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Selective fluorescence sensor for Cu^{2+} with a novel triazole Schiff-base derivative with coumarin units

Abstract: Novel triazole Schiff-base derivative **3** bearing a coumarin unit was synthesized by the reaction of 4-formylbenzocoumarin (**1**) with 3,5-diphenyl-4-amino-1,2,4-triazole (**2**). The structure of the product was characterized by means of IR, MS, ^{1}H NMR, ^{13}C NMR, and elemental analysis. The UV-vis absorption and fluorescence emission spectra of compound **3** exhibit blue-shifted absorption and fluorescent enhancement upon chelation to cupric ion. Fluorometric titration revealed a 2:1 ligand to metal ratio in the complex and the binding constant of 4.62×10^{6} M^{-1}.

Keywords: cupric ion; coumarin; fluorescent; recognition; Schiff bases; UV-vis.

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Introduction

Selective recognition and sensing of transition metal ions have become a focus of numerous studies in supramolecular chemistry owing to their importance in chemical, biological, and environmental processes [1–4]. Among the essential heavy metal ions in the human body, Cu^{2+} is third in abundance after Fe^{3+} and Zn^{2+}, and it plays important roles in many fundamental physiological processes. Either deficiency or overdose of copper can induce some serious diseases [5–7]. Consequently, much attention has been given to the development of selective Cu^{2+} sensors [8–10]. However, owing to the low concentrations at which this metal ion is present in biosystems, high-sensitivity probes are necessary for practical applications.

Schiff bases are known to form stable complexes with transition metal ions and to display different optical properties from the ligand itself. Recently, there have been some excellent studies on chemosensors and molecular logic gates based on Schiff bases [11–13], the nitrogen atoms which easily coordinate metal ions. Owing to their intrinsic high fluorescence quantum yield, good water solubility, and viability for chemical transformations, coumarin derivatives have attracted much attention as some of the most popular fluorophores amenable to a novel sensor design [14, 15]. In this paper, a novel Schiff-base derivative bearing a coumarin unit **3** was synthesized, characterized, and its recognition ability for Cu^{2+} was studied. The results showed that probe **3** is an excellent selective probe for Cu^{2+} in the presence of other metal ions.

Results and discussion

The target product **3** was synthesized using a three-step procedure as shown in Scheme 1. The preparation of the intermediate products **1** and **2** has been reported previously [16, 17]. The desired triazole Schiff-base derivative **3** was obtained by condensation of **1** with **2**. The target compound was characterized by IR, MS, ^{1}H NMR, ^{13}C NMR, and elemental analysis.

UV-vis spectroscopic changes of the prepared chemosensing ensemble upon addition of various cations (Ca^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Mg^{2+}, Na^{+}, Al^{3+}, Fe^{3+}, Ag^{+}) are shown in Figure 1. A significant change in the absorption intensity is observed upon addition of Cu^{2+}. No influence on the ultraviolet absorption of **3** is observed in the presence of other tested ions. Thus, it can be concluded that compound **3** selectively recognizes Cu^{2+}.

As shown in Figure 2, compound **3** exhibits a weak fluorescence emission at 551 nm in CH_3OH/DMF medium. After addition of Cu^{2+} to the solution of compound **3**, the fluorescence intensity is enhanced remarkably, that is, the emission intensity is increased 12-fold. Fluorescence enhancement observed for **3** is attributed to the formation of the **3**-Cu^{2+} complex, as a result of which the electron transfer from nitrogen atoms to the coumarin fluorophore is suppressed, resulting in fluorescent enhancement. Importantly, no change in fluorescence occurs in the presence of the other cations including Ca^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Mg^{2+}, Na^{+}, Al^{3+}, Fe^{3+}, Hg^{2+}, and Ag^{+} (not shown).

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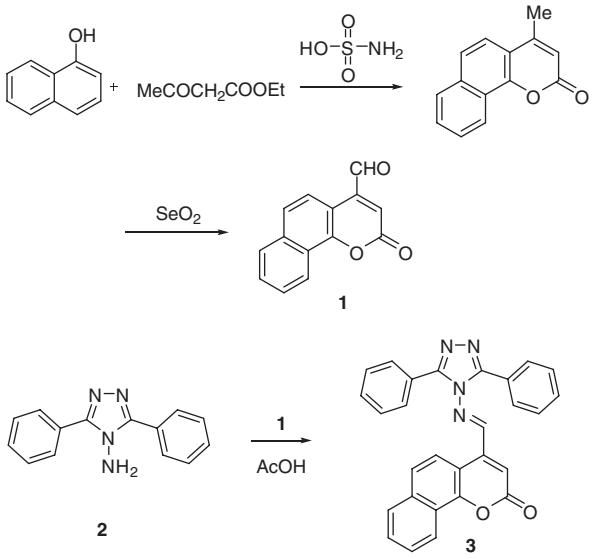

Scheme 1 Synthesis of the triazole Schiff-base derivative **3**.

