DOI: 10.1002/cjoc.201200260

A Highly Copper-Selective Ratiometric Fluorescent Sensor Based on BODIPY

Huang, Jinlong(黄金龙) Wang, Bo(王波) Ye, Jianguo(叶建国) Liu, Bin(刘斌)
Qiu, Huayu(邱化玉) Yin, Shouchun*(尹守春)

College of Material Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou, Zhejiang 310036, China

A new ratiometric fluorescent sensor (**1**) for Cu^{2+} based on 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) with di(2-picolyl)amine (DPA) as ion recognition subunit has been synthesized and investigated in this work. The binding abilities of **1** towards different metal ions such as alkali and alkaline earth metal ions (Na^+, K^+, Mg^{2+}, Ca^{2+}) and other metal ions (Ba^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+}, Fe^{3+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Hg^{2+}, Ag^+) have been examined by UV-vis and fluorescence spectroscopies. **1** displays high selectivity for Cu^{2+} among all test metal ions and a ~10-fold fluorescence enhancement in I_{582}/I_{558} upon excitation at visible excitation wavelength. The binding mode of **1** and Cu^{2+} is a 1∶1 stoichiometry determined via studies of Job plot, the nonlinear fitting of the fluorometric titration and ESI mass.

Keywords BODIPY, chemosensor, copper(II), ratiometric measurement, spectroscopic properties

Introduction

Because it is an essential trace element in biological systems and an important environmental pollutant, there has been great interest in the development of fluorescent chemosensors for Cu^{2+} in recent years.[1,2] Cu^{2+} plays an important role in many biological processes, however, if the level exceeds cellular needs, Cu^{2+} can cause oxidative stress and disorders associated with neurodegenerative diseases, such as Menkes disease, Wilson disease, and Alzheimer's disease.[3] Most of the reported Cu^{2+} ion fluorescent chemosensors work in a "turn-off" or "turn-on" mode with changes only in fluorescent probes intensity.[4-30] However, the simple change of fluorescence intensity is interfered easily by various factors, such as probe concentration, sample environments, and variabilities in the efficiency of excitation and emission wavelength. A ratiometric fluorescent measurement is desirable to eliminate those effects, which uses a ratio of the fluorescent intensities at two different wavelengths, providing a built-in correction to eliminate most of the ambiguities.[31-34] Thus, there is still strong demand for the development of efficient Cu^{2+}-selective fluorescent sensor, especially ratiometric probes that can be excited in the visible wavelength region.

BODIPY (4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) is a popular fluorescent dye with widespread applications as fluorescent chemosensor because BODIPY has a lot of valuable characteristics, such as high fluorescence quantum yields, relatively strong and sharp absorption and emission in the visible region, and chemical stability. Furthermore, BODIPY dyes are amenable to structural modification so that spectral shifts in the absorption and emission bands can be generated by introducing the appropriate substituent group.[35,36]

Herein, we report the synthesis and metal sensing properties of a new ratiometric BODIPY-fluorescent chemosensor, 5-*N*-(2-picolyl)amine-4,4-difluoro-3-methoxyl-8-(4-tolyl)-4-bora-3a,4a-diaza-s-indacene (**1**). **1** shows a high selectivity toward Cu^{2+} over all the tested metal ions and ~10-fold fluorescence ratio change after Cu^{2+} binding upon excitation at 535 nm in CH_3CN.

Experimental

Materials

3,5-Dichloro-8-(4-tolyl)BODIPY was synthesized according to literature procedures.[37] Sodium methoxide di(2-picolyl)amine, and sodium hydride were purchased from Aldrich and used without further purification. The metal salts [$AgClO_4$, $Ba(ClO_4)_2$, $Ca(ClO_4)_2$, $Cd(ClO_4)_2$, $Co(ClO_4)_2$, $Cu(ClO_4)_2 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, $FeCl_3$, $Hg(ClO_4)_2$, $KClO_4$, $Mg(ClO_4)_2$, $NaClO_4$, $Ni(ClO_4)_2 \cdot 6H_2O$, $Pb(ClO_4)_2 \cdot 3H_2O$ and $Zn(ClO_4)_2$] were purchased from Aldrich.

