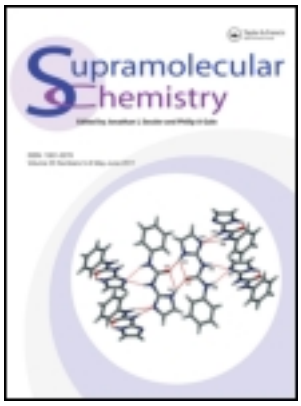

Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsch20

New tripodal and dipodal colorimetric sensors for anions based on tris/bis-urea/thiourea moieties

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Version of record first published: 28 Nov 2011.

To cite this article: Vimal K. Bhardwaj, Sanyog Sharma, Narinder Singh, Maninder Singh Hundal & Geeta Hundal (2011): New tripodal and dipodal colorimetric sensors for anions based on tris/bis-urea/thiourea moieties, Supramolecular Chemistry, 23:12, 790-800

To link to this article: http://dx.doi.org/10.1080/10610278.2011.593629

Supramolecular Chemistry
Vol. 23, No. 12, December 2011, 790–800

New tripodal and dipodal colorimetric sensors for anions based on tris/bis-urea/thiourea moieties

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(*Received 6 September 2010; final version received 26 April 2011*)

Seven neutral tripodal and dipodal receptors having mesitylene/triethylbenzene as core moiety, urea/thiourea as binding groups and *p*-nitrobenzene as signalling unit have been reported. The receptors act as selective colorimetric, naked eye sensors for small and spherical F^- ion with some interference from tetrahedral $H_2PO_4^-$ ions. Thiourea derivatives form stable 1:1 H-bonded complexes with F^- anion and to some extent with $H_2PO_4^-$ anions, whereas for urea derivatives, the recognition is simply based on acid–base reaction between ureidic protons and basic F^- ions and is a completely reversible phenomenon. The pre-organisation of thiourea derivatives coupled with their high-intrinsic acidity is supposed to help them in the formation of strong H-bonded complexes with F^- anion. The urea-based receptors do not respond at lower concentrations of the anion, but at higher concentrations, they undergo completely reversible deprotonation concomitant with a colorimetric change, with the production of stable $[HF_2]^-$ anion.

Keywords: 1,3,5-trimethyl/triethyl benzene core; urea/thiourea binding units; H-bonding; deprotonation; anion sensing

1. Introduction

Simple synthetic receptors capable of recognising anions serve as important tools for detecting chemically, biologically and environmentally important analytes (*1*, *2*). Many systems reported are based on amide (*1c*, *3*), pyrrole (*4*), urea/thiourea (*5*), azo dyes (*6*), naphthalene/-naphthalimide (*7*), porphyrin containing neutral hosts (*8*) or polyammonium (*9*), guanidinium, amidinium and thiouronium (*10*) containing cationic hosts. While designing and synthesising anion binding hosts, pre-organisation, charge and lability of the receptors are some of the features to be taken into consideration (*11*). As for the pre-organisation factor, binding of guests with the pre-organised macrocyclic systems is relatively simple to understand, but the binding processes of 'conformationally flexible' podands remain intangible.

However the latter, by virtue of this property, becomes more interesting for they may show anion-dependent conformational behaviour, thus acquiring a conformation which may best accommodate the guest in cognizance with size and other electronic factors. There are many examples for dipodal and tripodal hosts in the literature which are based on substituted benzene as core and various binding/reporting units to give neutral or cationic receptors for optical anion sensing (*6b*, *12*). Anslyn and co-workers (*13*) have reported many neutral tripodal receptors that are based on the principle of indicator displacement assay. Imidazolium-, benzoimidazolium- and pyridinium-based tripodal receptors have also been reported (*12a*, *b*, *d*) which have used weak C–H···X interaction for anion binding. Among various types of neutral chemosensors mentioned above, those based on urea and thiourea give strong, directional H-bond donors and can easily be accommodated in other pre-organised scaffolds (*14*). There are many examples in which the monopodal (*15*) and dipodal (*16*) urea/thiourea-based receptors have been used for the recognition of different anions, but very few reports on their tripodal (*11*, *12d*, *17*) analogues are available, specifically on the neutral ones. Steed and coworkers have reported N core-based neutral tris-urea receptors (*18*) and benzene core-based tris-urea pyridinium receptors (*12d*) sensing Cl^- ion. In an extensive study of the geometric effects, Davis and co-workers have reported 'cholapods' which are steroid-based tris-urea/thiourea receptors (*19*).

We herein report five tripodal and two dipodal urea/thiourea-based neutral receptors (Scheme 1) with nitrophenyl groups to enhance both hydrogen bond donor tendency and acidity and to act as a colorimetric signalling subunit. The aim of the study is to compare the binding ability of the thiourea versus urea group as a part of the tripodal and dipodal receptors. We have also tried to study the effectiveness of the tripodal pseudo-cavity being generated in the 'three up' conformation of the hexasubstituted central benzene core (*20*) in solution to hold ions of different geometry.

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ISSN 1061-0278 print/ISSN 1029-0478 online

