Synthesis of a Novel Anthraquinone Diamino-Bridged Bis(β-cyclodextrin) and Its Cooperative Binding toward Guest Molecules

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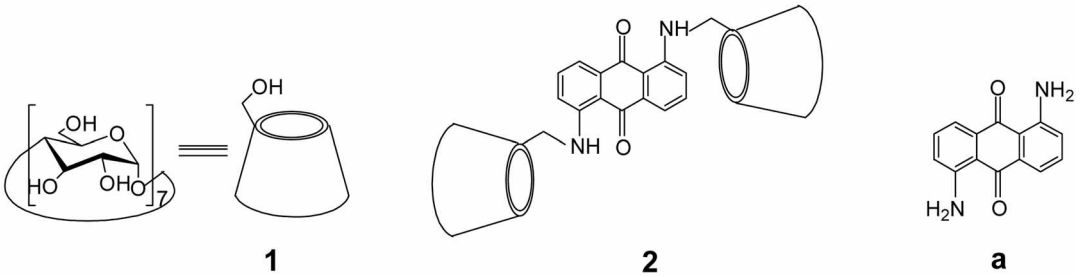
A novel anthraquinone diamino-bridged bis(β-cyclodextrin) **2** was synthesized. The inclusion complexation behaviors of the native β-cyclodextrin **1** and the novel bis(β-cyclodextrin) **2** with guests, such as acridine red (AR), neutral red (NR), ammonium 8-anilino-1-naphthalenesulfonate (ANS), sodium 2-(*p*-toluidinyl) naphthalenesulfonate (TNS) and rhodamine B (RhB) were investigation by fluorescence, circular dichroism and 2D NMR spectroscopy. The spectral titrations were performed in phosphate buffer (pH 7.20) at 25 °C to give the complex stability constants (*K*s) and Gibbs free energy changes ($-\Delta G^0$) for the stoichiometric 1:1 inclusion complexation of host **1** and **2** with guests. The results indicated that the novel bis(β-cyclodextrin) **2** greatly enhanced the original binding affinity of the native β-cyclodextrin **1**. Typically, bis(β-cyclodextrin) **2** showed the highest binding constant towards ANS up to 34.8 times higher than that of **1**. The 2D NMR spectra of bis(β-cyclodextrin) **2** with RhB and TNS were performed to confirm the binding mode. The increased binding affinity and molecular selectivity of guests by bis(β-cyclodextrin) **2** were discussed from the viewpoint of the size/shape-fit concept and multipoint recognition mechanism.

Key Words : Bridged bis(β-cyclodextrin), Guest molecule, Molecular recognition, Cooperative binding mode, Inclusion complexation

Introduction

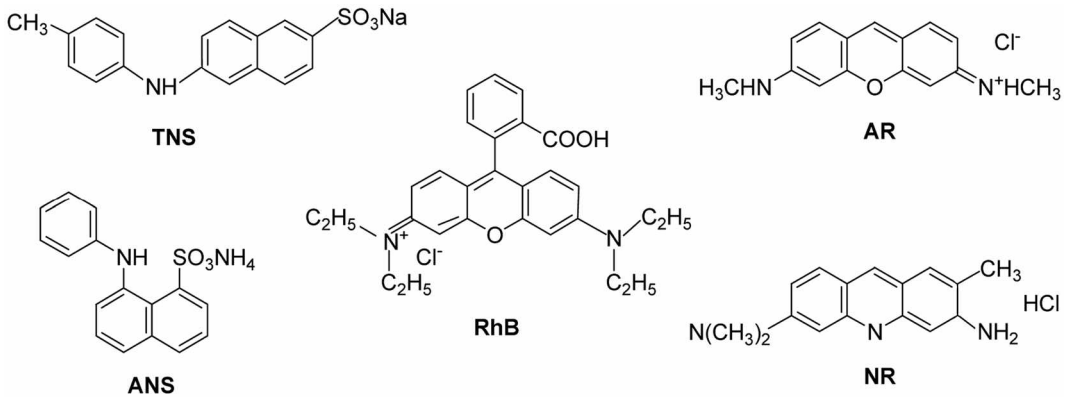
Native and chemically modified cycloedxtrins (CDs), served as synthetic receptors (hosts) of supramolecular systems, display dramatically different binding behaviors toward guest molecules.[1-5] Possessing two appropriately-located hydrophobic cavities in a single molecule, bridged bis(β-CD)s with simple tether can remarkably enhance the original molecular binding affinity and molecular selectivity of the native β-CD for specific guests through the cooperative multiple recognition. This fascinating property enables them to be employed successfully in several areas of science and technology as an excellent model system mimicking substrate-specific interaction of enzymes.[6,7] Consequently, a number of bis(β-CD)s have been designed and synthesized to examine and compare the molecular binding affinity of native β-CD and bridged bis(β-CD)s and also to gain insights into factors governing the inclusion complexation phenomena between the host bis(β-CD)s and guest molecules.[8-10] Recently, we have shown that the aromatic diamino-bridged bis(β-CD)s form more stable complexes with some guest molecules through cooperative binding of one guest molecule by two β-CD moieties.[11] These studies have helped us understanding the multiple recognition mechanism and the induced-fit interactions between the host bis(β-CD)s and guest molecules and prompted us to further investigate the inclusion complexation behavior of other bridged bis(β-CD)s.

