Journal of Luminescence 203 (2018) 113–120

Contents lists available at ScienceDirect

Journal of Luminescence

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

A novel turn on and reversible sensor for Al^{3+} and its applications in bioimaging

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ARTICLE INFO

Keywords:
Aluminum ions
Reversibility
Fluorescence probe
Fluorescent imaging
Coordination

ABSTRACT

A new and non-toxic probe **1** is synthesized and acted as fluorogenic sensor for Al^{3+} detection in CH_3CH_2OH / H_2O (1: 1, *v* / *v*). Besides the specific Al^{3+} induced a yellow solution of probe **1** to turn to colorless and with a 33 - fold fluorescence enhancement at 440 nm. Probe **1** is highly selective to Al^{3+} among other tested metal ions and anions with the detection limit is 0.37 μM. What's more, the binding constant between probe **1** and Al^{3+} is $7.62 \times 10^6\ M^{-1}$. The mechanism is confirmed by ESI - MS and a stoichiometric ratio of 1: 1 between probe **1** and Al^{3+}. The reversible "off-on" Al^{3+} response, fine cell permeability and cell imaging ability displays that its potential application in both environmental and Al^{3+} polluted biological samples.

1. Introduction

Aluminum is one of the most abundant metallic element in the earth's crust, which is widely used in daily life, such as cooking utensils, water purification, aluminum-based pharmaceuticals, packing materials and aerospace industry [1–6]. Although, it is convenient for us to use aluminum in life, excessive amount of aluminum is harmful to plant growth and human body [7–11]. For example, acid rain enhances the concentration of Al^{3+} in the environment and too high concentration of Al^{3+} may cause deleterious consequence to the growth of plants. In addition, when people are long-term exposed to Al^{3+} or excessive amount of Al^{3+} is intake, people could easily suffer from various diseases, due to the accumulation of Al^{3+} in different organs [12–18]. Moreover, when Al^{3+} is enriched in brain tissue, it will cause severe damages to the central nervous system, and further lead to extreme risks of neurological diseases [6,18]. Hence, the World Health Organization (WHO) recommended that the daily human intake of aluminum should be controlled within 10 mg and a tolerable weekly dietary intake should be controlled at 7 mg/kg of the body weight. The WHO also limited the concentration of Al^{3+} in drinking water is less than 7.41 μM [19]. Considering the potential impact of Al^{3+} on the environment and human health, it is required for us to detect Al^{3+} in life.

The most commonly used methods for detecting Al^{3+} include inductively coupled plasma optical emission spectrometry (ICP - OES) [20], inductively coupled plasma mass spectrometry (ICP - MS) [21], graphite furnace atomic absorption spectrometry (GF - AAS) [22], and atomic fluorescence spectroscopy (AFS) [23]. However, these methods have a few defects, such as operation process is complex and technology request is high. Nowadays, fluorescent probe has attracted considerable interest because of the high sensitivity, high selectivity, rapid response rate and simple manipulation [24–27]. It is reported that naphthalene and its derivatives have been chosen as ideal components of some fluorescent chemosensors [28–34], owing to the low fluorescence quantum yield, the short fluorescence life time, and the ability to act both as a donor as well as an acceptor [35].

In this paper, a novel fluorescent probe **1** is designed and synthesized to detect Al^{3+} via fluorescence method. The probe **1** emitted no luminescence in CH_3CH_2OH / H_2O (1: 1, *v* / *v*) solution. With the incremental addition of Al^{3+}, the characteristic emission at 440 nm is enhanced gradually. The response showed high selectivity for Al^{3+} compared with other common metal ions and anions. The binding strength for Al^{3+} is high and the limit of detection is low. The mechanism is proposed that a 1:1 complex was formed between probe **1** and Al^{3+}. Besides, probe **1** has good cell-membrane permeability and thus can be used to detect Al^{3+} within living cells.

