Water-soluble and highly selective fluorescent sensor from naphthol aldehyde-tris derivate for aluminium ion detection

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ABSTRACT

In the paper, a highly selective aluminum ion fluorescent probe based on naphthalene derivate has been synthesized and characterized systemically. The probe molecule for aluminum ion exhibits excellent water solubility, and it shows strong blue fluorescence under ultraviolet light, which is attributed to the Photoinduced Electron Transfer (PET) process. In addition, the large association constant between probe and aluminum ion is $1.19 \times 10^8 \, M^{-1}$, which is obtained by fluorescent measurement. Moreover, the binding site of L with Al^{3+} is determined by ^{1}HNMR titration experiment.

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1. Introduction

Aluminium is the third most prevalent (8.3% by weight) metallic element in the earth. The detection of aluminum is necessary due to its potential toxicity and extensive application in packing materials, clinical drugs, food additives and water purification et al. [1–5]. Despite being a non-essential element in living organism, some relevant aluminium compounds are frequently utilized as pharmaceutical drugs in the human body [6,7]. The drug aspirin containing aluminium glycinate is commonly used as an analgesic. Additionally, the WHO (World Health Organization) prescribed the average human intake of aluminum as around 3–10 mg day^{-1} with a weekly dietary intake of 7 mg kg^{-1} body weight. Aluminium has been proved to be a neurotoxin for a long time, and the abnormal content of aluminium can cause many health hazards such as Alzheimer's disease, osteomalacia and the risk of breast cancer, meanwhile, it can damage the brains and kidneys [8–12]. Furthermore, high concentration of aluminium in ecosystem is toxic to plants, fish, algae and other species, and can enter into human body along with biocycle to lead to other relevant diseases [13,14].

Taking account of the harm of aluminium on environment and health, the efficient testing methods toward aluminium has been a challenging task. Compared with the traditional detection methods (graphite furnace atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry), spectrofluorimetry has been widely used due to its sensitivity, selectivity and operational simplification. Fluorescent probe has been regarded as an effective method for tracing relevant ions and shows its unique potential advantages [15–18]. In recent years, some fluorescent probes toward aluminium ion like coumarin, 8-hydroxyquinoline and imidazoline et al. have been reported and synthesized [19–21], but some metal ions (Cu^{2+}, Zn^{2+}, Fe^{3+} et al.) can interfere with the detection of aluminium ion, because the metal ions exhibit more effective combining capacity with the fluorescent probes [22,23]. Additionally, in general, aluminium ion exists in aqueous environment and most of the reported Al^{3+} fluorescent probes have weak water-solubility, which limits its application value, so the good water-solubility of fluorescent probe is also necessary for its practical application. Based on the features, there is a great demand for the design and synthesis of highly selective, sensitive and water-soluble fluorescent probe for detecting aluminium ion in natural environment and living organism.

Naphthalene moiety has been proved as an ideal fluorophore, and its correlative derivates have been synthesized as effective
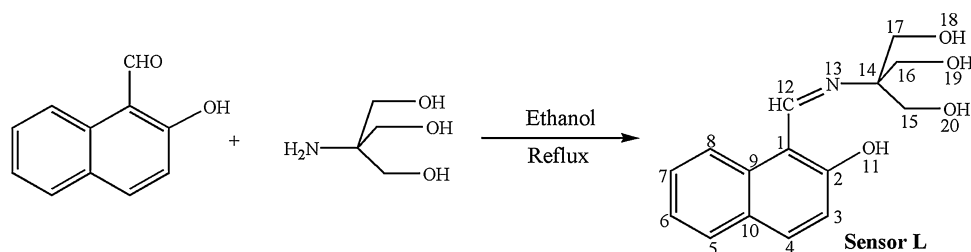
Scheme 1. The synthetic route of corresponding fluorescent sensor naphthol aldehyde-tris(hydroxymethyl)aminomethane schiff-base (**L**).

fluorescent probe in determination of some metal ions [24–27]. Especially, some highly selective fluorescent probes for Al^{3+} using naphthalene derivates have been reported in recent years [28–30], they exhibited high signal response toward and showed good application prospect, but all the fluorescent sensors need organic solvent to enhance the dissolving property of the sensors during the process of measuring. In the present investigation, we describe the synthesis of a novel naphthalene derivate as fluorescent probe of Al^{3+}, which derives from naphthol aldehyde and tris(hydroxymethyl)aminomethane (Tris). The existence of water-soluble organic group tris in the compound enhances water-solubility of the fluorescent probe largely. Moreover, the strong binding property between fluorescent probe and Al^{3+} leads to high selectivity over competing metal ions. Herein, the water-solubility and high selectivity will enhance the application prospect of the fluorescent probe for Al^{3+} in environment monitoring and biological analysis.

2. Experimental sections

2.1. Materials

Naphthol aldehyde and tris(hydroxymethyl)aminomethane was purchased from aladdin reagent corporation. All the chemicals were of reagent grade and were used without further purification.

All spectroscopic measurements were performed in HEPES buffer solution (pH = 7.0).

