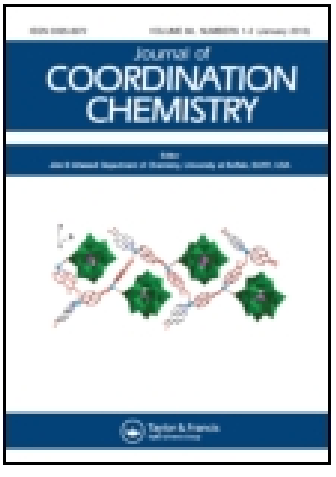


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

An off-on fluorescent sensor with high selectivity and sensitivity for Fe(III)

Junmei An[a], Tianrong Li[a], Baodui Wang[a], Zhengyin Yang[a] & Mihui Yan[a]

[a] State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, PR China

Accepted author version posted online: 13 Mar 2014.Published online: 04 Apr 2014.

To cite this article: Junmei An, Tianrong Li, Baodui Wang, Zhengyin Yang & Mihui Yan (2014) An off-on fluorescent sensor with high selectivity and sensitivity for Fe(III), Journal of Coordination Chemistry, 67:5, 921-928, DOI: 10.1080/00958972.2014.903474

To link to this article: http://dx.doi.org/10.1080/00958972.2014.903474

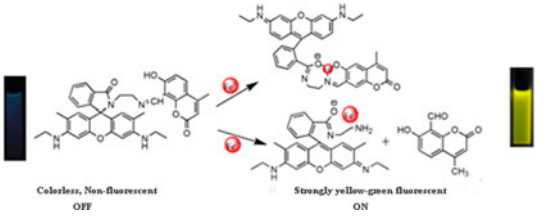
Journal of Coordination Chemistry, 2014
Vol. 67, No. 5, 921–928, http://dx.doi.org/10.1080/00958972.2014.903474

An off-on fluorescent sensor with high selectivity and sensitivity for Fe(III)

JUNMEI AN, TIANRONG LI, BAODUI WANG, ZHENGYIN YANG* and MIHUI YAN

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, PR China

(*Received 7 September 2013; accepted 10 February 2014*)



A new fluorescent derivative (**1**) containing coumarin exhibits Fe(III)-selective strong yellow-green fluorescence in ethanol. This compound could be used as an "off-on" chemosensor and allow the detection of Fe^{3+} by monitoring changes in absorption and fluorescence spectra. Upon addition of Fe^{3+}, an overall emission change of 125-fold was observed. High selectivity and sensitivity were observed over other metal ions, mainly due to the spirolactam ring-opening power of Fe^{3+}. The detection limit was as low as 5.6 ppb. Photo-induced electron transfer, coupled with intramolecular charge transfer are proposed to account for the observed spectral response.

Keywords: Fluorescent derivative; Fe^{3+} probe; Selectivity; Sensitivity; Detection limit

1. Introduction

Design of highly selective and sensitive fluorescent chemosensors for heavy and transition metal cations is an area of intense research activity [1]. As one of the most essential trace elements in biological systems, Fe^{3+} performs a major role in many biochemical processes at the cellular level [2]. High levels of Fe^{3+} within the body have been associated with increasing incidence of certain cancers and dysfunction of certain organs, such as the heart, pancreas, and liver [3]. Recent research suggests that Fe^{3+} could also be involved in the underlying mechanisms of many neurodegenerative diseases, such as Parkinson's disease and Alzheimer's disease [4]. Therefore, a convenient and rapid method for analysis of Fe^{3+} in biological samples has important consequences in biological and environmental concerns. Much effort has been devoted to the development of Fe^{3+}-selective fluorescent

*Corresponding author. Email: yangzy@lzu.edu.cn

chemosensors. Unfortunately, there have been few fluorescent chemosensors for Fe^{3+} because of the fluorescent quenching of the paramagnetic Fe^{3+} [5]. Recently, Lee *et al.* [6] developed a Fe^{3+}-selective sensor that could demonstrate sensitive and selective detection of intracellular Fe^{3+} in hepatocytes. At present, research related to this area is of great and interest.

