

A new fluorescent chemosensor for Fe³⁺ based upon 2,5-diphenylfuran and 8-hydroxyquinoline



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ABSTRACT

A new fluorescent chemosensor based upon 2,5-diphenylfuran and 8-hydroxyquinoline was designed and synthesized. Its structure 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 Fe³⁺ ion with high selectivity among a series of cations in aqueous DMF. This sensor forms a 1:1 complex with Fe³⁺ and displays fluorescent quenching.

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1. Introduction

The design of fluorescent chemosensors for various metal ions is an important area because of their fundamental role in medical, environmental and biological applications [1–4]. 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]. 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 reported Fe³⁺-selective fluorescent sensors are relatively rare [6–15] despite the widespread applications of Fe³⁺. Therefore, designing a highly selective sensor for Fe³⁺ is still a challenge.

8-Hydroxyquinoline (HQ) was employed widely in designing chemosensors for detection transition metal ions, such as, Cu²⁺ [16], Cd²⁺ [17], Mg²⁺ [18], Zn²⁺ [19,20], Al³⁺ [21,22], and Hg²⁺ [23,24] due to its good photostability and strong ability to complex metal ions. To develop new fluorescent sensors based on 8-hydroxyquinoline, we designed a new 8-hydroxyquinoline derivative **1**. The primary test showed that **1** possesses a highly selective response of

fluorescence quenching toward Fe³⁺ in aqueous DMF solution. To the best of our knowledge, it is the first example of Fe³⁺-selective fluorescent sensor based on 8-hydroxyquinoline in aqueous 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, MnCl₂·4H₂O, KCl, NaCl, CuCl₂·2H₂O, NiCl₂·6H₂O, CdCl₂·2H₂O, HgCl₂, FeCl₃·6H₂O, MgCl₂·6H₂O, CrCl₃·6H₂O, Pb(NO₃)₂, FeSO₄·7H₂O.

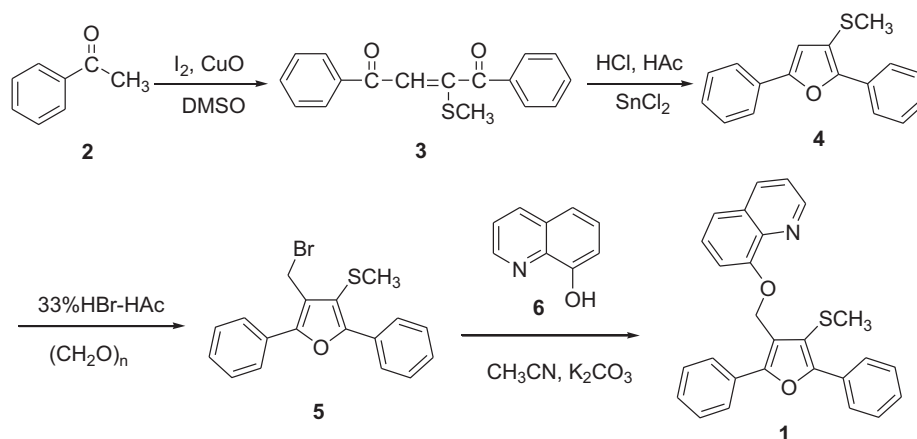
2.2. Apparatus

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 298 K).

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Scheme 1. Synthesis of sensor 1.

2.3. Synthesis

The synthetic route of the compound **1** is shown in Scheme 1.

2.3.1. Synthesis of 3-(bromomethyl)-4-(methylthio)-2,5-diphenylfuran (**5**)

3-(Methylthio)-2,5-diphenylfuran (**4**) was prepared according to literatures [25]. To a solution of 0.64 g of paraformaldehyde in 6.0 g of 33% hydrogen bromide-acetic acid reagent was added a solution of 0.54 g (2 mmol) of compound **4** in 6 ml of glacial acetic acid. The mixture was stirred for 2 h after which time the crystals which formed were filtered off, and consequently recrystallized from ethanol to afford pure compound **5** (0.51 g, 71.5%) as a pale solid. M.p.: 160–161 °C. IR (KBr, cm^{-1}): 1632, 1389, 1203, 768, 676. ^1H NMR (CDCl_3 , 300 MHz): δ 8.03–8.01 (m, 2H), 7.54–7.86 (m, 2H), 7.35–7.52 (m, 6H), 4.75 (s, 2H) 2.48 (s, 3H); EI-MS: m/z 358.2, 359 [M+1], 360 [M+2], 361 [M+3].

