Detection of Neutral Organic Compounds by Excimer-forming Bichromophoric γ-Cyclodextrins

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γ-Cyclodextrin derivatives bearing two 2-naphthylsulphonyl moieties show excimer emission that is markedly affected by the presence of guests, and can be used to detect a variety of neutral organic compounds.

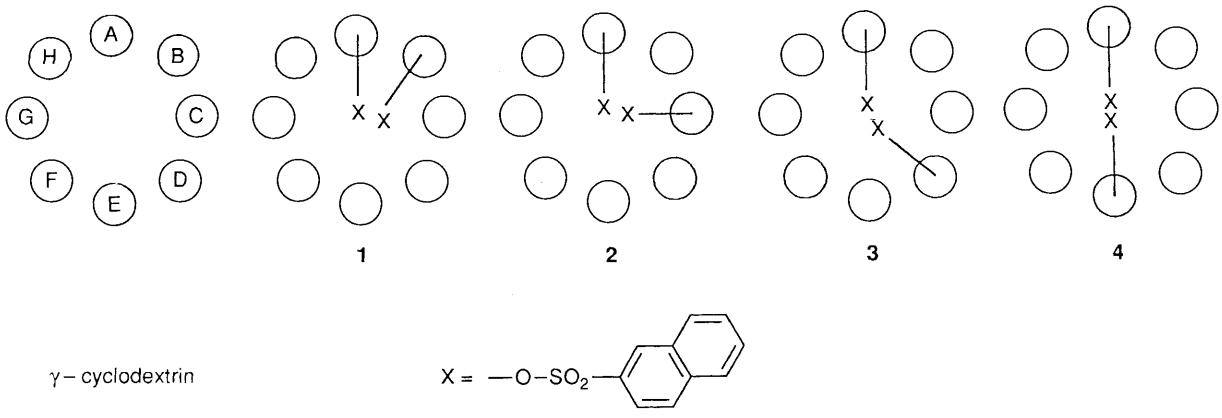
A number of ionophores have been prepared for detection of metal ions and ammonium cations by absorption and fluorescence changes induced by host–guest complexation.[1–3] However, attempts to detect neutral organic species have been rare.[4] Recently we prepared modified cyclodextrins that bear one aromatic moiety, the CD, absorption, or fluorescence spectra of which change upon complexation.[5–7] Although cyclodextrin derivatives have been shown to be useful for detecting organic species in solution, their guest selectivity has been limited because of the flexibility of the pendant. Here, we report unusually high molecular recognition ability attained by the modified γ-cyclodextrins **1–4** that bear two naphthyl moieties oriented rigidly in the γ-cyclodextrin cavity.

Compounds **1–4** were prepared by the reaction of 2-naphthylsulphonyl chloride with γ-cyclodextrin in pyridine and separated by HPLC with an ODS column.[8] These γ-cyclodextrin derivatives in 10% ethylene glycol aqueous solution exhibit exciton coupling bands in the naphthalene ^1B_b transition region (220–260 nm). The CD sign changes from positive to negative for **1** and **3** and from negative to positive for **2** and **4** as the wavelength changes from a longer to a shorter one. The exciton coupling patterns indicate that the two naphthyl rings are twisted clockwise (R-helicity) for **1** and **3** and counterclockwise (S-helicity) for **2** and **4**. This asymmetric twisting occurring in the chiral γ-cyclodextrin framework suggests that the naphthyl moieties are rigidly oriented in the γ-cyclodextrin cavities. The intensities of the exciton coupling bands of these hosts decreased upon binding one guest molecule, except for **1**, which exhibited limited CD variations. The guest-induced weakening of the CD intensities

Table 1 Guest-induced variations of excimer emission intensities[a]

	$\Delta I_{ex}/I_{ex}^{0}$ [b](%)			
	1	**2**	**3**	**4**
Cyclohexanol	0	−2	0	0
1-ACA[c]	−4	12	21	8
(−)-Borneol	−8	13	20	4
Cyclododecanol	4	65	91	10

[a] 25 °C in 10% ethylene glycol aqueous solution. Excitation wavelength is 290 nm; [host] = 0.02; [guest] = 0.2 mmol dm^{-3}. [b] $\Delta I_{ex} = I_{ex} - I_{ex}^{0}$. [c] Adamantane-1-carboxylic acid.