http://dx.doi.org/10.1080/10610278.2011.593629
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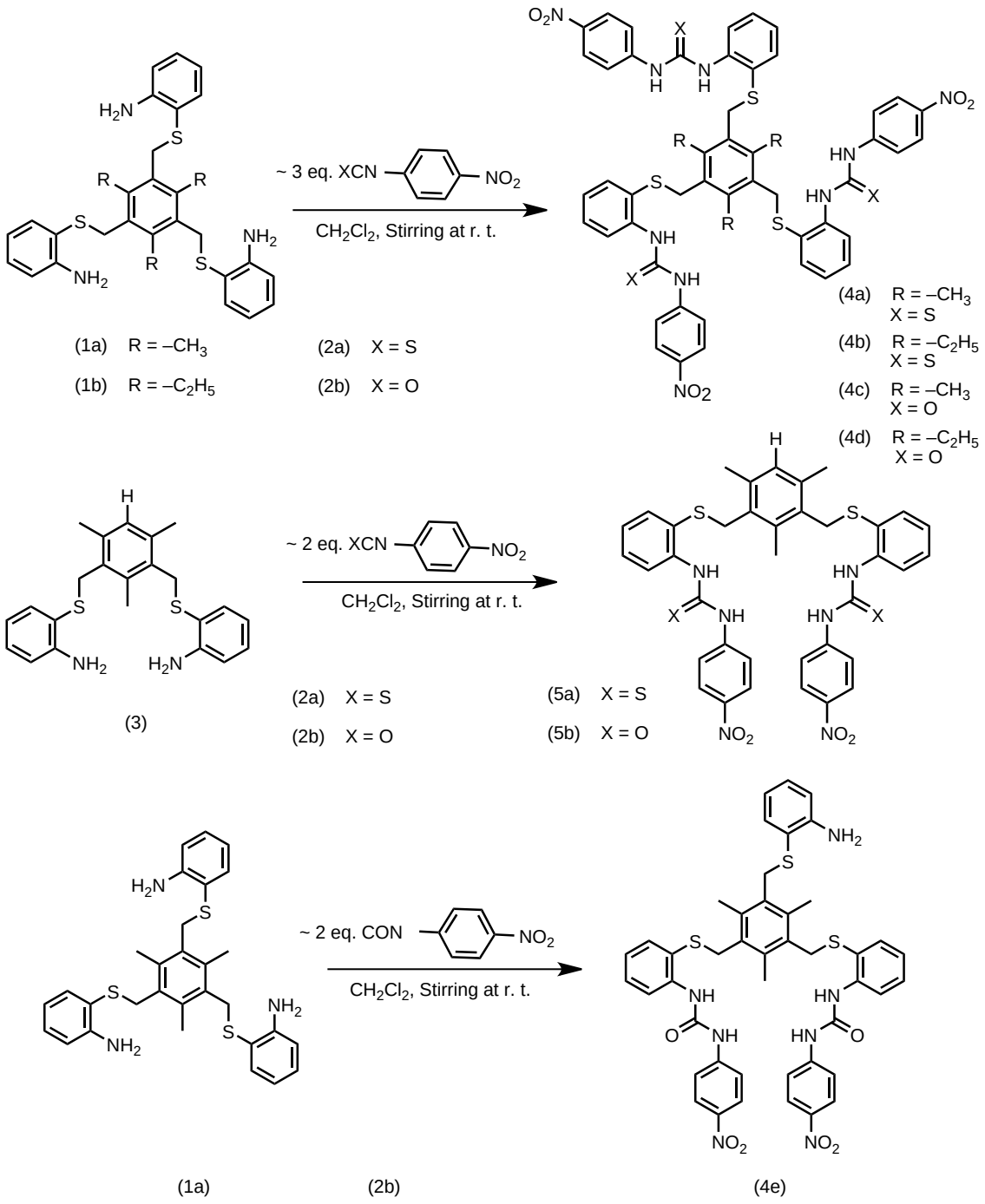

Scheme 1.

2. Results and discussion

Thiourea- and urea-based dipodal and tripodal receptors **4** and **5** were synthesised by reacting tripodal (*21*) **1** and dipodal **3** amines with 4-nitrophenyl isothiocyanate or 4-nitrophenyl isocyanate in dichloromethane. These were characterised by elemental analyses, IR, ^{1}H, ^{13}C NMR and UV–vis absorption spectroscopy. Their IR spectra show the presence of C═O or C═S stretching bands around $\sim$1490–1590 cm^{-1} and a band around $\sim$3050–3290 cm^{-1} characterising the presence of NH groups. The ^{1}H NMR spectra of **4** and **5** show signals lying in the range $\sim\delta$ 9.44–10.44 and $\sim\delta$ 8.41–10.08 ppm corresponding to thioureidic and ureidic protons, respectively. The appearance of only one signal for one kind of protons indicates that the two/three podes in the receptors are chemically equivalent which suggests an 'all up' conformation (*20*) for them. Alternatively, it may be due

to very rapid flipping of one conformation over the other due to rotation about C_{aryl}—$C_{methyl/ethyl}$ bonds, a rotation that has to be faster on the NMR scale. The available NMR evidence really cannot decide between the two. However, Anslyn and coworkers (*20b*) have already shown that *ababab* kind of conformation in the case of 1,3,5-R-2,4,6-R′ substituted arene-based receptors is thermodynamically more stable than its next conformation. Therefore, there is a very high probability of having a *cis,cis,cis* conformation for these ligands, at least in the solution state. CHN data are also in accordance with the molecular formulae.

2.1 Anion binding studies of chromogenic receptors

Investigations of anion recognition and anion selective behaviour of various receptors were carried out using UV–vis spectroscopy. The spectral changes upon the addition of various anions were determined in DMSO. The UV–vis spectra of each of the receptors **4** and **5** show a strong band at $\lambda_{max} \sim 355$ nm, characterised as an intra-ligand charge transfer band (ICT) which changes significantly upon addition of a small amount of tetrabutylammonium fluoride (TBAF) and in some cases, of tetrabutylammonium dihydrogen phosphate.

2.1.1 Thiourea derivatives

There were no changes in the spectra of thiourea receptors (*4a*, *4b*, *5a*) upon addition of tetrabutylammonium salts of other anions such as Cl^-, Br^-, I^-, NO_3^-, CN^-, ClO_4^-, AcO^- and HSO_4^- (Figure S1 of the Supplementary Information, available online).

2.1.1.1 Binding with fluoride ions. On addition of F^- ion into thiourea ligands, the absorption band at ~ 360 nm disappears and a new band at ~ 417 nm appears with a red shift of $\Delta\lambda_{max} \sim 57$ nm (Table 1) owing to the formation of a H-bonded complex. The complex formation on addition of F^- ion solution can be visually perceived through a colour change from pale to bright yellow. To learn more about the binding properties of these receptors for F^-, spectrophotometric titrations we carried out. A gradual decrease in the absorption of the band at 355 nm with a simultaneous increase in the absorption at 410 nm was seen (Figure 1, Figures S2 and S3 of the Supplementary Information, available online) on increasing the concentration of F^- ion solution for all three receptors. There is no emergence of any other band at much higher concentrations of TBAF (even up to 50×10^3 equivalents, Figure S4 of the Supplementary Information, available online).

