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## A Ratiometric Tetrazolylpyridine-Based "Turn-On" Fluorescent Chemosensor for Zinc(II) Ion in Aqueous Media

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The highly selective ratiometric "turn-on" fluorescent sensing of  $Zn^{2+}$  ion involving 2-(1*H*-tetrazole-5-yl)pyridine (**2PT**) in aqueous medium is reported, which is not observed when other metal ions are present. Upon **2PT** binding selectively with  $Zn^{2+}$  ion, a fluorescence enhancement is observed that is

Introduction

Zinc, an essential trace element, is the second most abundant metal in the human body<sup>[1]</sup> that plays a vital role in numerous biological processes, such as peptide synthesis, DNA synthesis, RNA transcription,<sup>[2]</sup> metabolism of cells, metalloenzyme regulation, and neurophysiology, and it also induces the formation of  $\beta$ -amyloid, which is related to neurological function. More than 100 enzymes, such as peptidases,<sup>[3]</sup> carbonic anhydrases,<sup>[4]</sup> and alcohol dehydrogenases,<sup>[5]</sup> require zinc for their catalytic activity.<sup>[6]</sup> Labile zinc is found in the cells of mammalian brain, pancreas, and prostate. Zinc and its compounds are widely used in various industries, such as electroplating, rubber, dye, wood preservatives, ointments, batteries, paint, and pharmaceuticals.<sup>[7]</sup>

Uncontrolled release of zinc from mossy fiber terminals causes brain injury, stroke, or neuronal death.<sup>[8]</sup> Studies show that a lack of zinc in the body causes prostate cancer, diabetes, Alzheimer's disease,<sup>[9]</sup> night blindness,<sup>[10]</sup> growth retardation, and skin lesions, and affects gene expression and enzyme activity.<sup>[11]</sup> Thus, in view of its biological relevance and importance, a selective sensor for the monitoring of zinc is essential.

Although there are several analyses available to detect zinc ion, such as atomic absorption spectrometry (AAS),<sup>[12]</sup> inductively coupled plasma mass spectrometry,<sup>[13]</sup> and voltammetry,<sup>[14]</sup> they are all expensive and time-consuming. Recently, many zinc sensors have been developed using the quinolone

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attributed to an enhancement of localized emission and suppression of excited-state intramolecular proton transfer. The described sensing system involving **2PT** is also successfully applied to the detection of Zn<sup>2+</sup> ion in real samples with a detection limit of  $7.5 \times 10^{-7}$  m.

moiety,<sup>[15]</sup> cyclam,<sup>[16]</sup> Znpyr,<sup>[17]</sup> Schiff base,<sup>[18]</sup> thiophene-based moieties,<sup>[19]</sup> pyrazoline and pyrazole moieties,<sup>[20]</sup> and rhodamine-based moieties.<sup>[21]</sup> However, construction of selective and ratiometric sensors for  $Zn^{2+}$  remains in high demand. Thus considerable attention has been focused on developing simple, inexpensive, ratiometric, "turn-on" sensors for  $Zn^{2+}$  selective determination. Also, understanding the biological and environmental roles of  $Zn^{2+}$  requires robust and versatile methods for quantification. The goal has been to devise "turn-on" fluorescent sensors for  $Zn^{2+}$ . However, these turn-on signals are insufficient for quantification.<sup>[22]</sup> An alternative approach involves developing sensors that display a change in the ratio of multiple emission bands, thus providing quantification rescent sensors for zinc were available recently.<sup>[23]</sup>

Our interest in developing chemosensors for biologically important cations,<sup>[24]</sup> anions,<sup>[25]</sup> and neutral molecules<sup>[26]</sup> prompted us to develop a simple ratiometric fluorescence chemosensor involving 2-(1*H*-tetrazole-5-yl)pyridine (**2PT**) for the selective sensing of Zn<sup>2+</sup>, which involves excited-state intramolecular proton transfer (ESIPT). Though several ESIPT sensors for Zn<sup>2+</sup> have been reported,<sup>[27]</sup> the present system is very simple and is employed in aqueous medium.

