A selectively rhodamine-based colorimetric probe for detecting copper(II) ion

Jiangang Zhang, Li Zhang, Yanli Wei, Jianbing Chao, Shaomin Shuang,
Zongwei Cai, Chuan Dong

PII: S1386-1425(14)00554-X
DOI: http://dx.doi.org/10.1016/j.saa.2014.04.006
Reference: SAA 11964

To appear in: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*

Received Date: 13 January 2014
Revised Date: 28 February 2014
Accepted Date: 2 April 2014

Please cite this article as: J. Zhang, L. Zhang, Y. Wei, J. Chao, S. Shuang, Z. Cai, C. Dong, A selectively rhodamine-based colorimetric probe for detecting copper(II) ion, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2014), doi: http://dx.doi.org/10.1016/j.saa.2014.04.006

A selectively rhodamine-based colorimetric probe for detecting copper（Ⅱ）ion

Jiangang Zhang[a,b], Li Zhang[a,b], Yanli Wei[a], Jianbing Chao[a], Shaomin Shuang[a], Zongwei Cai[a], Chuan Dong*[a]

[a]*College of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, P.R. China*
[b]*School of Arts and Sciences, Shanxi Agricultural University, Taigu 030801, P.R. China*

ABSTRACT

A novel rhodamine derivative 3-bromo-5-methylsalicylaldehyde rhodamine B hydrazone (BMSRH) has been synthesized by reacting rhodamine B hydrazide with 3-bromo-5-methylsalicylaldehyde and developed as a new colorimetric probe for the selective and sensitive detection of Cu^{2+}. Addition of Cu^{2+} to the solution of BMSRH results in a rapid color change from colorless to red together with an obvious new band appeared at 552nm in the UV-vis absorption spectra. This change is attributed to the spirocycle form of BMSRH opened via coordination with Cu^{2+} in a 1:1 stoichiometry and their association constant is determined as 3.2×10^4 $L\cdot mol^{-1}$. Experimental results indicate that the BMSRH can provide a rapid, selective and sensitive response to Cu^{2+} with a linear dynamic range 0.667-240 μmol/L. Common interferent ions do not show any interference on the Cu^{2+} determination. It is anticipated that BMSRH can be a good candidate probe and has potential application for Cu^{2+} determination. The proposed probe exhibits the following advantages: a quick, simple and facile synthesis.

Keywords**:** Rhodamine; Colorimetric; Probe; Copper; 3-bromo-5-methylsalicylaldehyde; Hydrazine

---

[*] Corresponding authors: E-mail: dc@sxu.edu.cn (C. Dong); Tel: +86-351-7018613; Fax: +86-351-7018613.

1. Introduction

Copper is an essential transition element to human health. It is very important in various physiological processes, such as bone formation, hematopoietic function, cellular respiration, prevention of cardiovascular diseases and connective tissue development [1]. Copper, together with certain protein, can also produces numerous critical enzymes for life such as cytochrome c oxidase, tyrosinase and superoxide dismutase [2-5]. A deficiency of copper(Ⅱ) can lead to anemia and arteriosclerosis, whereas excess copper can be harmful and even cause Alzheimer's and Parkinson's diseases [6,7]. The U.S. Environmental Protection Agency (EPA) has set the maximum allowable level of copper in drinking water at 1.3ppm [8]. In addition, copper(Ⅱ) is also used as the plant diseases treatment, colorant of china and as preservatives for wood and leather in industry. Its potential toxic effects on human beings continue to be challenging problems throughout the world. Consequently, effective detection of copper(Ⅱ) in food, industrial and physiological samples is of importance and considerable effort has been made toward the development of highly selective and sensitive ways to detect copper(Ⅱ) including atomic absorption spectrometry [9 -11], inductively coupled plasma mass spectroscopy (ICPMS) [12], inductively coupled plasma atomic emission spectrometry (ICP-AES) [13]. However, those methods are usually complicated, time-consuming, and costly. Recently, Colormetric and fluorescent methods proved to be a more powerful technique for ion detections because of their high selectivity and ease of fabrication. Many of these systems consists of a large rigid π-conjugated system such as fluoresceins [14-16], coumarins [17-20], quinolines [21], rhodamines [22-37], BODIPY dyes [38-40], calixarenes [41-44], polythiophene [45] and they have the obvious spectra absorption or strong fluorescence. Tang′s [46] group have developed the first near-infrared fluorescent probe toward Cu^{2+} and successfully applied to biological imaging. Compared with fluorimetry, Colormetry has its advantage due to the simplicity and low capital cost of the assay, it is easy observation by the naked eye and no requirement for sophisticated instruments. Shen′s [47] group and Yao′s [48] group have also developed a colorimetric method for the Cu^{2+} assay using click chemistry.

The fluorescein and rhodanmine family dyes are the ideal objectives for fabrication of colorimetric sensors because of their distinctive structure. Ring-opening of their spirolactam structure can lead to an obvious color change and a large rigid π-conjugated system with some excellent spectroscopic properties, such as long absorption and emission wavelength, high fluorescence quantum yield, visible-range extinction coefficients and high stability to light. By this main feature, in recent years, fluorescein and rhodamine compounds are usually introduced to construct optical sensor for many different target molecules especially transition metal ions, such as Zn^{2+} [14], Cu^{2+} [15,16,23-29,37], Hg^{2+} [30-34], Fe^{3+} [35] and Pb^{2+} [36]. Given the importance of the copper ions to our life, it is still desirable to develop some new probes for Cu^{2+} in terms of better sensitivity and selectivity.

In the present study, we designed and synthesized a novel rhodamine-based compound, 3-bromo-5-methylsalicylaldehyde rhodamine B hydrazone (BMSRH), for rapid, selective and sensitive response to Cu^{2+} ion in acetonitrile and water media. The BMSRH bears a cleavable active amide bond and exhibits a highly selective color reaction with Cu^{2+} in acetonitrile and water solutions. Addition of Cu^{2+} to the solution of BMSRH results in a rapid color change from colorless to red together with an obvious new band appeared at 552nm in the UV-vis absorption spectra. Addition of other common alkali-, alkaline earth-, trasition- and rare earth metal ions had not any changes in color or UV-vis absorption spectra. BMSRH is a naked-eye chemosensor for detection of Cu^{2+} with facile, fast and selective features.

2. Experimental

2.1. Chemicals and Instruments

Rhodamine B and 3-bromo-5-methylsalicylaldehyde was purchased from Aladdin Chemical Co., Ltd. (Shanghai, China), hydrazine hydrate(85%, Beijing Xudong Chemical Plant), other material for synthesis were used without further purification. All chemicals used were analytical grade. Deionized water was used throughout the work.