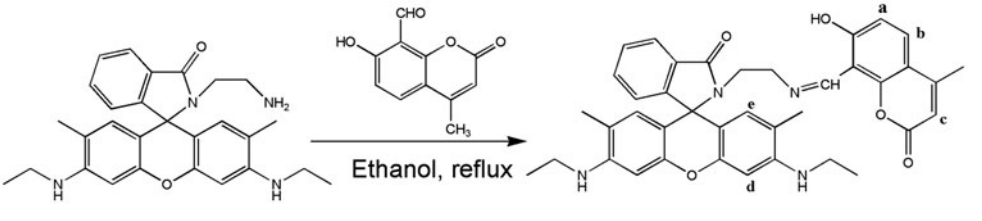
Several methods have been reported for detecting iron including atomic absorption spectroscopy [7], colorimetry [8], spectrophotometry [9–11], and voltammetry [12], which are costly, time-consuming, generally require sophisticated equipment, tedious sample preparation procedures, and trained operators. On the other hand, fluorescent signaling has been widely used in environmental and biological science [13], with rhodamine used extensively as a fluorescent labeling reagent and a dye laser source [14] owing to its simplicity, low detection limit, the capability for special recognition [15], and excellent photo-physical properties [16]. Recently, on the basis of spirolactam to ring-open the amide equilibrium of rhodamine, a number of rhodamine dyes have been utilized for detection of metal ions, such as Cu^{2+} [17–19], Pb^{2+} [20], Hg^{2+} [21–31], and Cr^{3+} [32]. Although rhodamine derivatives are the most widely studied and used fluorescent labeling reagent and a dye laser source, very few investigations have been carried out on their coumarin analogs.

We report in this paper a new "off-on" fluorescent sensor **1** (scheme 1) for Fe^{3+}. The chemosensor was designed on the basis of a coumarin–rhodamine scaffold as PET platform. The structure of **1** was confirmed by ^1H NMR, mass data, IR spectra, and elemental analysis. Compared with other metal ions examined, the new fluorescent sensor **1** showed very high selectivity and sensitivity towards Fe^{3+} in ethanol, thus indicating further potential for cellular imaging.

2. Experimental

2.1. *Material and measurements*

All solvents and reagents were obtained from commercial suppliers and used without purification. ^1H NMR spectra were measured on a Bruker Avance DRX 300-MHz spectrometer with TMS as an internal standard. ESI-MS were determined on a Bruker Esquire 6000 spectrometer. UV–vis absorption spectra were recorded on a Perkin Elmer Lambda 35 UV–vis spectrophotometer. Fluorescence spectra were generated on a Hitachi RF-5301 spectrophotometer equipped with quartz cuvettes of 1 cm path length. Elemental analyses were carried out on an Elemental Vario EL analyzer. IR spectra were obtained in KBr disks on a Therrno Mattson FTIR spectrometer from 4000 to 400 cm^{-1}. The melting points of the compounds were determined on a Beijing XT4-100× microscopic melting point apparatus.



Scheme 1. Synthesis of chemosensor **1**.

2.2. *Synthesis*

8-Formyl-7-hydroyl-4-methylcoumarin [33] and rhodamine-6G hydrazide [18] were prepared following literature methods.

In a 250 mL three-necked round bottom flask, 8-formyl-7-hydroyl-4-methylcoumarin (a) (0.245 g, 1.2 mM) was dissolved in hot ethanol (35 mL) and heated to reflux in an oil bath. Then, a solution of rhodamine-6G hydrazide (b) (0.468 g, 1 mM) in ethanol (80 mL) was added dropwise to the flask in 1 h and the mixture was heated under reflux for 12 h. Finally, the yellow precipitate was filtered, dried, and obtained with a yield of 80.8% (0.518 g). The crude product was purified by recrystallization from DMF to give 0.302 g of **1** as a white solid (58.3%, m.p. > 300 °C). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 1.31 (t, 6H, J = 8.0 Hz), 1.88 (d, 6H, J = 9.0 Hz), 2.36 (s, 3H), 3.19 (d, 4H, J = 10.5 Hz), 3.33 (t, 2H, J = 5.8 Hz), 3.52 (t, 2H, J = 6.1 Hz), 6.02 (s, 1H), 6.23 (s, 2H), 6.37 (s, 2H), 6.74 (d, 1H, J = 6.9 Hz), 7.07 (s, 1H), 7.47 (d, 2H, J = 12.0 Hz), 7.71 (d, 1H, J = 7.9 Hz), 7.96 (d, 1H, J = 7.9 Hz), 8.51 (s, 1H). ESI-MS: m/z 561.5 $(M + H)^+$. IR (KBr, cm^{-1}): $\nu_{C=O\ (Amide)}$: 1730, $\nu_{(Schiff\text{-}base)\ C=N}$: 1632. Elemental Analysis (Calcd for $C_{31}H_{20}N_2O_7$): C, 72.58 (72.86); H, 6.01 (5.92); N, 8.80 (8.72).

