Fluorescent behaviour in host–guest interactions. Part 3.† Fluorescent sensing for organic guests using three types of amino-β-cyclodextrins‡

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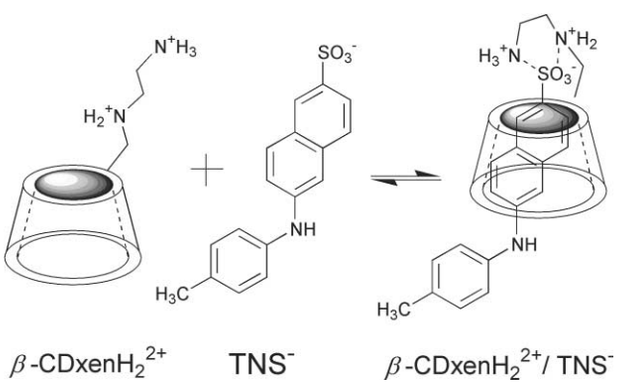
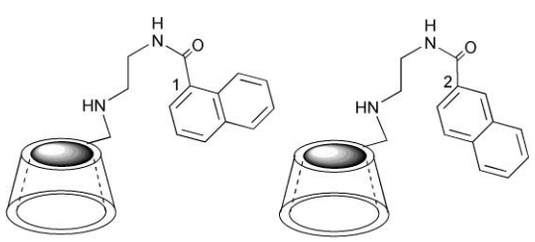
The pH- and temperature-dependent fluorescence behaviour in aqueous solution of three amino-β-cyclodextrins (amino-β-CDx), **1**, **2** and **3**, bearing an amide-linked naphthalene probe has been investigated. The emission intensity at λ_{max}(em) of **1** decreased dramatically with increasing temperature. The pH-dependent fluorescence spectrum was also recorded. Operation of the in–out equilibrium of the naphthalene probe of **1** was mainly analyzed using ^{1}H NMR and circular dichroism spectra. The application of **1** to organic-guest sensing is demonstrated by several examples. These findings suggest that the new host molecule, **1**, will be an excellent CDx-based fluorescent sensor for temperature, pH and neutral organic guests.

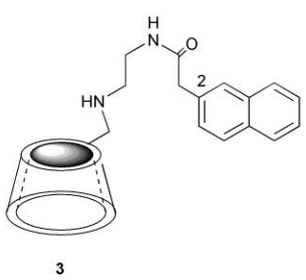
Introduction

Cyclodextrins (CDx) as a supramolecular host have an internal hydrophobic cavity like a "molecular flask" providing a non-polar environment for various types of guest molecules in aqueous solution.[1] The recent use of CDx as building blocks for the construction of supramolecular species such as rotaxanes, dendrimers and for application in lipophilic chiral sensing in solution represents a new, contemporary field in CDx chemistry.[2–4] The molecular recognition process in aqueous solution of several anionic azo compounds by α-cyclodextrin has been a subject of our particular attention as a dynamic model for enzyme–substrate processes.[5–7] Also, weak interactions such as electrostatic forces have been found to be effective in selectivity and enhancement of the binding properties of some amino-β-cyclodextrins.[8] Strong binding of doubly-protonated β-CDxenH_2^{2+} with fluorescent 2-(4-toluidino)-naphthalene-6-sulfonate (TNS) anion was observed owing to the electrostatic interactions between the $-SO_3^-$ group of TNS and the $-NH_2^+-CH_2CH_2-NH_3^+$ moiety of β-CDxenH_2.[8c]



Fluorescent artificial cyclodextrins have been received considerable attention in sensory,[8c,9] biochemical[10] and photoelectronic[11] applications. The CDx cavity as a binding site and the appended fluorophore as a signaling unit with the spacer group are indispensable for the substrate specific-responsive function. Pyrene-appended cyclodextrin derivatives have often been used because of the larger change in fluorescence intensity after complexation with substrate,[9k] but their solubility in water was not adequate. In the present study, we prepared water-soluble naphthalene-appended amino-β-cyclodextrin hosts (**1**, **2** and **3**) to carry out the guest sensing in aqueous solution.





Experimental

Materials and synthesis

Guaranteed-grade β-cyclodextrin (Wako Pure Chemical Ind. Ltd.) was used without further purification. Monotosylated

† For Part 2, see ref. 13.
‡ Electronic supplementary information (ESI) available: Figs. S1–S3. See http://www.rsc.org/suppdata/p2/b1/b108204n/

