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A Highly Selective and Sensitive Fluorescent Turn-on Probe for Al³⁺ Based on Naphthalimide Schiff Base

Hongping Peng¹ · Kesheng Shen¹ · Shanshan Mao¹ · Xinkui Shi¹ · Yuling Xu¹ · Stephen Opeyemi Aderinto¹ · Huilu Wu¹

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Abstract A simple and highly selective aluminium ion fluorescent probe (N-n-butyl-4-[3,3'-((2-aminoethyl)azanediyl)bis(N '-(2-hydroxy-3-methoxybenzylidene)-propanehydrazide)]-1,8naphthalimide) (P-1) employing 1,8-naphthalimide as the fluorophore group and Schiff base as the recognition group has been successfully synthesized and systemically characterized. The structure of probe P-1 has been established by single crystal X-ray. The photophysical properties of probe P-1 revealed that the values of the fluorescence quantum yield are higher in non-polar solvents than in polar solvents. Compared with the free P-1, the fluorescence intensity of P-1 shows a significant fluorescence enhancement in the presence of Al^{3+} without any significant interference from other cations and anions. In addition, from the UV-vis titration, fluorescence titration. Job's plot and ¹H NMR spectra analysis, we could primarily confirm that three important coordinative sites of P-1 for Al³⁺ were from imine nitrogen and tertiary amine nitrogen and formed a 1:1 complex. The fluorescence intensity for the (P-1) showed a good linearity with the concentration of Al^{3+} in the range of 3.0–10.0 μ M, with a detection limit of 8.65 × 10⁻⁸ M and a binding constant (K_b) of 4.95×10^4 M⁻¹. It is worthy of note that the probe P-1 was successfully applied in detection of Al³⁺ in Yellow River and tap water samples.

Keywords Fluorescent probe · 1,8-Naphthalimide · Aluminium ion · Schiff base

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Huilu Wu wuhuilu@163.com

Introduction

Aluminium is the most abundant metallic element (after oxygen and silicon) in the earth and is found in its ionic form Al^{3+} in most animal and plant tissues as well as in natural water owing to acidic rain and human activities [1, 2]. Nevertheless, aluminium has severe toxicity and is a non-essential element for biological systems; high concentration of aluminum ion not only hampers plant growth but has also been implicated in various neurodegenerative and neurological disorders, such as Alzheimer's disease, dialysis encephalopathy, and problems in bone and muscles, etc. [3–8]. For this reason, the development of effective methods for the detection of concentration levels of aluminium in the environment and some scientific fields is not only crucial but also timely [9–12].

In recent years, the design and synthesis of highly selective and sensitive fluorescent probes for biologically and environmentally important ionic species have attracted a great deal of attention [13–17]. Compared with the traditional detection methods (atomic absorption spectrometry, flame atomic absorption spectroscopy, inductively coupled plasma atomic emission spectrometry, mass spectrometry) [18–21], fluorescent probes with high sensitivity, selectivity, rapidity, inexpensive and easy operational procedure have currently attracted significant interests [22–26]. Along this line, many researchers have developed and reported highly sensitive Al³⁺ ion probes based on Schiff base [27, 28], quinolone [29], rhodamine [30, 31], 1,8-naphthalimide [32–34].

In general, as a hard acid, Al^{3+} prefers a matching hard base as a binding receptor, and this demands the structure of the probe had better can provide a nitrogen–oxygen-rich coordination environment [35–38]. The structure of probe **P-1** contains nitrogen–oxygen-rich coordination environments which provide enough binding sites for metal ions and satisfy a prerequisite for the design of the efficient fluorescent probe.

¹ School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou, Gansu 730070, People's Republic of China

Experimental

Materials and Measurements

All chemicals were obtained from commercial suppliers and used without further purification. Dilute hydrochloric acid or sodium hydroxide was used for adjusting the pH values. HEPES buffer (pH = 7.4) was prepared using double-distilled water. Stock solutions of various metal ions (1 mM) were prepared using the nitrate salt of each metal in double-distilled water. The intermediate compounds 2–4 were synthesized according to the literature [39–41].

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. ¹H and ¹³C NMR spectra were obtained with a Mercury plus 400 MHz NMR spectrometer with TMS as internal standard and DMSO- d_6 as solvent. IR spectra were recorded from 4000 to 400 cm⁻¹ with a Nicolet FT-VERTEX 70 spectrometer using KBr pellets. Electrospray ionization mass spectra (ESI-MS) were obtained on a BRUKER micrOTOF-Q system. UV spectra were measured with LabTech Bluestar Plus UV Visible Spectrophotometer. Fluorescence spectra were measured with Lengguang Tech. F97 Pro Spectrofluorometer. Thin-layer chromatography (TLC) was done using silica gel 60F₂₅₄ plates (Merck KGaA).

Synthesis of the Probe

Synthesis of Compound 2

A suspension of 4-bromo-1,8-naphthalic anhydride **1** (15 g, 54 mmol) and n-butylamine (7.90 g, 108 mmol) in 300 mL of ethanol was refluxed with stirring for 3 h. After the reaction was complete, the reaction mixture was cooled to room temperature and the solid phase was filtered off, washed with ethanol and dried to give pure 4-bromo-*N*-n-butyl-1,8-naphthalimide **2** as light yellow solid (17 g, 94.5%). M.p. 107–109 °C.

