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S. L. Ashok Kumar[a], M. Saravana Kumar[a], P. B. Sreeja[b], A. Sreekanth[a]*

[a]Department of Chemistry, Centre of Excellence in Corrosion and Surface Engineering, National Institute of Technology- Tiruchirappalli, Tiruchirappalli 620015, Tamilnadu, India.

[b]Department of Chemistry, Chirst University, Bangalore- 560029, Karnataka, India.

*1 Corresponding Author
Dr. A. Sreekanth, Assistant Professor, Department of Chemistry, National Institute of Technology-Tiruchirappalli, Tiruchirappalli-620015, Tamilnadu, India
E-mail: sreekanth@nitt.edu
Tel: +91 431 2503642
Fax: +91 431 2500133

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S. L. Ashok Kumar[a], M. Saravana Kumar[a], P. B. Sreeja[b], A. Sreekanth[a]*

[a]Department of Chemistry, Centre of Excellence in Corrosion and Surface Engineering, National Institute of Technology- Tiruchirappalli, Tiruchirappalli 620015, Tamilnadu, India.

[b]Department of Chemistry, Chirst University, Bangalore- 560029, Karnataka, India.

Abstract

Two novel heterocyclic thiosemicarbazone derivatives have been synthesized, and characterized, by means of spectroscopic and single crystal X-ray diffraction methods. Their chromophoric -fluorogenic response towards anions in competing solvent dimethyl sulfoxide (DMSO) was studied. The receptor shows selective recognition towards fluoride anion. The binding affinity of the receptors with fluoride anion was calculated using UV-visible and fluorescence spectroscopic techniques.

Keywords: Thiosemicarbazone, Heterocyclic, Chromophoric and fluorogenic sensor, Single Crystal XRD, UV-visible spectroscopy, Deprotonation.

1. Introduction

The design of host molecules that can recognize and sense anions selectively through visible, electrochemical and optical responses has received considerable interest in recent years because of the important roles played by the anions in biological, industrial, and environmental processes.[1-6] Molecules that possess functional groups such as amides, [7,8] ureas /thioureas, [9-12] guanidinium [13] and ammonium [14] derivatives have proven to be particularly effective in this regard as they are able to bind anions using directional hydrogen bonding interactions. The attachment of such functional groups with a suitable chromophoric part either covalently or intermolecularly provides a complete receptor that can intimate binding information either by a color change, fluorescence or both. Several reviews on anion binding in this regard using luminescent sensors have appeared. [15-17] Despite the significant development in this domain, the search for new luminescent sensors with structural simplicity and easy synthesis has recently been of keen interest in molecular recognition research. Thiosemicarbazones are thiourea derivatives having unique structural properties and chemical properties and have recently gained interest in the anion sensing. [18] They are easily synthesized in high yields and are found to be highly specific with low detection limits. We have synthesized two different chemosensors receptors for fluoride 2-acetlyfuran N(4)-cyclohexyl thiosemicarbazones (H_2L^1) and 2-acetlythiophene N(4)-cyclohexyl thiosemicarbazones (H_2L^2) (Figure 1) which function as dual mode sensors toward fluoride with much lower detection limits in biologically competing solvents like DMF and DMSO.

Figure 1

2. Experiment

2.1. Materials and Methods.

2-acetylfuran (Alfa), 2-acetylthiophene (Alfa), cyclohexyl isothiocyanate (Aldrich), and tetra-n-butylammonium (TBA) salts (Aldrich) were stored in vacuum desiccators containing self-indicating silica-gel and were used as received. Analytical grade DMSO and other solvents (Merck) were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III, 400 MHz in $CDCl_3$ at 298 K with TMS as an internal standard. FT- IR spectra were measured on a Perkin-Elmer FT-IR spectrometer using KBr pellets. UV- visible and Fluorescence spectra were recorded in 1 cm path length quartz cell on PG Instrument T90+

spectrophotometer and JASCO FP-8300 spectrofluorophotometer, respectively. Elemental analyses of both the receptor (H_2L^1 and H_2L^2) were carried out using Elementar Vario EL III CHNS.

2.2. General procedure: Ethanolic solutions of cyclohexyl isothiocyanate (0.706 g, 5 mmol) and hydrazine hydrate (0.250 g, 5 mmol) were mixed with constant stirring. The stirring was continued for 1 hour and then the white product, N(4)-cyclohexyl thiosemicarbazide formed was filtered, washed, dried and recrystallized from ethanol.

N(4)-cyclohexyl thiosemicarbazide (0.346 g, 2 mmol) was dissolved in methanol (30 mL) and was added to the appropriate ketones [2–acetylfuron (0.231 g, 2.1 mmol), 2–acetylthiophene (0.265 g, 2.1 mmol)] dissolved in methanol (5 mL), and the reaction mixture was continuously refluxed for 6 h after adding a few drops of acetic acid. The reaction mixture was kept aside for slow evaporation at room temperature. After one week time, the product has been isolated as a pale yellow solid in both the cases.

