doi:10.1246/cl.2011.279

Colorimetric "Naked-eye" Highly Selective Detection of Cu(II) Ion by a Simple Chemosensor: An Experimental and Theoretical Modeling

Sasanka Dalapati, Sankar Jana, and Nikhil Guchhait*
Department of Chemistry, University of Calcutta, 92 A. P. C. Road, Kolkata 700 009, India

(Received December 15, 2010; CL-101062)

The selectivity and sensitivity of *N*,*N*′-bis(4-diethylaminosalicylidene)hydrazine (sensor **1**) toward Cu^{2+} ion have been established both by distinct "naked-eye" color change as well as UV–vis spectrophotometry. Sensor **1** formed 1:1 complex with Cu^{2+} ion where the most stable s-trans form of the sensor is trapped in the high energy conformer. Single-crystal X-ray structure of sensor **1** supports its s-trans conformation. Theoretical calculations support well the experimental result.

Heavy-metal pollution arises from many sources in the environment which do not decay and thereby pose a challenge for detection and remediation. Though minute quantities of heavy metals are essential for living organisms playing important roles in biological, environmental, and chemical systems,[1] excessive amounts have damaging effects on the organisms.[2] Some transition and post-transition metals though normally toxic, are however, beneficial to living organisms under certain conditions. These metal ions are carcinogenic or toxic in nature, affecting the central nervous system and other organs. Therefore, quantitative determination of metal ions is very important. In this context, synthesis of highly selective colorimetric chemosensors for transition and heavy metal ions has been a challenge to chemists for many years. Cu^{2+} ion in particularly, is one of the essential trace nutrients to all plant and animals as it plays an important role in various physiologic processes.[3] On the contrary, Cu^{2+} ions are toxic when its level exceeds cellular needs thereby affecting kidney, bones, liver, skin, and teeth. It also possesses the ability to displace other metal ions which act as cofactors in enzyme-catalyzed reactions.[4]

To date, several methods have been reported to determine trace amounts of Cu^{2+} ions in μM range. These methods are mainly based on either quenching or enhancement[5] of the sensor's fluorescence in the presence of Cu^{2+} ion, but the structure of chemosensors are found to be quite complex and synthetic methods are complicated and troublesome. On the other hand, UV–vis absorption spectroscopy and colorimetric "naked-eye" detection techniques have gained comparatively faster attention than other techniques due to simplicity, high sensitivity, and cost effectiveness.[1,6] Herein we report a simple synthetic chemosensor **1** which can be used as a highly selective sensor toward Cu^{2+} ion both by using UV–vis spectroscopy and "naked-eye" color change.

The sensor *N*,*N*′-bis(4-diethylaminosalicylidene)hydrazine[7] has been synthesized by a simple one-step process from 4-diethylaminosalicylaldehyde (4-DEAS) (Scheme S1). Both 4-DAES and sensor **1** have been characterized by ^{1}H, ^{13}C NMR, C, H, N analysis, mass spectrometry, and single-crystal X-ray analysis (Figure S1, Table S1; Supporting Information (SI)).[13]

The ORTEP drawing of the X-ray structure of sensor **1** (Figure 1)[8] shows that two aldehyde groups are condensed with one diamine unit to from a di-Schiff base compound (s-trans form, sensor **1**). The packing of the molecules is controlled by two types of intermolecular interactions, namely hydrogen bonding (H-bonding) interaction and C–H/π interactions. The H-bonding interaction present through O(1)–H(10)···N(1) with O(1)–N(1) distance is 2.64 Å and donor–acceptor distance is 1.89 Å. A C–H/π interaction was found in the crystal packing, where the H(3) interact with Cg(1) with the distance of 2.77 Å (Cg represents the centroid of phenyl ring).

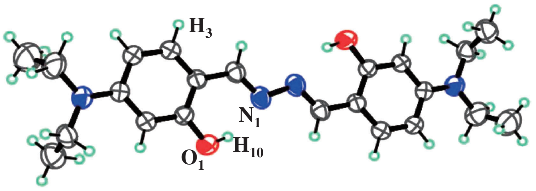

Figure 1. ORTEP view of sensor **1** with ellipsoids at 50% probability.

