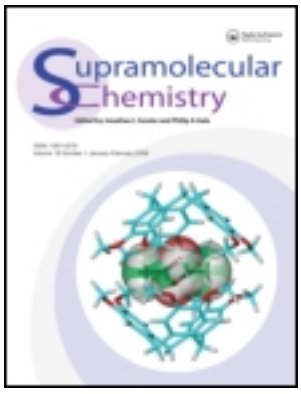

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Push-pull effect and synergistic discrimination of β-cyclodextrin and 18-crown-6

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Push–pull effect and synergistic discrimination of β-cyclodextrin and 18-crown-6

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The present work was devoted to the study of the effect of one host (18-crown-6, 18C6) on the binding behaviour of the other host (β-cyclodextrin, β-CD) to amphiphilic guests such as sodium dodecylbenzene sulphonate (SDBS) and D- and L-tryptophan (D- and L-Trp). Our results indicated that different combinations of the two hosts exhibited different push–pull effects in their binding process to SDBS, and the extent of the push–pull effect was dramatically dependent on the initial stoichiometric ratios of the two hosts. That is to say, the effect of 18C6 on the binding behaviour of β-CD to SDBS was not linear with its mole fraction, but first decreased and then increased with the increase in its mole fraction. On the other hand, there was a concentration dependence on synergistic effect of 18C6 and β-CD on the binding behaviour to D- or L-Trp. And there were rather remarkable differences in the molecular recognition abilities (K_L/K_D) of β-CD to D- and L-Trp in the presence of 18C6, such as free β-CD (0.48), 18C6–β-CD-**a** (0.27), 18C6–β-CD-**b** (0.86), 18C6–β-CD-**c** (1.17), 18C6–β-CD-**d** (1.72) and 18C6–β-CD-**e** (2.31). These results clearly revealed the important role of 18C6 in mediating the intermolecular interaction between the amphiphilic guests and β-CD, providing a new insight into the mutual effect between two hosts in multicomponent systems.

Keywords: β-cyclodextrin; push–pull effect; molecule–ion interaction; chiral discrimination

Introduction

β-Cyclodextrins (β-CD) and 18-crown-6 (18C6) are two of the most important macrocyclic hosts in organic chemistry (*1–4*). The former is an oligosaccharide consisting of seven glucose units, having the ability to form inclusion complexes with various organic guests due to its hydrophilic surface and hydrophobic central cavity (*5–8*). And the latter is a cyclic polyether, exhibiting the property to interact with many cations because of its hydrophobic surface and hydrophilic core (*9–11*). Isolation, structural determination, synthesis and properties of them and their derivatives have been extensively investigated by numerous organic chemists until now (*12–14*).

On the one hand, some applications concerning the micelle formation of surfactants in the presence of β-CD and 18C6 were reported in the past (*15–17*). For instance, Bakshi reported that the micelles of a series of surfactants were denatured with increasing the concentration of β-CD in the mixed solutions of 18C6 and β-CD (*18*). Liu and his co-workers found that β-CD–crown ether conjugates showed a strong binding ability and a high structural selectivity to charged guest molecules (*19*). These studies led us to adopt a different strategy for understanding whether there was a push–pull effect in the binding process of β-CD and 18C6 to surfactants. Accordingly, sodium dodecylbenzene sulphonate (SDBS) was chosen as a guest to evaluate whether there is a correlation between initial stoichiometric ratios of the double macrocyclic hosts and binding results. Our results demonstrated the presence of a mixed-induced push–pull effect in the ternary system and revealed that the extent of the push–pull effect was closely associated with the initial molar ratio of the two hosts.

