Analytical Methods

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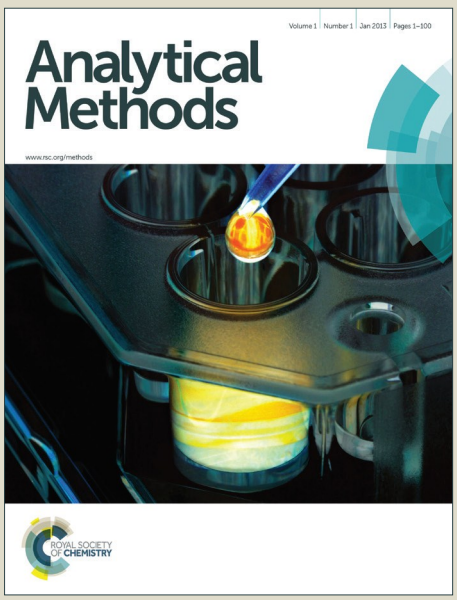

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A 'chromogenic' and 'fluorogenic' bis-Schiff base sensor for rapid detection of hydrazine both in solution and vapour phase

Anupam Ghorai, Jahangir Mondal, Sumantra Bhattacharya and Goutam Kumar Patra*

Abstract

A novel, convenient and rapid method has been developed, for the first time, for visual detection of hydrazine exploiting a simple, cost-effective Schiff base ligand, **L** as a fluorescent–colorimetric probe. The sensing behaviour is based on hydrogen bonding recognition. The probe could selectively distinguish hydrazine with an OFF–ON fluorescence signal change and the visible colour change from yellow to colourless at room temperature within 10 seconds. It exhibits exclusive selectivity towards hydrazine over different amines, metal cations and anions. The sensitivity of the fluorescent based assay (0.1 μM or 3.2 ppb) for hydrazine is far below the TLV (threshold limit value) set by the World Health Organization (WHO) and United States Environmental Protection Agency (USEPA). DFT and TDDFT calculations were performed on the molecule of **L** in order to get the structural information and to get better insight into the sensing mechanism. The probe can be successfully used for vapour-phase discrimination of hydrazine by the TLC plate technique and shows good practical applicability in detection of hydrazine in water and urine samples.

Corresponding Author: Tel.: 91 7587312992, *E-mail*: patra29in@yahoo.co.in

Introduction

Design and synthesis of functional molecules that could serve as molecular devices for sensing, switching, and signalling selectivity enjoys a great deal of interest of modern researchers in sensing arena and becomes an active area of current research.[1] The selective and sensitive detection of trace hydrazine has achieved increasing attention in recent years due to its multidisciplinary applications like emulsifier, corrosion inhibitor, antioxidant, photographic developer, pesticide, insecticide and plant growth regulator.[2-6] As a highly reactive base, hydrazine plays vital roles in the pharmaceutical, chemical, textile and agricultural industries. It is also used as high-energy rocket-fuel in propulsion and missile systems because of its detonable characteristics.[7-12] However, its extensive use is contemporaneous with its serious toxic and adverse health effects to environment as well as human body. As a neurotoxin, it can induce carcinogenic and mutagenic effects causing severe damage to the liver, lungs, kidneys and human central nervous system along with nose irritation, temporary blindness, pulmonary edema and damage of DNA.[13-17] Notably, hydrazine and its derivatives are classified as group B2 human carcinogens with a low threshold limit value (TLV) of 10 ppb by World Health Organization (WHO) and United States Environmental Protection Agency (USEPA).[18-20] Therefore, reliable analytical approach for hydrazine detection with satisfactory sensitivity and selectivity is a significant issue to address.

To date, various traditional analytical techniques, including chromatography-mass spectrometry,[21-24] titrimetry,[25-28] spectrophotometry,[29-31] potentiometry[32,33] and electrochemical methods[34-36] have been proposed for hydrazine analysis. But most of these methods involve tedious protocols and time-consuming procedures for real-time and on-site analysis.[37,38] So, search for simple but reliable detection methods for the rapid and sensitive detection of hydrazine both qualitatively and quantitatively is still a great challenge. However, these limitations can be surpassed by designing simple fluorescent chemo-sensor. These have some obvious advantages like non-invasiveness, high sensitivity, and spatiotemporal resolution.[39-42] A number of fluorescent sensors for hydrazine have been reported,[43-46] but very few reports of 'naked eye' and 'fluorescent' probes for hydrazine are available in the literature.[47-49] Recently, a fluorescent-colorimetric hydrazine sensor has been reported by Lee et al.[47] Raju et al.[48] reported a colorimetric hydrazine sensor which shows fluorescence. A similar molecule was reported by Cui almost at the same time.[49] In each case, sensing mechanism were based either on chemical reactions or by using nanoparticles. However, hydrogen bonding-induced sensing of hydrazine hydrate has been rarely observed in literature. Zhao et al.[50] reported a hydrazine sensor of this type but there the sensing

process was assisted by expensive gold nanoparticles and thus limits its application in constructing a device. Moreover, this sensor does not exhibit any fluorescence property.

