A Simplified and Turn-on Fluorescence Chemosensor Based on Coumarin Derivative for Detection of Aluminium(III) Ion in Pure Aqueous Solution

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A novel chemosensor **L** based on coumarin Schiff-base was synthesized and investigated. Sensor **L** showed remarkable selectivity for Al^{3+} in Tris-HCl aqueous buffer solution (pH 7.2), and the selectivity was not affected by the presence of a large excess of other competitive ions. The sensor responded rapidly to Al^{3+} in aqueous solutions with a 2:1 stoichiometry. Meanwhile, it indicated significant improvement of quantum efficiency and ideal fluorescent lifetime.

Keywords Coumarin derivative, fluorescent chemosensor, L-serine, aluminium(III) ion

(Received May 11, 2015; Accepted June 25, 2015; Published October 10, 2015)

Introduction

Aluminum is the most abundant element in the earth and is widely used in our daily life, such as in food additives, medicines and the production of light alloy, *etc.*¹ In organisms, aluminium which is present as Al³⁺, is highly important in order to maintain the health. However, an excess of Al³⁺ has severe toxicity, which not only influences plant growth² but also damages the central nervous system to cause human illnesses like dementia and impairment of memory, idiopathic Parkinson's disease, Alzheimer's disease and even breast cancer.³⁻⁷ Therefore, it is necessary to develop a simple and convenient method to detect Al³⁺ for environmental and biological studies.

Sensing analysis technology has attracted significant focus because of the advantages including capability of visualization, easy operational procedure, rapid response time, cost effective equipment, convenience afforded due to the lack of need for expensive instruments and complex operation steps, high sensitivity and selectivity.⁸⁻²¹, The technology has been applied for the determination of medicine,²²⁻²⁵ biomolecules,²⁶⁻²⁹ TNP,³⁰ metal ions,³¹⁻⁵⁰ anions,⁵¹ and so on.⁵²

Fluorescent sensors, as an important sensing analysis method, have also attracted received considerable attention for visual detection of metal ions. In recent years, a series of fluorescent sensors for Al³⁺ have so far been reported. Among them (Table S1, Supporting Information), some were operated in organic solvent or in aqueous solution of organic solvent,⁵³⁻⁵⁶ others showed less sensitivity to Al³⁺ with poor detection limits,^{57,58} and still others were severely disturbed by Hg²⁺, Cu²⁺ or Fe³⁺ in the process of Al³⁺ detection.^{55,59-62} Hence, the development of novel, pure water-soluble, sensitive and interference-free fluorescent chemosensors for Al³⁺ detection is still highly desired.

In this work, we designed a water-soluble fluorescence

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chemosensor for Al³⁺ based on a coumarin derivative. The sensor system was composed of a coumarin fluorophore and a receptor of L-serine. By virtue of their excellent properties, such as a high fluorescence quantum yield, large Stokes shift, low toxicity, ease of modification and visible wavelength emission, coumarin and its derivatives have an ideal skeleton structure for the construct ion of various fluorescent probes.⁶³ L-serine not only can combine with metal ions but also greatly enhances the water solubility of coumarin derivative. Therefore, compared with above-mentioned sensors, Sensor L has been proven to be a simple, convenient, rapid synthesis of a probe that shows excellent water solubility, high selectivity and sensitivity, the advantage of low cost, and visual fluorescent switching behav towards aluminium ions. Sensor L is shown in Scheme 1.

Experimental

Melting point was determined using an SGW X-4 digital melting point apparatus (Shanghai Instrument Physical Optics Instrument Co., Ltd.). ¹H NMR spectrum was run on a Varian Mercury-Plus 300 NMR spectrometer using TMS as the internal standard (Varian, San Diego, CA). Elemental analysis was taken with a Vario EL CHNS elemental analyzer (Elementar, Germany). Mass spectrum was recorded with a VG ZAB-HS double focusing mass spectrometer (Thermo Onix Ltd., UK). Fluorescence spectra, fluorescence lifetime and quantum efficiency were measured with a Fluorolog 3-TSCPC (Horiba Jobin Yvon Inc., France). All chemicals were purchased from Aladdin Industrial Corp. (China) and used without further purification. The solvents were purified using standard methods.

Preparation of 8-formyl-7-hydroxy-4-methylcoumarin: A solution of 8-formyl-7-hydroxy-4-methylcoumarin was prepared by the known method.⁶⁸ First, 7-hydroxy-4-methylcoumarin (5.00 g, 0.0284 mol) and hexamine (10.0 g, 0.071 mol) in acetic acid (37 mL) were stirred for 5.5 h at 95°C. Then, hydrochloric acid (75 mL, HCl: $H_2O = 84:100$, v/v) was added and further

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Scheme 1 Synthetic route of compound L.



