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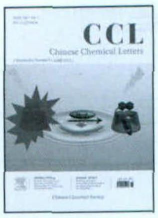

Original article

Selective binding of bile salts by β-cyclodextrin derivatives with appended quinolyl arms

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ABSTRACT

Two β-cyclodextrin derivatives bearing appended quinolyl and isoquinolyl arms, *i.e.* mono-(6-quinolyl-6-deoxy)-β-cyclodextrin (**1**) and mono-(6-isoquinolyl-6-deoxy)-β-cyclodextrin (**2**) were synthesized in satisfactory yields and fully characterized. Their original conformations and binding behaviors toward four bile salt guests, that is, sodium cholate (CA), sodium deoxycholate (DCA), sodium glycocholate (GCA), and sodium taurocholate (TCA), were investigated by means of fluorescence, circular dichroism and 2D NMR spectroscopy. The study of solution structures revealed that both quinolyl and isoquinolyl arms were located outside the cyclodextrin cavity. The results obtained from the fluorescence titrations showed that the binding abilities of hosts **1** and **2** with selected bile salts varied in an order of DCA > CA > GCA. The selective binding of hosts toward bile salt guests was discussed from the viewpoints of induced-fit and multiple binding.

1. Introduction

Cyclodextrins (CDs) are a class of macrocyclic oligosaccharides consisting of six, seven, or eight glucose units linked by α-1,4-glucose bonds and capable of accommodating various inorganic, organic, and biological molecules into their hydrophobic cavities to form stable host–guest inclusion complexes [1–3]. In recent years, molecular recognition based on CD and CD derivatives has received increasing attention in chemistry, biology and many other fields [4–9]. It is thoroughly documented that introducing a fluorophore into the β-CD cavity, as a spectral probe, makes it simple and convenient to investigate the inclusion behaviors with optically silent guest molecules. Consequently, the binding of a fluorescent-labeled CD can be quantitatively determined by analyzing the spectral changes which are induced by guest inclusion. As a result, a number of β-CD derivatives possessing fluorescent groups have been designed and synthesized, and their binding behaviors with model molecules have been investigated by spectral titration [10–14].

Among numerous guest molecules, bile salts, containing a steroid skeleton, are a group of important surfactant-like biological, amphipathic compounds. They not only assist in the digestion of fats, but also interact with antibiotics, such as neomycin, clidamycin, kanamycin, and lincomycin [15]. Because the hydrophobic cavity of β-CD well matches the size of bile salts, molecular binding between bile salts and CDs has been widely studied. For example, Tato and co-workers studied the binding modes of β-CD and its derivatives in D_2O by ROESY experiments, observing different binding modes upon inclusion complexation with bile salts [16]. Previously, we also reported the molecular recognition behavior of mono-[6-*O*-(8-hydroxyquinolyl)]-β-CD and several permethylated β-CD derivatives toward bile salts [17,18]. In the present work, we synthesized a pair of positively charged β-CD derivatives bearing appended quinolyl and isoquinolyl arms and investigated their molecular binding behavior toward four bile salts (CA, DCA, TCA, and GCA) by the circular dichroism, 2D NMR and fluorescence spectral titration experiments (Scheme 1).

2. Experimental

All bile salt guests were purchased from Sigma and used without further purification. Mono-6-indo-β-CD (6-I-β-CD) was synthesized following the procedure previously reported [19]. Mono-[6-*O*-(8-hydroxyquinolyl)]-β-CD (**3**) were synthesized according to reference method [20]. Disodium hydrogen phosphate and sodium dihydrogen phosphate were dissolved in distilled, deionized water to make a 0.1 mol/L phosphate buffer solution of pH 7.20, which was used in the spectral measurements. In the fluorescence titrations, the concentration of host CDs kept constant (1.0×10^{-5} mol/L), and the concentrations of bile salts varied from 0 to 2×10^{-3} mol/L. Binding constants were determined by plotting changes of the emission intensity at 381 nm versus the concentrations of guest.

