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Chromogenic ‘naked eye’ and fluorogenic ‘turn on' sensor for mercury metal ion using thiophene based Schiff base

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Abstract

2-((3-methylthiophen-2-yl)methyleneamino)benzenethiol (Probe 1) has been synthesized and successfully applied for the selective recognition of mercury metal ion and utilized as a fluorescence turn-on sensor for Hg^{2+} ion detection via chelation enhanced fluorescence (CHEF). The mechanism of the interaction of Probe 1 with the metal ion has been inculcated by the absorption, emission, ^{1}H-NMR, MALDI-TOF Mass analysis that intimate the favourable coordination of Hg^{2+} metal ion by the mercapto unit. The 2:1 stoichiometry of the sensor complex 1 + Hg^{2+} was calculated from the Job’s plot based on UV-Vis absorption spectra. The binding constant (log β_2) of the 1+Hg^{2+} complex was found 13.36 by Hill Plot. The limit of detection (LOD) was also calculated from the fluorescence emission titration that was found 20 μM. Moreover the density functional theory (DFT) studies were investigated for the 1+Hg^{2+} binding mechanism. Cyclic Voltammograms were also satisfied the Hg^{2+} binding with probe 1.

Introduction:

Many human disorders caused by the exposure of the toxic metal ion: like Mercury, Lead, Cadmium, Silver. Many efforts devoted to the development of fluorogenic and colorimetric sensor for the highly toxic mercury ion. Mercury metal ion is highly toxic, non-biodegradable[1] and hazardous in nature[2-4], toxic for human, including brain, kidney and lung damage. The results of mercury poisoning in several diseases, including Acrodynia, and Minamata disease. The toxicity of Hg^{2+} in human caused by the easily coordination with biological ligands such as proteins, DNA and enzymes due to its affinity towards thiol group. Its significant presence hazards to public health because of its presence in drinking water. Therefore, the development of rapid, cost-effective and enzyme-free colorimetric sensors for the easy and fast detection of toxic metal ions by the naked

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

eye without resorting to any expensive instruments is still an active ongoing research area.

The sources of Hg^{2+} contamination in water include gold mining, rubber processing, fertilizer industries, Oil refining, wood pulping. All the different forms of mercury ion as zero oxidation, mercuric ion in Hg^{2+}, mercurous in Hg_2^{2+}, have toxic effects on environment. Due to the bioaccumulation and magnification of Hg^{2+} in the aquatic food chain, Hg^{2+} have serious environmental toxification. So construction of chemosensor for Hg^{2+} ion detection is demanded. Due to the low level of metal in the samples and complexity of the matrices, the analysis of metal ions in the environment, clinical, industrial and biological samples is still a challenging task. Many sensors have been reported based on fluorescence 'turn-off' response due to quenching nature of heavy metal Hg^{2+} ion having large spin-orbit coupling constant[5-9], recently several 'turn-on' fluorescence sensor for Hg^{2+} ion reported[10-15]. However, the chemosensor detect Hg^{2+} ion via enhanced fluorescence are very rare. We herein report a new sensor motif to detect the Hg^{2+} through a fluorescence"turn-on" response in partial aqueous medium.

World Health Organization (WHO) and Environmental Protection Agency (EPA) have defined the limited concentration of these metal ions in drinking water. There are many important techniques which facilitate the quantification of these metal ions like: Atomic Absorbtion Spectroscopy (AAS) and ICP-MS[16-19]. Due to their high cost and high maintenance, colorimetric sensors have been developed. For the recognition of soft, heavy metal ion Hg^{2+}, the nitrogen and sulphur binding site might be a choice as it is present in the thiophene based Schiff base.

1. Experimental Section:

1.1. Reagents and Instrumentation:

Chloride and Nitrate salts of Metal ions were all of analytical reagent grade and purchased from Merck. These reagents were used without further purification. 3-methylthiophene-2-Carbaldehyde, 2-Aminothiophenol, 3-Aminophenol were purchased from Sigma-Aldrich. The UV-Vis analysis of all the solutions was recorded on a Shimadzu, UV-3600 double beam spectrophotometer using 10 mm path length silica cell. IR spectra were recorded with a Perkin Elmer FT-IR 1000 spectrophotometer as films between KBr. CHNS Analysis was recorded on an Elementar model Vario EL-III. NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer. MALDI-TOF Mass Spectra were recorded on Bruker Ultra-fleXtreme-TN-MALDI-TOF Spectrometer using HABA as a matrix. Fluorescence emission spectra were recorded using RF-5301PC with a standard quartz cell of 3 cm path length. Cyclic voltammetric studies were carried out at room temperature on a CH**I760E** electroanalyser. The potential range were +1.5000 V to −1.5000 V at a scan rate of 0.1 V/s using glassy carbon electrode as working electrode, Ag/AgCl electrode as reference electrode and Pt wire as auxiliary electrode, and 0.1 M tetrabutylammonium perchlorate (TBAP) were used as supporting electrolyte. All solutions were purged with nitrogen before the experiment. DFT Computation studies were organized in the Gaussian 09 W programme in gas phase using B3LYP function with 6-31G (d, p) for metal free ligand and LANL2DZ for the metal - ligand complex.

