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Two birds with one stone: Multifunctional and highly selective fluorescent probe for distinguishing Zn^{2+} from Cd^{2+} and selective recognition of sulfide anion

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ABSTRACT

A coumarin-based multifunctional fluorescent sensor containing a di-2-picolylamine (DPA) moiety (**1**) was presented. Interestingly, this probe could similarly act as ON-OFF type fluorescent sensor for Co^{2+} and Cu^{2+}, then in situ generated **1-Co(II)** and **1-Cu(II)** ensembles could further serve as OFF-ON type fluorescent sensors to achieve the discrimination of Zn^{2+} from Cd^{2+} and selective recognition of sulfide anion in aqueous solution via displacement approach, respectively. Specially, **1-Cu(II)** could permeate the cell membrane and could be used in fluorescence imaging of S^{2-} in living biological samples. These ON-OFF-ON type fluorescent sensors exhibited high selectivity and sensitivity towards the targets.

1. Introduction

The development of selective and efficient signaling approaches to monitor various chemically and biologically relevant species has attained significant interest in recent years. Considering its practicality, simplicity and convenience, it is not difficult to find that detecting in vitro or in vivo biologically pertinent species by fluorescent sensors can be advantageous compared with the traditionally developed detection techniques [1–4]. However, most of the probes reported only respond to one analyte and the sensors responding to two or more are rarely, though multifunctional probes are in an urgent demand. To design a sensor directly interacting with different analytes, different acting sites or different interaction modes should be considered, thus increasing the design difficulty [5–7]. Hence, a new design strategy should be explored. Recently, Ren group reported two DNA/ligand/ion-based ensembles for fluorescence turn on detection of cysteine and histidine by changing the metal ions (Cu^{2+} for histidine and Hg^{2+} for cysteine, respectively) [8]. This new method is simple in design and fast in operation and is more convenient and promising than other methods for detecting two or more analytes.

In the past few years, the selective detection of biological metals with fluorescent chemosensors is an attractive research field [9–11]. Zn^{2+} and Cd^{2+}, which have similar coordination properties, are difficult to distinguish because they are both group IIB elements in the periodic table. As we know, zinc is the second most abundant transition metal ion in the human body, and it is an essential cofactor in many biological processes [12–18]. In sharp contrast, Cd^{2+}, which is known as a toxic metal ion, plays a totally different role in biochemical processes and can cause severe diseases [19–24]. Thus, it is imperative to develop a selective and efficient method for monitoring and distinguishing Zn^{2+} and Cd^{2+}, which would offer a promising approach to study their different behaviors in biological, toxicological, and environmental circumstances. However, only a limited fluorescent probes that could distinguish Zn^{2+} [12–18] and Cd^{2+} [19–24] have been reported till now. Di-2-picolylamine (DPA) is usually reported to serve as a Zn^{2+} chelator, but the usage of DPA often results in a poor selectivity for Zn^{2+} because of its strong binding ability to other heavy metal ions [25–27]. That is to say, traditional means using coordination of metals with DPA is tough to discriminate Zn^{2+} from Cd^{2+} directly, and new strategies should be exploited to improve the Zn^{2+} selectivity of this old receptor.

On the other hand, sulfide anion is a toxic traditional pollutant and it is widespread in the environment, owing to industrial processes and biological metabolism [28]. Gradual and cumulative damage can be caused by continuous exposure to sulfide anion, such as loss of consciousness, irritation of mucous membranes, and suffocation [29]. Once changed to HS^- or H_2S, it becomes even more toxic and caustic. Therefore, it is important to develop a

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rapid and sensitive method for immediate sulfide monitoring in aqueous media and in biological systems. It is well-known that sulfide can react with copper ions to form a very stable CuS species, which has a low solubility product constant, thus Cu(II) ensemble might be a good probe for S^{2-} detection [30–32,35].

Herein, we presented a multifunctional and highly selective fluorescent probe **1**, which consists of coumarin as fluorophore and DPA as receptor. Ensemble **1-Co(II)** can serve as a chemosensing reporter for Zn^{2+}, and **1-Cu(II)** can serve as a chemosensing ensemble for selective recognition of S^{2-}. Thus, a determination for Zn^{2+} and S^{2-} separately is achieved by combining probe **1** with different metal ions, which is simple and convenient.

2. Experimental section

2.1. General

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AM400 NMR spectrometer. Proton Chemical shifts of NMR spectra were given in ppm relative to internals reference TMS. ESI-MS and HRMS spectral data were recorded on a Finnigan LCQ^{DECA} and a BrukerDaltonics Bio TOF mass spectrometer, respectively. Fluorescence emission spectra were obtained using FluoroMax-4 Spectrofluorophotometer (HORIBA JobinYvon) at 298 K. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. All the solvents were dried according to the standard methods prior to use. All of the solvents were either HPLC or spectroscopic grade in the optical spectroscopic studies.

2.2. Fluorescence analysis

Co^{2+} titration: Fluorescence emission spectra were obtained with a Xenon lamp and 1.0 cm quartz cells. The probe **1** (15 μL, 1 mM, DMSO) was added to a quartz cell containing 3.0 mL HEPES (20 mM, pH=7.4). Then appropriate aliquots of $CoCl_2$ (0.5 mM) were added to the mixture and the fluorescence was measured. The excitation and emission slits were set to 2.0 and 2.0 nm, respectively.

Zn^{2+} titration: Fluorescence titration of Zn^{2+} was conducted by adding appropriate aliquots of $Zn(NO_3)_2$ (0.5 mM) into the in situ generated solution of **1-Co(II)** (5 μM).

S^{2-} titration: Fluorescence titration of S^{2-} was conducted by adding appropriate aliquots ofNa_2S (0.5 mM) into the in situ generated solution of **1-Cu(II)** (5 μM).