#### **Results and Discussion**

#### Synthesis and characterization of the probe

Compounds **2PT** and 4-(1*H*-tetrazole-5-yl)pyridine (**4PT**) were prepared by following the literature procedure<sup>[28]</sup> using picolinonitrile and sodium azide in the presence of  $ZnCl_2$  as a catalyst (Scheme 1), and the products were characterized by NMR spectroscopy (Figures S1–S4 in the Supporting Information) and ESI-MS (Figures S5 and S6). As  $ZnCl_2$  is used as a catalyst during the synthesis of the probe, care is taken to remove it completely from the reaction mixture and the synthesized **2PT** 



Scheme 1. Synthesis of 2PT and 4PT.

is also analyzed by AAS for the absence of  $Zn^{2+}$ . The UV/Vis spectrum of **2PT** shows absorptions at 274 and 232 nm (Figure S7). The emission spectra show two emission peaks for **2PT** at 331 and 381 nm when excited at 275 nm (Figure S8), which are ascribable to localized emission (331 nm) and ESIPT emission (381 nm).<sup>[29]</sup>

#### Zn<sup>2+</sup> ion sensing studies

Compound **2PT** contains pyridine and tetrazole nitrogen atoms, so it will provide a good platform for binding metal ions. To study the cation binding ability of **2PT**, fluorescence titrations were performed with various cations, such as Li<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Hg<sup>2+</sup>, in aqueous medium. Figure 1 shows that, except for the Zn<sup>2+</sup> ion, all the other metal ions show poor response.



Figure 1. Emission spectra of 2PT  $(5 \times 10^{-5} \text{ mol L}^{-1})$  in the presence of  $Zn^{2+}$  and various other metal ions, such as Li<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Hg<sup>2+</sup>  $(5 \times 10^{-5} \text{ mol L}^{-1})$ .

Upon addition of  $Zn^{2+}$  ion, the peak at 379 nm decreased in intensity and the peak at 331 nm exhibited increased intensity with a slight blueshift to 327 nm with an isoemissive point at 376 nm. This observation was ascribed to the formation of a five-membered ring complex between **2PT** and  $Zn^{2+}$ , which was further confirmed by ESI-MS.

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#### Fluorescence titration of 2PT with Zn<sup>2+</sup>

To find out the sensitivity of  $Zn^{2+}$  detection, the concentration of  $Zn^{2+}$  was increased from 0 to  $1 \times 10^{-5}$  M. The fluorescence intensity increased linearly with an increase in the concentration of  $Zn^{2+}$  from 0 to  $1 \times 10^{-5}$  M (Figure 2). The value of the linearly dependent coefficient ( $R^2$ ) was found to be 0.997 and the limit of detection was  $7.5 \times 10^{-7}$  mol L<sup>-1</sup> ( $3.3 \sigma$  slope<sup>-1</sup>).<sup>[30]</sup> An isoemissive point appeared at 376 nm, which indicates that only a 1:1 complex was formed in fluorescence titration. The binding constant value was found to be  $1.392 \times 10^5$  m<sup>-1</sup>, which indicates strong binding between **2PT** and  $Zn^{2+}$ .



**Figure 2.** Fluorescence emission spectra of **2PT** ( $5 \times 10^{-5} \text{ mol L}^{-1}$ ) upon addition of 0 to  $1 \times 10^{-5} \text{ m Zn}^{2+}$  ( $\lambda_{ex} = 275 \text{ nm}$ ,  $\lambda_{em} = 327$  and 379 nm; blueshift 331 to 326 nm). Isoemissive point = 376 nm. Inset: linear increase in fluorescence intensity with increasing concentration of  $\text{Zn}^{2+}$ .

