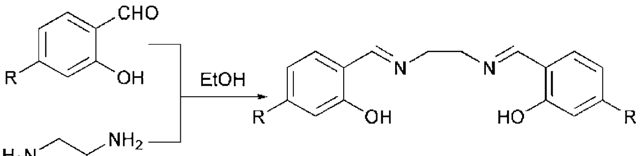
doi:10.1246/cl.2011.1082

A Highly Selective Colorimetric Chemosensor for Mn^{2+} Based on Bis(*N*-salicylidene)ethylenediamine in Pure Aqueous Solution

Chao Gou, Haiqiang Wu, Sisi Jiang, Chenglin Yi, Jing Luo,* and Xiaoya Liu*
School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, P. R. China

(Received June 16, 2011; CL-110505; E-mail: lxy@jiangnan.edu.cn)

A novel easily available chemosensor **1** based on bis(*N*-salicylidene)ethylenediamine was reported, which exhibits highly selective and sensitive recognition toward Mn^{2+} in pure aqueous solution over a wide range of tested metal ions with a clear naked eye color change from colorless to red. This represents the first reported colorimetric chemosensor capable of detecting Mn^{2+} in aqueous solution.



1 R=N(Et)$_2$ **2** R=H

Scheme 1. Chemical structure of sensors **1** and **2**.

Metal ion recognition and sensing has become a fast growing field of research due to their potential application in chemistry, biomedicine, and environmental studies. In particular, the study of metal ion sensing using fluorescent or colorimetric sensors has been actively studied, and great achievements in this field have been obtained in the past few years.[1] Compared to fluorescent sensors, colorimetric sensors have gained more importance and wide acceptance due to low costs and easy detections by naked eye rather than using costly instrumental setups.[2] Therefore, a great effort has been invested in developing simple-to-make and naked-eye colorimetric sensors for sensing of metal ions.[3]

Manganese is an essential trace element found in many enzymes. However, it is toxic at higher concentration level.[4] Overexposure to this metal can damage some tissues and cells of the human body such as brain, bone, and blood to cause heart problems and progressive, permanent, neurodegenerative damage, resulting in syndromes similar to idiopathic Parkinson's disease with few options for treatment and no cure.[5] Manganese is used in various products such as batteries, fertilizers, pesticides, ceramics, gasoline additives, and dietary supplements. Thus, it is found in soil, water, plants, and animals. Consequently, a rapid and convenient method for the determination of manganese becomes more and more important in environmental samples. A number of techniques such as X-ray fluorescence,[6] atomic absorption spectrometry,[7] anodic stripping voltammetry,[8] and inductively coupled plasma atomic emission spectrometry (ICP-AES) have been used for manganese determination, which normally require good infrastructure backup and expertise. So far, the detection of Mn^{2+} by using observable colorimetric chemosensors had been rarely reported in the literature.[9]

Schiff-base derivatives are known to have strong binding ability to metal ions and display different optical properties from the ligands themselves, which make them good candidates for cation probes.[10] This kind of molecule can be easily synthesized by the condensation reactions of salicylaldehyde and amine derivatives.[11] Recently, there has been some excellent work on chemosensors based on the Schiff bases. Gao and his coworkers designed and synthesized 4-chloro-*N*-salicylideneaniline, a highly selective and sensitive chemosensor complex for the detection of Zn^{2+}.[12] Bhardwaj et al. synthesized a new Schiff base, tripodal receptor capable of functioning as a sensor for Ag^{+}.[13] Wang et al. synthesized a chemosensor for Cu^{2+} based on a Schiff base, which could behave as a colorimetric "naked eye" and fluorescent chemosensor for the detection of Cu^{2+} and Zn^{2+} bifunctionally in tetrahydrofuran (THF) solution.[14]

