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ARTICLE

An "off-on-off" fluorescent probe for sequential detection of Zn^{2+} and hydrogen sulfide in aqueous solution

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Zhengping Dong*, Xuanduong Le, Panpan Zhou, Chunxu Dong, Jiantai Ma*

A novel selective fluorescent chemosensor (**L1**) based on 8-aminoquinoline was synthesized and characterized. The sensor exhibited remarkable selectivity for Zn^{2+} in the presence of other cations in aqueous solution. Density functional theory calculation results on **L1** and the **L1-Zn** complex are well consistent with the experimental results. Once combined with Zn^{2+}, the complex **L1-Zn** displayed high specificity for H_2S. As HS^- is equivalent of H_2S in physiological solution, HS^- was selected to represent H_2S in this work. Among various anions, only HS^- induced the revival of fluorescence of **L1**. The signal transduction occurs via reversible formation-separation of complex **L1-Zn** and ZnS. **L1** and the sequential complex **L1-Zn** have ideal chemical and spectroscopic properties that satisfy the criteria for further Zn^{2+} and H_2S sensing in biological and environmental applications.

Introduction

Design and synthesis of fluorescent sensors for cations, anions and biomolecules are hot research filed recent years.[1] To date, a great number of fluorescent sensors have been synthesized for Hg^{2+}, Cu^{2+}, Zn^{2+}, F^-, $H_2PO_4^-$, glutathione, cysteine etc.[2-8] Among all the fluorescent sensors been reported, chemosensors with dual sensing function is very interesting, and design this type of chemosensors is very meaningful, especially the sensors used for sequential detection of human body essential metal ions and biomolecules.

Among most of the human body essential elements, zinc ion (Zn^{2+}) is actively involved in numerous biochemical processes such as structural co-factors, regulator of enzymes, DNA binding, catalytic centers, and neuronal signal transmission.[9-11] However, Zn^{2+} deficiency or imbalanced Zn^{2+} distribution within the body, organ, or cell will lead to a broad range of pathologies, such as neuropathic, immune, endocrine, and gastro-enterological systems.[12, 13] As a result, development of fluorescent sensors for Zn^{2+} has attracted significant attention because of their high sensitivity and operational simplicity for real-time analysis.[14] Several studies focusing on improving and increasing the sensitivity and selectivity of fluorescent probes for Zn^{2+} have been reported in the literatures.[15-23]

On the other hand, hydrogen sulfide (H_2S) has emerged as the third endogenous gaseous signaling compound (gasotransmitter) after NO and CO,[24-27] although traditionally considered as a toxic gas for its rotten egg smell. Endogenous H_2S is biosynthesized by at least three separate enzymes: cystathionine-b-synthase (CBS), cystathionine-g-lyase (CSE), and 3-mercaptopyruvate sulfurtransferase (3-MST).[28] It is reported that H_2S also appeared to regulate inflammation. Nonetheless, some research studies also have indicated that the H_2S levels are related to Down syndrome and Alzheimer's disease.[29] These findings highlight importance of H_2S homeostasis. Therefore, detection of H_2S in living systems has attracted great attention recently.[30, 31] Fluorescence imaging through staining with a fluorescent probe is now one of the most attractive molecular imaging techniques for the *in vivo* detection of biomolecules owing to its high sensitivity/selectivity, non-invasiveness, and aptness for living cells, tissues, and living small animals, thus developing fluorescent probes for H_2S detection is now drawing much attention.[32, 33] A few fluorescent probes for H_2S have been reported in recent years.[34-41] Some could even be used for imaging of intracellular H_2S. Most of the reported chemodosimeters are based on the specific H_2S-induced reactions, such as azide reduction, and nucleophilic reaction to achieve strong fluorescence. However, these sensors may have some drawbacks, most of them display a response time between 20 minutes to 2 hours, and also not easy to reuse. While the fluorescent sensor based on cations removal sensing mechanisms could real-time imaging of quick H_2S-related biological processes.[41-43]

