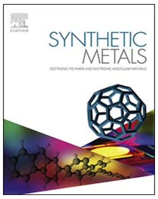
Synthetic Metals 232 (2017) 17–24

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



A highly selective colorimetric and fluorescent turn-on chemosensor for Zn^{2+} and its logic gate behavior

Na-Na Li, Yu-Qing Ma, Shuang Zeng, Ya-Tong Liu, Xue-Jiao Sun, Zhi-Yong Xing*

Department of Applied Chemistry, College of Science, Northeast Agricultural University, Harbin 150030, PR China, PR China

ARTICLE INFO

Keywords:
Quinoline
Chemosensor
X-ray crystallography
Zn^{2+}
Logic gate

ABSTRACT

A novel quinoline-based fluorescent chemosensor L was synthesized and characterized by ^{1}H NMR, ^{13}C NMR, HRMS and X-ray Crystallography. L showed a significant fluorescent enhancement (120-fold) and color change upon the addition of Zn^{2+} attributed to the joint contribution of the PET and CHEF processes. The binding ratio of the **L**–Zn^{2+} complex was 1:1 confirmed by the ^{1} HNMR, mass-spectral analysis and Job plot, and the detection limit for Zn^{2+} was as low as 5.2×10^{-7} M. **L** was successfully applied to the determination of Zn^{2+} in real water samples. Moreover, the fluorescent signals of **L** were utilized to built an INHIBIT logic gate.

1. Introduction

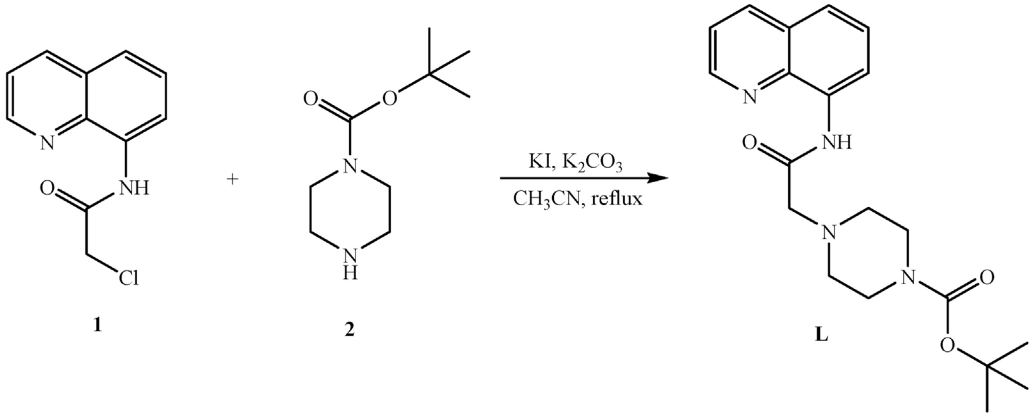
Zinc, the second most abundant transition metal after iron in the human body, plays an important role in numerous cellular functions including neural signal transmission, apoptosis, DNA synthesis, modulation of diverse ion channels and gene transcription [1–6]. Nevertheless, some serious diseases, such as Alzheimer, infantile diarrhea, cerebral ischemia and epilepsy are associated with the disorder of Zn^{2+} metabolism [7–12]. Moreover, pollution due to transition metals such as Zn^{2+} has been a threat to the human health and environment [13–16]. Therefore, it is crucial to develop a rapid and sensitive method for detection of Zn^{2+} in environmental and biological systems. Up to now, some analytical methods including atomic absorption spectrometry (AAS) [17], inductively coupled plasma mass spectroscopy (ICP-MS) [18], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [19], electrochemistry [20–26], ion selective membrane [27–52] have been developed for detection of metal ions. However, complicated pretreatment, consuming time, expensive instrumentation and large sample amount have limited their application.

During the last decades, fluorescent chemosensors have attracted significant attention due to high sensitivity, simplicity, low-cost, convenience and real time bio-imaging [53–61]. Although a large number of fluorescent probes based on various fluorophores have been reported for selective detection of Zn^{2+}, problems such as insolubility in water, complicated synthesis process, and disturbance from other transition metal ions (especially Cd^{2+}, which is in the same group of the periodic table and shows similar properties to Zn^{2+}) remains [62–64]. Therefore, the development of a highly selective sensing system for Zn^{2+} has become an attractive challenge. 8-aminoquinoline is a widely used building block for construction of fluorescent chemosensors for transition metals due to favorable biocompatibility and interesting photophysical properties [65–67]. Some chemosensors for detection Zn^{2+} using that building block involved different mechanisms, such as photoinduced electron transfer (PET) [68–72], internal charge transfer (ICT) [73–77], chelation enhanced fluorescence (CHEF) [78], twisted intramolecular charge transfer (TICT) [79], excited-state intermolecular proton transfer (ESIPT) [80], and inhabition of C=N isomerization [81]. Moreover, several Zn^{2+} chemosensors [82–85] have been developed on the basis of multi-mechanism which will amplify recognition process by producing multiple signals to a greater extent to improve selectivity and sensitivity. However, to the best of our knowledge, the Zn^{2+} chemosensor based on the combination of intramolecular charge transfer (PET) and chelation enhanced fluorescence (CHEF) mechanism with the 8-aminoquinoline fluorophore as the signaling unit has been scarcely reported. Taking the above statements into consideration, chemosensor **L** was designed and synthesized by a facile condensation between compound **1** and **2** (Scheme 1). Optical properties were investigated using UV–vis and fluorescence response of the **L** to Zn^{2+}. As we expected, **L** showed excellent selectivity and sensitivity with a fluorescence enhancement to Zn^{2+} over other tested cations, especially distinguishing Zn^{2+} from Cd^{2+} in $CH_3OH{-}H_2O$ (4:1, v/v, containing 0.01 M HEPES buffer, pH = 7.0). Furthermore, chemosensor **L** was successfully applied in detection of Zn^{2+} in real water samples. We also found that the fluorescence signal of chemosensor **L** could be used as an INHIBIT logic gate controlled by two chemical inputs Zn^{2+} (Input 1) and Cu^{2+} (Input 2).

