



ESIPT-based ratiometric probe for Zn²⁺ detection based on BINOL framework



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ABSTRACT

A ratiometric BINOL-based fluorescent probe for Zn²⁺ detection was rationally designed and synthesized. Based on the excited-state intramolecular proton transfer (ESIPT) mechanisms, the probe exhibited a significant variation on emission wavelengths with shifts more than 100 nm after combining with Zn²⁺, with emission colors changing from yellow to blue. Good selectivity and sensitivity of the probe toward Zn²⁺ could be found in aqueous solution. Sensing mechanism was proposed on the basis of fluorescence, absorption, ESI mass spectrometry, IR spectra, and CD spectra.

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Introduction

As the second most abundant transition metal ion in the human body, Zn²⁺ plays a myriad of roles in various biochemical processes, such as gene transcription, regulation of metalloenzymes, neural signal transmission, and apoptosis.¹ Zinc imbalance is closely related to a number of pathological disorders, such as Alzheimer's disease, epilepsy, Parkinson's disease, ischemic stroke, and infantile diarrhea.² Numerous previous work³ have demonstrated that among various analytical methods available, the method of fluorescent probe had become one of the best choices for detecting and tracking Zn²⁺ in vitro and in vivo due to its simplicity, cost effectiveness, and high sensitivity.⁴ However, among the reported probes, many of them still have drawbacks, such as tedious organic synthesis and poor selectivity,^{3b,f} especially interference from Cu²⁺, Cd²⁺, and Hg²⁺, which possess very similar chemical property. Therefore, it remains a significant challenge to develop a sensitive and selective fluorescent probe for Zn²⁺.

A ratiometric sensor is highly desirable as it reduces or eliminates the adverse effects of change of environment around the probe. The excited state intramolecular proton transfer (ESIPT) strategy has drawn much attention in the design of ratiometric fluorescent sensors, because of its large Stokes shift, which offers an advantage that it minimizes the self-absorption and eliminates the interference

from auto-fluorescence for bioimaging applications.⁵ The fluorescence of ESIPT chromophores can be perturbed by many intermolecular interactions, such as removal of the hydrogen involved in the ESIPT process, thus paving way for sensing metal ions.

Optically active 1,1'-bi-2-naphthol (BINOL) and its derivatives have attracted tremendous research interests in asymmetric catalysis and fluorescent enantioselective recognition due to their backbone, which can be modified by strategic placement of functional groups based on steric and electronic properties. However, there are few reports on the recognition toward metal ions based on BINOL.⁶

Herein, we report our research concerning the design, synthesis, and properties of novel material 3,3'-bis(4,5-diphenyl-1*H*-imidazol-2-yl)-[1,1'-binaphthalene]-2,2'-diol, which will be called **1** below. It is noteworthy that **1** can be utilized as a selective fluorescent Zn²⁺ probe based on the strategy of removal of the H-bond as well as the resulting ESIPT modulated fluorescence off-on response. The probe is composed of 4,5-diphenyl-1*H*-imidazol dye and a BINOL skeleton as both the fluorophore and the recognition unit. The emission of **1** exhibited a pronounced red shift due to the effective ESIPT process. The coordination of the OH group with Zn²⁺ will turn off ESIPT, thus the probe mainly displays normal emission, resulting in a substantial ratiometric response.

Results and discussion

The synthesis of chemosensor **1** was outlined in Scheme 1. 3,3'-Dialdehyde-BINOL (**2**) have been synthesized from

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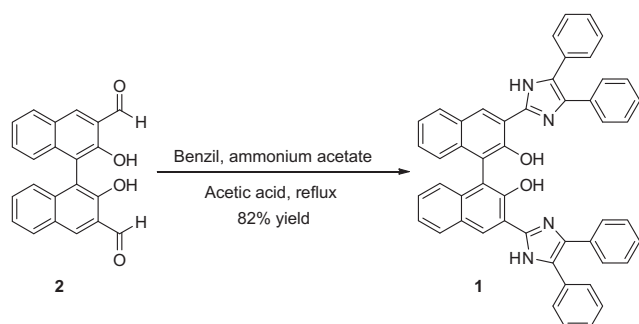
1,1'-bi-2-naphthol (BINOL) according to literature procedures (Scheme S1),⁷ then **2** was refluxed with benzil and ammonium acetate in acetic acid to afford **1** as the pale yellow solid in 82% yield. The structure of **1** was characterized by ¹H NMR, ¹³C NMR, and a high resolution mass spectrometry (HRMS).

