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Sequential recognition of zinc ion and hydrogen sulfide by a new quinoline derivative with logic gate behavior

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A Schiff base-type fluorescent chemosensor **L** has been synthesized and characterized to relay recognition of Zn^{2+} and H_2S. Among various metal ions, only Zn^{2+} induces the fluorescence enhancement of the sensor **L** and results in an "Off-On" type sensing with excellent selectivity and high sensitivity in aqueous solution. The lowest detection limit for Zn^{2+} is 1×10^{-7} M. Density functional theory calculation for **L** and the resultant zinc complex is also performed in this study. The chemosensor also exhibits fluorescence quenching with Cu^{2+} in aqueous solution. Fluorescent changes of **L** upon the addition of Zn^{2+} and Cu^{2+} is utilized as an INHIBIT logic gate at the molecular level, using Zn^{2+} and Cu^{2+} as chemical inputs and the fluorescence intensity signal as output. On the other hand, the consequent product of **L** and Zn^{2+}, **L-2Zn**, is an excellent indicator for H_2S for depriving Zn^{2+} from the complex **L-2Zn**. Its H_2S sensing behavior is not interfered by reduced glutathione (GSH), L-cysteine (L-Cys), and even bovine serum albumin (BSA) indicates that **L-2Zn** is able to detect H_2S without any distinct interference from these biological thiols. The addition of H_2S leads the fluorescence quenching of **L-2Zn**, forming an "On-Off" type sensing system. Therefore, the sensing process for Zn^{2+} and sequential for H_2S is a reversible one, and also constitutes an "Off–On–Off" type fluorescence monitoring system. This Zn^{2+} and H_2S sequential recognition via fluorescence relay enhancement and quenching make probe **L** have a potential utility for Zn^{2+} and H_2S detection in aqueous media and biological samples.

Introduction

Fluorescent sensors for selective detection of various biologically and environmentally relevant metal ions, such as the zinc ion (Zn^{2+}) have recently attracted great attention. Zn^{2+} is the second most abundant metal ion in human body, which plays a great role in physiological and metabolic processes.[1-3] However, the lack of Zn^{2+} could result in an increasing risk of kinds of diseases.[4, 5] Thus the development of new and efficient systems for sensing Zn^{2+} is of great current interest. Among several chemical tools, fluorescent probes provide the optimal choice to detect Zn^{2+} in biological samples due to the simplicity and high sensitivity. In this regard, a variety of fluorescent Zn^{2+} probes have been developed based on various fluorophores.[6-9] From another viewpoint, a number of fluorescent sensors have been reported as molecular logic gates.[10, 11] The use of molecular logic gates has become very popular for miniaturization of the information process using ions, photons, pH, temperature or certain molecules as an input whereby the observable changes in optical or electrochemical signals are output data.[12]

On the other hand, organic compounds as sensors for metal ions and resultant metal complexes as sensors for anions or biomolecules have gained popularity recently.[13-19] Some of the sequential detection systems work through cation displacement assay. For instance, the fluorescent sensor binding with the metal ion displays a significant change in the fluorescence intensity. Then the resultant metal ion complex acts as an ideal candidate for the recognition of anions through the liberation of the sensor from the metal complex due to strong affinity of the anion towards the metal ion; consequently bringing a considerable change in the fluorescence profile of the receptor-metal complex.[20]

Among most of the human body essential biomolecules, hydrogen sulfide (H_2S) acts as the third endogenous gaseous signaling compound (gasotransmitter) after NO and CO.[21-24] Altered levels of H_2S have been linked to many diseases,[25, 26] for example, at a low concentration, H_2S can produce personal distress, while at a higher concentration, it can result in loss of consciousness, permanent brain damage, or even death through asphyxiation.[27] Therefore, detection of H_2S in living systems has attracted great attention recently.[28-30] A few fluorescent sensors for H_2S have been reported over the last two years.[31-34] However, most of the reported sensors are based on the specific H_2S-induced reactions and have some drawbacks such as the response time is too long and not easy to recover. To solve these problems, fluorescent sensors based on cations displacement sensing mechanisms would be the best choice, because the cations displacement process usually occurs in a matter of seconds. The recovered organic fluorophores could coordinate with cations and be reused to recognize H_2S. Therefore, it would be highly desirable to employ an organic metal complex as a fluorescence probe for H_2S. In this regard, the pioneer work was reported by Tetsuo Nagano's lab,[35] they developed a novel fluorescent probe with high selectivity and sensitivity based on azamacrocyclic Cu^{2+} complex chemistry for H_2S.