The binding between **2PT** and  $Zn^{2+}$  is also confirmed by the Job's plot and ESI-MS. The complex formation is in good agreement with a 1:1 stoichiometry by Job's plot from the emission data (Figure S9). In ESI-MS, for **2PT** an *m*/*z* value was observed at 146.19 (**2PT**-H). When 1.0 equivalent of  $Zn^{2+}$  is added, a new peak appears at *m*/*z* 281.97 indicating formation of a  $Zn^{2+}$ –**2PT** complex (**2PT** +  $ZnCI_2$ –H; Figure 3).

#### Competitive binding study of 2PT

To investigate the efficiency of **2PT** in detecting Zn<sup>2+</sup>, a competitive assay was performed in the presence of other cations. The binding behavior investigation of **2PT** towards different cations (Li<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Hg<sup>2+</sup>) was investigated by fluorescence spectroscopy (Figure 4). Interestingly, **2PT** senses Zn<sup>2+</sup> selectively even though other metal ions are present in the mixture, and a similar result is also observed in the literature.<sup>[31]</sup> On the addition of paramagnetic metals, such as Co<sup>2+</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup>, significant fluorescence quenching was observed. This is a result of the quenching pathway involving low-lying d–d states<sup>[32]</sup> in the Co<sup>2+</sup>, Ni<sup>2+</sup>, and Cu<sup>2+</sup> and also the energy transfer from the



Figure 3. ESI-MS spectrum of 2PT with  $Zn^{2+}$  (2PT +  $ZnCl_2$ -H).



**Figure 4.** Bar chart showing the fluorescence selectivity of **2PT**  $(5 \times 10^{-5} \text{ mol L}^{-1})$  towards  $Zn^{2+}$  in the presence of other metal ions  $(5 \times 10^{-5} \text{ mol L}^{-1})$ . The red bars represent the fluorescence intensity of **2PT** in the presence of one equivalent of other metal ions. The green bars represent the fluorescence intensity of one equivalent of **2PT** containing one equivalent of other metal ions and  $Zn^{2+}$  ions.

photoexcited state of the ligand to the empty d orbital of the metals.<sup>[33]</sup> This finding indicates that the  $Zn^{2+}$ -dependent fluorescence response of **2PT** is not affected by the presence of other metal ions.

#### NMR titration

The interaction of **2PT** with  $Zn^{2+}$  was also analyzed by <sup>1</sup>H NMR spectroscopy to ascertain the binding between **2PT** and  $Zn^{2+}$ . Significant chemical shift changes were observed for protons a, b, and c of **2PT** in its <sup>1</sup>H NMR spectra (all deshielded, which is indicative of binding between **2PT** and  $Zn^{2+}$ ) while adding  $Zn^{2+}$ , which is shown in Figure 5.

# Cyclic voltammetric studies of 2PT

The selectivity for  $Zn^{2+}$  was further confirmed by cyclic voltammetric study of **2PT** (5×  $10^{-5}$  mol L<sup>-1</sup>) with various metal ions, such as Li<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Hg<sup>2+</sup> (5×  $10^{-5}$  mol L<sup>-1</sup>). Figure 6shows that only in the presence of Zn<sup>2+</sup> ion does the reduction peak current increase and with other metal

ions no significant changes are observed, which indicates that **2PT** binds strongly with  $Zn^{2+}$  ion (5×10<sup>-5</sup> mol L<sup>-1</sup>).

#### Effect of pH

As the influence of pH on the probe is very important for biological applications, in the present study it is noted that effective binding is observed at pH 6–7. At low pH values, the binding of  $Zn^{2+}$  is decreased owing to the competitive binding between H<sup>+</sup> and  $Zn^{2+}$ . When the pH was increased beyond 7, a negligible effect was observed on the fluorescence intensity. The fact that the probe operates effectively in the pH range



Figure 5. <sup>1</sup>H NMR spectra of 2PT with one equivalent of  $Zn^{2+}$  in  $[D_6]DMSO$ .

