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A New Fluorescence Turn-On Probe for Aluminum(III) with High Selectivity and Sensitivity, and its Application to Bioimaging

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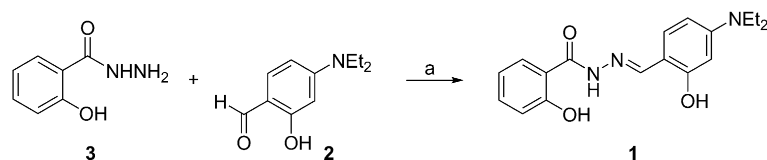
The development of novel selective probes with high sensitivity for the detection of Al^{3+} is widely considered an important research goal due to the importance of such probes in medicine, living systems and the environment. Here, we describe a new fluorescent probe, *N*′-(4-diethylamino-2-hydroxybenzylidene)-2-hydroxybenzohydrazide (**1**), for Al^{3+}. Probe **1** was evaluated in a solution of acetonitrile/water (1:1 *v*/*v*). Compared with previously reported probes for Al^{3+}, probe **1** can be synthesized easily and in high yield. A Job plot confirmed that probe **1** is able to complex Al^{3+} in a 1:1 ratio, and the binding constant was determined to be 4.25×10^{8} M^{-1}. Moreover, the detection limit was as low as 6.7×10^{-9} M, suggesting that probe **1** has a high sensitivity. Common coexistent metal ions, such as K^{+}, Co^{2+}, Ca^{2+}, Ba^{2+}, Ni^{2+}, Pb^{2+}, Hg^{2+}, Ce^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}, showed little or no interference in the detection of Al^{3+} in solution, demonstrating the high selectivity of the probe. Finally, the ability of probe **1** to act as a fluorescent probe for Al^{3+} in living systems was evaluated in Gram-negative bacteria, *Escherichia coli*, and confocal laser scanning microscopy confirmed its utility. The results of this study suggest that **1** has appropriate properties to be developed for application as a fluorescent probe of Al^{3+} for use in biological studies.

Introduction

It is widely considered meaningful to develop new selective and sensitive chemosensors for the detection of metal ions due to their important roles in medicine, living systems, and the environment.[1,2] Among metals, aluminum is the third most prevalent element (8.3% by weight) in the earth's crust. Acid rain can leach aluminum from soil and increases the concentration of free Al^{3+} in surface water, which is detrimental to growing plants.[3–5] Consequently, about 40% of the world's acidic soil is caused by aluminum toxicity.[6–8] Furthermore, people are widely exposed to aluminum because of its widespread use in food additives, aluminum-based pharmaceuticals, and so on.[9–10] The toxicity of aluminum leads to damage to the central nervous system (CNS), which is suspected to be involved in neurodegenerative diseases such as Alzheimer's and Parkinson's diseases.[11,12] The World Health Organization (WHO) reported that the average daily human intake of aluminum is approximately 3–10 mg.[13,14] However, compared with other metal ions, the detection of Al^{3+} has always been a great challenge because of its poor coordination ability, strong hydration ability, and the lack of spectroscopic characteristics.[15–17] To date, many fluorescent probes have been developed to detect Al^{3+}.[18–32]



Scheme 1. Synthesis of chemosensor **1**. *Reagents and conditions*: a) Piperidine, EtOH, 81%.[34]

To the best of our knowledge, although many Schiff base derivatives bearing a fluorescent moiety have been used to detect various metal ions,[33] Schiff base-type Al^{3+} sensors used for bioimaging remain rare.[20,28,30,32d] Here, we report a previously identified Schiff base derivative (**1**)[34] (Scheme 1) as the fluorescent turn-on probe for detection of Al^{3+}. Compared with the reported probes for Al^{3+}, probe **1** can be synthesized easily in high yields. Common coexistent metal ions showed little or no interference in the detection of Al^{3+}, demonstrating the high selectivity of probe **1**. More importantly, the detect limit of probe **1** towards Al^{3+} is extremely low (6.7×10^{-9} M), suggesting its high sensitivity. These advantages

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are helpful to its further application in areas such as bioimaging.

