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New rhodamine-based turn-on and colorimetric probe for copper(II) ion with high selectivity and sensitivity

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A new rhodamine-based derivative fluorescent probe (**L**) was synthesized as a highly selective and turn-on fluorescent probe for quantitative detection of Cu^{2+} exhibiting an almost 200-fold fluorescence increase. Moreover, the X-ray single crystal structure of the probe had also been measured. Besides, the fluorescent probe can also be considered as a good OFF–ON switch for Cu^{2+} with naked-eye colour change from colorless to pink. The 1:1 binding ratio between chemosensor **L** and Cu^{2+} was investigated using Job's plot method, ^{1}H NMR titration and ESI-MS. The probe exhibited excellent selectivity and sensitivity toward Cu^{2+} with little interference, meanwhile the detection limit of Cu^{2+} was at a quite lower micromolar level.

Key words: rhodamine, turn on, fluorescent probe, naked-eye detection, Cu^{2+}

1. Introduction

In recent years, the design and synthesis of highly selective fluorescent probe for detecting transition and heavy metal ions is one of the most important research areas in chemistry because of their potential applications in clinical biochemistry and environmental research [1]. Among various transition and heavy metal ions, Cu^{2+} ranks the third most abundant in the human body besides zinc and iron, and plays an important role in the areas of biological and environmental systems [2–6]. However, copper is

highly toxic to some organisms such as many bacteria and viruses if their levels exceed cellular needs, elevated concentrations of copper hamper the self-purification capability of the sea or rivers and destroy the biological reprocessing systems in water. Alteration in the cellular homeostasis of copper ions was reported to be connected with some serious neurodegenerative diseases such as Alzheimer's disease and prion diseases [7–10]. Accordingly, monitoring the concentration of Cu^{2+} in environmental samples is of considerable significance for environment protection and human health.

In the past decade, considerable attention has been focused on the design of fluorescent chemosensors for Cu^{2+} due to the highly sensitive, quick, and nondestructive advantages of the fluorescent method [11, 12]. Most of the classic and early-reported cation probe, however, generally undergo fluorescence quenching upon the binding of Cu^{2+} due to the fluorescence quenching nature of paramagnetic Cu^{2+} and give a "turn-off" signal [13–19]. Moreover, the selectivity for Cu^{2+} over other metal ions, such as Fe^{3+}, Pb^{2+} and Hg^{2+}, is not very satisfactory for some of the probes [20–25]. To overcome these disadvantages, fluoroionophores which show a selective response to Cu^{2+} by a copper-amplified fluorescence emission have been well developed in recent years [26, 27].

Rhodamine framework seems to be an ideal model to construct "turn-on" fluorescent probe because of it's a spirolactam ring-opening system [28–32]. Moreover, rhodamine derivatives have excellent spectroscopic properties such as long absorption and emission wavelength, large molar extinction coefficient, and high fluorescence quantum yield [33, 34]. Recently, a spirolactam to ring-opening amide process was utilized for the detection of metal ions [35]. In this paper, we reported the design and synthesis of a new rhodamine spirolactam-based chemosensor (**L**). It showed a "turn-on" fluorogenic and colorimetirc recognition functions toward Cu^{2+} in N, N-dimethylformamide (DMF) aqueous solution with remarkably high sensitivity and selectivity. This fluorescent probe may play a critical role in the detection of Cu^{2+} in environmental pollution.

2. Experimental

2.1 Materials and measurement

All the materials for the syntheses were commercially available and used as received without further purification. DMF was of analytical reagent grade. All aqueous solution was prepared using freshly deionized water. The solutions of the metal ions were prepared from their chloride salts except that Ag^+ was prepared from its nitrate salts. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX spectrometer operating at 400 MHz. UV-visible absorption spectra were recorded on a TU-1900 double-beam UV−Vis Spectrophotometer. Fluorescence emission spectra were recorded on a FluoroMax-4 Spectrofluorometer (Horiba Jobin Yvon Inc., France), excitation and emission slits of 5.0 nm were used for the measurements of fluorescence. Elemental analyses (C, H, N) was conducted using a Perkin-Elmer 240 elemental analyzer. Electrospray ionization time-of-flight mass spectrometry (MS) spectra were measured on a LC‐MSD‐Trap‐XCT instrument. Melting points were determined on an X-4 microscope electron thermal apparatus.

