Spectrochimica Acta Part A 79 (2011) 370–375

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

4-Salicylideneamino-3-methyl-1,2,4-triazole-5-thione as a sensor for aniline recognition

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ARTICLE INFO

Article history:
Received 2 December 2010
Received in revised form 2 March 2011
Accepted 11 March 2011

Keywords:
Schiff base
Sensor
Aniline
Benzene-1,4-diamine
UV–visible spectroscopy
^{1}H NMR titration
Photoluminescence

ABSTRACT

Tridentate triazole based Schiff base 4-salicylideneamino-3-methyl-1,2,4-triazole-5-thione has been found to selectively detect toxic aromatic amines such as aniline and benzene-1,4-diamine by simple titration techniques like UV–visible, fluorescence spectral studies (PL) and ^{1}H NMR titrations. The Schiff base receptor utilizes, thione sulfur, NH-thione and the phenolic hydroxyl group to form hydrogen bonded adduct of aniline and benzene-1,4-diamine with high binding affinity, followed by a slow removal of the corresponding hydrogens thus providing a promising candidate and an unique receptor for toxic aromatic amines.

1. Introduction

Most of the aromatic amines are found to be toxic in humans leading to bladder cancer when inhaled [1]. Aniline is one of the most toxic among the aromatic amine family, but has a wide spread application as a precursor to more complex chemicals. The toxicity of aniline and similar types of compounds on humans is well documented [2,3], with an oral lethal dose being 50–500 mg/kg for a grown man. The primary toxicity of aniline is characterized by methemoglobinemia; the increased production of methemoglobin can cause interference with the oxygen-carrying capacity of the blood. Despite its structural simplicity, the metabolism of aniline is complex and hence it is important to find out a good receptor to sense the aniline.

Only few synthetic receptors have been developed in the recent past due to the challenge in binding of the guest molecule (aniline) with the synthetic receptors developed. Such systems are generally composed of anion binding sites and the chromogenic moieties. When anions interact with the sensor via electrostatic, hydrogen bonding, coordination to a metal center, hydrophobic interaction, or a combination of any two or more of these interactions, the sensor can output binding information either by its altered behavior in fluorescence or in absorption spectra [4,5]. Li et al., have used 2,6-Bis(2-benzimidazolyl)pyridine and showed it to be an efficient receptor for binding aniline with high affinity [6]. It is observed that the host–guest complex formed between the 2,6-Bis(2-benzimidazolyl)pyridine and aniline is very stable, where 2,6-Bis(2-benzimidazolyl)pyridine utilizes not only its cavity but also the imine nitrogen located on the outer core to form a stable complex. Encouraged by this, we investigated the sensing behavior of 4-salicylideneamino-3-methyl-1,2,4-triazole-5-thione [7] against aniline and benzene-1,4-diamine. There are only few reports on aniline sensors and Schiff base functioning as aniline receptor has not been found anywhere in the literature.

2. Experimental

2.1. Materials and methods

Thiocarbohydrazide, glacial acetic acid, salicylaldehyde, aniline (G1) and benzene-1,4-diamine (G2) were purchased from Aldrich Chemicals and were used without further purification. 4-Salicylideneamino-3-methyl-1,2,4-triazole-5-thione and 4-amino-3-methyl-1,2,4-triazole-5-thione was synthesized according to the literature methods [7,8]. Acetonitrile was purified using the standard procedure. Titration of the receptor molecule 4-salicylideneamino-3-methyl-1,2,4-triazole-5-thione (receptor) with the guest molecules was performed cautiously by careful additions of G1 aliquots in to the acetonitrile solution of the receptor. The ratios of receptor/G1 and receptor/G2 are given as follows, A: pure receptor (1×10^{-5} mol/L); B: 1:0.2 (1×10^{-5} mol/L:0.2×10^{-5} mol/L); C: 1:0.4 (1×10^{-5} mol/L:0.4×10^{-5} mol/L); D: 1:0.6

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doi:10.1016/j.saa.2011.03.030