Bearing the above considerations in mind, in this study, a fluorescent sensor based on quinoline group has been synthesized. It's well known that many quinoline based fluorescent sensors have excellent selectivity for Zn^{2+} sensing.[16, 44-46] The synthesized sensor **L1** with weak fluorescence was also used for Zn^{2+} sensing, and the complex **L1-Zn** exhibited stronger fluorescence. In the sequential anions detection, it was found that **L1-Zn** had excellent HS^- selectivity for depriving Zn^{2+} from the complex **L1-Zn** gave weak fluorescence of **L1**. In other words, **L1-Zn** has excellent selectivity for H_2S as HS^- is equivalent of H_2S in physiological solution. So, the monitoring process both for Zn^{2+} and H_2S is reversible and the fluorescence monitoring system is an "off-on-off" type. What's more, compared with other probes for ions and anions, **L1** can

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sequentially sense Zn^{2+} and H_2S in aqueous solution. And the **L1-Zn** ensemble can detect H_2S within two minutes, which is much faster than other sensors based on H_2S-induced reactions. Therefore, the chemosensor has potential applications in biological systems for Zn^{2+} and H_2S detection.

Experimental Sections

Reagents and Instrumentation

8-Aminoquinoline, Glycine and 4-Methyl-Phenol were purchased from Aldrich. Cationic compounds such as $NaClO_4$, $KClO_4$, $Mg(ClO_4)_2$, $Ca(ClO_4)_2$, $Fe(ClO_4)_3$, $Co(ClO_4)_2$, $Ni(ClO_4)_2$, $Cu(ClO_4)_2$, $Zn(ClO_4)_2$, $Cd(ClO_4)_2$, $Al(ClO_4)_3$, $Pb(ClO_4)_2$, $AgClO_4$, $ZnCl_2$ and $Hg(ClO_4)_2$ were purchased from Aldrich and used as received. All the anions as their sodium salts used in the titrations were also purchased from Aldrich and used as received. All the 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.

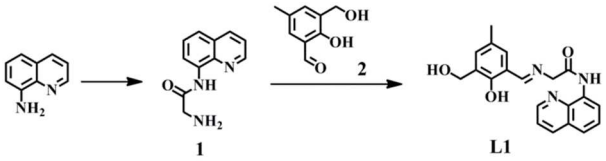
^1H NMR and ^{13}C NMR spectra were taken on a 400 MHz Nuclear Magnetic Resonance Spectrometer (JEOL, JNM-GX400). All the absorption and emission spectra were recorded at room temperature. UV-vis absorption spectra were determined on a Varian UV-Cary100 spectrophotometer. Steady state luminescence spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer with excitation wavelength of 345 nm. Quantum yields were determined by an absolute method using an integrating sphere on Edinburgh Instrument FLS920.

Synthesis of compound 1

Compound **1** was obtained by the procedure of literature.[47] The yield in this study is 82%. ^1H-NMR ($CDCl_3$, 400 MHz): δ=2.03 (s, 2H, -NH_2), 3.59 (s, 2H, CH_2NH_2), 7.30-7.46 (m, 3H), 8.01 (m, 1H), 8.76 (m, 2H), 11.22 (s, NHCO, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 45.7, 115.9, 121.1, 121.3, 126.8, 127.6, 133.8, 135.7, 138.4, 148.1, 171.3 ppm. EI (M/z): 201.

Synthesis of compound 2

NaOH solution (1 M) was added dropwise to 21 mL of 4-Methyl-Phenol with vigorous stirring until the mixture turned into purple. Then, formaldehyde (37 wt%, 60 mL) was added to the reaction solution and the reaction temperature was maintained at 50 °C for 3 h. And then CO_2 was bubbled through the solution to give a milky precipitate. The milky precipitate (5 g) was added to 100 mL $CHCl_3$ with 30 g activated MnO_2. The reaction mixture was heated and reflux for 10 h. The crude product was purified by silica gel column chromatography (cyclohexane/ethyl acetate=4:1) to give compound **2** (3.32 g, yield 67%). ^1HNMR ($CDCl_3$, 400 MHz): δ=2.28 (s, 3H, Ar-CH_3), 3.10 (s, H, CH_2-OH), 4.66 (s, 2H, Ar-CH_2), 7.20, (s, 1H, Ar-H), 7.36 (s, 1H, Ar-H), 9.77 (1H, HC=N), 11.08 (1H, Ar-OH) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.1, 59.8, 119.8, 128.9, 128.9, 132.3, 136.6, 156.9, 196.5 ppm. ESI: 167.2 (M+H).



