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A "turn-on" fluorescent chemosensor for aluminum ion and cell imaging application

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ABSTRACT

A simple and efficient fluorescent chemosensor for Al^{3+} is reported in the paper. The chemosensor is obtained by dehydration reaction of 2-hydroxy-1-naphthaldehyde and 2-aminophenol. The chemosensor has high selectivity and sensitivity for Al^{3+} and displays fluorescence "off–on" switch signal. The detection limit of the chemosensor for Al^{3+} can reach 1.0×10^{-7} M in DMSO/H_2O (1:9, v/v) solution. The mass spectra and Job's plot analysis confirm the 1:1 stoichiometry between chemosensor and Al^{3+}. Potential utilization of the probe as an intracellular sensor of Al^{3+} in human cancer (HiSa) cells is also examined by confocal fluorescence microscopy.

1. Introduction

Aluminum is the third most prevalent (8.3% by weight) metallic element in the earth. It has been widely used in packing materials, clinical drugs, food additives and water purification et al. [1–4]. The excess of aluminum can cause many health hazards such as Alzheimer's disease [5,6], Parkinson's disease [7], Osteomalacia [8], and even to the risk of cancer of the breast [9]. Additionally, the World Health Organization (WHO) prescribed the average daily human intake of aluminum as around 3–10 mg with a weekly tolerable dietary intake of 7 mg · kg^{-1} body weight. The WHO has listed aluminum as a source of food pollution and limited its drinking water concentration to 7.41 mM [10]. Therefore, it is necessary and highly desirable to develop some analytical methods for detecting and controlling the concentration levels of aluminum in the environmental and biological systems.

In the past ten years, several methods used for quantification of aluminum ion are atomic absorption spectrometry (AAS) [11,12], inductively coupled plasma mass spectroscopy (ICPMS) [13], inductively coupled plasma atomic emission spectrometry (ICP-AES) [14], electrochemical method [15,16] and fluorescent chemosensors. Compared with other methods, the fluorescence method can provide a simple and cost-effective detection way together with high sensitivity, good selectivity, short response time, and real-time monitoring [17,18]. However, the poor coordination ability of aluminum ion makes it develop slowly. It is because, as a hard acid, aluminum ion prefers to coordinate with hard base such as N and O atoms. Schiff bases (imine) are well known to be good ligands for metal ions [19,20]. Several publications have demonstrated that Schiff bases with proper placement of additional N or O as donor atoms can form stable complexes with transition metal ions and have been used as the ionophore in optical sensors for determining various cations [21–23].

Herein, we designed and prepared a simple chemosensor 1-{[(2-hydroxyphenyl)-imino]methyl}naphthalen-2-ol (HPIN) with Schiff-base unit and naphthalene group. Based on photoinduced electron transfer (PET) mechanism, the fluorescence of HPIN happens obvious enhancement with the interaction of HPIN with Al^{3+}. The mass spectra and Job's plot titration curve are used to study the bonding ratio of HPIN and Al^{3+}. In order to develop potential utilization of HPIN, as intracellular sensors, the interaction of HPIN with Al^{3+} in human cancer (HiSa) cells is examined by confocal fluorescence microscopy.

2. Experimental

2.1. Materials and instruments

All chemicals were obtained from commercial suppliers and used without further purification. ^{1}H NMR spectra were recorded on Bruker 300 MHz spectrometers, the chemical shifts (δ) were reported as ppm in DMSO-d_6. IR spectra were recorded with a ThermoFisher Nicolet iS5 FT-IR spectrophotometer as KBr pellets with absorption reported in cm^{-1}. Elemental analyses were measured on a EuroVector EA3000

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elemental analyzer. ESI-MS spectra were recorded on an Agilent 6520 Accurate-Mass Q-TOF LC/MS mass spectrometer. UV–visible (UV–vis) spectra were measured with a Varian 50 BIO spectrophotometer. Fluorescence spectra were recorded on an F-4600 fluorescence spectrophotometer equipped with quartz cuvettes of 1 cm path length at room temperature. Both the excitation and emission slit widths were 5.0 nm.