(1×10^{-5} mol/L:0.6 $\times 10^{-5}$ mol/L); E: 1:0.8 (1×10^{-5} mol/L:0.8 $\times 10^{-5}$ mol/L); F: 1:1 (1×10^{-5} mol/L:1 $\times 10^{-5}$ mol/L); G: 1:1.2 (1×10^{-5} mol/L:1.2 $\times 10^{-5}$ mol/L); H: 1:1.4 (1×10^{-5} mol/L:1.4 $\times 10^{-5}$ mol/L); I: 1:1.6 (1×10^{-5} mol/L:1.6 $\times 10^{-5}$ mol/L); J: 1:1.8 (1×10^{-5} mol/L:1.8 $\times 10^{-5}$ mol/L); K: 1:2 (1×10^{-5} mol/L:2 $\times 10^{-5}$ mol/L); L: 1:2.2 (1×10^{-5} mol/L:2.2 $\times 10^{-5}$ mol/L); M: 1:2.4 (1×10^{-5} mol/L:2.4 $\times 10^{-5}$ mol/L);N: 1:4 (1×10^{-5} mol/L:4 $\times 10^{-5}$ mol/L); O: 1:10 (1×10^{-5} mol/L:10 $\times 10^{-5}$ mol/L); P: 1:20 (1×10^{-5} mol/L:20 $\times 10^{-5}$ mol/L); Q: 1:30 (1×10^{-5} mol/L:30 $\times 10^{-5}$ mol/L); R: 1:40 (1×10^{-5} mol/L:40 $\times 10^{-5}$ mol/L); and S: 1:50 (1×10^{-5} mol/L:50 $\times 10^{-5}$ mol/L). A quartz cell (1 cm width) was used to record their corresponding UV–visible and fluorescence spectra at 298 K.

2.2. Synthesis of 4-salicylideneamino-3-methyl-1,2,4-triazole-5-thione (receptor)

4-Amino-3-methyl-1,2,4-triazole-5-thione (1 g, 0.0072 mol) and salicylaldehyde (0.88 g, 0.0072 mol) were dissolved in methanol and the resulting solution was gently refluxed for 2 h with constant stirring. The precipitate obtained was filtered out and kept for crystallization dissolving in methanol and chloroform mixture. Fine colorless single crystals obtained upon slow evaporation at room temperature in 5 days were used for single X-ray diffraction. Experimental results of elemental analysis. Calc. for $C_{10}H_{10}N_4OS$: C, 51.27; H, 4.30; N, 23.91; O, 6.83; S, 13.69. Found: C, 51.05; H, 4.10; N, 23.75; O, 6.51; S, 13.53%. NMR data ^{1}H NMR (δ, ppm DMSO-d_6, 400 MHz): 13.69 (br, s, –NH, 1H), 10.43 (s, –OH, 1H), 10.14 (s, CH=N, 1H), 6.97–7.89 (m, Ar, 4H), 2.35 (s, C–CH_3, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): 165.7, 162.7, 159.7, 148.4, 134.7, 133.6, 120.2, 117.5, 116.08, 11.1. IR data (KBr disc, cm^{-1}): 3433, 3105, 1603, 1590, 1298, 1264. UV–visible: [acetonitrile, λ_{max} cm^{-1} (ε M^{-1} cm^{-1})]: 46,940 (97,800), 39,060 (34,000), 30,300 (12,000).

2.3. Physical measurements

All experiments were carried out at room temperature, unless otherwise mentioned. ^{1}H NMR and ^{13}C NMR (100 MHz) were recorded on a Bruker Avance III 400 MHz in DMSO-d_6 at 298 K with TMS as an internal standard. D_2O exchange was performed by adding 1 drop of D_2O to the NMR tube containing the compound in DMSO-d_6. UV–visible spectra were measured using an ultraviolet spectrometer, PG-90+ (PG Instruments UK). Photoluminescence data (PL hereafter) were recorded in a JASCO FP – 6200 spectrofluorometer. FT-IR spectra were recorded in PerkinElmer-BX instrument. Both the UV–visible and fluorescence spectra are recorded using a 1 cm path length quartz cell. High Performance Liquid Chromatography (HPLC) of the receptor were recorded in SHIMADZU CLASS VP^{TM}-SPD-M20A with the mobile phase acetonitrile:water mixture system (50:50), and the column used for recording the chromatogram was Luna 5 μ C18(2) 100A. All measurements were carried out in the air at room temperature without being specified.

2.4. X-ray crystallography

A colorless monoclinic block crystal having approximate dimensions 0.35 mm × 0.30 mm × 0.25 mm was sealed in a glass capillary, and intensity data were measured at room temperature (296 K) on a Bruker Kappa APEXII diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. All structures were solved by direct methods and refined by fullmatrix least-squares calculations with the SHELXTL-PLUS software package [9]. Absorption corrections were employed using SADABS (T_{max} 0.9319 and T_{min} 0.9065). The non-hydrogen atoms were refined anisotropically and all hydrogen atoms were found from the difference Fourier map and refined isotropically with displacement coefficients U(H) = 1.2 U(C) or 1.5 U(C_{methyl}). However the crystal structure and related data is reported else were [7], the structural refinement parameters were also found to be the same to that of the reported data.