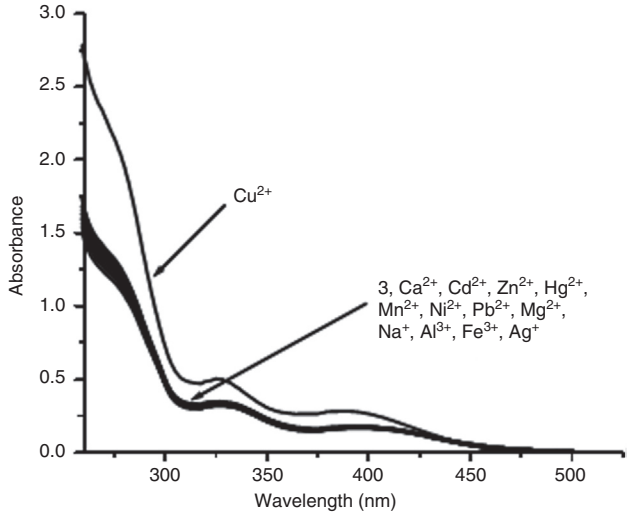

Figure 1 UV-vis spectra of compound **3** (10 μM) upon addition of various metal ions (20 μM) in a mixture of CH_3OH/DMF (9:1).

The sensitivity of the fluorescent probe **3** was estimated by changing amounts of Cu^{2+} from 0 equiv to 3 equiv with regard to the ligand and quantitatively assessing the fluorescence emission intensity change (Figure 3). As already mentioned, before addition of Cu^{2+}, the ligand is almost nonemissive. After the gradual addition of Cu^{2+} to the ligand, a significant increase in fluorescence intensity can be observed. From these titrations, the association constant of compound **3** for Cu^{2+}, K_a =4.62×10^6, and the limit of detection, LOD =3.72×10^{-7} M, were obtained.

Job's plot was used to analyze the complexation ratio between compound **3** and Cu^{2+} ion. As shown in Figure 4,

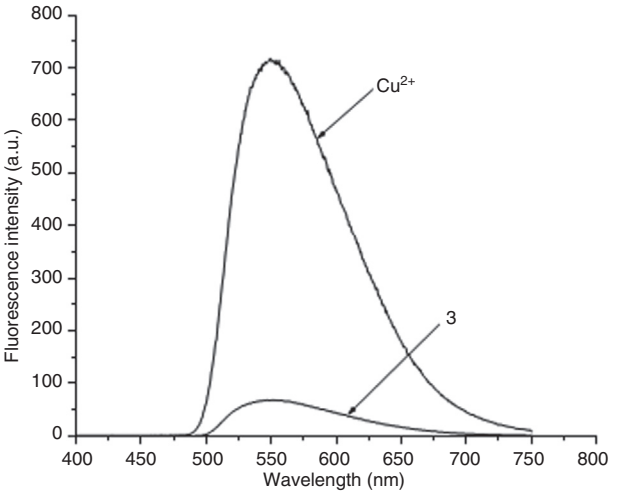

Figure 2 Fluorescence emission spectra of compound **3** upon addition of cupric ion (10 μM) in a mixture of CH_3OH/DMF (9:1).