Synthesis of Compound 3

A solution of ethylenediamine (12.2 g, 201.67 mmol) was weighed and put in 100 mL of round-bottom flask and heated to a temperature of 65 °C. Thereafter, 4-bromo-*N*-n-butyl-1,8-naphthalimide 2 (1.0 g, 3.01 mmol) was added to the portion inside the 100 mL flask. The resulting mixture was heated to reflux for 3 h with stirring. After the reaction was complete, the reaction mixture was poured into the solution, and the precipitate formed was collected by filtration, washed with distilled water and dried. Recrystallized from toluene and dried to

afford 4-(2-aminoethyl) amino-*N*-n-butyl-1,8-naphthalimide **3** as yellow-orange solid (0.49 g, 52%). M.p. 129–132 °C.

Synthesis of Compound 4

To a solution of 4-(2-aminoethyl)amino-N-n-butyl-1,8naphthalimide **3** (2 g, 6.4 mmol) in 80 mL of methanol, a solution of methyl acrylate (5.5 g, 64 mmol) in 70 mL of methanol, was added dropwise for a period of 30 min. The reaction mixture was stirred for 2 days at room temperature and the excess of methyl acrylate was removed by vacuum filtration, and then dried under vacuum. The esterfunctionalized derivative **4** was obtained as orange oil (1.95 g, 62.7%).

Synthesis of Compound 5

A solution of 1,8-naphthalimide **4** (1 g, 2.07 mmol) in 20 ml of methanol was heated and dissolved. Then, a solution of hydrazine hydrate (7.77 g, 124.2 mmol) in 5 mL of methanol was added dropwise to the portion above at 5 °C for a period of 30 min. The reaction mixture was stirred for 48 h at room temperature, whereupon the precipitate formed was collected by filtration, washed with methanol and dried. Compound **5** was obtained as yellow solid (0.92 g, 92%). M.p. 175–177 °C. $R_f = 0.31$ (CH₂Cl₂/CH₃OH = 5:1). Anal. calcd. C 59.61; H 6.88; N 20.28%; found: C 59.63; H 6.86; N 20.26%.

Synthesis of P-1

Compound 5 (0.2 g, 0.41 mmol) was dissolved in absolute ethanol (10 mL). An excess of O-vanillin (0.25 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 and dried to give the final product (P-1) (0.29 g, 96.8%). M.p. 182–184 °C. IR (KBr; v/ cm⁻¹): 2956.8, 1681.7, 1644.0.UV-Visible (in DMF, nm): 286, 437. Anal. calcd. C 63.90; H 6.03; N 13.04%; found: C 63.93; H 6.07; N 13.01%. M-S($[C_{40}H_{45}N_7O_8] + 1$) m/z = 752.3663. ¹H NMR (DMSO- d_6 , 400 MHz): δ (ppm) = 11.56(d, 2H); 11.24(s, 2H); 10.84 (d, 2H); 9.38 (d, 1H); 8.52 (dd, 1H, J = 28 Hz; 8.31 (d, 1H, J = 8.0 Hz); 8.23(d, 1H, 12 Hz); 7.55–7.59 (m, 1H, J = 16 Hz); 7.46–7.50(m, 1H, J = 16 Hz); 7.13 (d, 1H, J = 8 Hz); 6.96 (d, 1H, J = 8 Hz); 6.89 (d, 1H, J = 8 Hz; 6.74 (dd, 1H, J = 24 Hz); 3.96–3.99 (m, 2H); 3.79 (s, 6H); 3.47 (s, 2H); 2.80-2.92(m, 8H), 2.45(d, 2H); 1.55-1.59 (m, 2H); 1.31–1.36 (m, 2H); 0.91–0.94 (m, 3H).¹³C NMR (DMSO- d_6 , 400 MHz): δ (ppm) = 173.61, 168.12, 164.04, 163.26, 150.62, 148.22, 147.50, 147.14, 146.32, 141.24, 134.39, 130.64, 129.64, 128.30, 124.60, 122.15, 121.37, 120.78, 120.43, 119.44, 119.07, 118.94, 118.29, 114.04, 113.05, 108.45, 104.23, 56.18, 51.66, 49.67, 49.11, 41,25,

41.07, 40.33, 39.50, 39.34, 32.72, 30.38, 20.32, 14.17. (Fig. S1-S3).

Single Crystal X-Ray Structure Analysis of P-1

The structure of **P-1** was confirmed by single crystal X-ray crystallography. The ORTEP diagram of **P-1** with atomic numbering scheme is shown in Fig. 1. Important crystallographic data and refinement parameters are given in Table 1, while the selected bond lengths and bond angles are listed in Table 2. The bond lengths of C(21)–O(3), (1.221 Å) and C(22)–N(5), (1.273 Å) are consistent with the double bond characters of the>C = O and >C = N– bonds [42], respectively.

Results and Discussion

The desired probe **P-1** was synthesized utilizing a five-step procedure as shown in Scheme 1 and characterized by elemental analyses, IR, ESI-MS, ¹H NMR and ¹³C NMR.