Absorption spectra were taken on a TU-1901 double-beam UV–vis absorption spectrophotometer (Beijing Purkinje General Instrument Co., LTD, Beijing, China). Fluorescence spectra were recorded on a Cary Eclipse spectrofluorometer equipped with a 150 W xenon lamp source (Varian Australian PTY LTD, Victoria, Australia). Quartz cuvettes (path-length=1cm) was used in all spectrophotometric and fluorometric measurements. ^{1}H NMR and ^{13}C NMR measurements were performed on a Bruker DKX-300MHz NMR spectrometer (Bruker biospin, Switzerland). Mass spectroscopy was performed on VG Micro mass 7070H(ESI-MS). All the spectra were recorded at 298K. Elemental analyses were done on a Vario EL cube elemental analyzer (Elementar, Germany). Melting points were determined on a RD-1 melting point detector (Guoming, China).

2.2. Synthesis procedure

2.2.1. Synthesis of Rhodamine B hydrazide

Rhodamine B (4.79g, 10 mmol) was stirred in 50 mL of ethanol and excess hydrazine (12 ml, hydrazine content > 80%) was added dropwise. Then the reaction mixture was heated to reflux for 5h with stirring and monitoring with TLC, during which time the pink color disappeared gradually. After cooling to room temperature the solvent was removed on a rotary evaporator. The residue was dissolved in HCl (1M) and adjusted the solution to pH 7 by 0. 5 M NaOH. The resulting precipitate was filtered and washed many times with water to provide 3.94 g of RH as an off-white powder in

80% yield. ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ = 7.76 (m, 1H, ArH), 7.46 (m, 2H, ArH), 6.98 (m, 1H, ArH), 6.37–6.32 (d, 6H, xanthene-H), 4.27 (s, 2H, NH2), 3.32(q, 8H, NCH2CH3), 1.07 (t, 12H, NCH2CH3); ^{13}C NMR (DMSO-d$_6$) δ = 12.46, 43.7, 64.76, 97.42, 105.46, 107.79, 122.16, 123.51, 127.72, 128.12, 129.63, 132.39, 148.11, 151.9, 153.04, 165.29. MS, *m/z*: 457.2 ([RH + H]$^+$), 479.1 ([RH + Na]$^+$); [RH] calculated 456.2.

2.2.2. Synthesis of 3-bromo-5-methylsalicylaldehyde rhodamine B hydrazone (BMSRH)

BMSRH was synthesized by reaction of Rhodamine B hydrazide with 3-bromo-5-methylsalicylaldehyde in ethanol containing catalytic amount of acetic acid. To a solution of rhodamine hydrazide (0.99 g, 2 mmol) dissolved in 20 mL ethanol, 3-bromo-5-methylsalicylaldehyde (0.42g, 2 mmol) was added. The reaction mixture was heated to reflux for 8 h with stirring and monitoring with TLC, After the reaction, the mixture was cooled and an off-white precipitate appeared. The precipitate was separated by filtration and the crude product was recrystallized using methanol to provide 1.06 g of BMSRH as an off-white powder in 75% yield. Melting point: 153-154 °C. ^{1}H NMR (DMSO-d$_6$, 300 MHz, 25℃): δ 11.19 (s, 1H), 8.91 (s, N=C-H, 1H), 7.92(1H), 7.60(2H), 7.36(1H), 7.02(2H), 6.45-6.35(6H), 3.32(8H), 1.05(12H). ^{13}C NMR (DMSO-d$_6$, 75 MHz, 25℃): δ (ppm):11.55, 18.54, 42.84, 64.68 (C$_{spiro}$), 96.58, 103.36, 107.48, 108.84, 118.05, 122.40, 123.10, 126.84, 127.23, 128.22, 128.95, 129.83, 133.50, 134.19, 147.33, 147.84, 149.55, 150.32, 150.84, 151.80, 162.87. MS, *m/z*: 654.3([BMSRH + H]$^+$), 676.3 ([BMSRH + Na]$^+$); [BMSRH] calculated 653.3.

2.3. Cu^{2+} sensing measurement

A standard Cu^{2+} solution (2.0×10^{-3} mol/L) was prepared by dissolving copper chloride in deionized water. BMSRH stock solution (1.0×10^{-4} mol/L) was prepared in acetonitrile solution. In detection, BMSRH was diluted to 2.4×10^{-5} mol/L by B-R buffer (pH = 7.0). Each time 3.0 mL of 2.4×10^{-5} mol/L BMSRH was placed into a 1.0 cm path-length silica cuvette, and the required quantity of Cu^{2+} solution was added by a micro-pipette. 1 mins later the UV-vis spectra was measured. All the measurements were taken at room temperature. For the interference detection, solutions of Fe^{2+}, Co^{2+}, Zn^{2+}, Cr^{3+}, Pb^{2+}, Ni^{2+}, Sn^{2+}, Hg^{2+}, Mn^{2+}, Al^{3+}, Ba^{2+}, Mg^{2+}, Cu^{2+}, and Fe^{3+} from their chloride salts, Ag^+ from its nitrate salt and $Cr_2O_7^{2-}$from their sodium salts were used.

2.4. Job's plot measurements

1.0×10^{-4} mol/L stock solution of BMSRH in acetonitrile and a 1.0×10^{-4} mol/L stock solution of Cu^{2+} in H_2O were prepared, the stock solution of BMSRH and the Cu^{2+} stock solution were placed in a test tube to obtain a total volume of 3.6 mL, then diluted to 15 mL with acetonitrile / pH = 7.0 B-R buffer to get the test solution (nine test solutions were got; for the first test solution, 0.36 mL stock solution of BMSRH and 3.24 mL stock solution of Cu^{2+} were used, then diluted to 15 mL with pH = 7.0 B-R buffer; for the second test solution, 0.72 mL stock solution of BMSRH and 2.88 mL stock solution of Cu^{2+} were used; for the third test solution, 1.08 mL stock solution of BMSRH and 2.52 mL stock solution of Cu^{2+} were used; until 3.24 mL stock solution of BMSRH and 0.36 mL stock solution of Cu^{2+} were used to get the ninth test solution). All the measurements were performed with [BMSRH] + [Cu^{2+}] =24 μmol/L. The absorbances at 552 nm of these test solutions were recorded.

3. Results and discussion

3.1. Design and synthesis of BMSRH

A colormetric or fluorescence based metal ion probe usually comprises two major components: a chromophore and a ligand. Our considerations for synthesizing BMSRH are based on the facts: (1) 3-bromo-5-methylsalicylaldehyde can be readily reacted with amino of rhodamine hydrazide to form schiff′s base and contribute to a good coordination oxygen atom. (2)when coordination takes place, the spirocycle structure of rhodamine moiety will be opened and at the same time an obvious color and spectra change will be observed due to the formation of a large rigid π-conjugated system. Consequently, the BMSRH was synthesized by a simple two-step reaction for detecting Cu^{2+} (Fig. 1) and confirmed by ^{1}H NMR, ^{13}C NMR spectroscopy, and MS. The existence of spirocyclic ring structure in BMSRH was confirmed by the observation of ^{13}C NMR resonances at 64.68 ppm.

