Molecular Recognition and Complexation Thermodynamics of Dye Guest Molecules by Modified Cyclodextrins and Calixarenesulfonates

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The inclusion complexation behavior of some dye guest molecules with two kinds of molecular receptors, i.e., native α-, β-, and γ-cyclodextrins, and chemically modified β-cyclodextrins, and water-soluble calix[*n*]-arenesulfonates ($n = 4, 6, 8$) and their lower rim alkylated derivatives, has been investigated. It was found that the fluorescence intensity of guest molecules evidently changes upon the addition of molecular receptors. The calix[*n*]arenesulfonates ($n = 4, 6, 8$) cause gradual decreases in the fluorescence intensity, whereas native α-, β-, and γ-cyclodextrins cause gradual increases in the fluorescence intensity. Interestingly, the fluorescence intensity of dye guest molecules gradually increases upon the addition of the lower rim alkylated calix[*n*]-arenesulfonate derivatives ($n = 4, 6, 8$), in contrast to their parent calix[*n*]arenesulfonates ($n = 4, 6, 8$). Meanwhile, chemically modified cyclodextrins still show the same effect on the fluorescence intensity of dye guest molecules; however, the hydrophobicity or hydrophilicity of the substituent group influences the increment in the fluorescence intensity. The fluorescence phenomena are explained in terms of photophysical behavior on the basis of the changes in the fluorescence quantum yield and the molecular extinction coefficient of the guests due to the complexation with the two molecular receptors, i.e., cyclodextrins and calixarenesulfonates. The stability constants of the resulting complexes are determined via spectrofluorometric titration. The molecular recognition behavior is discussed from the viewpoint of size/shape-fit, electrostatic interaction, hydrogen-bonding, hydrophobic interactions, etc. The thermodynamic parameters for the inclusion complexation of guest molecules with the two kinds of molecular receptors were determined through van't Hoff analysis. The complexation mechanism is also discussed from the thermodynamic viewpoint.

Introduction

The inclusion complexation and molecular recognition are of current interest in host−guest chemistry or supramolecular chemistry.[1] In this field, the molecular receptors studied extensively include cyclodextrin,[2] calixarenes,[3] and cucurbituril.[4] Calixarenes and cucurbituril possess very limited solubility in aqueous solution. However, cucurbituril's solubility could be improved via the protonation or complexation with some metal cations, whereas calixarenes could be modified, e.g., via the sulfonation in the upper rim (para-positions), and be transformed into water-soluble molecular receptors, i.e., calixarenesulfonates.[5,6] Cyclodextrins, calixarenes, and cucurbituril possess a hydrophobic cavity, although their structural features and properties are distinctly different in nature.

The complexation behaviors of any one kind of these molecular receptors have been investigated extensively, especially for cyclodextrins. Native and chemically modified cyclodextrins[7] can accommodate a wide variety of inorganic, organic, and biological molecules in their hydrophobic cavity to form stable inclusion complexes, showing high molecular selectivity and enantioselectivity.[8,9,10] The water-soluble calixarenesulfonates have also been studied on the binding to several organic ammonium, some dye molecules, etc.[11−16] Cucurbituril was found to be able to form stable complexes with many metal cations and organic amines in acidic solution.[17]

Therefore, it would be interesting to compare the (inclusion) complexation behavior of the three molecular receptors, or at least any two of them. The improvement in the solubility in aqueous solution makes this possible. However, there are no reports on comparison studies of these three molecular receptors to our best knowledge. Furthermore, no report has been presented on the complexation of same guest with calixarenesulfonates and cucurbituril until now. Buschmann has investigated the complexation of several volatile organic molecules from the gas phase, organic dye molecules, and nonionic surfactant and poly(ethylene glycol)s with cucurbituril and cyclodextrins in aqueous solution via spectrofluorometric and calorimetric titration methods.[18] The complexation of auramine O with calixarenesulfonates and β-cyclodextrin was reported by Warner.[15a,d] In a preliminary communication, we have reported the inclusion complexation of acridine red dye molecule with calixarenesulfonates and native cyclodextrins.[19]

We present here the systematic study on the inclusion complexation of dye guest molecules, including acridine red (AR), acridine orange (AO), pyronine Y (PY), pyronine B (PB), sodium 6-toluidino-2-naphthalene sulfonate (TNS), Fluorscein (FL), and crystal violet (CV) (Chart 1), with the calix[*n*]-arenesulfonates ($n = 4, 6, 8$) and the lower rim (the phenolic hydroxyl groups) alkylated calix[n]arenesulfonates ($n = 6, 8$), and native and chemically modified cyclodextrins (Chart 2). The spectral phenomena upon the complexation are explained in terms of photophysical behavior on the basis of the changes in the fluorescence quantum yield and the molecular extinction coefficient of the guests due to the complexation with the two kinds of molecular receptors. The complexation thermodynamic

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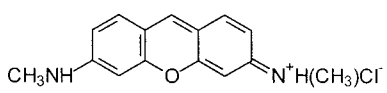
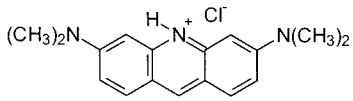
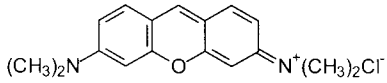
CHART 1: Molecular Structures of Dye Guest Molecules



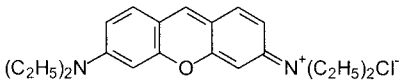
Acridine Red (AR)



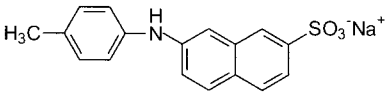
Acridine Orange (AO)



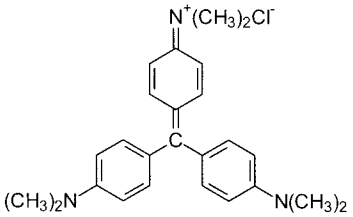
Pyronine Y (PY)



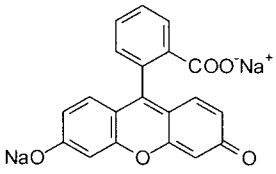
Pyronine B (PB)



Sodium 6-Toluidino-2-Naphthalene Sulfonate (TNS)



Crystal Violet (CV)



Fluorescein (FL)

parameters obtained via van't Hoff analysis can be used to elucidate the complexation mechanisms.

