Molecular Recognition Indicators of Modified Cyclodextrins Using Twisted Intramolecular Charge Transfer Fluorescence

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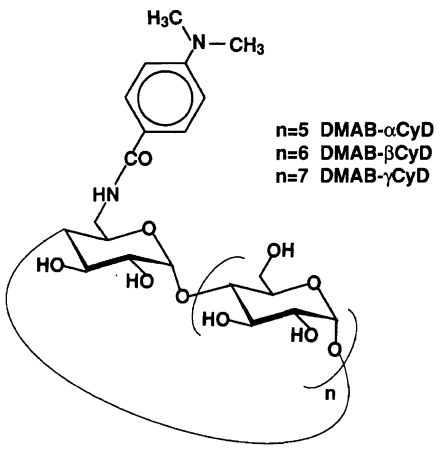
Modified α, β, and γ-cyclodextrins that bear one *p*-(dimethylamino)benzoyl (DMAB) moiety (DMAB-αCyD, DMAB-βCyD, and DMAB-γCyD, respectively) were synthesized as fluometric molecular recognition indicators. These three modified cyclodextrins show dual fluorescence arising from normal planar and twisted intramolecular charge transfer (TICT) excited states. Among them, the TICT emission was particularly great in the case of DMAB-βCyD. The TICT fluorescence intensity increased for DMAB-αCyD and DMAB-γCyD, and decreased for DMAB-βCyD when the hosts form inclusion complexes with guest molecules, and the variation of the TICT emission intensity was used as a sensitivity parameter. DMAB-αCyD was effective to detect chain compounds while DMAB-γCyD showed high sensitivities to bulky compounds including several steroids. Various guest compounds were detected by DMAB-βCyD, The orders of the sensitivities of the hosts were parallel with those of the binding constants except for the case of DMAB-γCyD. The results demonstrate that these fluorescent CyDs are useful as fluorescent indicators of molecular recognition.

Molecular recognition by artificial systems is a great desire of many chemists and has been intensively investigated. During the last two decade, many types of host molecules capable of recognizing molecules have been prepared and reported. Among many of these systems, fluorescent sensors of molecular recognition attract current interest particularly because of their high sensitivity.[1—7] Cyclodextrins (CyDs) are cyclic oligosaccharides which have six or more members of D-(+)-glucopyranose units and they are able to form inclusion complexes with various organic compounds in aqueous solution.[8,9] To detect organic compounds on the basis of this inclusion phenomenon, it is necessary to convert native CyDs to the hosts which have spectroscopic signs in response to the inclusion of guest species by the appropriate modification. Ueno et al. have synthesized chromophore-attached cyclodextrins and have shown that various organic compounds can be detected by using spectral changes of such modified CyDs.[3—7,10—12] With a view of constructing more powerful host–guest sensor systems, we have attempted to use the fluorescence arising from the twisted intramolecular charge transfer (TICT) excited state because of its remarkable property that the TICT emission is strongly affected by environmental polarity, changing its emission intensity and the peak position.[13—16]

p-(Dimethylamino)benzonitrile (DMABN) is a typical compound that is capable of exhibiting TICT fluorescence emission, but the TICT emission is hardly observed in aqueous solution, because the nonradiative decay rate is superior to that of the radiative one.[16] However in the presence of CyDs, DMABN exhibits enhanced TICT emission by forming inclusion complexes with CyDs in aqueous solution and then being located in the hydrophobic interior of the CyD cavity.[17—20] For constructing fluorescent indicators of molecular recognition on this basis, we have synthesized modified α-, β-, and γCyD, all having a *p*-(dimethylamino)benzoyl (DMAB) moiety, abbreviated DMAB-αCyD, DMAB-βCyD, and DMAB-γCyD, respectively (Chart 1), and observed that they actually act as indicators for detecting organic compounds in aqueous solution. Since the TICT emission is very sensitive to environmental polarity,[12—16] it is expected that they recognize not only size and shape but also the dipole or polarity of the guest molecules. It is also expected that the three DMAB-CyDs display characteristic molecular recognition abilities reflecting their different cavity sizes.

Experimental

Materials. α-, β-, and γCyD were kindly donated by Nihon Shokuhin Kako Co., Ltd. Acetonitrile and water which were used for fluorescence measurements as solvents



Mono-6-deoxy
-6-[*p*-(dimethylamino)benzoylamino]cyclodextrin

Chart 1. Structure of DMAB-CyDs.

were fluorescence spectroscopic grade of Cica Merck. All guest compounds were commercially guaranteed reagents.

Synthesis. DMAB-CyDs were synthesized by the reaction of 6-mono-deoxy-6-amino-α-, β-, or γ-cyclodextrin and *p*-(dimethylamino)benzoic acid in *N*,*N*-dimethylformamide below 0 °C in the presence of *N*,*N*-dicyclohexylcarbodiimide. The details were described in our previous paper.[21]

Measurements. Absorption, fluorescence, and circular dichroism spectra were measured by a Shimadzu UV3100 spectrophotometer, a Hitachi 850 spectrofluorometer, and a JASCO J-600 spectropolarimeter, respectively. The excitation wavelength was always 310 nm for fluorescence measurements.