2.3.2. Synthesis of 8-((4-(methylthio)-2,5-diphenylfuran-3-yl)methoxy)quinoline (**1**)

Compound **5** (0.358 g, 1.0 mmol) and quinolin-8-ol (**6**) (0.145 g, 1.0 mmol) was dissolved in CH_3CN (20 mL) and K_2CO_3 (0.55 g, 4.0 mmol) was added. The resultant mixture was refluxed for 3 h, cooled to room temperature, diluted with 2 N HCl (50 mL) and extracted with EtOAc (3×20 mL). The extracts were washed with brine (2×20 mL) and dried over anhydrous MgSO_4 . After filtration and rotary evaporation the residue was purified by flash chromatography with petroleum as eluent to give compound **1** (0.38 g, 65.2%) as a pale solid. Mp: 168–169 °C; IR (KBr, cm^{-1}): 3060, 2922, 1604, 1563, 1486, 1373, 1249, 1092, 970. ^1H NMR (300 MHz, CDCl_3): δ = 8.19–8.23 (m, 2H), 8.12–8.15 (m, 1H), 7.82–7.85 (m, 2H), 7.302–7.53 (m, 10H), 5.35 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ = 154.6, 152.8, 152.4, 1149.4, 140.4, 135.8, 130.4, 130.1, 129.5, 128.7, 128.5, 128.3, 126.7, 126.6, 126.1, 121.6, 120.7, 120.2, 116.9, 109.8, 61.9, 19.6. EI-MS: m/z 424.3 [M+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 CHCl_3 – CH_3OH (20:1, v/v) mixture at room temperature. The diffraction data was collected with a Bruker SMART CCD diffractometer using a graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) 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 $\text{C-H} = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$.

2.5. Analytical procedure

The stock solutions of **1** ($1.0 \times 10^{-5} \text{ M}$) were prepared by dissolving **1** in DMF/water (98:2, v/v) containing BR buffer (10 mM, pH = 7.0). The cationic stocks were all in H_2O with a concentration of $3.0 \times 10^{-3} \text{ M}$ 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 Fe^{3+} 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 314 nm.

3. Results and discussion

3.1. Synthesis and structural characteristics of **1**

The compound **1** was get by the reaction of quinolin-8-ol (**6**) with compound **5** in CH_3CN with K_2CO_3 as base under reflux. The yield of **1** was 65%. The structures of **1** were identified by using ^1H NMR, IR and MS. The structure of **1** was further confirmed 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 Triclinic space group P-1. The phenyl rings (C15–C20) and phenyl ring (C21–C26) are bonded to the furan ring at the atoms of C12 and C13. They are twisted away from the furan ring and form dihedral angles of 36.85° and 23.12° respectively, with the furan ring (O2–C12). The dihedral angle between them is 22.13° . The 8-hydroxyquinoline ring is connected with the furan ring at the atoms of C11 by a bridged methylene, the dihedral angle between them is 83.37° . Because of the presence of the electron-rich nitrogen, oxygen and sulfur atom in the possible cavity, **1** has the potential to bind guests.

Regarding the crystal structure of **1**, there is a intramolecular C26–H26...S1 hydrogen bond forming a pseudo six-membered. The molecules are connected by weak $\text{C-H} \cdots \pi$ interaction, which is

