



Cite this: DOI: 10.1039/c5nj00023h

A simple pincer-type chemosensor for reversible fluorescence turn-on detection of zinc ion at physiological pH range†

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Received (in Montpellier, France)
4th January 2015,
Accepted 16th March 2015

DOI: 10.1039/c5nj00023h

www.rsc.org/njc

A new, highly selective and sensitive pincer-type chemosensor (**Y**) for zinc ion with turn-on fluorescence behavior in physiological pH range solution was developed. **Y** is based on bi-hydrazone derivatives, which contain pyridine as the fluorescent group and a hydrazone bond as recognition site. The selectivity mechanism of **Y** for zinc is based on the combined effects of the inhibition of excited-state intramolecular proton transfer (ESIPT) and HC=N isomerization, as well as chelation-enhanced fluorescence. The entire process takes less than 15 seconds. The minimum detection limit of **Y** for zinc reaches 1.39×10^{-8} M. Moreover, **Y** can conveniently detect zinc in test strip form, and it can be recycled.

Introduction

The development of chemical probes for sensing metal ions^{1–6} and anions^{7–11} has received considerable attention due to their fundamental applications in chemical, environmental and biological fields. For example, despite the fact that zinc has significant roles in catalytic centers and serves as structural cofactor of many Zn²⁺-containing enzymes and DNA-binding proteins,^{12–17} an unregulated zinc level in the body may lead to a number of severe neurological diseases (e.g. Alzheimer's disease, cerebral ischemia, and epilepsy), developmental defects, and malfunctions.^{18–28} Therefore, considerable effort has been devoted to the development of efficient and selective methods to detect Zn²⁺. Numerous approaches, such as inductively coupled plasma atomic emission spectrometry,²⁹ atomic absorption spectroscopy,³⁰ and electrochemical methods,³¹ have been employed to detect both the metal ions and anions. However, most of these methods require sophisticated instrumentation, tedious sample preparation procedures, and trained operators. By contrast, fluorescence technology provides a convenient and easy method for monitoring the target ions.^{32–35} Methods using fluorescence have, therefore, attracted considerable attention in the detection of metal ions or anions, including Zn²⁺. Recently, simple chemosensors have become very popular among analysts because of their fast detection time and cost reduction.^{36–38} Meanwhile, multidentate donor ligands have the advantage that they can simultaneously

increase the electronic density and stabilize the coordination sphere of a transition metal (TM). In particular, the pincer-type motif featuring a tridentate, meridional coordinating ligand framework offers a myriad of opportunities for controlling the steric and electronic properties of TM complexes.³⁹ Generally, the side arms of a pincer ligand consist of neutral, two-electron Lewis donor moieties, which are connected through a linker group to a neutral or monoanionic anchoring site. Herein, we report the synthesis and sensing properties of a new hydrazone-based chemosensor **Y**, which is pincer-type, with both the hydrazone and an imine functional group. Our approach to designing this fluorescence-based, bi-functional chemosensor relies on the strong coordination capability of the hydrazone base with metal ions. Receptor **Y** showed a reversible, intense fluorescence enhancement in the presence of zinc ions in aqueous solutions at physiological pH range. Additionally, **Y** could also conveniently detect Zn²⁺ in the form of test strips.

Experimental section

Materials and physical methods

Fresh doubly distilled water was used throughout the experiment. All other reagents and solvents were commercially available at analytical grade and were used without further purification. ¹H NMR and ¹³C NMR spectra were recorded on a Mercury-400BB spectrometer at 400 MHz for ¹H. The chemical shifts, reported in ppm downfield from tetra spectra, were recorded with a Mercury-400BB spectrometer at 400 MHz (TMS, d scale with the solvent resonances as internal standards). Electrospray ionization mass spectra (ESI-MS) were measured on an Agilent 1100 LC-MSD-Trap-VL system. UV-visible spectra were recorded on a Shimadzu UV-2550

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5nj00023h

spectrometer. The photoluminescence spectra were performed on a Shimadzu RF-5301 fluorescence spectrophotometer. The melting points were measured on an X-4 digital melting-point apparatus (uncorrected). The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer.