2.2 Synthesis of the fluorescent probe ***L***

The rhodamine 6G hydrazide was prepared according to the literature method [36]. To a solution of methanol (15 mL) containing rhodamine 6G hydrazide (214.0 mg, 0.5 mmol) and 3-formyl-2-hydroxy-benzoic acid methyl ester (90.1 mg, 0.5 mmol), a few drops of glacial acetic acid were added into the mixture. The resulting solution was stirred at 68 °C refluxed for 2 h, and light pink precipitation was obtained after the solution cooled to room temperature. The precipitation was filtered off, washed with a mixture of methanol and diethyl ether (1:1, v/v) several times and dried under vacuum. The desired compound **L** was obtained in 86 % yield (253.8 mg). m.p: 246-248 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ = 11.10 (s, 1H), 8.74 (s, 1H), 8.05 (m, 1H), 7.91, (d, 1H), 7.75 (m, 1H), 7.50 (m, 2H), 7.07 (m, 1H), 6.81 (t, 1H), 6.44 (s, 2H), 6.36 (s, 2H), 3.91 (s, 3H), 3.52 (s, 2H), 3.23 (m, 4H), 1.90 (s, 6H), 1.33 (t, 6H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ = 169.58, 165.05, 159.87, 152.47, 151.34, 147.57, 142.80, 133.55, 132.91, 131.66, 128.52, 128.26, 127.64, 123.77, 123.44, 122.76, 118.61, 118.01, 113.86, 105.80, 96.84, 65.75, 52.24, 38.36, 16.71, 14.74. Anal. Calcd for $C_{35}H_{34}N_4O_5$: C, 71.17, H, 5.80, N, 9.49. Found: C, 71.21, H, 5.76, N, 9.51,. ESI-MS: $[M + H]^+$ 591.3.

2.3 X-ray crystallographic data collection and refinement of ***L***

Single-crystal X-ray diffraction data for **L** were conducted on a Bruker SMART APEX CCD diffractometer [37] with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature using the ω-scan technique. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods with SHELXS-97 [38] and refined with the full-matrix least-squares technique using the SHELXL-97 [39] program. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms of the organic ligand were included in the structure factor calculation at idealized positions using a riding model and refined isotropically. The hydrogen atoms of the solvent water molecules were located from the difference Fourier maps, then restrained at fixed positions and refined isotropically. Crystallographic data for **L** was provided in Table S1. Crystallographic data has been deposited with the Cambridge Crystallographic Data Center. CCDC reference number: 973784.

3. Results and Discussion

Our research involved the design, synthesis, and evaluation of the fluorescent probe **L**. As shown in Scheme 1 (Supporting Information), **L** was easily synthesized by simple reaction, and the characterization of the new compound ^{1}H NMR (Fig. S1), ^{13}C NMR (Fig. S2) was presented in Supporting Information. Single crystals of **L** suitable for X-ray diffraction were obtained by slow evaporation from a solvent mixture of tetrahydrofuran and DMF undisturbed at room temperature after about two weeks. X-ray single crystal structure for **L** was shown in Fig. 1. **L** crystallized in a monoclinic system with space group $P2_1/c$.

[inset Fig. 1]

3.1. The fluorescence emission spectroscopy of ***L*** *to* Cu^{2+}

To investigate the fluorescence selectivity toward special metal ions, the fluorescence selectivity experiments of various metal (Cu^{2+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Zn^{2+}, Al^{3+}, Cd^{2+}, Ba^{2+}, Ag^{+}, Hg^{2+}, Fe^{2+}, Ni^{2+} and Pb^{2+}) were carried out in DMF/H_2O (95:5). As

shown in Fig. 2, only Cu^{2+} has been successful to perturb the emission signal of **L**, but other cations can't affect the emission profiles. Upon the addition of 10 equiv of Cu^{2+}, a ''turn-on'' ratio over 200-fold was triggered because of the rhodamine ring-opening process (Scheme 2). In addition, according to the histogram (Fig. 2, inset), the high selectivity of **L** for Cu^{2+} over other metal ions were indicated obviously.

[inset Fig. 2 and scheme 2]

Fluorescence titration experiment (Fig. 3) using **L** and Cu^{2+} was performed in DMF/H_2O (95:5) at room temperature. Upon binding with ever-increasing Cu^{2+}, the fluorescence intensity was obviously enhanced. The emission spectrum of **L**, which was excited at 521 nm, exhibited an emission maximum at 559 nm with a low quantum yield (Φ = 0.0024) by using rhodamine 6G (Φ = 0.95) in ethanol as the reference [40]. Upon coordinating to Cu^{2+} (50 μM), the fluorescence intensity of emission band at 559 nm with a quantum yield (Φ = 0.473) was largely enhanced. From the changes in Cu^{2+} dependent fluorescence intensity the detection limit was estimated to be 9.12×10^{-7} M^{-1} (Fig. S3). Therefore, the probe **L** was sensitive enough to detect Cu^{2+}.

