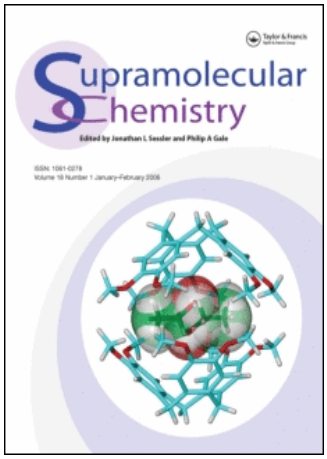

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# A Comparative Study of Complexation of β-Cyclodextrin, Calix[4]arenesulfonate and Cucurbit[7]uril with Dye Guests: Fluorescence Behavior and Binding Ability

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# A Comparative Study of Complexation of β-Cyclodextrin, Calix[4]arenesulfonate and Cucurbit[7]uril with Dye Guests: Fluorescence Behavior and Binding Ability

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**The complexation behaviors of acridine red (AR), neutral red (NR) and rhodamine B (RhB) dye guest molecules by three kinds of supramolecular hosts, including β-cyclodextrin (β-CD), calix[4]arene tetrasulfonate (C4AS) and cucurbit[7]uril (CB[7]), have been investigated by means of fluorescence spectra in aqueous citrate buffer solution (pH 6.0). The results obtained show that the three hosts, possessing different types of cavity, lead to various complexation-induced fluorescence of dye guests, and present different binding ability and molecular selectivity. The complexation stability constants decrease in the order of NR > AR > RhB for C4AS and CB[7] hosts, while in the order of RhB > AR > NR for β-CD host. Particularly, CB[7] displays the strongest binding ability with NR ($K_S = 33300\,M^{-1}$), and provides the molecular selectivity of 4.8 for NR/AR pairs. Although the binding ability of C4AS for present dye guests is weaker than CB[7], but the molecular selectivity of the two hosts are nearly equivalent. β-CD shows stronger binding ability with RhB ($K_S = 5880\,M^{-1}$) as comparison with CB[7] and C4AS. Furthermore, the solvent effects and salt effects during the course of complexation have also been investigated.**

*Keywords*: Dye; Fluorescence behavior; Cyclodextrin; Calixarene; Cucurbituril

## INTRODUCTION

In recent years, the inclusion complexation and molecular recognition are of considerable interest in host-guest chemistry or supramolecular chemistry [1,2]. In this field, cyclodextrins (CDs) [3], calixarenes (CAs) [4,5], and cucurbiturils (CBs) [6,7] as three most active synthetic receptors have been extensively studied. CDs are 1 → 4 α-linked cyclic oligomers of anhydroglucopyranose. CAs are a class of macrocycles that are generally made up of phenol units linked by methylene bridges. CBs are macrocyclic container molecules composed of glycoluril monomers joined by pairs of methylene bridges. Although the structural outlines of these three receptors all look like each other, possessing hydrophobic cavity, their intrinsical characteristics and inclusion properties differ much from each other: a) An equatorial symmetry plane is exhibited in the CBs structure which does not exist in the CDs and CAs, and thus, both cavity portals are identical in CBs and different in CDs and CAs. b) CDs and CBs are rigid molecules with a relatively fixed cavity compared to CAs, which are conformationally mobile molecules. c) During the course of molecular recognition, hydrophobic interactions are mainly dominating forces for CDs system [8–17], while π-stacking for CAs [18–21]. In the case of CBs, both hydrophobic interactions and ion-dipole interactions are crucial forces [22–34]. d) CDs' cavity possesses chiral micro-environment, and CDs present chiral recognition ability, while CBs and CAs are achiral receptors. So CDs often play an important role in the chiral recognition [35–38].