Scheme 1. Synthetic process of **L1**.

Synthesis of compound L1

Compound **2** (1.66 g, 10 mmol) and compound **1** (2.02 g, 10 mmol) were dissolved in anhydrous EtOH (60 mL). The mixture was stirred at 80 °C for 6 h under an argon atmosphere. The pale yellow precipitate was filtered and washed with EtOH several times to give **L1** (2.8 g, yield 80%). ^1HNMR (d-DMSO, 400 MHz, Fig. S1): δ=2.30 (s, 3H, Ar-CH_3), 4.64 (s, 2H, CH_2), 4.73 (s, 2H, Ar-CH_2), 5.15 (m, 1H, CH_2-OH), 7.21, (s, 1H, Ar-H), 7.36 (s, 1H, Ar-H), 7.61-7.71 (m, 3H, Ar-H), 8.40-8.43 (m, 1H, Ar-H), 8.65-8.68 (m, 2H, Ar-H), 8.89 (1H, HC=N), 10.63 (1H, Ar-NH) ppm. ^{13}C NMR (d-DMSO, 100 MHz, Fig. S2): δ 20.7, 58.1, 62.6, 116.6, 118.2, 122.7, 122.8, 127.4, 127.5, 128.3, 130.2, 130.6, 131.9, 134.4, 137.1, 149.5, 155.6, 168.1, 169.6 ppm. HRMS: 350.15 (M+H).

Results and Discussion

The synthesis of chemosensor **L1** was achieved from the condensation of compound **1** and compound **2** in yield of 80% (Scheme 1). Compound **1** was obtained by the procedure of literature. Compound **2** was synthesised by the reacting of 4-Methyl-Phenol and formaldehyde. All the compounds were characterized by ^1H NMR, ^{13}C NMR and mass spectrometry.

Absorption Spectroscopy of L1 and Zn^{2+}

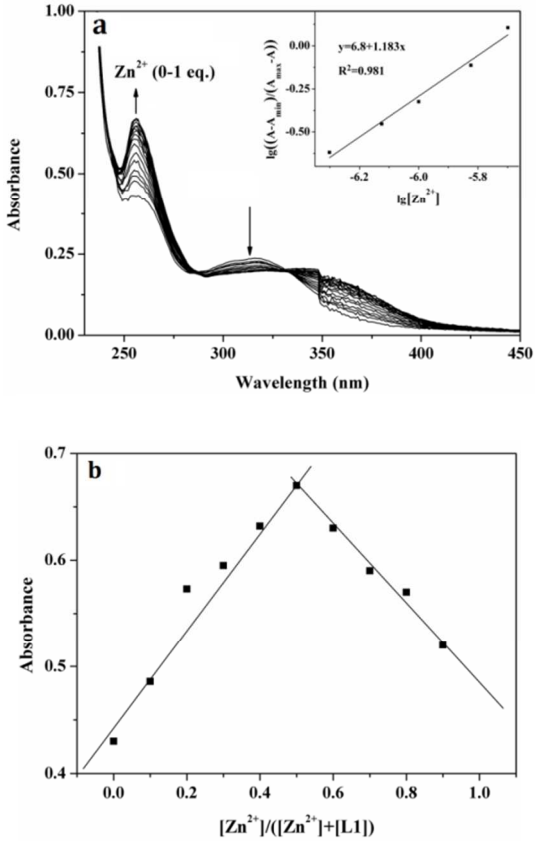


Fig. 1 (a) Uv-vis absorption of **L1** (10 μM) upon the addition of different concentrations of Zn^{2+} (0-1 eq.) in CH_3CN/Tris-HCl buffer solution (50 mM Tris, 50:50, v/v, pH 7.2). Inset: The nonlinear fitting (absorbance at 256 nm) of **L1**. **(b)** Job's plots of the complexation between **L1** and Zn^{2+}. Total concentration of [**L1**] + [Zn^{2+}] was kept constant at 20 μM.

