

Supplementary information

An Easy and Accessible Water-soluble Sensor for the Distinctive Fluorescence Detection of Zn²⁺ and Al³⁺ ions†

Experimental

Materials and instrumentation

Salicylaldehyde and 2-(2-Aminoethylamino)ethanol were obtained from aladdin-reagent. The solvents were used as received without further purification. Tap water was obtained from tap faucet (Nanshan District, Shenzhen, China. Sampling time: 14:00 on August 18th, 2015). Stock solutions of various cations (1 mM) were prepared using nitrate salts and chloride salts of analytical grade. Stock solution of SA (1 mM) was prepared in Tris buffer (10 mM, pH = 7.0) or tap water. Test solutions were prepared by placing 150 μ L of the probe stock solution into cuvettes, adding an appropriate aliquot of various metal ions solutions, and diluting the solution to 3 mL with Tris buffer (10 mM, pH = 7.0) or tap water. UV-vis spectra were recorded with SCINCO S-4100. A HORIBA Jobin Yvon SPEX spectro fluorimeter was used for fluorescence measurements. The excitation wavelength was 310 nm and the spectra were recorded in the range 330-600 nm. Both ¹H NMR (400 MHz) and ¹³C NMR spectra (100 MHz) of the compound were recorded on a Burkert Dpx spectrometer in CDCl₃ with tetramethylsilane as the internal standard. The high-resolution mass spectrum was performed on Bruker APEX IV.

Synthesis

A ethyl acetate solution (10.0 mL) of 2-(2-Aminoethylamino)ethanol (1.04 g, 10 mmol) was added dropwise to the solution (10 mL) of salicylaldehyde (1.22 g, 10 mmol) in methanol under stirring. Then the mixture was stirred for 3 h at room temperature to afford a yellow residue (the target product SA). SA was obtained via filtration and dried under vacuum in a 93% yield.

