Journal of Photochemistry and Photobiology A: Chemistry 315 (2016) 8–13

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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

A new colorimetric and turn-on fluorescent chemosensor for Al^{3+} in aqueous medium and its application in live-cell imaging

Fang Yu[a], Ling Jie Hou[a], Li Yuan Qin[a], Jian Bin Chao[a], Yu Wang[a,*], Wei Jun Jin[b,**]

[a] School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, PR China
[b] College of Chemistry, Beijing Normal University, Beijing 100875, PR China

ARTICLE INFO

Article history:
Received 4 July 2015
Received in revised form 6 September 2015
Accepted 8 September 2015
Available online 12 September 2015

Keywords:
Fluorescent chemosensor
Colorimetric
Al^{3+}
Naphthalene
Cell imaging
Aqueous medium

ABSTRACT

A new simple Schiff-base ligand 2-Hydroxy-1-naphthaldehyde-(2-pyridyl) hydrazone (HL) was synthesized and characterized as a fluorescent probe. In aqueous solution containing 10% ethanol (Hexamethylenetetramine-HCl buffer, pH5.3), HL selectively binds $Al^{3+}$to form a 1:1 ligand/metal complex, resulting in a color change from colorless to yellow–green and a significant fluorescence enhancement at 454 nm. The addition of EDTA quenches fluorescence of the HL·Al^{3+} complex, indicating that HL serves as a reversible chemosensor for Al^{3+}. Under the optimum conditions, the dynamic range of the system was found to be linear up to 4.0×10^{-6} M Al^{3+} ions with a limit of detection of 36.6 nM. The probe is very effective for detection of intracellular Al^{3+} through fluorescence microscopic imaging.

1. Introduction

As the third most prevalent element in the earth's crust and the most widely spread metal, Aluminum exists in its ionic form as Al^{3+} in most animal and plant tissues as well as in natural waters. Although Al^{3+} is widely used in our daily life, it is a non-essential element for living systems. Aluminum in excessive amounts not only hampers plant growth but damages the human nervous system and has been reported to induce neuronal disorder leading to Alzheimer's disease, Guamanian amyotrophic lateral sclerosis and Parkinsonism dementia [1]. As per the WHO norms, the permissible level of Al^{3+} in drinking water is 200 $\mu g\,L^{-1}$ (7.41 μM) [2]. Thus the detection of Al^{3+} in natural environment and living organisms is of considerable importance for human health. Out of various methods available for the detection of Al^{3+} ions, the spectrofluorometry has attracted much interest due to its high sensitivity, selectivity, rapidity and versatility. However, development of selective and sensitive fluorosensors for Al^{3+} is highly challenging for its poor coordination ability compared to transition metals [3]. Although a number of derivatives have been exploited hitherto for the fluorescence sensing of Al^{3+} by various workers [4–32], the majority of probes currently available cannot be operated in water let alone in buffered solution, which limited their practical applications. Hence, there is a great demand for the development of novel fluorescent chemosensors for Al^{3+} which satisfy several parameters viz. easy and economical synthetic procedure, water solubility and being suitable for cell imaging studies.

Schiff bases with proper placement of additional N or O as donor atoms can form stable complexes with transition metal ions. Hence, Schiff base derivatives incorporating a fluorescent moiety have been used for optical sensing of metal ions including Al^{3+} ions. However, examples of water-soluble sensors that can be used for imaging Al^{3+} in living cells are still quite limited in number [8,11,16,22,25,28,31]. Herein, we report on the synthesis of a very simple naphthalene-based Schiff base fluorescent probe, 2-hydxoxy-1-naphthaldehyde-(2-pyridyl) hydrazone (HL). HL has nitrogen and oxygen rich coordination environment which provides a hard base environment for hard acid Al^{3+}. We show that HL exhibits substantial color change and enhanced fluorescence upon complexation with Al^{3+}, which could be utilized as a selective colorimetric and fluorescent probe for Al^{3+} in aqueous media. Detection of Al^{3+} ions in living cell using fluorescence microscope was also demonstrated.