Based on these differences, comparative investigation of binding behaviors of CDs, CAs and CBs attracts us more and more interesting. In fact, we have reported the inclusion complexation of dye guest molecules with water soluble calixarene derivatives and native and chemically modified cyclodextrins in previous work, indicating that some dye guest molecules could form stable complexes with calix[*n*]arenesulfonates and cyclodextrins, but their fluorescence behaviors are entirely different

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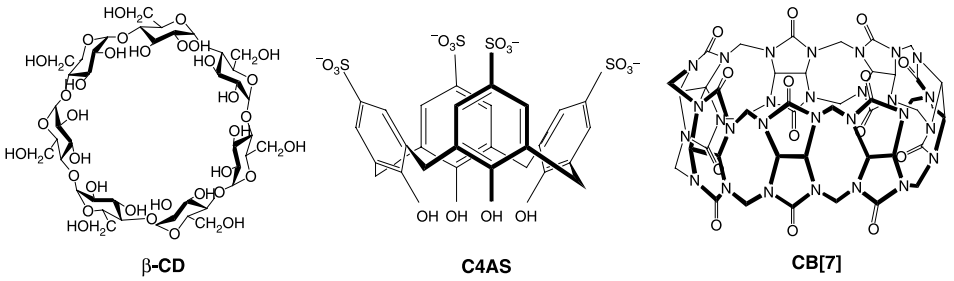


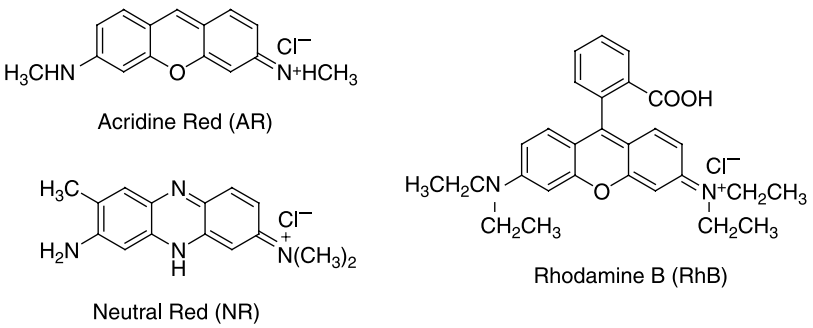

SCHEME 1 Molecular structures of hosts.

[39,40]. Moreover, Inoue, Kaifer and Kim *et al.* demonstrated a comparative study of the inclusion complexation of the ferrocene derivatives with cucurbituril and cyclodextrin, showing that all neutral and cationic guests form highly stable inclusion complexes with cucurbit[7]uril (CB[7]) and the negatively charged guest ferrocenecarboxylate was not bound by CB[7] at all, which are in sharp contrast to the binding behaviors of the same guests to β-cyclodextrin (β-CD), since all the guests form stable inclusion complexes with β-CD [41]. However, to the best of our knowledge, there are no reports on comparison studies of these three kinds of molecular receptors and even comparison studies of calixarenes and cucurbituril, although such comparative investigations are significant in selecting and designing different kind of host for binding a given guest with different binding strength. Among these three kinds of receptors and their derivatives, β-CD, calix[4]arene tetrasulfonate (C4AS) and CB[7] all are water-soluble ($2–3 \times 10^{-2}$ M for CB[7] [42–45], $1.6 \times 10^{-2}$ M for β-CD [43–45] and 0.1 M for C4AS [46]) and possess similar size of cavity. CB[7] has an internal cavity with a diameter of ca. 7.3 Å and a portal diameter of ca. 5.4 Å [43–45], and it is comparable in diameter to the β-CD cavity (6–7 Å) [47] and C4AS cavity (6.0–6.3 Å if approximated as a sphere) [48]. Therefore, in the present work, we selected these three typical receptors, β-CD, C4AS and CB[7] (Scheme 1), and investigated their binding behaviors with some dye guests through fluorescence titration experiments, such as acridine red (AR), neutral red (NR) and rhodamine B (RhB) (Scheme 2). Moreover, the salt effects and solvent effects have also been investigated that how they affect the molecular recognition abilities during the course of host-guest complexation. Previously, some binding behaviors of these dye guests have been reported by Singh [47], Nau [30] and our group [17,39,40], respectively. The present comparisons will further clarify the inclusion characteristics of CDs, CAs and CBs for dye guests. In addition, these investigations will illuminate how the solvent conditions affect the inclusion complexation of three typical hosts with dyes, including pH values, salt and solvent effects. These results obtained will serve us further understanding of the development of host-guest chemistry, such as the applications of dyes improved by host-guest recognition, including stabilizing additives of dye lasers [29], storing dilute dye solutions and the labeling of biological molecules (target light-up probes, molecular beacons, chip technology, immunoassays) [49,50].

