Tetrahedron 66 (2010) 1846–1851

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

2, 2′-Dihydroxyazobenzene-based fluorescent system for the colorimetric 'turn-on' sensing of cyanide

Jing Wang, Chang-Sik Ha *

Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Republic of Korea

ARTICLE INFO

Article history:
Received 3 December 2009
Received in revised form 7 January 2010
Accepted 7 January 2010
Available online 13 January 2010

Keywords:
2, 2′-Dihydroxyazobenzene (DHAB)
Cyanide
Indirect method
Color change
Chemosensor
Selectivity and sensitivity

ABSTRACT

2, 2′-Dihydroxyazobenzene (DHAB) demonstrated high sensitivity and low selectivity toward three anions: CN^-, CO_3^{2-}, and HCO_3^-. In the presence of Cu(II), complex DHAB–Cu(II) could give rise to enhanced fluorescence intensity by about 45-fold at 590 nm and visible red-to-reddish orange color change upon the addition of cyanide by utilizing an indirect method, while no changes were observed in the presence of other anions, including F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, CH_3COO^-, NO_3^-, CO_3^{2-} and HCO_3^-, and SO_4^{2-}, making the DHAB–Cu(II) complex a selective and sensitive cyanide chemosensor.

1. Introduction

Anions play a fundamental role in a wide range of chemical and biological processes.[1] However, in comparison with the relatively large number of cation chemosensors, the development of anion chemosensors is still a challenging area.[2] Considerable attention has been focused on finding better and more efficient ways to detect anions that can be potentially harmful to the environment or human health.[3,4] One such anion is cyanide (CN^-), which is probably one of the most toxic anions.[5,6] Despite its acute toxicity, cyanide or hydrogen cyanide is used in many industries such as synthetic fibers and resins, herbicides, gold extraction, etc., as well as is found in many foods and plants.[7] Therefore, reliable and efficient ways of detecting the presence of cyanide are quite necessary. Among various approaches for the detection of cyanide, fluorescence spectroscopy continues to play an important role in molecular sensing on account of its high sensitivity, rapid response rate, and relative low cost. Especially, colorimetric chemosensors are most desirable, which could be widely used owing to the low cost where a color change can be observed easily by the naked eye.[8] Therefore, fluorescence or colorimetric probes are particularly attractive.[9] More recently, metal-based receptors have been established as a class of anion receptors. The structural and geometrical flexibility of the metals provide an excellent way of organizing the anion binding groups (e.g., hydrogen bonding moieties) for optimal host–guest interactions.[10] Copper complexes have been developed as a new class for the detection of cyanide,[11] considering that cyanide could form very stable complex with copper ions.[12] Metal coordination compounds with 2,2′-dihydroxyazobenzene (DHAB) are well known.[13] However, there are no reports concerned with the sensing of anions involving DHAB.

Herein, for the first time, we demonstrated that DHAB has high sensitivity and low selectivity toward CN^-, CO_3^{2-}, and HCO_3^-. The high selectivity toward CN^- was realized by the complex DHAB–Cu(II), since the stability constant of the complex formed by the anion (CN^-) and the cation (Cu(II)) is larger than that of the complex (DHAB–Cu(II)) of the cation (Cu(II)) and its ligand (DHAB).[12] There are several advantages for this 'new' fluorescent system containing DHAB; first, the excitation (490 nm) and emission (590 nm) wavelengths for the detection of anions were in the visible range and large Stokes' shift of approximately 100 nm appeared in the presence of CN^-; second, the color change can be distinguished easily by the naked eyes without any instruments; third, the chemosensor for CN^- was monitored by the fluorescent type 'turn-on' to get the maximum signal-to-noise ratio; fourth, this observation indicates that the DHAB–metal complexes may be a 'new' and useful class for sensing of anions because DHAB can coordinate with many metal cations.[13]

---

* Corresponding author. Tel.: +82 51 510 2407; fax: +82 51 514 4331.
E-mail address: csha@pusan.ac.kr (C.-S. Ha).

0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.01.031

2. Results and discussion

2.1. Sensing of Cu(II) by DHAB

DHAB can coordinate with Cu(II) with 2/1 binding model (see Fig. 1),[13,14] however, there are no reports for the association constant (K_{ass}) between DHAB and Cu(II). DHAB (see Fig. 1) has two tautomeric forms, the azo form and the hydrazone form.[15a,b] Figure 2 shows the UV–vis spectra of the solution of DHAB in the presence and absence of copper ions. As indicated in Figure 2, the bands at approximately 325 nm were assigned to the π–π^* transition of the azo form and the bands at approximately 392 nm was assigned to the π–π^* transition of the hydrazone form.[15] After addition of transition metal ions Cu^{2+}, the typical absorption peak for the azo form of DHAB at 325 nm decreased and red-shifted, the peak for the hydrazone form of DHAB at around 392 nm disappeared, while a new absorption peak at around 499 nm appeared due to the formation of complex between DHAB and Cu(II). Molar extinction coefficient (ε) of **1** was 1333 M^{-1} cm^{-1} at 499 nm, while molar extinction coefficient (ε) of **1** in the presence of 3.0 equiv of Cu^{2+} was 20,133 M^{-1} cm^{-1} at 499 nm (Fig. 2). At the same time, the original light yellow solution of DHAB became red after adding Cu(II) (Fig. 3). The association constant (Fig. 2, right) of the complex formed between DHAB and copper ions was calculated to be K_{ass} of 2.24×10^{8} M^{-2} (R=0.997) (see Experimental part 4.6).[16] The plot of $C_{DHAB}/(A_{499}A_{DHAB})$ as a function $1/C_{DHAB}C_{Cu}$ (Fig. 2, right) reveals a straight line, further supporting the 2(DHAB)/1(Cu^{2+}) stoichiometry.[16]

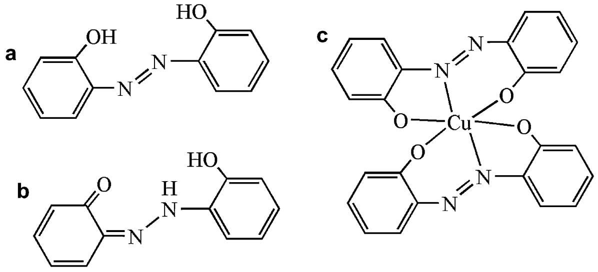


Figure 1. Two tautomeric forms of DHAB (a) azo form, (b) hydrazone form, and (c) the chemical structure of the Cu $(DHAB)_2$.

