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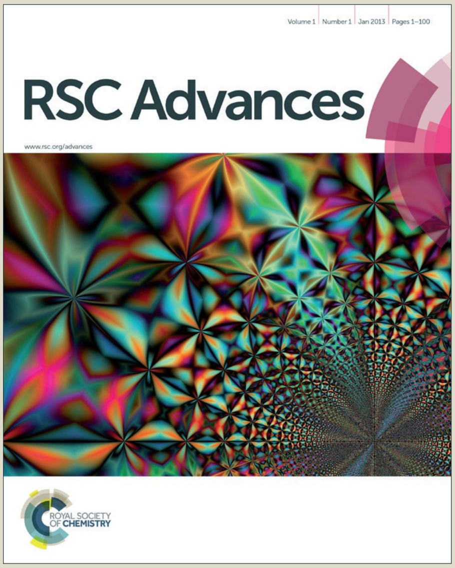

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An Easy and Accessible Water-soluble Sensor for the Distinctive Fluorescence Detection of Zn^{2+} and Al^{3+} ions†

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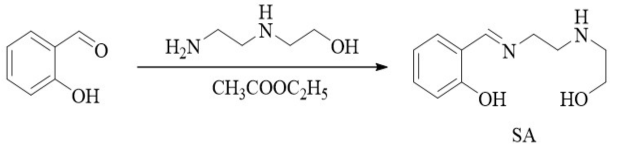
A water-soluble fluorescence sensor (SA) was facilely synthesized via a one-step condensation reaction between commercially available salicylaldehyde and 2-(2-aminoethylamino)ethanol with high yield. The addition of Zn^{2+} and Al^{3+} to SA showed drastic enhancements of the emission intensities in 458 nm and 376 nm respectively, whereas exhibited a negligible interference in the presence of typical competitive ions such as Fe^{3+}, Cr^{3+} Hg^{2+} and Cd^{2+}. This phenomenon indicates that SA may be helpful for rapid quantitative and qualitative detection of Zn^{2+} and Al^{3+}.

Fluorescence sensing[1-4] has gradually emerged as a significant and effective approach for the recognition of metal ions due to its simplicity, high sensitivity and instantaneous response. In the past decade, a considerable amount of sensors with excellent detection sensitivity and selectivity for diverse metal ions have been reported, however, there are still many challenges to be overcome. For example, most of the fluorescence detection process is conducted in pure organic or organic-water mixed solution ascribing to the insufficient water solubility of the sensor, which is inconvenient in practical quantitative and qualitative detection of the water contamination[5]. Besides, complicated multiple synthesis and purification steps accompanied with relatively low product yield of the chemosensor are also severe limitations for the large scale production and application. Consequently, it is highly desirable to design a sensor which is readily available with high yield, and is sensible for target ion in 100% aqueous solution.

Among the common metal ions, Zn^{2+} is the second most abundant transition metal ion in the human body which plays a significant role in various biological activities[6-8], and a deviation of Zn^{2+} concentrations from normal levels can increase the risk for diverse diseases. Al^{3+} toxicity is believed to retard plant growth[9] and arouse neuronal disorders which may induce Alzheimer's disease and Parkinson's disease[10, 11]. Until now, numerous fluorescence sensors for Zn^{2+} ion[12-17] and Al^{3+} ion[18-21] have been reported, but most of them have tedious synthetic step-outs. Besides, the detection of Al^{3+} is usually disturbed by other trivalent ions (Fe^{3+} and Cr^{3+})[22] while the detection of Zn^{2+} can be interfered by Cd^{2+}, owing to the similar electron configuration[23] in the recognition process. Consequently, relatively scarce fluorescence sensors capable of simultaneous discrimination of Zn^{2+} and Al^{3+} without any other interference have been reported[9, 24-30]. A water-soluble unit, 2-(2-aminoethylamino)ethanol, was strategically attached to salicylaldehyde template to improve the water solubility of probe thus meeting the needs of actual detection[31-33]. To the best of our knowledge, herein, it is the first time to develop the easy and accessible water-soluble fluorescence sensor for the distinct detections of Zn^{2+} and Al^{3+} ions with different fluorescence emission peak, which is convenient and economical for the quantitative determination of Zn^{2+} and Al^{3+} ions.



