Asian Journal of Chemistry; Vol. 25, No. 15 (2013), 8292-8296

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14722

A Highly Selective and Sensitive Fluorescent Sensor for Copper(II) Ion Characterized by One Dichlorofluorescein Moiety and Two Azathia-Crown Ether

YUZHU JIANG[1], ZHONG HUANG[2], HUAJUN DAI[1], LIHUA WANG[1], LIU YING[1] and XINGMING KOU[1,*]

[1]College of Chemistry, Sichuan University, Chengdu 610064, P.R. China
[2]Academy of Engineering Physics, Mianyang, Sichuan 621900, P.R. China

*Corresponding author: Fax: +8685412291; Tel: +13980995879; E-mail: kouxm@scu.edu.cn

(*Received*: 20 October 2012; *Accepted*: 19 August 2013) AJC-13936

A new fluorescent sensor **1**, which functionalized with one dichlorofluorescein moiety as fluorogenic signaling subunit and two azathia-crown ether macrocyclic as binding site was designed, synthesized and characterized. It was found that sensor **1** can selectively recognize Cu^{2+} by a remarkable emission quenching in DMSO-H_2O (1:1, v/v), which was attributed to the 1:2 complex formation between **1** and Cu^{2+}, while other ion including K^+, Na^+, Mg^{2+}, Zn^{2+}, Ba^{2+}, Co^{2+}, Ca^{2+}, Fe^{2+}, Fe^{3+}, Pb^{2+}, Pb^{2+}, Ni^{2+} and Ag^+ induced no or much small fluorescence changes. In addition, the sensor **1** exihibited a rapid, stable and linear response to Cu^{2+} in the concentration range from 5×10^{-7} to 1×10^{-5} mol L^{-1} with a detection limit as low as 8.7×10^{-8} mol L^{-1}. Furthermore, the sensor **1** was applied to practical determination of Cu^{2+} in different water samples with satisfactory results.

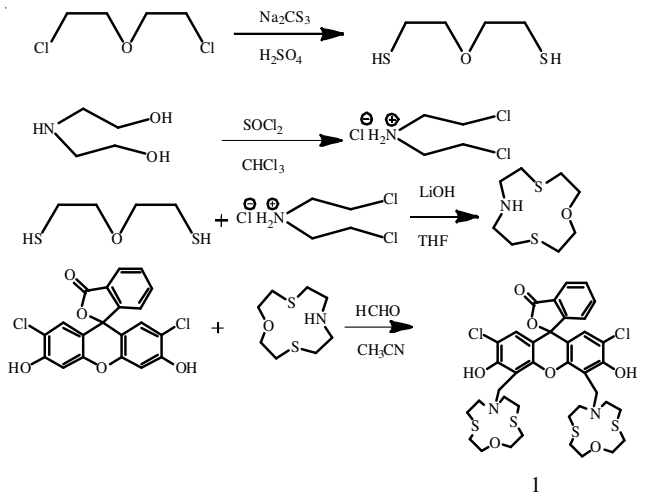
Key Words: Fuorescent probe, Azathia-crown ether, Dichlorofluorescein, Copper ion, Fluorescence quenching.

INTRODUCTION

Copper ions are essential for normal physiological processes of living things[1,2]. In humans, copper is the third most abundant transition metal ion[3-6], acting in several biological systems and also a cofactor in diverse biochemical processes of enzymes syntheses. Additionally, excessive amounts or defects in intake of copper ions cause several possible alterations to physiological processes[7,8], which result in systemic diseases and triggers, such as Menkes syndrome, amyotrophic lateral sclerosis and Wilson's disease[9]. At the same time, copper is an economically important element that is found in only trace quantities in the Earth's crust and main copper is often connected to effluents from septic tanks and municipal wastewaters, discharges from power plants as well as leaching from antifouling paints and pressure-treated docks pilings. It is well known that the free cupric ion is highly toxic for marine organisms[10,11]. Therefore, an efficient and reliable analytical systems for the trace levels of copper detection is urgent necessary. Thus far, various efficient and reproducible methods, such as atomic absorption spectrometry[12], inductively coupled plasma mass spectroscopy (ICP-MS)[13] and inductively coupled plasma atomic emission spectrometry (ICP-AES)[14] were established. However, most of these methods are usually complicated, time-consuming and costly. To the best of our knowledge, fluorescent probes are a class of superior sensors, which are extensively used in the field of heavy metal ion recognition and detection because of their sensitivity, simplicity and practicability[15]. So far, many effective fluorescent sensors for heavy metal ion including Cu^{2+} have been successfully developed[16-18]. However, there is still plenty of room for improvements in terms of fluorescence intensity quenching, selectivity, aqueous solubility, suitable fluorophores with a high fluorescence quantum yield and visible excitation and emission wavelengths, as well as availability without resorting to instruments.