Fig. 1 Molecular structure of P-1 in the crystal with displacement ellipsoids at the 15% probability level; hydrogen atoms are omitted for clarity

 Table 1
 Crystallographic data for P-1

Empirical formula	$C_{40} H_{45} N_7 O_8$
Formula weight	751.83
Temp (K)	296 (2)
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	P 21/c
a (Å)	16.3239(15)
b (Å)	17.1595(17)
c (Å)	13.7265(13)
α(。)	90
β(,)	99.097(2)
γ(。)	90
V (Å ³)	3796.6(6)
Z	4
Dcalc (g/cm ³)	1.315
$\mu (mm^{-1})$	0.093
F(0 0 0)	1592.0
Crystal size (mm)	$0.40 \times 0.38 \times 0.30$
θ range for data collection ($_{\circ}$)	1.26 to 25.50
No. of reflections collected	20,057
No. of independent reflections (Rint)	0.0456
Number of data/restraints/parameters	7080/21/502
Goodness-of-fit on F ²	1.025
R1, wR2 $^{a,b}[(I>2\sigma(I))]$	0.0590, 0.1631
R1, wR2 ^{a,b} (all data)	0.1185, 0.2148
Largest difference in peak and hole (e.Å ⁻³)	0.337, -0.223

 ${}^{u}\mathbf{R}_{1} = \Sigma ||\mathbf{F}_{0}| - |\mathbf{F}_{c}||\Sigma ||\mathbf{F}_{0}|$

 ${}^{b}R_{2} = [\Sigma w(|F_{0}{}^{2}| - |F_{c}{}^{2}|)^{2} / \Sigma w|F_{0}{}^{2}|^{2}]^{1/2}$

The structure of **P-1** was further established by single crystal X-ray crystallography. **P-1** shows remarkable solubility in polar aprotic solvents such as DMF, DMSO and THF; solubility in ethanol, methanol and MeCN; and partially soluble in water.

Table 2 Selected bond lengths (Å) and angles (1) in the P-1

Bond length		Bond angle	Bond angle		
C(30)-N(3)	1.480(4)	C(18)-N(3)-C(19)	111.4(3)		
C(19)-N(3)	1.465(4)	C(18)-N(3)-C(30)	112.2(3)		
N(5)-N(4)	1.372(3)	C(33)-N(7)-N(6)	118.8(4)		
C(22)-N(5)	1.273(3)	C(22)-N(5)-N(4)	120.0(2)		
N(6)-N(7)	1.354(4)	N(4)-C(21)-C(20)	115.5(3)		
C(33)-N(7)	1.284(5)	N(6)-C(32)-C(31)	116.0(4)		
C(21)-O(3)	1.221(4)	N(5)-C(22)-C(23)	119.7(3)		
C(32)-O(6) C(18)-N(3)	1.237(4) 1.457(4)	N(7)-C(33)-C(34)	120.1(4)		



Scheme 1 Synthesis of the fluorescent probe P-1

Photophysical Characteristics of P-1

The photophysical properties of the substituted 1,8naphthalimides are known to depend mainly on the polarization of their chromophoric systems. We therefore investigate the photophysical characteristics of **P-1** in organic solvents with different polarities. Table 3 summarizes its photophysical characteristics, where λ_A is the absorption maxima, λ_F is the fluorescence maxima, ε is the extinction coefficient, $_A - _F$ is the Stokes shift, and Φ_F is the fluorescence quantum yield.

As depicted from the data in Table 3, **P-1** absorbs in the near UV region with maxima at $\lambda_A = 413-442$ nm; the absorption could be ascribed to π - π^* transitions of the naphthalene ring. The respective fluorescence maxima are at 505–530 nm. The molar extinction coefficient (ε) is at 7708–15350 M⁻¹ cm⁻¹, corresponding to a S₀ \rightarrow S₁ transition. The polarity of the organic solvents is of great importance for the photophysical properties of **P-1** under study, most especially for the quantum fluorescence yield and Stokes shift. The Stokes shift is an important parameter, which indicates

 Table 3
 Photophysical characteristics of P-1

Organic solution	$\lambda_A(nm)$	$\epsilon(L \text{ mol}^{-1} \text{ cm}^{-1})$	$\lambda_{F}(nm)$	(cm^{-1})	$\Phi_{\rm F}$
DMSO	442	11,858	527	3396	0.21
acetonitrile	433	8525	519	3668	0.34
DMF	436	14,753	522	3622	0.22
methyl alcohol	413	15,350	530	4773	0.02
Ethanol	441	8495	527	3547	0.25
Acetone	434	9968	514	3428	0.71
THF	433	11,828	505	3293	0.97
dichloromethane	429	7708	509	3664	0.91
Trichloromethane	429	9908	508	3094	0.98



Fig. 2 Fluorescence intensity of P-1 (5 μ M) in the absence (**n**) and presence (*red dots*) of Al³⁺ (2.0 equiv) in different pH buffer solution. $\lambda_{Ex} = 350 \text{ nm}$

the difference in the properties and structure of the fluorophore between the ground state S₀, and the first exited state S₁. The Stokes shift was calculated by the equation: ($_{\rm A} - _{\rm F}$) = (1/ $\lambda_{\rm A}$ - 1/ $\lambda_{\rm F}$) × 10⁷ cm⁻¹.

The obtained Stokes shift values are in the 3094– 4773 cm⁻¹ region. It is obvious that the value of the Stokes shift depends on the solvent media, with polar solvents yielding larger Stokes shift values than non-polar solvents owing to their more favored hydrogen bond formation or dipole-dipole interactions (Table 3) [43–47]. The ability of probe **P-1** to emit absorbed light energy is characterized quantitatively by the fluorescence quantum yield $\Phi_{\rm F}$. The fluorescence quantum yield has been calculated on the basis of the absorption and fluorescence spectra using N-butyl-4-n-butylaminonaphthalimide ($\Phi_{\rm F} = 0.81$ in ethanol) according to eq. [48, 49]: $\Phi_{\rm F}=\Phi_{\rm res}[(S_{\rm sample}/S_{\rm ref})(A_{\rm ref}/A_{\rm sample})(n_{\rm sample}/n_{\rm ref})^2].$

Herein, $\Phi_{\rm F}$ is the emission quantum yield of the sample, $\Phi_{\rm ref}$ is the emission quantum yield of the standard; A_{ref} and A_{sample} represent the absorbance of the standard and sample at the excited wavelength respectively; while S_{ref} and S_{sample} are the integrated emission band areas of the standard and sample respectively; and n_{ref} and n_{sample} are the solvent refractive index of the standard and sample respectively. From Table 3, it is clear that the values of $\Phi_{\rm F}$ for probe **P-1** tend to become higher with decreasing polarity of the solvents; this can be explained by the photoinduced electron transfer processes, which are accelerated in polar solvents [50].