[inset Fig. 3]

*3.2. The UV–Vis absorption spectroscopy response of **L** to Cu^{2+}*

To get further insight into the binding of Cu^{2+} with **L**, the absorption spectra of **L** upon titration with Cu^{2+} was recorded (Fig. 4). Upon addition of Cu^{2+}, a new absorption band at 528 nm appeared with increasing intensity, which induced a clear color change from colorless to pink. Similar to other rhodamine spirolactam derivatives, **L** formed a nearly colorless and fluorescence inactive in DMF/H_2O (95:5), indicated that the spirolactam form predominantly existed [41]. The characteristic peak of the spirocycle carbon of **L** near 66 ppm in the ^{13}C NMR spectrum (Fig. S2) [42] and X-ray single crystal structure of **L** (Fig. 1) also supported this consideration. Upon interaction with Cu^{2+}, the spirolactam ring of **L** was opened and caused a significant enhancement of absorbance. Moreover, other metal cations exerted a negligible effect on the absorption response for **L**. The

association constant (K) for **L** binding to Cu^{2+} was determined from the absorption titration data following the reported method [43]. The association constant (K) of **L** with Cu^{2+} was $(2.439 \pm 0.456) \times 10^4$ (R = 0.999) from linear least-squares analysis obtained by Benesi-Hilderbrand plot (Fig. S4), which unambiguously demonstrated that **L** had a potent binding affinity for Cu^{2+}.

[inset Fig. 4]

*3.3. Coordination mode between **L** and Cu^{2+}*

Job's method for the fluorescence intensity was applied to determine the coordination mode of **L** to Cu^{2+}, by keeping the sum of the initial concentration of copper ion and **L** at 10 μM and the molar ratio of copper ion changing from 0 to 1 [44, 45]. The results showed the 1:1 stoichiometry of the complex between Cu^{2+} and **L** (Fig. 5). To further confirm the stoichiometry between **L** and Cu^{2+}, the ^1H NMR titration (Fig. S5) and ESI-MS spectrometry (Fig. S6) were both undertaken. Upon the addition of 1 equiv Cu^{2+}, the signals for these active protons (−OH and −CH=N−) shifted to downfield in certain degrees in comparison to those of **L**. The proton of −OH shifted from 10.99 to 11.10 due to the coordination "O" to "Cu^{2+}"and the proton of −CH=N− shifted from 8.86 to 8.92 due to the coordination "N" to "Cu^{2+}", the spirolactam ring of **L** was opened, which associated with the enhancement of fluorescent intensity in complex **L** + Cu^{2+}. And these active protons stopped changing after addition of another 1 equiv Cu^{2+}, the result also supported that **L** and Cu^{2+} formed a 1:1 ratio complex. ESI-MS measurements were carried out on by using methanol as mobile phase, a main peak at m/z 591.3 corresponding to $[\mathbf{L} + H]^+$. After the addition of 1 equiv of $CuCl_2$, a peak at m/z 755.3 appeared, coinciding exactly with that for the species of $[\mathbf{L} + Cu^{2+} + 2Cl^- + CH_3OH + H]^+$ which confirming the 1:1 formation of **L**–Cu^{2+} complex, too.

[inset Fig. 5]

3.4. Competition experiment

A very important parameter to evaluate the performance of a fluorescence probe is the ability to detect a specific cation in the vicinity of other competing ions. To further testify the specific selectivity of **L** for Cu^{2+}, the fluorescence intensity of **L** in the presence of

Cu^{2+} mixed with 10 equivalents other metal ions was carried out in DMF/H_2O (95:5), as shown in Fig. 6, no significant fluorescence intensity changes were observed. Furthermore, the anion responses to the detection systems were also investigated. Sufficient fluorescence enhancement was observed for probe **L** after the addition of Cu^{2+} in the presence of different anions (F^-, Cl^-, Br^-, I^-, AcO^-, ClO_4^-, $H_2PO_4^-$, HSO_4^-) (Fig. S7). All these results indicated that the probe **L** can be used as a good selective fluorescent probe for Cu^{2+} in the presence of a wide range of the environmentally relevant ions.

[inset Fig. 6]

3.5 The influence of solvent

The fluorescence behaviour of chemosensors **L** in different ratios of DMF/H_2O solution was investigated as shown in Fig. S8 in Supporting Information. Upon adding of 7 equiv Cu^{2+} and photoexcitation at 521 nm, the dilute aqueous solution of **L** hardly showed any fluorescence and then sharply enhanced when the DMF fraction was over 95%. In this work, DMF/H_2O (95:5) was used throughout the experiment.

*3.6. The reversibility of the binding of Cu^{2+} by **L***

Reversibility of target ion binding is a momentous character to a fluorescent probe. Consequently, we studied the chemical reversibility of the binding of **L** to Cu^{2+} in DMF/H_2O (95:5). As seen by the naked eye, the pink color of the solution of **L**-Cu^{2+} immediately disappeared upon the addition of excess Na_2S, the fluorescent intensity almost recovered to the original level (Fig. 7). The phenomenon could also be attributed to the fact that Cu^{2+} can coordinate with sulfide anions to form the stable species, CuS, with the low solubility product constant ($K_{SP} = 1.27 \times 10^{-36}$) [46], which indicated that addition of sulfide anions to the **L**-Cu^{2+} ensemble resulted in the release of the free **L**.