* E-mail: yinsc@ustc.edu; Tel.: 0086-571-28867899; Fax: 0086-571-28867899
Received March 18, 2012; accepted April 22, 2012; published online XXXX, 2012.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201200260 or from the author.

Instrumentation

^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance 400 operating at a frequency of 400 MHz for ^{1}H and 100 MHz for ^{13}C. Melting points were taken on a Beijing Taike X-5 melting point instrument and are uncorrected. Mass spectra were recorded on a Hewlett-Packard 5989 A mass spectrometer (ESI mode). High-resolution mass data were obtained with a Kratos MS50TC instrument.

UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 40 UV-vis spectrophotometer. Corrected steady-state excitation and emission spectra were obtained using a HITACHI F-2700 Fluorescence Spectrophotometer.

Experimental details for spectral studies

The sensor **1** was dissolved into spectroscopic grade CH_3CN. The concentration of the **1** solution for spectral analysis is 2 μmol/L. All the test metal ions were dissolved into deionized water. The concentration of the test metal ions was 3 mmol/L. For the sensitivity measurement, 100 μL of the test metal ions solution was added into 3 mL of the **1** solution (2 μmol/L).

Determination of quantum yields

For the determination of the relative fluorescence quantum yields (Φ_f) in solution, only dilute solutions with an absorbance below 0.1 at the excitation wavelength λ_{ex} were used. Cresyl violet in ethanol (Φ_f=0.55, λ_{ex}=535 nm) was used as fluorescence standards. [38] In all cases, correction for the solvent refractive index was applied. All spectra were recorded at room temperature using undegassed samples.

Determination of ground-state dissociation constant K_d

The ground-state dissociation constant K_d of the complex between **1** and Cu^{2+} was determined in CH_3CN solution by ratiometric fluorometric titration as a function of Cu^{2+} using the fluorescence emission spectra. Nonlinear fitting of Eq. (1) to the steady-state fluorimetric ratiometric data R recorded as a function of [Cu^{2+}] yields values of $K_d\xi$, R_{min}, R_{max}, and n. Since ξ—the ratio of the fluorescence signal of the free form of **1** over that of the bound form at the indicated wavelengths—is experimentally accessible, a value for K_d can be recovered from ratiometric excitation fluorescence data.

$$R=\frac{R_{max}\left[Cu^{2+}\right]^n+R_{min}K_d}{K_d\xi+\left[Cu^{2+}\right]^n} \quad (1)$$

In Eq. (1), R stands for the ratiometric emission fluorescence data at [Cu^{2+}], whereas R_{min} and R_{max} denote the ratiometric emission fluorescence data at minimal and maximal [Cu^{2+}], respectively, and n is the number of Cu^{2+} ions bound per probe molecule (*i.e.*, stoichiometry of binding). [39]

Synthesis of 5-chloro-4,4-difluoro-3-methoxyl-8-(4-tolyl)-4-bora-3a,4a-diaza-s-indacene (2)

To a solution of 3,5-dichloro-8-(4-tolyl)BODIPY (175 mg, 0.5 mmol) in 10 mL of methanol, sodium methoxide (54 mg, 1 mmol) was added. The reaction mixture was stirred at room temperature for 0.5 h under argon. After evaporating the solvent, 30 mL of water was added and the organic layer was extracted with CH_2Cl_2 (40 mL×3), dried by Mg_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with a mixture of CH_2Cl_2 and petroleum ether (1∶4, V∶V) to give red solid **2** (150 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.36 (d, J=8.0 Hz, 2H), 7.29 (d, J=7.6 Hz, 2H), 6.96 (d, J=4.4 Hz, 1H), 6.61 (d, J=4.0 Hz, 1H), 6.28 (d, J=4.0 Hz, 1H), 6.14 (d, J=4.8 Hz, 1H), 4.14 (3H, s, OCH_3), 2.45 (3H, s, CH_3); ^{13}C NMR (100 Mz, $CDCl_3$) δ: 169.5, 140.6, 136.9, 135.2, 132.2, 130.4, 130.0, 129.1, 115.3, 104.4, 59.2, 21.4; ESI-MS *m/z*: 369.5 [M+Na]$^+$.

