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Azophenol appended (thia)calix[4]arenes for colorimetric sensing of anions: A complexation induced extended conjugation

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ABSTRACT

Iminoazophenol appended calix[4]arene/thiacalix[4]arene derivatives **1** and **2** of cone and **3** of 1,3-alternate conformation have been synthesized and examined for their chromogenic anion recognition abilities towards different anions like fluoride, chloride, bromide, iodide, acetate, dihydrogenphosphate, nitrate and hydrogensulphate by UV–vis spectroscopy. Receptors **1**–**3** show an unusual red shift in UV–vis spectra upon binding with these anions, with a colour change visible to naked eye in case of fluoride, acetate and dihydrogenphosphate ions at lower concentration of anions. This red shift in the absorption spectra is accounted by anion complexation induced σ-extended conjugation.

1. Introduction

The selective recognition of anions plays an important role in biology, medicine, catalysis and environment [1–3]. During the last few years a large number of neutral anion receptors have been reported [4,5], majority of which include receptors which have functional groups such as amide [6], urea [7], pyrrole [8], thiourea [9] and sulphonamides [10] which are good hydrogen bond donors.

Recently, it has reported that hydroxyl groups of serine and tyrosine play an important role in anion-binding pockets of biological systems like ClC chloride channels [11,12], halorhodopsin [13,14]. Despite this important role there have been few developments in the design of hydroxyl group based anion recognition systems [15–18]. Our research work involves the design, synthesis and evaluation of calix[4]arene and thiacalix[4]arene based receptors selective for soft metal ions [19–23] and anions [24]. We recently reported new chloride ion selective sensors based on calix[4]arene possessing a urea/thiourea moieties [24]. Now, we have prepared new anion sensors **1** and **2** based on a calix[4]arene and thiacalix[4]arene of cone conformation possessing azophenyl moieties. We have also investigated the role of the phenolic moieties of (thia)calix[4]arene in anion binding using thiacalix[4]arene receptor **3** of 1,3-alternate having protected phenolic moiety.

These receptors **1**–**3**, undergo unusual red shift in the UV spectra upon interaction with anions. We propose that in the presence of anions, the azophenol moiety exerts push-pull phenomenon [25,26], which results in the σ-extended delocalization of the azophenol moiety resulting in the red shift of absorption band. Earlier Fabbrizzi et al., has reported π-extended conjugation for colorimetric sensing of fluoride ions [27]. We believe that this kind of σ-extended conjugation is unprecedented but a similar phenomenon has been reported by Kim et al. in the case of amidopyrene derivatives of calix[4]arene [28]. While this work was in progress Kandaswamy et al. reported a phenol based chromogenic sensors for fluoride ions [29,30].

2. Results and discussion

2.1. Synthesis

The receptors **1** [31], **2** [32] and **3** [33] were prepared by the reported methods (Fig. 1). Receptors **1** and **2**, contain four phenolic hydroxyl groups while receptor **3** contains two phenolic hydroxyl groups, as anion-binding moieties and two substituted phenyldiazo groups for monitoring the anion-binding event.

2.2. UV–vis studies

To evaluate the binding abilities of receptors **1**–**3** towards different anions and to establish the mode of binding, we carried out UV–vis experiments in THF, dimethyl sulphoxide (DMSO) and DMSO-H_2O (9:1, v/v). Receptor solutions (1×10^{-5} M) in THF were treated with the representative anions such as tetrabutylammonium (TBA) fluoride, chloride, bromide, iodide, acetate, dihydrogenphosphate, nitrate and hydrogensulphate. In the absence of anions, the absorption spectrum of receptor **1**/**2** is

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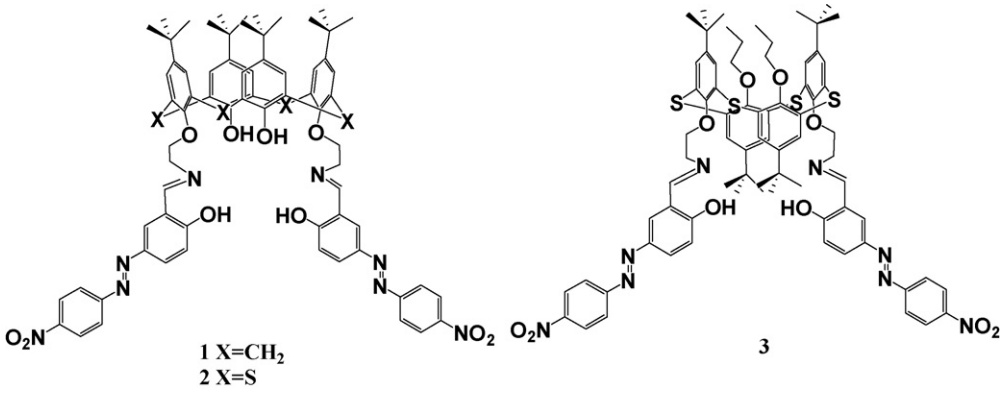


Fig. 1. Synthesis of azophenol derivatives **1**–**3**.

