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

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**Abstract**: 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 fluorescent groups and hydrazone bond as a recognition site. The selectivity mechanism of **Y** for zinc is based on a combinational effect of the inhibition of excited-state intramolecular proton transfer (ESIPT) and -HC=N- isomerization, and chelation-enhanced fluorescence. All process takes less than 15 seconds. The minimum detection limit **Y** to zinc could reach $1.39\times10^{-8}$ M. Moreover, **Y** can conveniently detect zinc in test form and can be used recycling.

**Keywords:** zinc iron, turn-on fluorescence, ESIPT, physiological range, recycling

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## Introduction

Development of chemical probes for the sensing of 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 structural cofactors of many $Zn^{2+}$ 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 $Zn^{2+}$. 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 instrumentations, tedious sample preparation procedures, and trained operators. By contrast, fluorescence technology provides a convenient and an easy monitoring of the target ions. [32-35] Detection methods using fluorescence have, therefore, attracted considerable attention in the detection of metal ions or anions, including $Zn^{2+}$. Recently, simple chemosensors have become very popular among the 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 has pincer-type with both hydrazone and an imine functional group. Our approach to design this fluorescence based bi-functional chemosensor relies on the strong coordination capability of a hydrazone-based to metal ions. Receptor **Y** showed a reversible intense fluorescence enhancement in the presence of zinc ions in physiological range pH aqueous solution. Additionally, **Y** could also conveniently detect $Zn^{2+}$ in its test strips.

**Experimental section**

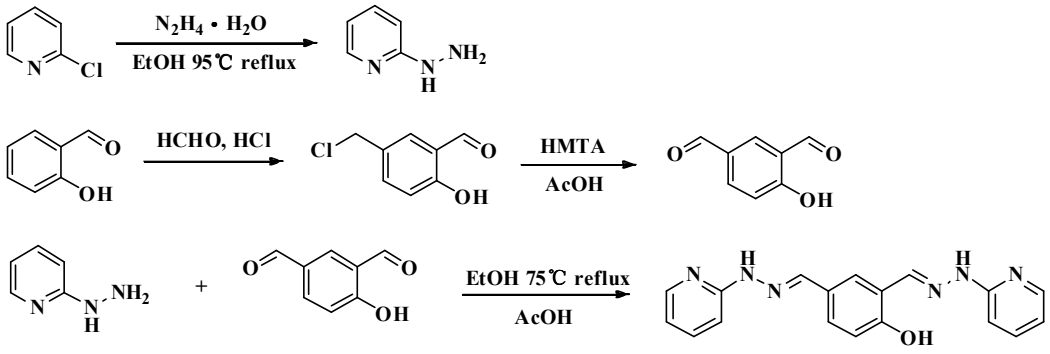
*Materials and physical methods*

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. $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on a Mercury-400BB spectrometer at 400 MHz for $^{1}H$. The chemical shifts are 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 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***

The compound **Y** can be readily prepared by a simple and lowcost 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℃). $^1$H 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**) IR (KBr) ν: 1622 cm$^{-1}$ (-HC=N-), 3422 cm$^{-1}$ (N-H). (**Fig. S8**) ESI-MS calcd for $[C_{18}H_{16}N_6O+H^+]^+$ 333.3592. Found 333.1727. (**Fig. S2**)




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

*General procedure for spectroscopy*

All the UV-vis experiments were carried out in a 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 ($2.0 \times 10^{-5}$ M) in all experiments. The perchlorate salts of $Fe^{3+}$, $Hg^{2+}$, $Ca^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Cr^{3+}$, and $Mg^{2+}$ 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 ($2.0 \times 10^{-5}$ M) in all experiments.

The perchlorate salts of the ions ($Fe^{3+}$, $Hg^{2+}$, $Ca^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Cr^{3+}$, and $Mg^{2+}$) were used for the fluorescence experiments. For $^1$H NMR titrations, the solution of **Y** was prepared in DMSO-$d_6$ and the appropriate concentrated solution of guest 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 $Zn^{2+}$ ions

To gain an insight into the fluorescent properties of receptor **Y** toward metal ions, the emission changes were measured with various metal ions in DMSO/$H_2O$ (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 $Zn^{2+}$. By contrast, upon addition of other metal ions such as $Fe^{3+}$, $Hg^{2+}$, $Ag^{+}$, $Ca^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$,