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β-CDxots at the O-6 position on the D-glucopyranosyl rings of β-CDx was synthesized by the reaction of β-CDx with toluene-*p*-sulfonyl chloride in pyridine at room temperature for 1.5 h. The β-CDxots thus obtained was dissolved in excess ethylenediamine (Tokyo Kasei) and the solution was heated at 70 °C for 1.5 h with stirring. The reaction mixture was poured into a large amount of acetone and the resultant white precipitate was collected and dried *in vacuo*. Purification of mono(6-*N*-(2-aminoethylamino-6-deoxy)-β-cyclodextrin (β-CDxen) as a precursor of the functionalized β-CDx derivatives was carried out by ion-exchange column chromatography through cation-exchange resin (Toyo-pearl 650M; 0.05 mol dm^{-3} NH_4HCO_3 aqueous solution as eluent). The purified β-CDxen was then coupled with 1- and 2-naphthoic acid and naphthalene-1-acetic acid by the usual *N*,*N*′-dicyclohexylcarbodiimide (DCC) method and precipitation with acetone and cation-exchange chromatography gave **1**, **2** and **3**, respectively. The elemental analysis of **1**, **2** and **3** was satisfactory, although solvent water molecules were usually bound. Found for **1**: C, 48.06; H, 6.51; N, 1.87. Calc. for $C_{55}H_{82}N_2O_{35}\cdot 3H_2O$: C, 47.69; H, 6.40; N, 2.02%. MS (FAB) *m*/*z* 1331 $[M + H]^+$. ^1H NMR (D_2O, 400 MHz) δ_H 3.3–3.9 (42H, CDx ring protons), 4.8–5.0 (7H, 1-H) and 7.4–8.0 (7H, aromatic protons). Found for **2**: C, 46.95; H, 6.29; N, 2.00. Calc. for $C_{55}H_{82}N_2O_{35}\cdot 3H_2O$: C, 47.69; H, 6.40; N, 2.02%. MS (FAB) *m*/*z* 1331 $[M + H]^+$. ^1H NMR (D_2O, 400 MHz) δ_H 3.3–3.9 (42H, CDx ring protons), 4.8–5.0 (7H, 1-H) and 7.6–8.3 (7H, aromatic protons). Found for **3**: C, 45.72; H, 6.52; N, 1.98. Calc. for $C_{56}H_{84}N_2O_{35}\cdot 5H_2O$: C, 46.86; H, 6.60; N, 1.95%. MS (FAB) *m*/*z* 1345 $[M + H]^+$. ^1H NMR (D_2O, 400 MHz) δ_H 2.5–2.7 (2H, CH_2), 3.3–3.8 ($COCH_2$, CDx ring protons), 4.8–5.0 (7H, 1-H) and 7.4–7.9 (7H, aromatic protons).

Measurements

Binding constants (K_f) of the inclusion complexes were determined fluorometrically using a Shimadzu RF-5300PC recording fluorescence spectrometer.[8c] The fluorescence measurements were performed by excitation at 295 nm. The pH values in solution were determined using a HORIBA pH meter B-112. The temperature was maintained between 10 and 80 °C using an external circulating water bath (Thomas Kagaku Co. Ltd., TRL-108H). Circular dichroism spectra were measured with a JASCO J-600C circular dichrometer.[12] The ^1H NMR spectra were obtained at various temperatures with a JEOL EX400 FT NMR spectrometer [with 2,2-dimethyl-2-silapentane-5-sulfonate sodium salt (DSS) as an external reference].

Result and discussion

Temperature-dependent fluorescence spectra of 1, 2 and 3

Strongly temperature-responsive fluorescence spectra of **1** in aqueous solution were observed over the temperature range between 25 and 80 °C as shown in Fig. S1. This phenomenon has been also found in other amino-β-cyclodextrins.[13] Excitation at 295 nm would produce a broad emission spectrum in both **1** and **2** (λ_{max}(em) ~378 and 360 nm respectively). On the other hand, the fluorescence spectrum of **3**, which has no π-conjugation with a methylene spacer between the carbonyl group and the naphthalene chromophore, shows a sharp peak at 330 nm with 340 (sh, m) and 355 (sh, w) nm, which is similar to that of 1-methylnaphthalene. Hamai and Hatamiya reported that such monomer fluorescence of 1-methylnaphthalene is slightly enhanced by increasing the β-CDx concentration.[14] At higher temperatures (70–80 °C), the fluorescence of **1** is effectively reduced (Fig. S1). In order to clarify the strong temperature-dependent fluorescence of **1**, we measured the ^1H NMR spectra of **1** at various temperatures between 10 and 60 °C (Fig. S2).

The protons, H-6 and H-7, at the head moiety of the naphthalene probe show a relatively large upfield-shift on decreasing the temperature. Furthermore, the well-separated signals arising from the anomeric protons (C_1-H) of the CDx ring of **1** became simplified as a more coalescent anomeric resonance. These results suggest that the head moiety of **1** may be less tightly included within the CDx cavity (self-inclusion) at the lower temperature and moved outside the cavity at the higher temperature.

Fig. 1 shows the induced circular dichroism (ICD) spectra

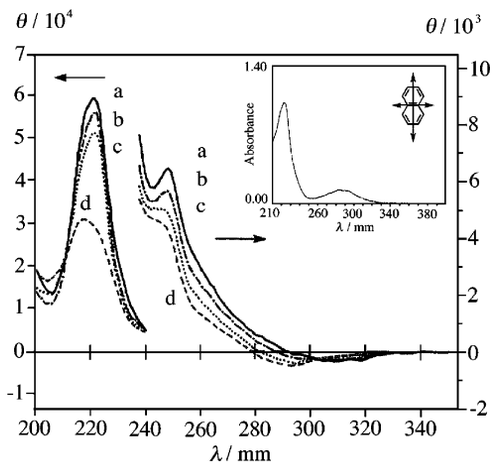
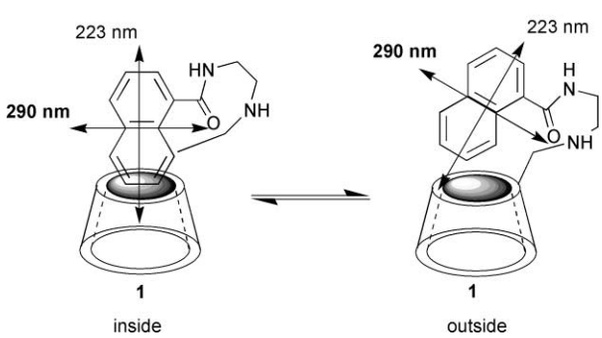