However, fluorescent sensors that can relay recognition of metal ions and H_2S are very rare. Inspired from the importance of sensing

Zn^{2+} and H_2S in physiological samples, design fluorescent sensors which can sequentially detect of Zn^{2+} and H_2S is very meaningful.

Bearing the above statement in mind, in this work, a fluorescent sensor for Zn^{2+} and the resultant Zn^{2+} complex as a sensor for H_2S has been designed. Firstly, a quinoline based Schiff base compound **L** was synthesized for the detection of Zn^{2+} since many quinoline based fluorescent sensors have excellent selectivity for zinc sensing.[36, 37] Density functional theory calculation for **L** and the resultant zinc complex is also carried out in this study. The fluorescent changes of **L** upon the addition of Zn^{2+} and Cu^{2+} are utilized as an INHIBIT logic gate at the molecular level. Secondly, the resultant complex **L-2Zn** was employed as a H_2S sensor for the depriving Zn^{2+} from the complex **L-2Zn**. As is well known that in aqueous state under the physiological pH, the major form of H_2S exists as HS^-, the ratio of HS^-:H_2S is approximately 3:1.[38] Thus, in this work, HS^- was used as the equivalent of H_2S. The **L-2Zn** ensemble can detect H_2S within two minutes, which is much faster than other sensors based on H_2S-induced reactions, such as azide reduction [21, 23, 39] and nucleophilic reaction to achieve strong fluorescence.[22, 30] Furthermore, this monitoring process both for Zn^{2+} and H_2S is an "Off–On–Off" monitoring system and could be extended to design new receptors for cations and anions detection in aqueous solutions.

Experimental

Reagents and Instrumentation

8-Aminoquinoline, Glycine, 4-Methyl-Phenol, all the cationic compounds and anionic compounds were purchased from Aldrich and used as received. All other chemicals were of the reagent-grade purchased from Tianjing Guangfu Chemical Companies and used as supplied. All solvents used for synthesis and measurements were redistilled before use.

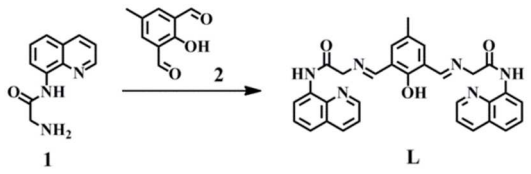
^1H NMR and ^{13}C NMR spectra were taken on a 400 MHz Varian Unity Inova spectrophotometer instrument. Solid State ^{13}C CP MAS NMR was obtained on Bruker Advance ⅡWB 400 M spectrometer at room temperature. All the absorption and emission spectra were recorded at room temperature. UV-Vis absorption spectra were determined on a Varian UV-Cary100 spectrophotometer. Steady state luminescence spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer with an excitation wavelength of 360 nm. Quantum yields were determined by an absolute method using an integrating sphere on Edinburgh Instrument FLS920. All the absorption and fluorescence spectra were recorded after 2 min when cations or anions were added.

UV-Vis and fluorescence titrations

Solutions of compound **L** were prepared in dry DMF (10^{-2} M). Metal perchlorates and anions were prepared in H_2O. In titration experiments, each time a 2 mL solution of ligand **L** (10 μM) was filled in a quartz cuvette (path length, 1 cm) and metal ions were added into the quartz cuvette by using a micro-pipette. For fluorescence measurements, excitation was provided at 360 nm, and emission was collected from 410 to 630 nm.

Synthesis of compound L

The synthesis of chemosensor **L** was achieved from the condensation of compound **1** and compound **2** in yield of 70% (Scheme 1, the detailed experimental sections see supporting information).



Scheme 1. Synthetic process of **L**.