Experimental Section

α-, *β*-, and *γ*-Cyclodextrins were obtained from Tokyo Kasei and dried under reduced pressure before use. The cyclodextrin derivatives were prepared according to the previous procedures: mono-(6-*O*-diphenoxyphosphoryl)-*β*-cyclodextrin (PhP-*β*-CD) and mono-(6-*O*-ethoxyhydroxyphosphoryl)-*β*-cyclodextrin (EtP-*β*-CD),[20] mono-[6-(benzylseleno)-6-deoxy]-*β*-cyclodextrin (BzSe-*β*-CD),[21,22] mono-[6-(phenylseleno)-6-deoxy]-*β*-cyclodextrin (PhSe-*β*-CD),[22,23] l-tryptophan-modified-*β*-cyclodextrin (l-Trp-*β*-CD),[10] mono-[6-(3-methyl-1-pyridinio)-6-deoxy]-*β*-cyclodextrin (*m*Py-*β*-CD).[22,24] 6-*O*-α-d-Glucosyl-*β*-cyclodextrin (G-*β*-CD) (CAS No. [92517-02-7]) was obtained from Sigma Chem. Co.

p-tert-Butylcalix[*n*]arenas ($n = 4, 6, 8$) were synthesized according to the literature procedures.[25,26,27] The complex of *p-tert*-butylcalix[6]arene with toluene was structurally characterized via single-crystal X-ray diffraction method.[28] Calix[n]arenes ($n = 4, 6, 8$) were obtained via the debutylation of corresponding *p-tert*-butylcalix[*n*]arnens by anhydrous aluminum chloride in the presence of phenol in toluene.[29] Calix[*n*]arenesulfonates ($n = 4, 6, 8$) were synthesized via the sulfonation of the corresponding calix[*n*]arenes ($n = 4, 6, 8$) in concentrate sulfuric acid (98%).[30] The alkylated derivatives of the calix[n]arenesulfonates ($n = 4, 6, 8$) were obtained via the alkylation in the lower rim of the corresponding calix[*n*]arenesulfonates ($n = 4, 6, 8$) with 1-bromopropane, 1-bromobutane, 1-bromoheptane, or 1-bromooctane (purified according to the standard procedures[31]) in the presence of sodium hydroxide in water-dimethyl sulfoxide mixture solvents,[11e,15a] and characterized.[16,32]

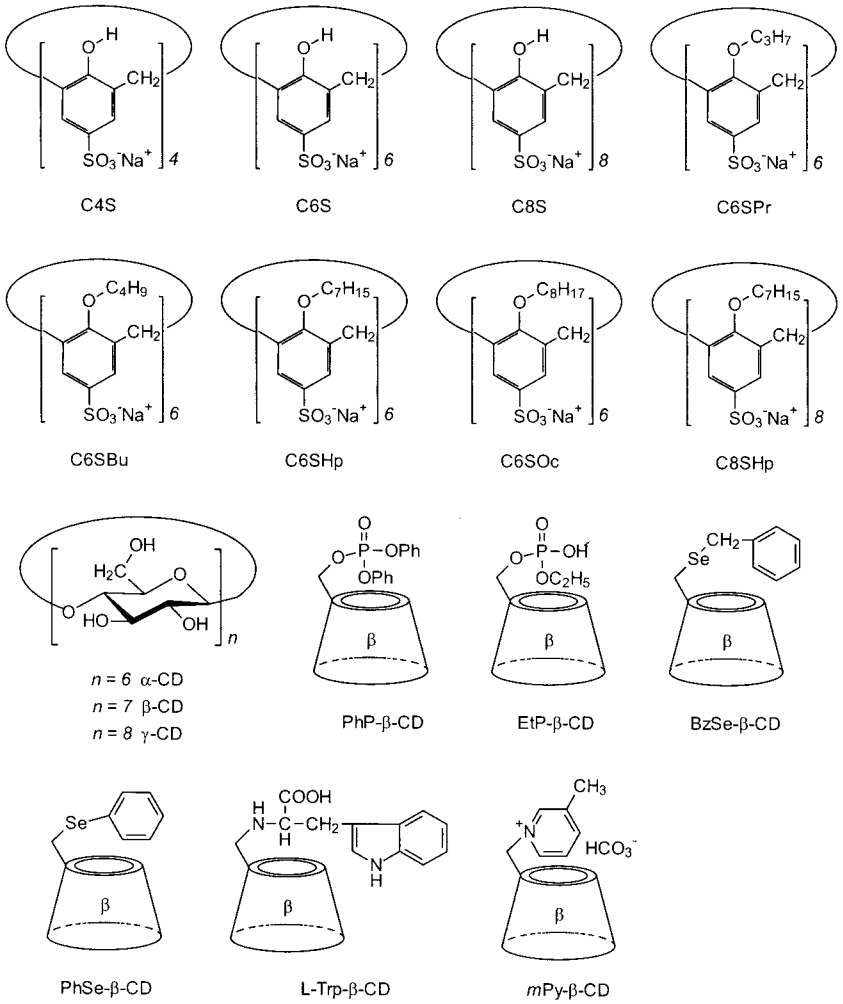
4-Phenolsulfonic acid, sodium salt dihydrate was purchased from Acros Organics. Acridine red (acridine red 3B, dimethyl diaminoxanthenyl chloride) (C. I. 45000) (AR) was purchased from Chroma-Gesellschaft Schmid & Co. Acridine orange (C. I. 46005) (AO) was obtained from Fluka Chem. Co. Pyronine Y (C. I. 45005) (PY) and pyronine B (C. I. 45010) (PB) were purchased from Chroma. 6-(*p*-Toluidino)-2-naphthalene sulfonic acid, sodium salt (99%) (TNS) was purchased from Aldrich Chem. Co. Crystal violet (C. I. 42555) (CV) and fluorescein, sodium salt (C. I. 45350) (FL) were commercially available from local supplier. All other chemicals were commercially available and used without further purification, except otherwise noted.

Citric acid monohydrate and sodium citrate dihydrate of analytical grade were dissolved in distilled, deionized water to make a 0.10 mol dm^{-3} citrate buffer solution of pH 6.00, which was used when taking measurements.

Concentrated stock solutions of the hosts and various guests were prepared in a 0.10 mol dm^{-3} citrate buffer solution. Considering the solubility and critical micelle concentration of calix[*n*]arenesulfonates ($n = 4, 6, 8$),[5a,b] the concentration of the stock host solution was as follows: α-, *β*-, and *γ*-Cyclodextrins, 10 mmol dm^{-3} (1 mmol $dm^{-3} = 1 \times 10^{-3}$ mol dm^{-3}); C4S, C6S, and C8S, 5 mmol dm^{-3}; C6SPr and C6SBu, 1 mmol dm^{-3}; C6SHp, C6Soc, C8SHp, and the *β*-cyclodextrin derivatives (PhP-*β*-CD, EtP-*β*-CD, BzSe-*β*-CD, PhSe-*β*-CD, l-Trp-*β*-CD, *m*Py-*β*-CD, and G-*β*-CD), 0.5 mmol dm^{-3}. The titration solutions were prepared in 10.0 mL (25.0 mL for the measurements at various temperatures) volumetric flasks with the host/guest molar ratio ranging from 0 to ~1200, which varies upon the stability constant of the complex formed.

Fluorescence spectra were measured using a JASCO spectrofluorometer model FP-715 using a conventional 1×1 cm quartz cell in a thermostated compartment, which was kept at a constant temperature through a Shimadzu TB-85 Thermo Bath unit. The excitation and emission bandwidths were set at 5 nm. The sample solutions containing acridine red dye at the

CHART 2: Molecular Structures of Calix[*n*]arenesulfonates ($n = 4, 6, 8$) and Modified Cyclodextrins



concentration of approximately $3-6 \times 10^{-6}$ mol dm^{-3} were excited at a specific wavelength to afford a strong emission (Table 1), and the fluorescence intensity at a wavelength near the emission maximum was used to determine the complex stability constants. The spectrofluorometric titration was performed at 20.0, 25.0, 30.0, 35.0, 40.0, and 45.0 °C to give the complexation thermodynamic parameters.

