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Highly sensitive and selective fluorescent 'turn-on' probe for determination of aluminum ion in aqueous solution

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Abstract

A novel fluorescent sensor, 1-((2-hydroxynaphthalen-1-yl)methylene)semicarbazide was synthesized and characterized by infrared spectra, elemental analysis, Electrospray ionization mass spectra. The fluorescent sensing behaviors of the sensor toward different metals ions, anions and amino acids were determined by UV-vis and fluorescence spectroscopy. The fluorescent sensor exhibited obvious changes in its electronic and fluorescent spectral behavior in the visible region of the spectrum in the presence of aluminum ion with the lower detection limit was 8.9×10^{-9} M.

KEYWORDS: Aluminum, Fluorescent Sensor, Schiff base, Detection limit

1. INTRODUCTION

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Aluminum(Al³⁺) is a polyvalent cation and the third abundant metal in the earth's crust, and it is widly used for water treatment, food additives, medicines and the production of light alloys in modern society ^[1-8]. However, the accumulation of aluminum in **the** human body can damage normal tissues and cells, **resulting** in human health problems, such as Alzheimer's disease^[9-11], Parkinson's disease^[12], lung cancer, breast cancer, and bladder cancer^[13,14]. Besides, the aluminium-containing adjuvants could trigger the cascade of immunological events such as chronic fatigue syndrome and macrophagic myofasciitis^[15]. **What's more**, the content of aluminium correlates with the reduction of the (Na⁺/K⁺)ATPase activity^[16,17]. In ddition, due to the high concentrations of aluminum appearing in acidified lakes and acidic soils worldwide^[18-20], the fish and the growing crop in these enviroment are also polluted ^[21]. Therefore, it is very important to determine and control aluminum ion in environment and **the human body**.

Recently, **a** great number of methods have been used for the detection of aluminum ion^[22-24] and others^[25-30]. Of them, the fluorescent detection for aluminum ion and others have attracted increasing attention, and have been used in a wide range of applications because of its operational homeliness^[31-35]. Moreover, a number of fluorescent sensors based on the schiff bases were used for the detection of aluminum ion have been reported , but the selectivity over anions and amino acids were not fully tested by previous reports^[36-41]. It is well known that Al³⁺ prefers a coordination sphere containing N and O as hard-base donor sites. Schiff bases are known to be good ligands which provide a hard-base environment for the hard-acid Al^{3+} [33,35,42].

In the present study, we attempted to design and synthesize an optical chemosensor for Al^{3+} . 1-((2-hydroxynaphthalen-1-yl)methylene)semicarbazide (*NS*) was chosen as the signaling subunit and its binding properties with other cation, antion and amino acid by the means of UV–vis and fluorescence spectroscopy. As expected, the chemosensor(*NS*) could recognize Al^{3+} over other cation, antion and amino acid.

2. EXPERIMENTAL

2.1 Materials And Methods

FT-IR spectra (4,000 - 400 cm⁻¹) were obtained on NICOLET380 FT-IR spectrometer in KBr disks (USA). Melting point was determined on a WRX-4 apparatus in a sealed capillary (China). UV - vis spectra were measured with Hewlett Packard HP-8453(China). ¹H and ¹³C NMR spectra were recorded at room temperature on a Varian 400MHz spectrometer in CD3OD(USA). The fluorescence spectra were obtained on Varian Cary ESe-NipSe-N fluorescence spectrometer with the excitation and emission slits are 2.5 nm (USA). Elemental analyses (EAs) were carried out with a VARI-EL elemental analyzer. Electrospray ionization mass spectra (ESI-MS) were measured on a Finnigan LCQ system in methanol/water solution(USA). All chemicals used

were of analytical grade and were used as received without any further purification and were obtained from Sigma–Aldrich (USA)and Alfa Aesar (USA)Chemical Reagent Co. All metal salts were introduced as their chlorate salts. Anions were purchased as sodium salts.