In the present study, we chose anthraquinone diamino-bridged bis(β-CD) as specific host molecule based on the consideration that anthracene diamines, possessing a rigid aromatic diamine tether, not only enhance hydrophobicity of the microenvironment, but also adjust the dimension of the hydrophobic cavity of CD. We wish to report our investigation results on the synthesis of anthraquinone diamino-bridged bis(β-CD) **2** (Scheme 1) and its binding behavior



1 **2** **a**

Scheme 1



Scheme 2

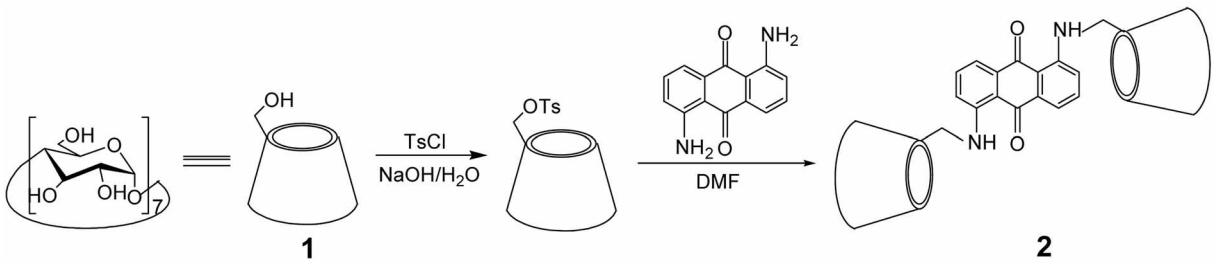
with some structure-related guest dye molecules (Scheme 2). The simple reason for choosing these typical guest dye molecules as spectral probe was that these fluorescent dyes were known to be very sensitive to environmental changes induced by CD hydrophobic cavity, which would enable us to investigate their inclusion complexation behavior with native and bridged bis(β-CD)s using fluorometric titration method. The inclusion complexation behavior of native β-CD **1** and the novel bis(β-CD) **2** was investigated at 25 °C in aqueous phosphate buffer solution (pH 7.20) by fluorescence, circular dichroism and 2D NMR spectroscopy. The results indicated that the binding affinity and molecular selectivity of bis(β-CD) **2** were greatly influenced by size/shape - fit between host and guest. 2D NMR spectra for the host - guest complexes further confirmed the cooperative binding of bis(β-CD) **2** toward guests. The cooperative binding modes of the novel bis(β-CD) **2** with TNS and RhB were deduced from the NOESY results.

Experimental Section

Materials. All guest dyes, including acridine red (AR), neutral red (NR), ammonium 8-anilino-1-naphthalenesulfonate (ANS), sodium 2-(*p*-toluidinyl) naphthalenesulfonate (TNS) and rhodamine B (RhB), were obtained form commercially sources and used without further purification. β-CD of reagent grade (Shanghai Reagent works) was recrystallized twice from water and dried under vacuum at 95 °C for 24 h prior to use. *N,N*-Dimethylformamide (DMF) was dried over calcium hydride for 2 days and then distilled under a reduced pressure prior to use. Mono[6-*O*-(*p*-toluenesulfonyl)]-β-CD was prepared from β-CD and *p*-toluenesulfonyl chloride in aqueous alkaline solution.[12] The phosphate buffer (0.10 mol·dm^{-3}, pH 7.20), used in the spectral measurements, was prepared from NaH_2PO_4 and Na_2HPO_4.