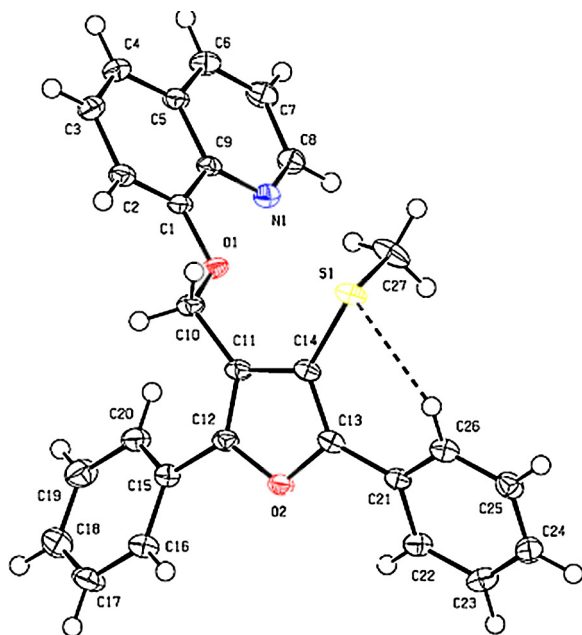


Fig. 1. The molecular structure of compound **1**, with displacement ellipsoids drawn at the 30% probability level.

important for the packing modes. C7...Cg1 3.6791(18) Å C18...Cg2 3.515(2) Å and C27...Cg3 3.3993(19) Å; and further assigned into layers via intramolecular hydrogen bond of C2–H2...S1, H2...S1 2.85, C2...S1 3.7835(17), C2–H2...S1 170° with the symmetry code of $-x, -y, 1-z$, along the b -axis and C25–H25...N1, H25...N1 2.53, C25...N1 3.302(2), C25–H25...N1 138° with the symmetry code of $-1+x, y, z$ (Fig. 2).

3.2. Spectral characteristics

The absorption spectrum of compound **1** exhibits a broad band at 314 nm at room temperature in DMF/water (98:2, v/v)

Table 1

Crystal structure data and structure refinement for **1**.

Empirical formula	C ₂₇ H ₂₁ NO ₂ S
Formula weight	423.51
Temperature	100(2) K
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
<i>a</i> (Å)	9.7449(16)
<i>b</i> (Å)	10.2333(17)
<i>c</i> (Å)	11.3236(18)
α	83.865(2)°
β	71.461(2)°
γ	79.360(2)°
<i>V</i> (Å ³)	31050.8(3)
<i>Z</i>	2
Density (calculated)	1.339 Mg/m ³
Index ranges	$-12 \leq h \leq 12, -11 \leq k \leq 13, -14 \leq l \leq 14$
<i>F</i> (000)	444
Crystal size	0.30 mm × 0.20 mm × 0.20 mm
θ range for data collection	1.90–28°
Reflections collected	7816
Independent reflections	4983 [$R_{\text{int}} = 0.0241$]
Max. and min. transmission	0.9651 and 0.9483
Data/restraints/parameters	4983/0/281
Goodness-of-fit on F^2	1.107
Absorption correction	None
Final <i>R</i> indices ($I > 2\sigma(I)$)	$R1 = 0.0435, wR2 = 0.1345$
<i>R</i> indices (all data)	$R1 = 0.0496, wR2 = 0.1510$
Largest diff. peak and hole	0.475 and $-0.548 \text{ e}^{-\text{Å}^{-3}}$

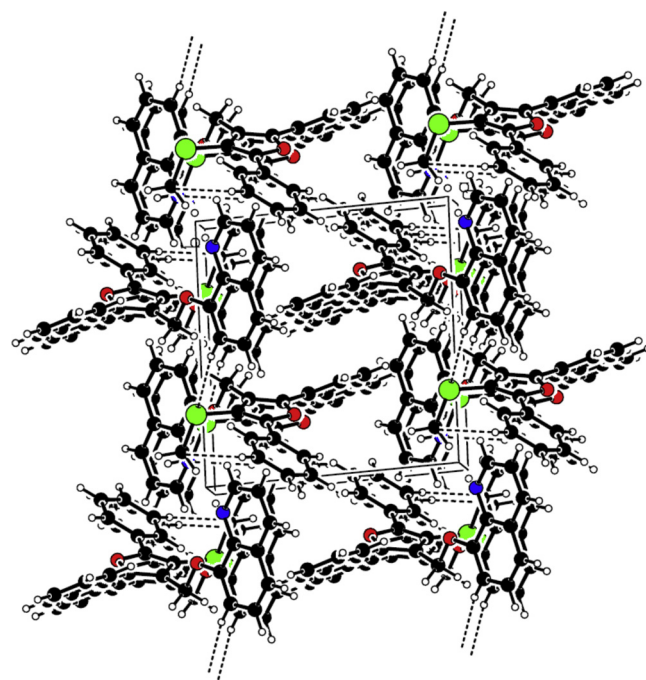


Fig. 2. A packing diagram for **1**, viewed along the c -axis. Dashed lines show arrays of hydrogen bonds.

