $R_f$  0.48, acetonitrile, water 5:1 by volume).<sup>4</sup> The solubility of 1 in pure water is poor, so a mixed solvent of water and dimethyl sulfoxide (9:1 by volume) was used for spectroscopic measurements.

Circular dichroism spectrum of 1 at 25 °C is shown in Figure 1. The signs of the induced c.d. bands are negative in the 240-260 nm region and positive in the 260-320 nm region. This exciton coupling observed for the  $^1L_a$  band demonstrates that the pair of naphthyl residues included in the  $\gamma$ -CD cavity has R-helicity.<sup>5</sup> Figure 1 shows also the spectrum in the presence of cyclododecanol, the positive band disappearing to give a new negative band. Similar c.d. changes were observed when other guests were added.

Binding constants at 25 °C of 1 for various guests have been determined by analysis of the changes of the dichroism intensity at 282 nm (Table 1).<sup>6</sup>

Table 1. Binding constants of 1 for various guests (25 °C)

guest	$K / \text{mol}^{-1} \text{ l}$
cyclohexanol	$21.7 \pm 0.4$
1-menthol	$329 \pm 32$
adamantanecarboxylic acid	$507 \pm 61$
1-borneol	$795 \pm 31$
cyclododecanol	$9730 \pm 570$

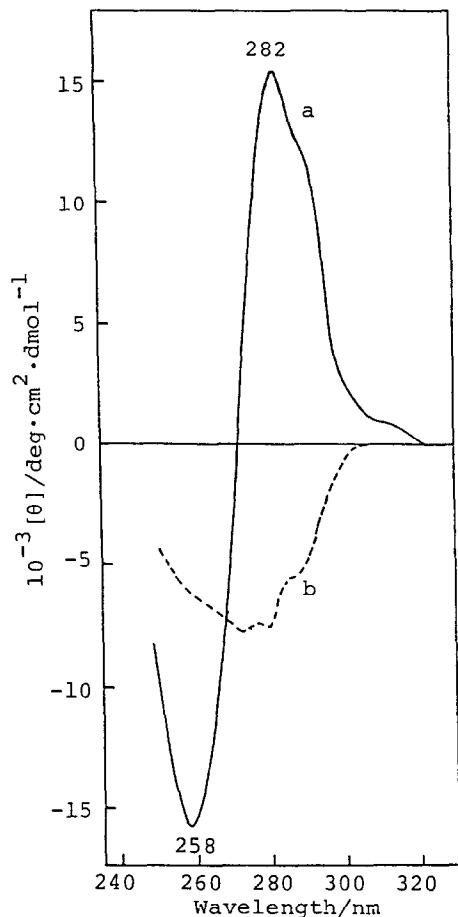


Fig. 1. Circular dichroism spectra of 1 ( $6.53 \times 10^{-5}$  M), alone (a) or in the presence of cyclododecanol (b,  $2.41 \times 10^{-4}$  M).

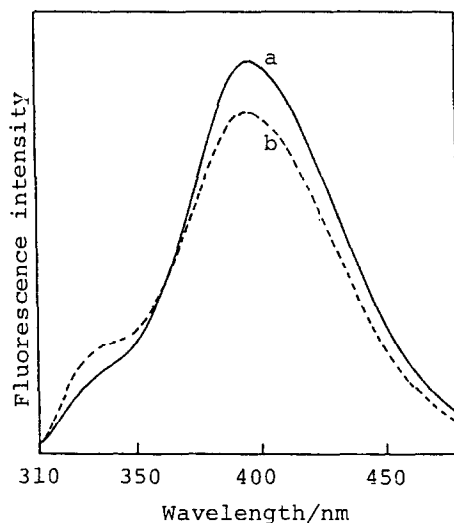
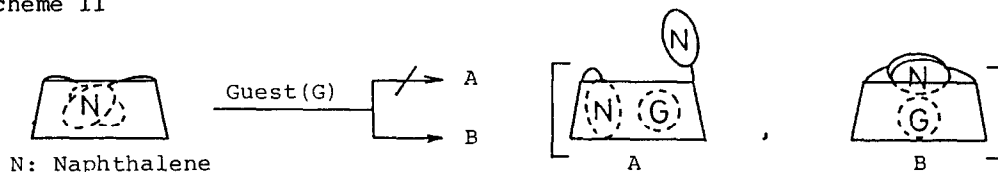


Fig. 2. Fluorescence spectra of 1 ( $6.53 \times 10^{-5}$  M), alone (a) or in the presence of adamantane-carboxylic acid (b,  $1.11 \times 10^{-3}$  M). Excitation wavelength is 290 nm.

The values of binding constants are smaller for smaller guests and larger for larger guests, ranging from  $21.7 \text{ mol}^{-1}$  l for cyclohexanol to  $9730 \text{ mol}^{-1}$  l for cyclododecanol.

Figure 2 shows fluorescence spectra of 1 at 25 °C. The solution containing no guest exhibits a marked excimer emission around 400 nm. The normal fluorescence around 330 nm is observed as a shoulder. The result indicates that face-to-face interaction needed for excimer formation is attained within the lifetime of excited singlet state of the naphthyl residues. It was also found that the spectral shape was hardly influenced by guest addition (Figure 2). If the structure of the 1-guest complexes is A-type (Scheme II), the excimer emission would have been diminished. One possible explanation for the fluorescence behavior of 1 is that the structure of the complexes is B-type. The geometry of the B-type is

Scheme II



consistent with the c.d. data since the parallel arrangement of the two naphthyl residues in the complexes should not show any exciton coupling band. This structure of the complex is different from the corresponding mono-substituted  $\gamma$ -CD in which the appended naphthyl residue acts as a spacer to narrow the large  $\gamma$ -CD cavity, being involved together with a guest molecule.<sup>7</sup>

As shown by above data and discussion, 1 can bind various guests into its cavity by changing the location of the two naphthyl residues. The two naphthyl residues seem to act as hydrophobic caps to promote binding of a guest molecule into the cavity. The conformational flexibility of 1 is different from the rigid frame of native cyclodextrins and provides a new aspect in host-guest chemistry.

#### References

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4. The positions substituted by the naphthyl residues are those sulfonated by *p,p'*-dichlorosulfonylazobenzene. Examination of Corey-Pauling-Koltun models shows that substitution is most likely to occur at A-D and A-E positions of primary side of  $\gamma$ -CD (see reference; I. Tabushi, K. Yamamura, and T. Nabeshima, J. Am. Chem. Soc., 1984, 106, 5267). The models also indicate that excimer can be formed for both isomers.
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