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A significant fluorescent "turn-on" chemosensor for Al³⁺ detection and application in real sample, logic gate and bioimaging

Shuang Zeng ^{a, 1}, Shi-Jie Li ^{b, 1}, Ting-Ting Liu ^a, Xue-Jiao Sun ^a, Zhi-Yong Xing ^{a, *}

^a Department of Applied Chemistry, College of Science, Northeast Agricultural University, Harbin

150030, PR China. Tel: +86 451 5519 1810, Fax: +86 451 5519 0317

^b College of Life Science, Northeast Agricultural University, Harbin 150030, PR China

* Corresponding authors

E-mail addresses: zyxing@neau.edu.cn

¹ These authors contributed equally to this work and should be considered co-first authors.

Abstract: A novel naphthaldehyde–benzothiazole conjugated sensor **Z** was successfully synthesized and characterized. Chemosensor **Z** showed highly selective and sensitive for the detection of Al^{3+} in DMF/H₂O (v/v, 4/6) attributed to the combined contribution of excited-state intramolecular proton transfer (ESIPT), C=N isomerization and chelation enhanced fluorescence (CHEF). The binding ratio of **Z** to Al^{3+} was 1:1 which was further determined by job's plot and HRMS. The detection limit was calculated 4.56×10^{-7} M and 5.09×10^{-8} M in corresponding Al^{3+} concentration range of 0-22 µM and 24-44 µM, respectively. Furthermore, **Z** was successfully practiced for the Al^{3+} quantitative analysis in real water samples, logic gate construction and bioimaging in human stromal cells (HSC).

Key Words: fluorescent; turn on; Al³⁺; cell imaging

1. Introduction

As we all known, metal ions play an important role in environmental and biological systems. As the third richest element in nature, the excessive accumulate of Al³⁺ in the human body can induce various diseases mainly exhibited in Alzheimer's disease, anemia, Parkinson's disease, hemochromatosis and amyotrophic lateral sclerosis [1-6]. Moreover, high concentrations of aluminum ions also have serious toxic effects on the ecosystem such as inhabitation of the growth of plant roots, damaging the living condition of freshwater fishes [7-9]. Undoubtedly, the monitoring of aluminum ions in environmental and biological systems is of important significance.

In recent years, compared with traditional analytical techniques, fluorescence based technology has gradually become a frontrunners in the field of analytical detection due to its merits including simple process of detecting samples, low cost, naked-eye recognition, high sensitivity and specificity [10-14]. Furthermore, fluorescent probes based on various derivatives such as rhodamine [15-19], naphthalene [20-22], benzothiazole [23-25] and naphthalimide [26-30] had been reported for the detection of metal ions. Although many fluorescent probes for identifying Al³⁺ were reported so far [31-39], due to these shortcomings of Al³⁺ such as strong hydration ability resulted in poor coordination and lack of spectroscopic characteristics, it is still more difficult in the detection of Al³⁺ than other metal ions [40, 41]. Therefore, designing a selective and sensitive fluorescent probe for Al³⁺ in aqueous media is still full of challenging.

2-(2'-Hydroxyphenyl) benzothiazole (HBT) is the most well-known ESIPT fluorophore, fluorescent probes are often designed using a strategy in which oxygen atoms on a phenolic hydroxyl coordinates with a metal ion to inhibit excited-state intramolecular proton transfer (ESIPT) to alter the fluorescent properties [42-44]. Especially, thiazole ring including N atom can

supply a hard base unit for the recognition the hard acid Al^{3+} [26, 38]. Moreover, 2-hydroxy-1naphthaldehyde is also an excellent building block which is usually to construct fluorescent schiffbase probe through condension of 2-hydroxy-1-naphthaldehyde (HNA) with various primary amines to achieve the detection of special analyte using the ESIPT mechanism [45, 46]. Herein, we designed and synthesized a novel fluorescent probe **Z**, which contained the deprotonation phenolic hydroxyl of HBT to provide more binding sites and the ESIPT-based fluorophore unit through the condension of hydrazine hydrate and 2-hydroxy-1-naphthaldehyde (Scheme 1). The result showed that sensor **Z** was highly specific for Al^{3+} ion through significant fluorescent "turnon" response in aqueous DMF (*N*, *N*-dimethylformamide) medium. The optical properties of sensor **Z** for Al^{3+} were investigated using fluorescence response, and its application in real sample detection, logic gate construction and cell imaging were also reported.