Receptor H_2L^1 (pale yellow). Yield: 89 %, M.P. 132-134^o C, Anal. Calc. for $C_{13}H_{19}N_3S_2$: C, 58.84; H, 7.22; N, 15.83; S, 12.08. Found: C, 58.57; H, 7.26; N, 15.45; S, 12.65 %. IR data (KBr, cm^{-1}) 1526 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.37 (4H, m, -CH_2), 1.48 (2H, m, -CH_2), 1.75 (4H, m, -CH_2), 2.24 (3H, s, CH_3), 4.30 (1H, m, -CH), 6.53 (2H, t, Ar), 6.72 (2H, d, Ar), 7.50 (2H, d, Ar), 8.47 (1H, br, HC–NH), 10.53 (1H, s, N–NH). ^{13}C NMR (100 MHz, $CDCl_3$): 176.22, 151.28, 149.15, 144.34, 137.99, 132.77, 53.18, 32.73, 25.52, 24.77, 12.50.

Receptor H_2L^2 (pale yellow). Fine yellow single crystals obtained upon slow evaporation of a solution of methanol at room temperature in 6 days were used for single crystal X-ray diffraction. Yield: 86 %, M.P. 216-218^o C, Anal. Calc. for $C_{13}H_{19}N_3S_2$: C, 55.59; H, 6.42; N, 14.53; S, 22.06. Found: C, 55.48; H, 6.80; N, 14.93; S, 22.79 %. IR data (KBr, cm^{-1}) 1529 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm) 1.30 (4H, m, -CH_2), 1.48 (2H, m, -CH_2), 1.75 (4H, m, -CH_2), 2.26 (3H, s, CH_3), 4.34 (1H, m, -CH), 7.03 (2H, t, Ar), 7.26 (2H, d, Ar), 7.33 (2H, d, Ar), 7.47 (1H, br, HC–NH), 8.42 (1H, s, N–NH). ^{13}C NMR (100 MHz, $CDCl_3$): 175.45, 142.75, 142.01, 128.00, 127.59, 127.17, 52.86, 32.52, 25.55, 24.55, 13.61.

2.3 X-ray crystallography.

Crystal H_2L^2 was mounted on a glass fibre and the intensity data were collected at room temperature (296 K) on a Bruker Kappa APEXII area-detector diffractometer equipped with

graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Unit cell dimensions and other parameters are listed in Table 1. All structures were solved by direct methods and refined by fullmatrix least-squares calculations with the SHELXTL-PLUS software package [19]. Absorption corrections were employed using SADABS (T_{max} 0.9597 and T_{min} 0.9404). The non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were found from the different Fourier map and refined isotropically.

Table 1

2.4. UV-visible and Fluorescence Titrations.

The stock solutions of receptors (1×10^{-3} mol L^{-1}) were prepared in DMSO. The TBA salts (F^-, Cl^-, Br^-, I^-, ClO_4^-, $H_2PO_4^-$, and AcO^-) solutions were prepared at a concentration of 1×10^{-2} mol L^{-1} in DMSO. Different equivalents of TBA salts (F^-, Cl^-, Br^-, I^-, ClO_4^-, $H_2PO_4^-$, and AcO^-) were added to the receptors and their corresponding UV- visible and fluorescence spectra were recorded at 298 K.

3. Result and Discussion

The structural formulae of receptors (H_2L^1 and H_2L^2) are shown in Figure 1. Both the receptors were well characterized by various analytical techniques such as, elemental analysis, UV- visible, FT–IR, ^1H, ^{13}C NMR and single crystal X-ray diffraction studies for H_2L^2. The elemental analyses found were in good agreement with the calculated values. Receptors were readily soluble in organic solvents such as DMF and DMSO. IR spectrum of the receptors showed characteristic stretching frequencies at 1526 (H_2L^1) and 1529 (H_2L^2), cm^{-1} ν(C=N) indicative of the newly formed azomethine group and stretching frequencies at 1213 (H_2L^1) and 1294 (H_2L^1) cm^{-1} ν(C=S) indicating that the thione form is dominating in the solid state. ^1H NMR spectrum of H_2L^1 showed two broad singlets at δ 8.47 and δ 10.53 ppm assignable to the NH protons present in the molecule, which disappears with the addition of D_2O. Similarly for H_2L^2 the corresponding two NH protons appeared at δ 7.47 and δ 8.42 respectively [20] which disappear with D_2O addition. H_2L^1 and H_2L^2 showed singlet protons at δ 2.27 and δ 2.26 corresponding to the ketone methyl group respectively. Receptors (H_2L^1, H_2L^2) heterocyclic aromatic ring protons appeared around δ 6.5–7.7 ppm accounting for two doublet protons and one triplet proton. The ^{13}C NMR spectrum of H_2L^1 and H_2L^2 showed well defined peaks at

176.22, 175.45 assignable to thione carbon (C=S) respectively. Azomethine carbon (–C=N) peaks appeared at δ 151.28, 142.75 respectively for H_2L^1 and H_2L^2.

Figure 1

3.1. Molecular and Crystal Structure of H_2L^2

The molecular structure of H_2L^2, along with the atom numbering scheme is given in Figure 2. The crystal data and structural refinement parameters are given in Table 1 and selected bond lengths and angles are given in Table 2. The receptor crystallized into a monoclinic lattice with the space group P21. The molecule exists in the E conformation with respect to the C5–N1 bond. However, the S2 and N1 atoms are in the E conformation with respect to the N2–C7 bond, and hence the thiosemicarbazone moiety as a whole exists in the EE conformation. This is contrary to the observations in 3-piperidyl and 3- hexamethyliminyl-di-2-pyridyl ketone thiosemicarbazones [21], which revealed a ZZ conformation for the thiosemicarbazone moiety. However, N4-methyl-di-2-pyridyl ketone thiosemicarbazone was observed to be in the ZE conformation [22]. In H_2L^1, the thiosemicarbazone moiety comprising of atoms N1, N2, C7, S2 and N3 is almost planar, with a maximum mean plane deviation of 0.0375(1) Å. A torsion angle of 174.48 (14) corresponding to the S2– C7–N2–N1 moiety implies a trans alignment of the thiocarbonyl S2 atom in H_2L^1. The azomethine bond, C5–N1 (1.281 (2) Å) is in conformity with a formal C=N double bond (1.28Å) and the C7–S2 bond distance of 1.671(2) Å, is very close to a formal C=S bond length (1.60Å) [23].

