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Hg^{2+} mediated quinazoline ensemble for highly selective recognition of Cysteine

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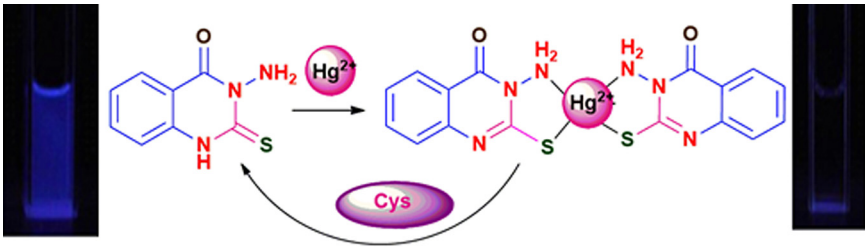
HIGHLIGHTS

- A quinazoline **A1** derived was synthesized and used to recognize Hg^{2+}.
- The Hg^{2+} detection limit (3.5×10^{-7} mol L^{-1}) is reported.
- This fluorescence change was further supported by DFT/TD-DFT calculations.
- The probe **A1** + Hg^{2+} ensemble is also further successfully utilized for detection of the Cysteine.
- This system can also be applied in real samples.

GRAPHICAL ABSTRACT



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ABSTRACT

A fluorimetric sensor for Hg^{2+} ion and Cysteine based on quinazoline platform was designed and synthesized by one step reaction and characterized by using common spectroscopic methods. Time Dependent Density Functional Theory calculations shows that probe behaves as "ON–OFF" fluorescent quenching sensor via electron transfer/heavy atom effect. Receptor was found to exhibit selective fluorescence quenching behavior over the other competitive metal ions, and also the receptor-Hg^{2+} ensemble act as an efficient "OFF–ON" sensor for Cysteine. Moreover this sensor has also been successfully applied to detection of Hg^{2+} in natural water samples with good recovery.

Introduction

In recent years the recognition and monitoring of the heavy metal ions such as Hg^{2+}, Pb^{2+}, Cd^{2+} and Cu^{2+} is one of the most challenging field [1–4]. Design and synthesis of selective sensor for Hg^{2+} is particularly important, since Hg^{2+} is hazardous metal and can cause detrimental effects on the environment even at very low concentration [5]. Mercury can easily penetrate through the skin and respiratory cell membranes and create difficulty in thyroid and adrenal hormone system [6]. Methyl mercury [7] derived from ionic/elemental mercury by bacteria affects a pregnant woman that reflects development delays in child [8,9]. The US Environmental Protection Agency (EPA) recommended a limit of 2 ppb of Hg^{2+} in potable water [10]. Due to these harmful effects, designing new chromophore for analysis of Hg^{2+} becomes significant. Various techniques such as atomic absorption spectroscopy [11], atomic emission spectroscopy [12], electro chemical methods [13,14] and photophysical methods have been used to detect the transition/heavy metal ions. Among these, photophysical methods are widely used due to its high selectivity, sensitivity and simple way of sample preparation. On the other hand intracellular thiol containing amino acids play vital role in biosynthesis and they are functional compounds of many proteins and enzymes

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[15–17]. Cysteine (Cys) and Homo Cysteine (Hcy) are biologically essential molecules required for the growth of cells and tissues in living systems. Especially the Cysteine levels are linked to many diseases such as Alzheimer, AIDS and cancer. Deficiency of Cysteine can cause delayed growth, liver damage, oedema, lethargy, fat loss, skin lesions and Psoriasis etc., [18,19].

Numerous fluorescent chemosensors designed for sensing Hg^{2+} based on coumarin derivatives [20,21], Hydroxyquinoline [22], Podants [23,24], Rhodamines [25], Pyrene derivatives [26], quinazoline [27] and heterocyclic based moieties [28] culminated in either large fluorescence enhancement or quenching phenomena. Huang et al. [29] reported anthraquinone containing thiourea subunit as a colorimetric sensor for Hg^{2+}. 2-Aminopyridine unit has been utilized for the fluorescent detection of Hg^{2+} by Ghosh et al. [30]. However most of the reported sensors have difficulty in distinguishing Hg^{2+} from Ag^{+} or Fe^{3+}, which compete with Hg^{2+} for the binding sites of the sensor molecule. Mechanisms such as photo induced electron transfer (PET) [31], intramolecular charge transfer (ICT) [32], twisted intramolecular charge transfer (TICT) [33], metal–ligand charge transfer (MLCT) [34] and fluorescence resonance energy transfer (FRET) [35] have been invoked to explain the observed enhancement or quenching of fluorescence. In many of the fluorescent chemosensors for Hg^{2+} there may be a large fluorescence quenching because of PET property and heavy atom effect [36,37]. Hitherto reported Hg^{2+} recognizing target compounds experienced multistep synthesis and tedious work-up. Therefore the design of sensors that can be easily synthesized for Hg^{2+} binding is of particular interest. The receptor containing nitrogen/oxygen and sulfur atom prefers the coordination of Hg^{2+} [38] over the competing transition metal ions. Besides Hg^{2+} various fluorescent chemosensors has been designed for the recognition of biological thiols based on different mechanism [39–43]. Due to the strong affinity of thiols towards Hg^{2+}, the thiol containing amino acids easily binds with the Hg^{2+} ions. Recently, Fu et al. [44] and Li et al. [45] proposed a squarine and thiacalixarene-Hg^{2+} ensemble fluorescence assay for thiol containing amino acids, which involves enervating synthetic procedures.

