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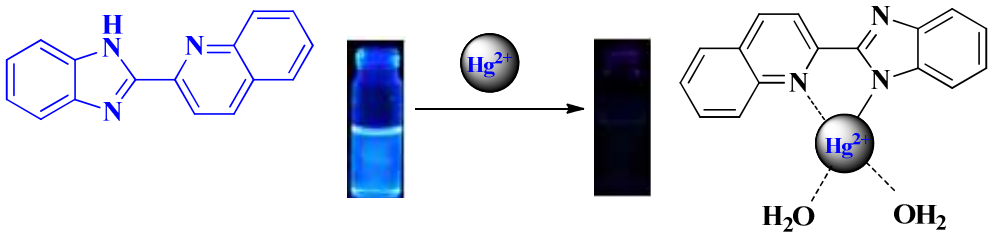

Graphical abstract: A novel and sulfur-free mercury specifically selective and highly sensitive fluorescent chemosensor **L** based on benzimidazole group and quinoline group as the fluorescence signal group had been designed and synthesized.

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PAPER

Highly selective and effective mercury (II) fluorescent sensor

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A novel mercury non-sulfur and simple fluorescent chemosensor **L** based on benzimidazole group and quinoline group as the fluorescence signal group has been designed and synthesized. The receptor could instantly detect Hg^{2+} cation over other cations such as Fe^{3+}, Ag^{+}, Ca^{2+} ,Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, and Mg^{2+} by fluorescence spectroscopy changes in H_2O/DMSO (1:9, v/v) solution with specific selectivity and high sensitivity. The fluorescence color of the solution containing sensor **L** induced a remarkable color change from blue to colorless only after the addition of Hg^{2+} in aqueous media while other cations did not cause obvious color change. Moreover, further study demonstrates the detection limit on fluorescence response of the sensor to Hg^{2+} is down to 9.56×10^{-9} M, which is far lower than the maximum level for mercury of 0.01 M in drinking water, from EPA guideline. Test strips based on **L** were fabricated, which could act as a convenient and efficient Hg^{2+} test kits. Thus, the probe should be potential application in an aqueous environment for the monitoring of mercury.

1. Introduction

Mercury (Hg^{2+}) is considered as one of the most toxic and dangerous element for the environment because it is widely distributed in natural phenomena and human activities, including oceanic and volcanic eruptions, wind erosion, water erosion, solid waste incineration, forest fires, and combustion of fossil fuels, electrical apparatus, batteries and industrial production [1-2]. Mercuric ion (Hg^{2+}), much more common than mercurous ion (Hg^{+}), is a caustic and carcinogenic material with high cellular toxicity, which can be converted into methyl mercury by bacteria in the environment, and subsequently accumulates in animals and plants and also enters into human body through the food chain [3]. As a strong neurotoxin, methylmercury ions can cause human health problems since it can easily pass through the skin and respiratory and cell membranes, leading to digestive, cardiac, kidney, DNA damage, mitosis impairment, and especially permanent damage to the central nervous system [4]. The United States Environmental Protection Agency (EPA) has set a maximum Hg^{2+} contaminant level in food and drinking water at 0.002 mgL^{-1} (0.01 M) [5]. Therefore, it is very important to detect the level of mercury in water and develop a simple yet environmentally friendly mercury sensor with high sensitivity and selectivity [6].

Development of organic molecules as receptors for the sensing of environmentally hazardous Hg^{2+} ions is of great importance due to its implications in broad areas of chemistry, biology, and environment. Recently, many sensitive fluorescent probes based on rhodamine [7], coumarin [8] or squaraine derivatives [9], as well as other fluorophores [10], have been developed to detect mercury ion. Among them, various molecular structure, the thioether containing crown ethers/acetals [11], podands [12], thioureas [13], amines/amides [14], spironolactone [15], heterocycles based moieties [16] etc. Appropriately appended with chromogenic and fluorescent moieties have found applications in developing Hg^{2+} sensors. Numerous analytical and sophisticated techniques have been used for the determination of mercury in real samples. These include atomic absorption spectrometry [17], inductively coupled plasma mass spectroscopy [18], spectrophotometry [19], neutron activation analysis [20], anodic stripping voltammetry [21], X-ray fluorescence spectrometry [22], electrothermal atomic absorption spectrometry [23], atomic fluorescence spectrometry [24], cold vapor atomic absorption spectrometry [25] and potentiometric ion-selective electrodes [26]. These methods has its own merits for mercury determination; however, they are also offers some problems such as expensive, limited sample adaptability, well-controlled experimental conditions, some inherent interference and time consuming procedures involving the use of sophisticated instrumentation, chemical sensors based on optical signal measurement are considered as the advanced techniques because of its operational simplicity, high selectivity, sensitivity, rapidity, cost effective, direct visual perception, and applicability to the