On the other hand, numerous efforts have been contributed to the design and preparation of new functional crown ethers and cyclodextrin derivatives, as well as their conjugates, in order to improve their binding affinities especially structural selectivities to chiral guests (*20–24*). For example, Suzuki and his collaborators gave an account of crown ether-tethered CD (*25*). They found that the presence of benzo-18C6 moiety favours the ability of CD to bind tryptophan (Trp) when compared to benzo-15-crown-5 moiety, and the secondary hydroxyl modification of CD was more advantageous during the discrimination process to D- and L-tryptophan (D- and L-Trp). Recently, our work has provided convincing spectral evidence that simple addition of a third component influenced the binding ability and discrimination behaviour of CDs to D- and L-Trp (*26*). These examples give a strong impression that a simple mixing behaviour of a pair of oppositely polarised hosts in different initial stoichiometries in an aqueous medium can regulate the discrimination behaviour of them to D- and L-Trp. Therefore, the ternary systems formed by two hosts 18C6 and β-CD with a guest D- or L-Trp were examined to determine which of the many possible combinations

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between the two hosts is most important in chiral discrimination. Our results indicated a synergistic effect of the double hosts in the binding process to D- or L-Trp. And, the concentration increase in 18C6 in the mixed solutions resulted in a stronger synergistic effect, but reversed the direction of discrimination at the same conditions.

This study provides important information about how push–pull effect and synergistic discrimination might actually occur by the simple mixing of the two kinds of hosts. We think that it is useful for the evaluation of host–guest inclusion phenomena and molecular recognition.

Experimental section

Materials

β-CD was purchased from Shanghai Chemical Reagent Company and recrystallised twice from deionised distilled water. SDBS procured from Shanghai Chemical Reagent Company. 18C6 was obtained from Shanghai Bangcheng Chemical Company. D- and L-Trp are chromatographic grades and are used without further purification. All other chemicals were of general purpose reagent grade unless otherwise stated. All samples were kept under the same conditions, i.e. stored in a vacuum drier under 298.2 K for 24 h before use.

Push–pull effect of 18C6 and β-CD in the binding process to SDBS in water

Stock solutions of 18C6 (1.21×10^{-1} mol dm^{-3}), β-CD (1.25×10^{-2} mol dm^{-3}) and SDBS (1.25×10^{-3} mol dm^{-3}) were freshly prepared by dissolving solid samples in deionised water. First, five series of binary host solutions were prepared in a volumetric flask of 25 ml by dissolving β-CD and 18C6 in the molar ratios: 1:1 (18C6–β-CD-**a**), 1:2.4 (18C6–β-CD-**b**), 1:4.3 (18C6–β-CD-**c**), 1:7 (18C6–β-CD-**d**) and 1:9.7 (18C6–β-CD-**e**). Each series was composed of 10 binary host solutions (*a*–*k*), in which the concentration of β-CD was changed from *a* to *k* in the range from 0 to 1.00×10^{-2} mol dm^{-3}, and the concentration of 18C6 was altered based on the molar ratios above and the concentration of β-CD. The binary solutions (50 samples) were heated for 2 h at 333.2 K under magnetic stirring. Subsequently, SDBS of 1.25 ml (1.00×10^{-3} mol dm^{-3}) and the binary host solutions of 12.5 ml were transferred to 25 ml volumetric flasks and diluted to volume with deionised water. And then, the ternary solutions were vigorously stirred for 2 h at 303.2 K. Before test, the solutions were stirred by ultrasonic agitation for 10 min at room temperature again. The pH values in all the ternary solutions did not show significant change (4.9 ± 0.1). Finally, the ternary solutions were measured using a UV–Vis spectrophotometer and a JC2000B-1 contact angle measuring instrument.

The binding constant (K) of β-CD to SDBS without and with 18C6 was determined by a double-reciprocal plot of absorbance vs. the concentrations of β-CD at 298.2 K using Equation (1) (*27*).

$$\frac{1}{A_{\max} - A_0} = \frac{1}{a} + \frac{1}{a \cdot K \cdot C_0}. \quad (1)$$

In this equation, A_0 and $A_{\max}$ are the absorbances of the SDBS in the absence and presence of β-CD at the maximum absorbance wavelength, respectively, and letting $A_{\max} - A_0 = \Delta A_{\max}$. a is a constant reflecting the difference between the molar extinction coefficients of the SDBS–β-CD and SDBS at the same wavelength, and C_0 is the initial concentration of β-CD in a solution. The initial concentration of SDBS is kept constant at 5.00×10^{-5} mol dm^{-3}, whereas the concentration of β-CD varies in the range from 0.00 to 50.00×10^{-4} mol dm^{-3}.