1.2. Synthesis of Probe 1 and 2:

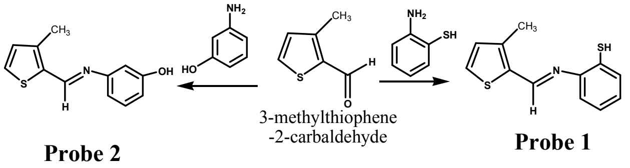
2-((3-methylthiophen-2-yl)methyleneamino)benzenethiol (Probe 1): Took 3-methylthiophene-2-carbaldehyde (2 mmol) in methanol solution in a round bottom flask and stirred till complete dissolution of aldehyde, after that add 2-amino thiophenol (2 mmol) and then reflux for 16 hrs, a yellowish precipitate of Probe 1 was formed recrystallised using ethanol.

Yield: 77%. Anal. Calc. for $C_{12}H_{11}NS_2$: C, 61.76; H, 4.75; N, 6.00, S, 27.48 Found: C, 62.01; H, 4.50; N, 6.71; S, 26.99. IR data (KBr,νmax/cm−1): Ar-H: 3117, S-H: 2359, C-N: 1568, C-C: 1414, C-O: 1247. UV-visible (MeOH, λmax/nm): 287, 355. ^{1}HNMR (DMSO,500 M Hz,δ/ppm) : 8.78 (s, 1H), 7.36 (d, 1H), 7.21 (d, 1H), 7.10 (t, 1H), 6.92 (dd, 1H), 6.87 (d, 1H), 6.83 (t, 1 H) 4.66 (s, 1H) 2.44 (s, 3H), ^{13}CNMR (DMSO, 125 MHz, δ/ppm) 151,148,142,136, 135, 131, 130, 128, 120, 115, 114, 83.

3-((3-methylthiophen-2-yl)methyleneamino)phenol (Probe 2): 3-methylhiophene-2-carbaldehyde (5 mmol) dissolved in methanol and the dropwise addition of a methanolic solution of 3-amino phenol (5 mmol) and refluxed this solution for 20 hrs, a brownish precipitate was occurred and recrystallised using ethanol.

Yield: 62%. Anal. Calc. for $C_{12}H_{11}NOS$: C, 66.33; H, 5.10; N, 6.45; O, 7.36; S, 14.76 Found: C, 66.10; H, 4.83; N, 6.79; O, 8.72; S, 13.56 IR data (KBr,νmax/cm−1): O-H: 3433, C-N: 1607, C-C: 1422, UV-visible (MeOH, λmax/nm): 383. ^{1}HNMR (DMSO,500 M Hz, δ/ppm): 8.65 (s, 1H), 7.38 (d, 1H), 7.24 (d, 1H), 6.95 (m, 4H), 3.19 (broad s, 1H), 2.48 (s, 3H), ^{13}CNMR (DMSO,125 M Hz,δ/ppm) 158, 150, 144, 141, 138, 136, 134, 131, 129, 122, 114, 55.

Structure of both Schiff bases shown in scheme 1. Characterization data of Probe 1 and 2 were shown in the supplementary information (Fig. S1 to Fig. S6).



Scheme 1. Synthesis of thiophene based Schiff base (Probe 1 and 2).

2. Results and Discussion:

Mercury ions have binding affinity with the sulphur atom because of the soft ligand. For this purpose, we proposed the synthesis of the ligand having mercapto unit and explored for the selective recognition of mercury ion. Mercury binds with the ligand moiety in linear pattern.

2.1. Naked eye detection of metal ion:

To investigate metal ion recognition with synthesized Schiff bases (Probe 1 and 2), colorimetric studies have been done with various metal ions. The solution of all the metal ions and Probe were prepared in methanol of 50 mM. 3 equivalents of metal solution were added to the Probe 1 solution, and the sudden color change of the Probe 1 from light yellow to yellowish orange was observed with the Hg^{2+} ion (Fig. 1). Further the selectivity of the Probe 1 towards mercury ion was confirmed by UV-Vis and fluorescence studies. Probe 2 did not show any change in color with different metal ions

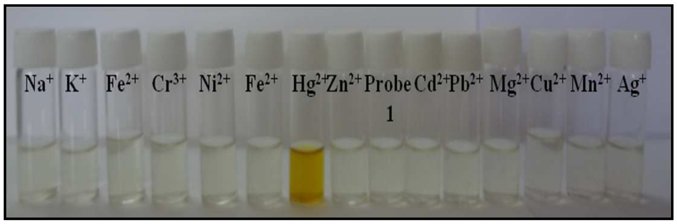


Fig. 1 Images of Colorimetric changes of Probe 1 with Hg^{2+} ion in Methanol/H_2O (8/2; v/v) solution.