2.3. *Analysis*

Stock solutions (1 mM) of **1** and the nitrate salts (Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ba^{2+}, Pb^{2+}, Ag^+, Hg^{2+}, and Fe^{3+}) were prepared in ethanol. Solutions of different anions (F^-, Cl^-, Br^-, I^-, NO_2^-, NO_3^-, SO_3^{2-}, SO_4^{2-}, HSO_4^-, CO_3^{2-}, HCO_3^-, ClO_3^-, ClO_4^-, $H_2PO_4^-$, and AcO^-) were prepared in water. Test solutions were prepared by placing 20 µL of the probe stock solution into cuvettes, adding an appropriate aliquot of each ion stock solution, and diluting the solution to 2 mL with ethanol. Both the excitation and emission slit widths were 3.0 nm.

3. Results and discussion

In the present study, we have chosen rhodamine and coumarin derivatives as the fluorophores in synthesizing the receptor molecule **1**. Details about the synthesis of **1** have been discussed above and its characterization data are presented in the Supplementary material (Supplemental data for this article can be accessed http://dx.doi.org/10.1080/00958972.2014.903474).

3.1. *Spectral studies*

The binding behavior of **1** was studied towards Fe^{3+} as its nitrate salt by UV–vis and fluorescence spectroscopy. The absorption spectrum of **1** in ethanol shows two absorptions around 305 and 415 nm (figure 1) due to coumarin, but there was no absorption observed above 500 nm in the absence of metal ions, indicating that only the ring-closed form was present. However, on addition of Fe^{3+} (0–1.0 equiv.), the intensity of the band around 305 and 415 nm increased in intensity and a new absorption band appeared at 538 nm along with a color change from colorless to pink. The formation of a new band around 538 nm is attributed to the interaction of Fe^{3+} with the receptor **1**, leading to the opening of the

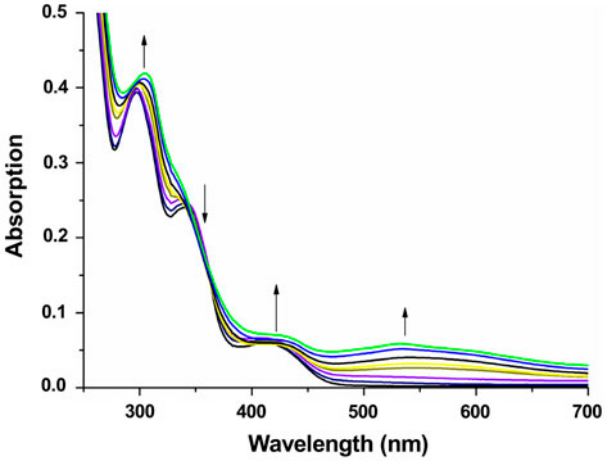


Figure 1. The changes of absorption spectrum of **1** (1.0×10^{-5} M) in ethanol upon addition of Fe^{3+} (0–1.0 equiv.) at room temperature.

