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PII:	\$1386-1425(16)30725-9
DOI:	doi: 10.1016/j.saa.2016.12.009
Reference:	SAA 14822

To appear in:

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

Received date:27 July 2016Revised date:7 December 2016Accepted date:12 December 2016

Please cite this article as: Jing-Han Hu, You Sun, Jing Qi, Qiao Li, Tai-Bao Wei , A new unsymmetrical azine derivative based on coumarin group as dual-modal sensor for CN- and fluorescent "OFF–ON" for Zn2+. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Saa(2016), doi: 10.1016/j.saa.2016.12.009

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#### A new unsymmetrical azine derivative based on coumarin group

#### as dual-modal sensor for CN<sup>-</sup> and fluorescent "OFF–ON" for

 $Zn^{2+}$ 

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#### **Abstract:**

A simple chemosensor **YS** based on coumarin group was designed and synthesized. Its structure was determined by single crystal X-ray diffraction analysis. In the presence of cyanide the sensor showed an immediate visible change in color from colorless to pale yellow by naked-eyes and produced a strong blue fluorescence rapidly in DMSO/H<sub>2</sub>O (3:7, v/v). The detection limit on fluorescence response of the sensor to  $CN^-$  is down to  $1.69 \times 10^{-7}$  M. In addition **YS** could show fluorescence turnon response rapidly for Zn<sup>2+</sup> over other metals ions such as Fe<sup>3+</sup>, Hg<sup>2+</sup>, Ag<sup>+</sup>, Ca<sup>2+</sup>,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Cr^{3+}$  and  $Mg^{2+}$  in aqueous solutions. Notably, this sensor served as a molecular switch, which was controlled by Zn<sup>2+</sup> and EDTA cyclically. Test strips based on **YS** were fabricated, which could act as a convenient and efficient  $CN^-$  and  $Zn^{2+}$  test kit. This chemosensor could achieve the detection of two ions, which need not depend on two different sensors.

**Keywords**: Chemosensor; Coumarin; CN<sup>-</sup>; Zn<sup>2+</sup>; DFT calculations.

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#### **1. Introduction**

Metals and anions both play important roles in daily life [1-3]. If eating some food by mistake such as cassavas and the kernels of apricot, the toxicity may directly lead to the death of human. The cyanide which is inhaled into living organisms could disrupt the mitochondrial electron-transport chain, further cause the decreased oxidative metabolism and oxygen utilization [4-7]. Even if the cyanide is so dangerous, they also have widespread use in the synthesis processes of a large amount of industrial products, such as nitriles, nylon, and fertilizers, as well as electroplating industry [8-11]. And zinc ion as the second most abundant transition-metal ion often involve in a variety of physiological and pathological processes for example gene expression, enzyme regulation, and catalytic function of protein [12-13]. Its most important applications in industry are producing zinc alloy and as a protective layer of other metals. Eating some toys surface containing zinc for a long time may lead to poisoning, which have emesis, diarrhea and other gastrointestinal symptoms. In other words, limited quantities of zinc are necessary for the living organism however excessive amounts may damage the life entity. [14-15] Thus, more enthusiastic has been sparked in exploring efficient methods that can selectively, sensitively and rapidly detect  $CN^{-}$  and  $Zn^{2+}$ .

At present, optical sensors which have a color or fluorescence change show a lot of merits, such as low cost, rapid response, convenience, high sensitivity and potential application [16-18]. As far as we known, the combination modes of host– $CN^-$  usually include these types: hydrogen boding interaction, deprotonation, addition reaction, coordination and so on [19-22]. Among these methods, deprotonation as a simple mechanism utilizing acidity of HCN are widely used in detection for  $CN^-$ . In recent years, more and more fluorescent sensors for  $Zn^{2+}$  are also reported, but they often

have interference problems from other metal ions or low water solubility [23-30]. At present, the sensors for single ion already could not satisfy demand. Hence the convenient, even multi-objects recognized sensors have become particularly imperative [31-33].

