RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

RSC Advances

RSCPublishing

ARTICLE

Multichannel Detection of Cu^{2+} Based on a Rhodamine-Ethynylferrocene Conjugate†

Cite this: DOI: 10.1039/xoxxoooooox

XingWen Cheng,[a] Yi Zhou,*[a] Yuan Fang,[a] QingQing Rui[a] and Cheng Yao*[ab]

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/advances

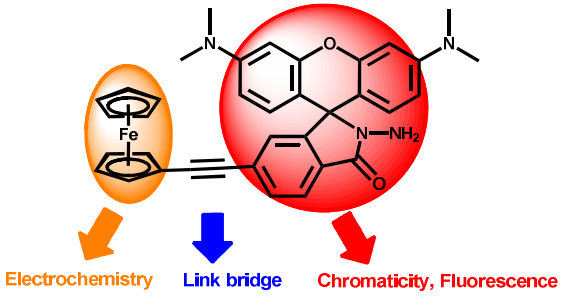
A novel multichannel chemosensor **DR3** juxtaposed with a rhodamine chromophore and the electrochemical characterization of an ethynylferrocene group was developed. This chemosensor could selectively recognized Cu^{2+} in the presence of other competing ions in a wide pH range, which exhibits the multi-response of UV/vis absorption, fluorescence emission, and electrochemical parameters.

Introduction

Recently, due to its innate advantages such as high sensitivity, selectivity and real-time monitoring, luminescent chemosensors for detection of transition metal have attracted increasing attention. It usually contain the reaction sites and an obvious change in optical characteristics upon host-guest interactions.[1] Among the transition metal, copper is the third most abundant essential heavy metal in the human body after zinc and iron and plays a crucial role in biological process. It forms as an important catalytic cofactor in redox chemistry for proteins.[2] However, the abnormal level of Cu^{2+} in living system may lead to various neurodegenerative diseases including Menkes, Wilson, and Alzheimer's diseases.[3-5] Thus, it is of significant importance to develop a luminescent chemosensor for monitoring Cu^{2+} in biological process. As far as we know, a large number of Cu^{2+}-chemosensors based on fluorescence enhancement have been reported.[6-19] Most of them are based on the changes of UV/vis absorption and fluorescence emission. But few multichannel Cu^{2+}-selective chemosensors have been developed so far through multiple responses including chromaticity, fluorescence, electrochemistry et. al. Compared with single signal detection, multichannel have higher sensitivity, better excellent selectivity and anti-interference ability. More importantly, multichannel detection system can make self-calibration measurements come true through different analytic methods.

Zade et. al. reported a thiophene-based salphen-type chemosensor for detection of Cu^{2+} and Zn^{2+} with electrochemical properties.[20] It is expected to introduce an excellent group to multichannel chemosensors which have electrochemical characteristics, realizing to establish multichannel analytic systems. Ferrocene has the brilliant ability to store electrons strengthening the coordination between the chemosensor and the metal ion.[21] It is well known that ferrocene-containing chemosensors exhibit the electrochemical response upon complexation of a suitable guest ion. Zhang and Zapata et. al also observed a significant potential shift of the Fe^{III}/Fe^{II} on coordination of an analyte, which exhibits a multi-responsive signaling.[22] The expanded work relied on rhodamine-based multichannel chemosensors for Cr^{3+} and Hg^{2+} et. al linked with ferrocene have been reported.[23] However, the multichannel Cu^{2+}-chemosensors have been barely mentioned to the best of our knowledge.[24]

Herein, we synthesized a novel multichannel chemosensor **DR3** for the detection of Cu^{2+} (Scheme 1). It is expected to achieve three-channel Cu^{2+}-selective chemosensor through introducing ferrocene group to the rhodamine chromophore. We designed the acetylene group linked with the electrochemical properties of a ferrocene group and chromatic, fluorescent rhodamine with ring-opening process, increasing multichannel output signaling upon interaction with Cu^{2+}. The chemosensor was introducing a hydrazide functional group to act as the potential reaction site for Cu^{2+}. Upon reacts with copper ion, the fluorescence and absorption intensity evidently increased due to the process of spirolactam ring-opening and hydrolysis. This multichannel chemosensor **DR3** exhibits suitable variations of absorption spectrum, fluorescence emission and electrochemical parameters.