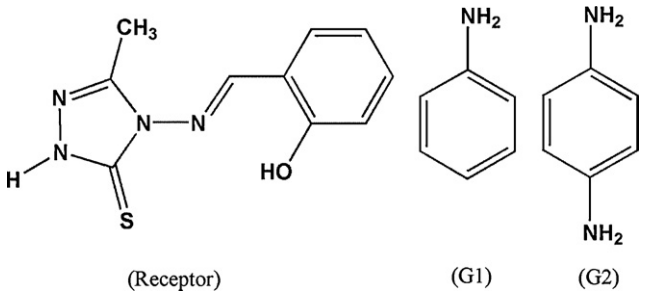


Fig. 1. Structural formulae of the receptor and guests (G1 and G2).

2.5. NMR titrations

All the ^{1}H NMR titrations were carried out at room temperature and the spectra were recorded on a Bruker Avance III, 400 MHz in DMSO-d_6 at 298 K with TMS as an internal standard. The receptor prepared as 1×10^{-4} M solutions (DMSO-d_6) and was titrated against the guest molecules by increasing its equivalents by 0.25 each time.

3. Results and discussion

4-Salicylideneamino-3-methyl-1,2,4-triazole-5-thione was synthesized by the condensation of the salicylaldehyde with triazole amine. Fig. 1 shows the chemical structure of the receptor along with guest molecules G1 and G2. Experimental results of elemental analysis are in good agreement with the calculated data. IR spectrum of the receptor showed a weak band at 3433 cm^{-1} corresponding to ν(NH) of the triazole ring system and a stretching band around 3105 cm^{-1} was assigned to ν(OH), various bands in the same region of 3067m, 2936s, 2759s cm^{-1} indicated that extensive hydrogen bonding interactions, may be present. It is later discussed that both these groups –NH and –OH plays a vital role in binding to the incoming guest molecule. Very sharp stretching band at 1603 cm^{-1} corresponding to ν(C=N), is observed which is very typical for azomethine groups and indicates the formation of the C=N after the reaction. A second stretch at 1590 cm^{-1} indicates the ν(C=N) in the triazole ring, other characteristic frequencies corresponding to 1505m, 1488m, 1412s, 1346m cm^{-1} are assigned to be those arising from the triazole moiety. The ν(C=S) stretching absorption appears at 1298 cm^{-1} and ν(C–N) thioamide appears at 1264 cm^{-1}. IR spectrum of the receptor gives an insight to the molecular functionality in general.

3.1. NMR spectra

^{1}H NMR spectrum of the compound have two sharp singlets in the region around $\delta \sim$ 10.1–10.4 ppm both accounting for single proton each, which accounts for the CH=N, phenolic –OH group as evident from a previous report [7] however they have not reported the NH proton, appearing as relatively broad singlet at δ 13.69 ppm as is evident that there are some quadrupole interaction from nitrogen. However, the proton is sufficiently labile and hence much deshielded. This is to be understood on the basis of extensive hydrogen bonding in the system. Both 10.43 and 13.69 peaks disappear on addition of D_2O confirming the functional groups. The assignment is also based on the hydrogen bonding interactions as

Table 1
Hydrogen bonding interactions.

D–H...A	H...A (Å)	D...A (Å)	∠D–H...A (°)
Intra O(1)–H(1O)...N(1)	1.98	2.6778	149
N(3)–H(3 N)...S(1)[a]	2.46	3.2650	175
Intra C(7)–H(7)...S(1)	2.49	3.1936	135
C(10)–H(10A)...S(1)[b]	2.83	3.7899	173

[a] $-x, -y, -z$.
[b] $1/2+x, 1/2-y, 1/2+z$.

seen in the crystal data (Table 1) which clearly shows an intramolecular hydrogen bonding for OH group, whereas –NH proton has an intermolecular hydrogen bonding. The ^{1}H NMR and ^{13}C NMR assignments are shown in Fig. 2.