2.2 Synthesis Of 1-((2-Hydroxynaphthalen-1-YI)Methylene)Semicarbazide (NS) 0.344 g(0.002 mo1) 2-hydroxy naphthalene formaldehyde was added to 6.00 mL ethanol with heating until it was dissolved. Then 0.150 g(0.002 mol) of semicarbazide in 7.00 mL water and 0.4 mL acetic acid was added drop-wise into the mentioned solution above. After the resulting solution was refluxed for 15 min with a constant stirring, light yellow solid was obtained and washed with ethanol and ether, respectively, recrystallized from dimethylbenzene, dried in vacuo. Yield, 67.8%. mp.:111-113°C. Elemental Analysis Calcd for $C_{12}H_{11}N_3O_2$: C: 62.87; H: 4.84; N: 18.33. Found: C: 62.86; H: 4.86; N: 18.33. IR(cm⁻¹, s strong, m medium, w weak): 3442m, v(O-H); 3346m, v(N-H); 1675s, v(C-H); 1625m, v(C=N). ¹H NMR (400 MHz, CD₃OD): 9.04 (1H, s), 7.19-7.89 (6H, s), 2.50 (4H, s). ¹C NMR (400 MHz, CD₃OD): 163.43, 162.12, 158.31, 152.64, 137.62, 133.72, 130.21, 126.91, 123.83, 120.44, 119.45, 117.25. Exact mass for NS: 229.09, ESI-MS: [NS+H]⁺ (m/z, 230.2473).

3. RESULTS AND DISCUSSION

3.1 Absorption Spectra Studies

Uv-vis titration experiments were conducted for evaluation of the formation of *NS*-Al³⁺ in solution. As shown in Figure 1, two main absorption peaks at 316 and 357 nm were observed in the absorption spectra of *NS*(25 μ M). Upon addition of Al³⁺, the two peaks show obvious red-shift and their intensities decrease gradually. Meanwhile, two new absorption peaks at 336 nm and 385nm appear and their intensities increase gradually. Moreover, there were three isosbestic points at 322, 352, 368 nm in the Uv-vis titration spectra. The results suggested the formation of a new compound between Al³⁺ and *NS*, which extends the conjugated system and leads to new absorption in the long wavelength region^[42,43]. The absorbance peaks have been hardly changed when the concentration of Al³⁺ was increased to 13 μ M.

3.2 Effect Of Ph On The Fluorescence Spectra

To evaluate the optimal determinations conditions, it is necessary to investigate pH effect on *NS* in the absence and presence of AI^{3+} . As shown in Figure 2, there is hardly change in the fluorescence spectra of *NS* with the addition of AI^{3+} at pH 1.0-12.0, while the remarkable change was found at pH range 4.0–6.0. The results showed the combination of protons and N atoms in –C=N– groups inhibits the coordination of AI^{3+} with *NS* at pH range 1.0–3.0, On the other hand, the fluorescence of *NS* has no response to AI^{3+} at high pH values because the hydrolysis happens between OH and $AI^{3+[44]}$. The optimal pH corresponding to the highest intensity is 6.0, which is within the biologically relevant pH range $(5.5-7.5)^{[45-47]}$, indicating that *NS* could be applied as an Al³⁺ sensor in biological organisms potentially.

3.3 Fluorescence Titration

On the basis of the above evaluation of optimal pH, fluorescence titration was performed to study the stoichiometric ratio of the NS-Al³⁺ complex in pH 6.0 buffer solution. The fluorescence enhancement of the NS in the presence of various concentrations of Al³⁺ was shown in Figure 3. The receptor NS do not show remarkable emission at 450 nm when the excitation wavelength is at 390 nm. However, upon the addition of Al³⁺ (2.5 μ M), the fluorescence intensity at 450 nm increases accordingly, but when the concentration of Al³⁺ was up to 10 μ M, the rising tendency slowed down gradually until stable.