Fig. 1 Circular dichroism spectra of **1** at various temperatures: 25 (a); 40 (b); 60 (c); 80 (d) °C. $\theta/10^4$ dm^3 mol^{-1} cm^{-1}.

of **1** at various temperatures. The ICD spectral changes provide precise structural information such as the orientation of the chromophore in the CDx cavity.[12] There are two main bands at 223(s) and 290(vw) nm which are attributed to the long- and short-axis polarized π–π* transition of the naphthalene chromophore.[12] If the long-axis polarized π–π* transition is almost parallel to the symmetry axis of CDx, a relatively strong positive ICD sign should be observed as shown in Fig. 1. Upon an increase in the temperature, the ICD intensity of **1** at 223 nm tends to decrease due to the disinclusion of the naphthalene chromophore (Scheme 1).



Scheme 1 In–out equilibrium for the naphthalene probe of **1**.

These findings are in accord with the NMR shifts at higher temperatures. At *ca.* 290 nm, a weak negative ICD sign was observed, suggesting that the short-axis polarized π–π* transition would be perpendicular to the CDx axis at the lower temperature. Fig. S3 shows the comparison of the temperature-dependence of fluorescence intensity (I_f) at λ_{max}(em) between **1**, **2** and **3**.

It is noteworthy that the control compound **3**, which has no π-conjugation system, shows a smaller temperature-dependence in its intensity. Therefore, compound **3** is not suitable as a fluorescence sensor upon binding the guest molecule (*vide infra*).

pH-Dependent fluorescence spectra of 1, 2 and 3

Fluorescent amino-β-cyclodextrin derivatives (**1**, **2** and **3**) have one amine site that can be protonated. Protonation of the amine site linked to the fluorophore may enhance the fluorescence of **1**, **2** and **3** owing to chelation-enhanced fluorescence[15] or a photo-induced electron-transfer (PET) mechanism.[16] Fig. 2 shows the pH-dependence of the fluorescence intensity (I_f) at λ_{max}(em) of **1**, **2** and **3**.

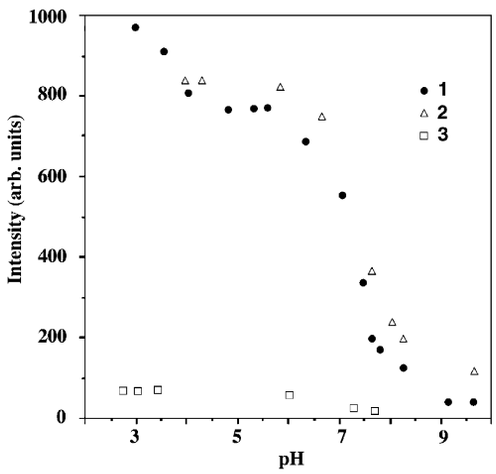
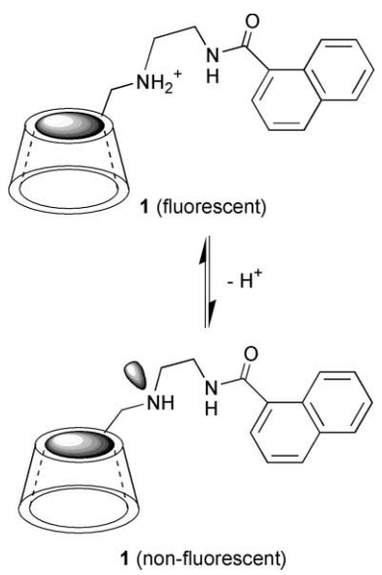


Fig. 2 Plots of fluorescence intensity at λ_{max}(em) *vs.* pH for **1**, **2** and **3** at 25 °C. [**1**] = [**2**] = [**3**] = 1.25×10^{-5} mol dm^{-3}.

The drastic decrease in I_f upon increasing the pH from 6 to 8 could be ascribed to the deprotonation of the amine protons as shown in Scheme 2. Since the ICD spectra of **1** at pH 4, 7 and 10



Scheme 2 Protolytic equilibrium of the amine proton of **1**.

almost coincide with each other (Fig. 3), no conformational change would occur upon protonation–deprotonation at the amine site. The fluorescence of **3** is only slightly sensitive to the pH in the solution.

Fluorescent sensing and guest-binding mechanism

The application of fluorophore-appended amino-β-cyclodextrin derivatives (**1**, **2** and **3**) to neutral guest sensing is described in this section using several organic guest systems (**G1**–**G4**).