3.2. Molecular and crystal structure of the receptor

Single crystal X-ray crystallography was carried out to confirm the structure of the molecule, since Schiff bases has a tendency to get hydrolyzed easily in solvents like methanol as well as very sensitive to pH. The molecular structure of the receptor has been reported earlier [7] were it crystallizes in to a monoclinic lattice with a space group of $P2_1/n$. The bond lengths and angles are unchanged however the compound exists as a monomer in our case. The previous report suggesting the molecule as centrosymmetric dimer structure of the molecule may be due to the extensive hydrogen bonding both inter as well as intra as seen in Fig. 3. The details of which are appended in Table 1. Since this type of aniline sensors is reportedly bind to the guest molecule via tridentate donor atoms through inter molecular hydrogen bonding interactions [6,10,11], we also suggest a similar type of mechanism operational in the solution of the compounds. It is clear from the NMR data as well as the titration data that the removal of NH proton is very easy, while still phenolic OH is difficult to remove with the addition of the guest to the receptor. Even though eventually phenolic OH disappears, the time taken for this change is not the same as to that of the NH removal which is instantaneous. The reason can be clearly seen from Fig. 3 as, the phenolic OH is engaged in an intramolecular hydrogen bonding with N1. There are previous reports of crystal structures of receptor and guest together [10,11] but our attempts to grow similar crystals failed.

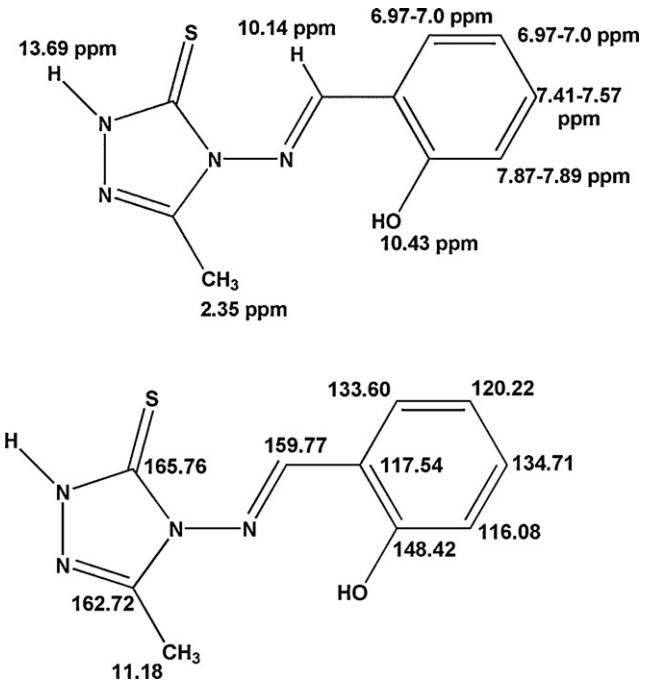


Fig. 2. ^{1}H NMR (top) and ^{13}C NMR (bottom) assignments for the receptor.

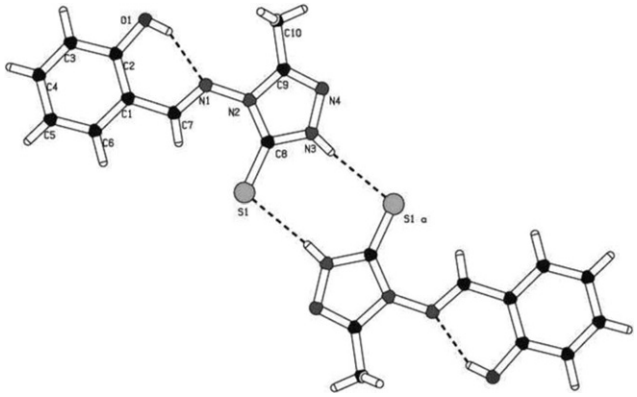


Fig. 3. PLATON plot showing intra and intermolecular hydrogen bonding in the compound.

3.3. High performance liquid chromatography of the receptor

Synthesized receptor 4-salicylideneamino-3-methyl-1,2,4-triazole-5-thione purity was confirmed using a HPLC, recorded with a mobile phase of acetonitrile:water system mixture (50:50), and the column used for recording the chromatogram was Luna 5 μ C18(2) 100A. Fig. 4 shows the HPLC chromatogram of the receptor molecule, which shows a single peak with an area percentage of 100, at a retention time 6.912 min, thus determining the purity of the receptor molecule used as a sensor. Purity of the receptor in HPLC hence provides the evidence that there is no other impurity in the system to interact with the incoming guest molecules.