[inset Fig. 7]

4. Conclusion

In summary, we have synthesized a new fluorescent probe (**L**) derived from rhodamine 6G, which showed "turn-on" response to Cu^{2+} based on rhodamine ring-opening approach, the X-ray single crystal structure of the probe has also been measured. The complex of

L-Cu^{2+} with a 1:1 stoichiometry was formed on the treatment with Cu^{2+}. **L** exhibited an excellent selectivity for Cu^{2+} with nearly 200-fold fluorescence enhancement compared with other metal ions. In addition, the fluorescence response of the probe could be switched "ON" and "OFF" by adding Cu^{2+} and Na_2S alternately with obvious colour change observed by naked eye. Furthermore, the chemosensor **L** has highly sensitive property for Cu^{2+} with a low detection limit. This fluorescent probe **L** may make contribution to solving the problem of environmental pollution caused by Cu^{2+}.

Acknowledgements

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References

[1] R. McRae, P. Bagchi, S. Sumalekshmy, C.J. Fahrni, Chem. Rev. 109 (2009) 4780.

[2] D.G. Barceloux, J. Toxicol. Clin. Toxicol. 37 (1999) 217.

[3] M.C. Linder, M. Hazegh-Azam, Am. J. Clin. Nutr. 63 (1996) 797.

[4] Y.J. Zheng, J. Orbulescu, X.J. Ji, F.M. Andreopoulos, S.M. Pham, R.M. Leblanc, J. Am. Chem. Soc. 125 (2003) 2680.

[5] Z.C. Xu, Y. Xiao, X.H. Qian, J.N. Cui, D.W. Cui, Org. Lett. 7 (2005) 889.

[6] I.A. Koval, P. Gamez, C. Belle, K. Selmeczi, J. Reedijk, Chem. Soc. Rev. 35 (2006) 814.

[7] C. Barranguet, F.P. van den Ende, M. Rutgers, A.M. Breure, M. Greijdanus, J.J. Sinke, W. Admiraal, Environ. Toxicol. Chem. 22 (2003) 1340.

[8] D.R. Brown, H. Kozlowski, Dalton Trans. 2004, 1907–1917.

[9] K.J. Barnham, A.I. Bush, Curr. Opin. Chem. Biol. 12 (2008) 222.

[10] R.R. Crichton, D.T. Dexter, R.J. Ward, Coord. Chem. Rev. 252 (2008) 1189.

[11] P. Jiang, Z. Guo, Coord. Chem. Rev. 248 (2004) 205.

[12] M.H. Lim, S.J. Lippard, Acc. Chem. Res. 40 (2007) 41.

[13] W. Breuer, S. Epsztejn, P. Millgram, I.Z. Cabantchik, Am. J. Physiol. 268 (1995)

1354.

[14] K.A. McCall, C.A. Fierke, Anal. Biochem. 284 (2000) 307.

[15] P. Chavez-Crooker, N. Garrido, G.A. Ahearn, J. Exp. Biol. 204 (2001) 1433.

[16] M. Royzen, Z. Dai, J.W. Canary, J. Am. Chem. Soc. 127 (2005) 1612.

[17] H.J. Kim, S.Y. Park, S. Yoon, J.S. Kim, Tetrahedron 64 (2008) 1294.

[18] N. Shao, J. Jin, H. Wang, Y. Zhang, R. Yang, W. Chan, Anal. Chem. 80 (2008) 3466.

[19] H.X. Wang, L. Yang, W.B. Zhang, Y. Zhou, B. Zhao, X.Y. Li, Inorg. Chim. Acta. 381 (2012) 111.

[20] Q.Y. Wu, E.V. Anslyn, J. Am. Chem. Soc. 126 (2004)14682.

[21] T. Gunnlaugsson, J.P. Leonard, N.S. Murray, Org. Lett. 6 (2004) 1557.

[22] A. Mokhir, R. Krämer, Chem. Commun. 2005, 2244.

[23] W-Y. Yao, K-X. Xu, H-J. Kong, L. Kou, Q-H. Zhang, C-J. Wang, Supramol. Chem. 25 (2013) 146.

[24] S. Ghosh, R. Manna, Supramol. Chem. 23 (2011) 558.

[25] K. Ghosh,; T. Sarkar, Supramol. Chem. 23 (2011) 435.

[26] X. Yu, A.J. Tong, P.Y. Jin, Y. Ju, Org. Lett. 8 (2006) 2863.

[27] N. Kaur, S. Kumar, Supramol. Chem. 23 (2011) 768.