2. Experimental

2.1. Materials and methods

All chemicals were analytical or spectroscopic grade which were obtained commercially and used without further purification. All metal ion solutions were prepared by its perchlorate or

nitrate salts.

Melting point was recorded on a Beijing XT4-100X microscopic melting point apparatus. FT-IR spectra were measured by SEWERE ALPHA-T (Bruker Company, DEU). ¹H NMR spectra and ¹³C NMR spectra were recorded on a Bruck AV-600 spectrometer using DMSO-d₆ as the solvent. The model of PHS-3C meter (Shanghai, China) was used for the pH measurement. Absorption spectra were recorded on a Shimadzu UV-2700 UV–vis spectrometer at 25 °C . Fluorescence measurements were measured on a Perkin Elmer LS55 fluorescence spectrometer. Mass spectra were determined on a Waters Xevo UPLC/G2-SQ Tof MS spectrometer.

The detection limit (LOD) of sensor Z for Al^{3+} was calculated based on $3\sigma/k$, where σ is the standard deviation of the blank measurements, and k is the slope of the intensity ratio versus sample concentration plot

The quantum yield was calculated according to the equation: $\Phi_{F(X)} = \Phi_{F(S)} (A_S F_X/A_X F_S)$ $(n_X/n_S)^2$. Where A is the absorbance at the excitation wavelength, F is the area under the corrected emission curve, and n is the refractive index of the solvents used. Subscripts S and X refer to the standard and to the unknown, respectively. The fluorescence quantum yield was determined by using quinine sulfate ($\Phi_{F(S)} = 0.55$) as reference with the literature method [47].

The Z-Al³⁺ complex was obtained as yellow solid by refluxing the solution of ethanol containing probe Z and Al(NO₃)₃·9H₂O, and the FT-IR spectrum of Z and Z-Al³⁺ complex were measured on a Perkin-Elmer IR spectrophotometer.

2.2. Synthesis

Compounds 1-3 were synthesized according to the previously reported method [39, 48].

2.2.1. Synthesis of compound 2

The compound **1** (400 mg, 1.64 mmol) and K₂CO₃ (456 mg, 3.32 mmol) were added into acetonitrile (14 mL). Then the ethyl bromoacetate (184 μ L, 1.64 mmol) was added dropwise to the mixture and refluxed for 1 h. After the solvent was removed under vacuum, the compound **2** was obtained by column chromatography on silica gel using ethyl acetate/dichloromethane (v/v, 1/50). Yield: 404 mg, 75%. ¹H NMR (600 MHz, DMSO) (Fig. S1) δ (ppm) 8.28 (s, 1H), 8.12 (d, J = 7.8 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 5.09 (s, 2H), 4.21 (q, J = 7.2 Hz, 2H), 2.37 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H).

2.2.2. Synthesis of compound 3

To a solution of compound 2 (200 mg, 0.62 mmol) in ethanol (20 mL) was added hydrazine hydrate (2 mL, 41.23 mmol) and the mixture was refluxed for 2 h under stirring. After the reaction was completed, the precipitate was filtered. Finally,washed it 5 times with ethanol to afford compound 3. Yield: 166 mg, 86%. ¹H NMR (600 MHz, DMSO) (Fig. S2) δ (ppm) 9.57 (s, 1H), 8.17 (d, J = 1.7 Hz, 1H), 8.12 (d, J = 7.8 Hz, 2H), 8.10 (d, J = 7.8 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 4.76 (s, 2H), 4.42 (s, 2H), 2.37 (s, 3H).

