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A novel HBT-based Schiff base for colorimetric detection of aluminum: Synthesis, characterization, spectral and DFT computational studies

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ABSTRACT

A novel Schiff base **L** was easily synthesized by the condensation reaction of 2-aminophenol and *p*-hydroxyphenylbenzothiazole (*p*-HBT) and could be used for detection of aluminum in ethanol as well as in aqueous solution. Among the detected metal ions, only Al^{3+} ion can induce a significant enhancement in fluorescence intensity. The lowest detection limit and the dissociation constants K_d for Al^{3+} are determined to be 8.24×10^{-9} M and 3.00×10^{-5} M, respectively. In addition, the binding details of **L**-Al^{3+} complex were investigated by means of infrared spectra, ^{1}H NMR titration and DFT computational studies, implying the fluorescence intensity enhanced by the inhibition of the ESIPT process in **L**, and further the formation of a large π-electron conjugation system.

1. Introduction

It is well known that aluminum is the third most abundant metal in nature and is widespread prevalence in food additives, aluminum-based pharmaceuticals, and storage/cooking utensils. This would inevitably lead to environmental pollution and accumulation in human body. Especially, excess accumulation of Al^{3+} would cause human illnesses in virtue of its toxicological effects on the central nervous system, such as dementia and encephalopathy, Parkinson's disease, and Alzheimer's disease [1–4]. Recent developments in the area of detection of biological relative metal ions and molecules by fluorescence technology remains to attract particular attention due to its simplicity, high selectivity, good sensitivity and non-destructive application in living cells [5–14]. Consequently, fluorescence probe is a powerful analytical tool for facile detection of aluminum and plays a very important role in environmental monitoring and biochemical assays.

To date, only a few of fluorescence probes for Al^{3+} have been achieved due to its poor coordination with Al^{3+}. Most of reported chemosensors for Al^{3+} are Schiff bases based on different fluorophore, such as rhodamine, BODIPY-derivatives, coumarin, naphthaldehyde, *etc.* [15–35]. To the best of our knowledge, none of fluorescence probes based on hydroxyphenylbenzothiazole (HBT) have been reported for detection of Al^{3+} up to now. HBT and its derivatives were widely applied in biological medicine, biochemistry, organic optoelectronic materials as well as for detection of metal ions or small biomolecules as fluorophores, due to their various bioactivities and prominent photo-physical properties [36,37]. Numerous excellent works on HBT derivatives have been reported [38–44].

It is worth noting that among the reported HBT-based probes, fluorescent mechanism is based on the excited-state intramolecular proton transfer (ESIPT) process in HBT due to the existence of O—H···N or O···H—N type hydrogen bonds as well as tautomerization between enol-imine and keto-amine forms [39–41,45,46]. With this in mind, a novel HBT-based Schiff base **L** has been designed. The coordination between Al^{3+} and **L** inhibited the ESIPT process in **L**, and further formed a large π-electron conjugation system, resulting in a significant fluorescence enhancement (Fig. 1). As depicted in Scheme 1, Schiff base **L** was easily synthesized by the condensation reaction of 2-aminophenol and *p*-hydroxyphenylbenzothiazole (*p*-HBT), and was fully characterized by NMR, ESI-MS and IR spectroscopy (Figs. S1–S5). Spectroscopic studies demonstrated that **L** exhibited highly sensitive and selective properties towards Al^{3+} over other metal ions. And the detailed binding mode of the probe **L** was confirmed by ^{1}H NMR titration, infrared spectra and DFT computational studies, for further supporting the fluorescent mechanism.

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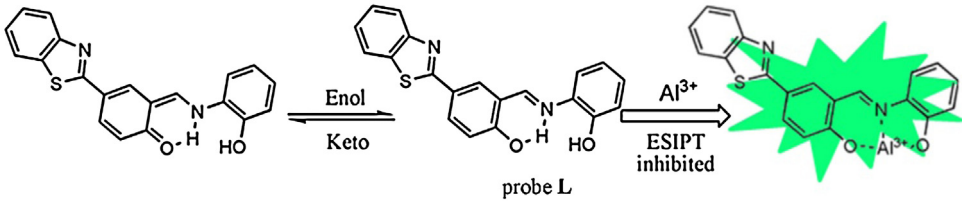
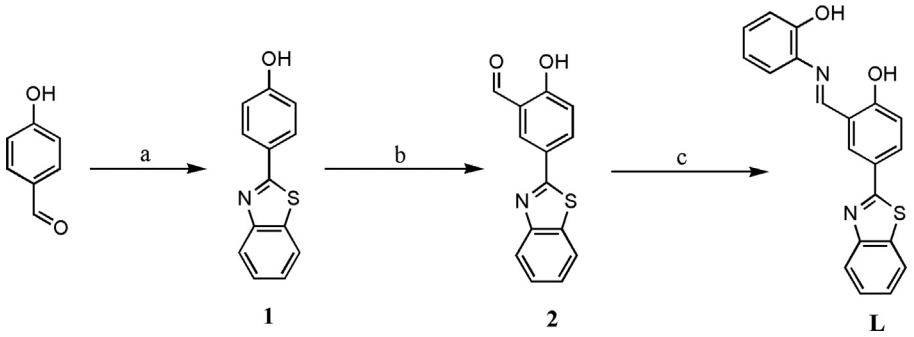


Fig. 1. Structures of Keto and Enol forms of probe **L** and proposed binding mode.