* Corresponding author. Fax: +86 351 7011688.
** Corresponding author. Fax: +86 1 58802146.
E-mail addresses: wangyu1168@sxu.edu.cn (Y. Wang), wjjin@bnu.edu.cn (W.J. Jin).

http://dx.doi.org/10.1016/j.jphotochem.2015.09.006
1010-6030/

2. Experimental

2.1. Materials and instrumentation

2-Hydroxy-1-naphthaldehyde (98%) was purchased from Energy Chemical (Shanghai, China). 2-Hydrazinopyridine was purchased from Aladdin Reagent Co. (Shanghai, China). All the other chemical reagents were of analytical grade and were used without further purification. Stock solutions of metal ions were prepared by dissolving their nitrates in water. Double distilled water was used throughout.

The UV absorption spectra were recorded on a UV-2450 spectrophotometer (Shimadzu, Japan). Fluorescence measurements were performed on a LS-55 spectrofluorimeter (PerkinElmer, USA). The samples were excited at 336 nm. The excitation and emission slits were set at 12 and 4 nm, respectively. IR spectra were taken as KBr pellets on a SHIMADZU 8400S infrared spectrometer (Nicolet, Waltham, Japan). The 1H NMR and 13C NMR spectra were recorded at 300 and 600 MHz at 298 K, using tetramethylsilane (TMS) as internal standard. Elemental analyses were performed using an Elementar Analysensteme Gmbh VarioEL analyzer. High resolution mass spectra were obtained on a Bruker micrOTOF-Q III mass spectrometer. The pH measurements were carried out on a pHS-3C acidometer (Shanghai Precision & Scientific Instrument Co., Ltd., China).

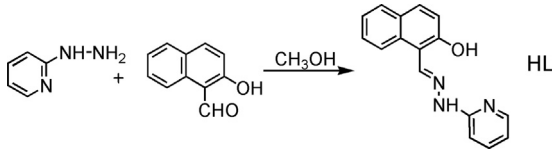
2.2. Synthesis of HL

The mixture of 2-Hydrazinopyridine (0.21 g, 2 mmol) and 2-Hydroxy-1-naphthaldehyde (0.36 g, 2 mmol) was refluxed for 3 h in CH_3OH (15 mL). After cooling to room temperature, the precipitate was filtered off and recrystallized from ethanol to give the product as a light-yellow solid (0.44 g, yield 84%). IR ν_{max} (KBr) 3442, 3175, 3008, 2954, 1598, 1594, 1443, 1316, 1279, 1161, 1101, 768, 739 cm^{-1}. ^1H NMR (DMSO-d6) δ: 11.92 (s, 1H, NH), 11.09(s, 1H, OH), 9.08 (s, 1H, HC=N), 8.38 (d, J = 8.11 Hz, 1H, ArH), 8.19 (t, J = 4.05 Hz,1H, ArH), 7.84 (m, 2H, ArH), 7.74 (t, J = 8.92 Hz, 1H, ArH), 7.60(t, J = 7.30 Hz, 1H, ArH), 7.41(m, 1H, ArH), 7.25 (d, J = 8.09 Hz, 1H, ArH), 7.00 (d, J = 8.11 Hz, 1H, ArH), 6.85 (m, 1H, ArH). ^{13}C NMR (DMSO-d6): 156.53, 156.20, 148.68, 139.59, 138.74, 131.58, 131.45, 129.30, 128.48, 127.86, 123.80, 121.84, 119.00, 115.76, 110.37, 106.42. HRMS(ESI): calcd. for $C_{16}H_{13}N_3O$ 264.1131(M + H), found: 264.1128. Elemental analysis: Calculated: C, 72.99; H, 4.98; N, 15.96. Found: C, 72.63; H, 4.96; N, 15.89 (Scheme 1).