The binding constant was calculated from the emission intensity - titration curve according to the equations (1) and $(2)^{[48]}$:

$$\frac{I - I_f}{I_b - I_f} = \frac{(b - (b^2 - 2k^2 C_t [Al^{3+}]/s)^{1/2})}{2kC_t}$$
(1)
$$b = 1 + kC_t + k[Al^{3+}]/2s$$
(2)

where I is the emission intensity observed at a given Al^{3+} concentration, I_f is the emission intensity of free *NS* in solution, I_b is the emission intensity of *NS* when fully bound to Al^{3+} (it is assumed that when further addition of Al^{3+} does not change the emission intensity, K is the equilibrium binding constant, C_t is the total *NS* concentration, [Al³⁺] is the Al^{3+} concentration, and s is the binding site. Both K and s are obtained from the best fit line. From Figure 4, we can obtained the equilibrium binding constant K between Al^{3+} with *NS* is 1.3×10^7 M⁻¹ and the binding site(s= [Al³⁺]/[*NS*]) is 0.43.

The limit of detection $(\text{LOD})^{[49,50]}$ was calculated based on the fluorescence titration. The emission intensity of *NS* without Al³⁺ was measured 10 times and the standard deviation of blank measurements was determined. A good linear relationship between the fluorescence intensity and the Al³⁺ concentration could be obtained in the 1.25 - 8.75 μ M concentration range (R² = 0.996). LOD was then calculated with the equation: LOD = $3\sigma_{bi}/m$, where σ_{bi} is the standard deviation of blank measurements, m is the slope between intensity versus sample concentration. LOD was measured to be 8.9 × 10⁻⁹ M, nearly the same capacity compared with other compounds ^[38]. In general, the concentration of Al³⁺ should be lower than (1.85×10⁻³ M) in drinking water, which means that our proposed fluorescent method based on probe *NS* is sensitive enough to monitor the water quality of drinking water.

3.4 Selectivity Experiment

The selectivity of *NS* for various common cations (Zn²⁺, Sr²⁺,Pb²⁺, Ni²⁺, Na⁺, Mg²⁺, K⁺, Hg²⁺, Fe³⁺, Cu²⁺, Cr³⁺, Co²⁺, Cd²⁺, Ca²⁺, Bi³⁺, Ba²⁺, Al³⁺, Ag⁺) were investigated in Tris-HCl buffered aqueous solution (25mM, pH=6.0). As shown in Figure 5, Al³⁺ treatment induces a large increase for the fluorescence intensity at 450 nm, whereas other

physiologically important metal ions, not only exist in living cells, such as Na⁺, K⁺, Mg²⁺, Ca²⁺, but also most heavy and transition metal ions such as Mn^{2+} , Cr^{3+} or some paramagnetic metal ions, such as Fe³⁺, Cu²⁺, Co²⁺, Ni²⁺, Zn²⁺, cause a slight fluorescence increasment at a 20-fold excess concentration.

In order to prove that the sensor was highly selective for Al^{3+} , other species existing in cells such as anions(SO_4^{2-} , SO_3^{2-} , PO_4^{3-} , NS^- , NO_3^- , MnO_4^- , IO_3^- , HPO_4^- , HCO_3^- , $H_2PO_4^-$, F⁻, CrO_4^{2-} , $Cr_2O_7^{2-}$, CO_3^{2-} , CNS^- , ClO_3^- , Cl^- , $C_2O_4^{2-}$, Br^- , $B_4O_7^{2-}$) and amino acids (Ile, Val, Asp, Ser, Pro, Tyr, Lys, Arg, Met, Gln, Glu, Gly, Ala, Phe, Leu) were determinated. The results show that both the anions and the amino acids have no interference on Al^{3+} determination, indicating that *NS* can be applied to detect Al^{3+} effectively(Figure 6-7).

3.5 The Preliminary Application Of The Sensor

The recovery of Al^{3+} from river water was studied with the proposed fluorescent sensor. First, the sample was concentrated by rotary evaporator. The fluorescence intensity of *NS* for the concentrated river water was investigated in Tris-HCl buffered aqueous solution (25mM, pH=6.0). The results demonstrated that the average amount was 1.21×10^{-4} M by fluorescence for 3 times, which was more or less the same as the result of the traditional flame atomic absorption spectrophotometry, 1.38×10^{-4} M. The experiment suggested that it was a convenient, accurate and reliable way to calculate the amount of Al3+ by the fluorescence sensor way.

