RSC Advances

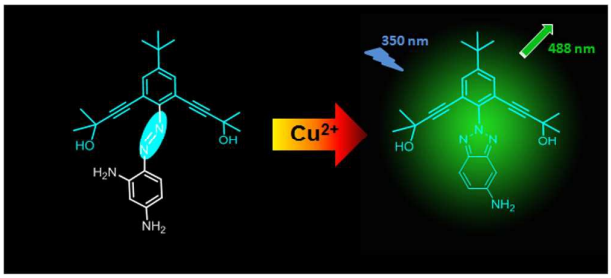
ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Development and cell imaging applications of a novel fluorescent probe for Cu^{2+}

Yuehua Yuan, Maozhong Tian,* Junling Wang, Hai Xie, Jun Qin, Feng Feng*

College of Chemistry and Chemistry Engineering, Shanxi Datong University, Datong 037009, People's Republic of China



A reactivity-based fluorescent probe was utilized to selectively detecting Cu^{2+} in aqueous solution and living cell.

Journal Name

ARTICLE

Development and cell imaging applications of a novel fluorescent probe for Cu^{2+}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Yue-Hua Yuan, Mao-Zhong Tian, * Jun-Ling Wang, Hai Xie, Jun Qin, Feng Feng*

A reactivity-based fluorescent probe **1** for Cu^{2+} was synthesized. The structure of this probe was characterized by infrared spectroscopy (IR), mass spectrometry (MS), X-ray crystallography, and ^{1}H NMR and ^{13}C NMR spectroscopy. Its photophysical as well as binding properties towards various metal ions were studied. Probe **1** showed highly sensitive and selective "Off-On" fluorescence changes with Cu^{2+} among various metal ions when excited at 350 nm. These selective changes were attributed to an oxidative cyclization reaction transforming nonemissive azoanilines into highly fluorescent benzotriazoles. Furthermore, fluorescence imaging experiments of Cu^{2+} ions in living cells demonstrated its value of practical applications in biological systems.

Introduction

The design and synthesis of mulitifunctionalized organic molecules with controlled properties on the molecular level remains a critical important target of chemistry, materials science and biology.[1-3] The development of fluorescent probes for various metal ions has received considerable attention due to their biological and environment important roles.[4] Among the various metal ions, copper ion has attracted a great deal of attention ascribing to its biological significance as a catalytic cofactor for a variety of metalloenzymes, including superoxide dismutase, cytochrome coxidase, and tyrosinase. However, under overloading conditions, copper ions exhibit toxicity in that it causes neurodegenerative diseases (e.g., Alzheimer's and Wilson's diseases) probably by its involvement in the production of reactive oxygen species.[5-9] Therefore, developing various techniques to monitor the concentration of Cu^{2+} in environmental water samples and visualize its cellular distribution in physiological processes has great significance for environment protection and human health.

Unlike other analytical techniques,[10-12] fluorescent probes for the determination of Cu^{2+} have had great popularity owing to the apparent advantages: sensitivity, specificity, simplicity, low cost, and rapid tracking of analytes in biological and environmental samples.[13-26] Nevertheless, the studies on fluorescent probes for detecting Cu^{2+} in aqueous solution have been so far scarce. On the one hand, the paramagnetic nature of Cu^{2+} always leads to an unavoidable fluorescence quenching effect;[27] on the other hand, due to the strong hydration ability of Cu^{2+} in water, high content of organic components are necessary for most fluorescent probes to exhibit satisfying analytical performances. Thus, the developing of novel "turn-on" fluorescent Cu^{2+} probes in aqueous solution is still a challenge. One alternative strategy of detecting Cu^{2+} is attributed to irreversible chemical reactions promoted by Cu^{2+}. In most cases, nonemissive probe molecules are converted to the emissive ones. Some probes for Cu^{2+} have been reported based on irreversible chemical reactions.[28-36] Many of these probes, however, suffer from some drawbacks: (1) they could not act in pure aqueous solvent; (2) they require specific reaction conditions such as acidic or basic pH media; and (3) they show cross-sensitivity toward other metal cations.