containing Britton–Robison buffer (10 mM, pH = 7.0). Binding affinities of compound **1** toward metal ions (K^+ , Na^+ , Cr^{3+} , Mg^{2+} , Hg^{2+} , Cd^{2+} , Zn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Mn^{2+} , Cu^{2+} , and Fe^{2+}) 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^+ , Cr^{3+} , Mg^{2+} , Hg^{2+} , Cd^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Mn^{2+} , and Fe^{2+} absorption curve did not obvious change, in the case of Cu^{2+} , absorption curve slight changed, whereas in the case of Fe^{3+} , the addition of Fe^{3+} ion caused a increase of absorption intensity at 314 nm, indicating the formation of a new complex between compound **1** and Fe^{3+} .

The UV–vis absorption spectra of compound **1** ($1 \times 10^{-5} \text{ M}$) in the presence of various concentrations of Fe^{3+} ion (0 – $15 \times 10^{-5} \text{ M}$) are shown in Fig. 4 and the inset shows the plots of changes as a function of increasing concentrations of Fe^{3+} . As shown in Fig. 4, the UV absorbance at 314 nm enhanced from 0.26 to 0.73, when

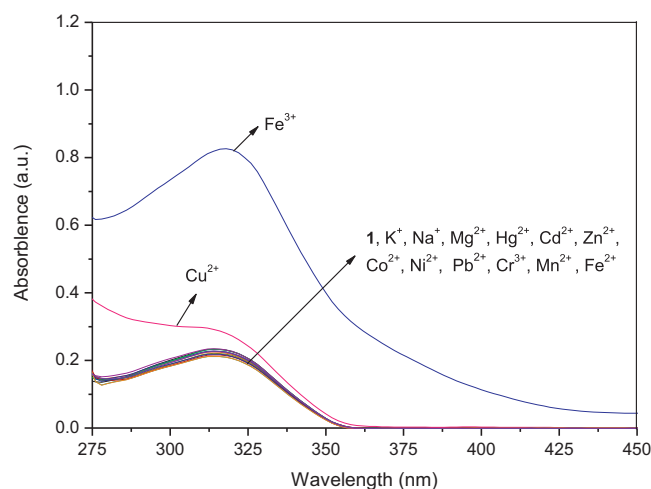


Fig. 3. UV–vis spectral changes of compound **1** ($1 \times 10^{-5} \text{ M}$) in DMF/water (98:2, v/v) containing Britton–Robison buffer (10 mM, pH = 7.0) upon additions of various metal ions ($10 \times 10^{-5} \text{ M}$).

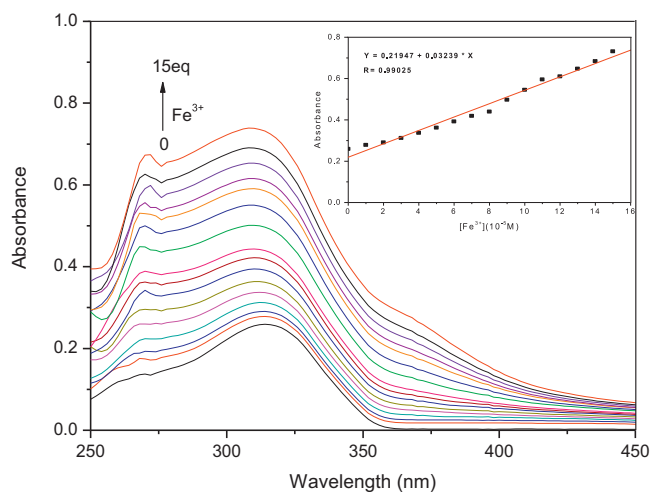


Fig. 4. UV absorbance spectra of **1** (1.0×10^{-5} M) in DMF/water (98:2, v/v) containing Britton–Robinson buffer (10 mM, pH = 7.0) upon the addition of various amounts of Fe^{3+} . The inset shows the absorbance intensity at $\lambda_{\text{max}} = 314$ nm as a function of Fe^{3+} concentration.

increasing concentration of Fe^{3+} from 0 to 15×10^{-5} M. A satisfactory linear relationship between UV–vis absorbance and Fe^{3+} concentration was observed with the correlation coefficient as high as 0.99.