Synthesis of 1,5-Diaminoanthraquinone-bridged-bis (6-amino-6-deoxy-β-CD) (2). As shown in Scheme 3. 1,5-diaminoanthraquinone (1.0 mmol, 0.28 g) and mono[6-*O*-(*p*-toluenesulfonyl)]-β-CD (2.2 mmol, 3.0 g) were dissolved in anhydrous DMF (30 mL), and the reaction mixture was stirred at 85 °C under nitrogen atmosphere for 4 days, followed by evaporation under reduced pressure to dryness. The residue was dissolved in a small amount of water, and the resultant solution was poured into acetone with vigorous stirring to obtain a brown-red precipitate. The crude product was collected by filtration and chromatographed on a Sephadex G-25 column with water as eluent to give the pure sample **2** (0.26 g, yield 11%). FAB-MS: m/z 2496 (M^+ + Na). ^{1}H NMR (D_2O, 500MHz, TMS, ppm): δ 3.4-3.9 (m, 84H), 4.9-5.0 (m, 14H), 7.0-7.6 (m, 6H). FT-IR (KBr) ν/cm^{-1}: 3406, 2927, 1632, 1418, 1366, 1155, 1078, 1027, 937, 854, 758, 707. UV/vis (H_2O) λ_{max}/nm (ε/M^{-1} cm^{-1}): 228 (4792), 261 (448). Anal. Calcd. for $C_{97}H_{150}O_{68}N_2 \cdot 12H_2O$: C, 43.99; H, 6.62; N, 1.06. Found: C, 43.06; H, 6.90; N, 1.09.

Instruments. Combustion analyses were performed on an Elementar Vario EL III. ^{1}H NMR spectra were recorded in on a Bruker AV.DRX5 instrument operated at 500 MHz. FT-IR spectra were obtained on a Bruker Tensor 27. Fluorescence spectra were measured in a conventional quartz cell (10 × 10 × 45 mm) at 25 °C on a Hitachi F-4500 spectrometer equipped with a constant-temperature water bath, with the excitation and emission slits of 10 nm width. The excitation wavelengths for AR, NR, ANS, TNS and RhB



Scheme 3

were 490, 510, 350, 366, and 520 nm, respectively. UV and Circular dichroism spectra were performed on a Shimadzu UV2401 PC spectrometer and a JASCO 810 spectropolarimeter, respectively.

Results and Discussion

Conformational Analysis. It has been amply demonstrated that the inclusion of a chromophoric achiral guest/moiety in a chiral host such as CDs produces induced circular dichroism (ICD) signals at the wavelengths at which the guest chromophore has absorbance.[13,14] To examine the original conformation of the bridged bis(*β*-CD) **2** possessing chromophoric achiral tether in an aqueous solution, its ICD spectrum was measured at 25 °C. As shown in Figure 1, bis(*β*-CD) **2** presented a moderate intensities positive Cotton effect peaks at 211 nm ($\Delta\varepsilon$ = +1.39 M^{-1} cm^{-1}) and a weak positive Cotton effect peaks at 276 nm ($\Delta\varepsilon$ = +0.17 M^{-1} cm^{-1}), attributed to the ^1L_a and ^1L_b band, respectively. According to the empirical rule proposed by Kajtar[15] and Harata[16], the sign of ICD signal depends on the orientation of the transition dipole moment of the chromophore with respect to the dipole moment of the CD. For the chromophore located inside the CD cavity, its electronic transition parallel to the CD axis gives a positive ICD signal, whereas the perpendicular transitions gives a negative signal, but this situation is reversed for the chromophore located outside the CD cavity. We propose that the anthraquinone ring of bis(*β*-CD) **2** might be located outside the CD cavity, where both the ^1L_a and ^1L_b transition moments were nearly perpendicular to the CD axis, resulting in the two positive Cotton effect peaks. This might favor the penetration of guest molecule into the cavities of bis(*β*-CD) **2**.

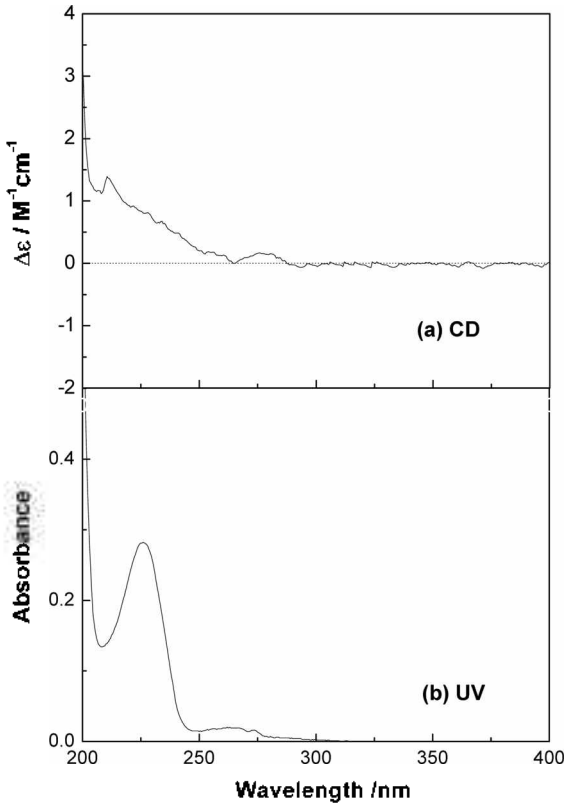


Figure 1. (a) Circular dichroism spectrum and (b) absorption spectrum of bis(*β*-CD) **2** (1.0×10^{-4} M) in phosphate buffer (pH 7.20) at 25 °C.