In the present study, we have synthesized the probe **A1** from 2-aminobenzohydrazide with CS_2 in single step process according to a literature procedure [46,47]. Recently, Thar et al. reported the same probe as an electrochemical sensor for silver by employing stripping voltammetry method [48]. **A1** is highly selective and sensitive turn-off fluorescent sensor for Hg^{2+} which could be utilized to quantify Hg^{2+} levels for health care and environmental monitoring. Further we applied the **A1 + Hg^{2+}** ensemble as a turn-on fluorescence sensor for Cysteine.

Materials and methods

General

2-Aminobenzohydrazide, amino acids was purchased from Sigma–Aldrich. Carbon disulphide and metal chloride salts were obtained from Merck. All the solvents were of analytical grade. ^{1}H and ^{13}C NMR was measured on BRUKER (Advance) 300 MHz instrument. UV–Visible spectra were recorded on a JASCO V-550 spectrophotometer, fluorescence analysis were done by using JASCO-spectrofluorimeter. Electro spray ionization mass spectrometer studies were carried out by using LCQ fleet thermo fisher instruments limited, US. The pH measurements were made with a Model PHS-25B meter. DFT calculations were carried out at the B3LYP/LANL2DZ level by using the Gaussian 03 program.

Synthesis of 3-amino-2-thioxo-2,3-dihydroquinazolin-4(1H)-one (**A1**)

Ethanolic solution containing 2-aminobenzohydrazide (0.483 g, 3.2 mmol), sodium hydroxide (0.13 g, 3.2 mmol) and carbon disulphide (0.25 g, 3.2 mmol) was refluxed for 15 h. The excess solvent was distilled off under reduced pressure. The residue was washed with water and treated with 1:1 HCl and subsequently washed several times with water. Recrystallized from ethanol to get a white solid (Scheme 1). Yield: 65%. Melting point: 205–207 °C. ^{1}H NMR (300 MHz, DMSO) ppm δ 14.72 (s, 1H), 7.53 (dd, J = 8.0, 1.4 Hz, 1H), 7.29–7.23 (m, 1H), 6.90–6.85 (m, 1H), 6.65 (dd, J = 11.1, 4.0 Hz, 1H), 6.17 (s, 2H).^{13}C NMR (75 MHz, $CDCl_3$): 181.107, 165.899, 152.385, 137.796, 132.192, 121.264, 120.873, 108.351. ESI–MS: observed: 192.06 $(M–H)^{-}$. Calculated: 193.12. (Figs. S1–S3). Anal. Found: C: 56.25, H: 6.2, N: 27.8, Cal. for: C: 56.01, H: 5.99, N: 28.0%.

Calculation of binding constant

The association constant of Hg^{2+} was calculated from the fluorescence titration data using the following equation:

$$\ln[(F - F_0)/(F\infty - F)] = n\ln[Hg^{2+}] + n\ln\ (\text{Kasscn})$$

In above equation, n refers to the number of Mercury ions associating with each molecule of **A1**, Kasscn refers to the association constant, F_0, F and $F\infty$ refers to the fluorescence intensities solution of chemosensor **A1** alone, **A1** with any concentration of Hg^{2+}, and at high concentration of Hg^{2+} ion.