Results and Discussion

Sensing Mechanism of Three Types of TICT-Fluorescent Cyclodextrins. Figures 1a and 1b show the fluorescence and circular dichroism (CD) spectra of DMAB-αCyD, host alone and in the presence of 2.5×10^{-3} mol dm^{-3} of 1-pentanol as a guest. DMAB-αCyD could not include its DMAB moiety in the cavity because of its narrow cavity size and the rigidity of the amide bond that links the DMAB moiety to αCyD. But, upon guest addition, the normal planar (NP) emission intensity decreased while TICT emission intensity increased. The results indicate that environmental polarity around the DMAB moiety was changed by forming an intermolecular inclusion complex with the guest molecule. Water molecules around the DMAB moiety are likely to be removed when the guest is included, thus resulting in the decrease of the environmental polarity around the DMAB moiety that may arise from the contact of the hydrophobic surface of the guest with the DMAB moiety. The guest addition also caused an increase of the intensity of the CD band. In this case, the DMAB moiety acts as a cap near the rim of the αCyD (Fig. 4, (1)).

Figure 2a shows the fluorescence spectra of DMAB-βCyD, host alone and in the presence of 2.5×10^{-5} mol dm^{-3} of *l*-borneol as a guest. The TICT emission of DMAB-βCyD is very strong and its peak position shifts by 45 nm to shorter wavelength region than other two hosts. This observation suggests that the DMAB moiety of DMAB-βCyD exists in a more hydrophobic environment than that of the others. The marked decrease in the TICT emission intensity induced by *l*-borneol suggests that the environment around the DMAB moiety of the host changes associated with complexation between the host and the guest. In this context, we measured CD spectra to study the structure of this host and the complex. Figure 2b shows the CD spectra of DMAB-βCyD. The host exhibits a CD pattern with positive and negative bands around 310 nm and changes it to a simple negative one upon guest binding. The CD pattern with a pair of negative and positive bands suggests the existence of conformational isomers and the change to the simple negative CD pattern may reflect the fact that the DMAB moiety of DMAB-βCyD is excluded from inside to outside of the cavity by forming an intermolecular inclusion complex with the guest molecule (Fig. 4, (2)). Therefore, an induced-fit type of guest binding[22] occurs in this case and it is confirmed that DMAB-βCyD decreases the TICT emission, changing the environment around the DMAB moiety from the hydrophobic interior to the polar water environment. The details of the conformational features of DMAB-βCyD were described in our previous paper.[21]

Figure 3a shows the fluorescence spectra of DMAB-γCyD, host alone and in the presence of cyclododecanol as a guest. Although γCyD has a cavity that is large enough to include the DMAB moiety, the enhancement of the TICT emission of DMAB-γCyD is limited. Figure 3b shows the CD spectra of DMAB-γCyD, host alone and in the presence of cyclododecanol. The simple negative CD pattern of DMAB-γCyD suggests that DMAB-γCyD does not include its DMAB moiety tightly in its cavity. These result indicate that the cavity of γCyD is too large to form a stable intramolecular inclusion complex. However, both the NP and the TICT emission of DMAB-γCyD are enhanced while that of the CD intensity diminished with increasing concentration of the guest. These results suggest that the DMAB moiety may act as a spacer or a cap[23] in the complexes depending on the affinity of the guest species (Fig. 4, (3)). In such inclusion compounds, the hydrophobic nature of the environment around the DMAB moiety may be enhanced by inclusion of the guest molecule, leading to the enhanced emission intensities.

Fluorescent Indicators of Molecular Recognition. The value of $\Delta I/I^\circ$ was used as the measure of the sensitivity of DMAB-CyDs, where $\Delta I = I - I^\circ$, and I and I° are the emission intensities in the presence and the absence of a guest, both being used with subscripts NP and TICT as shown by I_{NP} and I_{TICT} for the NP and TICT emission intensities, respectively. Binding constants of DMAB-CyDs for various guest compounds were obtained from guest-induced emission variations by the least-square curve fitting analysis[24,25] done with a Benesi–Hildebrand type equation[26] of 1 : 1 host : guest stoichiometry (Chart 2). In any case, experimental data coincide with the theoretical curve finely, confirming that DMAB-CyDs form complexes with 1 : 1 stoichiometry.

Detection of Acyclic Compounds. αCyD is an appropriate host for the acyclic compounds. Previously, it was shown that linear aliphatic alcohols form inclusion complexes with αCyD.[27—29] To test the sensitivities of DMAB-αCyD, we selected seven alcohols which have linear or branched structures. When 1-pentanol was added to the aqueous solution of DMAB-αCyD, the NP emission intensity diminished while that of the TICT emission increased. DMAB-αCyD shows higher sensitivities for linear alcohols and larger binding constants than for correspond-

