Bull. Chem. Soc. Jpn., 70, 1339—1346 (1997)

Fluorescent Sensors for Molecules. Guest-Responsive Monomer and Excimer Fluorescence of 6A,6B-; 6A,6C-; 6A,6D-; and 6A,6E-Bis(2-naphthylsulfonyl)-γ-cyclodextrins

Fumio Hamada,* Shingo Minato,† Tetsuo Osa,† and Akihiko Ueno,*,††

Department of Materials Engineering and Applied Chemistry, Mining College, Akita University, Tegata, Akita 010

†Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980

††Department of Bioengineering, Faculty of Bioscience and Biotechnology, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227

(Received October 16, 1996)

Flexible hosts, 6A,6B-; 6A,6C-; 6A,6D-; and 6A,6E-bis(2-naphthylsulfonyl)-γ-cyclodextrins (γ-**1**, γ-**2**, γ-**3**, and γ-**4**, respectively) were used as fluorescent sensors with which a variety of organic compounds were detected by naphthalene excimer and monomer emissions. In a 10 vol% ethylene glycol aqueous solution, γ-**1** exhibits almost pure monomer fluorescence while γ-**2**, γ-**3**, and γ-**4** exhibit both monomer and excimer emissions. The intensities of the emissions changed upon addition of guest species, particularly in the case of γ-**2** and γ-**3**, and the guest-induced intensity variations were used as sensitivity factors of the sensors. When (−)-borneol (**5**), cyclohexanol (**6**), cyclododecanol (**7**), and 1-adamantanecarboxylic acid (**8**) were added to each host solution, γ-**2**, γ-**3**, and γ-**4** increased the excimer emission intensity but decreased the monomer one, the absolute intensity variations being **6** < **5**≈**8** < **7**. When geraniol (**9**), nerol (**10**), and (−)-menthol (**11**) were added, the hosts decreased intensities in both monomer and excimer emissions for **9** and **10** while their emission variations for **11** were similar to those of **5**. For steroids such as cholic acid (**12**), deoxycholic acid (**13**), chenodeoxycholic acid (**14**), and ursodeoxycholic acid (**15**), γ-**4** showed depression in the excimer emission and enhancement in the monomer one while γ-**2** and γ-**3** showed complicated features in which the excimer emission was enhanced with the order of **15** < **14** < **13**≈**12** but the monomer one was depressed or enhanced depending on the hosts. All these data demonstrate that the hosts can be used as sensors for molecular recognition.

Detection of molecules by fluorescent sensors is of current interest.[1—17] One of the mechanisms for sensing is the use of host–guest complexation phenomena of cyclodextrin (CD) derivatives. CDs are cyclic compounds composed of D-glucose units connected by α-1,4-linkages; they form inclusion complexes with a variety of organic compounds in aqueous solution.[18,19] When the inclusion phenomena of CDs are investigated, spectroscopically active guests should be used because CDs are basically inert with respect to optical spectroscopy. CDs can, however, become spectroscopically active compounds by modification with chromophores, and spectroscopically inert guests can probably be recognized by the spectral change of modified CDs upon addition of a guest. Recently, some chromophore-modified CDs have shown remarkable variations in their circular dichroism, absorption, or fluorescence spectra associated with the formation of inclusion complexes; on this basis they have been used as sensors or indicators of molecules in aqueous solution.[4—17] A color-change indicator for molecules has also been constructed by attaching a pH indicator to β-CD.[10] We report here excimer-forming γ-CD derivatives (γ-**1**, γ-**2**, γ-**3**, and γ-**4**) as fluorescent sensors of molecular recognition. γ-CD has eight glucose units and can form 1 : 2 complexes by including two guest molecules in its large cavity.[20,21] We previously reported that a γ-CD derivative bearing two 2-naphthylacetyl moieties forms an intramolecular complex in which the appended moieties are included in the γ-CD cavity and interact with each other.[22] The intramolecular complex was converted into intermolecular complexes upon addition of guest species, changing the location of the moieties from inside to outside of the CD cavities. However, this host exhibits almost no fluorescence variation upon a guest addition, showing predominant excimer emission both before and after a guest binding. In view of constructing sensors capable of detecting guest species by guest responsive fluorescence variations, we prepared γ-CD derivatives that have two 2-naphthylthio moieties and observed remarkable guest-induced fluorescence enhancement.[8] However, the γ-CD derivatives exhibit almost no excimer emission either in the absence or in the presence of guest species, and consequently their abilities as sensors were limited. Under this circumstance, we examined the fluorescence behavior of γ-CD derivatives γ-**1**, γ-**2**, γ-**3**, and γ-**4**, which bear two 2-naphthylsulfonyl moieties at AB, AC, AD, and AE glucose units, respectively (Chart 1), and found that they change both monomer and excimer emissions together with induced circular dichroism (ICD) upon a guest addition.[6,7] The finding indicated that they can be used as sensors for detecting vari-

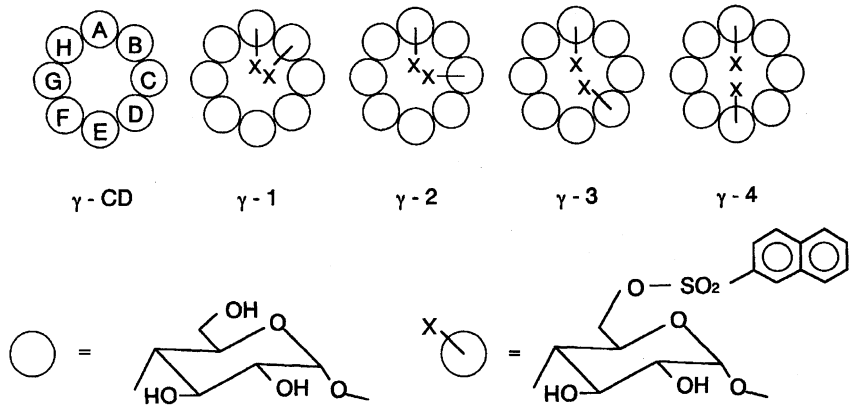

Chart 1.

ous organic compounds. In this report, we show the details of the sensor abilities of the fluorescent CDs, together with the abilities of the corresponding β-CD derivatives.