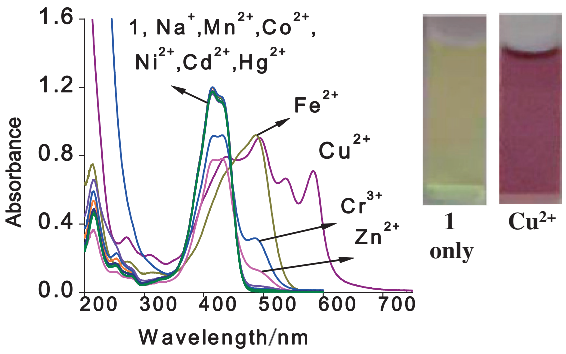

Figure 2. Absorption spectra of sensor **1** only and sensor **1** with various metal ions (perchlorate and chloride salts, SI[13]), $[M^{2+}] = 31.23\,\mu M$, $[\mathbf{1}] = 1.4\,\mu M$, M = Na, Mn, Fe, Co, Ni, Cu, Zn, Cd, Hg, and Cr ions. (Inset) visual color of **1** only (sensor **1**) and **1** in presence of Cu^{2+} ion in acetonitrile.

As depicted in Figure 2, the UV–vis spectra of sensor **1** in acetonitrile (ACN) solvent show a doublet with peak maxima at 415 nm and a shoulder peak at 436 nm. On addition of Cu^{2+} ion in ACN medium at room temperature the absorption spectrum shows a remarkable change both in shape and position. Three new red-shifted bands at 487, 538, and 584 nm appear with concomitant decrement of initial absorbance at 415 and ≈436 nm. A distinct "naked-eye" color change from lemon yellow to purple is observed from bare sensor to the Cu^{2+} ion solution. Bathochromic shift of the three new bands are 72, 123, and 169 nm, respectively (with respect to the band at 415 nm). In the case of addition of other metal ions, the change in the shape of the absorption spectra of the sensor **1** is different

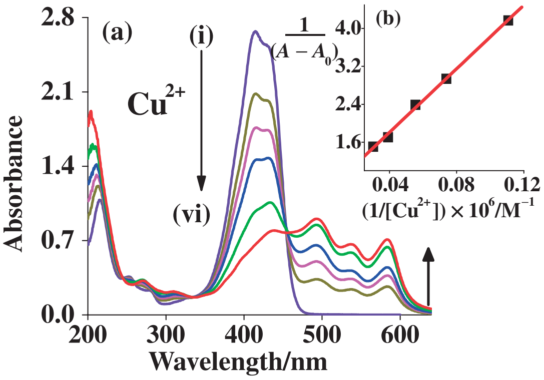

Figure 3. (a) Titration of sensor **1** with $Cu(ClO_4)_2 \cdot 6H_2O$ salt in acetonitrile solvent, where (i) to (vi) $[Cu^{2+}] = 0$, 9.04, 13.55, 18.05, 25.55, and 33.03 µM respectively. $[\mathbf{1}] = 1.6$ µM. (b) Ratiometric titration curve, optical density as a funtion of Cu^{2+} concentrations (B–H plot) at 538 nm.

(Figure S2).[13] The only band at 487 nm with appreciable intensity is observed in the case of addition of Fe^{2+}, Zn^{2+}, Cr^{3+}, and Co^{2+} ions. As seen in Figure 2, other metal ions such as Na^+, Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Hg^{2+} ions have almost no effect on the absorption peak of the bare sensor.