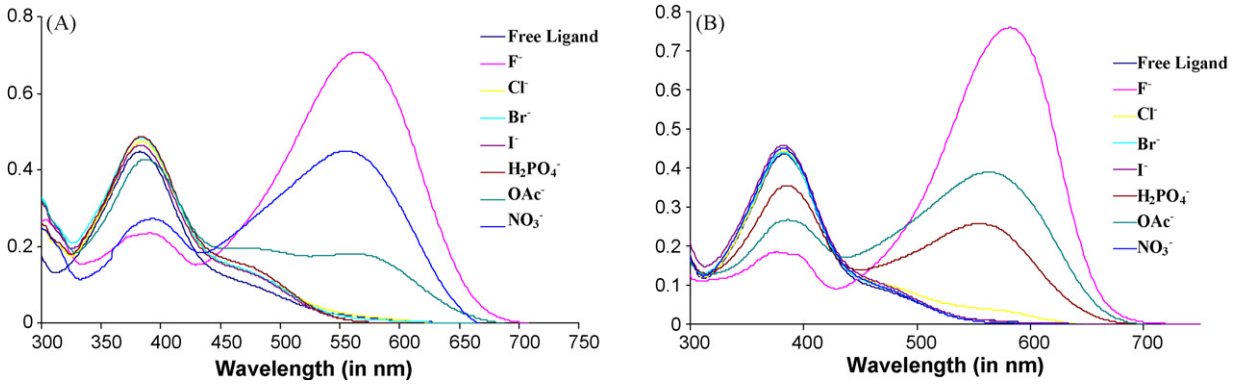


Fig. 2. UV–vis absorption spectra of (A) receptor **1** and (B) receptor **2** in THF (1×10^{-5} M) upon addition of 2 mol equiv. of different anions.

characterized by the presence of one absorption maximum peak at 383/385 nm (Fig. 2A and B). The absorption spectra of receptors **1** and **2** in the presence of different anions are shown in Fig. 2A and B, respectively. It was found that the UV–vis absorption bands of receptors **1** and **2** are red shifted to 583 nm ($\Delta\lambda$ 200 nm) and 567 nm ($\Delta\lambda$ 182 nm) as fluoride ions come in contact with solutions of these receptors. Similarly, new red shifted absorption bands were observed at 570 and 558 nm in the presence of acetate ions and weak absorption bands at 556 and 561 nm upon addition of $H_2PO_4^-$ ions. However, there was absolutely no change in the absorption spectrum of receptors **1** and **2** in the presence of chloride, bromide, iodide, nitrate and hydrogensulphate ions at this particular concentration (Fig. 2A and B).

Upon addition of increasing amounts of tetrabutylammonium fluoride to the solution of receptor **1**, the absorption band at 383 nm decreases with the formation of a new red shifted absorption band at 583 nm (Fig. 3A). Similarly, upon addition of increasing amounts of tetrabutylammonium fluoride to a solution of receptor **2** in THF, the absorption band at 385 nm decreases with the formation of a new red shifted absorption band at 567 nm (Fig. 3B). The UV–vis titration profile of receptors **1** and **2** with F^- ions showed ratiometric behaviour upon addition of 2.0 equiv. of F^- ions (insets in Fig. 3A and B). The relative absorption intensity (I_{583}/I_{383}) of receptor **1** was 0.0 and it increases to 4.5 with addition of 2.0 equiv. of fluoride ion. Similar ratiometric behaviour is also observed for receptor **2** upon addition of 2.0 equiv. of fluoride ion.