Scheme 1. Design of Cu^{2+} multichannel chemosensor **DR3**

[a] College of Science, Nanjing Tech University, Nanjing 211816, China
[b] State Key Laboratory of Coordination Chemistry, Nanjing University, Jiangsu 210093, China. E-mail: zhouyi624@126.com and yaocheng@njtech.edu.cn; Tel: +86-25-5813-9482; Fax: +86-25-5813-9482

† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/b000000x

Experimental section

Materials and measurements

All reagents were purchased from commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance 500 or Brucker Avance 400 spectrometer in $CDCl_3$. Electrospray ionization mass spectra (ESI-MS) were measured on a Micromass LCTTM system. UV–visible spectra were recorded on a Perkin–Elmer 35 spectrometer and Fluorescence measurements were performed on a Perkin-Elmer LS 50B fluorescence spectrophotometer. Electrochemical measurements were performed with an Eco Chemie Autolab. The pH measurements were made with a PHS-3C Precision Ph/mV Meter. TLC analysis was conducted on silica gel plates and chromatography was performed over silica gel (mesh 300-400).

UV/vis and fluorescence experiments

A stock solution of 1.0 mM **DR3** was prepared in acetonitrile. $Cu(NO_3)_2{\cdot}3H_2O$ was dissolved in doubly distilled water to form a 5.0 mM stock solution. For competing metal ions, various metal ions solutions of $NaNO_3$, $Co(NO_3)_2$, KNO_3, $Zn(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $MnCl_2{\cdot}4H_2O$, $Pb(NO_3)_2$, $HgCl_2$, $AgNO_3$, $Ba(NO_3)_2$ were used. Before fluorescence and UV/vis titration investigation was conducted, the stock solution of **DR3** was mixed with the stock solutions of metal salts in a 10 ml volumetric flask and diluted with H_2O and CH_3CN to volume. Spectral data were recorded at 2 min after the addition. For fluorescence measurements, excitation was provided at 530 nm, and emission was collected from 546 to 700 nm. The wide pH was adjusted by HCl or NaOH solutions.

Electrochemical test

Electrochemical characteristics was tested according to a literature.[23] All measurements for DPV were carried out in a one-compartment cell under N_2 gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and a silver reference electrode. All measurements for CV were carried out in a one-compartment cell under N_2 gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode reference electrode. The supported electrolyte was a 0.10 mol/L CH_3CN solution of tetrabutyl ammonium hexafluorophosphate (Bu_4NPF_6). The scan rate was 100 mV/s.

Synthesis of compound DR1

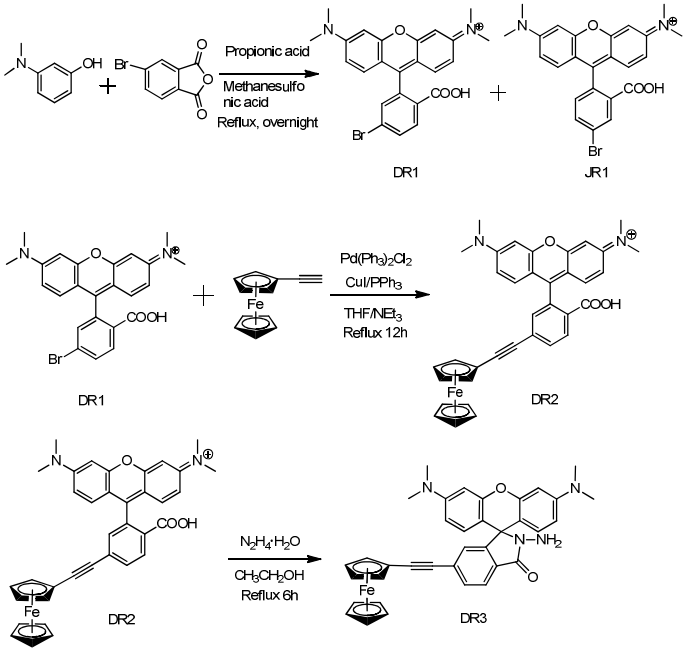
Compound **DR1** was synthesized according to a literature.[9] **JR1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, J = 8.1 Hz, 1H, Ar-H), 7.70 (dd, J = 8.1, 1.6 Hz, 1H, Ar-H), 7.32 (d, J = 1.5 Hz, 1H, Ar-H), 6.66 – 6.57 (m, 2H, Ar-H), 6.48 (d, J = 2.5 Hz, 2H, Ar-H), 6.41 (dd, J = 8.8, 2.6 Hz, 2H, Ar-H), 2.99 (s, 12H, -CH_3); **DR1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12 (d, J = 1.7 Hz, 1H, Ar-H), 7.83 – 7.66 (m, 1H, Ar-H), 7.05 (t, J = 8.8 Hz, 1H, Ar-H), 6.67 – 6.55 (m, 2H, Ar-H), 6.48 (d, J = 2.5 Hz, 2H, Ar-H), 6.41 (dd, J = 8.9, 2.6 Hz, 2H, Ar-H), 2.99 (s, 12H, -CH_3).