2.2. UV-Vis Studies of Probe 1 and 2 with metal ion:

To know the selectively recognition of Hg^{2+} to the Probe 1, UV-Vis studies were carried out methanol/H_2O (8/2:v/v solution). Probe 1 was shown absorption peaks at 287 nm due to π-π* transition and 355 nm due to n-π* transition. Upon the addition of mercury solution to the Probe 1 solution (50 mm) a new absorption band was occurring at 430 nm in UV-Vis spectra due to the metal recognition (Fig. 2a), and other metal ion was not showing any significant changes in UV-Vis spectra with Probe 1. Probe 2 did not show any absorption changes upon addition of metal ions (Fig. 2b).

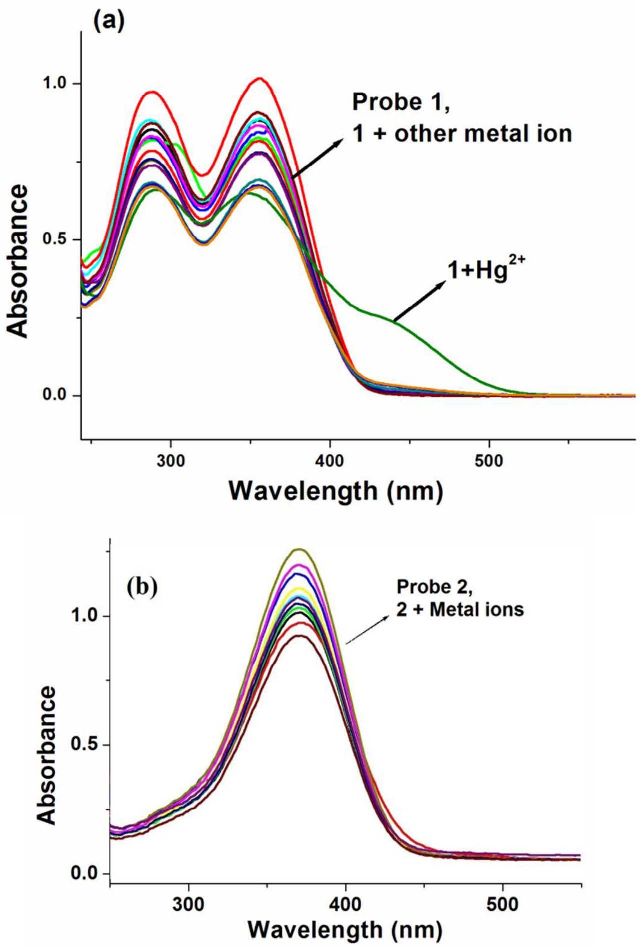


Fig. 2 UV-Vis Spectra of Probe 1 (a) and Probe 2 (b) with different metal ions.

To know the binding stoichiometry of $1+Hg^{2+}$ complex, equimolar solutions of Probe 1 and Hg^{2+} ion were prepared (50 µM in methanol) and absorption spectra were taken by the continuous variation of 1 and Hg^{2+} solution.