Moving along these lines, we have developed a series of chemosensors for Hg^{2+} detection[19,20]. In this paper, we designed and synthesized a novel fluorescent chemosensor **1** (**Scheme-I**) for Cu^{2+} based on intramolecular charge transfer mechanism (ICT)[21,22], which is an effective signaling mechanism employed in the design of fluorescent sensors. As usual, the chemosensor is composed of two sections, namely a binding site and a signaling subunit connected through a covalent bond. The binding site is responsible for the interaction with the host and is designed bearing in mind supramolecular chemistry principles in order to achieve a high degree of complementarity between both components. The interaction between the binding site and the host is transformed in an easy-to observe output by the signalling subunit. Due to its superior properties to coordinate with heavy and transition metal ions[23-26], azathia-crown ether was chosen as receptors of sensor **1**. Similarly,

dichlorofluorescein moiety, which is widely used as a fluorophore with high fluorescence quantum yield and visible light excitation, was selected as signaling subunit in sensor **1**[27]. Sensor **1** shows a selective response for Cu^{2+} in the presence of other related heavy and transition metal ions in a wide pH range from 3 to 6 and a remarkable fluorescence quenching, which was ascribed to the suppressing of intramolecular charge transfer in sensor **1**. Keeping this in mind, a highly selective, sensitive and rapid-response fluorescent chemosensor **1** containing one signaling subunit and two binding sites was developed.



1

Scheme-I: Synthetic route of **1**

EXPERIMENTAL

Water used was twice-distilled through out all experiments. All the chemicals were of analytic grade and used as received. Dimethyl sulfoxide, sodium sulfide, carbon disulfide, concentrated sulfuric acid (98 %), thionyl chloride, concentrated hydrochloric acid (37 %), triethylamine, dichloromethane, chloroform, sodium carbonate, acetonitrile, tetrahydrofuran, diethanol amine, diethyl ether, ethanol, lithium hydroxide, paraformaldehyde were obtained from Chengdu KeLong Chemical Reagents Factory, dichlorofluorescein and dichlorodiethyl sulfide were purchased from Bailingwei Chemical Company. All the reagents used as received without further purification. Both acetonitrile and triethylamine were prepared by refluxing with calcium hydride and distilled at atmospheric pressure. Lithium hydroxide was dried at 120 ºC for about 10 h in vacuum oven.

Fluorescence spectrometric data were obtained on a Hitachi F-4500 fluorescence spectrophotometer with a 1-cm quartz cell. ^{1}H NMR spectra were determined on a Varian UNITY INVOA-400 MHz spectrometer. Mass spectra (MS) were measured on an API-3000LC/MS/MS spectrometer. Melting points were measured with a XRC-I melting point apparatus. The IR spectrometric data were obtained on a Perkin Elmer 16PC FT-IR spectrometer. All pH measurements were obtained on a pH-25 pH meter.

Synthesis: β,β-dimercaptodiethyl ether[20]. To a solution of sodium sulfide (48 g, 200 mmol) dissolved in 30 mL water, 25 mL of carbon disulfide (600 mmol) was added dropwise at room temperature. Then the reaction mixture was warmed to 40 ºC and allowed to stirred for 6 h. The excess carbon disulfide was removed by distillation at normal pressure. Then the procreant turkey red liquid was diluted with 75 mL of water, giving a transparent solution. Then 40 mL of carbon disulfide (0.3 mol) was added dropwise to the aqueous sodium trithiocarbonate obtained above at 20 ºC. Then the reaction mixture was allowed to stir for 5 h at 65 ºC. The resulting basic solution was extracted three times with ether after cooling to remove unreacted material and other nonacid impurity. Then sulfuric acid (3 mol L^{-1}) was added to the aqueous layer to adjust pH to 2 and the acidic aqueous medium was extracted four times with ether. The combined extract was washed with water until it became neutral and dried over anhydrous magnesium sulfate. Distillation at reduced pressure (15 mm Hg) after removing solvent gave β,β-dimercaptodi-ethyl ether as a colourless but quite odoriferous liquid in 65 % yield. Bp.: 110 ºC (15 mm Hg). ^{1}H NMR (ppm, $CDCl_3$, 400 MHz): δ 1.56-1.52 (t, 2H, SH), 2.62-2.57 (m, 4H, SCH_2), 3.51-3.48 (t, 4H, OCH_2). MS (*m/z*): 137 [M^{-1}].

