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Recognition of Al³⁺ based on a naphthalene-based "Off-On" chemosensor in near 100% aqueous media

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Abstract: An efficient fluorescent Al^{3+} sensor, 2-hydroxy-1-naphthylaldehyde nicotinoyl hydrazone (HL) has been designed and synthesized. The receptor shows "off–on" fluorescent responses toward Al^{3+} in near 100% aqueous media. other relevant metal ions such as Li⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cu²⁺, Co²⁺, Mn²⁺, Ni²⁺, Zn²⁺, Ba²⁺, Fe²⁺, Cd²⁺, Hg²⁺, Pb²⁺, Sc³⁺, Fe³⁺, Cr³⁺ caused almost no fluorescence increase. The reason for this phenomenon is that the addition of Al³⁺ to the solution of HL induce the formation of a 1:1 stoichiometry of the binding mode of L-Al(III) which inhibits the excited-state intramolecular proton transfer (ESIPT) and photoinduced electron transfer (PET). More importantly, the reversibility of the recognition process of HL was performed by adding a Al³⁺ bonding agent Na₂EDTA. **...Keywords**: naphthalene; fluorescence sensor; Al³⁺; aqueous media; ESIPT/PET

1. Introduction

The development of selective and sensitive fluorescent sensor for the detection of metal ions has received more and more attention due to fundamental roles in medicine,

living systems and the environment [1-5]. Among metals, aluminium, the most abundant metal on earth, found in natural waters and most biological tissues is in its ionic form Al^{3+} , nevertheless, Al^{3+} also be potentially toxic, high concentration of Al^{3+} can hamper plant growth, kill fish and other species in aquatic ecosystems. More importantly, as a non-essential element for living systems, the superfluous ingestion of Al^{3+} is responsible for a serious of diseases, such as Alzheimer's disease, osteoporosis, etc [6-14]. In 1989, the WHO listed aluminum ion as a source of food pollution and limited its concentration in drinking water to 200 mg L⁻¹[15]. Therefore, Owing to the importance of Al^{3+} , it is necessary to develop a fluorescent probe for detecting the excessive of aluminum ions in the environment.

In recent decades, the reported Al^{3+} -selective fluorescent sensor is becoming increasingly more common [16-20]. However, most of them worked well in organic solvents or mixed solvents which are difficult for practical application. The design of fluorescent sensor in water or in near 100% aqueous media is still a challenge.

Naphthalene with short fluorescence life-time, low fluorescence quantum yield is extensively suitable to act as an ideal component of a fluorescent chemosensor [21-23]. Schiff-bases are well known to be good ligands, which provide nitrogen–oxygen-rich coordination environments as hard-base donor sites [24-25]. Therefore, it can be conceived that 2-hydroxy-1-naphthaldehyde schiff-bases would develop a fluorescent probe for detection of Al³⁺. Additionally, 2-hydroxy-1-naphthaldehyde schiff-bases are characterised by the existence of the -OH…N intramolecular hydrogen bond which is a prerequisite for ESIPT process [26-27]. More specifically, the ESIPT process commonly involves the transfer of a proton donor (-OH, $-NH_2$) to an adjacent proton acceptor (-C=O, -N=) through a six-membered ring of hydrogen-bonding configuration. In the presence of AI^{3+} , the proton of the donor will be removed, as a result, the excited-state intramolecular proton transfer process is inhibited and a significant emission enhancement can be observed [28-32].

With this in mind, we report a naphthalene-based "Off-On" chemosensor for distinct detection of Al^{3+} which was synthesized by 2-hydroxy-1-naphthylaldehyde and nicotinohydrazide (Scheme 1). The hydroxyl group of HL forms an intramolecular hydrogen bond with the adjacent imine bond (–CH=N–), which gives ESIPT. The hydroxyl and adjacent "hydrazone" groups also provide a strong binding site to Al^{3+} . Upon addition of Al^{3+} , the sensor displays a large fluorescence enhancement at 474 nm, which is because that the Al binding turned off the ESIPT and PET.

2. Experimental

2.1 General information

All chemicals were obtained from commercial suppliers and used without further purification. JNM-ECS400 instruments using TMS as an internal standard, Bruker esquire 6000 ESI-MS spectrometer, Perkin Elmer Lambda 35 UV-Vis spectrophotometer. Hitachi RF-5301 spectrophotometer equipped with quartz cell of 1 cm path length, Beijing XT4-100x microscopic melting point apparatus were also used for the characterization of novel compound.