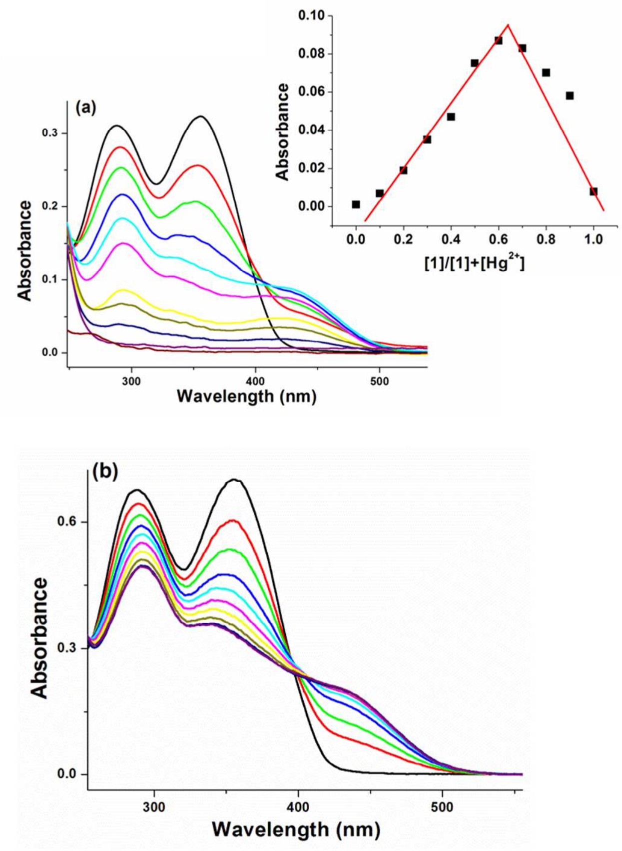


Fig. 3 (a) UV-Vis spectra with continuous variation in mole fraction of Probe 1 and metal ion, inset shows a Jobs plot with equimolar concentration (50 µM). (b) UV-Vis spectra showing the isosbestic point (100 µM).

Fig. 3a is showing the changes in absorption spectra and Job's plot[20] which show the 2:1 stoichiometry. UV-Vis spectra were shown changes while the addition of Hg^{2+} ion in Probe 1(100 µM), a concomitant increase in the absorbance at 430 nm and decreased in the absorbance at 355 nm and 287 nm. The formation of the isosbestic point confirmed (Fig. 3b) the changes of uncomplexed species (Probe 1) to complex species ($1+Hg^{2+}$). The red shift in UV-Vis spectra (90 nm) have responsible for the sudden color change of the solution of the Probe 1, i.e., light yellow to yellowish orange upon the addition of Hg^{2+} ion. The new absorption band was occurring due to the intramolecular charge transfer between Probe 1 and mercury metal ion.

2.3. Fluorescence Emission Spectra with metal ion:

All the experiments were carried out in methanol/H_2O. Initially, the Probe 1 (20 µM) in methanol/H_2O; (8/2: v/v solution) was tested for the metal ion 60 µM (3 equiv.) ions (Na^+, K^+, Fe^{2+}, Cr^{3+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, Hg^{2+}, and Ag^+).

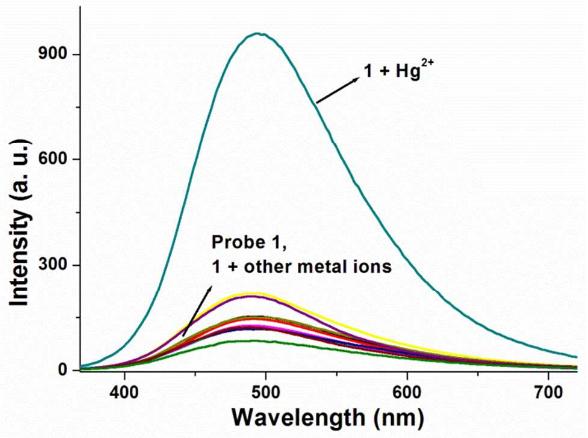


Fig. 4 Fluorescence Spectra of Probe 1 (5 µM) towards different metal ion in methanol/water (8/2=v/v; solution) (λ_{ex}= 365 nm).

Upon treating Probe 1 with 3 equiv. of metal ions, exhibited the turn-on emission occurred at 503 nm with Hg^{2+} ion (λ_{ex}=365 nm) (Fig. 4). The 'turn on' fluorescence selectivity of Hg^{2+} ion was caused by chelation enhanced fluorescence (CHEF). The covalent bond formation between the –SH group and Hg^{2+} ion exhibit the enhanced fluorescence response.

Table 1. UV-Vis and fluorescence wavelength of Probe 1 and 1+Hg^{2+} and LOD calculated by fluorescence titration.

Sample	UV (nm) Study	Fluorescence Study	LOD by fluorescence titration
Probe 1	287, 355nm	-	-
1+Hg^{2+}	287, 355, 430 nm	503 nm enhanced fluorescence	20µM

From the UV-Vis studies and fluorescence studies, it was found that the Probe 1 is highly selective for Hg^{2+} ion (Table 1), for the confirmation of above selectivity, the single and dual metal study has done with Probe 1. In the course of dual-metal studies, two equal amounts of both metal ion Hg^{2+} and other metal ions (60µM+60µM) were used. The interference effect of secondary metal ion for the selectivity of Hg^{2+} ion was also carried out and shown in Fig. 5. The blue bar indicates the single metal ion (Na^+, K^+, Fe^{2+}, Cr^{3+}, Ni^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, Hg^{2+}, and Ag^+) with Probe 1 and red bar indicates the 1+Hg^{2+} with interfering ion. Fig. 5 has shown enhanced fluorescence intensity with Hg^{2+} ion and no other metal ion were shown the enhancement in fluorescence intensity. No metal ions were interfering the selectivity of Hg^{2+} (red bar). So with the help of interference study it was surely confirmed that the Probe 1 was highly selective and sensitive for Hg^{2+} metal ion.