$Cd^{2+}$, $Pb^{2+}$, $Cr^{3+}$ and $Mg^{2+}$, either no or a slight increase in intensity was observed (**Fig. 1**). To this end, it is noteworthy that, **Y** can act as a ''turn-on'' sensor for $Zn^{2+}$ and differentiate $Zn^{2+}$ from $Cd^{2+}$, which had been a major problem almost always in the past. [40-43] This preferential fluorescence enhancement for $Zn^{2+}$ might be due to the formation of a chelate complex (rigid system) between **Y** and the $Zn^{2+}$ ion, leading to the chelation-enhanced fluorescence (CHEF) effect. [44] Additionally, receptor **Y** is a poor fluorescent due to the combined effects: (a) isomerization of the -HC=N- double bonds in the excited state [45] and (b) excited-state intramolecular proton transfer (ESIPT), involving the hydroxy proton of the 4-hydroxyisophthalaldehyde moiety (**Scheme 2**). [46] Upon stable chelation with the zinc ion, the -HC=N- isomerization and ESIPT might be inhibited, leading to a fluorescence enhancement.

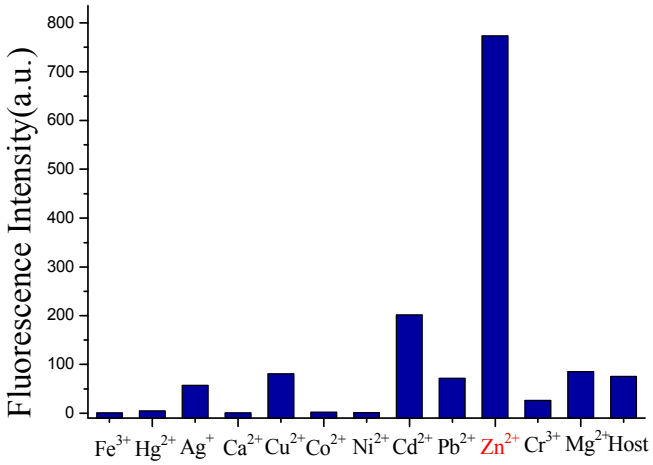
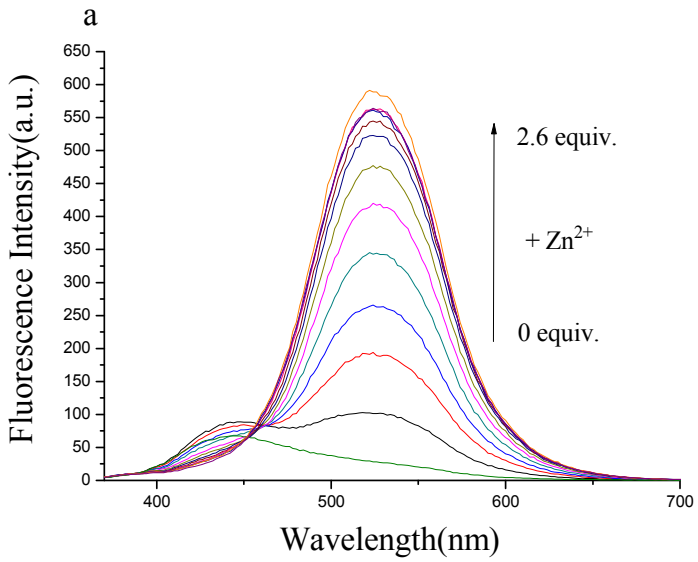



**Fig. 1** Bar graph shows the relative emission intensity of **Y** (c= $2\times10^{-5}$ M) in the presence of different metal ions (10 equiv.) such as $Fe^{3+}$, $Hg^{2+}$, $Ag^{+}$, $Ca^{2+}$, $Cu^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Cr^{3+}$ and $Mg^{2+}$ with an excitation of 355 nm in DMSO/$H_2O$ (v/v = 9/1) HEPES buffer solutions at pH = 7.2 of **Y** at 524 nm.