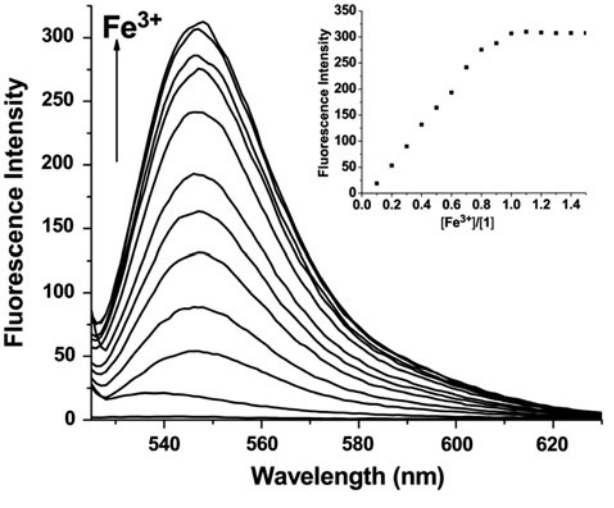


Figure 2. Plot of the changes in the fluorescence spectral pattern for receptor **1** (1×10^{-5} M) in the presence of varying $[Fe(NO_3)_3]$ (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 equiv.) in ethanol ($\lambda_{ex} = 500$ nm, $\lambda_{em} = 550$ nm, excitation and emission slit 3 nm).
Inset: the increase in fluorescence emission intensity related to the amounts of Fe^{3+} added.

spirolactam ring. Meanwhile, two isosbestic points at 350 and 368 nm were observed, which indicate the formation of a compound of **1** with Fe^{3+}. Higher concentrations of Fe^{3+} do not lead to any further change, suggesting that a 1 : 1 stoichiometry of Fe^{3+} and **1** was formed.

Figure 2 shows the fluorescence spectra of **1** exposed to ethanol containing different concentrations of Fe^{3+} (0–1.2 equiv.) recorded at an excitation wavelength of 500 nm and

emission wavelength of 525–630 nm. Upon addition of Fe^{3+}, the fluorescence emission intensity of the dosimeter at $\lambda_{ex} = 500$ nm and $\lambda_{em} = 550$ nm was increased 125-fold. As shown from the inset of figure 1, the emission intensity of **1** increased linearly as a function of Fe^{3+} concentration and it was saturated at l.0 equiv. of Fe^{3+}, which indicates formation of a 1 : 1 complex. The optical properties of **1** and its complex are mainly dominated by the rhodamine group. The remarkable fluorescence enhancement at 550 nm belongs to the fluorescent open-ring moiety. So, it can be presumed that Fe^{3+} leads to spirocycle opening of **1** via coordination as shown in scheme 2.

The relationship between the fluorescence intensity I and concentration of Fe^{3+} was $I = 3.654 \times 10^6$ c-18.492 (figure S1). The linear range of the method was found to be 1.0×10^{-5} to 7.0×10^{-5} M L^{-1} Fe^{3+} with a correlation coefficient of $R^2 = 0.9968$. The detection limit of **1** as fluorescence sensor for analysis of Fe^{3+} ions was 5.6 ppb (figure S2), which indicates that **1** was highly sensitive to Fe^{3+}. Fluorescence quantum yield measurements were carried out for the sensor to understand its fluorescence behavior observed. The fluorescence quantum yield (Φ) of **1** in the free and Fe^{3+}-bound state was 0.04 and 0.29, respectively.

3.2. *Application value studies*

Selectivity is a very important parameter to evaluate the performance of a new fluorescent probe. A highly selective response to the target over other potentially competing species is a necessity. The nitrate salts of Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ba^{2+}, Pb^{2+}, Ag^+, Hg^{2+}, and Fe^{3+} ions were used to evaluate the selectivity of **1** (10 μM) in ethanol. Among these metal ions, **1** showed selective fluorescence enhancement only with Fe^{3+} among the various metal ions examined in ethanol, indicating that **1** displayed a high Fe^{3+} selectivity (figure 3). Furthermore, competition experiments of Fe^{3+} mixed with the above-mentioned metal ions show that no significant variation is