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**Figure 6.** Cyclic voltammetric profile of **2PT** ( $5 \times 10^{-5} \text{ mol L}^{-1}$ ) with various metal ions ( $5 \times 10^{-5} \text{ mol L}^{-1}$ ), with platinum as working electrode and counter electrode, Ag/AgCl in 3 m NaCl as reference electrode, and 0.1 m KCl as electrolyte. Scan rate: 100 mV. Potential range: -1 to +1 V.

around 6–7 indicates that it is suitable for biological applications.

#### Mechanism of Zn<sup>2+</sup> selective sensing

The remarkable fluorescence enhancement in the localized emission (LE) band is attributed to the complexation of **2PT** with  $Zn^{2+}$ . According to Pearson's hard and soft acids and bases theory,  $Zn^{2+}$  (a borderline acid) can interact preferentially with pyridine nitrogen atoms (a borderline base) in both pyridine and tetrazole rings of **2PT**. In the absence of  $Zn^{2+}$ , an excited-state intramolecular hydrogen atom transfer between the tetrazole N–H and N atom of the pyridyl ring occurs (ESIPT). Upon  $Zn^{2+}$  binding with **2PT**, ESIPT is suppressed with a concomitant increase in the LE band of **2PT**, which is aided by the planarity of the  $Zn^{2+}$ –**2PT** complex (Figure 7).

The above mechanism is further supported by using **4PT** as a probe. In the case of **4PT**, no change in fluorescence is observed upon addition of metal ions (Figure S11). This study supports the finding that the N atoms of the pyridyl ring and the tetrazole ring are responsible for the complexation of **2PT** with  $Zn^{2+}$ .



Figure 7. Illustration of the sensing mechanism of  $Zn^{2+}$  detection.

#### Theoretical calculation

The geometries of the sensor **2PT** and of **2PT** with  $Zn^{2+}$  ion were optimized using DFT at the B3LYP/6-31G and B3LYP/LANL2D(d) levels, respectively, by using the Gaussian 03 package.<sup>[34]</sup> The optimized geometries of **2PT** and its 1:1 complex with  $Zn^{2+}$  are given in Figure 8.



Figure 8. Proposed optimized geometries of 2PT and 2PT with Zn<sup>2+</sup>.

In the HOMO and LUMO of the energy level diagram of **2PT**, the electron densities are distributed over the 2-pyridyl moiety in the HOMO and the tetrazolyl moiety in the LUMO (Figure 9). Upon binding of  $Zn^{2+}$  with **2PT**, the electron density distributed over the 2-pyridyl moiety still has the HOMO character whereas the  $Zn^{2+}$  has the LUMO character. This observation strongly supports the proposed mechanism.



Figure 9. Frontier molecular orbitals optimized at the B3LYP/LANL2DZ(d) level of theory.

The present method for  $Zn^{2+}$  detection is very sensitive and selective, and comparable to other methods reported earlier (Table 1).

#### Real sample analysis

To evaluate the practical applicability of probe **2PT** to real samples, analysis was performed for the detection of  $Zn^{2+}$  in well water and drinking water, which

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<b>Table 1.</b> Comparison of the <b>2PT</b> probe with reported sensor systems for Zn <sup>2+</sup> detection.			
Sensing probe	Method	Limit of detection	

		actection	
8-aminoquinoline-functionalized silica nanoparticle	fluorescence	0.1 μм	[35]
microfabricated bismuth electrodes	electrochemical	6 μм	[14]
pyrazole and pyrazoline	fluorescence	0.24 μм	[20]
solid-state ion-selective electrode based on polypyrrole conducting polymer nanofilm	potentiometric	1.0×10 <sup>-5</sup> м	[36]
phenylbenzoxazole-amide-cyclen linkage as a ratiometric fluorescent receptor	fluorescence	0.6 µм	[23]
click-functionalized poly(p-phenylene ethynylene)s	fluorescence	1 μм	[37]
tripodal zinc sensor	fluorescence	3.2 μм	[23b]
ordered mesoporous silica material (MCM-41) functionalized with	fluorescence	0.1 μм	[38]
N-(quinolin-8-yl)-2-[3-(triethoxysilyl)propylamino]acetamide			
di- and tripyrrins	fluorescence	2.7×10 <sup>-7</sup> м	[39]
cyclam-based "clickates"	fluorescence	75 μм	[40]
click-generated cyclam-based zinc(II) sensor	fluorescence	2 μм	[41]
porphyrin-based sensor	fluorescence	1.8 μм	[42]
2PT	fluorescence	7.5×10 <sup>-7</sup> м	this study

