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Conformational transition effects of anion recognition by calix[4]arene derivatives

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A calix[4]arene derivative (**3**) possessing naphthalene sulfonyl amide groups has been synthesised in satisfactory yield. Furthermore, its conformation and anion-binding behaviours are systemically investigated by the methods of fluorescence spectrometry, ^{1}H NMR spectrometry and X-ray crystallography. The results indicate that compound **3** assumes two different configurations in polar/apolar solutions, and therefore presents the interestingly solvent-dependent binding properties for anions. It is demonstrated that hydrogen-bonding interactions do play a great role in the conformation of **3** and its anion recognition.

Keywords: calixarene; fluorescence spectroscopy; anionic recognition

Introduction

Anion recognition, a highly active topic in supramolecular chemistry, has gained extensive attention. This can be attributed to the significance of anions in many fields including biological, medical, environmental and chemical sciences (*1*). Therefore, much endeavour has been focused on the design of various artificial receptors for anion binding and sensing (*2*). In this regard, receptors based on calixarene have a part to play in the development of anion recognition (*3*). Calixarenes, which are described as 'macrocycles with (almost) unlimited possibilities' for their facile modification, represent a particularly important class of the host molecules (*4*). As anions exhibit a wide range of geometries, calixarene receptors are endowed with pronounced binding abilities and selectivities for anion guests that their large size and flexible framework (even different conformational preferences). In other words, the conformational flexibility of calixarene receptors endows them with particular adaptability in binding properties. In recent years, calixarenes have been widely employed in the anion recognition as probes and sensors, such as chromogenic chemosensors, colorimetric sensors and electrochemical sensors, etc. (*5*). For example, calix[4]arene derivatives containing amide ferrocene units are able to act as electrochemical sensors for carboxylate anions (*6*). The colorimetric anion sensors based on calix[4]arene form a highly symmetrical and pre-organised cavity, giving rise to a colour change in the UV–vis spectra upon pyrophosphate and fluoride (*7*).

On the other hand, compared to anion-sensing systems including the naked eyes, electrochemical and optical responses (*7, 8*), the fluorescent sensor is especially attractive and valuable on account of its high sensitivity (*9*). For example, as reported by Tian et al. a fluoride ion-triggered dual fluorescence molecular switch could be regulated 'ON–OFF' and 'OFF–ON' by different excitations (*10*). In another case, a tripodal fluorescent receptor bearing benzimidazole motifs was shown to act as a selective sensor for iodide even in the presence of other ions in 10% aqueous CH_3CN (*11*). Meanwhile, the fluorescent anion sensing based on calixarene receptors is also undergoing preliminary investigations (*9b, 12, 13*). Kim et al. (*14*) developed a bifunctional fluorescent chemosensor based on calix[4]arene capable of detecting the fluoride anion. In another work, a 2-site chloride-selective 1,3-alternate calix[4]arene derivative utilised Cl^- to induce the conformational 'unstacking' of the pyrene moieties (*15*). More recently, we have reported a fluorescent sensor for anions based on modified calix[4]-arene bearing imidazo[4,5-*f*]-1,10-phenanthroline groups, which can efficiently recognise F^- and AcO^-, even through naked eyes (*16*). However, to the best of our knowledge, the effect of a solvent on calixarene-based anion recognition has been less of a concern. This is interesting as the flexible conformations of calixarene derivatives must rely on solvents to some extent (*17*).

In the present study, we wish to report the syntheses and characterisation of 5,11,17,23-tetra-*tert*-butyl-25,27-bis(2-naphthalenesulfonyl aminoethoxy)-26,28-dihydroxycalix[4]arene (**3**) (Scheme 1). Furthermore, the fluorescent sensing of **3** upon complexation with an anionic guest was observed in a variety of solvents. It is worth noting that the binding behaviour of **3** for anions is dramatically solvent dependent. This can be attributed to its variable structures elicited by solvent polarity.

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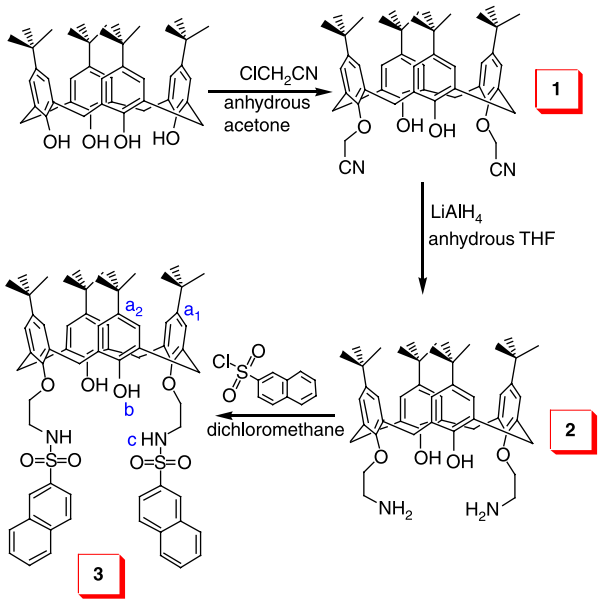


Scheme 1. Synthesis routes to compound **3**.