Calculation of detection limit

LOD was calculated based on the standard deviation of the response (SD) and the slope of the calibration curve (S) at levels approximating the LOD according to the formula:

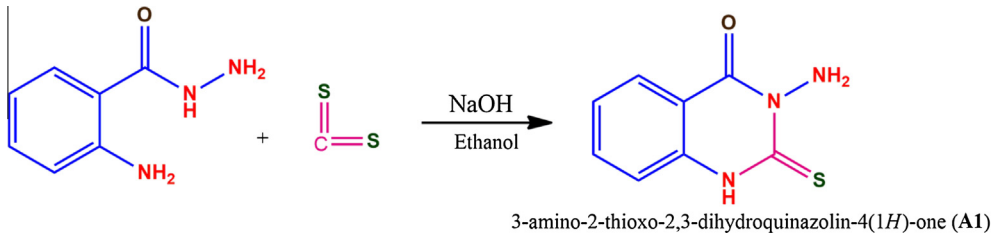
$$\text{LOD} = 3(\text{SD}/\text{S})$$

Results and discussions

To get an insight into the selectivity, UV–Visible measurements of the probe **A1** were carried out with the addition of various metal ions. The UV–Visible spectrum of probe **A1** shows two peaks at 284 nm and 334 nm. Upon incremental addition of chloride salt of Hg^{2+} (0–2.0 eq) absorption maximum of probe at 284 nm shifted rapidly and the band at 334 nm decreased. In the presence of Hg^{2+} the band at 284 nm is blue shifted to 276 nm. This blue shift along with hypochromism may be attributable to the binding of Hg^{2+} with the probe **A1** (Fig. S4). Only Hg^{2+} ion addition show changes in the absorption spectra, while the addition of other metal ions such as Cu^{2+}, Co^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+}, Ba^{2+}, Al^{3+}, Ca^{2+}, Cr^{3+}, K^{+} and Na^{+} did not show any shift in the band wavelengths (Fig. 1). So the receptor **A1** was a selective and sensitive sensor probe for Hg^{2+} ions.

The probe **A1** exhibits a strong emission when excited at 350 nm. The photonics of the **A1** was further explored with the addition of other metal ions such as Cu^{2+}, Co^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+}, Ba^{2+}, Al^{3+}, Ca^{2+}, Cr^{3+}, K^{+} and Na^{+} including Hg^{2+}. Among the metal ions investigated only Hg^{2+} selectively quenches the fluorescence intensity of **A1** (Fig. 2). While the other alkali such as Na^{+} and K^{+}, alkaline such as Ca^{2+} and Mg^{2+} and transition metal ions Cu^{2+}, Co^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+} and Ag^{+} exhibit no fluorescence quenching response under the same spectroscopic condition used for the Hg^{2+}.

Upon addition of Hg^{2+} from 0 to 2.0 eq the fluorescence intensity started quenching steadily (Fig. 3). The fluorescence quenching



Scheme 1. Synthesis of probe (**A1**).

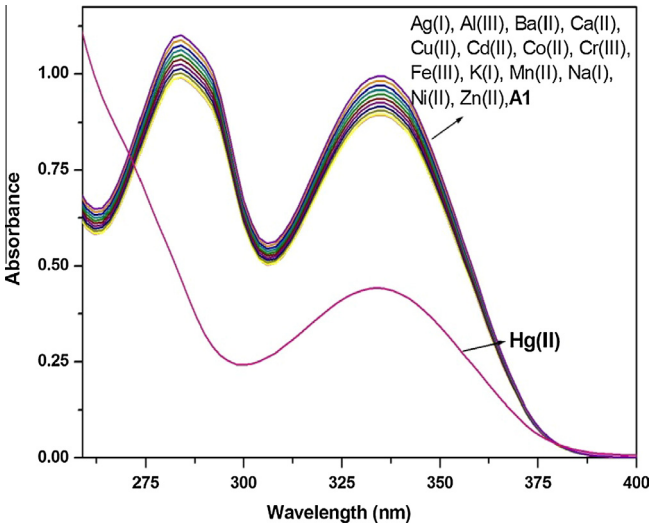


Fig. 1. UV–Visible spectra of (A1) 3-amino-2-thioxo-2,3-dihydroquinazolin-4(1H)-one upon addition of Hg^{2+} ion and other transition metal ions such as Cu^{2+}, Co^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+}, Ba^{2+}, Al^{3+}, Ca^{2+}, Cr^{3+}, K^{+} and Na^{+} (0–2 equiv.) in DMSO:H_2O (1:9, V/V).