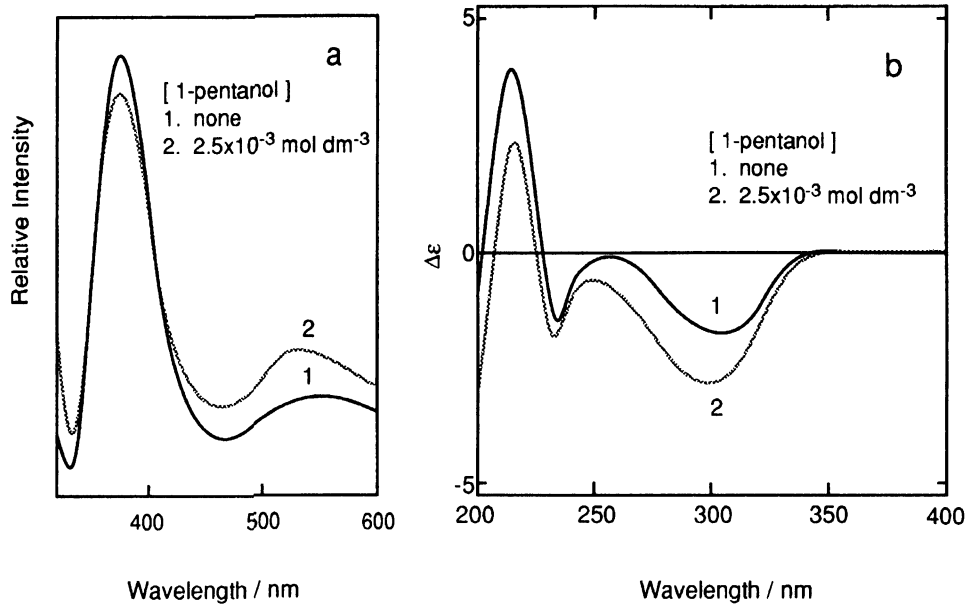


Fig. 1. Fluorescence spectra (a) and CD spectra (b) of DMAB-αCyD (2.5×10^{-5} mol dm^{-3}), respectively in aqueous solution, alone and in the presence of 1-pentanol (2.5×10^{-3} mol dm^{-3}).

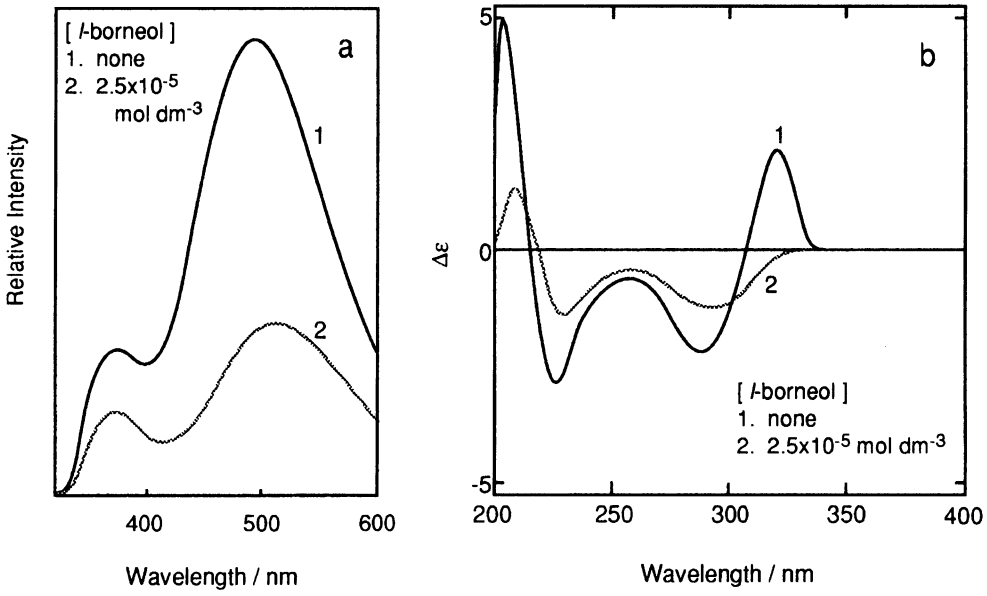


Fig. 2. Fluorescence spectra (a) and CD spectra (b) of DMAB-βCyD (2.5×10^{-5} mol dm^{-3}), respectively in aqueous solution, alone and in the presence of *l*-borneol (2.5×10^{-5} mol dm^{-3}).

ing branched ones (Table 1). We can discriminate alcohols by using both parameters of $\Delta I_{NP}/I^{\circ}_{NP}$ and $\Delta I_{TICT}/I^{\circ}_{TICT}$. For example, 2-methyl-1-propanol (isobutyl alcohol) and 1-hexanol gives the same value of $\Delta I_{TICT}/I^{\circ}_{TICT}$ (0.056) but their value of $\Delta I_{NP}/I^{\circ}_{NP}$ are different (−0.014 and −0.108 for 2-methyl-1-propanol and 1-hexanol, respectively). The absolute values of the sensitivity parameters ($\Delta I_{NP}/I^{\circ}_{NP}$ and $\Delta I_{TICT}/I^{\circ}_{TICT}$) of DMAB-$\alpha$CyD for alcohols which has the same carbon number, are in the orders of 1-butanol > 2-methyl-1-propanol > 2-methyl-2-propanol (*t*-butyl alcohol), and 1-pentanol > 3-methyl-1-butanol (isopentyl alcohol) > 2-methyl-2-butanol (*t*-pentyl alcohol) and the order of the binding constants is paralleled to that of the sensitivity parameters. These results suggest that linear alcohols are included in the cavity of αCyD more easily than branched ones and exhibit marked fluorescence variations. For linear alcohols, the orders of the binding constants and $\Delta I_{NP}/I^{\circ}_{NP}$ are 1-hexanol > 1-pentanol > 1-butanol while that of $\Delta I_{TICT}/I^{\circ}_{TICT}$ is 1-pentanol > 1-butanol > 1-hexanol. This inconsistency may be related to the fact that 1-butanol and 1-pentanol are straight in the cavity of αCyD while 1-hexanol changes its conformation to fit the cavity.[28]