This study is a part of our ongoing effort to design and synthesise fluorogenic chemosensor.[51,52] Herein we have utilised a simple Schiff base **L** as a fluorescent–colorimetric probe, which can selectively sense hydrazine over several amines, metal cations and anions through hydrogen bonding interaction. It can act as a rapid and selective naked-eye, fluorescent, as well as absorbance sensor for hydrazine both in aqueous and alcoholic medium. The probe can also be used for vapour-phase detection of hydrazine. The probe **L** is very easy to synthesize, eco-friendly, and cost effective. The sensing process does not involve any complicated buffer-making procedure and use of nanoparticles. To the best of our knowledge, this is the first report of a simple Schiff base acting as a hydrazine sensor in an aqueous and alcoholic medium and also for hydrazine gas.

Experimental

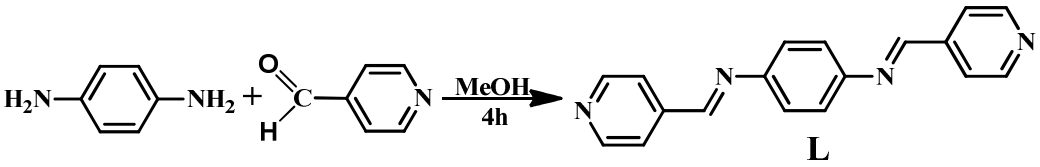
General information

The chemicals and solvents were purchased from Sigma-Aldrich Chemicals Private Limited and were used without further purification. Melting points were determined on a hot-plate melting point apparatus in an open-mouth capillary and were uncorrected. The measurements of pH were done using a digital pH meter (Merck). ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Brucker 400 MHz instrument. High resolution mass (HRMS) spectra were recorded on Waters mass spectrometer using mixed solvent HPLC methanol and triple distilled water. UV/Visible spectra were recorded on a Shimadzu UV 1800 spectrophotometer using a 10 mm path length quartz cuvette and the fluorescence experiment was done using PTI fluorescence spectrophotometer using a fluorescence cell of 10 mm path. Human urine sample collection and determination of hydrazine in those samples were performed in the Dept. of Microbiology, CIMS Hospital, Bilaspur in conformity with IEC guidelines regarding conduct of research and requirement of informed consent. Informed consent was obtained for any experimentation with human subjects.

Synthesis and characterisation of L

To a dehydrated methanolic solution of p-phenylenediamine (0.108 g, 1 mmol, in 50 mL methanol) pyridine-4-carboxaldehyde in methanol (0.214 g, 2 mmol, in 5 mL methanol) was

added. The mixture was refluxed for 4h at 45^{0}C, maintaining dry condition. A yellow precipitate obtained was filtered and washed several times with *n*-hexane and then again recrystallized in methanol and dried in a vacuum to obtain the pure yellow solid (Scheme 1). Yield: 82%. M.P.- 205^{0}C. ^{1}H NMR: (DMSO-d_6, δ ppm, TMS): 10.08 (s, 2H); 8.86 (d, 4H); 7.79 (d, 4H) and 7.44 (d, 2H) (Fig. S1); ^{13}C NMR: (DMSO-d_6, δ ppm, TMS): 160.4, 152.1, 150, 148.6, 142.9, 122.6, 114 (Fig. S2). FT-IR: (KBr, cm^{-1}): 1597.08 (C=N) (Fig. S3). ESI-MS: m/z [M +2H$^+$], 288.48 (100%) (Fig. S4). Anal. calcd for $C_{18}H_{14}N_4$: C, 75.50; H, 4.93; N, 19.57%. Found C,75.54; H,4.91; N,19.59%.



Scheme 1 Synthetic procedure of the receptor **L**.

UV-Vis titrations

The chemosensor **L** (2.86 mg, 0.01 mmol) was dissolved in methanol-water solvent mixture (4/6, v/v, 10 mL) and 30 μL of this was diluted to 3 mL with the solvent mixture to make a final concentration of 10μM. Hydrazine (0.1 mmol) was dissolved in 10 mL of triple distilled water and 1.5–90 μL of the hydrazine solution (10 mM) were transferred to the solution of **L** (10 μM) prepared above. After mixing them for a few seconds, UV-Vis spectra were obtained at room temperature.

Fluorescence Titration

L (2.86 mg) was dissolved in 10 mL of mixed solvent CH_3OH–H_2O (4/6, v/v) to make a solution of 1×10^{-3} M and 30 μL of this solution were diluted with 2.97 mL of solvent mixture to make the final concentration of 10 μM. Hydrazine (0.1 mmol) was dissolved in triple distilled water (10 mL) and 1.5–90 μL of this solution (10 mM) were transferred to each receptor solution (10 μM) to give 0.5–30 equiv. After mixing them for a few seconds, fluorescence spectra were obtained at room temperature.

pH effect test

A series of buffers with pH values ranging from 2 to 12 was prepared using 100 mM HEPES buffer. After the solution with a desired pH was achieved, receptor **L** (2.86 mg, 0.01 mmol) was dissolved in methanol (10 mL), and then 30 μL of this solution (1 mM) was diluted to 3

mL with above-mentioned buffers to make the final concentration of 10 μM. Hydrazine (0.1mmol) was dissolved in HEPES buffer (10 mL, pH 7.00). 30 μL of the hydrazine solution (10 mM) were transferred to each receptor solution (10 μM) prepared above. After mixing them for a few seconds, fluorescence spectra were obtained at room temperature.