Synthesis of 5-*N*-(2-picolyl)amine-4,4-difluoro-3-methoxyl-8-(4-tolyl)-4-bora-3a,4a-diaza-s-indacene (1)

To a solution of **2** (100 mg, 0.29 mmol) and di(2-picolyl)amine (40 mg, 0.4 mmol) in 15 mL of acetonitrile, sodium hydride (14 mg, 0.6 mmol) was added. The reaction mixture was refluxed for 3 h under argon. After evaporating the solvent, 30 mL of water was added and the organic layer was extracted with CH_2Cl_2 (40 mL×3), dried by $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting with a mixture of CH_2Cl_2 and ethyl acetate (4∶1, V∶V) to give red solid **1** (84 mg, 57% yield). m.p. 183—185 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (d, J=4.5 Hz, 2H), 7.64 (t, J=7.8 Hz, 2H), 7.49 (d, J=7.8 Hz, 2H), 7.33 (d, J=7.8 Hz, 2H), 7.22 (d, J=7.8 Hz, 2H), 7.15 (t, J=6.2 Hz, 2H), 6.67 (d, J=4.8 Hz, 1H), 6.47 (d, J=4.2 Hz, 1H), 6.06 (d, J=4.8 Hz, 1H), 5,75 (d, J=4.2 Hz, 1H), 5.10 (s, 4H, $N(CH_2)_2$), 4.00 (s, 3H, OCH_3), 2.42 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.5, 161.7, 157.4, 149.2, 139.1, 137.0, 134.8, 132.7, 132.6, 131.6, 130.5, 128.7, 126.3, 124.2, 122.4, 122.1, 111.2, 95.5, 58.3, 58.2, 21.3; ESI-MS *m/z*: 532.2 [M+Na]$^+$. HRMS calcd for $C_{29}H_{26}BF_2N_5O$ 509.2198, found 509.2250.

Results and Discussion

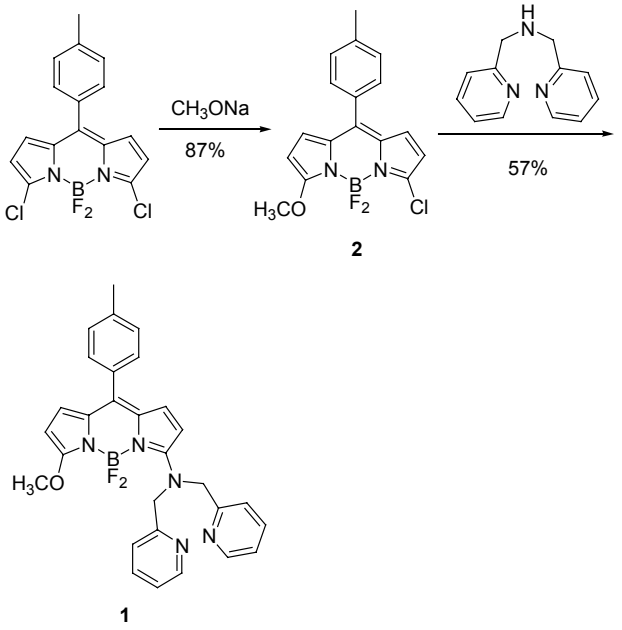
Synthesis of chemosensor 1

To synthesize sensor **1**, 3,5-dichloroBODIPY was first prepared according to a previously reported procedure. As reported in Wim's work, 3,5-dichloroBODIPY can be substituted with many different nucleophiles, such as oxygen, nitrogen, sulfur, and carbon centred nucleophiles, which turns out to be a very successful approach for preparing a variety of symmetric and asymmetric BODIPY compounds with substitution pat-