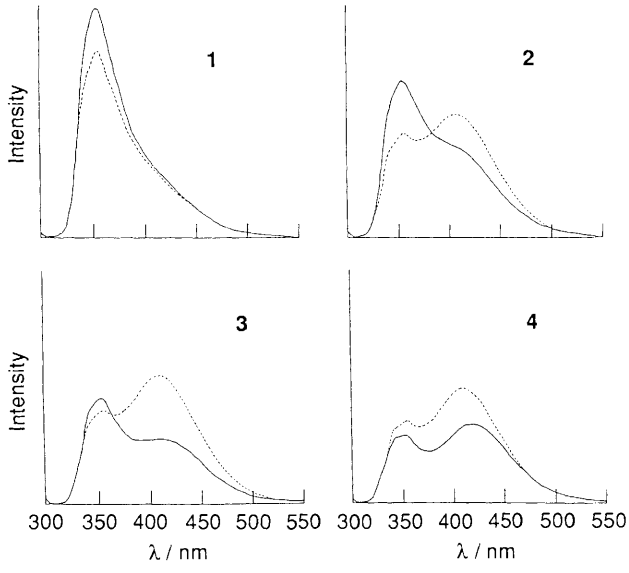
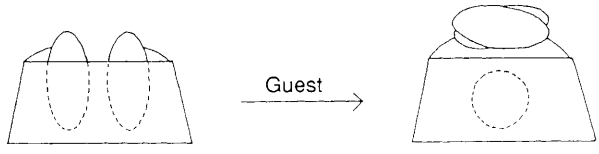


Fig. 1 Fluorescence spectra of **1–4**, alone (0.02 mmol dm^{-3}, —), or in the presence of (−)-borneol (2.0 mmol dm^{-3}, – – –) in 10% ethylene glycol aqueous solution

suggests that the location of the naphthyl moieties changes from inside to outside the host cavity in order to accommodate the guest molecule in the cavities.

Fig. 1 shows the fluorescence spectra of **1–4** in 10% ethylene glycol aqueous solution at 25 °C together with the spectra in the presence of (−)-borneol as the guest. The spectrum of **1** is composed of mainly monomer emission with a peak around 355 nm, indicating that, in spite of their proximal location along the cyclodextrin rim, it is difficult for the two naphthalene rings in **1** to be in the face-to-face orientation that is a prerequisite for excimer formation. In contrast to **1**, hosts **2–4** exhibit a strong excimer emission around 410 nm. The excimer emission is enhanced by complexation with (−)-borneol. This result indicates that it is easier for the naphthalene rings in **2–4** to attain the face-to-face orientation in intermolecular complexes than intramolecular complexes. The CD and fluorescence data suggest that **2–4** undergo the conformation change as shown in Scheme 1.

Table 1 shows variations in the excimer emission intensity induced by several guests (0.2 mmol dm^{-3}). The increase in the excimer emission ($\Delta I_{ex} = I_{ex} - I_{ex}^0$), where I_{ex}^0 and I_{ex} are emission intensities at 410 nm before and after guest addition, respectively, may be used as a parameter which reflects the sensitivities of the hosts. Examination of the data indicates



that the $\Delta I_{ex}/I_{ex}^0$ value markedly depends on the kind of host and guest. Among the four hosts, **3** shows the highest sensitivity for guests with the selectivity order of cyclododecanol > adamantane-1-carboxylic acid (1-ACA) ≈ (−)-borneol > cyclohexanol. Both **2** and **4** also show similar trends in guest binding. The $\Delta I_{ex}/I_{ex}^0$ values may be correlated with binding constants between the hosts and the guests. To confirm this point, we estimated the binding constants of **3** for the guests by analysing the guest-induced variations in the excimer emission, and obtained values of 19 500, 1210 and 650 dm^3 mol^{-1} for cyclododecanol, (−)-borneol, and 1-ACA, respectively. Although the magnitudes roughly coincide with the sensitivity data, the intensity of the excimer emission might also be dependent on the structures of the complexes. These systems may be applicable for detecting a variety of organic compounds by fluorescence variations of the hosts even if the compounds are optically inert.

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