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A new selective pyrazoline-based fluorescent chemosensor for Cu^{2+} in aqueous solution

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1. Introduction

The selective detection of transition and heavy metal ions is very important in various fields of chemical and biological science as well as in the protection of our environment [1]. Cu^{2+} is an important transition metal ion because it is not only an environmental pollutant at high concentrations [2,3], but also an essential trace element for many biological process and systems [4,5]. Therefore, many studies concerning Cu²⁺ sensing by synthesized colorimetric/fluorescent probes based on quinoline [6], fluorescein [7], pyrene [8,9], rhodamine [10–16], azobenzene [17,18], coumarin [19-21], 1,8-naphthalimide [22-25], anthraquinone [26-29] and other fluorophores [30,31] have been reported and investigated. However, there is still an intense demand for new efficient Cu²⁺ optical chemosensors, especially those that are simple to synthesize, and can work in aqueous solution with high selectivity and sensitivity; very important factors for potential biological applications [32]. Studies related to this area are a great challenge and continue to be of widespread interest.

1,3,5-Triaryl-2-pyrazolines, with their rigid but only partly unsaturated central pyrazoline ring, are well-known fluorescent

ABSTRACT

A new pyrazoline derivate was designed and synthesized. The structure of the pyrazoline was confirmed by single crystal X-ray diffraction and its photophysical properties were studied by absorption and fluorescence spectra. This compound can be used to determine Cu^{2+} ion with high selectivity and sensitivity among a series of cations in aqueous tetrahydrofuran. This sensor forms a 1:1 complex with Cu^{2+} and displays fluorescent quenching.

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compounds widely used in fluorescence dyes emitting blue fluorescence with high fluorescence quantum yield [33,34]; additionally these compounds have found application in electroluminescence [35–39]. However, to the best of our knowledge, only a few examples have been reported on the interactions between pyrazoline derivatives and zinc ion [40–42]. Herein, we report the synthesis of two new pyrazoline derivative **1** and **2**, and study the properties of their UV–vis absorption and fluorescence emission. Compound **1** can be used to determine Cu^{2+} ion with high selectivity and a low detection limit in aqueous solution.

2. Experimental

2.1. Apparatus

NMR spectra were measured on a Varian Mercury 300 spectrometer operating at 300 MHz for ¹H and 75 MHz for ¹³C relative to tetramethylsilane as internal standard.

HRMS were obtained on an Apex-Ultra MS equipped with an electrospray source. IR spectra were recorded on a Perkin–Elmer PE-983 infrared spectrometer as KBr pellets with absorption reported in cm⁻¹. All pH measurements were made with a Model PHS-3C pH meter (Shanghai, China) and operated at room temperature about 298 K. Absorption spectra were determined on UV-2501 PC spectrophotometer. Fluorescence spectra measurements were performed on a FluoroMax-P spectrofluorimeter equipped with a xenon discharge lamp, 1 cm quartz cells at room



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temperature (about 298 K). The X-ray crystal structure determinations of **1** were obtained on a Bruker SMART APEX CCD system.

2.2. Reagents

Deionized water was used throughout the experiments. All the reagents were purchased from commercial suppliers and used without further purification. The salts used in stock solutions of metal ions were $CoCl_2 \cdot 6H_2O$, $ZnCl_2$, $MnCl_2 \cdot 4H_2O$, KCl, NaCl, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, $CdCl_2 \cdot 2H_2O$, $HgCl_2$, $FeCl_3 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$, $Pb(NO_3)_2$. HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer solution (pH = 7.4) was prepared using 20 mM HEPES, and proper amount of aqueous sodium hydroxide under adjustment by a pH meter.

2.3. Synthesis of pyrazoline derivatives 1 and 2

The synthetic route to compounds **1** and **2** is shown in Scheme 1. Starting materials 2-hydrazinobenzothiazole (**3**) [43], chalcone (**4**) [44] and chalcone (**5**) [45] were prepared according to the literature. To a stirred solution of chalcone (**4**) and (**5**) (1.0 mmol) in AcOH (15 mL) was added 2-hydrazinobenzothiazole (**3**) (0.165 g, 1.0 mmol). The reaction mixture was heated under reflux for 6 h. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature and the solvent was evaporated in vacuo, and the crude product was washed with water, and consequently recrystallized from ethanol to afford pure compound **1** as a white solid (24.1 mg, 0.65 mmol, 65%) and compound **2** as a white solid (24.9 mg, 0.70 mmol, 70%).