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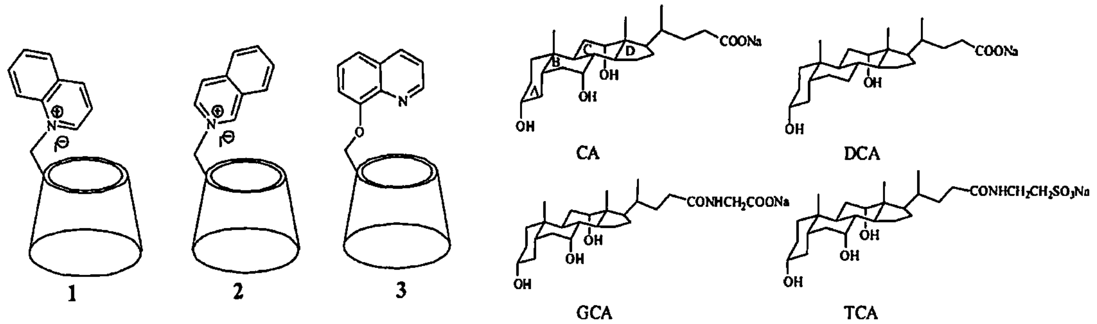

Scheme 1. Structures of host molecules and guest molecules.

2.1. *Synthesis of mono-(6-1-quinolyl-6-deoxy)-β-CD (1)*

Dry quinoline (4.7 mL, 40.25 mmol) was added to a solution of DMF (25 mL) containing mono-6-indo-β-CD (2 g, 1.61 mmol). The mixture was allowed to react with stirring at 80 °C for 24 h. The resulting dark red solution was poured into acetone (300 mL), and the precipitate was collected by filtration. The precipitate obtained was dissolved in a minimal amount of hot water and was added to acetone (200 mL), and the precipitate formed was collected by filtration. This procedure was repeated again. The crude product obtained was subsequently recrystallized from distilled water. After drying in vaccuo, a pure light yellow sample was obtained in 21% yield. ESI-MS: 1246.8 ([M−I]$^+$). ^{1}H NMR (400 MHz, D_2O): δ 9.72 (s, 1H, Ar-H), 8.47 (d, 1H, J = 7.1 Hz, Ar-H), 8.43–8.34 (m, 2H, Ar-H), 8.27–8.14 (m, 2H, Ar-H), 8.05–7.95 (m, 1H, Ar-H), 5.30 (d, 1H, J = 12.8 Hz, C-6 H of CD), 5.09–4.85 (m, 7H, C-1 H of CD), 4.35–4.24 (m, 1 H, C-6 H of CD), 4.15–3.18 (m, 40H, C-2,3,4,5,6 H of CD). ^{13}C NMR (100 MHz, D_2O): δ 150.1, 137.9, 137.8, 134.8, 131.7, 130.3, 127.5, 127.3, 126.5, 102.1, 102.0, 101.8, 101.6, 101.3, 83.3, 81.7, 81.1, 80.8, 80.6, 73.0, 72.6, 72.4, 72.0, 71.7, 71.5, 71.0, 70.7, 61.9, 60.3, 58.6. Elemental Anal. Calcd. for **1**: $C_{51}H_{76}INO_{34}\cdot 3H_2O$: C 42.89, H 5.79, N 0.98; Found: C 42.96, H 5.54, N 1.12.

2.2. *Synthesis of mono-(6-2-isoquinolyl-6-deoxy)-β-CD (2)*

Mono-(6-2-isoquinolyl-6-deoxy)-β-CD (**2**) was synthesized in 18% yield using a similar method to the synthesis of **1**. ESI-MS: 1246.8 ([M−I]$^+$). ^{1}H NMR (400 MHz, D_2O): δ 9.69 (s, 1H, Ar-H), 8.45 (d, 1H, J = 6.9 Hz, Ar-H), 8.41–8.31 (m, 2H, Ar-H), 8.23–8.13 (m, 2H, Ar-H), 7.97 (t, 1H, J = 7.5 Hz, Ar-H), 5.28 (d, 1H, J = 12.5 Hz, C-6 H of CD), 5.14–4.82 (m, 7H, C-1 H of CD), 4.26 (t, 1H, J = 9.2 Hz, C-6 H of CD); 4.15–3.11 (m, 40H, C-2,3,4,5,6 H of CD). ^{13}C NMR (100 MHz, D_2O): δ 150.2, 137.9, 137.8, 134.8, 131.7, 130.3, 127.5, 127.3, 126.5, 102.1, 101.9, 101.8, 101.6, 101.3, 83.2, 81.7, 81.1, 80.8, 80.6, 73.0, 72.7, 72.4, 72.0, 71.7, 71.5, 71.0, 70.7, 61.9, 60.3, 58.6. Elemental Anal. Calcd. for **2**: $C_{51}H_{76}INO_{34}\cdot 6H_2O$: C 41.33, H 5.98, N 0.95; Found: C 41.45, H 5.69, N 1.10.