Figure 1.

3.2. UV-vis spectra of interaction of BMSRH with Cu^{2+}

The UV-visible absorption spectra of BMSRH in the presence of Cu^{2+} are displayed in Fig. 2. The BMSRH had nearly no absorption over 552nm region, which was ascribed to the closed spirolactam form of BMSRH. When Cu^{2+} was added into the solution of BMSRH, it can chelate with BMSRH, induce ring-opening at C-N bond in spirolactam and generate a rhodamine-type intermediate with a new absorption peak appeared at 552nm and its absorbance increased gradually with the increase of Cu^{2+} concentration. Correspondingly, the solution of BMSRH changed from colorless to red. The significant spectra and color change indicated that BMSRH was a sensitive naked-eye indicator for Cu^{2+}. The analytical characteristics of BMSRH to Cu^{2+} based on the absorption spectra have also been exploited The results showed that the absorbance value changes (ΔA) as a function to the concentration of Cu^{2+} ion had a good linear range of 6.67×10^{-7} to 2.4×10^{-4} mol/L with the linear regression equation of $\Delta A=4.45\times10^{4}[Cu^{2+}]-0.03438$ (Fig. 3a). Further, according to linear Benesi-Hildebrand expression (Fig. 3b), the measured absorbance value $[1/(A-A_0)]$ at 552 nm varied as a function of $1/[Cu^{2+}]$ in a good linear relationship (r=0.9964), which was an indication that the composition of BMSRH/Cu^{2+} complex was 1:1[49,50]. The stability constant given by the slope of the straight line (Benesi–Hildebrand method) was 3.2×10^{4} mol/L, It could be seen that BMSRH formed stable complex with Cu^{2+}.

Figure 2.

Figure 3.

3.3. Time-dependence in the detection process of Cu^{2+}

To investigate the Cu^{2+} detection ability, time-dependence on the UV-vis absorption spectra of the reaction systems was investigated (as shown in Fig. 4). Low, medium and high concentration of Cu^{2+} standard solution in the linear range was tested. Upon addition various concentrations (2 μM, 10μM, 20μM) of Cu^{2+}, the interaction of BMSRH with Cu^{2+} was completed in less than 1 min. One min later three absorbance at 552 nm of the system get to maximum and does not increase with more reaction time, which indicated that the BMSRH could rapidly react with Cu^{2+} and the spirocycle of BMSRH could be opened in a very short time under the experimental conditions. It means the method could be used for real-time detection of Cu^{2+} and 1 mins was also selected as the detection time in this paper.

Figure 4.

3.4. Job's plot analyses

For further determination the stoichiometry between BMSRH and Cu^{2+}, Job's plot analyses was also used (Fig. 5). A plot of f absorbances versus the molecular fraction of [BMSRH]/([BMSRH]+[Cu^{2+}]) was provided in Fig. 6. All the analyses were performed with [BMSRH] + [Cu^{2+}] = 24 μmol/L. The maximum absorbance intensity was appeared when the molecular fraction of Cu^{2+} was close to 0.5, which indicated a 1:1 stoichiometry of the BMSRH to Cu^{2+} in the inclusion complex. It was consistent with the result of linear Benesi-Hildebrand expression.

Figure 5.

3.5. Selectivity investigation

Selectivity is an important characteristic of an ion-selective chemosensor. To examine the selectivity of BMSRH toward Cu^{2+}, the effect of a wide range of environmentally and physiologically active metal ions was investigated using the UV-vis spectra and the result were shown in Fig. 6. Under the same conditions, in the presence of other competive metals, the BMSRH has no absorption at 552nm and the color of solution has not any change. Only Cu^{2+} was present, a strong new absorption peak appeared at 552nm, and the color of the solution changed from colorless to red immediately. Furthermore, The possible interferences by other metal ions were further assessed through competitive experiments, the UV-vis spectra were measured by the treatment of 24 μmol/L Cu^{2+} in the presence of 48 μmol/L other interfering metal ions. As shown in Fig. 6. The absorption spectra of BMSRH solutions had similarly influence with that of Cu^{2+} was lonely present., the tested background ions showed almost no interference with the detection of Cu^{2+}.These results demonstrated that BMSRH showed excellent selectivity to Cu^{2+} over other competitive cations and the detection of Cu^{2+} was hardly affected by these coexistent common metal ions.

Figure 6.

3.6. Interaction mechanism of BMSRH binding to Cu^{2+}

The proposed mechanisms of detection and the structures of the probes, both with and without the addition of Cu^{2+} were shown in Fig. 7. As other rhodamine-based probes, BMSRH had spirocycle and open-cycle forms, The spirocycle form was colorless and non-fluorescent. Addition of Cu^{2+} makes the spirocycle open via coordination and obvious color with spectra change appear (Fig. 9). On addition of EDTA to the solution of BMSRH containing Cu^{2+}, the change of color and spectra disappeared again, this process could be repeated many times. These findings indicated that BMSRH reversibly coordinated with Cu^{2+}, rather than other possible reactions. Ring-opening of the spirocyle form resulted in a large rigid π-conjugated system but did not generate strong fluorescence emission. This phenomenon was own to the paramagnetic effect from spin-orbit coupling of the Cu^{2+} inducing fluorescence quenching of BMSRH. Similar phenomena were also observed in other experiments [51-53].

Figure 7.

In order to better understand the reaction mechanism of BMSRH and Cu^{2+}, ^{13}C NMR titration was performed to assess their interaction(Fig. 8). ^{13}C NMR spectra of BMSRH－Cu^{2+} compared to that of BMSRH showed the involvement of carbonyl oxygen of BMSRH in complex formation. The reduction in the ^{13}C-resonance at 64.68ppm confirms the opening of spirolactam ring upon complex formation with Cu^{2+} ions. Meanwhile, new characteristic absorption peaks appeared at 552nm in the presence of Cu^{2+} proved the spirolactam moiety of rhodamine backbone ring-opening because of the coordination of Cu^{2+} to BMSRH.

Figure 8.

