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4-(8′-Hydroxyquinolin-7′-yl)methyleneimino-1-phenyl-2,3-dimethyl-5-pyzole as a fluorescent chemosensor for aluminum ion in acid aqueous medium

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ABSTRACT

A new fluorescent Al^{3+}-sensor (**L**) was designed and synthesized from 8-hydroxyquinoline-7-carbaldehyde (HQ7A) and 4-aminopyrine. The sensor exhibited high selectivity and sensitivity "off-on" fluorescent responses toward Al^{3+} in methanol/water (1:9, v/v, acetate buffer, pH 4.5), with about 26-fold enhancement in fluorescence intensity and high sensitivity with the detection limit for Al^{3+} as low as 10^{-7} M level. The sensor showed a significant fluorescent enhancement for Al^{3+} over a wide range of tested metal ions. These suggested that **L** could be served as a highly selective and sensitive fluorescence sensor for aluminum ion in acid medium, indicating the potential application in acid aqueous environment.

1. Introduction

Aluminum is the third most abundant element in the earth's crust. Al^{3+} exists widely in the environment due to acidic rain and human activities. Al^{3+} affects the activity of gastrointestinal enzymes and excess Al^{3+} is toxic in the central nervous system. The World Health Organization (WTO) recommends an average daily human intake of Al^{3+} of around 3–10 mg kg^{-1} and the tolerable weekly dietary intake as 7 mg kg^{-1} body weight. Excessive exposure of the human body to Al^{3+} leads to many diseases such as Alzheimer's disease and Parkinson's disease, bone softening, smoking related diseases and chronic renal failure. Since there is a close association between Al^{3+} and human health, the investigation of Al^{3+} detection attracts more and more attention [1–9]. Compared with other metal cations, the detection of Al^{3+} has always been problematic because of its poor coordination ability, strong hydration ability and the lack of spectroscopic characteristics [10–12]. Therefore, it is of considerable importance to construct probes for selective detection of Al^{3+} [13–19].

In addition, the toxicity influences agricultural production in acidic soils (pH ≤ 5.5) [20,21]. In acid condition, solubility of aluminum minerals raises the amount of available Al^{3+}, and it was found to be more toxic in weak acid aqueous environment [22]. Toxicity of aluminum ion is often highly concerned due to its wide distribution in acid environment. Although several fluorescence sensors for Al^{3+} have been designed and synthesized, most of them were operated in organic solvent, which limited their applications, and very few fluorescent chemosensors for Al^{3+} in acid aqueous medium have been found in literature [23]. So it is a significant work to design and synthesize highly selective and sensitive fluorescence chemosensor for Al^{3+} in acid aqueous medium. 8-Hydroxyquinoline (HQ) as a desirable fluorophore and binding moiety was employed widely in designing chemosensors for detection of transition metal ions [24–29]. But only few Al^{3+} fluorescence sensors derived from HQ were synthesized up to now [30].

Design of a fluorescent probe is generally based on intramolecular charge transfer (ICT) [31], photoinduced electron transfer (PET) [32], chelation-enhanced fluorescence (CHEF) [33], fluorescence resonance energy transfer (FRET) [34], and excited-state intramolecular proton transfer (ESIPT) [35]. Among these mechanisms, excited state intramolecular proton transfer (ESIPT)-based chemosensors are ideal candidates for fluorescence probes because of the almost complete lack of spectral overlap between absorption and emission [36,37]. Furthermore, in some particular conditions, single signaling response cannot meet practical requirements. In this case, a combination of two or more conventional mechanisms would be valuable since such a multi-mechanism will usually produce multiple signals to amplify recognition events to

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a greater extent and improve selectivity and sensitivity. In fact, several fluorescent probes have been developed on the basis of multi-mechanism [38–40]. For example, Bojinov et al. reported a pH probe based on PET/FRET/ICT multi-mechanism. Chen et al. also applied FRET/ICT multi-mechanism to design a sensor to detection of Zn^{2+}. However, the combination use of PET and ESIPT mechanism has been scarcely explored till now [41,42]. As a result, there is still a high demand to develop new fluorescent probes based on PET/ESIPT multi-mechanism.