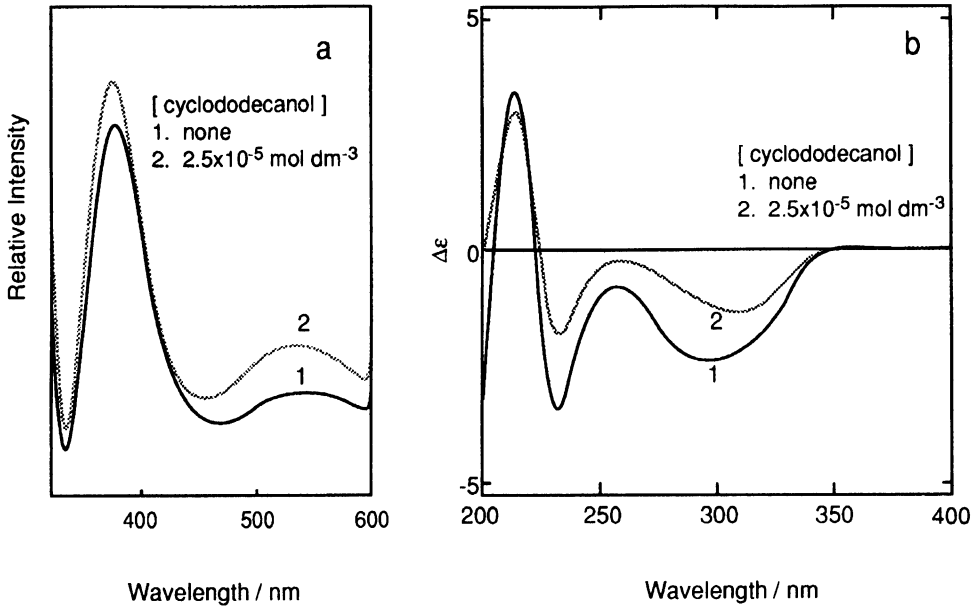


Fig. 3. Fluorescence spectra (a) and CD spectra (b) of DMAB-γCyD (2.5×10^{-5} mol dm^{-3}) in aqueous solution, alone and in the presence of cyclododecanol (2.5×10^{-5} mol dm^{-3}).

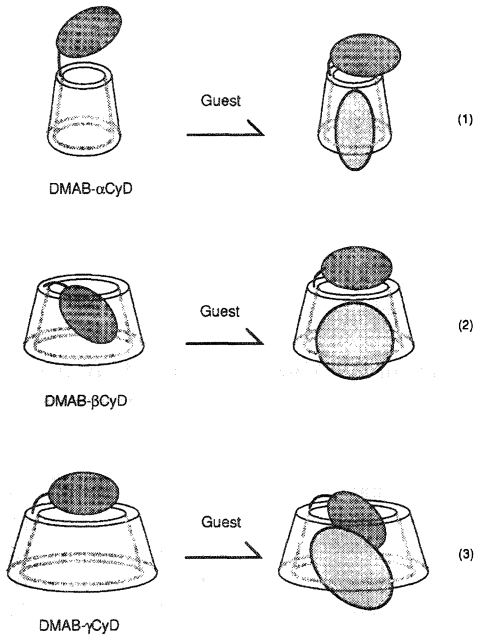


Fig. 4. Schematic illustration for three types of induced-fit guest binding of DMAB-CyDs.

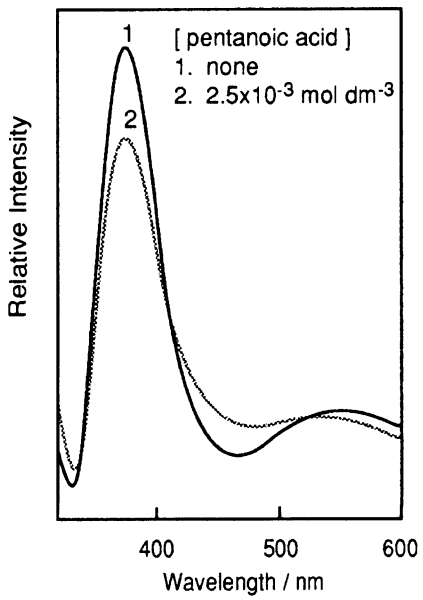


Fig. 5. Fluorescence spectra of DMAB-αCyD (2.5×10^{-5} mol dm^{-3}) in aqueous solution, alone and in the presence of 1-pentanoic acid (2.5×10^{-3} mol dm^{-3}).