2. Experimental

2.1. Materials

Propane-1,3-diamine, 2-hydroxybenzaldehyde and 2-hydroxy-1-naphthaldehyde were purchased from Shanghai. The salts solutions of metal ions, such as NaCl, KCl, $MgCl_2{\cdot}6H_2O$, $CaCl_2$, $BaCl_2$, $CrCl_3{\cdot}6H_2O$,

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https://doi.org/10.1016/j.jlumin.2018.06.047
Received 9 May 2018; Received in revised form 6 June 2018; Accepted 15 June 2018
Available online 18 June 2018
0022-2313/

$CoCl_2·6H_2O$, $MnCl_2·4H_2O$, $FeCl_3·6H_2O$, $NiCl_2·6H_2O$, $CuCl_2·2H_2O$, $CdCl_2·6H_2O$, $ZnCl_2$, SrCl, $AlCl_3$, $Pb(NO_3)_2$, $Bi(NO_3)_3$, $AgNO_3$, $SnCI_2$, $SrCI_2$, NH_4CI, $HgCI_2$ and the salts solutions of anions such as NaCl, KBr, KI, Na_2SO_4, Na_3PO_4, NaH_2PO_4, NaOH, $NaHCO_3$, $NaNO_3$, NaBr, $Na_2C_2O_4·H_2O$, NaF, Na_2HPO_4, $Na_2S_2O_3$, $NaNO_2$, NaAC·H_2O, $Na_2P_2O_7$, $Na_2B_4O_7$ were purchased from Shanghai Experiment Reagent Co., Ltd (Shanghai, China). Deionized water was used to prepare all aqueous solutions. All other chemicals used were of analytical grade.

2.2. Physical measurements

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker DRX 400 spectrometer with TMS as the internal standard. FT-IRspectra (4000 − 400 cm^{-1}) were obtained on NICOLET380 FT-IR spectrometer in KBr disks. Elemental analyses (EAs) were carried out with a VARI-EL elemental analyzer. Electrospray ionization mass spectra (ESI - MS) were measured on a Triple TOF TM 5600$^+$ system. Fluorescence spectral data were obtained by means of a RF-5301 fluorescence spectrophotometer. Ultraviolet spectrum was performed on UV-1800 ENG 240 V.

2.3. Measurement procedure

Fluorescence spectrum and UV–vis procedure were performed in a quartz optical cell of 1.0 cm optical path length at room temperature. All fluorescence measurements were carried out upon excitation at 370 nm, slit widths were 3 nm and 5 nm. The fluorescence procedures were as follows: metal ions and anions were gradually added to a C_2H_5OH / H_2O (v: v = 1: 1) solution containing 1.0 μM of probe **1**, then the titration experiment and interference experiment were tested. In the experiment of UV–vis spectral, 10 μM probe **1** was prepared in a quartz cell containing C_2H_5OH / H_2O (v: v = 1: 1) and 1 × 10^{-3} M Al^{3+} was gradually added. All fluorescence spectral and UV–vis data were recorded after the ion addition.

2.4. Calculations of the Binding Constant

The binding constant was calculated from the emission intensity titration curve according to Eqs. (1) and (2) [36].

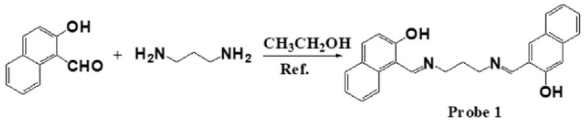
$$\frac{I_a - I_f}{I_b - I_f} = \frac{(b - (b^2 - 2K^2C_t[Al^{3+}]/s)^{1/2})}{2KC_t}. \quad (1)$$

$$b = 1 + KC_t + K[Al^{3+}]/2s. \quad (2)$$

Where I_a is the emission intensity observed at a given Al^{3+} concentration, I_f is the emission intensity of free probe **1** in solution, I_b is the emission intensity of probe **1** when fully bound to Al^{3+}, K is the equilibrium binding constant, C_t is the total probe **1** concentration, [Al^{3+}] is the Al^{3+} concentration, and s is the binding site size. Both K and s are obtained from the best fit line.

2.5. Cell Incubation and Imaging

HepG2 cells were cultured at 37 °C in a 5% CO_2 atmosphere and grown in DMEM supplemented with 10% fetal bovine serum (FBS) and 0.1% antibiotic-antimycoticmix antibiotic supplement. Afterwards, the cells were washed with 1×PBS and incubated in the medium containing probe **1** (final concentration: 10 μM) at 37 °C under 5% CO_2 for 30 min, and then treated with $AlCl_3$ (final concentration: 40 μM) for another 30 min. Subsequently, the cells were washed with 1 × PBS to remove the excessive dye. Next, the culture medium was removed, and the cells were washed with 1 × PBS for three times. Finally, the cells were imaged on a Leica-LCS-SP8-STED laser confocal fluorescence microscope.