Herein, for these reasons, we present the design, synthesis, and spectral properties of 4-(8′-hydroxyquinolin-7′-yl)methyleneimino-1-phenyl-2,3-dimethyl-5-pyzole (**L**) chemosensor, acting as Al^{3+} selective fluorescent sensor in acid aqueous medium, which was a novel Schiff-base of 8-hydroxyquinoline-7-carbaldehyde (HQ7A) synthesized from 8-hydroxyquinoline by the Reimer-Tiemann reaction according to the former literature [43–48]. Upon binding with Al^{3+}, the molecular structure changed from flexible to rigid, and the PET and ESIPT effects were inhibited efficiently, so the fluorescence intensity was increased dramatically.

2. Experimental

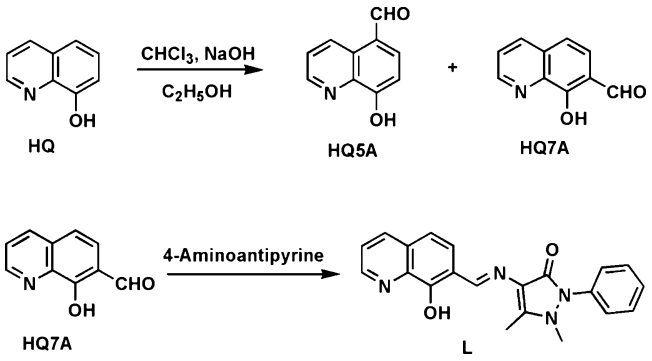
2.1. Materials and instrumentation

All chemicals were obtained from commercial suppliers and used without further purification. The solutions of metal ions were performed from their nitrate salts. Double-distilled water was used throughout the experiments. ^{1}H NMR and ^{13}C NMR spectra were measured on the Bruker 400 MHz instruments using TMS as an internal standard. UV–vis absorption spectra were determined on a Shimadzu UV-240 spectrophotometer. Fluorescence spectra were recorded on a Hitachi RF-4500 spectrophotometer equipped with quartz cuvettes of 1 cm path length. IR spectra were obtained in KBr discs on a Thermo Mattson FT-IR spectrometer in the 4000–400 cm^{-1} region.

2.2. Synthesis

2.2.1. The synthesis for 8-hydroxyquinoline-7-carbaldehyde (HQ7A)

14.5 g (0.1 mol) of 8-HQ in a 250 ml three-necked round-bottomed flask was dissolved in 60 ml ethanol; then the aqueous sodium hydroxide (35 g in 60 ml of water) was added with a mass of yellow phenolate precipitation appearing. It was heated to make the precipitate dissolve, then the solution was refluxed while chloroform 32 ml was added dropwise in 1 h and refluxed continuously for 12 h at 100 °C. Then ethanol and excess chloroform were distilled off. The residue was diluted with 200 ml water and poured into 500 ml beaker. The solution was slowly and carefully acidified with 1 M hydrochloric acid to pH 4.0 or so; a mass of brown precipitate was formed. The precipitate was filtered and dried, then continuously extracted with chloroform. The extract contains several compounds, and chloroform was distilled off to get brown crude product. Then the crude product was purified by column chromatography with a mixture of petroleum ethylacetate (v/v = 40:1) to afford yellow-pink HQ5A. Subsequently, it was eluted with a gradient of petroleum ethylacetate (v/v = 20:1) to get white solid HQ7A. The two products were crystallized from chloroform and anhydrous methanol to give HQ5A. Mp: 178–179 °C, 1.9 g, yield 11%, as pink needles; for HQ7A, mp: 179–180 °C, 0.8 g, yield 4.6%, as light yellow needles. **NOE ^{1}H NMR** In the NOE difference spectra, the resonances of H-6 were enhanced by irradiation of H-7 (-CHO) (Fig. S1). **HQ7A** (400 MHz, $CDCl_3$), **^{1}H NMR** δ: 10.36 (s, $H^7$1H), 8.93 (d, J = 4.0 Hz, 1H, H^2), 8.16 (d, J = 8.4 Hz, 1H, H^4), 7.75 (d, J = 8.6 Hz, 1H, H^6), 7.58 (dd, J = 8.2, 4.2 Hz, 1H, H^3), 7.37 (d, J = 8.6 Hz, 1H, H^5) (Fig. S2). **^{13}C NMR** (100 MHz, $CDCl_3$), δ: 192.88, 159.10, 149.52, 139.22, 136.05, 132.35, 125.81, 124.57, 118.37, 117.59 (Fig. S3). **IR** (KBr, cm^{-1}): 3080, 2854, 1675, 1508, 1389, 1227, 1138, 937, 835, 771, 728, 660, 473.