Our research group has a longstanding interest in molecular recognition [34-37]. Furthermore, there are few literatures about simultaneously detecting  $CN^{-}$  and  $Zn^{2+}$ . Herein, we designed and synthesized an unsymmetrical azine derivative chemosensor (**YS**) for respective recognition of  $CN^{-}$  and  $Zn^{2+}$ . Sensor **YS** showed blue fluorescent and UV-vis selectivity for  $CN^-$  in DMSO/H<sub>2</sub>O (3:7, v/v) binary solution over other anions based on a simple deprotonated mechanism. The detection limit of the probe for the cyanide anion was below the ppm level, which was much lower than the permitted limit of cyanide anions. And in the presence of  $Zn^{2+}$ , sensor **YS** showed a green fluorescence response at  $\lambda_{max} = 510$  nm. The coumarin group was introduced as fluorophore to achieve fluorescent recognition. Differently from the previous reports, here, we considered whether recyclable project could be achieved by adding of the EDTA to affect the intramolecular charge of the molecular and induce fluorescence color changes. In addition, compared with other reported sensors for  $CN^{-}$  and  $Zn^{2+}$  in the table (In SI), the sensor **YS** as a simple and inexpensive compound had preferable sensitivity and water solubility, it was worth mentioning that YS could achieve the detection of two ions in different mix-aqueous solution. So the compound YS could be used as a potential optical sensor for  $CN^{-}$  and  $Zn^{2+}$  ions. At the same time, the mechanism of this process was verified by spectroscopic methods including <sup>1</sup>H NMR, UV-vis, and mass spectrometry.

#### 2. Experimental

#### 2.1. Materials and physical methods

All reagents and solvents were commercially available at analytical grade without further purification. Double–distilled water was purified by standard methods and was used throughout the experiment. Tetrabutylammonium salt of anions ( $F^-$ ,  $CI^-$ ,  $Br^-$ ,  $\Gamma^-$ ,  $AcO^-$ ,  $H_2PO_4^-$ ,  $HSO_4^-$ , and  $CIO_4^-$ ), perchlorate salt of cations ( $Fe^{3+}$ ,  $Hg^{2+}$ ,  $Ag^+$ ,  $Ca^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Cr^{3+}$  and  $Mg^{2+}$ ), sodium salt of anions ( $CN^-$  and  $SCN^-$ ) and HEPES were purchased from Alfa-Aesar Chemical Reagent Co. and stored in a vacuum desiccator.

Melting points were measured on an X–4 digital melting-point apparatus. The infrared spectra were performed on a Digilab FTS–3000 FT–IR spectrophotometer. <sup>1</sup>H NMR and <sup>12</sup>C NMR were recorded on a Mercury–400BB at 400 MHz spectra. For <sup>1</sup>H NMR titrations, the sensor of stock solutions was prepared in DMSO– $d_6$ , the cyanide and zinc ions were prepared in D<sub>2</sub>O. Aliquots of the two solutions were mixed directly in NMR tubes. Electrospray ionization mass spectra (ESI–MS) were measured on an Agilent 1100 LC–MSD–Trap–VL system. UV–vis spectra were recorded on a Shimadzu UV–2550 spectrometer. Photoluminescence spectra were performed on a Shimadzu RF–5301 fluorescence spectrophotometer. The structure of sensor **YS** was further confirmed by single–crystal X–ray diffraction.

