Dyes and Pigments 97 (2013) 297–302

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

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

A highly selective chemosensor for colorimetric detection of Fe^{3+} and fluorescence turn-on response of Zn^{2+}

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ARTICLE INFO

Article history:
Received 21 June 2012
Received in revised form
6 October 2012
Accepted 21 December 2012
Available online 16 January 2013

Keywords:
Iron(III)
Zinc(II)
Colorimetric sensor
Fluorescence switch
Schiff base
Naked eye

ABSTRACT

A simple cation sensor bearing naphthol O–H and imine group was designed and synthesized, which showed both colorimetric detection for Fe^{3+} and fluorescence turn-on response for Zn^{2+}. Meanwhile the distinct color change and the rapid enhancement of fluorescence emission provide naked eyes detections. Moreover, the sensing of Zn^{2+} was found to be reversible, with the Zn^{2+}-induced emission spectra being quenched upon addition of EDTA. Even more important, this sensor provides a novel approach for selectively recognizing the most important two trace elements at the same time, for Fe^{3+} by UV–vis spectra and Zn^{2+} by emission spectra.

1. Introduction

In the past decade, the development of chemosensors with high selectivity and sensitivity has been a great interest field in supramolecular chemistry, especially for those in detecting biological active metal ions [1–8]. Iron and zinc, as the most two abundant and essential trace elements in the human body, play significant roles in various fundamental biological processes, such as cellular metabolism, energy generation, oxygen transport, gene expression, neurotransmission and regulation of metalloenzymes [9,10]. However, if unregulated, Fe^{3+} and Zn^{2+} can cause many severe diseases, such as β-thalassemia, Friedreich's ataxia, Alzheimer's disease, Parkinson's disease and epilepsy [11]. Moreover, excessive of these two ions is also harmful to the environment [12]. Thus, it is so imperative to develop analytic and detective methods for sensitive sensing of these two ions, because of their potential applications in clinical biochemistry and in environmental research.

Accordingly, a variety of sensing devices, involving Schiff bases, polythiacrown ethers, calix[n]arenes and tripodal derivatives have been reported and used with some success in biological applications for the selective detection of these two ions [13–16]. Nevertheless, most of the colorimetric as well as fluorescent sensors usually function in detecting Fe^{3+} or Zn^{2+} individually [17–19]. This limits their practical applications for detecting these two ions in a physiological environment. Moreover, their preparations require laborious multistep organic synthesis, which renders their discovery processes slow and causes prohibitively high cost. Chemosensors for selectively detecting both Fe^{3+} and Zn^{2+} by different approaches are relatively rare. In this context, the design and synthesis of simple, facile, low-cost and efficient sensors for selectively recognition of Fe^{3+} and Zn^{2+} remains of great interest, particularly for those showed both colorimetric and fluorometric properties.

Our research group has a longstanding interest in molecular recognition [20–22]. Herein, we reported the cation selective properties of a simple Schiff base (sensor **L**), which was synthesized in one step by the facile Schiff base condensation reaction of 2-hydroxy-1-napthaldehyde with 2-aminopyridine (Scheme 1). The strategy employed in the design of this sensor is as follows. Firstly, we introduced nitrogen and oxygen heteroatoms as chelating sites. Secondly, a naphthalene group was introduced as chromophore and fluorophore to achieve "naked-eye" recognitions. Thirdly, a Schiff base structure was used to significantly enhance intramolecular charge transfer (ICT) [23,24]. Finally, the sensor was designed with ease of synthesis and low cost. We are very gratifying to see that the results go as we expected, sensor **L**

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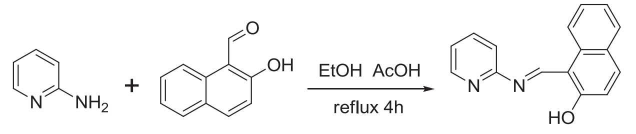
0143-7208/$ – see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.dyepig.2012.12.025



Scheme 1. Synthetic procedures for sensor **L**.

not only shows colorimetric, selective recognition for Fe^{3+} but also expresses an OFF–ON fluorescent selectivity for Zn^{2+} in DMSO. The excellent selectivity and strong affinity for Fe^{3+} is due to the ICT between naphthol O–H and N=CH group, while the enhancement of fluorescence spectra for Zn^{2+} is based on the coordination of Zn^{2+} to the sensor via the "O" and "N" heteroatoms.

2. Experimental

2.1. Materials and physical methods

^1H NMR and ^{13}C NMR spectra were recorded on a Mercury-400BB spectrometer at 400 MHz. ^1H chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards) UV–vis spectra were recorded on a Shimadzu UV-2550 spectrometer. The fluorescence spectra were recorded with a Shimadzu RF-5301 spectrofluorimeter. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. All reagents used were of analytical grade.

