Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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First published on: 16 July 2007

To cite this Article Kumar, Manoj , babu, J. Nagendra , Bhalla, Vandana and Athwal, Navdeep Singh(2007) 'Visible Colorimetric Sensor for Fluoride Ion Based on *o*-Phenylenediamine', Supramolecular Chemistry, 19: 7, 511 — 516, First published on: 16 July 2007 (iFirst)

To link to this Article: DOI: 10.1080/10610270601145436

URL: http://dx.doi.org/10.1080/10610270601145436

Supramolecular Chemistry, October–November 2007 Vol. 19(7), pp. 511–516

Taylor & Francis
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Visible Colorimetric Sensor for Fluoride Ion Based on *o*-Phenylenediamine

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(Received 19 October 2006; Accepted 29 November 2006)

A new chromogenic receptor based on 1,2-phenylene derivative containing thiourea moieties is synthesized and examined for its anion binding ability by UV–Vis and ^{1}H NMR studies. The results show that the receptor has selective colorimetric sensing of fluoride over all other anions like chloride, bromide, iodide, nitrate, hydrogen sulphate and acetate.

Keywords: Colorimetric sensor; Thiourea; *o*-Phenylenediamine; Fluoride ion

INTRODUCTION

The selective recognition of anions play an important role in biology, medicine, catalysis and environment studies [1–3]. The basic design of anionic receptors usually has groups like amides [4–6], ureas [7], pyrroles [8,9] and thioureas [10,11] which donate a hydrogen bond to the anion and a sensing moiety which undergo spectroscopic or electrochemical change upon anion binding [12,13]. The receptors which undergo spectroscopic changes normally have fluorogenic [12,14] or chromogenic [12,15–17] moieties attached to the receptors by covalent bond. Receptors with fluorogenic subunits require expensive instrumentation for anion sensing which is their major limitation. On the other hand receptors with chromogenic subunits are interesting as the anion determination can be carried out easily with naked eye without requiring any expensive instrument. Gale [18] and Gunnlaugsson [19] developed a number of colorimetric anion sensors having urea/thiourea binding units in different structural scaffolds [10,11,20–22] and containing different types of chromogenic moieties like naphthalimide [23,24] and *p*-nitrophenyl [18]. Apart from this, chromogenic anion receptors containing azophenol [25], diazo group [26], anthraquinone [27] and acridinedione [28] have also been developed.

Among the biologically important anions, fluoride is of particular interest owing to its role in preventing dental caries [29], in the treatment for osteoporosis [30]. Further, these ions are also associated with nerve gases, in the analysis of drinking water and refinement of uranium used in the nuclear weapon manufacture. The excess of fluoride can lead to fluorosis [31–33], which is a type of fluoride toxicity that generally manifests itself clinically in terms of increase in bone density. Thus, the diversity of its functions, both beneficial and otherwise, makes the detection of fluoride ion important. A number of receptors selective for fluoride ion have been reported [34–41], but there are a few number of visible colorimetric sensors for fluoride ions [42–45]. While this manuscript was in preparation, Gale *et al.* [46] and Kim *et al.* [47], reported *o*-phenylenediamine based receptors having urea moieties which selectively complex carboxylate and fluoride ions. In continuation of our research program for the synthesis of receptors [48–51] for soft metal ions we have now designed and synthesized a specific chemosensor for fluoride ion based on *o*-phenylenediamine which has thiourea moieties for interaction with the anion and a *p*-nitrophenyl groups as signaling units. The presence of electron withdrawing group is expected to increase the acidity of the thiourea protons and hence enhance their anion binding ability through hydrogen bonding.