Results and Discussion

Probe **1** was soluble in acetonitrile and slightly soluble in water. Therefore, the selectivity of **1** to various metal ions, namely K^+, Co^{2+}, Ca^{2+}, Ba^{2+}, Ni^{2+}, Pb^{2+}, Hg^{2+}, Ce^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}, Al^{3+} (5.0 equiv), was examined in an acetonitrile/water solution (1:1 *v*/*v*). As shown in Figure 1, probe **1** alone displays very weak fluorescence when excited at 400 nm. The addition of 5.0 equiv of K^+, Co^{2+}, Ca^{2+}, Ba^{2+}, Ni^{2+}, Pb^{2+}, Hg^{2+}, Ce^{2+}, Zn^{2+}, Cd^{2+}, or Fe^{3+} had no obvious effect on the fluorescence of probe **1**. However, upon addition of 5.0 equiv of Al^{3+}, the emission intensity was largely enhanced at 467 nm.

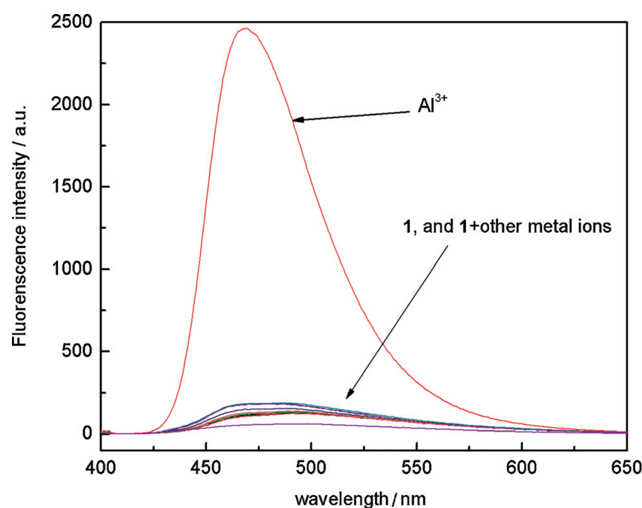

Figure 1. Fluorescence responses of **1** (5 μM, λ_{ex} = 400 nm) upon addition of 5.0 equiv of various metal ions in CH_3CN/H_2O (1:1 *v*/*v*).

Achieving a highly selective response to the targeted analyte over a complex background of potentially competitive species is an important requirement for a chemosensor. Thus, the competitive experiments were then carried out by addition of 10.0 equiv of A^{l3+} to the solutions of **1** in the presence of 100.0 equiv of other metal ions, in order to validate the high selectivity of **1** as a chemosensor for the detection of Al^{3+}. As shown in Figure 2, there is nearly no interference for the detection of Al^{3+} in the presence of other metal ions. These results demonstrate that **1** displays a high selectivity for Al^{3+} in the acetonitrile/water solution (1:1 *v*/*v*).

The UV-vis absorption of **1** in acetonitrile/water (1:1 *v*/*v*) was investigated by spectrophotometric titration. As shown in Figure 3 a, in the presence of Al^{3+} (5.0 equiv), a new absorbance band appears at approximately 350 nm. However, no obvious changes in the UV-vis absorption spectra of **1** were observed in the presence of other metal ions. Furthermore, the absorbance peak at ~350 nm increased gradually upon gradual addition of Al^{3+} to the solution of **1** (Figure 3 b).

