



A new dihydrazone based “turn on” fluorescent sensor for Zn(II) ion in aqueous medium



R. Borthakur^a, U. Thapa^a, M. Asthana^b, S. Mitra^{a,*}, K. Ismail^a, R.A. Lal^{a,*}

^a Centre for Advanced Studies in Chemistry, North-Eastern Hill University, Shillong 793022, Meghalaya, India

^b Department of Chemistry, Centre of Advanced Study, Banaras Hindu University, Varanasi 221005, Uttar Pradesh, India

ARTICLE INFO

Article history:

Received 17 September 2014

Received in revised form 21 November 2014

Accepted 10 December 2014

Available online 11 December 2014

Keywords:

Succinoyldihydrazone fluorescent sensor

Zinc ion

Chelation-enhanced fluorescence (CHEF)

Binding constant

Detection limit

ABSTRACT

A new simple dihydrazone based colorimetric and fluorescent “turn-on” chemosensor (disalicylaldehyde succinoyldihydrazone, **I**) for Zn(II) was designed and synthesized. The photophysical behavior of the ligand and metal coordinated complex was characterized by steady state and time-resolved fluorescence, density functional theory calculation in combination with ¹H NMR and mass spectroscopy results. The compound acts as a highly selective and sensitive detector of Zn(II) in aqueous medium with almost six times increase in fluorescence intensity. The optimum condition for sensing ability of **I** with a detection limit of ca. 2 μM of Zn(II) was found at solution pH 8.6 and at excitation wavelength of 380 nm. The other interfering elements, including Cd(II), show either no or very little change in fluorescence intensity under similar experimental conditions.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

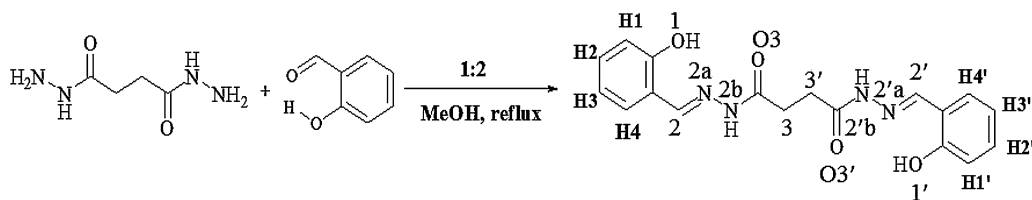
The development of fluorogenic sensors for transition-metal ions is particularly attractive because of their simplicity, high sensitivity, and instantaneous response [1–4]. The sensors that undergo fluorescence enhancement in the presence of metal ions are preferred because these allow a lower detection limit and high-speed spatial resolution via microscopic imaging [5–8]. Among the different chemical sensors, fluorescence-based sensors offer unparalleled sensitivity and thus have garnered significant interest [9]. Among the various metal ions present in human body, zinc is the second most abundant [10–13] and essential trace element that plays important roles in influencing DNA synthesis, gene expression, apoptosis, immune system function, and the activity of enzymes such as carbonic anhydrase and matrix metalloproteinase [14]. Although Zn(II) is considered to be relatively nontoxic, particularly if taken orally, overloading of this element damages several organisms [15–19]. Therefore, detecting Zn(II) ion in both environmental and biological samples is of significant interest and importance. Arguably, greatest interest has already been focused on the development of sensors for the detection of Zn(II) [20,21]; yet, limitations exist such as insufficient selectivity and/or sensitivity. Among the reported fluorescent probes especially developed for Zn(II), many cannot distinguish cadmium from zinc [22–25], because of their interfering chemical properties.

Therefore, searching for a new chemosensor which would react with Zn(II) with high selectivity is still an active field as well as a challenge for analytical research chemists. Moreover, both in environmental and biological systems, zinc-sensor interacts commonly in aqueous solution [15]. Therefore, a highly selective, non-toxic, easily synthesizable and water-soluble zinc sensor that can operate at physiological pH, to sense zinc levels over the broad concentration range known to be present in biological systems still needs to be developed.