Experimental

Materials. The host compounds γ-**1**, γ-**2**, γ-**3**, and γ-**4** were prepared according to the procedures reported previously.[23] The guest compounds **5**—**15** listed in Table 1 and ethylene glycol were commercially guaranteed reagents (Chart 2).

Measurements. The solubility ranges of the hosts were limited, so a 10 vol% ethylene glycol aqueous solution was used as the solvent. The solution of each host was prepared by adding an ethylene glycol solution of γ-**1**, γ-**2**, γ-**3**, and γ-**4** (24 mL) to a 10 vol% ethylene glycol aqueous solution (3 mL) so as to make the concentration of the resultant solution 2.0×10^{-5} M (M = mol dm^{-3}). Circular dichroism and fluorescence spectra were measured at 25 °C with a JASCO J-400X spectrophotodichrometer and a JASCO FP-770 spectrofluorometer, respectively. The fluorescence measurements were performed by excitation at 290 nm.

Determination of Binding Constants. The binding constants of γ-**1**, γ-**2**, γ-**3**, and γ-**4** for (−)-borneol (**5**), cyclododecanol (**7**), and 1-adamantanecarboxylic acid (**8**) were obtained from guest-induced circular dichroism variations for a peak (238, 243, and 220 nm for γ-**1**, γ-**3**, and γ-**4**, respectively) or a trough (238 nm for γ-**2**) observed below 250 nm.[21] The values for steroid compounds were obtained from guest-induced fluorescence variations around 410 nm by employing a Benesi–Hildebrand type equation as reported previously.[24]

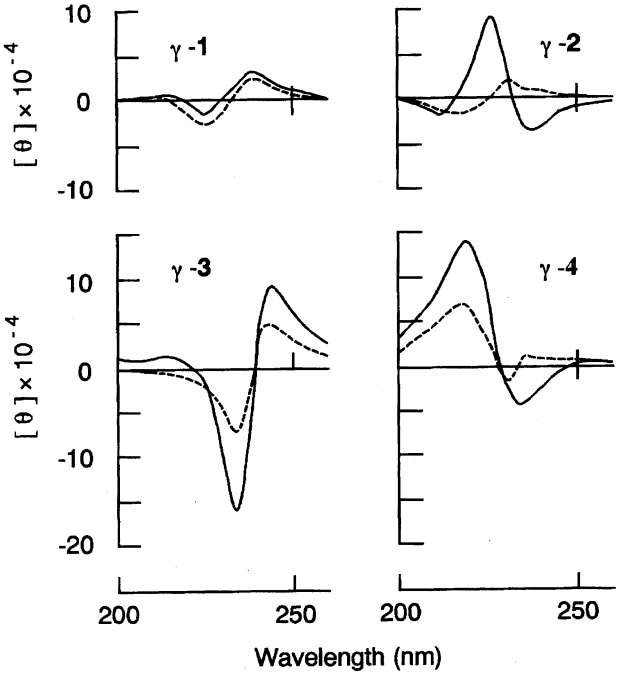

Fig. 1. Induced incular dichroism spectra of γ-**1**, γ-**2**, γ-**3**, and γ-**4** alone (0.02 mM, —) or in the presence of (−)-borneol (1 mM, - - -) in a 10 vol% ethylene glycol aqueous solution.

Results and Discussion

Induced Circular Dichroism (ICD) Spectra. Figure 1 shows ICD spectra of four hosts, γ-**1**–γ-**4**, alone or with (−)-borneol (**5**) in a 10 vol% ethylene glycol aqueous solution. All hosts examined exhibit exciton coupling bands in the naphthalene ^1B_b transition region (220—260 nm). The ICD sign changes from positive to negative for γ-**1** and γ-**3** and from negative to positive for γ-**2** and γ-**4** as wavelength changes from a longer to a shorter value. The exciton coupling patterns indicate that the two naphthyl rings are twisted clockwise (*R*-helicity) for γ-**1** and γ-**3** and counterclockwise (*S*-helicity) for γ-**2** and γ-**4**.[25] This asymmetric twisting occurring in the chiral γ-CD framework suggests that the two naphthyl moieties are rigidly oriented in the γ-CD cavity. The intensities of the exciton coupling bands of these hosts decreased upon binding a guest molecule of (−)-borneol (**5**), except for γ-**1**, which exhibited limited ICD variations. On the other hand, few guest-induced UV absorption variations of these hosts were observed. The guest-induced weakening of the ICD intensities suqqests that the location of the naphthyl moieties changes from inside to outside of the host cavity in order to accommodate the guest molecule in the cavities.