2.2. Synthesis of sensor L

The synthesis of sensor **L** is outlined in Scheme 1, by a facile Schiff base condensation reaction: 2-hydroxy-1-napthaldehyde (2.0 mmol, 0.35 g) was added to the solution of 2-aminopyridine (2.2 mmol, 0.21 g) in ethanol (25 ml), and several drops of acetic acid was added to the solution as catalyst. The reaction mixture was refluxed for 4 h. After cooling to room temperature, yellow precipitates was filtered, washed three times with hot absolute ethanol to give a yellow powder product **L** (0.36 g, yield: 80%). m.p. 183 °C, ^1H NMR (DMSO-d_6, 400 MHz) δ 15.21 (s 1H, OH), δ 9.84 (s 1H, NH), 6.84 ~ 8.53 (m 10H, ArH). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 177.93, 152.87, 150.69, 149.07, 139.14, 133.74, 129.39, 128.85, 126.55, 124.37, 124.02, 121.71, 119.75, 118.86, 115.25, 108.09. IR (KBr, cm^{-1}) v: 1560.41 (C=C), 1618.27 (CH=N), 3055.24 (ArH), 3444.38 (O–H) cm^{-1}. Anal. Calcd. for $C_{16}H_{12}N_2O$: C 77.41, H 4.84, N 11.29; Found C 77.38, H 4.84, N 11.25. Scheme 1.

2.3. General procedure for UV–vis experiments

All UV–vis spectroscopy was carried out just after the addition of perchlorate metal salts in DMSO solution, while keeping the ligand concentration constant (2.0×10^{-5} M) on a Shimadzu UV-2550 spectrometer. The solution of metal ions were prepared from the perchlorate salts of Fe^{3+}, Hg^{2+}, Ag^+, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Mg^{2+}.

2.4. General procedure for fluorescence experiments

All fluorescence spectroscopy was carried out just after the addition of perchlorate metal salts in DMSO solution, while keeping the ligand concentration constant (5.0×10^{-6} M) on a Shimadzu RF-5301spectrometer. The solution of metal ions were prepared from the perchlorate salts of Fe^{3+}, Hg^{2+}, Ag^+, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Mg^{2+}.

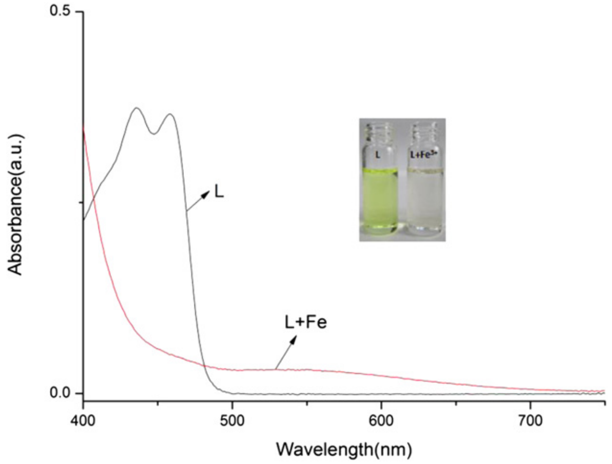


Fig. 1. Absorption changes of sensor **L** (2.0×10^{-5} M) in DMSO upon addition of 20 equivalents of Fe^{3+}, acquired after 180 min.

3. Results and discussions

3.1. Absorption spectroscopic studies on metal ions

The recognition profiles of sensor **L** toward various metal cations, Fe^{3+}, Hg^{2+}, Ag^+, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Mg^{2+}were primarily investigated by UV–vis spectroscopy in DMSO. The results show that **L** generated the largest signal in the presence of Fe^{3+}, when 20 equivalents of Fe^{3+} was added to the solution of sensor **L**, after 180 min, we found sensor **L** responded with a dramatic color change, from yellow to colorless, which could be easily detected by the naked eye. In the corresponding UV–vis

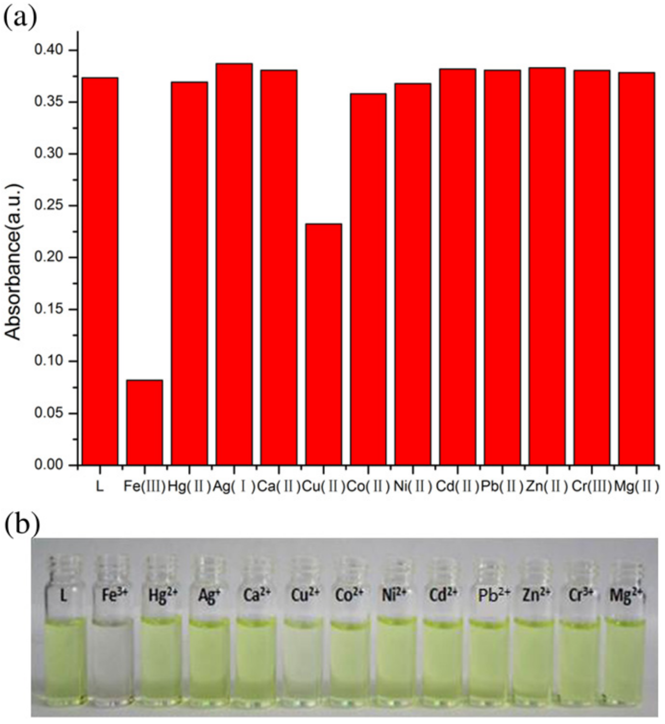


Fig. 2. (a) Absorption changes of sensor **L** (2.0×10^{-5} M) in DMSO upon addition of 20 equivalents of different perchlorate salts acquired after 180 min. (b) Color changes observed for L (2.0×10^{-5} M) upon the addition of Fe^{3+}, Hg^{2+}, Ag^+, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Mg^{2+} (1:20 equiv.) in DMSO.