Chiral discrimination of 18C6, β-CD and their mixed solutions to D- and L-Trp in water

To characterise the interactions between the host solutions and D- and L-Trp in aqueous solution, the initial concentrations of D- and L-Trp in the ternary systems were held constant at 5.00×10^{-5} mol dm^{-3}, whereas the concentration of β-CD in each of the five binary host solutions: 1:1 (18C6–β-CD-**a**), 1:2.4 (18C6–β-CD-**b**), 1:4.3 (18C6–β-CD-**c**), 1:7 (18C6–β-CD-**d**) and 1:9.7 (18C6–β-CD-**e**), was varied in the range from 0.00 to 9.00×10^{-3} mol dm^{-3} (*a*–*j*), and the concentration of 18C6 was altered based on the molar ratios above and the concentration of β-CD. The mixed solutions of D- and L-Trp with the binary host solutions of different concentrations were stirred in a beaker for 0.5 h at 303.2 K. Before test, the solutions were further stirred by ultrasonic agitation for 10 min. The pH values did not show significant change in all the mixed solutions (5.9 ± 0.1). And then, the mixed solutions were measured using a SLM-Aminco AB-2 spectrofluorimeter.

The K values of β-CD to D- or L-Trp without and with 18C6 were determined at 298.2 K by Equation (2) (*26*).

$$\frac{1}{F_0 - F_i} = \frac{1}{(F_0 - F_\infty) \cdot K \cdot [\mathrm{CD}]_i} + \frac{1}{F_0 - F_\infty}, \quad (2)$$

where F_0 and F_i are the fluorescence intensities of D- or L-Trp in the absence (blank) and presence of β-CD, F_∞ is the fluorescence intensity of the complex of D- or L-Trp with β-CD and $[\mathrm{CD}]_i$ is the concentration of β-CD after each addition. The initial concentrations of D- or L-Trp are kept constant at 5.00×10^{-5} mol dm^{-3}, whereas the concentration of β-CD varies in the range from 0.00 to 90.00×10^{-4} mol dm^{-3}.

Table 1. Values (α) of pure water and SDBS (5.00×10^{-5} mol dm^{-3}) in the absence and presence of β-CD (5.00×10^{-4} mol dm^{-3}), 18C6 (5.00×10^{-4} mol dm^{-3}) and the binary host solutions (the concentration of β-CD is kept at a constant of 5.00×10^{-4} mol dm^{-3}).

Samples	α (°)	Samples	α (°)
H_2O	66.8	SDBS–H_2O	42.6
β-CD–H_2O	58.7	β-CD–SDBS–H_2O	49.4
18C6–H_2O	66.1	18C6–SDBS–H_2O	55.8
18C6–β-CD-**a**–H_2O	62.6	18C6–β-CD-**a**–SDBS–H_2O	58.5
18C6–β-CD-**c**–H_2O	64.7	18C6–β-CD-**c**–SDBS–H_2O	64.2

Instruments and methods

UV–Vis spectra were recorded on a Shimadzu UV 2401-(PC) spectrometer in the range 190–350 nm. Fluorescence experiments were conducted on a SLM-Aminco AB-2 spectrofluorimeter (SLM Instruments) using a quartz cuvette of 3 mm path length with excitation and emission slit widths of 3 nm at 298.2 K. All pH values of solutions were determined at room temperature using a pHS-3C digital pH-meter (Shanghai Jinmai Experimental Instrument Factory, Shanghai, China) equipped with a combined glass–calomel electrode.

Contact angles (α) were measured on a JC2000B contact-angle measuring instrument (Zhongchen Digital Equipment Co., Zhongchuan, China), equipped with a CCD camera (Daheng, DH-HV1303UM, 1280 × 1024). All measurements were carried out at 298.2 K. The static contact angle of a liquid droplet (5 μl) on a planar surface surrounded by air under room temperature can be determined from the classical Young's equation (*28*, *29*). The contact angles obtained were an average of five measurements.