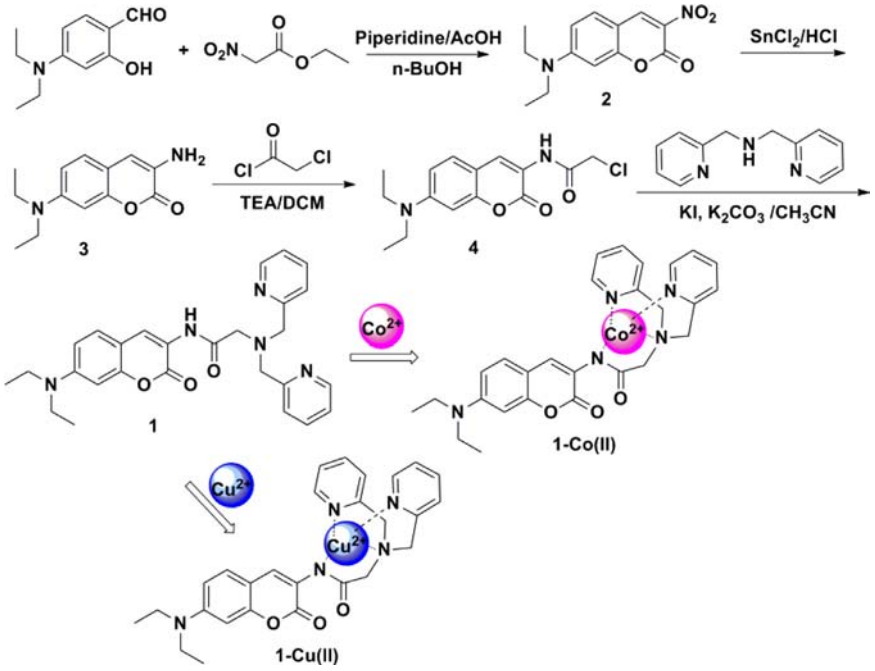
2.2.1. Preparation and characterization of *1*

Compounds **2**–**4** were prepared following the literature as shown in Scheme 1 [33].

Compound **4** (90 mg, 0.29 mmol), di-2-picolylamine (DPA) (70 mg, 0.35 mmol), anhydrous K_2CO_3 (80 mg, 0.58 mmol), and potassium iodide (30 mg) were added to acetonitrile (50 mL). After stirring and refluxing for 10 h under nitrogen atmosphere, the mixture was cooled to room temperature, and the solvent was removed under reduced pressure to obtain a yellow oil, which was purified by silica gel column chromatography (CH_2Cl_2/MeOH= 100/1) to afford **1** as yellow semi-solid in yield of 72% (98 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (s, 1H), 8.53–8.46 (m, 2H), 8.45 (s, 1H), 7.63 (td, J=7.6, 1.0 Hz, 2H), 7.56 (d, J=7.6 Hz, 2H), 7.17 (d, J=8.7 Hz, 1H), 7.10 (dd, J=6.6, 5.6 Hz, 2H), 6.51 (dd, J=8.8, 1.9 Hz, 1H), 6.42 (d, J=2.1 Hz, 1H), 3.87 (s, 4H), 3.36 (s, 2H), 3.31 (q, J=7.0 Hz, 4H), 1.11 (t, J=7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 159.4, 157.8, 152.9, 149.3, 136.9, 128.6, 125.5, 123.4, 122.5, 119.0, 109.5, 108.4, 97.4, 63.1, 55.8, 44.7, 12.5. HRMS calcd for $C_{27}H_{29}N_5O_3$ $[M+H]^+$: 472.2349; found: 472.2338.

3. Results and discussion

In connection with our continuing research of sensors for biologically and environmentally important components [34–37], we presented a multifunctional and highly selective probe to challenge the discrimination of Zn^{2+} from Cd^{2+} and recognition of S^{2-} in aqueous solution. 7-Diethylamino coumarin is chosen as the fluorophore due to its good photostability, large Stokes shift and high quantum yield [38,39]. DPA acts as the binding unit for metal ions because of its strong binding ability towards divalent heavy metal ions, even though its poor selectivity still remains to be



Scheme 1. The preparation of **1** and the ensemble formation of **1** with Co^{2+} and Cu^{2+}.

a problem. Compound **1** was prepared via simple process (Scheme 1) and characterized by ^{1}H NMR, ^{13}C NMR and HRMS.

To understand the coordination ability of the probe **1**, the fluorescence response of **1** (5 μM) toward common cations was tested in HEPES (20 mM, pH=7.4, containing 0.5% DMSO as cosolvent). As shown in Fig. 1, a strong fluorescence of **1** was observed at 500 nm. With the addition of main group ions like Na^{+}, Ca^{2+} and Mg^{2+}, there was no or little effect on the emission of probe **1**. However, quenching effect was observed when heavy transition metal ions Hg^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} were added, which was also observed in other DPA-appended fluorescence probes. [5]As reported, both Zn^{2+} and Cd^{2+} caused similar fluorescence changes during to their similar properties. The addition of Cd^{2+} induced a red shift from 500 nm to 505 nm, while the addition of Zn^{2+} could make the emission peak shift to 516 nm. The similar red shifts led to a difficult discrimination of Zn^{2+} from Cd^{2+}. Thus, probe **1** seems to be a terrible sensor towards Zn^{2+}.

Recently, some fluorescent sensors for anions [40,41] and thiols [42–44] based on displacement approach have been developed, as well as for cations [45,46]. Inspired by this, we speculated whether we could develop an ensemble consisting of compound **1** and some kind of cations to detect Zn^{2+}. Since Co^{2+} and Cu^{2+} can completely quench the fluorescence of **1**, the binding mode between **1** and these two cations were studied as well as in situ generated complexes of them and probe **1**.

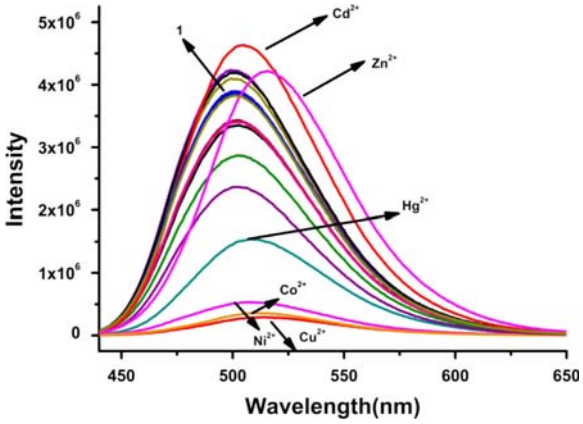


Fig. 1. Fluorescence spectra (λ_{ex}= 410 nm) of **1** (5 μM) in the presence of various metal cations (10 equiv of Na^{+}, K^{+}, Li^{+}, Mg^{2+}, Fe^{3+}, Cd^{2+}, Ba^{2+}, Ca^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+}, Pb^{2+}, Hg^{2+}, Al^{3+}, Mn^{2+}, Ag^{+}, Cu^{2+}, Zn^{2+}) in HEPES solution (20 mM, pH=7.4, containing 0.5% DMSO as cosolvent).