The fluorescence titration spectra of **1** with Fe^{3+} shows an emission maximum peak at 389 nm (Fig. 5). The fluorescence quantum yield of compound **1** in the absence of Fe^{3+} was calculated to be 0.052 with respect to quinine sulphate in 0.1 N H_2SO_4 solution ($\Phi_s = 0.54$) [26]. As Fe^{3+} ion was gradually titrated, the fluorescence intensity of compound **1** gradually decreased and when the amount of Fe^{3+} ion added was about 15×10^{-5} M, the fluorescence intensity reduced to 17.0% of the initial one. The quantum yield of **1** was calculated to be 0.011 in the presence of Fe^{3+} ion (15×10^{-5} M). To determine the stoichiometry of compound **1** and Fe^{3+} ion in the complex, Job's method [27] was employed by using the emission changes at 389 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 association constant was calculated to be $6.45 \times 10^3 \text{ M}^{-1}$ (error limits $\leq 10\%$) by a Benesi–Hildebrand

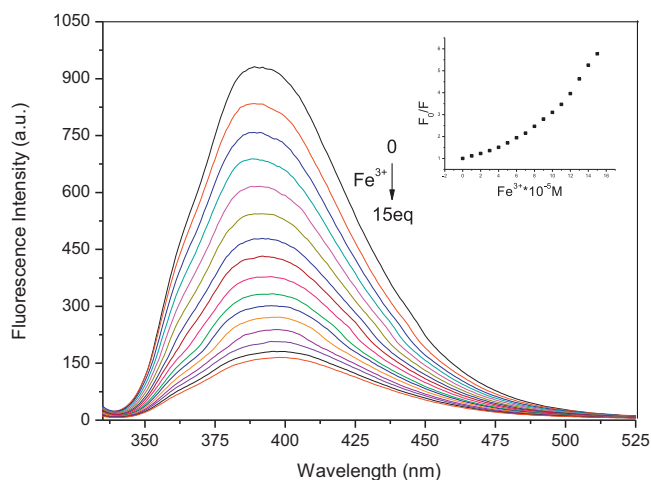


Fig. 5. Fluorescence emission spectra of compound **1** (1.0×10^{-5} M) was titrated with $\text{Fe}(\text{H}_2\text{O})_6\text{Cl}_3$ in DMF/water (98:2, v/v) containing Britton–Robinson buffer (10 mM, pH = 7.0). The concentration of Fe^{3+} : $1\text{--}15 \times 10^{-5}$ M.

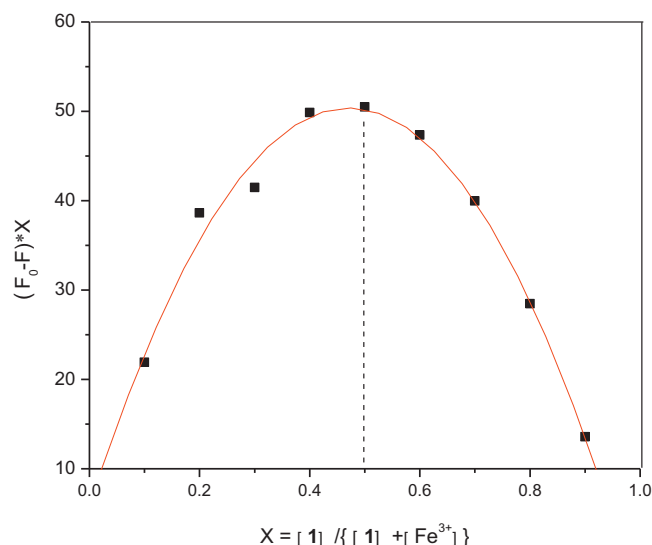


Fig. 6. Job's plot for determining the stoichiometry for **1** and Fe^{3+} in DMF/water (98:2, v/v) containing Britton–Robinson buffer (10 mM, pH = 7.0). Total concentration = 1.0×10^{-5} M.

plot [28] (Fig. 7). The detection limit, based on the definition by IUPAC ($C_{\text{DL}} = 3 \text{ Sb/m}$) [29], was found to be 9.7×10^{-7} M from 10 blank solutions.

