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A new selective fluorescent sensor for Fe³⁺ based on a pyrazoline derivative

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Abstract

A new pyrazoline derivative 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 Fe^{3+} ion with high selectivity among a series of cations in tetrahydrofuran and even in aqueous tetrahydrofuran. This sensor forms a 1:1 complex with Fe^{3+} and displays fluorescent quenching.

Key words

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Pyrazoline, Fluorescent sensor, Iron(III) ions, Selective

1. Introdution

Selective signalling of chemically and biologically important metal ions has always gained much research attention in supramolecular chemistry[1]. Of particular interest is the development of chemosensors for the heavy and transition metal ions because of their toxic impacts on our environment[2] and many important roles in living system[3]. As an important physiologically relevant metal ion, Fe³⁺ ion plays an indispensable role in many biochemical processes at the cellular level[4], and both its deficiency and excess can induce a variety of diseases[5]. Therefore, the determination of traces of iron ion in clinical, medicinal, environmental and different industrial samples has been an important topic in environmental and biological analysis. However, the examples of Fe³⁺-selective fluorescent sensors are still scarce[6-15] owing to its easy to be interfered by other transition-metal ions such as Cu²⁺ and Co²⁺. Therefore, designing a highly selective sensor for Fe³⁺ is still a challenge.

1,3,5-Triaryl-2-pyrazolines, with their rigid but only partly unsaturated central pyrazoline ring, are well-known fluorescent compounds widely used in fluorescent dyes emitting blue fluorescence with high fluorescence quantum yield [16-20] and electroluminescence fields [21–27], However, to the best of our knowledge, only a few examples have been reported on the interactions between pyrazoline derivatives and zinc ion [28–30]. Recently, we had reported a selective pyrazoline-based fluorescent chemosensor for Cu²⁺[31]. In continuing our research to develop new

fluorescent chemsensors based on pyrazoline chromophore, we design a new pyrazoline derivative **1**, in which a pyridine ring and a benzothiazole moiety are bonded to the pyrazoline ring, and hope this molecule to adopt a rigid Y-shaped conformation, which might be able to bind selectively with a metal ion. The primary test showed that **1** possesses a highly selective response of fluorescence quenching toward Fe^{3+} in THF and even in THF/H₂O (95:5, v/v) solution.

2. Experimental

2.1. Reagents

All the reagents were purchased from commercial suppliers and used without further purification. The salts used in stock solutions of metal ions were CoCl₂·6H₂O, ZnCl₂, NaCl, CuCl₂·2H₂O, NiCl₂·6H₂O, KCl, CdCl₂·2H₂O, HgCl₂, FeCl₃·6H₂O, Mg(ClO₄)₂, Al(NO₃)₃·9H₂O.

2.2. 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. MS spectra were obtained on a Finnigan Trace MS spectrometer. IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption reported in cm⁻¹. 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 temperature (about 298K).

2.3. Synthesis of 2-(5-(4-Chlorophenyl)-3-(pyridin-2-yl)-4,5-dihydropyrazol-1-yl)

benzo[d] thiazole (1)

The synthetic route of the proposed compound **1** is shown in Scheme 1. Starting materials chalcone (2)[32] and 2-hydrazinobenzothiazole (3)[33] were prepared according to literatures. To a stirred solution of chalcone 2 (0.243 g, 1.0 mmol) in AcOH (15 mL) was added 2-hydrazinylpyridine (3) (0.165 g, 1.0 mmol). The reaction mixture was refluxed for 4 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 yellow solid, yield 62%; M.p.:220–221 °C; IR (v_{max}, KBr, cm⁻¹): 3053, 2987, 2921, 1755, 1724, 1459, 1421, 1261, 1150, 757, 692; ¹H NMR (CDCl₃), δ (ppm): 8.58–8.60(m, 1H, Ar-H), 8.17–8.19(m,1H, Ar–H), 7.76(d,1H, 1.5Hz), 7.54(d,1H, J = 8.1 Hz, Ar–H), 7.65(m,1H, J = 8.1 Hz, Ar-H), 7.25-7.32(m, 6H,Ar-H), 7.09-7.14(m, 1H,Ar-H), 5.80(dd, 1H, J = 5.4, 5.4 Hz, pyrazoline-H), 4.05(dd, 1H, J = 12, 12 Hz, 12 Hz)pyrazoline-H), 3.49(dd, 1H, J = 5.4, 5.4 Hz, pyrazoline-H). ¹³C NMR (CDCl₃), δ (ppm): 43.29, 63.41, 120.30, 120.80, 121.36, 122.17, 124.09, 125.76, 127.49, 128.98, 131.69, 133.46, 136.25, 139.59, 149.37, 150.41, 152.31, 153.93, 162.89, ESI mass spectrometry: m/z 391.1 (100% $[M+H]^+$); M^+ calculated 390.1.