Ultraviolet−visible spectra were measured employing a Shimadzu UV-2401PC using a conventional 1 cm path (1×0.25 cm) quartz cell in a thermostated compartment, which was kept at 25 °C through a Shimadzu TB-85 Thermo Bath unit. The sample solutions contained crystal violet (CV) at the concentration of ca. 1×10^{-5} mol dm^{-3}.

Results and Discussion

1. Ultraviolet Spectral Behavior of Crystal Violet upon the Inclusion Complexation of *β*-Cyclodextrin and Calix[6]-arenesulfonate. From the spectral changes of spectrophotometric titration, it was evident that the inclusion complexation of crystal violet with C6S and *β*-cyclodextrin are distinctly different. Crystal violet shows strong absorption at 583 nm, upon the addition of *β*-cyclodextrin, the absorbance gradually decreases, and the peak shifts to 590 nm (bathochromic/red shift), however, the shape of the absorption peak does not change markedly. While adding C6S, the shape of the absorption curve changes, the peak at 583 nm decreases rapidly, and a peak at 536 nm appears and increases gradually, showing that there exist strong interactions between C6S and crystal violet. However, the complex stability constants could not be determined from the data obtained from the spectrophotometric titration.

2. Fluorescent Behavior of the Inclusion Complexation of Dye Guest Molecules with Calix[*n*]arenesulfonates ($n = 4, 6, 8$) and Cyclodextrin Derivatives. The fluorescence intensity of acridine red dye increased remarkably, and the emission peak gradually shifted from 560 to 553 nm (*β*-cyclodextrin) upon the complexation with the cyclodextrins. However, the order of the fluorescence intensity changes is based on the size/shape-fit concept, i.e., *β*-cyclodextrin > *γ*-cyclodextrin > α-cyclodextrin, which is same as that of hypsochromic/blue shift, 7, 1, and 0 nm for *β*-, *γ*-, and α-cyclodextrins, respectively (Table 1). Apparently, the acridine red dye molecule inserts into the hydrophobic cavity of the cyclodextrin, and the resulting hydrophobic interaction led to the hypsochromic/blue shift and the fluorescence enhancement.

The fluorescence intensity of acridine red dye decreased markedly upon the addition of calix[*n*]arenesulfonates, and the order of the fluorescence intensity changes is not the same as that of cyclodextrins, but is consistent with the size of the calixarene ring, i.e., calix[4]arenesulfonate < calix[6]arenesulfonate < calix[8]arenesulfonate. Although sulfonates could yield a quenching effect, it was found that, in the control titration experiment of acridine red dye molecule with 4-phenolsulfonate, i.e., the monomeric unit of calix[*n*]arenesulfonates (equiv: 0−1270), the quenching effect is limited and/or negligible, as

TABLE 1: Excitation and Emission Wavelength for the Dye Guest Molecules in the Absence and in the Presence of Host Compounds in Citrate Buffer Solution (0.10 mol dm^{-3}, pH 6.00) at 25.0 °C

guest	host	excitation wavelength/nm	emission wavelength/nm (without host)	emission shift or wavelength/nm (with host)
Acridine Red (AR)		493	560	
	α-CD			0
	β-CD			−7
	γ-CD			−1
	C4S			0
	C6S			+3
	C8S			0
	C6SPr			+2
	C6SBu			+5
	C6SHp			+6 → +4
	C6SOc			+7 → +4
	C8SHp			+5 → +4
	PhP-β-CD			−5
	PhSe-β-CD			−6
	BzSe-β-CD			−5
	EtP-β-CD			−5
	G-β-CD			−5
	l-Trp-β-CD			−5
	*m*Py-β-CD			−2
Acridine Orange (AO)		489	530	
	C6S			+3
Pyronine Y (PY)		525	552	
	C4S			0
	C6S			+3
	C8S			−4
Pyronine B (PB)		525	551	
	C4S			0
	C6S			+3
	C8S			−4
Fluorescein (FL)		482	512	
	β-CD			0
6-Toluidino-2-Naphthalene Sulfonate (TNS)		322		
	α-CD			478
	β-CD			482
	γ-CD			475

compared with the changes in fluorescence intensity upon the addition of calix[*n*]arenesulfonates. Furthermore, the emission peak at 561 nm does not shift. However, C6S caused a bathochromic/red shift (3 nm: 560 → 563 nm), although C4S and C8S almost do not cause any evident shift (Table 1). Therefore, the decreases in fluorescence intensity of acridine red upon the addition of calixarenesulfonates were mainly attributed to the inclusion complexation, not just to the simple quenching effect of sulfonate groups. The electrostatic interaction between the positively charged acridine red molecule and the negatively charged substituent groups in the flexible calixarene ring, as well as the hydrogen bonding, restricted the internal rotation, which should lead to fluorescence enhancement. However, the polarity or hydrophilicity around the dye molecule that resulted from the hydrogen bonding and electrostatic interaction afforded a much larger quenching effect. From the observed results, the cavity of the water-soluble calixarenes was found to display little hydrophobicity. From the bathochromic/red shift and the decrease in fluorescence intensity, it could be drawn that the acridine red dye molecule formed a host−guest inclusion complex with calix[*n*]arenesulfonates, although we do not have any direct evidence for the inclusion by calixarene hosts, and we could not rule out the possibility of the formation of an "external-type" complex, especially for C4S.

It is clearly seen that the fluorescence intensity of acridine red dye was enhanced upon the addition of chemically modified β-cyclodextrins: BzSe-β-CD (Figure 1a), PhSe-β-CD, PhP-β-CD, EtP-β-CD, and G-β-CD (Figure 1b). However, the hydrophobicity/hydrophilicity of the substituent group at C-6 position in one glucopyranose unit influences the increment in the fluorescence intensity of acridine red dye molecule, to some extent (Figures 1a and 1b). The hypsochromic/blue shifts caused by these β-cyclodextrin derivatives become smaller, ∼5 nm, as compared with that of the native β-cyclodextrin, which could be due to the microstructural change of the hydrophobic cyclodextrin cavity upon the asymmetric substitution and the resulted hindrance effect. As the case are l-Trp-β-CD and *m*Py-β-CD, although the hypsochromic/blue shift is only 2 nm for *m*Py-β-CD. However, the limited changes in the fluorescence intensity are irregular and/or negligible, showing no evidence on the complex formation, which could be attributed to the electrostatic repulsion. Because the 3-methyl-1-pyridinio substituent in *m*Py-β-CD is a positively charged group, and the amino group in the l-tryptophan residue in l-Trp-β-CD is in protonation state at pH 6.0 in the citrate buffer solution.