environmental and biological milieus. It is distinctly demonstrated that searching for production and development of mercury sensors is quite necessary.

Our research group has a longstanding interest in molecular recognition [27]. Herein, we have elaborately designed and synthesized a non-sulfur, simple and easy to prepare benzimidazole derivatives fluorescent chemosensor (**L**, Scheme 1) for Hg^{2+} ion, according to the chelation-enhanced quenching (CHEQ) mechanism, in which the quinoline groups act as fluorophore, benzimidazole groups into the same sensor molecule, to allow the coordination capacity required to chelate mercury ion. Sensor **L** showed fluorescent selectivity for Hg^{2+} in DMSO/H_2O (9:1, v/v) binary solution over other common physiologically important metal ions. The detection limit on fluorescence response of the sensor to Hg^{2+} is down to 9.56×10^{-9} M, which is far lower than the maximum level for mercury of 0.01 M in drinking water, from EPA guideline, and indicates that this sensor could potentially be useful as a probe for monitoring Hg^{2+} levels. The mechanism of this process has been investigated by ^{1}H NMR and IR spectrum and ESI-mass spectrometry.

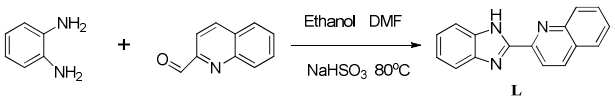
2. Experimental section

2.1. Materials and physical methods

Fresh double distilled water was used throughout the experiment. The inorganic salts $Ca(ClO_4)_2\cdot6H_2O$, $Mg(ClO_4)_2\cdot6H_2O$, $Cd(ClO_4)_2\cdot6H_2O$, $Fe(ClO_4)_3\cdot6H_2O$, $Hg(ClO_4)_3\cdot6H_2O$, $Co(ClO_4)_2\cdot6H_2O$, $Ni(ClO_4)_2\cdot6H_2O$, $Cu(ClO_4)_2\cdot6H_2O$, $Zn(ClO_4)_2\cdot6H_2O$, $Pb(ClO_4)_2\cdot3H_2O$, $AgClO_4\cdot H_2O$, $Cr(ClO_4)_3\cdot6H_2O$ and N-2-hydroxyethylpiperazine-N'-2-ethanesulfonic acid (HEPES) were purchased from Alfa Aesar Chemical Reagent Co. (Tianjin, China). All solvents and other reagents were of analytical grade. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Mercury-400BB spectrometer at 400 MHz and 100 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards) UV-vis spectra were recorded on a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were performed on a Shimadzu RF-5301 fluorescence spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus was purchased from Beijing Tech Instrument Co. (uncorrected). Infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer.

2.2. Synthesis of sensor L

The synthesis route of sensor **L** is demonstrated in Scheme 1. To an ethanol solution (25 mL) of 2-quinolinecarbaldehyde (0.786g, 5 mmol) and $NaHSO_3$ (0.624g, 6 mmol) as a catalyst was stirred 4h at the room temperature, and added a DMF (15 mL) of *O*-phenylenediamine (0.54g, 5 mmol) to the mixed solution. Then, the reaction of mixture solution was stirred at 353 K for 2 h. After cooling to room temperature, and dropwise added the pale white solution reaction solution to the 450 mL of distilled water, produced a large number of white precipitation, quietly placed, filtered, and washed with distilled water three times, then recrystallized with absolute ethanol to get white crystal of **L** (0.98g, 80%) (m.p. 107-110□), ^{1}H NMR (DMSO-d_6, 400MHz) δ: 13.21 (s, 1H), 8.56 (d, J = 8.3 Hz, 1H), 8.49 (d, J = 8.5 Hz, 1H), 8.17 (d, J = 8.3 Hz, 1H), 8.08 (d, J = 7.9 Hz, 1H), 7.88 (t, J = 7.6 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.69 (t, J = 7.3 Hz, 1H), 7.62 (d, J = 7.5 Hz, 1H), 7.28 (dd, J = 13.4, 7.4 Hz, 3H); IR (KBr, cm^{-1}) ν: 3482 (–NH), 1659 (C=N–H), 3060 (Ar–H); ESI-MS calcd for $C_{16}H_{11}N_3$+H 246.10, found 246.07.