Scheme 1. Synthesis of HQ5A, HQ7A and fluorescence chemosensor **L**.

2.2.2. The synthesis of 4-(8′-hydroxyquinolin-7′-yl) methyleneimino-1-phenyl-2,3-dimethyl-5-pyzole (**L**)

HQ7A (346 mg, 2 mmol) was dissolved in hot ethanol (15 ml); then added a solution of 4-aminoantipryrine (406 mg, 2 mmol) in 5 ml ethanol. Then the solution was reflux for 8 h under stirring and some light yellow precipitant appeared. The mixture was filtered and dried under vacuum to obtain a light yellow powder of 526 mg (Scheme 1). Mp: 231–233 °C, yield 78%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ: 15.15 (s, 1H, OH), 9.99 (d, 1H, CH=N), 8.95 (dd, J = 4.4, 1.6 Hz, 1H), 8.05 (d, J = 8.4, 1.6 Hz, 1H,), 7.27–7.54 (8H, H-Ar), 3.23 (3H, $-CH_3$), 2.51 (3H, $-CH_3$) (Fig. S4). **^{13}C NMR** (100 MHz, $CDCl_3$): 160.0, 159.3, 158.5, 149.5, 149.2, 140.0, 135.5, 134.1, 130.2, 129.2, 128.0, 127.3, 124.6, 122.5, 117.2, 116.4, 115.5, 35.4, 10.0 (Fig. S5). **IR** (KBr, cm^{-1}): 3425.2, 2929.0, 1648.7, 1582.8, 1491.5, 1489.6, 1378.1, 1310.2, 1276.1, 1139.0, 1099.9, 867.0, 829.2, 804.7, 764.0, 700.8, 588.1.

2.3. Analysis

The receptor could be dissolved in water when 10% (v/v) of methanol was added. To obtain a selective Al^{3+} fluorescence chemosensor operated under acid aqueous solution, the value of pH was adjusted to 4.5 by acetate buffer and all the following studies were carried out in aqueous solution containing 10% methanol (acetate buffer, pH 4.5) at room temperature. Stock solutions of various cations (1 mM) were prepared using nitrate salts. A stock solution of **L** (1 mM) was prepared. The solution of **L** was then diluted to 10 μM in methanol/water (1:9, v/v, acetate buffer, pH 4.5). In titration experiments, each time a 2 ml solution of **L** (10 μM) was filled in 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. Spectral data were recorded at 2 min after addition of the ions. In selectivity experiments, the test samples were prepared by placing appropriate amounts of ions stock into 2 ml solution of **L** (10 μM). For fluorescence measurements, both the excitation and emission slit widths were 3 nm.

3. Results and discussion

3.1. UV–vis and fluorescence spectra of chemosensor **L** with Al^{3+}

The binding properties of **L** with Al^{3+} were studied by UV–vis titration in the above aqueous solution (Fig. 1). Upon addition of increasing amount of Al^{3+} (0–2 equiv.), the absorption bands at