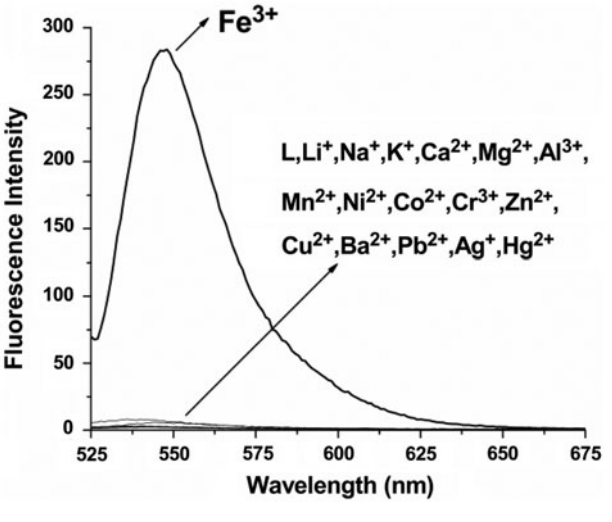


Figure 3. Fluorescence emission spectra of **1** (1.0×10^{-5} M) upon addition of 1.0 equiv. of Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ba^{2+}, Pb^{2+}, Ag^+, Hg^{2+} and Fe^{3+} in ethanol. The excitation was at 500 nm, and the emission was at 550 nm, excitation and emission slit width of 3 nm.

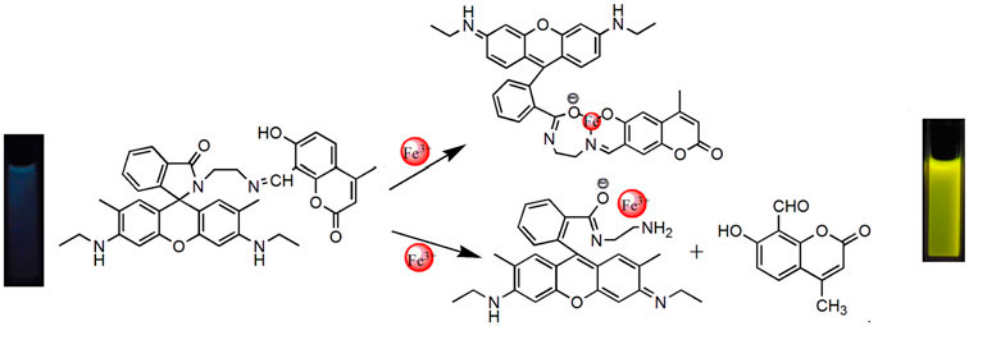
observed in fluorescence intensity (figure S3). Moreover, competition experiments of Fe^{3+} mixed with different anions (F^-, Cl^-, Br^-, I^-, NO_2^-, NO_3^-, SO_3^{2-}, SO_4^{2-}, HSO_4^-, CO_3^{2-}, HCO_3^-, ClO_3^-, ClO_4^-, $H_2PO_4^-$, and AcO^-) were tested (figure S4). The response of **1** for Fe^{3+} in the presence of ClO_4^- and AcO^- is relatively low but clearly detectable. Relatively low interference was observed for detection of Fe^{3+} in the presence of other anions. These facts indicate that **1** can be used as a selective fluorescent sensor for Fe^{3+} in the presence of most competing metal ions. According to the similar binding sites of the reported fluorescent chemosensor [5b, 34], the high selectivity and competitive behavior for Fe^{3+} of the probe are ascribed to the chemical structure of **1** containing oxygens and nitrogens in a special arrangement (scheme 2).

To test if the proposed complex could be reversed, a reversibility experiment was also carried out. Because of the high stability of the EDTA–Fe^{3+} complex, it could be expected that addition of EDTA will capture Fe^{3+} from the metal–ligand complex and release free **1**. Therefore, 1.0 equiv. of EDTA (20 μM) was added to the Fe^{3+} (20 μM) complex of **1** (20 μM) in ethanol. The addition of Na_2EDTA to the solution of **1**–Fe^{3+} complex resulted in gradual quenching of the fluorescence intensity at $\lambda_{em} = 550$ nm (figure S5). These results demonstrate that Fe^{3+} binding of **1** is chemically reversible, beneficial for the dynamic monitoring of the concentration change of Fe^{3+} in various samples.

3.3. *Binding properties and Job's plot*

The plot of measured fluorescence $F_0/(F - F_0)$ against $1/[Fe^{3+}]$ showed a linear relationship confirming the formation of a 1 : 1 complex between **1** and Fe^{3+}. The association constant (K_a) of **1** for Fe^{3+} was calculated to be $1.1 \times 10^7\ M^{-1}$ from the plot, which unambiguously demonstrates the strong binding ability of **1** with Fe^{3+} (figure S6). The linear equation is $y = 9.0652 \times 10^{-8}x - 0.0026$, with a correlation coefficient of $R^2 = 0.9925$.

