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Novel fluorescent sensor for detection of Cu(II) in aqueous solution

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Abstract

A novel fluorescent chemosensor based on aminonaphthol, which can selectively recognize copper(II) over other metal ions in aqueous solution within a broad pH span, was synthesized.

Keywords: Molecular recognition; Aminonaphthol; Chemosensor; Copper(II); Aqueous solution; Fluorescence quenching

1. Introduction

Detection of metal ions by fluorescent chemosensor in aqueous solution has been receiving much attention in recent years. This is mainly due to the potential application in clinical biochemistry and environment. There are already many fluorescent chemosensors developed so far [1–4], and many of them are commercially available [5,6]. However, fluorescent chemosensors for selective detection of transition metal ions, especially Cu^{2+}, in aqueous solution are rather rare [7–9] although copper is third in abundance (next for iron and zinc) among the essential heavy metals in the human body and plays an important role in various physiological processes. On the other hand, it was also known that copper ion, despite being an essential element in biological systems, has a toxic impact on the microorganisms at even submicromolar concentrations. Thus, it is highly desirable to design and synthesize novel sensors for copper ions with high selectivity and sensitivity in aqueous solution. Indeed, some sensors for copper ions have been developed recently [10,11]. They are mainly based on anthracenyl and dansyl moieties, most notably anthracenylated peptide and dansylated peptide [12–14]. In these cases, the fluorescent moiety is covalently linked to the recognition moiety via a spacer to form PET system, and the change of fluorescent intensity can be observed through PET process between an acceptor (ligand) and a fluorophore generally [15]. Therefore, there is still a need for development of fluorescent sensors for detection of divalent copper with improved selectivity and sensitivity in aqueous solution by using new fluorophores. As part of our efforts to develop fluorescent chemosensors by using new fluorophores [16–20], herein, we now wish to report a new Cu^{2+}-sensitive fluorescent sensor (aminonaphthol derivative), in which the fluorescent moiety itself acts as a ligand for metal cations. In this intrinsic fluorescent ligand, metal cation binding may affect the fluorescent properties dramatically. This fluorescent chemosensor also shows a good selectivity and sensitivity for divalent copper cation over other cations, such as Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Fe^{2+}, Cr^{3+}, Cd^{2+}, Pb^{2+} and alkali and alkaline earth cations as well in aqueous solution within a broad pH range.

2. Experimental

2.1. Apparatus

^{1}H NMR spectra were recorded on a Varian GEMANA-300 spectrometer. Fluorescence spectra were recorded with a Hitachi F4500 spectrophotometer. Mass spectra were recorded on a Finnigan 4021C MS-spectrometer.

2.2. Reagents

2-Hydroxy-l-naphthaldehyde, 4-aminoantipyrine and $NaBH_4$ were purchased from Aldrich and used as received. All cationic chlorides used were analytical grade and were from Beijing Chemical Works.

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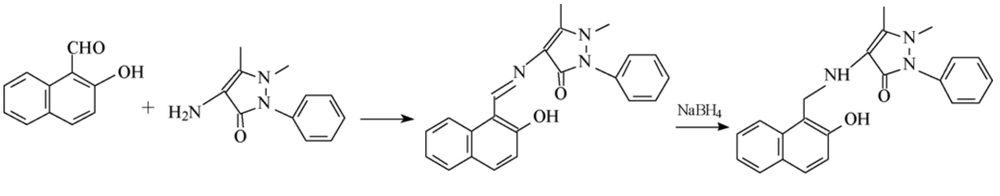


Compound 1

Fig. 1. Synthesis route of compound **1**.