3.7. Test of the method

The accuracy of this newly designed method was tested by recovery experiment. The solution of Cu^{2+} was prepared to the concentration of 2 mmol/L by dissolving $CuCl_2 \cdot 2H_2O$ in water. Each time 3ml 24 μmol/L BMSRH in CH_3CN/H_2O solution (1:1 v/v, 20 mmol/L B-R buffer at pH 7.0) was placed into a 1.0 cm path-length silica cuvette. Low, medium and high concentration of Cu^{2+} standard in the linear range was then added into the BMSRH solution by a micro-pipette and the concentration of Cu^{2+} were 2.00, 20 and 100 μmol/L, respectively. After 1 min, the UV-visible absorption spectrum was recorded. We obtained the found content of Cu^{2+} by the equation of $\Delta A=4.45\times10^4[Cu^{2+}]-0.03438$ and the result were showed in Table 1. From the date, the original and obtained contents were approximately consistent, and the RSD% < 2%. Besides, From the results of many times, the recovery of Cu^{2+} were kept within the range of 96%-103% and the average recovery(%) was 97.70%, which indicated that the designed method was reliable. BMSRH could be a potential candidate as a simple-to-use and naked-eye probe for Cu^{2+} determination.

Table 1

Conclusion

In summary, A novel rhodamine derivative BMSRH has been successfully synthesized by the reaction of rhodamine B hydrazide and 3-bromo-5-methylsalicylaldehyde. Its sensing characteristics to Cu^{2+} was further investigated using UV-vis spectroscopies. In the presence of Cu^{2+}, the BMSRH displayed an obvious color change from colorless to red together with UV-vis absorption spectra change in a very short time. As the result of coordination of BMSRH with Cu^{2+} in a 1:1 stoichiometric ratio, their ring-opening reaction mechanisms were proposed. Futhermore, BMSRH exhibited a good selectivity and sensitivity towards Cu^{2+} over other common competitive alkali, alkaline earth and transition metal ions. The proposed probe exhibits the following advantages: a quick, simple and facile synthesis. This phenomenon made the real-time, simple-to-use and naked-eye detection of Cu^{2+} possible.

Acknowledgements

Financial supports from the National Natural Science Foundation of China (21175086) and Natural Science Foundation for Young Scientists of Shanxi Province (2010021010-2) are gratefully acknowledged. This work was also supported by the project of Hundred Talents Program of Shanxi Province.

References

[1] Y.H. Chan, J. X. Chen, Q. Liu, S. E. Wark, D. H. Song, L. D. Batteas, Analytical Chemistry 82 (2010) 3671-3678.

[2] H. Ye, F. Ge, Y.M. Zhou, J.T. Liu, B.X. Zhao, Spectrochimica Acta A 112 (2013) 132-138.

[3] S.Q. Wang, Y. Gao, H.Y. Wang, X.X Zheng, S. Li, Y.R. Zhang, B.X. Zhao, Spectrochimica Acta A 106 (2013) 110-117.

[4] J. Liang, M. Qin, R. Xu, X. Gao, Y. Shen, Q. Xu, Y. Cao, W. Wang, Chemical Communications 48 (2012) 3890-3892.

[5] M. Shellaiah, Y.C. Rajan, H.C. Lin, Journal of Material Chemistry 22 (2012) 8976-8987.

[6] G. L. Millhauser. Accouts of Chemical Research 37 (2004) 79-85.

[7] E. Gaggelli, H. Kozlowski, D. Valensin, G. Valensin, Chemical Reviews.106 (2006) 1995-2044.

[8] J. W. Liu, Y. Lu, Journal of the American Chemical Society 129 (2007) 9838-9839.

[9] T. W. Lin, S. D. Huang, Analytical Chemistry 73 (2001) 4319-4325.

[10] N. Pourreza, R. Hoveizavi, Analytical Chimica Acta 549 (2005) 124-128.

[11] M. S. Chan, S. D. Huang, Talanta 51(2001) 373-380.

[12] J. Wu, E. A. Boyle, Analytical Chemistry 69 (1997) 2464-2470.

[13] Y. Liu, P. Liang, L. Guo, Talanta 68 (2005) 25-30.

[14] L. Jiang, L. Wang, M. Guo, G. Yin, R.Y. Wang, Sensors and Actuators B 156 (2011) 825-831.

[15] F.J. Huo, C.X. Yin, Y.T. Yang, Analytical Chemistry 84 (2012) 2219-2223.

[16] T.R. Li, Z.Y. Yang, Y. Li, Z.C. Liu, G.F. Qi, B.D. Wang, Dyes and Pigments 88 (2011) 103-108.

[17] Y.J. Jiang, B.S. Moon, M.S. Park, B.G. Kang, J.Y. Kwon, J.S.J. Hong, Y.J Yoon, K.D. Lee, J. Yoon, Tetrahedron Letters 47 (2006) 2707-2710.

[18] H.S. Jung, P.S. Kwon, J.W. Lee, J.I. Kim, C.S. Hong, J.W. Kim, S. Yan, J.Y. Lee, J.H. Lee, T. Joo, Journal of the American Chemical Society 131 (2009) 2008-2012.

[19] A. Helal, M.H.O. Rashid, C.H. Choi, H.S. Kim, Tetrahedron 67 (2011) 2794-2802.

[20] Q. Lin, P. Chen, J. Liu, Y.P. Fu, Y.M. Zhang, T.B. Wei, Dyes and Pigments 98 (2013) 100 -105.

[21] A.P. Silva, H.Q. Gunaratne, T. Gunnlaugsson, A.J. Huxley, C.P. McCoy, J.T. Rademacher, T.E Rice, Chemical Reviews 97 (1997) 1515-1566.

[22] S.C. Kang, S.W. Kim, Y.K. Yang, S. Bae, J.S. Tae, Tetrahedron Letters 50 (2009) 2010 -2012.

[23] M.L. Zhao, X.F.Yang, S.F. He, L.P.Wang, Sensors and Actuators B 135 (2009) 625-631.

[24] C.W.Yu, LX.. Chen, J. Zhang, J.H. Li, P. Liu, W.H. Wang, B. Yan, Talanta 85 (2011) 1627-1633.

[25] Z.Q. Hu, X.M. Wang, Y.C. Feng, L. Ding, H.Y. Lu, Dyes and Pigments 88 (2011) 257-261.

[26] M. Dong, T.H. Ma, A.J. Zhang, Y.M. Dong, Y.W. Wang, Y. Peng, Dyes and Pigments 87 (2010)164-172.

[27] X.Q. Chen, M.J. Jou, H.Y. Lee, S. Kou, J. Lim, S.W. Nam, S. Park, K.M. Kim, J. Yoon, Sensors and Actuators B-chem 137 (2009) 597-602.

[28] Y. Zhou, F. Wang, Y.M. Kim, S.J. Kim, J.Y. Yoon, Organic Letters 11 (2009) 4442-4445.

[29] L. Jiang, B. Zhang, J. Sun, G. Yin, T.M. Shang, L. Wang, R.Y. Wang, Journal of Inorganic Chemistry 26 (2010) 1750-1755.