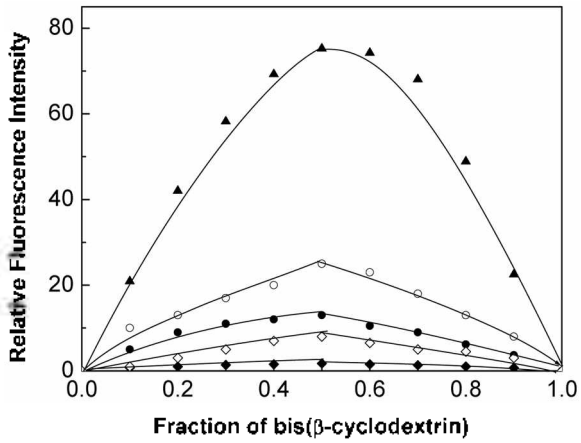


Figure 2. Continuous variation plots of **2**/guests system ([bis(*β*-CD) unit] + [guest] = 3.2×10^{-5} M). ◆: **2**/TNS system, ○: **2**/RhB system, ●: **2**/NR system, □: **2**/AR system and ▲: **2**/ANS system.

Inclusion Complexation Stoichiometry. The stoichiometry for the inclusion complexation of hosts **1**and **2** with representative guests, *i.e.*, AR, NR, TNS, ANS and RhB were determined by the continuous variation method. The continuous variation plots for **2**/guests systems are illustrated in Figure 2. In the concentration range studied, the plot for bis(*β*-CD) **2** unit peaked at a molar fraction of 0.5, suggesting a 1:1 inclusion complexation between host and guest.

Fluorescence Titration. Fluorescent spectral titrations of native *β*-CD **1** and bis(*β*-CD) **2** with guests were performed at 25 °C in aqueous phosphate buffer solution (pH 7.20) to quantitatively assess the inclusion complexation behavior of these compounds. In the fluorescence spectral titration experiments, the concentration of guests were kept constant, while the concentration of hosts were varied. The spectral changes depended critically on the formation of new species, *i.e.*, host-/guest inclusion complex, showing fluorescence enhancement or quenching. Figure 3(a) shows the typical spectral changes of TNS with gradual addition of bis(*β*-CD) **2**. As illustrated in Figure 3(a), the stepwise addition of a known amount of the bis(*β*-CD) **2** to a dilute TNS solution (2.5 *μ*M) caused significant enhancement in fluorescence intensity, accompanying appreciable hypsochromic shifts (3 nm, 445 → 442 nm from trace a to trace j) of the emission peaks. However, in the control experiments, the fluorescence intensities of the dye guests were not appreciably affected by the addition of **a** under identical conditions. Since TNS, just like ANS, is only weakly fluorescent in highly polar media such as water but becomes extremely fluorescent in nonpolar environments, the increase in fluorescence intensity of TNS observed was attributed to the incorporation of the TNS aromatic group into the nonploar cavities of bis(*β*-CD) **2**. Furthermore, this enhancement was due to a combination

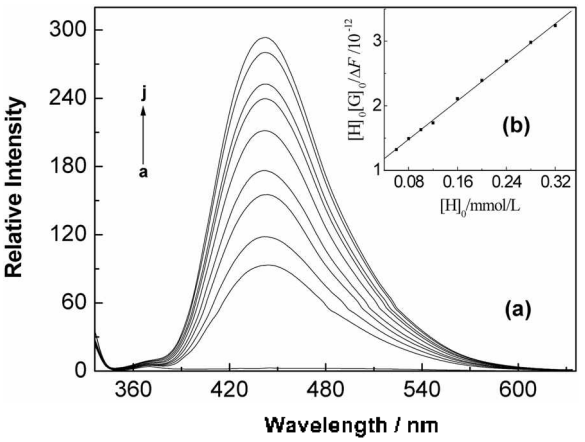


Figure 3. (a) Fluorescence spectral changes of TNS (2.5 μM) upon addition of bis(β-CD) **2** in phosphate buffer (pH = 7.20); The concentration of host **2** (from a to j): 0, 60, 80, 100, 120, 160, 200, 240, 280, 320 m M, respectively. λ_{ex} = 327 nm. (b) Typical plots of $[H]_0[G]_0/\Delta F$ versus $[H]_0$ for the inclusion complexation of bis(β-CD) **2** with TNS in aqueous phosphate buffer solution (pH = 7.20) at 25 °C.