Experimental section

Materials

Chloroform was distilled and stored over 4 Å molecular sieves before use. All other solvents such as DMSO and CH_3CN were of ultra-pure grade quality, and used without further purification. All anions were used in the form of their tetrabutylammonium salts, and the tetrabutylammonium fluoride was used as its trihydrate, no efforts were made to drying. The intermediate 5,11,17,23-tetra-*tert*-butyl-25,27-bis(2-cyanomethoxy)-26,28-dihydroxycalix[4]arene (**1**) as well as 5,11,17,23-tetra-*tert*-butyl-25,27-bis(2-aminoethoxy)-26,28-dihydroxycalix[4]arene (**2**) were prepared according to the literature procedures (*18*). The reaction of compound **2** with 2-naphthalene sulfonyl chloride afforded **3** in satisfied yield. All the synthesised compounds were characterised with ^{1}H NMR, ESI-MS, etc., which are found to be in good agreement with their structures.

Measurements

Melting points were measured by an XT-4 apparatus and are uncorrected. The ^{1}H NMR spectra were recorded on a Varian Mercury Plus 400 MHz or Bruker AV300 (300 MHz) instrument. The IR spectra were recorded on Shimadzu Bio-Rad FTS 135 instruments. Elemental analyses were performed on a Perkin-Elmer 2400C instrument. Fluorescence spectra were measured in a conventional quartz cell (10 × 10 × 45 mm) at 25.0 ± 0.1°C with an Edinburgh Analytical Instruments FLS920 spectrometer (Edinburgh Instruments, Edinburgh, UK). The sample solutions were excited at a host concentration of 2×10^{-5} mol dm^{-3} at 287 nm in DMSO and 1×10^{-4} mol dm^{-3} at 294 nm in $CHCl_3$ to give a strong emission. The fluorescence intensity of **3** peaked at 329 nm in DMSO and 421 nm in $CHCl_3$ was used to determine the complex stability constants.

*Synthesis of 5,11,17,23-tetra-***tert***-butyl-25,27-bis(2-naphthalenesulfonyl aminoethoxy)-26,28-dihydroxycalix-[4]arene (3)*

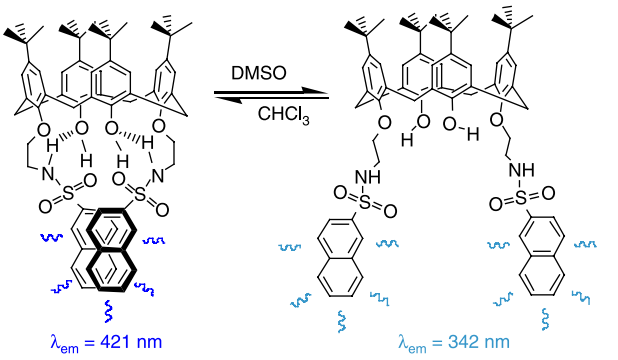
5,11,17,23-Tetra-*tert*-butyl-25,27-bis(2-aminoethoxy)-26,28-dihydroxycalix[4]arene **2** (0.74 g, 1 mmol) was dissolved in dichloromethane (20 ml), and then 2-naphthalene sulfonyl chloride (0.50 g, 2.2 mmol) and triethylamine (3 ml, 4 mmol) were added. The reaction mixture was stirred at room temperature for 8 h and then evaporated to dryness. The solid residue was purified by silica gel column chromatography using dichloromethane/methanol 20:1 as an eluent affording a white solid, recrystalised by dichloromethane/methanol, giving the product as a white needle solid (0.88 g, 79%), mp 262–264°C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS, ppm), δ 8.47 (s, 2H), 8.43 (s, 2H), 7.92 (m, 6H), 7.82 (d, $J = 6.0$ Hz, 2H), 7.63 (t, $J = 7.2$ Hz, 2H), 7.55 (t, $J = 7.2$ Hz, 2H), 7.44 (t, $J = 4.2$ Hz, 2H), 6.94 (s, 4H), 6.90 (s, 4H), 4.06 (d, $J = 6.6$ Hz, 4H, CH_{ax}), 3.98 (t, $J = 4.0$ Hz, 4H), 3.62 (q, $J = 6.8$ Hz, 4H), 3.15 (d, $J = 6.6$ Hz,4H, CH_{eq}), 1.23 (s, 18H), 1.07 (s, 18H); ESI-MS *m/z* 1115.4 (M^+). 1138.6 $(M + Na)^+$, IR (KBr cm^{-1}) 3284.1, 3055.0, 2957.6, 2868.7, 1771.0, 1698.4, 1650.8, 1483.6, 1459.8, 1331.8, 1161.1, 747.6, 658.7, 550.1. Anal. calcd for $C_{68}H_{78}N_2O_8S_2$: C, 73.22; H, 7.05; N, 2.51; found: C, 73.62; H, 7.25; N, 2.30.

