Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 138 (2015) 603–608

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Fluorescence sensors for Zn^{2+} based on conjugated indole Schiff base

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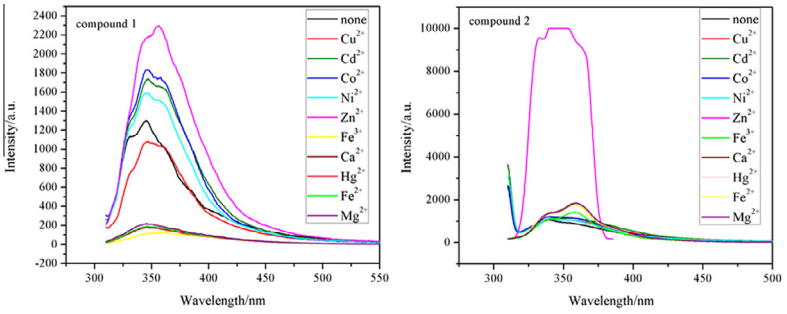
HIGHLIGHTS

- Two novel fluorescence probes were designed and synthesized.
- Experiments and theoretical calculations showed that compounds have outstanding fluorescence properties.
- The probes exhibited excellent sensitivity and selectivity for Zn^{2+}.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 June 2014
Received in revised form 27 September 2014
Accepted 19 November 2014
Available online 11 December 2014

Keywords:
Fluorescence sensors
Schiff base
Indole
p-Phenylenediamine
Zn^{2+}

ABSTRACT

Two novel fluorescence probes based on conjugated Schiff base for the detection of Zn^{2+} were developed. Corresponding molecular geometries, orbital energies, electron contributions and absorption properties of the fluorescence probes were calculated at B3LYP/6-31G* by density functional theory. The fluorescence properties of the probes were investigated by UV–vis and fluorescence spectrometer. Results indicate that the probes exhibit excellent sensitivity and selectivity for Zn^{2+} compared with metal ions examined. For example, the enhancement efficiency of the compound **2** for Zn^{2+} is up to 846%. The detection limit of the sensor toward Zn^{2+} could low to 1.0×10^{-7} M. Moreover, mechanisms for the high selectivity and sensitivity of the probes to Zn^{2+} were studied.

Introduction

Zinc as one of the essential trace elements in human body plays crucial roles in various biological and metabolic processes, such as brain function, gene transcription, neural signal transmission and immune function [1,2]. On the other side, the deviation of Zn^{2+} concentrations from normal levels may result in an increased risk of many diseases, such as Alzheimer's disease, hepatosplenomegaly, infantile diarrhea and amyotrophic lateral [3,4]. The World Health Organization has reported that more than 40% of the children in Africa and Asia suffered from the stunted growth problem which is probably caused by the lack of zinc elements. Moreover, Zn^{2+} is also a potent environment killer. Therefore, it is of great current interest to find a simple and efficient method for the detection of Zn^{2+} in the biological system and environment.

In the past few years, many fluorescence probes have been designed and synthesized to detect metal ions because of their high selectivity, simplicity, cost-effectiveness and facile operation [5–8]. For example, Wu et al. reported a simple off-on Zn^{2+} fluorescence probe with high selectivity benefited from chelation enhanced fluorescence effect (CHEF), C=N isomerization mechanism and the inhibition of photoinduced electron transfer [9]. Zhang et al. reported a turn-on fluorescence probe L with naphthol hydroxyl and imide groups, fluorescence enhanced when Zn^{2+} was added into the dimethyl sulfoxide solution of L [10]. Lippard et al. had designed a series of Zn^{2+} fluorescent probes based on PET

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http://dx.doi.org/10.1016/j.saa.2014.11.098
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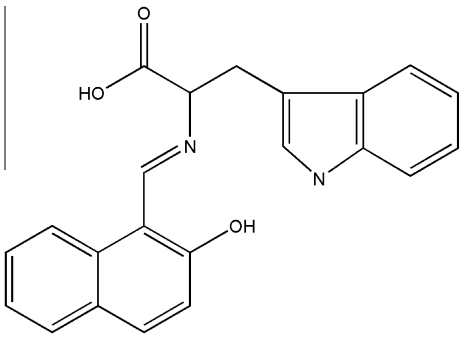


Fig. 1. The structure of the compound from Ref. [21].

mechanism using DPA as the receptor [11,12]. However, all the above Zn^{2+} fluorescent probes are hard to synthesis. Schiff base has attracted much attentions since it contains C=N group with a lone electron pair and can be synthesized by simple methods. It has been applied to many fields, such as medicine [13] and fluorescent sensors [14,15]. To date, many fluorescent probes for Zn^{2+} based on Schiff base have been reported [16–20]. However, the applications of fluorescent probes for Zn^{2+} are limited due to the instability or the lack of adequate selectivity. Furthermore, many fluorescent probes are vulnerable to interference by other metal ions, such as Cd^{2+} which chemical properties are so similar to Zn^{2+}. Therefore, the development of attractive synthetic methods for novel fluorescent probes based on Schiff base is of great significance.

