Supramolecular Interactions of Ionic Liquids with *p*-sulfonated calix[4]arene using a New Type of Fluorescent Probe

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Summary: Coptisine (COP) emits weak fluorescence in acidic (pH 2) aqueous solution. However, a remarkable increase in fluorescence intensity is observed when *p*-sulfonated calix[4]arene (SC4A) is added to the aqueous solution. With the addition of ionic liquid, the aqueous solution of COP-SC4A complexes considerably quenches fluorescence intensity. The supramolecular interactions of SC4A with three types of 1-butyl-3-methylimidazolium ionic liquids (C_4MIm^+) were examined based on this fluorescent probe system. The 1-butyl-imidazolium moiety of ionic liquid was embedded in the SC4A cavity, and the counter anion slightly affected the binding capacity of the ionic liquid. ^{1}H-NMR studies and molecular modeling theoretical calculations confirmed the formation of inclusion complexes.

Keywords: Coptisine, Ionic liquids, *p*-sulfonated calix[4]arene, Supramolecular interactions, Fluorescence intensity

Introduction

Molecular recognition and self-assembly properties of macrocyclic compounds have been extensively investigated because of their extensive applications in drug delivery, nanotechnology, and separation techniques [1-3]. *p*-Sulfonated calix[4]arene (SC4A, Fig. 1), a macrocycle oligomer of para-substituted phenolic residues bridged by methylene groups, is among the host molecules in supramolecular chemistry. SC4A often adopts a cone conformation that preferentially binds to metal ions [4, 5], biomolecules [6], and cationic organic compounds [7-9], such as protonated amines and pyridinium salts. A high fluorescence intensity enhancement is observed after the encapsulation of berberine alkaloid in SC4A [10]. Biczók et al. [11, 12] investigated the interactions between SC4A and ionic liquid with differences in thermodynamics and alkyl chains (as shown by spectroscopy), among others. However, the stability of SC4A interaction with ionic liquids with the same alkyl chains but different anion complexes has not been examined systematically.

Ionic liquids are considered environmentally benign solvents because of their high thermal stability, negligible vapor pressure, nonflammable characteristics, and easily adjustable properties. Ionic liquids can form micelles or microemulsions in aqueous solutions [13-15], and they have been used in extraction and separation methods [16, 17]. Alteration of the cation or the anion leads to changes in viscosity, melting point, water miscibility, and density as well as the creation of task-specific ionic liquids [13]. Viscosity of ionic liquids decrease markedly with the addition of a small quantity of SC4A or SC6A [18], as a result of the host-guest chemical interaction, which is confirmed by ^{1}H-NMRand thermodynamics analyses [11, 19]. The stability of SC4A-ionic liquid interaction when both compounds have the same alkyl chains but different anion complexes has not been examined systematically. Coptisine (COP, Fig. 1), a clinically important natural isoquinoline alkaloid, is used as a probe to demonstrate the encapsulation of three types of ionic liquids (C_4MIm^+, Fig. 1) in SC4A. COP is chosen because its fluorescence properties are highly sensitive to the microenvironment [20].

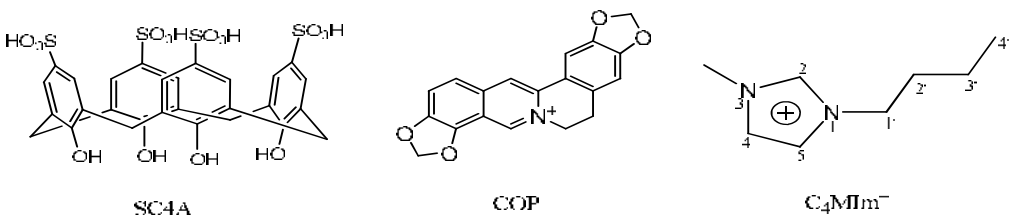

Fig. 1: The structures of SC4A, COP, C_4MIm^+.