The colourless single crystal of **3** was collected along with its mother liquor ($CHCl_3/CH_3OH$, 1:2) for the X-ray crystallographic analyses. The X-ray intensity data for **3** were collected on a Rigaku MM-007 rotating anode diffractometer equipped with a Saturn CCD area detector system using monochromated Mo-Kα ($\lambda = 0.71070$ Å) radiation at $T = 113(2)$ K. Data collection and reduction were performed by the program Crystalclear. X-ray structural data: $C_{70}H_{84.75}N_6Cl_{1.25}N_2O_{9.59}S_2$, $M = 1215.94$, triclinic, $a = 14.644(5)$ Å, $b = 15.452(5)$ Å, $c = 15.457(5)$ Å, $\alpha = 71.378(15)°$, $\beta = 78.886(17)°$, $\gamma = 81.376(18)°$, space group $P\bar{1}$, $Z = 2$, calculated density 1.247, crystal dimensions (mm^3): 0.30 × 0.28 × 0.20, $\mu = 0.193$ mm^{-1}, 24,801 measured reflections of which 11,378 were unique ($R_{(int)} = 0.1139$), final R indices [$I/\sigma(I) > 2$]: $R_1 = 0.1898$, $wR_2 = 0.4854$, R indices (all data): $R_1 = 0.2194$, $wR_2 = 0.4594$, GOF on F^2 1.452. CCDC-673360 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

Results and discussion

Conformation of 3

It is well known that calixarenes possess a scaffold of conformational flexibility and are easily able to alter their conformations. The conformation of calix[4]arene will be restricted by means of a proper chemical modification; the attachment of bulky-enough appendages to a calix[4]arene platform inhibits the oxygen-through-the-annulus rotation and results in conformational immobility (*4c*). Nevertheless, the platform of calix[4]arene derivatives is still flexible, and depends on the inclusion/complexation of guests or even polarity of solvents. Accordingly, the conformational behaviour of **3** is primarily investigated in different solvents (DMSO, CH_3CN, CH_2Cl_2 and $CHCl_3$) by fluorescent and NMR spectra before measuring its recognition ability towards anion guests. The fluorescence spectra of **3** detected in solvents with different polarities are shown in Figure 1. In $CHCl_3$, compound **3** exhibits two sets of fluorescent emissions: the weaker one peaked at 342 nm represents the typical monomer emission of naphthalene; the stronger one with $\lambda_{max} = 421$ nm is the characteristic of the excimer emission of naphthalene (*19*). It indicates that there is a clear overlapping between the two naphthalene substitutes on the lower rim of calix[4]arene. Contrarily, in DMSO, compound **3** exhibits only the monomer emission peaked at 342 nm. Moreover, the fluorescence spectra of **3** in CH_2Cl_2 and CH_3CN were also performed, showing a stronger excimer emission in CH_2Cl_2 while a weaker one in CH_3CN. It can be seen that the relative intensity sequence of excimer emission is opposite to the polarity sequence of four solvents: DMSO $>$ CH_3CN $>$ $CH_2Cl_2 \approx CHCl_3$. This shows that the conformation of **3** is subtly solvent dependent, maybe arising from hydrogen-bonding interactions. As shown in Scheme 2, in the apolar solvent such as $CHCl_3$,



Scheme 2. Possible conformation of compound **3** in $CHCl_3$ or DMSO.

the NH groups form dual intramolecular hydrogen bonds with oxygens of neighbouring phenolic hydroxyl groups (*20*), leading to the $\pi\cdots\pi$ dimer of naphthalene groups, whereas such hydrogen bonds do not exist in the polar solution of **3** (DMSO), and therefore the two naphthalene groups are apart from each other and assume the distal form. The present explanation is further validated by the measurement of fluorescent spectra of **3** in various mixtures of $CHCl_3$ and DMSO (Figure 2). By sequential augmentation of the DMSO ratio in mixing solvents, the excimer emission of **3** gradually weakened while its monomer emission concomitantly increased. We attributed this result to an ultimate disruption of the intramolecular hydrogen bonds, which allows **3** a new configuration to be adopted, where the naphthalene groups cannot come into proximity and form an excimer (*21*).