(Scheme 1)

2.4. X-ray crystallography 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 = 0.93Å and U_{iso}(H) = 1.2U_{eq}(C).

2.5. Analytical procedure and Quantum yield

The stock solutions of $1(1.0 \times 10^{-5} \text{ M})$ were prepared by dissolving 1 in THF and in THF/water(95:5, v/v) containing HEPES buffer(10mM, pH= 7.4). The cationic stocks were all in EtOH 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 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 Fe³⁺ 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, the excitation was at 352 nm.

3. Results and discussion

3.1. Synthesis and structural characteristics of 1

The 3, 5-diaryl pyrazoline derivative 1 was obtained by the reaction of chalcone (2)

with 2-hydrazinobenzothiazole (3) in AcOH under reflux. The yield of **1** was 62%. The structures of **1** were identified by using ¹H NMR, IR and MS. The structure of **1** was further comfirmed by X-ray diffraction analysis.

The molecular view of 1 is shown in Fig. 1. A summary of crystallographic data collection parameters and refinement parameters for 1 are compiled in Table 1. The structure of compound 1 is crystallized in Orthorhombic space group Pbcn. One benzene moiety, one pyridine ring and a 2-hydrazinobenzothiazole 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 [34]. In the crystal of 1, torsion angle C7–N2–C8–C16 of 66.85° shows C7 in the pyridazine moiety adopts an antiperiplanar conformation with respect to the C16 atom of the benzene ring. In the asymmetry unit, the pyrazoline ring, pyridine ring and 2-hydrazinobenzothiazole are almost coplanar. And the pyrazoline ring makes dihedral angles with pyridine and 2-hydrazinobenzothiazole of 4.07(1)° and $5.29(1)^{\circ}$, respectively, while the dihedral angle between pyrazoline and benzene moiety is 85.42(1)°.

(Fig. 1).

(Table 1)

The packing diagram of the compound 1 is shown in Fig. 2. The molecules are

connected by weak $\pi \cdot \cdot \pi$ interactions and C–H··· π interaction. C6 ··Cg3 3.512(2)Å C15···Cg5 3.789(2)Å and C21 ··Cg1 3.6800(18)Å.

(Fig. 2)

3.2. Spectral characteristics

The absorption spectrum of compound **1** exhibits a broad band at 354 nm at room temperature in THF. Binding affinities of compound **1** toward various metal ions were evaluated by UV–vis spectroscopy measurements. Upon addition of these metal ions, the absorption spectrum changes in different manner as shown in Fig. 3. In the case of K^+ , Na⁺, Cr³⁺, Zn²⁺, Cd²⁺, Co²⁺, Cu²⁺, Hg²⁺, Mg²⁺, Mn²⁺, Ni²⁺, Al³⁺, and Pb²⁺, the absorption curve did not obvious change, whereas in the case of Fe³⁺, the addition of Fe³⁺ ion caused a increase of absorption intensity at 354 nm, accompanied by the obvious hypsochromic shift of the absorption peak (from 354 to 337 nm). indicating the formation of a new complex between compound **1** and Fe³⁺.

(Fig. 3.)