[30] J.S. Wu, I.C. Hwang, K.S. Kim, Organic Letters 9 (2007) 907-910.

[31] Y.K. Yang, K.J. Yook, J. Tae, Journal of the American Chemical Society 127 (2005)16760-16761.

[32] S.K. Ko, Y.K. Yang, J. Tae, Journal of the American Chemical Society 128 (2006)14150-14155.

[33] H. Yang, Z.G. Zhou, K.W. Huang, M.X. Yu, F.Y. Li, T. Yi, Organic Letters 9 (2007) 4729-4732.

[34] J.H. Soh, K.M.K. Swamy, S.K. Kim, S. Kim, S.H.Lee, J .Yoon, Tetrahedron Letters 48 (2007) 5966-5969.

[35] M. Zhang, Y.H. Gao, M.Y. Li, M.X. Yu, F.Y. Li, L. Li, Tetrahedron Letters 48 (2007) 3709-3712.

[36] J.Y. Kwon, Y.J. Jang, Y.J. Lee, K.M. Kim, M.S. Seo, W. Nam, Journal of the American Chemical Society 127 (2005) 10107-10111.

[37] F.B Yu, W.S, Zhang, P. Li, Y.L, Xing, L.L, Tong, J.P, Ma, B.Tang. Analyst 134 (2009) 1826-1833.

[38] X. Qi, E.J. Jun, S.J. Kim, J.S.J Hong, Y.J Yoon, J. Organic Chemstry 71 (2006) 2881-2884.

[39] L. Zeng, E.W. Miller, A. Pralle, E.Y. Isacoff, C.J Chang, Journal of the American Chemical Society 128 (2006) 10-11.

[40] K. Rurack, M. Kollmannsberger, U. Resch-Genger, J. Daub, Journal of the American Chemical Society 122 (2000) 968-969.

[41] S.Y. Li, Q.Y. Zheng, C.F. Chen, Z.T. Huang, Textrahedron:Asrymmetry 16 (2005) 2816-2820.

[42] Z. Liang, Z.L. Liu, L. Jiang, Y.H. Gao, Tetrahedron Letters 48 (2007)1629-1632.

[43] V. Bhalla, R. Kumar, M. Kumar, A. Dhir, Tetrahedron 63 (2007) 11153-11159.

[44] N. Singh, M. Kumar, G. Hundal, Tetrahedron 60 (2004) 5393-5405.

[45] Z.Y. Yao, B.H. Huang, X.P. Hu, L Zhang, D.P. Li, M. Guo, X.H. Zhang, H. Yuan and H.C. Wu, Analyst 138 (2013) 1649-1652.

[46] P. Li, X. Duan, Z.Z Chen,Y. Liu,T. Xie, L.B Fang,X.R Li, M. Yin, B. Tang, Chem. Commun., 47(2011) 7755-7757.

[47] Q.P. Shen, W.H. Li, S.Y. Tang, Y.F. Hu, Z. Nie, Y. Huang, S.Z.Huang, S.Z. Yao, Biosensors and Bioelectronics 41(2013) 663-338.

[48] Z.Y. Yao, Y.B. Yang, X.L. Chen, X.P. Hu, L Zhang, L. Liu, Y.L. Zhao and H.C. Wu, Analytical chemistry 85 (2013) 5650-5653.

[49] H.A. Benesi, J.H. Hildebrand, Journal of the American Chemical Society 71 (1949)2703-2707.

[50] M. Barra, C. Bohne, J.C. Scaiano, Journal of the American Chemical Society 112 (1990) 8075-8079.

[51] F.A. Abebe, C.S. Eribal, G. Ramakrishna, E. Sinn, Tetrahedron Letters 52 (2011) 5554-5558.

[52] L.M. Hyman, C.J. Stephenson, M.G. Dickens, K.D. Shimizu, K.J. Franz, Dalton Transactions 39 (2010) 568-576.

[53] X.T. Chen, Z.F. Li, Y. Xiang, A.J.Tong, Tetrahedron Letters 49 (2008) 4697- 4700.

CAPTIONS FOR FIGURES

Figure 1. Synthetic route for 3-bromo-5-methylsalicylaldehyde rhodamine B hydrazone (BMSRH).

Figure 2. The UV-visible absorption spectra of BMSRH (24 μmol/L, $CH_3CN/H_2O=1:1$) with various concentrations of Cu^{2+} at room temperature. (a) $[Cu^{2+}]$=1.33, 2.67, 4.0, 5.33, 6.67, 8.0, 9.33, 10.67, 12.0, 13.33, 14.67, 16.0, 17.33, 18.67, 20.0, 21.33, 22.67,and 24.0 μmol/L, respectively; (b) Inset image shows the corresponding colors change of BMSRH with the various concentrations of Cu^{2+} in natural light.

Figure 3. **(a)**Linear range calibration curve of determination of Cu^{2+} ion. (b) Benesi-Hildebrand plot of $1/(A-A_0)$ versus $1/[Cu^{2+}]$.

Figure 4. Time course of the response of BMSRH (22 μmol/L, B-R buffer, pH=7.0) to (a)2.0 μmol/L, (b)10 μmol/L, (c)20 μmol/L of Cu^{2+} in aqueous solution. Inset image shows the corresponding colors change of BMSRH with the various concentrations of Cu^{2+} in natural light.

Figure 5. Job's plot of BMSRH with Cu^{2+} in $CH_3CN/H_2O=1:1$ solution. Total concentration of BMSRH + Cu^{2+} was kept constant at 24 μmol/L. The absorbance at 552 nm was used.

Figure 6. UV-vis absorption spectra of BMSRH (24 μmol/L, $CH_3CN/H_2O=1:1$) in the presence of Cu^{2+} (24 μmol/L) and other cations x (48 μmol/L) including Cu^{2+}, Al^{3+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Fe^{2+}, Zn^{2+}, Ag^{+}, Mg^{2+}, Ba^{2+}, Cr^{3+}, $Cr_2O_7^{2-}$, Hg^{2+}, Mn^{2+}, Pb^{2+} , Sn^{2+}. Inset:the Columns plot of BMSRH (24 μmol/L, $CH_3CN/H_2O=1:1$) in the different metal ions and the image of the corresponding colors of BMSRH (24 μmol/L, $CH_3CN/H_2O=1:1$) in natural light in the presence of different metal ions.

Figure 7. Proposed binding mechanism of BMSRH with Cu^{2+}.