Synthesis of compound DR2

Compound **DR2** was synthesized according to a literature with some modification.[9] A mixture of **DR1** (0.5 mmol, 233 mg), ethynylferrocene (0.5 mmol, 157 mg), 35 mg (0.05 mmol) of $PdCl_2(PPh_3)_2$, and PPh_3 (26 mg, 0.1 mmol), 4.8 mg (0.025 mmol) of CuI, THF (20 mL), NEt_3 (5 mL) under nitrogen, upon the temperature reached 95 ºC and refluxed 12 h after completion of the reaction by TLC, evaporated the solvent, the crude product was purified by column chromatography with CH_2Cl_2/NEt_3 (v/v = 200/4) and afforded the target product **DR2** as a purplish red (247 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08 (d, J = 0.7 Hz, 1H, Ar-H), 7.75 – 7.66 (m, 1H, Ar-H), 7.13 (d, J = 7.9 Hz, 1H, Ar-H), 6.63 (d, J = 8.8 Hz, 2H, Ar-H), 6.48 (d, J = 2.5 Hz, 2H), 6.40 (dd, J = 8.9, 2.6 Hz, 2H, Ar-H), 4.55 (t, J = 1.8 Hz, 2H, ferrocene-H), 4.30 – 4.28 (m, 2H, ferrocene-H), 4.27 (d, J = 4.5 Hz, 5H, ferrocene-H), 2.99 (s, 12H, -CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 169.19, 152.91, 152.09, 151.91, 137.38, 128.75, 127.93, 127.34, 125.55, 124.08, 108.66, 106.40, 98.53, 90.75, 84.31, 71.62, 70.08, 69.19, 64.30, 46.15, 40.26. ESI-MS m/z 595.2 $[M]^+$.

Synthesis of compound DR3.

A solution of **DR2** (0.25 mmol, 160 mg), excess 98% $N_2H_4{\cdot}H_2O$ (1 mL) was resolved in 10 mL of ethanol and refluxed 6 h, evaporated the solvent the crude product was purified by column chromatography with EtOAc/PE (v/v = 3/2) get the desired product **DR3** (110 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (s, 1H, Ar-H), 7.55 (dd, J = 7.9, 1.4 Hz, 1H, Ar-H), 7.03 (d, J = 7.9 Hz, 1H, Ar-H), 6.52 (d, J = 8.8 Hz, 2H, Ar-H), 6.48 (d, J = 2.3 Hz, 2H, Ar-H), 6.39 – 6.36 (m, 2H, Ar-H), 4.52 (t, J = 1.7 Hz, 2H, ferrocene-H), 4.26 (s, 2H, ferrocene-H), 4.25 (s, 5H, ferrocene-H), 3.63 (s, 2H, -NH_2), 2.97 (s, 12H, -CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): 165.56, 153.48, 151.55, 150.33, 135.50, 130.21, 127.94, 125.94, 124.30, 123.79, 108.81, 105.22, 99.01, 89.69, 84.90, 71.55, 70.05, 69.35, 69.03, 65.89, 40.31. ESI-MS m/z 609.2 $[M + H]^+$.