In this paper, we synthesized a bis(*N*-salicylidene)ethylenediamine based derivative **1** functionalized with *N*,*N*-diethylamino moiety (Scheme 1) and studied its spectroscopic properties upon coordination with Mn^{2+}. Moreover, its analog **2** without *N*,*N*-diethylamino moiety was also synthesized for a control experiment. As shown in Scheme 1, **1** and **2** were synthesized by a simple and straightforward method with good yields by condensating diamine with corresponding salicylaldehyde derivatives in anhydrous ethanol.[15] In these compounds, two salicylaldimine moieties are connected by a C=N–CC–N=C bond which provides two amine-N and two phenolate-O binding sites to interact with metal ions and form salen metal complexes.[16] Among the various metal ions, the chemosensor **1** displayed highly selective colorimetric responses with significant color change upon the addition of Mn^{2+}. Another advantage of the chemosensor **1** is its solubility in water, which makes it possible to detect Mn^{2+} in pure aqueous media. Up to now, most of the reported colorimetric or fluorometric sensors were utilized in pure organic solvents or in mixed organic–aqueous media.[17] The design and synthesis of chemosensors that can work in pure aqueous solution with high selectivity and sensitivity, has become crucially important. Works related to this area are of great increasing interest. As far as we are aware, compound **1** is the first colorimetric sensor for detecting Mn^{2+} in pure aqueous solution.

The photophysical properties of **1** were investigated by monitoring its absorption spectral behavior upon addition of various metal ions such as Fe^{3+}, Cu^{2+}, Al^{3+}, Mn^{2+}, Co^{2+}, Ag^{+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Zn^{2+}, Hg^{2+}, Cr^{3+}, Mg^{2+}, Pb^{2+}, and Ni^{2+}. The spectroscopic studies were carried out in pure aqueous solution at pH 8.0 (20 mM boric acid–borax). As shown in Figure 1a, compound **1** exhibits two absorbance bands centered at 356 and 390 nm, which could be attributed to n–π^* transition of C=N and π–π^* transitions of benzene rings in **1**, respectively.[18] The addition of four equiv of metal ions, such as Ag^{+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Hg^{+}, Mg^{2+}, Pb^{2+}, and

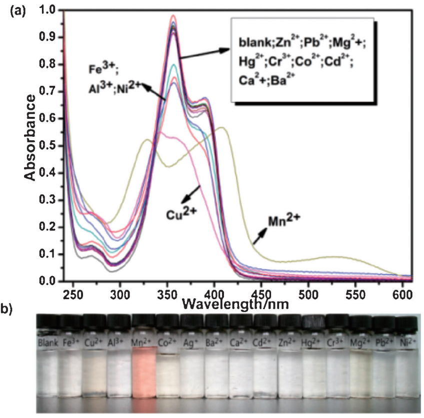


Figure 1. (a) UV–vis spectral changes of **1** (12.5 μM) in pure aqueous solution (20 mM boric acid–borax, pH 8.0) upon the addition of four equiv of different nitrate metal salts (50 μM). (b) Color changes of **1** (12.5 μM) in pure aqueous solution in the presence of four equiv of various cation ions.

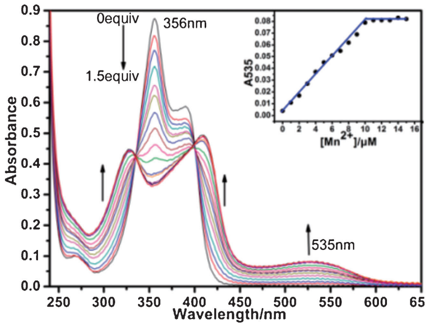


Figure 2. Absorbance spectra of **1** (12.5 μM) with increasing concentrations of Mn^{2+} in the form of nitrate salt in pure aqueous solution (20 mM boric acid–borax, pH 8.0). Inset: the absorbance at 535 nm as a function of Mn^{2+} concentration.

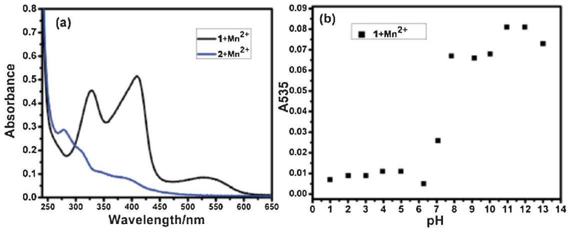


Figure 3. (a) The absorbance spectra of chemosensors **1** and **2** (12.5 μM) in pure aqueous solution (20 mM boric acid–borax, pH 8.0) in the presence of 25 μM Mn^{2+}. (b) The absorbance intensity of chemosensor **1** (12.5 μM) at 535 nm in the presence of Mn^{2+} (25 μM) at various pH values.