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Experimental

Reagent and chemicals

Coptisine (COP) was purchased from the Chinese National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China) without further purification. SC4A was synthesized according to the literature [21] and identified by IR, ^{1}H-NMR and element analysis. 1-butyl-3-methylimidazolium bromide ($C_4MIm^+Br^-$), 1-butyl-3-methyl-imidazolium chloride ($C_4MIm^+Cl^-$), and 1-butyl-3-methylimidazolium nitrate ($C_4MIm^+NO_3^-$) were purchased from Shanghai Cheng Jie Chemical Co., Ltd. (Shanghai, China). Ionic liquids were dried in high vacuum at 333 K for a day prior to use. Other chemicals were of analytical reagent grade. Double-distilled water was used in all experiments.

Apparatus

The UV–Vis absorption spectra were recorded at room temperature on a Cary 300 UV–Vis spectrometer(Varian Associates, America). Fluorescence spectra were measured with a Agilent Technologies Cary Eclipse Fluorescence spectrofluorometer equipped with a pulsed lamp. The slit width of both the excitation and emission monochromators was set at 5 nm. The fluorescence spectra were recorded at a scan rate of 600 nm min^{-1}. All measurements were performed in a standard 10 mm path–length quartz cell set to a temperature of 25.0 ± 0.5 ^{o}C. The pH values were measured with a pHS-3TC digital precision pH meter (Shanghai, China). ^{1}H-NMR spectra was recorded using a Bruker DRX-600MHz spectrometer (Switzerland) in D_2O. Molecular modeling calculations were optimized at the B3LYP/6-31G (d) level of density functional theory with the Gaussian 03 program.

Spectral measurements of SC4A−COP inclusion complex

A 1.0 ml of 1.0 × 10^{-4} mol L^{-1} COP solution and an appropriate amount of 1.0 × 10^{-4} mol L^{-1} SC4A were added into 10 mL colorimetric flask, followed by 1.0 mL of 0.05 mol L^{-1} H_2SO_4 solution was used to adjust the system pH value. The solution was mixed and diluted to volume with double-distilled water. Fluorescence intensities (or absorption spectra) were determined after incubated for 15 min at room temperature.

Spectral measurements of SC4A−ionic liquid inclusion complex

Appropriate amount of ionic liquid was added to the mixture solution of 1.0 × 10^{-4} mol L^{-1} COP and 2.0 × 10^{-4} mol L^{-1} SC4A (at pH 2). Fluorescence intensities (or absorption spectra) were also determined after incubated for 15 min at room temperature.

Results and Discussion

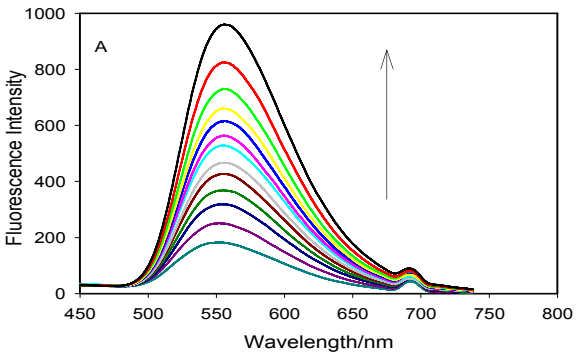
COP Binding to SC4A in water

From Fig. 2A, the maximum fluorescence wavelength of COP exhibited red shift and the intensity increased with the addition of gradually increasing amount of SC4A. This indicated that SC4A enhanced the fluorescence of the COP by the formation of the complex.

Fig. 2B displays the intensity change with SC4A concentration at 552.05 nm. For 1:1 inclusion complex, The association constant value for the inclusion complex can be determined by the typical double reciprocal (or Benesi − Hildebrand) plots [22]:

$$\frac{1}{F-F_0}=\frac{1}{(F_\infty-F_0)K[\mathrm{SC4A}]}+\frac{1}{(F_\infty-F_0)} \quad (1)$$

where F_∞ is the fluorescence intensity of the system when the guest has been completely encapsulated by the host SC4A; [SC4A] is the concentration of host SC4A and F_0 is the fluorescence intensity of COP without SC4A; while F is the fluorescence intensity at each SC4A concentration. And K is the binding constant of the complex.



