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A schiff-base receptor based naphthalimide derivative: Highly selective and colorimetric fluorescent turn-on sensor for Al^{3+}

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ABSTRACT

A new schiff-base receptor **L** based on naphthalimide had been investigated as a selective and sensitive chemosensor for Al^{3+} in CH_3OH. Upon addition of Al^{3+}, **L** showed a 39-fold enhancement at 508 nm with colorimetric and fluorometric dual-signaling response which might be induced by the integration of ICT and CHEF. A 1:1 stoichiometry for the **L**-Al^{3+} complex was formed with an association constant of $1.62 \times 10^4\ M^{-1}$, and the limit of detection for Al^{3+} was determined as 7.4 nM. In addition, the potential utility of **L** in sensing Al^{3+} was also examined in real water samples.

1. Introduction

Aluminum is the third most abundant element after oxygen and silicon in the earth's crust, accounting for approximately 8% of its mass [1]. It has been widely used in our daily life, such as food additives, packaging materials, construction and water treatment [2,3]. However, as non-essential element for living systems, excessive amounts of aluminum in human body may damage certain nervous system, tissues and cells and lead to a wide range of diseases such as Alzheimer' disease, Parkinson's disease and dialysis disease [4–7]. Moreover, excessive amounts of Al^{3+} in the environment can hamper plant growth and threaten the existence of fish [8,9]. According to the World Health Organization, the maximum concentration of Al^{3+} in drinking water should be restricted to 7.4 μM [10]. Thus, it is imperative to develop effective analytical methods for detection of Al^{3+} in environmental and biological systems.

Although many advanced analytical techniques have been applied in the detection of Al^{3+}, including atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry [11–13], most of these techniques are either time consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories [14,15]. During the last decades, the development of efficient fluorescence chemosensors has attracted intense interest due to their low cost, simplicity, high selectivity and sensitivity, real-time response and naked eye detection for Al^{3+} [16,17]. However, the detection of Al^{3+} is problematic because of its lack of spectroscopic characteristics and poor coordination ability compared to the transition metals [15,18]. So, it is still full of challenges in the development of excellent fluorescent sensors for selective determination of Al^{3+}.

Naphthalimide fluorophore has been widely used for the construction of excellent fluorescent chemosensors because of its desired properties such as remarkable chemical stability, a large Stokes shift, high fluorescent quantum yield and easy to modification [19–22]. In addition, some Al^{3+} fluorescent chemosensors have been recently reported based on multi-mechanism which exhibit excellent selectivity and sensitivity with multiple signals in the processing of recognition for Al^{3+} [23–26]. Nevertheless, to best of our knowledge, there is few report of the Al^{3+} chemosensor based on the combination of intramolecular charge transfer (ICT) and chelation enhanced fluorescence (CHEF) mechanisms with naphthalimide fluorophore. Herein, we report the design and synthesis of a novel schiff-base chemosensor **L** with the naphthalimide fluorophore as the signaling unit. Optical properties were investigated using UV–vis and fluorescence response of the **L** to Al^{3+}. We found that chemosensor **L** exhibited a selective colorimetric change and enhanced fluorescence for Al^{3+} over other examined metal ions. Furthermore, chemosensor **L** was successfully applied in detection of Al^{3+} in real water samples.

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2. Experimental

2.1. Materials

All solvents and reagents (analytical and spectroscopic grade) were purchased from commercial suppliers and used without further purification. Stock solution of **L** (0.1 mM) was prepared with chromatographic pure methanol. Stock solutions (0.01 M) of various metal ions were prepared using $NaClO_4$, $KClO_4$, $Mg(ClO_4)_2$, $Ba(ClO_4)_2$, $Zn(ClO_4)_2 \cdot 6H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$, $AgNO_3$, $Cd(NO_3)_2$, $Pb(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Fe(ClO_4)_3 \cdot xH_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $MnSO_4 \cdot H_2O$, $HgCl_2$, and $FeCl_2 \cdot 4H_2O$.

2.2. Physical measurement

^1H NMR spectra and ^{13}C NMR spectra were recorded on a Bruck AV-500 and Bruck AV-600 spectrometer. Chemical shifts (δ) are reported in ppm, using TMS (tetramethylsilane) as the internal standard and DMSO-d_6 as the solvent. Absorption spectra were recorded at 25 °C using a Pgeneral TU-1901 UV–vis spectrophotometer. Fluorescence measurements were performed on a Perkin Elmer LS55 fluorescence spectrometer. Mass spectra were measured on a Waters Xevo UPLC/G2-SQ Tof MS spectrometer. The melting point was determined on a Beijing XT4-100X microscopic melting point apparatus.