The azo derivative **1** has been designed and utilized to direct detection of Hg^{2+} in aqueous solution and living cells.[37] This study follows this mechanism whereby the detection of Hg^{2+} ion was based on the chelation enhanced fluorescence (chemosensor, λ_{ex}=430 nm); however, the recognition of Cu^{2+} ion was based on the irreversible chemical reactions promoted by Cu^{2+} (chemodosimeter, λ_{ex}=350 nm). To the best of our knowledge, incorporating both a chemosensor and a chemodosimeter onto this single molecular system for Hg^{2+} and Cu^{2+} ions has never been reported. The large fluorescence enhancement can be attributed to a rapid cyclization reaction triggered by Cu^{2+} ion in water. The fluorescence enhancement was so efficient that a large blue shift of 37 nm is observed for Cu^{2+} only. Furthermore, this probe was successfully applied to image Cu^{2+} in living cells. Lee and coworkers reported the analogous fluorescent probe for Cu^{2+}.[38]

Experimental section

Apparatus and materials

College of Chemistry and Environmental Engineering, Shanxi Datong University, Datong 037009, P. R. China. E-mail: tmzhong2002@163.com; feng-feng64@263.net; Fax: +86 352 6100028; Tel: +86 352 6100028

Electronic Supplementary Information (ESI) available: ^{1}H, ^{13}C NMR, IR, MS, UV-Vis and fluorescence spectra. CCDC-961622 (probe **1**). For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x

All the materials were obtained from commercial suppliers and were used without further purification. The solutions of metal ions were prepared from their nitrate salts except for $Hg(ClO_4)_2 \cdot 3H_2O$. Flash chromatography was carried out on silica gel SG1105 (200-300 mesh; Qingdao Makall). ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 400 MHz and 100 MHz, respectively. Chemical shifts (δ) were expressed in ppm relative to TMS and coupling constants (J) are in Hz. Matrix-assisted laser desorption/ionization reflectron time-of-flight (MALDI-TOF) mass spectrometry was performed with a BrukerBiflex III mass spectrometer. Elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer. Fluorescence excitation and emission spectra were recorded by using a JASCO FP6600 spectrophotometer in a quartzcell. UV−vis absorption spectra were measured on a JASCO V-579 spectrophotometer in a quartz cell. The cells were imaged by fluorescence microscopy (Olympus 1X71). The crystal data collection of **1** was performed on a CrysAlisPro diffractometer.

Synthesis of probe 1

To a stirred MeOH solution (5 mL) of 2,6-Bis(3-methyl-3-hydroxyl-1-butynyl)-4-*tert*-butylaniline (0.313 g, 1mmol) was added slowly conc. HCl (2.5 mL). The reaction mixture was kept at 0 °. An aqueous solution (1 mL) of $NaNO_2$ (75.9mg, 1.1 mmol) was added dropwise to generate the azonium intermediate, and the reaction mixture was stirred for 10 min. A solution of m-phenylenediamine (0.130 g, 1.2 mmol) and sodium hydroxide (0.150 g) in MeOH−H_2O (2:1, v/v; 9 mL) was kept at 0 °C. With stirring, the azonium intermediate was added dropwise to the m-phenylenediamine solution while maintaining the temperature of the reaction at 0 °C. After stirring for 30 min, water (50 mL) was added to induce precipitation of a red solid, which was isolated by filtration and washed thoroughly with water**,** and dried. Flash column chromatography on SiO_2 (hexane: EtOAc = 2:1, v/v) furnished compound **1** (391.5 mg, 0.906 mmol, yield = 91%).^{1}H NMR (400 MHz, DMSO-d_6, 298 K): δ 7.40, 7.38 (d, J = 8.8 Hz, 1H), 7.35 (s, 2H), 5.99 (m, 3H), 5.86 (d, J = 2.0 Hz, 1H), 5.34 (s, 2H), 1.41 (s, 12H), 1.28 (s, 9H).^{13}C NMR (100 MHz, CD_3OD, 298 K) δ 154.88, 154.73, 150.31, 147.21, 133.93, 132.11, 131.84, 117.08, 107.40, 99.10, 98.42, 81.47, 66.16, 35.34, 31.86, 31.58. FT-IR (thin film on KCl, cm^{-1}):3548, 3465, 3368, 2970, 2935, 2869, 1630, 1584, 1546, 1502, 1476, 1448, 1400, 1374, 1329, 1280, 1250, 1185, 1158, 1141, 945, 886, 820, 652, 579, 567, 452. MALDI-TOF Calcd for $C_{26}H_{32}N_4O_2$ $[M+H^+]^+$ 433.25; Found 433.17. Anal. Calcd for $C_{26}H_{32}N_4O_2$: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.27; H, 7.46; N, 12.99.

