ORIGINAL ARTICLE



# Novel Fluorometric Turn On Detection of Aluminum by Chalcone-Based Chemosensor in Aqueous Phase

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**Abstract** A novel, 100% water-soluble chalcone based chemosensing receptor {1-[3-(2-Hydroxy-phenyl)-3-oxo-propenyl]-naphthalen-2-yloxy}-acetic acid, **L** was synthesized and characterized. The receptor **L** is designed based on the chelation enhanced fluorescence (CHEF) mechanism. The chemosensing properties of **L** were evaluated by UV–vis and fluorescence spectrometric methods. It exhibits highly selective recognition ability towards aluminum ions in water over other metal ions. The binding stoichiometry of **L** – Al<sup>3+</sup> complex is 2:1 by means of Job's plot and the detection limit is  $5.66 \times 10^{-8}$  M.

KeywordsFluorometric  $\cdot$  Novel chalcone derivative  $\cdot$ Detection of aluminium  $\cdot$  CHEF  $\cdot$  Chemosensor

# Introduction

For the past few years, optical detection methods especially fluorescence technique for the detection of environmentally and biologically relevant species such as Al<sup>3+</sup>, Pb<sup>2+</sup> and Hg<sup>2+</sup> has received heightened concern. Compared to the conventional techniques such as mass spectrometry (MS) [1], atomic absorption spectrometry (AAS) [2] and inductively coupled plasma mass spectroscopy (ICP-MS) [3], fluorescent method was considered to be more desirable due to its high sensitivity and selectivity, easy to operate and low cost because no sophisticated instruments is required. Therefore, the design of such fluorescent chemosensors has become a research focus in supramolecular chemistry. In recent years, there are numerous fluorescent chemosensors have been reported but many of them have encountered interference caused by other metal ions [4, 5], multiple synthetic routes [6], high cost, poor water solubility and make use of other harmful organic solvents.

To the best of our knowledge, it is a challenging task to design a 100% water-soluble fluorescent chemosensor for specific detection of aluminium owing to its poor coordination ability and lack of spectroscopical properties [7, 8]. Aluminium exists as the most abundant metal in the earth crust and has been widely exploited over hundred decades ago due to its high thermal conductivity, light weight and excellent corrosion resistance. Unlike other trace elements, our human body does not require aluminium for living. Excessive exposure of body to aluminium which can be found in consumer items such as food additive, cosmetics, antiperspirants and water may lead to Alzheimer's diseases [9, 10], breast cancer [11, 12] and osteomalacia [13]. It also disturbed aquatic life and plant growth in the environment [14]. Hence, it is important to develop a new sensor that able to selectively detect Al<sup>3+</sup> ions in aqueous medium in order to minimize the adverse impacts exerted by aluminium to living organisms and environment.

Based on the literature review, there are few  $Al^{3+}$  chemosensors that exhibited their own forte [15] but they encountered interference from other analytes [16, 17] and often experiences the poor water solubility [18, 19]. Thus, in our work, we report a CHEF type fluorescent chemosensor L containing chalcone group which acts as a fluorophore unit and carboxyl group as a binding sites. Utilization of carboxyl group in our compound will increase the water solubility due to its hydrophilic nature and it is a hard base that will increase the selectivity towards  $Al^{3+}$  (hard

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Scheme 1 Synthesis of {1-[3-(2-Hydroxy-phenyl)-3-oxo-propenyl]-naphthalen-2-yloxy}-acetic acid L



acid) [20, 21]. The novel chemosensing receptor L exhibited completely water solubility and showed highly selective fluorometric response towards  $Al^{3+}$  only in water.

# Experimental

# **Chemicals and Instruments**

All the chemicals and solvents were used directly as received without further purification. 2-hydroxy-1-napthaldehyde and the perchlorate salts of all cations used (Ag<sup>+</sup>, Al<sup>3+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Hg<sup>2+</sup>, K<sup>+</sup>, Mn<sup>2+</sup>, Na<sup>+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup>) were obtained from Sigma–Aldrich. Ethyl chloroacetate was purchased from Merck. 2'-hydroxyacetophenone was obtained from Fluka. Potassium carbonate anhydrous was obtained from R & M Chemical. Potassium iodide, sodium hydroxide pellets, sodium sulfate anhydrous, acetone and ethanol were supplied from



Fig. 1 UV–vis absorption spectra of chemosensor L (100  $\mu$ M) in the absence and presence of various metal ions (100  $\mu$ M) in water

QRec. Fourier Transform Infrared (FT-IR) spectra data was recorded by using a Perkin Elmer 2000-FT-IR spectrophotometer. The Fourier Transform Nuclear Magnetic Resonance (FT-NMR) spectroscopy was carried out using a Bruker-Avance 500 MHz Ultrashield spectrometer. CHN microanalyses were performed by using a Perkin Elmer 2400 LS Series CHNS/O analyzer. Absorption spectra were recorded by Shimadzu model UV-2600 UV–Vis spectrophotometer. Fluorescence measurements were performed on a Perkin Elmer model LS55 fluorescence spectrometer. All the stock solutions for metal ion (1 mM) and **1** (1 mM) were prepared and operated in distilled water for the spectral measurements.

