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Highly Selective Quinoline-Based Fluorescent Probe for Copper(II) Ions

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A novel fluorescent probe based on 8-hydroxy-2-methyl quinoline has been designed and synthesized to detect Cu^{2+} ions. The probe showed a fluorescence turn-off response for Cu^{2+} over other metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ag^+, Cd^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+} and Pb^{2+} in CH_3CN/H_2O solution (v/v, 4:1, pH = 7.68) with specific selectivity and high sensitivity. The fluorescence emission of the probe was immediately quenched after addition of Cu^{2+} in CH_3CN/H_2O solution (v/v, 4:1, pH = 7.68) due to photoinduced electron transfer mechanism. The binding ratio between the probe and Cu^{2+} ions was determined to be 2:1.

Keywords: Quinoline, Fluorescence, Copper(II) ions.

INTRODUCTION

The highly selective and sensitive probes have attracted considerable attention because of their application in detecting many metal ions. Metal ions, especially transition metal ions, play significant roles in living systems and also have a negative and toxic impact on the environment [1-3]. So developing new methods for detecting important metal ions, such as Cu^{2+}, Hg^{2+}, Ag^+ [4,5], Fe^{3+} [6] and Zn^{2+} [7] has been an important research topic.

Detection of Cu^{2+} ions is meaningful for both living systems and environment because Cu^{2+} ions have been involved in several bioenergetics and metabolic processes as well as in environmental pollution. Many methods such as atomic absorption spectrometry and inductively coupled plasma mass spectrometry have been developed for detection of Cu^{2+}. However, these methods are both complicated and costly compared with fluorescence determination [8]. To find a simple and economic method for detecting Cu^{2+} is highly required. Fluorospectrophotomery is a good method which shows several advantages and high sensitive in determining metal ions compared with other methods. One of research focuses is to develop selective receptors for the transition metal copper ion [9]. Many synthetic receptors have been reported for recognizing and sensing copper ions [10-12].

In this paper, a new fluorescent probe **S1** has been developed using 8-hydroxy-2-methyl quinoline, ethyl 2-chloroethoxyl acetic acid and di-(2-picolyl)amine. The probe shows a remarkably quenching in CH_3CN/H_2O solutions (v/v, 4:1, pH = 7.68) after the addition of Cu^{2+} based on photoinduced electron transfer (PET) mechanism. The sensing abilities of the molecular probes to metal ions depended on the photophysical and electrochemical properties of the fluorophores moiety of probes. 8-Hydroxy-2-methyl quinoline is an efficient candidate for metal ion recognition and is widely used by many researchers for the synthesis of probes [13-17]. 8-Hydroxy-2-methyl quinoline has been employed to synthesis the probe **S1**. The synthesis and characterization of **S1** with its fluorescent response to Cu^{2+} is reported in this work.

EXPERIMENTAL

All chemical materials for synthesis and detection used in the experiments were of analytical grade and purchased from commercial suppliers.

General procedure: The synthetic procedures of the probe are depicted in **Scheme-I** [18].

Synthesis of compound 2: A mixture of 8-hydroxy-2-methylquinoline 1.622 g (10 mmol), ethyl 2-chloroethoxyl acetic acid 2.0766 g (10 mmol), KI (0.8 g) and K_2CO_3 (5.6 g) in acetonitrile (30 mL) was refluxed for 24 h. After cooling, the mixture was filtered and evaporated to generate crude residue, which was purified by chromatography (silica gel, petroleum ether/1-2 % ethyl acetate) to give 2.02 g oil. Yield: 70 %. ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.5 Hz, 1H), 7.36 (dd, J = 10.4, 5.4 Hz, 1H), 7.27 (dd, J = 12.7, 5.0 Hz, 2H), 7.13 (dd, J = 7.6, 1.0 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 4.15 (s, 2H), 3.82 (t, J = 5.8 Hz, 2H), 3.67 (t, J = 5.8 Hz, 2H), 2.70 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H).