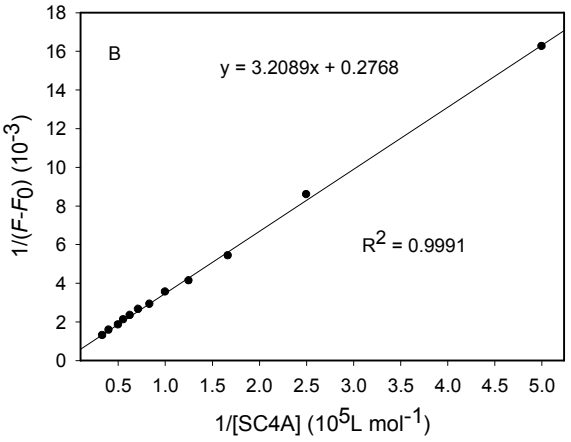


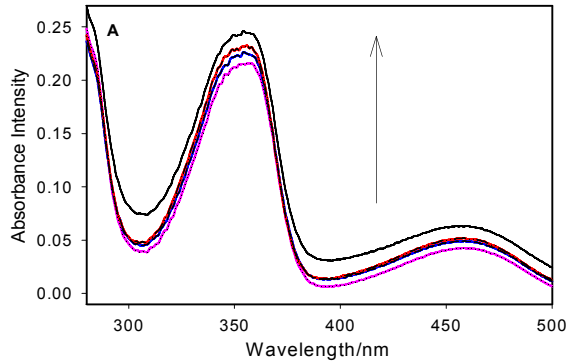
Fig. 2: (A) Variation of the fluorescence spectrum of COP aqueous solution on addition of different concentrations of SC4A (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5 and 3.0 $\times 10^{-4}$ mol L^{-1}). $C_{COP} = 1.0\times10^{-4}$ mol L^{-1}, λ_{em}= 552.05 nm. (B) Plots of $1/(F–F_0)$ versus 1/[SC4A] of SC4A-COP complex. It shows the linear double reciprocal plot indicating 1:1 complexation.

A good linear relationship was obtained when$1/(F - F_0)$ was plotted against 1/[SC4A], which supports the existence of a 1:1 complex ($R^2 = 0.9991$). The results showed that the regression equation was y = 3.2089x + 0.2768 and the binding constant was 8.63×10^3 L mol^{-1}.

Effect of ionic liquids on the formation of COP-SC4A complex

As a representative example, the UV absorption bands of COP-SC4A exhibited blue shift and hyperchromicity with addition of 1-butyl-3-methylimidazolium bromide($C_4MIm^+Br^-$), (Fig. 3A). Fluorescence spectra also confirmed the extrusion of COP form the SC4A cavity. When the ionic liquid concentration was increased, a significant fluorescence intensity diminution and a blue shift of the fluorescence maximum were observed (Fig. 3B). The changes were in the direction opposite to that shown in Fig. 2A, and these phenomena indicated that COP was extruded from SC4A cavity into the aqueous phase by ionic liquids. The gradual diminution of fluorescence intensity and the shift of the fluorescence maximum wavelength revealed the competitive displacement of COP by the ionic liquids.

The insets in Fig. 3B present the alteration of the fluorescence intensity diminution at 552.05 nm in the function of $C_4MIm^+Br^-$ concentration. Other two 1-butyl-3-methylimidazolium (C_4MIm^+) salts used in this study induced similar spectral alterations with COP−SC4A complex (Fig. 4).