CHINESE JOURNAL OF CHEMISTRY

terns that are difficult to synthesize by other way.[36] Thus, we use 3,5-dichloroBODIPY as starting material to synthesize **1** in two steps. As outlined in Scheme 1, one chlorine atom of 3,5-dichloroBODIPY was first substituted by a methoxy group upon addition of two equivalents of sodium methoxide in methanol at room temperature to afford the monosubstituted product **2** in good (87%) yield. The second chlorine atom of the isolated **2** was subsequently substituted by di(2-picolyl)-amine in refluxing acetonitrile with strong base (sodium hydride) because of the lower reactivity of the second chlorine resulting from the electron donating effect of the oxygen atom.

Scheme 1 Synthetic route to sensor **1**



Spectral characteristics with and without Cu^{2+}

The UV-vis absorption and fluorescence spectroscopic measurements and titration studies in the absence and presence of Cu^{2+} in CH_3CN solution were investigated after full characterization of the chemical structure by ^1H and ^{13}C NMR and MS spectroscopy. The UV-vis absorption spectrum of **1** in CH_3CN exhibited a main peak with a maximum at 535 nm assigned to the $S_0 \rightarrow S_1$ transition of the BODIPY chromophore (Figure 1). In addition, a weak absorption band at 502 nm corresponding to the $S_0 \rightarrow S_2$ transition of the BODIPY chromophore was also observed. When Cu^{2+} was added to **1** in CH_3CN solution, the intensity of the main absorbance peak at 535 nm gradually decreased while a new low energy broad band around 580 nm appeared and increased progressively with two isosbestic points at 491, 565 nm. After addition of solutions up to 20 μmol/L Cu^{2+}, the initial strong band at 535 nm almost disappeared, and the intensity of the low energy broad band at 573 nm increased very sharply with a new isosbestic point at 506 nm. The maximum intensity of absorption at 573 nm was reached when 36 μmol/L Cu^{2+} was added, and further addition of excess Cu^{2+} produced no significant changes in UV-vis spectra.

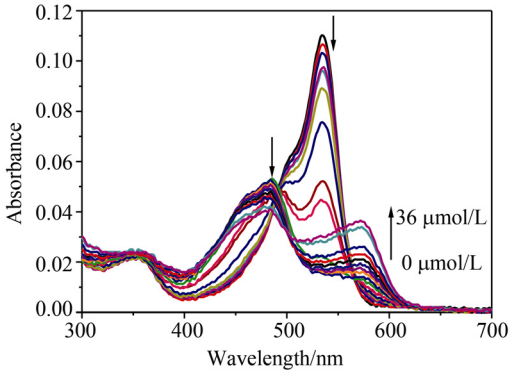


Figure 1 UV-vis absorption spectra of **1** (2 μmol/L) in the presence of different concentrations of Cu^{2+} (0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36 μmol/L) in CH_3CN.

The emission spectra of **1** and its fluorescence titration with Cu^{2+} were recorded in CH_3CN upon excitation at λ_{ex}=535 nm (Figure 2). The emission spectrum of free **1** displayed a weak peak with a maximum at 558 nm. Interestingly, after the addition of Cu^{2+} to chemosensor **1**, the fluorescence emission intensity at 558 nm decreased significantly and a new red-shifted emission band at 582 nm arising from the formation of a **1**-Cu^{2+} complex showed up. Correspondingly, the ratio of the fluorescent intensities at 582 nm and 558 nm (I_{582}/I_{558}) increased from 0.41 to 3.87 with the concentration of Cu^{2+} changed from 0 to 36 μmol/L, which made **1** serve as a ratiometric fluorescent sensor for Cu^{2+} (Figure 2).