Scheme 1. Synthesis of probe **L**. (a) 2-aminothiophenol, EtOH/HCl/H_2O_2; (b) hexamethylenetetramine, toluene/acetic acid, refluxed; (c) 2-aminophenol/ethanol, refluxed.

2. Experimental

2.1. Materials and instruments

All solvents and reagents (analytical grade) were obtained from commercial sources and used as received. Nuclear magnetic resonance spectra were recorded on Bruker 400 MHz instruments with TMS as an internal standard. Mass spectra were determined using a Bruker Daltonics esquire 6000 mass spectrometer and a micrOTOF Q-II (Bruker Daltonics) mass spectrometer. Melting point was measured with Yanaco micro-melting point apparatus. Infrared spectra were recorded in KBr on a NEXUS 670 spectrometer in the 4000–400 cm^{-1} region. Fluorescence spectra were performed with a thermo Scientific Lumina fluorescence spectrometer. Absorption spectra were carried out on an Evolution 220 UV-Visible spectrometer. The absolute fluorescent quantum yield was determined on a FL sp920.

2.2. Preparation of *L*

Compound **1** and **2** were synthesized according to reported literatures, respectively [42,47].

2.2.1. Synthesis of compound *1*

A solution of 2-aminothiophenol (625 mg, 5 mmol), *p*-hydroxybenzaldehyde (610 mg, 5 mmol), and ethanol (20 mL) was added in a 50 mL round-bottomed flask. Aq 37% HCl (15 mmol) were gradually added to the mixture, followed by aq 30% H_2O_2 (30 mmol). Then the mixture was stirred at room temperature for about 0.5 h, and the light white solid was obtained at a yield 75% by filtration. ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm): 9.90 (s, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.8 Hz, 2H), 7.51–7.47 (m, 1H), 7.39 (m, 1H), 6.97 (d, J = 8.4 Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm): 167.79, 160.91, 153.30, 133.98, 129.16, 126.57, 125.03, 123.72, 122.23, 122.15, 116.24. ESI–MS (m/z): 228.0 $[M+H]^+$, calcd. for $C_{13}H_9NOS$ = 227.04. Mp. 234–236 °C.

2.2.2. Synthesis of compound *2*

Compound **1** (429 mg, 1.89 mmol) was dissolved in toluene (15 mL) and acetic acid (15 mL). Hexamethylenetetramine (583 mg, 4.16 mmol) was added in one portion. The orange solution was refluxed until all the starting material was consumed (TLC monitor). The mixture was then cooled to room temperature and poured into 6 M HCl (30 mL). The product was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with saturated brine (40 mL), and then dried over Na_2SO_4. The crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum, 1/10) to provide compound **2** (169 mg, 35% yield) as light white powder. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 11.29 (s, 1H), 10.05 (s, 1H), 8.37 (d, J = 2.0 Hz, 1H), 8.25 (dd, J = 8.8, 2.4 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.52 (dd, J = 11.3, 4.0 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 196.37, 165.97, 163.50, 154.01, 135.72, 134.77, 132.72, 126.55, 126.06, 125.31, 123.05, 121.65, 120.63, 118.58. ESI–MS (m/z): 256.2 $[M+H]^+$, calcd. for $C_{14}H_9NO_2S$ = 255.04. Mp. 198–199 °C.

2.2.3. Synthesis of compound *L*

Compound **L** was synthesized according to the general synthetic method of Schiff base between the amine and aldehyde. Compound **2** (51 mg, 0.2 mmol) was dispersed in methanol (25 mL), and the mixture was heated until it is completely dissolved. 2-aminophenol (26 mg, 0.24 mmol) dispensed in methanol was added dropwise to the mixture. The mixture was stirred under refluxed condition to form a yellow precipitate. After refluxed for another 0.5 h, the precipitate was filtrated, washed with methanol for three times. Being dried under reduced pressure, the desired product **L** was obtained in 89% yield. ^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm): 14.73 (s, 1H), 9.93 (s, 1H), 9.22 (s, 1H), 8.41 (s, 1H), 8.14–8.09 (m, 2H), 8.01 (d, J = 8.0 Hz, 1H), 7.48 (m, 3H), 7.17 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 8.8 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.93 (t, J = 7.3 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ (ppm): 166.71, 164.97, 160.48, 153.61, 151.10, 134.16, 133.48, 131.71, 131.45, 128.51, 126.51, 125.05, 123.27, 122.33, 122.21, 119.65, 119.32, 119.22, 118.48, 116.56. ESI–MS (m/z): 347.0762 $[M+H]^+$, calcd. for $C_{20}H_{14}N_2O_2S$ = 346.08. Mp. 248–249 °C.