2.2.3. Synthesis of probe Z

The compound **3** (111 mg, 0.35 mmol) and 2-hydroxy-1-naphthaldehyde (61 mg, 0.35 mmol) were refluxed in ethanol (16 mL) for 5 h and the progress of reaction was monitored by TLC. After cooling to 25 °C, the probe **Z** as white solid was obtained by filtered and washed with ethanol. Yield: 156 mg, 94%. *E*-configuration: ¹H NMR (600 MHz, DMSO) (Fig. S3) δ (ppm) 12.43 (s, 1H, 67%), 12.05 (s, 1H, 67%), 9.33 (s, 1H, 67%), 8.29 (s, 1H), 8.28 (d, J = 10.2 Hz, 1H,

67%), 8.15 (d, J = 7.8 Hz, 1H, 67%), 8.08 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 9.0 Hz, 1H, 67%), 7.89 (d, J = 8.4 Hz, 1H), 7.57 (t, J = 8.4 Hz, 1H), 7.55 (t, J = 8.4 Hz, 1H, 67%), 7.44 (t, J = 7.8 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.35 (d, J = 7.2 Hz, 1H, 67%), 7.23 (d, J = 9.0 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H, 67%), 5.05 (s, 2H, 67%), 2.39 (d, J = 5.4 Hz, 3H). ¹³C NMR (151 MHz, DMSO) (Fig. 84) δ (ppm) 164.05, 162.84, 158.40, 154.37, 152.10, 147.58, 136.04, 133.43, 133.34, 132.04, 131.55, 129.47, 129.40, 128.32, 128.25, 126.75, 125.46, 124.06, 122.92, 122.33, 122.09, 121.60, 119.25, 114.61, 109.01, 67.94, 20.58.

Z-configuration: ¹H NMR (600 MHz, DMSO) (Fig. S3) δ (ppm) 11.70 (s, 1H, 33%), 10.74 (s, 1H, 33%), 8.91 (s, 1H, 33%), 8.76 (d, J = 9.0 Hz, 1H, 33%), 8.29 (s, 1H), 8.08 (d, J = 7.8 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H, 33%), 7.89 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H, 33%), 7.57 (t, J = 8.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H, 33%), 7.44 (t, J = 7.8 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.38 (t, J = 8.4 Hz, 1H, 33%), 7.38 (d, J = 8.4 Hz, 1H, 33%), 7.23 (d, J = 9.0 Hz, 1H), 5.48 (s, 1H, 33%), 2.39 (d, J = 5.0 Hz, 3H). ¹³C NMR (151 MHz, DMSO) (Fig. S4) δ (ppm) 168.29, 163.00, 157.40, 154.65, 152.03, 143.76, 136.14, 133.14, 133.01, 131.72, 130.67, 129.26, 129.16, 128.62, 128.37, 126.63, 125.30, 123.90, 122.84, 122.33, 122.18, 121.56, 118.59, 113.84, 110.68, 66.30, 20.58.

HRMS m/z (TOF MS ES⁺) (Fig. S5): calcd for $C_{27}H_{22}N_3O_3S$: 468.1382 [M+H]⁺, found:468.1383.

2.3. Cell Culture and Staining

The fibroblast cell line, human stromal cell line (HSC), was purchased from ATCC (CRL-4003). For maintained HSC, cells were routinely cultured in mixture medium (DMEM: F-12=1:1), which was supplemented with 10% heat-inactivated FBS, 100 U/mL penicillin, 100 µg/mL

streptomycin, and 1 mM sodiumpyruvate at 37 °C, 5% CO₂. 48-hour after plant HSC into 6-well plates with sterile cover glass at concentration of 10⁵ cells/well, the media would be changed to which without FBS or antibiotic. After the cells were incubated 2 hours with different amounts of Al^{3+} (0, 10 and 50 μ M), washed them 3 times with D-Hank's to remove excess Al^{3+} on the cell surface. Before stained with Z, cells were fixed by using a standard paraformaldehyde fixation protocol and were rinsed with DMD/H₂O (5/5, v/v). And then cells were stained by incubating for 2 hours with Z (1 × 10⁻⁴ M). Lastly, the cover glass were mounted over slide glass with anti-fluorescence quenching agent and imaged by fluorescence microscope.