Scheme 2. Synthesis of **DR3**

Results and discussion

DR3 was prepared based on a two steps route shown in Scheme 2. Firstly, compound **DR2** was achieved in 83% yield by a Sonogashira reaction in catalyst of $PdCl_2(PPh_3)_2$, PPh_3, and CuI. Then compound **DR2** reacts with hydrazine hydrate to obtain **DR3** in 73% yield by 6 h refluxing. These compounds were characterized and confirmed by ^{1}H NMR, ^{13}C NMR, ESI-MS (ESI, Fig. S1-6).

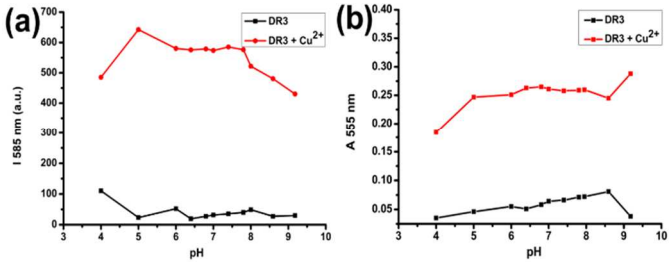


Fig. 1. (a) The fluorescence response of **DR3** (10 μm) at 585 nm before and after addition of 10 equiv Cu^{2+} with different pH condition. (b) The absorbance response of **DR3** (10 μm) at 555 nm before and after addition of 10 equiv Cu^{2+} with different pH condition.

As shown in Fig. 1a, the influence of pH on the fluorescence of **DR3** was investigated first. Under acidic conditions (pH < 5), ring opening of rhodamine occurred due to the protonation of chemosensor.[25] When the pH ranged from 5.0 to 9.0, no obvious characteristic fluorescence emission of rhodamine was observed. However, the addition of Cu^{2+} led to the fluorescence enhancement over a comparatively range (5.0-9.0), which is attributed to the ring-opening process of rhodamine and hydrosis. Multichannel Chemosensor **DR3** and **DR3**-Cu^{2+} remained unaffected in fluorescence intensity in the pH 6.0-8.0, suggesting that it was insensitive to pH around 7.0 and could be suitable for physiological conditions. This result was also same to the UV/vis spectra in range of pH 5-9, as illustrated in Fig.1b.

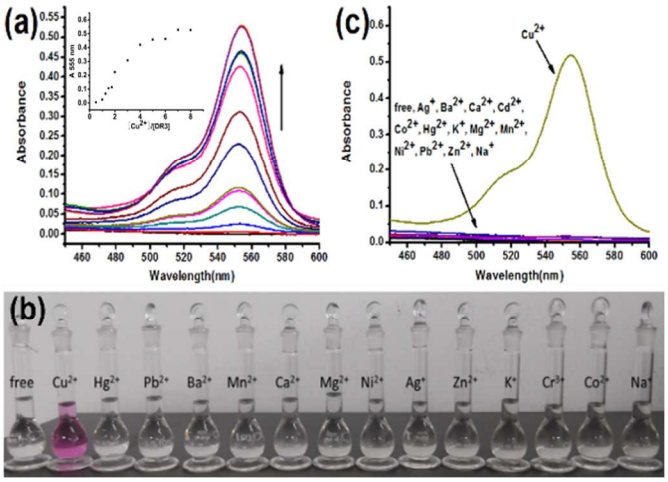


Fig. 2 (a) Absorption spectra of **DR3** (10 μM) in HEPES/CH_3CN (2:8, v/v, pH 7.0) solutions upon addition of increasing concentrations of 0-8 equiv $Cu(NO_3)_2{\cdot}3H_2O$. Insets: the absorbance at 555 nm as a function of Cu^{2+} concentrations. (b) Color changes upon adding different cations in HEPES/CH_3CN (2:8, v/v, pH 7.0) solutions. From left to right: free, Cu^{2+}, Hg^{2+}, Pb^{2+}, Ba^{2+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Ag^{+}, Zn^{2+}, K^{+}, Cr^{3+}, Co^{2+}, Na^{+}. (c) Absorption spectra of **DR3** in HEPES/CH_3CN (2:8, v/v, pH 7.0) solutions with 8 equiv of metal ions: free, Cu^{2+}, Hg^{2+}, Pb^{2+}, Ba^{2+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Ag^{+}, Zn^{2+}, K^{+}, Cr^{3+}, Co^{2+}, Na^{+}.

