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Spectrofluorimetric Study on Inclusion Behaviour of *p*-Sulfonated Calix[4,6]arene with 1,10-Phenanthroline

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The supramolecular interaction of 1,10-phenanthroline (Phen) with *p*-sulfonated calix[n]arenes (SCnA, n = 4, 6) were studied using spectrofluorimetry, ^{1}H NMR and molecular modeling calculations. The interaction mechanism of the inclusion complex was discussed and the various factors affecting the inclusion process were examined. It was found that the dramatic quenching of the fluorescence intensity of 1,10-phenanthroline was observed with the addition of the SCnA (n = 4, 6). This was due to 1,10-phenanthroline react with SCnA (n = 4, 6) to form stable complex. ^{1}H NMR titration spectra testified that 1,10-phenanthroline was penetrated into the hydrophobic cavity of SCnA (n = 4, 6). This finding was confirmed using molecular dynamics calculations and the thermodynamic parameters of the complex. The calculated stability constant results showed that the SC6A-Phen complex was more stable than SC4A-Phen.

Keywords: 1,10-Phenanthroline, *p*-Sulfonated calix[n]arenes, Inclusion interaction, Host-guest complexation, Spectrofluorometry.

INTRODUCTION

Calix[n]arenes are cyclic oligomers synthesized by condensation of a *p*-alkylated phenol and formaldehyde. They have a particular configuration because of their cavity, so they have the flexibility to adjust the cavity dimension and the ability to form inclusion compounds with a great variety of guests, from apolar compounds[1-5] to anions[6,7] and metallic cations[8-11]. This versatility makes the calixarenes family become the third major class of macrocyclic binding agents after crown-ethers and cyclodextrins. However, the poor solubility of calixarenes in aqueous solution limited their applications[12-14]. The sulfonation of calix[n]arenes on their *para* positions produces well highly water-soluble *p*-sulfonated calix[n]arenes (SCnA, Fig. 1a) which conquer the poor solubility of calixarenes in aqueous solution[15]. Recently, biological activity and potential application in medicine of *p*-sulfonated calix[n]arenes and its derivatives have caused the attention of people. Recently, many research papers have been published on the inclusion of various guests, like quaternary ammonium ions[16,17], methylammonium cations[18,19], dyes[20,21], native amino acids[22] and small neutral organic molecules[23] by *p*-sulfonated calix[n]arenes. Furthermore, *p*-sulfonated calix[n]arenes have been applied in the improvement of solubility and stability of drugs and enzyme mimics[24,25]. Nevertheless, comparing with the widely use of cyclodextrins in pharmaceutical fields and in many industrial products, related investigation of *p*-sulphonated calix[n]arenes and their derivatives is still in preliminary steps. Existing research on *p*-sulfonated calix[n]arenes focuses on the complex's inclusion ability and biological activity. Studies on its interaction with indicators are rare.

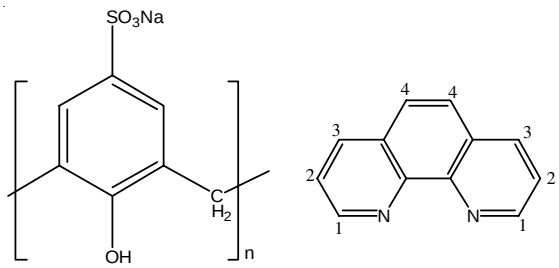

Fig. 1. Structure of *p*-sulfonated calyx[n]arene (n = 4, 6) and 1,10-phenanthroline

The compound 1,10-phenanthroline is an indicator[26], having good fluorescence properties and the ability to form stable complexes with a variety of transition metals. At pH levels of 4 to 5, 1,10-phenanthroline and ferrous ions form an orange-red complex[27], allowing the determination of iron content through spectrophotometry. The complex and its derivative formed with copper have DNA cleavage activity[28]. These complexes can hence be used as non-oxidative cleavage enzymes, having anticancer activity. Therefore, 1,10-phenanthroline is a very important indicator, research on the inter-

action of *p*-sulphonated calix[n]arenes and 1,10-phenanthroline has direct and practical significance. However, to the best of our knowledge, related research has never been reported.

