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A characteristic effect of pressure on inclusion complexation of phenothiazine dyes with *p*-sulfonatocalix[6]arene in a room-temperature ionic liquid

Naoya Inazumi · Shunzo Yamamoto · Yoshimi Sueishi

Abstract The inclusion complexation of *p*-sulfonatocalix[6]arene (Calix-S6) with three kinds of phenothiazine dyes was studied spectrophotometrically in a mixture of a room-temperature ionic liquid [bmim]BF$_4$ (1-butyl-3-methylimidazolium tetrafluoroborate) and ethanol. We have determined the association constants of Calix-S6 with phenothiazine dyes under external static pressure up to 767 bar in the [bmim]BF$_4$-ethanol and alcohol-water mixtures. With increasing external pressure, the inclusion equilibrium in the alcohol-water mixtures was shifted to the dissociation side. Conversely, the inclusion equilibrium of methylene blue (MB) and azure A (AA) in the ionic liquid mixture was shifted to the association side. From the analysis of the pressure effects, the reaction volumes ΔV for inclusion complexation were estimated as –7 to 9 cm^3 mol^{-1} in the [bmim]BF$_4$-ethanol mixture and 20–32 cm^3 mol^{-1} in the alcohol-water mixtures. Based on the results, we have suggested that there is a competing complexation between the included dye and [bmim]BF$_4$ molecules in the ionic liquid.

Keywords Calixarene · Inclusion complex · Pressure effect · Ionic liquid

Introduction

Calixarenes are macrocycle oligomers of para-substituted phenolic residues bridged by methylene groups.

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They are useful host molecules that can easily be modified with a wide variety of functional groups at the phenolic oxygens (lower rim) and at the para positions (upper rim) [1, 2]. The functionalization of the macrocycles by sulfonate groups allows water-soluble calixarenes, which are important for the molecular recognition of organic guests in water [3]. It is important to characterize the interactions and the mechanisms of inclusion complexation with *p*-sulfonatocalixarenes in aqueous solution. There are many reports of the complexation of cations with calixarenes. However, the studies on the inclusion complexation of organic molecules with water-soluble calixarenes have not been well established.

Ionic liquids are molten salts that are liquids at room temperature [4, 5] and have advantageous properties (negligible vapor pressure, nonflammable, high ionic conductivity, thermal stability, etc.). Ionic liquids attract a large amount of attention as chemical reaction media in green chemistry [6, 7]. Previous studies on the inclusion complexation of azobenzenes with cyclodextrins showed the considerable effects of solvent polarity on the inclusion equilibria [8]. In this connection, it is instructive to examine how room-temperature ionic liquids, which are sufficiently polar media, affect the inclusion complexation of calixarenes.

In a preliminary paper, we have examined the effects of pressure on inclusion complexation of methylene blue (MB) with *p*-sulfonatocalixarenes and reported the large effects of external pressure on the calixarene inclusion equilibria [9]. Pressure studies may be informative in characterizing the reaction mechanisms of chemical reactions. Since we have expertise in high-pressure technique, the present work was initiated

to obtain further insight into the inclusion behavior of
p-sulfonatocalixarene. We found a peculiar pressure
dependence of inclusion complexation of *p*-sulfonat-
ocalix[6]arene (Calix-S6) in an ionic liquid [bmim]BF$_4$
(1-butyl-3-methylimidazolium tetrafluoroborate) at
room temperature. Based on the results, using three
kinds of phenothiazine dyes, we performed a volu-
metric study on the inclusion behavior of Calix-S6 in
the ionic liquid.

Experimental

Materials

Methylene blue (MB), azure A (AA), and thionine
chloride (Th) were purchased from Croma Gesell-
schaft & Co., Aldrich, and Tokyo Chemical Industry
Co., respectively. The phenothiazine dyes were re-
crystallized from ethanol and dried under vacuum be-
fore use. *p*-Sulfonatocalix[6]arene was purchased from
Dojin Co. (Kumamoto, Japan) and used as received.
The ionic liquid [bmim]BF$_4$ was obtained from Fluka
(Sigma-Aldrich) and dried for 24 h under vacuum at
353 K. We used room-temperature ionic liquid
[bmim]BF$_4$ as a solvent, because [bmim]BF$_4$ does not
have absorption bands in a visible region. Reagent
grade methanol, ethanol, and 1-propanol were ob-
tained commercially (Wako Pure Chemicals, Osaka,
Japan). Alcohols and water were purified by distilla-
tion before use.