To further investigate the sensing properties of **Y**, a 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 plot [47] showed a 1 : 1 complexation stoichiometry between $Zn^{2+}$ and **Y** (**Fig. S3**), which was further confirmed by $^{1}H$ NMR titration analysis (**Fig. S4**). 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 $2.4 \times 10^{5}$ $M^{-2}$ from Li's equations. [48] Meanwhile, the fluorescence quantum yields (Φ) increase from 0.2 to 0.87. [49-50] These results indicate that pincer-type chemosensor **Y** reacts with $Zn^{2+}$ to form a complex. And in the UV-vis spectra corresponding, after adding $Zn^{2+}$ to **Y**, the maximum absorption peak red shift obviously, it is also supporting our conjecture. (**Fig. S5**)



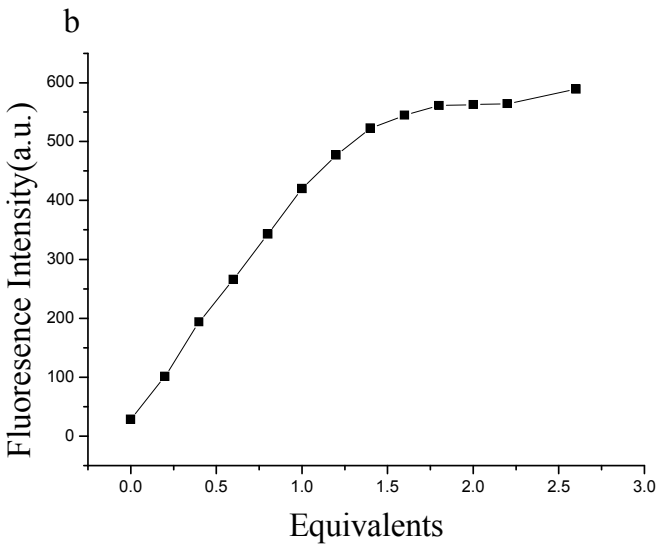



**Fig. 2** (a) Fluorescence spectral changes of **Y** (c= $2\times10^{-5}$ M) in the presence of different concentrations of $Zn^{2+}$ ions in DMSO/$H_2O$ (v/v = 9/1) HEPES buffer solutions at pH = 7.2. (b) Fluorescence intensity at 524 nm versus the number of equiv. of $Zn^{2+}$ added.

The detection limits of the **Y** for $Zn^{2+}$ calculated on the basis of $3s_B/S$ [51] (**Fig. S6**) were $1.39\times10^{-8}$ M for fluorescences spectra which is far lower than the WHO guidelines for drinking water (76 mM). [52-53] Meanwhile, the fluorimetric detection limits by naked-eyes of sensor **Y** for $Zn^{2+}$ were 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 was $2.0\times10^{-6}$ M.

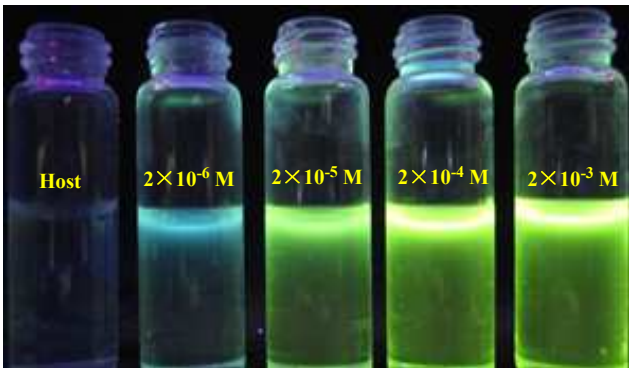


**Fig. 3.** Naked-eye detection limit under an UV-lamp at 365 nm. From left to right the concentration of $Zn^{2+}$ is $2.0\times10^{-6}$ mol/L, $2.0\times10^{-5}$ mol/L, $2.0\times10^{-4}$ mol/L, $2.0\times10^{-3}$ mol/L.

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**, other background metal ions had small or no obvious interference with the detection of $Zn^{2+}$ ions, except for $Cu^{2+}$, $Fe^{3+}$ and $Hg^{2+}$ in long time. 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 particular, distinguish $Zn^{2+}$ from $Cd^{2+}$ both having many common properties.[54]

Since the pH value affects the charge distribution of receptor **Y** or may change its inherent fluorescence properties, the effect of pH on the emission bands of **Y** in DMSO/$H_2O$ (v/v=9/1) HEPES buffer solution 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 physiological 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).