The UV/Vis spectrum of **DR3** in a solvent system of CH_3CN/HEPES 80:20 with titration of Cu^{2+} was shown in Fig. 2a. It exhibits almost no absorption in the visible wavelength range, indicating that chemosensor **DR3** is predominantly in the form of spirolactam. Upon addition of Cu^{2+}, a new absorption peak at 555 nm was observed, and the intensity gradually increased with increasing Cu^{2+} ion concentration. This could be attributed to the formation of ring-opened amide form of **DR3** upon interaction with Cu^{2+}. The inset in Fig. 2a showed the absorbance at 555 nm as a function of Cu^{2+} concentrations. The ring-opening mechanism was also confirmed by the color change of 10 μM **DR3** upon adding different cations (Fig. 2b). Among the metal ions, only Cu^{2+} can induce an obvious color change from colorless to pink in the solution of **DR3**, allowing colorimetric detection of Cu^{2+} by the naked eye. Fig. 2c shows the absorption response of **DR3** towards various metal ions in HEPES/CH_3CN (2:8, v/v, pH 7.0) solutions. Under identical condition, **DR3** exhibits almost no absorbance enhancement at around 555 nm on addition of Hg^{2+}, Pb^{2+}, Ba^{2+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Ag^{+}, Zn^{2+}, K^{+}, Cr^{3+}, Co^{2+}, Na^{+}, free. These results indicate that chemosensor **DR3** has the high selectivity towards Cu^{2+}.

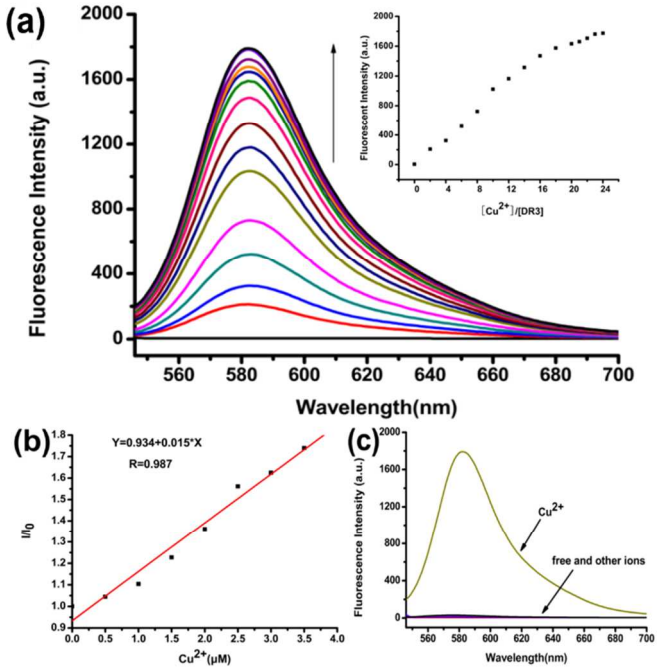


Fig. 3 (a) Fluorescence spectra of **DR3** in HEPES/CH_3CN (2:8, v/v, pH 7.0) solutions upon addition of increasing concentrations of 0-24 equiv Cu^{2+}. Inset: fluorescence intensity at 585 nm as a function of Hg^{2+} concentrations. (b) Fluorescence intensity at 585nm of **DR3** (10 μM) in HEPES/CH_3CN (2:8, v/v, pH 7.0) solutions as a function of Cu^{2+} concentration (0-3.5 μM). (c) Fluorescence intensity of **DR3** (10 μm) in HEPES/CH_3CN (2:8, v/v, pH 7.0) solutions upon addition of 24 equiv metal ions (blank, Cu^{2+}, Hg^{2+}, Pb^{2+}, Ba^{2+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Ag^{+}, Zn^{2+}, K^{+}, Cr^{3+}, Co^{2+}, Na^{+}).