In this work, the interaction between *p*-sulfonated calix-[4,6]arene and 1,10-phenanthroline in aqueous solutions was investigated through the spectrofluorometric titrations. Various factors affecting the inclusion process such as temperature, pH, surfactants, reaction time and the addition order of reagents were discussed. Thermodynamic property was also studied to obtain thermodynamic parameters of the complex. ^{1}H NMR study was performed to determine the possible binding mechanism of the interaction. We found that there was a strong interaction between 1,10-phenanthroline and *p*-sulfonated calix-[4,6]arene. Therefore, the possible application of the complex is as a fluorescence probe to determine other substances.

EXPERIMENTAL

Fluorescence spectra were obtained using a Agilent Technologies Cary Eclipse with an excitation wavelength of 227.96 nm and an emission wavelength of 362.92 nm. Both excitation and emission band widths were set at 5 nm. ^{1}H NMR spectra were obtained with a Bruker DRX-600MHz spectrometer (Switzerland). The pH was measured using a pHS-3TC digital precision pH meter (Shanghai, China). Molecular modeling calculations were optimized at the B3LYP/6-31G(d) level of density functional theory with the Gaussian 03 program.

All reagents used were of analytical-reagent grade or the best grade commercially. Doubly distilled water was used throughout. The 1,10-phenanthroline used in the experiment were purchased from Tianjin Municipality kermel Chemical Reagent limited liability company. The stock solution of 1×10^{-4} mol L^{-1} 1,10-phenanthroline were prepared by directly dissolving their powder in doubly distilled water. SC4A and SC6A were synthesized according to the literature[29] and identified by IR, ^{1}H NMR and element analysis. Stock solution of SC4A and SC6A were prepared directly with distilled water as 1×10^{-4} mol L^{-1}. Britton-Robinson buffer solution was prepared using a mixed acidic solution that contained 0.04 mol L^{-1} H_3PO_4, CH_3COOH and H_3BO_3, respectively and then was adjusted to accurate values by using 0.2 mol L^{-1} NaOH.

A 1 mL aliquot of the stock solution of 1,10-phenan-throline was transferred into a 10 mL volumetric flask and an appropriate amount of 1×10^{-4} mol L^{-1} SC4A was, respectively added, followed by 1 mL of Britton-Robinson buffer solution of pH = 6. The mixed solution was diluted to final volume with double-distilled water and stirred thoroughly and equilibrated at room temperature, the fluorescence intensities were determined after 20 min. The fluorescence intensity values of the solution and the blank solution were measured at 362.92 nm using an excitation wavelength of 227.96 nm. SC6A and 1,10-phenanthroline experimental procedures as above.

RESULTS AND DISCUSSION

Formation process of the complex: Aqueous solutions of 1,10-phenanthroline (1×10^{-5} mol L^{-1}) has strong fluorescence with using pH 6 Britton-Robinson buffer solution. Fig. 2 shows the fluorescence spectra of 1,10-phenanthroline in the absence and presence of SC4A and SC6A, respectively. The