of effects resulting from a specific host-guest inclusion complex formation including the protection of the bound fluorophore from external quenchers such as oxygen, the inhibition of the "free rotor" effect for the bound fluorophore, and the exposure of the bound flourophore to a less polar environment.[17] It was interesting to note that RhB displayed the opposite fluorescence behavior upon inclusion complexation by the bis(β-CD) **2** and native β-CD **1**. The fluorescence intensity of RhB was significantly enhanced upon addition of the bis(β-CD) **2**, but was decreased by adding the native β-CD **1**. Actually, the enhanced fluorescence intensity of RhB upon associating with bis(β-CD) **2** was attributed to the inclusion complexation of the fluorescent acid form of RhB in the pseudocavity formed by the anthraquinone diamine linker between two β-CD units, while the native β-CD **1** preferred to bind with the colorless lactonic form of RhB through hydrogen-bonding, thus resulting in the quenched fluorescence of RhB. The result indicated that the anthracene diamines tether of bridged bis(β-CD)s not only influenced the host-guest binding ability but also changed the fluorescence behavior of guest molecule.

Assuming 1:1 stoichiometry for the inclusion complexation of guest dyes (G) with CDs (H), where the two CD moieties in bis(β-CD) are treated as a single unit, the inclusion complexation is expressed by eq. (1) and the complex stability constant (K_S) is given by eq. (2).

$$H - G \overset{K_S}{\rightleftharpoons} G \cdot H \quad (1)$$

$$K_S = [H \cdot G]/[H][G] \quad (2)$$

$$\Delta F = \Delta\varepsilon[H \cdot G] \quad (3)$$

where ΔF and $\Delta\varepsilon$ denote the sequential changes of fluorescence intensity and the differential molar extinction coefficient of dye guest in the absence and presence of host β-CDs. Under the conditions employed, the initial concentration of the host β-CDs is much larger than that of guest molecules, *i.e.*, $[H]_0 >> [G]_0$. Therefore, the combination of eqs. (2) and (3) leads to the extended Benesi-Hildebrand equation (eq. 4), which is used to calculate the K_S (eq. 2) from the slope and intercept of $[H]_0[G]_0/\Delta F$ versus $[H]_0$ plots.

$$[H]_0[G]_0/\Delta F = (1/K_S\Delta F) + [H]_0/\Delta F \quad (4)$$

Figure 3(b) illustrates the result of such a treatment for the inclusion complexation of bis(β-CD) **2** with TNS, where the calculated $[H]_0[G]_0/\Delta F$ values were plotted against the $[H]_0$ values, generating an excellent linear curve. The complex stability constants (K_S) and the free energy changes($-\Delta G^\circ$) calculated from the slope and intercept are listed in Table 1.

Table 1. Complex Stability Constant (K_S) and Gibbs Free Energy Change ($-\Delta G^\circ$) for 1:1 Inclusion Complexation of Guests with β-CD **1** and Bis(β-CD)s **2** in Aqueous Buffer Solution (pH 7.20) at 25 °C

Host	Guest	λ^F_{max} /nm[a]	K_S (M^{-1})	Log K_S	$-\Delta G^\circ$ (kJ mol^{-1})
1	AR	552	2630 ± 50	3.42	19.51
	NR	575	480 ± 20	2.68	15.30
	TNS	472	3670 ± 60	3.56	20.31
	ANS	516	103 ± 5	2.01	11.47
	RhB	575	4240 ± 80	3.63	20.71
2	AR	554	4030 ± 100	3.60	20.54
	NR	573	1320 ± 50	3.12	17.80
	TNS	443	8470 ± 300	3.93	22.42
	ANS	483	3590 ± 100	3.55	20.26
	RhB	574	10700 ± 400	4.03	22.99

[a]Ultimate maximum fluorescence wavelength wave obtained upon addition of large excess of host, while the λ^F_{max}/nm[a] of AR, NR, ANS, TNS and RhB are 559, 598, 522, 445 and 575 nm, respectively.