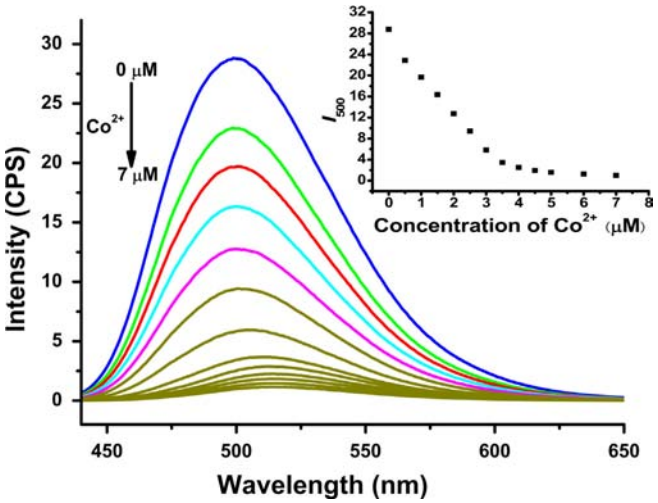


Fig. 2. The fluorescence titration of **1** (5 μM) toward Co^{2+} in HEPES solution (20 mM, pH=7.4, containing 0.5% DMSO as cosolvent) (λ_{ex}=410 nm, slits: 2 nm/2 nm).

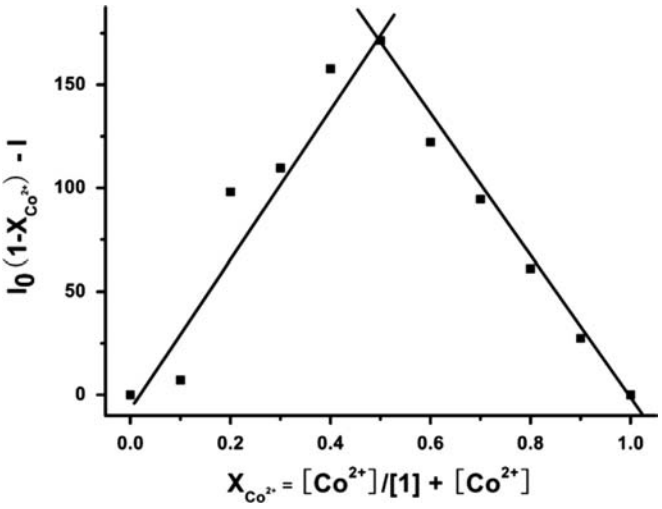


Fig. 3. The Job's plot of **1** toward Co^{2+}.

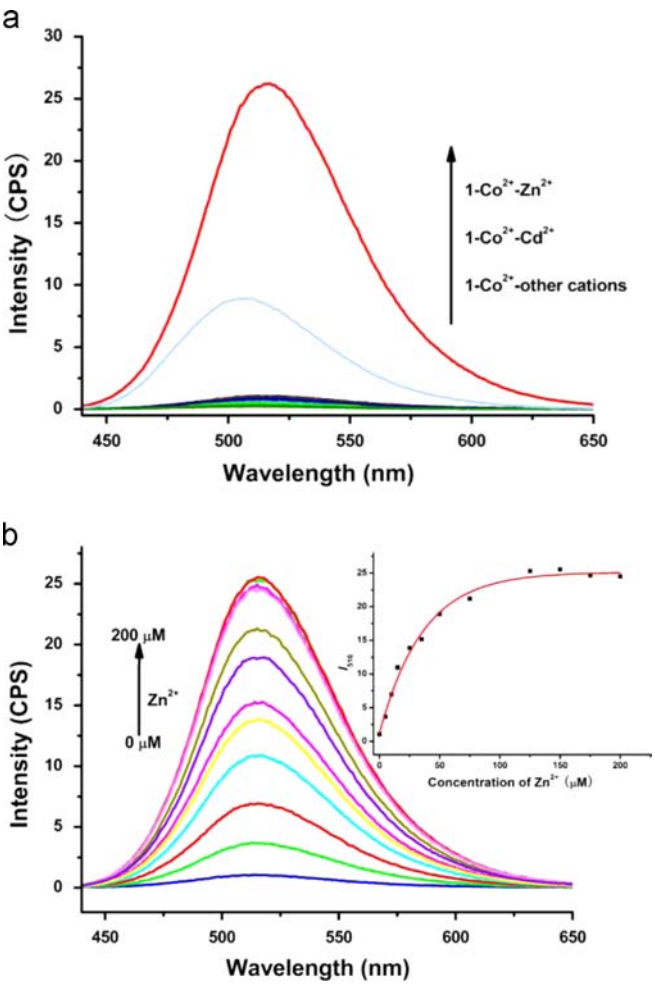


Fig. 4. (a) The fluorescence spectra of **1-Co(II)** (5 μM) in the presence of various cations (20 equiv of Ca^{2+}, Al^{3+}, Na^{+}, K^{+}, Mn^{2+}, Li^{+}, Mg^{2+}, Ba^{2+}, Ag^{+}, Pb^{2+}, Cr^{3+}, Ni^{2+}, Fe^{3+}, Hg^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}) in HEPES solution (20 mM, pH=7.4, containing 0.5% DMSO as cosolvent); (b) fluorescence spectra of **1+Co(II)** (5 μM) upon addition of Zn^{2+}(λ_{ex}=410 nm). Inset: the effect between **1-Co(II)** and Zn^{2+} at 516 nm.

First, the fluorescence titration of Co^{2+} toward probe **1** was tested. As shown in Fig. 2, gradual decrease could be observed when Co^{2+} ion was added to the solution of **1**, and the decrement came to an end when 5 μM Co^{2+} was added, indicating a 1: 1 complexation between **1** and Co^{2+}. Concomitantly, the quantum yield of **1** decreased from 41% to 1.3% (fluorescein in 1 N NaOH as reference, Φ=0.85). Meanwhile, a Job plot for the complexation also showed a 1: 1 stoichiometry from Fig. 3, which also could be further confirmed by ESI spectra (Fig. S1). The peak at *m/z* 529.24 corresponding to $[\mathbf{1}+Co^{2+}-H]^+$ was found and the original peak of **1** disappeared. The binding constant of **1-Co(II)** complex (K_1) was calculated to be $2.8\times10^5\ M^{-1}$ according to the fluorescence titration data (Fig. S2).