Synthesis of sensor molecule Y

Compound **Y** can be readily prepared by a simple and low-cost Schiff base reaction of 4-hydroxyisophthalaldehyde and 2-hydrazinylpyridine (Scheme 1). 4-Hydroxyisophthalaldehyde (0.7500 g, 5 mmol), 2-hydrazinylpyridine (0.5995 g, 5.5 mmol) and a catalytic amount of acetic acid (AcOH) were combined in hot absolute EtOH (30 mL). The solution was stirred under reflux for 4 hours. After cooling to room temperature, the dark yellow precipitate was filtered, washed three times with hot absolute ethanol, then recrystallized with EtOH to obtain a yellowy powdered product **Y** (4.31 mmol) in 86.2% yield (m.p. >300 °C). ¹H NMR (DMSO-*d*₆, 400 MHz) δ: 11.01 (s, 1H, O-H); δ: 10.80 (s, 1H, N-H); δ: 10.72 (s, 1H, N-H); δ: 8.31 (s, 1H, CH=N). (Fig. S1, ESI[†]) IR (KBr) ν: 1622 cm⁻¹ (-HC=N-), 3422 cm⁻¹ (N-H). (Fig. S8, ESI[†]) ESI-MS calcd for [C₁₈H₁₆N₆O + H⁺]⁺ 333.3592. Found 333.1727. (Fig. S2, ESI[†])

General procedure for spectroscopy

All the UV-vis experiments were carried out in DMSO solution on a Shimadzu UV-2550 spectrometer. Any changes in the UV-vis spectra of the synthesized compound were recorded upon the addition of perchlorate salts while keeping the ligand concentration constant (2.0 × 10⁻⁵ M) in all experiments. The perchlorate salts of Fe³⁺, Hg²⁺, Ca²⁺, Cu²⁺, Co²⁺, Ni²⁺, Cd²⁺, Pb²⁺, Zn²⁺, Cr³⁺, and Mg²⁺ were used for the UV-vis experiments.

Fluorescence spectroscopy was carried out in a DMSO solution on a Shimadzu RF-5301 spectrometer. Any changes in the fluorescence spectra of the synthesized compound were recorded upon the addition of perchlorate salts while keeping the ligand concentration constant (2.0 × 10⁻⁵ M) in all experiments.

The perchlorate salts of the ions (Fe³⁺, Hg²⁺, Ca²⁺, Cu²⁺, Co²⁺, Ni²⁺, Cd²⁺, Pb²⁺, Zn²⁺, Cr³⁺, and Mg²⁺) were used for the fluorescence experiments. For ¹H NMR titrations, the solution of **Y** was prepared in DMSO-*d*₆, and the appropriate concentration of test solutions was prepared in doubly distilled water. Aliquots of the two solutions were mixed directly in the NMR tubes.

Results and discussion

Fluorescence spectroscopic studies of **Y** toward Zn²⁺ ions

To gain insight into the fluorescent properties of receptor **Y** toward metal ions, the emission changes were measured with various metal ions in DMSO/H₂O (v/v = 9/1) HEPES buffer solutions at pH = 7.2. When excited at 355 nm, **Y** exhibited a weak fluorescence, which was much lower than that in the presence of Zn²⁺ (Fig. 1). By contrast, upon addition of other metal ions such as Fe³⁺, Hg²⁺, Ag⁺, Ca²⁺, Cu²⁺, Co²⁺, Ni²⁺, Cd²⁺, Pb²⁺, Cr³⁺ and Mg²⁺, either no increase or a slight increase in intensity was observed. To this end, it is noteworthy that **Y** can act as a “turn-on” sensor for Zn²⁺ and differentiate Zn²⁺ from Cd²⁺, which has almost always been a major problem in the past.⁴⁰⁻⁴³ This preferential fluorescence enhancement for Zn²⁺ might be due to the formation of a chelate complex (rigid system) between **Y** and the Zn²⁺ ion, leading to the chelation-enhanced fluorescence (CHEF) effect.⁴⁴ Additionally, receptor **Y** is a poor fluorescent due to the following combined effects: (a) isomerization of the -HC=N-double bonds in the excited state⁴⁵ and (b) excited-state intramolecular proton transfer (ESIPT), involving the hydroxy proton of the 4-hydroxyisophthalaldehyde moiety (Scheme 2).⁴⁶ Upon stable