3. Results and Discussion

3.1. Fluorescence studies of Z with different metal ions

Fluorescence selectivity experiments were conducted to investigate the fluorescence responses of **Z** in the presence of diverse metal ions. As shown in Fig. 1a, the probe **Z** (10 μ M) itself almost showed no significant fluorescent emission with low quantum yield ($\Phi_{F(s)} = 0.05$) in the solution of DMF/H₂O (4/6, v/v). This phenomenon might due to the probe **Z** exchanged in the keto-enol form which caused the occurrence of ESIPT mechanism (Scheme 1), and the C=N isomerization of **Z** also could greatly quench the fluorescence at the excited state [49, 50]. Upon the addition of tested metal ions into the solution of probe **Z**, the fluorescence spectra showed that only the addition of aluminum ions caused a remarkable fluorescence enhancement at 465 nm with higher quantum yield ($\Phi_{F(s)} = 0.82$) after excitation at 390 nm (Fig. 1a). At the same time, the easily visual detection of aluminum ions was also achieved under UV light of 365 nm, which mainly manifested in a significant color changing from colorless to bright blue (Fig. 1a Inset). This result could attribute to the coordination of **Z** with Al³⁺ through chelation–enhanced

fluorescence (CHEF) mechanism, which resulted in the inhibition of the ESIPT processes and



C=N isomerization and further increasing the rigidity of the molecular assembly [51, 52].

Fig. 1. (a) Fluorescence spectra of Z (10 μ M) upon addition of various metal ions (5 equiv.) in DMF/H₂O (4/6, v/v). Inset: The color change of Z after the addition of Al³⁺ under UV light of 365 nm; (b) Fluorescence spectral changes of Z (10 μ M) added with different concentrations of Al³⁺ in DMF/H₂O (4/6, v/v). Inset: The fluorescence intensity of Z at 440nm versus the concentrations of Al³⁺.

The excellent fluorescence selectivity of probe **Z** for AI^{3+} promoted us to further delve into the fluorescence titration experiments (Fig. 1b). The result showed that the fluorescence intensity of the probe **Z** gradually increased with the addition of AI^{3+} (0-5 equiv.) and almost no change when the addition of AI^{3+} was up to 5 equivalents. Interestingly, as shown in Fig. 2, the fluorescence intensity of **Z** has a good linear relationship with the concentration of AI^{3+} added in the concentration range of 0-22 μ M and 24-44 μ M, respectively. The detection limits (calculated using 3 σ /k, where σ is the standard deviation of the blank measurements, and k is the slope of the intensity ratio versus sample concentration plot, reported by previous report [42]) were calculated to be 4.56×10^{-7} M for the concentration ranging from 0 μ M to 22 μ M and 5.09×10^{-8} M for the concentration ranges of AI^{3+} indicated that the probe had the potential to quantitatively detect aluminum ions in different ranges. In addition, probe **Z** showed higher sensitivity to AI^{3+} according to the comparative analysis between **Z** and some previously reported sensors which

were summarized in Table 1.



Fig. 2. The fluorescence intensity of probe Z at 465 nm as a function of Al^{3+} concentration range (a) 0-22 μ M and (b) 24-44 μ M.