In connection with the reported result that αCyD also forms inclusion complexes with linear aliphatic carboxylic acids,[30] we have examined the sensitivities of DMAB-αCyD for six aliphatic carboxylic acids. Figure 5 shows the fluorescence emission spectra of DMAB-αCyD alone and in the presence of 2.5×10^{-3} M of 1-pentanoic acid. In this case, the NP emission diminished while the TICT emission was shifted to a shorter wavelength by addition of pentanoic acid (valeric acid). This result indicates that the environmental polarity around the DMAB moiety was reduced by the guest. This assertion is consistent with the previous argument that the TICT emission shifts toward longer wavelengths with increasing solvent polarity.[14—16] Similarly to the cases of alcohols, linear carboxylic acids decrease the absolute value of $\Delta I_{NP}/I^{\circ}_{NP}$ and the binding constants are greater than for branched ones. For carboxylic acids with the same carbon number, the absolute values of $\Delta I_{NP}/I^{\circ}_{NP}$ are in the order pentanoic acid (valeric acid) > 3-methylbutanoic acid (isovaleric

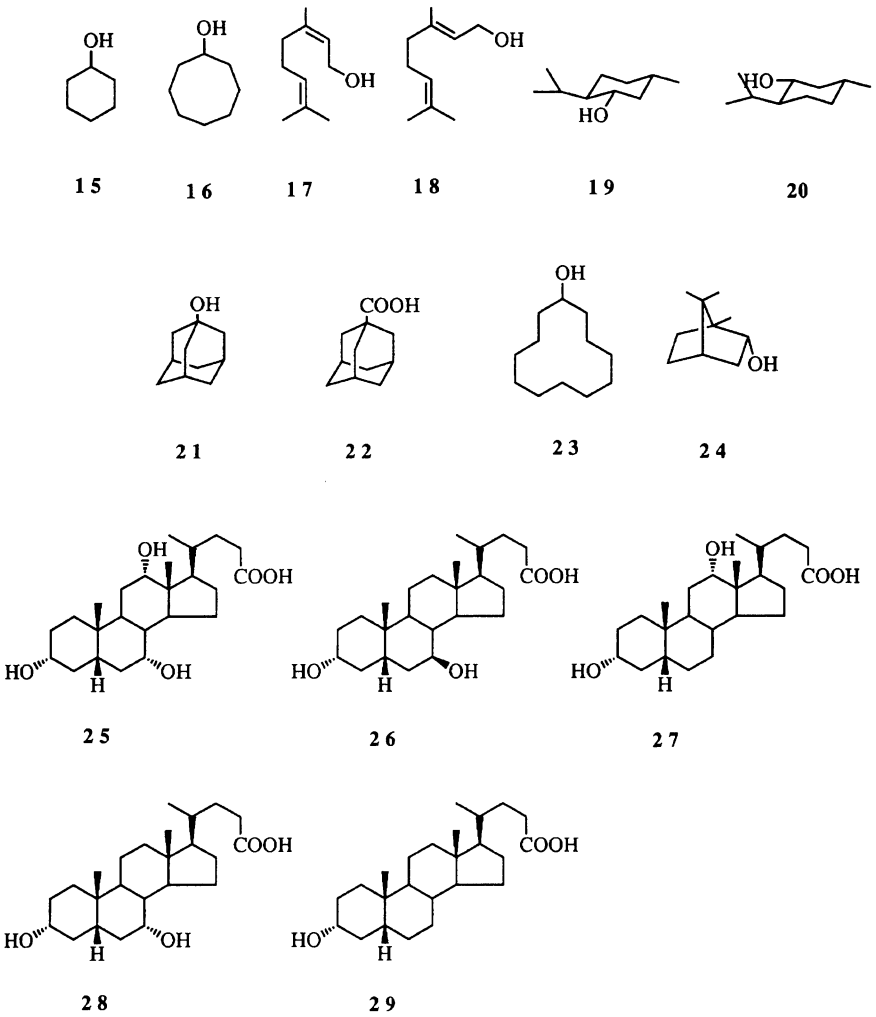


Chart 2. Structures of guest compounds.

Table 1. Guest-Induced Emission Variations and Binding Constants of DMAB-αCyD and DMAB-βCyD

Carbon number	Guest	DMAB-αCyD			DMAB-βCyD	
		$\Delta I_{NP}/I^{\circ}_{NP}$	$\Delta I_{TICT}/I^{\circ}_{TICT}$	K ($mol^{-1}\,dm^3$)	$\Delta I_{TICT}/I^{\circ}_{TICT}$	K ($mol^{-1}\,dm^3$)
4	1-Butanol (**1**)	−0.027	0.111	300	−0.105	56
	2-Methyl-1-propanol (**2**)	−0.014	0.056	—[b]	−0.210	110
	2-Methyl-2-propanol (**3**)	0.000	0.000	—[b]	−0.243	150
5	1-Pentanol (**4**)	−0.081	0.167	600	−0.195	100
	3-Methyl-1-butanol (**5**)	−0.027	0.111	250	−0.324	250
	2-Methyl-2-butanol (**6**)	−0.014	0.000	—[b]	−0.343	280
6	1-Hexanol (**7**)	−0.108	0.056	810	−0.433	320
4	Butanoic acid (**8**)	−0.095	—[a]	270	−0.305	130
	2-Methylpropanoic acid (**9**)	−0.068	—[a]	180	−0.316	150
5	Pentanoic acid (**11**)	−0.122	—[a]	340	−0.376	260
	3-Methylbutanoic acid (**12**)	−0.068	—[a]	220	−0.552	560
	2,2-Dimethylpropanoic acid (**13**)	−0.041	—[a]	200	−0.843	4000
6	Hexanoic acid (**14**)	−0.149	—[a]	520	−0.533	500