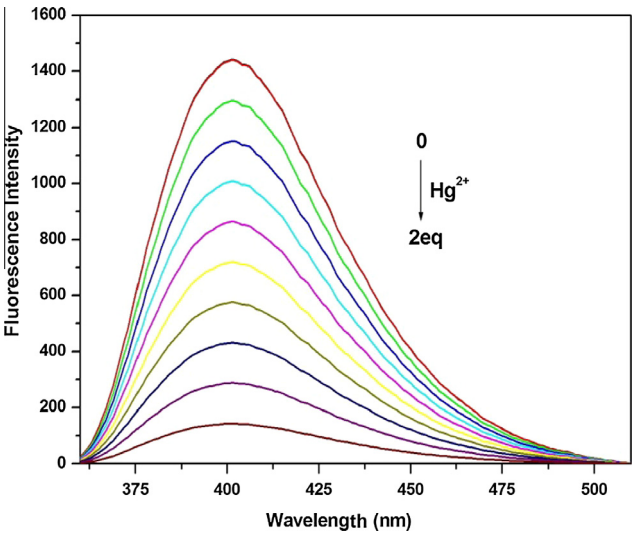


Fig. 3. Fluorescence emission spectra of (A1) 3-amino-2-thioxo-2,3-dihydroquinazolin-4(1H)-one upon addition of Hg^{2+} ion (0–2 equiv.) in DMSO:H_2O (1:9, V/V), (λ_{ex} = 350 nm, λ_{em} = 401 nm, slit:5 nm/5 nm).

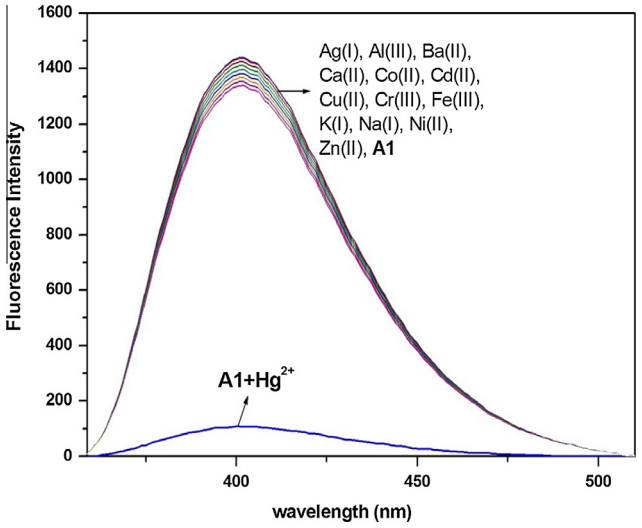


Fig. 2. Fluorescence emission spectra of (A1) 3-amino-2-thioxo-2,3-dihydroquinazolin-4(1H)-one (1×10^{-5} M) upon addition of Hg^{2+} ion and other transition metal ions such as Cu^{2+}, Co^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+}, Ba^{2+}, Al^{3+}, Ca^{2+}, Cr^{3+}, K^{+} and Na^{+} (0–2 equiv.) in DMSO:H_2O (1:9, V/V), (λ_{ex} = 350 nm, λ_{em} = 401 nm, slit:5 nm/5 nm).

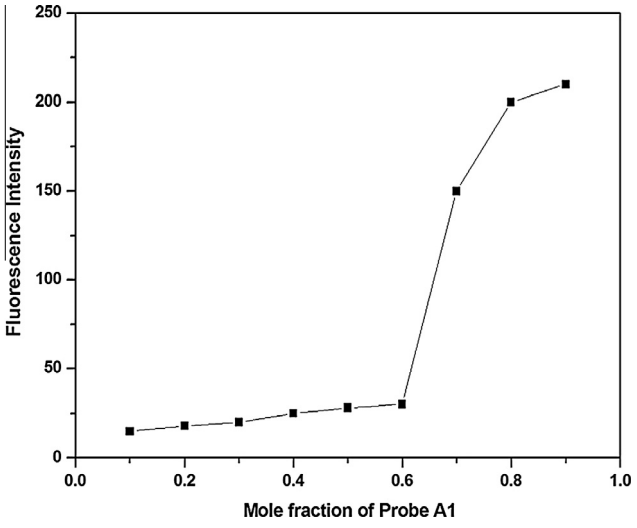


Fig. 4. The Job's plot mole fraction of probe vs fluorescence intensity at λ_{em} = 401 nm.

of probe upon complexation with Hg^{2+} may be attributable to the heavy atom effect followed by the electron transfer. Therefore **A1** is selective towards Hg^{2+} over various metal ions (Fig. S5).

