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Highly selective fluorescence turn-on sensor for hydrogen sulfide and imaging in living cells

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A displacement method of detecting hydrogen sulfide in aqueous media based on complex **L–Cu** ensemble is developed. Once combined with Cu^{2+}, complex **L–Cu** displayed high specificity for sulfide anion. Among the various anions, only sulfide anion induce the revival of fluoresecence of compound **L**, which is quenched by Cu^{2+}, resulting in turn-on type sensing sulfide anion. Complex **L–Cu** exhibits a highly sensitive fluorescent response toward S^{2-} by releasing compound **L** to give a remarkable change with 20-fold fluorescence intensity enhancement under 2 equivalent of S^{2-} added in Tris–HCl/ DMF (20 mM, 6/4, v/v), and also exhibits a dynamic response range for S^{2-} from 5×10^{-7} to 5×10^{-6} M, with a detection limit of 0.18 μM. In addition, the turn-on fluorescent change upon the addition of S^{2-} is also applied in cell imaging.

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1. Introduction

Hydrogen sulfide is well-known as a foul-smelling, corrosive, flammable, and deadly gas. The hydrogen sulfide can be widely found in water and wastewater samples not only owing to the activities of industry and agriculture but also thanks to microbial reduction of sulfate by an aerobic bacteria [1]. In the human body, H_2S is formed endogenously from cysteine and homocysteine by pyridoxal-50-phosphate-dependent enzymes, cystathionine-γ-lyase and cystathionine-β-synthetase [2]. Hydrogen sulfide is also a weak acid in aqueous solutions ($pK_a1=7.04$, $pK_a2=11.96$) [3], equilibrating mainly with HS^- at physiological pH. H_2S has been recently recognized as the third gasotransmitter together with carbon monoxide (CO) and nitric oxide (NO) [4], and it plays an important physiological role in many biological processes. However, abnormal levels of H_2S are associated with many types of diseases such as chronickidney disease, liver cirrhosis, and Down's syndrome [5–8]. Thus, it is of importance to develop a method to detect H_2S. Compared with traditional methods, such as titration, [9] inductively coupled plasma-atomic emission spectroscopy,[10] electrochemical methods,[11] and ion chromatography,[12] fluorescent sensing has received great attention of its simple operation and high selectivity and sensitivity.

Recently several elegant fluorescent probes for H_2S detection have been constructed [13–30]. Among these probes, there are two main pathways for hydrogen sulfide sensing. One is based on irreversible sulfide-specific chemical reactions, such as the strong reduction power [15–22] and nucleophilicity of hydrogen sulfide [23–27]. The other one is based on the displacement method of binding affinity with metals [28–30] of H_2S. However, most of the organic chemical reactions are time-consuming with poor selectivity and required relatively strict conditions, which limited the probes application. Furthermore, the probe based on nucleophilic substitution has the possible interference from thiol-containing amino acids, such as cysteine and homocysteine. Thus reversible sensors exploiting metal sulfide affinity [31–35] which is fast and stable attracted our special attention.

It is known that heavy and transition metal ions have a strong fluorescence quenching character. We considered that if the fluorescence of dyes can be efficiently quenched by heavy and transition metal ions due to complexation, this may provide a basis for the development of turn-on sensors for H_2S by the displacement method. Because sulfide is known to react with copper ions to form a very stable CuS species, which has a low-solubility product constant $k_{sp}=1.27\times10^{-36}$ [36]. Based on this hypothesis, we employ compound **L** reported by Lin'group [37], which is composed of 8-hydroxyquinoline group and the 1H-phenanthro[9,10-*d*]imidazol dye (Scheme 1), act as chelators for Cu^{2+}. We expected that Cu^{2+} would be released from compound **L–Cu** when S^{2-} binds to the Cu^{2+} center, resulting in fluorescence enhancement, whereas the **L–Cu** complex would retain its structure in the presence of high concentrations of GSH and Cys, showing no fluorescence enhancement.

2. Experimental

2.1. Materials and measurements

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification.

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Solvents used were purified and dried by standard methods prior to use. Twice-distilled water was used throughout all experiments. ESI–MS analyses were performed using a Waters Micromass ZQ-4000 spectrometer. Electronic absorption spectra were obtained on a U-3010 spectrometer; photoluminiscent spectra were recorded with a Hitachi F-2500 fluorescence spectrophotometer; cells imaging were performed with a OLYPUS-IX71 inverted fluorescence microscope; ^{1}H spectra were measured on an INOVA-400 spectrometer using TMS as an internal standard. TLC analyses were performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200–300), both of which were obtained from the Qingdao Ocean Chemicals.

2.2. Preparation of the test solution

The solutions of various testing species were prepared from KI, NaCl, KBr, NaN_3, $Na_2S_2O_3 \cdot 5H_2O$, Na_2SO_3, $NaNO_2$, CH_3COONa, Na_2CO_3, ascorbic acid, GSH, cysteine, H_2O_2, and NaClO in the twice-distilled water. Nitric oxide (NO) was generated from DEA/NONOate (stock solution 1 mM in 0.01M NaOH).

2.3. DFT calculations

Density functional theory (DFT) calculations were carried out with the Gassian 09 program package [38]. All the calculations were performed on systems in the gas phase using the Becke's three-parameter hybrid functional with the LYP correlation functional (B3LYP), and LANL2DZ basis set.