Colorimetric test kit

Chemosensor **L** (2.86 mg, 0.01 mmol) was dissolved in methanol (10 mL) to get 1 mM solution. Test kits were prepared by immersing filter-papers into this solution (1 mM), and then dried in air to get rid of the solvent. Hydrazine and different amines (aniline, urea, cyclohexyl amine, benzyl amine, thio urea, ethylenediamine, diethylenetriamine, phenyl hydrazine, diphenyl amine; 0.001 mmol) were dissolved in methanol (10 mL) to prepare 0.1 mM solution. The test kits prepared above were dipped into the methanol solution of hydrazine and different amines and then dried at room temperature.

Computational details

The GAUSSIAN-09 Revision C.01 program package was used for all calculations.[53] The gas phase geometries of the compound was fully optimized without any symmetry restrictions in singlet ground state with the gradient-corrected DFT level coupled with the hybrid exchange-correlation functional that uses Coulomb-attenuating method B3LYP.[54] Basis set 6-31++G was found to be suitable for the whole molecule. The electronic spectrum of the receptor **L** was calculated with the TD-DFT method and the solvent effect (in methanol) was simulated using the polarizing continuum model with the integral equation formalism (C-PCM).[55,56]

Results and discussion

DFT study on the receptor L

In order to get the structural information of **L** and to co-relate the spectral property, DFT calculations were performed on the molecule **L**. The geometry optimizations staring from gauss view structure of **L** lead to a global minimum as stationary level. The optimized structure of the **L** is shown in Fig. 1.The simulated absorption spectra of **L** in presence of the solvent employing the TD-DFT are in good agreements with the experimental data.[52]

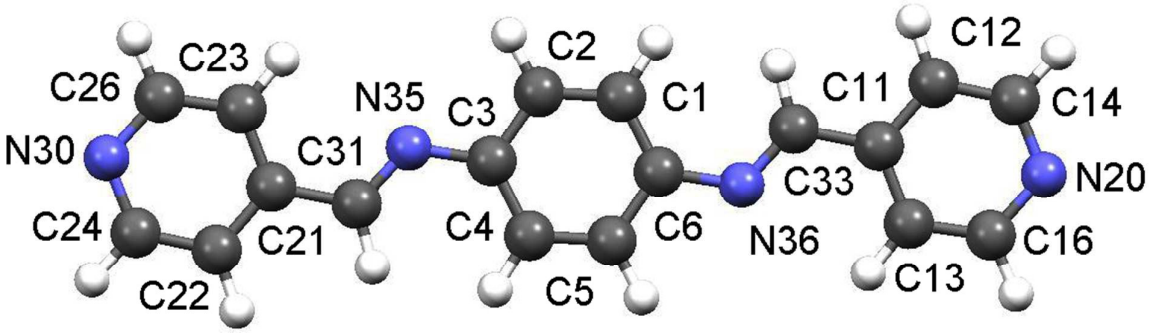


Fig. 1 Geometry optimized diagram of the molecule **L**.

UV/Vis absorption spectroscopy

To investigate the selectivity and specificity of the fluorescent-colorimetric sensing agent **L** for hydrazine, absorption and fluorescence studies of **L** were performed with other representative analytes, including common metal cations, anions and different amines under identical conditions. Remarkably, the results showed an excellent selectivity and specificity towards hydrazine over all other tested analytes. The probe **L** without hydrazine exhibited three absorption bands at 240, 288 and 380 nm. Among them two strong bands at 240 nm and 380 nm were assigned to the phenyl π- π* and n-π* electronic transition respectively. But addition of hydrazine to a solution of **L** led to an abrupt decrease in absorption intensity at 380 nm along with a colour change from yellow to colourless, which countenances the detection of hydrazine by naked eye. However absorption studies carried out with other amines, metal ions and anions (except Al^{3+} and HSO_3^- ions) showed no significant change, indicating their non-interactive nature with **L** (Fig. 2 and Fig. S5).

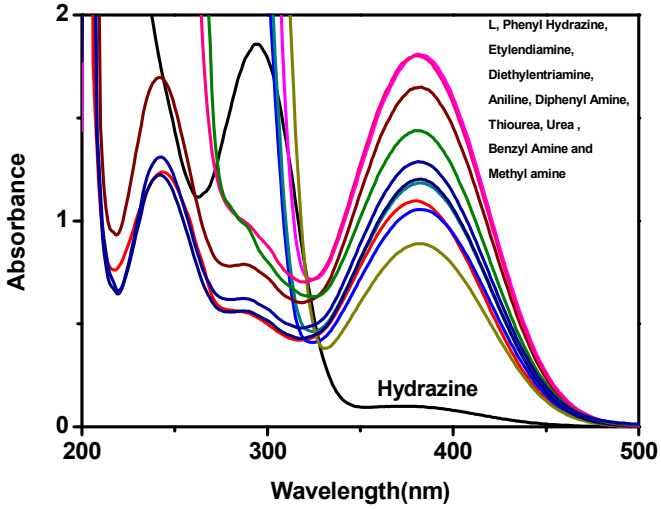


Fig. 2 Absorbance spectra of **L** (10 μM) before and after addition of various amines (10 equiv.)