Fig. 1 Fluorescence spectra of L (10.0 μ M, λ_{ex} = 335 nm) with addition of various metal ions (100.0 μ M) in aqueous solution (Tris-HCl, 10.0 mM, pH = 7.2).

heated for 45 min. After cooling, the mixture was poured into ice-water (375 mL) and extracted with ethyl acetate (150 mL × 3). The organic layer was dried over sodium sulfate and the solvent removed. The residue was purified by column chromatography on silica gel using dichloromethane as eluent ($R_f = 0.4$) to provide the product as a light yellow solid. Yield 0.9 g (15.5%). ¹H NMR (CDCl₃, δ ppm): 2.45 (s, 3H); 6.22 (s, 1H); 6.92 (d, J = 9.2 Hz, 1H); 7.74 (d, J = 8.8 Hz, 1H); 10.63 (s, 1H); 12.23(s, 1H). MS *m/z*: 205[M+H]⁺.

Preparation of 8-((s-2-carboxyl-1-hydroxy-2-ylimino)methyl)-7-hydroxy-4-methyl-2H-chromen-2-one (L): First, 8-formyl-7hydroxy-4-methylcoumarin (0.19 g, 0.1 mmol) and L-serine (0.11 g, 0.1 mmol) were dissolved in anhydrous ethanol (20 mL). The reaction mixture was refluxed for 8 h under nitrogen and then the mixture was cooled to room temperature. The precipitate was filtered off, washed with cold ethanol two times and dried in vacuum to give the desired product as a yellow solid. Yield 0.23 g (78.8%). m.p. 215.5 - 217.2°C. 1H NMR (d_6 -DMSO, δ ppm): 2.36 (s, 3H); 2.51 (s, 1H); 3.81 (m, 2H); 3.8 (m, 1H); 4.60 (s, 1H); 6.04 (s, 1H); 6.59 (d, J = 9.2Hz,1H); 7.63 (d, J = 9.2 Hz, 1H); 8.92 (s, 1H); 14.67 (s, 1H). 13C NMR (d_6 -DMSO, δ ppm): 18.96, 62.75, 67.15, 104.37, 107.06, 108.09, 119.14, 131.55, 155.06, 156.18, 160.04, 161.19, 170.61, 175.34. MS m/z: 292.2[M-H]+. Found, %: C, 58.02; H, 4.57; N, 4.79. Calculated for C₁₄H₁₃NO₆: C, 57.73; H, 4.50; N, 4.81.

Results and Discussion

In order to investigate the effect of various metal ions on the



Fig. 2 Fluorescence responses of L (10.0 μ M, $\lambda_{ex} = 335$ nm) to various metal ions (10.0 μ M) (black column) (10.0 equiv.), and upon the subsequent addition of Al³⁺ (red column) in aqueous solution (Tris-HCl, 10.0 mM, pH = 7.2).

fluorescence spectra of L, the ions Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Ba²⁺, Cr³⁺, Fe³⁺, Al³⁺, Ni²⁺, Cu²⁺, Zn²⁺, Ag⁺, Pb²⁺ and Hg²⁺ (as their nitrate salts) were used to evaluate the metal ion binding properties of L in aqueous solution (Tris-HCl, 10.0 mM, pH = 7.2). Figure 1 shows the changes in the fluorescence spectra of L upon addition of various metal ions. As shown in Fig. 1, compound L had a large effect only with Al³⁺ and Zn²⁺ among the metal ions examined. In the presence of Al³⁺ and Zn²⁺, L showed fluorescence enhancement so strong and a dramatic color change from colorless to light blue which could easily be identified by the naked eye under UV lamp during the detection process. Other metal ions gave no distinct response to L in the fluorescence spectra. This obvious feature reveals that compound L has high selectivity for Al³⁺ and Zn²⁺.

To further investigate the interference of other metal ions on the detection of Al³⁺, competition experiments were performed in which various metal ions (10.0 μ M) were added to a solution of L in the presence of Al³⁺. The total concentration of mixture ions was 100 times that of L; ions Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Ba²⁺, Cr³⁺, Fe³⁺, Al³⁺, Ni²⁺, Cu²⁺, Zn²⁺, Ag⁺, Pb²⁺ and Hg²⁺ (as their nitrate salts). As shown in Fig. 2, the addition of other metal ions, even a mixture of interference ions, resulted in hardly any change of the fluorescence intensity of L in the presence of Al³⁺. Nevertheless, the fluorescence intensity of L in the presence of Zn²⁺ was quenched dramatically with the addition of the mixture of competitive anions. The result suggested that L could be an effective sensor for the detection of Al³⁺ rather than Zn²⁺ in aqueous solution.

As shown in Fig. 3, the free ligand L (10.0 μ M) alone



Fig. 3 Fluorescence spectra of L (10.0 μ M, λ_{ex} = 335 nm) upon the titration of Al³⁺ (0 - 2.5 equivalent) in aqueous solution (Tris-HCl, 10.0 mM, pH = 7.2).