Fluorescence Spectra. Figure 2 shows fluorescence spectra of γ-**1**–γ-**4** in a 10 vol% ethylene glycol aqueous solution together with the spectra in the presence of cyclododecanol (**7**) as a guest. The spectrum of γ-**1** is mainly composed of monomer emission with a peak around 355 nm, indicating that, in spite of their proximal location along the rim of CD, it is difficult for the two naphthyl rings in γ-**1**

Table 1. Guest-Induced Intensity Variations of Monomer and Excimer Emissions of γ-**1**, γ-**2**, γ-**3**, and γ-**4** at 25 °C

Guest	Guest concn	$\Delta I_m/I_m^\circ$				$\Delta I_{ex}/I_{ex}^\circ$			
	mM	γ-**1**	γ-**2**	γ-**3**	γ-**4**	γ-**1**	γ-**2**	γ-**3**	γ-**4**
(−)-Borneol (**5**)	0.1	−0.02	−0.10	−0.03	0.0	0.0	0.09	0.14	0.02
	0.2	−0.04	−0.15	−0.03	0.04	−0.08	0.13	0.20	0.04
	2.0	−0.17	−0.32	−0.14	0.16	−0.02	0.33	0.74	0.32
Cyclohexanol (**6**)	0.2	0.01	−0.03	0.0	0.0	0.0	−0.02	0.0	0.0
	2.0	0.01	−0.04	0.0	0.0	0.0	0.0	0.03	0.0
	50	0.01	−0.18	−0.04	0.12	0.0	0.22	0.41	0.02
	100	−0.01	−0.20	−0.04	0.18	0.0	0.29	0.54	0.04
Cyclododecanol (**7**)	0.2	−0.16	−0.47	−0.37	−0.09	0.04	0.65	0.91	0.10
1-ACA (**8**)[a)]	0.2	−0.06	−0.12	−0.02	0.05	−0.04	0.12	0.21	0.08
Geraniol (**9**)	2.0	−0.20	−0.29	−0.17	−0.10	−0.20	−0.09	0.0	−0.06
Nerol (**10**)	2.0	−0.26	−0.34	−0.25	−0.16	−0.22	−0.07	−0.03	−0.10
(−)-Menthol (**11**)	2.0	−0.05	−0.14	−0.05	0.03	0.0	0.24	0.24	0.04
Cholic acid (**12**)	0.2	−0.06	−0.29	−0.17	0.07	−0.04	0.56	0.83	−0.11
Deoxycholic acid (**13**)	0.2	−0.15	−0.30	−0.21	0.04	−0.04	0.49	0.83	−0.15
Chenodeoxycholic acid (**14**)	0.2	−0.21	−0.09	0.12	0.43	−0.12	0.13	0.47	−0.23
Ursodeoxycholic acid (**15**)	0.2	−0.25	0.02	0.53	0.98	−0.17	−0.06	0.08	−0.19

a) 1-Adamantanecarboxylic acid.

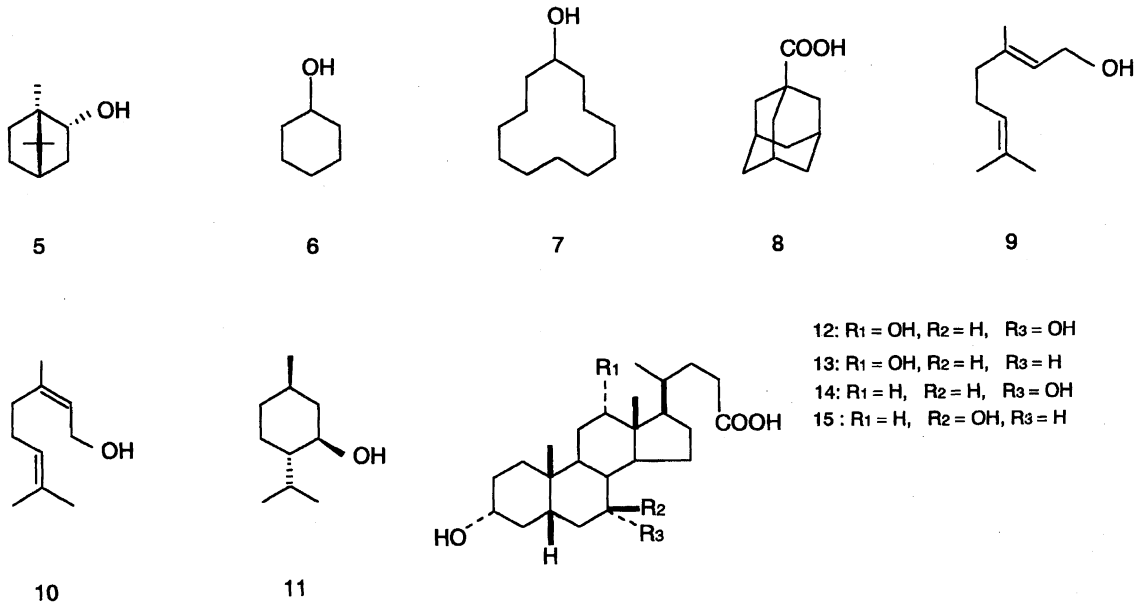

Chart 2.

to be the face-to-face orientation that is needed for excimer formation. In contrast to γ-**1**, the spectra of γ-**2**, γ-**3**, and γ-**4** exhibit a strong excimer emission around 410 nm. To clarify which the excimer emission is derived from intramolecular or intermolecular excimer formation, the intensity ratios of the excimer at 410 nm and monomer emission at 355 nm, I_{ex}/I_m, of γ-**4** at the concentrations of 2×10^{-7}, 2×10^{-6}, 2×10^{-5}, and 1×10^{-4}, M are studied. The ratios are obtained as the same. This fact means that there is no intermolecular 1 : 1 complex of γ-**4** at low or high concentration examined. The I_{ex}/I_m may be used as a parameter which reflects the tendency of each host to form an excimer. The ratios are in the order γ-**4** > γ-**3** > γ-**2** > γ-**1**, and consequently the face-to-face orientation of the naphthyl rings is most easily attained in γ-**4** (Fig. 3-A). The excimer intensity ratios of γ-**2** and γ-**3** were smaller than the ratio of γ-**4**, but the excimer emission was enhanced by the presence of **7**. This guest-induced enhancement may be caused by the conformational changes induced by accommodation of the guest in the cavities of γ-**2** and γ-**3**. Since the naphthyl moieties in the complexes of these hosts are probably located outside the cavity (Fig. 3-B), they can move more freely than in the interior of the cavity, this situation will result in the facilitated excimer formation. On the other hand, the excimer intensity ratio of γ-**4** slightly decreased due to the presence of **7**. This observation indicates that the orientation between the two naphthyl moieties of γ-**4**, which is most favorable for excimer formation among these hosts γ-**1**–γ-**4**, does not work effectively to make a host–guest complexation between γ-**4** and **7**.