3.4. UV–visible titration

The UV–visible spectrum of the receptor was recorded in acetonitirile showed significant absorptions at ca. 250 nm, 280 nm and 330 nm. In the case of thiosemicarbazone type systems these bands are assigned due to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions arising from thiocarbonyl group and azomethine group. However a clear distinction of them is often not possible. In the case of coordination normally there will be a bathochromic shift, along with a hyperchromic shift due to charge transfer transitions [12,13]. The change in optoelectronic properties with the addition of the guest was studied using the UV–visible spectral titrations. Fig. 5(A) demonstrates the absorption spectra upon the addition of G1 in to the acetonitrile solutions of the receptor. It can be seen in Fig. 5(A) and (B) that on increasing the concentration of G1 from 0 equivalents to higher concentration, a decrease of absorption around 330 nm occurs. Concurrently, a new absorption band around 275 nm with a higher intensity shows up. This new absorption band is due to the potential formation of a stable complex between the Schiff base receptor and the G1 [6,10,11]. Also we observed a formation of Isosbestic point at ~290 nm, indicating the presence of at least one species at equilibrium as indicated by Li and co-workers [6]. Upon higher G1 concentrations, the absorption spectra also exhibit characters of G1's absorption spectrum. The absorption at 330 nm becomes constant with the increasing concentration of G1. The absorption edge of G1 ends at 310 nm, the absorption peak around 330 nm is mainly dominated by the complex formed between the receptor and the G1 and also by the absorption due to the receptor. Throughout the spectral titration, the amount of free receptor tends to decrease as the formation of the complex between the receptor and G1 increases, until the complex achieves a balance state. Once

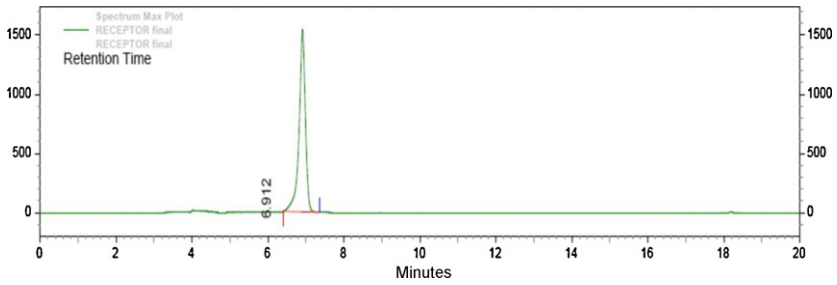


Fig. 4. HPLC of the receptor.

after reaching the balance state the absorption at 330 nm becomes constant invariably of any further increase in the concentration of the G1.

In the case of benzene-1,4-diamine (G2), we were unable to account the spectral evidence for the formation of stable complex between the receptor NH-thione and phenolic –OH groups with the G2 molecule unfortunately due to the strong absorption of G2 at ~324 nm which is quite close to the absorption maximum of the receptor, Fig. 6.

Even though Schiff bases are known to sense F^- anions, the present receptor does not sense any of the halides, neither visible change nor spectral changes. The experiments repeated in DMF and DMSO did not show any significant change in the spectral features indicating that even in competing solvents the receptor functioning is much better.

3.5. Fluorescence spectral studies

Fig. 7(A) shows the PL spectra upon the addition of the G1 in to the acetonitrile solution of the receptor. It can be seen from the spectra that the increase in the concentration of G1, the emission spectra of the receptor/G1 system increases without any quenching of the luminescence. As for the receptor/G1 system a new emission peak at 330 nm is perhaps due to the formation of receptor/G1 complex. Interestingly we also observed a spectral bathochromic shift from 315 nm to 330 nm confirming the stable receptor/G1 complex formed. Emission intensity increases as the concentration of G1 increases in the system.

Fig. 7(B) shows the PL spectra of receptor/G2 system. receptor shows an emission peak at 310 nm. Increasing the concentration of the G2, the emission spectra shows a clear bathochromic shift