3. Results and discussion

3.1. *Original conformations of hosts*

It is well-known that circular dichroism spectrometry has become a convenient method for investigating the conformation of CD derivatives. The inclusion of a chromophoric achiral guest/moiety in a β-CD cavity may produce induced circular dichroism (ICD) signals. In order to elucidate the conformation of hosts, the circular dichroism spectra were recorded at 25 °C in aqueous phosphate buffer solution (pH 7.2). As shown in Fig. 1, hosts **1** and **2** present quite similar circular dichroism signals in shape, indicating that the original conformations of hosts **1** and **2** should be similar. The circular dichroism spectra of hosts **1** and **2** show a weak positive Cotton effect peak around 230 nm (host **1**: $\Delta\varepsilon$ = 1.67 dm^3 mol^{-1} cm^{-1}; host **2**: $\Delta\varepsilon$ = 1.66 dm^3 mol^{-1} cm^{-1}) for the L_a transition band and a moderate negative Cotton effect peak around 245 nm (host **1**: $\Delta\varepsilon$ = −2.59 dm^3 mol^{-1} cm^{-1}; host **2**: $\Delta\varepsilon$ = −3.77 dm^3 mol^{-1} cm^{-1}) for the L_b transition band of quinolyl and isoquinolyl chromophores. According to the generally accepted empirical rule [21–23], the electronic transition parallel to the CD axis gives a positive ICD signal, whereas the perpendicular transition gives a negative signal. However, the situation is reversed for a guest located just outside the CD cavity. Therefore, it seems reasonable to conclude that the substituent chromophores of **1** and **2** were located outside the CD cavity with the L_a transition perpendicular to the β-CD axis and the L_b transition band parallel to the β-CD axis. Upon the inclusion complexation with CA, the circular dichroism signals of **1** and **2** are nearly unchanged. This phenomenon indicates that hosts **1** and **2** remain in their original location and orientation of the transition dipole moment of the chromophore after complexation with guest molecules. However, host **3** gives an absolutely different CD signal, showing two weak positive Cotton effect peaks at 239 nm ($\Delta\varepsilon$ = 0.93 dm^3 mol^{-1} cm^{-1}) and 300 nm ($\Delta\varepsilon$ = 0.26 dm^3 mol^{-1} cm^{-1}) that may be assigned to the L_a and L_b transition bands, respectively. This may indicate that the quinolyl group of **3** is incompletely, or only partially, included in the β-CD cavity to form self-included complexes, which is in good agreement with the previously reported conformation by 2D NMR [17].

The conformation of hosts **1** and **2** was further determined by the 2D NMR experiment. Generally, when the distance of the protons is closer than 0.4 nm spatially, nuclear Overhauser effect (NOE) cross-peaks will be observed in the NOESY or ROESY spectrum. Therefore, it is possible to conclude the location and orientation of the moiety in the β-CD cavity according to the assigned NOE correlations. Actually, no NOE cross-peaks are found between the isoquinolyl group and H3/H5 protons of β-CD cavity, except for the cross-peak between the protons of isoquinolyl group with H6 and H6′ protons of β-CD cavity. Hence, it is likely that the isoquinolyl group is not included in the β-CD cavity. In combination with the result of circular dichroism, it can be concluded that the isoquinolyl residue only remains above the rim of the CD cavity.

3.2. *Fluorescence spectral titrations*

The inclusion complexations of hosts **1** and **2** with the representative guests were quantitatively investigated by means of fluorescence titrations in aqueous phosphate buffer solution (pH 7.2) at 25 °C. As shown in Fig. 2, the fluorescence intensities of **1** and **2** continuously decrease upon the addition of CA, DCA and GCA. However, the fluorescence intensity almost remains unchanged with the addition of TCA. The stoichiometry for the inclusion complexation of hosts **1** and **2** with CA, DCA and GCA was