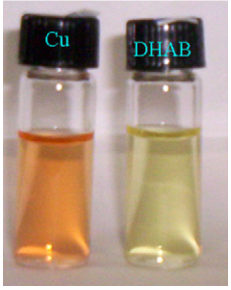


Figure 3. Color changes of DHAB (3×10^{-5} M) in the presence (left) and absence (right) of 3.0 equiv of copper ions in a mixture of H_2O–MeOH (1/1, v/v, 10 mM HEPES at pH 7.5).

2.2. Sensing of anions using DHAB

DHAB are well known coordination compounds with metals,[13] while there are no studies for the sensing of anions based on DHAB. For the first time, we tested the sensing ability of DHAB toward anions. The anions examined included the following F^-, Cl^-, Br^-, I^- with a spherical structure; CN^- with a linear structure; CO_3^{2-}, HCO_3^-, CH_3COO^-, $NO3^-$ with a trigonal planar structure; and SO_4^{2-}, $H_2PO_4^-$ with a tetrahedral structure.[17] Upon addition of CN^-, CO_3^{2-}, and HCO_3^- anions, the solution of DHAB changed from light yellow to red (Fig. 4). As illustrated in Figure 5, after addition of CN^-, CO_3^{2-}, and HCO_3^- anions, the typical absorption peak for DHAB at 325 nm decreased, the peak at around 392 nm disappeared, while a new absorption peak at around 480 nm appeared due to the formation of complex between DHAB and these three anions. With λ_{ex}=480 nm, DHAB does not show any fluorescence, however, DHAB displayed enhanced fluorescence intensity at approximately 590 nm above 45-fold and about 40-fold after adding CN^-/CO_3^{2-} and HCO_3^-, respectively (Fig. 6). Also large Stokes' shift of about 100 nm was observed (Fig. 7, Fig. S1 and Fig. S2). Minimal or no changes were observed with the other investigated anions for the solution color changes, absorption spectra, and fluorescence emission at approximately 590 nm (Figs. 4–6). It may be concluded that DHAB has sensitivity to CN^-, CO_3^{2-}, and HCO_3^- anions. Whereas it is difficult to distinguish CN^- from CO_3^{2-} and HCO_3^- anions, especially CO_3^{2-}, because changes of the solution color (light yellow to red), absorption spectra, and fluorescence spectra were almost the same after adding CN^- and CO_3^{2-}. Thus, DHAB has high sensitivity but low selectivity toward CN^-, the

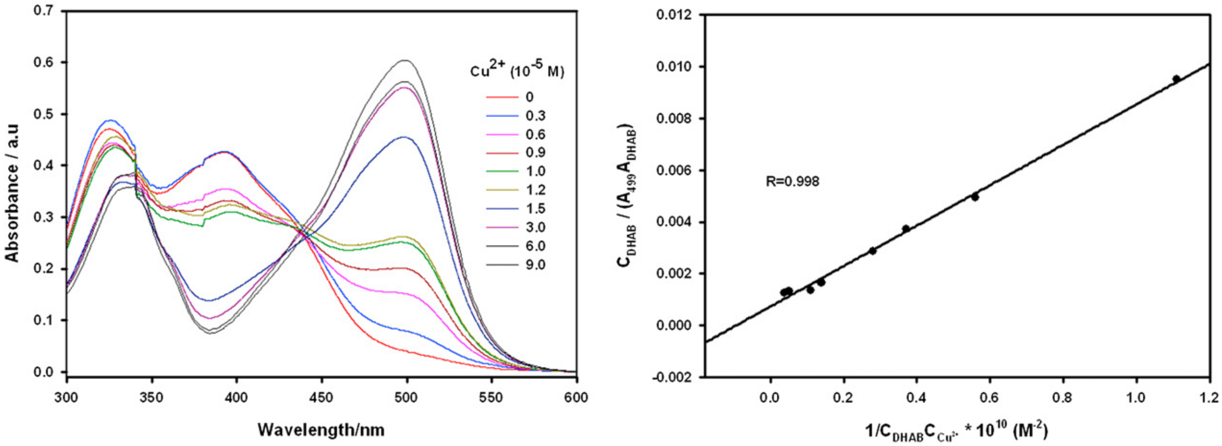


Figure 2. Absorption spectra of DHAB (3×10^{-5} M) in a mixture of H_2O–MeOH (1/1, v/v, 10 mM HEPES at pH 7.5) upon titrating different molar ratios of Cu^{2+} (left) and plot of $C_{DHAB}/(A_{499}A_{DHAB})$ against $1/C_{DHAB}C_{Cu}$ at 499 nm (right). See text for the definition of parameters.