#### 2.2. Synthesis of sensor molecule YS

The synthesis route of probe molecule **YS** is demonstrated in Scheme 1. 4– methyl–7–hydroxy–8–formyl–coumarin (0.41 g, 2 mmol), salicylaldehyde hydrazone (0.28 g, 2 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 h. After cooling to room temperature, the yellow precipitate was filtered, washed three times with hot absolute ethanol, then recrystallized with EtOH to obtain a yellowy powdered product **YS** in 82% yield. (m.p. 248–250°C). <sup>1</sup>H NMR (DMSO– $d_6$ , 400 MHz)  $\delta$ : 12.55 (s, 1H,

OH),  $\delta$ : 10.88 (s, 1H, OH),  $\delta$ : 9.30 (s, 1H, CH=N),  $\delta$ : 9.08 (s, 1H, CH=N),  $\delta$ : 6.29~7.82 (m, 7H, ArH),  $\delta$ : 2.51 (t, 3H, CH<sub>3</sub>) (Fig. S1); ESI–MS calcd for  $[C_{18}H_{15}N_2O_4 + H^+]^+$  323.32. Found 323.109. (Fig. S2) IR (KBr, cm<sup>-1</sup>) v: 3446.78, 2926.01, 1730.14, 1622.13, 1292.31, 1082.06, 758.02 (Fig. S3). The structure of sensor **YS** was further confirmed by single–crystal X–ray diffraction (Fig. 1).



Scheme 1 Synthesis of the sensor molecule YS.



Fig. 1 Single-crystal X-ray structure of sensor YS.

#### 3. Results and Discussion

#### 3.1 Sensing CN<sup>-</sup>

UV–vis absorption and fluorescence emission spectral response of chemosensor **YS** were tested with the anions ( $F^-$ ,  $CI^-$ ,  $Br^-$ ,  $I^-$ ,  $AcO^-$ ,  $H_2PO_4^-$ ,  $HSO_4^-$ ,  $CIO_4^-$ ,  $CN^-$  and SCN<sup>-</sup>) in DMSO/H<sub>2</sub>O (3:7, v/v) solutions. Only after addition of CN<sup>-</sup>, the

solution of **YS** resulted in an immediate change in color from colorless to pale yellow. In the corresponding UV–vis spectrum, a strong absorption band at 310 nm disappeared, while a new band developed at 372 nm (Fig. 2). All examined anions ( $F^-$ ,  $C\Gamma^-$ ,  $Br^-$ ,  $\Gamma^-$ ,  $AcO^-$ ,  $H_2PO_4^-$ ,  $HSO_4^-$ ,  $CIO_4^-$ , and  $SCN^-$ ) did not cause any obvious color and spectral changes. These results suggested that sensor **YS** displayed an excellent selectivity for  $CN^-$  over all other anions tested.

Compound **YS** alone displayed a weak, single fluorescence emission band at 430 nm when excited at 375 nm in DMSO/H<sub>2</sub>O (3:7, v/v). Changes in spectral pattern were observed only in the presence of added 50 equiv. of CN<sup>-</sup>, chemosensor **YS** produced a strong fluorescence response band and shifted toward 447 nm, and responded with a dramatic color change from colorless to blue. No change in spectral pattern for receptor **YS** in the presence of other anions suggested either a very weak or no interaction between these anions and the compound (Fig. 3).



**Fig. 2** UV–vis spectra changes of **YS** ( $2 \times 10^{-5}$  M) and in the presence of 50 equiv. of various anions in DMSO/H<sub>2</sub>O (3:7, v/v) binary solution at room temperature. Inset: Color changes observed upon the addition of various anions (50 equiv.) to solutions of sensor **YS** ( $2 \times 10^{-5}$  M) in DMSO/H<sub>2</sub>O (3:7, v/v) solutions.



**Fig. 3** Fluorescence spectra of **YS** ( $2 \times 10^{-5}$  M) and in the presence of 50 equiv. of various anions in DMSO/H<sub>2</sub>O (3:7, v/v) binary solution at room temperature. Inset: Color changes observed upon the addition of various anions (50 equiv.) to solutions of sensor **YS** ( $2 \times 10^{-5}$  M) in DMSO/H<sub>2</sub>O (3:7, v/v) solutions under a UV–lamp.