General methods for absorption and fluorescence studies

All spectroscopic measurements were performed in HEPES buffer solution (5.0×10^{-2} mol L^{-1}, pH = 7.4). Stock solutions (5.0×10^{-2} mol L^{-1}) of metal ions (metal nitrate, perchlorate for Hg^{2+}) were prepared in two-distilled water. The stock solution (1.0×10^{-2} mol L^{-1}) of probe **1** was prepared in DMSO. In titration experiments, each time a 3×10^{-3} L aqueous solution of **1** (1.0×10^{-2} mol L^{-1}) was filled in a quartz optical cell of 1 cm optical path length. Then various amount of Cu^{2+} stock solution was added into the quartz optical cell gradually by using a micro-pippet. Spectral data were recorded at 30 min after the addition. In selectivity experiment, the test samples were prepared by placing appropriate amounts of metal ion stock solution into 3×10^{-3} L aqueous solution of **1** (1.0×10^{-2} mol L^{-1}). For all measurements, excitation wavelength was at 350 nm, excitation and emission slit widths were 3 nm and 6 nm, respectively.

Determination of fluorescence quantum yields

The fluorescence efficiency of the probe was estimated by measuring their fluorescence quantum yield using Equation (1) on the basis of the absorption and fluorescence spectra taken in the solvent. Coumarin 30 (Φ = 0.67 in MeCN solution, λ_{exc}=380 nm) was used as a standard.[39] The sample absorbance was maintained < 0.1 to minimize internal absorption. Corrections were made to account for the differences in solvent refractive indexes.

$$\Phi_{sample} = \Phi_{st} \frac{S_u}{S_{st}} \frac{\lambda_{st}}{\lambda_u} \frac{n_{Du}^2}{n_{Dst}^2} \quad (1)$$

Where Φ_{st} the emission quantum yield of the standard, λ_{st} and λ_u represent the absorbance of the standard and sample at the excited wavelength, respectively, while S_{st} and S_u are the integrated emission band areas of the standard and sample, respectively, and n_{Dst} and n_{Du} are the solvent refractive index of the standard and sample, u and s refer the unknown and standard, respectively.

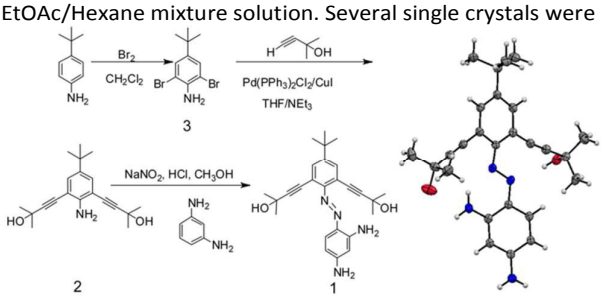
Cell lines and Cell Culture

HT-29 cell lines was purchased from cell culture center of Institute of Basic Medical Sciences, CAMS and cultured in Dulbecco's Modified Eagle's Medium , High Glucose (DMEM)/Ham's F12 (vol/vol=1:1) supplemented with 5% fetal calf serum. HT-29 cells were routinely cultured in DMEM (high glucose)/Ham's F12 medium containing 10% serum and harvested for subculture using trypsin (0.05%, Gibco/Invitrogen) and grown in a humidified atmosphere containing 5% CO_2 and 95% air at 37℃. Before experiment, the cells were pre-cultured.