2.1 Synthesis

2.2.1. Synthesis of 2-hydroxy-1-naphthaldehyde [33]

A mixture of 2-naphthol (10.5g, 73 mmol) and Hexamethylenetetramine (12g, 86 mmol) was dissolved in 20 ml of Acetic acid and stirred and heated for 1h at 50~60°C. Then rising the temperature to 90°C, H₂SO₄ (98%, 9 ml) was added dropwise by dropping funnel within 30 min. Upon completion, the reaction mixture was heated to 96°C and stirred for additional 6h, and then cooled to room temperature pouring into 100 ml H₂O. The crude product was filtered and washed to pH 7 with cold water. The final product was recrystallized from ethanol to afford **2** as a yellow solid and allowed to vacuum drying in low temperature. Yield: 55%, Mp: 79-80°C. ¹HNMR (400 MHz; CDCl₃) (Fig.S1) δ (ppm) = 13.1(s, 1H), 10.83(s, 1H), 8.36(d, 1H), 7.99(d, 1H), 7.81(d, 1H), 7.63(m, 1H,), 7.45(m, 1H), 7.15(d, 1H).

2.2.2. Synthesis of HL

An ethanol solution (20 mL) of nicotinohydrazide (0.274g, 2mmol) was added to another ethanol (20 mL) containing 2-hydroxy-1-naphthaldehyde (0.344g ,2 mmol). Then the solution was refluxing for 10 h under stirring. After cooling to room temperature, the mixture was filtered, washed 3 times with EtOH (3×10mL) and the final product was filtered, dried and recrystallized from ethanol and DMF to give the final product as yellow powder , Yield: 83%, Mp: 257-258°C. ¹HNMR (400 MHz; DMSO- d_6) (Fig.S2) δ (ppm) = 12.51(s, 1H), 12.22 (s, 1H), 9.43 (s, 1H), 9.11 (s, 1H), 8.76 (d, *J*=3.5 Hz 1H), 8.28 (d, *J*=7.6 Hz 1H), 8.24 (d, *J*=8.6 Hz 1H), 7.85~7.91 (m, 2H,), 7.56~7.61 (m, 2H,), 7.38 (t, *J*=7.5 Hz 1H), 7.20 (d, *J*=8.9 Hz 1H). ESI-MS (Fig.S3): [M+1]⁺: 292.10. [M+Na]⁺: 314.08. IR (KBr, cm⁻¹): (Fig.S4): 3217, 1691, 1596.

3. Results and discussion

3.1. Analysis

Stock solutions of various metal ions (10 mM) were prepared using nitrate salts. A stock solution of HL (2 mM) was prepared in DMF. Tris-HCl buffer stock solution prepared using 10 mM, 10 mM Tris and proper amount of HCl, The solution of HL was then diluted to 100 times in aqueous media (Tris-HCl, pH = 7.2). In experiments, each time a 2 mL solution of HL (20 μ L) was filled in the 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. Both the excitation and emission slit widths were 3 nm. 3.2. UV-vis titration

The chelating ability of HL with AI^{3+} was initially investigated by UV-Vis analysis in aqueous media (Tris-HCl, pH = 7.2). The changes in the absorption spectra of HL as a function of the concentration of AI^{3+} were shown in Fig. 1. In the absence of AI^{3+} , the receptor exhibited characteristic absorption bands at 317nm and 362 nm which should be assigned to $\pi \rightarrow \pi^*$ transitions of naphthalene ring [34-36]. Upon addition of AI^{3+} to aqueous solution of HL, the absorption bands at 317 nm and 362 gradually decreased while two new absorption bands appeared at 340 nm and 409 nm with increasing intensity. Moreover, two clear isosbestic points at 347 nm and 380 nm were observed, which clearly indicated the presence of new complex in equilibrium with the receptor. All of these might be attributed to the binding mode of HL with Al³⁺ which was further confirmed by ESI-MS, ¹HNMR titration, Job's plot analysis.