Fig. 4 (a) UV-vis spectra of **YS** (5.0  $\mu$ M) in response to CN<sup>-</sup> (0.0 to 22.4 equiv.) in DMSO/H<sub>2</sub>O (3:7, v/v) (b) Absorption of **YS** (2.0×10<sup>-5</sup> M) at 372 nm after adding of various anions.

The absorption spectral changes of **YS** on addition of cyanide (0.01 M) in DMSO/H<sub>2</sub>O (3:7, v/v) solutions were shown in Fig. 4a. The absorption band at 310 nm decreased, while a new band at 372 nm appeared. A clear isosbestic point at 356 nm indicated an interconversion into single discrete chemical species during the titration process. To validate the selectivity of sensor **YS**–CN<sup>-</sup>, the some tests were carried out using for other anions including  $F^-$ ,  $C\Gamma^-$ ,  $Br^-$ ,  $\Gamma^-$ ,  $AcO^-$ ,  $H_2PO_4^-$ ,  $HSO_4^-$ ,

 $ClO_4^-$ , and  $SCN^-$ . The presence of only those anions caused no change in UV–vis spectrum. However, in the presence of  $CN^-$  and the respectively competitive anions above described, the absorbance changes were similar to that in the presence of only  $CN^-$ . (Fig. 4b)

As shown in Fig. 5a, without  $CN^-$ , the sensor had almost no fluorescence, while the significant increase of the fluorescence intensity of the solution was observed at 447 nm upon gradual addition of  $CN^-$ . In addition, the interfering anions also did not influence the fluorescence spectrum. (Fig. 5b) These results indicated that **YS** was a highly selective  $CN^-$  sensor and had good antijamming capability.



**Fig. 5** (a) Fluorescence of **YS** in the presence of different concentration  $CN^-$  (0.0 to 6.7 equiv.) in DMSO/H<sub>2</sub>O (3:7, v/v) (b) Fluorescence of **YS** (2.0×10<sup>-5</sup> M) at 372 nm after adding of various anions.

In order to apply in real life, it was very necessary to detect the analytes at low concentrations. The detection limit of the fluorescence spectra measurements, was calculated on the basis of  $3S_B/S$  (where  $S_B$  is the standard deviation of the blank solution and S is the slope of the calibration curve), Fig. 6 showed the detection limit of  $1.69 \times 10^{-7}$  M for CN<sup>-</sup>, which was far lower than the maximum level for cyanide of  $1.9 \times 10^{-6}$  M in drinking water from WHO guidelines. Meanwhile, the fluorescence quantum yields increased from 0.27 to 0.76. (In SI)



**Fig. 6** Fluorescence detection limit spectra of **YS** ( $2 \times 10^{-5}$  M) in DMSO/H<sub>2</sub>O (3:7, v/v) solutions upon adding of a concentration of CN<sup>-</sup> ( $1 \times 10^{-3}$  M).

For practical applicability, the fluorescence spectra of the solution of **YS** at different pH in the absence and presence of  $CN^-$  were recorded. As shown in Fig. S4, without  $CN^-$ , the fluorescence of the solution of **YS** had no obvious change in the pH range 2–13. However, upon addition of  $CN^-$ , it could work well from 7 to 11.

According to <sup>1</sup>H NMR titration experiments were conducted to further investigate the interaction of **YS** with  $CN^-$  in DMSO-*d*<sub>6</sub>, as shown in Fig. 8. When 1.0 equiv.  $CN^-$  was added, the signal of  $-OH^1$  (coumarin rings) and  $-OH^2$  (benzene rings) respectively at 12.55 (s, 1H) and 10.88 (s, 1H) ppm had completely disappeared, which stated clearly the -OH had deprotonation process and the other aromatic ring proton signals gradually shifted to upfield due to the shielding effect. Therefore, <sup>1</sup>H NMR titration experiments suggested that the validity of the mechanism submitted and the cause of the fluorescence enhancement presented.