The UV–vis absorption spectra of $\mathbf{1}$ (1×10⁻⁵ M) in THF in the presence of various concentrations of Fe³⁺ ion (0–20×10⁻⁵ M) are shown in Fig. **4**, and the inset shows the plots of changes as a function of increasing concentrations of Fe³⁺. As shown in Fig. 4, the UV absorbance of **1** at 354 nm enhanced from 0.24 to 1.44 when increasing concentration of Fe³⁺ from 0 to 20×10⁻⁵ M. A satisfactory linear relationship between UV–vis absorbance and Fe³⁺ concentration was observed with the correlation

coefficient as high as 0.998.

(Fig. 4).

The fluorescence titration spectra of **1** in THF with Fe^{3+} shows an emission. maximum peak at 462 nm (Fig. 5). The fluorescence quantum yield of compound 1 in the absence of Fe^{3+} was calculated to be 0.48 with respect to quinine sulphate in 0.1 N H_2SO_4 solution ($\Phi_s = 0.54$) [35]. As Fe³⁺ ion was gradually titrated, the fluorescence intensity of compound 1 gradually decreased and when the amount of Fe^{3+} ion added was about 20×10^{-5} M, the fluorescence intensity almost reached minimum. The quantum yield of **1** was calculated to be 0.02 in the presence of Fe^{3+} ion (20×10⁻⁵M) and almost reduced to 4.2% of the initial one. To determine the stoichiometry of compound **1** and Fe^{3+} ion in the complex, Job's method [36] was employed by using the emission changes at 462 nm as a function of molar fraction of Fe^{3+} . A maximum emission was observed when the molar fraction of Fe^{3+} reached 0.5 (Fig. 6), indicating that Fe^{3+} ions form a 1:1 complex with the sensing compound. Based on the above fluorescence titration of **1** with Fe^{3+} , the Stern-Volmer constants (K_{sv}) was calculated to be 1.2×10⁴ M⁻¹by a modified Stern-Volmer plot[37] (Fig. 5, inset). The detection limit, based on the definition by IUPAC (C_{DL} =3Sb/m) [38], was found to be 1.4×10^{-6} M from 10 blank solutions.

(Fig. 5)

(Fig. 6)

The selectivity and tolerance of compound **1** in THF for Fe^{3+} ion over other metal cations such as K⁺, Na⁺, Cr³⁺, Mg²⁺, Hg²⁺, Cd²⁺, Zn²⁺, Co²⁺, Ni²⁺, Pb²⁺, Mn²⁺, Cu²⁺, and Al³⁺ ions were investigated by adding metal cations (10×10⁻⁵ M) to the solution of compound **1**(10×10⁻⁵M). As depicted in Fig. 7, Fe³⁺ 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 Fe³⁺ ion.

(Fig. 7)

To further gauge selectivity for Fe^{3^+} ion over other metal ions, competition experiments of Fe^{3^+} ion mixed with other metal ions were carried out from fluorescence spectra and the results are shown in Fig.8. The fluorescence intensity of **1** (1×10⁻⁵ M) in the presence of 10 equiv of the Fe³⁺ ion was almost unaffected by the addition of 10 equiv of competing metal ions (Cd²⁺, Cr³⁺, Cu²⁺, Hg²⁺, Mg²⁺, Mn²⁺, Zn²⁺, Co²⁺, Ni²⁺, K⁺, Al³⁺, and Na⁺). These results suggested that molecule **1** could be used as Fe³⁺ selective fluorescent chemosensor.

(Fig. 8)

In order to achieve a real application in infield monitoring. the photophysical properties of sensor **1** were also examined in THF/water(95:5, v/v) containing HEPES

buffer(10mM, pH=7.4) at a concentration level of 1×10^{-5} M. Changes of the UV-vis absorption spectra and fluorescence properties of **1** caused by various metal ions were shown in Fig. 9 and 10, respectively. The result showed Fe³⁺ also produced significant enhancement in the absorption spectra and quenching in the fluorescent emission of **1**, the other tested metals only show relatively insignificant changes. So it can be concluded that **1** also has higher selectivity for recognition of Fe³⁺ in anquous THF.