## EXPERIMENTAL SECTION

### General

Fluorescence spectra were measured using a JASCO spectrofluorometer model FP-750 using a conventional $10 \times 10 \times 45\,mm^3$ quartz cell in a thermostated compartment, which was kept at a constant temperature through a Shimadzu TB-85 Thermo Bath unit. The excitation wavelengths for AR, NR and RhB were 493, 510, and 520 nm, respectively. The sample solutions containing dye guests at the concentration




SCHEME 2 Molecular structures of dye guests.

of approximately 4–6 × $10^{-6}$ mol dm$^{-3}$ were excited at a specific wavelength to afford a strong emission. The titration solutions were prepared in 10 mL volumetric flasks with host/guest molar ratio ranging from 0 to ~400, which varies upon the stability constant of the complex formed.

### Materials

β-CD was obtained from Tokyo Kasei and dried under reduced pressure before use. C4AS [51] and CB[7] [52,53] were synthesized and purified according to the literature reports. AR, NR and RhB were purchased from Wako. 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 6.0, 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 (pH 6.0).

## RESULTS AND DISCUSSION

### Spectral Titrations

Spectral titrations of β-CD, C4AS and CB[7] with structurally related dye guests were performed at 25.0°C in a 0.10 mol dm$^{-3}$ citrate buffer solution of pH 6.0, to quantitatively assess the inclusion complexation behaviors of these compounds. The spectral changes depended critically on the formation of a new species, that is, a host-guest inclusion complex, showing the spectral enhancement or quenching. As shown in Fig. 1, the fluorescence intensity of RhB dye changed to a different extent with the addition of β-CD, C4AS and CB[7]. However, in the control experiments, under identical conditions the fluorescence intensities of the dye guests were not appreciably affected by the addition of pyranoglucose, 4-phenolsulfonate and glycoluril, i.e., the monomeric unit of β-CD, C4AS and CB[7]. These phenomena indicated that the dye guests must be included into the cavities of the three hosts, forming the host-guest inclusion complexes. The similar results are also observed in the spectral titrations of the other selected dyes with β-CD, C4AS and CB[7]. Assuming 1:1 inclusion complexation stoichiometry between the three hosts and dye guests, the complex stability constants (*K*s) could be calculated by analyzing the sequential changes in fluorescence intensity (Δ*F*) of dye that occurred with changes in host concentration. This analysis was carried out by using a nonlinear least-squares curve-fitting method. For each dye guest examined, the plot of Δ*F* as a function of $[H]_0$ gave an excellent fit ($R > 0.99$), verifying the validity of the 1:1 inclusion complexation stoichiometry assumed. In the repeated measurements, the *K*s values were reproducible within an error of ±5%. The complex stability constants (*K*s) obtained for all of the host-guest combinations are listed in Table I.