2.3. Preparation of compound *1*

Compound **1**, aminonaphthol derivative, was synthesized according to the route [21] shown in Fig. 1 and characterized by ^{1}H NMR, MS and elemental analysis. ^{1}H NMR (300 MHz, DMSO) δ 10.86 (s, 1H, ArOH), 7.92 (d, 2H, ArH), 7.78 (d, 2H, ArH), 7.64 (d, 2H, ArH), 7.49 (m, 2H, ArH), 7.33 (m, 2H, ArH), 7.10 (m, 1H, ArH), 5.03 (s, 1H, NH), 3.52 (s, 2H, $ArCH_2$), 2.54 (m, 3H, $C{=}CCH_3$), 2.13 (s, 3H, NCH_3); MS (*m*/*e*): 359 (358, 356, 265, 236, 188, 121, 57); anal. calcd. for $C_{22}H_{21}N_3O_2$: C 73.52%, H 5.89%, N 11.69%, O 8.90%. Found: C 73.79%, H 5.38%, N 11.66%, O 9.17%.

2.4. Sample preparation

The fluorescence spectra of compound **1** were measured in aqueous solution. The concentration of solution of compound **1** was 10^{-5} mol L^{-1}, and the concentration of stock solution of different metal salts used for the fluorescence titration is 10^{-3} mol L^{-1}. Two milliliter solution of compound **1** was filled in a quartz cell of 1 cm optical path length. Different stock solutions of metal salts were added into the quartz cell gradually by using a micro-syringe. The volume of metal salts stock solution added was less than 100 μL with the purpose of keeping the total volume of testing solution without obvious change. Excitation wavelength was 320 nm and the slit widths were 5 and 2.5 nm, respectively.

3. Results and discussion

The spectral and photophysical properties of compound **1** in organic solvents have ever been investigated in our group [21]. In this article, we will discuss its property in aqueous solution. From fluorescent spectra of compound **1** in aqueous solution (Fig. 2), two emission bands centered at 366 and 436 nm were observed, which could be assigned to the emission of the naphthol moiety and its deprotoned form, respectively. The assignment could be confirmed by its pH-sensitive fluorescence spectra. As shown in Fig. 2, the fluorescence spectrum of compound **1** shows no obvious change between pH 4 and 10. However, when the pH value of the solution is less than 4, the peak at 366 nm increases and that at 436 nm decreases concomitantly and vanishes completely at pH less than 0.9. This quenching process under strong acidic condition is related to the protonation of secondary amine between naphthol (pK_a ~ 4). On the other hand, when pH is more than 10, the emission peaked at 366 nm decreases with increasing pH value, and disappears ultimately at pH 13 due to the deprotonation of naphthol (pK_a ~ 10).

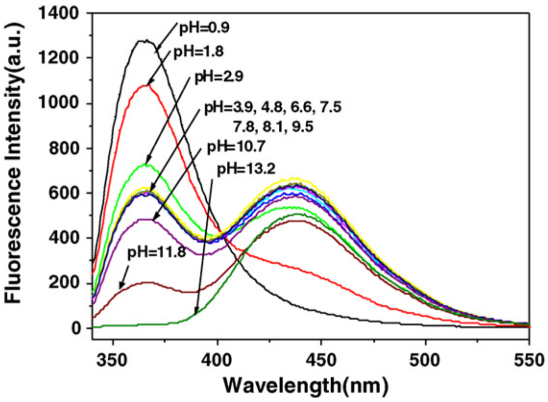


Fig. 2. Variation of fluorescence spectra of compound **1** (10 μM) in different pH conditions in aqueous solution at 25 °C.

The fluorescence of compound **1** in aqueous solution was quenched gradually upon addition of $CuCl_2$. A titration experiment was performed to determine the binding ratio and constant between compound **1** and Cu^{2+} (Fig. 3). The reason of fluorescence quenching of compound **1** is probably due to the occurrence of either an electron transfer or an electronic energy transfer involving the transition metal and the excited fluorophore as observed in other Cu^{2+}-recognition sensors [22,23]. Job's plot shows a complexation at a molar ratio of 1:1 occurred between compound **1** and Cu^{2+}(inset of Fig. 3). According to