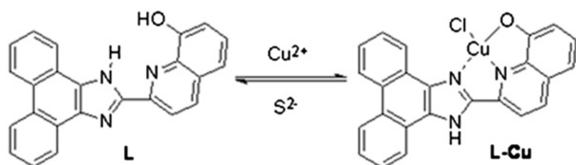
2.4. Cell culture and fluorescence imaging

The MCF-7 cells were grown in modified Eagle's medium (MEM) supplemented with 10% fetal bovine serum (FBS) in an atmosphere of 5% CO_2 and 95% air at 37 °C. The cells were plated on 12-well plates and allowed to adhere for 24 h. Immediately before the experiments, MCF-7 cells were pre-treated with compound **L** (5 μM) in the growth medium for 30 min and washed three times with PBS. Then the cells were incubated with Cu^{2+} (10 μM) for 30 min. Subsequently, the cells were washed three times with PBS to remove the remaining Cu^{2+} ions, the cells were further incubated with S^{2-} (10 μM) for 30 min and washed three times with PBS. Inverted microscope fluorescence imaging was performed with a OLYPUS-IX71 equipped with a CCD camera.

3. Results and discussion

3.1. Absorption and fluorescence spectra of compound L titrated with Cu^{2+}

With compound **L** in hand, we examined its optical properties with Cu^{2+}. The fluorescence titration of the Cu^{2+} ion was carried out using a solution of 5 μM of compound **L** in Tris–HCl/DMF (20 mM, 6/4, v/v). Initially, compound **L** displayed intense fluorescence in the 400–560 nm range (Fig. 1), addition of gradually increasing concentrations of Cu^{2+} caused a significant effect on the emission profile: the decrease of the emission band at around 445 nm, because Cu^{2+} has a strong fluorescence quenching character, and the solution fluorescence was quenched with 1 equivalent of Cu^{2+}, indicating that compound **L** binded with Cu^{2+}. In addition, the free compound **L** exhibited an absorption band at around 340 nm in Tris–HCl/DMF (20 mM, 6/4, v/v) (Fig. 2), introduction of Cu^{2+} elicited a large red shift (80 nm) in the absorption from 360 to 440 nm, and a distinct isosbestic at 400 nm was observed, suggesting that two species (compound **L** and the compound **L**–metal complex) were in equilibrium, further indicating that compound **L** binds with Cu^{2+}. As shown in Fig. 1 and its inset, the fluorescence of compound **L** was essentially completely quenched by 1 equivalent of Cu^{2+} ions. In good agreement with this finding, the Job plot also shows the formation of a 1:1 bonding mode between compound **L** and Cu^{2+} ions (Fig. 3). Based on the 1:1 binding mode, the binding constant derived from the fluorescence titration data was found to be 1.1×10^5 M^{-1}(Fig. 4).



Scheme 1. The proposed interaction mechanism of compound **L** with Cu^{2+}.

3.2. Fluorescence spectroscopy of **L–Cu** and S^{2-}

The above finding that the fluorescence of compound **L** could be almost completely quenched by Cu^{2+}, and the fact that Cu^{2+} can coordinate with sulfide anion to form the stable species, CuS (solubility product constant, $K_{sp}=1.27 \times 10^{-36}$) [19], rendered us to speculate that the **L–Cu** ensemble was promising as a turn-on fluorescent sensor for sulfide anions. To test this idea, compound **L** (5 μM) was preincubated with Cu^{2+} (10 μM), and the resulting ensemble was titrated with sulfide anions. As shown in Fig. 5, addition of sulfide induced a significant fluorescence turn-on response at 445 nm, and up to a 20-fold fluorescence enhancement was observed, indicating that addition of sulfide anions to the ensemble resulted in the release of the free compound **L**. Furthermore, the fluorescence intensities at 445 nm have an excellent linear relationship with the concentrations of sulfide anions from 0.5 to 5 μM (Fig. 6), and the detection limit (S/N=3) was calculated to 1.8×10^{-7} M, indicating that the ensemble was highly sensitive to sulfide anions. Besides, the fluorescence spectrum was recorded within 1 min after sulfide anion was added, and the intensity barely changed for more than 2 h, indicating that the monitoring system is a realtime and stable one.

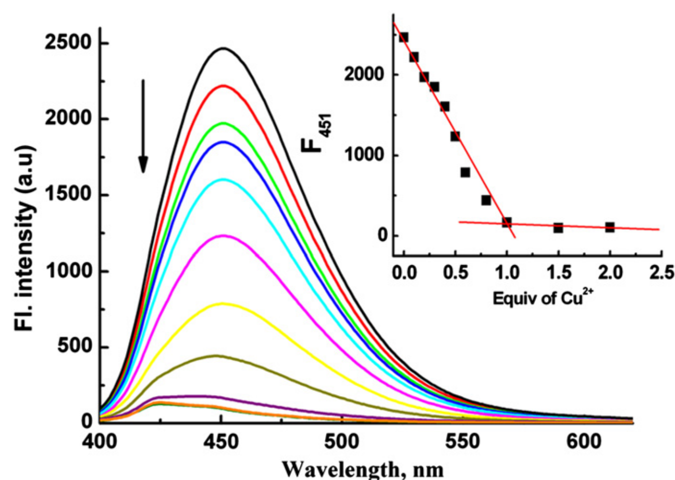


Fig. 1. Fluorescence spectra of compound **L** (5 μM) with the increasing concentrations of Cu^{2+} ions (0–2 equivalent) in Tris–HCl/ DMF (20 mM, 6/4, v/v). The inset shows the fluorescence intensity changes at 451 nm of compound **L** (5 μM)with the amount of Cu^{2+} ions.

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