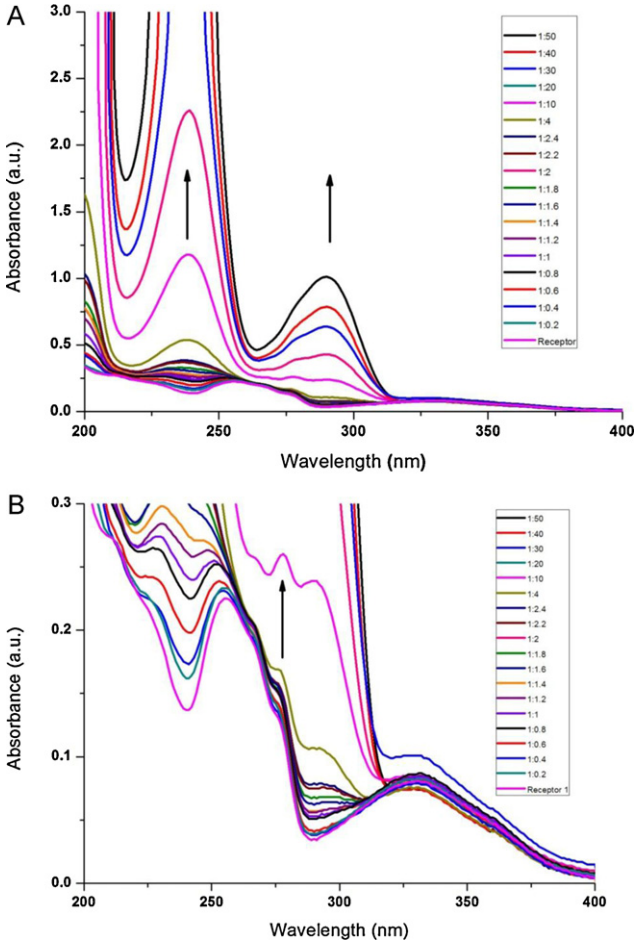


Fig. 5. (A) UV–visible spectra of receptor/G1 system recorded in acetonitrile. (B) A magnified view of absorption spectrum of receptor/G1 system recorded in acetonitrile.

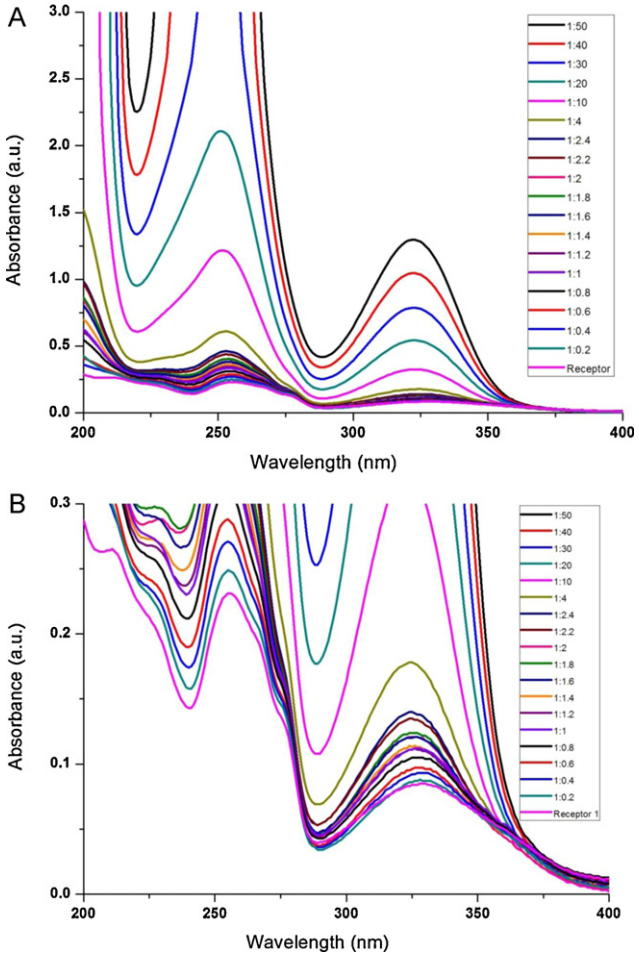


Fig. 6. (A) UV–visible spectra of receptor/G2 system recorded in acetonitrile. (B) A magnified view of absorption spectrum of receptor/G2 system.