Fig. 4 The plausible binding mode of L with Al³⁺, and fluorescence mechanism of PET processes.

displayed weak fluorescence intensity at 450 nm when it was excited at 335 nm in aqueous solution (Tris-HCl, 10.0 mM, pH = 7.2). Upon addition of Al^{3+} into the aqueous solution of L (10.0 µM), the fluorescence intensity clearly increased. When the concentration of Al³⁺ reached 2.0 equiv., the fluorescence intensity reached the maximum value (about 21-fold enhancement). This phenomenon is understood as a mechanism of PET (photo-induced electron-transfer).64,65 The lone pair electrons from the Schiff-base nitrogen atom and oxygen atom of L-serine contributed to the PET processes, which quenched the fluorescence emission of L. Then the quenched fluorescence could relapse dramatically upon chelating metal ion by inhibiting the PET processes and producing a highly efficient chelationenhanced fluorescence effect (Fig. 4). As a result, the fluorescence intensity of L ($\Phi_s = 0.87\%$) increased remarkably at 450 nm ($\Phi_F = 21.98\%$) upon the addition of Al³⁺ ions. Thus we can conclude that L may serve as a "turn-on" sensor for Al³⁺.

In order to further investigate the sensitivity of **L** to Al³⁺, the detection limits of **L** for Al³⁺ were tested upon excitation at 335 nm in aqueous solution.⁶⁶ As shown in Fig. 5, the plots of F/F_0 vs. Al³⁺ concentration (0 – 12.0 µM) show a good linear Stern-Volmer relationship: $F/F_0 = 5.73$ [Al³⁺] + 1.84 ($R_2 = 0.9903$), and the relative standard deviation for five repeated measurements of 0 µM of Al³⁺ was 1.27%. The detection limit (DL) for Al³⁺ was 6.65 × 10⁻⁸ mol/L (signal to noise ratio of



Fig. 5 The Stern-Volmer relationship plot of F/F_0 vs. [Al³⁺] in aqueous solution (Tris-HCl, 10.0 mM, pH = 7.2), DL = 6.65×10^{-7} mol/L; [L] = 10.0μ M; $\lambda_{ex} = 335$ nm.



Fig. 6 Benesi-Hildebrand plot ($\lambda_{ex} = 335 \text{ nm}$) of **L** and Al³⁺ in aqueous solution (Tris-HCl, 10.0 mM, pH = 7.2).

3:1) when the concentration of **L** was 10.0 μ M, which illustrated that the detection of **L** toward Al³⁺ was highly sensitive.

As shown in Fig. 6, the association constant K of the complex L-Al³⁺ was then calculated to be $9.50 \times 10^5 \text{ M}^{-1}$ with a linear relationship by the Benesi-Hildebrand method, Eq. (1).⁶⁷

$$\frac{1}{F - F_{\min}} = \frac{1}{K(F_{\max} - F_{\min})[Al^{3+}]} + \frac{1}{F_{\max} - F_{\min}}$$
(1)

To test the stoichiometry of the complexing behav of **L** with Al³⁺ in depth, the molar ratio method for the absorbance was applied. By keeping the total concentration of Al³⁺ and **L** at 20.0 μ M, and changing the molar ratio of **L** and Al³⁺ from 0 to 0.9, the fluorescence intensity of **L** in the absence (*F*₀) and presence (*F*) of Al³⁺ ion were determined, respectively. A plot of (*F* - *F*₀) *versus* [**L**]/([**L**]+[Al³⁺]) shows that the value goes through a maximum at a molar fraction of about 0.7, indicating a 2:1 stoichiometry complex formation exactly (Fig. 7).

Adaptability and also responsiveness were determined using the lifetimes of L and Al^{3+} by time-resolved fluorescence spectrofluorometer. The fluorescence lifetime was measured at

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1.6x10 1.4x10 1.2x10⁵ 1.0x10 8.0x104 6.0x10⁴ 4.0x10⁴ 0.3 0.2 0.5 0.6 0.9 0.1 0.4 0.7 0.8 [L]/([L]+[A1³⁺])

Fig. 7 Job's plot of the complexation between L and Al^{3+} , total concentration of L and Al^{3+} is 20.0 μ M.



Fig. 8 Fluorescence decay curves of L and L+Al³⁺ in aqueous solution (Tris-HCl, 10.0 mM, pH = 7.2) obtained at λ_{ex} = 335 nm.

the excitation 280 nm of NanoLED source. The decays of L were found to be monoexponential. The lifetime decays in the absence of Al^{3+} and in the presence of Al^{3+} are shown in Fig. 8. The average lifetimes of L and L+Al³⁺ were 4.77 ns (XSQ = 1.03) and 4.58 ns (XSQ = 1.13), respectively. The unapparent change of lifetime demonstrates that L possesses good responsiveness and adaptability to Al³⁺.

Conclusions

In conclusion, a water-soluble fluorescent chemosensor **L** for aluminium ion based on coumarin schiff-base conjugate has been designed and synthesized. It showed high sensitivity and selectivity for Al^{3+} recognition in comparison to other metal ions in aqueous solution. The sensor **L** exhibited 2:1 coordinates with Al^{3+} and high quantum efficiency in aqueous solution. We believe that the fluorescence sensor **L** may be utilized for the detection and analysis of various aluminum-related issues in environmental, biological and medical areas.

Acknowledgements

This work was supported by The Transformation of Scientific and Technological Achievements in Jiangsu Province Special Funds (BA2014123).

Supporting Information

Comparison of some chemosensors for Al³⁺ ions, and additional figures. These materials are available at http://www.jsac.or.jp/analsci/.

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