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ISSN 1061-0278 print/ISSN 1029-0478 online
DOI: 10.1080/10610270601145436

RESULTS AND DISCUSSION

Condensation of *o*-phenylenediamine **1** with 2.0 mol equiv. of *p*-nitrophenyl isothiocyanate **2** in refluxing tetrahydrofuran gave thiourea **3** in 52% yield (Scheme 1). The product separated as pure solid after adding hexane to the tetrahydrofuran solution, which gave satisfactory elemental analysis after one crystallization. The structure of compound **3** was confirmed from its spectroscopic and analytical data. The IR spectrum of **3** showed a C=S stretching band at 1300 cm^{-1} which indicates that the condensation has taken place. This was confirmed by FAB mass spectrum that showed a parent ion peak corresponding to 1:2 condensation products. The ^1H NMR spectrum of **3** showed two multiplets (2H each) due to *ortho*(H_e) and *meta*(H_f) hydrogens of phenylenediamine at δ 7.31–7.34 and 7.52–7.55, two doublets (4H each) due to the aromatic hydrogens (H_c and H_d) of *p*-nitrophenyl moiety at δ 7.90 and 8.20, a pair of singlets (2H each) due to thiourea protons (NH) at δ 9.67 and 10.63 respectively. These spectroscopic data corroborates the structure **3** for this compound.

UV–VIS STUDIES OF COMPOUND 3

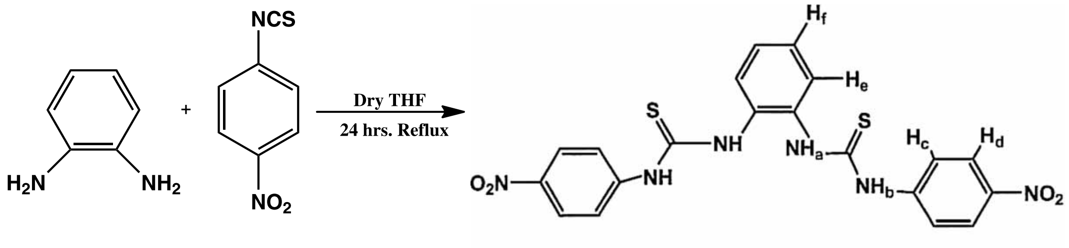
The UV–Vis spectroscopy has been extensively used to study a coordination system with a spectral change, which is a convenient method to determine the association constants of supramolecular complexes [52]. Receptor **3** contains four thiourea NH groups as hydrogen bond donor for anions and two *p*-nitrophenyl groups for monitoring the anion binding event. The recognition properties of receptor **3** (5×10^{-5} M) with various anions such as fluoride, chloride, bromide, iodide, acetate were monitored by UV–Vis spectroscopy in dry acetonitrile. In each case the counter cation was tetrabutylammonium ion. In the absence of anions, the absorption spectrum of **3** is characterized by the presence of one maxima at 338 nm. The absorption spectra of **3** in the presence of different anions is shown in Fig. 1.

From Fig. 1, it is clear that fluoride and acetate anions interact with the host **3**. The binding ability of **3** with fluoride and acetate ion was investigated by carrying out UV–Vis titrations. It was found that the UV–Vis absorption band of **3** in acetonitrile undergoes a red shift ($\Delta\lambda$ 119 nm) as a fluoride ion is complexed. Similarly, a new peak at 397 nm was observed in the case of acetate ions. This indicates that the fluoride and acetate ions were interacting with the receptor **3** with a different binding mode. The binding ability of **3** with fluoride and acetate ions was investigated by carrying out UV titrations. Upon addition of increasing amounts of tetrabutylammonium fluoride to the solution of **3**, a new peak appeared at 457 nm (Fig. 2). When fluoride ions come in contact with compound **3**, the intermolecular proton transfer takes place between thioureido nitrogen ($N{-}H_b$) and fluoride ion.

The modulation in the electron donating capabilities of the thioureido nitrogen ($N{-}H_b$) in the presence and in the absence of fluoride directly influences the intramolecular charge transfer (ICT) from the thioureido nitrogen atom ($N{-}H_b$) to the electron deficient *p*-nitrophenyl moiety [53]. In the absence of fluoride, ICT is inefficient while in the presence of fluoride the extent of ICT from thioureido nitrogen atom is enhanced facilitated by an intermolecular proton transfer from thioureido nitrogen ($N{-}H_b$) to fluoride ion.