In order to understand the binding mode of Hg^{2+} with **A1** job's plot measurements was carried out. Job's plot constructed from fluorescence titration data (Fig. 4), suggested the 2:1 binding between probe and Hg^{2+}. It was further supported by ESI–MS wherein the molecular ion peak at m/z = 609 corresponds to [(**A1**)$_2$ + Hg^{2+} + Na]$^{+}$ (Figs. S6 and S7). The fluorimetric titration profile shows a steady quenching of fluorescence with increase in concentration of Hg^{2+}. The binding constant [49] between probe

A1 and Hg^{2+} was $4.54 \times 10^2\ M^{-2}$ (Fig. S8). The detection limit [50,51] calculated by reported methods was found to be 3.5×10^{-7} M.

The influence of various metal ions conducted in the presence of Hg^{2+} (0.5 eq) with the addition of Cu^{2+}, Co^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Ag^{+}, Ba^{2+}, Al^{3+}, Ca^{2+}, Cr^{3+}, K^{+} and Na^{+} (1 eq) show no significant change in the fluorescence quenching in comparison with that observed by the addition of Hg^{2+} without the other transition metal ions. This result shows that probe has good sensitivity and selectivity towards Hg^{2+} over the other competitive metal ions (Fig. 5).

The influence of pH on fluorescence intensity of **A1** was investigated in the presence of acidic and basic medium (Fig. 6). The fluorescence intensity of **A1** completely vanished in the presence of higher pH (2–4 pH) values. Under 4–6 pH the intensity was quenched gradually along with the addition of acid and no new band was obtained. Quenching of fluorescence could be attributable to the protonation of primary amine and secondary amine of quinazoline moiety. However in lower pH range (9–12 pH), fluorescence intensity at 401 nm was shifted. When the medium became basic, a new emission band at 490 nm was appeared, which corresponds to the deprotonation of —NH attached with C=S and it can be stabilized by keto-thiol tautomerism. Besides the C—S^- ion forms hydrogen bond with the amine group, and this bond formation is the main criteria for the fluorescence shift and color change. More importantly **A1** exhibits blue to cyan fluorescence under basic medium and that can be visually detected. Thus, pH of 7 was selected as working range for their studies. ^{1}H NMR spectra of probe in DMSO-d_6 before and after the addition of hydrochloric acid and sodium hydroxide have been recorded (Fig. 7). Upon addition of 0.5 eq of hydrochloric acid, the signal of amine proton at 6.5 ppm became broad and N—H peak at 14.5 ppm disappeared due to the protonation of NH and NH_2. Whereas N—H peak at 14.55 ppm was slowly suppressed with incremental concentration of NaOH. At the same time, NH_2 proton peak at 6.55 ppm disappeared immediately. This clearly indicates that the NH and NH_2 peak was deprotonated in the presence of base.

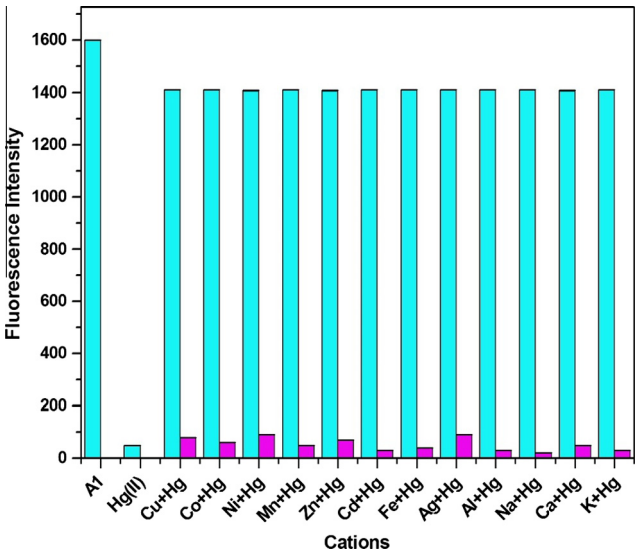


Fig. 5. Bar chart illustrating the selectivity in fluorescence response of probe **A1** for Hg^{2+} ion in the presence of other metal ions. The cyan bars represent the fluorescence intensity of **A1** in the presence of one equivalent of the other metal ions. The magenta bars represent the change in fluorescence intensity that occurs upon subsequent addition of one equivalent of Hg^{2+} to the solution containing probe **A1** and the other metal ions in DMSO/H_2O(1:9,v/v) 10 mM, (λ_{ex} = 350 nm, λ_{em} = 401 nm, slit:5 nm/5 nm).