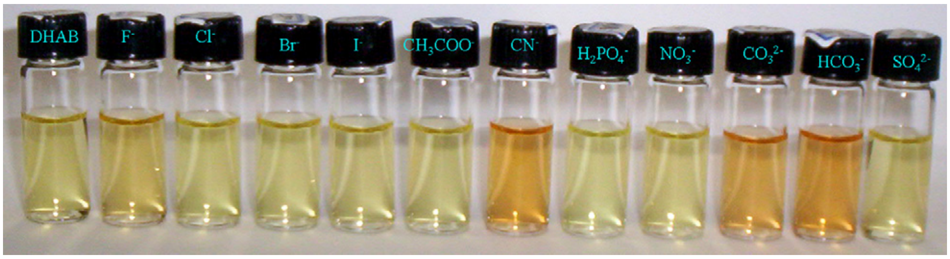


Figure 4. Photographs of DHAB (3×10^{-5} M) in a mixture of H_2O/MeOH (1/1, v/v, 10 mM HEPES at pH 7.5) in the presence of various anions (6.0×10^{-4} M). Anions from left to right: blank, F^-, Cl^-, Br^-, I^-, CH_3COO^-, CN^-, $H_2PO_4^-$, NO_3^-, CO_3^{2-}, HCO_3^-, and SO_4^{2-}.

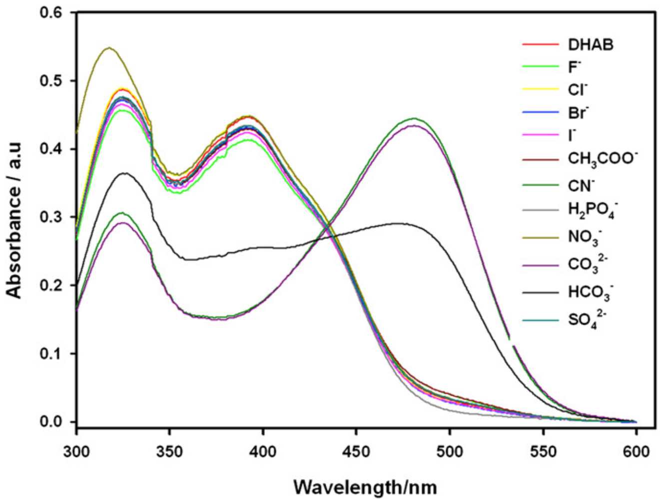


Figure 5. Absorption spectra changes of DHAB (3×10^{-5} M) in a mixture of H_2O–MeOH (1/1, v/v, 10 mM HEPES at pH 7.5) in the presence of various anions (6.0×10^{-4} M).

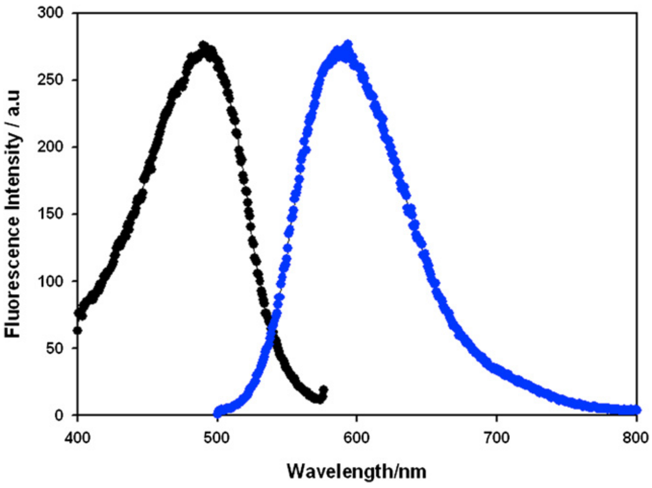


Figure 7. Excitation and emission spectra of DHAB (3×10^{-5} M) in a mixture of H_2O–MeOH (1/1, v/v, 10 mM HEPES at pH 7.5) in the presence of CN^- (6.0×10^{-4} M).

limitation of the selectivity inhibits its application for sensing of the toxic CN^-.

2.3. Selectivity of CN^- anion using DHAB–Cu(II) complex

The association constant of the complex formed between DHAB and copper ions 2.24×10^8 M^{-2} (Fig. 2) was much smaller than the stability constant of copper ions and cyanide.[11d] Thus, we expect that the limited selectivity of DHAB might be overcame if we used DHAB–Cu(II) instead of only DHAB because the added CN^- might capture the copper ions from the complex of DHAB–Cu(II), whereas CO_3^{2-} and HCO_3^- anions might be masked (Scheme 1).[11] As shown in Figures 8 and 9, only the addition of CN^- to the DHAB/Cu(II) complex solution caused the blue shifted and decreased absorption peak at around 500 nm and the enhancement of the fluorescent