This deprotonation process caused a high charge separation between acceptor and donor unit in **YS**, and consequently excellent electron delocalization to salicylaldehyde hydrazone unit. The excited states in the complexes were stabilized upon the binding of  $CN^-$ , resulting in a bathochromic shift in the absorption band with Dl = 60 nm for **YS**. Moreover, a new emission band at 533 nm for **YS** and  $CN^-$  was

observed. It possibly caused by a large charge separation between salicylaldehyde hydrazone unit and the coumarin rings resulting in a strong intramolecular charge transfer (ICT). Consequently, the observed fluorescence enhancement is most likely caused by the ICT. A schematic illustration was shown in Scheme 2. [38]



**Fig. 7** <sup>1</sup>H NMR titration in DMSO- $d_6$  upon addition of varying amounts CN<sup>-</sup>.



Scheme 2 The proposed reaction mechanism.

Generally, reaction-based chemosensors suffered from a long response time. In our case, the response of **YS** to  $CN^-$  was found to be very fast (Fig. 8). After addition of a solution of  $CN^-$ , the fluorescence emission intensity of **YS** in DMSO/H<sub>2</sub>O (3:7, v/v) solutions at 447 nm increased rapidly and reached a plateau in about 30 s. This

result suggested that the recognition profiles of sensor YS with  $CN^-$  was completed nearly instantly, so that  $CN^-$  ions were detected rapidly.



**Fig. 8** Fluorescence intensity of a solution of **YS**  $(2 \times 10^{-5} \text{ M})$  in DMSO/H<sub>2</sub>O (3:7, v/v) solutions at 446 nm after addition of 50 equivalents CN<sup>-</sup>.

The realization of quick response to cyanide is quite meaningful for the sensor in its practical application in portable sensing devices. To facilitate the use of **YS** for the detection of cyanide, test strips were prepared by immersing filter papers into a DMSO/H<sub>2</sub>O binary solution of **YS** (0.01 M) following by exposing it to air to dry it. Intriguingly, the fluorescence color can be changed immediately from purple to mazarine once the test paper was immersed into an aqueous solution (5  $\square$ M) of cyanide under UV irradiation (Fig. 9). Thereby, chemosensor **YS** exhibited excellent fluorescence sensing performance, which will be very useful for the fabrication of sensing devices with fast and convenient detection for cyanide and ions.



**Fig. 9** Photographs of **YS** (0.01 M) on test strips (a) only **YS**, (b) after immersion into water solutions with  $CN^{-}$ , (c) after immersion into water solutions with other anions,

(d) after immersion into water solutions with CN<sup>-</sup> and other anions under UV light respectively.

#### 3.2 Sensing Zn<sup>2+</sup>

To evaluate recognition studies of **YS**, Fe<sup>3+</sup>, Hg<sup>2+</sup>, Ag<sup>+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Cr<sup>3+</sup> and Mg<sup>2+</sup> ions were used to measure the selectivity and sensitivity of probe **YS** (20  $\mu$ M) in DMSO/H<sub>2</sub>O (pH=7.2, v/v=7:3) HEPES buffer solutions, and fluorescence spectra were recorded upon the addition of 20 equiv. of each of these metal ions. Only in the presence of Zn<sup>2+</sup>, sensor **YS** showed a strong fluorescence response at  $\lambda_{max} = 510$  nm, which responded with a dramatic color change from colourless to green by the naked eyes under the UV–lamp (365 nm) as shown in Fig. 10.



**Fig. 10** Fluorescence emission data of **YS** (20µM) and different metal ions in DMSO/H<sub>2</sub>O (pH=7.2, v/v=7:3) HEPES buffer solutions. ( $\lambda_{ex} = 475$  nm). Inset: Visual fluorescence emissions of sensor **YS** after the addition of Zn<sup>2+</sup>, Fe<sup>3+</sup>, Hg<sup>2+</sup>, Ag<sup>+</sup>, Ca<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cr<sup>3+</sup> and Mg<sup>2+</sup> (20 equiv.) in DMSO/H<sub>2</sub>O (pH=7.2, v/v=7:3) HEPES buffer solutions under the UV–lamp(365 nm).