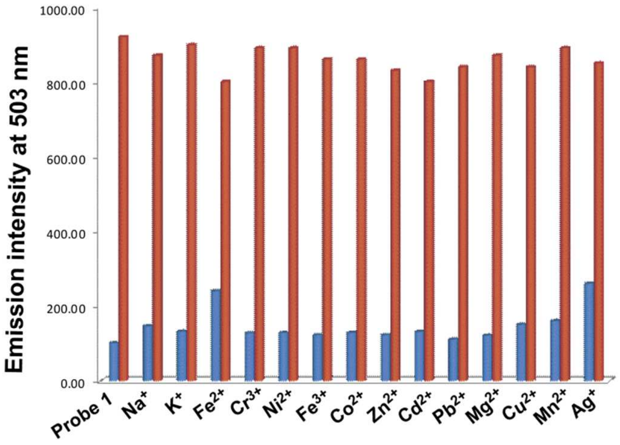


Fig. 5 Interference study with different metal ions at 503 nm in methanol/H_2O solution, Probe 1+ metal ions (blue bar) and 1 + metal ions + Hg^{2+} (red bar).

2.4. Fluorescence titration[21,22] of Hg^{2+} ion with Probe 1:

For the fluorescence titration, 10 µL aliquots addition of Hg^{2+} ions of fixed concentration was added to a 3 mL solution of Probe 1 (Fig. 6). Binding constant was calculated by fluorescence titration using Hill method[23].

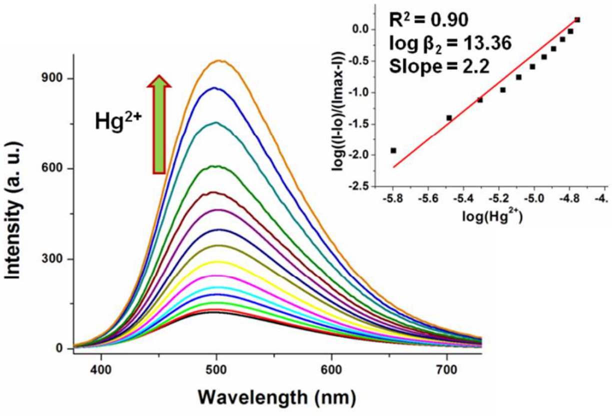


Fig. 6 Fluorescence Emission titration of Probe 1 with various concentration of Hg^{2+} metal ion.

The $\log\beta_2$ value for Hg^{2+} ion with Probe 1 was found to be 13.36 with 20 µM Limit of Detection (LOD)[24] (Fig. 7) which lowered than many reported literature.

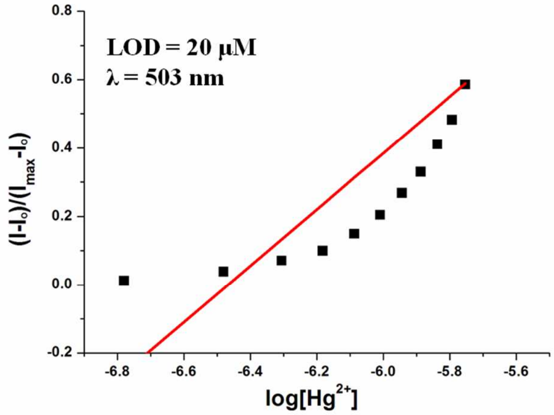


Fig. 7 Limit of detection (LOD) calculated by fluorescence emission spectra

2.5. pH studies:

The optical behaviour of the probe 1 with Hg^{2+} ion has been evaluated at varying pH by absorption and emission spectroscopy. All the above analysis was carried out at neutral pH. In the absorption analysis, spectra was remain same at pH 6-10, but in more alkaline medium (pH 11-14), disappearance of the absorption band at 421 nm, which was obtained due to the intramolecular charge transfer between the Probe 1 and Hg^{2+} ion, was found. At low pH 1-5 the total blue shift was occurring (Fig. 8). In the emission spectra probe 1 was shown enhancement in the intensity with Hg^{2+} ion, accordingly at pH 7-11. Probe 1 with Hg2+ at pH 1-6 has illustrated a marginal enhancement in emission intensity at 503 nm and a decrease in the emission intensity as we increase the pH 12 to 14 (Fig. 9). The whole study suggest that the chemosensor was properly used for the recognition of Hg^{2+} ion in pH 7-10.