With the above results in hand, the selectivity of **1-Co(II)** (5 μM) toward cations was measured. To our delight, a dramatic fluorescence enhancement (~27 fold) at 516 nm appeared when 100 μM Zn^{2+} was added to the solution and other cations caused negligible influence on the emission intensity, while the addition of 100 μM Cd^{2+} caused a moderate reinforcement (~8 fold) at 507 nm, as shown in Fig. 4a. Thus, a selective detection for Zn^{2+} can be achieved by utilizing a **1-Co(II)** ensemble and the obvious difference in the enhancement ratio (I/I_0, I refers to the fluorescence intensity after the addition of analyst; I_0 refers to the original fluorescence intensity of the ensemble) could lead to a discrimination of Zn^{2+} and Cd^{2+}. In addition, the cation selectivity experiment was also conducted using in situ generated **1-Cu(II)** ensemble (Fig. S3). The formation of a 1:1 bonding mode between **1** and Cu^{2+} has been proved in our previous study and the binding constant was calculated to be $1.3\times10^6\ M^{-1}$ [33]. Similar to **1-Co(II)**, the fluorescence of **1-Cu(II)** only increased upon addition of Zn^{2+} and Cd^{2+}. However, the intensity enhancements of **1-Cu(II)** induced by these two cations were not distinct enough. Accordingly, ensemble **1-Co(II)** was chosen for latter studying.

The fluorescence titration of Zn^{2+} toward **1-Co(II)** was then conducted to examine the interaction between Zn^{2+} and **1-Co(II)**, as shown in Fig. 4b. Upon the addition of Zn^{2+} to the solution, the fluorescence of **1-Co(II)** at 516 nm increased remarkably and the emission intensity remained steady when 125 μM Zn^{2+} was added, which might be due to the appearance of a new complex. The quantum yield of **1** increased from 1.3% to 17%. The detection limit was measured to be 5.7×10^{-7} M according to the titration profile [47]. To confirm this new complex, the ESI spectra of [**1-Co(II)**+Zn^{2+}]

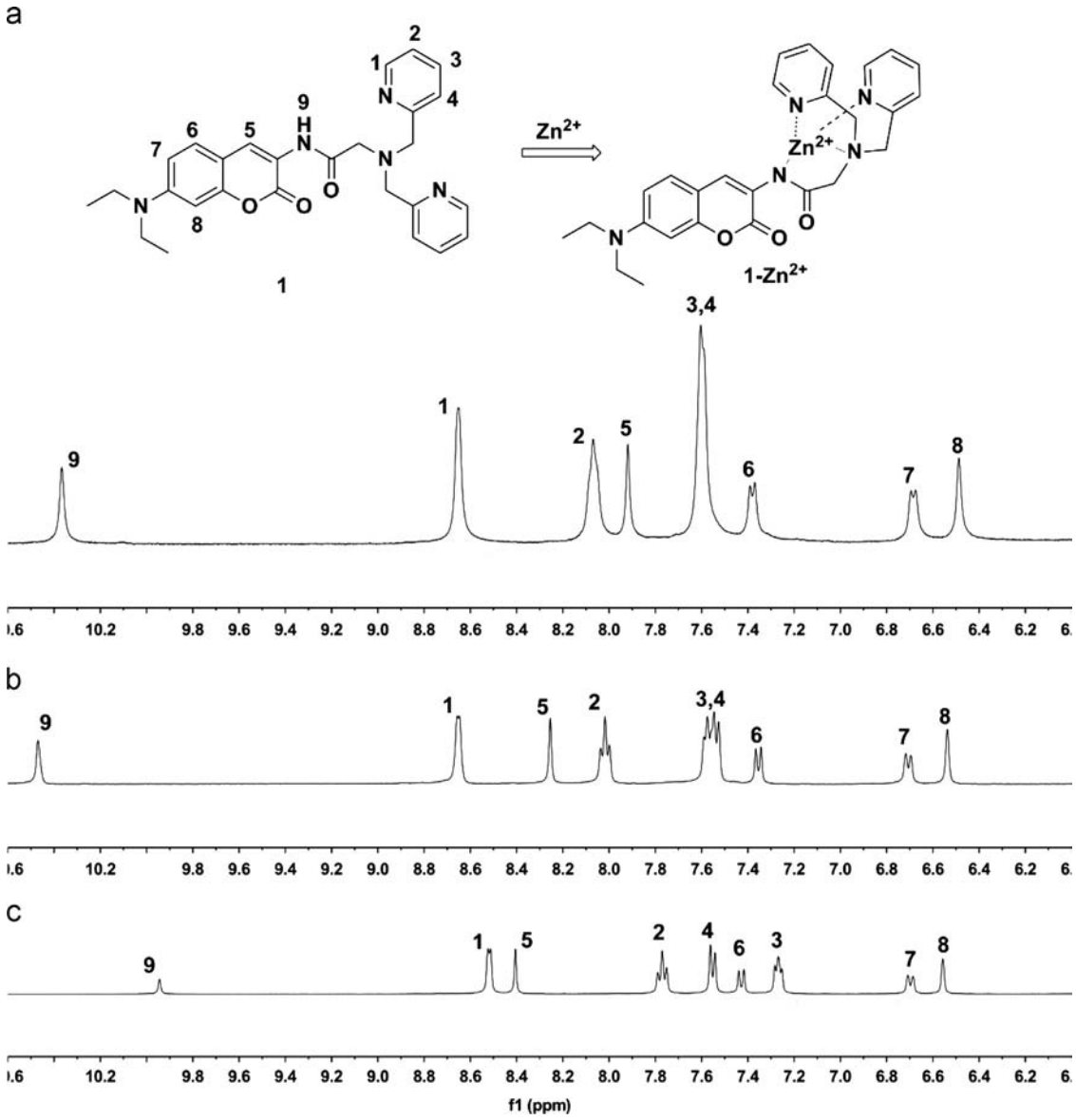


Fig. 5. Partial ^{1}H NMR spectra (400 MHz) of **1** (17.7 mM) in DMSO: (a) **1**+ 10 equiv of Zn^{2+}; (b) **1**+10 equiv of Cd^{2+}; (c) free **1** (aromatic area).