Stock solutions (1.0×10^{-3} M) of metal ions (metal chloride) were prepared using in two-distilled water. The stock solution of sensor **L** (1.0×10^{-3} M) was prepared in two-distilled water. In titration experiments, each time a 20 μL solution of **L** (1.0×10^{-3} M) was filled in a quartz optical cell of 1 cm optical path length. Then equal amount of Al^{3+} stock solution (5 μL) was added to the compound solution with micro-pippet. Spectral data was recorded at 1 min after addition. In selectivity experiment, the test samples were prepared by placing appropriate amounts of metal ion stock into 2 mL water solution of **L** (1.0×10^{-5} M). For fluorescence measurements, the excitation wavelength is at 320 nm.

The binding constant between **L** and Al^{3+} was calculated by the linear Benesi–Hildebrand expression [31,32]

$$I_0/(I - I_0) = I_0/[L] + I_0/[L].K_s.[M]$$

Where I is the change in the fluorescence intensity at 380 nm, K_s is the stability constant, and $[L]$ and $[M]$ are the concentrations of **L** and Al^{3+}, respectively. I_0 is the fluorescence intensity of L in the absence of Al^{3+}. On the basis of the plot of $1/I - I_0$ versus $1/[Al^{3+}]$, the stability constant can be obtained.

2.2. Physical measurement

^{1}HNMR spectra were recorded on a Bruker Avance III 400 spectrometer with TMS as an internal standard. The melting points of the compound were determined on a Beijing XT4-100X microscopic melting point apparatus. The UV–Vis spectra were recorded on a Perkin–Elmer Lambda-35 UV–Vis spectrophotometer. Fluorescence spectra were obtained on a Shimadzu RF-5301 spectrophotometer at room temperature. Elemental analysis was tested by vario EL analyzer.

3. Results and discussions

3.1. Synthesis of fluorescent sensor naphthol aldehyde-tris(hydroxymethyl) aminomethane schiff-base (**L**)

The synthetic route of naphthol aldehyde-tris(hydroxymethyl) aminomethane schiff-base is shown in Scheme 1. An ethanol solution (10 mL) of tris(hydroxymethyl)aminomethane (tris, 0.1 mol, 0.1211 g) was added to another ethanol (10 mL) containing naphthol aldehyde (0.1 mol, 0.1728 g), Then the solution was reflux for 2 h and cooled to room temperature. The mixture was filtered and dried under vacuum. Recrystallization from C_2H_5OH/H_2O (V:V = 1:1) gave the target product naphthol aldehyde-tris(hydroxymethyl) aminomethane schiff-base (**L**, 2-Hydroxymethyl-2-[(2-hydroxy-naphthalen-1-ylmethylene)-amino]-propane-1,3-diol), which was dried under vacuum. Yield, 86%. m.p: 258–260 °C. ^{1}HNMR (DMSO–d_6 400 MHz): δ 14.021–14.041 (1H, d,–O^{11}–H), δ 8.889–8.910 (1H, d,–C^3–H), δ 7.930–7.943 (1H, d,–C^4–H), δ 7.665–7.681 (1H, d,–C^5–H), δ 7.582–7.595 (1H, d,–C^8–H), δ 7.393-7.415 (1H, m,–C^3–H), δ 7.140–7.163 (1H, m,–C^4–H), δ 6.627–6.643 (1H, d,–C^{12}–H), δ 5.097 (3H, s,–$O^{18,19,20}$–H), δ 3.674–3.680 (6H, d,–$C^{15,16,17}$–H). Anal. Calcd for $C_{15}H_{17}O_4N_1$(%): C, 65.44; H, 6.22; N, 5.09. Found (%): C, 65.28; H, 6.31; N, 5.13.

3.2. Investigation of UV–vis spectrum between probe **L** and Al^{3+}

Fig. 1 shows the change in the UV–vis spectrum of sensor **L** (1.0×10^{-5} M) with addition of Al^{3+} (0–2 equiv) in HEPES (pH = 7.0)
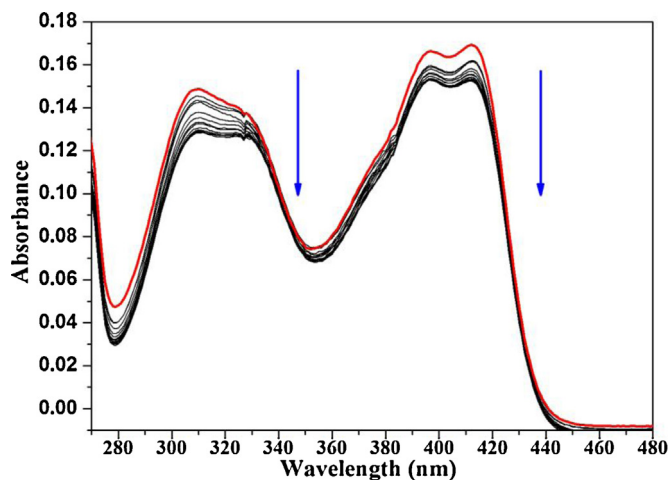

Fig. 1. The absorption spectra of **L** (1.0×10^{-5} M) in HEPES buffer media in the presence of different amounts of **Al^{3+}** (0–2 equiv).