Only Al^{3+} and HSO_3^- ions have some influence on absorption behaviour of **L** showing same type of colour change as was shown by hydrazine.[50] This indicates that under signalling conditions, the possible interference by common metal ions or anions is not of practical problem in hydrazine sensing by the probe **L**. In titration experiment, upon increasing the concentration of hydrazine, the absorbance of **L** at 380 nm almost vanished and one new peak was generated at 294 nm accompanied by a well-defined isosbestic point at 326 nm (Fig. 3).

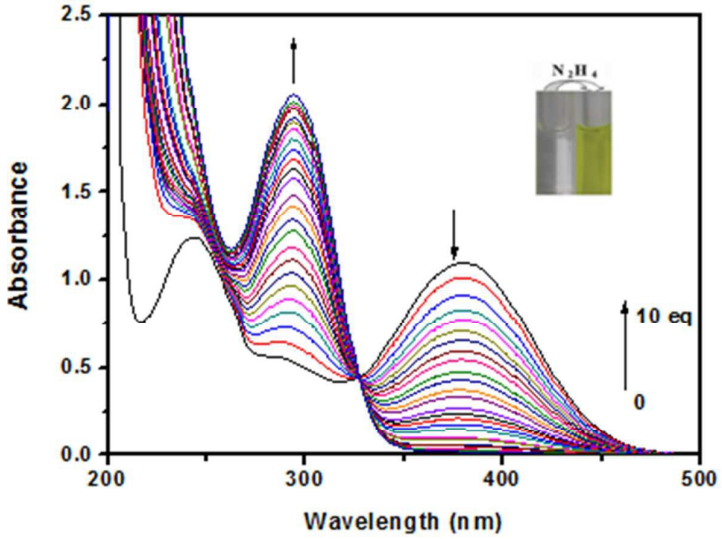


Fig. 3 Absorbance spectra of **L** (10μM) after addition of increasing amounts of N_2H_4 (up to 10 equiv.) in CH_3OH–H_2O (4/6, v/v) at room temperature.

The π conjugate system of the probe **L** undergoes intramolecular charge transfer (ICT) from the donor to the acceptor upon excitation by light, and so the association of hydrazine with **L** through hydrogen bonding interaction will affect the efficiency of intramolecular charge transfer and reduce the electron-donating ability of imino-nitrogen atoms leading to the decrease in intensity at 380 nm.

Fluorescence spectroscopy

The fluorimetric detection of hydrazine by **L** was also very much pronounced (Fig. 4). The low fluorescence intensity of **L** can be ascribed to the photo-induced electron transfer (PET) process caused by the electron transmission from the two terminal pyridyl nitrogen atoms to

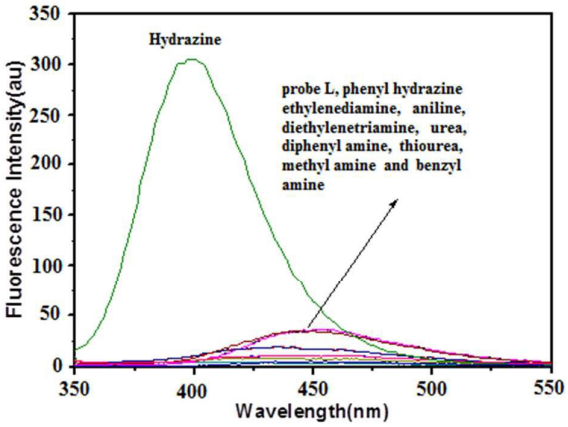
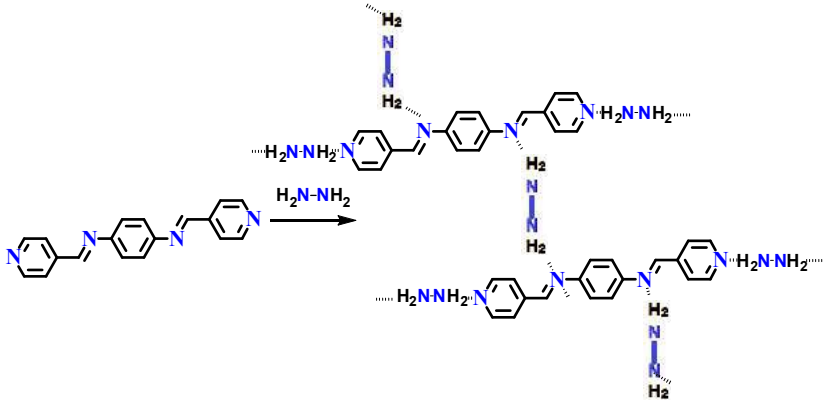


Fig. 4 Fluorescence spectra of probe **L** (10 μM) before and after the addition of various amines (2 equiv.) in CH_3OH–H_2O (4/6, v/v) λ_{ex}= 310 nm.

the large π-conjugation system including two >C=N– groups and three aromatic rings. On addition of hydrazine, the two terminal pyridyl nitrogen atoms and two imine nitrogen atoms of **L** formed H-bonds with the hydrogen atoms of hydrazine. As is well known, a hydrazine molecule contains two amino groups and two such units can easily form extended arrays of hydrogen bonding (NH---N) with the probe **L**, as shown in Scheme 2.



Scheme 2 Sensing process based on hydrogen bond recognition mechanism.