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The coordination of **L1** with Zn^{2+} was investigated by spectrophotometric titration in CH_3CN/Tris-HCl (50 mM Tris, 50:50, v/v, pH 7.2) at room temperature (The optimization of the solvent ratio see Fig. S3). To investigate the binding property of **L1** toward Zn^{2+}, we measured the UV-vis spectra of **L1** (10 μM) in the presence of various concentrations of Zn^{2+} (0-10 μM), as illustrated in Figure 1a. The absorbance of **L1** at 256 nm gradually increased with an increasing concentration of Zn^{2+}. Meanwhile, the absorption band at 315 nm gradually decreased. This absorption peaks intensity changes were likely due to the coordination of **L1** with Zn^{2+}.[48] No further absorbance enhancement was observed at 256 nm after 1 eq. of Zn^{2+} was added. Job's plot analysis of the UV-vis titrations revealed a maximum at about 0.5 mole fraction (Fig. 1b), indicating 1:1 binding stoichiometry between **L1** and Zn^{2+}. The changes that occurred in the UV-vis spectra arose from the coordination of Zn^{2+} to the N and O binding sites, which broke the intramolecular hydrogen bond of **L1**, increased its coplanarity of the conjugated system.[49]

The binding constant of **L1** for Zn^{2+} was also investigated through UV-vis titration. By assuming a 1:n stoichiometry for interaction between **L1** and Zn^{2+}, the association constant of **L1** for Zn^{2+} determined from the following equation [50] to be $\boldsymbol{K_{Zn^{2+}}}$=6.3×10^6 M^{-1}.

$$\lg\frac{\mathbf{A}-\mathbf{A}_{min}}{\mathbf{A}_{max}-\boldsymbol{A}} = \boldsymbol{lgK} + \boldsymbol{nlg}[\boldsymbol{M^{n+}}]$$

In the equation, K is the association constant, A_{max} is the absorbance of **L1** in the presence of excess amount of Zn^{2+}, A is the absorbance of **L1** obtained with various concentration of Zn^{2+}, A_{min} is the absorbance of **L1** without any cation. The nonlinear fitting of the titration curve also showed a 1:1 stoichiometry between **L1** and Zn^{2+} (Fig. 1a, inset). Thus, in accordance with the 1:1 stoichiometry, the possible binding mode between **L1** toward Zn^{2+} was proposed in Scheme 2.

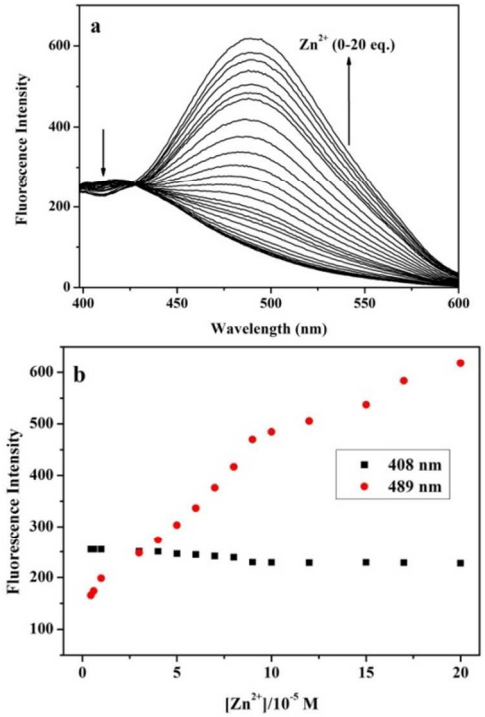

Fig. 2 (a) Fluorescence spectra of **L1** (10μM) in CH_3CN/Tris-HCl buffer solution (50 mM Tris, 50:50, v/v, pH 7.2) in the presence of different concentrations of Zn^{2+} (0–20 eq.). λ_{ex} = 345 nm. **(b)** Fluorescence intensity at 408 nm and 489 nm of **L1** as functions of Zn^{2+} concentration.