Results and discussion

Pull–push effect of 18C6 and β-CD in the binding process to SDBS

Values of α can be applied to monitor surface changes and evaluate intermolecular forces in a single aqueous phase (*30–33*). Table 1 summarises the changes in α values of pure water and SDBS solution after the addition of various hosts.

The α value of pure water is the highest in all cases. Obviously, the addition of SDBS, β-CD or 18C6 into water causes a decrease in the α value, and the magnitude of the decrease is dependent on the nature of components added. For example, the presence of SDBS at a lower concentration leads to an enormous decrease in the α value from 66.8 to 42.6°, but the addition of 18C6 only leads to a decrease of 0.7°. The decrease sequence of α values is 18C6 < 18C6–β-CD-**c** < 18C6–β-CD-**a** < β-CD < SDBS. However, when one or more hosts were added to the SDBS solution, α values increase in the order: β-CD < 18C6 < 18C6–β-CD-**a** < 18C6–β-CD-**c**.

These results indicate that the higher the concentration of 18C6, the lower the values of α in pure water, but the higher in the SDBS solution. This finding, as well as the divergence of the two sequences, may imply that the concentration of the hosts especially 18C6 plays a crucial role in mediating the intermolecular interaction among SDBS, 18C6 and β-CD.

Although the intermolecular complexation between β-CD or its derivatives and SDBS analogues were reported (*34*, *35*), there have been few data describing the effect of a third component as a host one on the complexation. Figure 1 indicates the effect of concentrations of β-CD especially 18C6 on the absorbance of SDBS. It should be noted that no absorbance was observed in this region from 190 to 310 nm for free 18C6 and β-CD. Two significant differences have been observed from this figure.

First, the addition of either 18C6–β-CD-**a** or 18C6–β-CD-**c** to SDBS solutions leads to not only a slight shift of the maximum absorption wavelength (λ_{max}) of free SDBS from 197 up to 199 m but also an increase (ΔA_{max}) of absorbance at the λ_{max}. Furthermore, the shift and increase (indicated by arrows) in absorption show an increasing

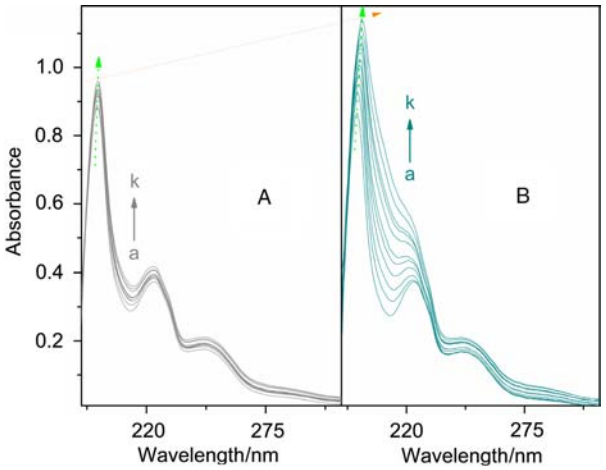

Figure 1. UV–Vis spectra of SDBS (5.00×10^{-5} mol dm^{-3}) upon the addition of (A) 18C6–β-CD-**a** and (B) 18C6–β-CD-**c**. The concentration range of β-CD is 0.00–5.00×10^{-3} mol dm^{-3} from *a* to *k*, and the concentration of 18C6 was altered based on both the initial molar ratios and the concentration of β-CD.

tendency with increasing total concentration of the mixed host solutions (from *a* to *k*).

Second, 18C6–β-CD-**c** always produces a larger effect than 18C6–β-CD-**a** at the same β-CD concentrations (indicated by arrow), which qualitatively explains the positive contribution of 18C6.

The differences provide evidence for the existence of the interaction between the two hosts and the guest SDBS. In order to further understand the nature of this interaction, other three host systems: 18C6–β-CD-**b**, 18C6–β-CD-**d**, 18C6–β-CD-**e** (see Supplementary Information, available online) as well as free 18C6 and β-CD are evaluated, and the results are shown in Figure 2. This figure gives us some insight into why this interaction occurs in the three components. Initially, SDBS has the weakest interaction with free 18C6 and a moderate interaction with free β-CD at the same concentrations. Next, except 18C6–β-CD-**a**, the other four binary host systems indicate a stronger interaction with the SDBS.