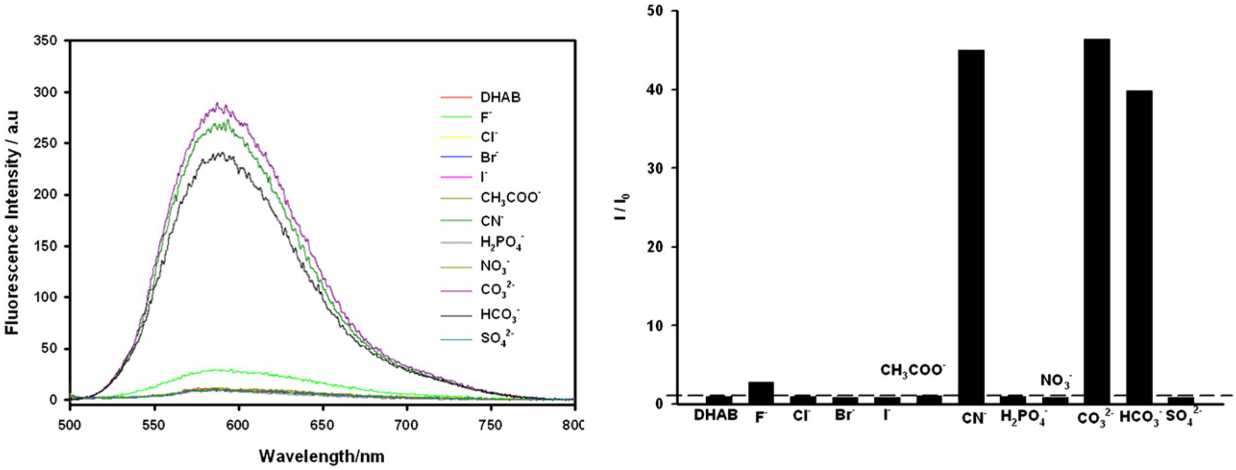
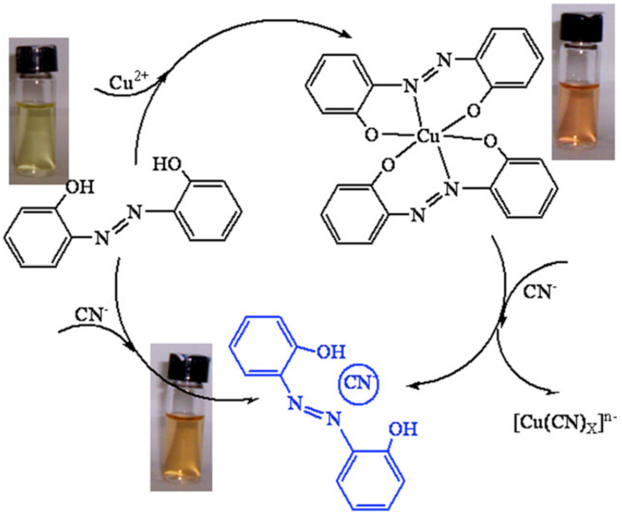


Figure 6. Fluorescence intensity changes of DHAB (3×10^{-5} M) in a mixture of H_2O/MeOH (1/1, v/v, 10 mM HEPES at pH 7.5) in the presence of various anions (6.0×10^{-4} M), λ_{ex}=480 nm. Anions from left to right: blank, F^-, Cl^-, Br^-, I^-, CH_3COO^-, CN^-, $H_2PO_4^-$, NO_3^-, CO_3^{2-}, HCO_3^-, and SO_4^{2-}. I and I_0 are the fluorescence intensity of DHAB in the presence and absence of various anions, respectively.



Scheme 1. The possible process for the sensing of cyanide (CN^-) based on 2, 2′-dihydroxyazobenzene (DHAB).

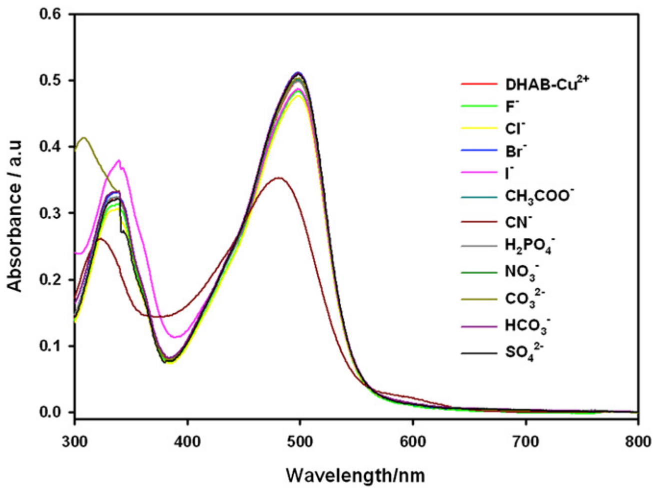


Figure 8. Absorption spectra changes of DHAB–Cu^{2+} (2.0×10^{-5} M/2.0×10^{-5} M) in a mixture of H_2O/MeOH (1/1, v/v, 10 mM HEPES at pH 7.5) in the presence of various anions (5.0×10^{-4} M).

intensity at 590 nm by about 45-fold, while there is almost no changes for both absorption spectra and fluorescent emission at 590 nm after adding other investigated anions, especially CO_3^{2-} and HCO_3^- anions. Thus, CO_3^{2-} and HCO_3^- anions were efficiently minimized by the complex of DHAB–Cu(II) and the high selectivity of DHAB–Cu(II) for CN^- was demonstrated (Figs. 8 and 9), which was attributed to the large stability constants (K_{ass}) between copper ions and cyanide anions ($[Cu(CN)_2]^-$, $K=1.00\times10^{24}$; $[Cu(CN)_4]^{3-}$, $K=2.00\times10^{30}$).[11] At first, the addition of copper ions to the solution of DHAB caused the appearance of the absorption peak at 499 nm (Figs. 2 and 8), indicating the formation of the complex of DHAB and copper ions, and the DHAB/Cu(II) did not show emission at 590 nm (Figs. 9 and 10); then in the second stage, due to the much higher stability constant of cyanide and copper ions, the added cyanide could snatch the copper ions from the complex of DHAB and copper ions (Scheme 1);[11] at last, the further added cyanide could coordinate with DHAB, which induced the increased emission at 590 nm by about 45-fold (Figs. 6 and 10) and the color changes of the solution was light yellow-red-reddish orange, which could be observed by the naked eyes without any instruments (Scheme 1). The plot (Fig. 10, right) of $I_0/(I-I_0)$ versus $[G]^{-2}$ shows a good linear relationship with $R=0.992$ based on the fluorescence titration experiments (Fig. 10, left), which supported the 1/2 binding model between DHAB and CN^- ions in the presence of copper ions.[18] The plot of $I_0/(I-I_0)$ versus $[G]^{-1}$ (Fig. S3), however, showed a poor linear relationship with $R=0.954$, suggesting that the 1/2 binding model between DHAB and CN^- ions was further confirmed. The association constant (K_{ass}) was estimated as 4.8×10^5 M^{-2} from the ratio of the y-intercept to the slope of the plot in Figure 10 (right).[18] Moreover, the sensitivity of DHAB in the presence of copper ions toward CN^- (Fig. S4) almost did not interfere in the existence of CO_3^{2-} and HCO_3^- anions, even when the concentrations of CO_3^{2-} and HCO_3^- ions were increased 30-fold compared to that of the CN^- ions. These results show that DHAB–Cu(II) system has a high selectivity and sensitivity for CN^- ions.