Sensitivity and Selectivity. Since the fluorescence in-

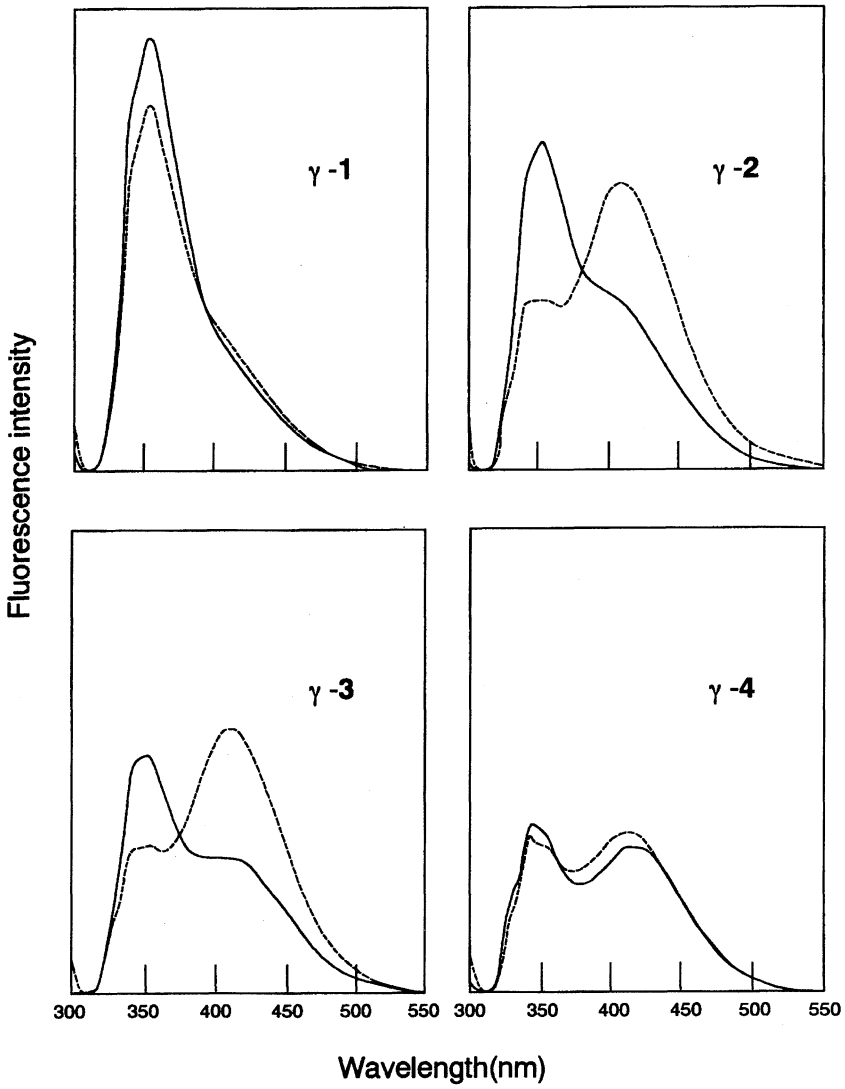

Fig. 2. Fluorescence spectra of γ-**1**, γ-**2**, γ-**3**, and γ-**4** alone (0.02 mM, ——) or in the presence of cyclododecanol (0.2 mM, - - -) in a 10 vol% ethylene glycol aqueous solution.

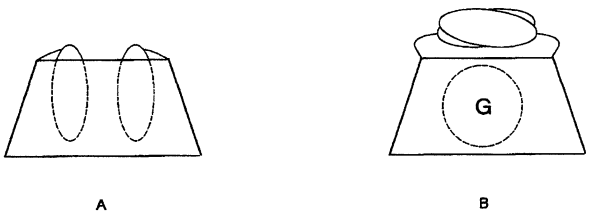

Fig. 3. Schematic representation of intramolecular (A) and intermolecular (B) complexes of γ-**1**–γ-**4**.

tensities of modified CDs are affected by the presence of guest molecules, they can be used as fluorescence sensors of molecules. Their sensing abilities for each guest molecule were evaluated by $\Delta I_m/I_m^\circ$ and $\Delta I_{ex}/I_{ex}^\circ$, where $\Delta I_m = I_m - I_m^\circ$, $\Delta I_{ex} = I_{ex} - I_{ex}^\circ$, and I_m° and I_m are intensities of the monomer emission around 355 nm of each host, alone and in the presence of guest, respectively, and I_{ex}° and I_{ex} are intensities of the excimer emission around 410 nm and abbreviated in the same manner as in the case of I_m. The data for eleven guests compounds were obtained at the guest concentration of 0.2 mM (**5**—**8**, **12**—**15**) and 2 mM (**9**—**11**), and are summarized in Table 1. Some of the results are shown in Figs. 4 and 5. Figure 4 shows the data of (−)-borneol (**5**), cyclohexanol (**6**), cyclododecanol (**7**), 1-adamantanecarboxylic acid (**8**), geraniol (**9**), nerol (**10**), and (−)-menthol (**11**). Compound **7** gave a typical response pattern of the hosts where excimer emission intensities were enhanced while monomer emission ones were depressed, demonstrating a complementary relationship between the excimer and the monomer emission intensities. Similar fluorescence behavior can also be seen to some extent except for open chain alcohols **9** and **10**, which exhibit depression both in excimer and monomer emission intensities. The exceptional behavior in the guest responsive fluorescence variation suggests that there exists a conformational change which is different from that shown in Fig. 3-A. One possible explanation for the fluorescence behavior of **9** and **10** is that each of the guests is included in the cavity together with one of the naphthyl moieties. This argument might be related to the fact that the geometrical discrimination of the hosts for the *trans* and *cis* guests was