Measurements

To avoid the dimerization of the dyes, we used alcohol-
water mixtures (1:1 v/v phosphate buffer) as a solvent.
A phosphate buffer was prepared from phosphate salts:
pH = 6.9 and ionic strength = 0.1. Dimerization of the
dyes was not observed in the ionic liquid [bmim]BF$_4$
while we utilized the mixture of [bmim]BF$_4$ and etha-
nol (10:1 v/v) as a solvent because the ionic liquid
[bmim]BF$_4$ is extremely viscous. Ethanol (E$_T$ = 217 kJ
mol^{-1}), which is comparable to the E$_T$ value (221 kJ
mol^{-1}) of [bmim]BF$_4$, was selected as a miscible sol-
vent. The spectral change of dyes in the presence of
excess Calix-S6 was monitored by using a Hitachi
U-3200 spectrophotometer (Tokyo, Japan); the reac-
tion temperature was controlled at 298 ± 0.1 K. The
high-pressure inner cell and the procedures for spectral
measurements under high pressures have been
described elsewhere [10]. The ^{1}H NMR spectra were
measured in D$_2$O and D$_2$O-CD$_3$OD with a Varian
Mercury 300 (300 MHz) at room temperature. Chem-

ical shifts were reported as δ values relative to HOD
(δ 4.79) and CHD$_2$OD (δ 3.31) as an internal standard
[11].

Results and discussion

Structure of the inclusion complex

To clarify the inclusion behavior of calixarene, we have
used three kinds of phenothiazine dyes as guest mol-
ecules (Fig. 1). We performed ^{1}H NMR measurements
for the inclusion complexes of phenothiazine dyes with
Calix-S6 and obtained useful information concerning
the complexation mode of the guest with the host.
Table 1 shows the changes ($\Delta\delta$) in the chemical shifts
of the protons of AA and Th in a CD$_3$OD-D$_2$O mix-
ture (1:1 v/v) together with the $\Delta\delta$ values of MB re-
ported previously [9]. The AA and Th protons were
assigned with reference to the NMR spectral data of
MB [9]. The upfield shifts of the guest protons indicate
an inclusion of the proton moiety into the calixarene
cavity [12–14]. From inspection of the data in Table 1,
we notice some interesting points. (1) In the inclusion
complex of AA, large chemical shift changes for the
C(2)-H, C(4)-H, and N-CH$_3$ protons are observed,
which is similar to the spectral shifts of the MB inclu-
sion complex. These changes indicate that the AA
molecule is encapsulated in the Calix-S6 cavity from
the –N(CH$_3$)$_2$ moiety side. (2) In the inclusion complex
of Th, the $|\Delta\delta|$ value of the C(1)-H proton is compa-
rable to those of the C(2)-H and C(4)-H protons,
suggesting that the C(1)-H proton is included in the
Calix-S6 cavity. Shinkai et al. reported that the con-
formation of water-soluble calixarenes is fixed into a
cone shape upon inclusion of guest molecules [15]. The
diameter of the Calix-S6 cavity has been evaluated as
being 0.56–1.17 nm at the sulfonato side and 0.48–
0.60 nm at the hydroxyl side [16]. The molecular size of
the phenothiazine dyes can be estimated by using Co-
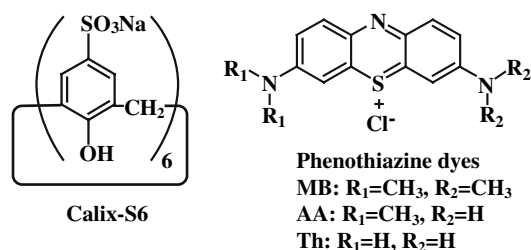rey–Pauling–Koltun (CPK) modeling. From these size

Fig. 1 Structures of *p*-sulfonatocalix[6]arene and phenothiazine
dyes

Table 1 Changes ($\Delta\delta$/ppm)[a] in chemical shifts of phenothiazine dyes in the presence of Calix-S6