Such hydrogen bonding impeded the PET process resulting in a significant fluorescence enhancement of **L-N_2H_4** adduct accompanied by a prominent blue shift of about 50 nm. As shown in Fig. 4, **L** exhibited an extremely weak fluorescence on excitation at 310 nm (Φ = 0.0157). But on addition of 2 equivalent of hydrazine, the fluorescence intensity was dramatically increased with high quantum yield (Φ = 0.63). Fig. 5 delineates the emission spectra of probe **L** via varying concentration of hydrazine from 0 to 10 equivalents. From the titration profile, the association constant for L–N_2H_4 was determined as 1.63×10^5 M^{-1} by a Hill plot (Fig. S6).

The Job plot analysis based on fluorescence indicated a 1:2 stoichiometric ratio which implies the attachment of two hydrazine molecules with one probe molecule (Fig. S7).

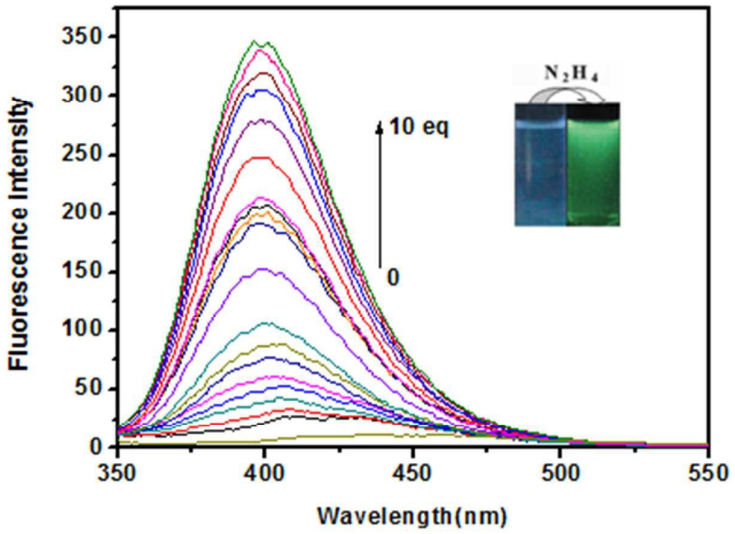


Fig. 5 Fluorescence spectra of **L** (10 μM) after the addition of increasing amounts of N_2H_4 (up to 10 equiv.) in CH_3OH–H_2O (4/6, v/v) at room temperature (λ_{ex} = 310 nm).

The enhanced fluorescence efficiency of **L-N_2H_4** adduct was around 14-fold greater than the control in absence of hydrazine. The inset in Fig. 5 shows the colour change of probe **L** upon addition of hydrazine based on the use of UV lamp with excitation at 365 nm. From this titration profile, we may conclude that fluorescence intensity varies almost linearly with the concentration of hydrazine in the range of 0–100 μM (linearly dependent coefficient R^2 = 0.996). The detection limit calculated on the basis of the definition given by IUPAC (C_{DL} = 3 Sb/m),[57] was 3.2 ppb which is far below the threshold limit value (10 ppb) (Fig. S8). These findings inferred that the chemo-sensor **L** was potentially useful for detection of hydrazine.

The selectivity behavior is obviously one of the most important characteristics of a chemosensor, that is, the relative sensor response for hydrazine over other analytes present in solution. In order to evaluate the selectivity of probe **L** towards hydrazine, fluorescence studies on **L** were performed with different amines, metal cations and anions under the similar conditions: the concentration of **L** was kept at 1.0×10^{-5} mol dm^{-3} and 2 equiv. of analytes were added. As shown in Fig. 6 and Fig. S9, no change in fluorescence intensity is observed in the emission spectra of **L** after addition of other analytes (except Al^{3+} and HSO_3^- ions). In presence of Al^{3+} and HSO_3^-, fluorescence intensity of **L** gets enhanced to some extent but this enhancement is smaller than that induced by hydrazine.

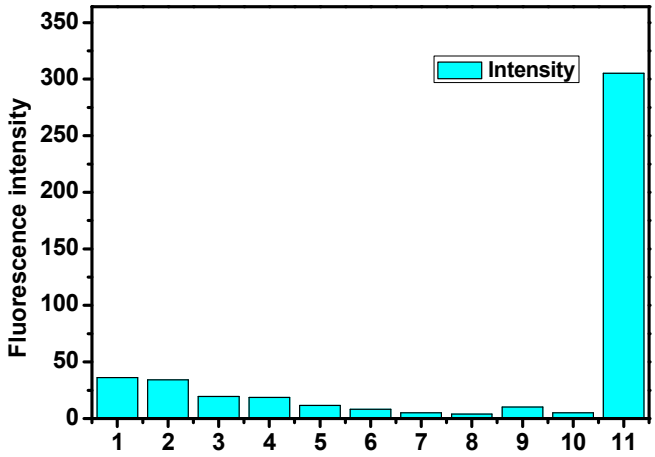


Fig. 6 Fluorescence responses of probe **L** (10 μM) to hydrazine and other amines (1. Phenyl hydrazine, 2. Ethylene diamine, 3. Aniline, 4. Diethylene triamine, 5. Urea, 6. Thio urea, 7. Diphenyl amine, 8. Methyl amine, 9. Benzyl amine, 10. only **L** and 11. Hydrazine). Each spectrum was recorded after 2 min.