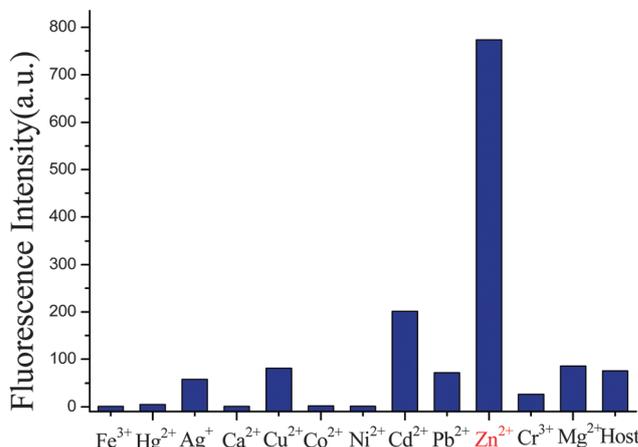
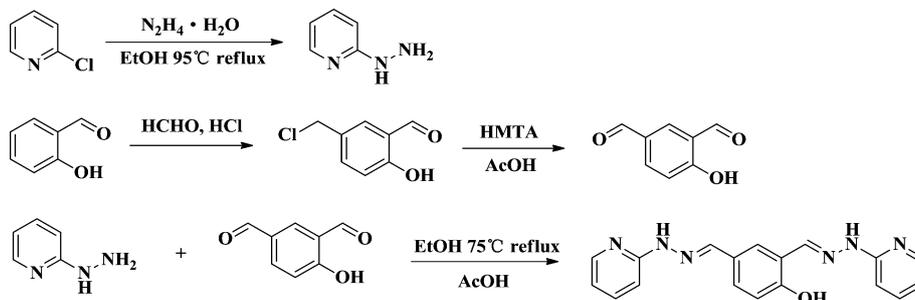
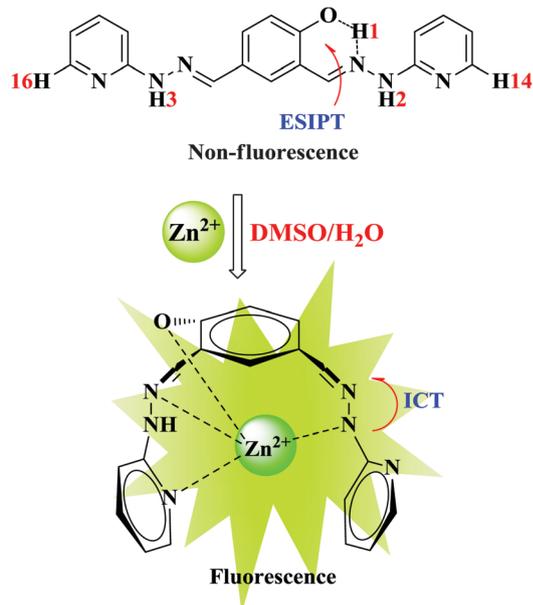


Fig. 1 Bar graph shows the relative emission intensity of **Y** ($c = 2 \times 10^{-5}$ M) in the presence of different metal ions (10 equiv.) such as Fe³⁺, Hg²⁺, Ag⁺, Ca²⁺, Cu²⁺, Co²⁺, Ni²⁺, Cd²⁺, Pb²⁺, Zn²⁺, Cr³⁺ and Mg²⁺ with an excitation of 355 nm in DMSO/H₂O (v/v = 9/1) HEPES buffer solutions at pH = 7.2 and 524 nm.