To validate the selectivity of **YS**, the same tests were carried out using  $Fe^{3+}$ ,  $Hg^{2+}$ ,  $Ag^+$ ,  $Ca^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Cr^{3+}$  and  $Mg^{2+}$  metal ions. None of these ions induced any significant changes in the fluorescence spectrum of the sensor. The

selectivity of **YS** for zinc ion over other metal ions was examined. Therefore, it was clear that all potentially competitive metal ions exerted no or little influence on the fluorescence detection of zinc ion in DMSO/H<sub>2</sub>O (pH=7.2, v/v=7:3) HEPES buffer solutions (Fig. 11).

![](_page_13_Figure_2.jpeg)

**Fig. 11** Fluorescence emission data of **YS** and different metal ions in DMSO/H<sub>2</sub>O (pH=7.2, v/v=7:3) HEPES buffer solutions (excitation wavelength = 475 nm).

To further investigate the interaction between **YS** and zinc ion, the fluorescence emission spectral variation of **YS** in DMSO/H<sub>2</sub>O (pH=7.2, v/v=7:3) HEPES buffer solutions was monitored during titrations with different concentrations of zinc ions from 0.0 to 8.4 equivalents (Fig. 12a). The binding constant  $K_a$  was determined to be  $2.91 \times 10^3 \text{ M}^{-1/2}$ . Meanwhile, the fluorescence quantum yields increased from 0.27 to 0.63. (In SI)

The detection limit is one of the most important parameters in ion sensing. For many practical purposes, it is very important to detect the analytes at low concentrations. The fluorimetric detection limits of sensor **YS** for  $Zn^{2+}$  were also determined. As shown in Fig. S5, the minimum concentration of  $Zn^{2+}$  that could be

observed though one order of magnitude lower for fluorescence naked eye detection was  $2.0 \times 10^{-5}$  M by using a UV lamp at 365 nm. In the meantime, the detection limit of the fluorescence spectra measurements, as calculated on the basis of  $3s_B/S$  (where  $s_B$  is the standard deviation of the blank solution and S is the slope of the calibration curve), Fig. 12b showed a detection limit of approximately  $6.1 \times 10^{-8}$  M for  $Zn^{2+}$ . Thus, **YS** can be applied to detect  $Zn^{2+}$  at an extremely low concentration level.

![](_page_14_Figure_2.jpeg)

**Fig. 12** (a) Fluorescence spectra of **YS-**Zn<sup>2+</sup> in the presence of different concentration of zinc ions (0.0–8.4 equiv.) in DMSO/H<sub>2</sub>O (pH=7.2, v/v=7:3) HEPES buffer solutions. (b) Fluorescent detection limit spectra of **YS** ( $2.0 \times 10^{-5}$  M) in DMSO/H<sub>2</sub>O (pH=7.2, v/v=7:3) HEPES buffer solutions upon adding of an increasing concentration of Zn<sup>2+</sup>.

With the  $Zn^{2+}$  concentration increasing, the fluorescent intensity remarkably increased at 510 nm. In order to gain an insight into the stoichiometry of the complex, the method of continuous variations was used as shown in Fig. 13. As expected, when the molar fraction of sensor **YS**-Zn<sup>2+</sup> was 0.35, the value approached a maximum, which revealed the possible formation of a 1:2 complex between the sensor Zn<sup>2+</sup> and **YS**.

![](_page_15_Figure_1.jpeg)

**Fig. 13** Job plot of **YS** and  $Zn^{2+}$ , which indicated that the stoichiometry of **YS**- $Zn^{2+}$  complex was 1:2.