The ^{1}H NMR experiments also provide a positive insight for the solvent-dependent configuration of **3**. According to Gutsche's theory (*22, 4a*), the difference between the axial and the equatorial protons of the

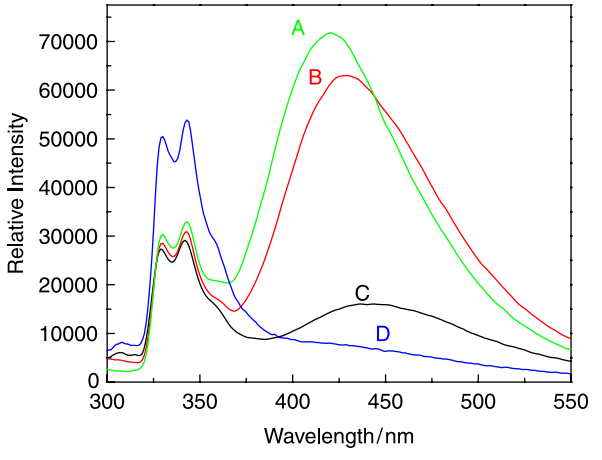


Figure 1. Fluorescence spectra of **3** (1.0×10^{-4} M) in (A) $CHCl_3$, (B) CH_2Cl_2, (C) CH_3CN and (D) DMSO at 25°C. $\lambda_{ex} = 294$ nm. Bandwidth (Ex): 1.8 nm; bandwidth (Em): 1.8 nm.

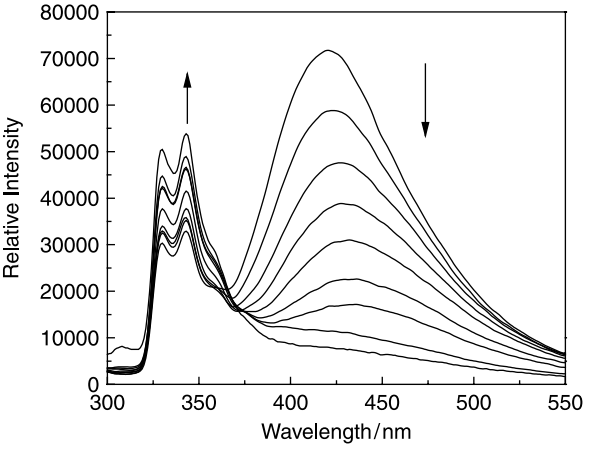


Figure 2. Fluorescence spectra of **3** (1.0×10^{-4} M) in different ratios of $CHCl_3$/DMSO (v/v) (from top to bottom: 100:0, 98:2, 94:6, 89:11, 84:16, 75:25, 66:34, 50:50, 0:100) at 25°C. $\lambda_{ex} = 294$ nm. Bandwidth (Ex): 1.8 nm; bandwidth (Em): 1.8 nm.

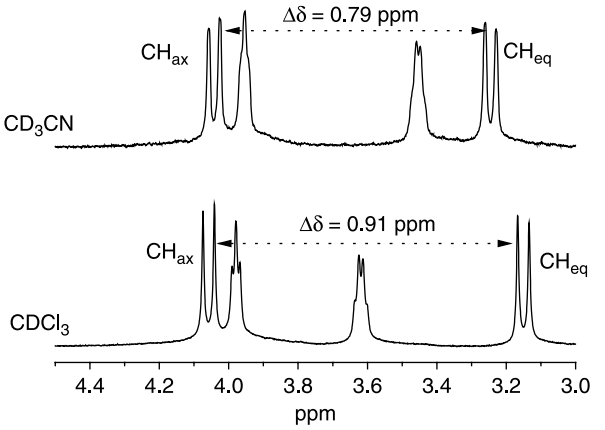


Figure 3. Partial ^{1}H NMR (400 MHz) of **3** (10 mM) in $CDCl_3$ and CD_3CN at room temperature.

methylene bridge in chemical shifts, $\Delta\delta_{ax\text{-}eq}$, provides an indicator about the conformation adopted in the solution. Comparatively, the ^{1}H NMR spectra of **3** are measured in either $CDCl_3$ or CD_3CN, showing that $\Delta\delta_{ax\text{-}eq} = 0.91$ ppm in $CDCl_3$ and $\Delta\delta_{ax\text{-}eq} = 0.79$ ppm in CD_3CN, respectively (Figure 3). As a result, compound **3** adopted a more distorted cone conformation in $CHCl_3$ than in CH_3CN, which mainly originated from the formation of the π···π dimer of naphthalene groups appended in the lower rim. The $\Delta\delta_{ax\text{-}eq}$ was also calculated in more polar DMSO-d_6 solution, and it is a pity that the signal of H_{eq} is somewhat overlapped with the peak of the DMSO-d_6 solvent at 3.3 ppm. Hence, the $\Delta\delta_{ax\text{-}eq}$ value is just estimated about 0.74–0.78 ppm (Figure S4), which is anticipatedly smaller than that in CH_3CN. In addition, the X-ray crystallographic structure of **3** (Figure S5) obtained from the $CHCl_3$–CH_3OH (1:2 v/v) solution shows that compound **3** exists in the distal form with two naphthalene groups away from each other owing to the high polarity of CH_3OH. The (*tert*-) C···C approaches of *trans-tert*-butyl groups are 8.913 and 9.197 Å, and the dihedral angles among the opposite aromatic rings are 48.4° and 70.3°, respectively. These data also indicate that the conformation of **3** with naphthalene groups in the distal form is distorted to a little extent.