Effect of pH

It is well-established that the performance of an electron donor/acceptor based fluorescence probe is highly dependent

Fig. 3 a UV–vis spectra of P-1 (10 μ M) in DMF-HEPES (ν/ν , 1:1) in the presence of different concentrations of Al³⁺(0, 1, 3, 6, 7, 9, 10, 12, 14, 15 μ M). **b** Absorbance at 375 nm as a function of the concentration of Al³⁺ ions



on the proton concentration; the optimization of pH on the efficiency of the probe is therefore very essential. The pH of the solution was suitably adjusted to values between 0 and 14 using 0.1 M HCl and/or NaOH. This pH range was studied so as to select the optimum conditions for the next experiments. As shown in Fig. 2, fluorescence pH titration shows that **P**-1– Al^{3+} exhibited a very stable fluorescence behavior in the pH range 5.0–8.0. Thus, the result of pH titration indicates that the probe **P**-1 could be used for the determination of Al^{3+} ions under neutral environmental (about 7) for the subsequent studies [51–53].

UV–Vis Titration

UV–vis titration experiments were carried out in DMF-HEPES (ν/ν , 1:1) at room temperature to understand the nature of binding of **P-1** (10 μ M) to Al³⁺. As shown in Fig. 3a, the absorption spectrum of the free **P-1** showed two absorption bands at 285 nm and 449 nm. Upon gradual addition of Al³⁺, a



Fig. 4 a Fluorescence spectra of P-1 (5 μ M) upon the addition of metal salts (50 μ M) of Na⁺, K⁺, Ca²⁺, Mg²⁺, Pb²⁺, Fe³⁺, Ni²⁺, Zn²⁺, Cu²⁺, Hg²⁺,Ag⁺ Co²⁺, Cr³⁺, Mn²⁺, Cd²⁺, and Al³⁺ in DMF-HEPES (1:1 ν/ν) solution (λ_{ex} : 350 nm). **b** Interference of other metal ions in a binary

new band appeared at 375 nm with increasing intensity and a clear isosbestic point at 301 nm was observed which clearly indicated the presence of a 1:1 stoichiometric complex in equilibrium with the receptor. In addition, the third band of **P-1** (at 447 nm) exhibited a red shift compared to the new band in the spectrum of [**P-1** + Al] (at 449 nm). The probable reason for these phenomena is the π - π transition. Figure 3b shows the plots of changes in 375 nm maxima as a function of increasing concentrations of Al³⁺. These phenomena indicated the formation of a new complex between ligand **P-1** and Al³⁺. Of course, all of these were further confirmed by fluorescence measurement.

Fluorescence titration of P-1 to Al³⁺

The selectivity of **P-1** was investigated upon the addition of several metal ions such as Na⁺, K⁺, Ca²⁺, Mg²⁺, Pb²⁺, Fe³⁺, Ni²⁺, Zn²⁺, Cu²⁺, Hg²⁺, Ag⁺, Co²⁺, Cr³⁺, Mn²⁺, Cd²⁺, and Al³⁺ in DMF-HEPES (ν/ν , 1:1) solution. As shown in



mixture solution of P-1 (5 μ M) + Al³⁺ (50 μ M) + Mⁿ⁺ (50 μ M), where Mⁿ⁺ = Na⁺, K⁺, Ca²⁺, Mg²⁺, Pb²⁺, Fe³⁺, Ni²⁺, Zn²⁺, Cu²⁺, Hg²⁺, Ag⁺, Co²⁺, Cr³⁺, Mn²⁺, Cd²⁺, and Al³⁺ in DMF-HEPES (1:1 ν/ν) solution (λ_{em} : 524 nm, λ_{ex} : 350 nm)



Wavelength(nm)

Fig. 4a, the free probe **P-1** displayed a weak fluorescence emission at 531 nm when it is excited at 350 nm. On addition of various metal ions to aqueous solution of **P-1**, there was no remarkable change in its fluorescence spectrum except in the case of Al^{3+} . Thus, the fluorescence intensity of **P-1** showed a large fluorescence enhancement along with a blue shift of 8 nm in the presence of Al^{3+} , which was enough for the selective detection of Al^{3+} .

To examine the affinity of **P-1** to AI^{3+} , competitive experiments in the presence of $AI^{3+}(50 \ \mu\text{M})$ mixed with other different metal ions were carried out in DMF-HEPES (*v*/v, 1:1) solution. As shown in Fig. 4b, relatively low interference was observed for the detection of AI^{3+} in the presence of other metal ions, which indicated that compound **P-1**– AI^{3+} system was hardly affected by these coexistent ions. Additionally, the effects of counter anions of the salts of various metal ions have been researched. The data of experiment showed P-1 + AI^{3+} probe complex with no such interference under neutral aqueous medium and the fluorescence intensity was insignificantly affected by counter anions of the salts of various metal ions (Fig. S4).