Scheme 1. Synthesis of probe **1**.

2.6. Synthesis of the probe 1

The synthesis of probe **1** is summarized in Scheme 1. 0.244 g 2-hydroxybenzaldehyde (2 mmol) and 0.148 g propane-1,3-diamine (2 mmol) were added to 25.00 mL ethanol and heated to reflux for 1 h, then 0.344 g 2-hydroxy-1-naphthaldehyde(2 mmol) was added to the reaction solution and heated to reflux for 1 h. The solution was filtered, after the reaction cooled to room temperature. Then the precipitation was collected and washed with ethanol and dried in vacuo. The yellow crystal was recrystallized from the mixed solution of ethanol and DMSO at room temperature. Yield: 68%. Calc. for $C_{25}H_{22}N_2O_2$: C, 78.51; H, 5.80; N, 7.32. Found: C: 78.51; H: 5.82; N: 7.32%. IR (cm^{-1}, s strong, m medium, w weak): 3445 m, ν (O - H), 1639 s, ν (C = N). ^{1}H NMR (400 MHz, DMSO) δ 14.20 (s, 2 H), 9.16 (d, J = 9.6 Hz, 2 H), 8.07 (d, J = 8.3 Hz, 2 H), 7.73 (s, 2 H), 7.63 (s, 2 H), 7.38 (d, J = 7.3 Hz, 2 H), 7.19 (t, J = 7.3 Hz, 2 H), 6.75 (d, J = 9.3 Hz, 2 H), 3.77 (d, J = 4.8 Hz, 4 H), 2.16 − 2.10 (m, 2 H). ^{13}C NMR (101 MHz, DMSO) δ 177.03 − 176.83 (m), 160.19 (s), 137.41 (s), 135.04 − 134.84 (m), 129.72 (s), 128.61 (s), 125.60 (s), 122.93 − 122.73 (m), 119.53 (s), 106.67 (s), 48.94 (s), 32.03 – 31.83 (m). Exact mass for probe **1**: 382.1681, ESI-MS (positive mode) [probe **1** + H^+]$^+$ (m / z, 383.1986).

3. Results and discussion

3.1. Synthesis and structural characterization of probe 1

As shown in Scheme 1, the probe **1** was obtained from the reaction of salicylaldehyde, propane-1,3-diamine and 2-hydroxy-1-naphthaldhyde in ethanol. Its chemical structure was determined by ^{1}H-NMR, ^{13}C-NMR, Elemental analyses (EAs), Electrospray ionization mass spectra (ESI - MS) and FT-IR spectra (IR) analysis(as shown in Supporting information Fig. S1–Fig. S4).

3.2. Selectivity over metal ions

To value the selectivity of probe **1** for Al^{3+}, the interference experiment was performed with a large number of metal ions. From Fig. 1, different solutions of probe **1** with the concentration is 1.0 μM in C_2H_5OH / H_2O (v: v = 1: 1) and added separately 20 equiva. selected metal ions, such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cr^{3+}, Co^{2+}, Mn^{2+},

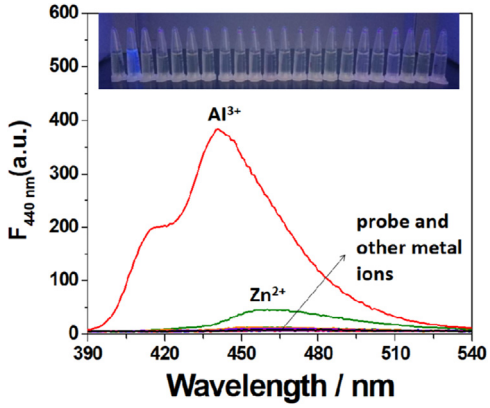


Fig. 1. Fluorescence responses of probe **1** upon the addition of several metal ions in C_2H_5OH / H_2O (v / v = 1 / 1). Inset: Corresponding fluorescent color under UV lamp.λ_{ex} = 370 nm, λ_{em} = 440 nm, slit:3 nm / 5 nm.