2-(1-(Benzo[d]thiazol-2-yl)-5-phenyl-4,5-dihydro-1H-pyrazol-3-yl)phenol (1). M.p.:206–207 °C; IR (ν_{max} , KBr, cm⁻¹): 3214, 1599, 1531,1440, 1316, 755; ¹H NMR (CDCl₃), δ (ppm): 3.44 (dd, 1H, *J* = 5.4, 5.4 Hz, pyridine-H), 4.05 (dd, 1H, *J* = 12.0, 12.0 Hz, pyridine-H), 5.81 (dd, 1H, *J* = 5.1, 5.1 Hz, pyrazoline-H), 6.90–6.93 (m, 1H, Ar–H), 7.08–7.38 (m, 10H, Ar–H), 7.52–7.55 (m, 1H, Ar–H), 7.64–7.67 (m, 1H, Ar–H), 10.06 (s, 1H, OH); ¹³C NMR (CDCl₃), δ (ppm): 162.3, 157.5, 154.8, 152.2, 140.6, 131.9, 131.3, 128.9, 128.1, 128.0, 125.9, 125.8, 122.2, 120.8, 120.2, 119.7, 117.1, 115.1, 62.2, 44.1; HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₂H₁₈N₃OS: 372.1165; found: 372.1168.

2-(3,5-Diphenyl-4,5-dihydropyrazol-1-yl) benzo[d]thiazole (**2**). M.p.:186–187 °C; IR (ν_{max} , KBr, cm⁻¹): 3080, 2385, 1601, 1537, 1440, 1274, 1126, 870, 753; ¹H NMR (CDCl₃), δ (ppm): 3.30 (dd, 1H, *J* = 5.1, 5.1 Hz, pyridine-H), 3.93 (dd, 1H, *J* = 11.7, 12.0 Hz, pyridine-H), 5.83 (dd, 1H, *J* = 5.1, 5.1 Hz, pyrazoline-H), 7.05–7.08 (m, 1H, Ar–H), 7.10–7.34 (m, 2H, Ar–H), 7.41–7.50 (m, 7H, Ar–H), 7.64–7.67 (m, 1H, Ar–H); 13 C NMR (CDCl₃), δ (ppm): 163.2, 152.6, 152.5, 141.2, 131.7, 131.2, 130.1, 128.9, 128.7, 127.8, 126.5, 125.9, 125.6, 121.8, 120.8, 120.1, 63.6, 43.7; HRMS (ESI): *m*/*z* [M + H]⁺ calcd for C₂₂H₁₈N₃S: 356.1216; found: 356.1217.

2.4. X-ray diffraction analysis of compound 1

Suitable single crystals of **1** for X-ray structural analysis were obtained by slow evaporation of a solution of **1** in CHCl₃–CH₃OH (20:1, v/v) mixture at room temperature. The diffraction data was collected with a Bruker SMART CCD diffractometer using a graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å) at 296(2) K. The structures were solved by direct methods with SHELXS-97 program and refinements on F^2 were performed with SHELXL-97 program by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. All H atoms were initially located in a difference Fourier map. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C).

2.5. Binding titration

The stock solutions of **1** and **2**(1.0×10^{-5} M) were prepared by dissolving **1** and **2** in THF/water (9:1, v/v) containing HEPES buffer (10 mM, pH = 7.4), respectively. The cationic stocks were all in H₂O with a concentration of 3.0×10^{-3} M for UV–vis absorption and fluorescence spectra analysis. For metal ion absorption and fluorescence titration experiments, each time 3 mL solution of **1** and **2** were filled in a quartz cell of 1 cm optical path length, and we increased concentrations of metal ions by stepwise addition of different equivalents using a micro-syringe. After each addition of Cu^{2+} ion, the solution was stirred for 3 min. The volume of cationic stock solution added was less than 100 µL with the purpose of keeping the total volume of testing solution without obvious change. For all measurements of fluorescence spectra of **1** and **2**, the excitation was at 355 nm and 349 nm, respectively.

3. Results and discussion

3.1. Synthesis and structural characteristics of 1 and 2

The 3, 5-diaryl pyrazoline derivative 1 was obtained by the reaction of chalcone (4) with 2-hydrazinobenzothiazole (3) in AcOH under reflux. To understand the crucial role of both the



Scheme 1. Synthesis of pyrazoline derivates 1 and 2.

phenol and thiazole providing a suitable binding site for metal ions, compound **2** was also prepared from chalcone (**5**) with 2-hydrazinobenzothiazole (**3**) in the same way. The yields of **1** and **2** were 65% and 70%, respectively. The structures of **1** and **2** were identified by using ¹H NMR, IR and MS. The structure of **1** was further confirmed by X-ray diffraction analysis.