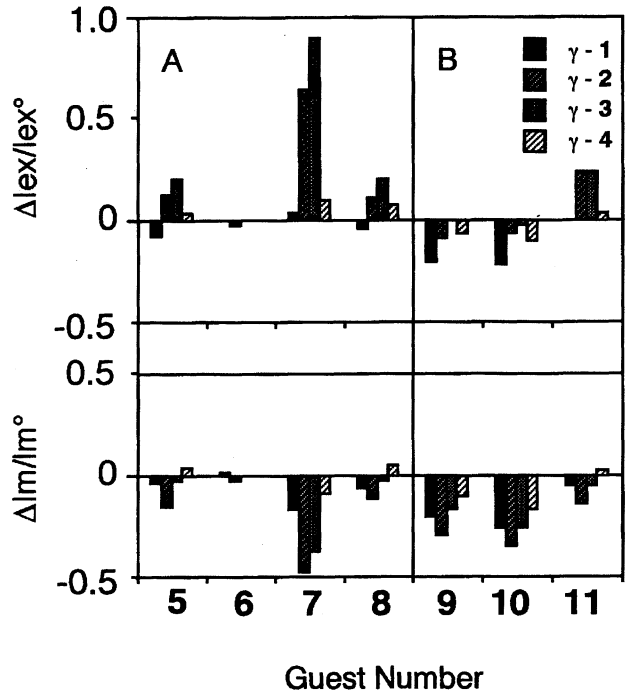

Fig. 4. Guest-induced variations of the excimer and monomer emission intensities of γ-**1**, γ-**2**, γ-**3**, and γ-**4** in a 10 vol% ethylene glycol aqueous solution for organic compounds **5**—**11** (A, 0.2 mM; B, 2.0 mM).

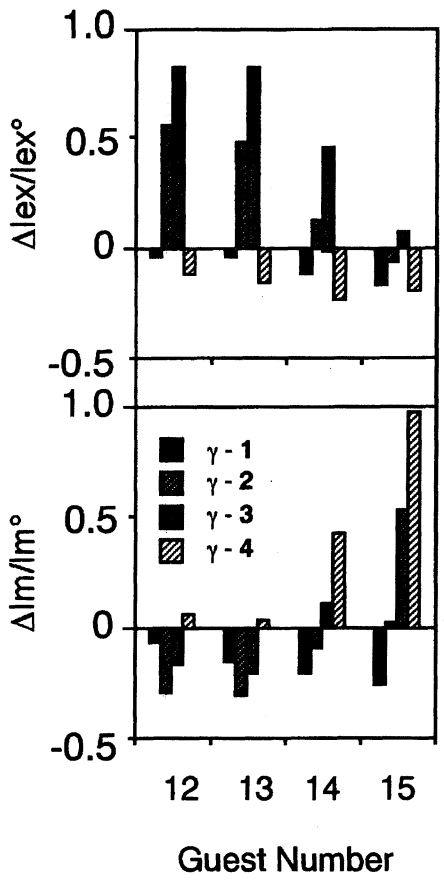

Fig. 5. Guest-induced variations of the excimer and monomer emission intensities of γ-**1**, γ-**2**, γ-**3**, and γ-**4** in a 10 vol% ethylene glycol aqueous solution for **12**—**15** (0.2 mM).