It confirms the existence of the thiosemicarbazone in the thione form in the solid state. The N2–N1 (1.368 (2)) and N3–C7 (1.322 (3)) bond distances in H_2L^2 are intermediate between formal single or double N–N and C–N bonds, giving evidence for an extended π delocalization along the thiosemicarbazone chain. In the molecule there exist intramolecular hydrogen bonding interaction, N2–H2A–S2 forming an eight-membered ring as clearly seen from the packing arrangement of the atoms as shown in Figure 3.

Figure 2, Figure 3, Table 2

3.2. Colorimetric analysis and UV visible spectra studies

The colorimetric analysis were conducted to test the interaction of the receptors (H_2L^1 and H_2L^2) with various anions such as fluoride, chloride, bromide, iodide, perchlorate,

dihydrogen phosphate and acetate anions were investigated in DMSO solution. Noticeable and appreciable color changes were observed when the receptors (H_2L^1 and H_2L^2) were treated with the fluoride anion, imparting an immediate color change from colorless to yellow color. However other anions failed to exhibit color changes on similar condition except, acetate anion which hardly produces any visible color change on interaction with the receptors as shown in Figure 4.

Figure 4

The UV-visible behavior of the receptors in DMSO solutions (5×10^{-5} mol L^{-1}) were studied at 298K in the presence of fluoride, chloride, bromide, iodide, perchlorate, dihydrogen phosphate and acetate anions. The receptors with addition (up to 3 equiv) of chloride, bromide, iodide, perchlorate and dihydrogen phosphate induced insignificant changes in the UV-visible spectra strongly suggesting that no coordination takes place. This behavior contrasts with that observed in the presence of basic anions, such as fluoride and acetate shown in Figure 5. The spectral profile of receptors shows the absorption peaks at 258 (H_2L^1) and 259 (H_2L^2) nm attributable to the $\pi\rightarrow\pi^*$ transitions. While a second absorption at 323 (H_2L^1) and 335 (H_2L^2) nm was observed which may be attributed to the $n\rightarrow\pi^*$ transitions. UV-visible titrations of the receptors (H_2L^1 and H_2L^2) with fluoride showed an intensity decrease and a small bathochromic shift in the absorption band corresponding to the $n\rightarrow\pi^*$ transitions and also subsequent formation of a new band appeared at 384 (H_2L^1) and 402 (H_2L^2) respectively. Moreover both the position of the new band and the relative intensity of the absorption band of the receptor with respect to the band upon addition of fluoride were dependent on the receptor used as shown in Figure 6. Whereas upon addition of acetate anion to the receptors showed a new peak with a less intensity at ≈ 360 (H_2L^1) and ≈ 390 (H_2L^2) nm.

Figure 5, Figure 6

Continuous variation method was used to determine the stoichiometric ratio of the receptors (H_2L^1 and H_2L^2) to the fluoride anion guest (Job's plot; Figure 7). A Job's plot [24] of the H_2L^1 and H_2L^2 with fluoride anion in DMSO shows the maxima at a molar fraction of 0.5. This indicates that the H_2L^1 and H_2L^2 bind with the fluoride anion in a 1:1 ratio during the initial stages of the reaction. Considering this result along with the other data, the binding mode of H_2L^1 and H_2L^2 to the fluoride anion is proposed as shown in Figure 8.

Figure 7, Figure 8

The binding stoichiometry of H_2L^1 and H_2L^2 were calculated in accordance with the Benesi-Hildebrand equation (shown in figure 9), [16] which was given as follows:

$$\frac{1}{A-A_0}=\frac{1}{A_\infty-A_0}\left[\frac{1}{K[F^-]_0}+1\right]$$

where A_0 is the absorbance of free receptor, A is the absorbance with a specific fluoride concentration, A_∞ is the absorbance with excess amount of F^-, K is the association constant (M^{-1}), and $[F^-]_0$ is the concentration of F^- added (M). The plot of $1/(A-A_0)$ against $1/[F]_0$ shows a linear relationship (R = 0.99), indicating that receptors associates with fluoride and acetate in a 1:1 stoichiometry. The association constant (K) of the receptors H_2L^1 and H_2L^2 with F^- was determined from the ratio of intercept/slope which is found to be $0.14 \times 10^4\ M^{-1}$ (H_2L^1) and $1.14 \times 10^4\ M^{-1}$ (H_2L^2), respectively. From the association constant values, it is inferred that H_2L^2 has more affinity toward fluoride anion as compared to that of H_2L^1. The spectra of receptors H_2L^1 and H_2L^2 did not show any appreciable change with the addition of other anion (AcO^-, Cl^-, Br^-, I^-, ClO_4^-, and $H_2PO_4^-$); hence association constants cannot be determined by using the spectra of both receptors H_2L^1 and H_2L^2 with other anions. The changes observed in the UV-visible spectrum upon fluoride addition were attributed to the formation of hydrogen-bonding complexes with the thiosemicarbazone groups that eventually resulted in a deprotonation [25-28]. The formation of hydrogen bonding complexes was reflected in relatively small variations in the absorption band of the receptor whereas deprotonation processes was related with the appearance of a new absorption band at longer wavelengths [29]. Moreover a close view of the results indicated that the final response of the receptors towards the tested anions is dependent on the heterocyclic ring system attached to the thiosemicarbazone group that modulated the acidity of the N-H protons.