4. CONCLUSION

In conclusion, a structurally characterized 1-((2-hydroxynaphthalen-1-yl)methylene) -semicarbazide (*NS*) demonstrates as a new sensor toward Al³⁺ in pH 6.0 Tris-HCl buffer solution. The sensor *NS* exhibited high selectivity for Al³⁺ over other important metal ions(Zn²⁺, Sr²⁺, Pb²⁺, Ni²⁺, Na⁺, Mg²⁺, k⁺, Hg²⁺, Fe³⁺, Cu²⁺, Cr³⁺, Co²⁺, Cd²⁺, Ca²⁺, Bi³⁺, Ba²⁺, Al³⁺, Ag⁺), anions(SO₄²⁻, SO₃²⁻, PO₄³⁻, NS⁻, NO₃⁻, MnO₄⁻, IO₃⁻, HPO₄⁻, HCO₃⁻, H₂PO₄⁻, F⁻, CrO₄²⁻, Cr₂O₇²⁻, CO₃²⁻, CNS⁻, ClO₃⁻, Cl⁻, C₂O₄²⁻, Br⁻, B₄O₇²⁻) and amino acids(Ile, Val, Asp, Ser, Pro, Tyr, Lys, Arg, Met, Gln, Glu, Gly, Ala, Phe, Leu) with the lower detection limit is 8.9×10^{-9} M. So this sensor may play an important role for detecting Al³⁺ in the biological and environmental system.

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Scheme 1. Synthesis the sensor of 2-hydroxy naphthalene formaldehyde.



Figure 1. UV–vis spectra changes of the sensor (2.5μ M) after addition of aluminum ion ($0, 2, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18 \mu$ M) at room temperature. **Inset**. Graph of the absorbance at 385 nm as a function of aluminum ion concentration.



Figure 2. Effect of pH on the fluorescence intensity of the sensor 2-hydroxy

naphthalene formaldehyde (2.5 μ M) at 450 nm with (Black) and without (Red) 1 equiv



Figure 3. The fluorescence spectra of the sensor ($2.5\mu M$) after addition of aluminum ion



 $(0, 1.25, 2.5, 3.75, 5, 6.25, 7.5, 8.75, 10, 11.25, 12.5, 13.75 \mu M)$ at room temperature.

Figure 4. Plot of (I- I_f)/(I_b - I_f) vs. [Aluminum ion] for the sensor **2-hydroxy naphthalene** formaldehyde. $\lambda_{ex} = 390$ nm. The best fit line (R²=0.996), superimposed on the data,

1.0 0.8 (l-lf)/(lb-lf) 0.6 R^2 = 0.99624 0.4 P1 12996428.26005 ? 0.43103 ? .02466 ? 272103.44871 P2 0.43103 0.2 0.0 0.000002 0.000003 0.000004 0.000005 0.000000 0.000001 The concentration of aluminum

according to 2 eq yields $K=1.3 \times 10^7 \text{ M}^{-1}$ and S=0.43.

Figure 5. The fluorescence responses (I_{450nm}) of sensor **2-hydroxy naphthalene**

formaldehyde (2.5 μ M) with various cations (50 μ M) in Tris-HCl buffer (pH=6.0)(λ ex =

390 nm).



Figure 6. The fluorescence responses (I_{450nm}) of the sensor **2-hydroxy naphthalene** formaldehyde (2.5µM) with various anions (50µM) in Tris-HCl buffer (pH=6.0)($\lambda ex =$



Figure 7. The fluorescence responses (I_{450nm}) of the sensor **2-hydroxy naphthalene**

formaldehyde (2.5µM) with various amino acids (50µM) in Tris-HCl buffer

Emission Signal AI³⁺ **Amino Acids** Wavelength (nm)

 $(pH=6.0)(\lambda ex = 390 \text{ nm}).$