Bis-(2-chloroethyl)amine hydrochloride[28] diethanolamine (21.9 g, 0.21 mol) was dissolved in chloroform (30 mL) in a 250 mL three necked round-bottomed flask keeping at 0 ºC. A solution of thionyl chloride (99.3 g, 0.84 mol) in chloroform (30 mL) was added dropwise to the above solution and stirred at 4-6 ºC for 2 h. Then the reaction mixture was placed at room temperature to react for 3 h and was heated to 60 ºC to react for 4 h. The reactant was then filtered and washed with chloroform to get a white solid *bis*-(2-chloroethyl)amine hydrochloride in 62 % yield. m.p.: 212-214 ºC. ^{1}H NMR (ppm, D_2O, 400 MHz): δ 3.49-3.46 (t, 4H, $ClCH_2$), 3.86-3.83 (t, 4H, NCH_2). IR (KBr, ν_{max}, cm^{-1}): 3423 (NH), 2952 (CH_2).

1-Oxa-4,7-dithia-10-azacyclododecane[29] a mixture of β,β'-dimercaptodiethyl ether (2.76 g, 120 mmol), *bis*-(2-chloroethyl)amine hydrochloride (3.58 g, 20 mmol) and lithium hydroxide (2.88 g,120 mmol) in absolute tetrahydrofuran (1500 mL) was refluxed under a nitrogen atmosphere for 5 days. The reaction mixture was filtered and then concentrated at reduced pressure. The residue was extracted three times with chloroform and the extract was washed with water. The solvent was removed after drying over anhydrous sodium sulfate. The crude product was recrystallized from hexane to give a white solid 1-oxa-4,7- dithia-10- azacyclododecane in 37 % yield. m.p.:62-63 º. ^{1}H NMR (ppm, $CDCl_3$, 400 MHz): δ 2.81-2.72 (m,13H, $CH_2SCH_2CH_2NH$), 3.58-3.56 (t, 4H, OCH_2). IR (KBr, ν_{max}, cm^{-1}): 3274, 3249 (NH), 2916, 2860, 2815 (CH_2), 1116 (OCH_2). MS (*m/z*): 208 $(M+1)^+$.

The sensor **1**[30] dichlorofluorescein (0.1368 g, 0.66 mmol) and paraformaldehyde (0.17 g, 5.66 mmol) were dissolved in acetonitrile (15 mL) in a 100 mL of three necked round-bottomed flask, then the mixture was refluxed under a nitrogen atmosphere for 0.5 h. With stirring, a solution of dichlorofluorescein (0.1245 g, 0.33 mmol) in 30 mL of CH_3CN-H_2O (1:1, v/v) was added to the above solution and then the mixture was refluxed for 24 h. The reaction mixture was first concentrated at reduced pressure to give a crude product. It was purified by silica gel chromatography using CH_2Cl_2-CH_3OH (10:1, v/v) as eluent, finally, a red solid was obtained by 45 % yield. The synthetic route of sensor **1** was shown in **Scheme-I**. ^{1}H

NMR (ppm, $CDCl_3$, 400 MHz): δ 2.83-2.67 (m, 24H, CH_2), 3.72-3.51 (m, 12H, CH_2), 6.79 (s, 2H, ArH), 7.31 (d, 1H, ArH), 7.66 (m, 2H, ArH), 8.20-8.16 (d, 1H, ArH); IR (KBr, ν_{max}, cm^{-1}): 3443 (OH), 2925 (CH_2), 1630.