These results highlight important details regarding the interaction. (1) There is a pull–push effect in the binding process of the two hosts to SDBS, and the pull–push effect is closely related to changes in the concentrations of 18C6 (first increase: C → E, and then decrease: E → G), and especially β-CD (always increases: a → e) in the ternary systems. (2) The weaker interaction between 18C6–β-CD-**a** and SDBS may be seen as a result of a sufficient inclusion between the cavity of β-CD and 18C6. A similar phenomenon also occurs when the molar ratio of 18C6 to β-CD is very high such as in the case of 18C6–β-CD-**d** or 18C6–β-CD-**e** (indicated by arrow in Figure 2).

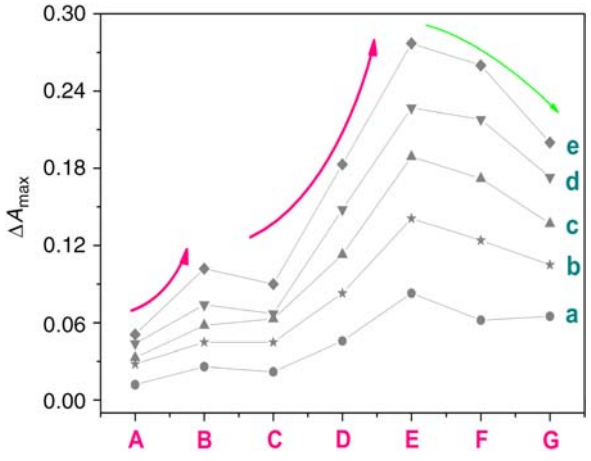

Figure 2. ΔA_{max} values of SDBS (5.00×10^{-5} mol dm^{-3}) at 197 nm upon the addition of (A) 18C6, (B) β-CD, (C) 18C6–β-CD-**a**, (D) 18C6–β-CD-**b**, (E) 18C6–β-CD-**c**, (F) 18C6–β-CD-**d** and (G) 18C6–β-CD-**e** at different concentrations (a) 1.00, (b) 2.00, (c) 3.00, (d) 4.00 and (e) 5.00×10^{-3} mol dm^{-3}. The concentrations represent the concentrations of β-CD in the binary host solutions from *a* to *e*, and the concentration of 18C6 was altered based on both the initial molar ratios and the concentration of β-CD.

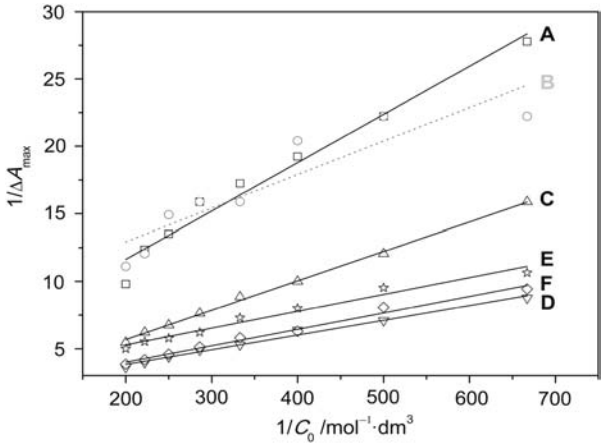

Figure 3. Plots of $1/\Delta A_{max}$ of SDBS vs. $1/C_0$ of β-CD in the binary and ternary systems formed by SDBS and (A) β-CD, (B) 18C6–β-CD-**a**, (C) 18C6–β-CD-**b**, (D) 18C6–β-CD-**c**, (E) 18C6–β-CD-**d** and (F) 18C6–β-CD-**e**. The concentration of SDBS is kept constant at 5.00×10^{-5} mol dm^{-3}, the concentration range of β-CD is 0.00 to 5.00×10^{-3} mol dm^{-3} and the concentration of 18C6 was altered based on the initial molar ratio as described in the Experimental Section.