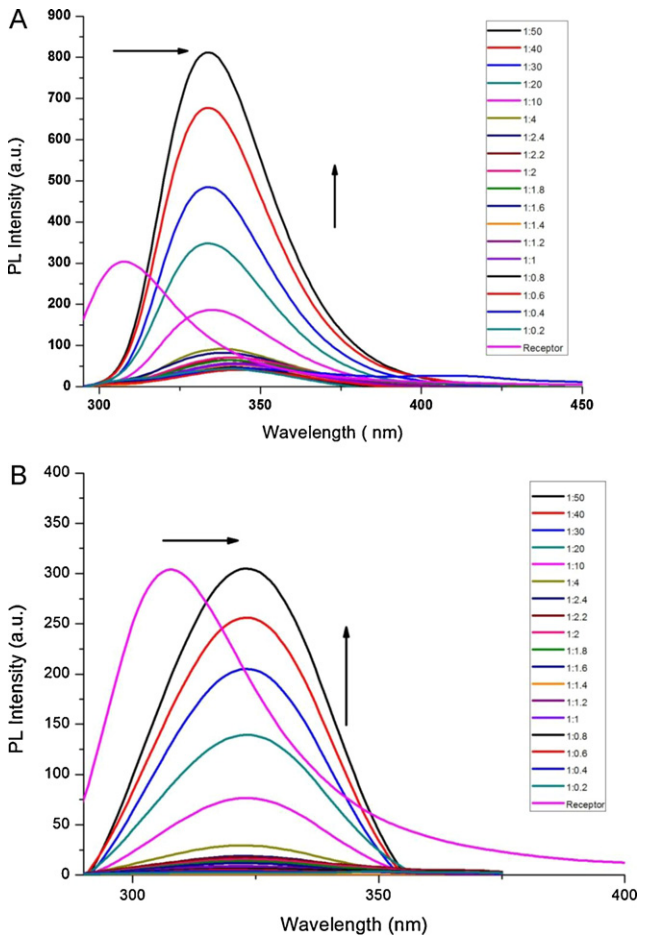
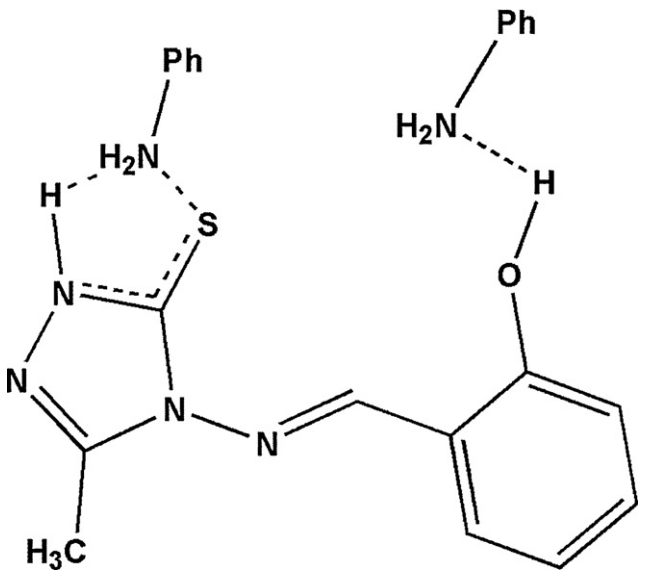


Fig. 7. (A) PL spectra of receptor and G1 system recorded in acetonitrile, excited at wavelength 275 nm, (B) PL spectra of receptor and G2 system recorded in acetonitrile, excited at wavelength 330 nm.

from 315 nm to 335 nm, it is thus confirmed that the PL spectral bathochromic shift are caused by the stable adduct between the receptor and the G2. Thus providing a strong evidence of the complex formed, which is overshadowed in the UV–visible absorption spectra for the same receptor/G2 system.



Scheme 1. Tentative coordination behavior of receptor towards G1.

3.6. ^1H NMR titration

UV–visible and PL spectra show that the titration of receptor with both the G1 and G2 form a new species which is leading to a new absorption band in UV–visible spectra and a clear bathochromic shift in PL spectral studies. To further look in to the nature of the receptor and guest molecule interactions and to understand the sensing behavior of the receptor towards the guest molecules ^{1}H NMR titration was conducted in DMSO-d_6. In the benzene-1,4-diamine case (G2), the new species formation was overshadowed by the strong absorption of G2 around 324 nm, thus no conclusion could be arrived from its absorption spectral data, but the formation of new species in the G2 with the receptor was evident from its bathochromic shift in the PL spectra.

^{1}H NMR titration of the receptor with aniline (G1) is shown in Fig. 8. Upon addition of 0.25 equiv of G1, the peaks at δ 13.69 ppm and δ 10.43 ppm, which were assigned to NH-thione of triazole moiety and phenolic –OH, respectively, were shifted slightly downfield and the intensity of both the peaks starts to decrease. This indicated the formation of a hydrogen bonding between the receptor and G1. With further addition of G1, the signal corresponding to –NH were disappeared and the signal of –OH too disappeared, but in very slow