---

* Corresponding author.
E-mail address: zyxing@neau.edu.cn (Z.-Y. Xing).

http://dx.doi.org/10.1016/j.synthmet.2017.07.017
Received 19 April 2017; Received in revised form 17 July 2017; Accepted 23 July 2017



Scheme 1. Synthesis of **L**.

2. Experimental

2.1. Materials and instrumentation

All chemical solvents and reagents were used as received from commercial sources without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruck AV-600 spectrometer. Chemical shifts (δ) are reported in ppm, relative to tetramethylsilane. Absorption spectra were recorded at 25 °C using a Pgeneral TU-1901 UV–vis spectrophotometer. Fluorescence measurements were performed on a Perkin Elmer LS55 fluorescence spectrometer. Mass spectra were measured on a Waters Xevo UPLC/G2-SQ TofMS spectrometer. The melting point was determined on a Beijing XT4-100X apparatus. Crystal data of L were collected on an Xcalibur, Eos, Gemini diffractometer with Mo Kα radiation (λ = 0.71073 Å) [86].

2.2. Synthesis

2.2.1. Synthesis of *L*

As shown in Scheme 1, according to the literature method [75], **L** was synthesized by coupling of 2-chloro-*N*-(quinol-8-yl)-Acetamide (**1**) and *tert*-butyl 1-piperazinecarboxylate (**2**) via one step reaction. *N*-boc-piperazine (0.447 g, 2.4 mmol), K_2CO_3 (0.276 g, 2 mmol) and KI

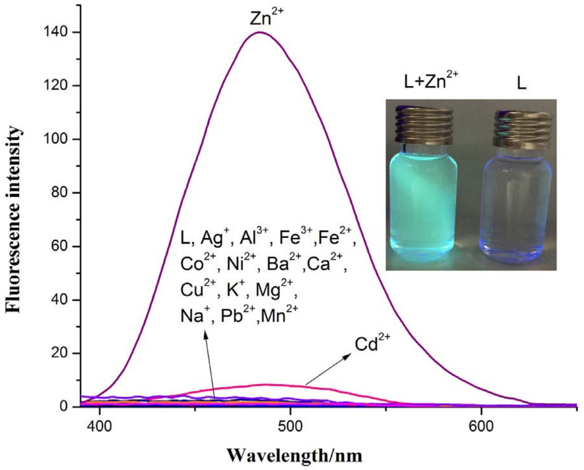


Fig. 2. Fluorescence spectra of **L** (50 μM) in the presence of various metal ions (200 μM) in $CH_3OH{-}H_2O$ (4:1, v/v, containing 0.01 M HEPES, pH = 7.0), (λ_{ex} = 360 nm). Inset: Fluorescence color changes of **L** solution before and after addition of Zn^{2+} under UV lamp at 365 nm.

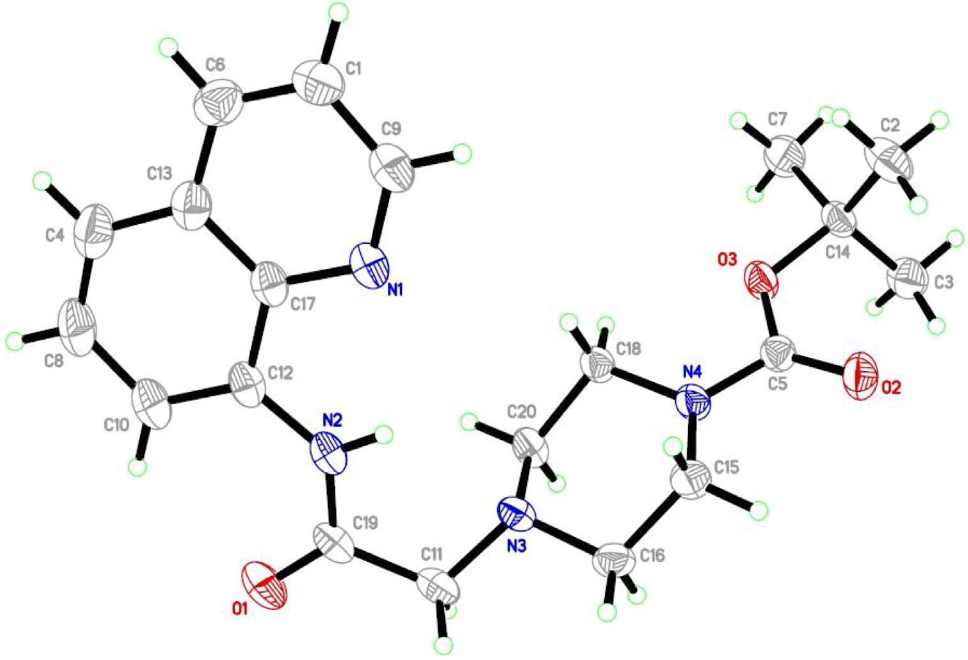


Fig. 1. X- ray crystal structure of **L**.