Scheme 1. Synthesis of the sensor **L.**

2.3. General procedure

All Fluorescence spectroscopy measurements was carried out after the addition of perchlorate metal salts in DMSO/H_2O (9:1, v/v), while keeping the ligand concentration constant (2.0×10^{-5} M) on a Shimadzu RF-5301 fluorescence spectrometer. The excitation wavelength was 352 nm. The solution of metal ions (4.0×10^{-3} M) were prepared from the perchlorate salts of Fe^{3+}, Hg^{2+}, Ag^{+}, Ca^{2+} ,Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, and Mg^{2+}.

For ^{1}H NMR titrations, two stock solutions were prepared in DMSO-d_6, one containing the sensor only and the second containing an appropriate concentration of the metal. Aliquots of the two solutions were mixed directly in NMR tubes.

Test strips were prepared by immersing filter papers into a DMSO/H_2O binary solution of **L** (0.01 M) followed by exposure to air until complete drying. The test strips containing this sensor **L** were utilized to detect Hg^{2+} and other cations.

3. Results and Discussion

Receptor was found to have limited solubility in water, and this compelled us to use these sensor in mixed solvent, such as H_2O/DMSO (1:9, v/v), for recognition studies of **L**. Fluorescence spectral response of chemosensor **L** was studied with aqueous solutions of the perchlorate metal salts of all common cationic analytes such as (Fe^{3+}, Ag^{+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, and Mg^{2+}) as well as Hg^{2+}. Changes in spectral pattern were observed in the presence of added 10 equivalent of Hg^{2+}, the solution of sensor **L** displayed a dramatical color change, from blue to colorless, in the fluorescence spectrum recorded the sensor (2.0×10^{-5} M) in a DMSO/H_2O (9:1, v/v) system **(**Figs 1 and 2). To validate the selectivity of sensor **L**, the same tests were also applied using competitive metal ions, and none of these ions induced any significant changes in the fluorescent spectrum and the test strips based on the sensor **L** (2×10^{-4} M) as depicted in Fig. 3. Thus, compound **L** shows high selectivity toward Hg^{2+}. Furthermore, the interferences from metal ions can be eliminated and displayed specific sensitivity to Hg^{2+}.

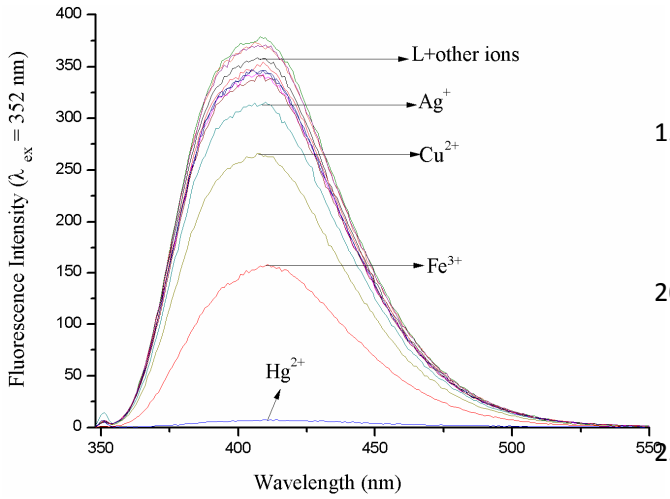


Fig. 1. Fluorescence spectra of **L** (2.0×10^{-5} M) and in the presence of 10 equiv. of various cations in H_2O/DMSO (1:9, v/v) binary solution at room temperature (λ_{ex} = 352 nm).