Schiff base ligands containing strong donor sites like phenoxo oxygen atoms as well as imine nitrogen atoms are excellent for catalysis and biological replication [26,27] for their special coordination ability with transition metal ions. In addition, Schiff base derivatives incorporating a fluorescent moiety are appealing tools for optical sensing of metal ions [28]. Salicylaldehyde Schiff bases are classical ligands for complexation with transition metal ions [4,15,21,29]. These ligands have at least one hydroxyl group, a coordination nitrogen atom and a delocalized pi-system [25]. Therefore, organic metal-chelate complexes of salicylaldehyde Schiff base ligands usually also should exhibit good luminescent properties [25–34].

Considering the special coordination ability of Schiff base ligands with transition metal ions, we report a new chemosensor (disalicylaldehyde succinoyldihydrazone) **I** for detection of Zn(II) ion in near aqueous media and in micro molar concentration range; thus providing a simple, cost-efficient method for trace detection of zinc ions in bio-chemical systems. Most importantly **I** can be readily prepared with high yield by a simple Schiff base

* Corresponding author. Tel.: 91 364 272 2634; fax.: +91 3642250486.
E-mail address: smitra@nehu.ac.in (S. Mitra).



Scheme 1. Synthesis of I.

condensation reaction and the fluorescence behavior of this ligand acts as “turn-on” type chemo-sensor, specifically for Zn(II).

2. Experimental

2.1. Materials and methods

All analytical reagent (AR) grade chemicals were obtained from the commercial sources. Metal acetate salts of different cations were purchased from Hi-Media, India. Diethyl succinate, hydrazine hydrate, salicylaldehyde were E-Merck, Qualigens, Hi-Media or equivalent grade reagents.

2.2. Synthesis of chemosensor I

The synthesis of **I** was accomplished as previously reported by us [31,32] and summarized in Scheme 1. In brief, **I** was synthesized by condensation of succinoyldihydrazine with salicylaldehyde in 1:2 molar ratios in methanol under reflux condition. The precipitate obtained was thoroughly washed with methanol and air dried to give **I** in 89% yield.

2.3. Characterization of I

Colour: White; Yield: 89%; M.p.: 250 °C; Anal. Calc. for $C_{18}H_{18}N_4O_4$ (354 g mol^{-1}): C, 61.02; H, 5.08; N, 15.82. Found: C, 61.23; H, 5.06; N, 15.69. IR (KBr, cm^{-1}): (3421, 3199) s $\nu(\text{OH} + \text{NH})$, 1659 s $\nu(\text{C}=\text{O})$, (1609 s, 1622) s $\nu(\text{C}=\text{N})$, 1269 s $\nu(\text{C}-\text{O})$; $^1\text{H NMR}$ (400 MHz, DMSO-d_6) (δ ppm): 11.72 (d, 1H, $J = 7.6 \text{ Hz}$, OH), 11.30 (d, $J = 5.2 \text{ Hz}$, 1H, OH), 11.16 (s, 1H, NH), 10.15 (s, 1H, NH), 8.33 (s, 1H, $\text{CH}=\text{N}$), 8.27 (s, 1H, $\text{CH}=\text{N}$), 6.8–7.6 (m, 8H, Ar–H), 2.91 (m, 2H, CH_2), 2.53 (m, 2H, CH_2); $^{13}\text{C NMR}$ (100 MHz, DMSO-d_6) (δ ppm): 26.5, 27.2, 116.1, 116.3, 119.2, 119.4, 126.7, 129.4, 130.8, 130.9, 140.8, 140.9, 146.2, 146.3, 156.3, 157.3, 167.2, 167.6; ESI-MS: m/z 377.64 $[\text{M} + \text{Na}]^+$, where $\text{M} = C_{18}H_{18}N_4O_4$ (Fig. S1).