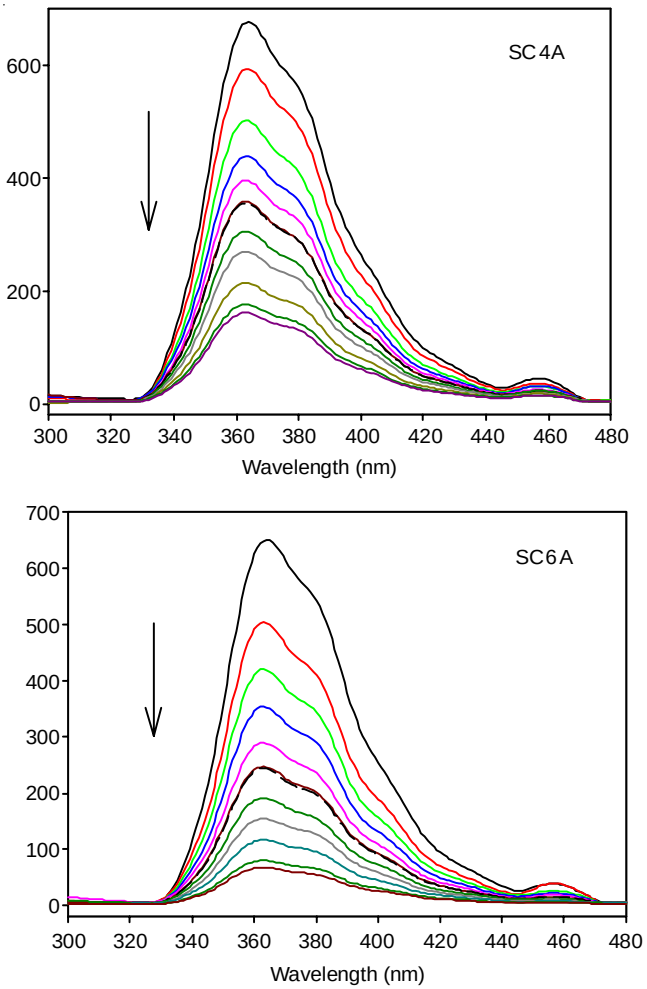

Fig. 2. Fluorescence spectra of 1,10-phenanthroline in different concentrations of SCnA (n = 4, 6) in Britton-Robinson buffer solutions. The concentrations of SCnA (10-4 mol L^{-1}): (1) 0; (2) 0.1; (3) 0.3; (4) 0.5; (5) 0.7; (6) 0.9; (7) 1.0; (8) 1.2; (9) 1.5; (10) 1.8; (11) 2.0. C Phen = 1×10^{-4} mol L^{-1}

fluorescence intensity of 1×10^{-5} mol L^{-1} 1,10-phenanthroline decreased markedly upon the addition of 1×10^{-4} mol L^{-1} SCnA (n = 4, 6) and SC6A experience a more obvious decline. Furthermore, the fluorescence quenching ($F-F_0$) values show good linear relationship with SCnA (n = 4, 6) concentration for a certain range of concentrations (Fig. 3). The marked fluorescence quenching and the slight blue-shift proved complex formation.

Stoichiometry and association constant of the inclusion complex: Assuming that SCnA and 1,10-phenanthroline forms a 1:1 ratio complex, the following expression can be written as follows:

$$\text{Phen} + \text{SCnA} \rightleftharpoons \text{Phen-SCnA} \quad (1)$$

If the equilibrium concentrations of 1,10-phenanthroline and SCnA were C_{Phen} and C_{SCnA}, respectively, the concentration of complex at equilibrium was $C_{Phen\text{-}SCnA}$, then:

$$K = \frac{C_{Phen\text{-}SCnA}}{C_{Phen} \times C_{SCnA}} \quad (2)$$

The association constant value for the inclusion complex can be determined by the typical double reciprocal (or Benesi-Hildebrand) plots:

$$\frac{1}{F - F_0} = \frac{1}{(F_\infty - F_0)KC_{SCnA}} + \frac{1}{F_\infty - F_0} \quad (3)$$