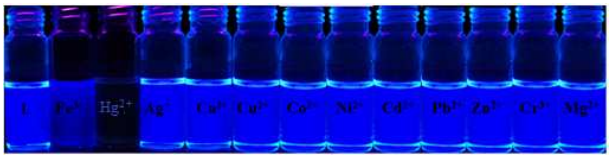
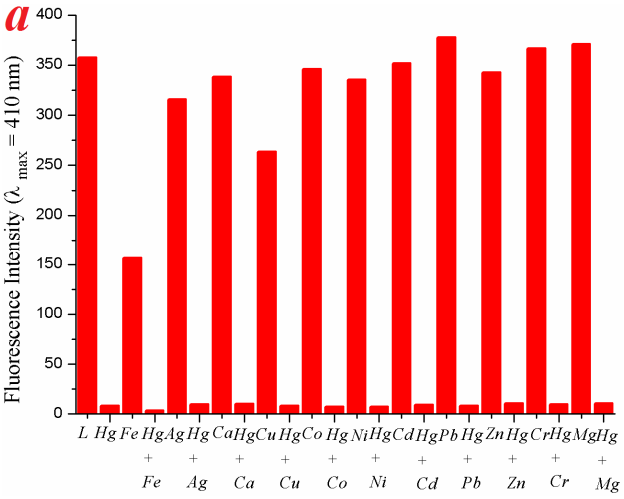


Fig. 2. Color changes observed upon the addition of various cations (10 equiv.) to solutions of sensor **L** (2×10^{-5} M) in DMSO/H_2O (9:1, v/v) under UV-lamp (365 nm).



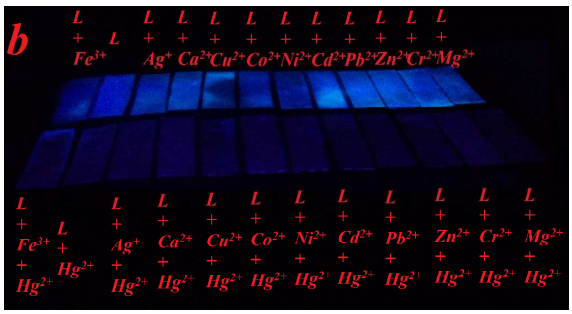


Fig. 3. a) Normalized change in the emission intensity of **L** (2×10^{-4} M) after addition of the Hg^{2+} ion (4×10^{-3} M) in the presence of an excess amount of other cations (4×10^{-3} M) in the DMSO/H_2O (9:1, v/v) solution. b) Photographs of the test strips based on **L** (2×10^{-4} M) after immersing the Hg^{2+} ion (4×10^{-4} M) in the presence of an excess amount of other cations (4×10^{-3} M) under irradiation at 365 nm.

Fluorescent titration was performed to gain insight into the recognition properties of receptor **L** as a Hg^{2+} probe (Fig. 4). The emission band at 410 nm of chemosensor **L** remarkably decreased as the Hg^{2+} (0.02 M) volume increased from 0 to 24 μL. In the meantime, the minimum concentration of Hg^{2+} that could be observed though one order of magnitude lower for fluorescence naked eye detection was 5.0×10^{-6} M, by using a UV lamp at 365 nm and the detection limit of the fluorescence spectra measurements, as calculated on the basis of $3S_B/S$ [28] (where S_B is the standard deviation of the blank solution and S is the slope of the calibration curve; Fig. 5), showed a detection limit of approximately 9.56×10^{-9} M for Hg^{2+}, which is far lower than the maximum level for mercury of 0.01 M in drinking water, from EPA guideline.