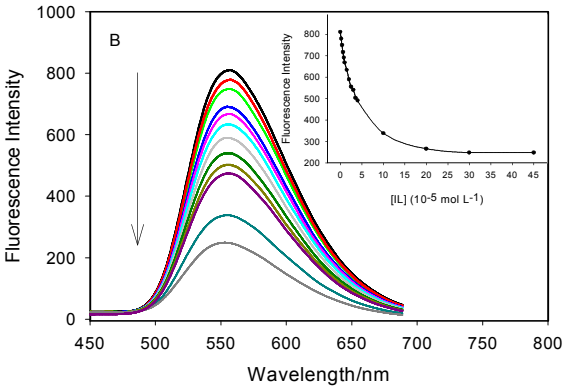


Fig. 3: (A) Absorption spectrum of 1.0×10^{-4} mol L^{-1} COP and 2.0×10^{-4} mol L^{-1} SC4A aqueous solution at pH 2 in the absence and presence of $C_4MIm^+Br^-$. (B) Fluorescence spectra of 1.0×10^{-4} mol L^{-1} COP and 2.0×10^{-4} mol L^{-1} SC4A at pH 2 in water in the presence of (0, 0.6, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 10, 20, 30 and 45) $\times 10^{-4}$ mol L^{-1} $C_4MIm^+Br^-$. Slit widths are 5 nm. Insets show the change of the fluorescence intensity at 552.05 nm in the function of $C_4MIm^+Br^-$ concentration.

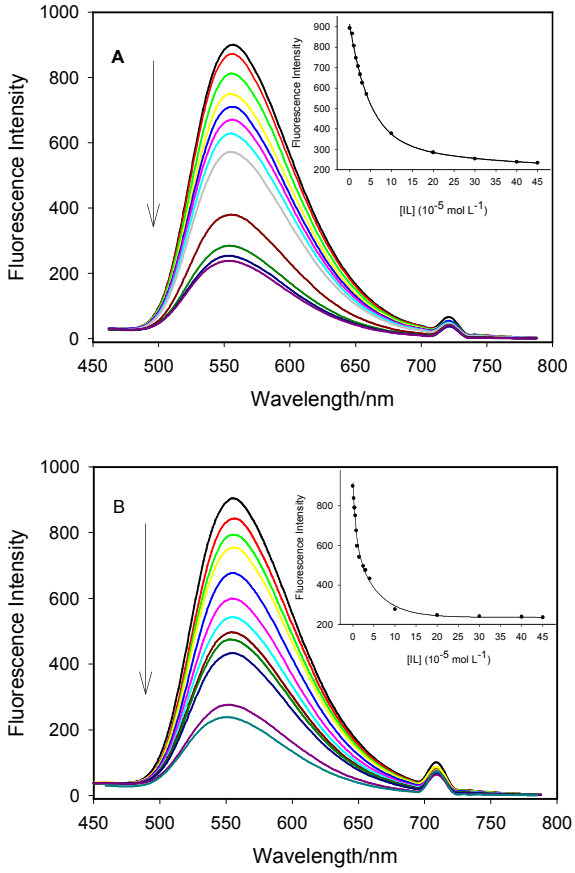


Fig. 4: (A) Fluorescence spectra of 1.0×10^{-4} mol L^{-1} COP and 2.0×10^{-4} mol L^{-1} SC4A at pH 2 in water in the presence of (0, 0.6, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 10, 20, 30 and 45) $\times 10^{-4}$ mol L^{-1} $C_4MIm^+Cl^-$. (B) Fluorescence spectra of 1.0×10^{-4} mol L^{-1} COP and 2.0×10^{-4} mol L^{-1} SC4A at pH 2 in water in the presence of (0, 0.6, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 10, 20, 30 and 45) $\times 10^{-4}$ mol L^{-1} $C_4MIm^+FB_4^-$. Slit widths are 5 nm. Insets show the change of the fluorescence intensity at 552.05 nm in the function of ionic liquid concentration.