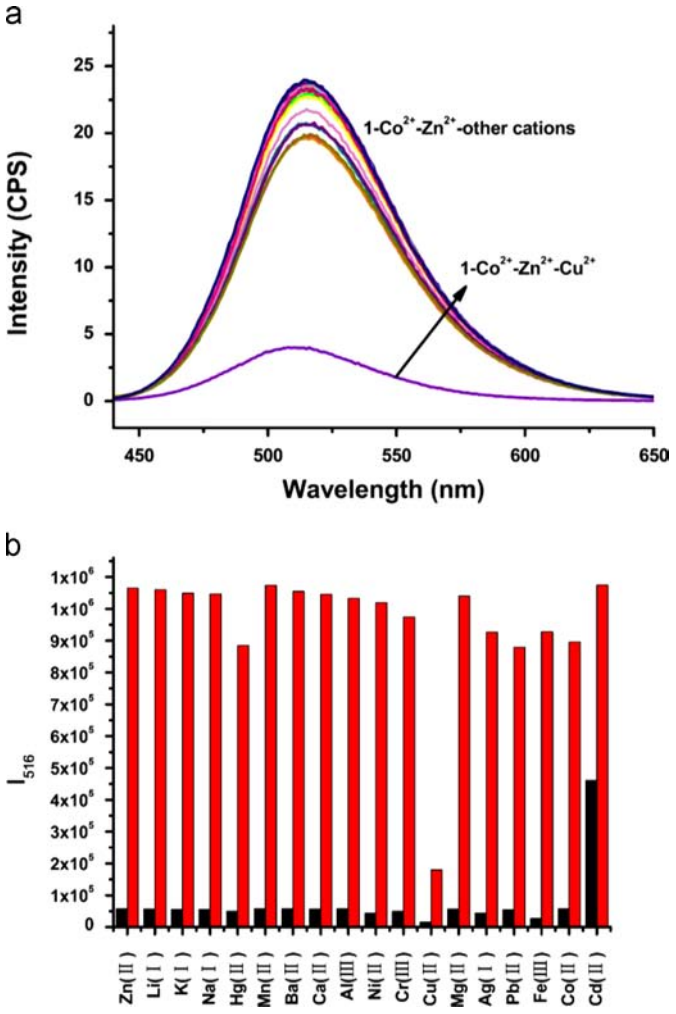


Fig. 6. (a) The fluorescence response of **1-Co(II)** (5 μM) to other cations (50 μM) in the presence of Zn^{2+} (50 μM) in HEPES (20 mM, pH=7.4, containing 0.5% DMSO as cosolvent); (b) Fluorescent intensity of **1-Co(II)** (5 μM) with selected cations (50 μM) in the absence (black bars) or presence (red bars) of Zn^{2+} (50 μM). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

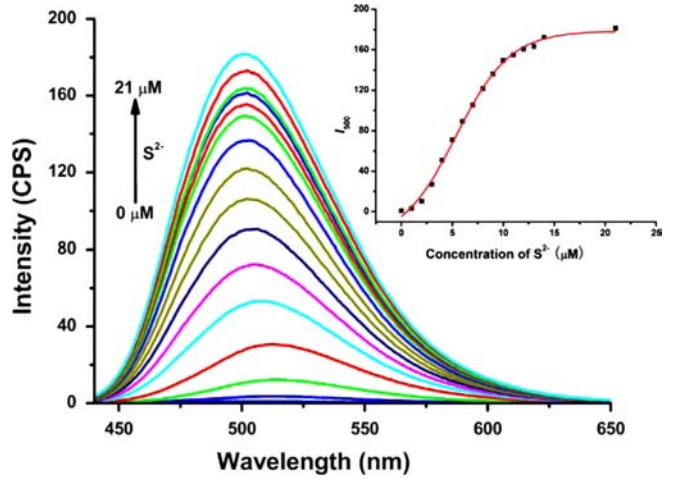


Fig. 7. (a) Fluorescence titration spectra (λ_{ex}= 410 nm) of **1-Cu(II)** (5 μM) toward S^{2-} in HEPES solution (20 mM, pH=7.4, containing 0.5% DMSO as cosolvent).

was obtained (Fig. S4). A new peak at *m/z* 534.22 was found to correspond to the $[\mathbf{1}+Zn^{2+}-H]^+$, and the peak at *m/z* 529.26 corresponding to $[\mathbf{1}+Co^{2+}-H]^+$ indicated the residual of **1-Co(II)**. Hence, with the addition of Zn^{2+} to **1-Co(II)**, Co^{2+} was displaced by Zn^{2+} to form a new **1-Zn(II)** complex due to a stronger binding ability of Zn^{2+} toward probe **1**, which further resulted in a fluorescence recovery of **1**. Based on the 1:1 binding mode resulting