In order to get further insight into the binding interaction between P-1 with Al^{3+} , we performed fluorescence titrations of the probe in the solution containing different concentrations of

 Al^{3+} ions. As shown in Fig. 5a, the probe P-1 showed a weak fluorescence signal at 531 nm when it is excited at 350 nm. With the addition of increasing concentration of Al^{3+} , probe P-1 exhibited a strong, increasing fluorescence enhancement at 524 nm. We proposed this phenomenon could be attributed to the formation of 1:1 ligand–metal complex inhibiting photoinduced electron transfer (PET) process and chelationenhanced fluorescence process. The nonlinear curve fitting of the fluorescence titration also gives a 1:1 stoichiometric ratio between probe P-1 and Al^{3+} (Fig. 5b). The results obtained consistent with the above UV titration measurements results.

3

6

 $[Al^{3+}](M)$

ģ

12

Binding constant has been determined using the modified Benesi–Hildebrand eq. [54]: $(F_{max}-F_0)/(F_x-F_0) = 1 + (1/K)$ $(1/[M]^n)$, where F_{max} , F_0 , F_x are the maximum fluorescence intensity of **P-1** in presence of Al³⁺ at saturation, fluorescence intensity of free **P-1** and intensity of **P-1** in presence of Al³⁺ at any intermediate concentration respectively. The plot of $(F_{max}-F_0)/(F_x-F_0)$ versus 1/[M] (where n = 1) (Fig. 6a) yielded the binding constant value as $4.95 \times 10^4 \text{ M}^{-1}$ (R = 0.99) (Error estimated to be 10%) [55, 56].

Figure 6b also showed the good linearity between the emission at 529 nm and concentrations of Al^{3+} in the range from 3.0 to 10.0 μ M, indicating that **P-1** can detect quantitatively relevant concentrations of Al^{3+} .

Fig. 6 a Determination of association constant of P-1 for Al³⁺ in DMF/HEPES (1:1, ν/ν , HEPES buffer, 10 mM, pH 7.4). **b** Emission intensities of P-1 (10 μ M) as a function of [Al³⁺]: em: 524 nm, ex: 350 nm. The detection limit is 7.88 × 10⁻⁸ M





Fig. 7 Job's plot for the determination of stoichiometry of $[P-1-Al^{3+}]$ system in DMF/HEPES (1:1, ν/ν , HEPES buffer, 10 mM, pH 7.4)

The detection limit based on the following equation: $3\sigma/k$, the detection limit reached at 8.65×10^{-8} M (where σ is the standard deviation of blank measurements, and k is the slope of the intensity versus sample concentration [57, 58]), which is below the WHO acceptable limit (7.4 μ M) in drinking water [59, 60]. Therefore, it means that the probe **P-1** can be used as a selective fluorescent probe for the detection and recognition of Al³⁺ in environmental analysis and analytical chemistry.

With interest to further validate the stoichiometry of **P-1** and Al^{3+} , Job's method was employed using the emission changes at 528 nm as a function of the molar fraction of Al^{3+} . As shown in Fig. 7, maximum emission was observed when the molar fraction of Al^{3+} reached 0.5, which is indicative of 1:1 complexation between **P-1** and Al^{3+} . Such a trend is consistent with the previous UV–vis titration and fluorescence titration results.

¹H NMR Titration

To study the detailed combination mode of Al³⁺ ions and **P-1**, ¹H NMR spectra of **P-1** upon the addition of Al^{3+} to solution of the probe in DMSO- d_6 were recorded. As shown in Fig. 8, the characteristic peak of the hydroxyl proton is located at 11.56 ppm. Upon the addition of 1.0 equiv. of Al^{3+} ions, the proton signals of -OH at 11.56 ppm neither disappeared nor underwent any chemical displacement, which means that -OH groups may not be deprotonated and involved in coordination. The proton peak of -CH = N- at 11.24 ppm was downfield shifted to a singlet at 11.84 ppm, and the protons on the benzene ring of Schiff base at 3.79-7.57 ppm also experienced a downfield shift to 3.81-7.72 ppm. It indicates that the nitrogen atom of the Schiff base may participate in coordination to Al³⁺ ions. In addition, the protons of ethylenediamine group undergone significant chemical shift from 2.45-3.47 ppm to 2.82-3.90 ppm, which indicates that the nitrogen atom of ethylenediamine group is also involved in coordination [61, 62].

In order to further demonstrate the stoichiometry between **P-1** and Al^{3+} ion, MALDI-TOF mass spectrometry was conducted. Mass peaks at m/z 778.3542 (calcd 778.38) corresponding to **[P-1 + Al^{3+}]^+**, and 752.3663 (calcd 752.37) corresponded to **[P-1 + H]^+** were clearly observed when Al^{3+} was added to **P-1**, which provided evidence for the formation of a 1:1 complex (Fig. S5). Therefore we could primarily confirm that three important coordinative sites of **P-1** for Al^{3+} were from imine nitrogen and tertiary amine nitrogen and formed a 1:1 complex as shown in Scheme 2.

Reversibility Study

The reversibility of the recognition process of **P-1** was performed by adding a bonding agent, Na₂EDTA. The addition





of Na₂EDTA to a mixture of **P-1** and Al^{3+} resulted in diminution of the fluorescence intensity at 530 nm, indicating the regeneration of the free probe **P-1** and a reversible coordination between **P-1** and Al^{3+} (Fig. S6). Upon the addition of Al^{3+} , the fluorescence intensity of **P-1** showed significant fluorescence enhancement at 530 nm again. The reversible response towards Al^{3+} meant that the receptor **P-1** could be used as a selective fluorescent probe for detection of Al^{3+} in such fields of environmental analysis and **P-1** is a chemosensor not a chemodosimeter of Al^{3+} .