To determine the stoichiometry of the **1**–Fe^{3+} complex, Job's method [35] was applied. The fluorescence emission was measured for each sample with the excitation wavelength at 500 nm, and the fluorescence intensities of **1** in the absence (I_0) and presence (I) of Fe^{3+} were determined, respectively. A plot of ΔI ($\Delta I = I - I_0$) *versus* X_M shows that the value goes through a maximum at molar fraction of about 0.5 (figure S7), indicating a 1 : 1 complex was formed. This 1 : 1 stoichiometry was further confirmed from results of the ESI-MS data with a peak of $[\mathbf{1} + Fe]^+$ at *m*/*z* 699.5 (figure S8).



Scheme 2. Schematic presentation showing Fe^{3+} binding mode of **1**.

3.4. *IR and NMR spectra*

IR spectra of **1** revealed that the peak at 1730 cm^{-1}, the characteristic frequency for the $C{=}O_{amide}$ bond of the rhodamine unit, shifted to 1607 cm^{-1} on coordination to Fe^{3+}, in the presence of 1.0 equiv. of the metal ion (figure S9). Such shift in the stretching frequency of the $C{=}O_{amide}$ bond of the rhodamine on binding to a metal ion was reported earlier [25]. This appreciable shift supports coordination of the $O_{>CO}$ of the fluorescent unit to Fe^{3+}. In the complex, the band at 616 cm^{-1} was assigned to $\nu_{(Fe-O)}$, which demonstrated the formation of a bond between iron and oxygen.

NMR spectroscopy has been widely used for studying the binding mode between coumarin–rhodamine hydrazone and metal cations. Coordination of the metal cation to the ligand induces conformational reorganization of the ligand and as a result, the chemical shifts of the protons near to the coordination site undergo certain changes [36].

^1H NMR shows appreciable downfield shifts of the associated aromatic protons (figure S10). These shifts were more pronounced for H_d and H_e protons ($\Delta\delta = 0.45,\ 0.32$ ppm), which revealed opening of the spirolactam ring on coordination to Fe^{3+} with associated inner charge transfer in the aromatic rings of the xanthene. Downfield shifts of H_a, H_b, and H_c ($\Delta\delta = 0.22$, 0.18, and 0.03 ppm, respectively) of the coumarin indicate involvement of its carbonyl oxygen in Fe^{3+} binding. The proton signals of H_f ($-CH_2N-$) shifted about 1.47 ppm, which demonstrated that nitrogen of the Schiff-base participated in coordination to Fe^{3+}.

Also, from the ESI-MS data, we found a peak at m/z 457.5 (figure S8) assigned to rhodamine 6G ethylenediamine [37]. So, the mechanism for the sensor to bind to Fe^{3+} should be complexation accompanied by hydrolysis and the possible binding mode for **1** to Fe^{3+} is suggested in scheme 2.

4. Conclusion

We have synthesized a fluorescence sensor (**1**) for Fe^{3+}, which has high sensitivity, selectivity, and low detection limit. **1** shows a 125-fold fluorescence enhancement in the presence of Fe^{3+} and has not been significantly affected by the presence of physiologically and environmentally important alkali, alkaline earth, and transition metal ions. Compared to previous work by Liu and Chavan [38, 39], the excitation wavelength of the sensor in this paper is 500 nm, which is in the visible region (400–700 nm). Therefore, the excitation light would not damage the cells or the damage could be overlooked. The quantum yield of the previous work by Jin [40] was 0.149. However, the fluorescence quantum yield of **1**–Fe^{3+} was found to be 0.29. The association constant (K_a) of **1** for Fe^{3+} was calculated to be $1.1 \times 10^7\ M^{-1}$, the association constant of previous work by Jia [41] was only $10^3\ M^{-1}$. In summary, we believe that the fluorescence sensor has potential application in environmental, biological, and medical areas.

Funding

This work is supported by the National Natural Science Foundation of China [grant number 81171337].

References

[1] (a) L. Prodi, F. Bolletta, M. Montalti, N. Zaccheroni. *Coord. Chem. Rev.*, **205**, 59 (2000); (b) K. Rurack. *Spectrochim.,* Acta, Part A, **57**, 2161 (2001).