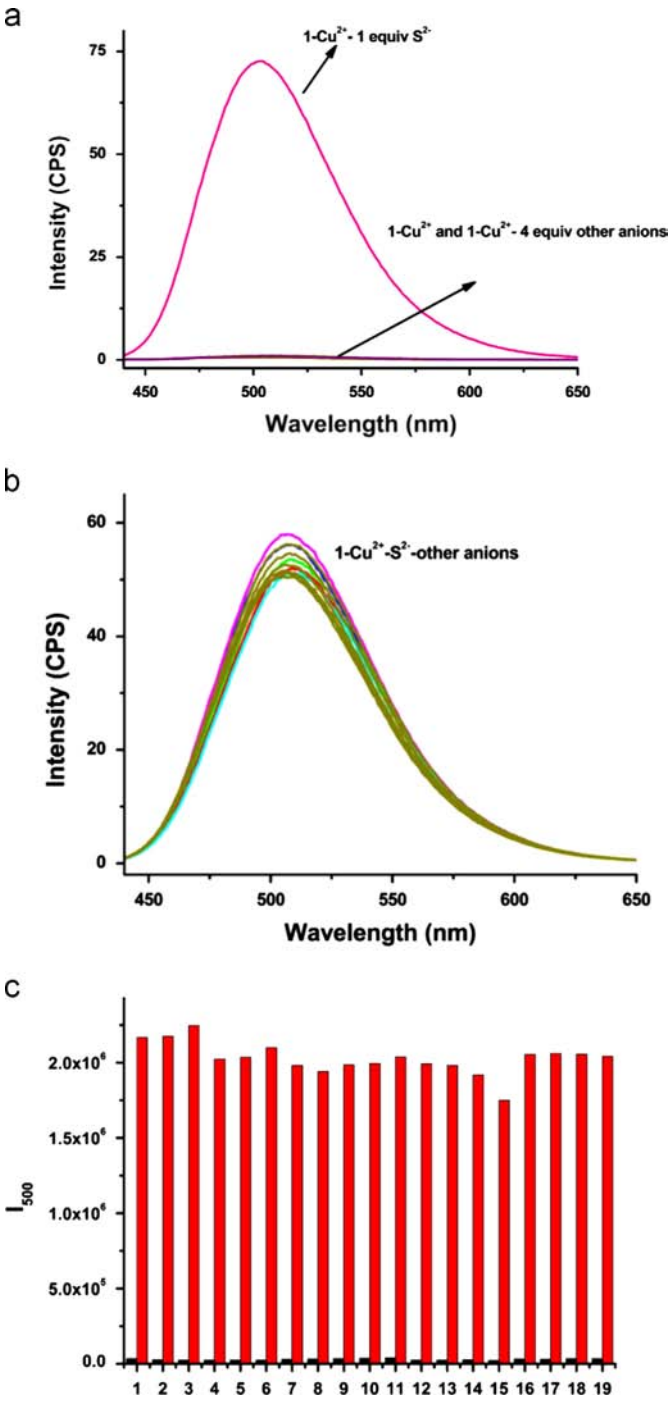


Fig. 8. (a) Fluorescence spectra of **1-Cu(II)** (5 μM) in the presence of various anions (10 equiv) in HEPES solution (20 mM, pH=7.4, containing 0.5% DMSO as cosolvent); (b) the fluorescence spectra of **1-Cu(II)** toward other anions (4 equiv) in the presence of sulfide (5 μM). (c) fluorescent intensity of **1-Cu(II)** (5 μM) with selected anions (20 μM) in the absence (black bars) or presence (red bars) of S^{2-} (5 μM). From 1 to 19: free, $P_2O_7^{4-}$, Cl^-, I^-, F^-, Br^-, HCO_3^-, SO_4^{2-}, CO_3^{2-}, NO_3^-, $H_2PO_4^-$, SO_3^{2-}, ATP, PO_4^{3-}, ACO$^-$, HSO_4^-, $S_2O_4^{2-}$, $S_2O_3^{2-}$ and $S_2O_5^{2-}$ (λ_{ex}=410 nm). (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

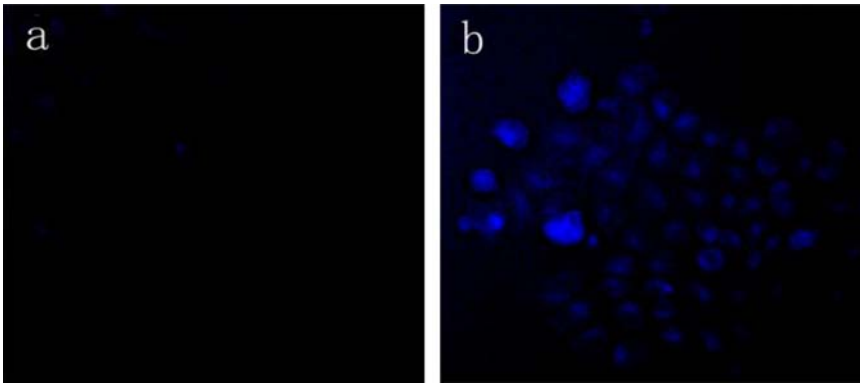


Fig. 9. Fluorescence images in HeLa cells. Cells were incubated with 5 μM **1-Cu(II)** in PBS buffer for 30 min (a); and then incubated with 20 μM S^{2-} for another 30 min (b).

from the ESI spectra, the association constant between Zn^{2+} and **1-Co(II)** (K_2) was calculated to be $1.2\times10^4\ M^{-1}$, and association constant (K_3)between **1** and Zn^{2+} was calculated to be $3.4\times10^9\ M^{-1}$ (Fig. S5). The much larger association constant between **1** and Zn^{2+} than that of **1** and Co^{2+} certainly opened the door for the displacement approach. Also, the solid **1-Co(II)** complex was also prepared by reaction of $Co(NO_3)_2$ and compound **1** in methanol to further confirm the displacement approach. As predicted, solid **1-Co (II)** complex exhibited a similar fluorescence response to Zn^{2+} and Cd^{2+} like **1-Co(II)** solution prepared in situ and also showed a moderate selectivity (Fig. S6).

To obtain detailed information about the interaction between **1** and Zn^{2+}, ^1H NMR titration was carried out in DMSO-d_6. As we could see from Fig. 5, when 50 μM Zn^{2+} was added to the solution of **1**, the peak of proton H9 was downfield shifted by 0.43 ppm (9.94–10.37), suggesting that Zn^{2+} was bound to imidic acid nitrogen [17]. The binding of the amide nitrogen with Zn^{2+} acted as an electron-withdrawing group, which led to the downfield shift of H9. The more or less upfield shifts of protons of coumarin (H5–8) could be attributed to the changes of electron density of coumarin induced by M–N bond formation. Additionally, the peaks of protonsH1–4 of pyridyl group were also downfield shifted obviously, indicating the binding of Zn^{2+} and pyridyl nitrogen. A large downfield shift of the peak of proton H10 referring to picolyl was promoted by the addition of Zn^{2+} (3.92 to 4.34–4.51) and was split into two sets of signals (Fig. S7), which was promoted by the strong binding between Zn^{2+} and aliphatic nitrogen of DPA. Thus, Zn^{2+} was bound to the three nitrogen atoms of DPA moiety and the imidic acid nitrogen. The same analysis was also realized between **1** and Cd^{2+}. Similar chemical shifts of aromatic protons were observed (Table S1). However, the difference between downfield shifts of proton H10 elicited by Zn^{2+} and Cd^{2+} was evident (0.59 and 0.19, respectively), which might indicate the stronger binding affinity of Zn^{2+} toward probe **1** than that of Cd^{2+} toward **1** and then be responsible for a selectivity for Zn^{2+} over Cd^{2+}.