It is also clearly seen that the fluorescence intensity of acridine red dye was enhanced upon the addition of alkylated calix[*n*]-arenesulfonates ($n = 6, 8$), which is interestingly different from those of their parent calix[*n*]arenesulfonates, and the emission peak showed a larger and faster bathochromic/red shift (4−7 nm) (Figure 1c for C6SOc − AR system) except C6SPr, as compared with their parent calix[n]arenesulfonate. The larger and faster shift may be attributed to the stronger binding of acridine red with alkylated calix[*n*]arenesulfonate derivatives. For the C6SPr series, the changes in the fluorescence intensity are also limited, irregular, and/or negligible, similar to the case for the positively charged β-cyclodextrin derivatives, l-Trp-β-CD and *m*Py-β-CD. However, we do not think this results from the failure of complex formation. On the contrary, the complex was formed between C6SPr and acridine red guest molecules. The fluorescence intensity shows the opposite behavior upon the addition of the parent and the alkylated calix[*n*]arenesulfonates, i.e., there is a transformation from fluorescence weakening effect for the parent calix[*n*]arenesulfonates to fluorescence enhancement effect for the lower rim alkylated calix[*n*]arenesulfonates. The C6SPr is just at the critical point, where the two effects fully cancel each other.

The alkylated calix[*n*]arenesulfonates ($n = 6, 8$) possessing long hydrophobic chain caused interesting chromic shift (5−7 → 4 nm). The largest bathochromic/red shift resulted when they were at the lowest concentration (equiv. ∼4). Upon the continuous addition of the alkylated calix[n]arenesulfonates, the bathochromic/red shift gradually decreased, e.g., 7 → 4 nm for C6SOc, i.e., a hypsochromic/blue-shifttendency was observed, which is due to the hydrophobicity contribution of the long chain, although the overall chromic shift is still bathochromic.

The alkylation in the lower rim converts the phenolic hydroxyl groups into ether bonds, which makes the hydrogen-bonding fail to form, or at least greatly weakens the degree of hydrogen-bonding. This is a partial contribution to the enhancement in the cavity hydrophobicity. On the other hand, the enlarged hydrophobic cavity is mostly attributed to the appended long hydrophobic alkyl chain. The enlargement in the hydrophobic cavity certainly leads to the fluorescence enhancement effect.

It is well-known that the hydrophobic environment would result in the fluorescence enhancement effect, and generally lead

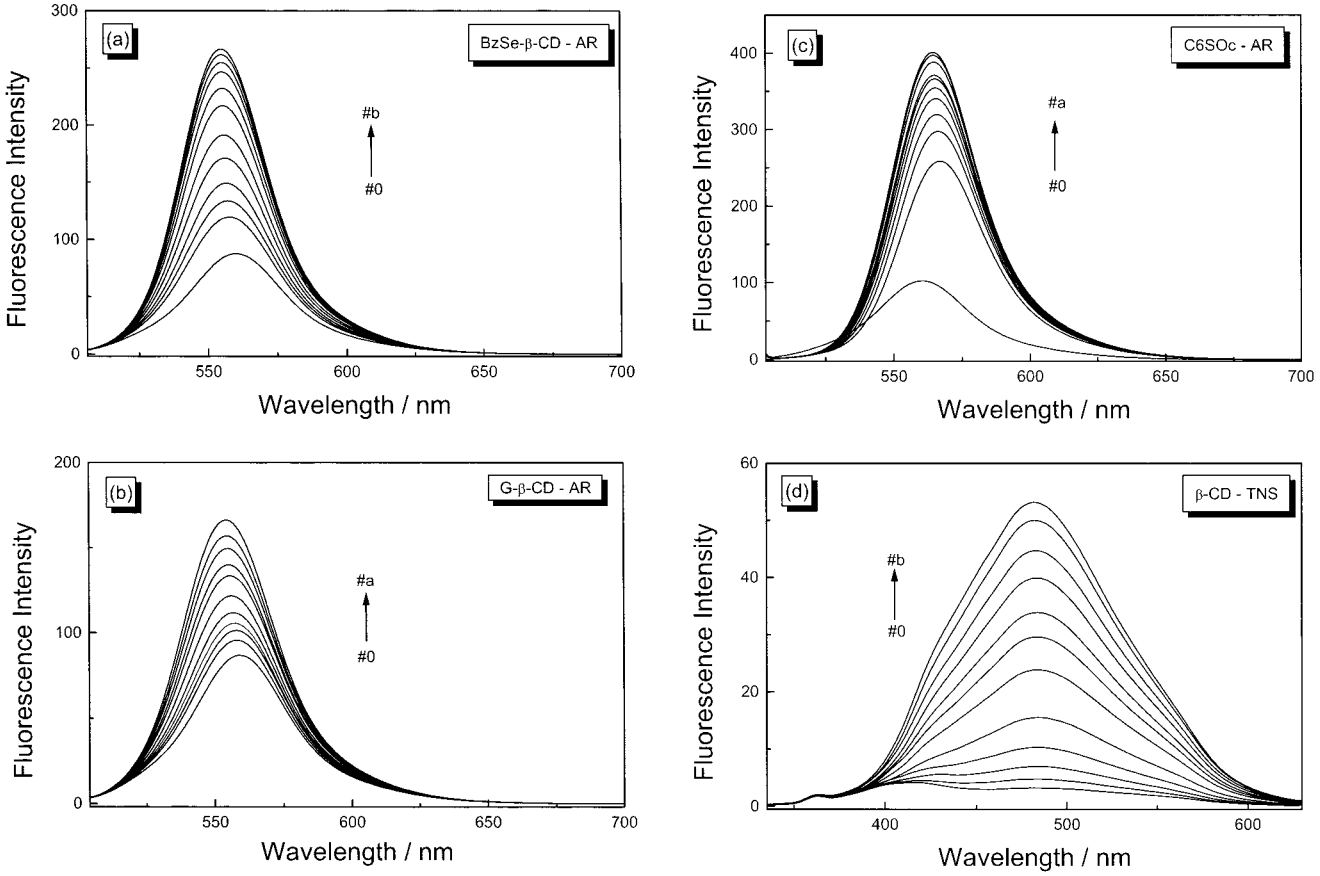


Figure 1. [a] Fluorescence spectra of acridine red dye (AR) (3.89×10^{-6} mol dm^{-3}) in the presence and absence of β-cyclodextrin derivative (BzSe-β-CD) (10^{-3} mol dm^{-3}): (0) 0; (1) 0.0205; (2) 0.0307; (3) 0.0410; (4) 0.0615; (5) 0.0819; (6) 0.123; (7) 0.164; (8) 0.205; (9) 0.246; (a) 0.287; (b) 0.328, in aqueous citrate buffer solution (pH 6.00) at 25.0 °C. [b] Fluorescence spectra of acridine red dye (AR) (3.89×10^{-6} mol dm^{-3}) in the presence and absence of β-cyclodextrin derivative (G-β-CD) (10^{-3} mol dm^{-3}): (0) 0; (1) 0.0310; (2) 0.0413; (3) 0.0619; (4) 0.0825; (5) 0.124; (6) 0.165; (7) 0.206; (8) 0.248; (9) 0.289; (a) 0.330, in aqueous citrate buffer solution (pH 6.00) at 25.0 °C. [c] Fluorescence spectra of acridine red dye (AR) (5.24×10^{-6} mol dm^{-3}) in the presence and absence of calix[6]arenesulfonate derivative (C6SOc) (10^{-3} mol dm^{-3}): (0) 0; (1) 0.0214; (2) 0.0321; (3) 0.0429; (4) 0.0535; (5) 0.0643; (6) 0.0750; (7) 0.0857; (8) 0.107; (9) 0.129; (a) 0.150, in aqueous citrate buffer solution (pH 6.00) at 25.0 °C. [d] Fluorescence spectra of sodium 6-toluidino-2-naphthalene sulfonate (TNS) (9.84×10^{-6} mol dm^{-3}) in the presence and absence of β-cyclodextrin (β-CD) (10^{-3} mol dm^{-3}): (0) 0; (1) 0.0107; (2) 0.0267; (3) 0.0533; (4) 0.107; (5) 0.213; (6) 0.320; (7) 0.427; (8) 0.640; (9) 0.851; (a) 1.277; (b) 1.703, in aqueous citrate buffer solution (pH 6.00) at 25.0 °C.