The titration curve of sensor **1** with Cu^{2+} ion is shown in Figure 3. The band at 584 nm can be attributed to the d–d transition of sensor **1**–Cu^{2+} complex.[4,9] The binding constants for sensor **1**–metal complexes have been determined from Figure 3b using the Benesi–Hildebrand (B–H) relation which indicate the formation of 1:1 complex between sensor **1** and Cu^{2+} ion with binding constant $1.38 \times 10^4\,M^{-1}$ (Table S2[13]). The peak at 538 nm arises due to formation of strongly chelating complex between sensor **1** and Cu^{2+} ion by deprotonation of two adjacent phenolic –OH groups[6,10] which is further confirmed by the mass spectra (Figure S1).[13] Cu^{2+} ion easily forms a strong internal-charge-transfer (ICT) complex[6] by deprotonation which causes an ICT in the metal complex and generates a new band at 538 nm.[5,11] The red-shifted band at 487 nm arises by protonation of sensor **1** due to the acidic nature of perchlorate salt (or $HClO_4$ formed by hydrolysis) or may be due to the similar binding nature of metal ions to that of proton (H^+) (Figure S2).[13] The bathochromic shift (72 nm) of the protonated species suggests that protonation takes place at the nitrogen present in the azine bridge or nitrogen in one of the diethyl amino ($–NEt_2$) groups. Protonation or metal binding favors the ICT or metal-induced charge-transfer (MICT) mechanism[10] which is responsible for the color change[6,10,11] from lemon yellow to pale yellow (Figure S4b).[13] Addition of individual metal ions such as Zn^{2+}, Co^{2+}, Fe^{2+}, and Cr^{3+} ion results in similar observation as acid effect (Figure S2).[13] This indicates 1:1 complexation between sensor **1** and any of the studied metal ions.

The titration curves with Fe^{2+} and Cr^{3+} ion (Figures S3a and S3b)[13] predict weaker complex formation than Cu^{2+} ion (Table S2[13]). Addition of Na^+, Mn^{2+}, Ni^{2+}, Cd^{2+}, and Hg^{2+} ions result in no significant change in the absorption spectra, which indicates the absence of binding of these metal ions with the sensor **1**. Due to stronger binding ability of Cu^{2+} ion and larger binding constant as well as greater free energy change (ΔG) (Table S2[13]), the chemosensor **1** can selectively detect only Cu^{2+} ion by differing absorption spectra and visual color change even in of the presence of other metal ions.

The selectivity of the sensor **1** toward the Cu^{2+} ion was further established by ion-competition experiments (Figure S4).[13] Addition of a mixture of ions to the ACN solution of chemosensor **1** results in almost similar response as Cu^{2+} ion itself. Only a little interference is observed due to the presence of other metal ions. A distinct color (lemon yellow to red, Figure S4b)[13] was observed when a mixture of ions is added to the ACN solution of sensor **1**. All the titration spectra (except in the case of Co^{2+} ion) show three clear isosbestic points at 253, 349, and 450 nm with decreasing the initial band of the sensor **1** at 415 and 436 nm, which indicates strong equilibrium between the complexed and uncomplexed form of the sensor **1** (Figures 3, S2,[13] and S4a[13]).[3]

Finally we have correlated the experimental findings with theoretical calculations. Structural calculations for sensor **1** and its Cu^{2+} complex were preformed using Gaussian 03 software at the density functional theory (DFT) level (SI[13]). Calculation shows that Conformer 1 (s-trans) is more stable than deformed s-trans conformer (Conformer 2, Figures S5, S6, and Table S3)[13] and it is expected that only Conformer 1 exists at room temperature. The absorption band of sensor **1** in ACN solvent was observed at 415 nm which is similar to that of calculated value (at 403.68 nm in vacuum). During the complexation process it is found that Cu^{2+} can form stable 1:1 complex when the two –OH groups are in the same side i.e., transformation from s-trans to high energy deformed s-trans form and generates cyclic six- and seven-member rings (Figure S7).[13] In the calculated structure of the complex, the Cu^{2+} ion is tetracoordinated and the binding sites are two O atom, one nitrogen lone pair, and water.[12] So in the presence of metal ion (especially Cu^{2+} ion) we can trap unstable high energy conformer from stable low energy conformer (sensor **1**).