RESULTS AND DISCUSSION

Fluorescence spectral characteristic of 1: The fluorescence behaviour of sensor **1** was investigated in DMSO-water (1:1, v/v) solvent systems. The excitation spectrum of sensor **1** was characterized by a maximum excitation at 500 nm. As shown in Fig. 1, the maximum emission wavelength was located at 546 nm. When Cu^{2+} was added to the solution of **1**, the fluorescence of **1** was quenched. In addition, the intensity of emission peak at 546 nm was found to be decreased gradually with the addition of Cu^{2+} to the solution of **1** and the maximum emission wavelength did not change, which constituted the basis for the recognition of Cu^{2+} with sensor **1** proposed in this work. At the same time, the coordination of sensor **1** and Cu^{2+} was found to be reversible by the changes of fluorescence. When 25 equiv. of Cu^{2+} was added to the solution of **1**, the fluorescence disappeared. While 25 times of concentration of EDTA is added subsequently, the fluorescence recovered at once, finally, fluorescence was quenched again upon the addition of Cu^{2+} (equiv). This phenomenon could be explained by intramolecular charge transfer mechanism (ICT), which is generally thought to be a typical signaling mechanism. Just as shown in **Scheme-II**, sensor **1** displayed intense fluorescence based on the charge transfer of electron-rich group (azathiacrown ether) to the electron-withdrawing group (dichlorofluorescein). After addition of Cu^{2+}, owning to the interaction between the fluorescent sensor **1** and Cu^{2+}, the above-mentioned ICT was suppressed. As a result, a fluorescence quenching was observed. Furthermore, the complexation stoichiometry of Cu^{2+} and **1** was studied and found to be 2:1 by the Job's plot, which was shown in Fig. 2.

Selectivity: Generally, high selectivity plays a vital role to determine whether a chemosensor is an excellent one or not, so the selectivity of sensor **1** has been studied in the presence of different alkali, alkaline earth and transition metal

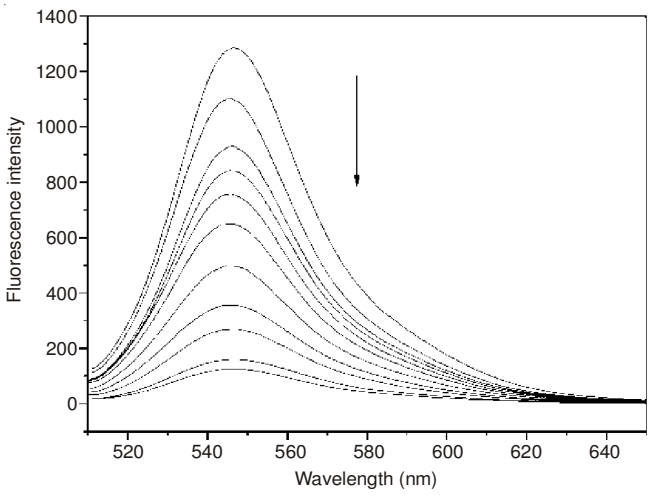
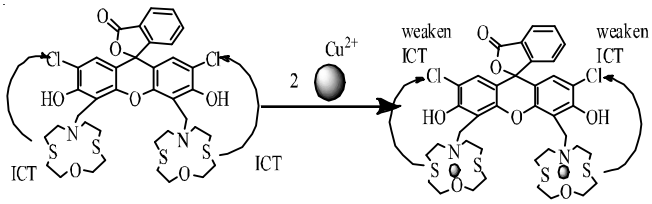


Fig. 1. Fluorescence titration of 1 (10^{-5} mol L^{-1}) with increasing concentration of Cu^{2+} (0.01, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 × 10^{-5} mol L^{-1}) in water-DMSO (1:1,v/v)



Scheme-II: Proposed binding mode of 1 with Cu^{2+} and sensing mechanis

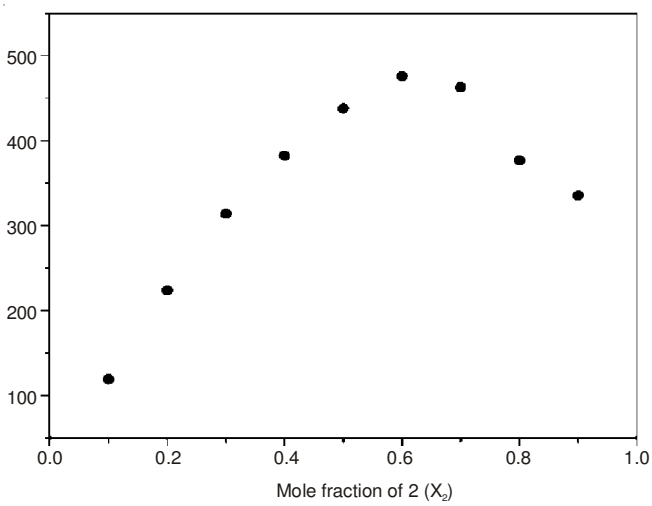


Fig. 2. Job's plot of 1-Cu^{2+} system in DMSO-water (1:1), [1]+[Cu^{2+}] = 1.0 × 10^{-5}