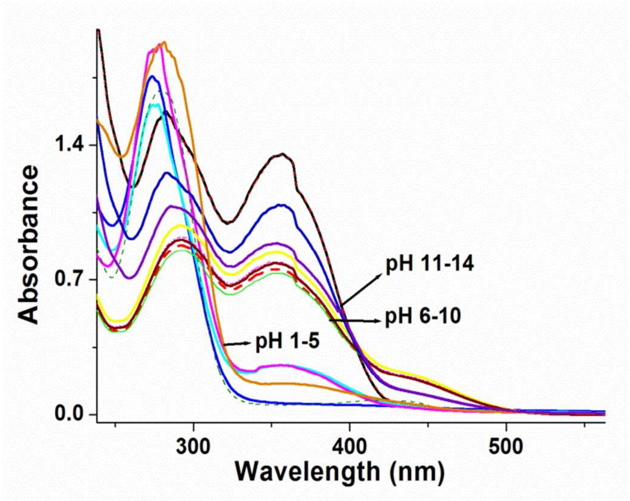


Fig. 8 Variation in the absorption spectra of Probe 1 with Hg^{2+} ion at different pHs in MeOH/H_2O solution.

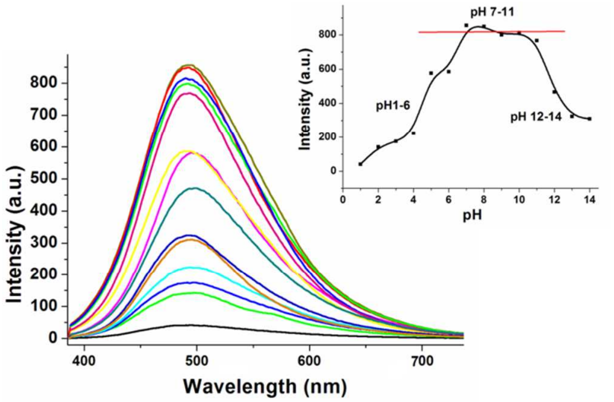


Fig. 9 Variation in the emission spectra of Probe 1 with Hg^{2+} ion at different pHs in MeOH/H_2O solution.

2.6. Stoichiometry of binding[25]:

Stoichiometry is the important tool of sensing mechanism to know the binding site of Probe 1, 2:1 stoichiometry of 1+Hg^{2+} complex was calculated using job's plot. By the job's plot it was confirmed that the absorption maxima was occurring at 0.66 mole fraction which facilitate the 2:1 Stoichiometry complex.

2.7. Nature of Binding Interaction:

To sustain this hypothesis of the interaction of probe 1 towards Hg^{2+} ion, ^{1}H-NMR studies have done. ^{1}H-NMR spectra of Probe 1 in $CDCl_3$ has shown the sharp singlet at δ 8.78 ppm of -CH proton (Ha) and doublets and triplets assigned to aromatic protons. The resonance signal appeared at δ 4.66 and 2.44 ppm assigned to -SH proton and -CH_3 proton. After the addition of Hg^{2+} ion the downfield shift of the aromatic protons ($\Delta\delta$=0.02) occurred due to the interaction of π-el$^-$ cloud of aromatic ring to Hg^{2+} metal ion, a significant downfield shift of the resonance signal of the -SH proton was occurring. With increasing the concentration of Hg^{2+} ion the -SH proton signal was completely disappeared. The ^{1}H NMR studies, as discussed thus, clearly suggested that, the complexation was occurred after complete deprotonation of mercapto proton.

Moreover, to confirm the stoichiometry of the 1+Hg^{2+} complex MALDI-TOF spectra was recorded (Fig. S7 in the Supporting Information) which showed a molecular ion peak, m/z at 667.356 (calcd. 667.022). ^{1}HNMR spectral data analysis of a complex, 1+Hg^{2+} and MALDI-TOF Spectra clearly suggested the interaction of the probe 1 with Hg^{2+} through the S atoms in mercapto unit in 2:1 stoichiometry (Fig. 10).

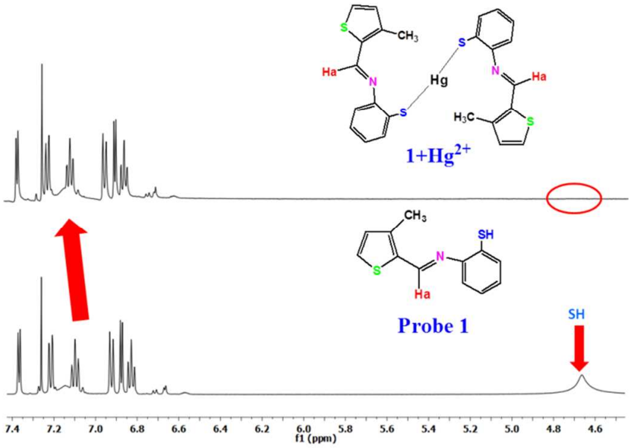


Fig. 10 ^{1}H-NMR spectra of Probe 1 and 1+Hg^{2+} in CDCl3 and possible mode of binding interaction.