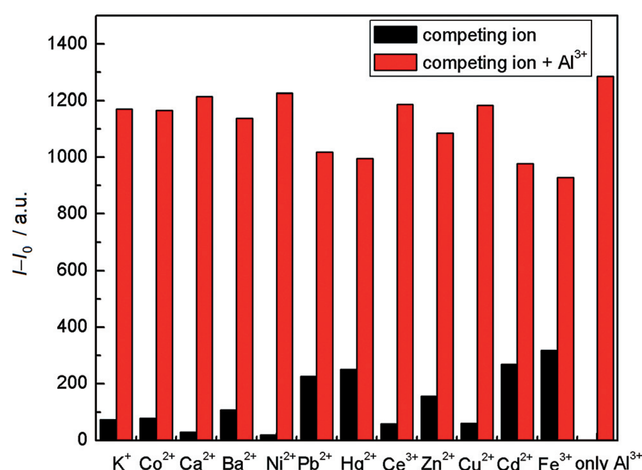

Figure 2. Fluorescence responses of **1** (5 μM) at 467 nm, in the absence and presence of different metal ions (5.0 equiv). The measured fluorescence intensity (I–I_0) of probe **1** in the presence of both the indicated metal ion (black bar) and the indicated metal ion plus 100 equiv Al^{3+} (red bar).

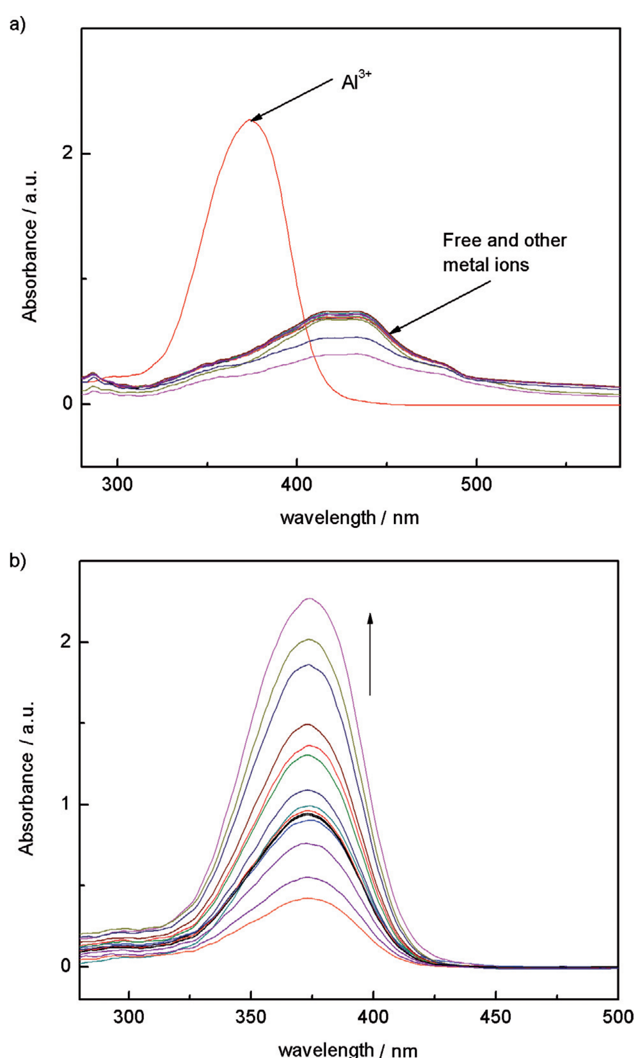

Figure 3. a) UV-vis absorption spectra of **1** upon addition of various metal ions (5.0 equiv) in CH_3CN/H_2O (1:1 *v*/*v*); b) Absorption titration spectra of **1** (5 μM) in CH_3CN/H_2O (1:1 *v*/*v*) in the presence of increasing concentrations of Al^{3+} (0–8 equiv).