Results and discussion

As shown in **Scheme 1**, 2,6-dibromo-4-(*tert*-butyl)aniline **3** was prepared by the treatment of p-*tert*-butylaniline with bromine following the reported procedures.[37] Compound **3** was then reacted with 2-methylbut-3-yn-2-ol under Sonogashira conditions to give 2,6-Bis(3-methyl-3- hydroxyl-1-butynyl)-4-*tert*-butylaniline **2**. Efficient azo coupling reaction between **2** and m-phenylenediamine afforded probe **1** in high yield. The structure of **1** was fully characterized by IR, ^{1}H NMR, ^{13}C NMR, MALDI-TOF mass spectroscopy and X-ray crystallography (see

supporting information). A single crystal of **1** was grown in EtOAc/Hexane mixture solution. Several single crystals were



Scheme 1 Synthesis of **1** (right, crystal structure of **1**).

obtained by the solvent partially evaporated and subjected to crystallographic structure analysis. X-ray crystallography investigation confirmed that the two benzene rings are twisted by a dihedral angle of 21.41°.

To obtain insight into the fluorescent properties of probe **1** toward metal ions as well as anions, fluorescence emission changes were studied for different metal ions (Fig. 1) and anions (Fig. S1), such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cd^{2+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Ag^+, Pb^{2+}, Zn^{2+}, Fe^{3+}, Hg^{2+}, Cu^{2+}, ClO_4^-, CO_3^{2-}, SO_4^{2-}, F^-, Cl^-, Br^-, $H_2PO_4^-$, $P_2O_7^{4-}$, Ac^- in 100% aqueous solution. With an excitation wavelength at 350 nm, probe **1** (10 μM) showed a very weak emission peak at 525 nm, and the addition of Cu^{2+} or Hg^{2+} induced the fluorescence enhancement of **1**, whereas no obvious variations were observed upon the addition of the above-mentioned other metal ions and anions. Only the addition of Cu^{2+} to the solution of **1** resulted in a clear hypsochromic shift of the fluorescence maximum of about 37 nm from 525 to 488 nm. Moreover, in the presence of miscellaneous competitive cations, the emission spectra of **1** displayed a similar pattern at near 488 nm to that with Cu^{2+} ions only, whereas Hg^{2+} prominently enhanced the fluorescence. Reversely, upon the addition of Fe^{3+} ions to the mixture of **1** and Cu^{2+} ions, the emission band at 488 nm was partly decreased (Fig. S2). These results clearly indicated that the probe **1** was highly specific for Cu^{2+} ions over other competitive cations in aqueous medium.

As shown in Fig. S3, free **1** exhibited an absorption band centered at 436 nm. When titrated by Cu^{2+} (0–30 μM), this band was gradually increased, and then decreased slightly and a new peak at 466 nm appeared simultaneously (red shift),

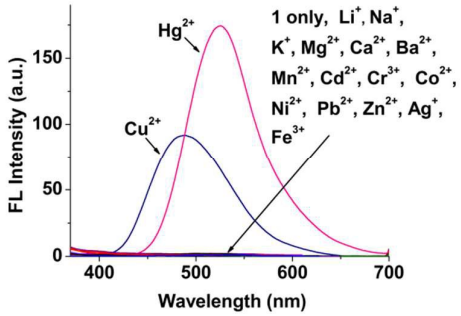


Fig.1 Fluorescent emission spectra of **1** (10 μM) upon addition of different metal ions (5.0 equivalents) in HEPES buffer (50 mM, containing 0.1M KNO_3, pH=7.4) solution. λ_{ex}=350 nm.