The pH dependence in aqueous media was examined using fluorescence emission spectroscopy (Fig. S6). Free **YS** was insensitive against H<sup>+</sup> and OH<sup>-</sup>. And when  $Zn^{2+}$  was added to the buffered solution of **YS** at different pH values, the results indicated that **YS** binding with  $Zn^{2+}$  occurred effectively in the range of pH = 7–12.In order to investigate the reversibility of **YS**, the addition of  $Zn^{2+}$  to the solution of sensor **YS** lead to fluorescence increasing. By addition of EDTA to the solution of **YS**–Zn<sup>2+</sup> complex, the emission intensity of **YS** diminishes. This "Off–On–Off" switching process could be repeated at several times with little fluorescent efficiency loss (Fig. 14).

![](_page_15_Figure_4.jpeg)

Fig. 14 Fluorescence study showing reversibility of  $Zn^{2+}$  coordination to **YS** by EDTA.

Generally, reaction-based chemosensors suffer from a long response time. In our case, the response of **YpriS** to  $Zn^{2+}$  was found to be very fast (Fig. S7). After addition of a solution of  $Zn^{2+}$ , the fluorescence emission intensity of **YS** in DMSO/H<sub>2</sub>O (pH=7.2, v/v=7:3) HEPES buffer solutions at 510 nm increased rapidly and reached a plateau in about 15 s. This result suggested that the recognition profiles of sensor **YS** with  $Zn^{2+}$  was completed nearly instantly, so that  $Zn^{2+}$  ions were detected rapidly.

In order to further validate the conjugation of **YS**–Zn<sup>2+</sup>, we did <sup>1</sup>H–NMR titration experiments As shown in Fig. 15, after adding 2.0 equivalents of zinc ions, the single  $-OH^1$  of coumarin group peak at 12.55 ppm decreased and gradually disappeared, due to binding to electron deficient Zn<sup>2+</sup>. Another hydroxyl proton peak (10.88 ppm) was gradually shifted downfield due to the addition of Zn<sup>2+</sup> destroying the intramolecular hydrogen bonding, which was leading to electron density decreased. The two proton peaks at 9.30 and 9.08 ppm corresponded to the protons of CH=N showed upfield shift. In addition, the aryl protons also had different changes in chemical shift.

![](_page_16_Figure_3.jpeg)

**Fig. 15** <sup>1</sup>H NMR titration in DMSO- $d_6$  upon addition of varying amounts  $Zn^{2+}$ .

In the ESI-MS spectra of **YS**–Zn<sup>2+</sup> complex, we found a new peak appeared at 707.08, which coincides well with that for the species  $[Zn^{2+}+2$  **YS** -H]<sup>+</sup> (m/z calcd. 707.11). A Job plot also indicated that Zn<sup>2+</sup> and **YS** ion form 1:2 adduct. Based on the above findings, we proposed that the reaction mechanism in this system may proceed through the route depicted in Scheme 3. The existence of hydrogen bonding blocked intramolecular energy transfer, which was leading to host molecule could not show fluorescence. Upon addition of Zn<sup>2+</sup>, the chelation of heteroatom with Zn<sup>2+</sup> resulted in the efficient inhibition for the PET process of the C=N group. As a result, YS-Zn<sup>2+</sup> showed strong fluorescence. [39-40]

![](_page_17_Figure_2.jpeg)

Scheme 3 Proposed mechanism for detection of  $Zn^{2+}$  by **YS**.

To facilitate the use of **YS** for the detection of zinc, test strips were prepared by immersing filter papers into a DMSO/H<sub>2</sub>O binary solution of **YS** (0.01 M) followed by exposure to air until complete drying. Intriguingly, the fluorescence color could be changed immediately from purple to grass green once the test paper was immersed into an aqueous solution (5  $\mu$ M) of Zn<sup>2+</sup> under UV-vis irradiation (Fig. 16). Thereby the sensor **YS** exhibited excellent fluorescence sensing performance, which would be very useful for the fabrication of sensing devices with fast and convenient detection for Zn<sup>2+</sup>.