The difference between the fluorescence of COP in water and SC4A cavity was exploited to determine the equilibrium constant of ionic liquid-SC4A complex (SC4A-IL) [11]. Two competing binding processes coexist in the solution containing COP, SC4A and free ionic liquid (IL):

$$\text{SC4A} + \text{COP} \; f \quad \text{SC4A-COP} \qquad (2)$$

$$\text{SC4A} + \text{IL} \; f \quad \text{SC4A-IL} \qquad (3)$$

The equilibrium constants are

$$K_{\text{SC4A-COP}} = \frac{[\text{SC4A-COP}]}{[\text{SC4A}][\text{COP}]} \qquad (4)$$

$$K_{\text{SC4A-IL}} = \frac{[\text{SC4A-IL}]}{[\text{SC4A}][\text{IL}]} \qquad (5)$$

Because the total ionic liquids concentration ($[IL]_T$) is the sum of the concentration of free ionic liquids ([IL]) and the ionic liquids embedded in SC4A ([SC4A–IL]), Eq. (5) alters to the following Eq. (6)

$$\frac{[\text{SC4A-IL}]}{\text{SC4A}} = K_{\text{SC4A-IL}}\left([\text{IL}]_T - [\text{SC4A-IL}]\right) \qquad (6)$$

The concentration of the free ionic liquid ([IL]) and the ionic liquid embedded in SC4A ([IL–SC4A]) can be obtained from the fluorescence intensities measured at a constant total COP concentration ($[COP]_T = 1.0 \times 10^{-4}$ mol L^{-1}) [23]

$$[\text{SC4A-IL}] = [\text{SC4A}]_T - \frac{F - F_0}{K_{\text{SC4A-COP}}(F_\infty - F)} - \frac{F - F_0}{F_\infty - F}[\text{COP}]_T \qquad (7)$$

$$[\text{SC4A}] = \frac{F - F_0}{K_{\text{SC4A-COP}}(F_\infty - F)} \qquad (8)$$

where F_0 is the fluorescence intensity of neat COP solution, F_∞ denotes the intensity of COP completely encapsulated by the host SC4A; whereas F represents the fluorescence intensity measured in the titration with IL at total SC4A concentration ($[SC4A]_T$). The [SC4A-IL] and [SC4A] values were calculated according to Eqs. (7) and (8) at each total ionic liquid concentration using K_{COP} and the fluorescence

intensities at 552.05 nm. Representative plot was given in Fig. 5 for the competitive displacement of COP from SC4A by 1-butyl-3-methylimidazolium bromide ($C_4MIm^+Br^-$). The binding constants of three kinds of ionic liquids with SC4A were obtained from the slopes and summarized in Table-1. Based on these results and the previous studies [11], it was deduced that the C_4MIm^+ cation was main responsible for the encapsulation in SC4A, and the counter anion affected the binding capacity of the ionic liquid slightly.

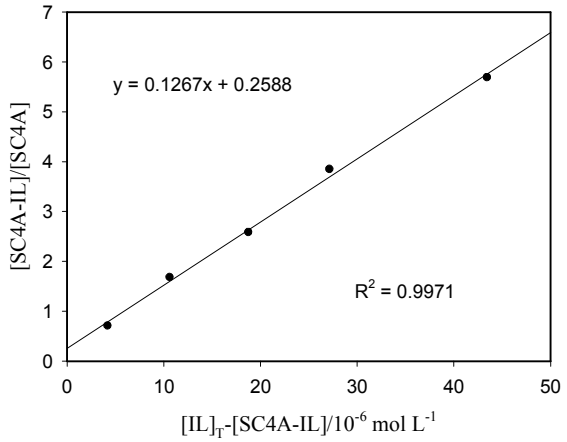


Fig. 5: Typical plot of [SC4A-IL]/[SC4A] in the function of ($[IL]_T$-[SC4A-IL]) in the SC4A-COP complex with the addition of $C_4MIm^+Br^-$.

Table-1: Equilibrium constants of ionic liquid binding to SC4A in aqueous solution at 298 K (pH 2).

Host compound	K^a/ L mol^{-1}
$C_4MIm^+Br^-$	1.27×10^5
$C_4MIm^+Cl^-$	9.83×10^4
$C_4MIm^+NO_3^-$	3.24×10^5

[a] The *K* values determined by competitive fluorimetric methods using COP as probe have experimental error of about 15%.