Guest[b]	C(1)-H	C(2)-H	C(4)-H	C(6)-H	C(8)-H	C(9)-H	N-CH$_3$
MB[c]	−0.08	−0.32	−0.32	(−0.32)	(−0.32)	(−0.08)	−0.44
AA[d]	−0.34	−0.58	−0.45	−0.13	−0.07	−0.08	−0.23
Th[e]	−0.34	−0.48	−0.32	(−0.32)	(−0.48)	(−0.34)	−

[a] $\Delta\delta = \delta$ (complex with Calix-S6) − δ (dye unbounded with Calix-S6). Negative values indicate upfield shifts

[b] MB: R$_1$ = R$_2$ = CH$_3$; AA: R$_1$ = CH$_3$ and R$_2$ = H; Th: R$_1$ = R$_2$ = H
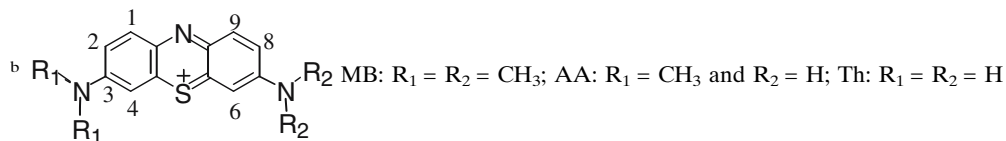
[c] Cited from Ref. 9. [Calix-S6]$_0$/[MB]$_0$ = 11

[d] [Calix-S6]$_0$/[AA]$_0$ = 1.0

[e] [Calix-S6]$_0$/[Th]$_0$ = 0.20

estimations and inspection of the CPK model, we concluded that: (1) the –NR$_2$ and C(4)-H moieties of both sides of the phenothiazine dyes are too large to be included in the Calix-S6 cavity; (2) in the inclusion complex, the –NR$_2$ group is located in the calixarene cavity; (3) the –S(δ+)– moiety of the phenothiazine dyes is located close to the –SO$_3^-$ groups of the calixarene cavity rim. The inclusion of dyes forces the –S(δ+)– moiety to interact with polar (negative) sulfonato groups; and (4) the 1:2 inclusion complexes between the phenothiazine dyes and Calix-S6 cannot be formed. Plausible structures of inclusion complexes

Fig. 2 Plausible structures of inclusion complexes of phenothiazine dyes with Calix-S6 based on ^{1}H NMR measurements

with phenothiazine dyes are illustrated in Fig. 2 based on these results.

Pressure effects on inclusion equilibria

Figure 3 shows the absorption spectra of thionine chloride (Th) in the [bmim]BF$_4$-ethanol mixture (10:1 v/v) upon consecutive additions of excess Calix-S6. The peak in the vicinity of 600 nm caused by the Th decreases with an increase in the Calix-S6 concentration. When Calix-S6 was added to the dye solution, MB, AA and Th in the ionic liquid mixture produce spectral changes similar to those of phenothiazine dyes in the alcohol-water mixtures. Previous UV-Vis and NMR studies on calixarene inclusion complexes have suggested that MB forms a 1:1 inclusion complex with Calix-S6 in the methanol-water mixture [9]. Under the
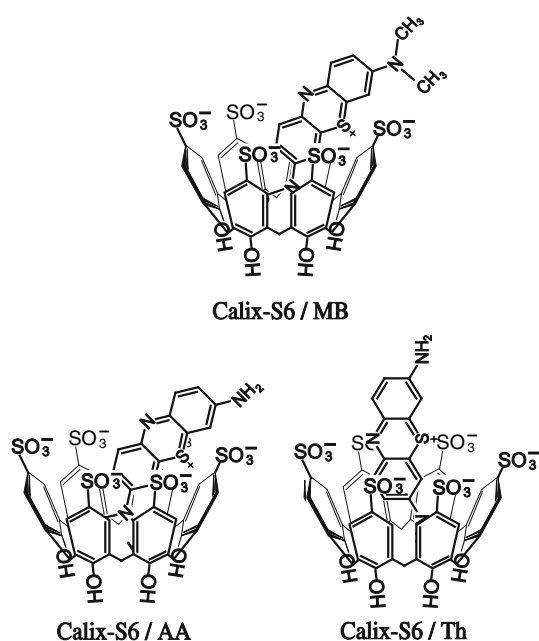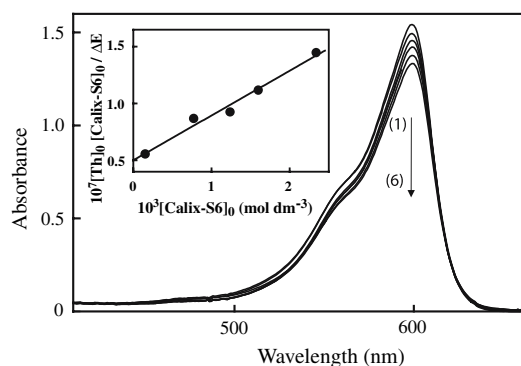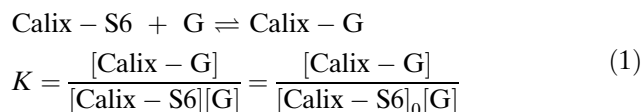