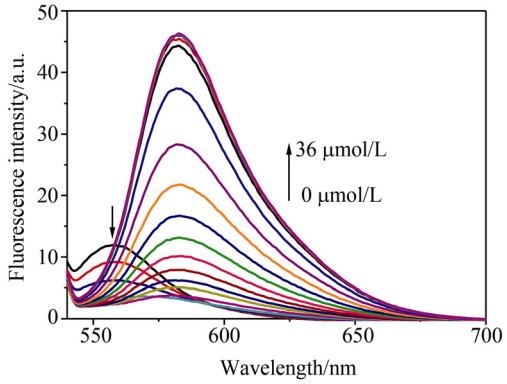


Figure 2 Fluorescent emission spectra of **1** (2 μmol/L) upon excitation at 535 nm in the presence of different concentrations of Cu^{2+} (0, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36 μmol/L) in CH_3CN.

The Φ_f values of free **1** and **1**-Cu^{2+} complex were 0.008 and 0.17, respectively. The low Φ_f value (0.008) for uncomplexed **1** could be attributed to an efficient quenching via an excited-stated intramolecular charge transfer (ICT) process from the nitrogen atom of the di(2-picolyl)amine moiety to the strongly electron-deficient BODIPY acceptor. Upon binding of Cu^{2+}, the electron-donating properties of the amine were reduced,

which resulted in an enhancement in the fluorescence intensity.[39]

Binding stoichiometry of 1 and Cu^{2+}

To determine the binding stoichiometry of **1** and Cu^{2+}, Job's method for the emission was employed. The total concentration of **1** and Cu^{2+} was kept at a constant 4 μmol/L, with a continuous variation of the molar fraction of Cu^{2+}. The change of the fluorescence intensity at 582 nm with the concentration ratio of **1** to Cu^{2+} was shown in Figure 3. When the molecular fraction of Cu^{2+} was about 0.5, the complex of **1** and Cu^{2+} exhibited a maximum fluorescence emission at 582 nm. This indicated that a 1∶1 stoichiometry is most possible for the binding mode of **1** and Cu^{2+}.

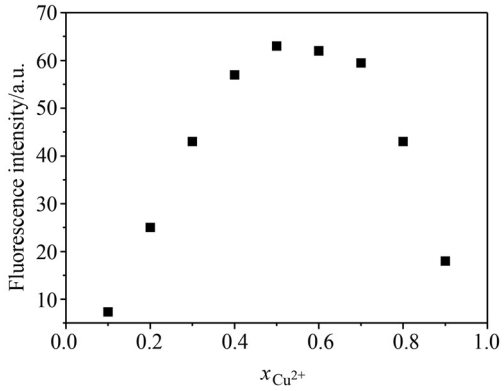


Figure 3 Job's plot of **1** and Cu^{2+}. The total concentrations of **1** and Cu^{2+} were kept at a constant 4 μmol/L in CH_3CN. Excitation was at 535 nm and emission intensity was measured at 582 nm.

Further evidences for proving a 1∶1 stoichiometry for the **1**-Cu^{2+} complex were the results of the nonlinear fitting of the fluorometric titration and ESI. Figure S1 showed the dependence of the intensity ratios of emission at 582 nm to that at 558 nm (I_{582}/I_{558}) on the concentrations of Cu^{2+} getting the data from Figure 2. With the increase of the concentration of Cu^{2+}, the intensity ratios of I_{582}/I_{558} were increasing, which reached the maximum values when 30 μmol/L Cu^{2+} was added. By the nonlinear fitting of the fluorometric titration data using equation 1, the stoichiometry of the complex of **1** and Cu^{2+} was obtained as 1∶1 and the disassociation constant (K_d) was 7.8±0.4 μmol/L. Figure S2 shows the ESI mass spectra of **1** and the **1**-Cu^{2+}complex. As shown in Figure S2, **1** showed two peaks at m/z=510.3 and 532.2 corresponding to $[1+H]^+$ and $[1+Na]^+$, respectively. After 15 equiv. of Cu^{2+} was added to **1** in CH_3CN, the peaks mentioned above decreased and a unique peak at m/z=572.2 corresponding to $[1+Cu-H]^+$ was clearly observed, which reveals a 1∶1 stoichiometry for the **1**-Cu^{2+} complex.