Based on Schiff base, Wu reported a fluorescent chemosensor which displayed specific recognition to Zn^{2+} [21], the structure is shown in Fig. 1. Molecules possessing C=N structure usually have high affinity in coordinating with metal ions, when it combines with the ions, the C=N isomerization would be prevented which resulted in the enhancement of fluorescence emission. Herein, we designed and synthesized two simple compounds based on conjugated Schiff base by condensation reactions of indole derivatives with *p*-phenylenediamine. As fluorescent probes, they displayed high selectivity and sensitivity for Zn^{2+} compared with other metal ions (Scheme 1).

Experimental

Materials

Analytical-grade 5-methoxyindole-3-carboxaldehyde, indole-3-carboxaldehyde and *p*-phenylenediamine were obtained from Aladdin. Methanol (CH_3OH, 99.5%, AR) was distilled before using, and glacial acetic acid (CH_3COOH, 99.5%, AR) was used without further purification. All the solvents were purchased from Guangfu Limited.

Instrumentation

Fourier Transform Infrared (FT-IR) spectra were conducted on Kumo TENSOR 27 FT-IR spectrometer by KBr tablet method. ^1H NMR and ^{13}C NMR spectra nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 spectrometer (resonance frequency of 400 MHz) operated in the Fourier transform mode. Dimethyl sulfoxide (DMSO) was used as the solvent. The melting points were measured on SGWX-4 micro melting point apparatus. All ultraviolet–visible (UV–vis) spectra were acquired on a TU-1901 UV–vis spectrofluorometer, using N,N-dimethylformamide (DMF) as the solvent. And fluorescence spectra were recorded using an F-4500 (Hitachi) spectrofluorometer.

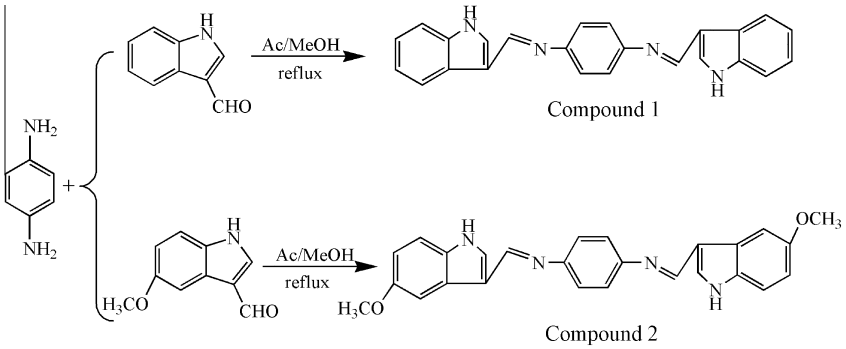
*Synthesis of the compounds **1** and **2***

*Synthesis of compound **1***

The general procedure for the synthesis of compound **1** was showed as follows. Indole-3-carboxaldehyde (2.88 g, 1.99×10^{-2} mol) and *p*-phenylenediamine (1.07 g, 1.00×10^{-2} mol) were added to a 100 mL four-neck round bottomed glass reactor and dissolved into absolute methanol (40 mL). When the solids were dispersed in the solvent completely at room temperature, four drops of glacial acetic acid was added dropwise to the solution. After refluxing for 6 h at 65 °C, yellow precipitate was obtained. After filtration, the powder was washed by ethanol for several times until the filtrate was colorless. Dried under vacuum for 6 h to give compound **1** as yellow solid (2.3 g, yield = 63.0%), Mp 330 °C. IR (cm^{-1}, KBr) ν/cm^{-1}: 1606.70 (C=N), 1575.84 (N-H), 1444.68, 856.39 (benzene ring, C—C), 1361.74 (C—N); ^1H NMR (DMSO-d_6, 400 MHz): 11.74 (s, 2H, —NH), 8.77 (s, 2H, —CH—), 8.40 (d, J = 7.6 Hz, 2H, —CH—), 8.00 (d, J = 2.4 Hz, 2H, —CH—), 7.49 (d, J = 7.6 Hz, 2H, —CH—), 7.27 (s, 2H, —CH—), 7.25 (d, J = 7.2 Hz, 2H, —CH—), 7.20 (d, J = 7.2 Hz, 2H, —CH—), 7.16 (d, J = 7.6 Hz, 2H, —CH—). ^{13}C NMR (DMSO-d_6, 100 MHz, δ, ppm): 154.2, 149.3, 137.1, 133.1, 124.8, 122.7, 121.1, 121.0, 120.7, 115.2, 111.5.

*Synthesis of compound **2***

Typical procedure employed for the synthesis of compound **2** was showed as follows. 5-methoxyindole-3-carboxaldehyde (2.89 g, 1.64×10^{-2} mol) and *p*-phenylenediamine (1.07 g, 1.0×10^{-2} mol) were dissolved in absolute methanol (40 mL) in a round-bottom flask equipped with a magnetic stirring bar, and the resultant solution was stirred at room temperature. When the solid dispersed in the solvent absolutely, four drops of glacial acetic acid was added. After that, the mixture was heated to



Scheme 1. The synthetic routes of compounds **1** and **2**.