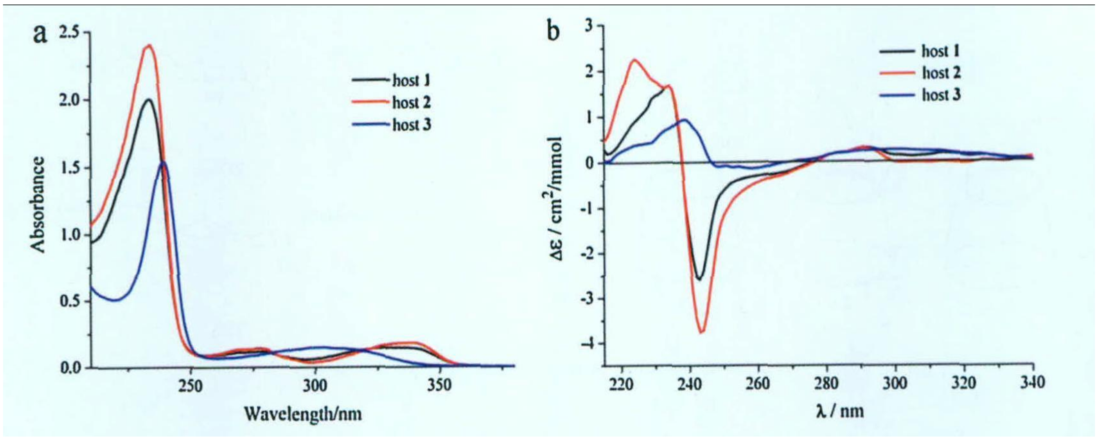

Fig. 1. (a) UV–vis absorption spectra (5.0×10^{-5} mol/L) of hosts **1**, **2** and **3** in phosphate buffer solution (pH 7.2) at 25 °C. (b) Circular dichroism spectra (1.0×10^{-4} mol/L) of hosts **1**, **2** and **3** in phosphate buffer solution (pH 7.2) at 25 °C.

determined by Job's method. As can be seen in Fig. 3, the Job's plot presents a maximum at a fraction of 0.5, confirming the formation of 1:1 inclusion complexation between host and guest. Similarly, the stoichiometry of 1:1 was obtained in other cases of host-guest inclusion complexation. After verifying 1:1 stoichiometry, the stability constants (K_S) values could be calculated according to the sequential changes in fluorescence intensity of hosts with the different concentrations of guests by using the nonlinear least-squares method [24]. The results along with the ΔG^0 values are listed in Table 1.

3.3. Binding mode

To obtain further information about the binding modes between bile salts and β-CDs, ROESY spectra were determined in D_2O at 25 °C. Generally, the bile salt molecule is identified with A, B, C, and D rings according to the previous report [15]. Meanwhile, the protons of β-CD and the steroid are marked with Hn and Gn, where n corresponds to the carbon number in β-CD and steroid, respectively. In the ROESY spectrum of **2**/DCA system (Fig. 4), the cross-peaks A and B were assigned to the NOE correlations between the H3/H5 protons of β-CD and the DCA's G18/G21 protons, respectively. Meanwhile, the cross-peaks C corresponded to the NOE correlations of the D ring and the hydrophobic tail of DCA with β-CD's H3/H5 protons, indicating that the D ring and the hydrophobic tail of DCA were accommodated in the β-CD cavity. Moreover, a clear cross-peak D corresponding to NOE correlation between the DCA's G23/G16 protons and the protons of isoquinolyl group was observed. From the above information, we deduced that the DCA was deeply included in the β-CD cavity from the wide opening with the tail and D ring located near the narrow opening.

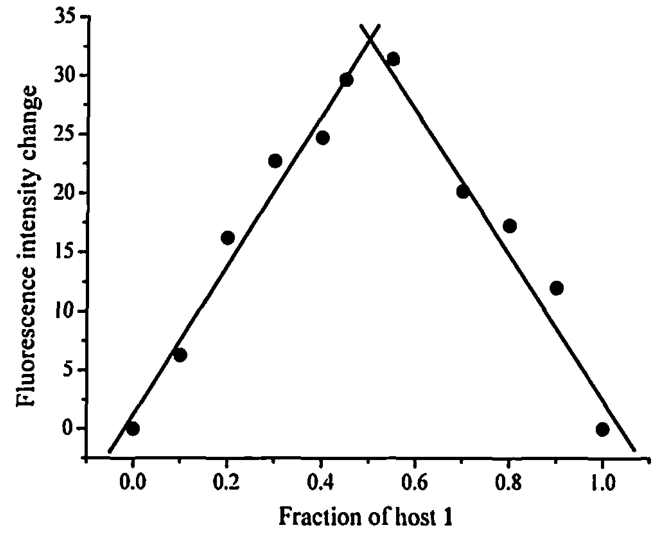

Fig. 3. Job's plot of host **1**/DCA system at 381 nm. ([host **1**] + [DCA] = 5×10^{-5} mol/L).