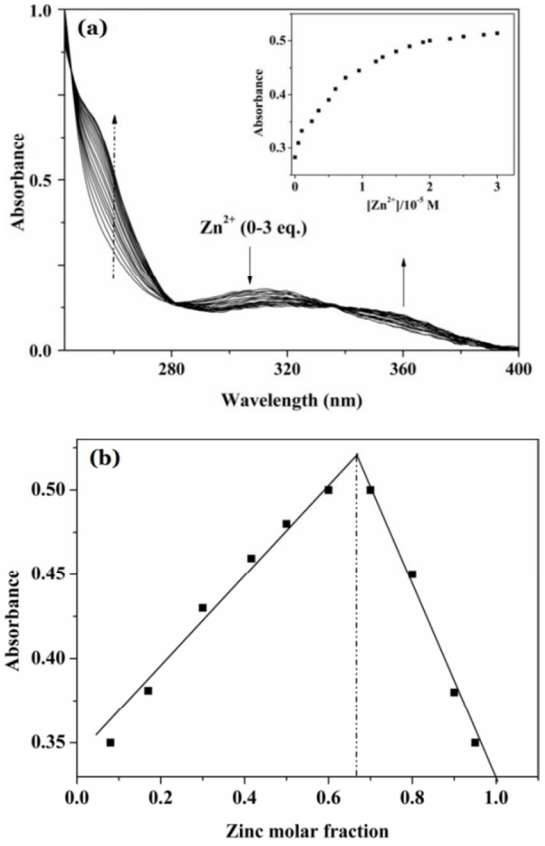


Fig. 1 (a) UV-Vis absorption of **L** (10 μM) upon the addition of different concentrations of Zn^{2+} (0-3 eq.) in CH_3CH_2OH/Tris-HCl buffer solution (50mM Tris, 50:50, v/v, pH 7.2), **(b)** Job's plot of Zn^{2+} and **L** with a total concentration of 30 μM.

Results and discussion

The condensation of glycine-N-8-quinolylamide with 4-Methyl-2, 6-Diformyl Phenol in ethanol furnished the quinoline based compound **L** in 70% yield (Scheme 1). It is well known that many quinoline based fluorescent sensors have excellent selectivity for zinc sensing.[40-47] Therefore, the synthesized compound **L** was firstly used as a zinc probe. And the sequential complex **L-2Zn** was used as a hydrogen sulfide sensor based on cations removal sensing mechanisms.[35]

Absorption Spectroscopy of L and Zn^{2+}

The binding behavior of compound **L** toward Zn^{2+} as its chloride salt was examined by UV-Vis spectroscopy. The titration experiment was carried out in CH_3CH_2OH/Tris-HCl buffer solution (50mM Tris, 50:50, v/v, pH 7.2) by adding aliquots of Zn^{2+}. The absorption spectrum of compound **L** (10 μM) was characterized by the presence of typical absorption bands at 320 nm due to the quinoline moiety

(Fig. 1). Upon addition of Zn^{2+} ions (0-3 eq.), the band at 320 nm was decreased slightly, while a new band at 260 nm was gradually increased. This absorption peaks intensity changes were likely due to the coordination of **L** with Zn^{2+}.[48] No obvious absorbance enhancement was observed at 260 nm when the concentration of Zn^{2+} increased from 2 to 3 equiv, indicating the exclusive formation of a 1:2 complex between L and Zn^{2+} (Fig. 1a inset). Job's plot also confirmed the 1:2 stoichiometric ratio of **L** with Zn^{2+} (Fig. 1b).

Fluorescence response of L and Zn^{2+}

Fluorescence spectroscopic study is also an important method to investigate the zinc-binding behavior of fluorescent probe **L**. In the fluorescence spectrum, compound **L** (10 μM) showed a weak emission at 482 nm when it was excited at 360 nm (Fig. 2). The weak fluorescence emission of compound **L** can be explained by two reasons as described in other reported quinoline-based sensors[42, 49, 50] and Schiff base-type sensors.[51] Firstly, the six nitrogen atoms of **L** can form intramolecular hydrogen bonds with hydrogen atoms in the absence of metal ions, which results in a photo-induced electron-transfer, and the de-excitation of the resulting tautomer occurs mainly through a non-radiative pathway.[42, 49, 50, 52] Secondly, C=N isomerization is also a decay process of excited states in compounds with an unbridged C=N structure so those compounds are often nonfluorescent.[51] As a result, compound **L** emits only weak fluorescence. Upon addition of 2.0 eq. of Zn^{2+} ions to the solution of sensor **L**, the intramolecular hydrogen bond is inhibited, the C=N isomerization is also be inhibited, thus leading to a significant increase in the fluorescence emission. The fluorescence intensity of **L** increased gradually as a function of Zn^{2+} ion concentration (Fig. 2 inset). When more than 2.0 eq. of Zn^{2+} was added, the fluorescence intensity became constant afterwards. The detection limit of **L** as a fluorescent sensor for the analysis of Zn^{2+} was found to be 0.1 μM from the titration experiment. The fluorescence quantum yields of compound **L** in the free state was found to be 7.9% and Zn^{2+}-bound state was found to be 11.33%.