Figure 9

3.3 Fluorescence spectral studies

The fluorescence behaviors of receptors (H_2L^1 and H_2L^2) were studied in DMSO. Fluorescence experiments were carried out with 384 and 402 nm as excitation wavelength of H_2L^1 and H_2L^2 respectively. When 0 - 3 equiv. of tetrabutylammonium fluoride were added to

the solution of receptors a concomitant increase of the fluorescence intensity was observed as shown in Figure 10. As also seen that the, addition of fluoride anion to H_2L^1 and H_2L^2 induced a slight red shifted emission band at 437 nm and 438 nm respectively. These are clear observations that the so called fluorescence enhancement comes by the removal of n→π* transitions which normally mask the π→π* transition which are mainly responsible for the emission behavior. Hence the recognition of a molecule does not simply involve a color change, but also involves serious electronic changes within the molecule affecting the HOMO and LUMO interactions considerably. In the same conditions, no significant spectra changes happened when 20 equiv. of other tetrabutylammonium anion salt were added.

Figure 10

The stability constant of the complex was calculated by the linear Benesi–Hildebrand expression [30] (shown in Figure 11).

$$\frac{1}{\Delta I} = \frac{1}{[R]\Delta X} + \frac{1}{K_{ass}[R]}\frac{1}{F}$$

where ΔI is the change in the fluorescence intensity at 437 (H_2L^1) and 438 (H_2L^2) nm, K_{ass} is the stability constant, ΔX is the difference of fluorescence quantum yields between the complex and receptor, and [R] and [F] are the concentrations of receptor and fluoride anion, respectively. On the basis of the plot of $1/\Delta I$ and 1/[F], the stability constant was determined to be 6.1×10^5 (H_2L^1) and 6.8×10^6 (H_2L^2) M^{-1} with a good linear relationship (R =0.99), which also indicates that the formation of the complex occurs with 1:1 stoichiometry . The results suggest H_2L^2 have high selective detection fluoride anion.

Figure 11

4. Conclusion

In conclusion, two chromogenic thiosemicarbazone receptors (H_2L^1 and H_2L^2) were synthesized in good yields via diazo coupling and condensation. Among them, the receptor H_2L^2 exhibits higher sensitive for the fluoride anion and there was a prominent color change in the system, which can be observed by naked-eye. Both the thiosemicarbazone derivatives have been designed to provide the anion recognition through H-bonding interactions employing thiourea -NH groups. However the results show that the deprotonation rather than the H-bonding is the key

factor triggering the chromogenic effect. Sensing ability and binding affinity of both the receptors towards fluoride was examined using techniques UV-visible and fluorescence spectroscopy. It has also been found that the receptors were highly sensitive and selective towards fluoride even in a biologically competing solvent like DMSO.

5. Supplementary information

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC 892725 for the H_2L^2. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (fax: +44-1223- 336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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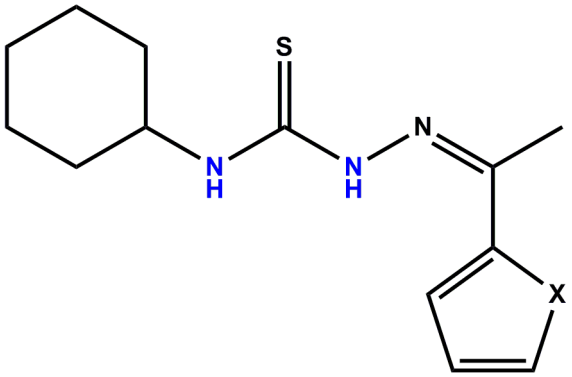
Figure 9: Benesi-Hildebrand plot UV-visible titration result receptor with F^- in DMSO (a) H_2L^1 (b) H_2L^2

Figure 10: Fluorescence spectra for receptor in DMSO solution with the addition (0- 3 eq.) of fluoride anion (a) H_2L^1 (b) H_2L^1.

Figure 11: Benesi-Hildebrand plot photo luminance titration result receptor with F^- in DMSO (a) H_2L^1 (b) H_2L^2.



	X
H_2L^1	O
H_2L^2	S

Figure 1: Structural formulae of the receptor (H_2L^1 & H_2L^2)

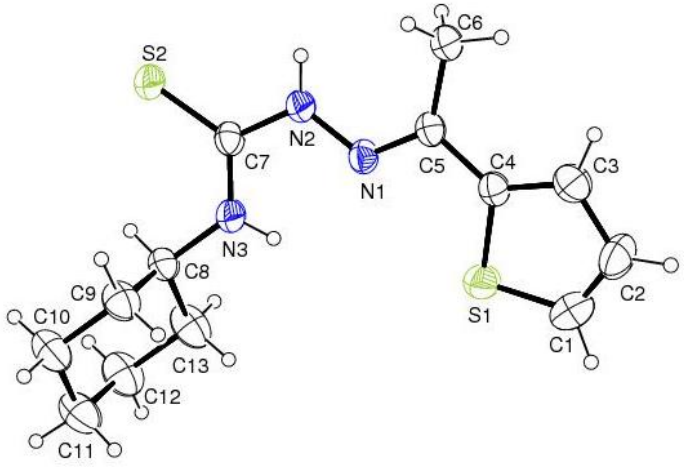


Figure 2: ORTEP of H_2L^2 showing the atom-numbering scheme.