2.8. Computational Studies:

Theoretical calculation[26] was conducted using density functional theory (DFT) method. Geometry optimized in Gas phase using Gaussian 09W computational program having B3LYP function by the basis set 6-31G(d, p) for metal free ligand and LANL2DZ for metal bind ligand. Computational studies of Probe 1 and 1+Hg^{2+} were also supplied the ligand to metal charge transfer. Fig 11 shown the optimized structure of the Probe 1 and 1+Hg^{2+} and HOMO-LUMO band gap, which confirm the ligand to metal charge transfer. To know the mechanism of binding interaction of Probe 1 with Hg^{2+}, optimized structure of 1+Hg^{2+} indicates the S-Hg-S linkage formation having 179.9º bond angle. Mercury metal forms complex with Schiff base in linear fashion. HOMO-LUMO band gap of 1+Hg^{2+} complex is decreased because of ligand to metal charge transfer occurring between Probe 1 and Hg^{2+} ion. The optimized structure and HOMO-LUMO diagram of Probe 2 was shown in Fig. S8.

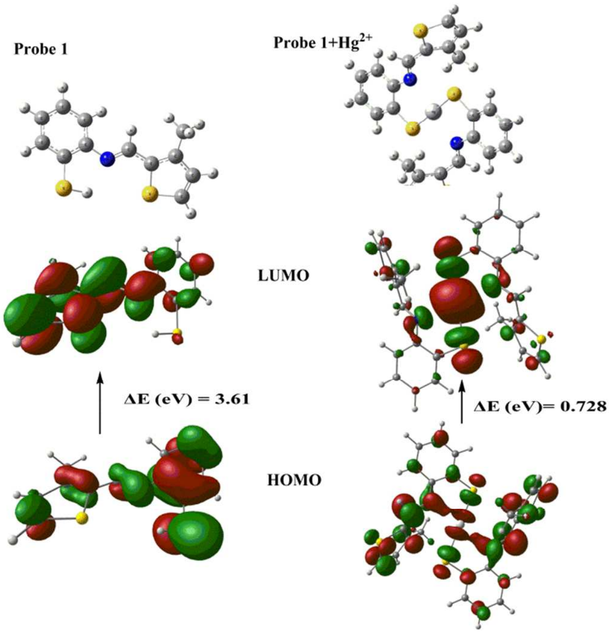


Fig. 11 DFT optimized structure and HOMO-LUMO band gap of Probe 1 and 1 + Hg^{2+} complex.

2.9. Cyclic Voltammetry:

Further, the electrochemical behavior of Probe 1, Probe 2 and Probe 1 with Hg^{2+} ion was tested in methanol solution. Cyclic voltammograms of Probe 1 having two irreversible reduction peak and three oxidation peak. Reduction peak was occurred at -1.22 and -0.635 V and oxidation peak at 0.202, 0.516 and 1.07 V. After the addition of a methanolic solution of Hg^{2+} ion, the first reduction potential of the Probe 1 was shown 0.131 V cathodic shift. First oxidation peak shown 0.373 V anodic shift. Probe 1 shown higher oxidation potential after binding with Hg^{2+} ion due to charge transfer from ligand to metal ion (Fig. 12). These results are also supported by theoretical calculation. All the CV data summarised in table 2. Cyclic voltammograms of Probe 2 having one irreversible reduction peak and two irreversible oxidation peak. Reduction peak was occurred at -0.60 V and oxidation peak occurred at 0.88 and 1.30 V. Cyclic voltammograms of Probe 2 mentioned in electronic supplementary information (Fig. S9).

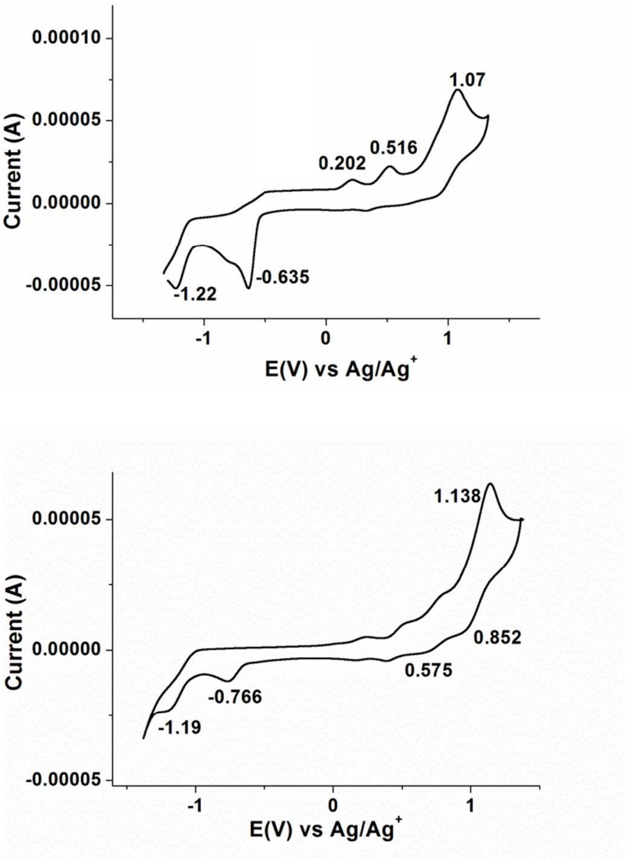


Fig. 12 Cyclic voltammograms of Probe 1 (top) and $1+Hg^{2+}$ (bottom) complex.