3. Conclusions

In conclusion, we report a ‘new’ colorimetric fluorescent ‘turn-on’ chemosensory (DHAB–Cu (II)) for CN^- ions by an indirect method. The detection of CN^- was monitored by fluorescence spectroscopy, which provides advantages over UV–vis spectroscopy[11] because of its high sensitivity, rapid response rate, and relative low cost. DHAB could coordinate with many metal cations and metal complexes can be used for the sensing of anions, [10,17] Thus,

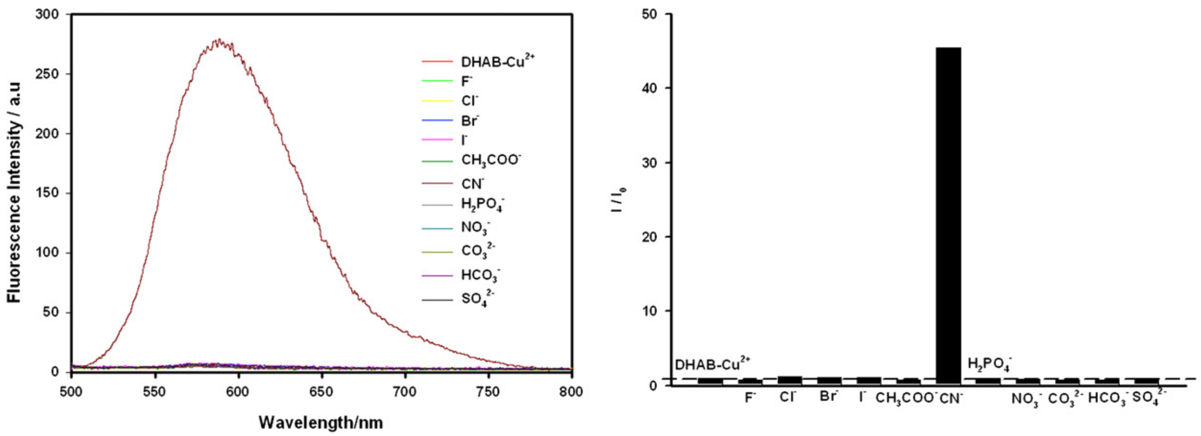


Figure 9. Fluorescence intensity changes of DHAB/Cu^{2+} (2.0×10^{-5} M/2.0×10^{-5} M) in a mixture of H_2O/MeOH (1/1, v/v, 10 mM HEPES at pH 7.5) in the presence of various anions (5.0×10^{-4} M), $\lambda_{ex}=490$ nm, $\lambda_{em}=590$ nm. Anions from left to right: blank, F^-, Cl^-, Br^-, I^-, CH_3COO^-, CN^-, $H_2PO_4^-$, NO_3^-, CO_3^{2-}, HCO_3^-, and SO_4^{2-}. I and I_0 are the fluorescence intensity of DHAB–Cu^{2+} in the presence and absence of various anions, respectively.

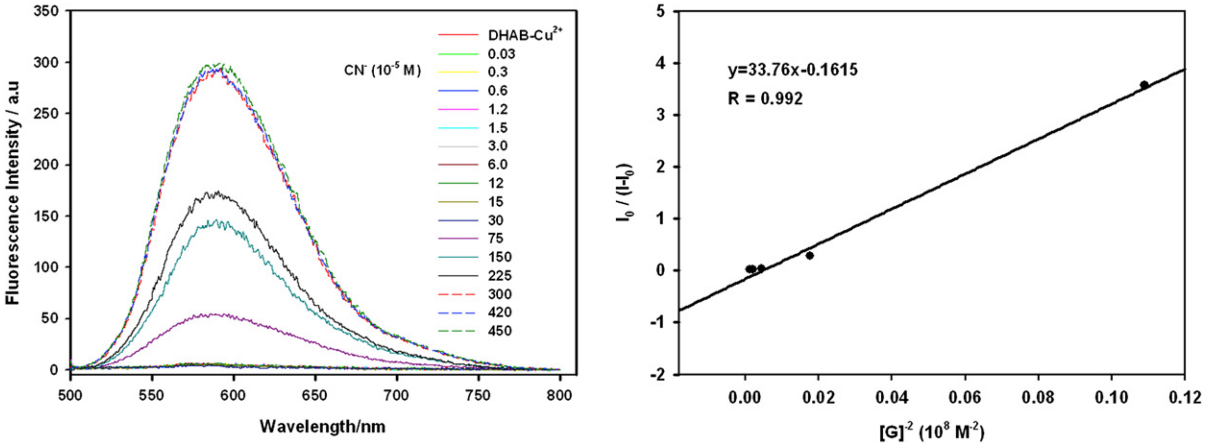


Figure 10. Fluorescence emission spectra of DHAB/Cu^{2+} (2.0×10^{-5} M/2.0×10^{-5} M) upon progressive addition of CN^- in a mixture of H_2O/MeOH (1/1, v/v, 10 mM HEPES at pH 7.5) (left) and the plot of $I_0/(I-I_0)$ versus $[G]^{-2}$ (right) based on 1/2 binding model. I_0 and I are the fluorescence intensity of DHAB–Cu^{2+} at 590 nm in the absence and presence of CN^- anions, respectively. $[G]$ is the concentration of CN^- anions.

this observation indicates that the DHAB–metal complexes may be useful fluorescent chemosensors for sensing of anions whose recognition process is based on the metal–ligand interaction. We are currently working along these lines.