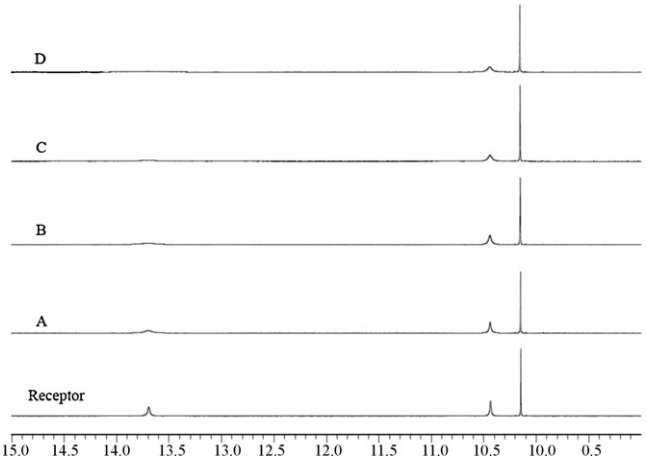


Fig. 8. ^{1}H NMR (400 MHz) spectra of receptor (1×10^{-4} M solutions in DMSO-d_6). Bottom one receptor only; (A) receptor + 0.25 equiv. of G1; (B) receptor + 0.5 equiv. of G1; (C) receptor + 0.75 equiv. of G1; (D) receptor + 1 equiv. of G1.

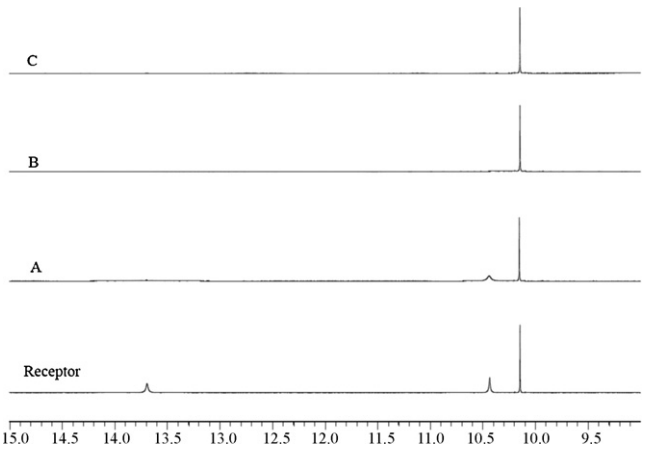


Fig. 9. ^{1}H NMR (400 MHz) spectra of receptor (1×10^{-4} M solutions in DMSO-d_6). Bottom one receptor only; (A) receptor + 0.25 equiv. of G2; (B) receptor + 0.5 equiv. of G2; (C) receptor + 1 equiv. of G2.

rate compared to the –NH signal. Binding mode of receptor and G1 is found to be in the ratio of 1:2 from the ^{1}H NMR titration results. Concluding from this the tentative binding mode of the receptor could be visualized as seen in Scheme 1.

^{1}H NMR titration of the receptor with benzene-1,4-diamine (G2) is shown in Fig. 9. In the case of G2, we found quiet interesting results with the addition of G2 to the NMR tube containing the receptor. Addition of the initial 0.25 equiv. of the G2, we found that the peak intensity of –NH and –OH disappeared drastically. Upon further addition of 0.25 equiv. of G2 to the receptor, resulting into a total of 0.5 equiv. the peaks corresponding to –NH and –OH disappeared completely, which clearly shows the new species formation between the receptor and the G2. Further addition of G2 has no change in the NMR spectrum. Binding mode of receptor and G2 is found to be in the ratio of 2:1 from the ^{1}H NMR titration results.

4. Conclusion

The tridentate triazole based Schiff base 4-salicylideneamino-3-methyl-1,2,4-triazole-5-thione has a highly optical sensitivity towards aniline and benzene-1,4-diamine. Crystal structure of the receptor as well as the NMR titrations also indicates that the binding to aniline and benzene-1,4-diamine might be due to extensive hydrogen bonding interaction. The sensing is even possible in competitive solvents like DMSO and DMF indicating that the present Schiff base is a promising sensor for aniline.

Supplementary information

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC 802088 for the receptor. 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).

Acknowledgements

AS acknowledges CSIR for a research grant (CSIR Sanction No. 01(2304)/09/EMR-II Dated 17.03.2009). AS is thankful to Dr. S. Abraham John, Associate Professor; Gandhigram Rural University, Tamilnadu, India for PL measurements and to Dr. Rohith P. John, Associate Professor, Department of Applied Chemistry, Indian School of Mines for XRD discussions. The authors are also thankful to SAIF-STIC at Cochin University of Science and Technology, Cochin 682 022, India for NMR as well as single crystal X-ray data.

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