Fig. 3 Absorption spectra of Th ([Th]$_0$ = 3.45 × 10^{-5} mol dm^{-3}) in [bmim]BF$_4$-ethanol mixture (10:1 v/v) at 298 K. Concentrations of Calix-S6 were (1) 0, (2) 1.55 × 10^{-4}, (3) 7.75 × 10^{-4}, (4) 1.24 × 10^{-3}, (5) 1.60 × 10^{-3}, and (6) 2.34 × 10^{-3} mol dm^{-3}. (Inset) Determination of inclusion equilibrium constant according to Eq. (4)

condition of [Calix-S6] » [dyes], the equilibria for the inclusion complexation of calixarene can expressed as:

$$Calix - S6 \; + \; G \rightleftharpoons Calix - G$$

$$K = \frac{[Calix - G]}{[Calix - S6][G]} = \frac{[Calix - G]}{[Calix - S6]_0[G]} \qquad (1)$$

The spectral data in Fig. 3 were analyzed according to the Benesi-Hildebrand Eq. (2) for the 1:1 complex formation. A linear relationship between $[Th]_0[Calix-S6]_0/\Delta E$ and $[Calix-S6]_0$ is shown in Fig. 3, indicating formation of the 1:1 inclusion complex.

$$\frac{[Th]_0[Calix - S6]_0}{\Delta E} = \frac{1}{K\Delta \varepsilon} + \frac{1}{\Delta \varepsilon}[Calix - S6]_0 \qquad (2)$$

where $[Th]_0$ and $[Calix-S6]_0$ are the total concentrations of Th and Calix-S6, respectively. $\Delta \varepsilon$ is the difference in the molar extinction coefficients for bound and unbound Th with Calix-S6 and ΔE is the change in the absorption intensity of the Th solution. The association constants K for the inclusion complexation with Calix-S6 in the ionic liquid mixture can be determined from the slope and intercept of Eq. (2). The association constants obtained in the [bmim]BF$_4$-ethanol mixture and alcohol-water mixtures are listed in Table 2.

The E$_T$ values are widely used as a measure of solvent polarity. Based on the absorption spectra of Reichardt's dye, the E$_T$-values in the alcohol-water mixtures were determined as 244, 230, and 225 kJ mol^{-1} for the mixtures of methanol-, ethanol-, and 1-propanol-water (1:1 v/v), respectively. The K values in the alcohol-water mixtures show a trend to increase with an increase in solvent polarity, which is similar to the formation of the inclusion complex with cyclodextrins because of hydrophobic interactions [8]. The E$_T$ value

of the ionic liquid mixture ([bmim]BF$_4$-ethanol (10:1 v/v)) used in this study was estimated to be 221 kJ mol^{-1}, which is smaller than those in the alcohol-water mixtures. The inclusion equilibrium constants K obtained in the [bmim]BF$_4$-ethanol mixture are extremely large compared with those expected from the E$_T$ values. The large association constants reflect the high degree of stability of the inclusion complex in the mixture of the ionic liquid. The high stability of the inclusion complex in the ionic liquid can be ascribed to the large difference between the environment in the ionic liquid and the environment in the calixarene cavity.