A typical example of the fluorescence spectral change of **1** upon addition of cyclohexanol (**G1**) at a constant pH is shown in Fig. 4. A gradual decrease in I_f indicates that the naphthalene

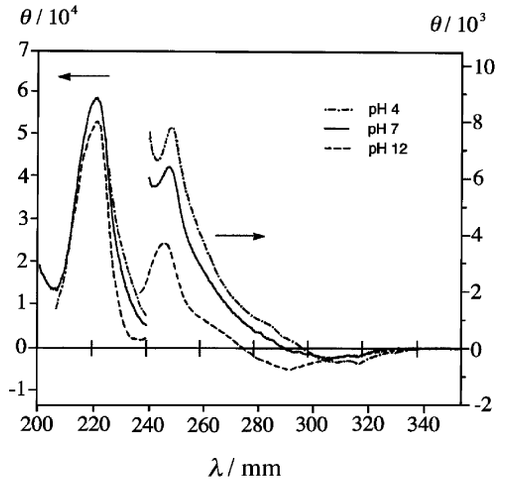
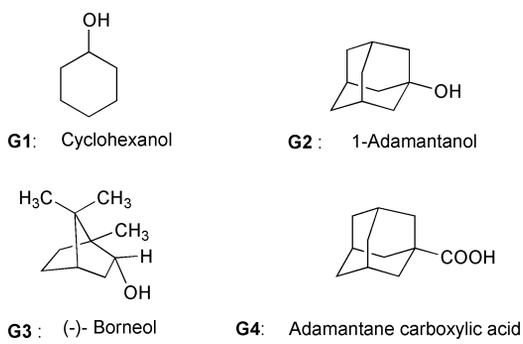


Fig. 3 Circular dichroism spectra of **1** at various pH. $\theta/10^4$ dm^3 mol^{-1} cm^{-1}.



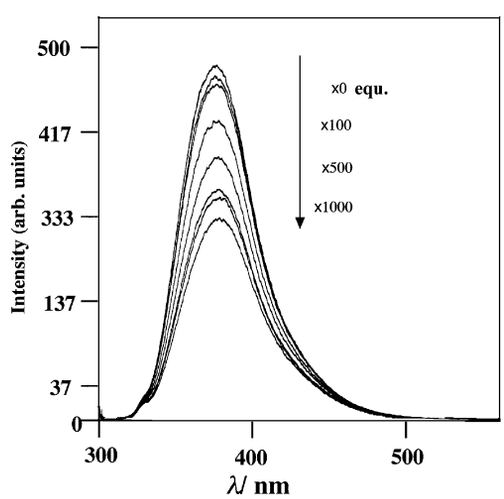


Fig. 4 Fluorescence spectra of **1** in aqueous solutions containing various concentrations of cyclohexanol (**G1**), [**1**] = 1.25×10^{-5} mol dm^{-3}. The excitation (λ_{ex} = 295 nm) and emission bandwidth were set at 5.0 and 3.0 nm.

fluorophore of **1** moves partially outside the CDx cavity upon binding with **G1**. The sensitivity of this host–guest system is limited by competition between complexation with the guest and self-inclusion of the fluorophore in the CDx cavity.[9a]

In order to elucidate the relationship between guest inclusion and the in–out equilibrium for the naphthalene probe of **1**, the ICD changes of **1** at various **G1** concentrations were measured (Fig. 5). The positive ICD sign of **1** at 223 nm, which is attributed to the long-axis polarization of the naphthalene probe, decreases drastically upon addition of **G1**. Further addition of **G1** would produce the negative ICD sign in this region. On the other hand, the negative ICD sign at 290 nm becomes a positive

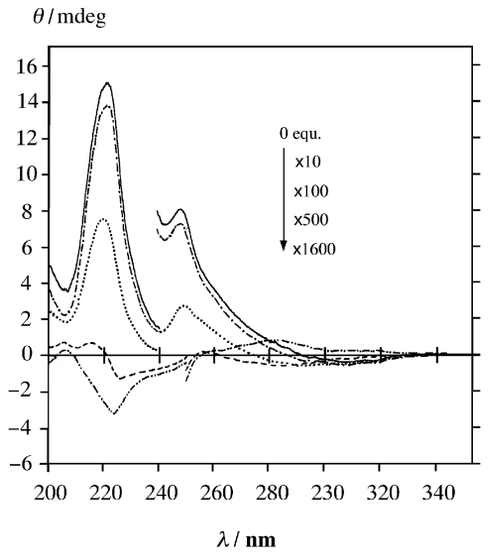
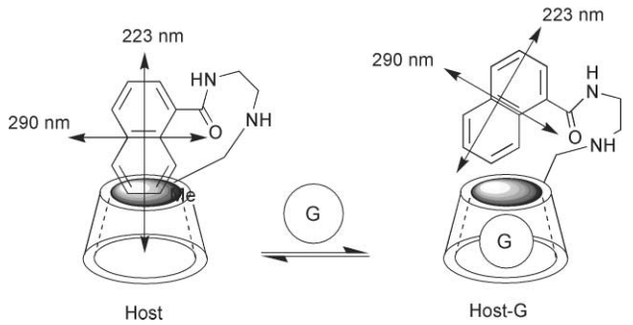


Fig. 5 Circular dichroism spectra of **1** containing various concentrations of cyclohexanol (**G1**).

value at the higher **G1** concentrations. These ICD changes suggest clearly that the long-axis and short-axis polarizations of the naphthalene probe of **1** would be brought nearly parallel and perpendicular to the CDx cavity, respectively, as shown in Scheme 3. Thus, the ICD method is a powerful tool to estimate



Scheme 3

the conformational changes upon binding between aromatic ring appended CDx and organic guests.[17]

In all cases, the binding of guests (**G1**–**G3**) in the CDx cavity of **1** resulted in a large decrease in I_f, indicating that the host **1** would be a excellent neutral-guest sensor.