Table 2. The redox potentials of Probe **1** and $1+Hg^{2+}$ in methanol at 298 K.

Sample	**Oxidation peak (V)**			**Reduction peak (V)**	
Probe 1	1.07	0.516	0.202	-0.635	-1.22
$1+Hg^{2+}$	1.13	0.852	0.575	-0.766	-1.19
Probe 2	1.30	0.88	-	-0.60	-

2.10. Reversibility of proposed sensor[27]:

The reversible behaviour of proposed sensor has been checked with EDTA disodium salt. The Probe 1 was showing the 'turn-on' fluorescence emission at 503 nm with Hg^{2+} metal ion in methanol/H2O (8/2: v/v solution). After the addition of 10mM of EDTA (in water) into the $1+Hg^{2+}$ solution (yellowish orange color), the fluorescence enhanced emission was quenched and the color was disappeared. Further the solution was reused for the chemosening of Hg^{2+} metal ion. The fluorescence intensity and reversible colorimetric images were shown in Fig. 13.

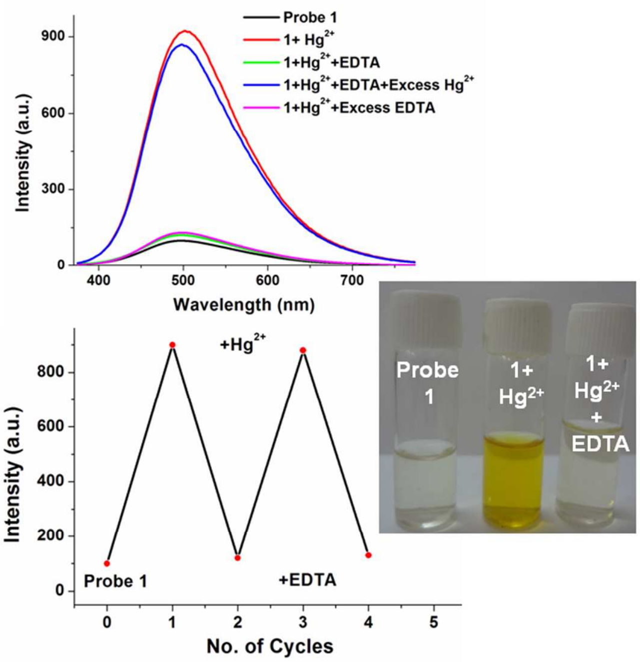


Fig. 13 Sensor reversibility and no. of cycle of $1+Hg^{2+}$ with EDTA.

The proposed chemosensor for Hg^{2+} metal ion has been compared with the previously reported literature. From the table 3, the proposed sensor results seem good with respect to Limit of Detection (LOD).

Table 3. Comparison of proposed chemosensor with previously reported literatures.

Previous Literature	Solvent	Limit of Detection (LOD)
Dalton Trans., 2013, 42, 4456[28]	CH_3CN	50 mM
Org. Biomol. Chem., 2012, 10, 5410[29]	$H_2O–CH_3CN$ (10 : 90, v/v)	0.226 mM
Tetrahedron Lett., 2010, 51, 3286[30]	CH_3CN–DDW	30 mM
Spectrochim. Acta, Part A, 2012, 93, 245[31]	DMSO	5.0 mM
Org. Lett., 2010, 12, 476[32]	C_2H_5OH/H_2O(1 : 1; v/v)	80μM
This Work	CH_3OH/H_2O (8/2; v/v)	20 μM

Conclusion:

Thiophene based Probe (1 and 2) has been synthesised and characterised by various spectroscopic techniques such as UV-Vis, FT-IR, NMR. Furthermore, Probe 1 was used for the fluorometric and colorimetric sensor for Hg^{2+} metal ion without any interference of other metal ions. The binding affinity of Hg^{2+} ion with Probe 1 was also confirmed by the optical studies, NMR, Mass studies, DFT optimization and electrochemical behaviour. The designed chemosensor was accomplished for the detection of Hg^{2+} ion in 20 μM in partially aqueous medium.

Acknowledgement

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