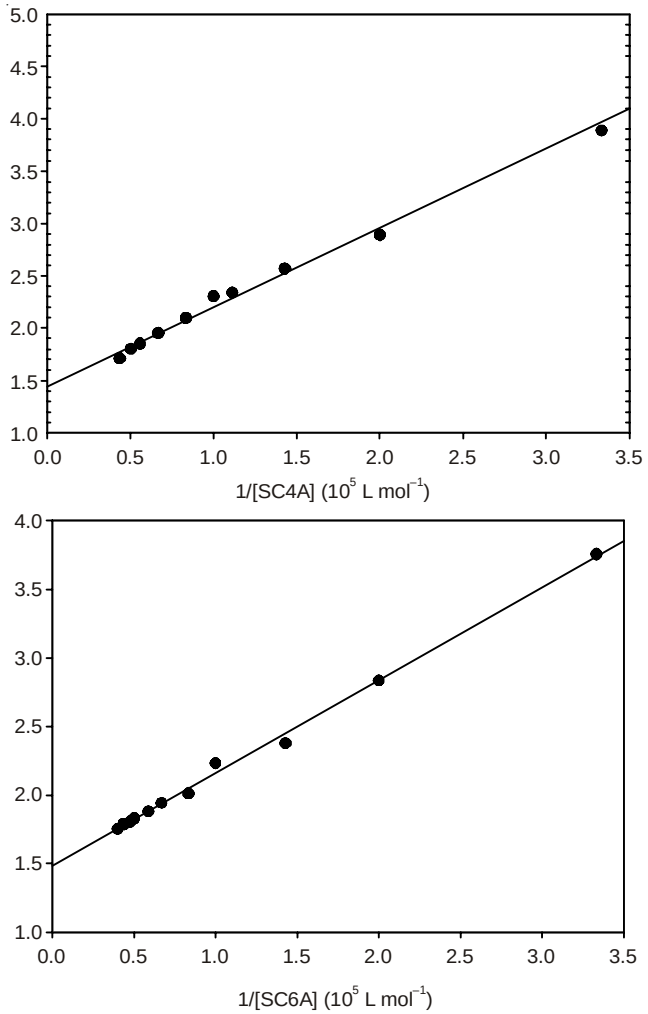

Fig. 3. Plot of $1/(F-F_0)$ *vs.* 1/[SCnA] of SCnA-Phen complex

where F_∞ is the fluorescence intensity of the system when the guest has been completely encapsulated by the host SCnA; C_{SCnA} is the concentration of host SCnA and F_0 is the fluorescence intensity of 1,10-phenanthroline without SCnA; while F is the fluorescence intensity at each SCnA concentration. And K is the binding constant of the complex. A good linear relationship was obtained when $1/(F-F_0)$ was plotted against $1/C_{SCnA}$, which supports the existence of a 1:1 complex ($R^2 > 0.99$, Fig. 3). The results showed that the apparent association constants for these 1:1 complexes at pH 6 were determined to be 1.90 × 105 and 2.19 × 105 L mol^{-1} in presence of SC4A and SC6A, respectively.

A representative Job's plot for the inclusion complexation of SCnA with 1,10-phenanthroline was shown in Fig. 4. The maximum of the curve was clearly at a mol fraction of 0.5, confirming the 1:1 ratio host-guest complex assembly formed in aqueous solution.

The thermodynamic parameters ΔH and ΔS of the inclusion process were determined from the temperature dependence of the binding constants using the van't Hoff equation.

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (4)$$

Thus, the thermodynamic parameters ΔH and ΔS were obtained from the slope and intercept of the plot of ln K *vs.* 1/T,

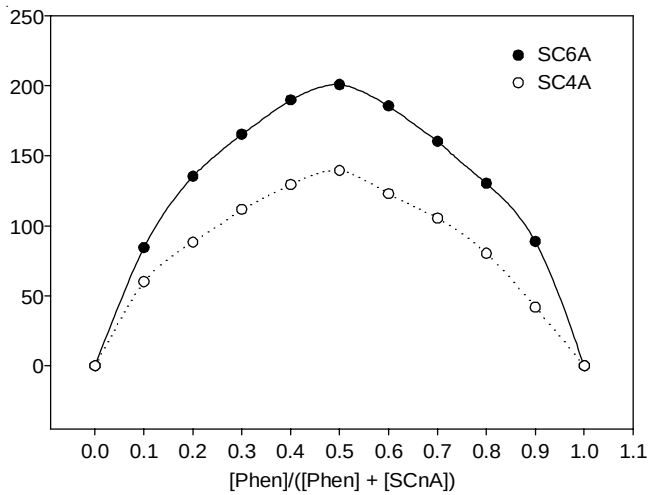

Fig. 4. Job's plot for the complexation of 1,10-phenanthroline with SCnA in Britton-Robinson buffer solution (pH 6) at 25 °C. ([Phen] + [SCnA]) = 1 × 10^{-5} mol L^{-1})

which was shown in Fig. 5. The results obtained are listed in Table-1. It can be seen that the complex has a negative ΔH and a larger negative ΔS, which indicates the formation of complex is mainly driven by the favorable enthalpy with a small entropic loss.