Ref.	Detection Medium	LOD	Binding Constants	Recovery	Application
[31]	Ethanol/H ₂ O (95/5, v/v)	5.2×10 ⁻⁸ M	1.74×10 ⁶ M ⁻¹	NR	test strips
[32]	DMSO/H ₂ O (1/1, v/v)	2.9×10⁻6 M	1.5×10 ³ M ⁻¹	EDTA ²⁻	cell imaging
[33]	Ethanol/H ₂ O (1:1, v/v)	3.7×10 ⁻⁷ M	7.62×10 ⁶ M ⁻¹	EDTA ²⁻	cell imaging
[35]	Ethanol/H ₂ O (7:3, v/v) HEPES pH = 7.4	1.0×10-7 M	1.83×10 ⁵ M ^{-1/2}	NR	cell imaging
[36]	Tris-HCl buffer pH=7.2	3.2×10 ⁻⁷ M	NR	EDTA ²⁻	real water samples
[37]	aqueous solution	4.1×10 ⁻⁹ M	4.67×10 ⁴ M ⁻¹	S ²⁻	cell imaging
[39]	DMF/H ₂ O (1/9, v/v)	1.9×10 ⁻⁷ M	1.04×10 ⁴ M ⁻¹	EDTA ²⁻	cell imaging real water samples
[41]	Ethanol	2.2×10 ⁻⁷ M	1.89×10 ⁴ M ⁻¹	EDTA ²⁻	None
[43]	HEPES buffer pH=7.4	2.2×10 ⁻⁶ M	NR	EDTA ²⁻	test strips cell imaging
This work	DMF/H ₂ O (4:6, v/v)	5.09×10 ⁻⁸ M	2.35×10 ⁴ M ⁻¹	EDTA ²⁻	cell imaging real water samples

Table 1 Comparison of different properties of Z with recently reported probes used as fluorescent sensor for Al³⁺.

LOD: The limit of detection; NR: Not reported in the corresponding paper.

To further investigate the selectivity of probe Z to Al^{3+} , the competitive experiment was conducted by mixing the DMF/H₂O solution containing probe Z (10 μ M) and Al^{3+} (50 μ M) with other tested metal ions (Fig. 3). As for the fluorescence intensity of Z-Al³⁺ system, it almost kept a

constant by the addition of large amounts of other metal ions except Cr^{3+} which had an ignorable effect on the intensity of chemosensor Z, indicating that the probe Z could quantitatively detect Al³⁺ in the presence of these tested metal ions.



Fig. 3. Fluorescence intensity of Z (10 μ M) at 465 nm upon addition of various metal ions (50 μ M) in the presence Al³⁺ (50 μ M) in DMF/H₂O (4/6, v/v), (λ_{ex} = 390nm).

3.2. Investigation of Binding sites and sensing mechanism

In order to better explicit the sensing mechanism of probe **Z** to Al^{3+} , the binding mode between the probe **Z** and Al^{3+} was first verified by Job's method and ESI-MS analysis. As shown in Fig. 4, when the mole fraction of Al^{3+} was reached 0.5, the fluorescence intensity of the complex **Z**- Al^{3+} reached the maximum, showing the 1:1 binding stoichiometry between probe **Z** and Al^{3+} . Furthermore, the ESI mass spectrum showed a peak at m/z 565.1497, designate to [**Z**- $2H^+ + Al^{3+} + DMF$] (calcd. m/z 565.1490) in the ESI mass spectrum (Fig. 5). The ESI-MS analysis matched with the Job's plot analysis and further confirmed the 1:1 binding mode of Z with Al^{3+} . Based on the Benesi–Hildebrand plot, the association constant was calculated as 1.45×10^4 M⁻¹ and 2.35×10^4 M⁻¹ for the concentration range 0-22 and 24-44 μ M, respectively (Figs. S6 and S7).

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900 700 1100 1200 1300 Fig. 5. ESI–MS spectrum of the DMF solution containing Z (50 μ M) and Al³⁺ (5 equiv.).