Fig. 3a shows the fluorescence spectra of **DR3** in HEPES/CH_3CN (2:8, v/v, pH 7.0) solutions with the addition of Cu^{2+}. Chemosensor **DR3** shows a very weak emission at around 585 nm upon excitation at 530 nm. When Cu^{2+} was added to the **DR3** buffer solution, fluorescence intensity at 585 nm was observed, attributed to the ring-opening process of rhodamine derivatives. The solution showed an approximately 274-fold enhancement in the fluorescence intensity. This fact means that DR3 could be acted as an off-on luminescence chemosensor for Cu^{2+}. The fluorescence intensity finally levelled off until the amount of added Cu^{2+} was 2.2 × 10^{-4} M (Fig. 3a inset). As an excellent luminescence chemosensor, it is important to have high selectivity. As illustrated in Fig. 3c,

additions of other metal ions including Hg^{2+}, Pb^{2+}, Ba^{2+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, Ni^{2+}, Ag^{+}, Zn^{2+}, K^{+}, Cr^{3+}, Co^{2+}, Na^{+} and free induced no obvious fluorescence enhancement under the same condition. These observations indicated that chemosensor **DR3** could selectively recognize Cu^{2+} in HEPES/CH_3CN (2:8, v/v, pH 7.0) solutions. For practical application the detection limit was also calculated as 6.85×10^{-6} M for Cu^{2+} (3σ/slope), which is sufficiently low for the detection of many chemical systems for Cu^{2+} (Fig. 3b).[26]

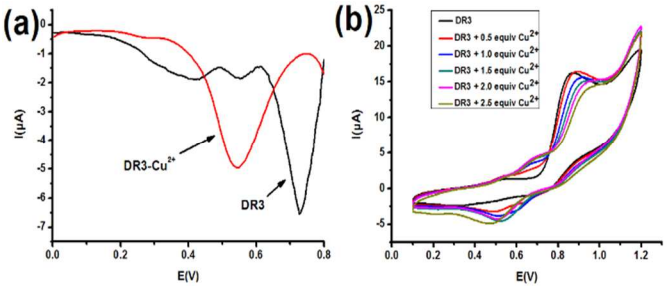


Fig. 4 (a) DPV of **DR3** (100 μM) in CH_3CN solution in the absence and presence of 1.6 equiv of Cu^{2+} with *n*-Bu_4NPF_6 as supporting electrolyte. (b) CV of **DR3** (100 μM) in CH_3CN solution in the absence and presence of Cu^{2+} with *n*-Bu_4NPF_6 as supporting electrolyte.

As designed, **DR3** shows an evident change in its reversible ferrocene/ferricinium redox cycles upon complexation. Differential pulse voltammetry (DPV) curves of **DR3** were recorded in CH_3CN solution containing 0.1 M *n*-tetrabutylammonium hexafluorophosphate (*n*-Bu_4NPF_6) as supporting electrolyte in the absence and presence of Cu^{2+}.[23a] As shown in Fig. 4a, a significant displacement was observed upon addition of Cu^{2+}. The oxidation peak was shifted in CH_3CN from 0.728 to 0.54V ($\Delta E_{1/2}$ = 188 mV). For cyclic voltammetry (CV), a significant shift of the redox potential of the ferrocenyl group was also observed (Fig. 4b). The CV behavior of chemosensor **DR3** was measured in CH_3CN, suggesting a reversible one-electron redox process. The addition of Cu^{2+} induces a positive shift of the ferrocene/ferricinium couple, which is attributed to the redox process of Cu^{2+}. This fact indicated that DR3 could be a multi-signal chemosensor for Cu^{2+} with electrochemical measurements.