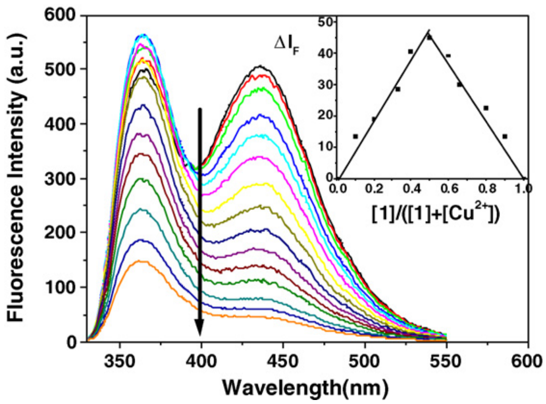


Fig. 3. Variation of fluorescence spectra of compound **1** (10 μM) upon addition of $CuCl_2$ (from 5 to 200 μM) in aqueous solution (pH 6.8, 25 °C) with an excitation of 320 nm. *Inset*: Job's plot for the binding of compound **1** with $CuCl_2$.

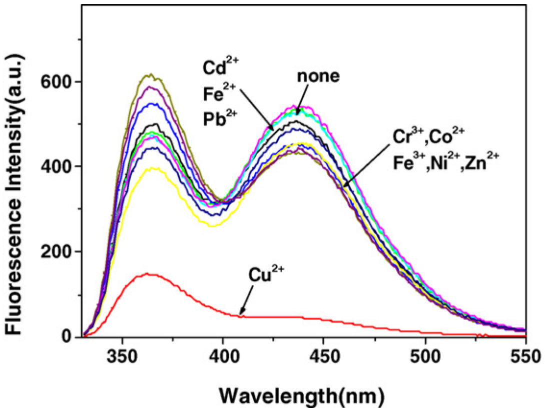
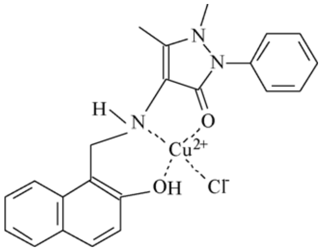


Fig. 4. Fluorescence spectra of compound **1** (10 μM) in aqueous solution (pH 6.8, 25 °C) upon addition of different metal chlorides (200 μM) with an excitation of 320 nm.



Scheme 1. Possible interaction mode between compound **1** and Cu^{2+}.

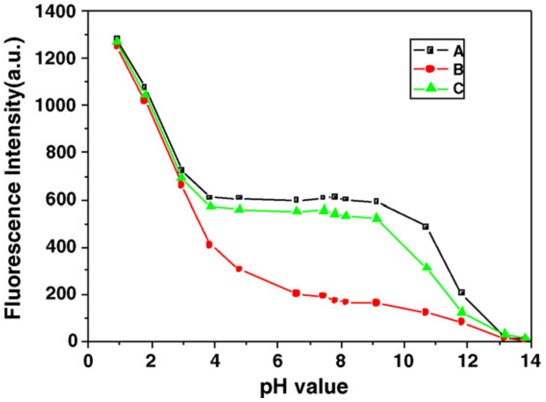


Fig. 5. Fluorescence intensity of compound **1** recorded at 366 nm at different pH conditions at 25 °C (a) 10 μM free **1**, (b) 10 μM **1** and 160 μM $CuCl_2$, (c) 10 μM **1** and miscellaneous metal ions including $ZnCl_2$, $CoCl_2$, $NiCl_2$, $FeCl_3$, $FeCl_2$, $CrCl_3$, $CdCl_2$ and $PbCl_2$, and each concentration is 20 μM, respectively.

1:1 stoichiometery, we further determined the stability constant between compound **1** and Cu^{2+} to be 4205 M^{-1} in aqueous solution by using a binding model reported in the literature [24].