Zn^{2+}, resulted in negligible changes in the absorption spectrum of **1**. A small decrease at 356 nm was observed in the presence of Fe^{3+}, Al^{3+}, and Ni^{2+}. On the other hand, Cu^{2+} induced slight blue-shift absorption with decreased molar absorption coefficient. The small UV–vis spectral changes observed in the presence of Fe^{3+}, Al^{3+}, Ni^{2+}, and Cu^{2+} is possibly due to the metal ion-catalyzed hydrolysis reaction of chemosensor **1**.[19] It is also observed that the color of the solutions after the addition of these ions remained relatively unchanged. Only Mn^{2+} caused obvious absorption changes, and a new absorption band centered at 535 nm appeared, resulting in a color change of the solution from colorless to red which was clearly visible to the naked eye (Figure 1b). These results indicated the compound **1** exhibited a high selectivity for Mn^{2+} over various other metal ions and thus, could serve as a good selective naked-eye chemosensor for Mn^{2+} in aqueous media.

To understand the coordination behavior between **1** and Mn^{2+}, a UV–vis absorption spectral titration experiment of **1** (12.5 μM) with Mn^{2+} (0 to 15 μM) in pure aqueous solution (20 mM boric acid–borax, pH 8.0) was carried out. As shown in Figure 2, the original absorption bands centered at 356 and 390 nm gradually decreased with the formation of two new absorption bands at 325 and 425 nm, generating two isosbestic points at 335 and 400 nm. These changes indicated the formation of a new complex between **1** and Mn^{2+}. In addition, a new absorption band centered at 535 nm appeared with increasing intensity with increasing Mn^{2+} concentration. Chemosensor **1**, which bears two strongly electron-donating *N*,*N*-diethylamino moiety groups on the side aromatic ring and the electron-accepting C=N moiety in the middle, is a type of a donor–acceptor–donor molecule.[14] The binding of Mn^{2+} with the imino nitrogen atom induced the decrease of the electron density of C=N units and strengthened its electron-accepting character, which could enhance the charge transfer from *N*,*N*-diethylamino moiety (donor) to C=N group (acceptor) units and consequently induce spectral changes. Therefore, the new long wavelength absorption band at 535 nm is most possibly attributed to an intramolecular charge-transfer (ICT) band. As expected, the ICT band was significantly influenced by the ability of donating electrons of the substituted group.[2d,20] To understand the crucial role of the *N*,*N*-diethylamino donor group, chemosensor **2** was synthesized. As shown in Figure 3a, unlike **1**, in the case of **2** which has no donor substitutions, no obvious ICT absorption band is observed after the addition of Mn^{2+}, confirming the important role of the *N*,*N*-diethylamino moiety and the ICT character of the 535 nm absorption band. Meanwhile, the intensity of the ICT absorption band at 535 nm is strongly pH dependant.[21] As shown in Figure 3b, the 535 nm ICT band is very weak in acidic condition (pH <7), possibly due to the protonation of the *N*,*N*-diethylamino moiety, leading to the decrease in the strength of the donating group and thus a weak ICT effect. To investigate the practical application of chemosensor **1**, the absorbance of the [**1** + Mn] complex at 535 nm as a function of pH was also recorded. The absorbance intensity of the [**1** + Mn] complex at 535 nm in pH >7 environment is much higher than that in pH <7 environment, which means the best pH working range of chemosensor **1** for the detection of Mn^{2+} is under near neutral and alkaline conditions (pH 7.5–13).

As shown in the inset of Figure 2, a nearly linear dependance of the absorbance at 535 nm as a function of Mn^{2+} concentration from 0 to 12.5 μM was observed. The absorbance at 535 nm reaches the maximum upon addition of nearly 1 equiv of Mn^{2+}. At the same time, the absorption changes were clearly visible to the naked eye, showing that the colorless solution of **1** became red upon titration with Mn^{2+}, even at 1 μM concentration (Figure 4a), which means that the detection limit for Mn^{2+} by naked eye was 1 μM, lower than the limit of

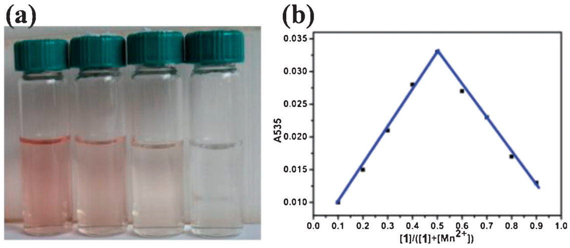
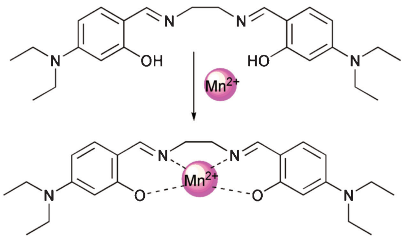


Figure 4. (a) Photographs of the aqueous solutions of **1** (12.5 μM) after addition of different concentrations of Mn^{2+}. Left to right: 10, 5, 1, and 0 μM. (b) Job's plot of the complex formed by **1** and Mn^{2+} at an invariant total concentration of 10 μM.