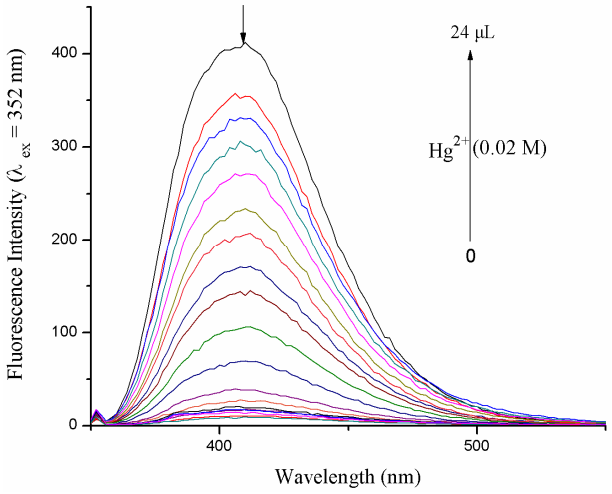
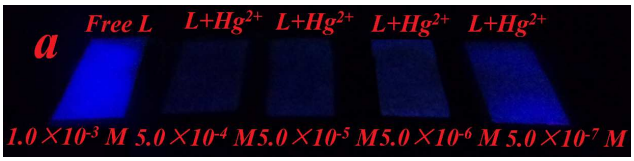


Fig. 4. Fluorescence titration spectra of **L** (2.0×10^{-5} M) in H_2O/DMSO (1:9, v/v) solution upon adding of an increasing concentration of Hg^{2+} (λ_{ex} = 352 nm).



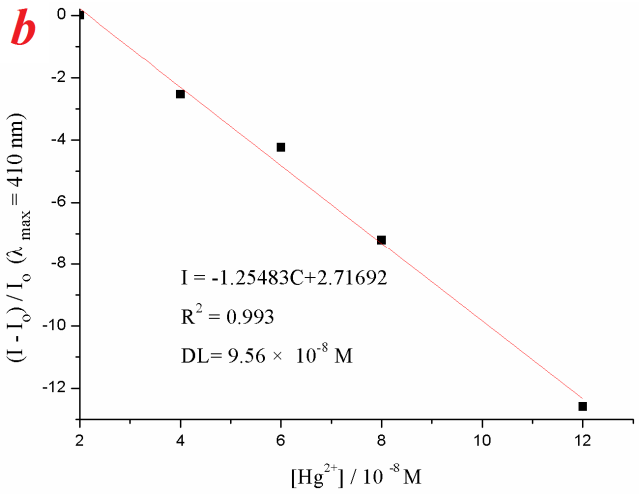
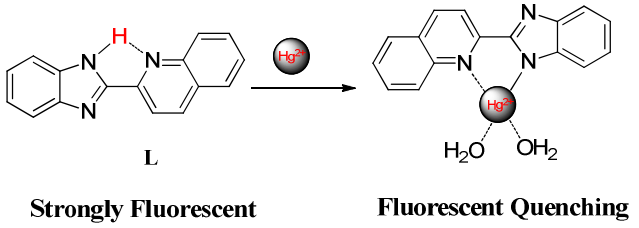


Fig. 5. a) Fluorescent changes upon the addition of Hg^{2+} at the indicated concentrations. Images were taken under white UV light at 365 nm. b) Fluorescence detection limit spectra of **L** (2.0×10^{-5} M) in H_2O/DMSO (1:9, v/v) solution upon adding of an concentration of Hg^{2+} (1.0×10^{-4} M).

We propose that the reaction mechanism in this system may proceed through the route depicted in Scheme 2. These results reveal that the sensor of **L** reacts toward Hg^{2+} and forms a organometallic compound. It leads to decreasing and destruction of the sensor conjugate rigid plane structure, the probe **L** shows fluorescence quenching by chelating effective. Therefore, it can be clearly seen the sensor **L** selective and sensitive response of mercury over other cations in aqueous media (H_2O/DMSO, 1:9, v/v).