817

959 2274

934.4743

975.2224

1233.4352

1346.4445

1451.3212

1500

597 1391

685 1495

484,1335

378.3226 439 1165

524.1230

326.096

248.0556

274,2743

5 0 200

In addition, the coordination mode of the probe Z with Al^{3+} was further analyzed by FT-IR spectra (Fig. S8) and ¹H NMR titration experiment. As for the FT-IR spectra of probe Z, the peaks at, 3305 cm⁻¹ and 1216 cm⁻¹, were attributed to O-H stretching and C-O stretching of phenolic hydroxyl, respectively. Moreover, peaks at 3217 cm⁻¹ and 1689 cm⁻¹ were assigned to N-H stretching and C=O stretching of amide, respectively. After complexation with Al^{3+} , the characteristic peaks of N-H absorption and C=O absorption of the amide were disappeared, and the appearance of an absorption peak at 1601 cm⁻¹, indicated that one probable binding site to Al³⁺ was O atom of the deprotonation of enolized amide group. Moreover, the characteristic OH vanished and the C-O moved to higher wavenumbers form 1216 cm⁻¹ to 1322 cm⁻¹, indicating the interaction of Al³⁺ with the O atom of deprotonated of phenolic hydroxyl.

¹H NMR titration was performed in DMSO-d₆ illustrated in Fig. 6, the protons of hydroxyl (H₁₄ and H₁₄) and the protons (H₁₆ and H₁₆) of amide was due to (*Z*)- and (*E*)-configurations resulting from the C=N isomerization of the probe **Z** itself. Upon the addition of Al³⁺, due to the difference in the two spatial configurations, the protons of hydroxyl (H₁₄) at 12.42 ppm and (H₁₄) at 10.74 ppm were all disappeared, indicating the coordination of Al³⁺ with oxygen atom came from the deprotonation of phenolic hydroxyl whatever in the (*E*)-configuration or (*Z*)-configuration.

According to the above analysis including Job's plot, ESI–MS, FT–IR spectra comparison and ¹H NMR titration, a plausible bonding fashion between **Z** and Al³⁺ was proposed (Scheme 2).

Scheme 2. Plausible binding fashion of probe Z with Al^{3+} ions.

3.3. Relationship between pH and fluorescence intensity of probe Z

Furthermore, in order to investigate the ability of probe **Z** on the recognition of Al^{3+} at different pH conditions, the fluorescent intensity of complex **Z**- Al^{3+} centred at 465 nm were measured at different pH ranging from 2 to 13 (Fig. 7). The result showed that probe **Z** itself was without any fluorescence emission in the range of pH from 2 to13. However, upon addition of Al^{3+} , the fluorescence intensity of the probe **Z** was significantly enhanced in the range of pH 4-7, which indicated that the probe **Z** could recognize Al^{3+} in neutral to acidic medium.

Fig. 7. The fluorescence intensity changes (λ_{em} = 465 nm) of Z and Z-Al³⁺ solution at various pH conditions (pH = 2-13).

3.4. Reversibility of Z for Al^{3+}

Reversibility, an important factor in determining whether a probe can be repeatedly detected, plays an important role in practical applications. In the reversibility experiment, based on the conclusion we had previously analyzed, the probe Z and the aluminum ion was coordinated in the

form of chelation to generate fluorescence, so we used the common metal complexing agent Na_2EDTA as chelating ligand to the solutions of Z-Al³⁺. Upon the addition of Na_2EDTA , the fluorescence spectra of Z-Al³⁺ were all similar to that of probe Z without addition of Al³⁺ (Fig. S9). Moreover, when Al³⁺ ions were added to the mixture of $Z + Al^{3+} + Na_2EDTA$, the fluorescence intensity turned on again (Fig. 8a), and the result showed that this reversible cycle could be repeated at least 5 times through alternate addition of Na_2EDTA and Al^{3+} (Fig. 8b). This result showed that this reversible cycle performance further enhanced the potential application of probe Z in construction of logic gate.

Fig. 8. (a) The color changes of solution Z upon alternate addition of Al³⁺ and EDTA under UV light ($\lambda_{em} = 365$ nm); (b) fluorescence intensity of Z at 465 nm by alternate addition of Al³⁺ and EDTA.

4. Application of chemosensor Z

4.1. Detection of Al^{3+} in real water samples

In order to investigate the applicability of the probe Z to the detection of Al^{3+} in real water samples, different concentrations of Al^{3+} were added to water samples, and the results were analyzed through the previously calculated linear relationship (Table 2). The results showed that the probe Z had high recovery and precision for the detection of Al^{3+} in these tested water samples, which also indicated that it could be applied to the analysis and detection of Al^{3+} in environmental water samples.