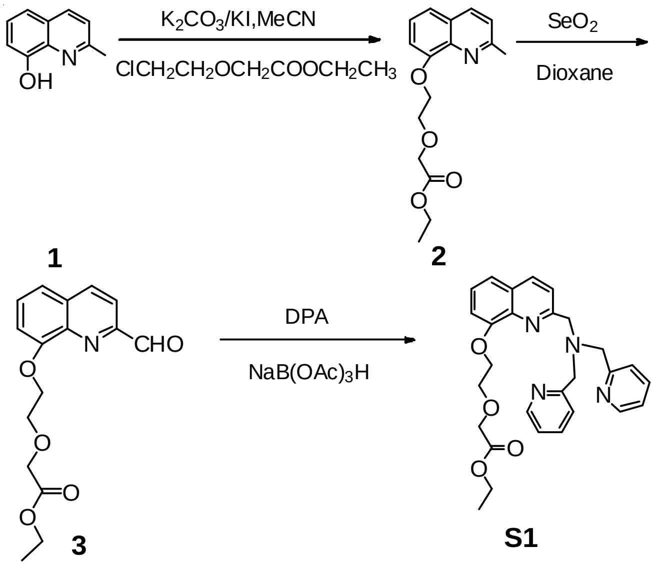
Synthesis of compound 3: Compound **2** (1.5 g) dissolved in dioxane (20 mL) was stirred and heated to 65 °C. To this solution was added SeO_2 (0.75 g). Then the temperature was increased to 80 °C. After reacting for 2 h, the mixture was cooled to room temperature. The precipitate in the solution was filtered off. Organic phase was concentrated. The yellow solid was obtained by recrystallization from ethyl acetate/hexane. ^1H NMR (500 MHz, DMSO) δ 10.12 (s, 1H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 4.45-4.40 (m, 2H), 4.37 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 4.03-4.00 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H).

Synthesis of the probe S1: A mixture of compound **3** (0.30 g, 1.0 mmol) in 1,2-dichloroethane (20 mL) was added the 2,2-dipicolylamine (DPA) (0.22 g, 1.0 mmol) and $NaB(OAc)_3H$ (0.30 g). The solution was stirred at room temperature overnight. Then the solution was acidified with 1 N HCl to pH 4-5 and neutralized with 1 N NaOH to pH 7-8. The organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 20 mL). The organic phase was combined and dried over $MgSO_4$. The solvents were evaporated to give crude solid which was further subjected for purification by column chromatography (CH_2Cl_2/CH_3OH = 100/1) provided product **1** as a brown solid (65 %) (**Scheme-I**). ^1H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 4.6 Hz, 2H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.79 (t, *J* = 10.5 Hz, 1H), 7.64 (ddd, *J* = 21.3, 10.8, 4.5 Hz, 4H), 7.44-7.28 (m, 2H), 7.21-7.10 (m, 2H), 7.07 (dd, *J* = 7.1, 1.1 Hz, 1H), 4.47-4.40 (m, 2H), 4.36 (s, 2H), 4.18 (dd, *J* = 14.5, 7.4 Hz, 2H), 4.17-4.13 (m, 2H), 4.10 (s, 2H), 3.94 (s, 4H), 1.24 (t, *J* = 7.1 Hz, 3H).

Detection method: The ^1H NMR spectra were recorded on a Bruker AVANCE-500 spectrometer. Fluorescence spectra were recorded using a Hitachi F-7000 spectrometer with excitation slit set at 2.5 nm and emission at 2.5 nm respectively. Stock solutions of **S1** were prepared (c = 2.5 mmol/L) in acetonitrile [19]. All stock solutions of metal ions were prepared from each of its individual salts dissolved (c = 10 mmol/L) in aqueous solution.

RESULTS AND DISCUSSION

Effects of metal ions on fluorescence spectra of probe **S1**: The probe **S1** was synthesized according to the route in the **Scheme-I**. All fluorescence spectra of **S1** were performed in CH_3CN/H_2O solutions (v/v, 4:1, pH = 7.68). The sensing ability of probe **S1** was tested by mixing it with the metal ions K^+, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ag^+, Ce^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+} and Pb^{2+}. Fig. 1a showed the fluorescence intensity of probe **S1** in the absence and presence of Cu^{2+}. The fluorescence quenching of **S1** was observed after addition of Cu^{2+} ions. Fig. 1b showed the effects of other metal ions on the fluorescence emission of **S1**. Negligible changes were caused by other metal ions in fluorescence emission spectra of **S1**. Therefore, probe **S1** showed a high selectivity for the transition metal ions Cu^{2+} and remarkable fluorescence "turn-off" response to Cu^{2+}.



