



Naphthalene-derived Al³⁺-selective fluorescent chemosensor based on PET and ESIPT in aqueous solution



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ABSTRACT

A simple fluorescent chemosensor **HL** based on naphthalene with high selectivity and sensitivity towards Al³⁺ over other commonly coexisting metal cations in fully aqueous solution to enhance the potential applications of the fluorescent chemosensor was developed. **HL** exhibited a significant fluorescence enhancement at 475 nm in the presence of Al³⁺ over other competitive metal ions with a low detection limit of 0.43 μM due to the inhibition of the photo induced electron transfer (PET) and the excited-state intramolecular proton transfer (ESIPT). The 1:1 binding stoichiometry between **HL** and Al³⁺ was corroborated by the Job plot and the ESI-MS spectrum. Importantly, the reversible recognition process of **HL** to Al³⁺ will make **HL** could be used circularly and repeatedly in practical applications by addition of Na₂EDTA. In addition, the binding behavior and sensing mechanism of **HL** to Al³⁺ were illustrated in detail by the ¹H NMR titration experiment.

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Introduction

The design and synthesis of fluorescent chemosensors for Al³⁺ continues to be a significant research subject. On the one hand, Al³⁺ has its impact on the environment and human health. On the other hand, fluorescent techniques show simplicity, high selectivity and sensitivity, on-site and real time monitoring, as well as low detection limit^{1–6} compared with traditional analytical methods for detecting Al³⁺ such as ion selective membrane, atomic absorption spectrometry, voltammetry, inductively coupled plasma mass spectrometry (ICP-MS), and liquid chromatography mass spectrometry.⁷ As the most prevalent metallic element (8.3% by weight) and the third most abundant element (after oxygen and silicon) in the earth's crust,^{8–10} aluminum is widely used in modern society involving industrial fields and daily life. In industrial fields, aluminum is diffusely used in water treatment, paper industry, dye production, textile industry, cosmetic preparations, production of light alloy, as well as manufacturing of cars and computers.^{11–16} Additionally, in daily life, aluminum is far and wide used in food additions, food packaging, aluminum-based pharmaceuticals, storage/cooking utensils, and electrical equipment.^{17–24} However, aluminum in excessive amounts would lead to environmental contamination and be toxic to human health.^{25,26} Particularly, excess aluminum in the human body interferes with the calcium metabolism, causing Osteomalacia, influences the

ingestion of iron in blood, causing microcytic hypochromic anemia, and also decreases liver and kidney function. Moreover, excess accumulation of Al³⁺ leads to malfunction of the central nervous system, which causes human illnesses such as encephalopathy, myopathy, dementia, Guamanian amyotrophic lateral sclerosis, Parkinson's disease, and Alzheimer's disease.^{27–33} Therefore, it's essential and crucial to design and synthesize some fluorescent chemosensors for detecting Al³⁺ in the environmental and biological systems.

The development of Al³⁺ fluorescent probe is rather slow compared with other common transition metal ions due to the lack of spectroscopic characteristics and poor coordination ability.³⁴ Recently, many various fluorescent chemosensors for detecting Al³⁺ have been reported. However, many of them have suffered from many drawbacks such as synthesis based on single mechanism causing poor selectivity and sensitivity,³⁵ tedious synthetic route,³⁶ poor water solubility,³⁶ and fluorogenic response in organic solvents making them difficult for practical applications.¹⁷ Thus, it's highly desirable to develop some fluorescent chemosensors based on multi-mechanism for the detection of Al³⁺ in aqueous solution. Owing to the short fluorescence life time,³⁴ the low fluorescence quantum yield,³⁴ and the ability to act both as a donor as well as an acceptor,³⁷ Naphthalene and its derivatives have been chosen as ideal components of some fluorescent chemosensors.