4. Experimental

4.1. Materials and instrumentations

DHAB, 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES), $CuCl_2$, NaF, NaCl, NaBr, KI, NaCN, CH_3COONa, NaH_2PO_4, $NaNO_3$, Na_2CO_3 and $NaHCO_3$, and Na_2SO_4 were commercially available, methanol (MeOH) was analytical grade, doubly distilled water was used. All spectroscopic measurements were performed in a mixture of H_2O–MeOH (1/1, v/v, 10 mM HEPES buffer solution, pH 7.5). The UV–vis spectra were measured using a Hitachi U-2010 spectrometer at 25 °C. The fluorescence emission spectra were measured using a Hitachi F-4500 spectrometer at 25 °C. Excitation slit size was 10.0 nm and emission slit size was also 10.0 nm. Scan speed was set at 240 nm/min.

4.2. Preparation of solutions for the sensing of Cu(II) by DHAB

A solution of DHAB (60 μM) was prepared in H_2O–MeOH (1/1, v/v, 10 mM HEPES buffer solution, pH 7.5); then 2.0 mL of the solution of DHAB was placed in a quartz cell (10.0 mm width) and the UV absorption spectrum was recorded before and after the addition of 2.0 mL of Cu^{2+} (0–180 μM) in H_2O/MeOH (1/1, v/v, 10 mM HEPES buffer solution, pH 7.5) to the solution of DHAB.

4.3. Preparation of solutions for the sensing of anions by DHAB

A solution of DHAB (30 μM) was prepared in H_2O–MeOH (1/1, v/v, 10 mM HEPES buffer solution, pH 7.5); then 4.0 mL of the solution of DHAB was placed in a quartz cell (10.0 mm width) and the UV absorption spectra and fluorescence spectra were recorded before and after the addition of 20.0 equiv of the investigated anions to the solution of DHAB. The fluorescence spectra of each solution were recorded with excitation at 480 nm. The anion recognition behavior of DHAB was evaluated from the changes in fluorescence spectra at the emission wavelength of 590 nm upon addition of that sodium salt.

4.4. Preparation of solutions for the sensing of anions by DHAB–Cu(II)

A solution of DHAB (20 μM) with Cu^{2+} (20 μM) was prepared in H_2O/MeOH (1/1, v/v, 10 mM HEPES buffer solution, pH 7.5); then 4.0 mL of the solution of DHAB–Cu (II) was placed in a quartz cell (10.0 mm width) and the UV absorption spectra and fluorescence spectra of each solution was recorded after adding 25 equiv of the investigated anions. The fluorescence spectra of each solution were recorded with excitation at 490 nm. The anion recognition behavior of DHAB was evaluated from the changes in fluorescence spectra at the emission wavelength of 590 nm upon the addition of that sodium salt.

4.5. Preparation of solutions for the sensing of CN^- by DHAB–Cu(II)

A stock solution of DHAB (40 μM) with Cu^{2+} (40 μM) was prepared in H_2O/MeOH (1/1, v/v, 10 mM HEPES buffer solution, pH 7.5); the solution of NaCN was introduced in portions and the UV absorption spectra and fluorescence intensity changes were recorded at room temperature each time.

4.6. Calculation of the association constant (K_{ass}) between DHAB and Cu(II)

Bearing the 2(DHAB)/1(Cu^{2+}) association stoichiometry in mind,[14] the relationship among absorbance of the mixture (A), the initially prepared DHAB concentration (C_0), and the concentration of copper ions (C_g) can be expressed by the following equation:[16]

$$\frac{C_0}{A-\varepsilon_M C_0}=\left[\frac{1}{k_a(\varepsilon_D-2\varepsilon_M)}\right]\frac{1}{C_0C_g}+\frac{4}{\varepsilon_D-2\varepsilon_M}$$

where ε_M and ε_D are molar extinction coefficients of the DHAB in the absence and presence of copper ions, respectively, at a wavelength of 499 nm. The association constant K_{ass} can thus be calculated to be 2.24×10^{8} M^{-2}, extracted from intercept/[4×slope].

Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) Grant funded by the Ministry of Education, Science and Technology, Korea (MEST) (Acceleration Research Program (No.

2009-0078791)), the Brain Korea 21 Project, and the MEST for the scholarship for foreign students (J.W.).

Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.01.031.