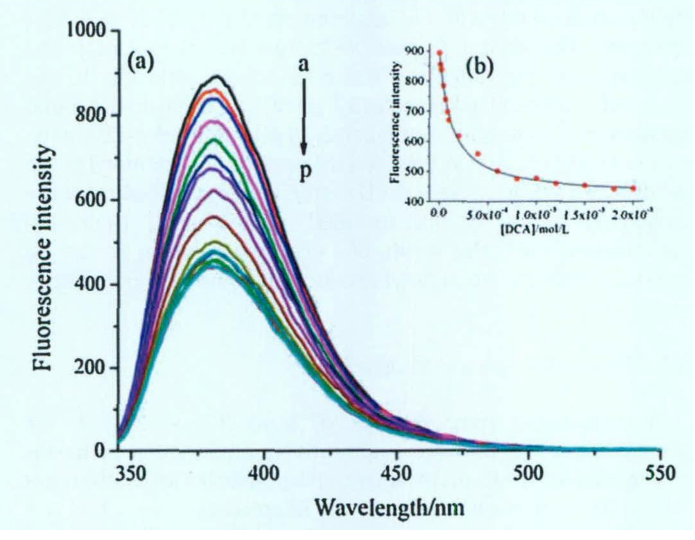

Fig. 2. (a) Fluorescence spectral changes of host **1** (1.0×10^{-5} mol/L) upon addition of DCA (0–2.0×10^{-3} mol/L) in 0.1 mol/L phosphate buffer solution (pH 7.2) at 25 °C. (b) Nonlinear least-squares analysis of the differential intensity to calculate the complex formation constant (K_S) (λ_{ex} = 342 nm, λ_{em} = 381 nm).

Table 1

Stability constants (K_S) and Gibbs free energy changes ($-\Delta G^0$) for the inclusion complexation of steroids with host **1**, **2** and **3** in phosphate buffer solution (pH 7.20) at 25 °C.

Hosts	Guests	K_S (L/mol)	ΔG^0 (kJ/mol)	logK_S
1	CA	5034 ± 185	−21.12	3.70
	DCA	7903 ± 437	−22.24	3.90
	GCA	2680 ± 105	−19.56	3.43
	TCA	[a]	[a]	[a]
2	CA	4434 ± 129	−20.81	3.65
	DCA	6921 ± 199	−21.91	3.84
	GCA	2572 ± 143	−19.46	3.41
	TCA	[a]	[a]	[a]
3	CA	2443 ± 123	−19.33	3.39
	DCA	3177 ± 17	−19.99	3.50
	GCA	2811 ± 33	−19.68	3.45
	TCA	2809 ± 46	−19.68	3.45

[a] The guest-induced variations of fluorescence emission are too small for these values to be determined.

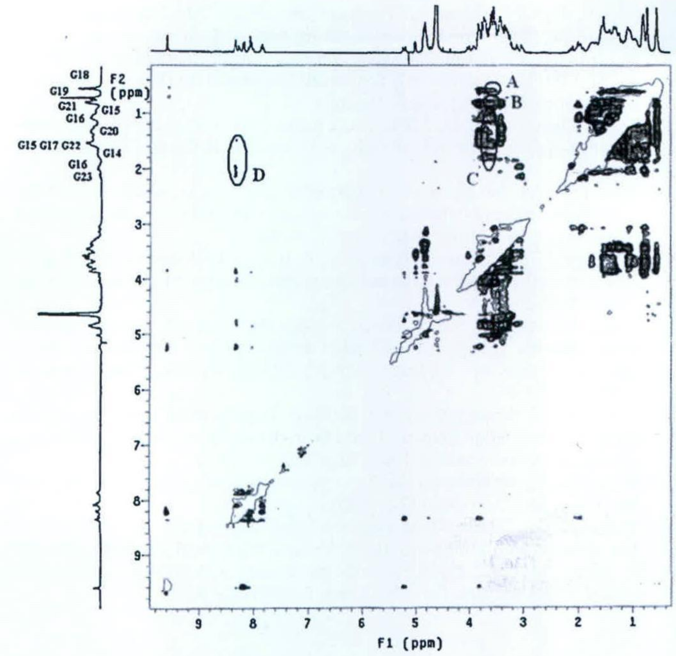

Fig. 4. ROESY spectrum of **2**/DCA (2.5 mmol/L and 5.2 mmol/L, respectively) with a mixing time of 260 ms at 298.1 K.