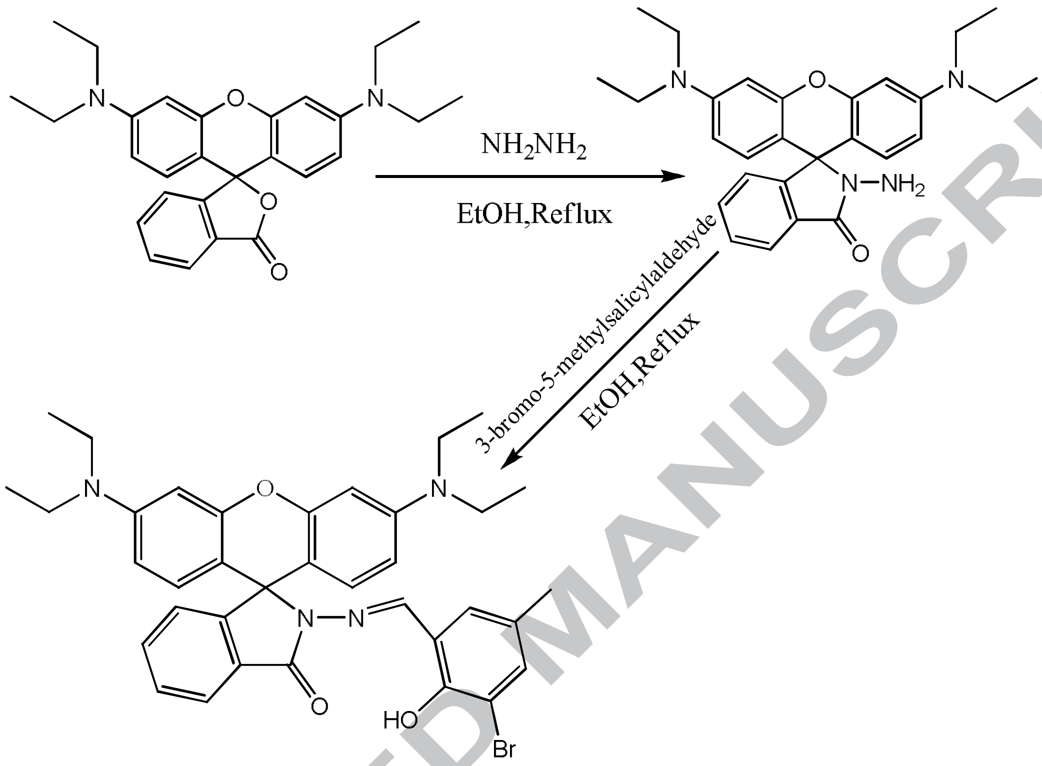
Figure 8. ^{13}C NMR spectra of BMSRH in the absence or presence of Cu^{2+} (a) BMSRH, (b) BMSRH + Cu^{2+}.

Table 1 Test experiment determination of Cu^{2+}.

	Original content of Cu^{2+} (μmol/L)	found content of Cu^{2+}. (μmol/L)[a]	RSD%	Recovery%	average recovery%
Day	2.00	2.00 ± 0.08	2.06	96 – 102.0	
	20.00	20.00 ± 0.48	0.82	97.6 – 102.4	
	100.00	100.00 ± 1.29	0.48	98.7 – 111.2	97.7
Days	2.00	2.00 ± 0.06	1.92	97.0 – 103	
	20.00	20.00 ± 0.52	0.66	97.4 – 102.5	
	100.00	100.00 ± 1.18	0.52	98.8 – 111.8	

[a] Every concentration were determinated 8 times

Figure 1



N
O
N
O
O
NH_2NH_2
EtOH,Reflux
N
O
N
N–NH_2
O
3-bromo-5-methylsalicylaldehyde
EtOH,Reflux
N
O
N
N–N
O
HO
Br

Figure 2

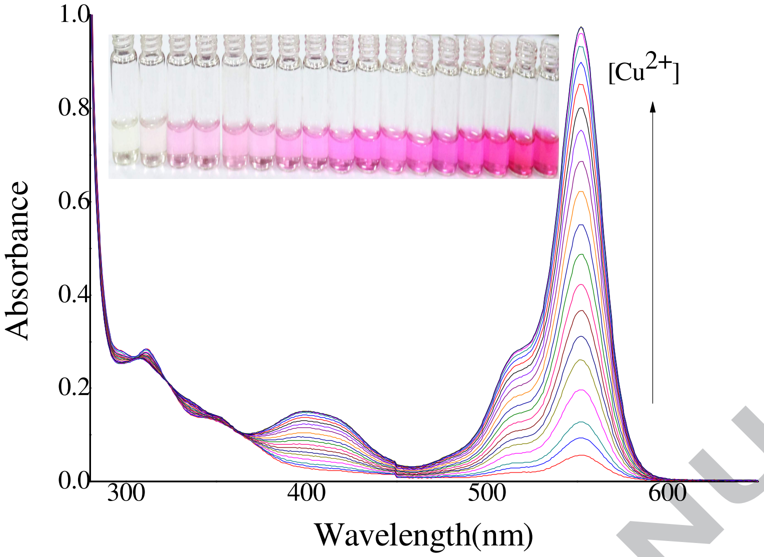


Figure 3

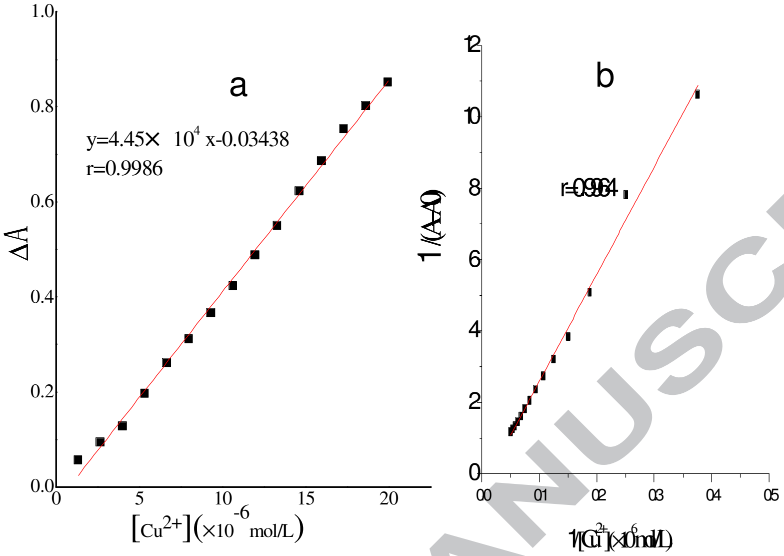

a
1.0
0.8
0.6
0.4
0.2
0.0
ΔA
0
5
10
15
20
y=4.45× 10^4 x-0.03438
r=0.9986
[Cu2+](×10-6 mol/L)
b
12
10
8
6
4
2
0
1/(A-A0)
r=0.9964
0.0
0.1
0.2
0.3
0.4
0.5
1/[Cu2+](×10^6 mol/L)