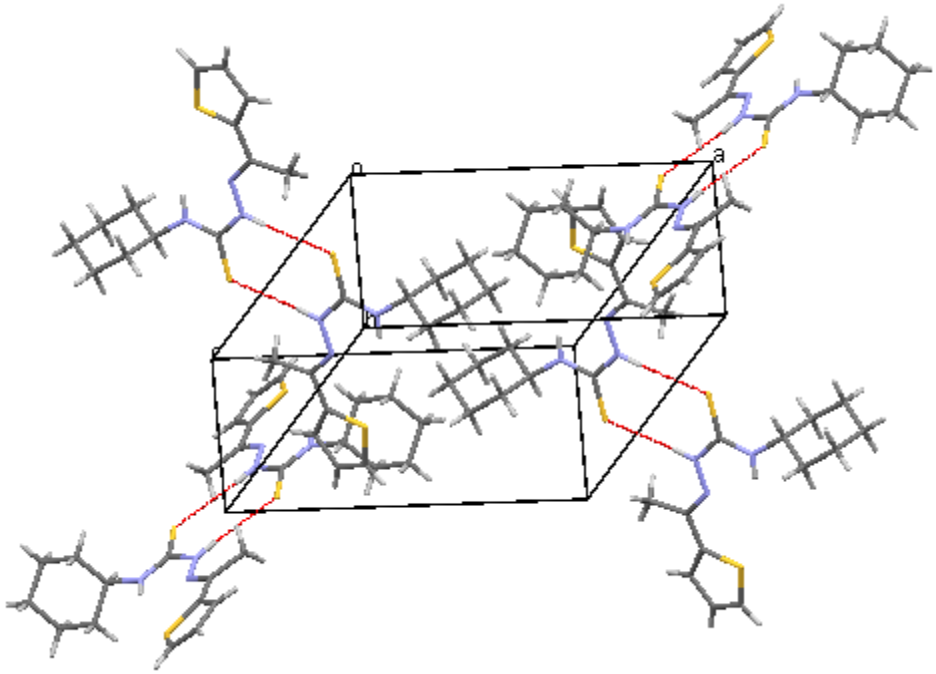


Figure 3: The crystal packing of (H_2L^2). Hydrogen bonds are shown as dashed lines of H_2L^2.

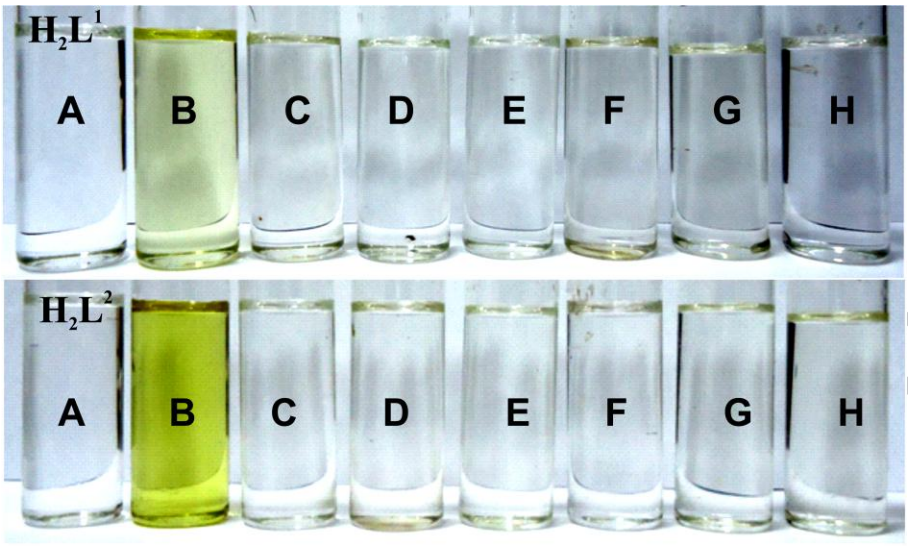


Figure 4: Color change of H_2L^1 and H_2L^2 (5×10^{-5} mol L^{-1}) in DMSO solution with the addition 3 eq. of TBA anions. A= Receptor, B = F^-, C = Cl^-, D = Br^-, E = I^-, F = ClO_4^-, G = $H_2PO_4^-$, H = AcO^- at 298 ± 0.1 K.