The spectral changes were used to calculate the binding constants of the receptors. Fitting the changes in UV–vis spectra of these receptors using SPECFIT program (*22*) showed that for all the three receptors, best fits were obtained considering species with 1:1 stoichiometry. This suggests a stable, symmetrical 1:1 H-bonded, *endo*-complex (*5c*) in which the fluoride anion is supposed to reside inside the pseudo-cavity formed by the receptor. The binding constants calculated for receptors **4** and **5** are given in Table 2. The stoichiometry of these complexes formed was also determined by Job's plot (*23*) and was found to be 1:1 (Figure S5 of the Supplementary Information, available online). To verify the phenomenon of recognition, a titration of **4b** with tetrabutylammonium hydroxide (TBAOH) was carried out in similar conditions. As TBAOH is a strong base, it is bound to produce deprotonation to the ligand. Indeed, the spectral changes here took place in two steps: first, the appearance of a new band at λ_{max} 412 nm which has been attributed to the formation of a strong H-bonded complex as with TBAF. It is followed by the appearance of a second band at λ_{max} 477 nm, at higher equivalents corresponding to the deprotonation of the receptor (Figure 2). However, even with TBAOH, the deprotonation emerges at a very high concentration of the OH^- ion (>100 equivalents) and a proper band starts forming only after the addition of 200 equivalents and ultimately attains saturation. Therefore, a band at λ_{max} 477 nm is considered to correspond to the deprotonation of the receptor.

The recognition of tripodal **4a, 4b** and dipodal **5a** with F^- was evident in the ^1H NMR titration experiment. The results of NMR titrations of **4a** with TBAF solution in

Table 1. Optical response of receptors **4** and **5** to fluoride and phosphate ions showing changes in absorption band.

	Original band	Shifted or new band	Shifted or new band		
Ligands	λ_{max} (ligand) ($\log \varepsilon$ $M^{-1}cm^{-1}$)(nm)	λ_{max} (ligand + F^-) ($\log \varepsilon$ $M^{-1}cm^{-1}$)(nm)	$\Delta\lambda_{max}$ for F^-	λ_{max} (ligand + $H_2PO_4^-$) ($\log \varepsilon$ $M^{-1}cm^{-1}$) (nm)	$\Delta\lambda_{max}$ for $H_2PO_4^-$ ($\log \varepsilon$ $M^{-1}cm^{-1}$)
4a	360	417	57	409	49
4b	355	410	55	370	15[a]
4c	351	478	127	474	123
4d	348	474	126	475	127
4e	350	477	127	473	123
5a	358	417	59	383	25
5b	353	475	122	475	122

[a] Very small intensity, seen only at high anion concentration.

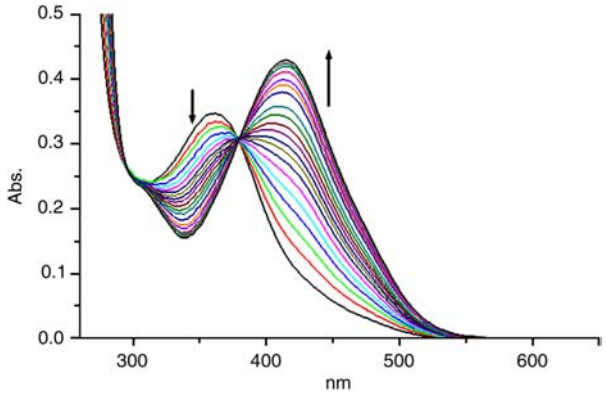

Figure 1. Changes in absorbance spectra of **5a** (10 μM) upon addition of TBAF (0–100 μM) in DMSO.

Table 2. Values of stability constants.

	4a	4b	5a
Log K_{a1} for F^-	4.14	4.65	5.13
Log K_{a1} for $H_2PO_4^-$	3.55	[a]	3.416

[a] The change was too small to be significant.

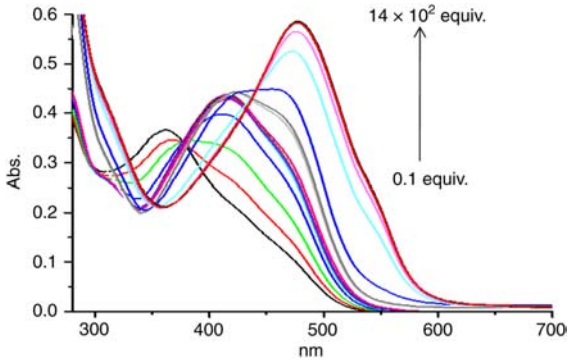

Figure 2. Changes in absorbance spectra of **4b** (10 μM) upon addition of TBAOH (0.1–14 × 10^2 equivalents).

DMSO-d_6 are shown in Figure 3. On addition of TBAF, signals due to both thiouredic protons H_1 and H_2 become broad and then disappear which may suggest their deprotonation. In many cases, however, the strong H-bonding also leads to the disappearance of the signals (*5f*, *24*) which seems to be the case presently since the UV–vis data (*vide supra*) have suggested H-bonding and not deprotonation in the case of thiourea derivatives. ^{1}H NMR spectrum of **4b** and **5a** in DMSO-d_6 (Figures S6 and S7 of the Supplementary Information, available online) also shows similar changes with the addition of F^- anion.

2.1.1.2 Binding with dihydrogen phosphate ions. With **4a, 4b** and **5a**, $H_2PO_4^-$ ions show lesser bathochromic shifts (Table 1) on increasing the concentration of the

