

# Synthesis and multi-response research of a highly selective fluorescent chemosensor for $\text{Zn}^{2+}$

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**Abstract.** A new 1,2,3-triazole receptor bearing quinoline groups have been prepared *via* “click” reaction. The compound shows significant fluorescent response to  $\text{Zn}^{2+}$  over other cations in  $\text{CH}_3\text{CN}$  solvent. Besides, electrochemical properties including cyclic voltammetry (CV) and differential-pulse voltammetry (DPV) tests are operated to reveal the complex also has good electrochemical response toward  $\text{Zn}^{2+}$ .

## 1. Introduction

Zinc and its derivatives play an essential role in many biological processes in human-beings, and it is the second most abundant transition metal ion in human body after iron [1]. Many diseases, like Alzheimer's disease, and epilepsy are associated with the disorder of  $\text{Zn}^{2+}$  metabolism [2]. Therefore, measurement of  $\text{Zn}^{2+}$  is important in the field of biology.

Sensitive chemosensors have attracted more and more attention in recent years because of their potential applications in analytical chemistry, biochemistry, environmental monitoring and convenience of use [3]. Among numerous synthetic methods, Cu(I)-catalyzed “click” reaction has provided an easy strategy for the linkage of 1,2,3-triazole which has good coordination abilities with metal cations to various functionalities. Besides, quinoline groups are rich in optical properties that can be detected easily in fluorescent tests. In this research, we report a new chemosensor toward  $\text{Zn}^{2+}$  containing both triazole and quinolone groups using ferrocene as the structural matrix.

## 2. Experiment

Synthesis of 8-(prop-2-ynyloxy) quinoline (1). 8.7g (60 mmol) 8-hydroxyquinoline was reacted with 8.5g (70mmol) 3-bromopropyne in 100 mL acetone with 30.0g (220mmol)  $\text{K}_2\text{CO}_3$  as a catalyst. The mixture was stirred in ice-salt bath for three days. When the reaction finished, the solvent was removed under vacuum, and the crude product was washed with petroleum ether for several times to remove the unreacted 8-hydroxyquinoline. 6.5g liquid compound 1 with a deep yellow colour was obtained in 46% yield.

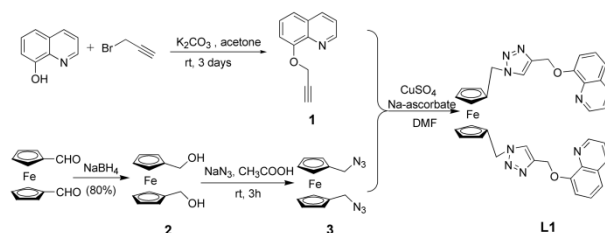


Figure 1. Synthesis route of the title compounds



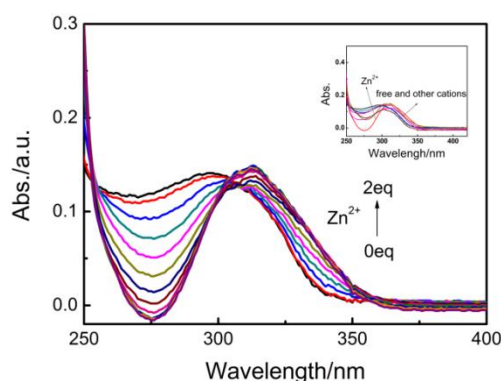
Synthesis of 1,1'-ferrocenedimethanol (**2**). The reactant 1,1'-ferrocenedicarboxaldehyde was synthesized by literature method [4]. 1.55g (6.4mmol) 1,1'-ferrocenedicarboxaldehyde was dissolved in 25 mL methanol stirring for 10 minutes at 0 °C. Then, 0.54g (14.1mmol) NaBH<sub>4</sub> was added into the mixture in batches for another 2 hours of stirring at room temperature. After the reaction, the solvent was removed under vacuum, the solid obtained was extracted with ethyl acetate. The organic layer was evaporated and subjected to the purification by silica-gel column chromatography to get 1.1g yellow needle-like crystals with a yield in 71% (m. p.=105-107 °C).