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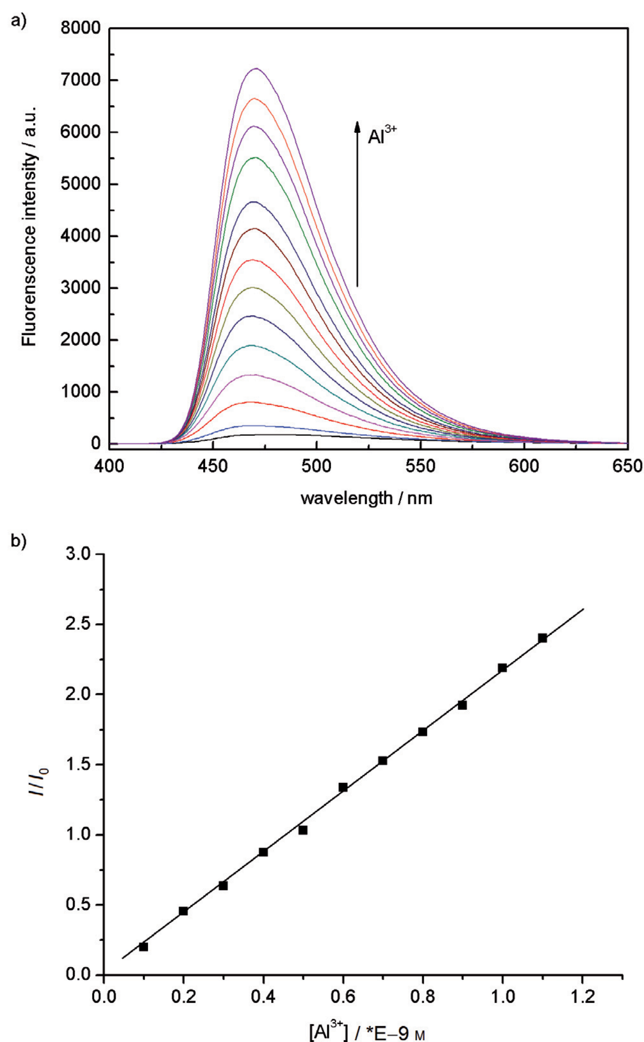

Figure 4. a) Fluorescence titration of **1** (5 μM) with Al^{3+} in CH_3CN/H_2O (1:1 *v/v*) with increasing concentrations of Al^{3+} (λ_{ex} = 400 nm); b) fluorescence of **1** (5 μM) at 467 nm as a function of Al^{3+} concentration ($0–8\times10^{-9}$ M).

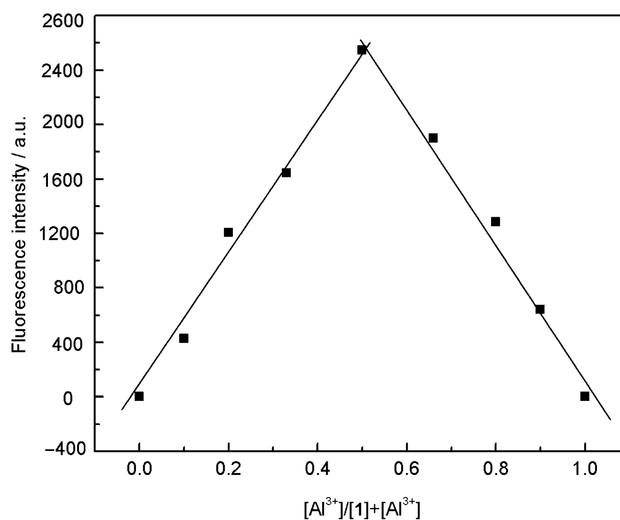

Figure 5. Job's plot to determine the stoichiometry of the **1**–Al^{3+} complex (λ_{ex} = 400 nm). Fluorescence at 467 nm was plotted as a function of the molar ratio: $[Al^{3+}]/([Al^{3+}]+[\mathbf{1}])$.