3.3. Selectivity studies and effects of metal ions

The selectivity of HL was investigated upon addition of several metal ions such as Li⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cu²⁺, Co²⁺, Mn²⁺, Ni²⁺, Zn²⁺, Ba²⁺, Fe²⁺, Cd²⁺, Hg²⁺, Pb²⁺, Sc³⁺, Fe³⁺, Cr³⁺ and Al³⁺ in aqueous media (Tris-HCl, pH = 7.2). As shown in Fig. 2, the free sensor showed no fluorescence emission at 474 nm when it was excited at 409 nm. Upon the addition of Al³⁺, the sensor showed a large fluorescence enhancement. This was because that the addition of Al³⁺ resulted in breaking intra-molecular hydrogen bond (OH····N) with the imine-nitrogen and the deprotonation of the naphthol hydroxyl, thus inhibiting excited state intramolecular proton transfer [28], [31-33], [37]. In addition, part of the reason was attributed to the chelation of the nitrogen atom of the –C=N group with Al³⁺, which induced the efficient inhibition for the PET process of the –C=N group [38-39] (Scheme 2). In contrast, addition of other relevant metal ions caused almost no fluorescence increase, which indicated HL was a highly selective fluorescent sensor for Al³⁺.

3.4. The practical applicability of HL

To check the practical applicability of HL as a selective fluorescent sensor for Al^{3+} , it was necessary to carry out the competition experiment and the reversible experiment in aqueous media (Tris-HCl, pH = 7.2). In competition experiment, the systems of other metal ions and Al^{3+} coexisted were examined in aqueous media. As shown in Fig. 3, the receptor HL was treated with 5.0 equiv of Al^{3+} in the presence of

other metal ions. We found that all the coexistent metal ions had no obvious interference with the detection of Al^{3+} except in the case of Cu^{2+} , which were attributed to their inherent to the magnetic property [40-41]. Reversibility is also a prerequisite in developing novel chemosensors for practical application, the reversibility of recognition of Al^{3+} was performed by adding Na₂EDTA which is a good sequesterant in aqueous media (Tris-HCl, pH = 7.2). As shown in Fig. 4, the sensor displayed significant fluorescence enhancement at 474 nm in the presence of Al^{3+} , the addition of Na₂EDTA to a mixture of HL and Al^{3+} resulted in diminution of the fluorescence intensity at 474 nm, which indicated the regeneration of the free receptor HL, then keep adding HL, the fluorescence intensity recovered again. Therefore, it means that the receptor HL can be used as a selective fluorescent sensor for detection and recognition of Al^{3+} in many fields.

In addition, the detection limit was also calculated based on the fluorescence titration (Fig. 5). As shown in Fig. S5, according to the following equation: detection limit: $3\sigma/K$, the detection limit reached at 4×10^{-6} m. Where σ was the standard deviation of blank measurements, and K was the slope between intensity versus sample concentration [42].

3.5. The complexation of HL with Al^{3+}

In order to validate the conjugation of L-Al, we carried out Job's plot in aqueous media (Tris-HCl, pH = 7.2). The total concentration of HL and Al³⁺ was 100 μ M. X_{Al}= ([Al³⁺]/ (Al³⁺] + [HL]. As shown in Fig. 6, the maximum point appeared at a mole

fraction of 0.5. The result has indicated that it was a 1:1 stoichiometry of the binding mode of HL and Al^{3+} which is further confirmed by the appearance of a peak at m/z 334.06 assignable to $[HL+H_2O+Al^{3+}-2H]^+$ and a peak at m/z 374.08, assignable to $[HL+ 2H_2O +Al^{3+}-3H+Na]^+$ in the ESI/MS (Fig. S6). Since the formation of a 1: 1 ligand-metal complex was confirmed by Job's plot analysis and ESI/MS, in combination with the fluorescence titration, the binding constant of HL with Al^{3+} also could be estimated using the Benesi–Hildebrand equation (A) [43],

$$1/(F_x - F_0) = 1/(F_{\max} - F_0) + (1/K[C])(1/(F_{\max} - F_0))$$

where F_0 , F_x , and F_{max} were the emission intensities (at 474 nm) of the organic moiety considered in the absence of metal ion, at an intermediate metal ion concentration, and at a concentration of complete interaction, respectively, and where K_a is the binding constant concentration, namely: $K_{L-Al} = 4 \times 10^3$ (Fig.S7)