In conclusion, we have reported simple Schiff base chemosensor *N*,*N′*-bis(4-diethylaminosalicylidene)hydrazine which can selectively detect Cu^{2+} ion in the µM (detection limit 2.4×10^{-6} M) range irrespective of the presence of other metal ions. Structurally the sensor **1** is of low energy stable s-trans geometry, but it transfers to high energy deformed s-trans geometry upon binding with metal i.e., metal-mediated trapping of high energy conformer. An excellent correlation has been observed between experimental results and theoretical calculations. A simple synthesis of sensor **1** also has significant advantage in practical applications because of its distinct "naked-eye" color change in the presence of Cu^{2+} ion itself (purple) and also in the presence of other metal ions (red).

This work is supported by grants from DST, India (Project No. SR/S1/PC/26/2008) to NG. S.D would like to acknowledge UGC, Utpal Rana and Saptarshi Biswas for their grateful contribution.

References and Notes

1 a) Z. Xu, X. Qian, J. Cui, *Org. Lett.* **2005**, *7*, 3029. b) L. H. Feng, Z. Chen, *Sens. Actuators, B* **2007**, *120*, 665. c) D. C. Kennedy, R. K. Lyn, J. P. Pezacki, *J. Am. Chem. Soc.* **2009**, *131*, 2444.
2 a) R. Sundari, M. Ahmad, L. Y. Heng, *Sens. Actuators, B* **2006**, *113*, 201. b) D. Ray, P. K. Bharadwaj, *Inorg. Chem.*

2008, *47*, 2252.

3 a) T. Mayr, I. Klimant, O. S. Wolfbeis, T. Werner, *Anal. Chim. Acta* **2002**, *462*, 1. b) V. K. Gupta, A. K. Jain, G. Maheshwari, H. Lang, Z. Ishtaiwi, *Sens. Actuators, B* **2006**, *117*, 99.

4 Z. Wang, X. Fan, D. Li, L. Feng, *Spectrochim. Acta, Part A* **2008**, *71*, 1224.

5 a) A. Mallick, M. C. Mandal, B. Halder, A. Chakrabarty, P. Das, N. Chattopadhyay, *J. Am. Chem. Soc.* **2006**, *128*, 3126. 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.

6 a) R. Sheng, P. Wang, Y. Gao, Y. Wu, W. Liu, J. Ma, H. Li, S. Wu, *Org. Lett.* **2008**, *10*, 5015. b) N. Shao, J. Y. Jin, H. Wang, Y. Zhang, R. H. Yang, W. H. Chan, *Anal. Chem.* **2008**, *80*, 3466. c) T. Gunnlaugsson, J. P. Leonard, N. S. Murray, *Org. Lett.* **2004**, *6*, 1557.

7 a) Y. Fu, G. Li, Z. Xu, J. Jiang, Faming Zhuanli Shenqing Gongkai Shuomingshu, petent CN 101403143, **2009**. b) Y. Fu, Q. He, H. Cao, J. Cheng, Faming Zhuanli Shenqing Gongkai Shuomingshu, petent CN 101619032, **2010**.

8 CCDC 804053 contains supplementary crystallographic data for sensor **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44-1223-336033; or e-mail: deposit@ccdc.cam.ac.uk.

9 B. Sarkar, M. S. Ray, Y.-Z. Li, Y. Song, A. Figuerola, E. Ruiz, J. Cirera, J. Cano, A. Ghosh, *Chem.—Eur. J.* **2007**, *13*, 9297.

10 a) Y. Fu, H. Li, W. Hu, *Eur. J. Org. Chem.* **2007**, 2459. b) J. Yoshino, N. Kano, T. Kawashima, *J. Org. Chem.* **2009**, *74*, 7496.

11 a) A. Caballero, R. Martínez, V. Lloveras, I. Ratera, J. Vidal-Gancedo, K. Wurst, A. Tárraga, P. Molina, J. Veciana, *J. Am. Chem. Soc.* **2005**, *127*, 15666. b) P. Mukhopadhyay, B. Sarkar, P. K. Bharadwaj, K. Nättinen, K. Rissanen, *Inorg. Chem.* **2003**, *42*, 4955.

12 M. Salavati-Niasari, A. Amiri, *Appl. Catal., A* **2005**, *290*, 46.

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