Fig. 6 shows the 1 : 1 (= host : guest) binding curves of **1** with **G1** and **G2** at various temperatures. The solid lines denote the theoretical curves that could be obtained using a curve-fitting method. Fig. 7 shows the fluorescence responses of **1** to the various temperatures and **G3** concentrations.

The low binding constant for the **1**–**G1** system (Table 1) indicates a less tight inclusion. Furthermore, steric hindrance between the naphthalene probe of **1** and the guest **G1** would lead to such a lower value (K_f = 107 M^{-1}) compared with that (K_f = 2000 M^{-1}) found for the dimethylaminobenzoyl-modified β-CDx–**G1** system.[9g] On the other hand, more compatible inclusion with adamantan-1-ol (**G2**) results in very high binding constants. Interestingly, the decrease in I_f (ΔI_f) of **2** with **G2** and **G3** was found to be too small to determine the exact K_f values, but their stability order would be almost similar to that in the **1**-**G2** and **1**-**G3** systems. No appreciable ΔI_f was observed in the **2**–**G1** and control compound **3** systems.

Thermodynamic parameters

From the van't Hoff plots (log K_f *vs.* $1/T$), we could evaluate the thermodynamic parameters such as $\Delta H°$ and $\Delta S°$ for the binding of **1** with **G1**, **G2** and **G3**. The free energy changes ($\Delta G°$) calculated from the slope and the intercept are listed in Table 1. It is well known that the inclusion reaction by native CDx is enthalpically favored ($\Delta H_{incl} < 0$) and the standard entropy ($\Delta S°_{incl}$) is either negative or positive.[5b,5c,18] Therefore, the negative $\Delta H°$ values in our cases (Table 1) indicate that the binding of **1** with **G1**–**G3** is exothermic. Compared with the **1**–**G1** system, the complexation of **1** with **G2** and **G3** is enthalpically less favorable but entropically more favorable. It is noteworthy that the comparative contribution of the positive $\Delta S°$ to the Gibbs energy term $\Delta G°$ found in both the **1**–**G2** and **1**–**G3** systems may result from a change in solvent structure in the bulky guests **G2** and **G3** and/or a conformational change in **1** upon binding with the bulky guests.

NMR sensing using the control compound 3

Although strongly temperature-dependent fluorescence spectra were observed in both the **1** and **2** systems as discussed above, the changes in their ^{1}H NMR spectra were relatively small. On the other hand, the temperature-dependence of the fluorescence spectrum of **3** was quite small, but its ^{1}H NMR spectrum was

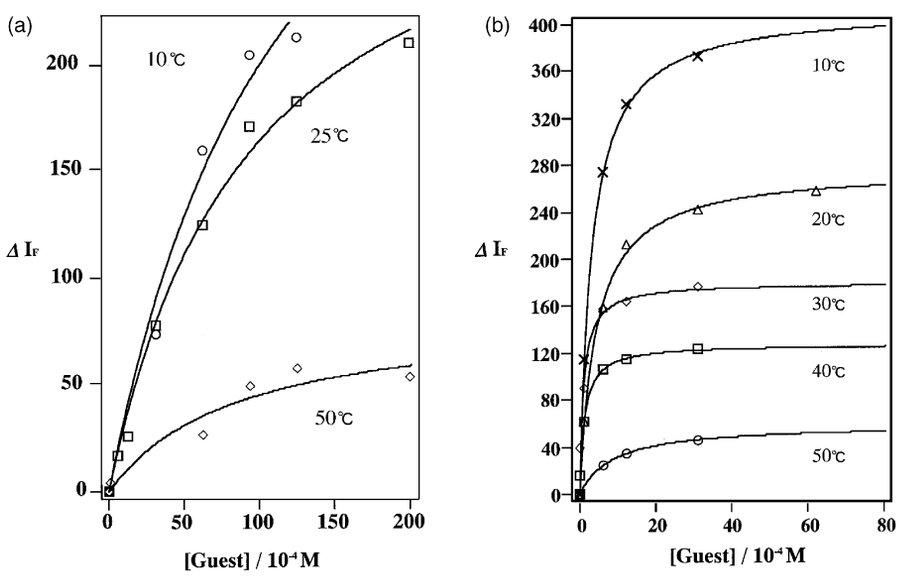


Fig. 6 Binding curves for the interaction of **1** with **G1** (a) and **G2** (b) at various temperatures.