[2] (a) B. D'Autreaux, N.L. Tucker, R. Dixon, S. Spiro. *Nature*, **437**, 769 (2005); (b) J.W. Lee, J.D. Helmann. *Nature*, **440**, 363 (2006); (c) H. Weizman, O. Ardon, B. Mester, J. Libman, O. Dwir, Y. Hadar, Y. Chen, A. Shanzer. *J. Am. Chem. Soc.*, **118**, 12368 (1996); (d) J.P. Sumner, R. Kopelman. *Analyst*, **130**, 528 (2005).

[3] (a) B.J. Halliwell. *Neurochem.*, **59**, 1609 (1992); (b) E.D. Weinberg. *Eur. J. Cancer Prev.*, **5**, 19 (1996); (c) D. Galaris, V. Skiada, A. Barbouti. *Cancer. Lett.*, **266**, 21 (2008).

[4] (a) R.R. Crichton, D.T. Dexte, R. Ward. *J. Coord. Chem. Rev.*, **252**, 1189 (2008); (b) A.S. Dornelles, V.A. Garcia, M.N. Lima, G. Vedana, L.A. Alcalde, M.R. Bogo, N. Schroeder. *Neurochem. Res.*, **35**, 564 (2010).

[5] (a) J.L. Bricks, A. Kovalchuk, C. Trieflinger, M. Nofz, M. Bueschel, I. Tolmachev, J. Daub, K. Rurack. *J. Am. Chem. Soc.*, **127**, 13522 (2005); (b) Y. Xiang, A. Tong. *J. Org. Lett. Organic.*, **8**, 1549 (2006); (c) X. Zhang, Y. Shiraishi, T. Hirai. *Tetrahedron. Lett.*, **48**, 5455 (2007); (d) L. Dong, C. Wu, X. Zeng, L. Mu, S.F. Xue, Z. Tao, J.X. Zhang. *Sens. Actuators. B.*, **145**, 433 (2010).

[6] M.H. Lee, T.V. Giap, S.H. Kim, Y.H. Lee, C. Kang, J.S. Kim. *Chem. Commun*, **46**, 1407 (2010).

[7] A. Ohashi, H. Ito, C. Kanai, H. Imura, K. Ohashi. *Talanta.*, **65**, 525 (2005).

[8] Z.Q. Liang, C.X. Wang, J.X. Yang, H.W. Gao, Y.P. Tiang, T.X. Tao, M.H. Jiang. *N. J. Chem*, **31**, 906 (2007).

[9] S. Lunvongsa, M. Oshima, S. Motomizu. *Talanta.*, **68**, 969 (2006).

[10] Z.O. Tesfaldet, J.F. Staden, R.I. Stefan. *Talanta.*, **64**, 1189 (2004).

[11] D.M.C. Gomes, M.A. Segundo, J.L.F.C. Lima, A.O.S.S. Rangel. *Talanta.*, **66**, 703 (2005).

[12] A. Bobrowski, K. Nowak, J. Zarebski. *Anal. Bioanal. Chem.*, **382**, 1691 (2005).

[13] (a) S. Malashikhin, N.S. Finney. *J. Am. Chem. Soc.*, **130**, 12846 (2008); (b) M.E. Ostergaard, P. Cheguru, M.R. Papasani, R.A. Hill, P.J. Hrdlicka. *J. Am. Chem. Soc.*, **132**, 14221 (2010); (c) S.S. Tan, S.J. Kim, E.T. Kool. *J. Am. Chem. Soc.*, **133**, 2664 (2011).

[14] (a) M.M. Pires, J. Chmielewski. *Org. Lett.*, **10**, 837 (2008); (b) S. Kou, H.N. Lee, D. Noort, K.M.K. Swamy, S.H. Kim, J.H. Soh, K.M. Lee, S.W. Nam, J. Yoon, S. Park. *Angew. Chem. Int. Ed.*, **47**, 872 (2008); (c) J.F. Zhang, Y. Zhou, J. Yoon, Y. Kim, S.J. Kim, J.S. Kim. *Org. Lett.*, **12**, 3852 (2010).

[15] R.W. Ramette, E.B. Sandell. *J. Am. Chem. Soc.*, **78**, 4872 (1956).