The free energy change (ΔG) was estimated from the following relationship:

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

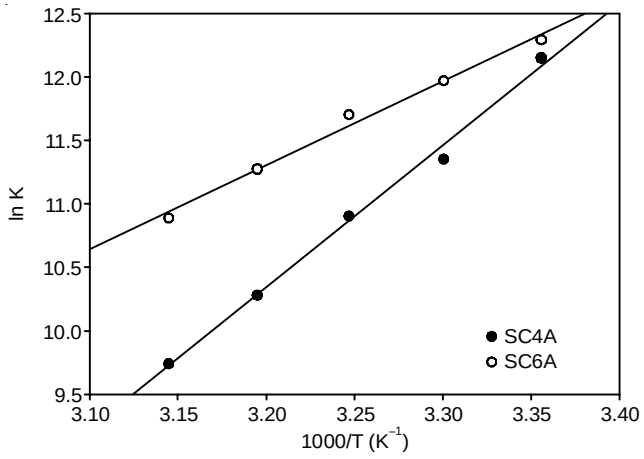

Fig. 5. Van't Hoff plot, pH 6, CPhen = 1 × 10^{-4} mol L^{-1}

From Table-1, it can be seen that the negative sign for free energy (ΔG) means that the interaction process was spontaneous. Hydrogen bonding, *p-p* interaction, electrostatic interaction, hydrophobic interaction, dipole-dipole or van der Waals would contribute to the favorable enthalpy change[30]. While the conformation change and the desolvation effect contributed to the entropic changes[31]. The entropy change originated from the entropic gain from the rearrangement of water molecules originally surrounding the host and guest molecules and the entropic loss from the decrease in the motion freedom in the complexation[32]. Higher temperature was disadvantageous to the formation of inclusion complexes. Therefore, the experiment should be conducted under a lower temperature. The present experiment was conducted at room temperature.

TABLE-2
COMPLEX ASSOCIATION CONSTANTS FOR 1:1 INTERMOLECULAR COMPLEXATION OF 1,10-PHENANTHROLINE WITH SCnA at DIFFERENT pH

		pH						
		2	4	6	7	8	10	12
		n = 1:1	n = 1:1	n = 1:1	n = 1:1	n = 1:1	n = 1:1	n = 1:1
SC4A	K	1.03×10^5	1.29×10^5	1.90×10^5	6.54×10^4	3.68×10^4	3.32×10^4	2.15×10^4
	R^2	0.9991	0.9994	0.9993	0.9994	0.9980	0.9990	0.9989
SC6A	K	1.59×10^5	2.03×10^5	2.19×10^5	1.63×10^5	1.29×10^5	8.69×10^4	4.75×10^4
	R^2	0.9985	0.9990	0.9967	0.9973	0.9968	0.9980	0.9999

Influence of pH: One of the most important factors affecting the stability of an inclusion complex is pH values. The pH dependence of association constants was studied over the pH range of 2 to 12. The formation of an inclusion complex between 1,10-phenanthroline and SCnA (n = 4, 6) was also measured by fluorescence spectra at different pH. From Table-2, significant changes in the stability constant at different acidity levels can be observed. The stability constants increased with increasing pH. At pH 6, the stability constants reached the maximum values, indicating that lower or higher pH would affect the stability of the inclusion complex. The binding constants were more sensitive to pH with increasing SCnA (n = 4, 6) cavity size, suggesting that the electrostatic interaction and the effect of structural matching were the dominant host-guest complex stabilizing factors.

Electrostatic interaction between the N atom of 1,10-phenanthroline and the negatively charged sulphonyl groups of SCnA (n = 4, 6) observably exists at pH 6. When the pH is increased from pH 6 to 12, or during a more basic condition, the electrostatic interaction between the 1,10-phenanthroline and SCnA (n = 4, 6) becomes gradually weaker. According to these observations, the binding constant at pH 6 is possibly larger than binding constants at other pH values. Coleman *et al.*[32] have also reported that with increasing pH, deprotonation of the SCnA (n = 4, 6) phenolic OH groups is reinforced, leading to strengthening of the hydrogen bonds among the phenolic hydroxyl groups. This allows conformation flexibility for the calixarene ring. As shown in Table-2, the association constants reached the maximum at pH 6 Britton-Robinson buffer solution. Hence, a buffer of pH 6 had been chosen for further studies.