2.4. Instrumentation

Mass spectrum was recorded on water ZQ 4000 Micromass Spectrometer in DMSO solution. $^1\text{H-NMR}$ spectra was recorded on a JEOL (300 MHz) spectrometer. The details of steady state and time-resolved fluorescence measurements are given elsewhere [35]. In brief, the UV/Vis and steady state fluorescence experiments were carried out with PerkinElmer Lambda-25 and Hitachi FL-4500 spectrophotometers, respectively; whereas, fluorescence life – times were determined in a nano-LED based time-resolved fluorimeter obtained from Photo Technology International (PTI) using TCSPC technique. The experimental solutions and/or buffers (TRIS buffer) were prepared with analytical grade type – II water obtained from Elix 10 water purification system (Millipore India Pvt. Ltd.). To ensure spectroscopic homogeneity, 0.5% (v/v) DMSO/water (TRIS buffer) solutions of **I** were prepared by mixing trace volume of stock DMSO solution of known concentration into the desired amount of water (TRIS buffer) medium. Spectroscopic investigations were carried out on this solution (hereinafter

referred as aqueous/buffer solution in the text) with an intention to verify **I** as a possible fluorescence based zinc sensor.

3. Results and discussions

3.1. Photophysical behavior of I: Proton dissociation in the excited state

3.1.1. Steady state spectral properties in solution

The solution phase UV–vis spectra of **I** show a single broad absorption peak at $\sim 330 \text{ nm}$ ($\epsilon_{\text{max}} \sim 2.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$). Excitation at the absorption peak also results a single broad emission peak at $\sim 470 \text{ nm}$ along with a small peak at $\sim 370 \text{ nm}$. The fluorescence excitation spectra corresponding to these two emissions appear at $\sim 380 \text{ nm}$ and $\sim 350 \text{ nm}$, respectively (Fig. 1). With increase in pH of the solution, the intensity of 370 nm decreases with a concomitant increase in the emission intensity at 470 nm. These results confirm that the normal form of **I** and its proton dissociated anionic structure give emission peaks at 370 and 470 nm, respectively. Thus the ground and excited state photophysical behaviour can be depicted as in a simple Jablonski type of diagram given in Scheme 2, which is further supported by time-resolved fluorescence and density functional theory (DFT) calculation results, discussed later.

3.1.2. Time-resolved fluorescence properties

Fluorescence lifetime of **I** is detected by nanosecond time-correlated single photon counting technique using 340 and 365 nm LED, respectively to excite the neutral and anionic forms and monitoring the emission at 380 and 460 nm, respectively. All the time-resolved data are collected in Table 1 and some of the representative decay profiles are shown in Fig 2. Apparently, all the fluorescence decays need three exponential function to reproduce the experimental data points with acceptable statistical

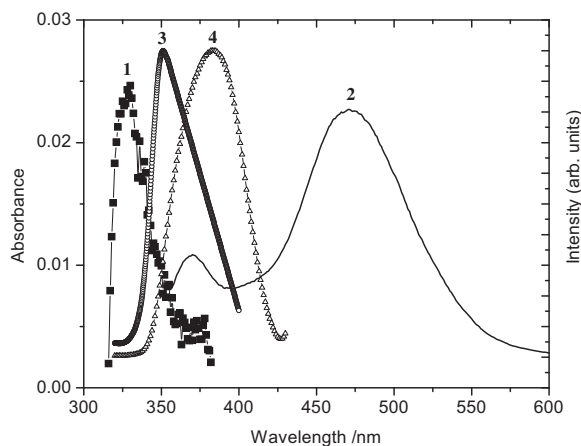


Fig. 1. Absorption (1), emission (2) and excitation spectra (3 & 4) of $1 \mu\text{M}$ solution of **I** in DMSO: Water (0.5%, v/v) solution at pH 7.4, $\lambda_{\text{mon}} = 370$ and 470 nm for (3) & (4), respectively.

Download English Version:

<https://daneshyari.com/en/article/26788>

Download Persian Version:

<https://daneshyari.com/article/26788>

[Daneshyari.com](https://daneshyari.com)