Hence, taking these factors into account, we have designed and synthesized a simple fluorescent chemosensor (**HL**) based on PET (photo induced electron transfer)³⁴ and ESIPT (excited-state intramolecular proton transfer)³⁸ for the detection of Al³⁺ in

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aqueous media, which enhanced the practical application of the chemosensor. The structure of **HL** was validated by ^1H NMR spectrum and the ESI mass spectrum. The 1:1 binding stoichiometry between **HL** and Al^{3+} was confirmed by the Job's plot titration curve and the mass spectrum data. In addition, the recognition process of **HL** towards Al^{3+} was chemically reversible in the presence of Na_2EDTA with a quite low detection limit (0.43 μM) of a micromolar concentration level.

Experimental section

Materials and instruments

The materials used for this study were obtained from commercial suppliers and used without further purification. ^1H NMR spectrum were measured on the JNM-ECS 400 MHz spectrometer. Chemical shifts are reported in ppm using TMS as an internal standard. ESI-MS were determined on a Bruker esquire 6000 spectrometer. UV–vis absorption spectrum were measured with a Shimadzu UV-240 spectrophotometer. Fluorescence spectrum were determined on a Hitachi RF-4500 spectrophotometer equipped with quartz cuvettes of 1 cm path length. The melting point was determined on a Beijing XT4-100x microscopic melting point apparatus.

Synthesis

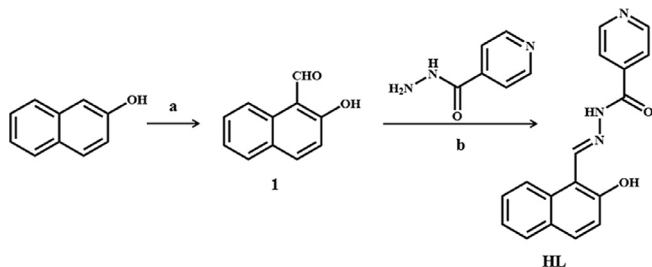
The synthetic route of **HL** (2-hydroxy-1-naphthaldehyde-(4-pyridinecarboxylic)-hydrazone) was shown in Scheme 1.

Synthesis of compound 1 (2-hydroxy-1-naphthaldehyde)³⁹

A 10.5 g of 2-naphthol was added to a solution of a 12 g of Hexamethylenetetramine (HMTA) in 20 ml of acetic acid and then the reaction solution was stirred and heated for 1 h at 50–60 °C. After rising the temperature to 90 °C, H_2SO_4 (98%, 10 ml) was added dropwise to the above solution within 40 min. Upon adding completely, the temperature of the system was raised to 96 °C rapidly and then the reaction solution was refluxed for 10 h with stirring at 96 °C. After cooling to room temperature, 100 ml of ice-water mixture was added to precipitate the crude product. The crude product was collected and washed with cold water until the pH of the filtrate was neutral. The final product was recrystallized from ethanol and dried in vacuum at low temperature to obtain a yellow solid. Yield: 76%; mp: 79–80 °C. ^1H NMR (400 MHz, CDCl_3 , TMS) (Fig. S1): δ_{H} ppm 13.16 (s, 1H), 10.81 (s, 1H), 8.34 (d, 1H, $J = 8.8\text{Hz}$), 7.98 (d, 1H, $J = 9.2\text{Hz}$), 7.80 (d, 1H, $J = 8\text{Hz}$), 7.62 (t, 1H, $J = 8\text{Hz}$), 7.44 (t, 1H, $J = 8\text{Hz}$), 7.14 (d, 1H, $J = 9.2\text{Hz}$).

Synthesis of 2-hydroxy-1-naphthaldehyde-(4-pyridinecarboxylic) hydrazone (**HL**)

2-Hydroxy-1-naphthaldehyde (0.69 g) and 4-pyridinecarboxylic hydrazide (0.55 g) were mixed in 20 ml ethanol and refluxed for 10 h under N_2 . After cooling to room temperature,



Scheme 1. The synthetic route of 2-hydroxy-1-naphthaldehyde-(4-pyridinecarboxylic).