The X-ray molecular view of **1** is shown in Fig. 1. A summary of crystallographic data collection parameters and refinement parameters for **1** is compiled in Table 1.

Compound **1** crystallized in an orthorhombic space group Pbcn. One benzene moiety, one phenol ring and a benzothiazole moiety are bonded to the pyrazoline ring at the atoms of C8, C10 and N2, respectively. Consistent with a pronounced electronic interaction, the bond lengths of C10–C11, N2–C7 are significantly shorter as would be expected for a single bond. Moreover, the bond lengths of N2–N3, N3–C10, C8–C9 agree well with the equivalent ones in similar structures [46]. In the crystal of **1**, torsion angle C7–N2–C8–C17 of 67.9(3)° shows C7 in the benzothiazole moiety adopts an synperiplanar conformation with respect to the C17 atom of the benzene ring. In the asymmetry unit, the pyrazoline ring, phenol ring makes dihedral angles with phenol and thiazole of $5.19(11)^\circ$ and $4.54(12)^\circ$, respectively, while the dihedral angle between pyrazoline and benzene moiety is $87.89(10)^\circ$.

Regarding the crystal structure of **1**, there is one intramolecular O1–H1…N3 hydrogen bond forming a pseudo six-membered ring. The packing diagram of compound **1** is shown in Fig. 2. The molecules are connected by weak $\pi \cdots \pi$ interactions and C–H… π interaction. Cl5…Cg4 3.661(2) Å Cl8…Cg2 2.998(2) Å.

3.2. Spectral characteristics

Initial studies on the UV–vis absorption and fluorescent emission revealed that **1** showed selectivity toward Cu^{2+} ions in THF/ water (9:1, v/v). As shown in Fig. 3, in the absence of Cu^{2+} , compound **1** exhibits a broad band at 352 nm (log $\varepsilon = 4.48$). Coordination of copper cation to **1** resulted in the formation of a new absorption band at 400 nm and synchronous decrease in the absorption band at 352 nm. In contrast to **1**, compound **2**, which has

Table 1

Crystal structure data and structure refinement for 1.

Empirical formula $C_{22}H_{17}N_3OS$	
Lormania Woldh 2/1/15	
romula weigin 571.45	
Temperature 296(2) K	
Wavelength (A) 0.71073	
Crystal system Orthorhombic	
Space group Pca2(1)	
a (Å) 26.585 (5)	
b (Å) 9.5587 (17)	
c (Å) 7.0731 (12)	
α 90°	
β 90°	
γ 90 °	
V (Å ³) 1797.4 (5)	
Ζ 4	
Density (calculated) 1.373 Mg/m ³	
Index ranges $-22 \le h \le 28, -13 \le k \le 13, -18 \le l \le$	18
F(000) 776	
Crystal size $0.16 \times 0.12 \times 0.05 \text{ mm}$	
θ Range for data collection 1.53–25.26°	
Reflections collected 11,100	
Independent reflections 3253 $[R_{(int)} = 0.0351]$	
Max. and min. transmission 0.9902 and 0.9691	
Data/restraints/parameters 3253/1/246	
Goodness-of-fit on F^2 1.063	
Absorption correction None	
Final <i>R</i> indices $(I > 2\sigma(I))$ $R1 = 0.0304$, $wR2 = 0.0752$	
<i>R</i> indices (all data) $R1 = 0.0381$, w $R2 = 0.0782$	
Largest diff. peak and hole $0.153 \text{ and } -0.155 \text{ e} ^{\text{A}^{-3}}$	

no hydroxyl group in the phenyl ring and exhibits two broad band at 294 nm (log ε = 4.69) and 350 nm (log ε = 4.42), did not revealed any significant changes in absorption and fluorescence emissions upon addition to 1 equiv of copper ion as shown in Fig. 3, which indicates the importance of a phenolic group as a binding site at the 3 position of the pyrazoline ring.

The UV–vis absorption spectra of compound $1 (1 \times 10^{-5} \text{ M})$ in the presence of various concentrations of Cu²⁺ ion $(0-3 \times 10^{-5} \text{ M})$ is shown in Fig. 4 and the inset shows the plots of changes in 352 and 400 nm maxima as a function of increasing concentrations of Cu²⁺. The absorbance of compound 1 at 352 nm gradually decreases with an increasing concentration of Cu²⁺ ion. Moreover, two isobestic points appears at 328 nm and 380 nm; new absorption peaks appear in the range 250–328 nm and 380–450 nm, and their absorption intensity gradually increases or decreases with the



Fig. 1. The molecular structure of compound 1, with displacement ellipsoids drawn at the 30% probability level.