Thus, we propose that the spectral changes in Fig. 2 are due to deprotonation of thiourea proton ($N{-}H_b$), this suggests that a negatively charged *p*-nitroanilide ion was formed, which causes a significant increase in the charge density on thioureido nitrogen atom. This enhanced the charge-transfer interactions between electron-rich and electron deficient moieties resulting in visible colour change [54] (Scheme 2). Similar results were obtained when relatively strong base Bu_4NOH was specifically employed. This further confirms our suspicion that the proton transfer between the thioureido group ($N{-}H_b$) of the sensor and the fluoride ions is responsible for the pronounced colour change.

Other examples of deprotonation of neutral hydrogen bond donor anion receptor systems with fluoride ions have been reported by Gale [18,55–57], Gunnlaugsson [19,58] and Fabbrizzi [59–61].



1 2 3

SCHEME 1 Synthesis of thioured derivative **3**.

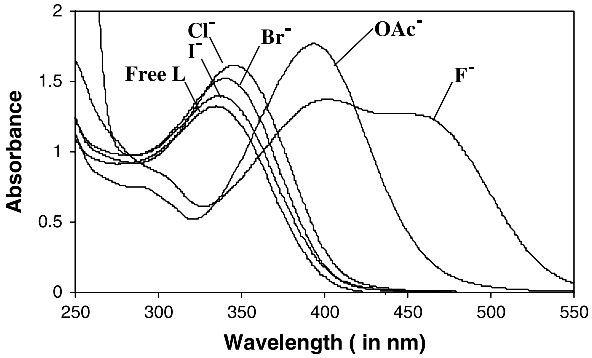


FIGURE 1 Absorption spectra of **3** in CH_3CN (5×10^{-5} M) upon addition of 10 Eq. of different anions.

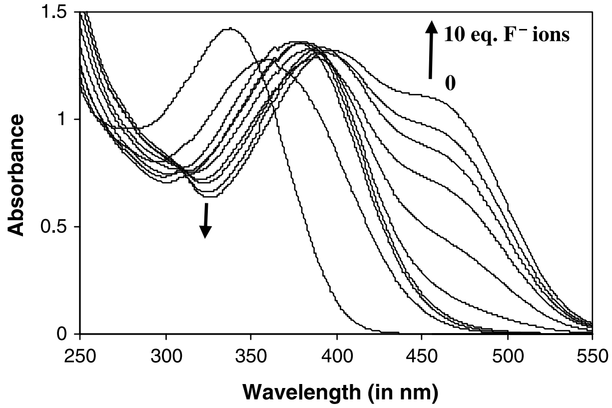


FIGURE 2 Absorption spectra of **3** (5×10^{-5} M) upon addition of tetrabutylammonium fluoride (0–10 Eq.) in CH_3CN.

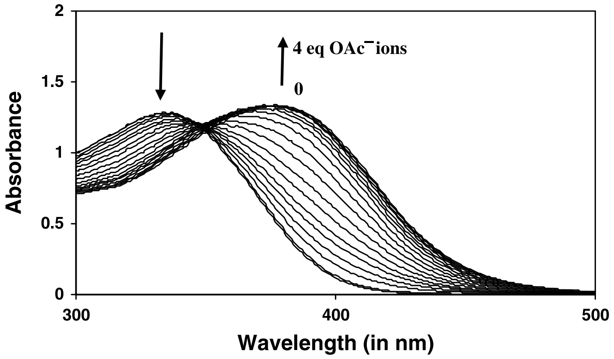


FIGURE 3 Absorption spectra of **3** (5×10^{-5} M) upon addition of tetrabutylammonium Acetate (0–4 Eq.) in CH_3CN.