TABLE-1
COMPLEX STABILITY CONSTANTS (K) AND THERMODYNAMIC PARAMETERS FOR 1:1 INTERMOLECULAR COMPLEXATION OF 1,10-PHENANTHROLINE WITH SCnA (n = 4, 6) IN BRITTON-ROBINSON BUFFER SOLUTION (pH = 6) AT DIFFERENT TEMPERATURE

	T (K)	K (L mol^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔS (J/(mol K)$^{-1}$)
SC4A	298	1.89×10^5	–92.83	–29.93	–211.06
	303	8.51×10^4		–28.88	
	308	5.44×10^4		–27.82	
	313	2.92×10^4		–26.77	
	318	1.70×10^4		–25.71	
SC6A	298	2.18×10^5	–55.13	–30.53	–82.56
	303	1.58×10^5		–30.11	
	308	1.12×10^5		–29.70	
	313	7.88×10^4		–29.29	
	318	5.36×10^4		–28.88	

Influence of surfactants: The influences of cationic surfactant cetyltrimethyl ammonium bromide (CTAB) and anionic surfactant sodium dodecyl sulfate (SDS) on SCnA-Phen inclusion complex were studied. As shown in Fig. 6, the fluorescence intensity of SCnA-Phen inclusion complex increased upon the addition of CTAB and SC4A-Phen inclusion complex experience a more obvious increase. When SDS was added, the fluorescence intensity of SCnA-Phen inclusion complex decreased and more decrease was observed in the SC4A-Phen system. According to the report[33], trimethyl ammonium cations can insert into the hydrophobic cavity of SCnA. CTAB molecules are trimethyl ammonium cationic surfactants, so CTAB compete with 1,10-phenanthroline in

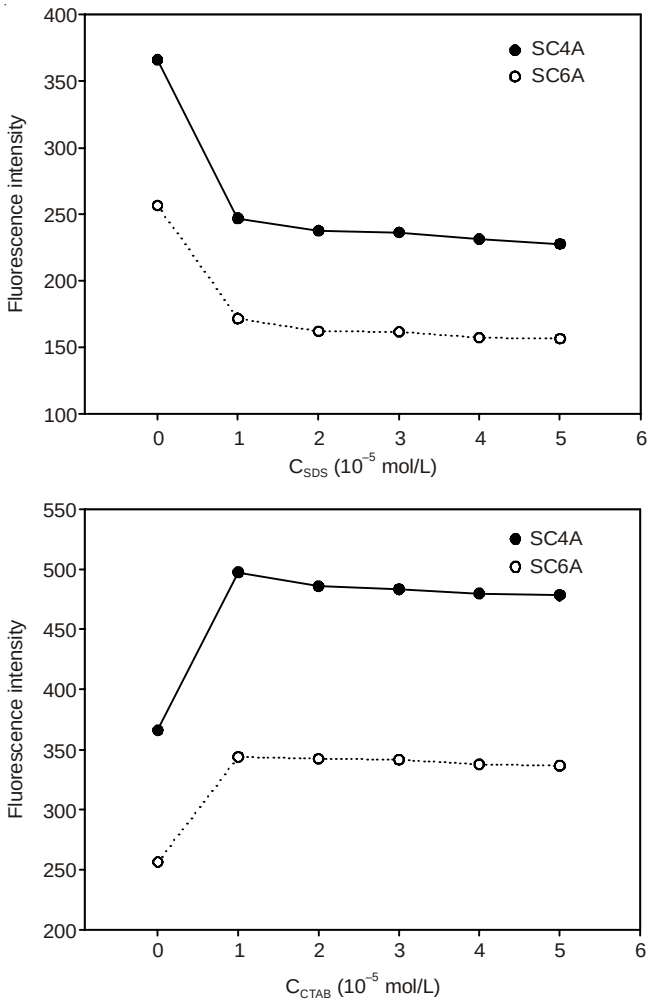

Fig. 6. Influence of CTAB and SDS concentration on the fluorescence intensity of Phen-SCnA, [Phen] = 1×10^{-4} mol/L, [SCnA] = 1×10^{-4} mol/L, pH = 6