not appreciable. In contrast to **9** and **10**, which give negative values both in $\Delta I_{ex}/I^{\circ}_{ex}$ and $\Delta I_m/I^{\circ}_m$, **11** exhibits a response pattern similar to that of **5** and **7** with a rough complementary relationship between the monomer and excimer emission intensities. When we use the values of $\Delta I_{ex}/I^{\circ}_{ex}$ and $\Delta I_m/I^{\circ}_m$ as the sensitivity factors, the order of the sensitivities of γ-**1**, γ-**2**, and γ-**3** for three alcohols **5**, **6**, and **7** was $\mathbf{6} < \mathbf{5} < \mathbf{7}$. These results can suggest that the size of **7** is more suitable to be included in the γ-CD cavity of the hosts than those of **5** and **6**. For derivatives bearing two 2-naphthythio moieties where each naphthalene ring is more closely connected to γ-CD framework than in the present systems, the same order of the sensitivities was observed.[8] The results suggest that the selectivity for guests is hardly affected by the length of the linkage between the chromophore and γ-CD. Figure 5 shows the sensitivity data for cholic acid (**12**), deoxycholic acid (**13**), chenodeoxycholic acid (**14**), and ursodeoxycholic acid (**15**). Compounds **14** and **15** are isomers with the difference in stereochemistry of the hydroxyl at C-7, and **13** is the regioisomer of **14** and **15** with one hydroxyl at C-12 in place of C-7 of **14** and **15**. It is interesting that γ-**3** and γ-**4** give positive $\Delta I_m/I^{\circ}_m$ values with remarkable intensities for **14** and **15**, in spite of the fact that the $\Delta I_m/I^{\circ}_m$ values are negative or close to zero in almost all cases including **5**—**13**. The unique fluorescence behavior of γ-**3** and γ-**4** might be related to the partial inclusion of **14** and **15**, which probably occurs from the wider secondary hydroxyl side of CD and permits the insertion of naphthyl moieties into the cavities with an orientation unsuitable for excimer formation. It is another important fact that the response patterns of γ-**1**, γ-**2**, γ-**3**, and γ-**4** as shown by $\Delta I_{ex}/I^{\circ}_{ex}$ and $\Delta I_m/I^{\circ}_m$ are different for each steroid. If we use the patterns, it might be possible to attribute a given pattern to a steroid. Among the complicated response features, it is noted that the sensitivity factors of γ-**2** and γ-**3** as shown by $\Delta I_{ex}/I^{\circ}_{ex}$ are $\mathbf{15} < \mathbf{14} < \mathbf{12} = \mathbf{13}$ while those of γ-**3** and γ-**4** as shown by $\Delta I_m/I^{\circ}_m$ are rather opposite, with the values in order of $\mathbf{12} = \mathbf{13} < \mathbf{14} < \mathbf{15}$. Consequently, in the present systems, the use of both factors of $\Delta I_{ex}/I^{\circ}_{ex}$ and $\Delta I_m/I^{\circ}_m$ may lead to deeper insight into the chemical structures of the guest species, and molecular recognition for steroids was reflected in the response patterns as well as in the values of the sensitivity factors.

Response Ranges. Figure 6 shows response curves of γ-**1**, γ-**2**, γ-**3**, and γ-**4** for **5**, **6**, and **12**. Since these guests were detected with remarkably different responses by the hosts both in $\Delta I_{ex}/I^{\circ}_{ex}$ and $\Delta I_m/I^{\circ}_m$ with the order of $\mathbf{6} < \mathbf{5} < \mathbf{12}$, they are expected to have different response ranges when the guest concentrations are varied. Although γ-**1** and γ-**4** give no clear concentration dependency for the guests, γ-**2** and γ-**3** show distinctly different curves, reflecting the sensitivities of the systems for the guests with response range of 10^{-5}—10^{-4} M, 10^{-4}—10^{-3} M, and above 10^{-3} M for **12**, **5**, and **6**, respectively.

Binding Constants. The binding constants of γ-**1**,

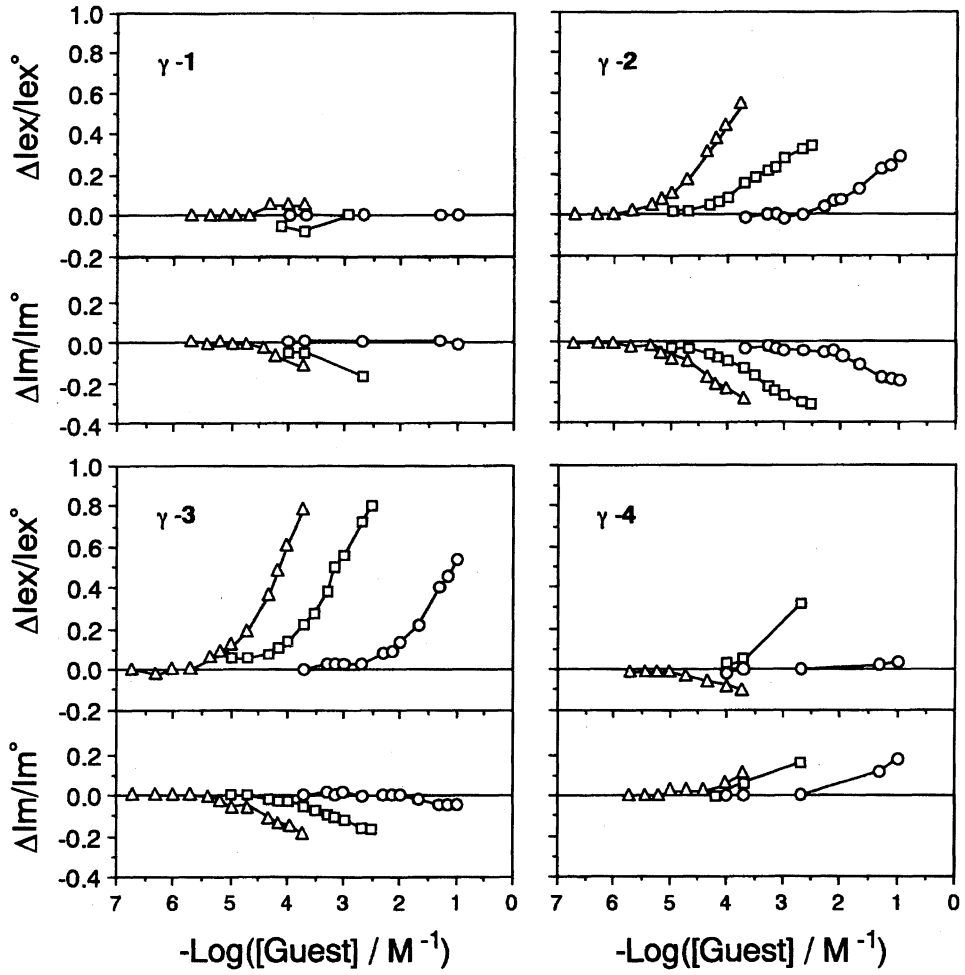

Fig. 6. Fluorescence variations of γ-**1**, γ-**2**, γ-**3**, and γ-**4** for cyclohexanol (○), (−)-borneol (□), and cholic acid (△) as a function of guest concentration.