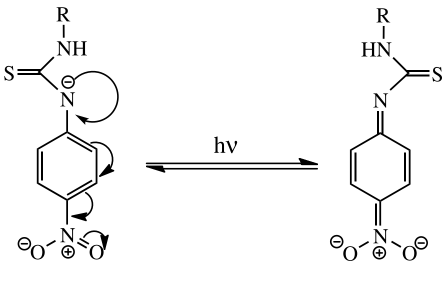
Many of these processes were recognised due to the colour changes that can occur upon deprotonation.

Upon addition of increasing amounts of tetrabutylammonium acetate to the solution of **3**, the absorption peak at 338 nm decreases while a new peak at 397 nm is appeared with a clear isosbestic point at 357 nm (Fig. 3). The isosbestic point in UV spectras indicates that there is a balance in the solution and the complex has been formed between the host and the guest. We propose that the new absorption band at 397 nm can be ascribed to charge transfer interactions between the electron- rich nitrogen atoms of the thiourea moieties and the electron deficient *p*-nitrophenyl units. When the acetate ions complex with compound **3**, hydrogen bonds were formed to form stable complex as a result of which the electron density in the supramolecular complex was considerably enhanced. This enhanced the charge interactions between electron-rich and electron deficient moieties resulting in visible colour change [54].

The stoichiometry of the **3-OAc⁻** complex was determined by the method of continuous variation. The total concentration of the compound **3** and OAc^- was constant (1.0×10^{-4} M), with a continuously varying molar fraction of guest ($[OAc^-]/[3] + [OAc^-]$).

Figure 4 shows the Job's plot of compound **3** with OAc^- ion at 397 nm. The absorbance at 397 nm approaches a maximum when the molar fraction of OAc^- is between 0.6–0.7, which means **3** and OAc^- formed a 1:2 complex.

Analysis of the UV-titrations of compound **3** with OAc^- ions were performed by means of SPECFIT programme (global analysis system V3.0 for 32-bit Window system), which uses singular value decomposition and non-linear regression modelling by the Leverberg–Marquardt method [62]. The global analysis showed that the titration curves



SCHEME 2 Charge transfer transition occuring in the deprotonated form of compound **3**.

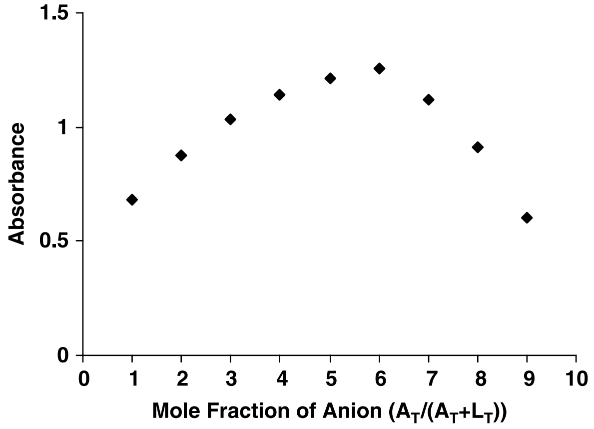


FIGURE 4 Job's plot of compound **3** with acetate ion. The total concentration $[3] + [OAc^-] = 1 \times 10^{-4}$ M.

TABLE I Binding constants of compound **3** with acetate anions in CH_3CN as determined from UV–Vis spectral data analysed by SPECFIT\32

	OAc^-	
Anion	$\log K_1$	$\log K_2$
	5.97	2.75

were consistent with the formation of two complexes, namely 1:1 and 1:2 (Ligand: Anion). The binding constants K_1 and K_2 of the sucessive equilibria were obtained from the titration data, analyzed by SPECFIT are given in Table I.

A noticeable colour change could be observed by naked eye by mixing the receptor **3** with different anions as shown in Fig. 5. Upon addition of F^- ion there is remarkable colour change from light yellow to red. On the other hand with OAc^- ion the colour changes from light yellow to light orange. However, on addition of other anions (Cl^-, Br^-, I^-, NO_3^-, HSO_4^-) no detectable colour changes were observed. Thus, there is a clear naked eye detection of fluoride and acetate ion.

