



An efficient sensor for relay recognition of Zn²⁺ and Cu²⁺ through fluorescence 'off-on-off' functionality



Lijun Tang*, Jia Zhao, Mingjun Cai, Pei Zhou, Keli Zhong, Shuhua Hou, Yanjiang Bian

Department of Chemistry, Liaoning Key Laboratory for the Synthesis and Application of Functional Compounds, Bohai University, Jinzhou 121013, China

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ABSTRACT

A new bis(8-carboxamidoquinoline) dangled binaphthol derivatized fluorescent sensor (**L**) was designed and synthesized. **L** behaves ratiometric response to Zn²⁺ with high selectivity accompanied by remarkable emission enhancement and red shift. The resultant **L**-Zn²⁺ complex can act as a Cu²⁺ sensing probe with fluorescence quenching behavior through direct Zn²⁺ ion replacement. Furthermore, the binding modes of Zn²⁺ and Cu²⁺ with **L** are elucidated by X-ray crystallographic analysis, respectively.

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Introduction

Development of fluorescent probes for sensing biologically and environmentally important heavy and transition metal (HTM) ions has received immense interest due to the fundamental roles they are played in chemical, biological, and environmental processes.¹ Zn²⁺, as the second-most abundant transition metal ion in human body and other mammals, plays critical roles in a wide variety of biological processes including gene transcription, signal transmission, and mammalian reproduction.² High zinc concentration in cells also pertains to some pathological processes such as Alzheimer's disease, epilepsy, and infantile diarrhea.³ Consequently, great efforts have been devoted to the design and synthesis of Zn²⁺ selective fluorescent probes due to the high sensitivity and easy operability of fluorescence technique.⁴ Cu²⁺, as the third-most abundant transition metal in human body, also plays pronounced roles in the fundamental physiological processes of organisms.⁵ However, under overloading conditions, copper produces toxicity and can result in neurodegenerative diseases.⁶ Designing effective fluorescent probes for Cu²⁺ ion has recently received immense attention.^{1c,7}

Metal complexed receptors have been widely employed in displacement assays for the recognition of biologically important anions through anion induced metal removal.⁸ Another valuable application of metal complexed receptors is in the detection of metal cation through metal ion replacement approach based on competitive binding of two metal ions with the ligand. Therefore, some fluorescent probes can be applied to relay recognition of metal

ions. Recently, studies on single probe for relay recognition of two metal ions, such as Zn²⁺/Cd²⁺,^{4s} Zn²⁺/Hg²⁺,⁹ Cu²⁺/Hg²⁺,¹⁰ and Zn²⁺/Al³⁺,¹¹ have received considerable attention. Although studies on single probe for Zn²⁺/Cu²⁺ metal ion recognition also have been explored,¹² only few works associated with relay recognition of Zn²⁺ and Cu²⁺ have so far been documented.^{12a,b}

Herein we report a bis(8-carboxamidoquinoline) dangled binaphthol derivative **L** (Scheme 1), which exhibits Zn²⁺ selective ratiometric fluorescence changes, the resultant **L**-Zn²⁺ complex behaves Cu²⁺ recognition with fluorescence turn-off process through Zn²⁺ ion replacement.