a) Emission maximum of the DMAB-αCyD shifted to shorter wavelengths but the value of $\Delta I_{TICT}/I^{\circ}_{TICT}$ is too small to be measured correctly. b) The guest-induced variation in the emission is too small to give correct binding constants. Host concentration: 2.5×10^{-5} mol dm^{-3}, All guest concentration: 2.5×10^{-3} mol dm^{-3}, Temperature: 25 °C.

acid) >2,2-dimethylpropanoic acid (pivalic acid). This order is consistent with that of the binding constants. On the other hand, for linear acids with different carbon numbers, the absolute values of $\Delta I_{NP}/I^{\circ}_{NP}$ and the binding constants are in the order hexanoic acid>pentanoic acid>butanoic acid. There is a great difference between

the alcohols and the carboxylic acids as shown by the fact that the host gave larger binding constants for carboxylic acids than for the corresponding alcohols, for example, the host gave binding constants 100 and 260 $mol^{-1}\,dm^3$ for 1-pentanol and pentanoic acid, respectively, while it gave a smaller sensitivity for the carboxylic acid than for the alcohol as measured by TICT emission. Although the reason for this difference is not clear, the results indicate that in the case of carboxylic acids the NP emission of DMAB-αCyD is more useful than the TICT one for the purpose of molecular sensing.

Chain compounds can also be discriminated by DMAB-βCyD. In contrast to the case of DMAB-αCyD, DMAB-βCyD showed high sensitivities and gave large binding constants for branched compounds (Table 1). Figure 6 show the fluorescent titration curves of DMAB-αCyD and DMAB-βCyD as a function of 1-pentanol (**1**) or 2-methyl-1-propanol (**2**) concentration. It is obvious that 1-pentanol causes larger changes in the emission spectrum of DMAB-αCyD than isopentyl alcohol. In the case of DMAB-βCyD, the vlaues of $\Delta I_{TICT}/I^{\circ}_{TICT}$ for alcohols that have five carbons are in the order 2-methyl-2-butanol (**6**) > 2-methyl-1-butanol (**5**) >1-pentanol (**4**). Conversely, in the case of DMAB-αCyD, both absolute values of $\Delta I_{NP}/I^{\circ}_{NP}$ and $\Delta I_{TICT}/I^{\circ}_{TICT}$ are in the reverse order. These results may be explained by the fact that ball-like compounds are more favorable to be included in the cavity of βCyD. Similarly to the case of the alcohols, aliphatic acids have the same tendency, that is, the absolute $\Delta I_{TICT}/I^{\circ}_{TICT}$ values of DMAB-βCyD for aliphatic acids with five carbons are in the order of 2,

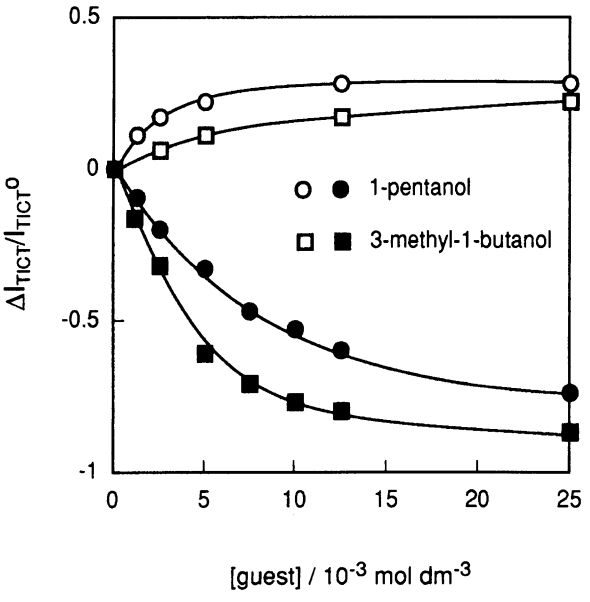


Fig. 6. Fluorescent titration curves of DMAB-αCyD (○, □) and DMAB-βCyD (●, ■) (2.5×10^{-5} mol dm^{-3}) as a function of the concentration of 1-pentanol (○, ●) or 3-methyl-1-butanol (□, ■).

2-dimethylpropanoic acid (**13**) >3-methylbutanoic acid (**12**) >pentanoic acid (**11**), but the absolute $\Delta I_{NP}/I^{\circ}_{NP}$ values of DMAB-αCyD are in the reverse order. The order of the binding constants are always paralleled to those of fluorescence responses. All these results suggest that DMAB-αCyD and DMAB-βCyD are sensitive to the size or shape of the guests.