Cations selectivity assays have been performed for sensor **L** with excitation energy of 360 nm while keeping other experimental conditions unchanged (Fig. 3, red bar). Figure 3 illustrated the fluorescence intensities of sensor **L** in the presence of various metal ions under physiological condition (CH_3CH_2OH/Tris-HCl buffer solution, pH 7.2). The results showed that, among the metal ions studied, only Zn^{2+} has a significant effect on the fluorescence intensity of sensor **L**. Other cations which exist at high concentrations in living cells, e.g., Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}, did not enhance the fluorescence intensity as shown in Figure 3. These results were presumably due to the poor complexation of alkali metals or alkaline earth metals with sensor **L**. However, the fluorescence increase of Cd^{2+} was also observed due to Zn^{2+} and Cd^{2+} are in the same group of periodic table and cause similar spectral changes while coordinated with fluorescent sensors.[45] While Cd^{2+} is rarely present in biological systems and would not cause any problem in biological applications.

The fluorescence intensity of sensor **L** in the presence of 5 eq. of Zn^{2+} mixed with various metal ions (5 eq.) were measured (Fig. 3, green bar) in the cations competition studies. In the presence of most of the investigated cations, the emission intensity of Zn^{2+}-bound **L** was unperturbed. While Cu^{2+}, Ni^{2+}, Co^{2+} and Fe^{3+} caused the fluorescence to quench to some extent, due to the displacement of Zn^{2+} by these cations.[49, 53] However, Cu^{2+}, Ni^{2+} and Co^{2+} ions would have little influence in vivo, since they exist at very low concentrations and are negligible in normal biological samples. Thus, Zn^{2+} can be distinguished from these investigated ions under physiological conditions.

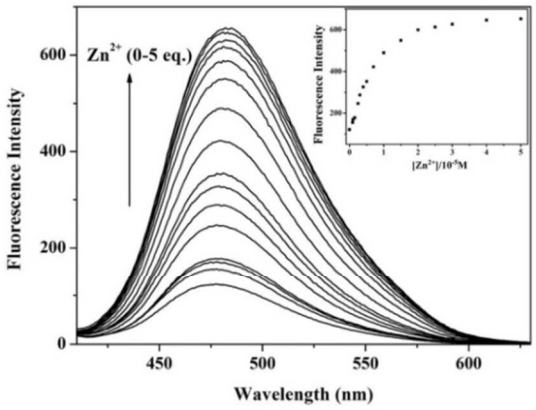


Fig. 2 Fluorescence spectra of **L** (10 μM) in CH_3CH_2OH/Tris-HCl buffer solution (50mM Tris, 50:50, v/v, pH 7.2) in the presence of different concentrations of Zn^{2+} (0–5 eq.). λ_{ex}=360 nm. **Inset:** Fluorescence intensity at 482 nm of **L** as functions of Zn^{2+} concentration.

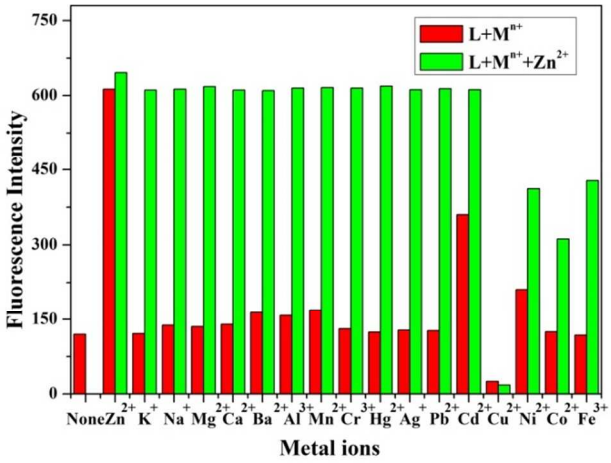


Fig. 3 Fluorescence response of **L** (10 μM) and different metal ions (5 eq) in CH_3CH_2OH/Tris-HCl buffer solution (50mM Tris, 50:50, v/v, pH 7.2). The red bars represent the addition 5 eq. of the various metal ions to a 10 μM solution of **L**. The green bars represent the change of the emission that occurs upon the subsequent addition of 5 eq. Zn^{2+} to the above solution. λ_{ex}=360 nm, λ_{em}=482 nm.

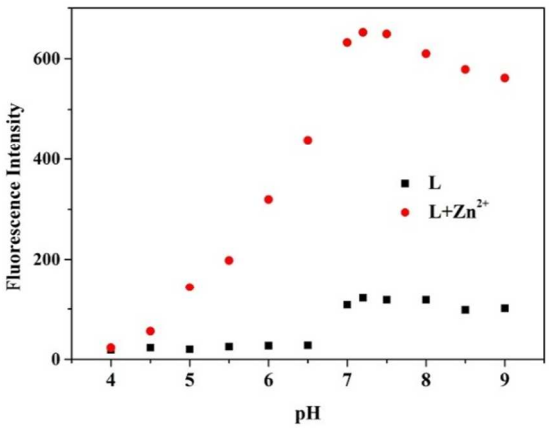


Fig. 4 Fluorescence intensity of **L** (10 μM) at various pH values in CH_3CH_2OH/Tris-HCl buffer solution (50mM Tris, 50:50, v/v) in the absence and presence of Zn^{2+} (5 eq.), λ_{ex}=360 nm.