Scheme-I: Synthesis procedure of probe **S1**

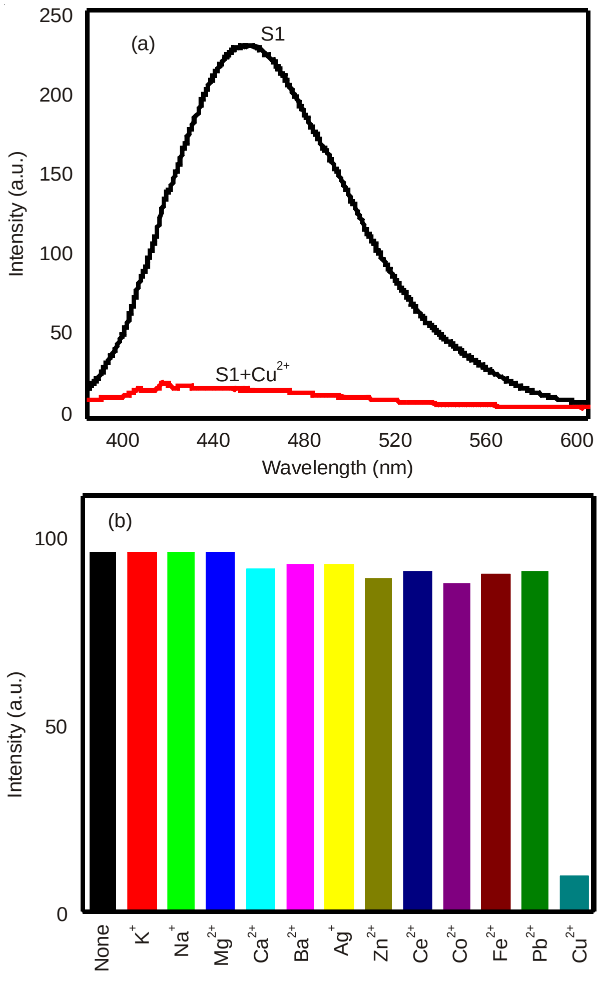


Fig. 1. Fluorescence spectra of **S1** (5 μmol/L) with addition of Cu^{2+} (50 μmol/L) (a) and in the presence of various metal ions (50 μmol/L Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ag^+, Zn^{2+}, Ce^{2+}, Co^{2+}, Fe^2, Pb^{2+} and Cu^{2+}) in CH_3CN/H_2O solutions (v/v, 4:1, pH = 7.68), λ_{ex} = 366 nm (b)

Binding properties of Cu^{2+} and S1: For investigating the binding properties of **S1** and Cu^{2+}, a fluorescence photometric titration at various concentrations of Cu^{2+} was carried out. The concentration of the probe was 5 μmol/L and the molar ratio of Cu^{2+} to **S1** varied from 0 to 2.5 equiv. Fig. 2 showed that the fluorescence intensity gradually decreased with increasing the concentration of Cu^{2+}. The insert showed

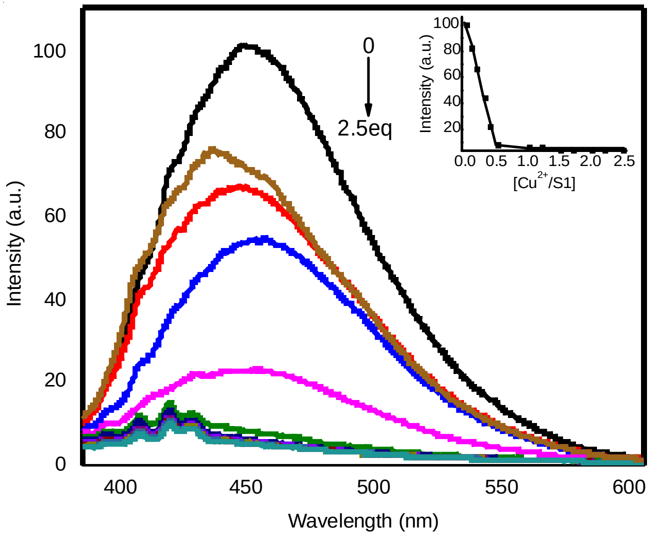


Fig. 2. Fluorescence spectra (λ_{em} = 446 nm) of **S1** (5 μmol/L) in the presence of various concentrations of Cu^{2+} (0, 0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 1.2, 1.5, 1.7, 2.0, 2.2, 2.5 equiv) in CH_3CN/H_2O solutions (v/v, 4:1, pH = 7.68). Insert: fluorescence intensity as a function of {Cu^{2+}/[**S1**]} concentration

