



# A fluorescent sensor for selective recognition of Al<sup>3+</sup> based on naphthalimide Schiff-base in aqueous media



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## ABSTRACT

In this paper, a new chemosensor **S1**, *N*-*n*-butyl-4-[3,3'-((2-aminoethyl)azanediyl)bis(*N'*-(2-hydroxybenzylidene)propanehy-drazide)]-1,8-naphthalimide, has been designed and synthesized as an “turn-on” sensor for the detection of Al<sup>3+</sup> with a high sensitivity and an excellent selectivity. The sensor **S1** comprises 1,8-naphthalimide moiety as the fluorophore and Schiff base as the binding site. The structure of sensor **S1** has been established by single crystal X-ray structure and common spectroscopic methods. As expected, it exhibited high selectivity and sensitivity for detecting Al<sup>3+</sup> over other commonly coexistent metal ions. The 1:1 binding stoichiometry of the metal complex was established on the basis of combined fluorescence titration, Job's plot, UV–vis titration and <sup>1</sup>H NMR spectra analysis. In addition, the sensor **S1** can be applied to the quantification of Al<sup>3+</sup> with a linear range covering from 1.0 to 10.0 μM and a detection limit of 1.78 × 10<sup>-7</sup> M. Much more than this, the sensor **S1** was preliminarily applied for the determination of Al<sup>3+</sup> in water samples from the Yellow River and tap water with satisfying results.

## 1. Introduction

Aluminum is the most abundant metallic element in the earth and is found in its ionic form Al<sup>3+</sup> in most animal and plant tissues and in natural waters because of acidic rain and human activities [1,2]. Additionally, aluminum has been widely used in modern life, such as food packaging, cookware, drinking water supplies, antiperspirants, deodorants, bleached flour, antacids and the manufacturing of cars and computers. However, the increase of Al<sup>3+</sup> concentration in the environment is deadly for growing plants and excess amounts of aluminum can induce many health issues, such as bone and joint diseases, neuronal disorder, dementia, myopathy etc. [3–5]. According to WHO, the average daily human intake of Al<sup>3+</sup> of around 3–10 mg and the weekly tolerable dietary intake of 7 mg/kg body weight [6–9]. Therefore, the detection of Al<sup>3+</sup> is essential, because of its concentration levels in the biosphere and its direct impact on human health.

Compared with the traditional detection methods for the detection of Al<sup>3+</sup>, the fluorescent method is popular due to its operational simplicity, high sensitivity and selectivity, naked eye detection and potentially use in medicinal and environmental research [10–14]. Chemosensor has been regarded as an effective method for tracing relevant ions and shows its unique potential advantages [15–18]. However, compared to other transition metal, detection of Al<sup>3+</sup> has always been a

great challenge due to its poor coordination ability, strong hydration ability and lack of spectroscopic characteristics which limit its application prospect [19,20].

Previous reports based on quinoline [21], fluorescein [22], rhodamine [23,24], azobenzene [25], coumarin [26–28], 1,8-naphthalimide [29–31] and other fluorophores [32,33] indicate that structures of most fluorescent sensors for Al<sup>3+</sup> contain nitrogen and oxygen-rich coordination environments providing a hard base environment for the hard acid Al<sup>3+</sup> [34–37]. Here, we have designed and synthesized a novel Schiff base ligand **S1** as a chemosensor for Al<sup>3+</sup> that satisfies a prerequisite for the design of the efficient fluorescent chemosensor.