Scheme 1 Synthesis of the sensor molecule **Y**.



Scheme 2 A possible sensing mechanism of the sensor **Y** to Zn^{2+} .

chelation with the zinc ion, $-\text{HC}=\text{N}-$ isomerization and ESIPT might be inhibited, leading to enhanced fluorescence.

To further investigate the sensing properties of **Y**, fluorimetric titration of **Y** was performed with the Zn^{2+} ion. As shown in Fig. 2, the emission intensity of **Y** at 524 nm steadily increased until the amount of Zn^{2+} reached 2.6 equiv. The Job plot⁴⁷ showed a 1:1 complexation stoichiometry between Zn^{2+} and **Y** (Fig. S3, ESI[†]), which was further confirmed by ¹H NMR titration analysis (Fig. S4, ESI[†]). Based on the Job plot analysis, we propose the structure of the Zn^{2+} -**Y** complex, as shown in Scheme 2. From the fluorescence titration data, the association constant for Zn^{2+} -**Y** complexation was determined to be $2.4 \times 10^5 \text{ M}^{-2}$ from Li's equations.⁴⁸ Meanwhile, the fluorescence quantum yield (Φ) increases from 0.2 to 0.87.^{49,50} These results indicate that the pincer-type chemosensor **Y** reacts with Zn^{2+} to form a complex. In the corresponding UV-vis spectra, after adding Zn^{2+} to **Y**, the maximum absorption peak red shifts obviously, which also supports our conjecture (Fig. S5, ESI[†]).

The detection limit of **Y** for Zn^{2+} calculated on the basis of $3s_B/s^{51}$ (Fig. S6, ESI[†]) is $1.39 \times 10^{-8} \text{ M}$ for fluorescence spectra, which is far lower than the WHO guidelines for drinking water (76 mM).^{52,53} Meanwhile, the fluorimetric detection limit of Zn^{2+} by the naked eye for sensor **Y** was also tested. As is shown in Fig. 3, the minimum concentration of Zn^{2+} for fluorescence color change under an UV lamp at 360 nm observed by the naked eye is $2.0 \times 10^{-6} \text{ M}$.

To further check the practical applicability of receptor **Y** as a Zn^{2+} -selective fluorescent sensor, we carried out competition experiments. **Y** was treated with 10 equiv. of Zn^{2+} in the presence of other metal ions (Fe^{3+} , Hg^{2+} , Ag^+ , Ca^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Cd^{3+} , Pb^{2+} , Cr^{3+} , Mg^{2+}) of the same concentration. As shown in Fig. S7 (ESI[†]), other background metal ions had little or no obvious interference with the detection of Zn^{2+} ions, except for Cu^{2+} , Fe^{3+} and Hg^{2+} , after a long time.