In addition to metal ion selectivity, the fluorescence intensity of sensor **L** at various pH values in the presence and absence of Zn^{2+} was also measured (Fig. 4). In the absence of Zn^{2+}, protons did not induce any obvious fluorescence enhancement in the range of pH < 6.5, but slight increase was observed at pH > 6.5. The reason was that the formation of the intramolecular hydrogen bond was forbidden in alkalinity solution. When Zn^{2+} was added, sensor **L** showed no appreciable sensing ability to Zn^{2+} at pH < 6.5, which should be due to the competition of H^+ below pH 6.5. However, sensor **L** exhibited satisfactory Zn^{2+} sensing abilities when the pH was increased to the range 6.5-9. At pH=7.2, the fluorescence intensity reached its maximum value, indicating that sensor **L** possessed the highest sensing ability in an environment similar to physiological environment (pH =7.2).

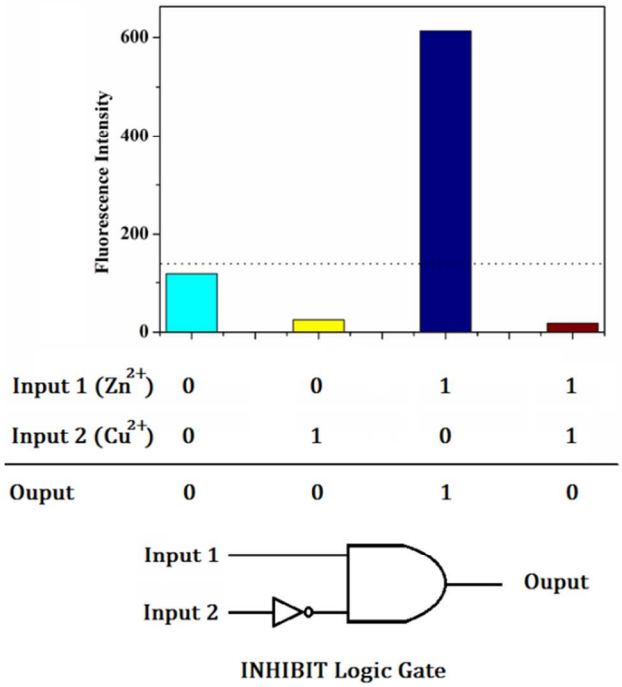


Fig. 5 The combinatorial logic scheme (top) of INHIBIT logic operations and the truth table (bottom).

Logic Gates Based on L with Zn^{2+} and Cu^{2+} as the Inputs

It has been reported that fluorescence sensors can act as logic gates.[10] Based on the interaction of **L** with Zn^{2+} and Cu^{2+} ions with subsequent changes of its emission intensity, a binary INHIBIT type logic gate by employing Zn^{2+} and Cu^{2+} as inputs was constructed. In order to elucidate the design of the logic gate, binary "0" and binary "1" are assigned to the inputs and outputs. For the input signals, binary "0" stands for no addition of Zn^{2+}/Cu^{2+}. Binary "1" denotes addition of Zn^{2+}/Cu^{2+}. The output values (fluorescence intensity) below a predefined threshold level are translated into binary "0", while the fluorescence output values above the threshold correspond to binary "1", in accordance with positive logic convention. The four possible input combinations are (0, 0), (1, 0), (0, 1) and (1, 1) shown in Figure 5. Free **L** shows a weak fluorescence emission at 482 nm ("0"). In the presence of Zn^{2+} ion the fluorescence is strong ("1"). In the presence of Cu^{2+} ion the fluorescence is low ("0"). In the simultaneous presence of both Zn^{2+} and Cu^{2+} ion, system still exhibits a low fluorescence ("0"). Therefore, A two-input INHIBIT logic gate was successfully mimicked for **L**.