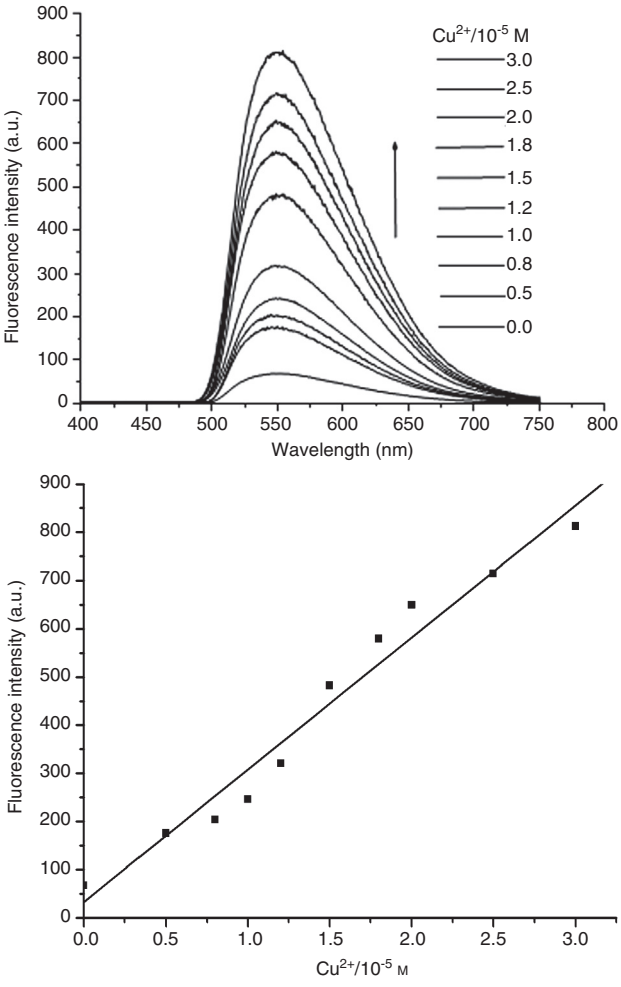

Figure 3 Fluorescence emission spectra of compound **3** (10 μM) for Cu^{2+} ion titration in a mixture of CH_3OH/DMF (9:1).

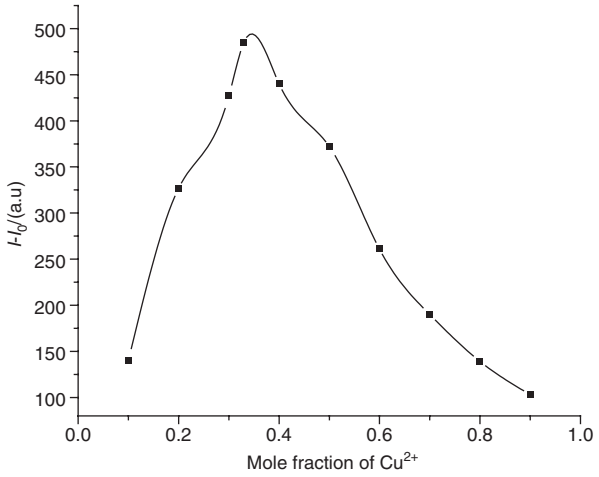

Figure 4 Job's plot for determining the stoichiometry of receptor **3** and Cu^{2+} ion in CH_3OH/DMF (9:1). I and I_0 are the fluorescence intensity of **3** in the presence and absence of Cu^{2+}, respectively. The total concentration of **3** and Cu^{2+} ion is 0.1 mM, λ_{ex}=392 nm.

the maximum point at the mole fraction of 0.33 indicates the complexation ratio of compound **3** and Cu^{2+} as 2:1.

Conclusion

A new triazole Schiff-base derivative was designed and synthesized. Compound **3** displays selective UV-vis absorption and fluorescence changes upon the addition of cupric ion. The design of Schiff-base hosts for selective binding of other ions is currently under investigation.

Experimental

Coumarin aldehyde **1** [17] and 3,5-diphenyl-4-amino-1,2,4-triazole **2** [16] were prepared as previously described. Other chemicals were obtained from Aladdin and used without further purification.

Synthesis of (*E*)-4-[(3,5-diphenyl-4*H*-1,2,4-triazol-4-ylimino)methyl]-2*H*-benzo[*h*]chromen-2-one (3)

A mixture of 3,5-diphenyl-4-amino-1,2,4-triazole **2** (0.02 mol), coumarin aldehyde **1** (0.02 mol), and glacial acetic acid (20 mL) was heated under reflux for 8 h, then cooled and filtered. The solid product **3** thus obtained was crystallized from ethanol: yield 61%; mp 247–249°C (dec); FT-IR (KBr): 3022, 2994, 2897, 1682, 1605, 1497, 1466, 1377, 1229, 843, 720 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ_H 8.569 (1H, s, CH=N), 8.474 (1H, s, Ar-H), 7.909 (5H, m, Ar-H), 7.712 (2H, m, Ar-H), 7.590 (7H, m, Ar-H), 7.505(1H, d, J = 9.0 Hz, Ar-H), 6.677 (1H, s, Ar-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 162.2, 160.4, 152.8, 151.8, 144.2, 136.0, 131.5, 130.5, 130.2, 129.9, 128.6, 127.2, 125.7, 123.7, 120.8, 118.8; ESI-MS: m/z 442.6 ($M + H^+$). Anal. Calcd for $C_{28}H_{18}N_4O_2$: C 76.01, H 4.10, N 12.66. Found: C 76.07, H 4.08, N 12.62.

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