to a bathochromic/red shift, whereas the hydrophilic environment would weaken the fluorescence intensity of the fluorophore and usually cause a hypsochromic/blue shift. Apparently, the native and modified cyclodextrins belong to the former type, which features fluorescence enhancement and bathochromic/red shift. Calix[*n*]arenesulfonates ($n = 4, 6, 8$) definitely belong to the later type with fluorescence weakening effect and hypsochromic/blue shift. Interestingly, the alkylated calix[*n*]-arenesulfonates ($n = 6, 8$) could cause the fluorescence enhancement effect and lead to a hypsochromic/blue shift, which is the same as their parent calixarenesulfonates. The fluorescence intensity (F) is proportional to the concentration of the fluorophore (c) in dilute solution (eq 1),[33] in which the coefficient is called the molar fluorescence intensity (ϵ_F).[34] The change in ϵ_F value results from changes in fluorescence quantum yield (ϕ_F) and the molecular extinction (absorption) coefficient (ϵ) under certain experimental conditions in which the intensity of incident light (I_0) and the thickness of the sample (l) are kept constant (eq 2)[33]

$$F = \epsilon_F c \tag{1}$$

$$\epsilon_F = (\ln 10)\phi_F I_0 \epsilon l \tag{2}$$

The alkylation in the lower rim enlarges the hydrophobic cavity of the calixarene ring, as mentioned before, which would result in a great increase in ϵ values, and thus fluorescence enhancement. Although the enhancement was canceled in part due to the decrease in fluorescence quantum yield as in the case of calixarenesulfonates, the alkylated calixarenesulfonate systems showed overall increases in the fluorescence intensity.

The fluorescence intensity of acridine orange (AO) decreases gradually upon the addition of calix[6]arenesulfonate, accompanying with a continuous hypsochromic/ blue shift (3 nm for highest concentration of C6S).

The fluorescence intensity of pyronine Y and pyronine B decreases gradually upon the addition of calix[n]arenesulfonates, and the order of the fluorescence intensity decrement is same as that of acridine red, i.e., C4S < C6S < C8S. The chromic shifts of pyronine Y and pyronine B are interesting, 0 nm for C4S, 3 nm bathochromic/red shift for C6S, and 4 nm hypsochromic/blue shift for C8S, respectively. The bathochromic/red shift (3 nm) is reasonable, due to the same reason as for acridine red. However, the hypsochromic/blue shift for C8S might be due to that the C8S is the most flexible one; it could adopt a structure via induced-fit concept to accommodate the guest molecules, showing more hydrophobicity and/or hydrophobic interaction to some extent. The changes in the fluorescence intensity and the shift are opposite to the profiles of

acridine red dye molecule with the alkylated calix[*n*]arenesulfonates ($n = 6, 8$). The hypsochromic/blue shift is due to the hydrophobicity and hydrophobic interactions between the host and the guest upon the induced-fitted structural changes. However, the marked decreases in fluorescence quantum yield ϕ_F value would play a determining role in the fluorescence intensity changes, which, although, may be canceled partially by the contribution from the increase in molecular extinction (absorption) coefficient ϵ value.

TNS shows very weak fluorescence in aqueous solution, making the detection of the emission peak difficult. It is well-known that TNS is very sensitive to the hydrophobic environment. Upon the addition of cyclodextrins, the fluorescence intensity was largely enhanced (Figure 1d), showing the same order of the increment as for acridine red dye: β- cyclodextrin > γ-cyclodextrin > α- cyclodextrin. The resulted emission peaks are at 478, 482, and 475 nm for α-, β-, and γ-cyclodextrins, respectively.

3. Spectrofluorometric Titration. For the spectrofluorometric titration, assuming a 1:1 stoichiometry, the inclusion complexation of the dye guest molecule (G) with the host compounds (H) (cyclodextrins or calix[n]arenesulfonates) is expressed by eq 3, and the complex stability constant (K_s) is given by eq 4

$$H + G \overset{K_S}{\rightleftharpoons} H \cdot G \tag{3}$$

$$K_S = \frac{[H \cdot G]}{[H] \cdot [G]} \tag{4}$$

where [H], [G], and [H•G] represent the equilibrium concentration of the host, the guest, and the formed complex, respectively.

From eq 1, we can obtain the following equations. (In this case, the guest is the fluorophore.)

$$F_0 = \epsilon_F[G]_0 \tag{5}$$

$$F = \epsilon_F[G] + \epsilon_F'[H \cdot G] = \epsilon_F[G]_0 + (\epsilon_F' - \epsilon_F)[H \cdot G] \tag{6}$$

where $[G]_0$ signifies the initial concentration of the guest fluorophore, ϵ_F and ϵ_F' represent the molar fluorescence intensity of the free guest and the complexed guest, i.e., the formed complex (H•G).

Subtracting eq 5 from eq 6, we obtain

$$\Delta F = F - F_0 = (\epsilon_F' - \epsilon_F)[H \cdot G] = \Delta\epsilon_F[H \cdot G] \tag{7}$$

where ΔF and $\Delta\epsilon_F$ denote the changes in the fluorescence intensity and molar fluorescence intensity of guest molecule upon complexation with cyclodextrins or calixarenesulfonates.

Further, from eqs 4 and 7, eq 8 can be derived

$$\Delta F^2 - \Delta\epsilon_F\left([H]_0 + [G]_0 + \frac{1}{K_S}\right)\Delta F + \Delta\epsilon_F{}^2[H]_0[G]_0 = 0 \tag{8}$$

and solving eq 7 for ΔF, we obtain

$$\Delta F = \frac{\Delta\epsilon_F\left([H]_0 + [G]_0 + \frac{1}{K_S}\right) \pm \sqrt{\Delta\epsilon_F{}^2\left([H]_0 + [G]_0 + \frac{1}{K_S}\right)^2 - 4\Delta\epsilon_F{}^2[H]_0[G]_0}}{2} \tag{9}$$

where the initial concentrations were designated $[H]_0$ and $[G]_0$ for the host and the guest, respectively.