The addition of increasing amounts of acetate ions to the solution of receptor **1** in THF resulted in similar change with the red shifted absorption band appearing at 570 nm (Fig. 4A). Likewise addition of increasing amounts of dihydrogenphosphate ions to the

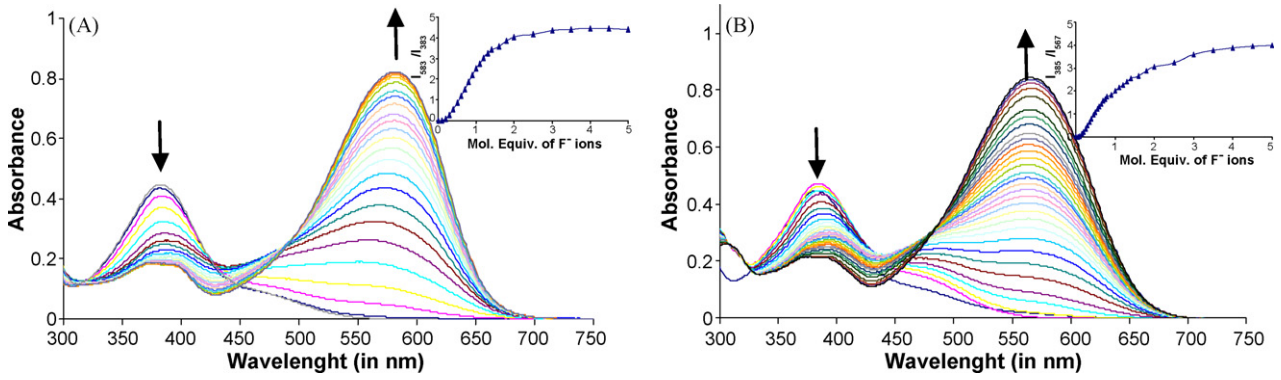


Fig. 3. UV–vis absorption spectra of (A) receptor **1** and (B) receptor **2** (1×10^{-5} M) upon addition of tetrabutylammonium fluoride (0–5 equiv.) in THF. Inset showing the ratiometric calibration curve as a function of fluoride ion concentration in equiv.

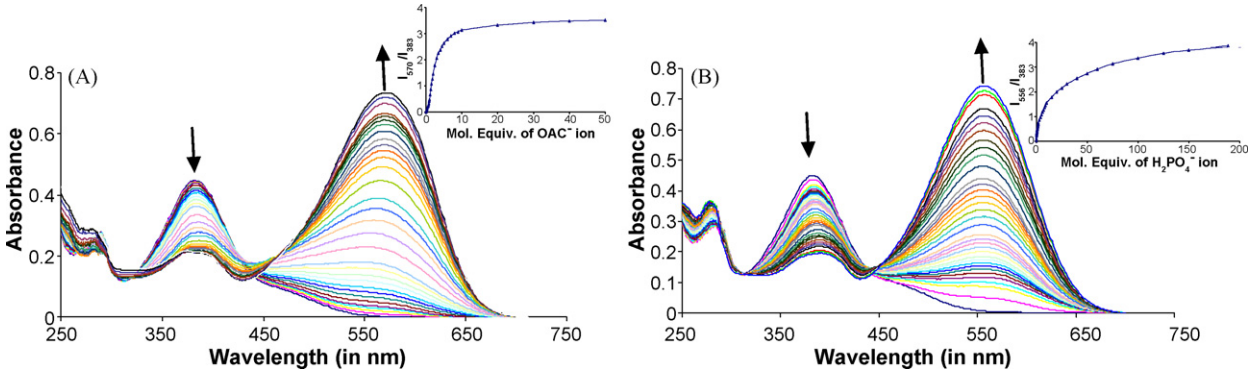


Fig. 4. UV–vis absorption spectra of receptor **1** in THF (1×10^{-5} M) upon addition of (A) tetrabutylammonium acetate (0–20 equiv.) and (B) tetrabutylammonium dihydrogen phosphate (0–100 equiv.). Inset showing the ratiometric calibration curve as a function of anion concentration in equiv.

solution of receptor **1** in THF results in the formation of new red shifted band at 556 nm (Fig. 4B). Similarly, upon addition of acetate and dihydrogenphosphate ions to the solution of receptor **2** in THF, the new red shifted absorption bands appeared at 552 and 563 nm, respectively (Table 1). The slope of the binding isotherm showed a saturation of response upon addition of 25 equiv. of acetate ions and 40 equiv. of dihydrogenphosphate ions in case of both of these receptors **1** and **2**.

Similar behaviour was observed for receptor **1**, upon addition of 1000 equiv. of anions like chloride and iodide, the difference in the wavelength ($\Delta\lambda$) being 173 and 187 nm, respectively as given in Table 1.