The selectivity and tolerance of compound **1** for Fe^{3+} ion over other metal cations such as K^+ , Na^+ , Cr^{3+} , Mg^{2+} , Hg^{2+} , Cd^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Fe^{2+} , Mn^{2+} , and Cu^{2+} ions were investigated by adding metal cations (10×10^{-5} M) to the solution of compound **1** (10×10^{-5} M). As depicted in Fig. 8, Fe^{3+} 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 Fe^{3+} ion.

To further gauge selectivity for Fe^{3+} ion over other metal ions, the competition experiments was also carried by adding 10 equiv. of other metal ions to the solution of **1** (1×10^{-5} M) in the presence of 10 equiv. of the Fe^{3+} ion and the results were shown in Fig. 9. No significant variation in fluorescence intensity was found except for a little quenching by Cu^{2+} , which indicates that the signaling of Fe^{3+} by **1** is hardly affected by these common coexistent metal ions.

The proposed binding mechanism of Fe^{3+} with **1** was shown in Fig. 10. It should be noted that other coordination sites of the six-coordinate iron may be occupied by the solvents and the

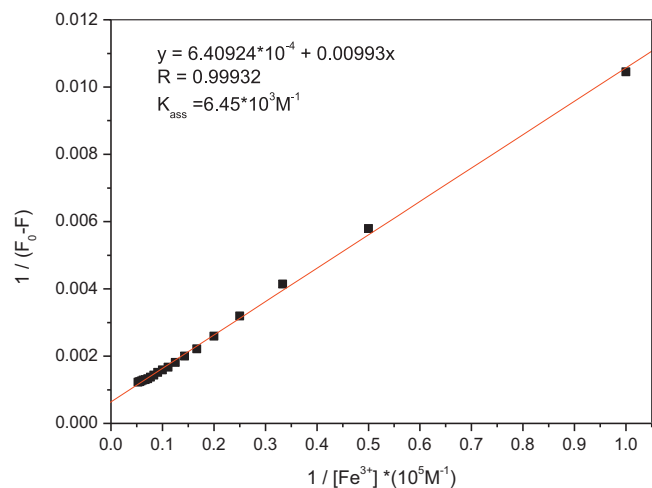


Fig. 7. Benesi–Hildebrand linear analysis plots of **1** at different Fe^{3+} concentration.

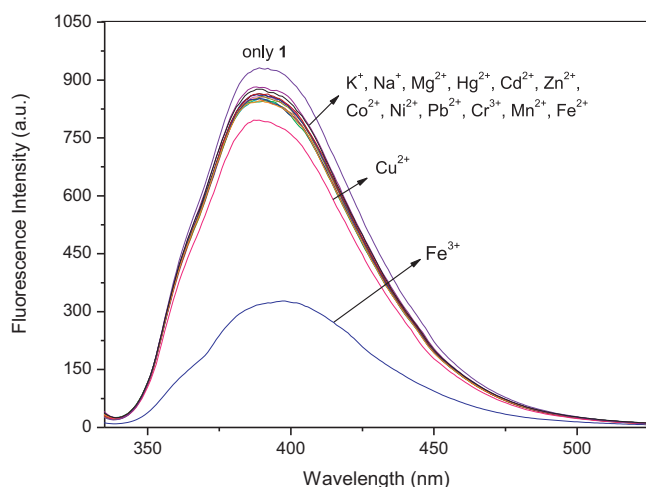


Fig. 8. Fluorescence spectra of **1** (1.0×10^{-5} M) in DMF/water (98:2, v/v) containing Britton–Robinson buffer (10 mM, pH = 7.0) in the presence of different metal ions (10 equiv.). Excited at 314 nm.