[28] Z.X. Han, X.B. Zhang, Z. Li, G.J. Mao, Z. Jin, G.L. Shen, R.Q. Yu, X.Y. Wu, Anal. Lett. 43 (2010) 2751.

[29] H. Kim, S-H. Kim, D-H. Lee, Y-A. Son, Supramol. Chem. 25 (2013) 87.

[30] Y. Xiang, Z.F. Li, X.T. Chen, A.J. Tong, Talanta 74 (2008) 1148.

[31] N. Li, W.X. Tang, Y. Xiang, A.J. Tong, P.Y. Jin, Y. Ju, Luminescence 25 (2010) 445.

[32] Y. Wang, H-Q. Wu, J-H. Sun, X-Y., Liu, J. Luo, M-Q. Chen, J Fluoresc 22 (2012) 799.

[33] J.R. Lakowicz, New York: Springer 2006, 67.

[34] J.L. Manzoori, M.H. Sorouraddin, A.M.H. Shabani, J. Anal. Atom. Spectrom. 13 (1998) 305.

[35] Y. Zhao, F. Wang, Y. Kim, S.J. Kim, J.Yoon, Org. Lett. 11 (2009) 4442.

[36] X.F. Yang, X.Q. Guo, Y.B. Zhao, Talanta. 57 (2002) 883.

[37] SMART and SAINT. *Area Detector Control and Integration Software;* Siemens Analytical X-Ray Systems, Inc.: Madison, WI, 1996.

[38] G.M. Sheldrick, SHELXS-97, *Program for solution of crystal structures*, University of Göttingen, Germany, 1997.

[39] G.M. Sheldrick, SHELXL-97, *Program for Crystal Structures Refinement;* University of Göttingen, Germany, 1997.

[40] L. Li, H.F. Qian, J.C. Ren, Chem. Commun. 2005, 528.

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

[42] U. Anthoni, C. Christophersen, P. Nielsen, A. Puschl, K. Schaumburg, Struct. Chem. 3 (1995) 161.

[43] M. Zhu, M.J. Yuan, X.F. Liu, J.L. Xu, J. Lv, C.S. Huang, H.B. Liu, Y.L. Li, S. Wang, D.B. Zhu, Org. Lett. 10 (2008) 1481.

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

[45] W.C. Vosburgh, G.R. Cooper, J. Am. Chem. Soc. 63 (1941) 437.

[46] Y.F. Zhu, D.H. Fan, W.Z. Shen, J. Phys. Chem. C. 112 (2008) 10402.

Fig. 1. X-ray single crystal structure for **L**.

Fig. 2. Fluorescence emission spectra of **L** (5 μM) in the presence of various metal ions (10 equiv for 1. Cu^{2+}, 2. Na^{+}, 3. K^{+}, 4. Mg^{2+}, 5. Ca^{2+}, 6. Mn^{2+}, 7. Co^{2+}, 8. Zn^{2+}, 9. Al^{3+}, 10. Cd^{2+}, 11. Ba^{2+}, 12. Ag^{+}, 13. Hg^{2+}, 14. Fe^{2+}, 15. Ni^{2+} and 16. Pb^{2+}) in DMF/H_2O (95:5). λ_{ex} = 521 nm.

Fig. 3. Fluorescence spectra of **L** (5 μM) in the presence of increasing concentration of Cu^{2+} (0–7 equiv). The excitation wavelength was 521 nm. Inset: (a) Linear relationship between the emission intensity at 559 nm and Cu^{2+} concentration from 0 to 15 μM; (b) Fluorescence change of **L** (5 μM) in the absence and presence of Cu^{2+} (50 μM) under UV light with an excitation of 365 nm.

Fig. 4. Absorption spectra of **L** (5 μM) with addition of different concentrations of Cu^{2+} (0–5 equiv) in DMF/H_2O (95:5). The inset showed the colour change under visible light, in the absence and presence of Cu^{2+} (25 μM) respectively.

Fig. 5. Job's plot method between chemosensor **L** and Cu^{2+}.

Fig. 6. The fluorescent response of **L** (5 μM) upon addition of different metal ions at 559 nm. The black bars represented the addition of various metal ions (50 μM), the red bars represented the change in the emission that occured upon the subsequent addition of Cu^{2+} (50 μM) to the above solution.

Fig. 7. Reversible fluorescence response of **L** to Cu^{2+} in DMF/H_2O (95:5). Green: 5 μM **L**; Blue: 5 μM **L** with 7 equiv Cu^{2+}; Red: 5 μM **L** with 7 equiv Cu^{2+} and then addition of 20 equiv sulfide ion (Na salt). Excitation was performed at 521 nm.

Scheme 2. Possible mechanism of the response of **L** to Cu^{2+}.