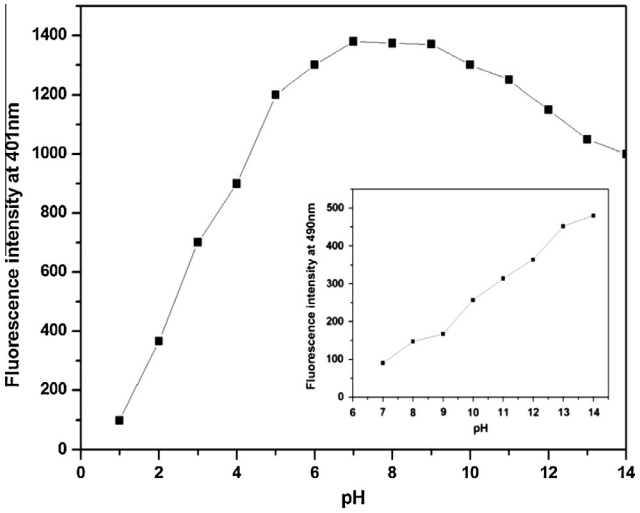


Fig. 6. pH Effect on the fluorescence intensity (at 401 nm) of solution **A1** (10 μM) in DMSO/H_2O (9:1, v/v). Inset shows the corresponding titration plot at 490 nm.

Real sample analysis of Hg^{2+}

In order to examine the practical applicability of the sensor developed herein, it was preliminarily applied to the determination of Hg^{2+} in natural water samples from River water, drinking water and tap water. Each recovery of Hg^{2+} was determined by comparing the results obtained before and after the addition of 0, 50, 100 μg of Hg^{2+} to the diluted water samples, the results obtained before and after the addition of Hg^{2+} to the water samples were listed in Table 1. The observed results show that A1 is able to measure the concentrations of spiked Hg^{2+} with good recovery. The recoveries of Hg^{2+} in these three were 97–98.9%, which validated the reliability and practicality of this method.

Detection of Cysteine

Cu^{2+} and Hg^{2+} are highly attractive for the thiol based amino acids, because these metal ions have high affinity towards the thiols [52–54]. The reversible nature of **A1** + Hg^{2+} ensemble was verified in the presence of different amino acids such as Aspartic acid (Asp), Cysteine (Cys), Glutamic acid (Glu), Glycine (Gly), Glutathione (GSH), Serine (Ser), Glutamine (Gln), Tyrosine (Tyr), Arginine (Arg), Lysine (Lys), Histidine (His), Alanine (Ala) and Valine (Val). Addition of Cysteine to the solution of **A1** + Hg^{2+} emission band at 401 nm was greatly increased; addition of other amino acids did not induce obvious change (Fig. 8). Upon addition of increasing concentration of Cysteine into the solution of **A1** + Hg^{2+} the fluorescence was restored by the removal of Hg^{2+} indicating that receptor **A1** is a reversible chemosensor (Fig. S9). The binding constant between Hg^{2+} and Cysteine was $6.41 \times 10^2\ M^{-2}$ (Fig. S10). The binding constant for the Hg^{2+}–Cysteine complex is higher [55] than that of **A1** + Hg^{2+}, hence the dissociation of **A1** + Hg^{2+} leads to the enhancement of fluorescence.

DFT calculations

In order to understand the fluorescence quenching process of **A1** with Hg^{2+}, DFT/TDDFT calculations were carried out with Gaussian 03 program [56]. The geometries of **A1**, (**A1**)$_2Hg^{2+}$ were optimized by B3LYP/631G and B3LYP/LanL2DZ methods respectively. The TD-DFT calculations of probe **A1** shows a transition at 348.29 (0.368). In probe HOMO resides on the receptor sulfur atom