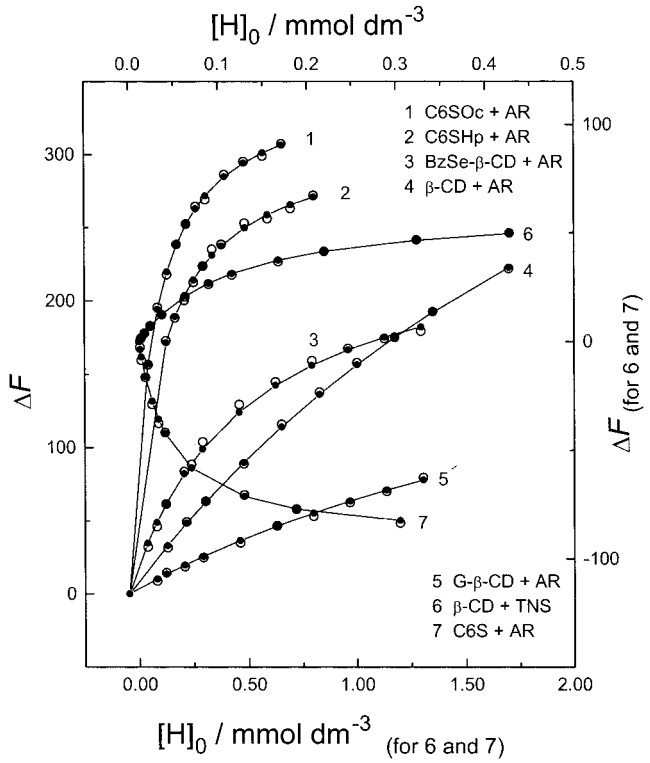


Figure 2. Curve-fitting plots for the spectrofluorometric titration: (1), C6SOc + AR; (2) C6SHp + AR; (3) BzSe-β-CD + AR; (4) β-CD + AR; (5) G-β-CD + AR; (6) β-CD + TNS; (7) C6S + AR.

Using the nonlinear curve-fitting approach,[10] the complex stability constant (K_S) and the change in molar fluorescence intensity ($\Delta\epsilon_F$) were calculated according to eq 9 using the data of ΔF observed at each initial host concentration $[H]_0$. Good curve-fitting plots further verify the 1:1 complex stoichiometry for each host−guest system. Typical curve-fitting plots are shown in Figure 2 for seven systems. The results are summarized in Table 2.

4. Complex Stability Constants and Molecular Recognition. The profiles of the stability constants for the dye guests with the two kinds of molecular receptors are shown in Figure 3. Comparing Figure 3 and the data in Table 2, it is seen that calix[*n*]arenesulfonates ($n = 4, 6, 8$) could form stable complexes with acridine red, pyronine Y, and pyronine B, showing similar molecular selectivity, i.e., the complex stability constants monotonically increase with the number of phenolic units in the calixarenes, C4S < C6S < C8S for each dye guest compounds. The ratios of complex stability constants (K_S) of C4S, C6S, and C8S with dye guest molecules are as follows: acridine red, 0.174:1:15.3; pyronine Y, 0.087:1:61.8; pyronine B, 0.075:1:36.9. This is due to the increases in cavity size and induced-fit concept resulting from the large flexibility of the calixarene rings. There are no significant differences among the K_S values of these three dye guests, acridine red, pyronine Y, and pyronine B, with a same calixarenesulfonate.

The profiles of the molecular selectivity of cyclodextrins are different from those of calixarenesulfonates. The stability constants of the inclusion complexation of acridine red with cyclodextrins show the order, β-cyclodextrin > γ-cyclodextrin > α-cyclodextrin, which embodies the size/shape-fit concept in the complexation process.

Because pyronine Y and pyronine B are larger than acridine red dye, although three of them possess high structural similarity,

TABLE 2: Stability Constants (log K_s) of Inclusion Complexation of Calix[*n*]arenesulfonates ($n = 4, 6, 8$) and Cyclodextrin Derivatives with Some Dye Molecules in Citrate Buffer Solution (0.10 mol dm^{-3}, pH 6.00) at 25.0 °C[a]

host	guest	K_s	log K_s	$-\Delta G$/kJ mol^{-1}
C4S	Acridine Red (AR)	1660	3.22	18.4
C6S	Acridine Red (AR)	9550	3.98	22.7
C8S	Acridine Red (AR)	146 000	5.16	29.5
α-CD	Acridine Red (AR)	49.7	1.70	9.68
β-CD	Acridine Red (AR)	1380	3.14	17.9
γ-CD	Acridine Red (AR)	117	2.07	11.8
β-CD	Crystal Violet (CV)	5850	3.77	21.5
C6S	Crystal Violet (CV)	- -		
C6S	Acridine Orange (AO)	416 000	5.62	32.1
β-CD	Acridine Orange (AO)	- -		
C4S	Pyronine Y (PY)	777	2.89	16.5
C6S	Pyronine Y (PY)	8950	3.95	22.6
C8S	Pyronine Y (PY)	553 000	5.74	32.8
α-CD	Pyronine Y (PY)			
β-CD	Pyronine Y (PY)			
γ-CD	Pyronine Y (PY)			
C4S	Pyronine B (PB)	790	2.90	16.5
C6S	Pyronine B (PB)	10 500	4.02	23.0
C8S	Pyronine B (PB)	387 000	5.59	31.9
α-CD	Pyronine B (PB)			
β-CD	Pyronine B (PB)			
γ-CD	Pyronine B (PB)			
C6S	Fluorescein (FL)			
β-CD	Fluorescein (FL)	11.7	1.07	6.10
C4S	6-Toluidino-2-Naphthalene Sulfonate (TNS)			
C6S	TNS			
C8S	TNS			
α-CD	TNS	53.8	1.73	9.88
β-CD	TNS	2420	3.38	19.3
γ-CD	TNS	176	2.25	12.8
PhP-*β*-CD	Acridine Red (AR)	2540	3.40	19.4
EtP-*β*-CD	Acridine Red (AR)	1190	3.08	17.6
PhSe-*β*-CD	Acridine Red (AR)	3660	3.56	20.3
BzSe-*β*-CD	Acridine Red (AR)	8050	3.91	22.3
G-*β*-CD	Acridine Red (AR)	1460	3.16	18.1
l-Trp-*β*-CD	Acridine Red (AR)			
*m*Py-*β*-CD	Acridine Red (AR)			
C6SPr	Acridine Red (AR)			
C6SBu	Acridine Red (AR)	22600	4.35	24.9
C6SHp	Acridine Red (AR)	31300	4.50	25.7
C6SOc	Acridine Red (AR)	42700	4.63	26.4
C8SHp	Acridine Red (AR)	165000	5.22	29.8

[a] Values are the averages of two or more independent runs; errors are less than 5% of the values reported in the table.

they fail to form stable complexes with cyclodextrins, due to the rigidity of the cyclodextrin cavity and the strict size/shape-fit concept.

TNS could form stable complexes with α-, *β*-, and *γ*-cyclodextrins, showing same molecular selectivity as for acridine red, *β*-cyclodextrin > *γ*-cyclodextrin > α-cyclodextrin. However, it could not form stable complexes with calixarenesulfonates, due to the electrostatic repulsion between the sulfonate groups in TNS and calixarenesulfonates.