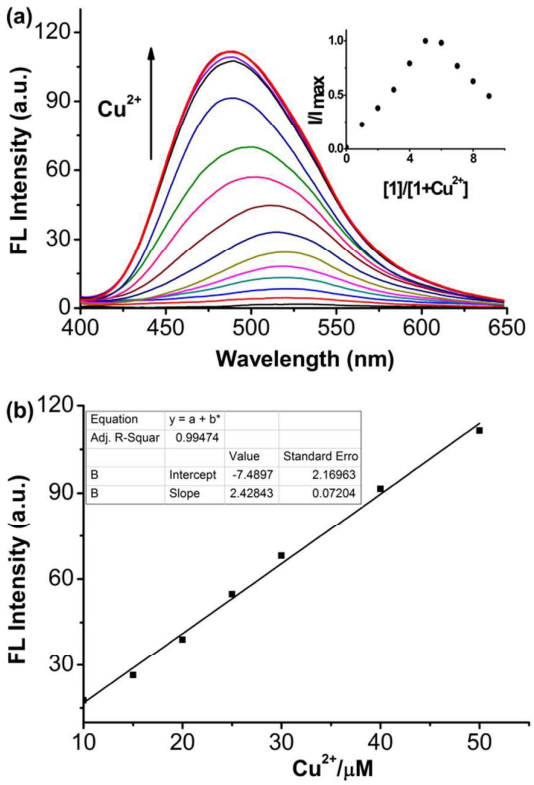
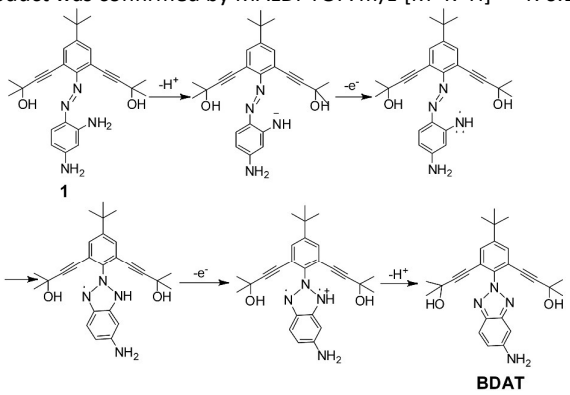


Fig. 2 (a) Emission spectra of **1** (10 μM) in the presence of Cu^{2+} (0, 3, 5, 7, 10, 15, 20, 25, 30, 40, 50, 60, 80, 100, 120 μM). Inset: Job's plot of **1**. (b) A plot of fluorescence intensity at λ_{em}=488 nm of **1** (10 μM) *vs* concentration of Cu^{2+} in HEPES (50 mM) solution (0.1 M KNO_3, pH = 7.4). λ_{ex}=350 nm. Excitation and emission slit widths were 3 and 6 nm, respectively.

indicating new species formed. The fluorescence titration of **1** toward Cu^{2+} was shown in Fig. 2a. Probe **1** showed a weak band with emission maxima at 525 nm upon excitation at 350 nm (Φ = 0.008). However, large fluorescent enhancements (131 fold, Φ = 0.313) were observed upon addition of Cu^{2+} to the solution of **1**. Notably, Cu^{2+} induced a blue-shift in the emission of **1** to 488 nm, while Hg^{2+} hardly caused shift in the emission of **1**. This difference in response allows **1** to easily distinguish between Cu^{2+} and Hg^{2+} in aqueous solution. A plot of $I_{488\ nm}$ vs Cu^{2+} concentration (Fig.2b) shows an excellent linear relationship (linearly dependent coefficient: R^2 = 0.9947) down to the value of [Cu^{2+}] = 10 μM, which is comparable to the U.S. Environmental Protection Agency (EPA) guideline of 1.3 ppm (= 21μM) Cu^{2+} in drinking water. A Job's plot indicates that the 1:1 stoichiometry of a binding event between **1** and Cu^{2+} (inset of Fig. 2a).