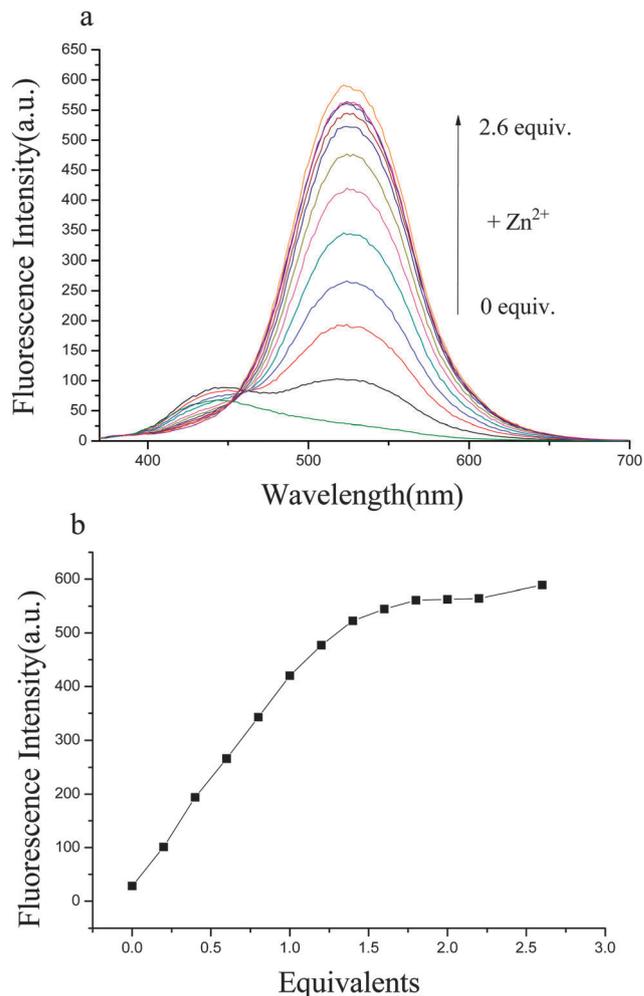


Fig. 2 (a) Fluorescence spectral changes of **Y** ($c = 2 \times 10^{-5} \text{ M}$) in the presence of different concentrations of Zn^{2+} ions in DMSO/ H_2O ($v/v = 9/1$) HEPES buffer solutions at $\text{pH} = 7.2$. (b) Fluorescence intensity at 524 nm versus the number of equiv. of Zn^{2+} added.

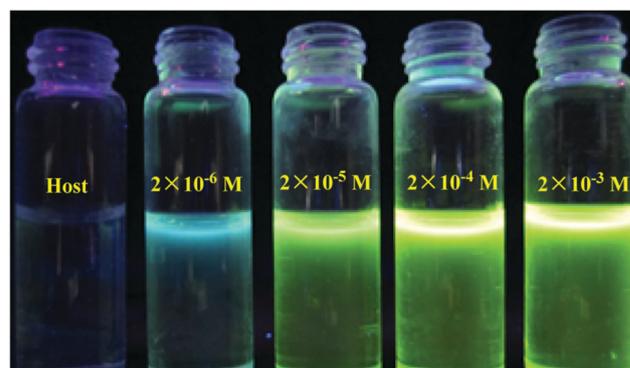


Fig. 3 Naked-eye detection limit under an UV lamp at 365 nm. From left to right, the concentration of Zn^{2+} is $2.0 \times 10^{-6} \text{ mol L}^{-1}$, $2.0 \times 10^{-5} \text{ mol L}^{-1}$, $2.0 \times 10^{-4} \text{ mol L}^{-1}$, and $2.0 \times 10^{-3} \text{ mol L}^{-1}$.

However, it is worth noting that cadmium ions hardly inhibited the fluorescence intensity of the Zn^{2+} -**Y** complex. Hence, these results suggest that **Y** could be a good sensor for Zn^{2+} and in

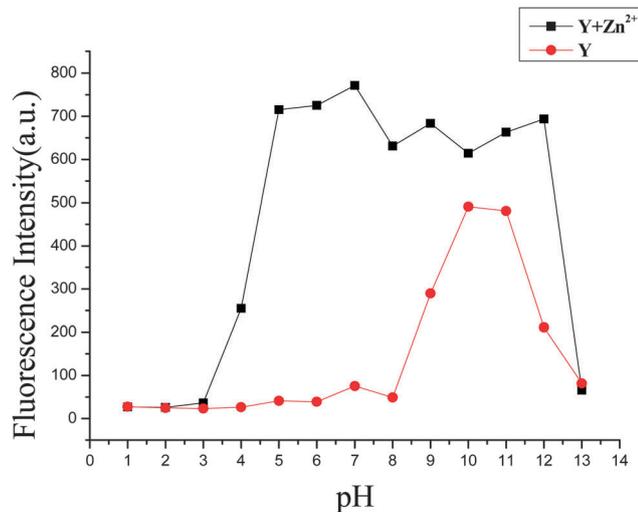


Fig. 4 pH value affects the charge distribution of receptor **Y** and **Y + Zn²⁺**.

particular, distinguish Zn^{2+} from Cd^{2+} , which have many common properties.⁵⁴