Fluorescence Response of L1 and Zn^{2+}

In fluorescence emission, free **L1** exhibits λ_{max}em at 408 nm upon excitation at 345 nm in CH_3CN/Tris-HCl (50 mM Tris, 50:50, v/v, pH 7.2) solution. Its quantum yield is 0.069. Upon addition of increasing Zn^{2+} (0-20 eq.), a remarkable 81 nm red-shift from 408 to 489 nm of fluorescence emission and an obvious increase in fluorescence intensity at 489 nm were observed with a quantum yield of 0.138 (Fig. 2). A well-defined isoemission point at 427 nm was also observed. The detection limit for Zn^{2+} is established at 10^{-7} M under current experimental conditions. The fluorescence changes of **L1** upon addition of Zn^{2+} can be described from Scheme 2. The three nitrogen atoms of **L1** 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. As a result of this process, **L1** emits only weak fluorescence. Once **L1** coordinated to Zn^{2+}, the intramolecular hydrogen bond is broken, thus enhancing fluorescence emission. Simultaneously, the deprotonation process strengthens the electron-donating ability from the nitrogen atom of the 8-amino group to the quinoline ring. And the electron transfer from the nitrogen atom of the heterocycle to the metal ion further enhances the ICT process.[51-53]

The fluorescence intensity of **L1** in the absence and presence of Zn^{2+} at various pH values was also measured. Because for many biological applications, it is very important that fluorescent sensor can be suitable for measuring specific metal ion in the physiological pH range[54, 55] As shown in Figure 3, in the absence of Zn^{2+}, protons did not induce any obvious fluorescence enhancement in the range of pH=4-7. When Zn^{2+} was added, **L1** had only weak fluorescence response to Zn^{2+} in the acidic environment due to the protonation of the amino group of **L1** leading to a weak coordination ability of Zn^{2+}, however, satisfactory Zn^{2+}-sensing abilities were exhibited when the pH was increased from 6.5 to 10. At pH=7.2, the fluorescence intensity reached its maximum value, indicating that **L1** possessed the highest sensing ability under the physiological pH window. The stability of fluorescence in near neutral and weak acidic media is very important for the practical applications of the Zn^{2+} probes in both environmental and biological analysis.

The selectivity and tolerance of **L1** for Zn^{2+} over other metal ions were investigated by adding excess amount of metal ions (2×10^{-4} M) to the solution of **L1** (10^{-5} M). The fluorescence intensity was chosen at 489 nm. As shown in Figure 4 (red bars), all biological relevant cations (i.e., Na^+, K^+, Ca^{2+}, and Mg^{2+}) were non-responsive to the probe **L1**. Other metal ions, including common transition metals, only had slightly influence on the fluorescence of **L1**. However, the fluorescence increase of Cd^{2+} was also observed. Because Zn^{2+} and Cd^{2+} are in the same group of the periodic table and cause similar spectral changes while coordinated with fluorescent sensors.[45]

To further explore the selectivity of **L1** for Zn^{2+}, the fluorescence intensity of **L1** in the presence of Zn^{2+} mixed with various metal ions (20 eq.) was also measured (Fig. 4, green bar). The emission intensity of Zn^{2+}-bound **L1** are unperturbed in the presence of most of the investigated cations except Cu^{2+}, Ni^{2+} and Co^{2+}, especially Cu^{2+} almost quenched the emission of **L1-Zn**. This phenomenon is owing to the displacement of Zn^{2+} by these cations.[49, 56] 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. Therefore, sensor **L1** has excellent selectivity for Zn^{2+} over other cations.

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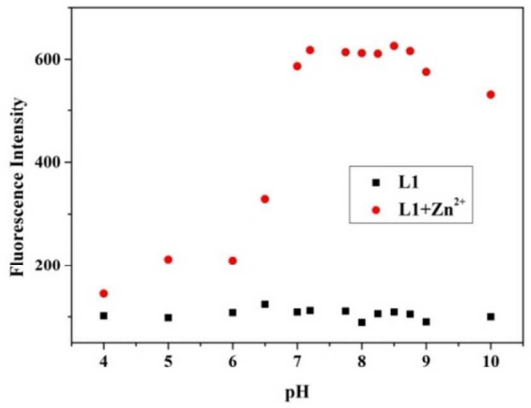


Fig. 3 Fluorescence intensity of **L1** (10 μM) at various pH values in CH_3CN/Tris-HCl buffer solution (50 mM Tris, 50:50, v/v) in the absence and presence of Zn^{2+} (20 eq.), λ_{ex}=345 nm.