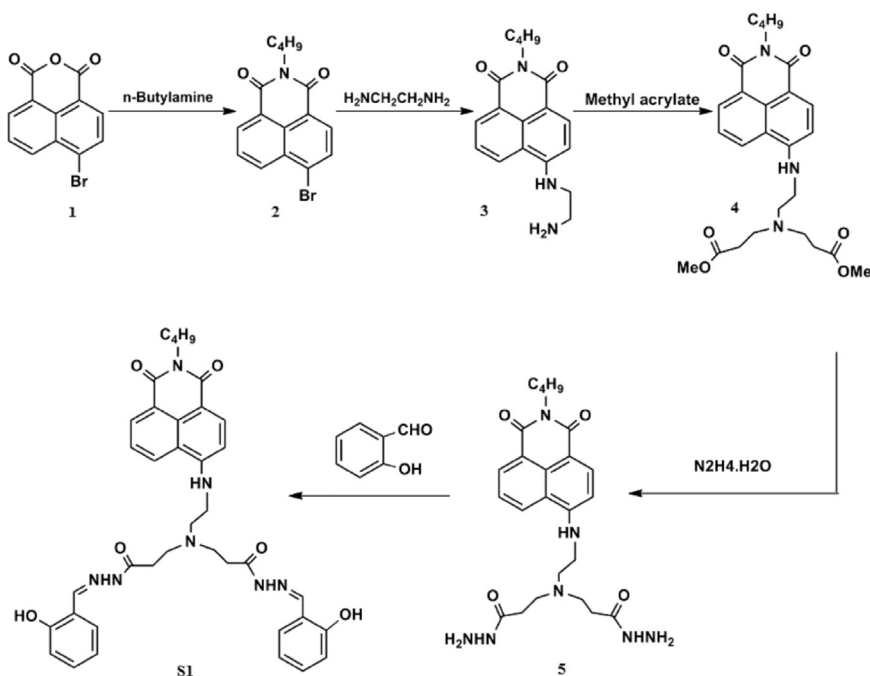
## 2. Experimental

### 2.1. Materials and measurements

All chemicals were obtained from commercial suppliers and used without further purification. *N*-butyl-4-*n*-butylamino-naphthalimide ( $\Phi_{ref} = 0.81$  in ethanol) was synthesized according to the literature [38]. Tris buffer (PH = 7.2) was prepared using double-distilled water. Stock solutions of various metal ions (1 mM) were prepared using nitrate salts in double-distilled water. pH adjustment was made with dilute hydrochloric acid and sodium hydroxide.

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Scheme 1. Synthesis of the sensor S1.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained with a Mercury plus 400 MHz NMR spectrometer with TMS as internal standard and  $\text{DMSO-}d_6$  as solvent. IR spectra were recorded from 4000 to  $400\text{ cm}^{-1}$  with a Nicolet FT-VERTEX 70 spectrometer using KBr pellets. UV spectra were measured with Lab-Tech Bluostar Plus UV Visible Spectrophotometer. Fluorescence spectra were measured with Lengguang Tech. F97 Pro Spectrofluorometer. Electrospray ionization mass spectra (ESI-MS) were obtained on a BRUKER micrOTOF-Q system. Thin-layer chromatography (TLC) involved silica gel 60F<sub>254</sub> plates (Merck KGaA). C, H and N elemental analyses were determined using a Carlo Erba 1106 elemental analyzer. The melting points of the compounds were determined on an XD-4 digital micro melting point apparatus.

## 2.2. Synthesis

The whole synthesis routes for P-1 are shown in Scheme 1. The intermediate compounds 2–4 were synthesized according to the literature [39–41].

### 2.2.1. Synthesis of compound 5

To a solution of 1,8-naphthalimide 4 (1 g, 2.07 mmol) in 20 mL of methanol was heated and dissolved, a solution of hydrazine hydrate (7.77 g, 124.2 mmol) in 5 mL of methanol was added dropwise at  $5^\circ\text{C}$  for a period of 30 min. The reaction mixture was stirred for 48 h at room temperature; the precipitate formed was collected by filtration, washed with methanol and dried. The compound 5 was obtained as yellow solid (0.92 g, 92%). Yield: 92%, m.p. 175–177  $^\circ\text{C}$ .  $R_f = 0.31$  ( $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH} = 5:1$ ). Anal. calcd. C 59.61; H 6.88; N 20.28%; found: C 59.73; H 6.66; N 20.36%.