Fluorescent sensing and selective binding

Based on the aforementioned results of diverse configurations of **3** in different solvents, the binding behaviours of **3** for various anions (including F^-, Cl^-, Br^-, HSO_4^-, $H_2PO_4^-$ and AcO^-) were further investigated by fluorescence spectroscopy in DMSO and $CHCl_3$ solutions, respectively. As shown in Figure 4 and Figures S7 and S8 (the fluorescence ratio $(I - I_0)/I_0$), the fluorescence of **3** was quenched to different intensities upon the addition of anions in both DMSO and $CHCl_3$ solutions. Among these

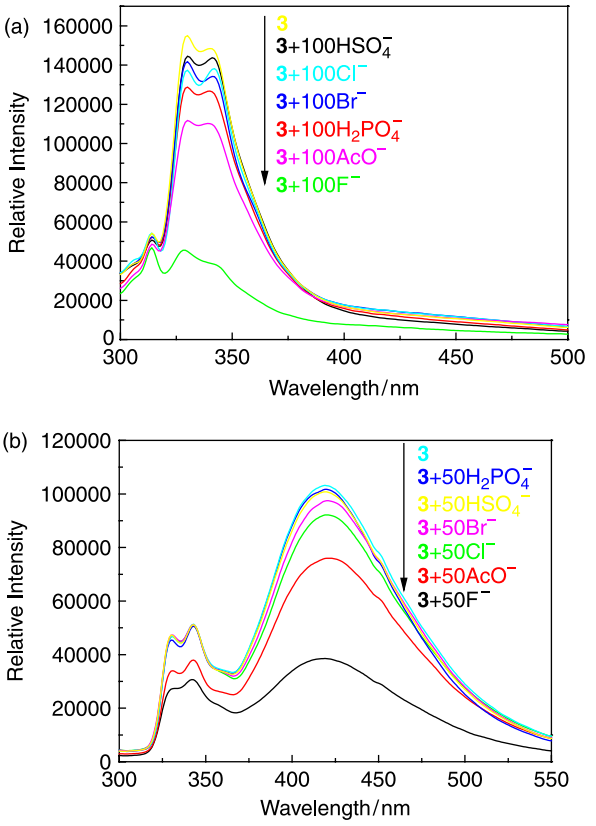


Figure 4. (a) Fluorescence spectra of **3** (2.0×10^{-5} M) in the absence and presence of 100 equiv. Br^-, Cl^-, $H_2PO_4^-$, HSO_4^-, AcO^- and F^- in DMSO at 25°C. $\lambda_{ex} = 287$ nm. Bandwidth (Ex): 2.5 nm; bandwidth (Em): 2.5 nm. (b) Fluorescence spectra of **3** (1.0×10^{-4} M) in the absence and presence of 50 equiv. anions in $CHCl_3$ at 25°C. $\lambda_{ex} = 294$ nm. Bandwidth (Ex): 2.0 nm; bandwidth (Em): 2.0 nm.

anions employed, F^- and AcO^- remarkably lead to the decrease of the fluorescent intensity of **3** while the other four only present a limited influence, which implies that host **3** provides preferable binding affinity for F^- and AcO^-, especially for F^-. For the case in DMSO solution, the quenching of monomer emission of **3** by F^- and AcO^- should be attributed to the enhanced photo-induced electron transfer (PET) effect upon complexation with anions. For the case in $CHCl_3$ solution, not only the monomer emission but also the excimer emission of **3** is clearly quenched upon the addition of F^- and AcO^-. One possible explanation for the quenching of emission is the PET effect upon the addition of anions too. The other is that the π···π dimer of naphthalene groups in **3** is destroyed, causing the reduction in the overlapping extent of two naphthalene groups. However, the judgement from the complex stability constant (mentioned as below) proves that the latter should be a minor reason for the quenching of the excimer emission of **3**. In the present experimental condition (1.0×10^{-4} M of **3**), most of **3** forms complex with F^- upon the addition of 50 equiv. F^-.