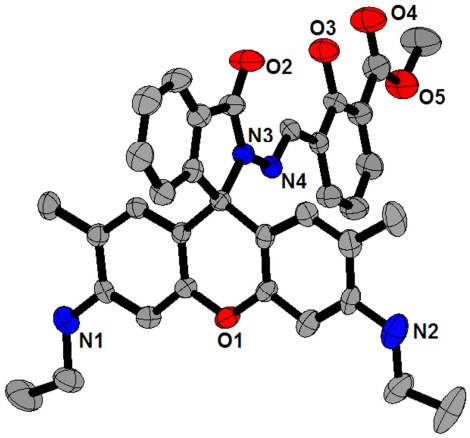
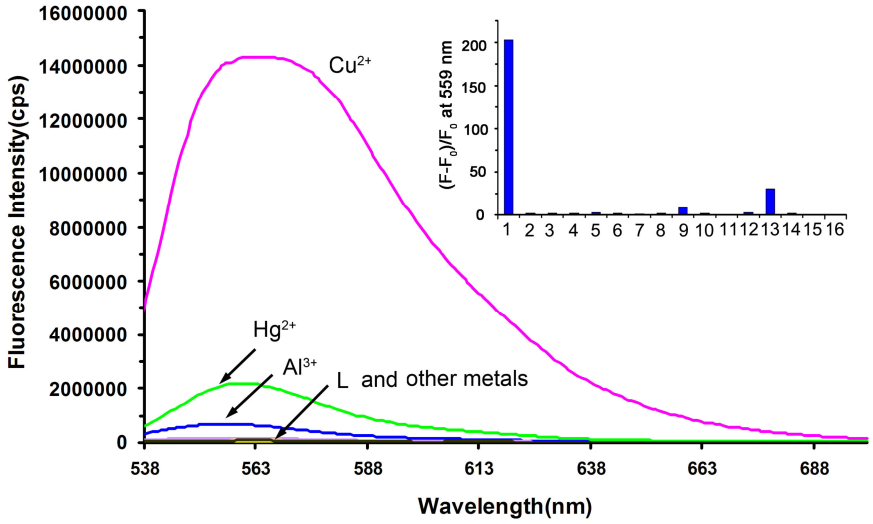


Fig. 1. X-ray single crystal structure for **L**. (All hydrogen atoms were omitted for clarity).



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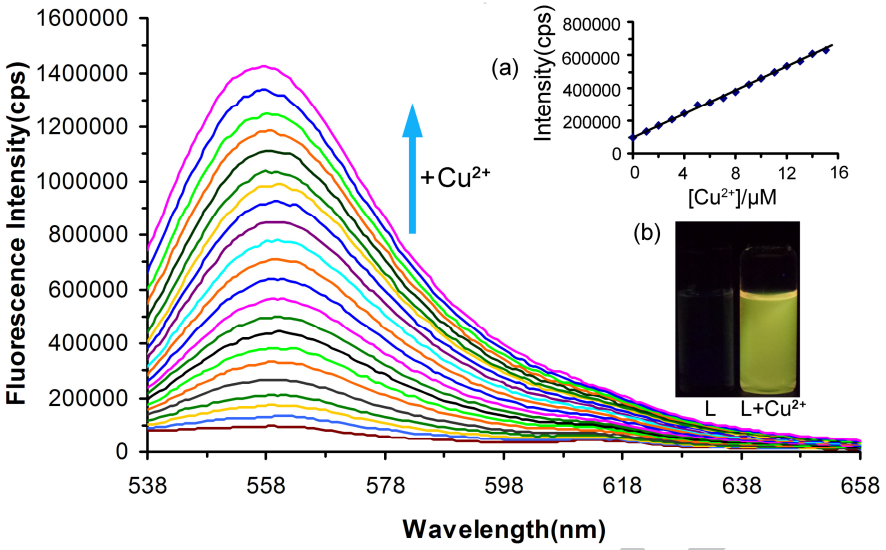

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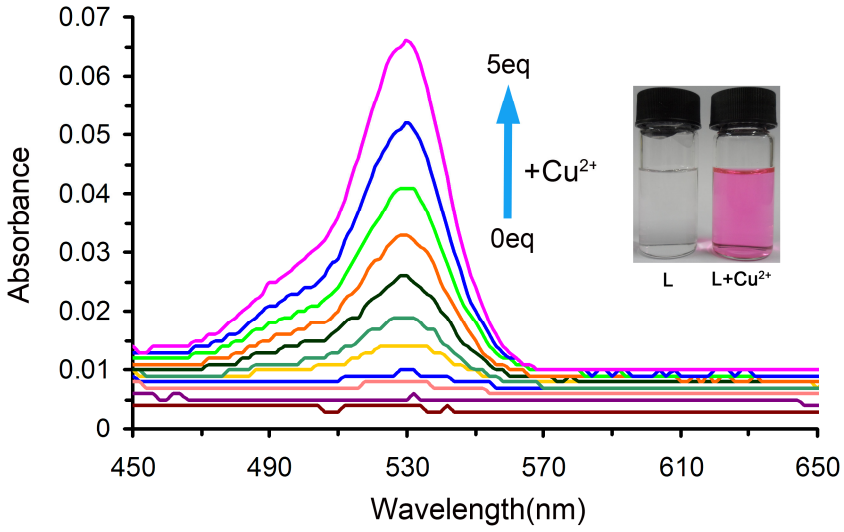