Application of P-1 for Al³⁺ Analysis in Water Samples

We examined the applicability of the proposed probe **P-1** in a practical sample for the determination of Al^{3+} in Yellow River and tap water samples. Yellow River water samples were obtained from the Yellow River (Lanzhou, China) while tap water samples were obtained from our school, Lanzhou Jiaotong University. The water was simply filtrated and showed that no Al^{3+} was present in them. All the water

 Table 4
 Recovery study of spiked determination of Al³⁺ in water samples

Sample	Al ³⁺ spiked (µM)	$\begin{array}{l} Al^{3+} recovered, mean^{a} \pm SD^{b} \\ (\mu M) \end{array}$	Recovery (%)
Yellow River water 1	5	5.03 ± 0.14	100.6
Yellow River water 2	7	7.13 ± 0.22	101.7
Yellow River water 3	9	8.97 ± 0.17	99.7
Tap water 1	5	4.95 ± 0.04	99
Tap water 2	7	7.08 ± 0.23	101.1
Tap water 3	9	9.31 ± 0.36	103.4

^a Mean of three determinations

^b SD standard deviation

samples were spiked with standard Al^{3+} solutions at different concentration levels and then analyzed with proposed probe. The results are shown in Table 4. One can see that the recovery study of spiked Al^{3+} determined by the **P-1**-based probe shows excellent results. The present probe seems useful for the determination of Al^{3+} in real samples.

Conclusion

In summary, we have successfully developed an efficient fluorescent Al^{3+} -probe (**P-1**) based on a naphthalimide derivative. **P-1** exhibited high selectivity and sensitivity for detecting Al^{3+} over other commonly coexistent metal ions in DMF-HEPES (ν/ν , 1:1) solution. The results of experiment studies further indicated that **P-1** and aluminum (III) ion formed a 1:1 complex that led to fluorescent enhancement. Above all, because of the low detection limit in aqueous solution, the probe could find potential applications to detect micromolar concentrations of Al^{3+} in both biological and environmental systems.

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References

- Wang Y, Hou LJ, Wu Y, Shi LL, Shang ZB, Jin WJ (2014) Alizarin Complexone as a highly selective ratiometric fluorescent probe for Al³⁺ detection in semi-aqueous solution. J Photoch Photobio A 281:40–46
- Qin J, Yang Z (2015) Selective fluorescent sensor for Al³⁺ using a novel quinoline derivative in aqueous solution. Synth Met 209: 570–576
- Perl DP, Gajdusek DC, Garruto RM, Yanagihara RT, Gibbs CJ (1982) Intraneuronal aluminium accumulation in amyotrophic

lateral sclerosis and parkinsonismdementia of Guam. Science 217: 1053–1055

- Perl DP, Brody AR (1980) Alzheimer's disease: X-ray spectrometric evidence of aluminum accumulation in neurofibrillary tanglebearing neurons. Science 208:297–299
- Tavakoli O, Yoshida H (2005) Effective recovery of harmful metal ions from squid wastes using subcritical and supercritical water treatments. Environ Sci Technol 39:2357–2363
- Weller DG, Gutierrez AJ, Rubio C, Revert C, Hardisson A (2010) Dietary intake of aluminum in a Spanish population (Canary islands). J Agric Food Chem 58:10452–10457
- 7. Valeur B, Leray I (2000) Design principles of fluorescent molecular sensors for cation recognition. Coord Chem Rev 205:3–40
- Fasman GD (1996) Aluminium and Alzheimer's disease: model studies. Coord Chem Rev 149:125–165
- Sen S, Mukherjee T, Chattopadhyay B, Moirangthem A, Basu A, Marek J, Chattopadhyay P (2012) A water soluble Al³⁺ selective colorimetric and fluorescent turn-on chemosensor and its application in living cell imaging. Analyst 137:3975–3981
- Shi XY, Wang H, Han TY, Feng X, Tong B, Shi JB, Zhi J, Dong YP (2012) A highly sensitive, single selective, real-time and turn-on fluorescent sensor for Al³⁺ detection in aqueous media. J Mater Chem 22:19296–19302
- Chen Y, Mi Y, Xie Q, Xiang J, Fan H, Luo X, Xia S (2013) A new off-on chemosensor for Al³⁺ and Cu²⁺ in two different systems based on a rhodamine B derivative. Anal Methods 5:4818–4823
- Choi YW, Park GJ, Na YJ, Jo HY, Lee SA, You GR, Kim C (2014) A single schiff base molecule for recognizing multiple metal ions: a fluorescence sensor for Zn(II) and Al(III) and colorimetric sensor for Fe(II) and Fe(III). Sensor Actuat B-Chem 194:343–352
- Maity D, Govindaraju T (2012) A differentially selective sensor with fluorescence turn-on response to Zn²⁺ and dual-mode ratiometric response to Al³⁺ in aqueous media. Chem Commun 48:1039–1041
- Ajayaghosh A, Carol P, Sreejith S (2005) A Ratiometric Fluorescence Probe for Selective Visual Sensing of Zn²⁺. J Am Chem Soc 127:14962–14963
- Zhang JF, Zhou Y, Yoon J, Kim JS (2011) Recent progress in fluorescent and colorimetric chemosensors for detection of precious metal ions (silver, gold and platinum ions). Chem Soc Rev 40: 3416–3429
- Maity D, Manna AK, Karthigeyan D, Kundu TK, Pati SK, Govindaraju T (2011) Visible–Near-Infrared and Fluorescent Copper Sensors Based on Julolidine Conjugates: Selective Detection and Fluorescence Imaging in Living Cells. Chem Eur J 17:11152–11161
- Sahana A, Banerjee A, Das S, Lohar S, Karak D, Sarkar B, Mukhopadhyay SK, Mukherjee AK, Das D (2011) A naphthalene-based Al³⁺ selective fluorescent sensor for living cell imaging. Org Biomol Chem 9:5523–5529
- Boevski IV, Daskalova N, Havezov I (2000) Determination of barium, chromium, cadmium, manganese, lead and zinc in atmospheric particulate matter by inductively coupled plasma atomic emission spectrometry (ICP-AES). Spectrochim Acta B 55:1643–1657
- Silvestre MD, Lagarda MJ, Farre R, Martinez-Costa C, Brines J (2000) Copper, iron and zinc determinations in human milk using FAAS with microwave digestion. Food Chem 68:95–99
- Weber G, Alt F, Messerschmidt J (1998) Characterization of lowmolecular-weight metal species in plant extracts by using HPLC with pulsed amperometric detection and cyclic voltammetry. J Fresenius Anal Chem 362:209–214
- Panayi AE, Spyrou NM, Iversen BS, White MA, Part P (2002) Determination of cadmium and zinc in Alzheimer's brain tissue using Inductively Coupled Plasma Mass Spectrometry. J Neurol Sci 195:1–10