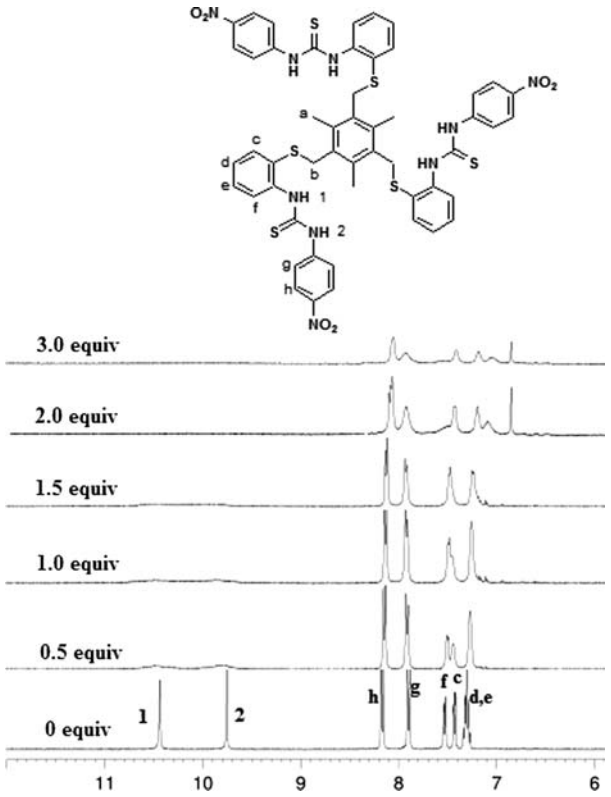

Figure 3. Changes in NMR titrations of **4a** (10 μM) with TBAF (0–3.0 molar equivalents) in DMSO-d_6.

anion (Figure S8 of the Supplementary Information, available online). From the extent of the shifts and the shapes of the spectra it is clear that the H-bonding interactions with the $H_2PO_4^-$ ions are strongest for **4a** followed by **5a** and **4b**, in this order. From the formation constants, we may deduce that for F^- ions, the acidity of thiourea derivatives varies as **5a** > **4b** > **4a**. With the less basic dihydrogen phosphate anions, this order may be formed as **4a** > **5a** > **4b**. A comparison clearly shows that the pre-organisation of the dipodal receptor is best suited for the spherical fluoride ion, whereas the tripodal receptor **4a** is more adapted to the tetrahedral dihydrogen phosphate anion.

2.1.2 *Urea derivatives*

2.1.2.1 Binding with fluoride ion. The UV–vis spectrophotometric titrations of receptors (**4c**–**4e**) with tetrabutylammonium salts of various anions show chromogenic response towards F^- ion (Figure S9 of the Supplementary Information, available online). On addition of TBAF (< 1 M equivalent), the absorption band at ~351 nm of receptors **4c** (Figure S10 of the Supplementary Information, available online), **4d** (Figure 4), **4e** (Figure S11 of the Supplementary Information, available online) and **5b** (Figure S12 of the Supplementary Information, available online) shows slight bathochromic shifts with a decrease in

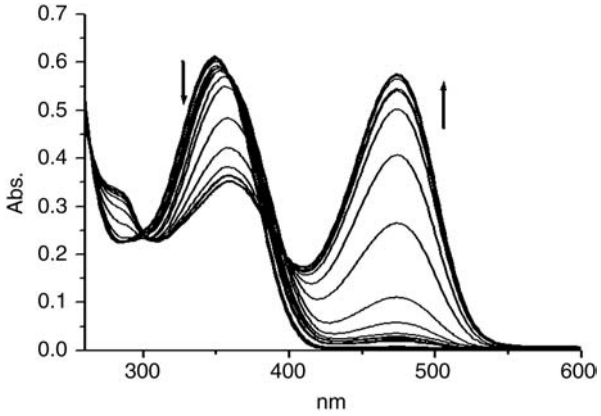

Figure 4. Changes in absorbance spectra of **4d** (10 μM) upon addition of TBAF (0–1100 μM) in DMSO.

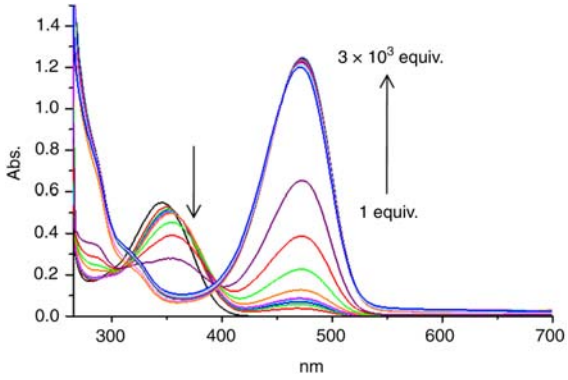

Figure 5. Changes in absorbance spectra of **4d** (10 μM) upon addition of TBAOH (1–3 × 10^3 equivalents) in DMSO.

its absorbance. From 1 M equivalent onwards, a new band appears at 474 nm which further grows on increasing the concentration of F^- ion (Table 1). These spectral changes are accompanied by visual colour changes from colourless to reddish yellow promising a naked eye detection of the F^- ion. There are three important differences in the behaviour of urea and thiourea derivatives here. First, the thiourea derivatives start responding at lower molar equivalents of the added anion solution and are saturated at ~2–3 equivalents, whereas the urea derivatives initiate significant response (after 1 equivalent) and are saturated at relatively much higher molar equivalents of the added anion (7–8 M equivalents). Second, the original band gets bathochromically shifted and gradually decreases in absorbance, but it does not disappear at any time and sustains even at saturation which is achieved at 10 times higher concentration of the anion. Finally, the spectral changes are transient and go back to the original situation shortly and the visual colour of the solution also reverts back. Urea derivatives, therefore, are not very sensitive to F^- ion at low concentrations due to their obviously low acidity. They show any significant response at ~8–10 equivalents of the anion and there they undergo deprotonation too fast to register any H-bonding step. Again, the acid–base titration of **4d** with TBAOH was used to confirm it. The titration (Figure 5) shows the emergence of a band at ~λ_{max} 474 nm ($\Delta\lambda$ ~125 nm, corresponding to deprotonation) with a simultaneous decrease in the absorption of the band at λ_{max} 348 nm and the latter disappearing completely after addition of 100 equivalents of the anion. The reversibility of the binding process observed in all the urea-based receptors further confirms the deprotonation step being involved. For this reason, at any given time, the accurate absorbance values for any given concentration of the anion could not be recorded; therefore, the formation constants of urea derivatives could not be calculated.