The alkylation in the lower rim of calixarenesulfonates enlarges their hydrophobic cavity, which makes them form stable complexes with acridine red. Moreover, the complex stability constants increases with the length of the hydrophobic alkyl chain, i.e., the number of carbon atoms in the chain, showing that the ratios of the stability constants are 1:2.4:3.3:4.5 for C6S, C6SPr, C6SBu, and C6SOc.

The modification in the primary side of *β*-cyclodextrin somewhat influence the complex stability constants with acridine red dye molecule. Hydrophobic groups show some contribution to the increase in the complex stability constants. However, G-*β*-CD and EtP-*β*-CD possessing hydrophilic groups do not show any evidence of the complexation enhancement, showing complex stability constant very close to their parent *β*-cyclodextrin.

5. Thermodynamic Parameters of Inclusion Complexation. The stability constants K_S of the inclusion complexation of acridine red dye guest molecule with several typical molecular receptors were determined via spectrofluorometric titration at various temperatures ranging from 20.0 to 45.0 °C, which were listed in Table 3.

The complexation thermodynamic parameters (ΔH and ΔS) were obtained by the slope and ordinate-intercept of van't Hoff analysis $\ln K_s \approx 1/T$ plots applying eq 10. The results obtained are listed in Table 4

$$\ln K_S = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{10}$$

Inspection of Table 4 indicates that the cyclodextrin series show cavity selectivity for *β*-cyclodextrin over its analogues upon complexation with acridine red, giving the stability constant order of *β*-cyclodextrin > *γ*-cyclodextrin > α-cyclodextrin. The relatively rigid cavity of *β*-cyclodextrin (~7.8 Å) is best size-fitted to the acridine red dye molecule, whereas the cavity of α-cyclodextrin (~5.7 Å) is small as compared to the dye molecule. However, the complex stability constant monotonically increases with the number of phenolic units in the calixarene ring, which is attributed mainly to the electrostatic interaction, rather than to the cavity size. Therefore, the electrostatic interaction plays a determining role in their complex stability. Furthermore, alkylation in the lower rim of calix[6]-arenesulfonate (C6SBu) enhances the complex stability, which is 2 times that of calix[6]arenesulfonate (C6S).

To visualize the complexation behavior of the two kinds of molecular receptors from the thermodynamic point of view, the free energy ($-\Delta G$), enthalpy ($-\Delta H$), and entropy changes ($T\Delta S$) for the inclusion complexation of acridine red dye guest are plotted for typical cyclodextrins and calixarenesulfonates in Figure 4. The complexation thermodynamic parameters in Table 4 indicate that the complexation of acridine red molecule with calix[6]arenesulfonate is mainly driven by the favorable enthalpic change with a small entropic loss (Figure 4), which is attributed to the intermolecular hosts-guest interactions, such as electrostatic interaction of the guest's cationic moiety with sulfonates and hydrogen bonding of the guest's CH_3NH moiety with the phenolic hydroxyl groups. This is consistent with Barra's results.[14] Meanwhile, the complexation behavior of C6SBu (Figure 4) is also driven by the enthalpic change, but with accompanying a small entropic gain. Although C6SBu could not form effective hydrogen bonds with the alkyloxy groups in its lower rim, the hydrophobic interaction and van der Waals forces, as well as the electrostatic interactions with sulfonate groups, would contribute to the favorable enthalpy change, which is less than that of C6S because the hydrophobic interaction and van der Waals forces are weaker than hydrogen bonding. The entropy change originates from the entropic gain from the rearrangement of water molecules originally surrounding the host and guest molecules, and the entropic loss from the decrease in the motion freedom upon the complexation. In the case of C6SBu, the entropic gain term should be larger than that of C6S due to the guest molecules included into the enhanced hydrophobic cavity (lower rim), and it would be expected to balance the entropic loss due to the restricted mobility of the guest molecules to a much greater extent than

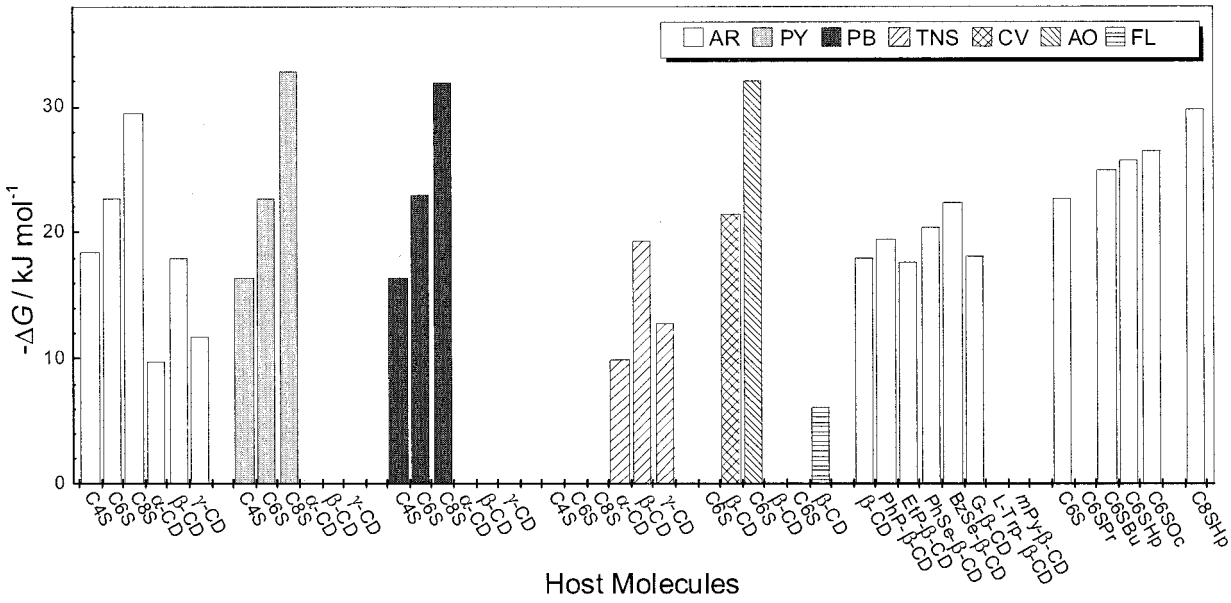


Figure 3. Profile of the free energy changes ($-\Delta G$) of inclusion complexation of calix[n]arenesulfonates ($n = 4, 6, 8$) and cyclodextrin derivatives with acridine red (AR), pyronine Y (PY), pyronine B (PB), sodium 6-toluidino-2-naphthalene sulfonate (TNS), crystal violet (CV) and fluorescein (FL) in citrate buffer solution (0.10 mol dm^{-3}, pH 6.00) at 25.0 °C.