Since the pH value affects the charge distribution of receptor **Y** and may change its inherent fluorescence properties, the effect of pH on the emission bands of **Y** in DMSO/H₂O (*v/v* = 9/1) HEPES buffer solution at pH = 7.2 was also studied (Fig. 4). The Zn^{2+} -**Y** complex showed a significant fluorescence response between pH 5 and 8, which includes the physiologically relevant range of pH 7.0–8.4.⁵⁵ These results indicate that Zn^{2+} could be clearly detected by the fluorescence spectral measurement using **Y** within the physiological pH range (pH = 7.0–8.4).

To further examine the binding mode of **Y** with Zn^{2+} , we performed ¹H NMR titrations in DMSO-*d*₆ (Fig. S4, ESI[†]). Upon addition of 0.1 equiv. of Zn^{2+} , protons of the hydroxyl (H1) started to disappear, and protons of hydrazone (H2, H3) were downshifted. At 1.0 equiv. of Zn^{2+} , H1 was deprotonated, and H3 took the proton transfer from 10.70 ppm to 5.78 ppm. This indicated that Zn^{2+} coordinated with the -O- of hydroxyl and -N- of hydrazone. Importantly, the proton of one pyridine (H16) underwent a tiny chemical shift, and another pyridine (H14) underwent no obvious chemical shift, indicating that only one of the two pyridine groups participates in the coordination process. Therefore, the ¹H NMR titration results support the structure of a 1 : 1 complex of **Y** and Zn^{2+} proposed by the Job plot analysis. Furthermore, in the IR spectra (Fig. S8, ESI[†]), the peak at 3422 cm⁻¹ (O-H) disappeared, which also supports this inference.

Fig. 5 reveals the reversibility of Zn^{2+} (**Y + Zn²⁺**) binding to **Y** (EDTA). This process was repeated several times without a large loss in the emission intensity. The switching was probably caused by the EDTA reduction of Zn^{2+} to [EDTA + Zn^{2+}]²⁻ to regenerate **Y**.

Motivated by the favorable features of sensor **Y** in solution, we prepared test strips by immersing filter papers (3 × 1 cm²) into the DMSO/H₂O (*v/v* = 9/1) HEPES buffer solution at pH = 7.2 of sensor **Y** (*c* = 1 × 10⁻³ M), and then dried them in air to

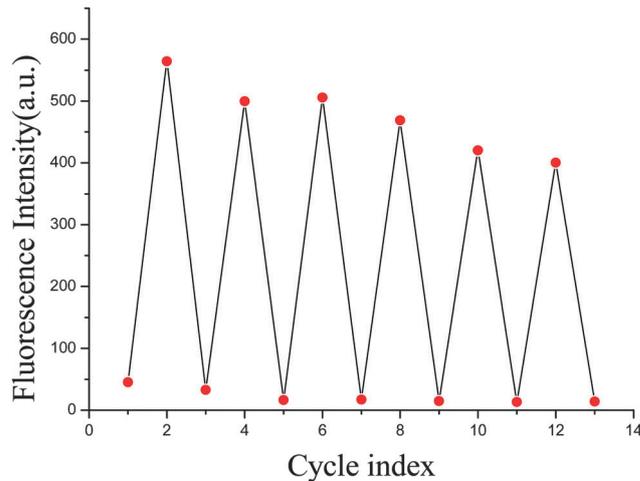


Fig. 5 Stepwise complexation–decomplexation cycles carried out in DMSO/H₂O (*v/v* = 9/1). Emission intensity changes at 524 nm of **Y** upon addition of 10 equiv. Zn^{2+} before and after treatment of 10 equiv. EDTA.