Binding Mode. Since two protons located closely in space can induce an NOE cross-peak between the relevant protons in the NOESY or ROESY spectrum, we performed 2D NMR experiments to further investigate the binding mode between the novel bis(β-CD) **2** and guest molecules. Figure 4 illustrates a typical NOESY spectrum for the inclusion complexation of bis(β-CD) **2** with TNS. As can be easily recognized, this spectrum showed the clear correlations between TNS protons and the interior protons (H-3, H-5) for the CD cavity. Through the ascription of these correlations, we found that the cross peak A corresponded to the correlation between the methyl protons of TNS and the interior protons of CD, and the cross-peak B corresponded to the correlation between the protons in the phenyl moiety (Ha, Hb) of TNS and the interior protons of CD, while cross-peak C corresponded to the correlation between the naphthalene protons (Hg, Hh) of TNS and the interior protons of CD. Moreover, it could be observed from the corss-peaks A, B and C that the corresponding TNS protons (Ha, Hb, Hg and Hh) all showed stronger correlations with the H-5 protons than with the H-3 protons of CD. Since the H-3 protons are located near the wide side of CD cavity, while the H-5 protons are near the narrow side, we deduced that the

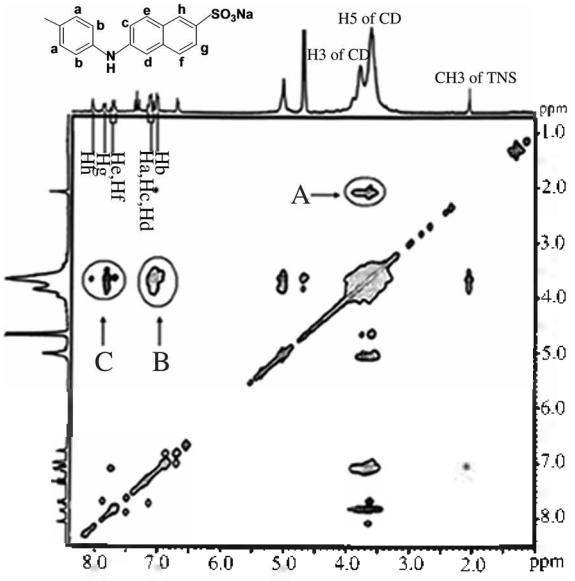


Figure 4. NOESY spectrum of bis(β-CD) **2** in the presence of TNS in D_2O ([bis(β-CD) **2**] = [TNS] = 5.0×10^{-3} M) with a mixing time of 600 ms at 298 K.

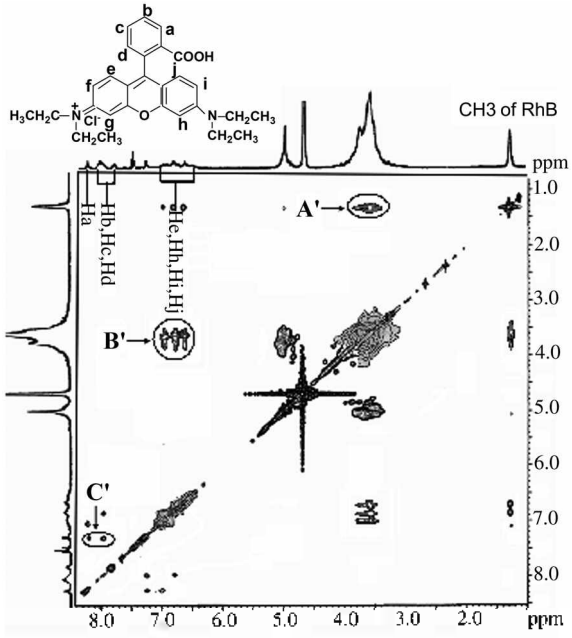


Figure 5. NOESY spectrum of bis(β-CD) **2** in the presence of RhB in D_2O ([bis(β-CD) **2**] = [RhB] = 5.0×10^{-3} M) with a mixing time of 600 ms at 298 K.

toluene and naphthalene units of TNS were respectively included in two CD cavities from the narrow side to give the sandwich inclusion complex (Figure 6a). In addition, the NOESY spectrum of the **2**/RhB system (Figure 5) further confirmed the cooperative binding mode of bis(β-CD) **2** toward guest. As shown in Figure 5, the CD's interior protons gave the NOE correlations with not only the methyl protons of diethylamino groups in RhB (cross-peak A') but also the aromatic protons of diethylaminophenyl in RhB (cross-peak B'). Moreover, the cross-peak C' clearly demonstrated the close distance between the anthracene protons of the linker group in bis(β-CD) **2** and the aromatic protons of the benzoate moiety in RhB. Therefore, we propose a possible binding mode in the inclusion complexation of RhB by bis(β-CD) **2** (Figure 6b). In this mode, two diethylaminophenyl groups of RhB were included in the hydrophobic CD cavities from the narrow side to form a "face-to-face" sandwich inclusion complex, while the benzoate branch of RhB was located partially or entirely in the pseudocavity formed by the linker groups of hosts. These results showed bis(β-CD) **2** might adopt a cooperative sandwich binding mode, where a guest molecule was cooperatively bound by two CD cavities from the smaller opening of the CDs (Figure 6). Thus, the guest molecule was more efficiently shielded from attack of solvent water by the cooperative inclusion complexation with CD cavities.