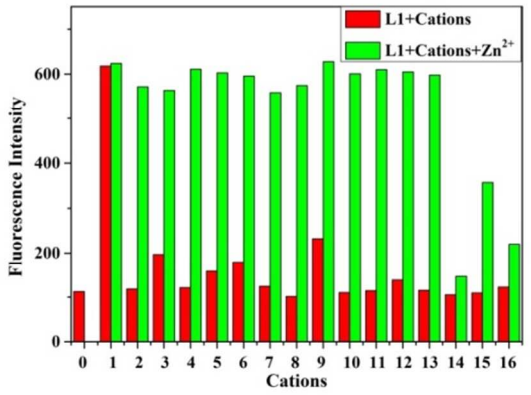


Fig. 4 Fluorescence response of **L1** (10 μM) and different metal ions (20 eq) in CH_3CN/Tris-HCl buffer solution (50 mM Tris, 50:50, v/v, pH 7.2). The red bars represent the addition 20 eq. of the various metal ions to a 10 μM solution of **L1** (0 None, 1 Zn^{2+}, 2 Ag^{+}, 3 Pb^{2+}, 4 K^{+}, 5 Na^{+}, 6 Mn^{2+}, 7 Hg^{2+}, 8 Cr^{3+}, 9 Cd^{2+}, 10 Ca^{2+}, 11 Ba^{2+}, 12 Al^{3+}, 13 Mg^{2+}, 14 Cu^{2+}, 15 Ni^{2+}, 16 Co^{2+}). The green bars represent the change of the emission that occurs upon the subsequent addition of 20 eq. Zn^{2+} to the above solution. λ_{ex} =345 nm, λ_{em} = 489 nm.

Quantum Mechanical Calculations

Furthermore, quantum mechanical calculations were carried out to identify the configuration of **L1-Zn**, in which the B3LYP [57, 58] functional was employed. The 6-31G(d,p) basis set was used for C, H, N, and O atoms, while the LANL2DZ basis set was used for Zn atom. The calculations were performed using the Gaussian 09 suite of programs.[59] The optimized configurations of L1 and L1-Zn are displayed in Figure 5a, b. It can be seen that the Zn^{2+} ion binds to **L1** well via four coordination sites, forming an almost planar structure. The Zn-O bond length is 1.939 Å (Zn-$O_{phenol\text{-}oxygen}$), and the Zn-N bond lengths are 2.029 Å (Zn-$N_{amino\text{-}nitrogen}$), 2.149 Å (Zn-$N_{quinoline\text{-}nitrogen}$) and 2.081 Å (Zn-$N_{schiff\ base\text{-}nitrogen}$). The results suggest that **L1** can provide suitable space to accommodate the Zn^{2+} ion.

In addition, the electronic properties of **L1** and **L1-Zn** complex were also discussed. It is known that the electronic distributions as well as the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) might be used to elucidate the changes in the fluorescent properties with metal cation coordination and detect the ratiometric response to metal cations.[60] For **L1**, the HOMO is mainly located on its aminoquinoline unit, while the LUMO spans over the whole molecule (Fig. 5c). Surprisingly, after the introduction of Zn^{2+} ion which forms **L1-Zn** complex, the HOMO almost covers the whole molecule, whereas the LUMO is mainly located on the aminoquinoline unit (Fig. 5d). Obviously, the binding of Zn^{2+} ion to **L1** enforces **L1** to redistribute its electron density, that is, there are considerable electrons transferring from aminoquinoline unit to phenol unit, leaving aminoquinoline unit as an electron-deficient region (i.e., the LUMO). As a result, the formed **L1-Zn** complex is stabilized. Compared to **L1**, the energy level of the HOMO of **L1-Zn** complex increases, but the LUMO decreases, so the HOMO-LUMO energy gap for **L1-Zn** complex is smaller than **L1**. These changes are closely associated with the electron redistribution. Therefore, it can be concluded that the enhanced fluorescence spectra upon the binding of Zn^{2+} ion to **L1** stems from the intramolecular electron transfer from the aminoquinoline unit to phenol unit.