Selectivity and tolerance of 1 to Cu^{2+} over other metal ions

To further explore the selectivity of **1** to Cu^{2+}, fluorescent spectra of **1** response to other metal ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Ag^+) that probably affected the fluorescence intensity were examined (Figures 4 and 5). As shown in Figure 4, titration of alkali and alkaline earth metal perchlorates did not show much change to the fluorescence intensities of **1**. The emission of **1** at 558 nm was partly quenched by Co^{2+}, Ni^{2+}, Hg^{2+}, and Pb^{2+}, whereas the titration of Cu^{2+} resulted in a remarkable red-shift and a great enhancement of the emission at 582 nm. However, variation of the fluorescence intensity ratio (I_{582}/I_{558}) was rather small when other selected metal perchlorates were titrated compared to Cu^{2+} as shown in white bars of Figure 5. Even Co^{2+}, Ni^{2+}, Hg^{2+}, or Pb^{2+} only induced a negligible effect on the fluorescence intensity ratio (I_{582}/I_{558}). These results clearly indicate that **1** shows good selectivity and sensitivity toward Cu^{2+}. The competition experiments were further conducted in the presence of Cu^{2+} at 30 μmol/L, followed by addition of 200 μmol/L of other metal ions, respectively. The competition experiments revealed that

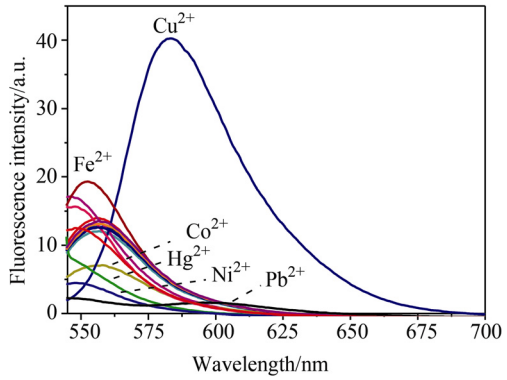


Figure 4 Fluorescence emission spectra of **1** (2 μmol/L) upon addition of various metal ions (100 μmol/L) in CH_3CN (λ_{ex}=535 nm).

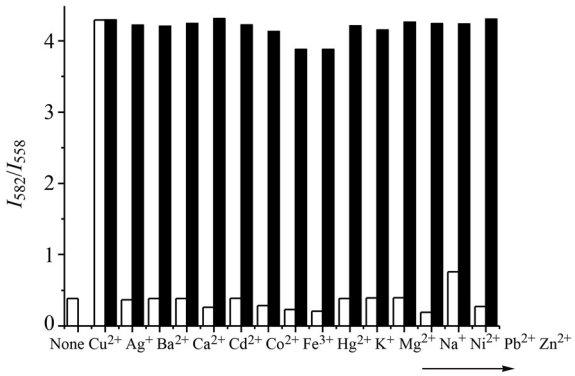


Figure 5 Metal ion selectivity profiles of **1** (2 μmol/L): white bars, fluorescence of **1** in the absence and the presence of the selected metal ions (100 μmol/L); black bars, fluorescence of **1** in the presence of 30 μmol/L Cu^{2+}, followed by the selected metal ions (200 μmol/L) except Cu^{2+}. All samples were measured in CH_3CN and excitation was at 535 nm.

the Cu^{2+}-induced ratiometric fluorescence response was unaffected in the presence of all the tested metal cations mentioned above (black bars in Figure 5). Therefore, the Cu^{2+}-selective binding ratiometric response to **1** can take place in the coexistance of the other competitive metal ions.

We have also investigated the effect of water content on the fluorescence measurement of **1**-Cu^{2+}. It has been found that the fluorescence signal of **1**-Cu^{2+} had already quenched and sensor **1** has no sensitivity to Cu^{2+} if the water content exceeded 10%.