2.2. UV–vis and fluorescence spectra studies

Stock solutions of various metal ions (1.0 mM) were prepared using nitrate salts. A stock solution of HPIN (1.0 mM) in DMSO was prepared. Double-distilled water was used throughout the experiments. The working solution of HPIN was then diluted to 1.0 μM in DMSO/H_2O (1:9, v/v) solution. In fluorescence titration experiments, each time a 2 mL solution of L (1.0 μM) was filled in a quartz optical cell of 1 cm optical path length, and the ions stock solution were added into the quartz optical cell gradually by using a pipette. The binding constants were obtained from the emission intensity data following the modified Benesi–Hildebrand equation [24] (A):

$$\frac{1}{F-F_{min}} = \frac{1}{K(F_{max}-F_{min})\left[Al^{3+}\right]} + \frac{1}{F_{max}-F_{min}}$$

where F_{min}, F, and F_{max} are the emission intensities of the organic moiety considered in the absence of aluminum ion, at an intermediate aluminum concentration, and at a concentration of complete interaction, respectively, and where K is the binding constant.

2.3. Preparation of HPIN and HPIN/Al^{3+} complex [25,26]

The fluorescent chemosensor 1-{[(2-hydroxyphenyl)imino]methyl} naphthalen-2-ol (HPIN) was designed and synthesized in one step as shown in Scheme 1. 2-Hydroxy-1-naphthaldehyde (1.72 g, 10.0 mmol) in 50 ml absolute ethanol was added drop wise into a solution of 2-aminophenol (1.09 g, 10.0 mmol) in 50 ml absolute ethanol under stirring. And then, the reaction mixture was further stirred for 4 h at room temperature until an orange-yellow precipitate appeared. The resulting precipitate was filtered and washed 2 times with ice ethanol. The solid obtained was recrystallized from ethanol to give orange-yellow crystals. Yield: 85%, m.p.: 252–253 °C. Anal. Calc. for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 78.27; H, 5.02; N, 5.09. IR (KBr pellet, cm^{-1}): 3427 (OH), 1632 (C = N); ^1H NMR (DMSO-d_6, δ_H, ppm): 10.32 (s, 1H), 9.51 (d, 1 H), 8.40 (d, 1 H), 7.95 (d, 1 H), 7.82 (d, 1 H), 7.69 (d, 1 H), 7.51 (t, 1 H), 7.29 (t, 1 H), 7.11 (d, 1 H), 7.01 (m, 2H), 6.79 (d, 1 H). ESI-MS (*m/z*): $[M + H]^+ = 264.1018$.

A mixture of HPIN (0.26 g, 1.0 mmol) and $Al(NO_3)_3 \cdot 9H_2O$ (0.38 g, 1.0 mmol) in 10 mL of methanol was stirred and refluxed for 5 h. The reaction mixture was concentrated by rotary evaporation and cooled to precipitate solid. The solid was collected on a Buchner funnel, washed thoroughly with methanol and dried at ambient temperature to obtain yellow brown solid. Yield 68%. IR (KBr pellet, cm^{-1}): 3423 (OH), 1621 (C = N), 1384 (NO_3). ESI-MS (*m/z*): $[(M - 2H) + Al(III)]^+ = 288.0584$, $[(M - 2H) + Al(III) + H_2O]^+ = 306.0701$, $[(M - 2H) + Al(III) + CH_3OH]^+ = 320.0859$, $[(M - 2H) + Al(III) + H_2O + Na]^+ = 329.0862$, $[(M - 2H) + Al(III) + 2H_2O + Na]^+ = 347.0969$, $[(M - 2H) + Al(III) + H_2O + CH_3OH + Na]^+ = 361.1125$, $[(M - 2H) + Al(III) + H_2O + NO_3 + 2]^+ = 370.1126$.