fluorescence intensity as a function of {[Cu^{2+}]/[**S1**]} concentration. No change in the fluorescence intensity of **S1** was observed when the value of {[Cu^{2+}]/[**S1**]} was at a molar ratio of 0.5, which indicated a 1:2 stoichiometry of the Cu^{2+} to **S1** in the complex. No shift of the emission spectra of **S1** with increasing Cu^{2+} concentration was observed, which was consistent with the photoinduced electron transfer mechanism. The lone electron pair in nitrogen atoms could coordinate with metal ions, so the coordination between 2,2-dipicolylamine group and Cu^{2+} ions resulted in the fluorescence quenching (**Scheme-II**).

Metal-ion competition studies: To study more about the influence of other metal ions on Cu^{2+} binding with the probe **S1**, competitive experiments with other metal ions (50 μmol/L) was conducted. When no metal ion was added to the solutions of **S1** (5 μmol/L), the fluorescence intensity was observed as the first black bar. Metal ions Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ag^{+}, Ce^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+} and Pb^{2+} were added to the solutions of the probe, the results were showed as the other black bars in Fig. 3. Then gray bars in Fig. 3 represented the fluorescence intensity changes after addition of Cu^{2+} (50 μmol/L).

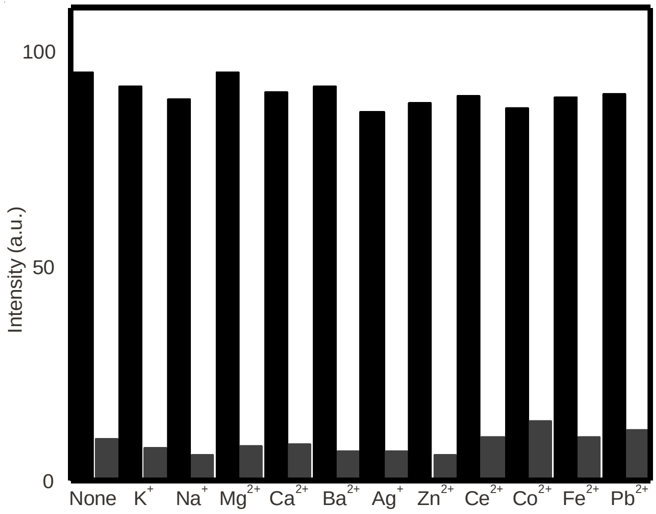


Fig. 3. λ_{em} = 446 nm, black bars represent the response of **S1** in the presence of other metal ions, Gray bars represent the fluorescence intensity when the above solutions was followed by 50 μmol/L Cu^{2+}

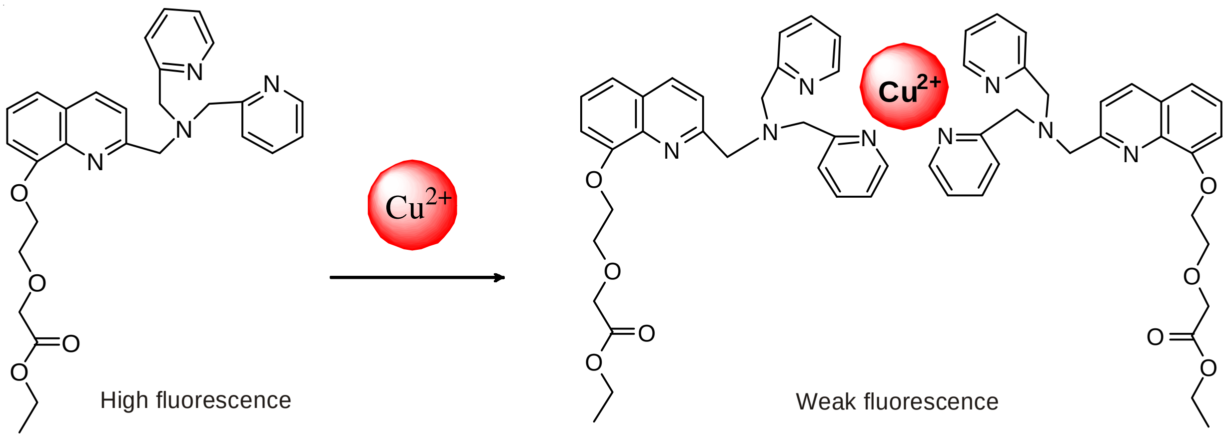
The results indicated that the probe still produced strongly fluorescence quenching with addition of other cations. Therefore other metal ions didn't have the ability to affect the fluorescence quenching of the probe in the presence of Cu^{2+}.

