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A highly selective fluorescence-enhanced chemosensor for Al^{3+} in aqueous solution based on a hybrid ligand from BINOL scaffold and β-amino alcohol

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ABSTRACT

A chemosensor (*R*)-**OH** bearing an amino alcohol group was synthesized for the highly selective fluorescent recognition of Al^{3+} with low limit of detection (16 *ppb*). "Turn-on" type fluorescence changes were observed upon the addition of Al^{3+} in aqueous solution. The significant enhancement (35.4-fold) of fluorescence intensity was ascribed to the complex formation between (*R*)-**OH** and Al^{3+} which denoted as the chelation-enhanced fluorescence (CHEF) process.

1. Introduction

Aluminum is the third most abundant metal in Earth's crust and extensively used in modern life, such as food packaging, cookware, drinking water supplies, antiperspirants, deodorants, bleached flour, antacids and the manufacturing of cars and computers [1–3]. Excess aluminum, however, can induce many health issues, such as Alzheimer's disease [4] and Parkinson's disease [5]. Furthermore, it is known that 40% of the world's acidic soils are caused by aluminum toxicity [6,7]. In view of the biological and environmental importance of aluminum, considerable effort has been devoted to the development of optical chemosensors for the facile detection of Al^{3+}. But, owing to the weak coordination and strong hydration ability of Al(III) in water, it is easily interfered by the variation of pH value of solution and the coexistence of interfering ions. In comparison with transition metal ions, relatively scarce examples of fluorescence chemosensors for Al^{3+} in either organic media [8–16] or aqueous solution [17–23] have been reported to date, among which only two examples [8,10] demonstrated significant fluorescence enhancement. Therefore, the design of highly selective chemosensor for Al^{3+} with "turn-on" type fluorescence changes remains highly desirable.

In connection with our continuing research of chemosensors based on 1,1′-Binaphthyl fluorophore [24,25], we previously reported a series of chemosensors for Al^{3+} based on BINOL derivatives containing β-amino acid moiety, which showed Al^{3+}-selective fluorescent enhancements in pure CH_3OH as a single-channel fluorescent chemosensor, while only (*R*)-**1** could be used as a double-channel fluorescent sensor in CH_3OH–water (1:99, v/v) [26]. In this work, we synthesized a conjugate (*R*)-**OH** based on BINOL and β-amino alcohol (Scheme 1), in order to explore whether the change of bonding sites affect selectivity and sensitivity. The further studies indicate that (*R*)-**OH** shows more superior Al^{3+}-selective fluorescence enhancement (35.4-fold) in CH_3OH–water (95:5, v/v) solutions as a single-channel fluorescent chemosensor with lower limit of detection (16 *ppb*) compared with the one from previous receptor (*R*)-**1** [26].

2. Experimental

2.1. General

All chemicals were obtained from commercial suppliers and used without further purification. Methanol was distilled from magnesium prior to use. Column chromatography was performed on silica gel (200–300 mesh). ^1H and ^{13}C NMR spectra were measured on the Bruker 400 MHz instruments using TMS as an internal standard. ESI−MS were determined on a Bruker esquire 6000 spectrometer. UV–Vis absorption spectra were determined on a Varian

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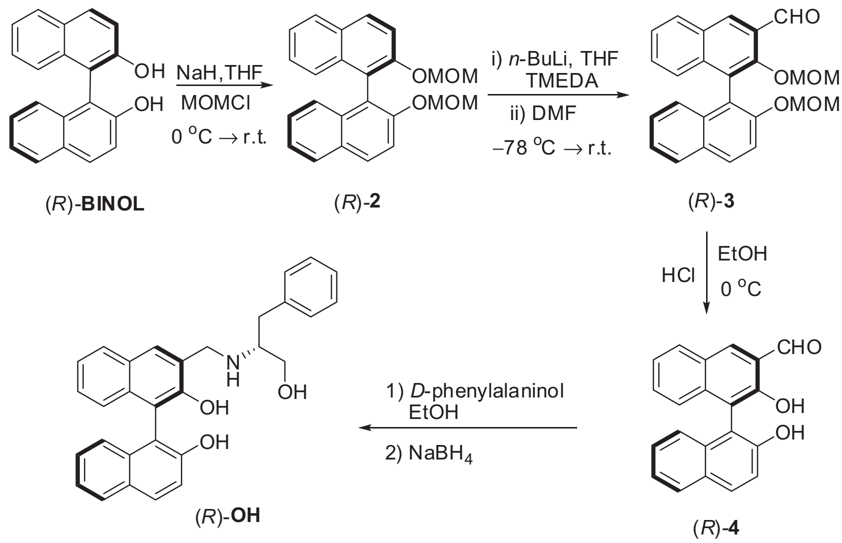

Scheme 1. The synthesis of compound (*R*)-**OH**.