The binding interaction of **1** with Cu^{2+} was investigated. **1** is a nonfluorescent compound. Upon the addition of Cu^{2+}, a bright fluorescence developed simutaneously. The above resulting solution was subsequently treated with excess EDTA, and the strong fluorescence of the **1**-Cu^{2+} was almost not affected upon addition of EDTA to the mixture of **1** and Cu^{2+}

ions, indicating that the interaction of 1 with Cu^{2+} is chemically irreversible. The formation of a new compound **BDAT** as product was confirmed by MALDI-TOF: *m/z* $[M+K+H]^{2+}$=470.1



Scheme 2 Oxidative Cyclization of **1**[a]

[a] For clarity, coordination of Cu^{2+} ions to the amino/azo N-donor is not shown. Alternative sequences of electron- and proton-transfer (ET and PT, respectively) steps could also be considered that avoid the development of highly charged intermediates in the net removal of $2H^+/2e^-$ from **1** to form **BDAT**.

(authentic **BDAT**: *m/z* $[M+K+H]^{2+}$=470.2) (Fig. S4). In addition, the IR spectra of **1** confirmed the presence of azo group due to the band in the frequency range 1443-1493 cm^{-1}. However, after binding Cu^{2+}, stretching frequency signal of the azo group disappeared. A strong band of appeared in the vicinity of 1635 cm^{-1} should be assigned to C=C and C=N bonds. There is a stretching frequency at 1076 cm^{-1}, which should be assigned to the stretching frequency of C-O and C-N bond (Fig. S5). These results clearly showed that **BDAT** was formed in the reaction. The turn-on response of fluorescence in this system may be proposed to proceed through the route shown in **Scheme 2**. The reaction mechanism most likely requires coordination of the Cu^{2+} to the amine/amide nitrogen atom to facilitate both PT and ET, with the possibility of azo nitrogen atom functioning as an additional ligand to assist metal binding. An oxidative cyclization reaction transforms nonemissive azoanilines into highly fluorescent benzotriazoles upon adding Cu^{2+}. No interference, such as paramagnetic quenching by free Cu^{2+} was observed, presumably due to the weak metal-binding affinity of the triazole in aqueous environment.[38]

It is well known that pH-insensitivity of probes is extremely valuable for practical applications. Therefore, the fluorescence spectra response of **1** in the absence and presence of Cu^{2+} in different pH values were evaluated (Fig. S6). Without Cu^{2+}, no obvious fluorescence change of **1** could be observed between pH 5 and 11. Upon addition of Cu^{2+}, **1** responded stably to Cu^{2+} in the same region with little interference by protons. These results indicate that **1** successfully react with Cu^{2+} and allow Cu^{2+} detection in a wide pH range.

To further demonstrate the practical applicability of the probe in biological samples, fluorescence imaging experiments were carried out in living cells (Fig. 3). Incubation of HT-29 cells with **1** (10 μM) for 0.5 h at 37 °C was followed by the addition of Cu^{2+} (50 μM) and then was incubated for another 0.5 h. The enhancement of fluorescence was observed. The results suggest that probe **1** can penetrate the cell membrane and can be used for imaging of Cu^{2+} in living cells potentially.

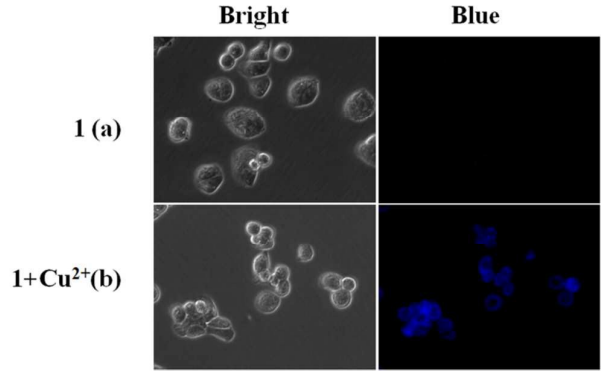


Fig. 3 Fluorescent images of Cu^{2+} in HT-29 cells. (a) Cells stained with 10 μM of **1** for 30 min. (b) Fluorescence image of HT-29 cells incubated with **1** for 30 min, washed two times, and then further incubated with 50 μM of Cu^{2+} for 30 min.