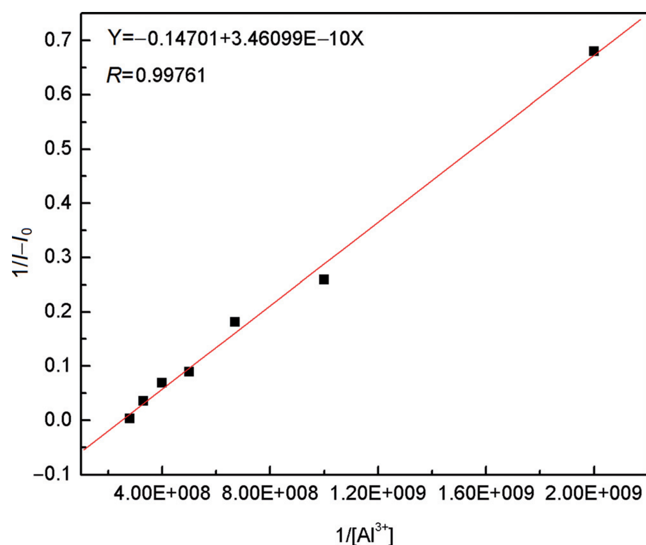

Figure 6. Benesi–Hildebrand plot (λ_{em} = 467 nm) of fluorescence intensity $1/(I-I_0)$ of **1** as a function of $1/[Al^{3+}]$.

Titration of a 5 μM solution of **1** in acetonitrile/water (1:1 *v/v*) by gradual addition of Al^{3+} was carried out. Upon incremental addition of Al^{3+}, the fluorescence intensity at 467 nm of **1** in solution increased gradually (Figure 4a). Figure 4b shows relative intensity (I/I_0) versus the concentration of Al^{3+} in the low concentration region up to 6.7×10^{-9} M, suggesting that probe **1** could act as a chemosensor for the detection of Al^{3+} with extraordinarily high sensitivity compared with other chemosensors.[18–32]

To investigate the binding stoichiometry of the **1**–Al^{3+} complex, a Job's plot based on fluorescence data was generated (Figure 5), showing a maximum emission intensity when the molecular fraction of Al^{3+} was approximately a half, suggesting that probe **1** complexes with Al^{3+} in a 1:1 ratio. According to the linear Benesi–Hildebrand expression,[35] the measured fluorescence intensity $1/(I-I_0)$ at 467 nm showed a linear relationship with $[\mathbf{1}]/[Al^{3+}]$. Using the Benesi–Hildebrand plot (Figure 6), the binding constant of the **1**–Al^{3+} complex was found to be 4.25×10^{8} M^{-1} (R = 0.998).

The pH influence on the sensitivity of probe **1** for Al^{3+} was also examined under various pH conditions (Figure 7). As expected, **1** was found to be weakly fluorescent in acetonitrile/water (1:1 *v/v*) and showed a significantly positive response (strong fluorescence) between pH 6.8 and 7.4 upon the addition of Al^{3+}. The biologically relevant pH range is 6.0–7.6,[20] thus, fluorescent probe **1** could be used to detect intracellular Al^{3+} without being affected by the physiological pH.

The ability of biosensing molecules to selectively monitor guest species in living systems recently attracted much attention due to their importance in biological applications.[36,37] Therefore, we evaluated fluorescent probe **1** against *Escherichia coli*, a Gram-negative bacteria, to demonstrate its potential application in biological systems. *E. coli* cells were incubat-

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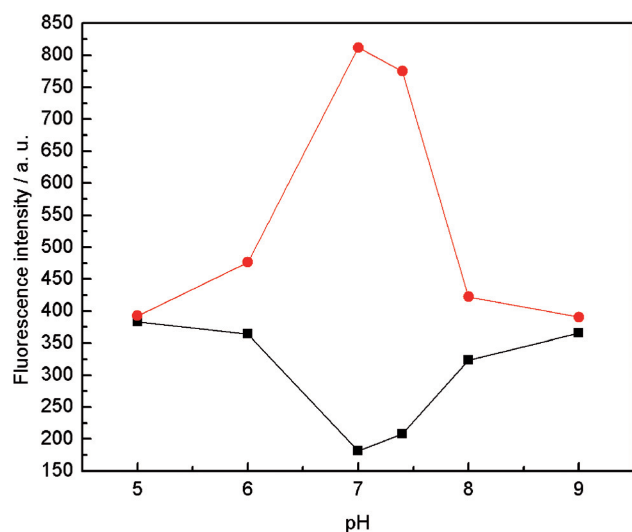