Figure 3 shows the double-reciprocal plots of $1/\Delta A_{max}$ vs. $1/C_0$. As seen in the figure, the solid curves (A, C, D–F) show fits to the data using Equation (1) with the correlation coefficients (r) of more than 0.96 for eight points. The K values for the binding behaviours of β-CD, 18C6–β-CD-**b**, 18C6–β-CD-**c**, 18C6–β-CD-**d** and 18C6–β-CD-**e** to SDBS were determined to be 124, 61, 151, 128 and 224 mol^{-1} dm^3, respectively, by means of slopes and intercepts of the linear plots (Figure 3) based on Equation (1) described in the experimental section.

The good linear correlations in the investigated concentration range probably suggest that the binding stoichiometries of β-CD to SDBS in these binary and ternary systems are 1:1. For 18C6–β-CD-**a**, there is a poor linear correlation (r, 0.81) of these data. In this case, the K value cannot be calculated exactly. The large difference in the K values at the same temperature conditions provides important information concerning the functional significance of 18C6 in the mixed solutions. The effect of 18C6 on the binding behaviour of β-CD to SDBS is not linear with its mole fraction, but first decreases from 124 to 61 mol^{-1} dm^3 and then increases with the increase in its mole fraction. And the K value in 18C6–β-CD-**e** system is much higher than free β-CD system, revealing the promotion effect of 18C6 at a high mole fraction on the binding behaviour.

The pull–push effect can be explained as a synergic process, in which the alkyl chain or aromatic ring of a dodecylbenzene sulphonate anion entered into the hydrophobic cavity of β-CD, forming an inclusion complex (*34*, *35*), whereas a sodium cation was captured by the hydrophilic cavity of 18C6, forming a coordination complex (*36–38*). Undoubtedly, the inclusion complexation

plays a more important role than the coordination interaction in weakening the electrostatic interaction between the sodium cation and the dodecylbenzene sulphonate anion, which causes the change in absorbance of SDBS.

Synergistic effect of 18C6 and β-CD in the binding and chiral discrimination processes to D- and L-Trp

It was reported that β-CD and its derivatives showed quite different binding abilities for D- and L-amino acids by forming 1:1 inclusion complexes in solution, so as to be successfully applied to the chiral discrimination between them (*26*, *39–41*). This allows us to assess whether such a pull–push effect of 18C6 and β-CD could be more effectively applied in this very important area. Figure 4 shows the fluorescence intensity curves of D- and L-Trp in the absence and presence of 18C6–β-CD-**a**, 18C6–β-CD-**c** and 18C6–β-CD-**e**.

Evidently, the addition of the mixed solutions of 18C6 and β-CD has caused an increase (indicated by arrows) in the fluorescence intensity of D- and L-Trp at 355 nm, and the increase exhibits a strong dependence on the total concentration of the two hosts in each of the ternary systems. This is similar to the case in Figure 1. Such a phenomenon could have an important implication that the presence of the hosts has resulted in a change in conformation of D- and L-Trp due to the binding of the hosts to them via intermolecular interactions.

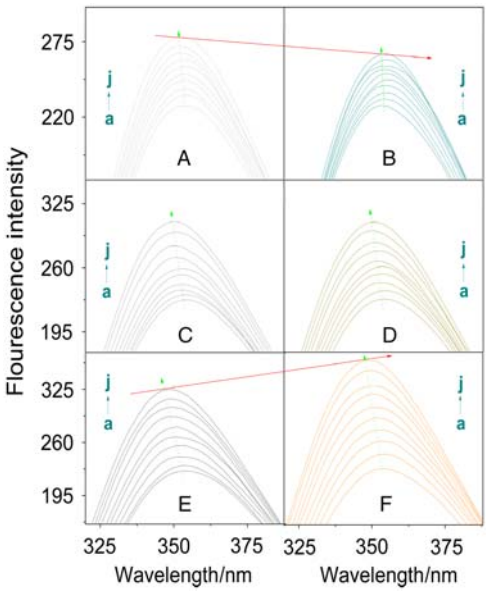

Figure 4. Fluorescence spectra of D- (left side), L-Trp (right side) (5.00×10^{-5} mol dm^{-3}) upon the addition of (A and B) 18C6–β-CD-**a**, (C and D) 18C6–β-CD-**c** and (E and F) 18C6–β-CD-**e**. The concentration range of β-CD in the binary host solutions is $0.00–9.00 \times 10^{-3}$ mol dm^{-3} from *a* to *j*, and the concentration of 18C6 was altered based on both the initial molar ratios and the concentration of β-CD.