in SCnA-Phen inclusion, release a fraction of 1,10-phenanthroline and lead to fluorescence intensity enhancement. It is confirmed that the 1,10-phenanthroline was included into the cavity of SCnA. As is known, SDS with negative charges and negative substituent groups (SO_3^{2-}) are in the flexible calixarene ring. Due to electrostatic repulsion between SDS and SCnA, the inclusion effect is more efficient between 1,10-phenanthroline and SCnA (n = 4, 6), with the descent of fluorescence intensities observed. As a result, electrostatic force plays an important role in the forming process of SCnA-Phen inclusion complex.

Influence of reaction time: The effect of reaction time was studied. As shown in Fig. 7, the results showed that the fluorescence intensity reached a minimum after the reagents had been added for 20 min. Hence, the reaction was carried out for 20 min, the subsequent fluorescence measurements were made after 20 min.

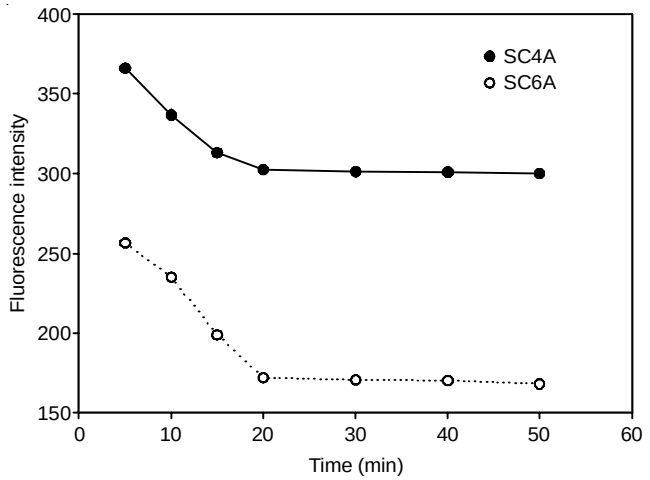

Fig. 7. Influence of reaction time on fluorescence intensity of the complex. [Phen] = 1 × 10^{-4} mol/L, [SCnA] = 1 × 10^{-4} mol/L, pH = 6

Influence of the addition order of reagents: The effect sequence of adding reagents on the fluorescence recovery was studied and the order: 1,10-Phenanthroline, SCnA (n = 4, 6), surfactants and buffer solution was proved to be the best suitable.

^{1}H NMR study and molecular modeling calculation: Molecular modeling calculations were optimized at the B3LYP/6-31G(d)[34] level of the density functional theory[35] using Gaussian 03 program. Results confirmed the inclusion of the 1,10-phenanthroline and SCnA.

Molecular modeling simulation was performed to obtain the optimized conformation of the host-guest complex (Fig. 8). To SC4A-Phen example, in the energy-minimized structure, the N atom of 1,10-phenanthroline react with negatively charged sulphonyl groups of SC4A and the N atom is located in the vicinity of a negatively charged sulphonyl groups. This state causes 1,10-phenanthroline molecules dispersed electron cloud density which, in turn, leads to fluorescence quenching.

To explore the possible inclusion model between SCnA (n = 4, 6) and 1,10-phenanthroline, ^{1}H NMR titration experiments were carried out in a pH 6 buffer solution at room temperature. The ^{1}H NMR spectra of 1,10-phenanthroline with SCnA (n = 4, 6) were shown in Fig. 9. The chemical shifts of

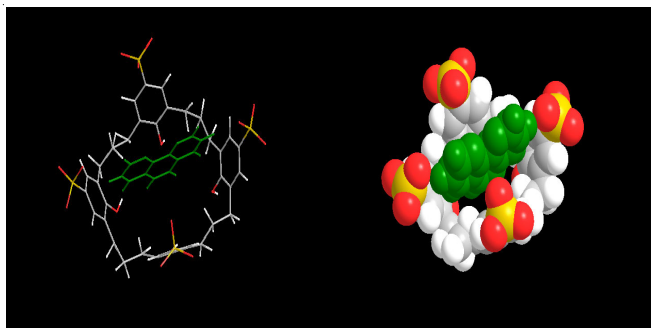

Fig. 8. Energy-minimized structure of SC4A-Phen complexes in the ground state using balls and tubes for the rendering of atoms. Color codes: 1,10-phenanthroline, green; SC4A, sulfur, yellow; oxygen, red; carbon, gray; hydrogen, white; lone-pair electron, powder