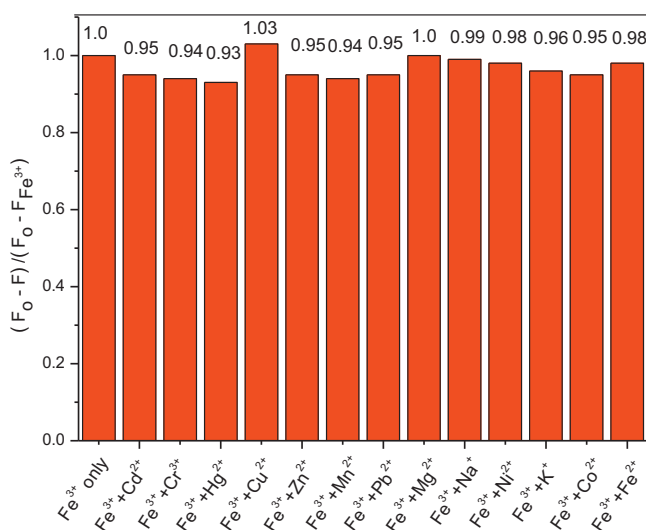


Fig. 9. Competitive experiments in the **1** + Fe^{3+} system with interfering metal ions. **1** = 1×10^{-5} M, $[\text{Fe}^{3+}] = 10 \times 10^{-5}$ M, and $[\text{M}^{n+}] = 10 \times 10^{-5}$ M. Excited at 314 nm and emission collected at 389 nm.

counteranions of Fe^{3+} . ESI mass spectra provide evidence of the formation of a 1:1 **1**– Fe^{3+} complex in 98% DMF solution (see Fig. S1 in Supplementary data). The peak at $m/z = 567.36$, corresponding to $[\text{1} + \text{Fe}^{3+} + 2\text{Cl}^- + \text{H}_2\text{O}]^+$, is observed when FeCl_3 (30 μM) is added to **1** (10 μM). Whereas free **1** exhibits a peak at $m/z = 424.34$, which corresponds to $[\text{1} + \text{H}]^+$ (Fig. S2). Moreover, the complexation of Fe^{3+}

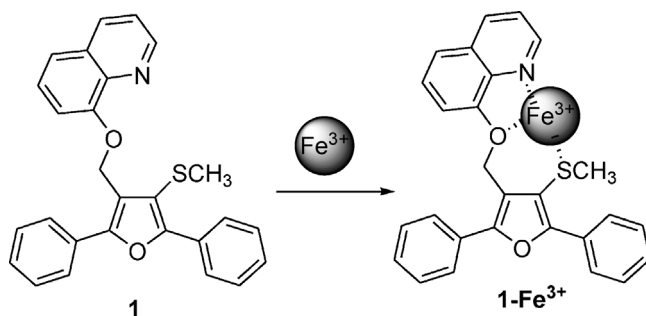


Fig. 10. Proposed binding model of **1** with Fe^{3+} .

ion requires the coordination of O, N atom of quinoline and S atom of methylthio group of **1**, which was supported by Fe^{3+} induced chemical shift of **1** changes in the ^1H NMR spectra (see Figs. S3 and S4 in Supplementary data). In the presence of 5.0 equiv. of Fe^{3+} ions, chemical shifts of proton NMR signals corresponding to the methylthio– CH_3 , the bridged $-\text{CH}_2-$ group was upfield shifted by 0.048 and 0.057 ppm, respectively. In the same way, obvious change in the chemical shifts of proton of quinoline–H is also can be observed owing to the binding of the Fe^{3+} . These results suggest that the quinoline and methylthio group are involved in the complexation with Fe^{3+} ion.

4. Conclusion

In summary, a new selective fluorescent sensor based on 2,5-diphenylfuran and 8-hydroxyquinoline was synthesized and used for the determination of Fe^{3+} ion with high selectivity in aqueous DMF. 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. 919472. Copy of this information may be obtained free of charge via <http://www.ccdc.cam.ac.uk> or from The Director, CCDC, 12 Union Road, Cambridge CB221EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk). Structural factors are available on request from the authors.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jphotochem.2013.07.009>.

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