The ^{1}H NMR titrations of the urea-based ligands offer some interesting results that might help in explaining the difference in behaviour between these urea/thiourea receptors. The most significant difference between the NMR spectra of thiourea and urea derivatives is that the spectra of the latter show the signal of H_f proton between the H_h and H_g protons. As a representative of the changes in the NMR spectra on gradual addition of TBAF, figure 6 shows them for ligand **5b**, which illustrates the presence of H_f protons at δ 7.928 ppm in between complex multiplets for H_h (δ 8.194) and H_g (δ 7.672). This significant downfield shift of H_f protons in comparison with their counterparts in thiourea derivatives indicates the presence of intramolecular H-bonding interactions between the H_f protons and the oxygen of —C═O group. Such intramolecular H-bonding interactions have earlier been reported in the simple monopodal urea-based receptors for F^- ions (*15a*). On addition of 0.25 equivalents of TBAF in **4d**, the signals H_1 and H_2 from the —NH protons (originally seen at δ 10.084 and 8.408 ppm) show a high-frequency shift with $\Delta\delta$ of 0.41 and 0.12 ppm, respectively. Subsequent addition of F^- anion shows the disappearance of the —NH protons. It is well known that for the —NH- containing receptors, one of the reasons of the penchant for F^- ions is the remarkable stability of HF_2^- ion (*5c*, *15a*, *25*, *26*). The presence of which may be clearly seen in the NMR spectra of the representative compound **4d** in the form of a telltale triplet at ~δ 16 ppm (Figure 7) taken on addition of 12 equivalents of the anion. Fluoride ion though is not a specially strong base (pK_a = 15 in DMSO) (*27*), however, the extreme stability of $[HF_2]^-$ is well documented (*14a*) and it is known to behave as a very strong base, second to OH^- only. The NMR titrations of **4c** (Figure S13 of the Supplementary Information, available online), **4d** (Figure S14 of the Supplementary Information, available online) and **4e** (Figure S15 of the Supplementary Information, available online) with TBAF also show deprotonation in the presence of F^- anion. The NH_2 protons in **4e** do not participate in the H-bonding signifying that the anion prefers to get encapsulated by the receptor instead of

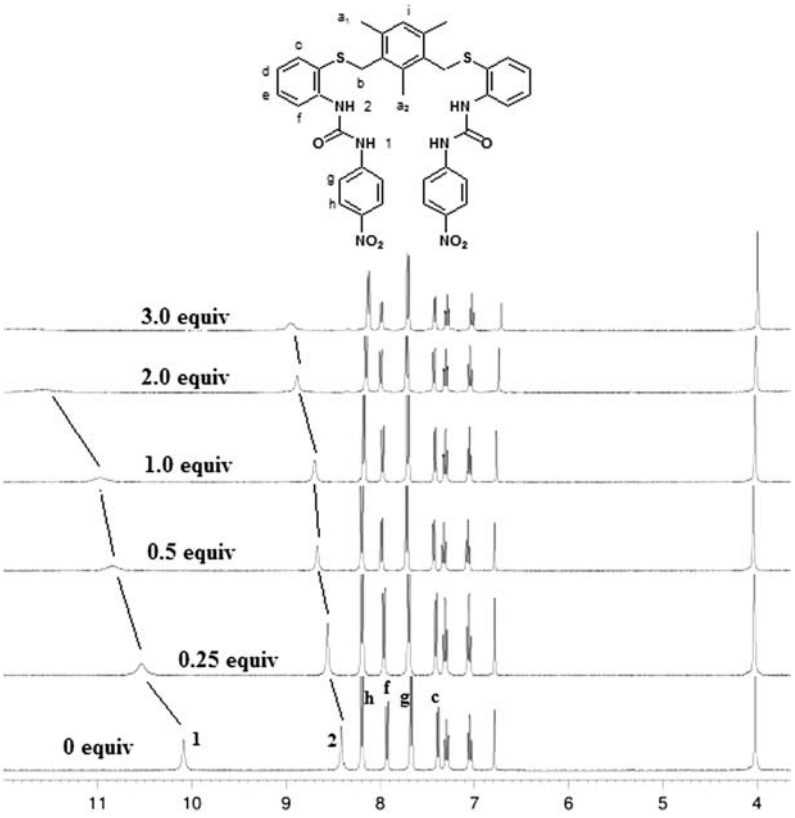

Figure 6. Changes in the NMR spectra of **5b** on stepwise increase in the concentration of TBAF in DMSO-d_6.

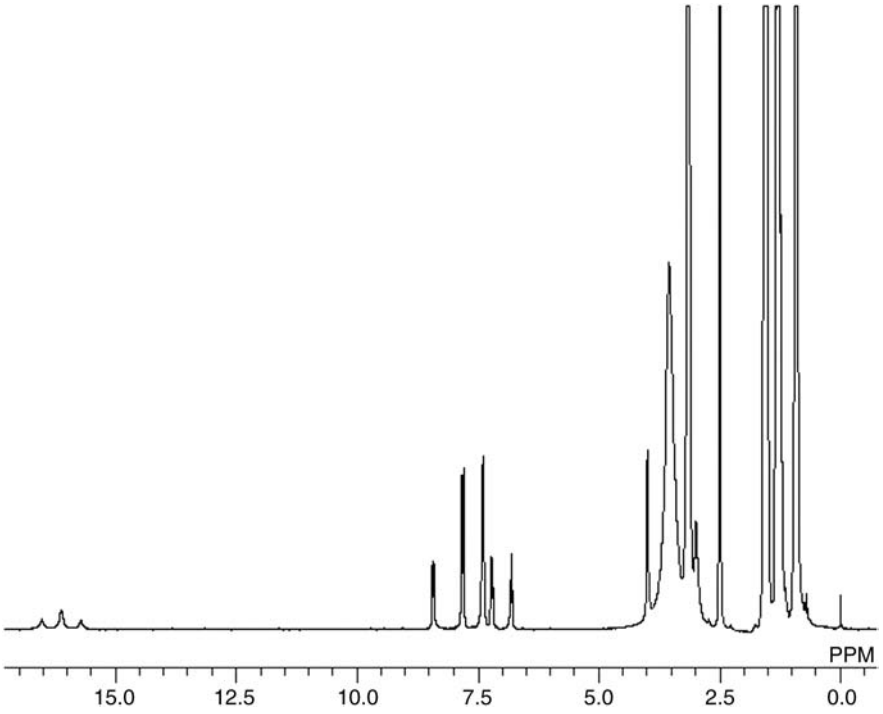

Figure 7. Appearance of a peak at δ 16 ppm corresponding to $[HF_2]^-$ ion in ^{1}H NMR on addition of 12 equivalents of TBAF to DMSO-d_6 solution of **4d**.

simply being H-bonded to a terminally attached potential H-bond donor (—NH_2 group).