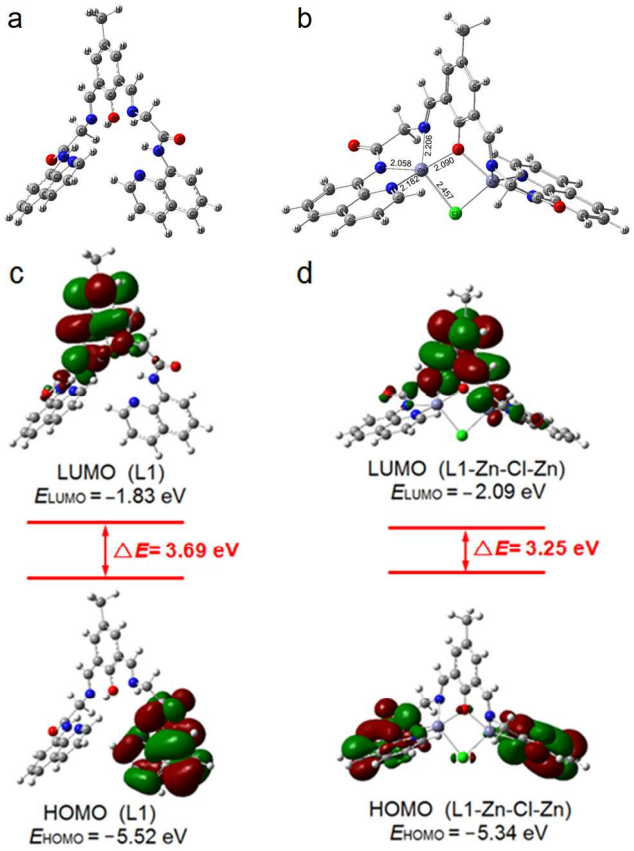


Fig. 6 The optimized configuration of (a) **L**, (b) **L** with Zn^{2+}. HOMO−LUMO energy gaps for respective compounds and interfacial plots of the orbitals: (c) free **L**, (d) **L-2Zn**.

Quantum Mechanical Calculations

Moreover, quantum mechanical calculations were carried out to confirm the configuration of **L-2Zn**, in which the B3LYP[54, 55] functional was used. For atoms C, H, N, Cl and O in this compound, the 6-31G (d,p) basis set was used, while the LANL2DZ basis set was used for Zn atom. The calculations were performed using the Gaussian 09 suite of programs.[56] The optimized configuration of **L** and **L-2Zn** complex are depicted in Figure 6a and b. The results show that there are two Zn^{2+} ions binding to **L** via five coordination sites, and the two Zn^{2+} ions coordinate with the O atom of *para*-methyl substituted phenol and one Cl atom simultaneously. The Zn−O bond length is 2.090 Å ($Zn-O_{phenol-oxygen}$), the Zn−Cl bond length is 2.457 Å, and the Zn−N bond lengths are 2.058 Å ($Zn-N_{amino-nitrogen}$), 2.182 Å ($Zn-N_{quinoline-nitrogen}$) and 2.206 Å ($Zn-N_{schiff\ base-nitrogen}$). It can be concluded that **L** can provide suitable space to accommodate the Zn^{2+} and Cl^- ions, forming a stable compound.

Additionally, the electronic properties of **L** and **L-2Zn** complex were also analyzed. It has been shown that the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as well as the electronic distributions may be used to explain the changes in the fluorescent properties with metal cation coordination and detect the ratiometric response to metal cations.[57, 58] With respect to **L**, the HOMO is mainly located on one of its aminoquinoline units, while the LUMO is mainly located on the phenol unit (Fig. 6c). But for the bindings of two Zn^{2+} and one Cl^- ions to **L**, the HOMO is mainly located on the two aminoquinoline units, whereas the LUMO is mainly located on

the phenol unit (Fig. 6d). Evidently, the bindings of two Zn^{2+} and one Cl^- ions to **L** enforce **L** to redistribute its electron density to stabilize the formed **L-2Zn** complex. Compared to **L**, the energy level of the HOMO of **L-2Zn** complex increases, but the LUMO decreases, so the HOMO-LUMO energy gaps for **L-2Zn** complex are smaller than **L**. These changes can be ascribed to the electron redistribution after the bindings. Thereby, it indicates that the enhanced fluorescence spectra upon the binding of two Zn^{2+} and one Cl^- ions to **L** arises from the energy level changes causing by the electron redistribution.