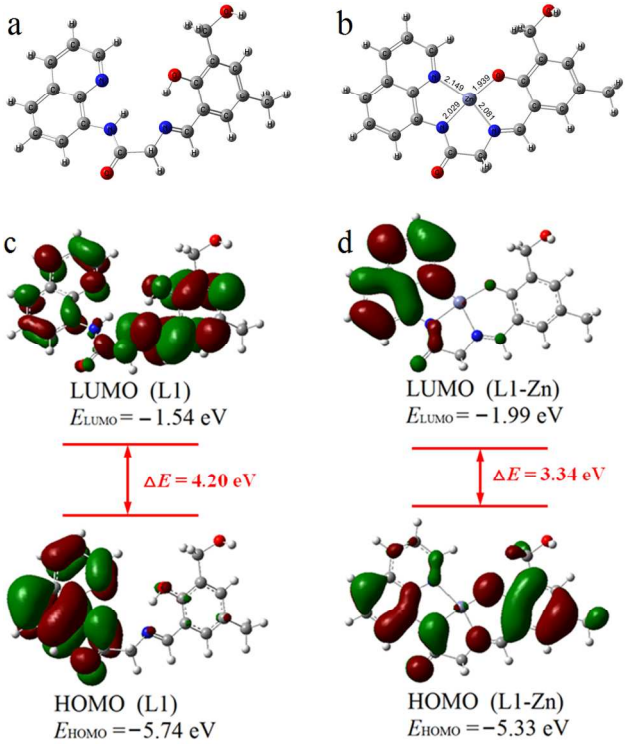
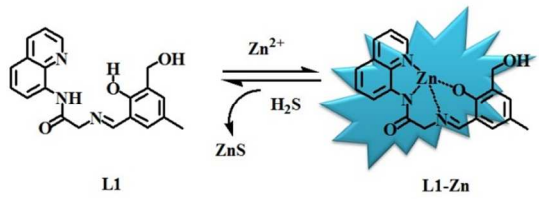


Fig. 5 The optimized configuration of (a) **L1**, (b) **L1** with Zn^{2+}. HOMO−LUMO energy gaps for respective compounds and interfacial plots of the orbitals: (c) free **L1**, (d) **L1-Zn**.



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

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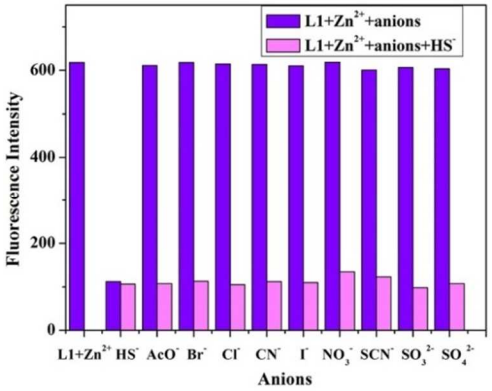

Fig. 6 Fluorescence response of **L1-Zn** (10 μM) and different anions (20 eq) in CH_3CN/Tris-HCl buffer solution (50 mM Tris, 50:50, v/v, pH 7.2). The purple bars represent the addition 20 eq. of the various anions to a 10 μM solution of **L1-Zn**. The pink bars represent the change of the emission that occurs upon the subsequent addition of 20 eq. HS^- to the above solution. λ_{ex} =345 nm, λ_{em} = 489 nm.

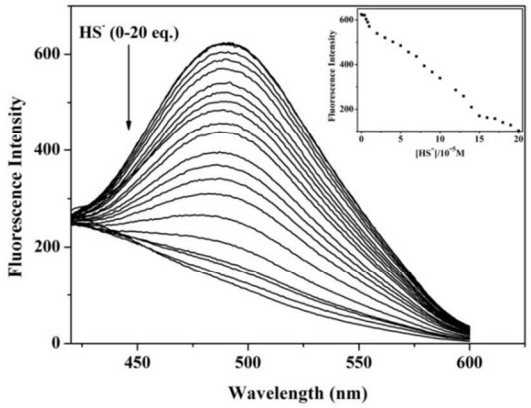

Fig. 7 Fluorescence spectra of **L1-Zn** (10 μM) in CH_3CN/Tris-HCl buffer solution (50 mM Tris, 50:50, v/v, pH 7.2) in the presence of different concentrations of H_2S (0–20 eq.). λ_{ex} = 345 nm. Inset, fluorescence intensity of **L1-Zn** at 489 nm as a function of H_2S concentration.