References and notes

1. (a) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacherand, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515; (b) Beer, P. D.; Gale, P. A. *Angew. Chem.* **2001**, *113*, 502; (c) Thomas, S. W., III; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339; (d) Yoon, J.; Kim, S. K.; Singh, N. J.; Kim, K. S. *Chem. Soc. Rev.* **2006**, *35*, 355; (e) Snowden, T. S.; Anslyn, E. V. *Curr. Opin. Chem. Biol.* **1999**, *3*, 740; (f) Rudkevich, D. M.; Brzozka, Z.; Palys, M.; Visser, H. C.; Verboom, W.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 467.
2. (a) Gale, P. A. *Coord. Chem. Rev.* **2000**, *199*, 181; (b) Gale, P. A. *Coord. Chem. Rev.* **2001**, *213*, 79; (c) Sessler, J. L.; Davis, J. M. *Acc. Chem. Res.* **2001**, *34*, 989; (d) Lee, D. H.; Kim, S. Y.; Hong, J. I. *Angew. Chem., Int. Ed.* **2004**, *43*, 4777; (e) Xu, Z. C.; Kim, G. H.; Han, S. J.; Jou, M. J.; Lee, C.; Shin, I.; Yoon, J. *Tetrahedron* **2009**, *65*, 2307; (f) Wang, H. H.; Gan, Q.; Wang, X. J.; Xue, L.; Liu, S. H.; Jiang, H. *Org. Lett.* **2007**, *9*, 4995; (g) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72.
3. (a) Berger, M.; Schmidtchen, F. P. *Chem. Rev.* **1997**, *97*, 1609; (b) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486; (c) Kulig, K. W. *Cyanide Toxicity*; U.S. Department of Health and Human Services: Atlanta, GA, 1991; (d) Lee, K. S.; Kim, H. J.; Kim, G. H.; Shin, I.; Hong, J. I. *Org. Lett.* **2008**, *10*, 49; (e) Kumar, R.; Bhalla, V.; Kumar, M. *Tetrahedron* **2008**, *64*, 8095.
4. (a) Prodi, L.; Bolletta, F.; Montalti, M.; Zaccheronii, N. *Coord. Chem. Rev.* **2000**, *205*, 59; (b) de Silva, A. P.; Fox, D. B.; Huxley, A. J. M.; Moody, T. S. *Coord. Chem. Rev.* **2000**, *205*, 41; (c) Valeur, B.; Leray, I. *Coord. Chem. Rev.* **2000**, *205*, 3; (d) Fabbrizzi, L.; Poggi, A. *Chem. Soc. Rev.* **1995**, *24*, 197; (e) Steed, J. W. *Chem. Commun.* **2006**, 2637; (f) Suksai, C.; Tuntulani, T. *Top. Curr. Chem.* **2005**, *255*, 163; (g) Beer, P. D.; Bayly, S. R. *Top. Curr. Chem.* **2005**, *255*, 125; (h) Gale, P. A. *Coord. Chem. Rev.* **2003**, *240*, 191.
5. (a) Yang, Y. K.; Tae, J. *Org. Lett.* **2006**, *8*, 5721; (b) Jin, W. J.; Fernández-Argüelles, M. T.; Costa-Fernández, J. M.; Pereiro, R.; Sanz-Medel, A. *Chem. Commun.* **2005**, 883; (c) García, F.; García, J. M.; García-Acosta, B.; Martínez-Máñez, R.; Sancenón, F.; Soto, J. *Chem. Commun.* **2005**, 2790; (d) Ros-Lis, J. V.; Martínez-Máñez, R.; Soto, J. *Chem. Commun.* **2001**, 2248; (e) Sun, S.; Lees, A. J. *Chem. Commun.* **2000**, 1687; (f) Chung, Y. M.; Raman, B.; Kim, D. S.; Ahn, K. H. *Chem. Commun.* **2006**, 186; (g) Palomares, E.; Martínez-díaz, M. V.; Torres, T.; Coronado, E. *Adv. Funct. Mater.* **2006**, *16*, 1166.
6. (a) Anzenbacher, P.; Tyson, D. S., Jr.; Jursiková, K.; Castellano, F. N. *J. Am. Chem. Soc.* **2002**, *124*, 6232; (b) Miyaji, H.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 154; (c) Zhang, Y.; Zhang, D.; Liu, C. *J. Phys. Chem. B* **2006**, *110*, 4671; (d) Liu, H.; Shao, X.; Jia, M.; Jiang, X.; Li, Z.; Chen, G. *Tetrahedron* **2005**, *61*, 8095; (e) Tomasulo, M.; Sortino, S.; White, A. J. P.; Raymo, F. M. *J. Org. Chem.* **2006**, *71*, 744.
7. Miller, G. C.; Pritsos, A. Cyanide: Social, Industrial and Economic Aspects. *Proceeding of the TMS Annual Meeting,* 2001; p 73.
8. (a) Xu, J.; Liu, K.; Di, D.; Shao, S.; Guo, Y. *Inorg. Chem. Commun.* **2007**, *10*, 681; (b) Suksai, C.; Tuntulani, T. *Chem. Soc. Rev.* **2003**, *32*, 192; (c) Wiskur, S. L.; AitHaddou, H.; Lavigne, J. J. V.; Anslyn, E. *Acc. Chem. Res.* **2001**, *34*, 963; (d) Lohr, H. G.; Vogtle, F. *Acc. Chem. Res.* **1985**, *18*, 65; (e) Sun, Y.; Liu, Y. L.; Guo, W. *Sens. Actuators, B* **2009**, *143*, 171.
9. (a) Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419; (b) Gunnlaugsson, T.; Glynn, M.; Tocci, G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev.* **2006**, *250*, 3094; (c) Martínez-Máñez, R.; Sancenón, F. *Coord. Chem. Rev.* **2006**, *250*, 3081.