Table 2 lists the influence of pressure on the inclusion equilibria of phenothiazine dyes with Calix-S6. The K values in the alcohol-water mixtures decrease as the external pressure increases. Conversely, the K values in the [bmim]BF$_4$-ethanol mixture increase with increasing pressure except for guest molecule Th. By using the K values in Table 2, the reaction volume ΔV at 1 bar can be evaluated according to the following thermodynamic equations. The results are listed in the right-hand column of Table 2.

$$\ln K = \; aP + b \qquad (3)$$

$$\Delta V = \; -RT(\partial \ln K/\partial P)_T - \; \kappa_T RT \qquad (4)$$

where κ_T is the isothermal compressibility of the solvent mixtures. These were estimated to be 2.63×10^{-5} bar, 4.43×10^{-5} bar, 4.92×10^{-5} bar, and 6.39×10^{-5} bar for [bmim]BF$_4$-ethanol, methanol-water, ethanol-water, and 1-propanol-water mixtures, respectively. In Calix-S6 complexation in the alcohol-water mixtures, all guest molecules showed large, positive ΔV values

Table 2 The equilibrium constants (K) and reaction volumes for inclusion complexation of Calix-S6 in various solvents at 298 K

Guest	Solvent[a]	$10^{-3}K$ (mol^{-1} dm^3)				ΔV (cm^3 mol^{-1})
		1 bar	196 bar	490 bar	767 bar	
MB	[bmim]BF$_4$-ethanol	9.87 ± 0.21	10.6 ± 0.3	11.3 ± 0.6	12.0 ± 0.4	–7.0 ± 0.3
MB	Methanol-H$_2$O	1.92 ± 0.05	1.49 ± 0.04	1.03 ± 0.04	0.749 ± 0.020	28.9 ± 0.4
MB	Ethanol-H$_2$O	1.07 ± 0.07	0.779 ± 0.042	0.568 ± 0.036	0.396 ± 0.013	29.7 ± 1.1
MB	1-Propanol-H$_2$O	0.678 ± 0.038	0.425 ± 0.012	0.327 ± 0.24	0.234 ± 0.09	30.4 ± 3.1
AA	[bmim]BF$_4$-ethanol	4.44 ± 0.35	4.78 ± 0.28	5.11 ± 0.25	5.51 ± 0.29	–7.3 ± 0.3
AA	Methanol-H$_2$O	4.71 ± 0.22	3.62 ± 0.15	2.56 ± 0.05	1.88 ± 0.03	28.1 ± 0.5
AA	Ethanol-H$_2$O	1.72 ± 0.06	1.34 ± 0.04	0.923 ± 0.017	0.640 ± 0.005	30.3 ± 0.1
AA	1-Propanol-H$_2$O	0.671 ± 0.031	0.533 ± 0.020	0.391 ± 0.014	0.230 ± 0.011	31.8 ± 2.3
Th	[bmim]BF$_4$-ethanol	2.96 ± 0.12	2.64 ± 0.19	2.42 ± 0.11	2.12 ± 0.07	9.5 ± 0.5
Th	Methanol-H$_2$O	3.07 ± 0.13	2.66 ± 0.16	1.93 ± 0.11	1.58 ± 0.06	20.7 ± 0.9
Th	Ethanol-H$_2$O	1.20 ± 0.04	0.953 ± 0.046	0.789 ± 0.028	0567 ± 0.025	21.7 ± 1.3
Th	1-Propanol-H$_2$O	0.532 ± 0.026	0.449 ± 0.025	0.323 ± 0.016	0.249 ± 0.014	23.1 ± 0.5

[a] [bmim]BF$_4$-ethanol (10:1 (*V/V*)), Methanol-H$_2$O (1:1 (*V/V*)), Ethanol-H$_2$O (1:1 (*V/V*)), and 1-Propanol-H$_2$O (1:1 (*V/V*))

while in the ionic liquid mixture, the ΔV values for MB and AA were negative and that for Th was positive. Further, the ΔV values in the alcohol-water mixtures become larger with decreasing solvent polarity.