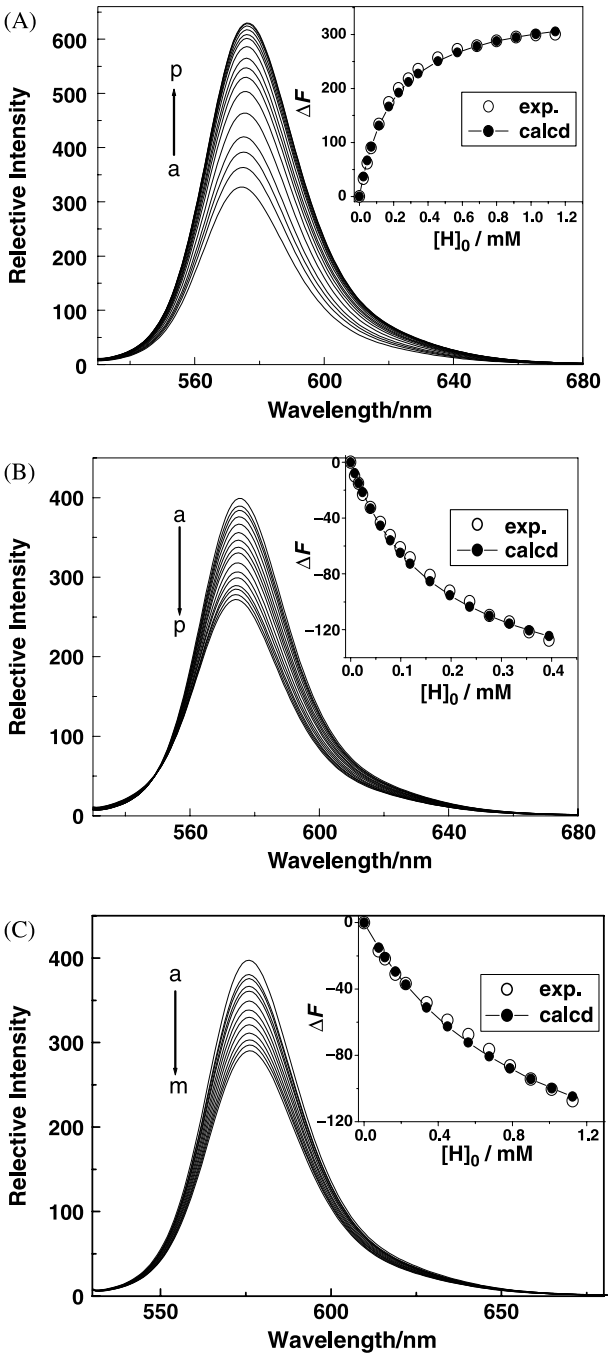



FIGURE 1 Fluorescence spectra of RhB in the presence and absence of CB[7] [A], β-CD [B] and C4AS [C] in aqueous citrate buffer solution (pH 6.0) at 25.0°C. Inset: the nonlinear least-squares analysis of the differential intensity (Δ*F*) to calculate the complex stability constant ($K_S$). [RhB] = 4.08–4.98 × $10^{-6}$ mol dm$^{-3}$, $[host]_{max}$ = 0.40–1.14 × $10^{-3}$ mol dm$^{-3}$. Inset: the nonlinear least-squares analysis of the differential intensity (Δ*F*) to calculate the complex stability constant ($K_S$).

TABLE I Stability constants ($K_S/M^{-1}$) of inclusion complexation of β-CD, C4AS and CB[7] with some dye molecules in citrate buffer solution (0.10 mol dm$^{-3}$, pH 6.0) at 25.0°C

| | CB[7] | β-CD | C4AS |
|---|---|---|---|
| Acridine red | 6890 ± 50 | 1380† | 1660† |
| Neutral red | 33300 ± 450 | ‡ | 8210 ± 210 |
| Rhodamine B | 5050 ± 40 | 5880 ± 120 | 1090 ± 45 |

† Ref. [39,40]. ‡ The spectral changes are too weak to calculate the *Ks* value

### Fluorescence Behavior

The fluorescence intensity of all three dye guests increases markedly upon the addition of CB[7], which is just contrary to C4AS. In the case of the addition of β-CD, the fluorescence intensity of AR and NR increases and that of RhB decreases. Apparently, these fluorescence enhancements of the emission bands were attributed to the inclusion of the molecules in the CB[7] or β-CD cavity. And the inclusion of guests into host cavity results in the decrease in the intramolecular rotational freedom of the guest molecule. For RhB guest, it presents different fluorescence behavior upon complexed by β-CD due to the equilibrium shift from the hydrophilic, fluorescent carboxylate ion form of RhB to the hydrophobic, nonfluorescent lactone form [54]. The decreases in fluorescence intensity of dyes upon the addition of C4AS were mainly attributed to the inclusion complexation, not just to the simple quenching effect of sulfonate groups [39,40]. The quenching phenomena can be rationalized in terms of efficient quenching through hydrogen atom abstraction from the phenolic hydroxyl groups and possibly, also exciplex formation with the aryl rings, which is a composite effect [55]. On the other hand, it can be validated by our previous work that calix[*n*]arenesulfonates modified by the alkylation in the lower rim can effectively cause the fluorescence intensity of the dye guest molecules to gradually increase [39,40]. The hypsochromic/bathochromic shifts of dyes fluorescence are neglectable upon the complexation with CD, CB7, and C4AS except an exceptional case of NR with CB7. Dramatically, the emission peak of NR showed a visible hypsochromic shift of 21 nm accompanied with the steep increase of fluorescence intensity upon complexation with CB7. This fluorescence behavior provides advantageous evidence that CB7 form strongly stable inclusion complex with NR guest, a conclusion which is also supported by the complex stability constants (see Table I).