For realistic applications, the suitable pH conditions of both the probe **L** and **L-N_2H_4** adduct were examined using 100 mM HEPES buffer. The variation of fluorescence intensity of both the probe **L** and **L-N_2H_4** at different pH were shown in Fig. 7. Remarkably this unprecedented nature of sensing also holds well in wide pH range (pH 4 -10). The intense and almost stable fluorescence of **L-N_2H_4** adduct in wide pH range warrants its application under physiological conditions, without any change in detection results.

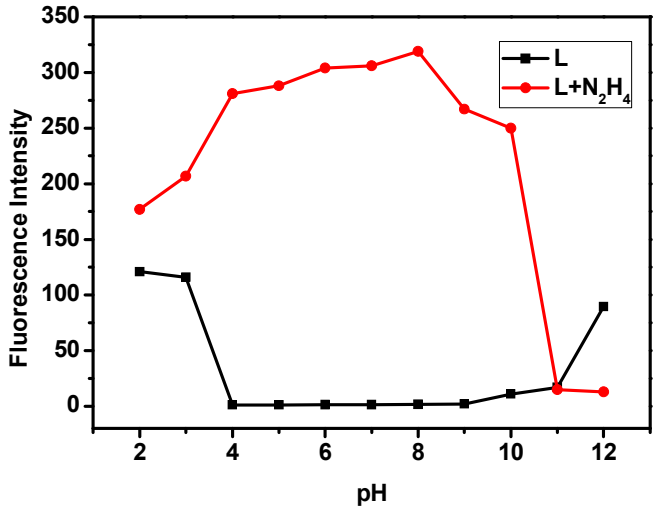


Fig. 7 Fluorescence intensity of **L** and **L-N_2H_4** at different pH at room temperature. Inset: intensity at 400 nm.

^{1}H NMR and HRMS spectral studies of the probe and the adduct

Furthermore, we investigated the ^{1}H-NMR spectra of the probe **L** in the presence of hydrazine and compared with that of the sensor **L**. It has been observed that on addition of hydrazine to the probe **L**, all the proton signals are shifted to lower δ values with respect to **L** due to formation of hydrogen bonding (Fig. 8). Most interestingly, a new peak is generated at 6.47 ppm which may be the signal of hydrogen of hydrazine. This observation clearly demonstrates the hydrogen bonding induced sensing mechanism of the probe **L**.

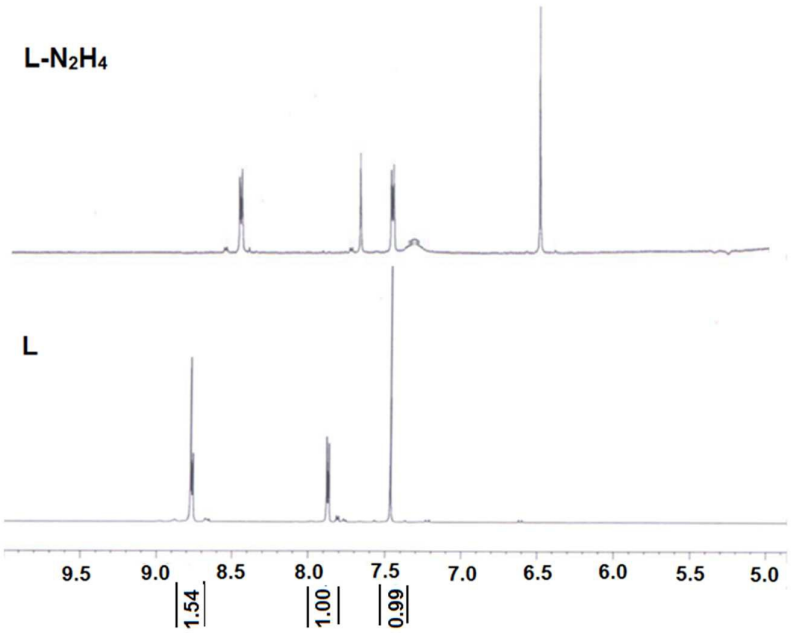


Fig. 8 Partial ^{1}H NMR spectra of the receptor **L** and its **N_2H_4** adduct, **L- N_2H_4** in d_6-DMSO.

Moreover, in HRMS spectral analysis of **L-N_2H_4**, (Fig. 9) the appearance of a peak at m/z: 414, assignable to [**L**+ 4 N_2H_4] further rationalize the phenomenon of hydrogen bonding between hydrazine and probe **L**.

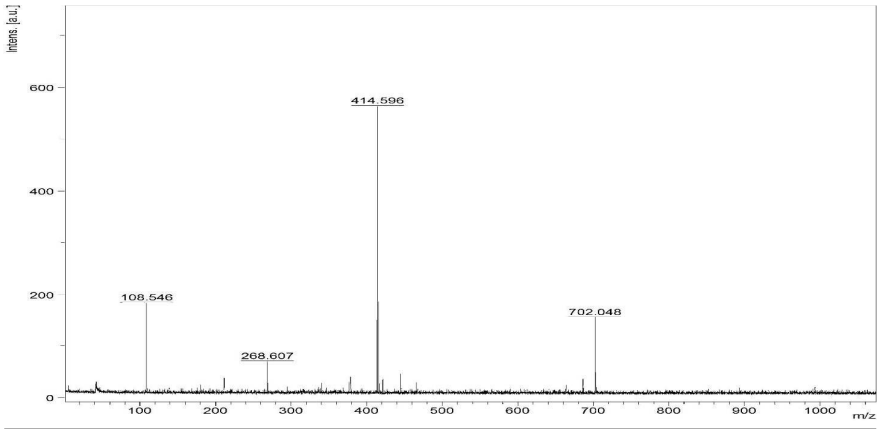


Fig. 9 HRMS spectrum of **L- N_2H_4** adduct.