(Fig. 9).

(Fig. 10)

The UV–vis absorption of $1 (1 \times 10^{-5} \text{ M})$ in THF/water(95:5, v/v) containing HEPES buffer(10mM, pH= 7.4) in the presence of various concentrations of Fe³⁺ ion (0–20×10⁻⁵ M) are shown in Fig. 11, and the inset shows the plots of changes as a function of increasing concentrations of Fe³⁺. As shown in Fig. 11, compound **1** exhibits a broad band at 354 nm. Coordination of Fe³⁺ to **1** resulted in the formation of a new absorption band at 318 nm and synchronous increase in the absorption band at 354 nm, accompanied by the obvious hypsochromic shift of the absorption peak (from 354 to 362 nm).A satisfactory linear relationship between UV–vis absorbance and Fe³⁺ concentration was observed with the correlation coefficient as high as 0.999.

(Fig. 11)

Similarly, fluorescence titration of **1** with Fe³⁺ was carried out in THF/water(95:5, v/v) containing HEPES buffer(10mM, pH=7.4) at a concentration level of 1×10^{-5} M. Addition of Fe³⁺ to the solition of **1** causes a quenching in the fluorescent emission of **1**(Fig. 12). When the amount of Fe³⁺ ion added was about 20×10^{-5} M, the fluorescence intensity reduced to 38.5% of the initial one. The calculated quantum yield of **1** with respect to quinine sulphate in 0.1 N H₂SO₄ solution ($\Phi_s = 0.54$) was reduced from 0.28 of the initial to 0.08. Job's plot of **1** with Fe³⁺ ions also indicating the formation of a 1:1 complex (Fig. 13). The Stern-Volmer constants (K_{sv}) was calculated in THF/water(95:5, v/v) containing HEPES buffer (10mM, pH=7.4) was 2.3×10^3 M⁻¹ (Fig. 12, inset). The detection limit was found to be 3.0×10^{-6} M from 10 blank solutions.

(Fig. 12)

(Fig. 13)

To investigate the mechanism of the fluorescence quenching for **1** by comparing with our previous report[31], Fe^{3+} may be easily establish coordinative interactions with the pyridine, pyrazoline, and benzo[d]thiazole moiety than other metal ions examined, the capture of Fe^{3+} resulted in the electron or energy transfer from **1** to Fe^{3+} ; thus, **1** showed quenching of the fluorescence for Fe^{3+} and provided a high selectivity for Fe^{3+} over the other tested metal ions.

4. Conclusion

In summary, a new selective fluorescent sensor based on a pyrazoline unit was synthesized and used for the determination of Fe^{3+} ion with high selectivity in THF and in THF/water(95:5, v/v) containing HEPES buffer(10mM, pH= 7.4). This sensor formed a 1:1 complex with Fe^{3+} and showed a fluorescent quenching.

Supplementary material

The crystallographic data (excluding structure factors) of **1** have been deposited with the Cambridge Crystallographic Center as supplementary publication no. 894133. Copy of this information may be obtained free of charge viawww: http://www.ccdc.cam.ac.uk or from The Director, CCDC, 12 Union Road, Cambridge CB221EZ, UK (fax: t44 1223/336 033; email: deposite@ccdc.cam.ac.uk). Structural factors are available on request from the authors.

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Empirical formua	C ₂₁ H ₁₅ ClN ₄ S
Formula weigh	390.88
Temperature	298(2) K
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pbcn
a (Å)	22.723(2)
b (Å)	11.0052(10)
c (Å)	14.6753(13)
α	90°
β	90°
γ	90°
$V(Å^3)$	3669.9(6)
Ζ	8
Density (calculated)	1.415 Mg/m ³
Index ranges	-22≤h≤28, -13≤k≤13, -18≤l≤18
F(000)	1616
Crystal size	0.20×0.10×0.10 mm
θ range for data collection	1.79 to 25.99°
Reflections collected	23756
Independent reflections	3599 [$R_{(int)} = 0.0268$]
Max.and min.transmission	0.9672 and 0.9359
Data/restraints/parameters	3599 / 0 / 245
Goodness-of-fit on F ²	1.092
Absorption correction	None
Final <i>R</i> indices $(I \ge 2\sigma(I))$	R1 = 0.0307, wR2 = 0.0885
R indices (all data)	R1 = 0.0395, $wR2 = 0.0930$
Largest diff. peak and hole	0.230 and -0.214 e $Å^{-3}$

Table 1.