Figure 4

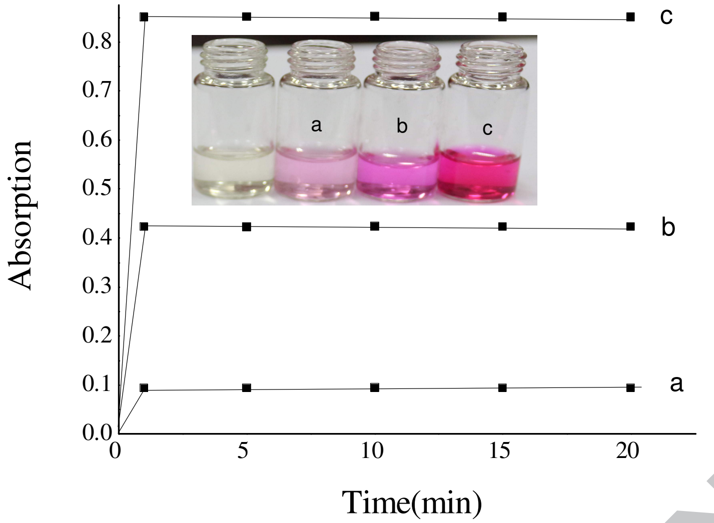


Figure 5

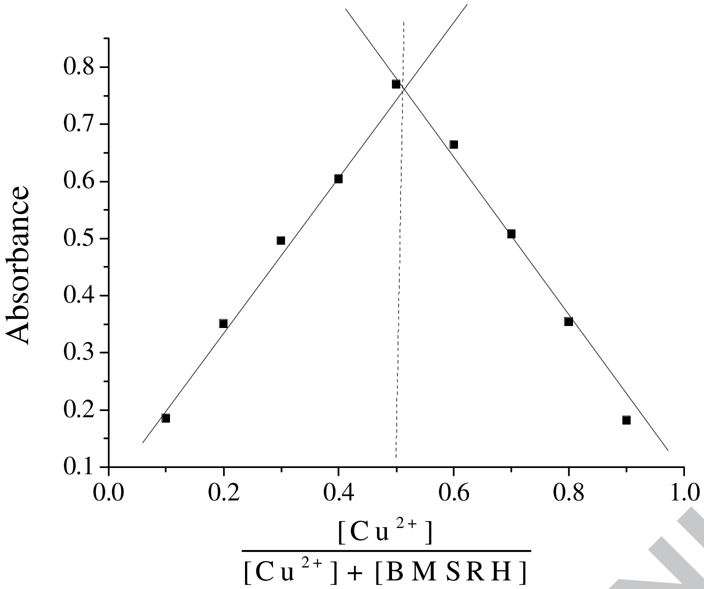

Absorbance
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.0
0.2
0.4
0.6
0.8
1.0
$\frac{[Cu^{2+}]}{[Cu^{2+}] + [BMSRH]}$

Figure 6

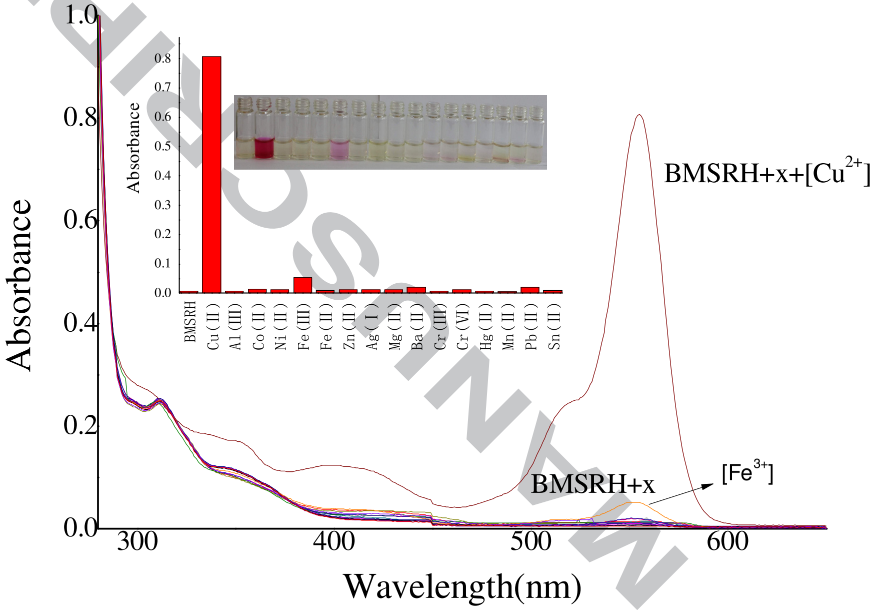

Absorbance
0.0
0.2
0.4
0.6
0.8
1.0
Wavelength(nm)
300
400
500
600
BMSRH+x+[Cu^{2+}]
BMSRH+x
[Fe^{3+}]
Absorbance
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
BMSRH
Cu(II)
Al(III)
Co(II)
Ni(II)
Fe(III)
Fe(II)
Zn(II)
Ag(I)
Mg(II)
Ba(II)
Cr(III)
Cr(VI)
Hg(II)
Mn(II)
Pb(II)
Sn(II)