2.1.2.2 With dihydrogen phosphate ions. For dihydrogen phosphate ions, only **4d** shows some significant recognition and the bathochromic shift of band starts with rather higher equivalents, i.e. from 20 equivalents onwards (Figure S16 of the Supplementary Information, available online). At higher concentrations of the anion, the band appears at ~474 nm, again signifying deprotonation. The ^{1}H NMR spectrum (Figure S17 of the Supplementary Information, available online) also shows absence of ureidic protons.

The H-bonding tendencies of a given donor group (e.g. the N—H fragment of urea/thiourea) depend upon its protonic acidity. Thiourea is more acidic than urea ($pK_a = 21.1$ and 26.9, respectively in DMSO) (*27*); thus, it is expected that thiourea- containing receptors bind more strongly with anions than their urea-based counterparts through H-bond interactions. Apart from that, the basicity and geometry of the anion, stability of HX_2^- anion formed, pre-organisation of the receptor and polarity of the solvent are also known to be important factors for deciding the specific anion selectivity and sensitivity. In the present case, the thiourea derivatives form stable H-bonded complexes with anions such on $H_2PO_4^-$ and F^-, which is not strictly according to the basicity scale because acetate is a stronger base than dihydrogenphosphate (*28*). It shows that the pre-organisation effect of the tripodal and dipodal structures of the receptors is effective in the recognition of the tetrahedral $H_2PO_4^-$ and preferably the smaller spherical F^- ions over other anions. The pre-organisation effect of the tripodal structure has been earlier found to be effective in reversing the selectivity pattern of these two oxoanions in contrast to their basicity pattern (*29*). For the F^- ion, flexibility of these podands seems to be good enough to stabilise a particular conformer that is a paradigm of the best compromise between the basicity and geometry and size of the guest anion, with dipodal receptor **5a** being much better than the tripodal ones. Such adaptability of these podands gives a very stable, symmetrical 1:1 H-bonded, *endo*-complex (*5c*) in which the fluoride anion is supposed to reside inside the pseudo-cavity formed by the receptor.

For the urea-based receptors, on the other hand, such a conformation that can bring the widely separated binding units to converge together is also induced only by the F^- ions or to a much lesser extent by the $H_2PO_4^-$ anion. However, they are probably not capable of encapsulaing the smaller F^- ion as efficiently as their thiourea counterparts. The latter besides having bigger S atoms in them face no risk of loosing stability on the account of intramolecular (Ar—H···O═C) H-bonding interactions on effectively encapsulating the anion and are thus more or less pre-organised for binding with F^- ion. Thus, the urea derivatives do not allow any significant colorimetric action from the receptors at lower concentrations of the anion. At higher concentrations, the receptors are simply deprotonated and a considerable concurrent change in the dipole moment of the systems produces larger bathochromic shift in the spectra. Again, the deprotonation is dependent on the basicity of the anion, hence bathochromic shift is much less for $H_2PO_4^-$ ion.

3. Conclusions

In this work, we have reported seven neutral tripodal and dipodal receptors based on urea/thiourea, which have the potential to act as colorimetric anion sensors. Thiourea derivatives are proved to be very selective and sensitive towards small and spherical F^- ion with some interference from tetrahedral $H_2PO_4^-$ ions. Their recognition act involves stable H-bonded complexes. Urea derivatives, on the other hand, are also selective for F^- ions but have very low sensitivity and work only at relatively higher concentrations of the anion. Their sensing process is simply based upon Lewis acid–base reaction which is completely reversible with time. The difference in the activity of the thiourea/urea receptors is highly dependent on their intrinsic acidity and conformational adaptability for F^- ions. The more acidic thiourea receptors are more flexible and adapt well to form H-bonded complexes. Urea derivatives, on the contrary, have to undergo significant conformational changes and they loose their intramolecular (—C═O···H_f) H-bonding if they have to give a tight size fit to small F^- ions that are not suitable to encapsulating the anion effectively. Hence, their 1:1 H-bonded complexes are not very stable. At higher concentrations, however, these receptors undergo deprotonation concomitant with a colorimetric change which is completely reversible. In general, the tripodal pseudo-cavity being generated in the 'three up' conformation of the hexasubstituted central benzene core in solution seems more suitable to hold either spherical F^- ion or tetrahedral dihydrogen phosphate anion over more basic 'Y'-shaped acetate ions, signifying the host–guest complementarity.

4. Experimental

4.1 General

All the commercially available chemicals were purchased from Aldrich and used without further purification**.** All solvents were dried by standard methods. Unless otherwise specified, chemicals were purchased from commercial suppliers and used without further purification. TLC was carried out on glass sheets pre-coated with silica gel. The ^{1}H and ^{13}C NMR spectra were carried out in $CDCl_3$ and DMSO-d_6 with TMS as an internal reference, on a 300 and 400 MHz NMR spectrometer. The infrared spectrum (KBr pellet) was recorded using PYE Unicam IR spectrophotometer in the range 400–4000 cm^{-1}. The

electronic absorption spectra were recorded on a Shimadzu Phramaspec UV-1700 UV–vis spectrophotometer. Compounds **2a** and **2b** were commercially available. The tripodal amines **1a** and **1b** were prepared as already reported by us (*21*).

4.2 Preparation of receptors

*4.2.1 Dipodal amine (**3**)*

Dipodal amine **3** was prepared by taking K_2CO_3 in dry acetonitrile along with 2-aminothiophenol (246 mg, 2.2 mmol). The reaction mixture was refluxed for 20 min and then dibromide (*30*) (306 mg, 1 mmol) was carefully added to it. The reaction mixture was refluxed for the next 8 h and the progress of the reaction was monitored by TLC. Upon completion of the reaction, K_2CO_3 was filtered off and acetonitrile was evaporated. The crude product was recrystallised from chloroform–methanol solvent mixture to get a pure white product. Yield 58–60%. mp 118°C; found: C, 69.91; H, 6.91; N, 6.81. Calcd for $C_{23}H_{26}N_2S_2$: C, 70.01; H, 6.64; N, 7.10%; IR (KBr, cm^{-1}) 3427 (s), 1301 (s), 1020 (s); δ_H (300 MHz, $CDCl_3$, Me_4Si) 2.30 (s, —CH_3, 6H), 2.33 (s, —CH_3, 3H), 3.99 (s, —CH_2, 4H), 4.36 (s, —NH_2, 4H), 6.62–6.67 (m, Ar, 4H), 6.83 (s, phenyl, 1H), 7.15 (t, Ar, 2H, $J = 9.3$ Hz), 7.35 (d, Ar, 1H, $J = 6.9$Hz); δ_C (75 MHz, $CDCl_3$, Me_4Si) 15.17, 19.73, 34.99, 114.84, 118.32, 118.60, 129.93, 130.22, 132.08, 136.12, 136.24, 136.46, 148.54.