Components in reaction volume

Conventionally, volume change (ΔV) accompanied by chemical reaction is divided into two terms: an intrinsic volume change and a volume change arising from reorganization of the solvent molecules. The volumetric contributions during formation of an inclusion complex can be expressed by two discrete volume changes [17, 18].

$$\Delta V = \Delta V_{inclu} + \Delta V_{desolv} \tag{5}$$

where ΔV_{inclu} and ΔV_{desolv} denote volume changes related to inclusion of guest molecules in the calixarene cavity ($\Delta V_{inclu} < 0$) and accompanying desolvation around the contact area of the dye and $-SO_3^-$ groups of Calix-S6 ($\Delta V_{desolv} > 0$), respectively. The magnitude of the ΔV values is related to the contributions of ΔV_{inclu} and ΔV_{desolv}. In the alcohol-water mixtures, the large positive ΔV values indicate that desolvation is extensive upon inclusion with Calix-S6. In the pressure effects on chemical reactions involving dipoles or charges in solution, the contribution of ΔV_{desolv} increases with a decrease in solvent polarity [17]. This is responsible for the increase in the ΔV values observed for the Calix-S6 inclusion complexation in the alcohol-water mixtures, which is taken as an evidence for the contribution of ΔV_{desolv}. The ΔV values for MB are comparable to those of AA owing to the similarity of the included moiety of guest molecules. This result supports the above structure of the inclusion complex shown based on the ^{1}H NMR study (Fig. 2). The ΔV values for Th are small compared with those for AA and MB. This is attributed to the size of the Th's moiety encapsulated by Calix-S6.

Judging from the small κ_T value of the [bmim]BF$_4$-ethanol mixture, the contribution of ΔV_{desolv} in the ionic liquid is assumed small. The positive ΔV value for Th in the [bmim]BF$_4$-ethanol mixture suggests that the additional volumetric contribution is required for the inclusion equilibrium in the ionic liquid. It is known that calixarenes form inclusion complexes with organic molecules as well as with cations [1]. Relatively small organic compounds such as methanol and ethanol do not form inclusion complexes with calix-S6 efficiently [1], while there is a possibility that Calix-S6 does associate with the [bmim]BF$_4$ molecule used as a solvent. We have examined the inclusion complexation of

Calix-S6 with [bmim]BF$_4$ by using ^{1}H NMR. Figure 4a shows the ^{1}H NMR spectrum of [bmim]BF$_4$ in D$_2$O (phosphate buffer pD = 6.9). The assignments of the [bmim]BF$_4$ protons were performed according to the report by Holbrey and Seddon [19]. When Calix-S6 was added to the [bmim]BF$_4$ solution, all peaks of the [bmim]BF$_4$ protons were shifted to a higher magnetic field (Fig. 4b). The upfield shifts of the guest protons indicate an encapsulation of the proton moiety into the hydrophobic cavity of calixarene [11–13]. Figure 4c shows the chemical shifts for the [bmim]BF$_4$ protons as a function of Calix-S6 concentration. Large shifts of the protons on the imidazolium ring of [bmim]BF$_4$ are observed, indicating the encapsulation of the imidazolium ring moiety by Calix-S6. By the method of continuous variation (Job's method) [20], using various ratios of [bmim]BF$_4$ to Calix-S6, the stoichiometry of the [bmim]BF$_4$-Calix-S6 complexes has been established. The Job's diagram for the C(2')-H$_2$ of the [bmim]BF$_4$ protons shows the minimum at a guest/(host + guest) ratio of 0.5 (Fig. 4d), indicating 1:1 inclusion complexation. Based on the results of the chemical shifts, a plausible structure of the inclusion complex of [bmim]BF$_4$ with Calix-S6 is depicted in Fig. 5. Figure 4c shows induced chemical shifts ($\Delta\delta$) for the [bmim] BF$_4$ protons upon addition of Calix-S6. The induced chemical shifts of NMR signals upon the 1:1 complexation can be expressed as [21, 22]:

$$\Delta\delta = \frac{\Delta\delta_{sat}}{2[G]_0}(\beta - \sqrt{\beta^2 - 4[G]_0[H]_0}) \tag{6}$$