Figure 7

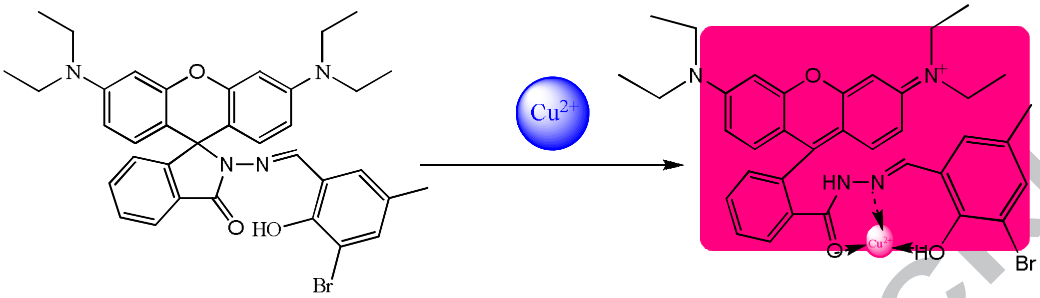
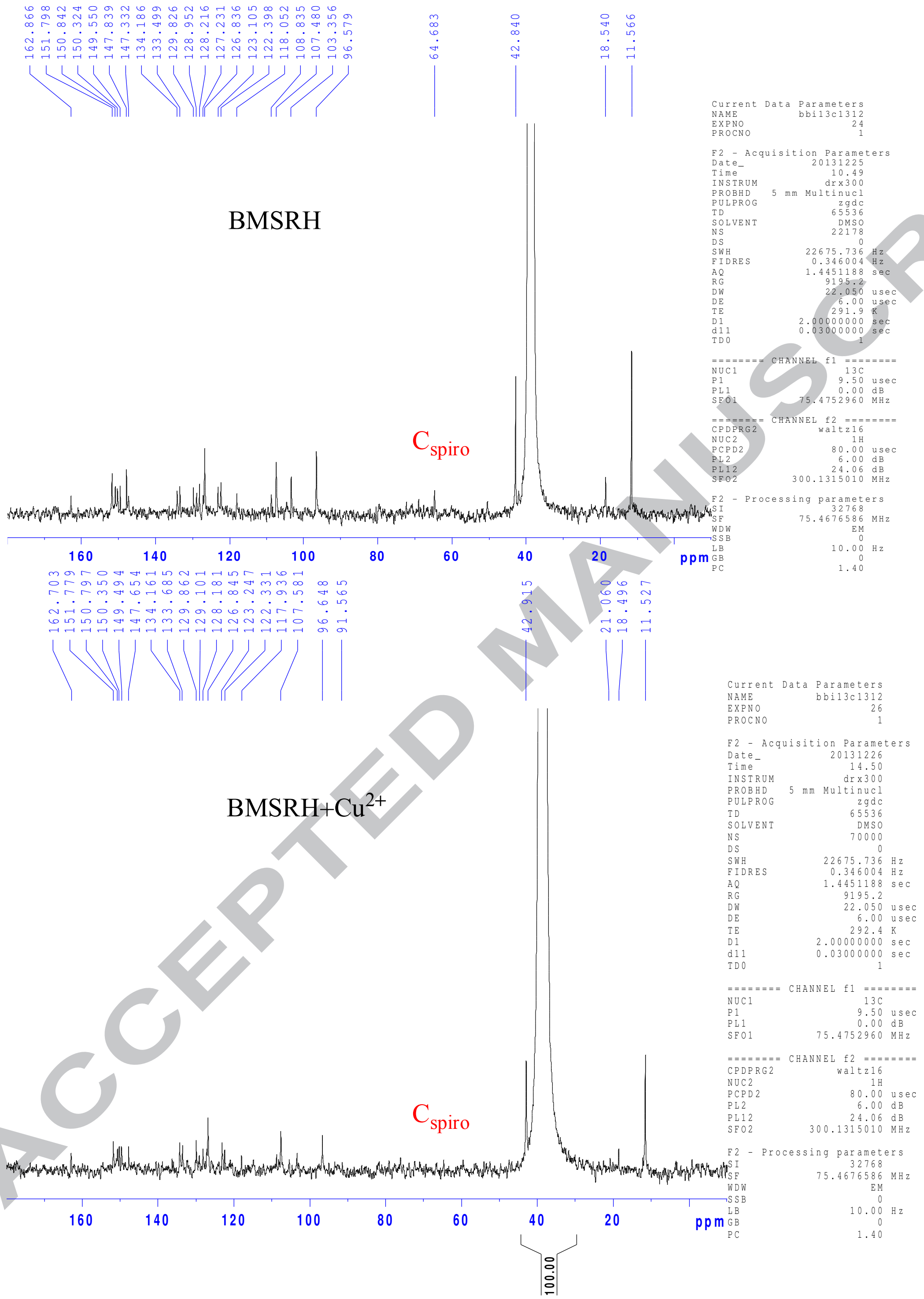


Figure 8



```
Current Data Parameters
NAME          bbi13c1312
EXPNO                 24
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131225
Time               10.49
INSTRUM           drx300
PROBHD   5 mm Multinucl
PULPROG             zgdc
TD                 65536
SOLVENT             DMSO
NS                 22178
DS                     0
SWH            22675.736 Hz
FIDRES          0.346004 Hz
AQ             1.4451188 sec
RG                9195.2
DW                22.050 usec
DE                  6.00 usec
TE                 291.9 K
D1            2.00000000 sec
d11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                 0.00 dB
SFO1          75.4752960 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 6.00 dB
PL12               24.06 dB
SFO2         300.1315010 MHz

F2 - Processing parameters
SI                 32768
SF            75.4676586 MHz
WDW                   EM
SSB                    0
LB                 10.00 Hz
GB                     0
PC                  1.40
```

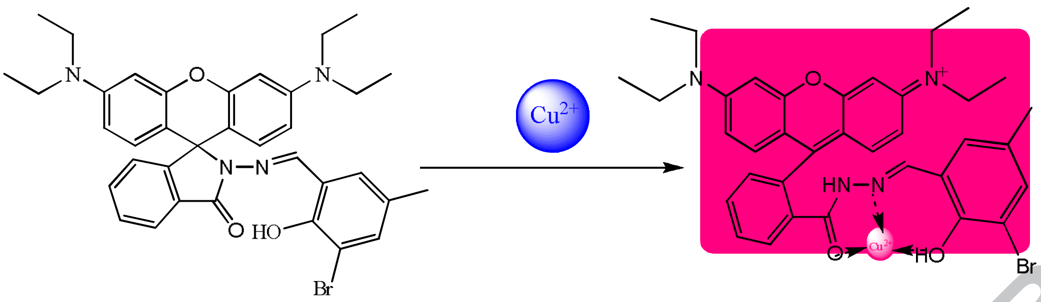
```
Current Data Parameters
NAME          bbi13c1312
EXPNO                 26
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131226
Time               14.50
INSTRUM           drx300
PROBHD   5 mm Multinucl
PULPROG             zgdc
TD                 65536
SOLVENT             DMSO
NS                 70000
DS                     0
SWH            22675.736 Hz
FIDRES          0.346004 Hz
AQ             1.4451188 sec
RG                9195.2
DW                22.050 usec
DE                  6.00 usec
TE                 292.4 K
D1            2.00000000 sec
d11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.50 usec
PL1                 0.00 dB
SFO1          75.4752960 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 6.00 dB
PL12               24.06 dB
SFO2         300.1315010 MHz

F2 - Processing parameters
SI                 32768
SF            75.4676586 MHz
WDW                   EM
SSB                    0
LB                 10.00 Hz
GB                     0
PC                  1.40
```



N
O
N
N
N
O
HO
Br
Cu2+
N
O
N+
HN
N
Cu2+
O
HO
Br

A novel rhodamine B derivative 3-bromo-5-methylsalicylaldehyde rhodamine B hydrazone (BMSRH) was synthesized and characterized.

BMSRH have a rapid, selective and sensitive response to Cu^{2+}.

The response of BMSRH to Cu^{2+} is reversible .

BMSRH can be a good colorimetric probe for Cu^{2+} determination .