- Kim S, Noh JY, Kim KY, Kim JH, Kang HK, Nam SW, Kim SH, Park S, Kim C, Kim J (2012) Salicylimine-Based Fluorescent Chemosensor for Aluminum Ions and Application to Bioimaging. Inorg Chem 51:3597–3602
- Lee JH, Kim HY, Kim SJ, Noh JY, Song EJ, Kim C, Kim JH (2013) Fluorescent dye containing phenol-pyridyl for selective detection of aluminum ions. Dyes Pigments 96:590–594
- 24. Han TY, Feng X, Tong B, Shi BJ, Chen L, Zhi JG, Dong YP (2012) A novel "turn-on" fluorescent chemosensor for the selective detection of Al³⁺based on aggregation-induced emission. Chem Commun 48:416–418
- Li C, Zhou Y, Li Y, Zou C, Kong X (2013) Efficient FRET-based colorimetric and ratiometric fluorescent chemosensor for Al³⁺ in living cells. Sensor Actuat B-Chem 186:360–366
- Liu YW, Chen CH, Wu AT (2012) A turn-on and reversible fluorescence sensor for Al³⁺ ion. Analyst 137:5201–5203
- Samanta S, Nath B, Baruah JB (2012) Hydrolytically stable Schiff base as highly sensitive aluminium sensor. Chem Commun 22:98– 100
- Liang CS, Bu WH, Li CL, Men GW, Deng MY, Jiangyao YK, Sun HC, Jiang SM (2015) A highly selective fluorescent sensor for Al³⁺ and the use of the resulting complex as a secondary sensor for PPi in aqueous media: its applicability in live cell imaging. Dalton Trans 44:11352–11359
- Park JS, Jeong S, Dho S, Lee M, Song C (2010) Colorimetric sensing of Cu²⁺ using a cyclodextrin–dye rotaxane. Dyes Pigments 87:49–54
- Zeng X, Dong L, Wu C, Mu L, Xue SF, Tao Z (2009) Highly sensitive chemosensor for Cu(II) and Hg(II) based on the tripodal rhodamine receptor. Sensor Actuat B-Chem 141:506–510
- Zhou Y, Wang F, Kim Y, Kim SJ, Yoon J (2009) Cu²⁺-Selective Ratiometric and "Off-On" Sensor Based on the Rhodamine Derivative Bearing Pyrene Group. Org Lett 11:4442–4445
- Xu Z, Xiao Y, Qian X, Cui J, Cui D (2005) Ratiometric and Selective Fluorescent Sensor for Cu^{II} Based on Internal Charge Transfer (ICT). Org Lett 7:889–892
- Huang J, Xu Y, Qian X (2009) A colorimetric sensor for Cu²⁺ in aqueous solution based on metal ion-induced deprotonation: deprotonation/protonation mediated by Cu²⁺-ligand interactions. Dalton Trans 1761–1766
- Zhang JF, Zhou Y, Yoon J, Kim Y, Kim SJ, Kim JS (2010) Naphthalimide Modified Rhodamine Derivative: Ratiometric and Selective Fluorescent Sensor for Cu²⁺ Based on Two Different Approaches. Org Lett 12:3852–3855
- Hsieh WH, Wan CF, Liao DJ, Wu AT (2012) A turn-on Schiff base fluorescence sensor for zinc ion. Tetrahedron Lett 53:5848–5851
- Jia TJ, Cao W, Zheng XJ, Jin LP (2013) A turn-on chemosensor based on naphthol-triazole for Al(III) and its application in bioimaging. Tetrahedron Lett 54:3471–3474
- Tiwari K, Mishra M, Singh VP (2013) A highly sensitive and selective fluorescent sensor for Al³⁺ ions based onthiophene-2-carboxylic acid hydrazide Schiff base. RSC Adv 3:12124–12132
- 38. Guha S, Lohar S, Sahana A, Banerjee A, Safin DA, Babashkina MG, Mitoraj MP, Bolte M, Garcia Y, Mukhopadhyaye SK, Das D (2013) A coumarin-based "turn-on" fluorescent sensor for the determination of Al³⁺: single crystal X-ray structure and cell staining properties. Dalton Trans 42:10198–10207
- Bojinov VB, Georgiev NI, Nikolov PS (2008) Synthesis and photophysical properties of fluorescence sensing ester- and amidoamine-functionalized 1,8-naphthalimides. J Photoch Photobio A 193:129–138
- Leng B, Zou L, Jiang J, Tian H (2009) Colorimetric detection of mercuric ion (Hg²⁺) in aqueous media using chemodosimeter-functionalized gold nanoparticles. Sensor Actuat B-Chem 140:162–169