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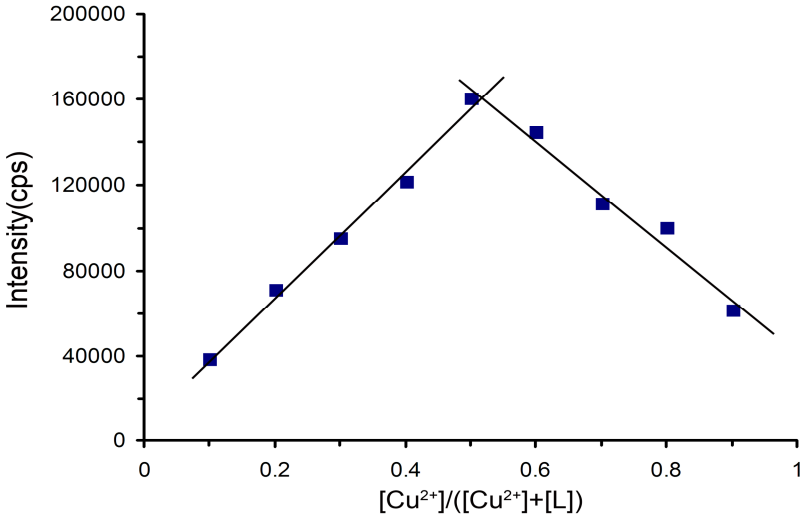


Fig. 5. Job's plot method between chemosensor **L** and Cu^{2+}.

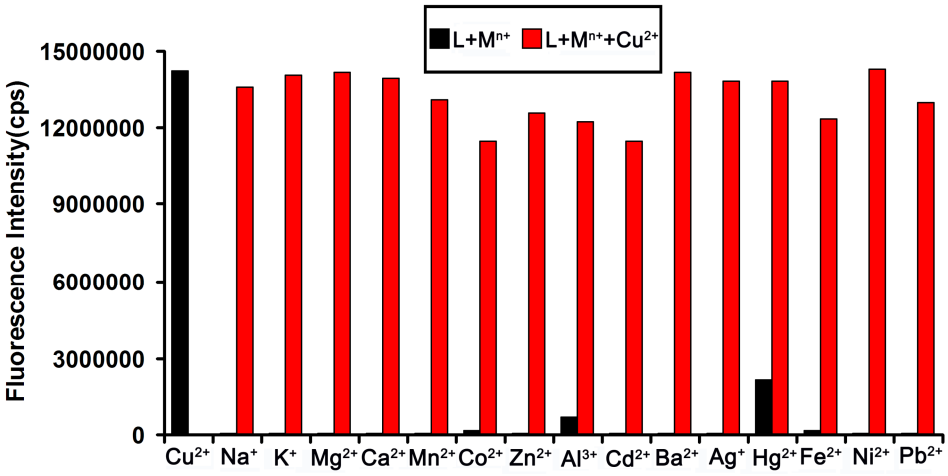


Fig. 6. The fluorescent response of **L** (5 μM) upon addition of different metal ions at 559 nm. The black bars represented the addition of various metal ions (50 μM), the red bars represented the change in the emission that occured upon the subsequent addition of Cu^{2+} (50 μM) to the above solution.