Molecular modeling calculation and ^{1}H-NMR study

COP exhibits weak fluorescence emission in aqueous solution because the isoquinoline and the substituted benzene rings in COP are not on the same plane. This configuration prevents a conjugated system from being formed. When SC4A was added into the aqueous solution of COP, the electrostatic attraction between the positive charge of the heterocyclic nitrogen of the COP and the high electron density of the sulfonyl groups of SC4A was induced. The apolar part of COP can penetrate into the host cavity. Inside the cavity, the degree of freedom of motion of the COP molecule is reduced, thus reducing the probability of radiationless transition. At the same time, the cavity can shield the excited single state of COP from probable quenching processes that usually occur in aqueous solutions.

Molecular modeling calculations were optimized at the B3LYP/6-31G(d) [24] level of density functional theory [25] with the Gaussian 03 program [26]. Results confirmed the partial inclusion of COP in the hydrophobic core of SC4A (Fig. 6A). In the energy-minimized structure, the methylenedioxy-isoquinoline moiety was embedded in SC4A, and the heterocyclic nitrogen was located near negatively charged sulfonyl groups. The partial immersion of COP in the hydrophobic cavity of SC4A reduced interaction with water. A less polar microenvironment was created, which subsequently led to fluorescence enhancement.

When C_4MIm^+ was added to the host-guest system of COP-SC4A, COP and C_4MIm^+ competed to bind with SC4A. Several parts of the COP molecule were expelled from the SC4A cavity when C_4MIm^+ was introduced. The energy-minimized structure of C_4MIm^+-SC4A complex is shown in Fig. 6B. The butyl chain and the imidazolium moiety were located inside the host, whereas the methyl chain was not encapsulated. The photochemical property of COP is strongly dependent on its local microenvironment. The addition of C_4MIm^+ resulted in the loss of COP occupancy in the SC4A hydrophobic cavity, which reduced the fluorescence intensity of the SC4A-COP complex. The competitive inclusion model is shown in Fig. 7.

To verify the accuracy of the molecular model by the competitive binding of the COP probe, C_4MIm^+ encapsulation in SC4A was examined by ^{1}H-NMR spectroscopy. Compared with the proton resonances of the unbound C4MIm$^+$ molecules, the signals of $H_{1'}$, $H_{2'}$, $H_{3'}$ and $H_{4'}$ protons of the bound C4MIm$^+$ significantly shifted upfield (Fig. 8). This behavior is characteristic of the butyl group of the molecule encapsulated in the SC4A cavity. By contrast, H-4 of the imidazolium moiety and methyl proton signals did not show chemical shifts, indicating a negligible interaction with SC4A. The results of ^{1}H-NMR experiments agree with the calculated structure of C_4MIm^+-SC4A complex

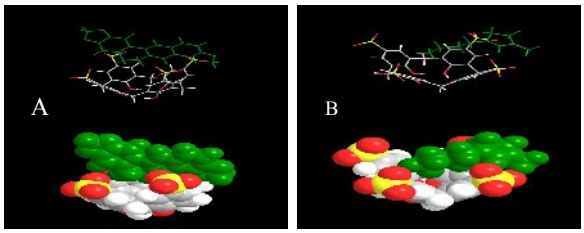


Fig. 6: Energy-minimized structure of A: COP-SC4A; B: C_4MIm^+-SC4A complexes in the ground state using balls and tubes for rendering the atoms. Color codes: for COP and C_4MIm^+, green; SC4A, oxygen red, nitrogen blue, carbon gray, hydrogen white.

Taken together, when C_4MIm^+ is added to the solution of COP-SC4A complex and the new equilibrium is reached, some parts of the COP molecules can be expelled from the SC4A cavities, resulting in reduced COP fluorescence intensity. Ion-dipole interaction between the sulfonic acid groups of SC4A and N^+ ion (of COP, and C_4MIm^+), and hydrogen bonding interaction leads to the formation of host-guest inclusion complex.