DFT Study on sensing mechanism

The sensing mechanism based on hydrogen bonding recognition was also well documented by DFT studies. To calculate the hydrogen bonding energy we have used the same basis sets and the same functional as used to optimize the structures of the ligand and hydrazine. Hydrazine can form hydrogen bonding with the ligand in two positions, viz. nitrogen in the chain and the terminal position of the pyridine ring (Fig. 10). In both the cases the initial distance between the hydrazine and the ligand is 2.0 Å. The hydrogen bonding energy for both the structures are tabulated in Table 1.

Table 1 Hydrogen bond energy of ligand-hydrazine mixture

Molecule	**Stability (kcal/mol) (BSSE corrected)**
Ligand-Hydrazine (with chain)	−2.84514775 (−2.55688429)
Ligand-Hydrazine (terminal)	−3.46386275 (−3.24373073)

The basis set super position error (BSSE) corrected values are also given in the parenthesis. From the Table 1 it is clear that the hydrogen bonding is stronger in the terminal one, than the chain.

We have also studied the excitation energies of both the systems (Table S1-Table S3). From these data we can conclude that the λ_{max} value of the hydrazine-ligand admixture does not change much from the original ligand. So possibility of charge transfer is less. This fact is further corroborated by Mülliken population analysis (Table S4). Mülliken population

analysis shows that the charge on ligand and hydrazine is not that high, thus, no significant charge transfer could take place.

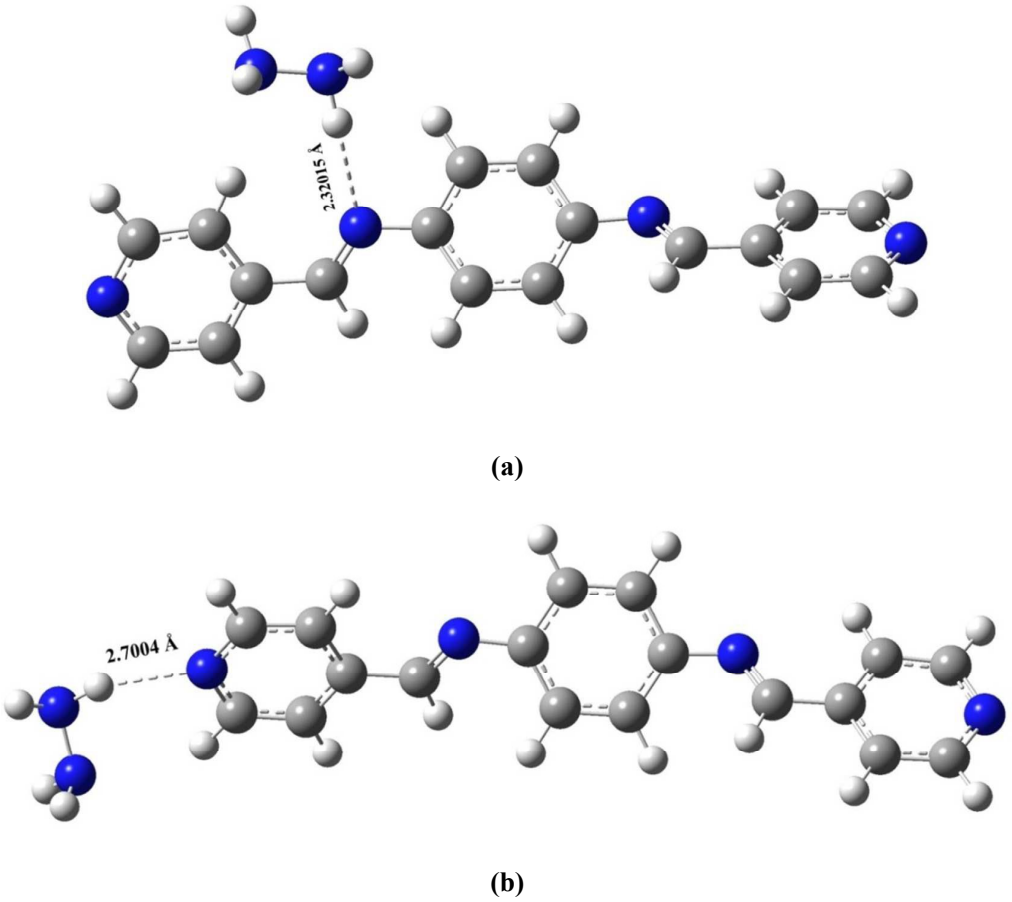


Fig. 10 The optimized structures of hydrazine and the ligand. (a) When hydrazine interact with the N atom of chain, (b) hydrazine interacts with terminal N. Hydrogen bonds are shown by dotted line (---) and the value is the distance of the optimum structure.