Molecular Binding Affinity and Molecular Selectivity. Native and simple modified CDs afford only very small binding constants probably due to the weak hydrophobic interactions. Bridged bis(β-CD)s, however, afford much more stable inclusion complexes through cooperative binding of two adjacent cavities and potential multiple recognition ability. The complex stability constants (*K*s) of bis(β-CD) **2** with the guest molecules are obviously larger than those of native β-CD **1** (Table 1). The bis(β-CD) **2** that gave the enhancement factors for each guest molecules was: 1.5 for AR, 2.8 for NR, 2.3 for TNS, 34.8 for ANS and 2.5 for RhB, respectively. By comparing the enhancement factor, we concluded that the curved guest ANS was more capable of cooperatively binding bis(β-CD) **2** than linear guests NR, AR, TNS and T-shaped guest RhB.

The importance of guest structure was more clearly demonstrated by comparing the host effect for each guest. The molecular selective profile of native β-CD **1** was in the

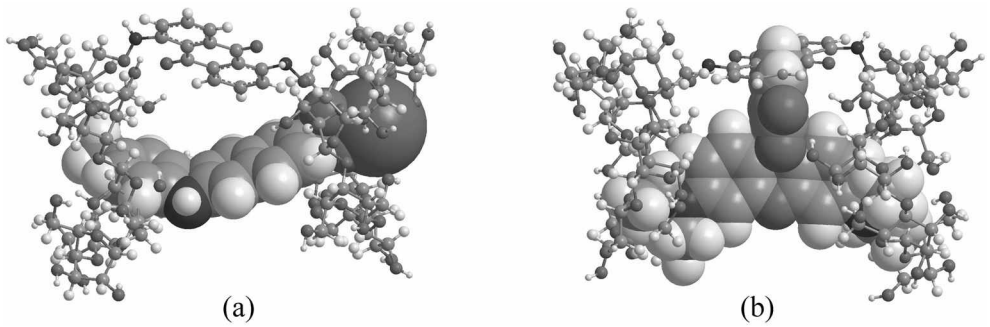


Figure 6. Possible inclusion binding modes of bis(β-CD) **2** (a) with TNS and (b) with RhB.

order of RhB > TNS > AR > NR > ANS. Bis(β-CD) **2** gave a similar selective sequence. that is. RhB > TNS > AR > ANS > NR. The guests RhB and TNS afforded higher complexation stability constants with hosts. An examination with the Core-Pauling-Koltun (CPK) molecular model demonstrat that the skeleton lengths of TNS (14.1 Å) and RhB (13.8 Å) are longer than those of AR (10.8 Å), NR (11.1 Å) and ANS (8.1 Å). Therefore, the stronger complexation might be attributed to the strict size-fit between TNS or RhB and CD. which enabled the long guests to penetrate more deeply into the CD cavity and thus gave the stronger van der Waals and hydrophobic interactions between host and guest. In a further investigation, guests TNS and ANS possessed the similar frameworks (naphthalenen ring moiety), but TNS was substituted at 2- and 6-positions. ANS at 1- and 8-postitons. Although native β-CD **1** and bis(β-CD) **2** gave the lower *K*s values for ANS rather than TNS, the enhanced molecular binding affinity by the cooperative binding of bis(β-CD) **2** for ANS was more remarkable than that for TNS. This might be attribute to the shape difference of the linear guest TNS and the curved guest ANS. The present results indicated that TNS could be embedded deeply into the cavity of the native β-CD **1** in the longitudinal direction, and the second cavity in the bis(β-CD) **2** merely enhanced the *K*s value by 2.3 times. while the guest ANS was only poorly accommodated in the cavity of native β-CD **1** due to the steric hindrance, and therefore the contribution of the second cavity in bis(β-CD) **2** was much more pronounced to give an enhancement of the *K*s by a factor of 34.8. Another interesting point is that. guests AR and NR. possessing a similar heterocycle anthracene moiety. gave entirely different binding constants upon inclusion complexation with native β-CD **1**. displaying the *K*s values of 2630 and 480 M^{-1} for the AR and NR, respectively. This result seems reasonable. since AR. which had small substituent. could be well-embedded in the cavity of β-CD in the longitudinal direction. while NR could partly penetrate into the CD cavity to form a weaker inclusion complex due to the steric hindrance. Compared with the native β-CD **1**. bis(β-CD) **2** more stable inclusion complexes with AR and NR through cooperative binding tow CD units. displaying a binding affinity sequence of AR > NR. These results further demonstrated that the size and shape of guest molecules were very important factors for enhancing the binding affinity of anthraquinone diamino bridged bis(β-CD) **2**.