To investigate the role of phenolic hydroxyl groups in anion binding, we carried out studies of thiacalix[4]arene receptor **3** of 1,3-alternate conformation, where the coordination environment was changed with the removal of the phenolic hydroxyl group from the coordination sphere. Receptor **3** exhibits an absorption band at 387 nm in the absence of anions. The absorption spectrum of receptor **3** undergoes a red shift from 387 to 583, 570 and 556 nm, respectively, as fluoride, acetate and dihydrogenphosphate ions come in contact with solution of receptor **3** (see supporting information S1).

Upon addition of increasing amounts of tetrabutylammonium fluoride to the solution of receptor **3**, the absorption band at 387 nm decreases with the formation of a new red shifted absorption band at 583 nm (Fig. 5). The UV–vis titration profile of receptor **3** with F^- ions showed ratiometric behaviour upon addition of 2.0 equiv. of F^- ions. The relative absorption intensity (I_{583}/I_{387}) of receptor **3** was 0.0 and it increases to 6.0 with addition of 2.0 equiv. of fluoride ion.

Similarly, red shifted absorption bands appeared on addition of various anions like chloride, iodide, dihydrogenphosphate and acetate, to the solution of receptor **3**. The respective bathochromic shift in the absorption bands is given in Table 1. From the results given in Table 1, it is clear that the anion recognition behaviour of the receptors **3** is similar to the anion recognition behaviour of receptors **1** and **2** which indicates that the phenolic hydroxyl groups of the thiacalix[4]arene moiety are not involved in the binding process. Thus, it may be concluded from these anion-binding studies that the anion prefers to bind the more acidic part i.e., the phenolic hydroxyl groups of the azophenol moiety [28].

Using pH studies we established that receptors **1** and **2** showed absorption bands at 518 and at 521 nm respectively in the UV–vis spectrum due to deprotonation of the azophenol moiety (see supporting information S2) while the anion induced red shifted bands appeared at 583, 555, 570, 556 and 570 nm upon addition of fluoride, chloride, iodide, dihydrogenphosphate and acetate ions, respectively (Table 1). Thus, from this observation, we could infer that the mode of interaction of these receptors with various anions is different from the deprotonation mechanism. Thus, in pursuit of establishing the mode and nature of interaction of anions with these receptors, we carried out further investigations of the anion recognition behaviour of receptors **1** and **2** in DMSO and DMSO-H_2O (9:1, v/v).

The absorption spectrum of receptor **1** (1×10^{-5} M) in DMSO showed two absorption maxima at 400 and 480 nm (Fig. 6). Similarly, the absorption spectrum of receptor **2** (1×10^{-5} M) in DMSO showed two absorption maxima at 407 and 477 nm (see supporting information S3). The absorption band at 400/407 nm is due to the azophenol moiety, while the band at 480/477 nm may be due to

Table 1
Bathochromic shift ($\Delta\lambda$, nm) in absorbance wavelength of (thia)calix[4]arene based azophenol receptors **1**–**3** (1×10^{-5} M) upon addition of tetrabutylammonium anions like F^-, Cl^-, I^-, $H_2PO_4^-$ and OAc^-.

Entry	Wavelength, λ_{max}	Azophenol based receptors		
		1	**2**	**3**
1	Free ligand	383	385	387
2	Free ligand + F^-	583	567	583
	$\Delta\lambda^*$	200	182	196
3	Free ligand + Cl^-	555	558	555
	$\Delta\lambda^*$	172	173	168
4	Free ligand + I^-	570	561	570
	$\Delta\lambda^*$	187	176	183
5	Free ligand + $H_2PO_4^-$	556	563	556
	$\Delta\lambda^*$	173	178	169
6	Free ligand + OAc^-	570	552	570
	$\Delta\lambda^*$	187	167	183

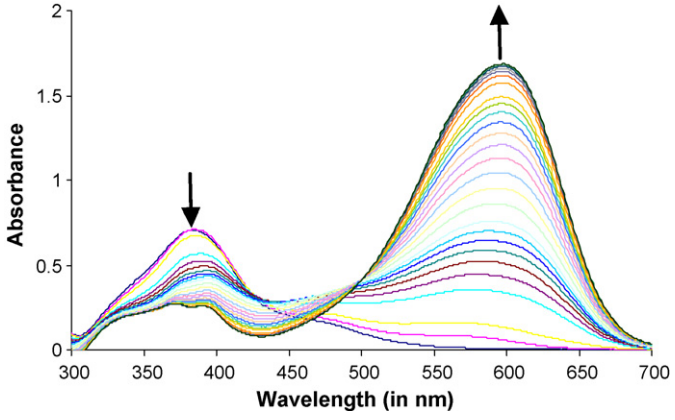


Fig. 5. UV–vis absorption spectra of receptor **3** in THF (1×10^{-5} M) upon addition of tetrabutylammonium fluoride (0–5 equiv.).