To investigate practical application, the detection limit of this new fluorescent chemosensor **1** was also evaluated. The fluorescence emission changes of **1** (2 μmol/L) upon addition of Cu^{2+} ions by 0.2 μmol/L in CH_3CN were shown in Figure S3. From Figure S3, it can be seen that the detection limit of sensor **1** for Cu^{2+} ions was 2.5×10^{-7} mol/L and the linear range was from 2.5×10^{-7} mol/L to 2.0×10^{-6} mol/L.

Conclusions

In conclusion, we have presented a new ratiometric Cu^{2+}-specific fluorescent chemosensor **1**. **1** displays high selectivity for Cu^{2+} over other metal ions and a ~10-fold fluorescence ratio change upon excitation at 535 nm in CH_3CN.

Acknowledgement

This work was financially supported by the National Natural Science Foundation of China (Nos. 91127032, 21174035), Zhejiang Provincial Natural Science Foundation of China (No. Y4100287), Program for Excellent Young Teachers in Hangzhou Normal University (No. HNUEYT 2011-01-019) and the Opening Foundation of Zhejing Provincial Top Key Discipline (No. 20110943).

References

[1] Gaggelli, E.; Kozlowski, H.; Valensin, D.; Valensin, G. *Chem. Rev.* **2006**, *106*, 1995.
[2] Que, E. L.; Domaille, D. W.; Chang, C. J. *Chem. Rev.* **2008**, *108*, 1517.
[3] Barnham, K. J.; Masters, C. L.; Bush, A. I. *Nat. Rev. Drug Discov.* **2004**, *3*, 205.
[4] Wen, Z. C.; Yang, R.; He, H.; Jiang, Y. B. *Chem. Commun.* **2006**, 106.
[5] Xiang, Y.; Tong, A. J.; Ju, Y. *Org. Lett.* **2006**, *8*, 2863.
[6] Xie, J.; Ménand, M.; Maisonneuve, S.; Métivier, R. *J. Org. Chem.* **2007**, *72*, 5980.
[7] Li, G. K.; Xu, Z. X.; Chen, C. F.; Huang, Z. T. *Chem. Commun.* **2008**, 1774.
[8] Yu, M. X.; Shi, M.; Chen, Z. G.; Li, F. Y.; Li, X. X.; Gao, Y. H.; Xu, J.; Yang, H.; Zhou, Z. G.; Yi, T.; Huang, C. H. *Chem. Eur. J.* **2008**, *14*, 6892.
[9] Jung, H. S.; Kwon, P. S.; Lee, J. W.; Kim, J. I.; Hong, C. S.; Kim, J. W.; Yan, S. H.; Lee, J. Y.; Lee, J. H.; Joo, T. H.; Kim, J. S. *J. Am. Chem. Soc.* **2009**, *131*, 2008.
[10] Chen, W. B.; Tu, X. J.; Guo, X. Q. *Chem. Commun.* **2009**, 1736.
[11] Zhao, Y.; Zhang, X. B.; Han, Z. X.; Qiao, L.; Li, C. Y.; Jian, L. X.; Shen, G. L.; Yu, R. Q. *Anal. Chem.* **2009**, *81*, 7022.
[12] Li, N.; Xiang, Y.; Tong, A. J. *Chem. Commun.* **2010**, *46*, 3363.
[13] Goswami, S.; Sen, D.; Das, N. K. *Org. Lett.* **2010**, *12*, 856.
[14] Guo, Z. Q.; Zhu, W. H.; Tian, H. *Macromolecules* **2010**, *43*, 739.
[15] Zhang, J. F.; Zhou, Y.; Yoon, J. Y.; Kim, Y.; Kim, S. J.; Kim, J. S. *Org. Lett.* **2010**, *12*, 3852.