Table 1 Binding constants and thermodynamic parameters for the inclusion reaction of host **1** with various guest molecules

Guest	K_f/mol^{-1} dm^{-3}	$\Delta G°$/kcal mol^{-1}	$\Delta H°$/kcal mol^{-1}	$\Delta S°$/cal mol^{-1} K^{-1}
Cyclohexanol (**G1**)	107 (293 K)	−2.77	−4.38 ± 0.02	−5.41 ± 0.07
Adamantan-1-ol (**G2**)	9800 (293 K)	−5.53	−2.65 ± 0.48	9.50 ± 1.59
(−)-Borneol (**G3**)	1149 (303 K)	−4.24	−2.33 ± 0.71	6.30 ± 2.38

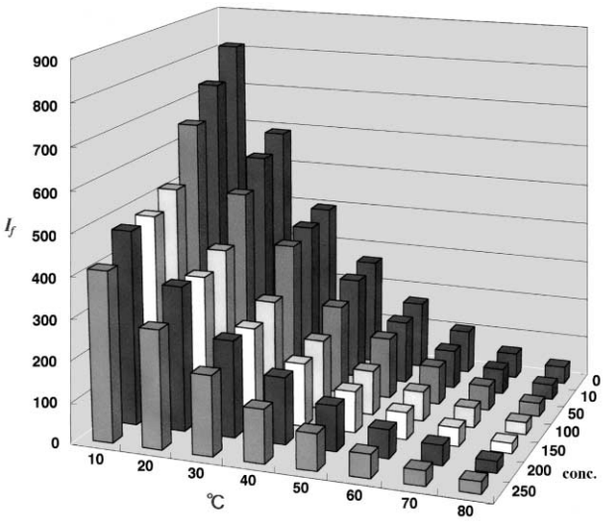


Fig. 7 Fluorescence sensing by **1** for temperature and (−)-borneol (**G3**) concentrations.

found to be strongly temperature-dependent. Comparison of the ^{1}H NMR spectra of 2-naphthylacetic acid (**2-NA**) and its β-CDx inclusion complex (β-CDx–**2-NA**) shown in Fig. 8(a) with the ^{1}H NMR spectrum of **3** at 30 °C [Fig. 8(b)] indicates that the naphthalene probe in **3** would be included within the CDx cavity at lower temperature.

The signals in the β-CDx–**2-NA** complex display some broadening and large upfield shifts of up to 0.2 ppm for the protons, H_5–H_8, inside the cavity. The H_1, H_3 and H_4 protons of **2-NA** at the methylene site remain well-separated signals. As the temperature is increased in solution, the protons H_5–H_8 in the head group of **3** tend to shift downfield owing to disinclusion from the CDx cavity, while the protons, H_1, H_3 and H_4, in the vicinity of the methyleneamide linkage shift a little.

The flexible motion of the naphthalene probe of **3** would be applicable to the NMR sensing of the guest molecules. Fig. 9 shows the ^{1}H NMR spectra of **3** in the absence and presence of adamantanecarboxylate anion (**G4**).

Upon inclusion with **G4**, the head protons, H_5–H_8, of **3** experience a large downfield shift, suggesting that the naphthalene probe moves outside the CDx cavity. Work towards the ^{1}H