2.3. General procedure

Typically, to a comparison tube containing 1.0 mL of HL stock solution and 1.0 mL of hexamethylenetetramine-HCl buffer solution of pH 5.3, an appropriate aliquot of Al^{3+} was added and the mixture was diluted to 5 mL with water. The mixed solution was shaken well and kept for 5 min before the absorption and fluorescence spectra were measured.

For competition experiments purpose, a solution of HL in water (4×10^{-6} M) was prepared, aliquots of Al^{3+} (12×10^{-6} M) and all other coexisting cation salt solutions (12×10^{-6} M) were added and the respective emission spectra was measured.



Scheme 1. Synthesis of HL.

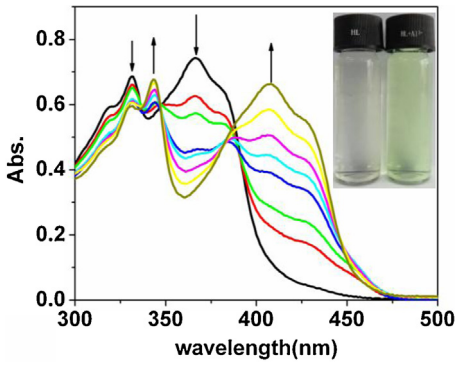


Fig. 1. Absorption spectra of HL (40 μM) in the presence of different concentrations of Al^{3+} (up to 3 equiv.) in EtOH/H_2O (1:9, v/v, pH 5.3). The inset shows visual color change of HL in the presence of Al^{3+} ions (3 equiv.). (For interpretation of the references to colour in the text, the reader is referred to the web version of this article.)

2.4. Cell imaging

In vitro experiments were performed using Human glioma cell line U251. U251 cells were cultured in DMEM medium, which was supplemented with 10% fetal bovine serum (FBS) in an atmosphere of 5% CO_2 at 37 °C. Immediately before the experiments, the cells were incubated with 50 μM HL in 0.1 M sterile PBS buffer for 30 min at room temperature. After incubation, the cells were washed with PBS buffer and incubated with Al^{3+} (150 μM) for additional 30 min at room temperature under 5% CO_2. The cells were washed three times with PBS buffer and the fluorescence intracellular images were obtained using an Olympus FV1000 confocal microscope (Tokyo, Japan) with a 40× objective (excited at 405 nm).

3. Results and discussion

3.1. Spectral characteristics of HL and HL–Al^{3+}

The spectroscopic properties of HL were investigated in an ethanol-water (1:9, v/v) solution at pH 5.3. As shown in Fig. 1, the UV/vis spectrum of free HL is characterized by two bands centered at 328 nm and 373 nm, which corresponds to π–π* transitions of pyridine and naphthalene ring, respectively [33,34]. The UV–vis response of HL to Al^{3+} shows an obvious concentration-dependent red shift of the maximum absorption peak from 373 nm to 415 nm. Well defined isosbestic points were obtained at 330, 350 and 380 nm, clearly indicating the formation of a complex between HL and Al^{3+}. The absorption spectral changes enable the observation of

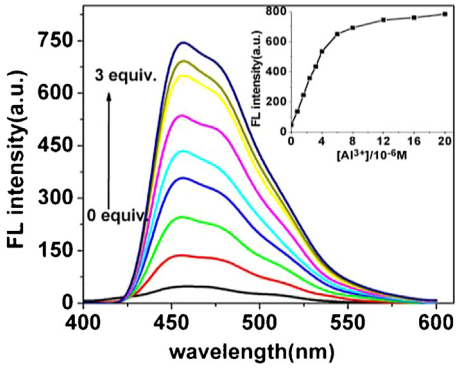


Fig. 2. Fluorescence spectra of HL (4 μM) in the presence of different concentrations of Al^{3+} (0–3 equiv.) in EtOH/H_2O (1:9, v/v, pH 5.3). The inset shows the fluorescence intensity of HL as a function of Al^{3+} ion concentration.