1,10-phenanthroline protons shifted to higher fields after complexation with SCnA (n = 4, 6) as compared with the free 1,10-phenanthroline. The shift value is gradually increased with the increase of the number of phenolic units of the calixarene ring. This implied that 1,10-phenanthroline may penetrate into the SCnA (n = 4, 6) cavity to form the inclusion complexes, leading to the shield of the 1,10-phenanthroline protons. Analysis of the ^{1}H NMR spectrum displayed that the presence of SCnA (n = 4, 6) caused significant upfield shifts for the proton of 1,10-phenanthroline, respectively. It suggested that the 1,10-phenanthroline was included into the cavity of SCnA (n = 4, 6)[36].

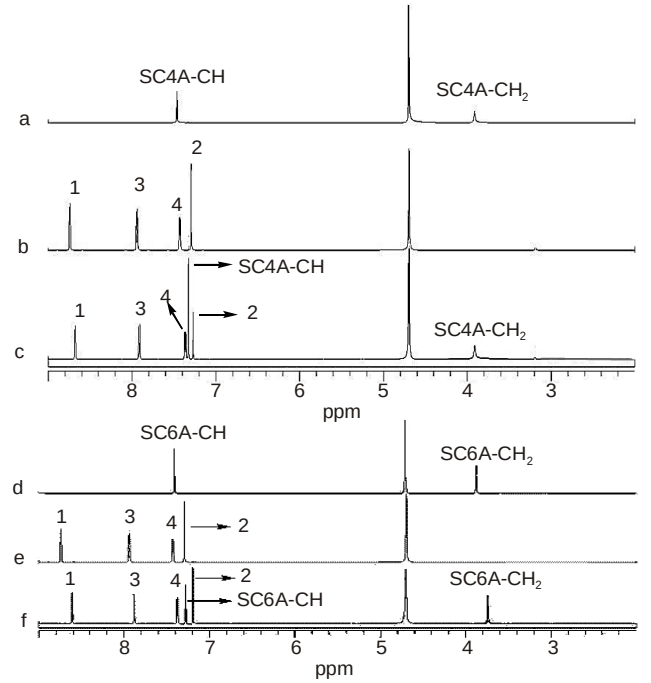

Fig. 9. ^{1}H NMR spectra (600 MHz) of SC4A (a), Phen-SC4A complex (b), Phen-SC4A complex (c), SC6A (d) , 1,10-phenanthroline (e), Phen-SC6A complex (f) in D_2O

Conclusion

The inclusion interaction between 1,10-phenanthroline and SCnA (n = 4, 6) was investigated and characterized by fluorescence spectroscopy and ^{1}H NMR. It was found that the fluorescence intensity of 1,10-phenanthroline guest molecule to gradually decreased with blue shifts upon the addition of

SCnA (n = 4, 6). 1:1 inclusion stoichiometry was verified and the inclusion constant was estimated. The binding ratio, enthalpy and entropy of the complex were calculated and analyzed, respectively. Various factors affecting the inclusion process such as temperature, pH, surfactants, reaction time and the addition order of reagents were examined. The results showed that the electrostatic interaction and structural matching effect were thought to play important roles in the formation of the host-guest complex. The possible inclusion model of 1,10-phenanthroline with SCnA (n = 4, 6) was proposed by ^{1}H NMR. Apparent chemical shift variations of 1,10-phenanthroline validated that the 1,10-phenanthroline was penetrated into the hydrophobic cavity of SCnA (n = 4, 6) to form host-guest complex. Molecular dynamic calculation was in agreement with the result obtained from ^{1}H NMR. It provided the useful information for the analytical application of 1,10-phenanthroline and stimulated further investigation to exploit the interactions between 1,10-phenanthroline and other calixarenes.

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