# Synthesis of (1-Formyl-naphthalen-2-yloxy)-acetic Acid Ethyl Ester (1)

0.7 0.6 0.5 Absorbance 0.4 0.3 0.2 0.1 0 300 350 400 450 250 500 Wavelength (nm)

Fig. 2 Absorption spectral changes of L (100  $\mu$ M) in the presence of different concentrations of Al<sup>3+</sup> ions in water

To a solution of 2-hydroxy-1-napthaldehyde (1.0 equiv.) and ethyl chloroacetate (1.0 equiv.) in acetone, potassium carbonate anhydrous (4.0 equiv.) was added followed by a pinch of

40

35

30

25

20

15

10

5

0

Fluorescence Intensity (au)



Fig. 3 Fluorescence emission spectra of sensor L (100  $\mu$ M) in water upon addition of metal perchlorate salts (1 equiv.) such as Ag<sup>+</sup>, Al<sup>3+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Hg<sup>2+</sup>, K<sup>+</sup>, Mn<sup>2+</sup>, Na<sup>+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup>

potassium iodide. After 24 h reflux, the reaction mixture was filtered off to remove  $K_2CO_3$  and the solvent was left to evaporate. The reaction mixture was treated with water and extracted with diethyl ether and the organic layer was dried on anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was washed with ethanol to afford a beige solid. Yield: 53%. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 500 MHz)  $\delta$ : 11.00 (s, 1H), 9.29 (d, 1H), 8.05–8.03 (d, 1H), 7.78–7.77 (d, 1H), 7.65–7.62 (t, 1H), 7.46–7.43 (t, 1H), 7.15–7.13 (d, 1H), 4.87 (s, 2H), 4.30–4.26 (q, 2H), 1.31–1.28 (t, 3H).

## Synthesis of {1-[3-(2-Hydroxy-phenyl)-3-oxo-propenyl]naphthalen-2-yloxy}-acetic Acid (L)

Compound 1 (1.0 equiv.) was added to a mixture of 2'-hydroxyacetophenone (1.0 equiv.) in ethanol and stirred for 15 min. A 10% sodium hydroxide solution was added and stirred for overnight. The precipitate formed was filtered and dried. The product was washed with acetonitrile



fluorescence at 575 nm of L as a function of Al<sup>3+</sup> concentration



Fig. 5 Competitive selectivity of L towards  $Al^{3+}$  in the presence of other metal ions (1 equiv.) in water

to get a yellow solid, L. Yield: 78%, FT-IR (KBr, cm<sup>-1</sup>): 3616.0 (O–H), 3373.4 (O–H<sub>COOH</sub>), 3010.9 (C–H), 1639.8 (C=O<sub>COOH</sub>), 1622.2 (C=O<sub>chalcone</sub>), 1252.7 (C–O<sub>COOH</sub>), 1151.9 (C–O<sub>ether</sub>). <sup>1</sup>H-NMR (D<sub>2</sub>O, 500 MHz) & 8.32–8.31 (d, 1H), 8.25–8.22 (d, 1H), 7.92–7.90 (d, 2H), 7.89–7.87 (d, 1H), 7.63–7.58 (m, 2H), 7.48–7.40 (m, 2H), 7.19–7.17 (d, 1H), 6.81–6.79 (d, 1H), 6.70–6.67 (t, 1H), 4.67 (s, 2H). <sup>13</sup>C-NMR (D<sub>2</sub>O, 500 MHz) & 198.48, 176.78, 169.46, 155.59, 136.19, 136.04, 135.08, 132.22, 132.01, 131.85, 130.65, 128.92, 128.68, 127.63, 124.21, 123.56, 122.56, 117.21, 114.02, 113.76, 67.69. Anal. calcd for C<sub>21</sub>H<sub>16</sub>O<sub>5</sub> (348.35): C, 72.41; H, 4.63. Found: C, 74.82; H, 4.50%.

#### **Results and Discussion**

The experimental route towards the synthesis of receptor  $\mathbf{L}$  is shown in Scheme 1. The synthesized receptor  $\mathbf{L}$  was



Fig. 6 Job's plot for the interaction of L with  $Al^{3+}$  in water indicating 2:1 stoichiometry for  $L-Al^{3+}$  complex



Fig. 7 Benesi-Hildebrant plot based on fluorescence intensity of L with added  ${\rm Al}^{3+}$  concentrations in water

further analyzed by CHN elemental analysis, FT-IR, <sup>1</sup>Hand <sup>13</sup>C-NMR. The cation recognition ability of receptor L was investigated by adding various metal ions (Ag<sup>+</sup>, Al<sup>3+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Hg<sup>2+</sup>, K<sup>+</sup>, Mn<sup>2+</sup>, Na<sup>+</sup>,  $Ni^{2+}$ ,  $Pb^{2+}$  and  $Zn^{2+}$ ) in water to the solution of receptor L (in H<sub>2</sub>O).