[16] Maity, D.; Manna, A. K.; Karthigeyan, D.; Kundu, T. K.; Pati, S. K.; Govindaraju, T. *Chem. Eur. J.* **2011**, *17*, 11152.
[17] Ko, K. C.; Wu, J. S.; Kim, H. J.; Kwon, P. S.; Kim, J. W.; Bartsch, R. A.; Lee, J. Y.; Kim, J. S. *Chem. Commun.* **2011**, *47*, 3165.
[18] Li, Z. X.; Zhang, L. F.; Wang, L.; Guo, Y. K.; Cai, L. H.; Yu, M. M.; Wei, L. H. *Chem. Commun.* **2011**, *47*, 5798.
[19] Liu, Y. L.; Sun, Y.; Du, J.; Lu, X.; Zhao, Y.; Chen, M. L.; Wang, P.; Guo, W. *Org. Biomol. Chem.* **2011**, *9*, 432.
[20] Liu, L. Z.; Dong, X. H.; Xiao, Y.; Lian, W. L.; Liu, Z. H. *Analyst* **2011**, *136*, 2139.
[21] Huang, L.; Cheng, J.; Xie, K. F.; Xi, P. X.; Hou, F. P.; Li, Z. P.; Xie, G. Q.; Shi, Y. J.; Liu, H. Y.; Bai, D. C.; Zeng, Z. Z. *Dalton Trans.* **2011**, *40*, 10815.
[22] Sirilaksanapong, S.; Sukwattanasinitt, M.; Rashatasakhon, P. *Chem. Commun.* **2012**, *48*, 293.
[23] Coskun, A.; Akkaya, E. U. *J. Am. Chem. Soc.* **2005**, *127*, 10464.
[24] Xu, Z.; Xiao, Y.; Qian, X.; Cui, J.; Cui, D. *Org. Lett.* **2005**, *7*, 889.
[25] Shao, N.; Jin, J.; Wang, H.; Zhang, Y.; Yang, R.; Chan, W. *Anal. Chem.* **2008**, *80*, 3466.
[26] Yin, S. C.; Leen, V.; Van Snick, S.; Boens, N.; Dehaen, W. *Chem. Commun.* **2010**, *46*, 6329.
[27] Lee, M.; Kim, H.; Yoon, S.; Park, N.; Kim, J. S. *Org. Lett.* **2008**, *10*, 213.
[28] Hu, M. B.; Li, H. X.; Chen, L. S.; Zhang, H. B.; Dong, C. *Chin. J. Chem.* **2009**, *27*, 513.
[29] Zou, Q.; Li, X.; Zhang, J. J.; Zhou, J.; Sun, B. B.; Tian, H. *Chem. Commun.* **2012**, *48*, 2095.
[30] Zhu, W. H.; Huang, X. M.; Guo, Z. Q.; Wu, X. M.; Yu, H. H.; Tian, H. *Chem. Commun.* **2012**, *48*, 1784.
[31] Lin, W.; Yuan, L.; Tan, W.; Feng, J.; Long, L. *Chem. Eur. J.* **2009**, *15*, 1030.
[32] Domaille, D. W.; Zeng, L.; Chang, C. J. *J. Am. Chem. Soc.* **2010**, *132*, 1194.
[33] Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891.
[34] Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 1184.
[35] Baruah, M.; Qin, W. W.; Basarić, N.; De Borggraeve, W. M.; Boens, N. *J. Org. Chem.* **2005**, *70*, 4152.
[36] Qin, W. W.; Rohand, T.; Dehaen, W.; Clifford, J. N.; Driesen, K.; Beljonne, D.; Van Averbeke, B.; Van der Auweraer, M.; Boens, N. *J. Phys. Chem. A* **2007**, *111*, 8588.
[37] Rohand, T.; Baruah, M.; Qin, W. W.; Boens, N.; Dehaen, W. *Chem. Commun.* **2006**, 266.
[38] Olmsted, J. *J. Phys. Chem.* **1979**, *83*, 2581.
[39] Baruah, M.; Qin, W. W.; Vallée, R. A. L.; Beljonne, D.; Rohand, T.; Dehaen, W.; Boens, N. *Org. Lett.* **2005**, *7*, 4377.

(Lu, Y.)