Water samples studied	Amount of standard Al ³⁺ added (µmol/L)	Total Al ³⁺ found (n=3) (μmol/L)	Recovery of Al ³⁺ (n=3) added (%)	RSD (%)	Relative error (%)
	5	4.96	99.20	0.90	-0.80
ultrapure water	8	8.03	100.38	0.39	0.37
	24	24.32	101.33	2.28	1.33
Tan water	5	5.24	104.80	0.51	4.80
(Department of	8	8.25	103.13	2.69	3.13
Chemistry)	24	24.36	101.50	1.91	1.5

Table 2 Determination of Al³⁺ in water samples.

4.2. Molecular Logic Gates

Based on the good reversible cycle performance of **Z** with Al^{3+} and EDTA, a logic gate could be implemented on Boolean logic operations, which was a INHIBIT logic gate (Fig. 9). Since there was significant fluorescence emission at 465 nm after the addition of Al^{3+} , we set the fluorescence signal at 465 nm as the output, the strong fluorescence intensity at 465 nm was On (1) state and weak for Off (0) state. Al^{3+} and EDTA were respectively set as inputs In 1 and inputs In 2, whose presence and absence were itemized as 1 and 0. According to the above mentioned basic logic gates, we further installed the memory storage device to implement the reset operation of the logic circuit. When the output was On (1) state, the input signal could be reset by the memory unit to return the output to the off (0) state. Hence, the above setting could make the entire process to be repeated for several times.

Fig. 9. (a) Logic circuit showing memory unit containing two inputs (In 1 and In 2) and one output; (b) corresponding truth table.

4.3. Cells Imaging

Considering imaging in biological systems was another important practical applicability for one probe, we used the human stromal cells (HSC) that was incubated different amounts of Al^{3+} and Z (0.1 mM) and then imaged by fluorescence microscope. As shown in Fig. 10 A and Fig. 10 B, the cells without any treatment and the cells incubated 2 hours with Z (0.1 mM) were all emit any intracellular fluorescence. When the cells was incubated of Al^{3+} (10 µM) and Z (0.1 mM), a weak blue fluorescence was detected (Fig. 10 C). When cells were further treated with Al^{3+} (50 µM) and Z (0.1 mM), the blue fluorescence was significantly increased (Fig. 10 D). These results indicated that the probe Z might became an Al^{3+} tracer in biological systems.

Fig. 10. (A) The cells without any treatment; (B) incubation of cells with \mathbf{Z} (0.1 mM) for 2 hours; (C) incubation of cells with Al³⁺ (10 μ M) and \mathbf{Z} (0.1 mM); (D) incubation of cells with Al³⁺ (50 μ M) and \mathbf{Z} (0.1 mM).

5. Conclusions

In summary, a novel naphthaldehyde–benzothiazole conjugated chemosensor Z was successfully synthesized and characterized. Chemosensor Z was achieved in highly selective and sensitive for the detection of Al³⁺ in DMF/H₂O (v/v, 4/6) through significant fluorescence turn on. The binding ratio of Z to Al³⁺ was 1:1 and the detection limit was calculated 4.56×10⁻⁷ M and

 5.09×10^{-8} M in corresponding Al³⁺ concentration range of 0-22 μ M and 24-44 μ M, respectively. Furthermore, **Z** was successfully practiced for the Al³⁺ quantity analysis in real water samples, logic gate and imaging in human stromal cells (HSC).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at

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25

Highlights

- Chemosensor **Z** was synthesized and characterized.
- Chemosensor **Z** exhibits significant fluorescence response to Al³⁺ with a 400-fold fluorescence enhancement
- The limit of detection (LOD) and binding constant for Al³⁺ were 5.09×10⁻⁸ M and 2.35×10⁴ M⁻¹, respectively.
- Z was successfully applied in real sample detection of Al³⁺ and cell imaging in HSC.