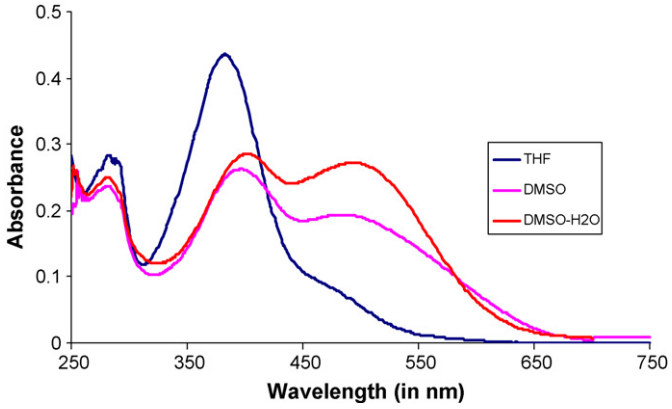
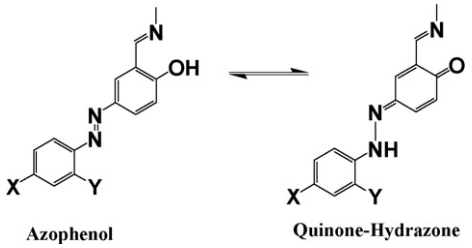


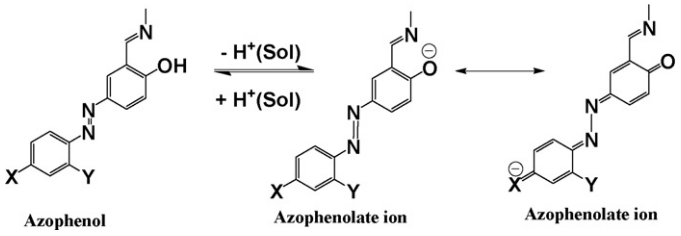
Fig. 6. UV–vis absorption spectra of receptor **1** (1×10^{-5} M) in THF/DMSO/DMSO-H_2O (9:1, v/v).



Scheme 1. Azophenol to quinone-hydrazone tautomerism in azophenol derivatives.

the quinone-hydrazone tautomer of the azophenol (Scheme 1) or can be due to the deprotonation of the receptor itself in presence of solvent (Scheme 2).

If the tautomerism of the azophenol and quinone-hydrazone (Scheme 1) is responsible for the formation of the absorption band at 480 nm, then these tautomeric forms should be stabilized towards the more polar species on addition of an acid or a base. However, it was observed that there was a small increase in the intensity of the band at 480 nm on addition of triethylamine, while



Scheme 2. Azophenol–Azophenolate equilibria in azophenol derivatives.

on adding trifluoroacetic acid (TFA) the absorption band at 480 nm decreases while the band at 381 nm increases (Fig. 7), which leads us to propose that tautomerism (Scheme 2) is certainly not responsible for the new absorption band at 480 nm. Thus, the absorption band at 480 nm might be due to the solvent induced partial deprotonation of the receptor.

The UV–vis absorption band of receptor **1** is red shifted to 581, 572 and 569 nm, respectively, as fluoride, acetate and dihydrogenphosphate ions come in contact with solutions of the receptor, however, there was absolutely no change in the absorption spectrum of receptor **1** in the presence of chloride, bromide, iodide, nitrate and hydrogensulphate ions at this particular concentration (see supporting information S4).

Upon addition of increasing amounts of tetrabutylammonium fluoride to the solution of receptor **1**, the absorption band at 400 nm decreases while a red shifted band appeared at 581 nm with an isosbestic point at 472 nm (Fig. 8). Thus, these results indicate that the deprotonation phenomenon is not operational rather the interaction of receptor **1** with fluoride ion is taking place in different mode.