UV-Cary100 spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4500 spectrophotometer equipped with quartz cuvettes of 1 cm path length. All pH measurements were made with a pH-10C digital pH meter.

2.2. Synthesis

Starting from (*R*)-1,1′-bi-2-naphthol (BINOL), (*R*)-2,2′-dihydroxy-1,1′-binaphthyl-3-carbaldehyde was synthesized according to a literature procedure [24,25,27].

2.2.1. (R)-2,2′-Bis(methoxymethyloxy)-1,1′-binaphthalene ((R)-2)

NaH (1.92 g, 80 mmol) was added to DMF (30 mL) on ice bath. (*R*)-BINOL ((*R*)-2,2′-dihydroxy-1,1′-binaphthyl) (10 g, 34 mmol) in DMF (50 mL) was dropped to this solution for 20 mim. After 30 min, MOMCl (Chloromethyl methyl ether) (6.4 g, 80 mmol) was added dropwise to the above solution over 20 min. The reaction was monitored by TLC. After stirring for 1 h, the reaction mixture was quenched with water and extracted with chloroform (2 × 100 mL). The crude product was purified by flash chromatography (Pet/EtOAc = 5:1) on silica gel to give 12.4 g of (*R*)-**2** (95% yield).

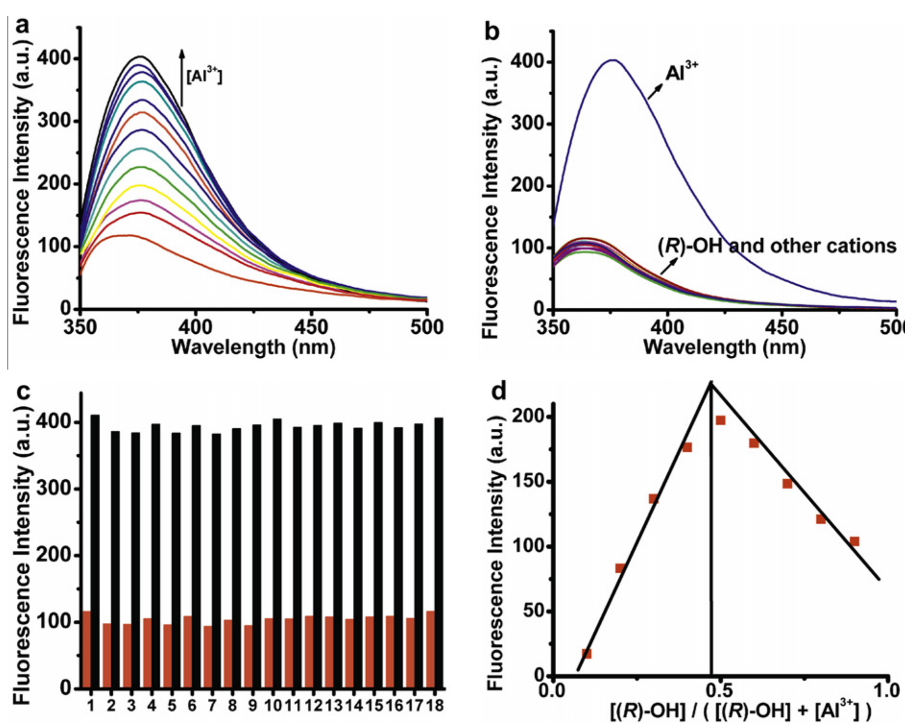

Fig. 1. (a) Fluorescent spectra of (*R*)-**OH** (20 μM) in the presence of different concentrations of Al^{3+} (0–1.0 equiv) in CH_3OH. (b) Fluorescence responses of (*R*)-**OH** (20 μM) in CH_3OH with 20 μM of Al^{3+}, Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Pb^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Ag^+, Zn^{2+}, Hg^{2+} and Cd^{2+}. Excitation wavelength was 337 nm. (b) Fluorescence responses of (*R*)-**OH** (20 μM) to various cations in CH_3OH at 375 nm. The orange bars represent the emission intensity of (*R*)-**OH** in the presence of other cations (20 μM). The black bars represent the emission intensity that occurs upon the subsequent addition of 20 μM of Al^{3+} to the above solution. From left to right: none, Ag^+, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^+, Li^+, Mg^{2+}, Mn^{2+}, Na^+, Ni^{2+}, Pb^{2+}, Hg^{2+} and Zn^{2+}. (d) Job's plot at 375 nm.