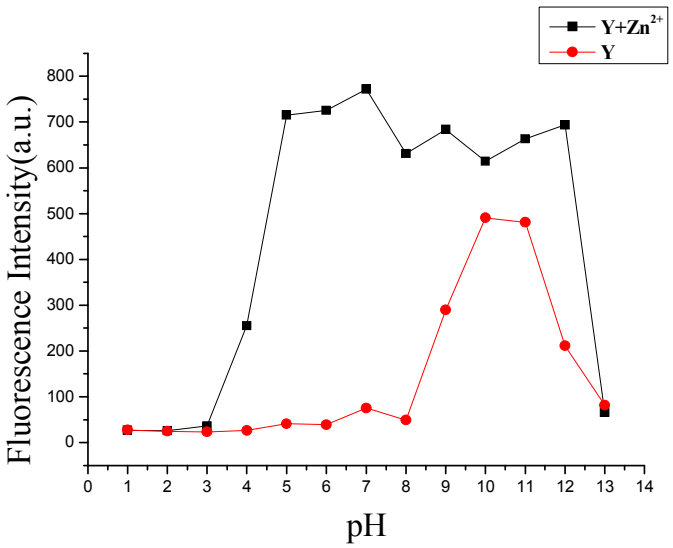



**Fig. 4** pH value affects the charge distribution of receptor **Y** and **Y**+$Zn^{2+}$.

In order to further examine the binding mode of **Y** with $Zn^{2+}$, we have performed $^1$H NMR titrations in DMSO-$d_6$ (**Fig. S4**). Upon addition of 0.1 equiv. of $Zn^{2+}$, the protons of hydroxyl (H1) was disappearing, protons of hydrazone (H2, H3) were downshifted. Start from 1.0 equiv. of $Zn^{2+}$, H1 deprotonation, H3 take the proton transfer from 10.70 ppm to 5.78 ppm. That indicated that $Zn^{2+}$ coordinated with –O: of hydroxyl, -N: of hydrazine respectively. Importantly, the proton of one pyridine (H16) underwent a tiny chemical shift change, and another one pyridine (H14) underwent no obvious chemical shift, it indicates that only one of two pyridine group participates in the coordination procession. Therefore, the $^1$H NMR titration results support the structure of a 1 : 1 complex of **Y** and $Zn^{2+}$ proposed by the Job plot analysis. And in IR spectra (**Fig. S8**), peak at 3422 $cm^{-1}$ (O-H) disappeared also illustrate the inferring.

Besides, **Fig. 5** revealed the reversibility of $Zn^{2+}$ (**Y** + $Zn^{2+}$) binding to **Y** (EDTA). This process was repeated several times without large loss of the emission intensity.

The switching was probably caused by the EDTA reduction of $Zn^{2+}$ to [EDTA+ $Zn^{2+}$]$^{2+}$ to regenerate **Y.**

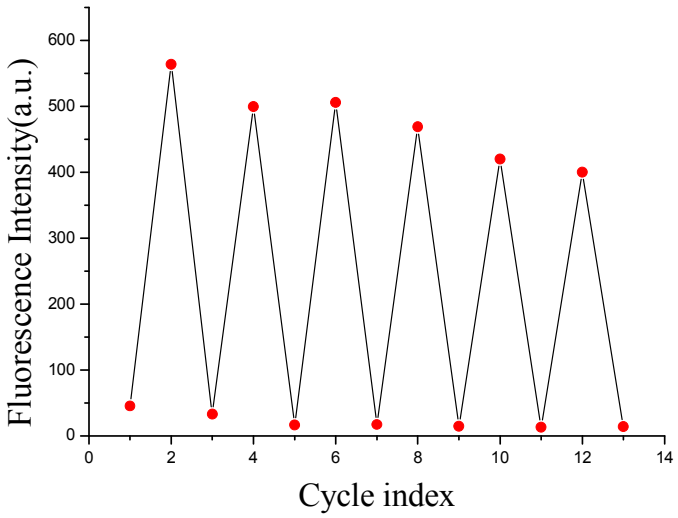



**Fig. 5.** Stepwise complexation/decomplexation cycles carried out in DMSO/$H_2O$ (v/v =9/1). Emission intensity changes at 524 nm of **Y** upon addition of 10 equiv. $Zn^{2+}$ before and after treatment of 10 equiv. EDTA.

Motivated by the favorable features of sensor **Y** in solution, we prepared test strips by immersing filter papers (3 × 1 $cm^2$) into the DMSO/$H_2O$ (v/v = 9/1) HEPES buffer solutions at pH = 7.2 of sensor **Y** (c=1 × $10^{-3}$ M) and then dried them in air to determine the suitability of a ‘dip-stick’ method for the detection of $Zn^{2+}$, similar to that commonly used for the pH measurement. When the test strips coated with **Y** (c=1 × $10^{-3}$ M) were immersed into the pure water solutions of $Zn^{2+}$, the obvious Kelly fluorescence appeared (**Fig. 6**). The development of such a ‘dip-sticks’ approach was extremely attractive for ‘in-the-field’ measurements that did not require any additional equipment. Therefore, the test strips of **Y** have excellent application value in the

detection of $Zn^{2+}$.