In mixed aqueous media (DMSO-H_2O 9:1, v/v), on addition of increasing amounts of tetrabutylammonium fluoride to the solution of receptor **1**, the absorption band at 400 nm decreases while the absorption band at 480 nm gradually shifts to 513 nm with increase in intensity (Fig. 9).

One interesting point to note here is the fact that in presence of all these anions like fluoride, chloride, bromide, iodide, acetate and dihydrogenphosphate, the new absorption band is formed at 513 nm, irrespective of the basicity of the anion (see supporting information S5). Thus, we propose that in such cases there may be a deprotonation of the azophenolic protons of the receptor upon addition of these anions.

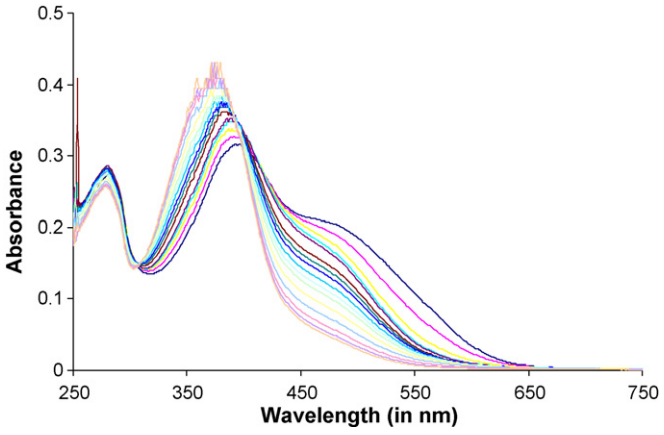
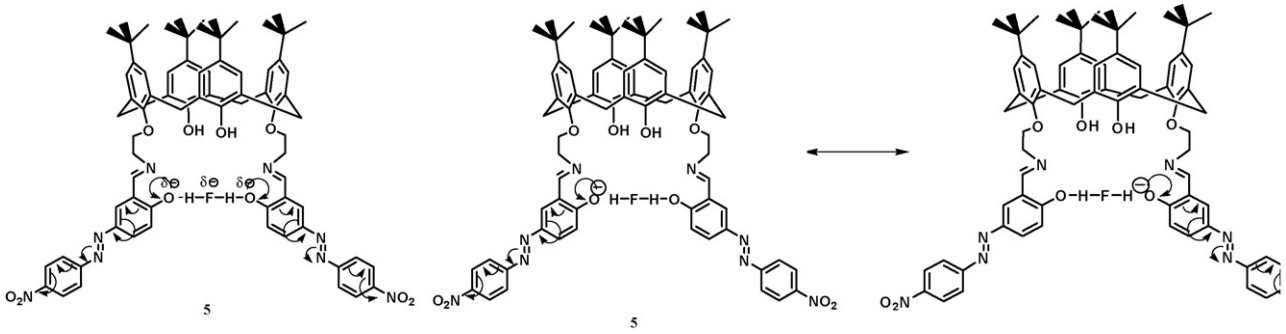


Fig. 7. UV–vis absorption spectra of receptor **1** (1×10^{-5} M) upon addition of trifluoroacetic acid (TFA) (0–100 equiv.).



Scheme 3. Representation of the receptor (**1**)-fluoride hydrogen bonded complex.

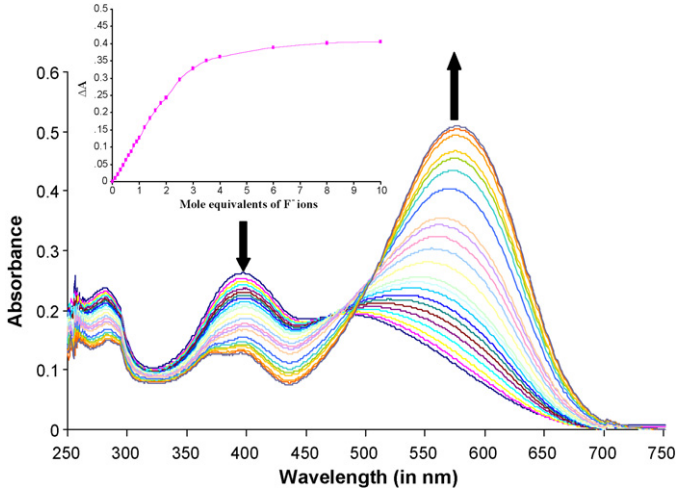


Fig. 8. UV–vis absorption spectra of receptor **1** in DMSO (1×10^{-5} M) upon addition of tetrabutylammonium fluoride (0–10 equiv.). Inset showing the ratiometric calibration curve (I_{581}/I_{400}) as a function of fluoride ion concentration in equiv.