Scheme 2. Possible sensing mechanism

The interaction and binding behavior between **L** and Hg^{2+} ion were investigated with their ^1H NMR titration experiments, as shown in Fig. 6. There was one intramolecular hydrogen bond in the sensor of **L**: NH···N=C. The formation of this hydrogen bond led to the ^1H NMR chemical shifts of NH appearing at low-field of the probe **L** at 13.21 ppm, and led to the sensor **L** of conjugate rigid plane structure increase and produce strong blue fluorescent. After the addition of 0.5 equivalent of Hg^{2+}, the NH peak of benzimidazole group at 13.21 ppm gradually disappeared, and increased the electronegativity of the whole ring. Thus, there were signal peaks of benzimidazole group showed a significant upfield shift. Meanwhile, Hg^{2+} coordinate N atom of the quinoline group and electronegativity of quinoline ring have been reduced, the signal of the hydrogen atoms in quinoline ring showed a significant downfield shift. These results indicated the Hg^{2+} chelate with N atom of the benzimidazole groups and N atom of the quinoline groups, and form a mercury complex. Therefore, the results of ^1H NMR titration experiments suggested that the validity of the mechanism submitted and the cause of the fluorescence quenching presented.

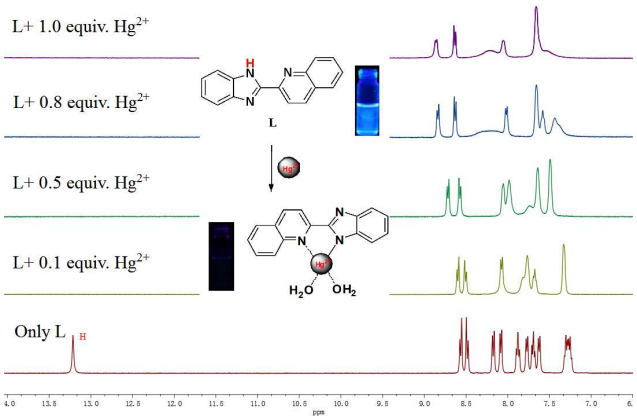


Fig. 6. Partial ^1H NMR spectra of **L** (0.01 M) and in the presence of varying amounts of Hg^{2+} (0.5 M).

To further investigate the interaction between sensor **L** and Hg^{2+}, the infrared spectra were performed and displayed in Fig. 7. The sensor **L** of the stretching vibration absorption peaks at 3482 cm^{-1} (−NH), 1659 cm^{-1} (C=N−H), 3060 cm^{-1} (Ar−H), compared with the **L**+Hg^{2+} compound the N−H peak at 3482 cm^{-1} disappeared, at the same time, the peak of (C=N−H) at 1659 cm^{-1} moved to 1619 cm^{-1}, the peak at 1120 cm^{-1} obvious enhanced, which demonstrated receptor **L** combined with Hg^{2+} and formed the new compound. Moreover, the mass spectrum obtained and confirmed the sensor **L** ion peak were detected at m/z 246.07 (ESI, † Fig. S3), which are corresponding to [**L**+H]$^+$, and the mercury complex ion peak appeared at m/z 481.99, which indicated the probe **L** react with Hg^{2+} (M = 200.6) and two H_2O (M = 36) to form a stable complex [**L**+Hg^{2+}+$2H_2O$] (ESI, † Fig. S4). In conclusion, the IR, ^1H NMR titration experiments and mass spectrum experiments suggested that the probable binding mode of chemosensor **L** and mercury.

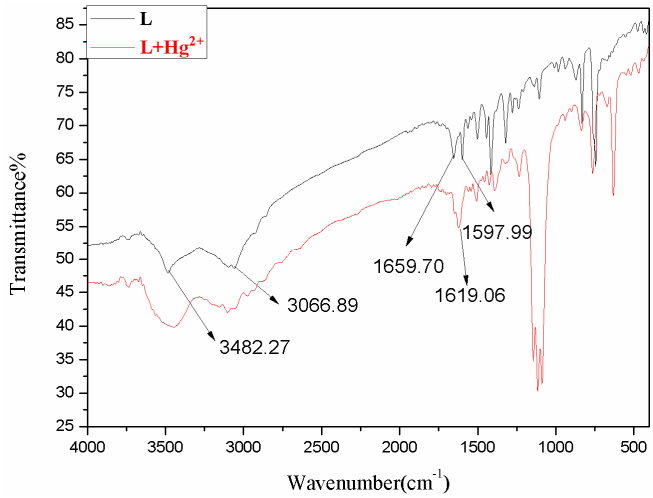


Fig. 7. Infrared spectra of **L** (black line) and its complex **L**+Hg^{2+} (red

line).