Effect of solvents and pH on the fluorescence emission of S1: To explore the effect of solvents on the fluorescence of the probe, the fluorescence intensity experiment of the probe in different solvents was carried out respectively. As shown in Fig. 4, acetonitrile was selected as the most suitable solvent in all the mentioned solvents to test the fluorescence of probe **S1**.

In addition, the effect of pH on fluorescence emission of the probe **S1** also has been discussed in present study. Fig. 5 showed when pH was around the neutral, the fluorescence emission of the probe was stronger than other pH conditions. Therefore, **S1** can be used for ratiometric detection of Cu^{2+} in the neutral solution without the adverse influence of other metal ions.

Conclusion

In conclusion, we have designed and synthesized a new fluorescent probe **S1** based on the photoinduced electron transfer (PET) mechanism. The probe is able to detect Cu^{2+}



Scheme-II: Proposed binding mechanism of Cu^{2+} with **S1**

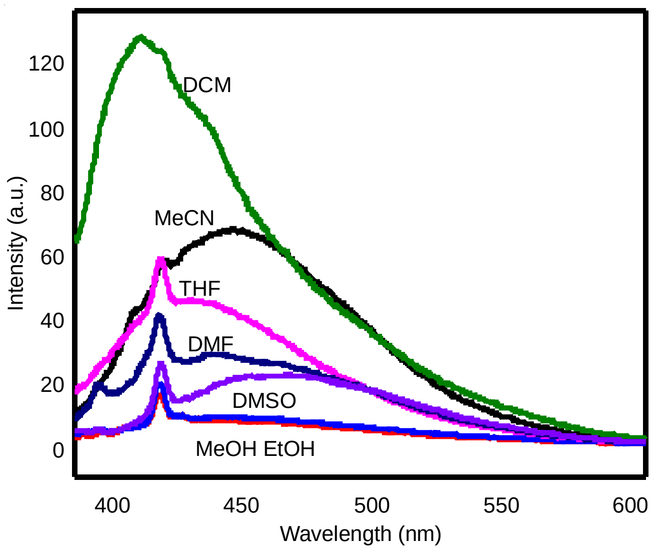


Fig. 4. Effect of solvents on the fluorescence emission of **S1**

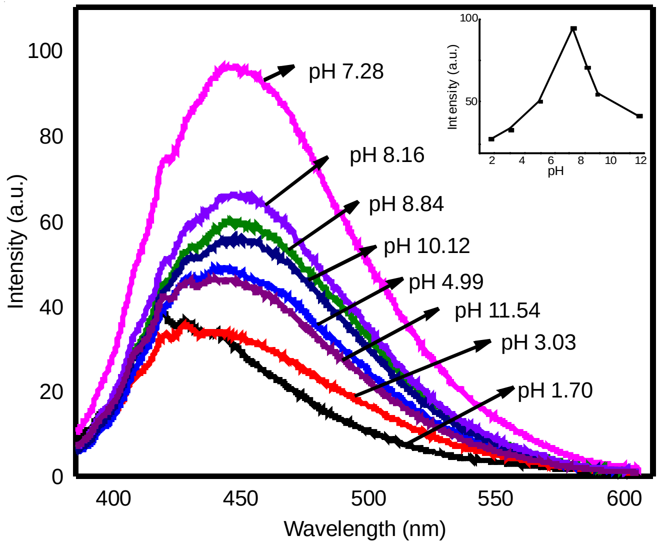


Fig. 5. Effect of pH on the fluorescence emission of **S1**

with remarkably fluorescence quenching better than other metal ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ag^+, Ce^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+} and Pb^{2+}) in CH_3CN/H_2O solutions (v/v, 4:1, pH = 7.68) and exhibited high sensitivity and selectivity for Cu^{2+} ions.

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