- Liu T, Zhang X, Qiao Q, Zou C, Feng L, Cui J, Xu Z (2013) A twophoton fluorescent probe for imaging hydrogen sulfide in living cells. Dyes Pigments 99:537–542
- 42. Singh DP, Raghuvanshi DS, Singh KN, Singh VP (2013) Synthesis, characterization and catalytic application of some novel binuclear transition metal complexes of bis-(2-acetylthiophene) oxaloyldihydrazone for C-N bond formation. J Mol Catal A Chem 379:21–29
- 43. Wang F, Xu YL, Aderinto SO, Peng HP, Zhang H, Wu HL (2017) A new highly effective fluorescent probe for Al³⁺ ions and its application in practical samples. J Photoch Photobio A 332:273–282
- 44. Xu YL, Aderinto SO, Wu HL, Peng HP, Zhang H, Zhang JW, Fan XY (2017) A highly selective fluorescent chemosensor based on naphthalimide and Schiff base units for Cu²⁺ detection in aqueous medium. Z Naturforsch B 72:35–41
- 45. Wu HL, Peng HP, Wang F, Zhang H, Chen CG, Zhang JW, Yang ZH (2017) Two 1,8- naphthalimides as proton-receptor fluorescent sensors for detecting pH. J Appl Spectrosc 83:931–937
- 46. Aderinto SO, Zhang H, Wu HL, Chen CY, Zhang JW, Peng HP, Yang ZH, Wang F (2017a) Synthesis and studies of two proton– receptor fluorescent probes based on 1,8-naphthalimide. Color Technol 133:40–49
- Wu HL, Chen CY, Zhang H, Peng HP, Wang F, Yang ZH, Zhang JW (2016) Two 1,8-naphthalimide-based proton-receptor fluorescent probes for pH determination. Chem Pap 70:685–694
- Chovelon JM, Grabchev I (2007) A novel fluorescent sensor for metal cations and protons based of bis-1,8-naphthalimide. Spectrochim Acta A 67:87–91
- Aderinto SO, Xu YL, Peng HP, Wang F, Wu HL, Fan XY (2017b) A highly Selective Fluorescent Sensor for Monitoring Cu²⁺ Ion: Synthesis, Characterization and Photophysical Properties. J Fluoresc 27:79–87
- Grabchev I, Qian X, Xiao Y, Zhang R (2002) Novel heterogeneous PET fluorescent sensors selective for transition metal ions or protons: polymers regularly labelled with naphthalimide. New J Chem 26:920
- Wee SS, Ng YH, Ng SM (2013) Synthesis of fluorescent carbon dots via simple acid hydrolysis of bovine serum albumin and its potential as sensitive sensing probe for lead (II) ions. Talanta 116: 71–76

- 52. Dong WK, Li XL, Wang L, Zhang Y, Ding YJ (2016) A new application of Salamo-type bisoximes: As a relay–sensor for Zn²⁺/Cu²⁺ and its novel complexes for successive sensing of H+/ OH–. Sensor Actuat B-Chem 229:370–378
- Dong WK, Akogun SF, Zhang Y, Sun YX, Dong XY (2017) A reversible "turn-on" fluorescent sensor for selective detection of Zn²⁺. Sensor Actuat B-Chem 238:723–734
- 54. Benesi HA, Hildebrand JH (1949) A Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons. J Am Chem Soc 71:2703–2707
- Thordarson P (2011) Determining association constants from titration experiments in supramolecular chemistry. Chem Soc Rev 40: 1305–1323
- 56. Forgues SF, LeBris MT, Gutte JP, Valuer B (1988) Ion-responsive fluorescent compounds. 1. Effect of cation binding on photophysical properties of benzoxazinone derivative linked to monoaza-15-crown-5. J Phys Chem 92:6233–6237
- 57. Lohani CR, Kim JM, Chung SY, Yoon J, Lee KH (2010) Colorimetric and fluorescent sensing of pyrophosphate in 100% aqueous solution by a system comprised of rhodamine B compound and Al³⁺ complex. Analyst 135:2079–2084
- Wu HL, Wang CP, Zhang JW, Zhang YH, Chen CY, Yang ZH, Fan XY (2015) 1,8-Naphthalimide derivative-based turn-off fluorescent probe for the detection of picrate in organic aqueous media. Z Naturforsch B 70:863–869
- 59. World Health Organization (2004) Guidelines for drinking water quality, third edn. World Health Organization, Geneva, p 301
- Jisha B, Resmi MR, Maya RJ, Varma RL (2013) Colorimetric detection of Al(III) ions based on triethylene glycol appended 8propyloxy quinoline ester. Tetrahedron Lett 54:4232–4236
- Sun Y, Hu JH, Qi J, Li JB (2016) A highly selective colorimetric and "turn-on" fluorimetric chemosensor for detecting CN⁻ based on unsymmetrical azine derivatives in aqueous media. Spectrochim Acta A 167:101–105
- 62. Hu JH, Sun Y, Qi J, Li Q, Wei TB (2017) A new unsymmetrical azine derivative based on coumarin group asdual-modal sensor for CN⁻ and fluorescent "OFF–ON" for Zn²⁺. Spectrochim Acta A 175:125–133