TABLE 3: Stability Constants (log K_s) of Inclusion Complexation of Calix[6]arenesulfonates and β-cyclodextrin Derivatives with Acridine Red (AR) in Citrate Buffer Solution (0.10 mol dm^{-3}, pH 6.00) at Various Temperature[a]

		log K_s					
host	guest	20.0 °C	25.0 °C	30.0 °C	35.0 °C	40.0 °C	45.0 °C
C6S	Acridine Red (AR)	4.056		3.914	3.842	3.676	3.573
C6SBu	Acridine Red (AR)		4.465	4.392	4.324	4.262	4.139
β-CD	Acridine Red (AR)		3.139	3.126	3.117	3.139	3.133
BzSe-β-CD	Acridine Red (AR)	3.929	3.883	3.810	3.727	3.689	
EtP-β-CD	Acridine Red (AR)	3.162	3.111		3.086	3.047	2.983

* Values are the averages of two or more independent runs; errors are less than 5% of the values reported in the table.

TABLE 4: Thermodynamic Parameters (kJ mol^{-1}) of Inclusion Complexation of Calix[*n*]arenesulfonates ($n = 4, 6, 8$) and β-cyclodextrin Derivatives with Guest Molecules

host	guest	log K_s	$-\Delta G$	$-\Delta H$	$T\Delta S$	ref
C6S	Acridine Red (AR)	3.98	22.7	34.7	−11.8	*a*
C6SBu	Acridine Red (AR)	4.46	25.5	24.4	1.11	*a*
β-CD	Acridine Red (AR)	3.14	17.9	0	17.8_5	*a*
BzSe-β-CD	Acridine Red (AR)	3.88	22.2	22.4	−0.31	*a*
EtP-β-CD	Acridine Red (AR)	3.11	17.7_5	9.0	8.8	*a*
C4S	*N*,*N*,*N*-Trimethyl-phenylammonium chloride (TMPA)	3.748	21.4	25.9	−4.48	*b*
C6S	TMPA	2.740	15.6	1.05	14.6	*b*
C8S	TMPA	3.716	21.2	0	21.2	*b*
C4S	*N*,*N*,*N*-Trimethyl-adamantanylammonium chloride (TMAA)	4.322	24.7	23.8	0.81	*b*
C6S	TMAA	3.000	17.1	0.63	16.6	*b*
C8S	TMAA	4.279	24.4	0	24.4	*b*
C4S	Phenol Blue (PB)	2.418	13.8	29.3	−15.9	*c*
C6S	Phenol Blue (PB)	2.691	15.4	26.8	−12.0	*c*
C8S	Phenol Blue (PB)	2.703	15.4	31.0	−16.3	*c*
C6SMe(methyl)	Phenol Blue (PB)	1.863	10.6	12.6	−3.14	*c*
C6SHx(hexyl)	Phenol Blue (PB)	3.435	19.6	0	20.1	*c*

[a] Data obtained in citrate buffer solution (0.10 mol dm^{-3}, pH 6.00) at 25.0 °C [b] Ref 11b. [c] Ref 14.

in the case of C6S, resulting in the slight overall entropic gain. However, the complexation of the acridine red dye molecule with β-cyclodextrin is entirely driven by the entropic increase (Figure 4). This is the typical case driven by the classical hydrophobic interaction in the inclusion complexation.[35,8,9] The hydrophobic interaction seems to be the main binding contribution in the cyclodextrin-acridine red complexation system. A reasonable explanation is the release of high-energy water molecules from the cavity upon complexation and the desolvation of acridine red dye molecules.

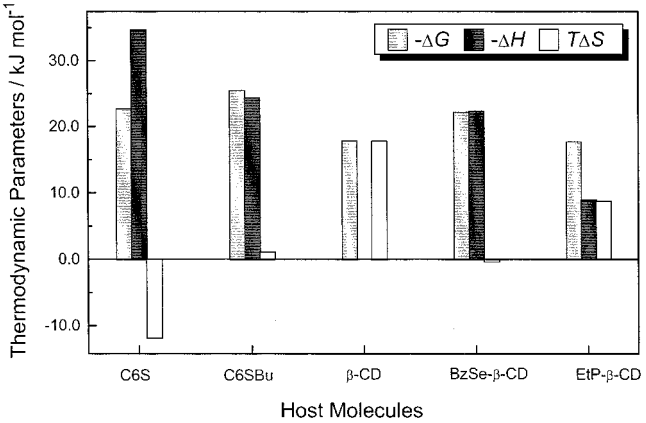


Figure 4. Profile of the changes in free energy ($-\Delta G$), enthalpy ($-\Delta H$), and entropy ($T\Delta S$) of inclusion complexation of calix[6]-arenesulfonates and β-cyclodextrin derivatives with acridine red (AR) in citrate buffer solution (0.10 mol dm^{-3}, pH 6.00) at 25.0 °C.

However, contrary to the parent β-cyclodextrin, the complexation of acridine red molecules with BzSe-β-CD possessing a hydrophobic substituent group is mainly driven by the favorable enthalpic changes accompanying with a very small entropic loss (Figure 4). The complexation of acridine red with EtP-β-CD possessing a hydrophilic substituent group is equally

driven by the enthalpic change and the entropic increase (Figure 4). This is consistent with the thermodynamic parameter profiles of the corresponding inclusion complexation of l-tryptophan with BzSe-β-CD and EtP-β-CD, respectively.[22]

6. $\Delta H - T\Delta S$ Compensation. The thermodynamic parameters for the complexation of several metal cations and positively charged organic guest with calix[n]arenesulfonates exhibited a compensatory extrathermodynamic relationship between ΔH and $T\Delta S$ values.[36] The slope (α) and intercept ($T\Delta S_0$) of the regression line of the $\Delta H - T\Delta S$ plot could be taken as measures of the conformational changes and the extent of desolvation upon the complexation.

Using the thermodynamics data ($n = 13$) obtained in this and previous studies listed in Table 4, the entropy changes ($T\Delta S$) for calixarenesulfonates were plotted against the enthalpy changes (ΔH) to give a good linear relationship (correlation coefficient $r = 0.941$). The large slope ($\alpha = 1.01$) and intercept ($T\Delta S_0 = 18.99$ kJ mol^{-1}) obtained from the regression line indicates that substantial conformational changes and extensive desolvation upon the complexation. These values are very close to those for modified cyclodextrins.[22]

Conclusion

An investigation of the complexation of some dye molecules with calix[*n*]arenesulfonates and cyclodextrins indicates that, although both molecular receptors possess a hydrophobic cavity, they lead to different profiles of the fluorescence intensity changes upon complex formation. The fluorescence intensity of the dye guest molecules gradually decreases upon the addition of calix[*n*]arenesulfonates, accompanying with hypsochromic/blue shifts. The fluorescence intensity of the dye guest molecules increases greatly upon the complexation of native cyclodextrins and chemically modified cyclodextrins, accompanying with bathochromic/red shifts. Interestingly, the alkylation in the lower rim of calix[*n*]arenesulfonates enlarges their hydrophobic cavity, causing the fluorescence intensity of the dye guest molecules to gradually increase, however, accompanying with hypsochromic/blue shifts. The calix[*n*]arenesulfonates and cyclodextrins could form stable complexes with some dye guest molecules and the complex stability constants were determined via the spectrofluorometric titration. Native and chemically modified cyclodextrins show high molecular selectivity based on the size/shape-fit concept. The thermodynamic parameters for the inclusion complexation obtained for typical molecular receptors are useful in elucidating the complexation mechanisms.

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