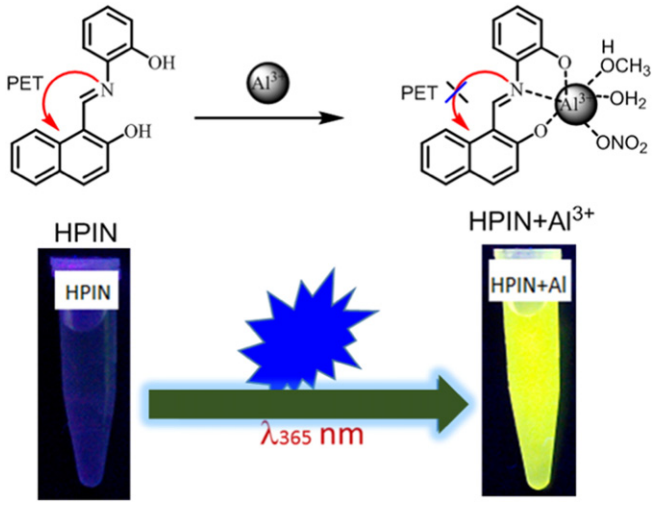
2.4. Cells culture and imaging

Under a humid atmosphere containing 5% CO_2, SiHa cells were grown in DMEM medium containing 10% FBS routinely, then harvested for subculture using trypsin (0.05%, Gibco/Invitrogen) at 37 °C. SiHa cells were incubated onto a 35 mm × 35 mm Petri dish with a glass bottom, then allowed to grow for 24 h for attachment, after which 1 mL of DMEM medium containing 10% 5 μM compound HPIN was used to incubate the SiHa cells at 37 °C for 5 h. The medium was replaced and phosphate-buffered saline (PBS, pH = 7.4) was used to wash the cells thrice. And two equivalent metal ion in PBS buffer solution were added into the dish and the cells were cultured at 37 °C for 1 h. The medium was replaced and phosphate-buffered saline (PBS, pH = 7.4) was used to wash the cells thrice. Then fresh medium with cytoplasm located dye (LysoTracker Red) was added and incubated. After washing thrice with PBS, the images of the cells were recorded on confocal laser scanning microscopy.

3. Results and discussion

3.1. UV–vis absorption and fluorescence emission spectra of HPIN with Al^{3+}

Firstly, the interaction of HPIN with Al^{3+} was investigated by UV–vis absorption spectrum. Fig. S1 shows the change of the UV–vis spectrum of HPIN with addition of Al^{3+} in DMSO/H_2O (1:9, v/v) solution. As can be seen from Fig. S1, Upon the addition of Al^{3+}, the absorption intensities of HPIN peaks about 450 nm (n–π* transition from imine) and 310 nm (π–π* transition from naphthalene) all gradual decrease with the solution



Scheme 1. The probable bonding model of HPIN with Al^{3+} and the color change of HPIN (2.0×10^{-5} mol/L) solution by introducing Al^{3+} (2.0×10^{-4} mol/L).

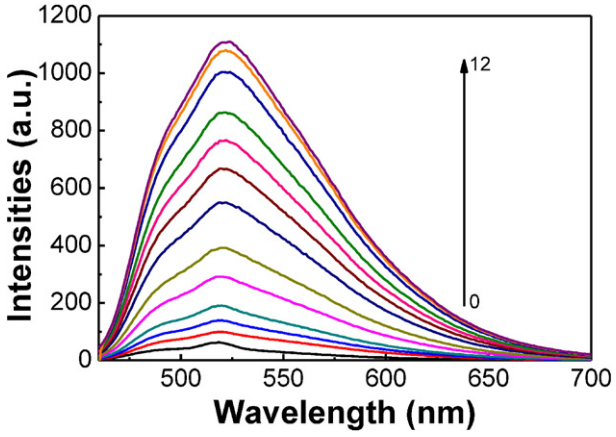


Fig. 1. Fluorescence spectra of HPIN (1.0×10^{-6} mol/L) in DMSO/H_2O (1:9, v/v) solution upon the addition of Al^{3+} (0, 0 mol/L; 1, 1.0×10^{-7} mol/L; 2, 2.0×10^{-7} mol/L; 3, 3.0×10^{-7} mol/L; 4, 4.0×10^{-7} mol/L; 5, 5.0×10^{-7} mol/L; 6, 6.0×10^{-7} mol/L; 7, 7.0×10^{-7} mol/L; 8, 8.0×10^{-7} mol/L; 9, 9.0×10^{-7} mol/L; 10, 1.0×10^{-6} mol/L; 11, 1.2×10^{-6} mol/L 12, 1.5×10^{-6} mol/L, respectively.) with an excitation of 440 nm.