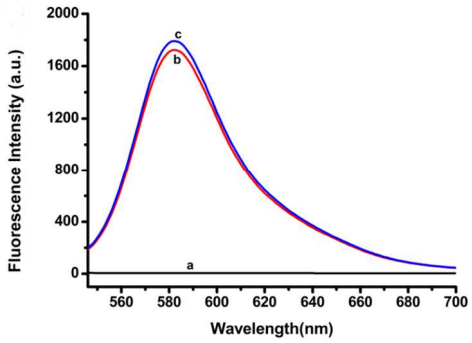
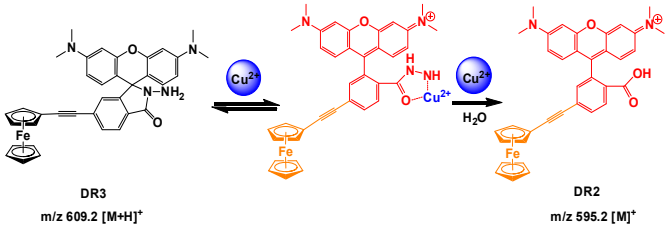


Fig. 5 Fluorescence spectra in HEPES/CH_3CN (2:8, v/v, pH 7.0) solutions: (a) **DR3** (10 μM); (b) **DR3** (10 μM) with Cu^{2+} (240 μM); (c) **DR3** (10 μM) with Cu^{2+} (240 μM) and then addition of EDTA (500 μM).

In order to explore mechanism, the reaction product of **DR3** and Cu^{2+} was detected by ESI spectra analyses (ESI, Fig. S7). The ion peak was detected at m/z 609.2, which was corresponding to [**DR3** + H]$^+$. In addition, the main ion peak at m/z 595.2 corresponding to intermediate **DR2** was detected after the addition of Cu^{2+} to **DR3** aqueous solution, which suggested that Cu^{2+} induces the hydrolysis and spirolactam ring-opening of rhodamine. To further confirm Cu^{2+} mediated hydrolysis, we have carried out the chemical reversibility experiment in the CH_3CN-water solution. Upon addition of 500 μM chelating agent EDTA to the **DR3**-Cu^{2+} complex in HEPES/CH_3CN (2:8, v/v, pH 7.0) solutions, the color and fluorescence intensity discovered no obvious changes (Fig. 5). These findings indicated that **DR3** is an irreversible luminescence chemosensors for Cu^{2+}. According to the obtained results, we proposed that the reaction process may proceed as the route depicted in Scheme 3.



Scheme 3 The proposed reaction mechanism of **DR3** with Cu^{2+}.

Conclusions

In summary, we have designed a multichannel chemosensor **DR3** for Cu^{2+} with the chromatic, fluorescent rhodamine derivatives and the electrochemical characterization of a ferrocenyl group. The novel chemosensor exhibits the multi-responsive colorimetric, fluorescent and electrochemical detection for Cu^{2+}. Multichannel chemosensor **DR3** could detect micromole level of Cu^{2+} and in a wide pH range (5.0-9.0). Above these results, we believe that **DR3** could be further used for monitoring intracellular Cu^{2+} ions in biological systems.

Acknowledgements

The authors are grateful for the financial support from the open fund of the State Key Laboratory of Materials-Oriented Chemical Engineering (KL13-07), the China Postdoctoral Science Foundation (2014M550287), Specialized Research Fund for the Doctoral Program of Higher Education (20123221110012), Jiangsu Planned Projects for Postdoctoral Research Funds, and State Key Laboratory of Coordination Chemistry of Nanjing University.

References

1 Y. Yang, Q. Zhao, W. Feng and F. Y. Li, *Chem. Rev.*, 2013, **113**, 192.
2 H. Tapiero, D. M. Townsend and K. D. Tew, *Biomed. Pharmacother.*, 2003, **57**, 386.
3 D. J. Waggoner, T. B. Bartnikas and J. D. Gitlin, *Neurobiol. Dis.*, 1999, **6**, 221.
4 C. Vulpe, B. Levinson, S. Whitney, S. Packman and J. Gitschier, *Nat. Genet.*, 1993, **3**, 7.
5 K. J. Barnham, C. L. Masters and A. I. Bush, *Nat. Rev. Drug. Discov.*, 2004, **3**, 205.
6 C. W. Yu, W. Ting, K. Xu, J. Zhao, M. H. Li, S. X. Weng and J. Zhang, *Dyes Pigm.*, 2013, **96**, 38.
7 A. F. Liu, L. Yang, Z. Y. Zhang, Z. L. Zhang and D. M. Xu, *Dyes Pigm.*, 2013, **99**, 472.