### Molecular Binding Ability and Selectivity

It is seen from the data in Table I that CB[7] and C4AS could form moderately stable complexes with positively charged guests, showing similar $K_S$ orders, i.e., NR > AR > RhB. It is worth mentioning that CB[7] includes NR most strongly with the highest complex stability constants ($K_S = 33300\,M^{-1}$), and the molecular selectivity for NR/AR pairs is high to 4.8. One reasonable explanation is that CB[7] can effectively bind the positive-charge portion of AR guest mainly through ion-dipole interactions, while for NR guest, the hydrogen bond interactions between the middle NH group in NR and C═O group in CB[7] possibly also play crucial role in the host-guest complexation besides the ion-dipole interactions. On the other hand, the binding behaviors of CB[7] for AR and NR guests is pH dependent. CB[7] prefers to include the positive-charged guests relative to neutral guests. At the present pH value (6.0), the NR and AR guests (pKa of NR: 6.8; pKa of AR: 7.4) are protonated more or less. Although the pKa value of AR is larger than that of NR, however, it has been well demonstrated that the pKa value of NR shifts dramatically from 6.8 to 8.8 upon complexation by CB[7]. Therefore, it also illuminates to some extent the great difference in binding affinity between AR and NR. Similarly, C4AS presents the molecular selectivity for NR/AR pairs of 4.9. For the complexation of C4AS with NR, AR guests, the host-guest charge effect together with the C—H$\cdots\pi$ interactions (between the guest $CH_3$ on positive-charge group and the host aromatic rings) may act as the mainly dominating forces, the $\pi\cdots\pi$ interactions are neglectable because the size of aromatic portion in guest is too large to be included into the C4AS cavity. In NR guest, there is one more $CH_3$ group (linked with $N^+$) as comparison with AR guest, which can be more strongly complexed by C4AS. It is a pity that the conclusive results of binding modes from NMR study cannot be obtained due to solubility limitations.

However, the $K_S$ sequence of β-CD with dyes is much different from CB7 and C4AS, and the $K_S$ values decrease in the order RhB > AR > NR. Particularly, the inclusion complexation of β-CD with NR is too weak to be determined by the method of fluorescence titrations because not only the two ends but also the middle portion of NR guest are high-polarity. For the same guest, the complex stability constants monotonically increase with CB[7] > C4AS, which may be explained by the rigidity of the CB[7] cavity and the strict size/shape fit concept, i.e., CB[7] cavity is more rigid and a bit larger than C4AS. RhB shows the strongest binding ability with β-CD host ($K_S = 5880\,M^{-1}$) as comparison with CB[7] and C4AS, possibly because RhB molecule exists in its spirocyclic form and complexes with β-CD in the phenyl—COOH moiety [54], resulting in stronger hydrophobic interactions. In addition, it should also be mentioned that the other intermolecular forces, i.e., polarizabilities of hosts

and hence dispersion interactions, may contribute differently to the binding of the guests. As reported before, the polarizabilities of β-CD, C4AS and CB[7] are 0.204, 0.245, and 0.12, respectively [55]. In other words, the polarizabilities of these three hosts decrease in the order of C4AS > β-CD > CB[7]. However, there is not any corresponding regularity about the host-guest $K_S$ values going with the change of polarizabilities. Therefore, we deduce that the polarizabilities of hosts are not very important during the course of complexation of dye guests.