ions. It is found that Cu^{2+} has caused the most obvious fluorescence quenching after 5 equiv of K^+, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Ag^+, Hg^{2+} and Cu^{2+} were added respectively. Except for Ag^+, other ions induce a little fluorescence quenching under identical conditions as depicted in Fig. 3. This indicated that sensor **1** owns high selectivity to Cu^{2+}, though Ag^+ may induce some interferences. To evaluate quantitatively the selectivity of sensor **1**, we have investigated the selectivity coefficients[31] of Cu^{2+} *via* the formula $S_{Cu^{2+}}/S_0$, $S_{Cu^{2+}}$ is the fluorescent change caused by Cu^{2+}, S_0 is the fluorescent change induced by other ions. The selectivity coefficients of Cu^{2+} against other metal ions were listed in

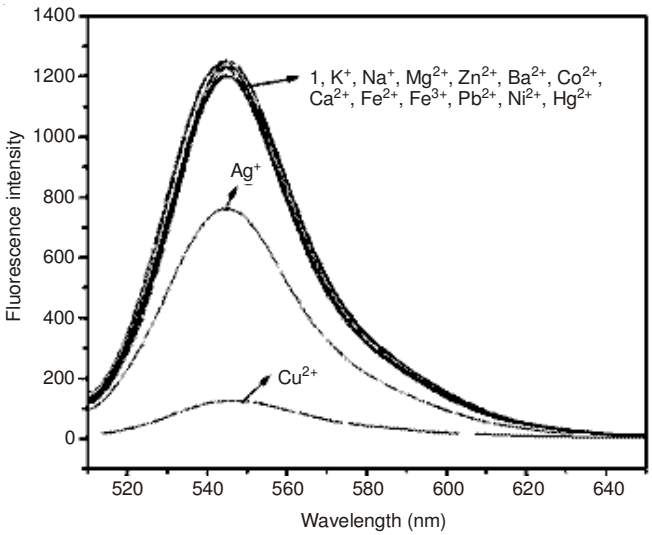


Fig. 3. Fluorescence spectra (excitation at 500 nm) of 1 in water-DMSO (1:1,v/v) and in the presence of 5 equiv of K^+, Na^+, Mg^{2+}, Zn^{2+}, Ba^{2+}, Co^{2+}, Ca^{2+}, Fe^{2+}, Fe^{3+}, Pb^{2+}, Pb^{2+}, Ni^{2+}, Ag^+, Cu^{2+}

Table-1. Apparently, **1** can recognize Cu^{2+} specifically in the presence of other metal ions. Actually, the azathia-crown ether moiety of sensor **1** played an important role in Cu^{2+} recognition. According to the theory of soft and hard acid-base, sulfur is a soft base, nitrogen is a middle-intensity base and Cu^{2+} is a soft acid, therefore, Cu^{2+} has a strong ability to coordinate with sulfur and nitrogen atoms to form a stable coordination compound, which gave **1** a high selectivity.

TABLE-1
SELECTIVITY COEFFICIENTS OF Cu^{2+} OVER OTHER SELECTED METAL IONS

Metal ion	Selectivity coefficient	Metal ion	Selectivity coefficient
Ca^{2+}	40.0	Cd^{2+}	40.1
Co^{2+}	42.7	Zn^{2+}	43.3
Fe^{3+}	42.5	Ni^{2+}	41.2
Ba^{2+}	44.5	Na^{+}	56.3
Mg^{2+}	46.5	K^{+}	56.0
Pb^{2+}	25.2	Fe^{2+}	47.4
Hg^{2+}	47.0	Ag^{+}	2.43

For further investigation the interference from other metal ions on the fluorescence determination of Cu^{2+}, quenching ratio[29] (I_0/I) change of **1** was studied, where I_0 is fluorescence intensity of **1**, I is the fluorescence intensity in the presence of 5 equiv. of Cu^{2+}, coexisting with 50 equiv. of other background metal ions, including K^+, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Hg^{2+}, Cd^{2+}, Pb^{2+}, Ag^+ respectively. The results was shown in Fig. 4. Clearly, the coexisted ions cause a little interference except Ag^+. All of these results indicated that the sensor **1** was of a good selectivity.