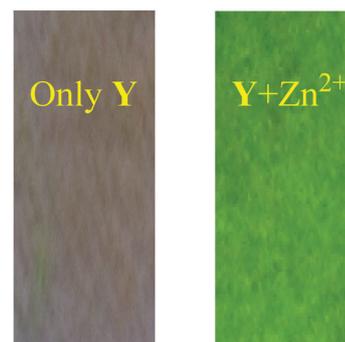


Fig. 6 Fluorescence change of the test strips of **Y** (*c* = 1 × 10⁻³ M) with Zn^{2+} in DMSO/H₂O (*v/v* = 9/1) HEPES buffer solution at pH = 7.2, under irradiation at 365 nm.

determine the suitability of a 'dip-stick' method for the detection of Zn^{2+} , similar to that commonly used for pH measurement. When the test strips coated with **Y** (*c* = 1 × 10⁻³ M) were immersed into the pure water solutions of Zn^{2+} , obvious Kelly fluorescence appeared (Fig. 6). The development of such a 'dip-stick' approach is extremely attractive for 'in-the-field' measurements that do not require any additional equipment. Therefore, the test strips of **Y** have excellent application value in the detection of Zn^{2+} .

As is well known, typical chemosensors always have the problem of long response time. In our case, the detection course of Zn^{2+} using **Y** was found to be relatively faster (Fig. 7). After adding the zinc ion, the fluorescence emission intensity of **Y** increased at 524 nm and reached the plateau region in less than 15 seconds, then remained quite stable, suggesting that the entire process of recognition might be completed instantly, and the chemosensor has rapid detection ability. Meanwhile, when the water ratio increased, the response time did not change a lot, and all reactions were completed within less than 1 min (Fig. S9, ESI[†]).

All the above changes indicated that the pyridine derivative-based, bis-schiff-base pincer-type **Y** can selectively detect Zn^{2+}

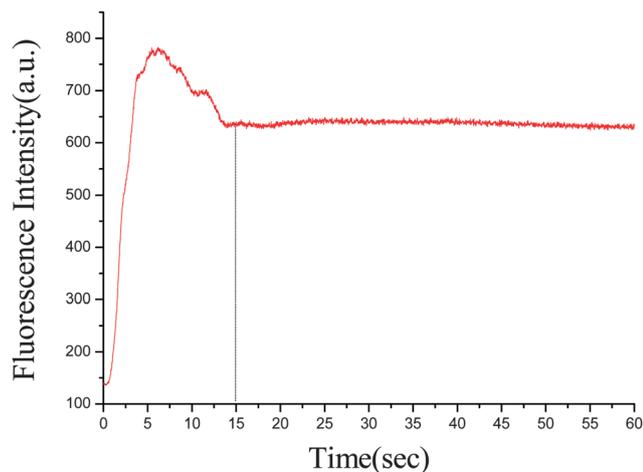


Fig. 7 Fluorescence intensity at 524 nm for **Y** ($c = 2.0 \times 10^{-5}$ M) in a mixture of DMSO/H₂O ($v/v = 9/1$) HEPES buffer solution at pH = 7.2 after the addition of 10 equivalents of Zn²⁺ ($c = 4 \times 10^{-3}$ M).

in DMSO/H₂O ($v/v = 9/1$) HEPES buffer solution at pH = 7.2. Meanwhile, this process leads to the fluorescence performance from the OFF state to the ON state due to blocking of the ESIPT process to identify Zn²⁺ (Scheme 2).

Conclusions

We have synthesized a pincer-type fluorescence sensor based on the combination of 4-hydroxyisophthalaldehyde and 2-hydra-zinylpyridine. The receptor **Y** exhibited a fluorescence enhancement upon binding to Zn²⁺ in aqueous solution of physiological pH range due to the combined effects of the inhibition of ESIPT and -HC=N- isomerization, as well as chelation-enhanced fluorescence (CHEF). The binding of the receptor **Y** and Zn²⁺ was also utilized in test strip form for convenience. Moreover, **Y** can be recycled, and the minimum detection limit of **Y** for zinc reaches 1.39×10^{-8} M.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (NSFC) (No. 21064006; 21161018; 21262032), the Natural Science Foundation of Gansu Province (1308RJZA221) and the Program for Changjiang Scholars and innovative Research Team at University of Ministry of Education of China (IRT1177).

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