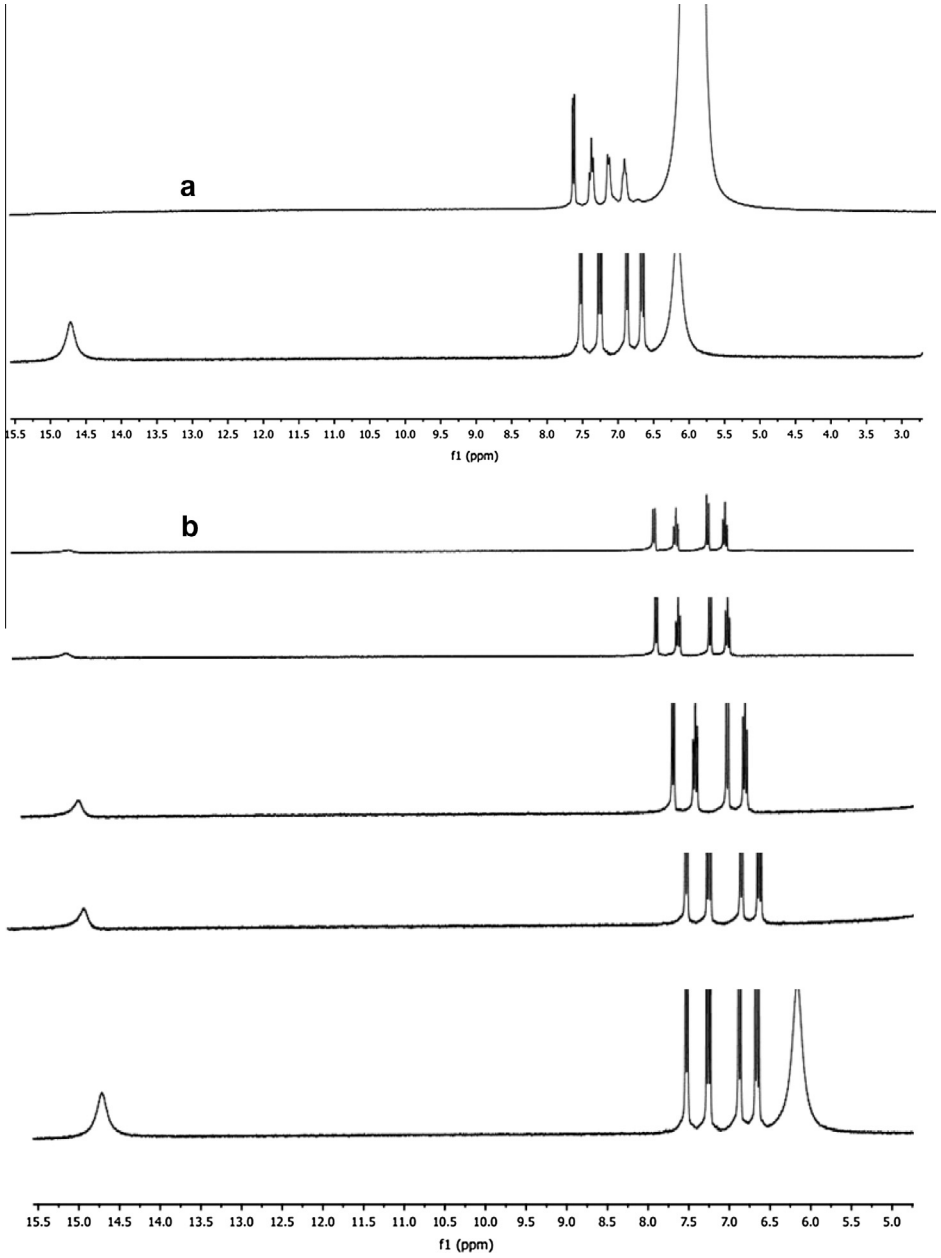


Fig. 7. ^{1}H NMR spectral changes of A1 in DMSO-d_6 in the presence of acid (a) base (b).

whereas LUMO spreads on the whole molecule and this HOMO–LUMO energy gap (λ_{cal} = 352 nm) corresponds to that of n–π^* transitions (Fig. 9).

Similar calculations for **A1 + Hg^{2+}** show two transitions with wavelength at 372.48 (0.0410), 322.46 (0.00881). After binding of Hg^{2+} with probe the LUMO has more metal character whereas the HOMO is essentially localized on the sulfur atom with little spread on fluorophore moiety and virtually not having metal character (Fig. 10).

Upon excitation with wavelength at 350 nm, it is expected that HOMO to LUMO transitions can occur while HOMO-1 to LUMO transitions may not occur due to very small oscillator strength. The HOMO to LUMO transitions leads to an electron transfer from fluorophore to Hg^{2+} metal center similar to the earlier reports of Fabbrizzi and Bergonzi et al. [57,58]. This results in reducing Hg^{2+} to Hg^{+}. Hg^{+} ion by virtue of being paramagnetic and heavy atom causes quenching of fluorescence.

Table 1
Determination of Hg^{2+} in drinking water, tap water and river water samples with A1.

Sample	Hg^{2+} added (μg L^{-1})	Hg^{2+} found (μg L^{-1})	Recovery (%)
Drinking water			
A	0	–	–
B	50	50.06[a] ± 0.01[b]	98.9
C	100	100.09 [a] ± 0.03[b]	99.0
Tap water			
A	0	–	–
B	50	50.02[a] ± 0.05[b]	99.7
C	100	100.00 [a] ± 0.07[b]	99.56
River water			
A	0	–	–
B	50	50.09 [a] ± 0.015[b]	97.8
C	100	100.04 [a] ± 0.06[b]	97.91

[a] Average of 3 measurements.
[b] Standard deviation.