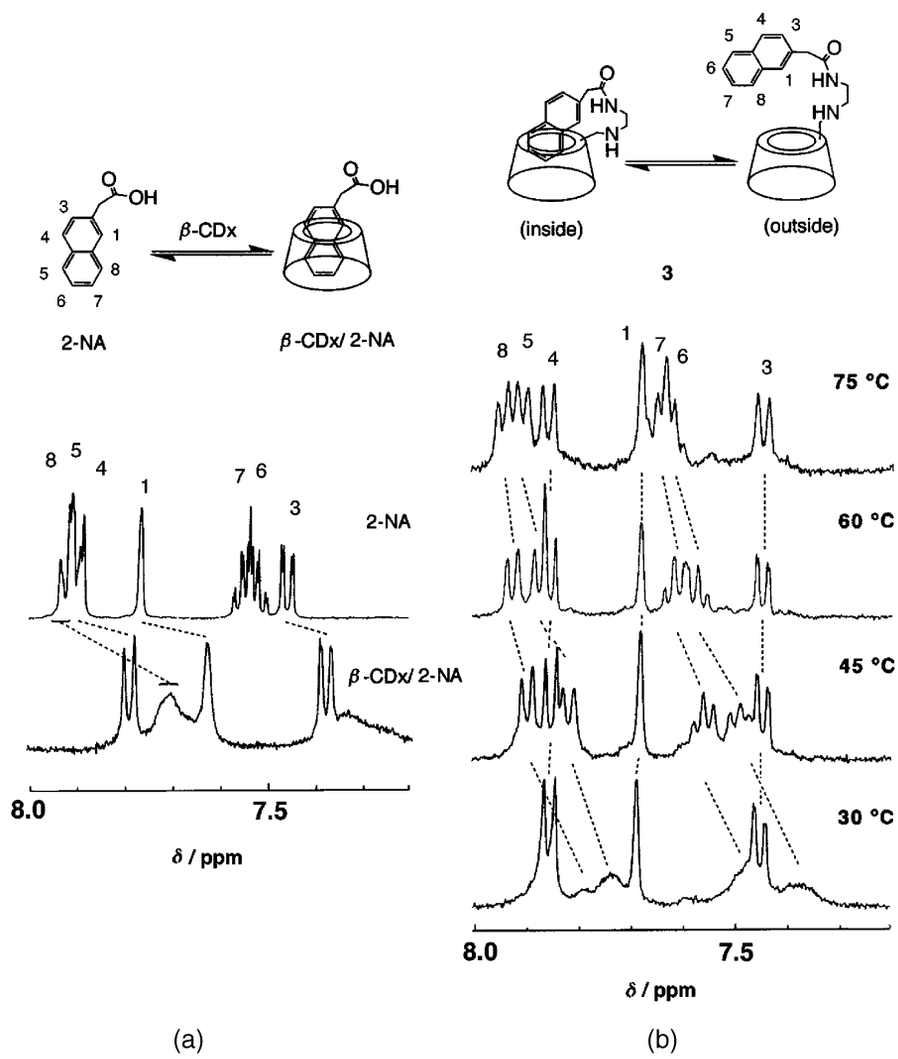


Fig. 8 ^{1}H NMR spectra of the aromatic region of β-CDx–**2-NA** and **3**. **2-NA** and β-CDx–**2-NA** complex at 30 °C in D_2O (a). **3** at various temperatures in D_2O (b).

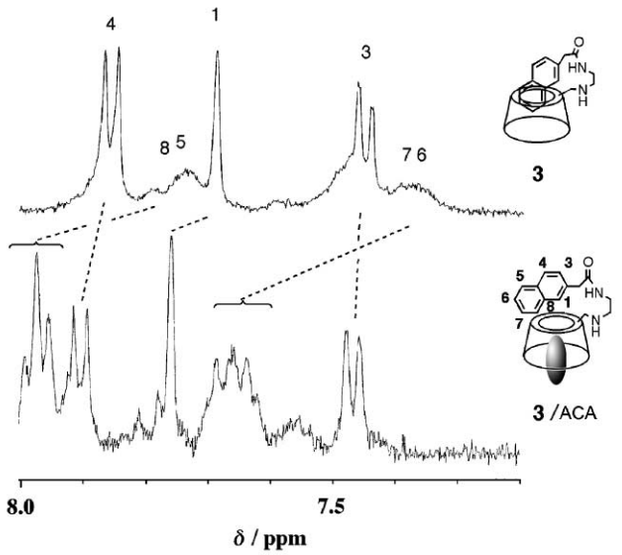


Fig. 9 ^{1}H NMR spectra of **3** and **3**–**G4** complex at 30 °C in D_2O.

NMR detection of some organic guests in aqueous solution using **3** is now in progress.

Conclusion

A systematic study using three hosts, **1**, **2** and **3**, clearly indicates that the naphthalene-appended amino-β-cyclodextrin, **1**, shows the highest sensitivity towards neutral-guest sensing in aqueous solution. It has been demonstrated that the fluorescence properties of **1**, **2** and **3** are strongly dependent on the temperature and pH in solution. Their fluorescent responses were also controlled by the geometrical position and π-conjugation of the probe. The thermodynamic parameters ($\Delta H°$ and $\Delta S°$) suggested that the conformational change of the naphthalene probe of **1** and the change in solvation around the guest play an important role in binding with the bulky guests. The data from the induced circular dichroism studies suggested that a fairly large conformational change takes place at the naphthalene probe of **1** on changing the temperature and binding with the guest.

References

1 M. L. Bender and M. Komiyama, *Cyclodextrin Chemistry*, Springer-Verlag, Heidelberg, 1978.

2 S. Anderson, T. D. W. Claridge and H. L. Anderson, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1310; S. Anderson, W. Clogg and H. L. Anderson, *Chem. Commun.*, 1998, 2379; S. Anderson, W. Clogg and H. L. Anderson, *Chem. Commun.*, 1998, 2773.

3 S. A. Nepogodiev and J. F. Stoddart, *Chem. Rev.*, 1998, **98**, 1959.

4 J. E. H. Buston, J. R. Toung and H. L. Anderson, *Chem. Commun.*, 2000, 905; C. Péan, C. Créminon, A. Wijkhuisen, J. Grassi, P. Guenot, P. Jéhan, J.-P. Dalbiez, B. Perly and F. Djedaïni-Pilard, *J. Chem. Soc., Perkin Trans. 2*, 2000, 853; A. J. Baer and D. H. Macartney, *Inorg. Chem.*, 2000, **39**, 1410; D. Armspach and D. Matt, *Chem. Commun.*, 1999, 1073; S. Weidner and Z. Pikramenou, *Chem. Commun.*, 1998, 1473; N. Schaschkle, S. Fiori, E. Weyher, C. Escrieut, D. Fourmy, G. Müller and L. Moroder, *J. Am. Chem. Soc.*, 1998, **120**, 7030; W. Hermann, M. Schneider and G. Wenz, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2511; A. Harada, J. Li. and M. Kamachi, *Chem. Commun.*, 1997, 1413; A. Harada, J. Li. and M. Kamachi, *J. Am. Chem. Soc.*, 1994, **116**, 3192; K. Harata, Y. Takenaka and N. Yoshida, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1667.