Compound **1** exhibits an excellent selectivity for Cu^{2+} over other cations, such as Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Fe^{2+}, Cr^{3+}, Cd^{2+}, Pb^{2+}, and alkali and alkaline earth cations. (No obvious change of fluorescence spectra of compound **1** upon addition of alkali and alkaline earth cations was observed, and these cations were not listed in Fig. 4 for clarity.) From Fig. 4, when 20 equivalents of Cu^{2+} were added to an aqueous solution of compound **1** (10 μM), the fluorescence intensity was substantially quenched. However, when several competitive transition metal ions including Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Fe^{2+}, Cr^{3+}, Cd^{2+}, Pb^{2+} were added, respectively, no obvious changes were observed. Relative fluorescence intensities of compound **1** binding these metal ions at 360 and 436 nm are shown in Table 1. The stability constants between **1** with these metal ions are all less than 300 M^{-1}. The selectivity for Cu^{2+} might be interpreted to the geometrical difference between Cu^{2+}-complex and other metal complexes as observed in other metal–ligand complexes [25]. In aqueous solutions, these ions generally form octahedral complexes. Due to the Jahn–Teller effect, coordinating interaction of the four equatorial sites is stronger than that of the remaining axial positions [26]. Consequently, four-coordinated Cu^{2+} complexes are generally characterized by a square planar geometry if there is no special geometrical constraints in ligands, just like in the present ligand—compound **1**. In contrast, there is usually no intrinsic preference for axial over equatorial coordination in other metal ions in aqueous solution. Therefore, compound **1** can be superior to bind Cu^{2+} over other metal ions. In this case, Cu^{2+} cation may locate at the center of the pseudocavity of compound **1** and coordinates with oxygen atom of naphthol, nitrogen atom of a secondary amino and oxygen atom of carbonyl group. Moreover, the counter anion Cl^- may also participate in the coordination as the fourth chelate group. The possible interaction mode between compound **1** and Cu^{2+} was shown in Scheme 1.

It is important to investigate the influence of the fluorescence spectra of compound **1** at different pH range in order to find a suitable pH span in which compound **1** can selectively detect Cu^{2+} efficiently. The fluorescent titration curve of compound **1** was measured with the change of pH. The fluorescence spectra of free **1** (Fig. 5, Curve A) exhibits a good plateau between pH 4 and 10, in which compound **1** is not affected by pH variation. The effect of pH on the fluorescence of **1**–Cu^{2+} solution (Curve B) exhibits a quite different feature from that of free 1. When the pH is less than 4, the fluorescence seems to be the same as that of curve A, which illustrates that the dissociation of **1**–Cu^{2+} is superior to complexation in strong acidic conditions. When pH is larger than 4, the fluorescence is deeply quenched, which is different from that of free **1**. Curve C shows the influence of several miscellaneous transition and heavy metal cations including Zn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Fe^{2+}, Cr^{3+}, Cd^{2+} and Pb^{2+}. Only small variation is observed comparing with Curve A between pH 4 and

Table 1
Relative fluorescence intensity of compound **1** upon addition of different metal ions

	None	Fe^{2+}	Co^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Cd^{2+}	Fe^{3+}	Cr^{3+}	Cu^{2+}
R_{If} (360 nm)	1	0.87	1.13	1.06	0.71	0.89	0.84	0.84	0.85	0.27
R_{If} (436 nm)	1	1.07	0.89	0.85	0.86	0.97	1.05	0.89	1.04	0.089

R_{If} denote relative fluorescence intensity.

10. Therefore, the ideal pH range for the detection of Cu^{2+} is 5–9, since in this pH region, Cu^{2+} causes a maximum quenching of the fluorescence of compound **1** while the other metal cations only have a marginal effect on the detection of Cu^{2+}. Such broad pH range makes it very meaningful during miscellaneous applications, such as the detection of ions of waste water, industrial trade analysis and physiological course, etc. Furthermore, its water-compatibility makes it not limited under practical applications in many fields.

4. Conclusion

A Cu^{2+}-sensitive fluorescent sensor based on a novel fluorophore (ligand), aminonaphthol, was synthesized. It shows a good selectivity for divalent copper over other metal cations in aqueous solution within a wide pH range. Development of other novel fluorescent chemosensors based on similar ligands is in progress.

Acknowledgements

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