![](_page_18_Picture_1.jpeg)

Fig. 16 Photographs of YS (0.01 M) on test strips (a) only YS under UV light, (b) after immersion into water solutions with  $Zn^{2+}$  under UV light, (c) after immersion into water solutions with other anions under UV light, (d) after immersion into water solution with  $Zn^{2+}$  and other ions under UV light.

#### **3.3 Theoretical calculations**

Further to confirm the proposed mechanism of sensor **YS** with  $CN^-$  and  $Zn^{2+}$ , we performed DFT calculations done at the B3LYP/6-311g (2d, p) level of theory. [41-42] The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of **YS** and the **YS**- $CN^-$  complex were investigated and shown in Fig. 17. Obviously, the HOMO–LUMO energy band gap of **YS** was 93.74 kcal/mol. it was higher than that of **YS**- $CN^-$  complex (87.48 kcal/mol), which caused the red–shift in the absorption band of **YS**. The presence of  $Zn^{2+}$  ions in compound **YS** caused the change of electron density. And the HOMO–LUMO energy band gap of **YS** was also higher than that of **YS**- $Zn^{2+}$  complex (80.78 kcal/mol). These calculations results were consistent with the experimental results.

![](_page_18_Figure_5.jpeg)

Fig. 17 Density functional theory computed diagrams of LUMOs, HOMOs and energy gaps of YS and YS–CN<sup>-</sup>, blue ball is nitrogen, grey ball is carbon, red ball both are oxygen and white ball is hydrogen.

![](_page_19_Figure_2.jpeg)

Fig. 18 Density functional theory computed diagrams of LUMOs, HOMOs and energy gaps of YS and YS– $Zn^{2+}$ , blue ball is nitrogen, grey ball is carbon, pink or red ball both are oxygen and white ball is hydrogen.

#### 4. Conclusion

In conclusion, we have presented a facile, rapid and efficient chemosensor **YS**, which could recognize CN and  $Zn^{2+}$  with different fluorescence changes and different mechanisms. Moreover, the detection limit on fluorescence response of the sensor to CN<sup>-</sup> is down to  $1.69 \times 10^{-7}$  M, which is far lower than the WHO guideline of  $1.9 \times 10^{-6}$  M. According to Job's plot and ESI-MS, binding stoichiometry of metal/ligand complex was found by fluorescence method as 2:1. In addition, test strips based on **YS** were fabricated, which could serve as a practical colorimetric and fluorimetric sensor to detect CN<sup>-</sup> and fluorescent "OFF–ON" for Zn<sup>2+</sup>. We believe this work provides an underlying applications for constructing a fluorescent sensor for highly selective and rapidly recognition of CN<sup>-</sup> and Zn<sup>2+</sup> ions based on different mechanisms respectively in aqueous.

#### Acknowledgment

This work was supported by the National Nature Science Foundation of China (no. 21467012).

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K CERTER MANUSCRIPT

### A new unsymmetrical azine derivative based on coumarin

### group as dual-modal sensor for CN<sup>-</sup> and fluorescent "OFF-

## **ON**" for Zn<sup>2+</sup> in aqueous media

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**Graphical abstract:** In this work, an unsymmetrical azine derivative chemosensor (**YS**) for respective recognition of  $CN^-$  and  $Zn^{2+}$  was designed and synthesized. Sensor **YS** exhibited high sensitivity and good selectivity for cyanide and zinc in aqueous solution.

![](_page_24_Figure_7.jpeg)

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#### Highlights

1. A structurally simple sensor could achieve the detection of two ions in aqueous solution.

2. This sensor was successfully applied to detect  $CN^-$  by dual-modal and showed fluorescence turn-on response rapidly for  $Zn^{2+}$  in aqueous solution.

3. Taking advantage of a simple mechanism of deprotonation.

4. Test strips based on **YS** were fabricated, which could act as a convenient and efficient  $CN^{-}$  and  $Zn^{2+}$  test kit.

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