To better understand the binding behavior of receptor HL with Al^{3+} , it is necessary to ¹HNMR titration besides the above experiments. The spectral differences were depicted in Fig. 7. In the absence of Al^{3+} , the spectra showed two singlets at 12.51 ppm (H_a) and 12.22 ppm (H_d) corresponding to phenolic -OH and -NH, respectively. The peak at 9.11 ppm (H_c) was assigned to -CH=N of HL. In the ¹H NMR of the neutral HL, the normal signal was located at about 10 ppm, the signal for –OH was obtained at a down field due to possibility of the formation of intramolecular hydrogen bonding with azomethine nitrogen which has been reported by related article [44-45]. In addition, the receptor did not show any peak attributed to enolic –OH proton indicating that they exist in keto forms. Upon complexation with Al^{3+} ions, the proton peak of the phenolic hydroxyl (H_a) at 12.51 ppm disappeared, the proton signal of the imine (H_d) downfield shifted by 0.22 ppm. A new broad signal appeared at 9.44 ppm, which was assigned to the imine-nitrogen of L-Al. Compared with the signal at 7.22 ppm (H_b), a new signal which appeared in the presence of Al^{3+} at 7.03 ppm upfield shifted by 0.19 ppm owing to the interaction HL with Al^{3+} . The results suggested that HL may chelate Al^{3+} through interactions with carboxylate oxygen, imine nitrogen and oxygen of naphthol hydroxyl group. The large differences of the IR spectra of the sensor (Fig.S8) in the absence and presence of Al^{3+} indicate further proved the combination of between the sensor and Al^{3+} as shown Table 1.

4. Conclusion

In summary, a highly selective and sensitive fluorescent sensor based on naphthalene derivative for Al^{3+} has been has been developed. The sensor shows great fluorescence turn-on upon binding Al^{3+} which inhibits ESIPT and PET. More importantly, because of lower detection limit in aqueous solution, the chemosensor may find potential applications to detect micromolar concentrations of Al^{3+} in both biological systems and the environment.

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Figure captions

Fig.1. Changes in the absorption spectra of HL (20 μ M) in near 100% aqueous media (Tris-HCl, pH = 7.2).at room temperature upon addition of different amounts of Al³⁺ ions (0- 5 equiv.).

Fig.2. Fluorescence spectra of HL (20 μ M) upon the addition of metal salts (5 equiv.) of Li⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cu²⁺, Co²⁺, Mn²⁺, Ni²⁺, Zn²⁺, Ba²⁺, Fe²⁺, Cd²⁺, Hg²⁺, Pb²⁺, Sc³⁺, Fe³⁺, Cr³⁺ and Al³⁺ in near 100% aqueous media (Tris-HCl, pH = 7.2).Excitation wavelength was 407 nm, slit = 3nm / 3nm.

Fig.3. Fluorescence intensity of HL and its complexation with Al^{3+} in the presence of various metal ions in near 100% aqueous media (Tris-HCl, pH = 7.2). Red bar: HL (20.0 μ M) and HL with 5 equiv. of Li⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cu²⁺, Co²⁺, Mn²⁺, Ni²⁺, Zn²⁺, Ba²⁺, Fe²⁺, Cd²⁺, Hg²⁺, Pb²⁺, Cr³⁺, and Sc³⁺ stated. Green bar: 20.0 μ M of HL and 5 equiv. of Al³⁺ with 5 equiv. of metal ions stated ($\lambda_{ex} = 407$ nm, slit = 3nm / 3nm.).

Fig.4. the reversibility of recognition of Al^{3+} was performed by adding Na₂EDTA in near 100% aqueous media (Tris-HCl, pH = 7.2). Black: HL, Blue: HL+Al³⁺, Green: HL+Al³⁺+ Na₂EDTA, Red: HL+Al³⁺+ Na₂EDTA+HL, (Ex =407nm, slit = 3nm / 3nm).

Fig.5. Fluorescence spectra of HL (20 μ M) in near 100% aqueous media (Tris-HCl, pH = 7.2), upon the addition of Al³⁺ (0-8equiv.) Inset: color of HL and HL+Al³⁺ system under UV lamp.