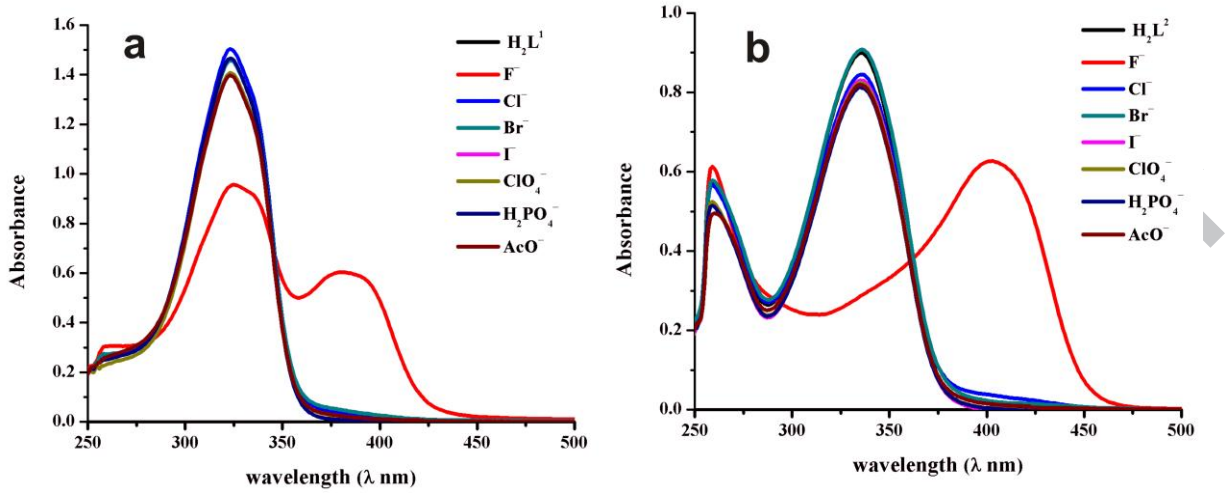


Figure 5: Absorption spectra of receptor with addition of different anions (3 eq.) as their TBA salts (a) H_2L^1 (b) H_2L^2

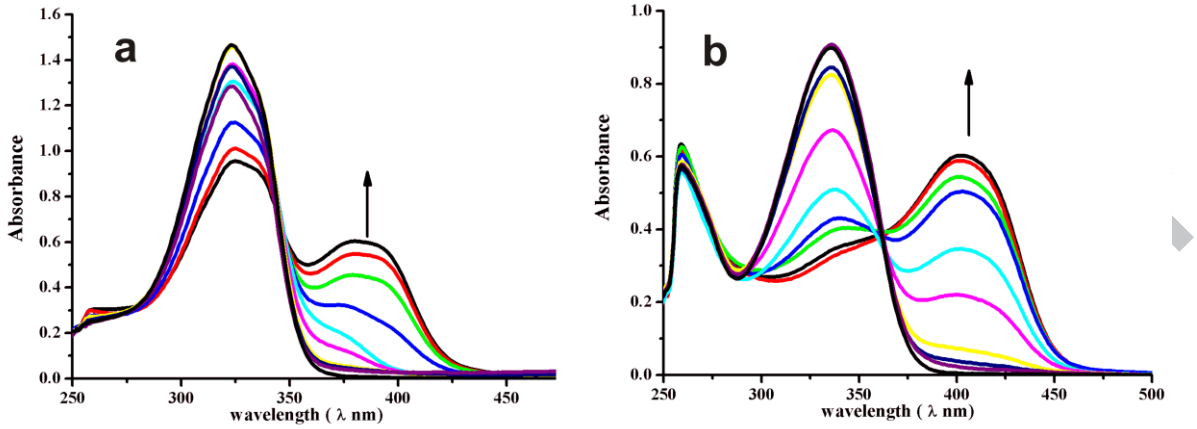


Figure 6: Absorption spectra of receptor with addition (0 – 3 eq.) of standard solution fluoride (a) H_2L^1 (b) H_2L^2

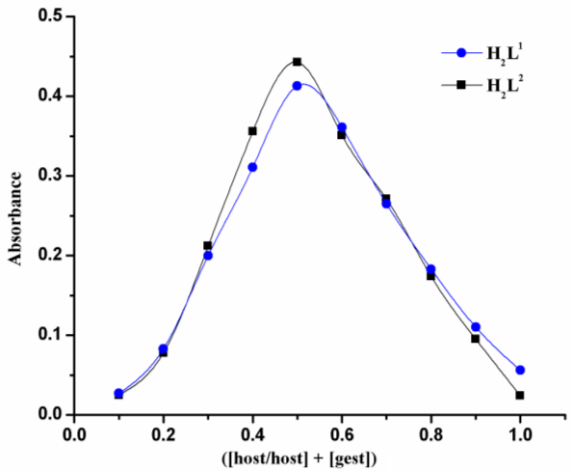


Figure 7: Job plot for complexation of receptor with F^- determined by absorption spectra, $[H_4L]$ + [anion] = 1×10^{-4} mol L^{-1} (a) H_2L^1 (b) H_2L^2

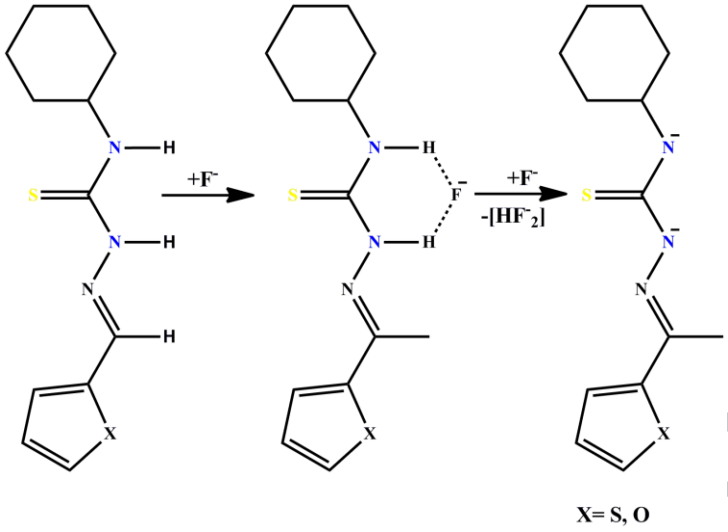


Figure 8: The proposed host–guest binding mode with fluoride anion in solution.