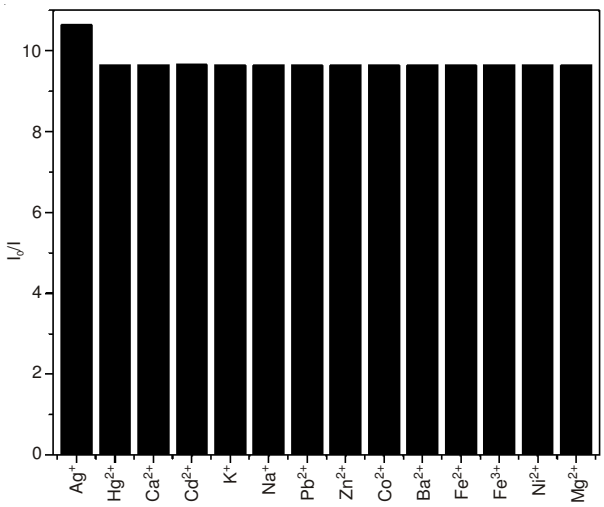


Fig. 4. Quenching ratio (I_0/I) of fluorescence intensity of 1 (1.0×10^{-5} mol L^{-1}) at 546 nm in the presence of 5 equiv. of Cu^{2+} upon addition of 50 equiv. of other metal ions respectively

Effect of pH: The intense fluorescence of the sensor **1** originates from dichlorofluorescein moiety, which was affected by pH in some extent. Therefore, the effect of pH on fluorescence intensity of the sensor **1** in the absence and presence of Cu^{2+} was studied. pH was controlled by buffer and Cu^{2+} concentration was fixed at 1×10^{-5} mol L^{-1} in the experiments. The results were shown in Fig. 5, it can be seen from the Fig. 5 that during the pH range from 3 to 6, the fluorescence intensity of **1** in the absence of Cu^{2+} showed a trend of slow decrease. When pH is higher than 6, the fluorescence intensity decreased greatly with the increasing pH, which might be induced by the isomerization of dichlorofluorescein[32]. Upon addition of Cu^{2+}, the fluorescence quenching varied barely with the pH in the range of 5-7. Nevertheless, with the pH varied form 3 to 5, fluorescence quenched much more intently, which may due to the protonation of the nitrogens of **1**. In order to avoid the interference caused by pH, the pH was controlled during 5-7 used phosphate buffer.

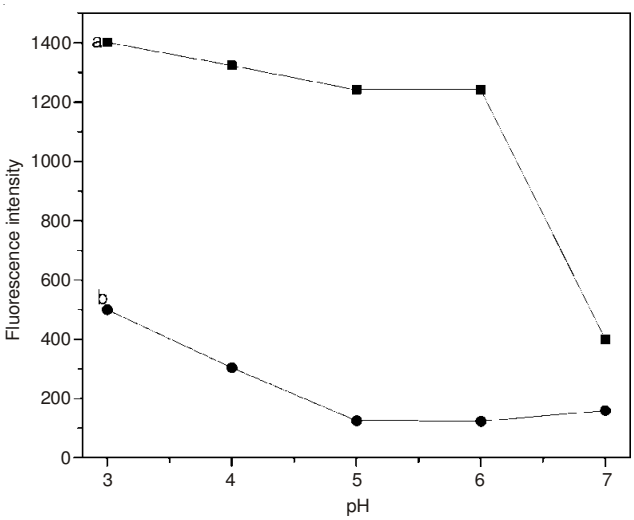


Fig. 5. Effect of pH on the fluorescence intensity of 1 [in the absence (a) and presence (b) of 5 equiv. of Cu^{2+}]

Detection limit and linear range: Under the optimal experiment condition, quenching ratio $(I_0-I)/I_0$ of **1** was linearly proportional to the concentration of Cu^{2+} in the range of 5.0×10^{-7}-1.0×10^{-5} mol L^{-1} with the correlation coefficient of 0.9947 and the linear regression equation was proposed to be $(I_0-I)/I_0 = 0.1003 \times 10^6 c + 0.0323$, where I_0 is the fluorescence intensity of 1, I is the fluorescence intensity in the presence of Cu^{2+}, c is the concentration of Cu^{2+}. The detection limit was as low as 8.7×10^{-8} mol L^{-1}, which was measured by following equation.

$$\text{Detection limit} = \frac{3\sigma_{bi}}{m}$$

where m is the slope of standard curve based on the fluorescence quenching ratio (I_0-I); I_0 of 1 *vs*. Cu^{2+} concentration. σ_{bi} Is the standard deviation of blank measurements (n = 11).