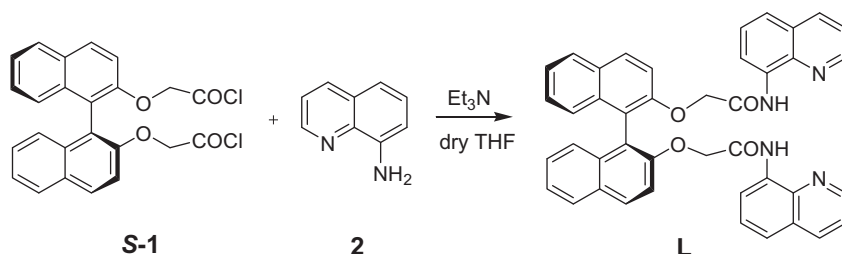
Results and discussion

Fluorescence recognition of Zn²⁺

Sensor **L** was prepared by condensation of **S-1**¹³ with 8-aminoquinoline (**2**) in dry THF, the structure of **L** was characterized by ¹H NMR, ¹³C NMR, and high resolution mass spectrometry (HRMS). To get insight into the metal ion selectivity of **L**, the fluorescence changes of **L** solution (10 μM) to various metal ions in aqueous solution (CH₃OH/H₂O, 9:1, v/v, HEPES 10 mM, pH 7.4) were investigated. Free **L** solution displays a weak emission band at 403 nm when excited at 324 nm, this can be attributed to the photoinduced electron transfer (PET) from the amide N atom to the excited singlet state of quinoline.¹⁴ On addition of 1.0 equiv of Zn²⁺ to **L** solution, the emission at 403 nm of **L** decreased accompanied with the appearance of a strong emission band at 507 nm and a remarkable red shift of 104 nm. Addition of Cu²⁺ ions induced an obvious fluorescence quenching, which means that Cu²⁺ ions also can bind with **L** but lead to fluorescence quenching due to its paramagnetic prop-

* Corresponding author. Tel.: +86 416 3400302.

E-mail address: ljtang@bhu.edu.cn (L. Tang).



Scheme 1. Synthesis of sensor L.

erty. Whereas, other cations such as Hg^{2+} , Ag^+ , Pb^{2+} , Sr^{2+} , Ba^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Al^{3+} , Cr^{3+} , Ca^{2+} , Mg^{2+} , K^+ , and Na^+ did not promote any significant fluorescence spectra changes (Fig. 1). The Zn^{2+} binding induced emission enhancement may come from the chelation-enhanced fluorescence (CHEF) effect, which suppresses the PET process. A Zn^{2+} induced deprotonation of amide NH was also suspected, which increased the electron-donating ability of the amine group to the quinoline moiety, which further enhanced the intramolecular charge transfer (ICT) process from the nitrogen atom of heterocycle to the metal ion and thus led to the Zn^{2+} induced red-shifted emission.¹⁵ Similar to some typical reported Zn^{2+} -selective fluorescent sensors, the main reason for the high selectivity of sensor L to Zn^{2+} can be attributed to the high binding affinity of aminoquinoline moiety to Zn^{2+} ion.^{14a,15a-c}

Subsequently, fluorescence titration of L by increasing amounts of Zn^{2+} was examined (Fig. 2). Upon incremental addition of Zn^{2+} , ratiometric fluorescence changes were observed. The original emission intensity at 403 nm was gradually decreased, concomitantly, the newly formed emission band at 507 nm was gradually increased. The fluorescence changes terminated when 1 equiv of Zn^{2+} was employed. The well-defined isoemissive point appearing at 432 nm demonstrates the existence of an equilibrium in the solution. The intensity ratio of $F_{507\text{nm}}/F_{403\text{nm}}$ exhibited a nice linearity against the added Zn^{2+} concentration between the range of 0–9 μM (inset in Fig. 2). Benesi–Hildebrand analysis of the titration profiles based on 1:1 binding mode¹⁶ resulted in a nice linearity (Fig. S1), indicating the 1:1 binding stoichiometry of Zn^{2+} and L, and the binding constant was estimated to be $1.2 \times 10^4 \text{ M}^{-1}$. The 1:1 binding ratio was also supported by Job's plot investigation

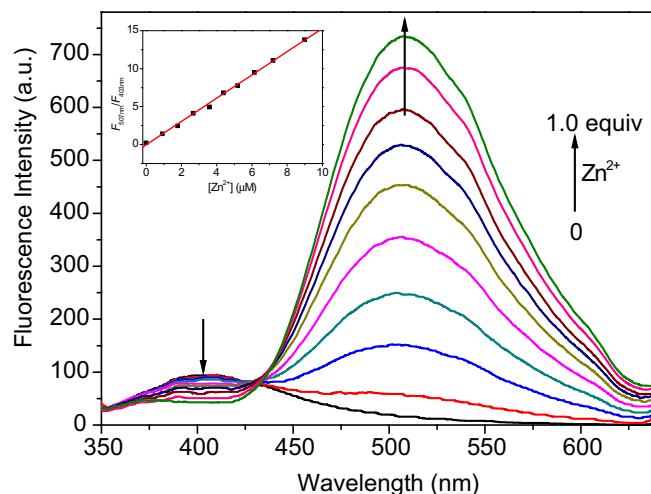


Figure 2. Fluorescence spectrum changes of L solution (10 μM , $\text{CH}_3\text{OH}/\text{H}_2\text{O}$, 9:1, v/v, HEPES 10 mM, pH 7.4) upon addition of different amounts of Zn^{2+} ions (0–1.0 equiv). $\lambda_{\text{ex}} = 324 \text{ nm}$. Inset: linear dependence of intensity ratio ($F_{507\text{nm}}/F_{403\text{nm}}$) on Zn^{2+} concentration.