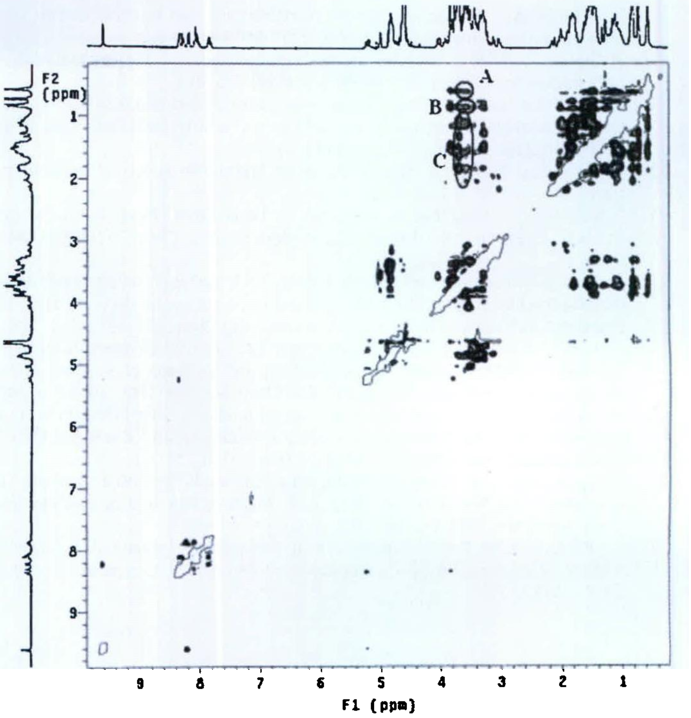

Fig. 5. ROESY spectrum of **2**/CA (2.5 mmol/L and 5.2 mmol/L, respectively) with a mixing time of 260 ms at 298.1 K.

In the ROESY spectrum of **2**/CA system (Fig. 5), the cross-peaks A and B were assigned to the NOE correlations between the H3/H5 protons of β-CD and G18/G21 protons of CA. The cross-peaks C corresponded to the NOE correlations of the CA's D ring and the tail chain with the β-CD's H3/H5 protons. By comparing the NOE signals of **2**/DCA and **2**/CA systems, it was determined that, in **2**/DCA system, the correlation intensity of the D ring and tail chain with β-CD's H3 proton was same as the corresponding intensity with β-CD's H5 proton. However, the correlation intensity of the D ring and tail chain with β-CD's H3 proton was stronger than the corresponding intensity with β-CD's H5 proton in **2**/CA system. This may indicate that DCA penetrated into the β-CD cavity of **2** more deeply than CA, which was consistent with the K_S values obtained from fluorescence titrations.

3.4. Binding ability

As shown in Table 1, the binding abilities of hosts **1** and **2** with bile salts guests decreased in the following order of DCA > CA > GCA, however, the inclusion constant of hosts **1** and **2** with TCA cannot be measured by fluorescence spectra. This seems reasonable, because the depth that DCA inserts into the β-CD cavity is deeper than that of CA and GCA. In addition, TCA possesses a highly hydrophilic sulfonate tail, which is very unfavorable for its interactions with the hydrophobic cavity of β-CD. Thus, the fluorescence of hosts **1** and **2** barely changed with the addition of TCA.

4. Conclusion

In summary, a pair of β-CD derivatives modified with quinolyl and isoquinolyl chromophores have been successfully synthesized, and their binding behaviors toward four typical bile salts (CA, DCA, GCA, and TCA) were carefully studied. The results obtained from the circular dichroism and 2D NMR showed that the quinolyl and isoquinolyl chromophores of **1** and **2** were not self-included into the β-CD cavity, and only remained on the edge of the β-CD cavity. Upon the inclusion complexation, DCA penetrated into the β-CD cavity more deeply than CA, and the binding abilities decreased in the order of DCA > CA > GCA.

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