More importantly, Figure 4 reveals that changes in fluorescence intensity are closely mirrored by changes in the concentration of 18C6 in the ternary systems. For example, 18C6–β-CD-**e** (E and F) shows a much stronger binding ability to either D- or L-Trp than 18C6–β-CD-**c** (C and D), and especially 18C6–β-CD-**a** (A and B) at the same β-CD concentrations. This observation emphasises the importance of 18C6 in assisting binding of D- or L-Trp to β-CD. Surprisingly, and most importantly, 18C6–β-CD-**a** and 18C6–β-CD-**e** showed a completely reverse response (indicated by arrows, one increases and the other decreases) to D- and L-Trp. The former has a stronger association with D-Trp, but the latter has a more marked binding effect on L-Trp. However, no such a clear increase or decrease correlation exists in 18C6–β-CD-**c**. This result is very suggestive and useful for all who are interested in the chiral discrimination and molecular recognition.

In order to further investigate the role of the two hosts in the chiral discrimination process to D- and L-Trp, we summarise the changes (ΔF) in fluorescence intensity of D- and L-Trp in the absence and presence of a series of hosts, including free 18C6 and β-CD and give the differences ($\Delta\Delta F$) of ΔF values between D- and L-Trp in Figure 5.

Figure 5 provides some information to evaluate the role of the two hosts. First, 18C6 has a similar, low binding ability to D- and L-Trp, and the binding behaviour is independent of the change in 18C6 concentration.

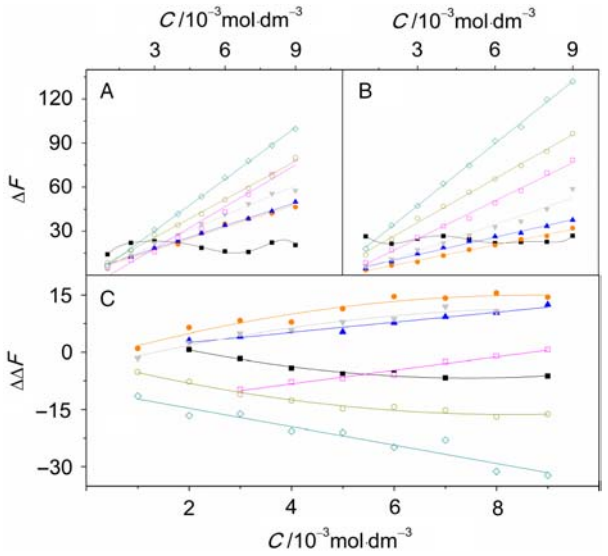

Figure 5. ΔF values of (A) D-, (B) L-Trp (5×10^{-5} mol dm^{-3}) in the absence and presence of different concentrations (*C*, $0.00–9.00 \times 10^{-3}$ mol dm^{-3}) of 18C6 (■), β-CD (●), 18C6–β-CD-**a** (▲), 18C6–β-CD-**b** (▼), 18C6–β-CD-**c** (□),18C6–β-CD-**d** (○) and 18C6–β-CD-**e** (◇) and $\Delta\Delta F$ values between D- and L-Trp (C). The concentration range of β-CD in the binary host solution is $0.00–9.00 \times 10^{-3}$ mol dm^{-3} from *a* to *j*, and the concentration of 18C6 was altered based on both the initial molar ratios and the concentration of β-CD.

However, there is a concentration-dependent increase in the binding of Trp to β-CD, as well as all the binary host systems.

Second, 18C6–β-CD-**c** has a poor ability to distinguish between D- and L-Trp with the increase in total concentration of the mixed hosts, as seen from Figure 5(C). Nevertheless, like 18C6–β-CD-**a**, β-CD and 18C6–β-CD-**b** present a higher affinity for D-Trp (see Supplementary Information, available online), thus indicating the ability to discriminate between the isomers. And the discrimination ability is enhanced with increasing total concentration of the mixed hosts. On the contrary, the situation of 18C6–β-CD-**d** is somewhat similar to that of 18C6–β-CD-**e** (see Supplementary Information, available online), having a higher affinity for L-Trp.