[16] J.R. Lakowicz. *Principles of Fluorescence Spectroscopy*, 3rd Edn, p. 67, Springer, New York, NY (2006).

[17] Y. Xiang, A.J. Tong, P.Y. Jin, Y. Ju. *Org. Lett.*, **8**, 2863 (2006).

[18] V. Dujols, F. Ford, A.W. Czarnik. *J. Am. Chem. Soc.*, **119**, 7386 (1997).

[19] Y.R. Kim, H.J. Kim, J.S. Kim, H. Kim. *Adv. Mater.*, **20**, 4428 (2008).

[20] J.Y. Kwon, Y.J. Jang, Y.J. Lee, K.M. Kim, M.S. Seo, W. Nam, J. Yoon. *J. Am. Chem. Soc.*, **127**, 10107 (2005).

[21] X.Q. Zhan, Z.H. Qian, H. Zheng, S.B. Yu, Z. Lan, J.G. Xu. *Chem. Commun.*, **16**, 1859 (2008).

[22] J.H. Huang, Y.F. Xu, X.H. Qian. *J. Org. Chem.*, **74**, 2167 (2009).

[23] J.S. Wu, I.C. Hwang, K.S. Kim, J.S. Kim. *Org. Lett.*, **9**, 907 (2007).

[24] H. Zheng, Z.H. Qian, L. Xu, F.F. Yuan, L.D. Lan, J.G. Xu. *Org. Lett.*, **8**, 859 (2006).

[25] M.H. Lee, J.S. Wu, J.W. Lee, J.H. Jung, J.S. Kim. *Org. Lett.*, **9**, 2501 (2007).

[26] S.K. Ko, Y.K. Yang, J. Tae, I. Shin. *J. Am. Chem. Soc.*, **128**, 14150 (2006).

[27] H. Yang, Z.G. Zhou, K.W. Huang, M.X. Yu, F.Y. Li, T. Yi, C.H. Huang. *Org. Lett.*, **9**, 4729 (2007).

[28] W. Huang, C. Song, C. He, G. Lv, X. Hu, X. Zhu, C. Duan. *Inorg. Chem.*, **48**, 5061 (2009).

[29] X.Q. Chen, S.W. Nam, M.J. Jou, Y. Kim, S.J. Kim, S. Park, J. Yoon. *Org. Lett.*, **10**, 5235 (2008).

[30] C.Y. Wang, K.M.C. Wong. *Inorg. Chem.*, **52**, 13432 (2013).

[31] E. Karakus, M. Üçüncü, M. Emrullahoğlu. *Chem. Commun.*, **50**, 1119 (2014).

[32] A.J. Weerasinghe, C. Shmiesing, E. Sinn. *Tetrahedron. Lett.*, **50**, 6407 (2009).

[33] D.R. Bender, D. Kanne, J.D. Frazier, H. Rapoport. *J. Org. Chem.*, **48**, 2709 (1983).

[34] B.D. Wang, J. Hai, Z.C. Liu, Q. Wang, Z.Y. Yang, S.H. Sun. *Angew. Chem. Int. Ed.*, **49**, 4576 (2010).

[35] P. Job. *Ann. Chim.*, **9**, 113 (1928).

[36] A.J. Pearson, W.J. Xiao. *J. Org. Chem.*, **68**, 5369 (2003).

[37] M.H. Lee, T.V. Giap, S.H. Kim, Y.H. Lee, C. Kang, J.S. Kim. *Chem. Commun.*, **46**, 1407 (2010).

[38] C.J. Liu, Z.Y. Yang, M.H. Yan. *J. Coord. Chem.*, **65**, 3845 (2012).

[39] S.S. Chavan, B.A. Yamgar, B.G. Bharate. *J. Coord. Chem.*, **66**, 1837 (2013).

[40] X.L. Jin, Z.Y. Yang, T.R. Li, B.D. Wang, Y. Li, M.H. Yan, C.J. Liu, J.M. An. *J. Coord. Chem.*, **66**, 300 (2013).

[41] X. Jia, X.T. Yu, G.L. Zhang, W.S. Liu, W.W. Qin. *J. Coord. Chem.*, **66**, 662 (2013).