Detection of Cyclic Compounds. The cavity size of αCyD is too small to penetrate cyclic compounds and DMAB-αCyD showed no response to cyclic compounds, so we used DMAB-βCyD and DMAB-γCyD for detection of cyclic compounds. We have selected fifteen compounds as guests in order to test the sensitivities of DMAB-βCyD and DMAB-γCyD. It is noted that the sensitivity parameter of $\Delta I_{TICT}/I^{\circ}_{TICT}$ of DMAB-βCyD is negative because in any case the DMAB moiety of the host is excluded from the cavity by the guest binding while that of DMAB-γCyD is positive in response to the guest-induced enhancement in the TICT. The results are summarized in Table 2. In the case of DMAB-βCyD, all of the guests were detected at the same concentration as that of the host (2.5×10^{-5} mol dm^{-3}) and the orders of sensitivities and binding constants are roughly parallel to each other. Among mono-cyclic alcohols, cyclooctanol (**16**) showed the highest sensitivity and the largest binding constants. The binding constants of DMAB-βCyD for cyclooctanol is 25-fold and 1.8-fold larger than those of cyclohexanol (**15**) and cyclododecanol (**23**), respectively. The result suggests that the size of cyclooctanol is most suitable to the cavity of the βCyD among these three monocyclic alcohols. Nerol (**17**) and geraniol (**18**) are cis and trans isomers, respectively. DMAB-βCyD has a larger absolute value and binding constant for the cis one. DMAB-βCyD shows the highest sensitivity (largest absolute value of $\Delta I_{TICT}/I^{\circ}_{TICT}=-0.93$) and largest binding constant (220000 $mol^{-1}\,dm^3$) for 1-adamantanecarboxylic acid. This guest might form a tight complex with the host because of its ball-like shape and suitable size. *l*-Borneol (**24**) is a bicyclic alcohol that was detected by DMAB-βCyD with higher response and gave larger binding constant than monocyclic alcohols like cyclooctanol. DMAB-βCyD shows chiral discrimination, detecting *l*-menthol (**20**) with 1.4-fold preference than *d*-menthol (**19**). On the other hand, five steroidal compounds were well discriminated by DMAB-βCyD in spite of the fact that they have the same steroidal framework for the major part of the molecules. Although ursodeoxycholic acid (**26**) and chenodeoxycholic acid (**28**) are geometrical isomers having different stereochemistry for the hydroxyl group at C-7, their binding constants were very different, that is, ursodeoxycholic acid has the binding constant of 178000 $mol^{-1}\,dm^3$, which is 3.5-fold larger than that of chenodeoxycholic acid. However, ursodeoxycholic acid was detected with almost the same value of $\Delta I_{TICT}/I^{\circ}_{TICT}$ as that of chenodeoxycholic acid. Deoxycholic acid (**27**), which is another isomer of ursode-

Table 2. Guest-Induced Emission Variations and Binding Constants of DMAB-βCyD and DMAB-γCyD

Guest	DMAB-βCyD		DMAB-γCyD	
	$\Delta I_{TICT}/I^{\circ}_{TICT}$	K ($mol^{-1}\,dm^3$)	$\Delta I_{TICT}/I^{\circ}_{TICT}$	K ($mol^{-1}\,dm^3$)
Cyclohexanol (**15**)	−0.12[a]	2000	—	—
Cyclooctanol (**16**)	−0.33[a]	50000	0.29[c]	200
Nerol (**17**)	−0.17[a]	4000	0.36[c]	600
Geraniol (**18**)	−0.14[a]	3000	0.14[c]	500
d-Menthol (**19**)	−0.25[a]	10000	0.36[b]	840
l-Menthol (**20**)	−0.36[a]	18000	0.36[b]	840
1-Adamantanol (**21**)	−0.84[a]	128000	0.29[b]	6000
1-Adamantancarboxylic acid (**22**)	−0.93[a]	220000	0.43[b]	11000
Cyclododecanol (**23**)	−0.26[a]	28000	0.29[a]	36000
l-Borneol (**24**)	−0.65[a]	59000	0.14[a]	20000
Cholic acid (**25**)	−0.27[a]	27000	0.14[a]	4100
Ursodeoxycholic acid (**26**)	−0.93[a]	178000	0.36[a]	35000
Deoxycholic acid (**27**)	−0.32[a]	47000	0.57[a]	22000
Chenodeoxycholic acid (**28**)	−0.82[a]	51000	0.43[a]	58000
Lithocholic acid (**29**)	−0.83[a]	158000	0.71[a]	84000

Guest concentration: a) 2.5×10^{-5} mol dm^{-3}; b) 2.5×10^{-4} mol dm^{-3}; c) 2.5×10^{-3} mol dm^{-3}. Host concentration: 2.5×10^{-5} mol dm^{-3}, Temperature: 25 °C.

oxycholic acid with the hydroxyl group at C-12 in place of at C-7, was detected with 39% of the sensitivity and 92% of the binding constant of chenodeoxycholic acid. Regardless of the 3.1-fold larger binding constant with compared with that of chenodeoxycholic acid, lithocholic acid (**29**) was detected with almost the same value of $\Delta I_{TICT}/I^{\circ}_{TICT}$. On the other hand, cholic acid (**25**), which has one more hydroxyl group than chenodeoxycholic acid, had 53% of the binding constant and 33% of the $\Delta I_{TICT}/I^{\circ}_{TICT}$ value, respectively, of those of chenodeoxycholic acid.