From these UV studies, we observe that addition of anions like fluoride, acetate and dihydrogenphosphate to these (thia)calix[4]arene derivatives **1–3** bearing azophenol moieties, in THF and DMSO show an unusual red shift in the absorption bands, whereas addition of various anions to the solution of these receptors in mixed aqueous environment (DMSO-H_2O, 9:1 v/v), showed an anion–induced deprotonation of these receptors.

To further evaluate the intermolecular interactions between the azophenol calix[4]arene derivative **1** and anions, we also carried out ^{1}H NMR studies in DMSO-d_6 (Fig. 10). The ^{1}H NMR spectrum of receptor **1** showed a singlet at δ 9.83 ppm for the phenolic protons of azophenol moiety, which undergoes a complexation induced upfield shift of 1.20 ppm in presence of 1 mol equiv. of fluoride ion.

Thus, the ^{1}H NMR studies show that a hydrogen bonded complex is formed between the receptor **1** and the anion. Similar upfield shift of the hydrogen bonding protons have been observed by Fabbrizzi et al. [27] who propose an enhanced π-extended conjugation in presence of fluoride ion, based on an iminothiourea receptor. In light of all these spectroscopic studies, we propose that there is a intermolecular proton transfer from azophenol to fluoride ion which form hydrogen bond with other phenolic proton in the near

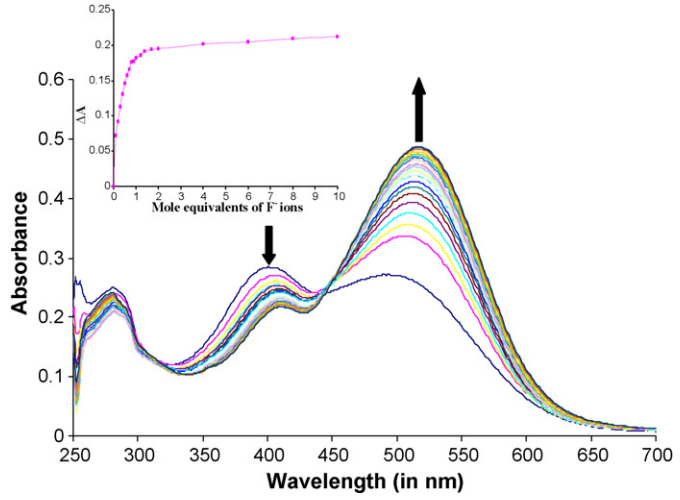


Fig. 9. UV–vis absorption spectra of receptor **1** (1×10^{-5} M) upon addition of TBA fluoride (0–10 equiv.). Inset showing the binding isotherm at 513 nm as a function of anion concentration in equiv.

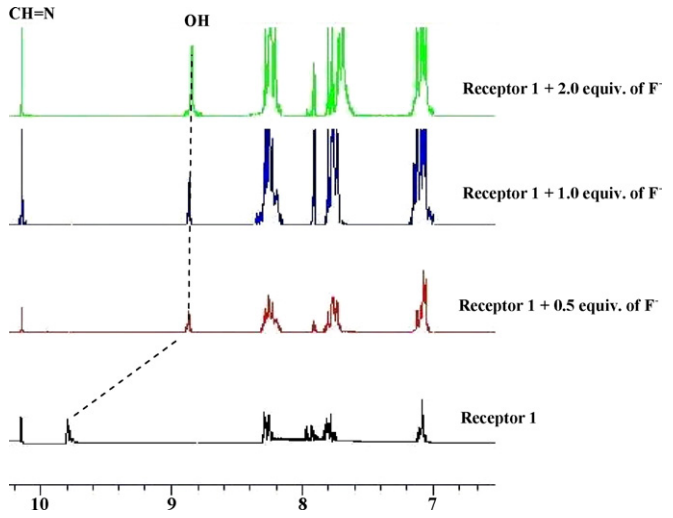


Fig. 10. Partial ^{1}H NMR spectra of receptor **1** (10 mM) in DMSO-d_6 in the presence of fluoride ions.

Table 2
Binding constants ($\log \beta_{11}$) of receptors **1–3** with various anions in THF at 298 K.