*4.2.2 Tripodal ligand (**4a**)*

Compound **4a** was prepared by dissolving **1a** (*21a*) (531 mg, 1.0 mmol) and **2a** (577 mg, 3.2 mmol) in dry dichloromethane separately. The two solutions were mixed and the reaction mixture was stirred at room temperature. After 30 min, yellow precipitates separated out. These were filtered and dried under vacuum. Yield 74%. mp 134–138°C; found: C, 57.41; H, 4.45; N, 11.13; S, 17.99. Calcd for $C_{51}H_{45}N_9O_6S_6$: C, 57.12; H, 4.23; N, 11.76; S, 17.94%; IR (KBr, cm^{-1}) 1507 (C═S), 3216 (NH); δ_H (300 MHz, DMSO + $CDCl_3$, Me_4Si) 2.40 (s, —CH_3, 9H), 4.09 (s, —CH_2, 6H), 7.23 (br, Ar, 6H), 7.45–7.46 (br, Ar, 3H), 7.57 (br, Ar, 3H), 7.959 (d, Ar, 6H, $J = 9.0$ Hz), 8.13 (d, Ar, 6H, $J = 9.3$ Hz), 9.50 (s, —NH, 3H), 10.42 (s, —NH, 3H); δ_C (75 MHz, DMSO, Me_4Si) 15.76, 33.86, 54.97, 112.58, 121.78, 124.40, 126.54, 127.66, 128.88, 131.17, 134.70, 136.47, 137.22, 142.54, 146.20, 180.35.

*4.2.3 Tripodal ligand (**4b**)*

Compound **4b** was prepared by the same method as that of **4a** except that (573 mg, 1.0 mmol) **1b** (*21b*) was taken instead of **1a**. Pure product is solid and light yellow. Yield 52%. mp 125°C; found: C, 58.78; H, 4.78; N, 10.97; S, 17.47. Calcd for $C_{54}H_{51}N_9O_6S_6$: C, 58.20; H, 4.61; N, 11.31; S, 17.26%; IR (KBr, cm^{-1}) 1498 (C═S), 3065 (NH); δ_H (300 MHz, DMSO + $CDCl_3$, Me_4Si) 1.20 (br, —CH_3, 9H), 2.90 (br, —CH_2, 6H), 4.08 (s, —CH_2, 6H), 7.31 (br, Ar, 6H), 7.47 (br, Ar, 3H), 7.55–7.57 (br, Ar, 3H), 7.98–7.15 (m, Ar, 12H), 9.46 (s, —NH, 3H), 10.44 (s, —NH, 3H); δ_C (75 MHz, DMSO, Me_4Si) 15.01, 21.65, 32.26, 119.85, 122.82, 125.19, 126.12, 127.77, 128.74, 132.51, 135.75, 141.40, 142.04, 144.69, 144.00, 178.97.

*4.2.4 Tripodal ligand (**4c**)*

Compound **4c** was prepared by dissolving **1a** (531 mg, 1.0 mmol) and **2b** (525.18 mg, 3.2 mmol) in dry dichloromethane separately. The two solutions were mixed and the reaction mixture was stirred for 1 h at room temperature. After completion of the reaction, solvent was evaporated and product was recrystallised from methanol. Pure product is solid and yellow. Yield 40%. mp 267°C; found: C, 59.49; H, 4.79; N, 12.86; S, 9.87. Calcd for $C_{51}H_{45}N_9O_9S_3$: C, 59.81; H, 4.43; N, 12.31; S, 9.39%; IR (KBr, cm^{-1}) 1635 (C═O), 3500 (NH); δ_H (300 MHz, DMSO + $CDCl_3$, Me_4Si) 2.07 (s, —CH_3, 9H), 4.0 (s, —CH_2, 6H), 7.05 (d, Ar, 3H, $J = 8.1$ Hz), 7.36–7.39 (m, Ar, 6H), 7.65 (d, Ar, 6H, $J = 9.3$ Hz), 7.86 (d, Ar, 3H, $J = 8.4$ Hz), 7.18 (d, Ar, 6H, $J = 9$ Hz), 8.35 (s, —NH, 3H), 10.0 (s, —NH, 3H); δ_C (75 MHz, DMSO, Me_4Si) 15.65 (—CH_3), 34.85, 54.97, 117.47, 121.91, 124.12, 125.27, 128.15, 131.40, 132.37, 138.28, 141.15, 143.00, 146.40, 151.96, 187.17.

*4.2.5 Tripodal ligand (**4d**)*

Compound **4d** was prepared by the same method as that of **4c** except that (573 mg, 1.0 mmol) **1b** was taken instead of **1a**. Pure product is solid and light yellow. Yield 51%. mp 210°C; found: C, 60.21; H, 4.67; N, 11.27; S, 8.87. Calcd for $C_{54}H_{51}N_9O_9S_3$: C, 60.83; H, 4.82; N, 11.82; S, 9.02%; IR (KBr, cm^{-1}) 1501 (C═O), 3290 (NH); δ_H (300 MHz, DMSO + $CDCl_3$, Me_4Si) 1.20 (br, —CH_3, 9H), 2.94 (br, —CH_2, 6H), 4.07 (s, —CH_2, 6H), 7.13 (d, Ar, 3H, $J = 7.2$ Hz), 7.37 (d, Ar, 3H, $J = 6.9$ Hz), 7.42–7.45 (m, Ar, 3H), 7.66 (d, Ar, 6H, $J = 8.7$ Hz), 7.92–7.95 (m, Ar, 3H), 7.95–8.11 (m, Ar, 6H), 8.30 (s, —NH, 3H), 9.87 (s, —NH, 3H); δ_C (75 MHz, DMSO, Me_4Si) 14.50, 21.43, 32.24, 115.80, 121.13, 122.82, 123.40, 125.37, 126.16, 128.84, 129.42, 136.04, 139.80, 141.68, 144.78, 150.7.