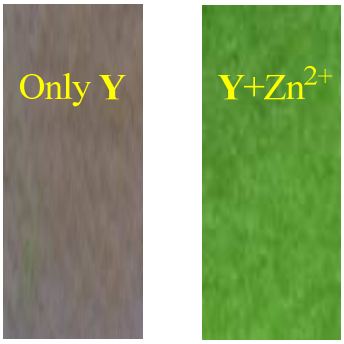



**Fig. 6** Fluorescence change of the test strips of **Y** (c=1 × $10^{-3}$ M) with $Zn^{2+}$ in DMSO/$H_2O$ (v/v = 9/1) HEPES buffer solutions at pH = 7.2 under irradiation at 365 nm.

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

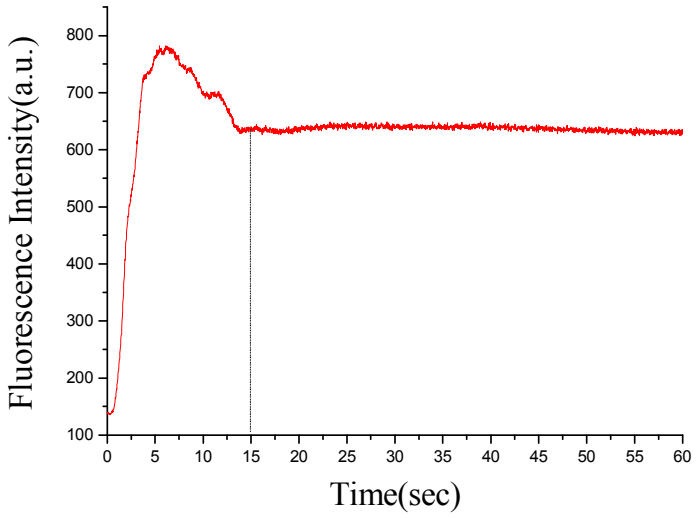
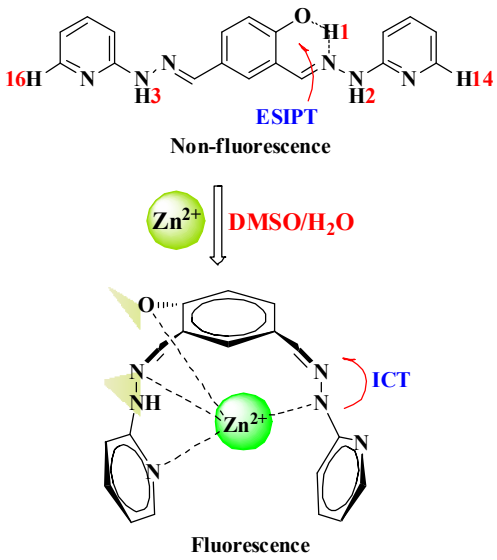



**Fig. 7.** Fluorescence intensity at 524 nm for **Y** ($c=2.0\times10^{-5}$ M) in a mixture of DMSO/$H_2O$ (v/v=9/1) solution pH=7.2 buffer system of HEPES after addition of 10 equivalents of $Zn^{2+}$ ($c=4\times10^{-3}$ M).

All above these changes indicated that pyridine derivative-based of bis-schiff-base pincer-type **Y** can specific selective detection of $Zn^{2+}$ in DMSO/$H_2O$ (v/v = 9/1) HEPES buffer solutions at pH = 7.2. Meanwhile, this process leads to the fluorescence performance from the OFF state to ON state due to blocking the ESIPT process to identify $Zn^{2+}$. (**Scheme 2**)




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

## Conclusions

We have synthesized a pincer-type fluorescence sensor based on the combination of 4-hydroxyisophthalaldehyde and 2-hydrazinylpyridine. The receptor **Y** exhibited a fluorescence enhancement upon binding to $Zn^{2+}$ in physiological pH range aqueous solution due to a combinational effect of the inhibition of ESIPT and -HC=N- isomerization and the chelation-enhanced fluorescence (CHEF) effect. The binding of the receptor **Y** and $Zn^{2+}$ was also made as test-strips for convenience. Moreover, it can be used recycling and the minimum detection limit **Y** to zinc could reach $1.39\times10^{-8}$ M.

## Acknowledgements

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