Fig. 2. A packing diagram for **1**, viewed along the *a*-axis. Dashed lines show arrays of hydrogen bonds.



Fig. 3. UV-vis spectra of compound $\mathbf{1}(-)$ and $\mathbf{2}(-)$ (1×10^{-5} M) (a) in the absence, and (b) in the presence of 1 equiv of CuCl₂ in THF/water (9:1, v/v) containing HEPES buffer (10 mM, pH = 7.4). Fluorescence spectra of $\mathbf{1}(-)$ and $\mathbf{2}(-)$ (c) in the absence and (d) in the presence of 1 equiv of CuCl₂ in THF/water (9:1, v/v) containing HEPES buffer (10 mM, pH = 7.4).



Fig. 4. UV–vis titration of compound **1** (1×10^{-5} M) in THF/water (9:1, v/v) containing HEPES buffer (10 mM, pH = 7.4) with increasing amount of Cu²⁺ ($0-3 \times 10^{-5}$ M). Inset: Absorbance plot of compound **1** against increasing of Cu²⁺ at λ_{max} 352 and 400 nm.

addition of Cu^{2+} ion, respectively. This absorption peak is likely due to the coordination of compound **1** with Cu^{2+} ion.

The fluorescence titration spectra of 1 with Cu^{2+} shows an emission maximum peak at 438 nm (Fig. 5a). The fluorescence quantum yield (Φ_u) of **1** in the absence of Cu²⁺ was calculated to be 0.20 with respect to quinine sulfate in 0.1 N H₂SO₄ solution $(\Phi_{\rm s} = 0.54)$ [47]. As Cu²⁺ ion was gradually titrated, the fluorescence intensity of compound 1 gradually decreased and when the amount of Cu^{2+} ion added was about 1×10^{-5} M, the fluorescence intensity almost reached a minimum. The quantum yield of **1** was calculated to be 0.025 in the presence of Cu^{2+} ion $(1 \times 10^{-5} \text{ M})$ and almost reduced to 12% of the initial one. When more Cu^{2+} was titrated, the fluorescence intensity showed negligible changes. The nonlinear curve fitting of the fluorescence titration (inset) gives a 1:1 stoichiometric ratio between compound **1** and Cu²⁺. Moreover, a Job's plot [48], which exhibits a maximum at 0.5 M fraction of Cu^{2+} , further indicates that only a 1:1 complex is formed (Fig. 5b). Based on the above fluorescence titration of 1 with Cu^{2+} , the association constant was calculated to be 9.3 \times $10^4~M^{-1}(error~limits \le 10\%)by$ a Benesi-Hildebrand plot [49] (Fig. 6). The detection limit, based on the definition by IUPAC ($C_{DL} = 3 \text{ Sb/m}$) [50], was found to be 8.7×10^{-8} M from 10 blank solutions.

The selectivity and tolerance of compound **1** for copper ion over other metal cations were investigated by adding metal cations



Fig. 5. (a)Fluorescence emission spectra of **1** (10^{-5} M) was titrated with Cu²⁺ (0– 2.0 equiv.) in THF/water (9:1, v/v) containing HEPES buffer (10 mM, pH = 7.4). Inset: variations of fluorescence intensity of compound **1** (10^{-5} M) at 438 nm vs. equivalents of [Cu²⁺] [**1**]. (b) Job's plot for determining the stoichiometry for **1** and Cu²⁺ in THF/ water (9:1, v/v) containing HEPES buffer (10 mM, pH = 7.4). Total concentration = 1.0×10^{-5} M.



Fig. 6. Benesi-Hildebrand linear analysis plots of 1 at different Cu²⁺ concentration.



Fig. 7. UV–vis spectral changes of compound 1 (1 \times 10⁻⁵ M) in THF/water (9:1, v/v) containing HEPES buffer (10 mM, pH = 7.4) upon additions of various metal ions (1 \times 10⁻⁵ M).

 $(5 \times 10^{-5} \text{ M})$ to the solution of compound $1(1 \times 10^{-5} \text{ M})$. As depicted in Fig. 7, there was no obvious new absorption band at 400 nm and synchronous decrease in the absorption band at 352 nm with any other metal ions.