^{1}H NMR STUDIES

^{1}H NMR spectroscopy has been widely used to investigate receptor substrate interactions as it provides details of interactions between the host and the guest. To evaluate the intermolecular interactions between the compound **3** with acetate and fluoride anions, we carried out ^{1}H NMR studies in DMSO-d_6. The addition of one equivalent of tetrabutylammonium fluoride to a solution of compound **3** in DMSO-d_6 results in complexation induced shift of different protons of compound **3** (Fig. 6).

The multiplets due to H_e and H_f protons of the *o*-phenylene moiety are shifted upfield by 0.14 ppm and 0.27 ppm respectively. This upfield shift could be the result of enhanced resonance of phenyl ring from the anionic character of thiourea nitrogen. The thioureido protons NH_b disappear upon addition of F^- ion while NH_a protons show a large downfield shift of 1.0 ppm. The disappearance of NH_b proton clearly indicate that the proton transfer interaction between compound **3** and F^- involve the thioureido proton. However, when more than one equivalent of fluoride ions were added H_f protons

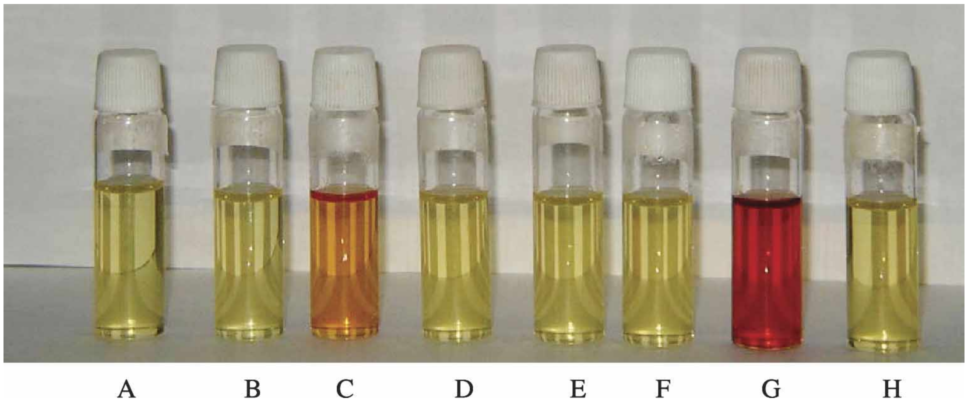


FIGURE 5 Colour changes of compound **3** (5×10^{-5} M) in CH_3CN upon addition of tetrabutylammonium anion (5×10^{-4} M). A = free ligand, B = nitrate, C = acetate, D = iodide, E = bromide, F = chloride, G = fluoride, H = hydrogen sulphate (colour in online version).