5 (*a*) A. Seiyama, N. Yoshida and M. Fujimoto, *Chem. Lett.*, 1985, 1013; (*b*) N. Yoshida and M. Fujimoto, *J. Phys. Chem.*, 1987, **91**, 6691; (*c*) N. Yoshida, A. Seiyama and M. Fujimoto, *J. Phys. Chem.*, 1990, **94**, 4246; (*d*) N. Yoshida and K. Hayashi, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1285; (*e*) N. Yoshida, *J. Chem. Soc., Perkin Trans. 2*, 1995, 2249; (*f*) N. Yoshida and Y. Fujita, *J. Phys. Chem.*, 1995, **99**, 3671; (*g*) N. Yoshida, H. Yamaguchi and M. Higashi, *J. Phys. Chem.*, 1998, **102**, 1523.

6 A. Örstan and J. F. Wojcik, *Carbohydr. Res.*, 1988, **176**, 149.

7 A. Hersey and B. H. Robinson, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 2039.

8 (*a*) T. Kitae, T. Nakayama and K. Kano, *J. Chem. Soc., Perkin Trans. 2*, 1998, 207; (*b*) H. Monzen, N. Yoshida and M. Fujimoto, *Chem. Lett.*, 1988, 1129; (*c*) N. Ito and N. Yoshida, *J. Chem. Soc., Perkin Trans. 2*, 1996, 965; (*d*) A. K. Yatsimirsky and A. V. Eliseev, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1769; (*e*) A. V. Eliseev and H.-J. Schneider, *J. Am. Chem. Soc.*, 1994, **116**, 6081; (*f*) N. Yoshida, K. Harata and N. Ito, *Supramol. Chem.*, 1998, **10**, 63.

9 (*a*) M. R. deJong, J. F. J. Engbersen, J. Husktens and D. N. Reinhondt, *Chem. Eur. J.*, 2000, **6**, 4034; (*b*) M. Narita, F. Hamada, I. Suzuki and T. Osa, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2751; (*c*) R. Corradini, A. Dossena, G. Galaverna, R. Marchelli, A. Paragia and G. Sartor, *J. Org. Chem.*, 1997, **62**, 6283; (*d*) C. T. Bibeau, B. K. Hubbard and C. J. Abelt, *Chem. Commun.*, 1997, 437; (*e*) S. R. McAlpine and M. A. Garcia-Garibay, *J. Am. Chem. Soc.*, 1996, **118**, 2750; (*f*) B. K. Hubbard, L. A. Beilstein, C. E. Heath and C. J. Abelt, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1005; (*g*) K. Hamasaki, H. Ikeda, A. Nakamura, A. Ueno, F. Toda, I. Suzuki and T. Osa, *J. Am. Chem. Soc.*, 1993, **115**, 5035; (*h*) K. Takahashi, *J. Chem. Soc., Chem. Commun.*, 1991, 929; (*i*) A. Ueno, *Anal. Chem.*, 1990, **62**, 2461; (*j*) A. Ueno, S. Minato, I. Suzuki, M. Fukushima, M. Okubo, T. Osa, F. Hamada and K. Murai, *Chem. Lett.*, 1990, 605; (*k*) A. Ueno, I. Suzuki and T. Osa, *J. Am. Chem. Soc.*, 1989, **111**, 6391; (*l*) A. Ueno, F. Morikawa, T. Osa, F. Hamada and K. Murai, *J. Am. Chem. Soc.*, 1988, **100**, 4323.

10 M. Eddaoudi, H. P.-Lopez, S. F. de Lamotte, D. Ficheux, P. Prognon and A. W. Coleman, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1711; S. Matsumura, S. Sakamoto, A. Ueno and H. Mihara, *Chem. Eur. J.*, 2000, **6**, 1781.

11 R. A. Bissell and A. P. de Silva, *J. Chem. Soc., Chem. Commun.*, 1991, 1148; M. A. Mortellaro, W. K. Hartman and D. G. Nocera, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1945; H. F. Nelissen, A. F. J. Schut, F. Venema, M. C. Feiters and R. J. M. Nolte, *Chem. Commun.*, 2000, 57.

12 N. Yoshida, H. Yamaguchi, T. Iwao and M. Higashi, *J. Chem. Soc., Perkin Trans. 2*, 1999, 379.

13 H. Nakashima, Y. Takenaka, M. Higashi and N. Yoshida, *J. Chem. Soc., Perkin Trans. 2*, 2001, 2096.

14 S. Hamai and A. Hatamiya, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2469.

15 *Fluorescent Chemosensors for Ion and Molecular Recognition*, ed. A. W. Czarnik, *ACS Symp. Ser.*, 1993, 538.

16 L. Fabbrizzi, M. Licchelli, P. Pallavicini, A. Perotti, A. Taglietti and D. Sacchi, *Chem. Eur. J.*, 1996, **2**, 75.

17 Y. Inoue, K. Yamamoto, T. Wada, S. Everitt, X.-M. Gao, Z.-J. Hou, L.-H. Tong, S.-K. Jiang and H.-M. Wu, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1807; G. Vecchio, D. L. Mendola and E. Rizzarelli, *J. Supramol. Chem.*, 2001, **1**, 87.

18 R. I. Gelb, L. M. Schwartz, B. Cardelonio, H.-S. Fuhrmann, R. F. Jonson and D. A. Laufer, *J. Am. Chem. Soc.*, 1981, **103**, 1750.