γ-**2**, γ-**3**, and γ-**4** for several guests were obtained to examine the correlation between the fluorescence variations and the binding abilities of the hosts. The results are shown in Table 2. The binding constants are in the orders **5** < **8** < **7** for γ-**1** and γ-**2** and **8** < **5** < **7** for γ-**3** and γ-**4**, the roughly parallel with the sensitivity factors. In contrast, the order of the binding constants of each host for steroidal compounds is neither parallel with the order of the sensitivity factor of $\Delta I_{ex}/I^{\circ}_{ex}$ nor with that of $\Delta I_{m}/I^{\circ}_{m}$. This means that the sensitivity value gives a relative, but not an absolute, measure of the sensing ability.

Pattern Recognition of Organic Compounds. We have previously reported sensor abilities of β-**1**, β-**2**, and β-**3**,[7,11] which have 2-naphthylsulfonyl moieties at AB, AC, and AD glucose units of β-CD, respectively (Chart 3). They undergo a guest-induced conformational change from intramolecular complexes, in which one naphthyl moiety is included in the cavity, to intermolecular complexes, in which two naphthyl

Table 2. Binding Constants for Guests in a 10% Ethylene Glycol Aqueous Solution at 25 °C[a)]

	K/M^{-1}			
Guest	γ-**1**	γ-**2**	γ-**3**	γ-**4**
5	1960	2660	1210	1770
7	62100	21800	19500	31000
8	3270	4020	649	568
12	b)	13600	9100	18300
13	b)	25200	26400	b)
14	b)	27100	7300	370
15	b)	b)	7000	13400

a) Determined by circulardichroism for **5**, **7**, and **8**, or by fluorescence variations for **12**, **13**, **14**, and **15**.
b) Values were not accurately determined because of the small fluorescence variations.

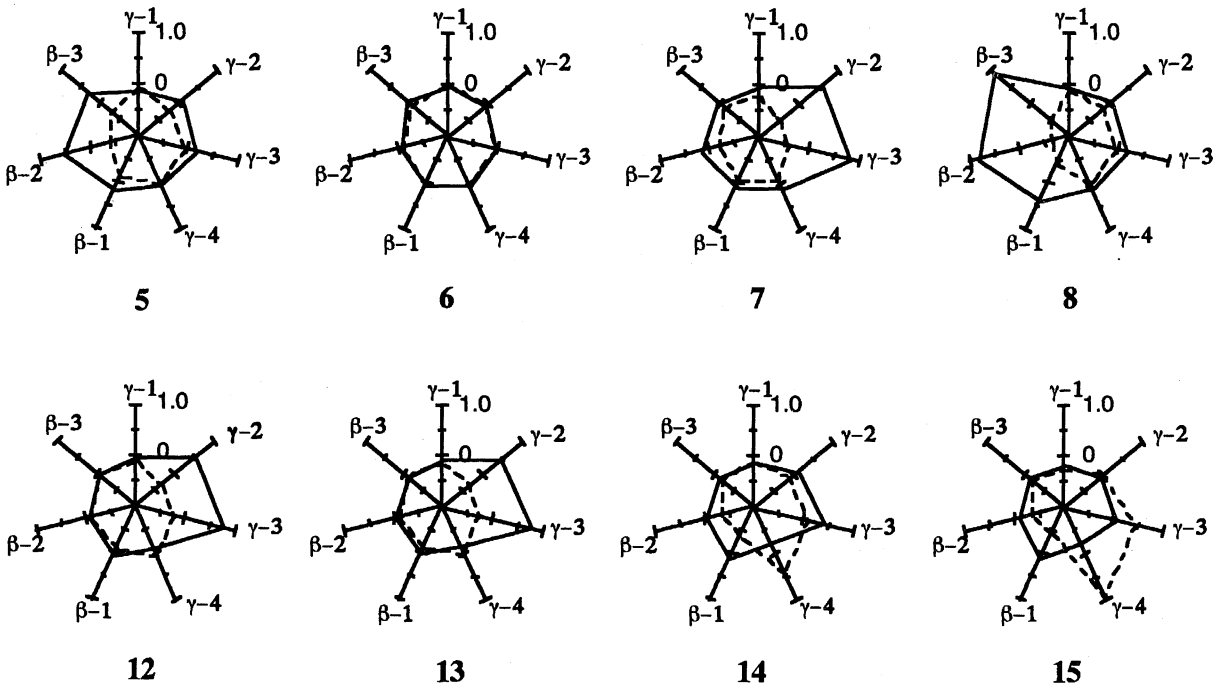

Fig. 7. Variations of excimer (—) and monomer (- - -) emissions of the seven hosts (0.02 mM) induced by various organic guests (0.2 mM).

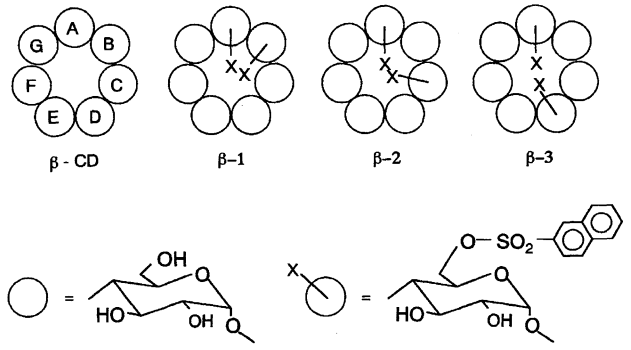

Chart 3.