8 S. L. Hu, S. S. Zhang, Y. Hu, Q. Tao and A. X. Wu, *Dyes Pigm.*, 2013, **96**, 509.
9 J. L. Fan, P. Zhan, M. M. Hu, W. Sun, J. Z. Tang, J. Y. Wang, S. G. Sun, F. L. Song and X. J. Peng, *Org. Lett.*, 2013, **15**, 492.
10 M. Kumar, N. Kumar, V. Bhalla, P. R. Sharma and T. Kaur, *Org. Lett.*, 2012, **14**, 406.
11 Z. Q. Hua, X. M. Wang, Y. C. Feng, L. Ding and H. Y. Lu, *Dyes Pigm.*, 2011, **88**, 257.
12 J. L. Liu, C. Y. Li and F. Y. Li, *J. Mater. Chem.*, 2011, **21**, 7175.
13 P. H. Xie, F. Q. Guo, D. Li, X. Y. Liu and L. Liu, *J. Lumin.*, 2011, **131**, 104.
14 D. P. Wang, Y. Shiraishi and T. Hirai, *Chem. Commun.*, 2011, **47**, 2673.
15 W. Y. Liu, H. Y. Li, B. X. Zhao and J. Y. Miao, *Org. Biomol. Chem.*, 2011, **9**, 4802.
16 C. W. Yu, J. Zhang, R. Wang and L. G. Chen, *Org. Biomol. Chem.*, 2010, **8**, 5277.
17 V. Dujols, F. Ford and A. W. Czarnik, *J. Am. Chem. Soc.*, 1997, **119**, 7386.
18 J. T. Yeh, W. C. Chen, S. R. Liu and S. P. Wu, *New J. Chem.*, 2014, **38**, 4434.
19 X. M. Wu, Z. Q. Guo, Y. Z. Wu, S. Q. Zhu, T. D. James and W. H. Zhu, *ACS Appl. Mater. Interfaces*, 2013, **5**, 12215.
20 A. K. Asatkar, S. P. Senanayak, A. Bedi, S. Panda, K. S. Narayan and S. S. Zade, *Chem. Commun.*, 2014, **50**, 7036.
21 (a) A. P. D. Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, T. J. M. Huxley, C. P. Mccoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515; (b) W. H. Zhu, L. W. Song, Y. H. Yang and H. Tian, *Chem. Eur. J.*, 2012, **18**, 13388; (c) M. Li, Z. Q. Guo, W. H. Zhu, F. Marken and T. D. James, *Chem. Commum.*, **51**, 1293.
22 (a) B. C. Zhu, C. C. Gao, Y. Z. Zhao, C. Y. Liu, Y. M. Li, Q. Wei, Z. M. Ma, B. Du and X. L. Zhang, *Chem. Commun.*, 2011, **47**, 8656; (b) F. Zapata, A. Caballero, A. Espinosa, A. Tarraga and P. Molina, *Org. Lett.*, 2007, **9**, 2385.
23 (a) K. W. Huang, H. Yang, Z. G. Zhou, M. X. Yu, F. Y. Li, X. Gao, T. Yi and C. H. Huang, *Org. Lett.*, 2008, **10**, 2557; (b) X. Q. Chen, S. W. Nam, M. J. Jou, Y. M. Kim, S. J. Kim, S. S. Park and J. Y. Yoon, *Org. Lett.*, 2008, **10**, 5235; (c) H. Yang, Z. G. Zhou, K. W. Huang, M. X. Yu, F. Y. Li, T. Yi and C. H. Huang. *Org. Lett.*, 2007, **9**, 4729.
24 Y. S. Mi, Z. Cao, Y. T. Chen, Q. F. Xie, Y. Y. Xu, Y. F. Luo, J. J. Shi and J. N. Xiang, *Analyst*, 2013, **138**, 5274.
25 Y. Xiang and A. J. Tong, *Org. Lett.*, 2006, **8**, 1549.
26 D. N. Beatrice, M. Jerome, L. Dominique and F. F. Suzanne, *Inorg. Chem.*, 2006, **45**, 5691.