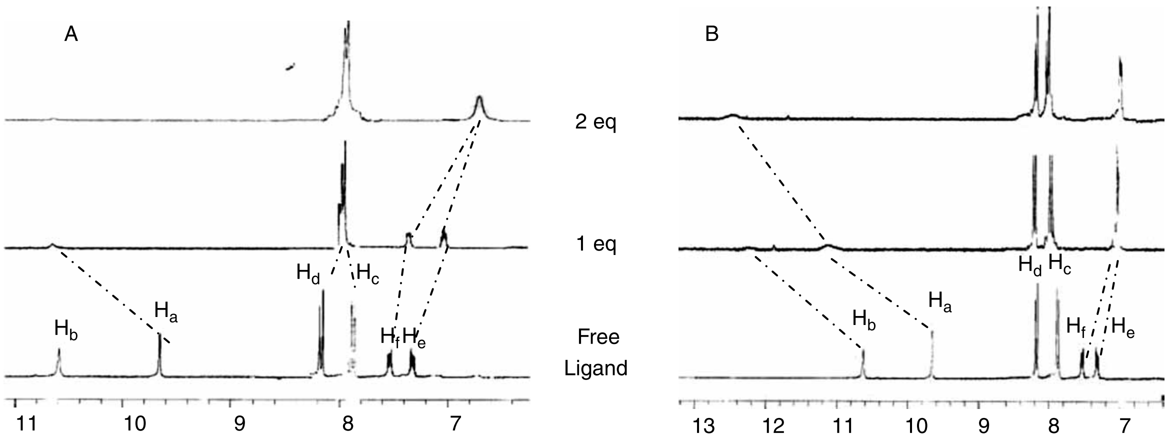


FIGURE 6 ^{1}H-NMR spectra of compound **3** in presence of (**A**) tetrabutylammonium fluoride (0–2 Eq.) (**B**) tetrabutylammonium acetate (0–2 Eq.) in DMSO-d_6.

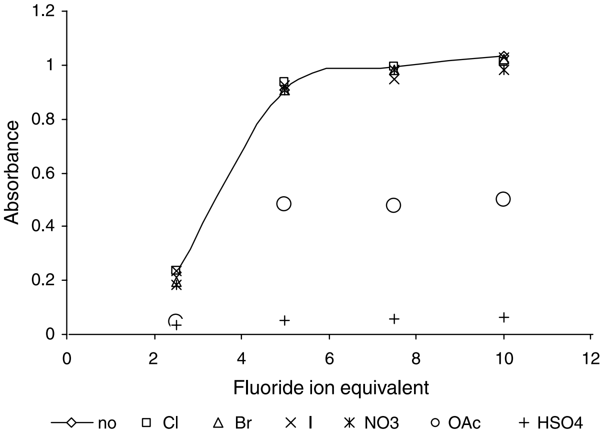


FIGURE 7 Absorbance of compound **3** (5×10^{-5} M) to various equivalents of fluoride (2.5, 5, 7.5, 10 Eq.) in the presence of interfering anions (10 Eq.) at $\lambda_{max} = 457$ nm. In CH_3CN.

were further shifted upfield by 0.59 ppm and all the thioureido NH protons disappeared. The addition of one equivalent of tetrabutylammonium acetate ion to compound **3** showed remarkable changes in the NMR spectra. The thioureido protons NH_a and NH_b shifted downfield by 1.48 ppm and 1.62 ppm respectively. H_e and H_f protons of phenylene moiety shifted upfield by 0.15 ppm and 0.27 ppm respectively. On adding two equivalents of acetate anion, H_e and H_f protons were further shifted upfield by 0.20 ppm and 0.32 ppm respectively. The H_c protons were shifted downfield by 0.21 ppm, while NH_a protons were further shifted downfield by 3.04 ppm. This indicates the complex between compound **3** and acetate anion has been formed by hydrogen bonding.

To test the practical applicability of compound **3** as F^- selective chromogenic sensor competitive experiments were carried out in the presence of F^- at variable equivalents namely 0.125, 0.250, 0.375, 0.50 mM mixed with various background anions such as Cl^-, Br^-, I^-, OAc^-, HSO_4^- and NO_3^- ions at 0.50 mM respectively. As shown in Fig. 7 except for HSO_4^- and OAc^-, other background anions had small or no obvious interference with the detection of F^- ions. These results suggest that compound **3** could be used as a potential F^- selective colorimeric sensor.

EXPERIMENTAL

All reagents were purchased from Aldrich/Fluka and used without further purification. Acetonitrile was dried using P_2O_5 followed by a treatment with K_2CO_3 and CaH_2. UV Spectra was recorded on SCHIMADZU UV-1601 spectrophotometer, with a quartz cuvette (path length: 1 cm). The cell holder was thermostated at 25°C. ^1H NMR spectra were recorded on JEOL-FT NMR-AL 300 MHz spectrophotometer using DMSO-d_6 as solvent and TMS as internal standard. Solutions of compound **3** and tetrabutylammonium anions for UV studies were prepared in CH_3CN AR grade. All spectrophotometric titration curve were fitted with SPECFIT\32 software.