It was worthly note that the bridged bis(β-CD) **2** not only greatly enhanced the original binding affinity of the native β-CD. but also extended its molecular selectivity for T-shaped guest RhB. As AR and RhB contained analogous tricyclic fragments (Scheme 2). the native β-CD **1** displayed close *K*s value for linear guest AR and T-shaped guest RhB. and showed lower molecular selectivity (about 1.6) for the RhB/AR pair. However. host **2** showed lower *K*s value (4030) for AR and the highest *K*s value (10700) for RhB. This might be attribute to the fact that the tether length and the relative rigidity of the bridged chain in **2** were unsuitable for the binding of the linear guest AR. On the other hand, attributing to the linker group of bis(β-CD) **2** could supply a well - organized pseudo cavity, which in turn provided additional binding interaction with the branch fragment of RhB to form a sandwich inclusion complex, the bis(β-CD) **2** displayed the highest *K*s values for RhB among the examined guests, and significantly enhanced molecular selectivity for the RhB/AR pair, that is 1.7 times higher than the corresponding value of the native β-CD **1**.

In summary, we succeeded in preparing a novel anthraquinone diamino-bridged bis(β-CD) 2. Further investigations demonstrated that the novel bridged bis(β-CD) **2** greatly enhanced the original binding affinity of the native β-CD by the cooperative binding of one guest molecular in the two closely located β-CD cavities. giving the highest binding affinity towards ANS up to 34.8 times and the enhancement of molecular selectivity for RhB/AR pair by 1.7 times as compared with the native β-CD. The size/shape matching concept between host and guest dominated the stability of the inclusion complexes formed by the novel bis(β-CD) **2** and guests molecules.

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References and Notes

1. Szejti. J. *Chem. Rev.* **1998**. *98*. 1743-1754.
2. Dentuto. P. L.: Catucci. L.: Cosma. P.: Fini. P.: Agostiano. A.: D'Accolti. L.: Trevithick-Sutton. C. C.: Foote. C. S. *J. Phys. Chem. B* **2005**. *109*, 1313-1317.
3. Zhao. Y.: Yang. Z. M.: Li. Z. Y.: Li. B. Y.: A. F.: Bi. X. J. *Chin. J. Inorg. Chem.* **2006**, *22*, 679-684.
4. Zhao. Y.: Liu. X. Q.: Zhao. Y.: Liu. P.: Li. C. *Chin. J. Anal. Chem.* **2006**. *34*. 959-962.
5. Ali. S. M.: Asmat. F.: Koketsu. M. *Bull. Korean Chem. Soc.* **2006**. *27*. 1397-1400.
6. Michels. J. J.; Huskens. J.; Reinhoudt. D. N. *J. Am. Chem. Soc.* **2002**. *124*, 2056-2064.
7. De. J. M. R.: Engbersen. J. F. J.: Huskens. J.: Reinhoudt. D. N. *Chem. Eur. J.* **2000**. *6*. 4034-4040.
8. Liu. Y.: Yang. Y. W.: Chen. Y.: Ding. F. *Bioorgan. Med. Chem.* **2005**. *13*, 963-971.
9. Liu. Y.; Chen. Y. *Accounts Chem. Res.* **2006**, *39*, 681-691.
10. Breslow. R.: Dong. S. D. *Chem. Rev.* **1998**, *98*. 1997-2012.
11. Zhao. Y.: Yang. Z. M.: Zhu. H. Y.: Gu. J.: Wang. Y. F. *Acta Phys.-Chim. Sin.* **2007**. *23*. 394-398.
12. Petter. R. C.: Salek. J. S.: Sikorski. C. T.: Kumaravel. G.: Lin. F. T. *J. Am. Chem. Soc.* **1990**. *112*, 3860-3868.
13. Connors. K. A. *Chem. Rev.* **1997**, *97*. 1325-1357.
14. Park. K. K.; Kim. Y. S.; Jung. H. K.; Song. H. E.; Park. J. W. *Bull. Korean Chem. Soc.* **2000**. *21*. 1119-1124.
15. Kajtar. M.: Horvath-Toro. C.: Kuthi. E.: Szejtli. J. *Acta Chim. Acad. Sci. Hung.* **1982**. *110*. 327-355.
16. Harata. K.: Uedaira. H. *Bull. Chem. Soc. Jpn.* **1975**. *48*. 375-378.
17. Fraiji. E. K.: Cregan. T. R.; Werner. T. C. *Appl. Spectrosc.* **1994**. *48*. 79-84.