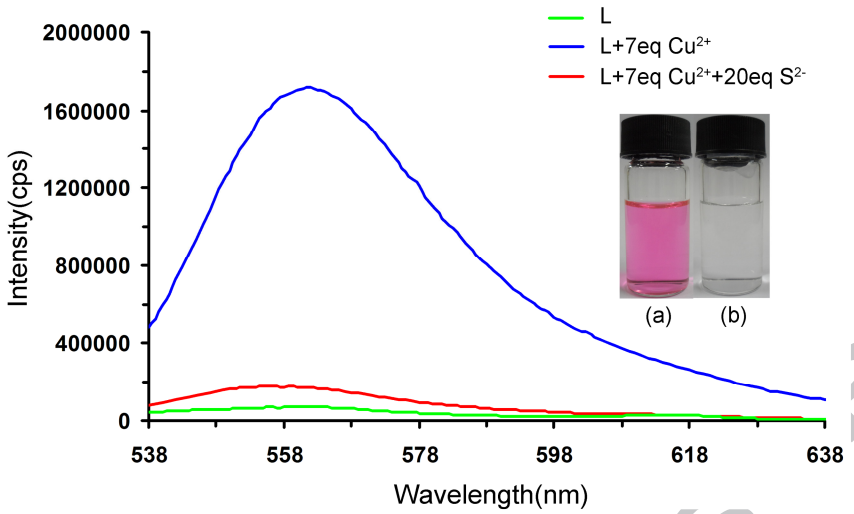
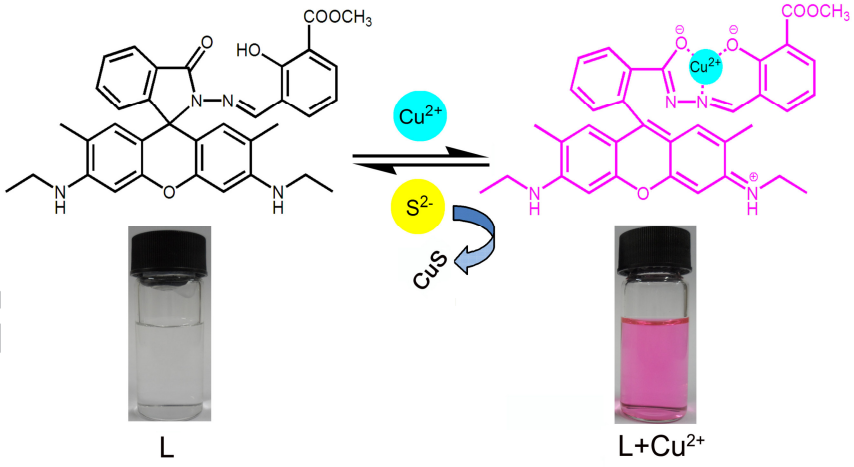


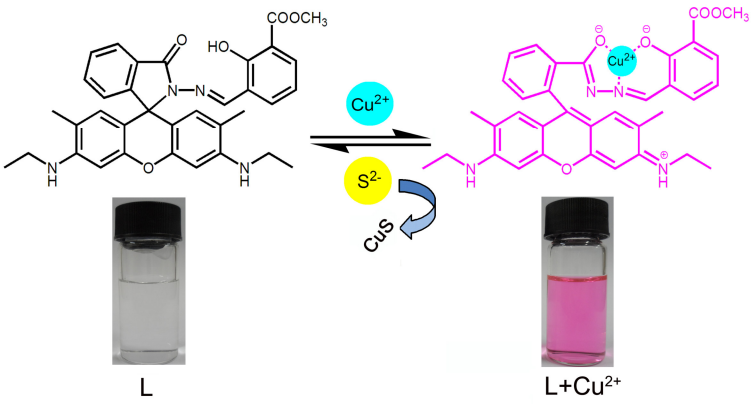
Fig. 7. Reversible fluorescence response of **L** to Cu^{2+} in DMF/H_2O (95:5). Green: 5 μM **L**; Blue: 5 μM **L** with 7 equiv Cu^{2+}; Red: 5 μM **L** with 7 equiv Cu^{2+} and then addition of 20 equiv sulfide ion (Na salt). Excitation was performed at 521 nm.



Scheme 2. Possible mechanism of the response of **L** to Cu^{2+}.

New rhodamine-based turn-on and colorimetric probe for copper(II) ion with high selectivity and sensitivity

Yan Fu[a], Qiao-Feng Tian[b], Yan-Qin Guo[a], Shuang-Quan Zang[a*]



New rhodamine-based turn-on and colorimetric probe for copper(II) ion with high selectivity and sensitivity

Yan Fu[a], Qiao-Feng Tian[b], Yan-Qin Guo[a], Shuang-Quan Zang[a*]

A new rhodamine-based derivative fluorescent probe (**L**) was synthesized as a highly selective and turn-on fluorescent probe for quantitative detection of Cu^{2+} exhibiting an almost 200-fold fluorescence increase. Moreover, the X-ray single crystal structure of the probe had also been measured. Besides, the fluorescent probe can also be considered as a good OFF–ON switch for Cu^{2+} with naked-eye colour change from colorless to pink. The 1:1 binding ratio between chemosensor **L** and Cu^{2+} was investigated using Job's plot method, ^{1}H NMR titration and ESI-MS. The probe exhibited excellent selectivity and sensitivity toward Cu^{2+} with little interference, meanwhile the detection limit of Cu^{2+} was at a quite lower micromolar level.

►A new fluorescent probe (**L**) exhibited significant fluorescence enhancement upon binding with Cu^{2+} over 200-fold.

►**L** showed naked-eye detection of Cu^{2+} from colorless to pink.

►**L** exhibited good selectivity for Cu^{2+} over other metal ions with little interference.