To examine the Zn^{2+}-determination of **1-Co(II)** ensemble in practice, competition experiments were also performed upon addition of 100 μM of other cations to **1-Co(II)** solution in the presence of 100 μM Zn^{2+}. As Fig. 6 shows, all the tested metals caused negelectable influence on the detection except Cu^{2+}. Hence, **1-Co(II)** seems to be a desirable probe to distinguish Zn^{2+} from Cd^{2+}. Therefore, a void probe **1** for cations can selectively detect Zn^{2+} by exploiting a **1-Co(II)** ensemble.

It is well known that sulfide can react with copper ions to form a very stable CuS species, which has a low solubility product constant $k_{sp}=6.3\times10^{-36}$ [48]. We doubted whether **1-Cu(II)** ensemble could recognize sulfide anion by exploiting CuS affinity among the various approaches to sensing sulfide anions.

The fluorescence spectra of **1-Cu(II)** upon addition of sulfide was explored to further testify the feasibility of the probe in HEPES solution (20 mM, pH=7.4, containing 0.5% DMSO as cosolvent), as shown in Fig. 7. Upon the addition of S^{2-}, the fluorescence of probe **1** at 500 nm increased gradually and the emission intensity remained constant when up to 21 μM $S^{2-}$was added. The detection limit was calculated to be 1.3×10^{-7} M. Thus, ensemble **1-Cu (II)** can serve as an OFF-ON type probe toward sulfide.

Subsequently, the selectivity of **1-Cu(II)** toward anions was measured. As shown in Fig. 8a, the addition of 20 μM other anions ($P_2O_7^{4-}$, Cl^-, I^-, F^-, Br^-, HCO_3^-, SO_4^{2-}, CO_3^{2-}, NO_3^-, $H_2PO_4^-$, SO_3^{2-}, ATP, PO_4^{3-}, AcO^-, HSO_4^-, $S_2O_4^{2-}$, $S_2O_3^{2-}$ and $S_2O_5^{2-}$) to **1-Cu(II)** had no effect on the emission at 500 nm, while the addition of 5 μM S^{2-} induced an apparent enhancement. The quantum yield of **1** increased from 0.85% to 32%, subsequently. This result suggested that ensemble **1-Cu(II)** exhibited a high selectivity for S^{2-} over other anions including sulfur-containing anions due to the formation of CuS. Moreover, as Fig. 8b displays, in the presence of miscellaneous competitive anions, S^{2-} still exhibited a similar fluorescence enhancement effect, indicating that **1-Cu(II)** could be used as a selective S^{2-} sensor and would not be interfered by other anions. To confirm the abstraction of Cu^{2+} from ensemble **1-Cu(II)** by S^{2-}, the ESI spectra of [**1-Cu(II)**+S^{2-}] was obtained (Figs. S8 and S9). Before the addition of S^{2-}, the peak at m/z ~533.15 corresponding to $[\mathbf{1}+Cu^{2+}-H]^+$ was found and no peak referring to **1** was observed. However, the addition of S^{2-} led to the observation of a new peak at m/z 494.29 in relation to $[\mathbf{1}+Na]^+$. Thus, the formation of CuS released compound **1** then restored its fluorescence. The displacement approach was also confirmed by the interaction between the solid **1-Cu(II)** complex and S^{2-} (Fig. S10).

To demonstrate the biological application of the ensemble, the experiments of fluorescence imaging of cells were carried out on HeLa cells with **1-Cu(II)**. After being cultured with HeLa cells (5 μM **1-Cu(II)** in PBS buffer for 30 min at 37 °C), it gave a weak intracellular luminescence, as shown in Fig. 9a. However, when the cells were subsequently incubated with S^{2-} (20 μM) at 37 °C for another 30 min, the dark blue luminescence became brighter obviously, which was clearly visible by the naked-eye from Fig. 9b. The results revealed that **1-Cu(II)** could permeate the cell membrane and could be used in fluorescence imaging of S^{2-} in living biological samples.

4. Conclusion

In conclusion, a multifunctional fluorescent probe **1** via the formation of different **1**-metal complexes was presented. They could selectively detect the substrates in aqueous solution via displacement approach. To be specific, **1-Co(II)** ensemble displayed high specificity for discrimination of Zn^{2+} from Cd^{2+}

although **1** itself showed no profound selectivity to cations. On the other hand, the quenched fluorescence of the in situ generated **1-Cu(II)** ensemble could recover upon the addition of sulfide anion, realizing the selective recognition of sulfide anion without considerable interference in the presence of other anions and common biological species. The solid **1-Co(II)** complex and **1-Cu (II)** complex were prepared by reactions of $Co(NO_3)_2$ and $Cu(NO_3)_2$ and compound **1** in methanol, respectively, and they displayed the same fluorescence response toward the analytes as they did when they were prepared in situ. Meanwhile, **1-Cu(II)** could permeate the cell membrane and could be used in fluorescence imaging of S^{2-} in living biological samples. Thus, these results are significant and interesting for a new generation of molecular recognition systems that can detect two or more analytes with a single small molecule without complicated designs.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.07.020.