	F^-	Cl^-	Br^-	I^-	$H_2PO_4^-$	OAc^-	NO_3^-	HSO_4^-
1	6.79	1.87	–	0.98	4.15	4.87	–	–
2	5.76	2.19	–	2.63	3.86	4.73	–	–
3	5.81	2.15	–	2.83	3.92	4.45	–	–

vicinity leading to the formation of adduct 5 (Scheme 3). Thus, we believe that this unusual red shift of >90–200 nm in presence of anions is a result of anion induced extended conjugation of the azophenol moiety. This extended delocalization is expected to reduce the energy of the π–π^* transition. As a consequence, the absorption band is shifted to longer wavelength leading to a colour change from yellow to blue in presence of fluoride ion. Kim et al. have reported similar adduct on amidopyrene derivative of calix[4]arene [28].

Analysis of the UV titrations of compounds **1–3** with all the anions was performed by means of SPECFIT programme [34] which showed that the titration curves were consistent with the formation of 1:1 (receptor:anion) complex and the stability constant values obtained from the titration data are given in Table 2. From Table 2 it is clear that the binding constants follow the order $F^- > AcO^- > H_2PO_4^- > Cl^- > I^-$. Further, the binding constant of fluoride ion with receptor **1** is ten times the binding constant with receptors **2** and **3**. This indicates that the increase in the cavity of thiacalix[4]arene results in the lower binding efficiency of the receptors **2** and **3**.

A noticeable colour change could be observed by naked eye by mixing the receptor **1** (1×10^{-5} M) with anions (2×10^{-5} M) as shown in (Fig. 11). In particular, it was remarkable that a light yellow coloured receptor solution became purple upon addition of fluoride ions in tetrahydrofuran and light purple or light pink when acetate or dihydrogenphosphate ions were added to the receptor

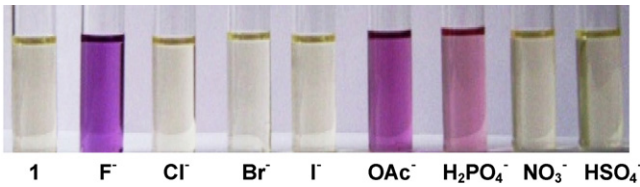


Fig. 11. Colour changes of receptor **1** (1×10^{-5} M) in THF upon addition of tetrabutylammonium anions (2×10^{-5} M).

solution. However, in the case of all other anions no detectable colour changes were observed upon addition of 2 mol equiv. of anions (Cl^-, Br^-, I^-, NO_3^- and HSO_4^-) to the solution of 1. Thus, there is a clear naked eye detection of fluoride ions.

3. Conclusions

To sum up, we have demonstrated the use of easy to prepare iminoazophenol receptors **1**–**3** as a chromogenic sensor for anions. These receptors respond with charge transfer by a push–pull mechanism in conjunction with a σ-bond conjugated hybrid complex. However, in mixed aqueous solution (DMSO-H_2O), upon addition of anion, these receptors show a true deprotonation.

4. Experimental

4.1. General procedures

All reagents were purchased from Aldrich and were used without further purification. THF was dried over sodium and benzophenone and kept over molecular sieves overnight before use. UV Spectra was recorded on SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length: 1 cm). The cell holder was thermostatted at 25 °C. ^1H and ^{13}C NMR spectra were recorded on JEOL-FT NMR-AL 300 MHz spectrophotometer using $CDCl_3$/DMSO-d_6 as solvent and TMS as internal standards. Solvents used for UV studies were THF AR grade/DMSO HPLC grade/double distilled water. All spectrophotometric titrations curve were fitted with SPECFIT\32 software.

4.2. UV–vis studies

UV–vis titrations were performed on 1×10^{-5} M solution of ligands **1**–**3** in THF/DMSO/DMSO-H_2O. Typically, aliquots of freshly prepared Bu_4NX (X = F^-, Cl^-, Br^-, I, OAc^- and NO_3^-) solutions ($1–10^{-3}$ M in THF) were added and the UV–vis spectra of the samples were recorded.

4.3. ^1H NMR titration

Stock solution (10 mM) of compound 1 was prepared in DMSO-d_6/$CDCl_3$. Similarly, Stock solutions (20 mM) of anions (fluoride, chloride, bromide, iodide, acetate and nitrate as their tetrabutylammonium salts) were prepared in DMSO-d_6/$CDCl_3$ for the ^1H NMR experiments.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2009.11.028.

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