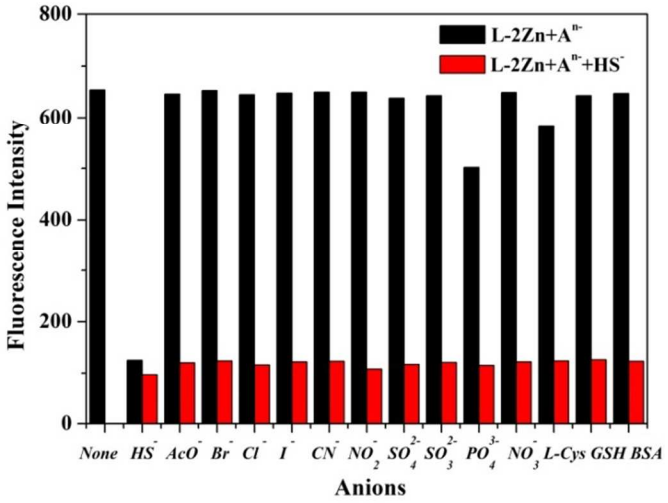


Fig. 7 Fluorescence response of **L-2Zn** (10 μM) and different anions (10 eq.) in CH_3CH_2OH/Tris-HCl buffer solution (50mM Tris, 50:50, v/v, pH 7.2). The black bars represent the addition 10 eq. of the various anions to a 10 μM solution of **L-2Zn**. The red bars represent the change of the emission that occurs upon the subsequent addition of 5 eq. HS^- to the above solution. λ_{ex}=360 nm, λ_{em}=482 nm.

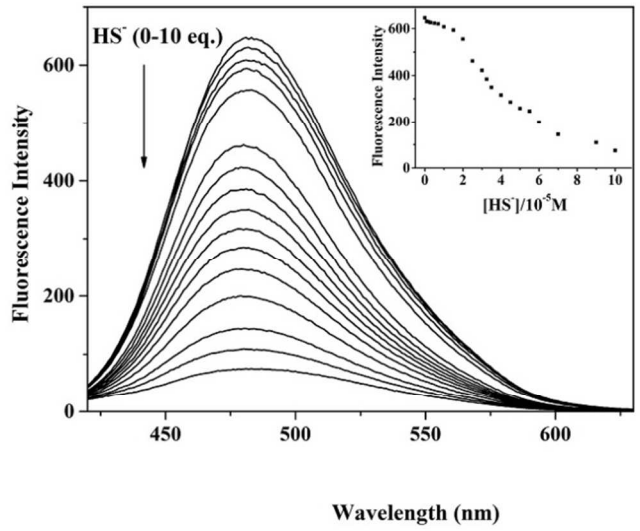
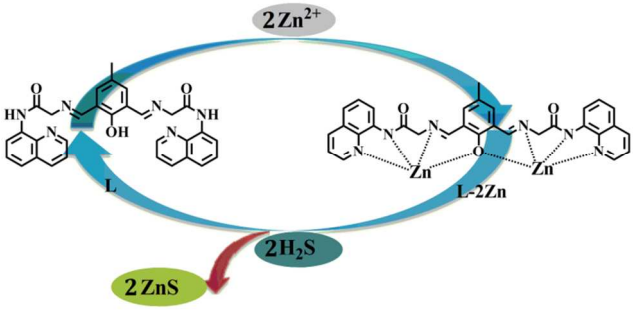


Fig. 8 Fluorescence spectra of **L-2Zn** (10 μM) in CH_3CH_2OH/Tris-HCl buffer solution (50mM Tris, 50:50, v/v, pH 7.2) in the presence of different concentrations of H_2S (0–5 eq.). λ_{ex} = 360 nm. Inset, fluorescence intensity of **L-2Zn** at 482 nm as a function of H_2S. concentration.



Scheme 2. The proposed mechanism of the sensing of Zn^{2+} and H_2S.

Fluorescence Spectroscopy of L-2Zn and H_2S

The recovery and reuse are important properties of the chemosensor toward the analyte.[59-61] In this study, considering the fact that Zn^{2+} can coordinate with sulfide anions to form a highly stable species ZnS, which has an extremely small solubility product constant (1.2×10^{-23}), the obtained fluorescence on **L-2Zn** system is regarded as a promising ensemble for fluorescence "On-Off" detection of H_2S via Zn^{2+} displacement approach. And in the H_2S selectivity experiment, it is very exciting and noteworthy that compound **L** can be regenerated only by adding HS^- to the solution containing **L-2Zn**. Thus, a sequential detection system is constructed, not only for Zn^{2+} detection, but also for the sensing of H_2S, as HS^- is equivalent of H_2S in physiological solution. [38]

In addition, competition experiments were also carried out to explore the anti-interference ability of **L-2Zn**. Complex **L-2Zn** (10 μM) was treated with 10 eq. of various anions, including AcO^-, Br^-, Cl^-, I^-, CN^-, NO_3^-, NO_2^-, SO_3^{2-}, PO_4^{3-} and SO_4^{2-}. As shown in Figure 7 (black bar), only HS^- caused remarkably fluorescence quenching, while PO_4^{3-} gave a slightly decrease in the fluorescence intensity. In the anion competition experiments, the **L-2Zn** ensemble (10μM) was treated with HS^- (10 eq.) in the presence of various tested anions (10 eq.) in pH 7.2 CH_3CH_2OH/Tris-HCl (50mM Tris, 50:50, v/v) buffer. And the results showed that all the relevant anions tested have virtually no influence on the fluorescence detection of HS^- (Fig. 7, red bar). In addition, some thiolcontaining amino acids such as reduced glutathione (GSH), L-cysteine (L-Cys), and even bovine serum albumin (BSA) were also examined to further evaluate the H_2S selectivity. As other reported organic metal complex fluorescent probe for H_2S,[35] addition of these thiolcontaining amino acids to **L-2Zn** did not induce noticeable fluorescence intensity changes. Thus, the complex **L-2Zn** has a very high selectivity for H_2S.