The pH dependence of the sensor **L** in HEPES buffer system was also checked by Fluorescent spectroscopy. Mercury ion was added to the buffered solution of **L** at different pH values. No apparent changes of the fluorescence spectra were observed, the results indicated that the binding of **L** with the Hg^{2+} can work well in the range of pH 2.0-11.0 (Fig. 8).

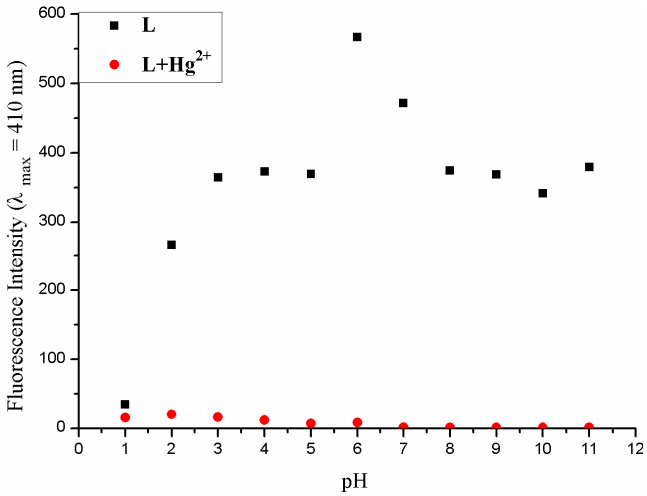


Fig. 8. Effect of pH on the fluorescence spectra of **L** (2.0×10^{-5} M) and **L** in response to Hg^{2+} (10 equiv.) from 1 to11 in DMSO/H_2O (9:1, v/v, containing 0.01 M HEPES) solution..

To facilitate the use of **L** for the detection of mercury, test strips were prepared by immersing filter papers into a DMSO/H_2O binary solution of **L** (0.01 M) followed by exposure to air until complete drying. Intriguingly, the fluorescence color can be changed immediately from blue to colorless once the test paper was immersed into an aqueous solution (5 μM) of mercury under UV irradiation. The same procedures were done for mercury and different cations (Fig. 9). The immersion of these test strips in the solution mixture of other cations (5 μM), did not cause any color change, and the blue of the strips remained unaffected. When these strips were immersed in the solution of mercury again, the color changed immediately. Thereby chemosensor **L** exhibits excellent fluorescence sensing performance, which will be very useful for the fabrication of sensing devices with fast and convenient detection for mercury and cations.

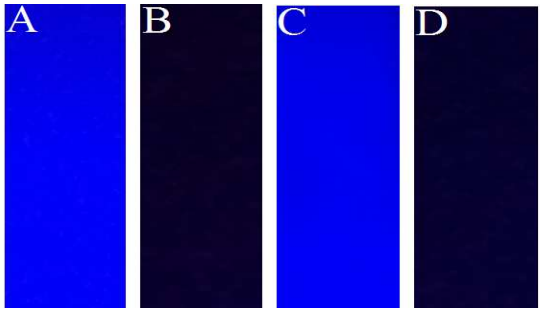


Fig. 9. Photographs of **L** on test strips (A) only **L**, (B) after immersion into water solutions with Hg^{2+}, (C) after immersion into water solutions with other cations, (D) after immersion into water solutions with Hg^{2+} and other cations under irradiation at 365 nm.

4. Conclusions

A non-sulfur, facile and efficient chemosensor **L** of mercury ion has been designed and synthesized. The sensor **L** shown specially selective and highly sensitive fluorescence recognition for Hg^{2+} in DMSO/H_2O (9:1, v/v) solutions. This work shows a new approach for the detection of mercury ion. Moreover, the sensor demonstrates the detection limit on fluorescence response of the sensor to Hg^{2+} is down to 9.56×10^{-9} M, which is far lower than the maximum level for mercury of 0.01 M in drinking water, from EPA guideline. In addition, test strips based on **L** were fabricated, which could serve as a practical fluorescent sensor to detect Hg^{2+} in field measurements or in test kits. Thus, we believe that these characteristics of **L** make it attractive for further molecular modifications and underlying applications as fluorescence sensor for mercury.

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Notes and references

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