# UV-vis Titration of Probe L Towards Al<sup>3+</sup>

The chemosensing behavior of L was initially studied by UV-vis analysis. As shown in Fig. 1, the free receptor L showed a maximum absorbance at 399 nm which corresponds to  $\pi \rightarrow \pi^*$  transition of the chalcone group. Addition of Al<sup>3+</sup> ions resulted in red shift to 416 nm due to the binding of aluminum with the receptor. The other cations Ag<sup>+</sup>, Ca<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Hg<sup>2+</sup>, K<sup>+</sup>, Mn<sup>2+</sup>, Na<sup>+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> with L did not show any color change. Therefore, Al<sup>3+</sup> could be easily identified among all other cations. As compared to Al<sup>3+</sup>, addition of Cu<sup>2+</sup> lead to a slight red shift which might be due to the minor interaction with receptor L. UV-vis titration experiments (Fig. 2) were further conducted in order to get more information on binding properties of receptor L towards Al<sup>3+</sup>. On treating L with increasing concentration of Al<sup>3+</sup> ions, the existence



8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.55.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 f1 (ppm)

Fig. 8 <sup>1</sup>H-NMR titration of L with Al<sup>3+</sup> in D<sub>2</sub>O

of an isosbestic point at 435 nm clearly suggests the conversion of receptor L1 into the  $L1-Al^{3+}$  complex.

# Fluorescent Study upon Binding Affinity of Probe L Toward Al<sup>3+</sup>

Studies of the fluorescent response behaviors of L towards different metal ions were then carried out in water (Fig. 3). The receptor  $\mathbf{L}$  alone exhibited negligible fluorescent emission upon excitation at 420 nm. However, after the addition of  $Al^{3+}$ , the receptor L showed a fluorescent emission at 575 nm. Although the fluorescence intensity for L after addition of  $Al^{3+}$  was not high enough, but sufficient fluorescence enhancement was observed for  $Al^{3+}$  only indicating that sensor L shows high selectivity towards Al<sup>3+</sup> over other metal ions. Further investigation of binding affinity of sensor L with Al<sup>3+</sup> was performed by fluorescent titration experiments (Fig. 4). The fluorescent intensity increases gradually when receptor L was titrated with  $Al^{3+}$ . This can be explained by the activation of chelation enhanced fluorescence (CHEF) as the complexation of L with  $Al^{3+}$  brings rigidity to the system [22]. High selectivity plays an important role in order to be a prominent chemosensor. The limit of detection was calculated based on fluorescence titration which is  $5.66 \times 10^{-8}$  M.

### **Competition with Other Cations**

To explore the specificity of **L** for the detection of  $Al^{3+}$ , competition experiment was performed. From the bar chart displayed in Fig. 5, no significant interference was observed in the presence of competing metal ions and the fluorescence enhancement induced by  $Al^{3+}$  was retained. Interestingly, all the metal ions including  $Cu^{2+}$  and  $Fe^{2+}$  which are known as fluorescence quenchers were unable to decrease the fluorescence intensity of the **L**-  $Al^{3+}$  complex. Therefore, there is no metal ion that able to alter the fluorescence response of **L** towards  $Al^{3+}$ .

### Job's Plot Measurements

The binding stoichiometry of chemosensor L with  $Al^{3+}$  was indicated by Job's plot method. The presence of a maximum absorbance at mole fraction 0.6 shows the formation of a hexa-coordinated complex of 2 molecules of L with 1 molecule of  $Al^{3+}$  ion. The binding mode was proposed as shown in Fig. 6. From the fluorescence titration results, the association constant for L-  $Al^{3+}$  in water was determined as  $0.21 \times 10^2 \text{ M}^{-2}$  by a Benesi-Hildebrant plot in Fig. 7. To further confirm the binding mode, the <sup>1</sup>H-NMR titration experiments (Fig. 8) of L with  $Al^{3+}$  in D<sub>2</sub>O was conducted. The absence of the protons of

carboxyl and hydroxyl groups was due to the hydrogen-deuterium exchange in  $D_2O$ . When the  $Al^{3+}$  was coordinated with sensor **L**, the shifting in resonance signals and peaks broadening occurred. Most of the aromatic protons shifted upfield or downfield to some extent due to the change in electron density of the aromatic rings. The oxymethylene protons were shifted upfield by 0.11 ppm from 4.67 to 4.56 ppm. These results suggested that the two oxygen atoms of carboxyl and hydroxyl groups and the oxygen atom of the oxymethylene group involved in coordination.

# Conclusions

In conclusion, a new 100% water soluble chalcone-based fluorescene turn-on chemosensor L has been designed and synthesized for the detection of  $Al^{3+}$  ions. Sensor L can be used as a selective fluorescence sensor for  $Al^{3+}$  due to its high binding affinity towards  $Al^{3+}$  which can be explained by the formation of a predominant interaction between L and  $Al^{3+}$  and high ionic potential of  $Al^{3+}$ . This completely water-soluble nature of a sensing material is rare which enables L to detect aluminium ion without any use of solvent.

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