The mechanism of the sensing of H_2S can be described in Scheme 2. When Zn^{2+} is added, the intramolecular hydrogen bond of compound **L** is broken, the lone pair of electrons on the nitrogen atoms are involved in coordination with the Zn^{2+}, leading to a significant increase in the fluorescence emission. And the fluorescence is recovered by the addition of H_2S to **L-2Zn** ensemble, which is attributed to the low solubility product constant of ZnS. With alternately adding Zn^{2+} and H_2S, compound **L** shows an "Off-On-Off" type fluorescence change, meaning that the detection process is a reversible one for sequential sensing.[62]

To further understand the sensing behavior of **L-2Zn** to H_2S, the H_2S titration experiment was conducted. The fluorescence titration experiments of **L-2Zn** with H_2S were recorded in pH 7.2 CH_3CH_2OH/Tris-HCl (50mM Tris, 50:50, v/v) buffer solution. As can be seen in Figure 8, in the absence of H_2S, the free **L-2Zn** displayed quite high fluorescence. Importantly, with the addition of NaHS (0-10 eq.), the fluorescence intensity of **L-2Zn** decreased

gradually at 482 nm due to the depriving Zn^{2+} from the complex **L-2Zn**. The detection limit of H_2S could reach up to 10^{-6} M level from the titration experiment.

Conclusion

In conclusion, we have synthesized a multi-responsive and selective sensor **L** as a probe to monitor Zn^{2+} and sequential detection of H_2S. The receptor showed high sensitivity and selectivity for Zn^{2+} detection with a detection limit of 10^{-7} M. And the density functional theory calculation of sensor **L** and **L-Zn** was further studied; the results are well consistent with the experimental results. The fluorescent intensity of compound **L** can be recovered by adding HS^- to the Zn^{2+} sensing system via Zn^{2+} displacement approach. Therefore, the Zn^{2+} complex can be used for H_2S recognition. With alternately adding Zn^{2+} and H_2S, compound **L** shows an "Off-On-Off" type fluorescence change, meaning that the detection process is a reversible one. And the cation displacement approach employing a metal-complex for anion recognition allows for the design new receptors for sensitive anion detection in aqueous solutions.

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Notes and references

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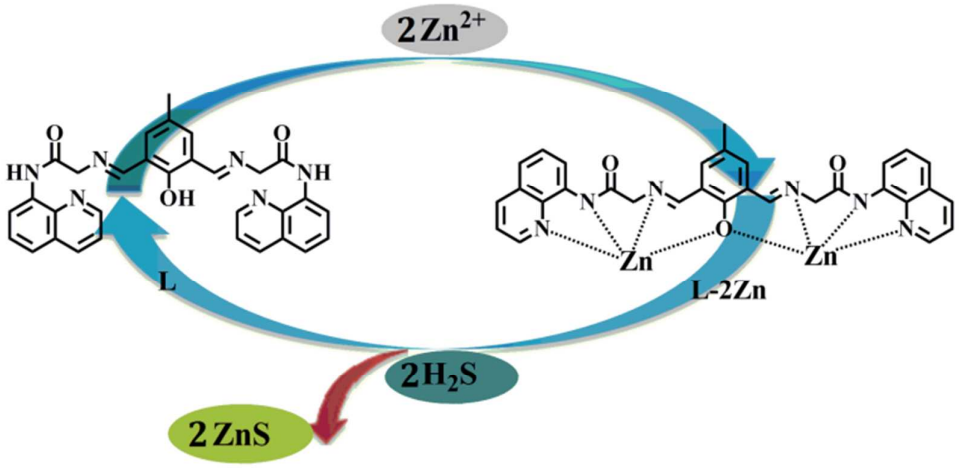
Graphical Abstract



A Schiff base-type fluorescent chemosensor L has been synthesized for Zn^{2+} detection, and the consequent product of L and Zn^{2+}, L-2Zn, is an excellent indicator for H_2S for depriving Zn^{2+} from the complex L-2Zn.