Scheme 1 Schematic illustration of the synthesis of fluorescent chemosensor SA.

The fluorescence probe was obtained via one-step condensation reaction between salicylaldehyde and 2-(2-aminoethylamino)ethanol at room temperature[34, 39], as is illustrated in Scheme 1. The yield is as high as 93%. Molecular structure of the probe was confirmed by ^1H NMR, ^{13}C NMR and HR-MS analysis (Fig. S1-S3). The modification of 2-(2-aminoethylamino)ethanol endows the probe SA with excellent water solubility, which is advantageous for the following heavy metal ion detection process.

The fluorescence response of SA (50 μM) toward various metal ions (250 μM) was investigated in Tris buffer (10 mM, pH

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= 7.0). As shown in Fig. 1, free SA gave almost no fluorescence emission changes and was silent toward most of the metal ion such as Na^+, K^+, Mg^{2+}, Ni^{2+}, Ba^{2+}, Cd^{2+}, Ca^{2+}, Hg^{2+}, Cu^{2+}, Pb^{2+}, Fe^{3+} and Cr^{3+}. However, the fluorescence signal of SA showed immediate changes upon the addition of Zn^{2+} and Al^{3+} ions. Surprisingly, Zn^{2+} and Al^{3+} can be distinguished through the different fluorescence emission peak. An emission band centered at 458 nm was observed with an obvious fluorescence turn-on after the addition of Zn^{2+} ion. As for Al^{3+} ion, a much more significant fluorescence blue shift from 496 nm to 376 nm was achieved, accompanied with a distinctive enhancement of fluorescence intensity. These fluorescence changes can be attributed to the formation of a chelate complex between metal ions and SA, causing the chelation-enhanced fluorescence (CHEF) effect[35, 36].

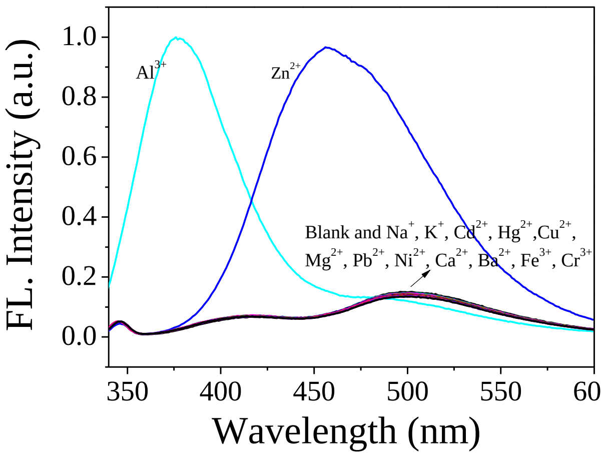

Fig .1 Fluorescence spectra of SA (50 μM) in Tris buffer (10 mM, pH = 7.0) in the absence and presence of 250 μM of various metal ions, λ_{ex} =310 nm