Synthesis of 1,1'-diazidomethylferrocene (**3**). 2.4g NaN<sub>3</sub> was added into 40 mL acetic acid solution of 0.3g (1.58mmol) 1,1'-ferrocenedimethanol, the mixture was stirred for 3 hours at room temperature. After the reaction, the mixture was diluted with ethyl acetate, and washed with NaHCO<sub>3</sub> saturated aqueous solution. Then, the organic layer was evaporated and the crude product was purified with silica-gel column chromatography to give the compound **3** as yellow syrup.

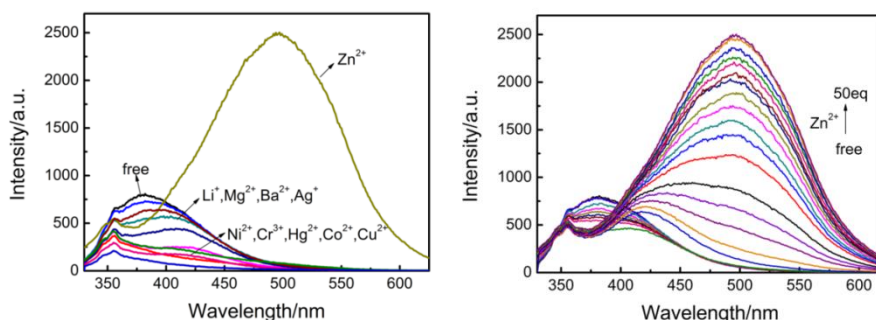
Synthesis of the title compound **L1**. A mixture of 8-(prop-2-ynyloxy) quinoline (293mg, 1.6mmol) and 1,1'-diazidomethylferrocene (190 mg, 0.64 mmol) was dissolved in 10mL DMF. Then, 64mg (0.26 mmol) CuSO<sub>4</sub> and 51 mg (0.26 mmol) sodium ascorbate were added into the above solution as a catalyst. The mixture was stirred for 8hours under nitrogen atmosphere. After the reaction, NaCl saturated aqueous solution was added into the resultant mixture, lots of yellow flocculent precipitate appeared immediately. The mixture was filtered and washed with water for several times to harvest the yellow solid **L1** (386mg) with a high yield in 91% (m.p.=93-96 °C). <sup>1</sup>HNMR (CDCl<sub>3</sub>) δ(ppm): 8.90(d, *J*=2.8Hz, 2H), 8.11(d, *J*=8.0Hz, 2H), 7.67(s, 2H), 7.36-7.43(m, 6H), 7.33(d, *J*=7.2Hz, 2H), 5.53(s, 4H), 5.16(s, 4H), 4.15(d, *J*=14.4Hz, 8H). IR (KBr, cm<sup>-1</sup>): 1632 cm<sup>-1</sup>, 1569 cm<sup>-1</sup>, 1500 cm<sup>-1</sup>, 1468 cm<sup>-1</sup>, 1260 cm<sup>-1</sup>, 1050 cm<sup>-1</sup>.

### 3. Results and discussion

In this work, we have synthesized a novel ferrocene-based multi-response chemosensor (**L1**) for Zn<sup>2+</sup> detection using the “click” reaction method. The synthesis route is shown in Figure 1. To obtain an insight into the sensing properties of **L1** towards metal ions, the UV-visible absorption spectra are examined with different cations such as Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ba<sup>2+</sup>, Hg<sup>2+</sup>, Cr<sup>3+</sup>, Zn<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, and Ag<sup>+</sup> in CH<sub>3</sub>CN (see Figure 2). There is a broad band at 300nm in the UV-vis absorption spectrum of **L1** in CH<sub>3</sub>CN. Upon the addition of Zn<sup>2+</sup> to 2 equivalents, the absorption band gradually decreases until disappears, and a new absorption band appears at 312nm, which could be due to the coordination of **L1** and Zn<sup>2+</sup>. Furthermore, the isosbestic point at 305nm implies the undoubted conversion of free **L1** to a zinc complex.



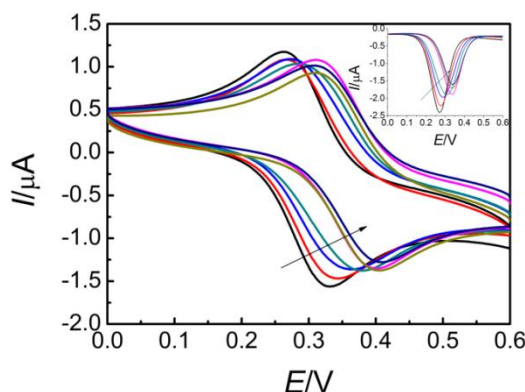
**Figure 2.** UV-vis spectra of **L1**( $2 \times 10^{-5}$ M) upon addition of 0-2 equiv. of Zn<sup>2+</sup> in CH<sub>3</sub>CN solution.  
Inset: UV-vis spectra of **L1** upon addition of 2 equiv. of various of cations in CH<sub>3</sub>CN solution.