Figure 7. Effect of pH on the fluorescence intensity of chemosensor **1** (5 μM) (■) at 467 nm, and **1** upon addition of 10 equiv Al^{3+} in CH_3CN/H_2O (1:1 *v/v*) (●).

ed with **1** (10 μM) for one hour at 37 °C, after which time no obvious fluorescence could be detected (Figure 8 a). In contrast, a strong fluorescent image was observed in *E. coli* cells incubated with both **1** and Al^{3+} (Figure 8 b). The bright field transmission image of the *E. coli* cells (Figure 8 c) was exactly consistent with the fluorescence image in Figure 8 b. These results suggested that **1** is cell-membrane permeable and could be used for detecting Al^{3+} within living systems.

Conclusion

We have synthesized a probe (**1**) that could selectively detect Al^{3+} with high sensitivity. Upon the formation of the **1**–Al^{3+} complex, obvious detectable changes in absorbance and fluorescence were observed. The recognition behavior of probe **1** towards Al^{3+} was carefully investigated by experimental studies to give the binding stoichiometry and binding constant, and the level of detection limit, which is extremely low. More importantly, confocal laser scanning microscopy showed the application of fluorescent probe **1** as an imaging reagent for detection of Al^{3+} in *E. coli*, demonstrating its value in practical applications in biological systems.

Experimental Section

General materials and methods: All materials for synthesis of probe **1** were obtained in analytical grade from Alfa Aesar, A Johnson Matthey Company, and used without further purification. All solvents used in spectroscopic experiments were spectroscopic grade. Distilled, deionized water was used throughout the experiments.

NMR spectra were recorded on a Bruker DRX spectrometer operating at 500 MHz or 125 MHz (Bruker Scientific Technology Co. Ltd, Beijing, P. R. China). Chemical shifts (δ) are reported in parts per million (ppm) relative to an internal standard (TMS). A Hitachi F-4500 spectrofluorometer (Hitachi High Technologies Co. Ltd, Shanghai, P. R. China) was used for fluorescence measurements. Absorption spectra were recorded with a Techcomp UV-8500 spectrophotometer (Shanghai Techcomp Scientific Instrument Co. Ltd, Shanghai, P. R. China).

Synthesis of *N'*-(4-diethylamino-2-hydroxybenzylidene)-2-hydroxybenzohydrazide (1):[34] A solution of 2-hydroxybenzohydrazide (**3**) (1.52 g, 10 mmol), 4-(diethylamino)salicylaldehyde (**2**) (1.93 g, 10 mmol), and piperidine (0.50 mL) in EtOH (25 mL) was heated at reflux for 4 h. The resulting yellow precipitate was isolated by filtration and then washed with EtOH to give the crude product. Purification by column chromatography (hexane/EtOAc, 2:1→1:1) gave the title compound as a pale yellow solid (2.77 g, 81 % yield): ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ=8.48 (s, 1 H), 7.87 (d, J=6.5 Hz, 1 H), 7.44–7.42 (m, 1 H), 7.29 (d, J=8.5 Hz, 1 H), 6.97–6.93 (m, 2 H), 6.38 (d, J=8.5 Hz, 1 H), 6.24 (s, 1 H), 3.38 (q, J=7.0 Hz, 4 H), 1.09 ppm (t, J=7.0 Hz, 6 H); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ=165.0, 159.8, 159.6, 150.2, 134.5, 132.1, 129.2, 119.5, 117.8, 116.0, 48.5, 11.7 ppm; MS (ESI): m/z=327 $[M]^+$. Characterization data are in line with those reported in Ref. [34].