We have also assumed another possibility of formation of $^{-}NH\text{-}NH_3^{+}$ zwitterions in the solution such that charge transfer can take place from the ligand to $^{-}NH\text{-}NH_3^{+}$ or hydrazine (Fig. S10). From Mülliken charge analysis we have seen that the amount of charge transfer from ligand to hydrazine or $^{-}NH\text{-}NH_3^{+}$ is negligible. So we can conclude that the hydrogen bonding plays an important role for this phenomenon.

Detection of hydrazine in vapour phase and in aqueous solution

To check the practical applicability, the probe **L** was tested for hydrazine in vapour phase. The chemosensor **L** could rapidly and effectively sense hydrazine gas. This experiment was carried out using a TLC plate coated with **L**. A 0.1 mM solution of the L was prepared in

methanol. A TLC plate was dipped into it and dried at room temperature for 30 min to get rid of the solvent. The TLC plate was kept in a conical flask. Excess of hydrazine gas was then passed into the flask for 10 second. The colour of the TLC plate changed from yellow to colourless within 10 second (Fig. 11).

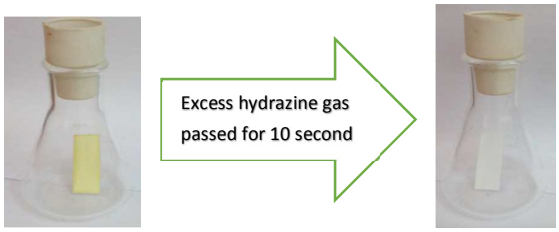


Fig. 11 Change in colour of TLC plate in presence of hydrazine gas.

To further establish the application potential of probe **L**, the test kits were utilized to sense hydrazine among different amines. When the test kits, coated with probe **L** were added to different amine solutions, the obvious colour change from yellow to colourless was observed only in the case of hydrazine solution, as shown in Fig. 12. Therefore, the test kits coated with probe **L** would be convenient for detecting hydrazine. These results showed that receptor **L** could be a valuable practical sensor for environmental analyses of hydrazine.

Fig. 12 Photographs of the test kits with **L** (0.5 mM) for detecting hydrazine in aqueous solution with other amines.

Determination of hydrazine in real samples

In order to evaluate the practical feasibility of the sensor for determination of hydrazine, water samples collected from tap and rain water and human urine samples were employed (Table 2). The spiked hydrazine concentrations were of 10 and 20 μM. The determined concentrations are: tap water (11.6 and 19.3 μM); rain water (12.7 and 21.5 μM) and urine sample (8.9 and 19.1).The corresponding recoveries are: tap water (116% and 96%); rain water (127% and 107%) and urine sample (89% and 95%). Appreciable recoveries achieved in the determination of hydrazine in various water samples and human urine samples revealed good practical feasibility of the sensor in quantitative estimation of hydrazine in different environmental and biological samples.

Table 2 Determination of hydrazine in different water samples

Samples	Added(μM)	Found(μM)	Recovery (%)	RSD*(%)
Tap water	10	11.6	116	2.1
	20	19.3	96	1.5
Rain water	10	12.7	127	1.8
	20	21.5	107	2.7
Urine sample	10	8.9	89	2.2
	20	19.1	95	1.3

*Relative Standard Deviation of 3 individual measurements.

Conclusion

In summary, for first time, we have developed a simple Schiff base **L** as a fluorescent-colorimetric probe which can efficiently detect hydrazine in vapour and solution phase through hydrogen bond recognition. The probe could selectively distinguish hydrazine with an OFF–ON fluorescence signal change and the visible colour changes from yellow to colourless at room temperature within 10 second. The detection limit of **L** was found to be 3.2 ppb, which is fairly below TLV limit set by the USEPA. Interestingly, the probe has sufficient potentiality to operate in wide pH range. Importantly, probe **L** has been successfully applied for sensing of hydrazine in different environmental and biological samples by an easy and practical method, providing a convenient way for hydrazine detection. Most of the chemo-sensors for hydrazine available in literature are based on chemical reactions. But the hydrogen bonding induced sensing of hydrazine is rarely observed.

Acknowledgements

G.K.P would like to thank the Department of Science and Technology and Department of Biotechnology, Government of India, New Delhi for financial support. The authors are grateful to Dr. R. Murthy, Medical Superintendent, CIMS Hospital Bilaspur for allowing them to perform few experiments in CIMS Hospital Bilaspur.

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GRAPHICAL ABSTRACT

A 'chromogenic' and 'fluorogenic' bis-Schiff base sensor for rapid detection of hydrazine both in solution and vapour phase

Anupam Ghorai, Jahangir Mondal, Sumantra Bhattacharya and Goutam Kumar Patra*

Department of Chemistry, Guru Ghasidas Vishwavidyalaya, Bilaspur (C.G)

A simple, cost effective Schiff base ligand has been exploited as a fluorescent-colorimetric probe for rapid detection of hydrazine both in liquid and gas phase via a novel and facile way. The sensing behaviour is based on hydrogen bonding recognition supported by DFT and TDDFT studies. The probe shows good practical applicability in different environmental and biological samples.