2.3. General information

For the spectroscopic determination, stock solution of **L** was diluted with methanol to a final test concentration of 1×10^{-5} M. Test solutions for selectivity experiments were prepared by placing 10 mL of **L** solution (1×10^{-5} M) into volumetric flasks followed by adding 50 µL of each metal ion stock solution (0.01 M) with micropipette. The vials were shaken for a few seconds and the absorption and fluorescence spectra were recorded. Test solutions for titration experiments were prepared by placing 10 mL of **L** solution (1×10^{-5} M) into volumetric flasks followed by adding an appropriate aliquot of Al^{3+} stock solution (0.01 M) with micropipette. The vials were shaken for a few seconds and the absorption and fluorescence spectra were recorded. For all measurements of fluorescence spectra, excitation wavelength was 401 nm, and the excitation and emission slit widths were 10 nm and 15 nm, respectively.

The binding constant between **L** and Al^{3+} was calculated from the fluorescence intensity data using the modified Benesi-Hildebrand equation shown below [27,28]:

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

where, F_{min}, F and F_{max} are the fluorescence intensities of **L** in the absence of Al^{3+}, at an intermediate Al^{3+} concentration, and at a concentration of complete interaction, respectively. K: Binding constant.

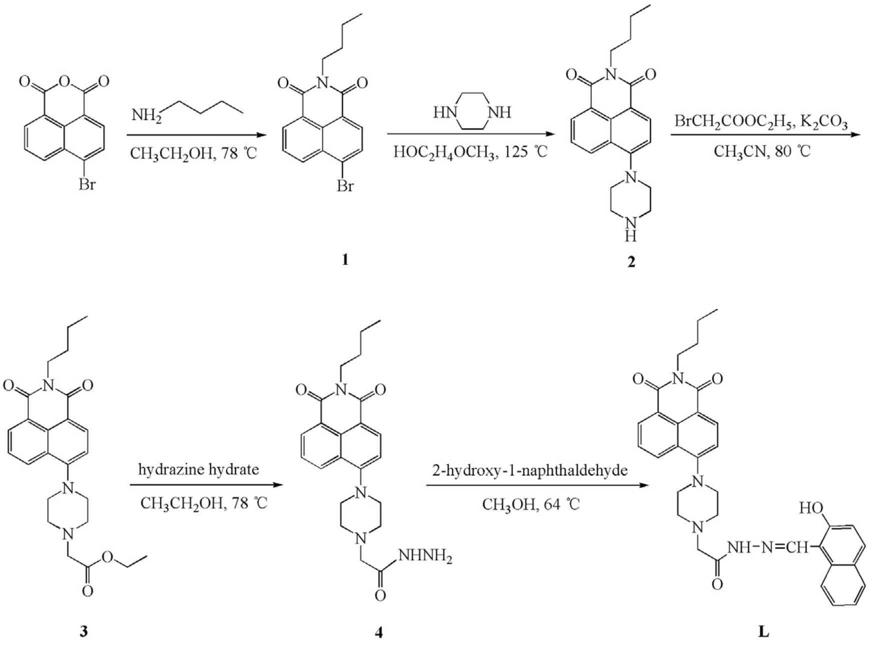
2.4. Synthesis

2.4.1. Synthesis of compounds 1–3

As shown in Scheme 1, the compounds **1–3** were prepared according to the reported procedures [29–31].

2.4.2. Synthesis of compound 4

An ethanol solution (10 mL) of hydrazine hydrate (1100 mg, 8.79 mmol) was added dropwise to an ethanol solution (55 mL) containing compound **3** (950 mg, 1.77 mmol) at room temperature. Then the mixture was refluxed for 7 h under stirring. After cooling to room temperature and vacuum concentration, the residue was further purified by silica gel column chromatography using methanol/chloroform (1:10, v/v) as the eluent to afford yellow powder solid **4** (480 mg, yield: 58%); m.p. 168–169 °C. ^1H NMR (600 MHz, DMSO-d_6) (Fig. S1) δ (ppm): 9.02 (s, 1H), 8.51–8.23 (m, 3H), 7.81–7.72 (m, 1H), 7.30 (dd, J=16.4, 8.0 Hz, 1H), 4.28 (s, 2H), 4.07–3.94 (m, 2H), 3.25 (s, 4H), 3.09 (s, 2H), 2.78 (s, 4H), 1.60 (dt, J = 14.3, 7.2 Hz, 2H), 1.43–1.29 (m, 2H), 1.04–0.82 (m, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) (Fig. S2) δ (ppm): 168.61, 163.94, 163.42, 156.04, 132.59, 131.02, 130.88, 129.51, 126.41, 125.70, 122.97, 115.93, 115.44, 60.18, 53.21, 52.98, 39.59, 30.18, 20.27, 14.19. HRMS m/z (TOF MS ES^+) (Fig. S3): calcd for $C_{22}H_{27}N_5O_3 + H^+$, 410.2192 $[M+H]^+$; Found: 410.2186.



Scheme 1. Synthesis of chemosensor **L**.