Fig. 4











Fig. 8









Fig. 11



Fig. 12



Fig. 13

Captions:

Scheme 1 Synthesis of pyrazoline derivate 1.

Fig. 1. The molecular structure of compound 1, with displacement ellipsoids drawn at

the 30% probability level.

 Table 1 Crystal structure data and structure refinement for 1.

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

Fig. 3. UV–vis spectral changes of compound **1** (1×10^{-5} M) in THF upon additions of various metal ions (10×10^{-5} M).

Fig. 4. UV absorbance spectra of $1(1.0 \times 10^{-5} \text{ M})$ upon the addition of various amounts of Fe³⁺. The inset shows the absorbance intensity at $\lambda max = 354$ nm as a function of Fe³⁺ concentration.

Fig. 5. Fluorescence emission spectra of compound $1 (1 \times 10^{-5} \text{ M})$ in THF were titrated with Fe³⁺(0–20 equiv); Inset: modified Stern–Volmer plot of the emission data.

Fig. 6. Job's plot for determining the stoichiometry for 1 and Fe^{3+} in THF. Total concentration =1.0 ×10⁻⁵ M.

Fig. 7. Fluorescence spectra of $1 (1 \times 10^{-5} \text{M})$ in the presence of different metal ions (10 equiv) in THF.

Fig. 8. Competitive experiments in the $\mathbf{1} + \text{Fe}^{3+}$ system with interfering metal ions. [1] = 1×10^{-5} M, $[\text{Fe}^{3+}] = 10 \times 10^{-5}$ M, and $[\text{M}^{n+}] = 10 \times 10^{-5}$ M. Excited at 352 nm and emission collected at 462 nm.

Fig. 9. UV–vis spectral changes of compound **1** (1×10^{-5} M) in THF/water(95:5, v/v) containing HEPES buffer(10mM, pH= 7.4) upon additions of various metal ions ($10 \times$

 10^{-5} M).

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Fig. 10. Fluorescence spectra of **1** (10^{-5} M) in THF/water(95:5, v/v) containing HEPES buffer(10mM, pH= 7.4) in the presence of different metal ions (10 equiv), Excited at 352 nm.

Fig. 11. UV absorbance spectra of $1(1.0 \times 10^{-5} \text{ M})$ in THF/water(95:5, v/v) containing HEPES buffer(10mM, pH= 7.4) upon the addition of various amounts of Fe³⁺. The inset shows the absorbance intensity at λ max =354 nm as a function of Fe³⁺ concentration.

Fig. 12. Fluorescence emission spectra of **1** (10^{-5} M) was titrated with Fe³⁺(0–20 equiv.) in THF/water(95:5, v/v) containing HEPES buffer(10mM, pH= 7.4); Inset: modified Stern–Volmer plot of the emission data.

Fig. 13. Job's plot for determining the stoichiometry for 1 and Fe^{3+} in THF/water(95:5, v/v) containing HEPES buffer(10mM, pH= 7.4). Total concentration =1.0 ×10⁻⁵ M.

Graphical Abstract



Pyrazoline derivate 1 for selective detection of Fe³⁺ with fluorescence quenching

Highlights

- The pyrazoline derived sensor is simple to synthesize.
- ► The structure of the pyrazoline was confirmed by single crystal X-ray diffraction.
- This sensor can be used to determine Fe^{3+} ion with high selectivity.
- It is the first example of Fe^{3+} ion fluorescent chemosensor based on pyrazoline SIL