Conclusion

In conclusion, metal-induced chemical transformation of azo dye molecules has been exploited for the selective detection of copper ions. Cu^{2+} induced a highly selective "turn-on" fluorescence enhancement in aqueous buffer. A 131 fold fluorescence enhancement was observed upon the addition of Cu^{2+}. Moreover, this probe shows a broad working pH range (5-11) for response to Cu^{2+}. Fluorecence microscopy experiments indicated that probe **1** could be applied to the cell-imaging of Cu^{2+} using HT-29 cells. This work also implies that simple structural modification of azo dyes can easily contribute to new Cu^{2+} selective fluorescent probes.

Acknowledgements

This study was supported by the National Nature Science Foundation of China (21175085 and 21375083) and the Shanxi Scholarship Council of China (No. 20090980).

Notes and references

1 M. H. Lee, Z. Yang, C. W. Lim, Y. H. Lee, S. Dongbang, C. Kang and J. S. Kim, *Chem. Rev.*, 2013, **113**, 5071.
2 Y. J. Li, T. F. Liu, H. B. Liu, M. Z. Tian, and Y. L. Li, *Acc. Chem. Res.*, 2014, **47**, 1186.
3 Y. B. Guo, L. Xu, H. B. Liu, Y. J. Li, C. M. Che and Y. L. Li, *Adv. Mater.*,2015, **27**, 985.
4 G. W. Gokel, W. M. Leevy, and M. E. Weber, *Chem. Rev.*, 2004, **104**, 2723.
5 L. Tapia, M. Suazo, C. Hodar, V. Cambiazo, and M. Gonzalez, *Biometals*, 2003, **16**, 169.
6 H. Sigel, Dekker, New York, 1981.
7 D. J. Waggoner, T. B. Bartnikas, and J. D. Gitlin, *Neurobiol. Dis.*, 1999, **6**, 221.
8 F. Tisato, C. Marzano, M. Porchia, M. Pellei, and C. Santini, *Med. Res. Rev.*, 2010, **30**, 708.