(Fig. S2). Moreover, the detection limit of L to Zn^{2+} was evaluated to be $1.51 \times 10^{-6} \text{ M}$ (Fig. S3).¹⁷

Fluorescence competition experiments were then conducted to further validate the high selectivity of L to Zn^{2+} (Fig. 3). When 1.0 equiv of Zn^{2+} was added to L solution containing the same amount of other metal ions such as Hg^{2+} , Ag^+ , Pb^{2+} , Sr^{2+} , Ba^{2+} ,

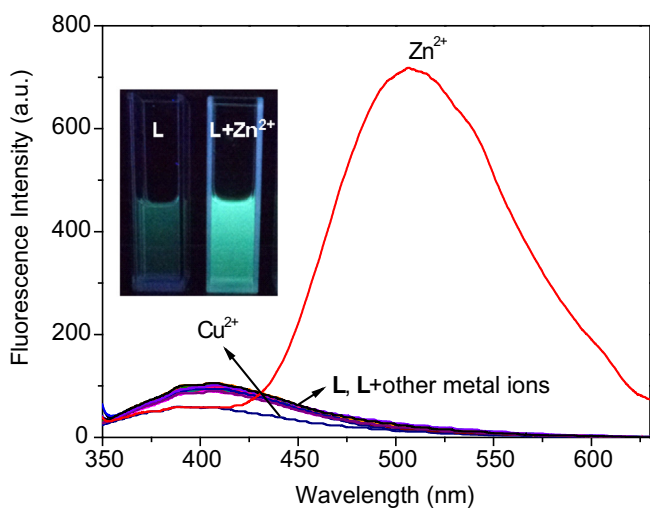


Figure 1. Fluorescence spectra of L solution (10 μM , $\text{CH}_3\text{OH}/\text{H}_2\text{O}$, 9:1, v/v, HEPES 10 mM, pH 7.4) in the absence and presence of various metal ions (1.0 equiv of Zn^{2+} , Hg^{2+} , Ag^+ , Pb^{2+} , Sr^{2+} , Ba^{2+} , Cd^{2+} , Ni^{2+} , Co^{2+} , Fe^{2+} , Fe^{3+} , Mn^{2+} , Cu^{2+} , Al^{3+} , Cr^{3+} , Ca^{2+} , Mg^{2+} , K^+ , and Na^+). Inset: naked-eye observable fluorescence changes of L solution before and after addition of Zn^{2+} .

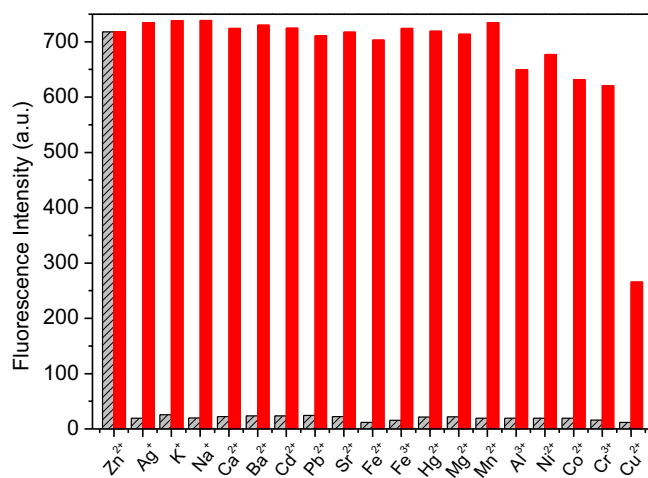


Figure 3. Fluorescence responses of L solution (10 μM , $\text{CH}_3\text{OH}/\text{H}_2\text{O}$, 9:1, v/v, HEPES 10 mM, pH 7.4) to various metal ions. The gray bars represent the emission intensity of L solution on addition of 1.0 equiv of different metal ions; the red bars represent the emission intensity of the metal ion containing solution upon further addition of 1.0 equiv of Zn^{2+} . $\lambda_{\text{ex}} = 324 \text{ nm}$, $\lambda_{\text{em}} = 507 \text{ nm}$.

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