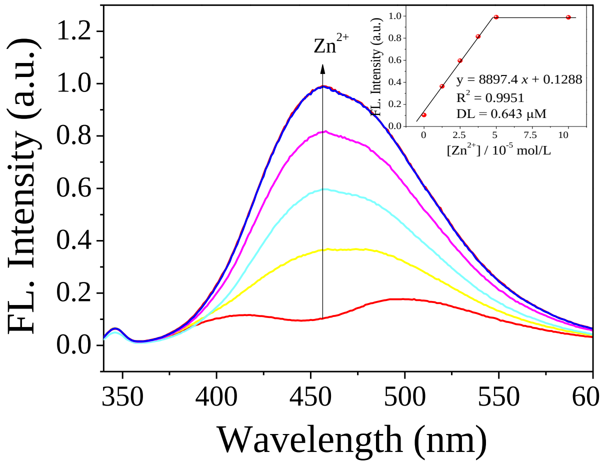

Fig. 2 Fluorescence spectra of SA (50 μM) in the presence of increasing concentrations of Zn^{2+} in Tris buffer (10 mM, pH = 7.0). Inset: fluorescence intensity at 458 nm as a function of $[Zn^{2+}]$, λ_{ex} =310 nm

The fluorescence detection capacity of SA (50 μM) toward Zn^{2+} was evaluated by fluorescence titration experiments in Tris buffer (10 mM, pH = 7.0). As shown in Fig. 2, relative weak fluorescence emission was observed in the absent of any metal ion. With the increasing concentration of Zn^{2+}, the fluorometric titration curve firstly showed a steady and smooth enhancement, and then gradually reached equilibrium as the concentration of Zn^{2+} ion was greater than 50 μM, indicating that the recognition molar ratio of probe SA to Zn^{2+} ion might be 1:1. Plotting of the fluorescence intensity (458 nm) versus the concentration of Zn^{2+} (0-50 μM) afforded a good linear relationship as shown in the inset of Fig. 2. The detection limit (DL) of SA toward Zn^{2+} ion was calculated to 0.643 μM according to the equation DL = 3 S_{b1}/S[37], where S_{b1} is the standard deviation of the blank sample, S is the slope of the calibration curve.

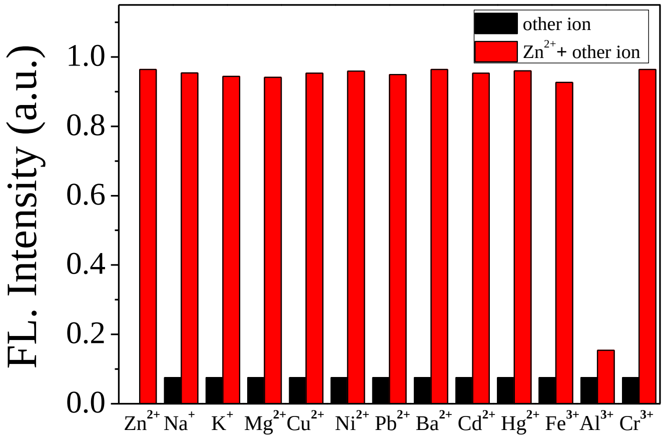

Fig. 3 Fluorescence intensity at 458 nm of SA (50 μM) in the presence of selected metal ions (250 μM) in Tris buffer solution (10 mM, pH = 7.0). The black bars represent the intensity of SA in the presence of selected cations; the red bars represent the intensity upon an addition of Zn^{2+} (250 μM) to a solution of SA in the presence of selected cations