### 2.2.2. Synthesis of S1

Compound 5 (0.2 g, 0.41 mmol) was dissolved in absolute ethanol (10 mL). An excess of salicylic aldehyde (0.2 g, 1.65 mmol) in 10 mL of ethanol was added dropwise for a period of 10 min. The reaction mixture was refluxed for 4 h. After the mixture was cooled to room temperature, the precipitate produced was filtered and washed with ethanol. Yield: 75.9%. m.p. 178–179  $^\circ\text{C}$ . IR (KBr;  $\nu/\text{cm}^{-1}$ ): 3200.2, 2957.6, 1684.5, 1665.4, 1650.2. UV–Visible (in methanol, nm): 255 ( $\epsilon = 33013$ ), 281 ( $\epsilon = 33585$ ), 388 ( $\epsilon = 14493$ ). Anal. calcd. C 65.98; H 5.97; N 14.17%; found: C 65.83; H 5.74; N 14.30%. M-S( $[\text{C}_{38}\text{H}_{41}\text{N}_7\text{O}_6]$

+ 1)  $m/z = 692.3436$ .  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz):  $\delta$  (ppm) = 11.59(d, 2H), 11.25(s, 2H); 11.11 (d, 2H); 10.05 (s, 1H); 8.50–8.56 (m, 1H,  $J = 24$  Hz); 8.31 (d, 1H,  $J = 8$  Hz); 8.22(s, 1H); 8.19 (d, 2H,  $J = 8$  Hz); 7.47–7.59(m, 2H,  $J = 48$  Hz); 7.26 (t, 2H,  $J = 20$  Hz); 7.17 (t, 1H,  $J = 12$  Hz); 6.77–6.84 (m, 2H,  $J = 28$  Hz); 6.74 (d, 1H,  $J = 12$  Hz); 3.97 (s, 2H); 3.48 (s, 2H); 2.82–2.93 (m, 8H); 2.47 (d, 2 H); 1.57 (d, 2H); 1.31–1.36 (m, 2H); 0.93 (t, 3H).  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ , 400 MHz):  $\delta$  (ppm) = 173.54, 168.14, 164.02, 163.24, 157.73, 156.77, 150.64, 147.25, 141.50, 134.41, 131.42, 131.19, 130.68, 129.92, 129.66, 128.34, 126.97, 124.58, 122.18, 120.40, 119.69, 119.41, 118.69, 116.60, 116.44, 108.45, 104.23, 51.65, 49.76, 49.57, 49.08, 41.24, 41.09, 39.34, 32.69, 30.39, 20.33, 14.18.

### 2.3. Single crystal X-ray structure analysis of S1

Sensor S1 was well characterized using physico-chemical and spectroscopic tools along with the detailed structural analysis by single crystal X-ray crystallography. Fig. 1 shows the ORTEP diagram of S1 with atomic numbering scheme. The crystallographic data and relevant refinement parameters are tabulated in Table 1 and the selected bond lengths and bond angles are listed in Table 2. The bond lengths of C(25)–O(4), (1.221 Å) and C(26)–N(7), (1.275 Å) are consistent with the double bond characters of the  $>\text{C}=\text{O}$  and  $>\text{C}=\text{N}$  bonds [42–46], respectively.

## 3. Results and discussion

Scheme 1 gives the full synthesis of S1 in five simple steps. The structure of S1 was confirmed by elemental analyses, IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and ESI–MS [47,48]. In order to verify whether S1 is the target product we want to design and synthesize, we performed a single crystal X-ray structure analysis. The C–N bond distances are 1.275(4) Å and 1.277(4) Å [ $\text{N}(7) = \text{C}(26)$ ,  $\text{N}(5) = \text{C}(22)$ ], which are consistent with a slight elongation of the C–N double bond, indicating the formation of Schiff base [42,49–52]. The bond angles of  $\text{C}(26)\text{--N}(7)\text{--N}(6) = 117.2(3)$ ,  $\text{C}(22)\text{--N}(5)\text{--N}(4) = 117.3(3)$ ,  $\text{N}(7)\text{--C}(26)\text{--C}(33) = 121.6(4)$  and  $\text{N}(5)\text{--C}(22)\text{--C}(27) = 121.4(3)$  are close to  $120^\circ$ . The sensing property of S1 in methanol–Tris (1:1 v/v) solution was confirmed by spectroscopic analysis. S1 exhibited good solubility in various organic and polar solvents including THF, DMF and DMSO;

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