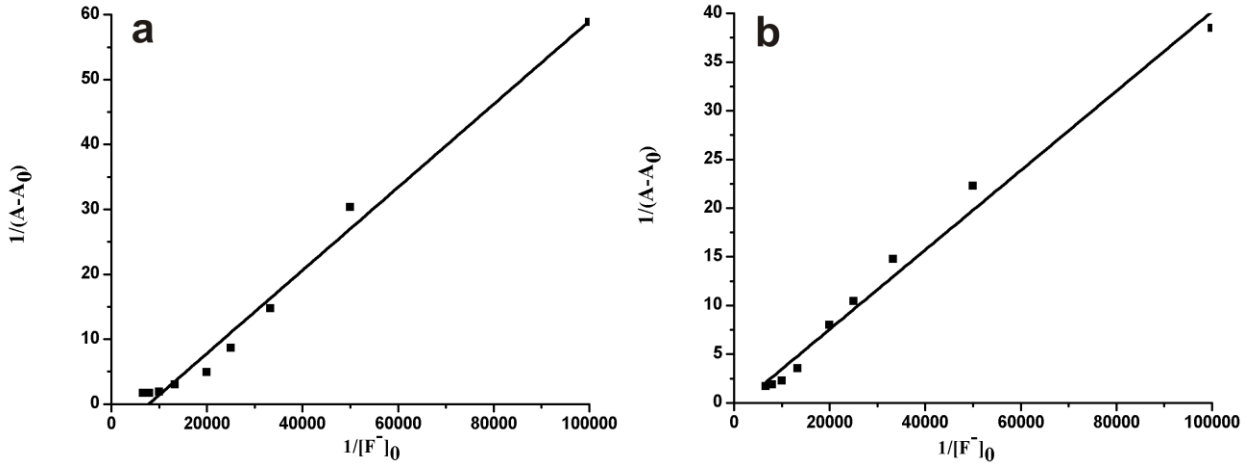


Figure 9: Benesi-Hildebrand plot UV-visible titration result receptor with F^- in DMSO (a) H_2L^1 (b) H_2L^2

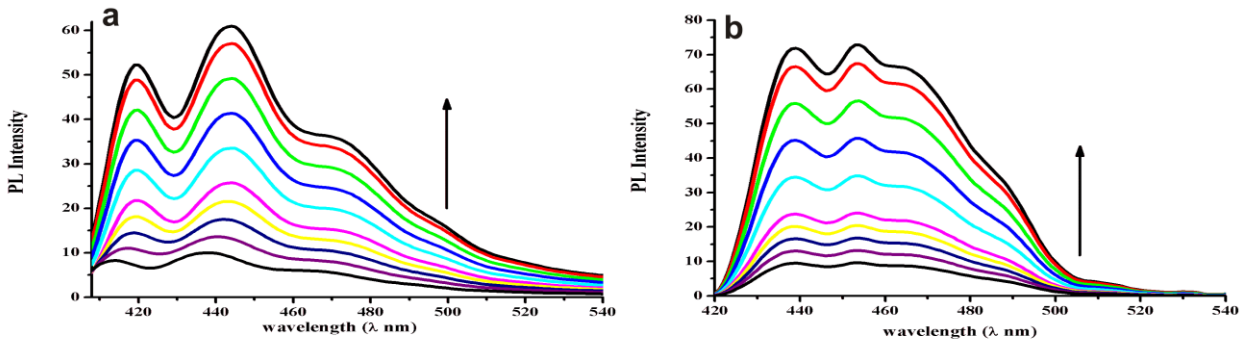


Figure 10: Fluorescence spectra for receptor in DMSO solution with the addition (0- 3 eq.) of fluoride anion (a) H_2L^1 (b) H_2L^1