Fig. 8 shows that Cu^{2+} produced significant quenching in the fluorescent emission of **1**, the other tested metals only show relatively insignificant changes. This means that sensor **1** has a high selectivity to Cu^{2+} ion. And from the photograph shown in Fig. 8, we can see the stronger blue emission of compound **1** without addition of Cu^{2+} ion under the irradiation at 365 nm than with addition of 1×10^{-5} M Cu^{2+} ion.

To further gauge selectivity for copper ion over other metal ions, competition experiments of Cu^{2+} ion mixed with other metal ions were carried out from fluorescence spectra and the results are shown in Fig. 9. The fluorescence intensity of $1 (1 \times 10^{-5} \text{ M})$ in the presence of 1 equiv of the Cu^{2+} ion was almost unaffected by the addition of 5 equiv of competing metal ions (K⁺, Na⁺, Cd²⁺, Fe³⁺,



Fig. 8. Fluorescence spectra of 1 (1 × 10⁻⁵ M) in THF/water (9:1, v/v) containing HEPES buffer (10 mM, pH = 7.4) in the presence of different metal ions (1 equiv). Inset: Photos of 1 in THF/water (9:1, v/v) containing HEPES buffer (10 mM, pH = 7.4) without and with addition of Cu²⁺ under the irradiation of UV light at 365 nm.



Fig. 9. Competitive experiments in the $1 + Cu^{2+}$ system with interfering metal ions. [1] = 1×10^{-5} M, $[Cu^{2+}] = 1 \times 10^{-5}$ M, and $[M^{n+}] = 5 \times 10^{-5}$ M. Excited at 355 nm and emission collected at 438 nm.

 Mn^{2+} , Mg^{2+} , Co^{2+} , Ni^{2+} , Hg^{2+} , Pb^{2+} and Zn^{2+}). These results suggested that molecule **1** could be used as Cu^{2+} selective fluorescent chemosensor.

Additionally, in order to explore the effects of anionic counterions on the sensing behavior of compound **1** to Cu^{2+} ion, fluorescence responses of compound **1** to sulfate, chloride, and nitrate salts of copper were conducted in the THF/water (9:1, v/v) containing HEPES buffer (10 mM, pH = 7.4). As can be seen from Fig. 10, there were no obvious changes in the fluorescence responses of compound **1** to CuSO₄, CuCl₂, and Cu(NO₃)₂.

To gain further insight into the fluorescent signaling behavior of compound 1 toward Cu²⁺ ion, the effect of EDTA on the fluorescence signaling of the $1-Cu^{2+}$ system was investigated. When 1×10^{-5} M EDTA was added into the $1-Cu^{2+}$ system, the fluorescence intensity increased to the fluorescence intensity of compound 1 without Cu²⁺ ion as shown in Fig. 11. This is attributed



Fig. 10. Fluorescence spectra of **1** (10^{-5} M) in THF/water (9:1, v/v) containing HEPES buffer (10 mM, pH = 7.4) in the presence of different copper salts (10^{-5} M). Excited at 355 nm.



Fig. 11. Fluorescence spectra of $1-Cu^{2+}(10^{-5} \text{ M in THF/water } (9:1, v/v)$ containing HEPES buffer (10 mM, pH = 7.4), excitation at 389 nm, buffered by 10 mM HEPES, pH 7.4) upon addition of EDTA (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 equiv).

to the stronger complexation of Cu^{2+} ion with EDTA than with sensor 1.

To investigate the mechanism of the fluorescence quenching for 1, Cu^{2+} may be easily establish coordinative interactions with the phenol, pyrazoline, and benzo[d]thiazole moiety than other metal ions examined, the capture of Cu^{2+} resulted in the electron or energy transfer from 1 to Cu^{2+} ; thus, 1 showed quenching of the fluorescence for Cu^{2+} and provided a high selectivity for Cu^{2+} over the other tested metal ions.

4. Conclusion

In summary, a new highly selective fluorescent sensor based on a pyrazoline unit was synthesized and used for the determination of Cu²⁺ ion with high selectivity and a low detection limit in THF/ water (9:1, v/v) containing HEPES buffer (10 mM, pH = 7.4). This sensor formed a 1:1 complex with Cu²⁺ and showed a fluorescent quenching with good tolerance of other metal ions. Moreover, this sensor is very sensitive with fluorometric detection limit of 8.7×10^{-8} M.

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Appendix A. Supplementary material

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2012.09.019.

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