Possible interference from other cations in the fluorescence detection of Zn^{2+} ions was also tested. Competitive ions were first added into the detection solution, and Zn^{2+} ions were added 20 minutes later. The fluorescence emission curves were then recorded and the changes of fluorescence intensity at 458 nm before and after the addition Zn^{2+} were displayed in Fig. 3. It is obvious that most of the detection systems exhibited minimum interference in the detection of Zn^{2+} even in the presence of typical competitive ions Cd^{2+} and Hg^{2+}. However, the detection process of Zn^{2+} can be affected by Al^{3+}, suggesting that SA has a binding affinity toward Al^{3+} higher than that of Zn^{2+}. The association constant (K_a) between the probe and the two ions was then calculated according to the reported work[38]. The equilibrium constant K_a between SA and Zn^{2+} ion was 3.06 × 10^8, while the data was 4.96 × 10^8 for SA and Al^{3+} ion. The formation of more stable SA-Al^{3+} complex can be ascribed to that hard Lewis acid Al^{3+} tends to have a high binding affinity toward the probe under the hard base environment offered by SA[26]. We tried to select ammonium fluoride and tartaric acid as screening agent of Al^{3+} in HAc-NaAc buffer (60 mM, pH=6, ω_{NH_4F}=0.02, $\omega_{tartaric\ acid}$=0.07) (Fig. S4). The results indicate that there was no obvious interferences (fluorescence intensity decreased to 94% of original intensity) in detecting Zn^{2+} in the presence of 5 equivalents of Al^{3+} under the above detection system. Fluorescence spectroscopic titration experiments (Fig. S5-S6) showed that there was a negligible fluorescence enhancement (blue line, slope K_1 = 0.017) with the concentration of Zn^{2+} ranging from 0 μM to 15 μM (0 - 0.3 eq.). With increasing concentrations of Zn^{2+}, the titration reaction curve showed a steady enhancement (red line, slope K_2 =1.073), and gradually reached equilibrium as the concentration of Zn^{2+} was greater than 60 μM. This phenomenon means that sensitive detection of Zn^{2+} in the presence of Al^{3+} when the concentration of Zn^{2+} is less than 15 μM has not been achieved using this method.

Similarly, the fluorescence detection capacity of SA (50 μM) toward Al^{3+} was recorded in Fig. 4. With the increasing concentration of Al^{3+}, the fluorometric titration curve showed a steady and smooth enhancement, accompanied with a much more fluorescence blue shift, which is significant to the distinctive detection of Zn^{2+} and Al^{3+} ions respectively. Plotting of the fluorescence intensity (376 nm) versus the concentration of Al^{3+} (0-50 μM) also afforded a good linear relationship as shown in the inset of Fig. 4. The detection limit of probe SA toward Al^{3+} was 0.611 μM, there were no obvious interferences in the presence of Fe^{3+}, Cr^{3+}, Zn^{2+}, and other cations as shown in Fig. 5.

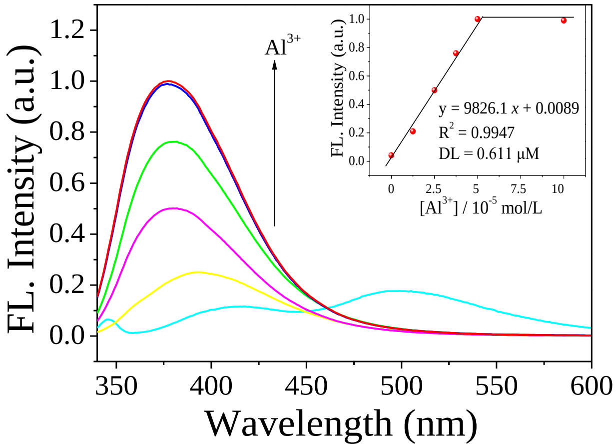

Fig. 4 Fluorescence spectra of SA (50 μM) in the presence of increasing concentrations of Al^{3+} in Tris buffer (10 mM, pH = 7.0). Inset: fluorescence intensity at 376 nm as a function of $[Al^{3+}]$, λ_{ex} =310 nm

A sample with tap water background has been detected to evaluate the potential application of chemosensor SA in detecting Zn^{2+} and Al^{3+}. Zn^{2+} and Al^{3+} was deliberately introduced to simulate contaminated tap water. 200 mL tap water was obtained from tap faucet (Nanshan District, Shenzhen, China. Sampling time: 14:00 on August 18th, 2015). The water sample in the beaker was kept still for 24 hours. Then the tap water could be used as testing solution for fluorescent analysis. As shown in Fig. S7-S8, the fluorescence intensity increased linearly (R^2 = 0.9954) upon the addition of Zn^{2+} (0-50 μM). The result indicated the suitability of this chemosensor for the determination of Zn^{2+} in real sample. Similar phenomenon can also be observed in the fluorescence sensing of Al^{3+} (Fig. S9-S10). The fluorescence intensity increased linearly (R^2 = 0.9945) upon the addition of Al^{3+} (0-50 μM).