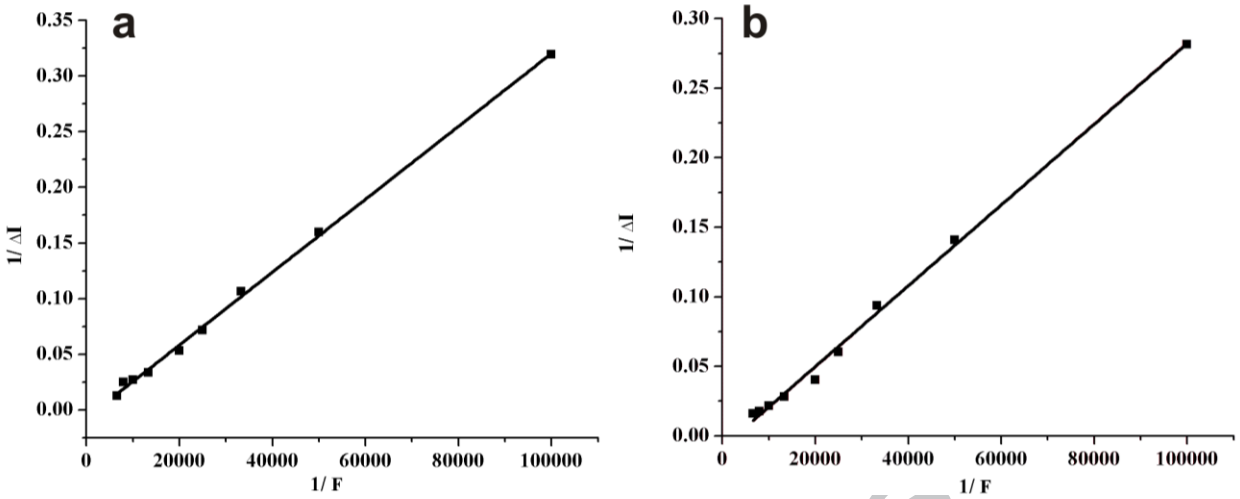


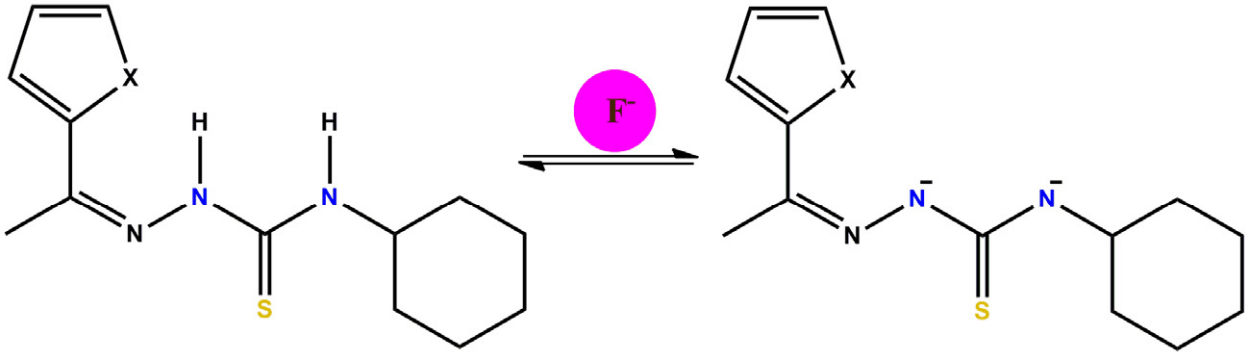
Figure 11: Benesi-Hildebrand plot photo luminance titration result receptor with F^- in DMSO (a) H_2L^1 (b) H_2L^2.

Table 1: Crystal data and structure refinement information for H_2L^2.

	H_2L^2
Empirical formula	C_{13} H_{19} N_3 S_2
Formula weight	281.43
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P12/c1
Unit cell dimensions	a = 13.0370(5) Å alpha = 90 deg. b = 5.7580(2) Å beta = 96.7000(10) deg. c = 19.9200(6) Å gamma = 90 deg.
Volume	1485.12(9) A^3
Z, Calculated density	4, 1.259 Mg/m^3
Absorption coefficient	0.346 mm^-1
F(000)	600
Crystal size	0.30 x 0.20 x 0.20 mm
Theta range for data	2.06 to 25.00 deg.
collection	-15<=h<=15, -6<=k<=4, -23<=l<=23
Limiting indices	13464 / 2599 [R(int) = 0.0282]
Reflections collected / unique	= 25.00
Completeness to theta	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9863 and 0.9031
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2599 / 198 / 241
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0347, wR2 = 0.0859
R indices (all data)	R1 = 0.0540, wR2 = 0.1002
Largest diff. peak and hole	0.217 and -0.138 e.A^-3

Table 2: Selected bond lengths (Å) and bond angles (°) for H_2L^2

Selected bonds	Value (Å)	Selected angles	(°)
C(2)-S(1')	1.637(3)	C(1)-C(2)-S(1')	120.1(3)
C(4)-S(1')	1.587(7)	S(1')-C(4)-S(1)	117.2(3)
C(4)-S(1)	1.649(6)	C(1)-S(1)-C(4)	92.74(16)
C(5)-N(1)	1.687(3)	C(2)-S(1')-C(4)	93.3(4)
C(7)-N(3)	1.281(2)	N(1)-C(5)-C(4)	115.15(17)
C(7)-N(2)	1.322(3)	N(1)-C(5)-C(6)	125.05(18)
C(7)-S(2)	1.362(2)	C(4)-C(5)-C(6)	119.79(16)
C(8)-N(3)	1.671(2)	H(6A)-C(6)-H(6B)	109.5
N(1)-N(2)	1.455(2)	N(3)-C(7)-N(2)	114.94(18)
N(2)-H(2A)	1.368(2)	N(3)-C(7)-S(2)	124.76(15)
N(3)-H(3A)	0.859(15)	N(2)-C(7)-S(2)	120.29(15)
		N(3)-C(8)-C(9)	115.2(3)
		N(3)-C(8)-C(13)	108.7(3)
		N(3)-C(8)-C(9')	103.2(5)
		N(3)-C(8)-H(8)	103.9(15)
		C(5)-N(1)-N(2)	119.80(16)
		C(7)-N(2)-N(1)	117.83(17)
		C(7)-N(2)-H(2A)	115.9(13)
		N(1)-N(2)-H(2A)	125.8(13)
		C(7)-N(3)-C(8)	126.00(19)
		C(7)-N(3)-H(3A)	117.4(15)
		C(8)-N(3)-H(3A)	116.6(15)



X = O (H_2L^1), S (H_2L^2)

Research highlights

- New heterocyclic thiosemicarbazone derivatives have been prepared and characterized.
- It is a very good naked eye detection sensor for the fluoride anion
- The Chemosensor is novel with sensing unit directly attached to the signaling unit for easy signaling.