*4.2.6 Tripodal ligand (**4e**)*

Compound **4e** was prepared by dissolving **1a** (531 mg, 1.0 mmol) and **2b** (361.06 mg, 2.2 mmol) in dry dichloromethane separately. The two solutions were mixed and the reaction mixture was stirred at room temperature. After 30 min, the yellow precipitate separated. This was filtered and dried under vacuum. Yield 68%. mp 215°C; found: C,

61.89; H, 5.09; N, 11.86; S, 10.87. Calcd for $C_{54}H_{51}N_9O_9S_3$: C, 61.45; H, 4.81; N, 11.40; S, 11.19%; IR (KBr, cm^{-1}) 1497 (C═O), 3285 (NH); δ_H (300 MHz, DMSO + $CDCl_3$, Me_4Si) 2.21 (s, —CH_3, 3H), 2.25 (s, —CH_3, 3H), 2.29 (s, —CH_3, 3H), 3.87 (s, —CH_2, 2H), 4.02 (s, —CH_2, 2H), 4.07 (s, —CH_2, 2H), 5.28 (s, —NH_2, 2H), 6.50 (t, Ar, 1H, $J = 7.2$ Hz), 6.72 (d, Ar, 1H, $J = 8.1$ Hz), 7.0–7.15 (m, Ar, 4H), 7.25–7.32 (m, Ar, 2H), 7.36–7.43 (m, Ar, 2H), 7.64–7.68 (m, Ar, 4H), 7.89 (t, Ar, 2H, $J = 8.4$ Hz), 8.16–8.23 (m, Ar, 4H), 8.35 (s, —NH, 1H), 8.37 (s, —NH, 1H), 10.0 (s, —NH, 1H) 10.03 (s, —NH, 1H); δ_C (75 MHz, DMSO, Me_4Si) 15.79, 34.84, 79.41, 85.40, 114.47, 116.94, 117.04, 117.32, 119.37, 119.62, 123.50, 126.12, 125.27, 128.34, 129.83, 130.67, 132.25, 132.45, 133.82, 134.80, 135.10, 135.80, 136.14, 143.0, 145.80, 149.30, 149.46, 152.96, 163.26.

4.2.7 *Dipodal ligand (**5a**)*

Compound **5a** was prepared by dissolving **3** (394 mg, 1.0 mmol) and **2a** (577 mg, 3.2) in dichloromethane. The mixture was stirred at room temperature. After 30 min, the yellow precipitates separated out which were filtered and dried under vacuum. Yield 51%. mp 158–160°C; found: C, 58.46; H, 4.83; N, 11.25; S, 17.87. Calcd for $C_{37}H_{34}N_6O_4S_4$: C, 58.86; H, 4.54; N, 11.13; S, 16.99%; IR (KBr, cm^{-1}) 1592 (C═S), 3171 (NH); δ_H (300 MHz, DMSO + $CDCl_3$, Me_4Si) 2.31 (s, —CH_3, 6H), 2.39 (s, —CH_3, 3H), 4.08 (s, —CH_2, 4H), 6.83 (s, phenyl, 1H), 7.28 (br, Ar, 4H), 7.47 (br, Ar, 2H), 7.62 (s, Ar, 2H), 7.98 (br, Ar, 4H), 8.14 (d, Ar, 4H, $J = 7.8$ Hz), 9.44 (s, —NH, 2H), 10.44 (s, —NH, 2H); δ_C (75 MHz, DMSO, Me_4Si) 14.98, 19.32, 33.18, 112.35, 121.51, 124.37, 126.37, 127.36, 128.62, 129.58, 129.97, 130.60, 134.61, 136.61, 137.25, 142.32, 146.10, 152.46.

4.2.8 *Dipodal ligand (**5b**)*

Compound **5b** was prepared by the same method as that of **5a** except that (525.18 mg, 3.2 mmol) **2b** was taken instead of **2a**. Pure product is solid and light yellow. Yield 77%. mp 140°C; found: C, 68.29; H, 5.02; N, 11.13; S, 8.51. Calcd for $C_{37}H_{34}N_6O_6S_2$: C, 61.48; H, 4.74; N, 11.63; S, 8.87%; IR (KBr, cm^{-1}) 1501 (C═S), 3308 (NH); δ_H (300 MHz, DMSO + $CDCl_3$, Me_4Si) 2.08 (s, —CH_3, 6H), 2.30 (s, —CH_3, 3H), 4.06 (s, —CH_2, 4H), 6.79 (s, phenyl, 1H), 7.03–7.06 (m, Ar, 2H), 7.27–7.31 (m, Ar, 2H), 7.39 (d, Ar, 2H, $J = 5.1$ Hz), 7.67 (d, Ar, 4H, $J = 6.9$ Hz), 7.93 (d, Ar, 2H, $J = 5.7$ Hz), 8.195 (d, Ar, 4H, $J = 6.9$ Hz), 8.41 (s, 2H, —NH), 10.08 (s, 2H, —NH); δ_C (75 MHz, DMSO, Me_4Si) 15.47, 19.68, 34.90, 117.98, 122.26, 124.67, 125.70, 126.13, 128.96, 130.38, 131.56, 133.62, 136.53, 136.73, 139.05, 141.65, 146.77, 152.46.

4.3 *Anion recognition studies*

Anion binding ability of receptors was determined by generally preparing solutions containing 10 μM of receptor (unless specified otherwise) and 100 μM of tetrabutylammonium salts of a particular anion in DMSO. Changes in the electronic absorption spectra of the receptors were observed. The anion binding ability of receptors with TBAF was investigated using UV–vis titration experiments.

Acknowledgements

GH thanks the CSIR (India) for research grant No. 01 (2104)/07/EMR-II. VKB and SS thank CSIR and UGC for fellowships.

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