According to the description above, we notice that the binary host systems present several completely different meanings. (1) There is always a positive relationship between 18C6 and β-CD in the binding process for D- or L-Trp, showing a synergic effect. It is possibly involved in the interaction between 18C6 and the NH_3^+ of Trp. (2) At a low or a high molar ratio, for example 18C6–β-CD-**a** and 18C6–β-CD-**e**, there is a positive attitude towards the chiral discrimination between D- and L-Trp in comparison with free β-CD. (3) At a moderate molar ratio, such as 18C6–β-CD-**b** especially 18C6–β-CD-**c**, leads to a negative attitude in the chiral discrimination process. In short, the binding and discrimination behaviours of the binary host systems are dominated by the composition effect, highly depending on the molar ratio of the two hosts used for their preparation.

The values of *K* are determined based on Equation (2) and shown in Figure 6. From the bar diagram, it is clear that the binding behaviours of β-CD to D- and L-Trp in the presence of 18C6 are related to the variation of the mole fraction of 18C6. In particular, the molecular recognition abilities (K_L/K_D) of β-CD to D- and L-Trp in the presence of 18C6 indicate rather remarkable differences, for example free β-CD (0.48), 18C6–β-CD-**a** (0.27), 18C6–β-CD-**b** (0.86), 18C6–β-CD-**c** (1.17), 18C6–β-CD-**d** (1.72) and 18C6–β-CD-**e** (2.31). These results clearly demonstrate the important role of 18C6 in mediating the intermolecular interaction between Trp and β-CD.

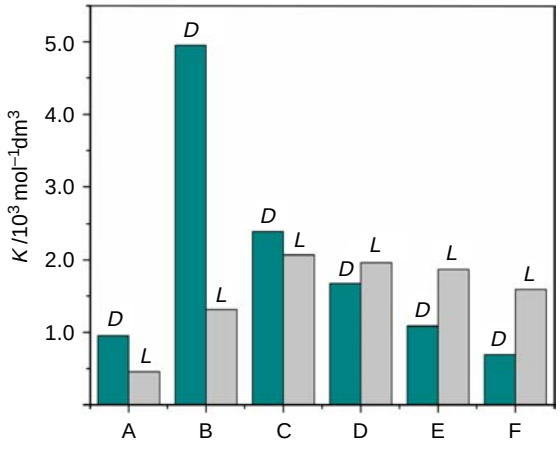

Figure 6. The *K* values of (A) β-CD, (B) 18C6–β-CD-**a**, (C) 18C6–β-CD-**b**, (D) 18C6–β-CD-**c**, (E) 18C6–β-CD-**d** and (F) 18C6–β-CD-**e** with D- and L-Trp.

Conclusions

The study demonstrated that there is a composition effect of two hosts: 18C6 and β-CD in solution and that such an effect can result in a synergistic effect in the binding process to amphiphilic guests such as SDBS and Trp. More importantly, a host concentration-dependent chiral discrimination between D- and L-Trp was observed. And the difference in the binding behaviours of β-CD to D- and L-Trp can be enlarged in the presence of 18C6 through the variation of the mole fraction of 18C6. This observation clearly reflects the significant role of 18C6 in mediating the intermolecular interaction between β-CD and the two forms of Trp. 18C6 and β-CD are only two representatives of an extensive group of hosts. In this regard, this study opens a large window of possibilities for future research. There is no doubt that it will interest numerous researchers including organic chemists, analytical chemists, especially supramolecular chemists.

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Supplementary information available: (1) UV–Vis spectra of SDBS upon the addition of 18C6, β-CD, 18C6–β-CD-**b**, 18C6–β-CD-**d** and 18C6–β-CD-**e** and (2) Fluorescence spectra of D-, L-Trp upon the addition of 18C6, β-CD, 18C6–β-CD-**b** and 18C6–β-CD-**d** are available.

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