DMAB-γCyD is also useful to detect various compounds including cyclododecanol, *l*-borneol, and the five steroidal compounds using the same concentration (2.5×10^{-5} mol dm^{-3}) for the host and the guests, but the order of the sensitivities was not parallel with that of the binding constants. For example, deoxycholic acid gave the larger value of $\Delta I_{TICT}/I^{\circ}_{TICT}$ (0.57) than ursodeoxycholic acid ($\Delta I_{TICT}/I^{\circ}_{TICT}=0.36$, binding constant: $K=35000$ $mol^{-1}\,dm^3$), chenodeoxycholic acid ($\Delta I_{TICT}/I^{\circ}_{TICT}=0.43$, $K=58000$ $mol^{-1}\,dm^3$) and cyclododecanol ($\Delta I_{TICT}/I^{\circ}_{TICT}=0.29$, $K=36000$ $mol^{-1}\,dm^3$), but its binding constant is the smallest ($K=22000$ $mol^{-1}\,dm^3$). These results suggest that the sensitivity parameter displayed by the TICT emission intensity is not solely governed by the affinity of the complex formation and it is influenced by the other factors such as the polarity, dipole, shape or size of the guest compounds. Since the guest enhanced fluorescence intensities and the CD results suggest that the DMAB moiety of DMAB-γCyD may act as a spacer or a cap, structural features of the complexation may be complicated. In the case that the DMAB moiety and the guest molecule are co-included in the cavity resulting in mutual contact, the TICT excited state of the DMAB moiety may be affected by various factors such as polarity, dipole, shape, and size of the counterpart guest. As a results, DMAB-γCyD can distinguish chenodeoxycholic acid and lithocholic acid, which were not discriminated by DMAB-βCyD.

Figure 7 shows the fluorescent titration curves of DMAB-βCyD and DMAB-γCyD for 1-adamantanol and cyclooctanol. The response ranges of DMAB-βCyD for 1-adamantanol and cyclooctanol are between 2.5×10^{-5}—2.5×10^{-4} mol dm^{-3}. However, in the case of DMAB-γCyD, higher concentrations ranges of 2.5×10^{-4}—2.5×10^{-3} mol dm^{-3} and 2.5×10^{-3}—2.5×10^{-2} mol dm^{-3} are required for 1-

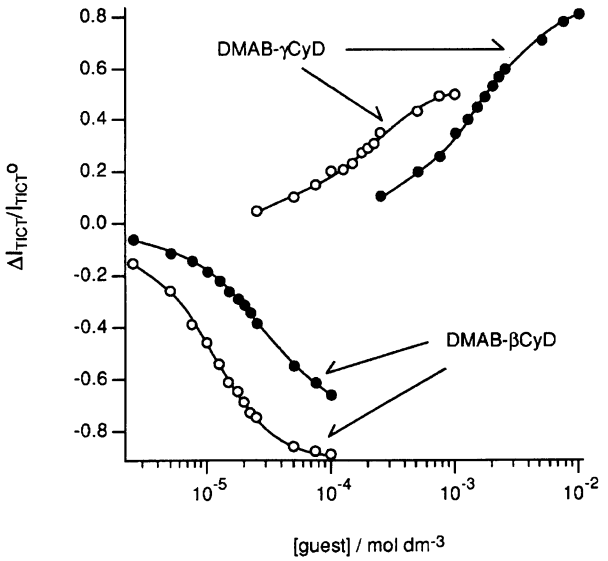


Fig. 7. Fluorescent titration curves of DMAB-βCyD and DMAB-γCyD (2.5×10^{-5} mol dm^{-3}) as a function of 1-adamantanol (○) and cyclooctanol (●).

adamantanol and cyclooctanol, respectively. This result is consistent with the fact that DMAB-βCyD gave larger binding constants than DMAB-γCyD did except for cyclododecanol and chenodeoxycholic acid. All these features suggest that the cavity size of DMAB-βCyD is favorable to form tight inclusion complexes with most of the guest compounds examined here.

Conclusion

DMAB-CyDs are good examples of fluorescent molecular indicators. They show guest responsive dual emissions that reflect shape, size, polarity, and dipole of the guest compounds as well as host-guest binding strength. DMAB-αCyD is effective to detect the chain compounds such as aliphatic alcohols but showed no response to cyclic compounds. DMAB-γCyD has high sensitivities to the large cyclic compounds and steroidal compounds but showed no response to aliphatic compounds. DMAB-βCyD is effective in detecting all types of guest molecules examined in this research. These results demonstrate that each of these modified CyDs has its own characteristic and various types of organic species can be detected by these fluorescent CyDs. Since there are many fluorophores that exhibit TICT fluorescence, it is possible to construct a variety of fluorescent indicators, each having different molecular recognition ability. A study along this line is now under way.

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