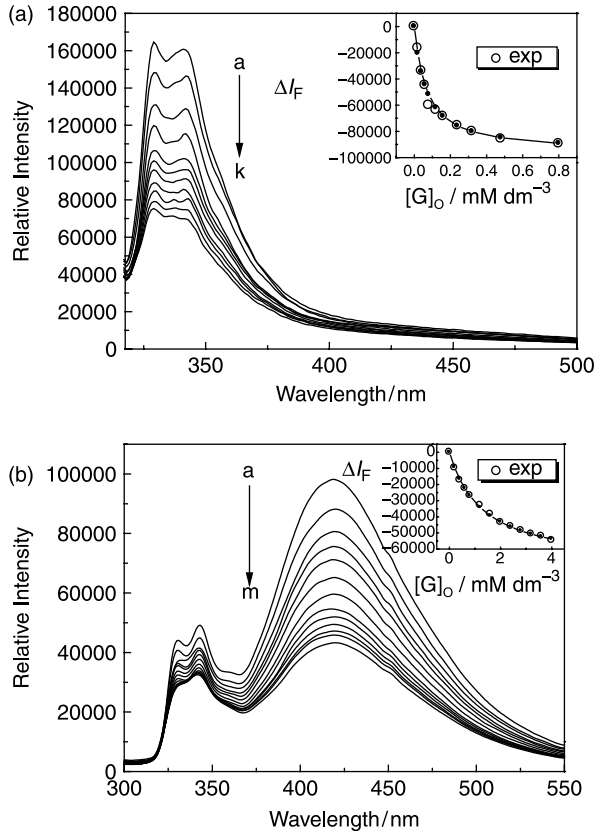


Figure 5. (a) Fluorescence spectral changes of **3** (2.0×10^{-5} M) upon the addition of F^- ($0–8.0 \times 10^{-4}$ M from a to k) in DMSO at 25°C, $\lambda_{ex} = 287$ nm. Bandwidth (Ex): 2.5 nm; bandwidth (Em): 2.5 nm. (b) Fluorescence spectral changes of **3** (1.0×10^{-4} M) upon the addition of F^- ($0–4.0 \times 10^{-3}$ M from a to m) in $CHCl_3$ at 25°C, $\lambda_{ex} = 294$ nm. Bandwidth (Ex): 2.0 nm; bandwidth (Em): 2.0 nm. Inset: the nonlinear least-squares analysis (inset) of the differential intensity (ΔI_f) for calculating the complex stability constants (K_S).

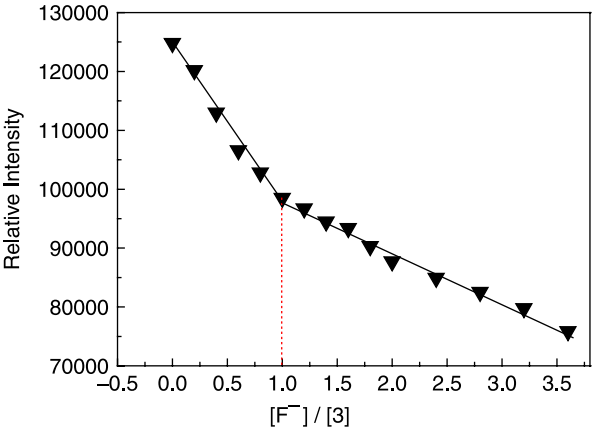


Figure 6. Mole ratio plot for the binding of F^- anion with **3** in DMSO ($\lambda_{em} = 329$ nm).

So the excimer emission of **3** should nearly disappear if the π···π dimer of naphthalenes is thoroughly overcome by F^-, which does not accord with the factual experimental phenomena. Moreover, the relative ratio of excimer/monomer decreased upon the addition of F^- or AcO^- (from 1.98 to 1.24 upon the addition of 50 equiv. F^- to **3**), which indicates the overlapping extent of the dimer to be partially weakened (*12d*).