Selective Optical Response of Complex L1-Zn to H_2S

When sensor L1 was used for Zn^{2+} sensing, excess amount of cations (20 eq.) were added. To examine the sequential H_2S sensing, the above mixture was incubated with some representative anion species. In this work, NaHS was used as the equivalent of H_2S. It is 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.[61] As shown in Figure 6 (purple bar), when 20 eq. of HS^-, ACO^-, Br^-, Cl^-, CN^-, I^-, NO_3^-, SCN^-, SO_3^{2-} and SO_4^{2-} were added to the solution of **L1-Zn** (10μM), only HS^- caused remarkably fluorescence quenching. The reason is that among the investigated anions, only HS^- could form insoluble substances with Zn^{2+}. Because all the fluorescence titrations were carried out at the pH 7.2 to simulate the biological pH, OH^- was not investigated. Thus, the spectroscopic studies suggest that the **L1-Zn** ensemble has a high selectivity for H_2S over other test anions at the biological pH, which may be attributed to the low solubility product constant of ZnS.

To investigate whether the **L1-Zn** ensemble could still retain the sensing response to H_2S under the potential competition of other relevant anions, the ensemble (10μM) was treated with HS^- (20 eq.) in the presence of various tested anions (20 eq.) in pH 7.2 CH_3CN/Tris-HCl (50 mM Tris, 50:50, v/v) buffer. As displayed in Figure 6 (pink bar), all the relevant anions tested have virtually no influence on the fluorescence detection of HS^-. Besides, the fluorescence spectrum was recorded after 2 minutes when HS^- was added, and the intensity barely changed for more than 1 h, indicating that the monitoring system is very stable. Thus, the ensemble seems to be useful for selectively sensing H_2S in physiological solution even involving these relevant anions.

On the other hand, the titration curve of H_2S was also investigated in CH_3CN/Tris-HCl (50:50, v/v, pH 7.2) solution. As can be seen in Figure 7, the fluorescence intensity of **L1-Zn** (10 μM) at 489 nm gradually decreased with the increasing of the concentration of HS^- (from 0-20 eq.). The detection limit of H_2S could reach up to 1.2×10^{-6} M from the titration experiment. In this study, chemosensor **L1** had just weak fluorescence. When Zn^{2+} was added, the fluorescence intensity at 489 nm significantly increased. And the fluorescence was recovered with the addition of H_2S to **L1-Zn** ensemble, thus constituted a reversible monitoring process. It is also worth mentioning that the fluorescence monitoring system could be described as an "off–on–off" type (Scheme 2).

Conclusions

In summary, we reported in this study a dual function fluorescent sensor for sequential detection of Zn^{2+} and H_2S. The sensor **L1** displayed highly selectivity and sensitivity for Zn^{2+} over other common cations like other reported quinoline based fluorescent probes. The consequent product of **L1** and Zn^{2+}, **L1-Zn**, was an excellent indicator for H_2S for depriving Zn^{2+} from the complex **L1-Zn**. And the **L1-Zn** ensemble has a high selectivity for H_2S over other test anions. The chemosensor **L1** exposed weak fluorescence, which was enhanced by Zn^{2+}, then recovered with the addition of H_2S. Therefore, that constituted an "off–on–off" type fluorescence monitoring system, meaning that the process was a reversible one. We believe this strategy will be useful for the design of more sensitive and selective probes for the detection of H_2S in biological systems.

Acknowledgements

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Notes and references

College of Chemistry and Chemical Engineering, Gansu Provincial Engineering Laboratory for Chemical Catalysis, Lanzhou University, Lanzhou, PR China. E-mail address: dongzhp@lzu.edu.cn (Zhengping Dong), majiantai@lzu.edu.cn (Jiantai Ma). Tel.: +86 0931 8912577; fax: +86 0931 8912582.

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