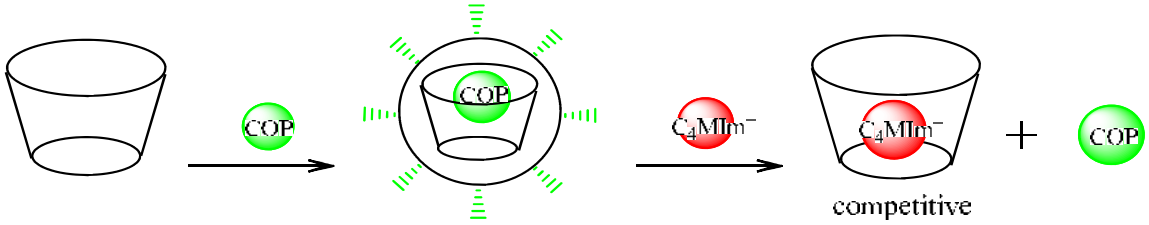


Fig. 7: The competition diagram for the SC4A cavity between C_4MIm^+ and COP.

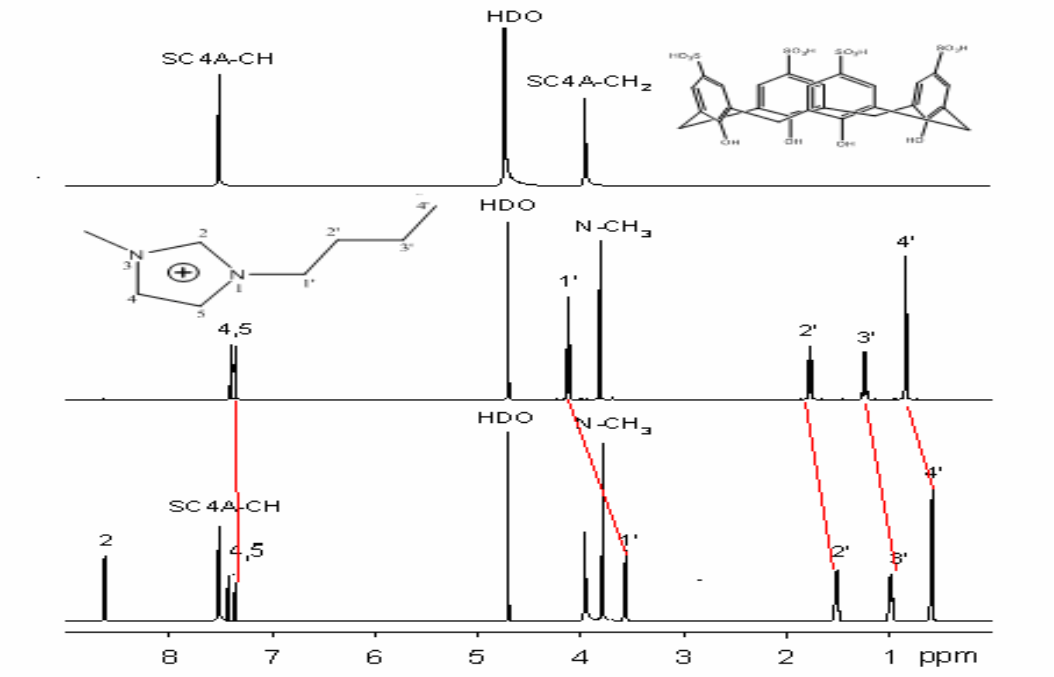


Fig. 8: ^{1}H-NMR(600 MHz) spectrum of SC4A (upper), $C_4MIm^+Br^-$ (middle) and SC4A-$C_4MIm^+Br^-$ complex (lower) in D_2O.

Conclusion

COP is a good fluorescent probe for investigating the binding of ionic liquids to SC4A in water at pH 2. COP was extruded from the SC4A cavity into the aqueous environment by 1-buty-3-methylimidazolium- type ionic liquids. ^{1}H-NMR spectra and density functional theory calculations suggested that the 1-butyl-imidazolium moiety was embedded in the hydrophobic interior of the host, whereas the methyl chain was not encapsulated. The variation in encapsulation state did not significantly affect the inclusion complex formation possibly because the negative charge on the upper rim of the SC4A cavity precluded the anion ingression within the cavity. Moreover, the C_4MIm^+ cation was encapsulated into SC4A.

Acknowledgments

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