Synthesis of 1,1′-(1,2-Phenylene)bis(3-[4-nitrophenyl])thiourea (3)

1,2-diaminobenzene (216 mg, 2.0 mmol) was dissolved in dry THF (15.0 ml) and then 4-nitrophenyl isothiocyanate (720 mg, 4.0 mmol) was added and the reaction mixture refluxed at 60–70°C for 24 hrs. After the completion of reaction (TLC), the volume of the solvent was reduced to 5 ml and then about 20 ml of hexane was added. A yellow coloured precipitates were formed which were filtered, washed with hexane and recrystallised using tetrahydofuran and methanol mixture (1:1). m.p.: 220°C; Yield: (0.480 g, 52%); ^1H NMR (300 MHz, DMSO-d_6): δ 7.31–7.34 (m, 2H, H_e), 7.52–7.55 (m, 2H, H_f), 7.90 (d, J = 14.7 Hz, 4H, H_d), 8.20 (d, J = 15.9 Hz, 4H, H_c), 9.67 (s, 2H, NH_a), 10.63, (s, 2H, NH_b); Anal. Calcd for $C_{20}H_{16}S_2N_6O_4$: C, 51.28; H, 3.41; N, 17.94; Found: C, 51.42; H, 3.49; N, 17.75; IR (KBr) ν_{max} cm^{-1} 1090 (C=S), 1300 (NO_2), 3150 (NH). FAB-MS m/z 469(M + 1)$^+$.

UV Studies

UV–Vis titrations were carried out by adding varying amounts of the anions (fluoride and acetate) to the solution of compound **3** (5×10^{-5} M) and the UV spectra of the resulting solutions were recorded.

Determination of Stoichiometry of the Acetate Complex

The stoichiometry was determined by the continuous variation method (Job's Plot). The ligand **3** and tetrabutylammonium acetate were dissolved in dry CH_3CN separately at appropriate concentrations, which were then mixed and made up with the solvent to control the concentrations. The sum of the total concentration of the ligand $[L]_T$ and anion $[A^-]_T$ namely $[L]_T + [A^-]_T$ was maintained to be 0.1 mM in CH_3CN. At the same time, the ratio $[L]_T/[A^-]_T$ was varied from 1:9 to 9:1. After recording the UV-spectrum of these solutions, the absorbance value at 397 nm respectively for acetate ion were plotted against the mole fraction of the anions. The maximum was observed at $[A^-]_T/[L]_T + [A^-]_T$ between 0.6–0.7 which implied the stoichiometry to be 1:2 for acetate ions.

CONCLUSION

In conclusion a new colorimetric sensor based on *o*-phenylenediamine having thiourea moieties is synthesized by the reaction of *o*-phenylenediamine **1** and the *p*-nitrophenyl isothiocyanate **2**. The receptor **3** selectively recognizes biologically important acetate and fluoride ions over Cl^-, Br^-, I^-, NO_3^- and HSO_4^- ions in acetonitrile. The receptor also shows naked eye detection of F^- and OAc^-. There was distinct colour change from light yellow to red and light yellow to light orange when fluoride and acetate ions were added to receptor **3**. Thus we have shown that a simple anion receptor in which 4-nitrophenyl thiourea binding site is attached to a simple benzene ring is a suitable colorimetric sensor for fluoride and acetate ions.

Acknowledgements

MK and VB are thankful to CSIR (New Delhi) for financial support [project no. 01(1934)/04/EMR-II]. JNB is thankful to CSIR for a junior research fellowship. We are also thankful to Central Drug Research Institute (CDRI), Lucknow, for FAB mass spectra, DST for support under FIST programme, UGC for SAP programme and Guru Nanak Dev University for providing research facilities.

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