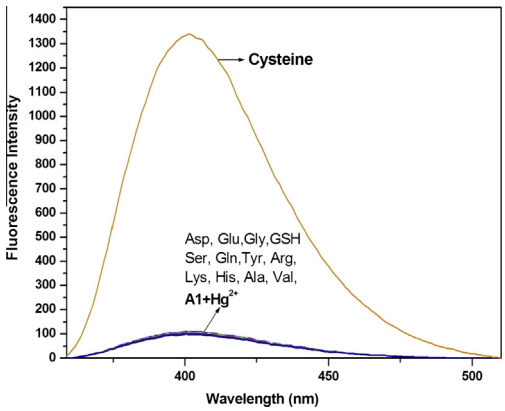


Fig. 8. Fluorescence emission spectra of A1 + Hg^{2+} upon addition of increasing concentration of Cysteine and other amino acids such as Asp, Glu, Gly, GSH, Ser, Gln, Tyr, Arg, Lys, His, Ala and Val in DMSO:H_2O(1:9, v/v) (λ_{ex} = 350 nm, λ_{em} = 401 nm, slit:5 nm/5 nm).

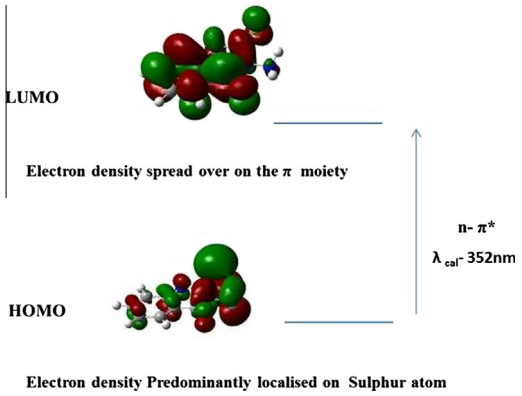


Fig. 9. Calculated electronic transitions of probe A1.

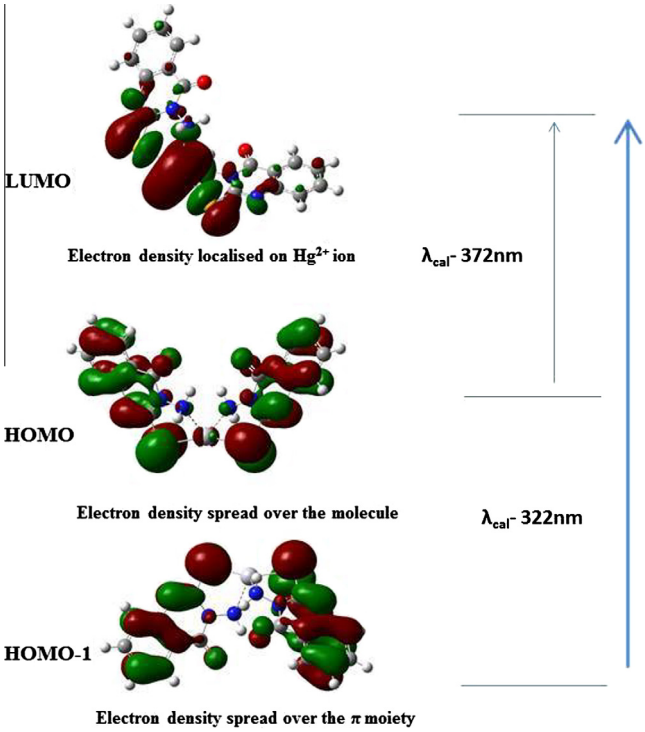


Fig. 10. Calculated electronic transitions of A1 + Hg^{2+}.

Conclusion

We have shown that the fluorescent probe (3-amino-2-thioxo-2, 3-dihydroquinazolin-4(1H)-one) **A1** is selective and sensitive for detection of Hg^{2+} chloride in aqueous medium. Addition of Hg^{2+} to the probe **A1** shows large fluorescence quenching and it is highly selective towards Hg^{2+} over the other competing metal ions and however the quenching of fluorescence was reversible by using Cysteine. The probe **A1** binds with Hg^{2+} in 2:1 stoichiometry as confirmed by job's plot and ESI–MS studies. From TD-DFT calculation, the fluorescence quenching of **A1** with Hg^{2+} was ascertained, heavy atom effect followed by electron transfer mechanism. Furthermore, practical applications are carried out. The probe exhibited high selectivity toward Hg^{2+} in natural water samples with satisfactory recovery.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.12.054.

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