To investigate quantitatively the binding ability of **3** for anions, the titrations of fluorimetry have been performed in DMSO and $CHCl_3$, giving the corresponding complex stability constants (K_S). The typical fluorescent spectra of titration between **3** and F^- in DMSO and $CHCl_3$ are shown in Figure 5. The K_S values of complex **3**·F^- were calculated by utilising the nonlinear least-squares method, which are well fitted with 1:1 host–guest stoichiometry: $K_S = 16{,}300 \pm 800\ M^{-1}$ in DMSO and $900 \pm 80\ M^{-1}$ in $CHCl_3$. The host–guest stoichiometry was further identified by the mole ratio plot (Figure 6) that there is obvious inflexion at 1.0 ($[F^-]/[\mathbf{3}]$). In the same way, the K_S values of complex **3**·AcO^- were also obtained: $K_S = 3500 \pm 130\ M^{-1}$ in DMSO and $120 \pm 10\ M^{-1}$ in $CHCl_3$. For the other anions (Cl^-, Br^-, HSO_4^- and $H_2PO_4^-$), the fluorescent changes in both DMSO and $CHCl_3$ were too small to be used for calculating the complex stability constants. It can be seen that host **3** presents the strongest binding affinity towards F^- among all anions examined in either polar or apolar solutions, which may arise from its strong electronegativity and basicity. Particularly, it should be mentioned that the solvents exert an extraordinary influence over the host–guest complexation: such as the K_S (**3**·F^-) in DMSO is 18 times higher than that in $CHCl_3$; the K_S (**3**·AcO^-) in DMSO is 29 times higher than that in $CHCl_3$. It may be a result from some reasons of the diverse configurations of **3** and the different polarities of solvents or others, which will be discussed in detail in the undermentioned section of ^{1}H NMR spectra.

^{1}H NMR spectra

To clearly understand the above binding and fluorescent behaviours between host **3** and anions, we carried out the ^{1}H NMR experiments of **3** in the absence or presence of F^-. The results obtained are illustrated in Figure 7 (in (a) $CDCl_3$ and (b) DMSO-d_6), displaying that there is a pronounced difference of host–guest binding manners between $CHCl_3$ and DMSO. For host **3** in $CDCl_3$, upon the addition of 1 equiv. F^-, the proton signal of H_b becomes invisible, suggesting that there exist hydrogen-bonding interactions between F^- and two phenolic hydroxyls at the low rim of **3**. And then, the signal of H_c proton does not change any more upon the gradual addition of F^-, which means that NH groups do not

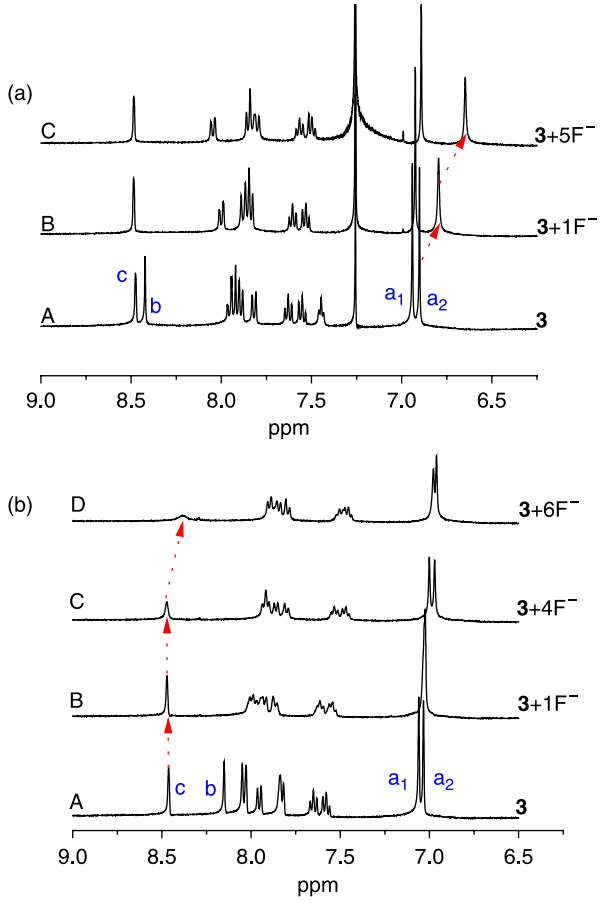
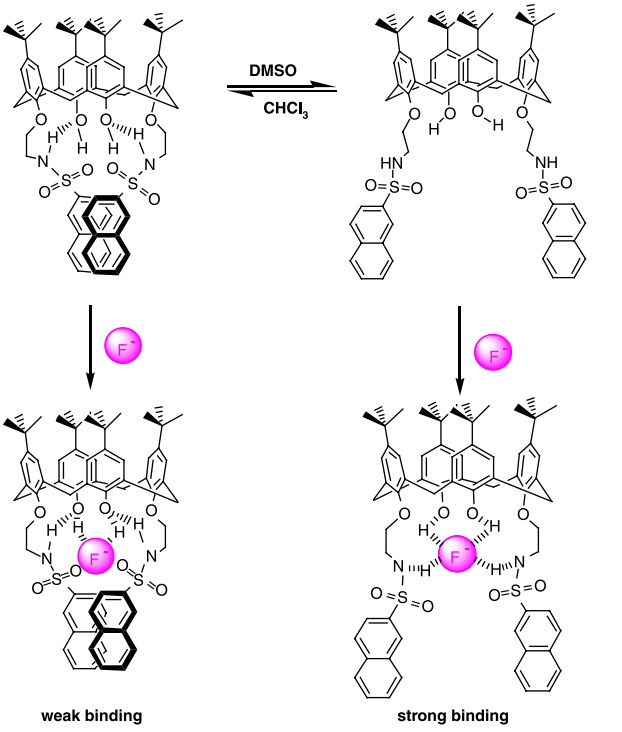