Scheme 2. The proposed binding mechanism of **1** with Mn^{2+}.

0.4 mg L^{-1} (ca. 8 μM) defined by the World Health Organization (WHO).

To further explore the binding mechanism, Job's plot of the UV–vis titrations of Mn^{2+} with a total concentration of 10 μM is shown in Figure 4b. A maximum absorption was observed when the molar fraction reached 0.5, which is indicative of a 1:1 stoichiometric complexation between **1** and Mn^{2+} for the newly formed species. The ESI mass spectrum of a mixture of **1** and $Mn(NO_3)_2$ also revealed the formation of a 1:1 metal–ligand complex through the metal coordination interaction, with a major signal at $m/z = 463.2039$ for $[\mathbf{1} + Mn^{2+} - H]^+$ (calcd 463.1906) (Figure S8[22]). The association constant of the newly formed complex at 298 K was then determined to be $1.129 \times 10^4\,M^{-1}$ with a good linear relationship ($R = 0.997$) by a 1:1 binding mode (Figure S7[22]). The proposed binding mode of **1** for the 1:1 equilibrium with Mn^{2+} is shown in Scheme 2. Upon the addition of Mn^{2+} to **1**, Mn^{2+} was coordinated by the two phenolic hydroxy oxygen atoms and two nitrogen atoms.

The selectivity of **1** (12.5 μM) to Mn^{2+} (25 μM) was further demonstrated in the presence of two equiv of other metal ions. As shown in Figure S9,[22] the absorbance intensity of **1** and Mn^{2+} at 535 nm was almost unaffected by the presence of other metal ions such as Ag^+, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Hg^{2+}, Mg^{2+}, and Zn^{2+}. Only the presence of Pb^{2+} caused about 25% decrease of absorbance intensity of **1** at 535 nm.

In summary, we have developed a novel, easily available colorimetric sensor **1** based on bis(*N*-salicylidene)ethylenediamine which exhibits highly selective and sensitive recognition toward Mn^{2+} in pure aqueous solution. The recognition of Mn^{2+} gave rise to color change from colorless to red which was clearly visible to the naked eye. This is, to the best of our knowledge, the first reported example of a colorimetric chemosensor capable of detecting Mn^{2+} in pure aqueous solution. Furthermore, it could work over a wide pH range from 7.5 to 13.0, which is important for practical use. We believe that this sensor, with sensitive and selective naked eye responses as well as wide pH working range, can be used for many practical applications in chemical, environmental, and biological systems. We are currently working toward the development of such a device by grafting **1** onto functional polymers.

This work was supported by the Natural Science Foundation of China (Grant Nos. 20974041 and 50673038) and the Fundamental Research Funds for the Central Universities (No. JUSRP11108).

References and Notes

1 a) Q. He, E. W. Miller, A. P. Wong, C. J. Chang, *J. Am. Chem. Soc.* **2006**, *128*, 9316. b) 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, J. S. Kim, *J. Am. Chem. Soc.* **2009**, *131*, 2008. c) X. Peng, J. Du, J. Fan, J. Wang, Y. Wu, J. Zhao, S. Sun, T. Xu, *J. Am. Chem. Soc.* **2007**, *129*, 1500. d) C. Chen, R. Wang, L. Guo, N. Fu, H. Dong, Y. Yuan, *Org. Lett.* **2011**, *13*, 1162. e) S. K. Kim, K. M. K. Swamy, S.-Y. Chung, H. N. Kim, M. J. Kim, Y. Jeong, J. Yoon, *Tetrahedron Lett.* **2010**, *51*, 3286. f) S. O. Obare, C. J. Murphy, *Inorg. Chem.* **2001**, *40*, 6080. g) Z. Liu, H. Xu, C. Song, D. Huang, L. Sheng, R. Shi, *Chem. Lett.* **2011**, *40*, 75.