To get insight into the metal ion selectivity of **1**, the fluorescence changes of **1** solution (10 μM) to various metal ions in aqueous solution (CH₃OH/H₂O, 9:1, v/v, HEPES 20 mM, pH 7.2) were investigated. Free **1** solution displayed an emission band at 549 nm when excited at 330 nm, which could be attributed to the relaxation of the keto form to the ground state. Upon addition of 5.0 equiv of Zn²⁺ to **1** solution, the emission at 549 nm was decreased, accompanied with the appearance of a strong emission band at 427 nm and a remarkable hypochromatic shift of 122 nm. Whereas, the addition of other cations such as Ag⁺, Pb²⁺, Ba²⁺, Cd²⁺, Ni²⁺, Co²⁺, Fe²⁺, Fe³⁺, Mn²⁺, Al³⁺, Cr³⁺, Ca²⁺, Mg²⁺, K⁺, and Na⁺ have caused less change in the fluorescence of probe **1** except for Cu²⁺ and Hg²⁺ which led to the fluorescence quenching of the ESIPT band (Fig. 1).

The dramatic fluorescence response to the binding of **1**-Zn²⁺ may be ascribed to (i) the deprotonation of phenolic-OH and the cause of restriction of excited-state induced proton transfer (ESIPT), (ii) the prohibition of intramolecular electron-transfer process, and (iii) the chelation-enhancement of fluorescence process along with the lowering of vibrational loss due to the rigid molecular structure of the complex.⁸ The UV-Vis absorption spectra of **1** in the presence of various metal ions were also studied (Fig. S9), while there was interference by the addition of Cu²⁺ and Hg²⁺.

The mode of coordination of **1** with Zn²⁺ ions was initially investigated by UV-Vis titration. As shown in Figure 2. The free receptor showed a maximum absorption wavelength at 373 nm. Upon the addition of Zn²⁺ ions, the maximum absorbance exhibited an obvious bathochromic shift from 373 to 388 nm, and the ratio of absorbance ($A_{388\text{ nm}}/A_{373\text{ nm}}$) increased linearly from 0.23 to 0.92 by adding Zn²⁺ ions (Fig. 2). Meanwhile, the absorbance at 337 nm was decreased, while the absorbance at 250 nm and 290 nm were increased simultaneously. In addition, two clear isosbestic points were observed at 296 nm and 383 nm.

Subsequently, fluorescence titration of **1** by increasing the amounts of Zn²⁺ was examined (Fig. 3). Upon incremental addition of Zn²⁺, ratiometric fluorescence changes were observed. The original emission intensity at 549 nm was gradually decreased, and concomitantly, the newly formed emission band at 427 nm was gradually increased. The ratio of fluorescence intensity ($F_{427\text{ nm}}/F_{549\text{ nm}}$) increased from 0 to 43.8 with nonlinear relationship on addition of Zn²⁺ ions (Fig. 3). The well-defined isoemissive point appearing at 500 nm demonstrated the presence of a new complex in equilibrium with the receptor.^{6c} Notably, the fluorescence intensity of **1** at both 427 nm and 549 nm has well fitted linear relationships with [Zn²⁺] in the range of 0.0–10.0 μM ($R^2 = 0.99395$ and 0.99784) (Fig. 4), which suggested that **1** could be served as an efficient ratiometric fluorescent probe for Zn²⁺



Scheme 1. Synthetic route of **1**.