$$\beta = \frac{1}{K_1} + [G]_0 + [H]_0 \tag{7}$$

where $[G]_0$ and $[H]_0$ denote the initial concentrations of guest (dyes) and host (Calix-S6), respectively. K_1 is an association constant for the inclusion complexation of [bmim]BF$_4$ with Calix-S6 and $\Delta\delta_{sat}$ is the saturated value of induced chemical shifts. The value of $\Delta\delta_{sat}$ was determined from curve fitting for the NMR titration curve (Fig. 4c). Using the value of $\Delta\delta_{sat}$, nonlinear least-square fits of induced chemical shifts to Eq. (6) yield the value of $K_1 = (1.48 \pm 0.12) \times 10^3$ mol^{-1} dm^3 for the 1:1 inclusion complex.

As suggested above, Calix-S6 forms an inclusion complex with [bmim]BF$_4$. Upon inclusion of dyes in the ionic liquid, one included [bmim]BF$_4$ molecule is repelled out from the calixarene cavity. The volumetric contribution for the inclusion equilibrium in the ionic liquid is expressed as follows [18]:

Fig. 4 ^{1}H NMR spectra of [bmim]BF$_4$ ([[bmim]BF$_4$]$_0$ = 4.90 × 10^{-3} mol dm^{-3}) in D$_2$O. (**a**) [Calix-S6]$_0$ = 0 mol dm^{-3}. (**b**) [Calix-S6]$_0$ = 5.82 × 10^{-3} mol dm^{-3}. (**c**) Changes in chemical shifts of the [bmim]BF$_4$ protons at various Calix-S6 concentrations ([Calix-S6]$_0$ = 0–4.36 × 10^{-3} mol dm^{-3}); ○: C(4')-H$_3$, ●: C(3')-H$_2$, △: C(2')-H$_2$, ▲: C(1')-H$_2$, □: C(2)-H, ■: C(4)-H, ▽: C(5)-H, ▼: N(3)-CH$_3$. (**d**) Continuous variation plots (Job's plot) derived from the ^{1}H NMR data (C(2')-H$_2$ in (**c**)) for the [bmim]BF$_4$ and Calix-S6 system
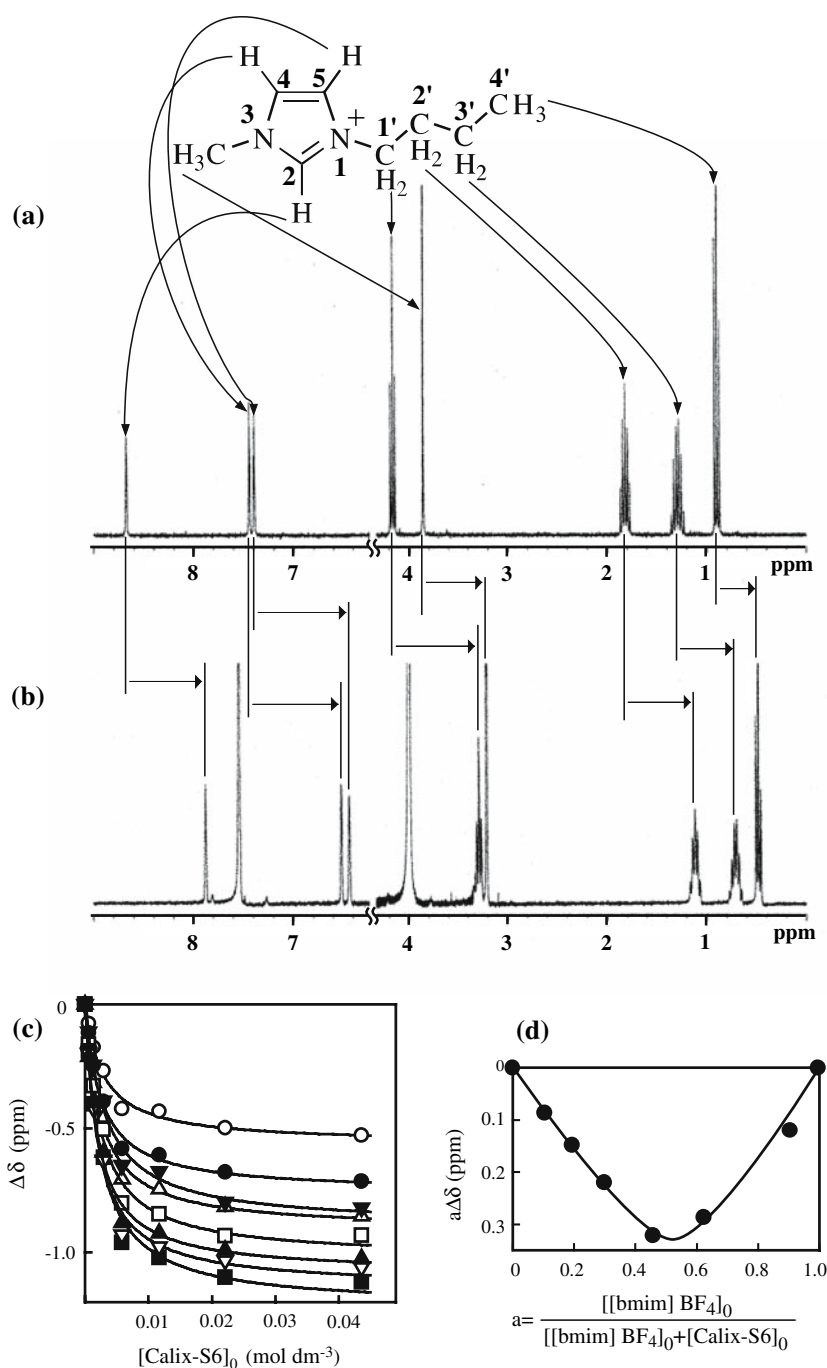
$$\Delta V = \Delta V_{\text{inclu}} + \Delta V_{\text{desolv}} + \Delta V_{\text{repel}} \qquad (8)$$