### Environment Effects

It is well known that the environment effects, including pH values, solvent effects and salt effects, should significantly affect the *K*s values and molecular selectivity upon complexation of host with guest. For example, the binding behaviors of NR guest with CB[7] and β-CD have been studied at different pH values, acidic and basic conditions, respectively. Their results obtained show that complexation of NR by CB[7] is stronger for the protonated form ($K_S = 6 \times 10^5\,M^{-1}$ at pH 2.0) than the unprotonated form ($K_S = 6.5 \times 10^3\,M^{-1}$ at pH 11.0) [30]. The present pH value studied is nearly neutral, and then the binding constant ($K_S = 3.3 \times 10^4\ M^{-1}$ at pH 6.0) of CB[7] with NR is in the range between those of pH 2.0 and pH 11.0. That is to say, the binding ability of CB[7] with NR is pH-sensitive, increasing sharply while accompanied with the decrease of pH values, owing to the protonation of NR guest. On the other hand, complexation of NR by β-CD is stronger for the neutral form ($K_S = 4.11 \times 10^2\,M^{-1}$) than the protonated form ($K_S$ is apparently too weak to detect), which is mainly because the protonated form is more hydrophilic [47]. Similarly, the binding constant of β-CD with NR cannot be obtained at present case of weak acidic condition yet. The inclusion phenomena of β-CD upon pH change are distinct from those of CB[7]. This is mainly attributed to the intrinsic difference of included driving forces between CB[7] and β-CD, as mentioned in the Introduction. For C4AS cases, most like CB[7], the binding ability for charge-changed guests also increases sharply accompanied with the decrease of pH values among the certain pH range [21,56–58].

Moreover, Warner *et al.* have demonstrated that the addition of a small amount of organic solvents, such as alcohols, could alter the binding abilities of cyclodextrin hosts toward model substrates in aqueous solution [59–62]. Kaifer and coworkers have demonstrated that the $K_S$ values of CB[7]-methyl viologen complex decrease with increasing ionic strength, with more pronounced effects for solutions containing divalent $Ca^{2+}$ ions than for solutions containing monovalent $Na^+$ ions [63]. And Nau *et al.* reported the salt effects of host-guest complexation between cucurbit[6]uril and various guests [64]. To the best of our knowledge, however, the solvent effects upon the binding abilities of cucurbit[n]uril ($n = 5$, 6, 7, 8) and calix[*n*]arenesulfonates ($n = 4$, 5, 6, 8) and the salt effects upon the binding abilities of cyclodextrins and calix[*n*]arenesulfonates have been studied less frequently. Hence, it is interesting to study the effects of solvent and salt in the host-guest binding behaviors.

To examine the influence of solvents on the binding abilities of three kinds of hosts toward dye guests, we performed the fluorescence titration experiments in which a small amount (4%, by volume) of methanol was added to the citrate buffer solution (pH 6.0), and the binding constants of β-CD, C4AS and CB[7] toward dye guests in the presence and absence of methanol were quantitatively assessed. The results for a representative RhB system are listed in Table II.

From Table II, it can be seen that the binding constant of the β-CD–RhB complex increased ($5880 \rightarrow 8310\,M^{-1}$), while those of CB7 and C4AS complexes decreased ($5050 \rightarrow 1442\,M^{-1}$ for CB[7]–RhB; $1092 \rightarrow 496\,M^{-1}$ for C4AS–RhB) upon addition of a small amount of methanol. During the course of complexation of β-CD with guests, hydrophobic interactions are the mainly driving forces. It has been well documented that the addition of alcohols could extrude water from the cavity and make the cavity more hydrophobic, and thus strengthen the binding of guests. On the other hand, some main noncovalent interactions working between host and guest, such as electrostatic and hydrogen bond interactions, would be weakened to some extent when some water molecules were replaced by alcohols. The ion-dipole and electrostatic interactions play great role in the complexation of CB[7]/C4AS with RhB, respectively. Therefore, the addition of methanol weakened the binding ability of CB[7]/C4AS with dye guests. In addition, the $K_S$ value of CB[7]–RhB decreases (3.5 times) to more extent than that of C4AS–RhB