References

[1] A.P. de Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1997) 1515–1566.
[2] P.D Beer, P.A. Gale, Angew. Chem. Int. Ed. 40 (2001) 486–516.
[3] L. Pu, Chem. Rev. 104 (2004) 1687–1716.
[4] A. Lippert, G.C.R. Van de Bittner, C.J. Chang, Acc. Chem. Res. 44 (2011) 793–804.
[5] L. Yuan, W. Lin, Y. Xie, B. Chen, S. Zhu, J. Am. Chem. Soc. 134 (2012) 1305–1315.
[6] X. Sun, Y.-W. Wang, Y. Peng, Org. Lett. 14 (2012) 3420–3423.
[7] D. Srikun, A.E Albers, C.J. Chang, Chem. Sci. 2 (2011) 1156–1165.
[8] F. Pu, Z. Huang, J. Ren, X. Qu, Anal. Chem. 82 (2010) 821–8216.
[9] C Bargossi, M.C Fiorini, M Montalti, L Prodi, N Zaccheroni, Coord. Chem. Rev. 208 (2000) 17–32.
[10] E.L. Que, D.W. Domaille, C.J. Chang, Chem. Rev. 108 (2008) 1517–1549.
[11] E.M. Nolan, S.J. Lippard, Chem. Rev. 108 (2008) 3443–3480.
[12] E.M. Nolan, S.J. Lippard, Acc. Chem. Res. 42 (2009) 193–203.
[13] Z. Xu, J. Yoon, D.R. Spring, Chem. Soc. Rev. 39 (2010) 1996–2006.
[14] B. Tang, H. Huang, K. Xu, L. Tong, G. Yang, X. Liu, L. An, Chem. Commun. (2006) 3609–3611.
[15] Y. Mikata, A. Yamanaka, A. Yamashita, S. Yano, Inorg. Chem. 47 (2008) 7295–7301.
[16] F. Qian, C. Zhang, Y. Zhang, W. He, X. Gao, P. Hu, Z. Guo, J. Am. Chem. Soc. 131 (2009) 1460–1468.
[17] Z. Xu, K. Baek, H.N. Kim, J. Cui, X. Qian, D.R. Spring, I. Shin, J. Yoon, J. Am. Chem. Soc. 132 (2010) 601–610.
[18] J. Wang, W. Lin, W. Li, Chem. Eur. J. 18 (2012) 13629–13632.
[19] W. Liu, L. Xu, R. Sheng, P. Wang, H. Li, S. Wu, Org. Lett. 9 (2007) 3829–3832.
[20] M. Taki, M. Desaki, A. Ojida, S. Iyoshi, T. Hirayama, I. Hamachi, Y. Yamamoto, J. Am. Chem. Soc. 130 (2008) 12564–12565.
[21] Z. Liu, C. Zhang, W. He, Z. Yang, X. Gao, Z. Guo, Chem. Commun. 46 (2010) 6138–6140.
[22] X. Peng, J. Du, J. Fan, J. Wang, Y. Wu, J. Zhao, S. Sun, T. Xu, J. Am. Chem. Soc. 129 (2007) 1500–1501.
[23] T. Cheng, Y. Xu, S. Zhang, W. Zhu, X. Qian, L. Duan, J. Am. Chem. Soc. 130 (2008) 16160–16161.
[24] Q. Zhao, R. Li, S. Xing, X. Liu, T. Hu, X. Bu, Inorg. Chem. 50 (2011) 10041–10046.
[25] Z. Xu, X. Liu, J. Pan, D.R. Spring, Chem. Commun. 48 (2012) 4764–4766.
[26] L. Xue, C. Liu, H. Jiang, Chem. Commun. (2009) 1061–1063.
[27] Z. Liu, C. Zhang, Y. Chen, W. He, Z. Guo, Chem. Commun. 48 (2012) 8365–8367.
[28] V.S Lin, C.J. Chang, Curr. Opin. Chem. Biol. 16 (2012) 595–601.
[29] R.E Gosselin, R.P Smith, H.C Hodge, et al., Clinical Toxicology of Commercial Products, pp, 5th ed., Williams &Wilkins, Baltimore, MD198–202.
[30] F Hou, L. Huang, P. Xi, J. Cheng, X. Zhao, G. Xie, Y. Shi, F. Cheng, X. Yao, D. Bai, Z. Zeng, Inorg. Chem. 51 (2012) 2454–2460.
[31] K Sasakura, K Hanaoka, N Shibuya, Y Mikami, Y Kimura, T Komatsu, T Ueno, T Terai, H Kimura, T Nagano, J. Am. Chem. Soc. 133 (2011) 18003–18005.
[32] X. Lou, H. Mu, R. Gong, E. Fu, J. Qin, Z. Li, Analyst 136 (2011) 684–687.
[33] J.-T Hou, K. Li, K.-K Yu, M.-Y Wu, X.-Q Yu, Org. Biomol. Chem. 11 (2013) 717–720.
[34] Q.-S. Lu, L. Dong, J. Zhang, J. Li, L. Jiang, Y. Huang, S. Qin, C.-W. Hu, X.-Q. Yu, Org. Lett. 11 (2009) 669–672.
[35] M.-Q. Wang, K. Li, J.-T. Hou, M.-Y. Wu, Z. Huang, X.-Q. Yu, J. Org. Chem. 77 (2012) 8350–8354.
[36] X. Chen, Z. Huang, S.-Y. Chen, K. Li, X.-Q. Yu, L. Pu, J. Am. Chem. Soc. 132 (2010) 7297–7299.
[37] M.-Y. Wu, K. Li, J.-T. Hou, Z. Huang, X.-Q Yu, Org. Biomol. Chem. 10 (2012) 8342–8347.
[38] A. Helal, M.H. Or Rashid, C.-H. Choi, H.-S. Kim, Tetrahedron 67 (2011) 2794–2802.
[39] L. Yuan, W. Lin, J. Song, Y. Yang, Chem. Commun. 47 (2011) 12691–12693.
[40] B.L. Ma, F. Zeng, F.Y. Zheng, S.Z. Wu, Chem. Eur. J. 17 (2011) 14844–14850.
[41] X. Cao, W. Lin, L. He, Org. Lett. 13 (2011) 4716–4719.
[42] H.S. Jung, J.H. Han, Y. Habata, C. Kang, J.S. Kim, Chem. Commun. 47 (2011) 5142–5144.
[43] X.-F. Yang, P. Liu, L. Wang, M. Zhao, J. Fluoresc. 18 (2008) 453–459.
[44] Y.-K. Yang, S. Shim, J. Tae, Chem. Commun. 46 (2010) 7766–7768.
[45] L. Xue, Q. Liu, H. Jiang, Org. Lett. 11 (2009) 3454–3457.
[46] Z. Huang, J. Du, J. Zhang, X.-Q. Yu, L. Pu, Anal. Methods 48 (2012) 3412–3414.
[47] M. Shortreed, R. Kopelman, M. Kuhn, B. Hoyland, Anal. Chem. 68 (1996) 1414–1418.
[48] Y.F. Zhu, D.H. Fan, W.Z. Shen, J. Phys. Chem. C 112 (2008) 10402–10406.