where ΔV_{repel} denotes the volume change caused by [bmim]BF$_4$ repelled from the Calix-S6 cavity ($\Delta V_{\text{repel}} > 0$). ΔV_{desolv} in the ionic liquid can be assumed to be small: $\Delta V_{\text{desolv}} \sim 0$ and $\Delta V = \Delta V_{\text{inclu}} + \Delta V_{\text{repel}}$. Therefore, the negative ΔV values for MB and AA in the [bmim]BF$_4$-ethanol mixture indicate that $|\Delta V_{\text{inclu}}(\text{MB})| > \Delta V_{\text{repel}}$, and the positive ΔV value for

Th in the ionic liquid mixture is responsible for the smaller molecular size of Th ($|\Delta V_{\text{inclu}}(\text{MB})| > |\Delta V_{\text{inclu}}(\text{Th})|$), resulting in $|\Delta V_{\text{inclu}}(\text{Th})| < \Delta V_{\text{repel}}$.

In summary, we show the inclusion complex formation of the ionic liquid [bmim]BF$_4$ with Calix-S6 and the high degree of stability of the inclusion complex of phenothiazine dyes with Calix-S6 in the ionic liquid mixture. Although the present analysis of high-pressure results utilized a simplified model, the data show
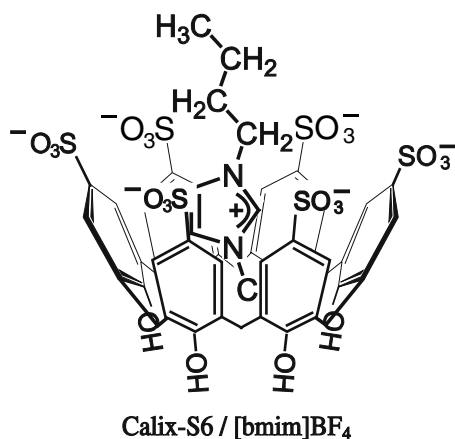
Fig. 5 Plausible structure of inclusion complex of [bmim]BF$_4$ with Calix-S6

that the [bmim]BF$_4$ molecules repelled from the calixarene cavity upon complex formation may be an important aspect of calixarene inclusion complex formation in the ionic liquid [bmim]BF$_4$ at room temperature. We believe that a study of high pressure on inclusion complexes might provide useful insights into the establishment of inclusion behavior.

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