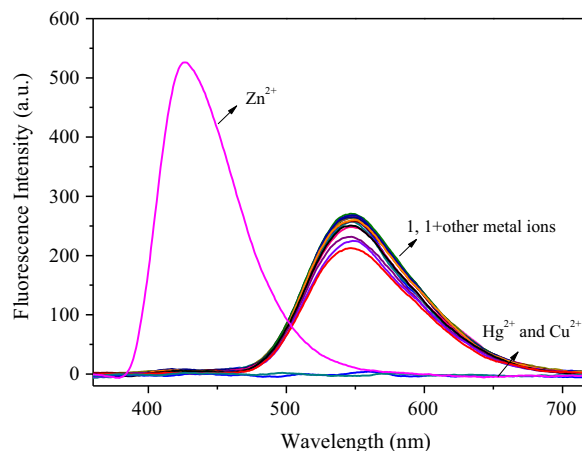


Figure 1. Fluorescence spectra of **1** solution (10 μM, CH₃OH/H₂O, 9:1, v/v, HEPES 20 mM, pH 7.2) in the absence and presence of various metal ions (5.0 equiv of Zn²⁺, Hg²⁺, Cu²⁺, Ag⁺, Pb²⁺, Ba²⁺, Cd²⁺, Ni²⁺, Co²⁺, Fe²⁺, Fe³⁺, Mn²⁺, Al³⁺, Cr³⁺, Ca²⁺, Mg²⁺, K⁺ and Na⁺). $\lambda_{\text{ex}} = 330$ nm.

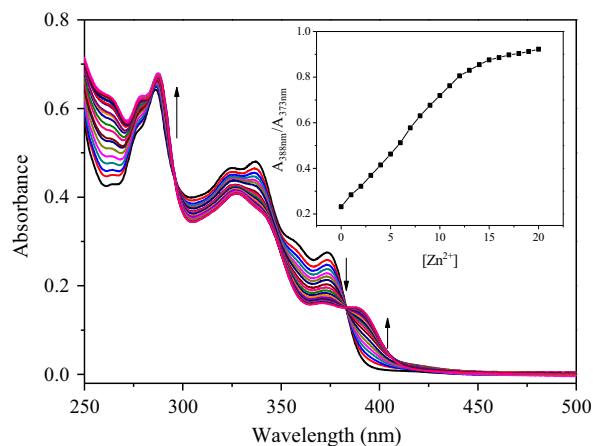


Figure 2. Absorption spectra changes of **1** solution (10 μM, CH₃OH/H₂O, 9:1, v/v, HEPES 20 mM, pH 7.2) upon the addition of different amounts of Zn²⁺ ions (0–2.0 equiv). Inset: the linear relationship between the ratio of absorbance ($A_{388\text{ nm}}/A_{373\text{ nm}}$) and the concentration of Zn²⁺.

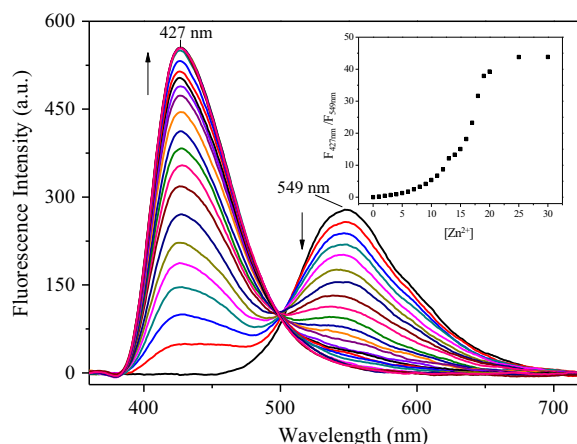


Figure 3. Fluorescence spectra changes of **1** solution (10 μM, CH₃OH/H₂O, 9:1, v/v, HEPES 20 mM, pH 7.2) upon addition of different amounts of Zn²⁺ ions (0–2.0 equiv). $\lambda_{\text{ex}} = 330$ nm. Inset: the nonlinear relationship between the ratio of fluorescence intensity ($F_{427\text{ nm}}/F_{549\text{ nm}}$) and the concentration of Zn²⁺.

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