TABLE II Complex stability constants (*K*s) and Gibbs free energy changes ($-\Delta G°$) for formation of the inclusion complex between the hosts and RhB in citrate buffer solution (0.10 mol dm$^{-3}$, pH 6.0) containing methanol (4 vol%) or 0.4 M NaCl aqueous solution at 298.15 K

| Host | Addition | *K*s ($M^{-1}$) | $-\Delta G°$ (kJ mol$^{-1}$) |
|---|---|---|---|
| CB7 | None | 5050 | 21.1 |
| | Methanol | 1442 | 18.0 |
| | NaCl | 887 | 16.8 |
| β-CD | None | 5880 | 21.5 |
| | Methanol | 8310 | 22.4 |
| | NaCl | 3330 | 20.1 |
| C4AS | None | 1090 | 17.3 |
| | Methanol | 496 | 15.4 |
| | NaCl | 339 | 14.4 |

(2.2 times). According to the results reported before [65,66], C4AS does not accommodate methanol molecule at all. So the addition of methanol hardly takes any effect to the cavity of C4AS. For CB[7], the case may be different because CB can form stable complexes with alcohol guests [67]. Some methanol molecules may enter into the cavity of CB[7], possibly taking some additional disadvantage of the complexation between host and guest.

In order to compare salt effects, a moderate concentration (0.4 M) of NaCl was added to the citrate buffer solution (pH 6.0) in the fluorescence titration experiments, and the binding constants of β-CD, C4AS and CB[7] toward dye guests in the presence and absence of NaCl were quantitatively assessed. As can be seen from Table II, the salt effects are very pronounced on the formation of CB[7] and C4AS inclusion complexes since the binding constant decreases 5.7 times and 3.2 times respectively. The dramatic decrease of binding ability is mainly caused by the competing ion-dipole or electrostatic interactions between $Na^+$ and RhB molecule. In addition, the $K_S$ value of CB[7]–RhB decreases to more extent than that of C4AS–RhB, which can be well explained that CB[7] possibly shows stronger binding ability ($K_S = 1700\,M^{-1}$ for the complexation of $Na^+$ with CB[6]) [68] toward $Na^+$ than C4AS ($K_S = 75\,M^{-1}$ at pH 2.4, $85\,M^{-1}$ at pH 7.4) [69]. Moreover, according to the results reported before, CB[7] can form very stable complex ($K_S > 50{,}000\,M^{-1}$) with Rhodamine 6G (possess similar structure with RhB) in water [29]. The present complexation of CB[7] with RhB only present the $K_S$ value of $5050\,M^{-1}$ because there are already $\sim$0.2 mM $Na^+$ in the citrate buffer solution. This shows that the existence of $Na^+$ ion indeed can decrease the binding ability of CB[7] with dye guests to much extent. In contrast, salt effects are inapparent on the complexation between β-CD and dye guest due to the weak β-CD–salt interactions. So the binding strength of guests with CB[7] and C4AS can be effectively modulated by adding salts.

## CONCLUSION

The above comparative investigations on the molecular recognition behaviors of β-CD, C4AS and CB[7] revealed that the fluorescence behaviors of dye guests changes to different extent upon complexation with these three hosts, and their binding abilities differ much from each other. CB[7] always cause the enhanced fluorescence of dye guests, while contrarily, C4AS always cause the quenched fluorescence of dyes. Moreover, the emission peak of NR showed a dramatically hypsochromic shift of 21 nm accompanied with the steep increase of fluorescence intensity upon complexation with CB[7], which further present the strongest complexation stability. The complexation stability constants decrease in the order of CB[7] > C4AS > β-CD for the linear dye guests (AR and NR), while in the order of β-CD > CB[7] > C4AS for the triangular RhB guest. In addition, the pH values, solvent effects and salt effects also exert extraordinary influence over the binding ability of the three kinds of hosts with guests. Addition of a small amount of methanol can enhance the binding affinity of β-CD, while by contraries, decrease that of CB[7] and C4AS. All the binding abilities of three hosts decrease upon addition of NaCl salt, particularly to most extent for CB[7] owing to the strong competitive complexation between dye guests and $Na^+$. Therefore, the different photophysical behaviors and selective binding of dye guests represent the respective characteristics of these three hosts.

### *Acknowledgements*

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