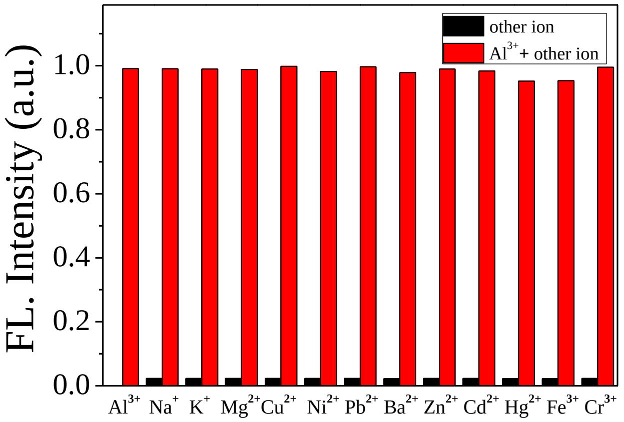

Fig. 5 Fluorescence intensity at 376 nm of SA (50 μM) in the presence of selected metal ions (250 μM) in Tris buffer solution (10 mM, pH = 7.0). The black bars represent the intensity of SA in the presence of selected cations; the red bars represent the intensity upon an addition of Al^{3+} (250 μM) to a solution

HR-MS measurements (Fig. S11) and FT-IR (Fig. S13) were utilized to analyse the binding mode of sensor SA towards Zn^{2+} ion. In Fig. S11, the peak located at m/z 271.0409 (calcd=271.0420) corresponding to $[SA+Zn^{2+}-H^{+}]^{+}$ can be clearly observed when 5 equiv. of $ZnCl_2$ was added to the solution containing probe SA. In Fig. S13 the characteristic absorption peak of C=N double bond at 1577 cm^{-1} shifted to 1544 cm^{-1}, and the characteristic absorption peak of C-O bond at 1045 cm^{-1} shifted to 1014 cm^{-1} in the presence of Zn^{2+} ion, indicating that the N atom of the Schiff base and the O atom of alcoholic hydroxyl ($-CH_2OH$) were actually involved in the recognition of Zn^{2+}. Considering the strong acidity (δ=13.38 ppm) of the phenolic hydroxyl group in SA, the H of phenolic hydroxyl was easy to leave, which also agreed with reported work[25, 26, 39]. The binding mode of sensor SA towards Al^{3+} was further confirmed by high-resolution mass spectrum (Fig. S12), in which the peak at m/z 233.0861 (calcd=233.0865) corresponding to $[L+Al^{3+}-2H^{+}]^{+}$ was clearly observed when 5 equiv of $Al(ClO_4)_3$ was added to probe SA. According to these results, the probable binding modes of SA with Zn^{2+} and Al^{3+} ions were proposed as shown in Fig. S14.

In conclusion, we report the one-step synthesis and characterization of a new fluorescence chemosensor for the distinct detections of Zn^{2+} and Al^{3+}, and it can be used in pure aqueous solution. An obvious fluorescence turn-on with a slight blue shift (centered at 458 nm) was observed after the addition of Zn^{2+} ion. However, much more significant fluorescence blue shift was achieved for SA-Al^{3+} complex, accompanied with a distinctive intensity enhancement (centered at 376 nm). The detection limit of SA for Zn^{2+} and Al^{3+} are both at the micromolar level without the disturbances from Na^{+}, K^{+}, Mg^{2+}, Ni^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, Pb^{2+}, Fe^{3+} and Cr^{3+}, which is comparable to the recommended maximum contaminant level (MCL) for Zn^{2+} (1.0 mg/L, 15.3 μM) and Al^{3+} (0.2 mg/L, 7.4 μM) in drinking water.

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