Fig.6. Job's plot for determining the stoichiometry of HL and Al^{3+} in near 100% aqueous media (Tris-HCl, pH = 7.2) ($X_{Al}=[Al^{3+}]/([Al^{3+}] + [HL])$), the total concentration of HL and Al^{3+} was 100 μ M).

Fig.7. ¹HNMR spectra of HL with $Al(NO_3)_39H_2O$ in DMSO-d₆: (I) HL; (II) HL with 1.0 eq. of Al^{3+} ; (III) HL with 2 eq. of Al^{3+} .

Table 1 Major IR data of the receptor and its complexe.

Scheme1 Synthesis of HL

Scheme 2 Proposed mechanism for detection of Al³⁺ by HL.



Fig.1. Changes in the absorption spectra of HL (20 μ M) in near 100% aqueous media (Tris-HCl, pH = 7.2).at room temperature upon addition of different amounts of Al³⁺ ions (0- 5 equiv.).



Fig.2. Fluorescence spectra of HL (20 μ M) upon the addition of metal salts (5 equiv.) of Li⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cu²⁺, Co²⁺, Mn²⁺, Ni²⁺, Zn²⁺, Ba²⁺, Fe²⁺, Cd²⁺, Hg²⁺, Pb²⁺, Fe³⁺, Sc³⁺, Cr³⁺, and Al³⁺ in near 100% aqueous media (Tris-HCl, pH = 7.2).Excitation wavelength was 407 nm, slit = 3nm / 3nm.



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Fig.4. the reversibility of recognition of AI^{3+} was performed by adding Na₂EDTA in near 100% aqueous media (Tris-HCl, pH = 7.2). Black: HL, Blue: HL+ AI^{3+} , Green: HL+ AI^{3+} + Na₂EDTA, Red: HL+ AI^{3+} + Na₂EDTA+HL, (Ex =407nm, slit = 3nm / 3nm).



Fig.5. Fluorescence spectra of HL (20 μ M) in near 100% aqueous media (Tris-HCl, pH = 7.2), upon the addition of Al³⁺ (0-8equiv.) Inset: color of HL and HL+Al³⁺ system under UV lamp.



Fig.6. Job's plot for determining the stoichiometry of HL and Al^{3+} in near 100% aqueous media (Tris-HCl, pH = 7.2) ($X_{Al}=[Al^{3+}]/([Al^{3+}] + [HL])$), the total concentration of HL and Al^{3+} was 100 μ M)



Fig.7. ¹HNMR spectra of HL with $Al(NO_3)_39H_2O$ in DMSO-d₆: (I) HL; (II) HL with 1.0 eq. of Al^{3+} ; (III) HL with 2 eq. of Al^{3+} .

| Compound | v(naphthalene-OH) cm ⁻¹ | v(benzovl-C=O) cm ⁻¹ | v(-C=N) cm ⁻¹ | v (M–O) cm ⁻¹ |
|-----------------------|------------------------------------|---------------------------------|--------------------------|--------------------------|
| HL | 3217 | 1691 | 1596 | |
| L-A1 | weak | 1620 | 1544 | 582 |
| Δv(cm ⁻¹) | | 71 | 52 | |

 Table 1 Major IR data of the receptor and its complexe.



Scheme1 Synthesis of HL



Scheme 2 Proposed mechanism for detection of Al³⁺ by HL.

| Compound | v(naphthalene-OH) cm ⁻¹ | v(benzoyl-C=O) cm ⁻¹ | $v(-C=N) \text{ cm}^{-1}$ | v (M–O) cm ⁻¹ |
|---------------------|------------------------------------|---------------------------------|---------------------------|--------------------------|
| HL | 3217 | 1691 | 1596 | |
| L-Al | weak | 1620 | 1544 | 582 |
| $\Delta v(cm^{-1})$ | _ | 71 | 52 | 7 – 1 |
| | | | | |

Highlights

- 1. The sensor shows "off-on" fluorescent responses toward Al^{3+} in aqueous media.
- 2. The detection limit reached at 10^{-6} m in near 100% aqueous media.

The sensor shows "turn-on" fluorescent responses toward Al³⁺ in near 100% aqueous media. The reason for this phenomenon is that the addition of Al^{3+} to the solution of HL result in the formation of a 1:1 stoichiometry of the binding mode of ister interester inter L-Al which inhibits the excited-state intramolecular proton transfer (ESIPT) and



Em=474nm