2 a) R. Sheng, P. Wang, Y. Gao, Y. Wu, W. Liu, J. Ma, H. Li, S. Wu, *Org. Lett.* **2008**, *10*, 5015. b) R. Sheng, P. Wang, W. Liu, X. Wu, S. Wu, *Sens. Actuators, B* **2008**, *128*, 507. c) E. Coronado, J. R. Galán-Mascarós, C. Martí-Gastaldo, E. Palomares, J. R. Durrant, R. Vilar, M. Gratzel, Md. K. Nazeeruddin, *J. Am. Chem. Soc.* **2005**, *127*, 12351. d) Y. Zeng, G. Zhang, D. Zhang, D. Zhu, *Tetrahedron Lett.* **2008**, *49*, 7391.

3 a) P. Kaur, S. Kaur, A. Mahajan, K. Singh, *Inorg. Chem. Commun.* **2008**, *11*, 626. b) P. Kaur, S. Kaur, K. Singh, *Inorg. Chem. Commun.* **2009**, *12*, 978. c) H.-B. Sun, S.-J. Liu, T.-C. Ma, N.-N. Song, Q. Zhao, W. Huang, *New J. Chem.* **2011**, *35*, 1194.

4 a) F. S. Archibald, I. Fridovich, *Arch. Biochem. Biophys.* **1982**, *214*, 452. b) V. Bencko, M. Cikrt, *J. Hyg., Epidemiol., Microbiol., Immunol.* **1984**, *28*, 139.

5 a) A. Barbeau, *Neurotoxicology* **1984**, *5*, 13. b) I. Mena, S. Fuenzalida, G. C. Cotzias, *Neurology* **1967**, *17*, 128. c) J. Crossgrove, W. Zheng, *NMR Biomed.* **2004**, *17*, 544.

6 H. Bilinski, Ž. Kwokal, M. Branica, *Water Res.* **1996**, *30*, 495.

7 C. Sarzanini, O. Abollino, E. Mentasti, *Anal. Chim. Acta* **2001**, *435*, 343.

8 O. M. S. Filipe, C. M. A. Brett, *Talanta* **2003**, *61*, 643.

9 V. K. Gupta, A. K. Jain, G. Maheshwari, *Talanta* **2007**, *72*, 49.

10 a) H.-y. Li, S. Gao, Z. Xi, *Inorg. Chem. Commun.* **2009**, *12*, 300. b) L. Li, Y.-Q. Dang, H.-W. Li, B. Wang, Y. Wu, *Tetrahedron Lett.* **2010**, *51*, 618.

11 W. C. Gilbert, L. T. Taylor, J. G. Dillard, *J. Am. Chem. Soc.* **1973**, *95*, 2477.

12 L. Gao, Y. Wang, J. Wang, L. Huang, L. Shi, X. Fan, Z. Zou, T. Yu, M. Zhu, Z. Li, *Inorg. Chem.* **2006**, *45*, 6844.

13 V. K. Bhardwaj, A. P. S. Pannu, N. Singh, M. S. Hundal, G. Hundal, *Tetrahedron* **2008**, *64*, 5384.

14 S. Wang, G. Men, L. Zhao, Q. Hou, S. Jiang, *Sens. Actuators, B* **2010**, *145*, 826.

15 M. Salavati-Niasari, M. Bazarganipour, *Appl. Surf. Sci.* **2009**, *255*, 7610.

16 Y. N. Belokon, M. North, T. D. Churkina, N. S. Ikonnikov, V. I. Maleev, *Tetrahedron* **2001**, *57*, 2491.

17 K. S. Moon, N. Singh, G. W. Lee, D. O. Jang, *Tetrahedron* **2007**, *63*, 9106.

18 W. Tang, Y. Xiang, A. Tong, *J. Org. Chem.* **2009**, *74*, 2163.

19 R. Alarcón, M. Silva, M. Valcárcel, *Anal. Lett.* **1982**, *15*, 891.

20 D. Ray, A. Nag, A. Jana, D. Goswami, P. K. Bharadwaj, *Inorg. Chim. Acta* **2010**, *363*, 2824.

21 S. Derinkuyu, K. Ertekin, O. Oter, S. Denizalti, E. Cetinkaya, *Dyes Pigm.* **2008**, *76*, 133.

22 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.