9 W. Chouyyok, Y. Shin, J. Davidson, W. D. Samuels, N. H. LaFemina, R. D. Rutledge, G. E. Fryxell, T. Sangvanich, and W. Yantasee, *Environ. Sci. Technol.,* 2010, **44**, 6390.
10 M. Lin, M. Cho, W. S. Choe, J. B. Yoo, and Y. Lee, *Biosens. Bioelectron.*, 2010, **26**, 940.
11 N. Pourreza, and R. Hoveizavi, *Anal. Chim. Acta.*, 2005, **549**, 124.
12 J.S. Becker, M.V. Zoriy, C. Pickhardt, N. Palomero-Gallagher, and K. Zilles, *Anal. Chem.*, 2005, **77**, 3208.
13 M. Taki, S. Iyoshi, A. Ojida, I. Hamachi, and Y. Yamamoto, *J. Am. Chem. Soc.*, 2010, **132**, 5938.
14 K. L. Ciesienski, L. M. Hyman, S. Derisavifard, and K. J. Franz, *Inorg. Chem.*, 2010, **49**, 6808.
15 K. C. Ko, J. S. Wu, H. J. Kim, P. S. Kwon, J. W. Kim, R. A. Bartsch, J. Y. Lee, and J. S. Kim, *Chem. Commu.*, 2011, **47**, 3165.
16 L.N. Wang, J.X. Yan, W.W. Qin, W.S. Liu, and R. Wang, *Dyes. Pigm.*, 2012, **92**, 1083.
17 J. G. Huang, M. Tang, M. Liu, M. Zhou, Z. G. Liu, Y. Cao, M. Y. Zhu, S. G. Liu, and W. B. Zeng, *Dyes. Pigm.*, 2014, **107**, 1.
18 S. P. Wu, Z. M. Huang, S. R. Liu, and P. K. Chung, *J. Fluoresc.*, 2012, **22**, 253.
19 M. Q. Wang, K. Li, I. T. Hou, M. Y. Wu, Z. Huang, and X. Q. Yu, *J. Org. Chem.*, 2012, **77**, 8350.
20 Z. P. Liu, C. L. Zhang, X. Q. Wang, W. J. He, and Z. J. Guo, *Org. Lett.*, 2012, **14**, 4378.
21 S. L. Hu, S. S. Zhang, Y. Hu, Q. Tao, and A. X. Wu, *Dyes. Pigm.*, 2013, **96**, 509.
22 L. Y. Yang, Q. Song, K. Damit-Og, and H. S. Cao, *Actuat. B-Chem.*, 2013, **176**, 181.
23 M. Z. Tian, M. M. Hu, J. L. Fan, X. J. Peng, J. Y. Wang, S. G. Sun, and R. Zhang, *Bioorg. Med. Chem. Lett.*, 2013, **23**, 2916.
24 J. Q. Tian, Q. Liu, A. M. Asiri, A. O. Al-Youbi, and X. P. Sun, *Anal. Chem.*, 2013, **85**, 5595.
25 S. Pu, L. Ma, G. Liu, H. Ding, and B. Chen, *Dyes. Pigm.,* 2015, **113**, 70.
26 H. Zhu, J. L. Fan, B. H. Wang, and X. J. Peng, *Chem. Soc. Rev.*, 2015, **44**, 4337.
27 A. P. de Silva, H. Q. Gunaratne, T. Gunnlaugsson, A. J. Huxley, C. P. McCoy, J. T. Rademacher, and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515.
28 Y. Xiang, A. Tong, P. Jin, and Y. Ju, *Org. Lett.*, 2006, **8**, 2863.
29 X. Zhang, Y. Shiraishi, and T. Hirai, *Org. Lett.*, 2007, **9**, 5039.
30 K. M. K. Swamy, S.-K. Ko, S. K. Kwon, H. N. Lee, C. Mao, J.-M. Kim, K.-H .Lee, J. Kim, I. Shin, and J. Yoon, *Chem. Commun.*, 2008, **45**, 5915.
31 Y. Zhao, X.-B. Zhang, Z.-X. Han, L. Qiao, C.-Y. Li, L.-X. Jian, G.-L. Shen, and R. -Q. Yu, *Anal. Chem.*, 2009, **81**, 7022.
32 N. Li, Y. Xiang, A. Tong, *Chem. Commun.*, 2010, **46**, 3363.
33 J. J. Du, M. M. Hu, J. L. Fan, and X. J. Peng, *Chem. Soc. Rev.*, 2012, 41, 4511.
34 S. I. Reja, V. Bhalla, S. Manchanda, G. Kaur, M. Kumar, *Rsc. Adv.*, 2014, **4**, 43470.
35 Y.-Y. Zhu, X. Zhang, H. Guo, and Z.-J. Zhu, *Rsc. Adv.*, 2014, **4**, 45791.
36 C. Yang, Y. Chen, K. Wu, T. Wei, J. Wang, S. Zhang, and Y. Han, *Anal. Methods*, 2015, **7**, 3327.
37 M. Z. Tian, L. B. Liu, Y. J. Li, R. F. Hu, T. F. Liu, H. B. Liu, S. Wang, and Y. L. Li, *Chem. Commu.*, 2014, **50**, 2055.
38 J. Jo, H. Y. Lee, W. Liu, A. Olasz, C. H. Chen, and D. Lee, *J. Am. Chem. Soc.,* 2012, **134**, 16000
39 A. T. R. Williams, S. A. Winfield, and J. N. Miller, *Analyst*, 1983, **108**, 1067.