Effect of reaction time: For an excellent chemosensor, fast response is a matter of necessity. Consequently, the effect of reaction time on the binding process of Cu^{2+} to 1 was investigated. The results are depicted in Fig. 6. As shown in Fig. 6, the fluorescence intensity reached the plateau region after 2 to 3 s and kept stable until to 1200 s. This indicated that the response time of **1** to Cu^{2+} is very short, which was owed to the fast and complete reaction between **1** and Cu^{2+}. Consequently, we can obtain the fluorescence emission spectrum of **1** immediately upon addition of Cu^{2+}.

Stability constant: As stated above, **1** shows high selectivity to Cu^{2+}, which can be attributed to its excellent coordination with Cu^{2+}. So stability constant of coordination compound was measured to investigate its stability. Stability constant was obtained by following formula:

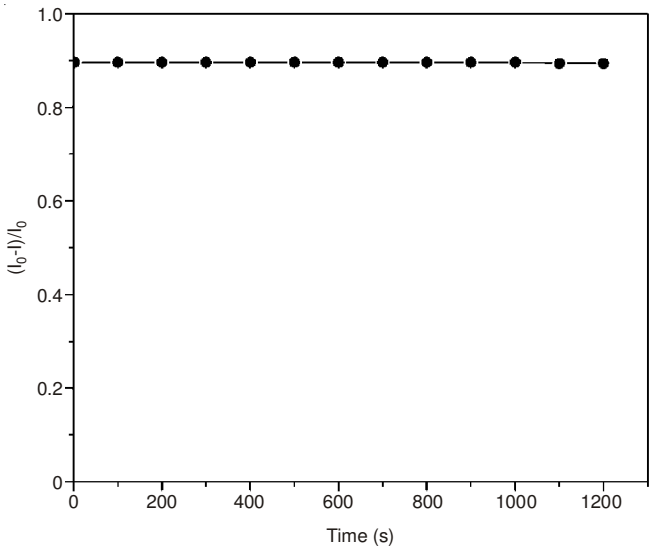


Fig. 6. Effect of reaction time on the fluorescence intensity of 1 in the presence of Cu^{2+}

$$Y = Y_0 + \frac{Y_{lim} - Y_0}{2}\left\{1 + \frac{C_M}{C_L} + \frac{1}{K_s C_L} - \left[\left(1 + \frac{C_M}{C_L} + \frac{1}{K_S C_L}\right)^2 - 4\frac{C_M}{C_L}\right]^{\frac{1}{2}}\right\}$$

where y is fluorescence intensity of **1** in the presence of Cu^{2+}, Y_0 is fluorescence intensity without Cu^{2+}. C_M represents the concentration of Cu^{2+}, C_L is the concentration of 1, stability constant is expressed by K_s. As a result, the association constant between **1** and Cu^{2+} was estimated to be 7.0×10^6.

Preliminary analytical applications: To investigate the practical application of chemosensor **1**, it was applied to determine Cu^{2+} concentration in drinking water, tap water and river water samples. The river water was first filtered to remove insoluble substance. All the samples were tested by chemosensor 1 and the analytical results are shown in Table-2. It can be found from the results in Table-2 that chemosensor **1** exhibited good recovery for the determination of spiked Cu^{2+}. This indicated that chemosensor **1** was applicable to detect Cu^{2+} in real samples.

TABLE-2
DETERMINATION RESULTS OF Cu^{2+}

	Cu^{2+} spiked (mol L^{-1})	Cu^{2+} recovered (mol L^{-1})	Recovery (%)
Drinking water			
1	0	Not detected	-
2	1.20×10^{-6}	$(1.19 \pm 0.02) \times 10^{-6}$	99.2
3	3.60×10^{-6}	$(3.61 \pm 0.01) \times 10^{-6}$	100.3
Tap water			
1	0	Not detected	-
2	1.20×10^{-6}	$(1.18 \pm 0.02) \times 10^{-6}$	98.3
3	3.60×10^{-6}	$(3.53 \pm 0.03) \times 10^{-6}$	98.1
River water			
1	0	Not detected	-
2	1.20×10^{-6}	$(1.17 \pm 0.02) \times 10^{-6}$	97.5
3	3.60×10^{-6}	$(3.45 \pm 0.04) \times 10^{-6}$	95.8

Conclusion

In summary, the investigation described above has resulted in the development of a highly selective and sensitive chemosensor 1 for Cu^{2+} based on ICT mechanism. The system, which using a novel strategy by designing a molecule containing one fluorophore and two ionophores, has displayed a considerable selectivity for Cu^{2+}. In addition, sensor **1** showed fairly low detection limit for Cu^{2+}, which was as low as 8.7×10^{-8} mol L^{-1}, this was attributed to the specific affinity of Cu^{2+} for 1. In addition, the proposed sensor **1** was successfully applied to the determination of Cu^{2+} in water samples with satisfatory results.