moieties are excluded from the cavity to form excimers. It is interesting to examine the responses of the seven hosts for each guest compound. Figure 7 shows both $\Delta I_{ex}/I^{\circ}_{ex}$ (solid line) and $\Delta I_{m}/I^{\circ}_{m}$ (broken line) of the seven hosts for each guest at the guest concentration of 0.2 mM. In this presentation, **6**, whose responses are small or negligible, exhibits a symmetrical heptagon and the solid and the broken lines are almost overlapped near the zero value. However, other guests such as **5**, **7** and **8** give expanded solid lines and shrunken broken lines with distorted shapes of the heptagon. In the case of steroidal compounds, the expansion of the solid line toward β-CD derivatives is small while the expansion of the solid line toward γ-**3** is remarkable for **12** and **13**. Among all guests examined, the crossings of the solid and broken lines are remarkable for **14** and **15**. These results demonstrate that each guest has its own shapes when the responses of the plural sensors are used and that the shape representation is an indication of molecular recognition of the hosts.

Conclusion

Host γ-**1** exhibits an almost pure monomer fluorescence while γ-**2**, γ-**3**, and γ-**4** exhibit both monomer and excimer emissions. Organic compounds in aqueous solution were selectively detected by variations of guest-responsive monomer and excimer emissions of the hosts. The fluorescent sensory system using the hosts is very convenient and useful to detect organic molecules, because the chemical modifications of a guest, even spectroscopically inert or neutral guests, are not necessary; that is, a guest can be examined directly in the system. The set of seven sensors including three β-CD derivatives of this series from shape-different heptagons for different guests from monomer and excimer responses. Molecular recognition as indicated by such shape representation for the responses of plural sensors might become an important approach to sensing molecules.

The authors would like to thank Nihon Shokuhin Kako Co., Ltd. for a generous gift of γ-cyclodextrin. This work was supported by Grants-in Aid for Scientific Research from Ministry of Education, Science, Sports and Culture.

References

1) A. W. Czarnik, in "Frontiers in Supramolecular Organic Chemistry and Photochemistry," VCH, Weinheim (1991), p. 109.

2) A. Ueno and T. Osa, in "Photochemistry in Organized and Constrained Media," VCH, New York (1991), p. 739.

3) J. Yoon and A. W. Czarnik, *J. Am. Chem. Soc.*, **114**, 5874 (1992).

4) A. Ueno, S. Minato, I. Suzuki, M. Fukushima, M. Ohkubo, T. Osa, F. Hamada, and K. Murai, *Chem. Lett.*, **1990**, 605.

5) A. Ueno, I. Suzuki, and T. Osa, *Anal. Chem.*, **62**, 2461 (1990).
6) S. Minato, T. Osa, and A. Ueno, *J. Chem. Soc., Chem. Commun.*, **1991**, 107.
7) S. Minato, T. Osa, M. Morita, A. Nakamura, H. Ikeda, F. Toda, and A. Ueno, *Photochem. Photobiol.*, **54**, 593 (1991).
8) A. Ueno, S. Minato, and T. Osa, *Anal. Chem.*, **64**, 1154 (1992).
9) A. Ueno, Q. Chen, and T. Osa, *Anal. Chem.*, **64**, 1650 (1992).
10) A. Ueno, T. Kuwabara, A. Nakamura, and F. Toda, *Nature*, **356**, 136 (1992).
11) A. Ueno, S. Minato, and T. Osa, *Anal. Chem.*, **64**, 2562 (1992).
12) F. Hamada, Y. Kondo, R. Ito, I. Suzuki, T. Osa, and A. Ueno, *J. Inclusion Phenom.*, **15**, 273 (1993).
13) F. Hamada, Y. Kondo, K. Ishikawa, H. Ito, I. Suzuki, T. Osa, and A. Ueno, *J. Inclusion Phenom.*, **17**, 267 (1994).
14) F. Hamada, K. Ishikawa, R. Ito, H. Shibuya, I. Suzuki, T. Osa, and A. Ueno, *J. Inclusion Phenom.*, **20**, 43 (1995).
15) F. Hamada, K. Ishikawa, I. Tamura, and A. Ueno, *Anal. Sci.*, **11**, 935 (1995).
16) B. K. Hubbard, L. A. Beilstein, C. E. Heath, and C. J. Abelt, *J. Chem Soc., Perkin Trans. 2*, **1996**, 1005.
17) M. Eddaoudi, H. Parrot-Lopez, S. F. de Lamotte, D. Ficheux, P. Prognon, and A. W. Colemann, *J. Chem Soc., Perkin Trans. 2*, **1996**, 1711.
18) M. L. Bender and M. Komiyama, "Cyclodextrin Chemistry," Springer-Verlag, New York (1977).
19) J. Szejtli, "Cyclodextrin Technology," Kluwer, Dordrecht (1988).
20) A. Ueno, K. Takahashi, and T. Osa, *J. Chem Soc., Chem. Commun.*, **1980**, 921.
21) H. Hirai, N. Toshima, and S. Uenoyama, *Bull. Chem. Soc. Jpn.*, **58**, 1156 (1985).
22) A. Ueno, F. Moriwaki, T. Osa, F. Hamada, and K. Murai, *Bull. Chem. Soc. Jpn.*, **59**, 465 (1986).
23) A. Ueno, F. Moriwaki, A. Azuma, and T. Osa, *J. Org. Chem.*, **54**, 295 (1989).
24) A. Ueno, Y. Tomita, and T. Osa, *Chem. Lett.*, **1983**, 1635.
25) N. Harada and K. Nakanishi, "Circular Dichromic Spectroscopy, Exciton Coupling in Organic Stereochemistry," Tokyo-Kagaku-Dojin, Tokyo (1982).