**Figure 3.** Emission spectra ( $\lambda_{\text{ex}}=320\text{nm}$ ) of **L1** ( $2\times 10^{-5}\text{M}$ ) upon addition of 50 equiv. of various of cations in  $\text{CH}_3\text{CN}$  solution (left); Changes in emission spectra of **L1** ( $2\times 10^{-5}\text{M}$ ) upon addition of 0-50 equiv. of  $\text{Zn}^{2+}$  in  $\text{CH}_3\text{CN}$  solution (right).

The emission titration experiments (see Figure 3) reveals that **L1** shows distinct fluorescent sensing to  $\text{Zn}^{2+}$ , which is consisted with the UV-vis results. When **L1** is exposed in 50 equiv. of various of cations in  $\text{CH}_3\text{CN}$  solution, only **L1**- $\text{Zn}^{2+}$  couples shows a great increasing fluorescent emission which is from the new emission band at 496nm. By contrast, **L1**-other cation couples quench their emissions at 381nm which may be ascribed to the quenching effect of a photo-induced electron transfer process from quinolone to triazole [5]. In fact, the emission band of **L1** is also quenched by the addition of  $\text{Zn}^{2+}$  at the first stage as the other **L1**-cation couples, when the large amount of  $\text{Zn}^{2+}$  added, the new emission band with a distinct red shift appears. It may be due to the formation of rigid structure caused by the chelation from the neighbouring triazoles to  $\text{Zn}^{2+}$ .

Ferrocene-contained compounds often have good electrochemical properties. Cyclic voltammetry (CV) and differential-pulse voltammetry (DPV) titrations are operated for several cations to **L1** (see Figure 4). The electrochemical data are listed in Table 1. The oxidation potential shifts 79mV positively with the reduction potential shifts 47mV positively in the CV curves when  $\text{Zn}^{2+}$  is added (68mV for DPV test), which could be attributed to the difficulty of ferrocene-oxidation, a result of coordination between **L1** and  $\text{Zn}^{2+}$ .



**Figure 4.** Cyclic voltammetry (CV) and differential-pulse voltammetry (DPV) tests for the  $\text{Zn}^{2+}$  titration to **L1** ( $2\times 10^{-4}\text{M}$ ).

**Table 1.** Cyclic voltammetry (CV) and differential-pulse voltammetry (DPV) data for the titration of several cations to **L1**.

Compound	$E/V(\text{CV})^a E_{\text{pa}}$	$E/V(\text{CV}) E_{\text{pc}}$	$E_{1/2}$	$\Delta E_{1/2}$	$E/V(\text{DPV})^b$
<b>L2</b>	0.332	0.261	0.297		0.272
+ $\text{Hg}^{2+}$	0.366	--	--	--	0.368
+ $\text{Cu}^{2+}$	0.389	0.299	0.344	0.047	0.320
+ $\text{Zn}^{2+}$	0.411	0.308	0.360	0.063	0.340
+ $\text{Cr}^{3+}$	0.331	0.264	0.298	0.001	0.276

+Ni <sup>2+</sup>	0.382	0.292	0.337	0.040	0.312
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<sup>a</sup> CV,  $E_{1/2}$  and  $\Delta E$  vs. Ag<sup>+</sup>/Ag, the  $E_{1/2}$  of unsubstituted ferrocene is 0.037 V vs. Ag<sup>+</sup>/Ag.

<sup>b</sup> DPV,  $E_{dpv}$  vs. Ag<sup>+</sup>/Ag, 50 ms pulse width.

#### 4. Conclusion

A novel ferrocene-based multi-response chemosensor **L1** is synthesized successfully. UV-vis spectra, fluorescent emission spectra, and electrochemical tests reveal the compound shows high sensitivity and selectivity toward Zn<sup>2+</sup>. Designing based on the present studies could be further modified to develop more systems for ion probes.

#### Acknowledgments

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