ACKNOWLEDGEMENTS

The authors gratefully acknowledged Analytical and Testing Center, Sichuan University.

REFERENCES

1. R.F.H. Viguier, Hulme and A.N. Helmet, *J. Am. Chem. Soc.*, **128**, 11370 (2006).
2. H.S. Jung, P.S. Kwon, J.W. Lee and J.I. Kim, *J. Am. Chem. Soc.*, **131**, 2008 (2009).
3. M.C. Linder, M. Hazegh-Azam, *Am. J. Clin. Nutr.*, **63**, 797 (1996).
4. R. Uauy, M. Olivares and M. Gonzalez, *Am. J. Clin. Nutr.*, **167**, 952 (1998).
5. X.J. Xie and Y. Qin, *Sens. Actuators B.*, **156**, 213 (2001).
6. W.-H. Hu and Q.-Z. Zhai, *Asian J. Chem.*, **24**, 3191 (2012).
7. S.A. El-Safty, A.A. Ismail and A. Shahat, *Talanta*, **83**, 1341 (2011).
8. M. Kumar, N. Kumar and V. Bhalla, *Org. Lett.*, **14**, 406 (2012).
9. C.H. Zong, K.L. Ai, G. Zhang, H.W. Li and L.H. Lu, *Anal. Chem.*, **83**, 3126 (2011).
10. T.R. Li, Z.Y. Yang and Y. Li, *Dyes Pigments*, **88**, 103 (2011).
11. L. Feng, Y. Zhang, L.Y. Wen, Z. Shen and Y.F. Guan, *Talanta*, **84**, 913 (2011).
12. T.W. Lin and S.D. Huang, *Anal. Chem.*, **73**, 4319 (2001).
13. J. Wu and E.A. Boyle, *Anal. Chem.*, **69**, 2464 (1997).
14. Y. Liu, P. Liang and L. Guo, *Talanta*, **68**, 25 (2005).
15. Y. Zhou, F. Wang, Y.M. Kim, S.-J. Kim and J.Y. Yoon, *Org. Lett.*, **11**, 4442 (2009).
16. F.-J. Huo, C.-X. Yin and Y.-T. Yang, *Anal. Chem.*, **84**, 2219 (2012).
17. M.S. Royzen, Z.H. Dai and J.W. Canary, *J. Am. Chem. Soc.*, **22**, 1612 (2005).
18. H.J. Kim, J.Y. Hong, A. Hong, S. Ham, J.H. Lee and J.S. Kim, *Org. Lett.*, **10**, 1963 (2008).
19. Z.C. Xu, Y. Xiao, X.H. Qian, J.N. Cui and D.W. Cui. *Org. Lett.*, **7**, 889 (2005).
20. D.H. Jun, L. Fei and Q.Q. Gao, *Luminescence*, **26**, 523 (2011).
21. J.B. Wang, X.H. Qian and J.N. Cui, *J. Org Chem.*, **71**, 4308 (2006).
22. J.S. Yang, Y.D. Lin and S.S. Wang, *J. Org. Chem.*, **70**, 6066 (2005).
23. Y. Yan, Y. Hu, G.P. Zhao and X.M. Kou, *Dyes Pigments*, **79**, 210 (2008).
24. A.A. Abbas, *Tetrahedron*, **60**, 1541 (2004).
25. R. Battaloglu, A.I. Pekacar and Y.K. Yildiz, *Asian J. Chem.*, **24**, 2377 (2012).
26. M.H. Kim, J.H. Noh, S. Kim, S. Ahn and S.-K. Chang, *Dyes Pigments*, **82**, 341 (2009).
27. H. Yin, Y.F. Xu and X.H. Qian, *Bioorg. Med. Chem.*, **15**, 56 (2007).
28. Y. Habata and F. Osaka, *Dalton Trans.*, **18**, 36 (2006).
29. E.M. Zahran, V. Gavalas, M. Valiente and L.G. Bachas, *Anal. Chem.*, **82**, 3622 (2010).
30. Y.L. Zhang, P.T. Jing and Q.H. Zeng, *J. Phys. Chem.*, **113**, 1886 (2009).
31. D. Yang, H.-L. Wang and Z.-N. Sun, *Am. Chem. Soc.*, **18**, 6004 (2006).
32. S. Goswami and R. Chakrabarty, *Tetrahedron Lett.*, **43**, 5910 (2009).