10. (a) Jose, D. A.; Mishra, S.; Ghosh, A.; Shrivastav, A.; Mishra, S. K.; Das, A. *Org. Lett.* **2007**, *9*, 1979; (b) Vilar, R. *Eur. J. Inorg. Chem.* **2008**, 357; (c) Ojida, A.; Nonaka, H.; Miyahara, Y.; Tamaru, S.; Sada, K.; Hamachi, I. *Angew. Chem., Int. Ed.* **2006**, *45*, 5518; (d) Rhee, H. W.; Choi, H. Y.; Han, K.; Hong, J. I. *J. Am. Chem. Soc.* **2007**, *129*, 4524; (e) Zhao, Q.; Liu, S.; Shi, M.; Li, F.; Jing, H.; Yi, T.; Huang, C. *Organometallics* **2007**, *26*, 5922; (f) O'Neil, E. J.; Smith, B. D. *Coord. Chem. Rev.* **2006**, *250*, 3068; (g) Beer, P. D.; Hayes, E. J. *Coord. Chem. Rev.* **2003**, *240*, 167; (h) Männel-Croisé, C.; Zelder, F. *Inorg. Chem.* **2009**, *48*, 1272; (i) Shang, L.; Dong, S. *Anal. Chem.* **2009**, *81*, 1465; (j) Zeng, Q.; Zhang, L. Y.; Li, Z.; Qin, J. G.; Tang, B. Z. *Polymer* **2009**, *50*, 434; (k) Lin, L. R.; Fang, W.; Yu, Y.; Huang, R. B.; Zheng, L. S. *Spectrochim. Acta, Part A* **2007**, *67*, 1403; (l) Kim, M. J.; Swamy, K. M. K.; Lee, K. M.; Jagdale, A. R.; Kim, Y.; Kim, S. J.; Yoo, K. H.; Yoon, J. *Chem. Commun.* **2009**, 7215; (m) Choi, M. G.; Cha, S.; Lee, H.; Jeon, H. L.; Chang, S. K. *Chem. Commun.* **2009**, 7390.
11. (a) Lou, X. D.; Qin, J. G.; Li, Z. *Analyst* **2009**, *134*, 2071; (b) Li, Z. A.; Lou, X. D.; Yu, H. B.; Li, Z.; Qin, J. G. *Macromolecules* **2008**, *41*, 7433; (c) Lou, X. D.; Zhang, L. Y.; Qin, J. G.; Li, Z. *Chem. Commun.* **2008**, 5848; (d) Lou, X. D.; Qiang, L.; Qin, J. G.; Li, Z. *ACS Appl. Mater. Inter.* **2009**. doi:10.1021/am900467b; (e) Guliyev, R; Buyukcakir, O.; Sozmen, F.; Bozdemir, O. A. *Tetrahedron Lett.* **2009**, *50*, 5139; (f) Chung, S. Y.; Nam, S. W.; Lim, J.; Park, S.; Yoon, J. *Chem. Commun.* **2009**, 2866; (g) Xu, Z. C.; Chen, X. Q.; Kim, H. N.; Yoon, J. *Chem. Soc. Rev.* **2010**. doi:10.1039/b907368j
12. Song, T.; Xu, J.; Cheng, G. *Inorganic Chemistry*; Higher Education: Beijing, 2004.
13. (a) Price, R. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 6, p 35; (b) Grychtol, K.; Mennike, W. *Ullmann's Encyclopedia of Industrial Chemistry*; Chemie: Weinheim, 1990; Vol. A16, 299; (c) Abildgaard, J.; Hansen, P. E.; Josephsen, J.; Lycka, A. *Inorg. Chem.* **1994**, *33*, 5271; (d) Nag, J. K.; Chattopadhyay, P.; Mishra, T. K.; Sinha, C. *J. Indian Chem. Soc.* **2000**, *77*, 270; (e) Dutta, S.; Basu, P.; Chakravorty, A. *Inorg. Chem.* **1991**, *30*, 4031; (f) Chakravarty, J.; Dutta, S.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1993**, 2857; (g) Chakravarty, J.; Dutta, S.; Chandra, S. K.; Basu, P.; Chakravorty, A. *Inorg. Chem.* **1993**, *32*, 4249; (h) Dutta, S.; Basu, P.; Chakravorty, A. *Inorg. Chem.* **1993**, *32*, 5543; (i) Hintermaier, F.; Kuehlwein, F.; Robl, C.; Beck, W. *Z. Anorg. Allg. Chem.* **1995**, *621*, 829; (j) Adams, H.; Bucknall, R. M.; Fenton, D. E.; Garcia, M.; Oakes, J. *Polyhedron* **1998**, *17*, 4169; (k) Besslera, K. E.; Santosa, J. A.; Deflona, V. M.; Lemosa, S. S.; Niquet, E. Z. *Anorg. Allg. Chem.* **2004**, *630*, 742; (l) Lahiri, G. K.; Bhattacharya, S.; Mukherjee, M.; Mukherjee, A. K.; Chakravorty, A. *Inorg. Chem.* **1987**, *26*, 3359; (m) Cuny, G. D.; Landgrebe, K. D.; Smith, T. P. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 237; (n) Iki, N.; Hoshino, H.; Yotsuyanagi, T. *Anal. Chem.* **2000**, *72*, 4812; (o) Badea, M.; Olar, R.; Emandi, A. *J. Therm. Anal. Calorim* **2006**, *84*, 601.
14. Constantinescu, C.; Emandi, A.; Vasiliu, C.; Negrila, C.; Logofatu, C.; Cotarlan, C.; Lazarescu, M. *Appl. Surf. Sci.* **2009**, *255*, 5480.
15. (a) Bershtein, I. Y.; Ginzburg, O. F. *Russ. Chem. Rev.* **1972**, 4197; (b) Dedkov, Y. M.; Kotov, A. V. *Russ. Chem. Bull.* **1973**, *22*, 1289; (c) Wang, J.; Ha, C. S. *Tetrahedron* **2009**, *65*, 6959.
16. Ho, M. L.; Hsieh, J. M.; Lai, C. W.; Peng, H. C.; Kang, C. C.; Wu, I. C.; Lai, C. H.; Chen, Y. C.; Chou, P. T. *J. Phys. Chem. C* **2009**, *113*, 1686.
17. Wang, J.; Liu, H. B.; Wang, W.; Kim, I.; Ha, C. S. *Dalton Trans.* **2009**, *47*, 10422.
18. Wong, W. L.; Huang, K. H.; Teng, P. F.; Lee, C. S.; Kwong, H. L. *Chem. Commun.* **2004**, 384.