the precipitate was collected and washed 3 times with ethanol. Then the final product was recrystallized from ethanol and dried in vacuum to give a yellow solid. Yield: 79%; mp: 257 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, TMS) (Fig. S2): δ_{H} ppm 12.49 (s, 1H), 12.37 (s, 1H), 9.44 (s, 1H), 8.80 (d, 1H, $J = 2.0\text{Hz}$), 8.78 (d, 1H, $J = 2.0\text{Hz}$), 8.28 (d, 1H, $J = 8.0\text{Hz}$), 7.92 (d, 1H, $J = 8.0\text{Hz}$), 7.88 (s, 1H), 7.86 (d, 1H, $J = 2.0\text{Hz}$), 7.84 (d, 1H, $J = 2.0\text{Hz}$), 7.58 (m, 1H), 7.38 (t, 1H, $J = 3.6\text{Hz}$), 7.21 (d, 1H, $J = 8.0\text{Hz}$). ^{13}C NMR (400 MHz, $\text{DMSO-}d_6$, TMS) (Fig. S3): δ_{C} ppm 109.05, 119.36, 121.48, 121.97, 124.15, 128.39, 128.44, 129.53, 132.13, 133.66, 140.32, 148.51, 151.02, 158.72, 161.55 (C=O). ESI-MS (Fig. S4) calculated for $[\text{M} + \text{H}]^+$ 292.3166, found 292.1458.

UV–vis and fluorescence spectrum measurements

Stock solutions of 5×10^{-3} M various metal ions and **HL** were prepared in ethanol. Additionally, the stock solution of 5×10^{-3} M Na_2EDTA was prepared in distilled water. All absorption and emission spectrum were performed in a quartz optical cell of 1 cm optical path length at room temperature. All fluorescence measurements were carried out upon excitation at 415 nm. Both excitation and emission slit widths were 3 nm.

Results and discussion

To find out the effect of solvent in the fluorogenic response of **HL** towards Al^{3+} , we recorded the emission changes in different solvents (Fig. S5). The fluorescence intensity of **HL** enhanced about 500-fold accompanied with the split of the fluorescence emission spectrum upon addition of Al^{3+} in methanol. The fluorescence intensity of **HL** strengthened approximately 400-fold and the phenomenon of the split still existed after the addition of Al^{3+} in ethanol. Furthermore, the fluorescence intensity of **HL** had different extent of enhancement and the phenomenon of the split still existed upon addition of Al^{3+} in other solvents. It was notable that the fluorescence intensity of **HL** enhanced about 550-fold and those bands just merge together due to increased inhomogeneity after the addition of Al^{3+} in water. Thus, further UV/vis and fluorescent studies were carried out in aqueous solution.

UV–vis studies of **HL** towards Al^{3+}

The UV/vis spectrum of **HL** towards various metal ions (Na^+ , K^+ , Ag^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , Cd^{2+} , Co^{2+} , Pb^{2+} , Mn^{2+} , Hg^{2+} , Cr^{3+} , Fe^{3+} , and Al^{3+}) was illustrated in Fig. 1a. In the absence of Al^{3+} , **HL** exhibited characteristic absorption bands at 325 nm and 366 nm which should be assigned to $\Pi \rightarrow \Pi^*$ transitions of naphthalene ring.^{40–42} Upon addition of Al^{3+} to **HL** solution, a new absorption peak at 432 nm appeared, while other metal ions showed no absorption peak at 432 nm under the identical conditions. Thus, **HL** could serve as a highly selective fluorescent probe for Al^{3+} .

The absorption titrations of **HL** towards Al^{3+} were carried out in aqueous solution (Fig. 1b). Upon gradual addition of Al^{3+} to **HL** solution, the absorption bands at 325 nm and 366 nm gradually decreased while the new absorption band at 432 nm appeared with increasing intensity. Meanwhile, an isobestic point at 400 nm was observed. These results indicated that the formation of a new stable complex between **HL** and Al^{3+} . Moreover, the absorbance spectrum of **HL** exhibited no remarkable changes and the intensity of absorption remained constant more than 1 equiv. of Al^{3+} , demonstrating the 1:1 binding stoichiometry between **HL** and Al^{3+} .

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