Fluorometric and UV-vis titrations: Solutions (5.0 mM) of K^+, Co^{2+}, Ca^{2+}, Ba^{2+}, Ni^{2+}, Pb^{2+}, Hg^{2+}, Ce^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}, and Al^{3+} in CH_3CN/H_2O (1:1 *v/v*) were prepared from the chloride or ni-

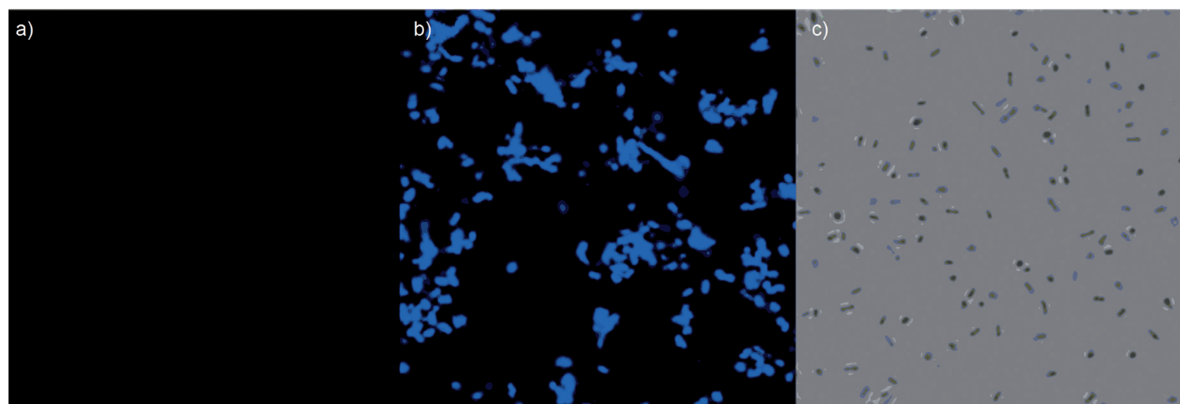

Figure 8. Confocal fluorescence images of *E. coli*. a) Bacteria after incubation with probe **1** (10.0 μM) for 1 h; b) bacteria after incubation with $AlCl_3$ (200 μM) in DMSO/H_2O (1:1 *v/v*) for 10 min, then with **1** (10.0 μM) for 1 h; c) bright field image of *E. coli*. The images were taken at 2000× magnification, and the size of each square presented is 25 μm×25 μm.

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trate salt. A solution (5 μм) of probe **1** in CH_3CN/H_2O (1:1 *v/v*) was also prepared for titration purposes. Titrations were carried out at room temperature.

During titration, 5.0 mм metal ion solution was added using a micro-injector to a solution of **1** (5 μм, 3 mL); the volume of metal ion solution could be ignored compared to that of **1**. Measurements were taken after 2 h. Excitation and emission slits of 5.0 nm were used for all the measurements of fluorescence.

Preparation of *E. coli* cells: *E. coli* was obtained from the Qingdao Institute of Bioenergy and Bioprocess Technology (QIBEBT) of the Chinese Academy of Sciences (CAS). Nutrient broth and trypticase soy broth were obtained from Aladdin Reagent Company (Shanghai, China).

After incubation at 37 °C for 24 h, stock cultures were maintained on trypticase soy agar slants at 4 °C. A loop of bacteria was resuspended in nutrient broth (5 mL) and trypticase soy broth (50 mL) without glucose (1.5% trypticase, 0.5% soytone, and 0.5% NaCl). The culture broth was incubated with shaking for 15–18 h at 37 °C. Bacteria were washed with sterile 0.85% saline (4–5 mL) and then centrifuged twice (3000 rpm, rt, 30 min) to remove culture medium from the bacterial pellet. Before use, bacteria were resuspended in 0.025 м phosphate buffer (pH 6.8) (4 mL).

Confocal fluorescence imaging: Confocal fluorescence imaging was performed on a Leica TCS SP5 laser scanning confocal microscope (Leica Microsystems, Wetzlar, Germany), with a blue diode laser (50 mW, $\lambda_{ex}=405$ nm) and acquisition as *xyz* at a speed of 400 Hz.

Acknowledgements

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Keywords: aluminum(III) · bioimaging · fluorescent probes · selectivity · sensitivity

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