Figure 7. Partial ^{1}H NMR (400 MHz) of **3** (10 mM) in (a) $CDCl_3$ at room temperature: (A) compound **3** only, (B) **3** + 1 equiv. of F^-, (C) **3** + 5 equiv. of F^-; in (b) DMSO-d_6: (A) compound **3** only, (B) **3** + 1 equiv. of F^-, (C) **3** + 4 equiv. of F^-, (D) **3** + 6 equiv. of F^-.



Scheme 3. Reasonable structures of complexes **3**·F^- in $CHCl_3$ or DMSO.

interact with F^- in $CDCl_3$, and the primary hydrogen-bonding interactions between NH groups and oxygens of phenolic hydroxyl groups still remain. It also indicates the retainment of the π···π dimer of naphthalene groups when host **3** complexed with F^-. Moreover, the $\Delta\delta$ value of the aromatic protons (H_{a1} and H_{a2}) of **3** enlarged gradually accompanied with the augmentation of F^- as shown in Figure 7(a) (from 0.04 to 0.24 ppm), which implies that the cone shape of **3** is pinched to more extent upon complexation with F^- in $CDCl_3$. In the meanwhile, the distortion of the conformation of **3** by F^- is also validated by the $\Delta\delta_{ax\text{-}eq}$ value increases from 0.91 to 1.06 ppm. In contrast to the case in $CDCl_3$, both the H_b and H_c protons of **3** disappeared upon the stepwise addition of F^- in DMSO-d_6. It indicates that not only OH but also NH groups of **3** participate in binding with F^- in DMSO. It should also be mentioned that the protons of OH vanish prior to those of NH, possibly owing to the different acidities between NH and OH groups in **3** (*13, 14*). In addition, there is only a slight change for the $\Delta\delta$ value between H_{a1} and H_{a2}, showing that the conformation of calixarene does not obviously distorted upon complexation with F^- in DMSO. Therefore, it can be seen that host **3** contributes only two hydrogen bonds donated by phenolic hydroxyls to capture F^- in $CHCl_3$, which is accompanied with some loss of conformational freedom, whereas host **3** contributes four hydrogen bonds donated by both OH and NH groups to capture tightly F^- in DMSO almost without any loss of conformational freedom. Consider that the dehydrated fluoride has been shown to be a strong Lewis base (*23*) enough to deprotonate the NH of sulfonamides in DMSO (*24*). One then should see deprotonation after the addition of F^- to **3**, such deprotonation would give rise to the formation of HF_2^- with concomitant new long wavelength absorption emergence (*25, 9m*) (similar deprotonation was reported by Fabbrizzi (*2e, 8d*), and Gunnlaugsson et al. (*7, 8g*)). However, this absorption at long wavelength was not observed in the absorption spectra within the measurement range (40 equiv. F^-). It is possible that the reactivity of fluoride may be dimmed by complexation to the water molecules introduced by the salt itself in the very beginning. Therefore, we can conclude that for F^-, the binding occurs by the hydrogen bond as mentioned before within the measuring range in this paper (*26*). The deduced binding manners are illustrated in Scheme 3, which is in good agreement with the phenomena from the

fluorescence spectra. The results obtained by ^{1}H NMR measurements clearly present the rational explanation for such large diversity of the binding affinities of **3** for anions in DMSO and $CHCl_3$.

Conclusion

In summary, the fluorescent behaviour of the calix[4]arene derivative upon complexation with the anion was investigated. In polar solutions, host **3** displays only the fluorescence of monomer emission; whereas in apolar solutions, host **3** displays the fluorescence of both monomer and excimer emissions. This indicates that there are alternative conformations of **3** in solvents with different polarities: the two lower-rim naphthalene groups exist in the distal form in polar solutions while the $\pi\cdots\pi$ dimer form in apolar solutions. Further investigations on the anion-binding behaviours show that host **3** provides the highest complex stability constants for F^- in both DMSO and $CHCl_3$ solutions. However, the complex stability differs much from each other in different solvents. That is, host **3** presents strong binding affinity for F^- and AcO^- in DMSO while weak binding affinity in $CHCl_3$. ^{1}H NMR measurements indicate that the hydrogen-bonding interactions and pre-organised structure of **3** are two key factors of influencing the anion-binding properties. The present work will serve us further understanding and design of potential anion fluorescent sensors based on calixarenes.

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