Table 2. Results of $Zn^{2+}$ sensing in drinking water and well water.							
Sample	$Zn^{2+}$ spiked [µм L <sup>-1</sup> ]	$Zn^{2+}$ found [µм L <sup>-1</sup> ]	Recovery [%]				
Well water							
1	0	-	-				
2	100	$100.2^{[a]} \!\pm\! 0.43^{[b]}$	101.5				
3	200	$200.1^{[a]}\!\pm\!0.30^{[b]}$	101.3				
Drinking water							
1	0	-	-				
2	100	$100.7^{[a]} \pm 0.21^{[b]}$	101				
3	200	$200.6^{[a]}\!\pm\!0.14^{[b]}$	99				
[a] Mean values of three determinations. [b] Related standard deviation.							

was collected from our campus. To remove the insoluble materials, the collected water sample was filtered. All the samples with or without addition of  $Zn^{2+}$  ion concentrations of 100 or 200  $\mu$ m were analyzed with **2PT**. The observed results are shown in Table 2, which also includes recovery data. These prove the practicality of the reported probe **2PT** for the detection of  $Zn^{2+}$  in real water samples without any interference from other metal ions.

## Conclusion

We have reported 2-(1*H*-tetrazole-5-yl)pyridine (**2PT**) as a simple, ratiometric, selective, and rapid "turn-on" chemosensor for  $Zn^{2+}$  ion based on an excited-state intramolecular proton transfer mechanism at the micromolar level in aqueous medium. Compound **2PT** shows selectivity toward  $Zn^{2+}$  in the presence of other metal ions, such as Li<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Hg<sup>2+</sup>. The ligand forms a 1:1 complex with Zn<sup>2+</sup>, which is evident from fluorescence titration, the Job's plot, and ESI-MS. The high binding constant value (1.392×10<sup>5</sup> m<sup>-1</sup>) indicates that strong binding occurs between **2PT** and Zn<sup>2+</sup>. With a detection limit of  $7.5 \times 10^{-7}$  mol L<sup>-1</sup>, **2PT** senses Zn<sup>2+</sup> effectively at a pH range of 6–7 in aqueous solu-

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tion, which is suitable for biological studies. The **2PT** is also applicable to real sample analyses for  $Zn^{2+}$  in well water and drinking water.

## **Experimental Section**

UV/visible absorption spectra were recorded by using the JASCO Spectra Manager (V-550) in a 1 cm path length quartz cuvette. All fluorescence measurements were performed on a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon) with excitation slit set at 5.0 nm band pass and emission at 5.0 nm band pass in a 1 cm quartz cell. Electrospray ionization mass spectrometry (ESI-MS) analysis was performed in the positive and nega-

tive ion modes on a liquid chromatography-ion-trap mass spectrometry instrument (LCQ Fleet, Thermo Fisher Instruments Limited, USA). The samples were introduced into the ion source by the infusion method at flow rate 1  $\mu$ Lmin<sup>-1</sup>. The capillary voltage of the mass spectrometer was 33 V, with source voltage 4.98 kV for the mass scale (*m*/*z* 50–400). A CH1205 electrochemical analyzer (CH Instruments, USA) and a standard three-electrode cell containing a platinum wire auxiliary electrode, a saturated calomel reference electrode, and a platinum electrode as working electrode were employed for electrochemical studies. DFT calculations were performed at the B3LYP/LANL2DZ(d) level by using the Gaussian 03 program.

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Ref

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