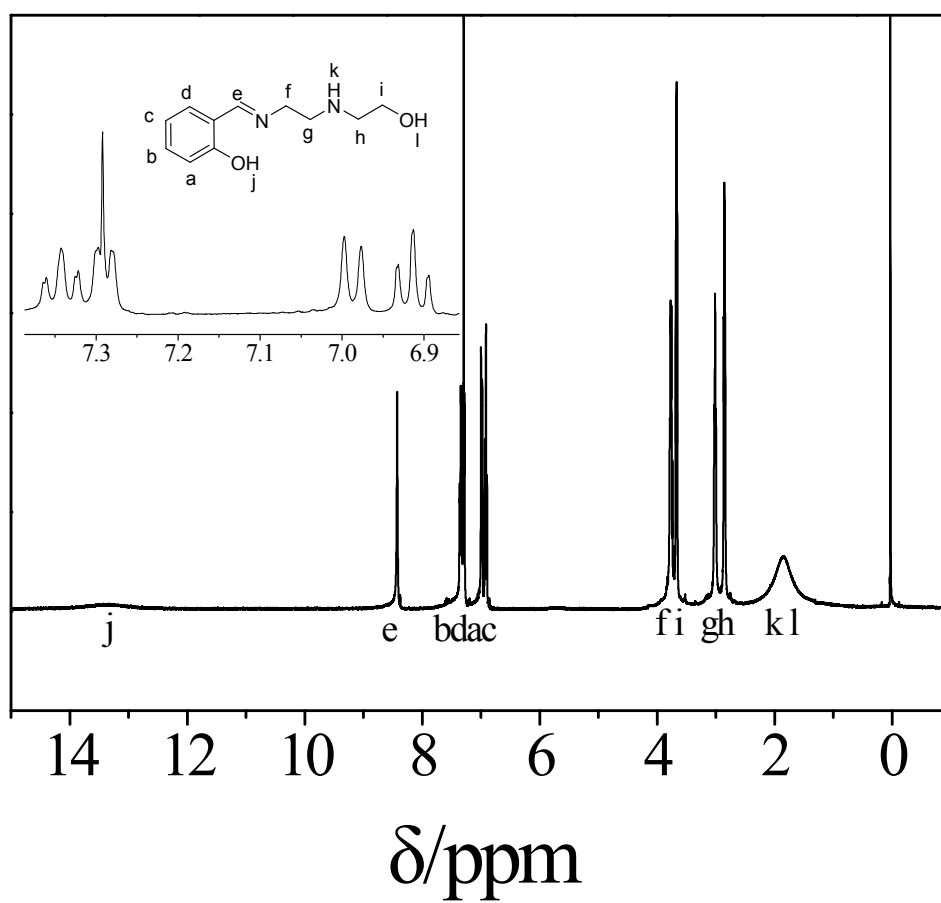


Fig. S1 ^1H NMR spectrum of SA. ^1H NMR (400 MHz, CDCl_3) δ : 13.38 (br, 1H), 8.43 (s, 1H), 7.34 (t, $J = 8.5$ Hz, 1H), 7.29 (d, $J = 6.3$ Hz, 1H), 6.99 (d, $J = 8.2$ Hz, 1H), 6.91 (t, $J = 7.4$ Hz, 1H), 3.82 – 3.73 (m, 2H), 3.71 – 3.64 (m, 2H), 3.06 – 2.97 (m, 2H), 2.92 – 2.81 (m, 2H), 1.87 (br, 2H).

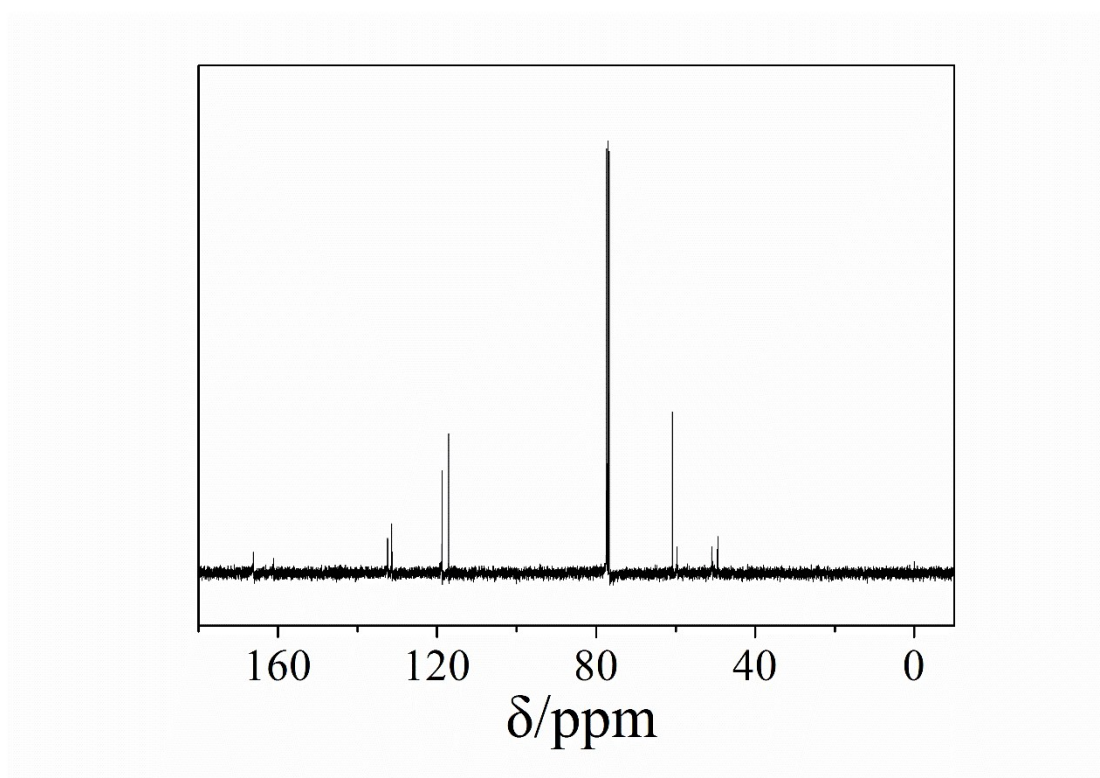


Fig. S2 ¹³C NMR spectrum of SA. ¹³C NMR (100 MHz, CDCl₃) δ: 166.20, 161.16, 132.42, 131.37, 118.71, 117.08, 60.86, 59.70, 50.88, 49.43.

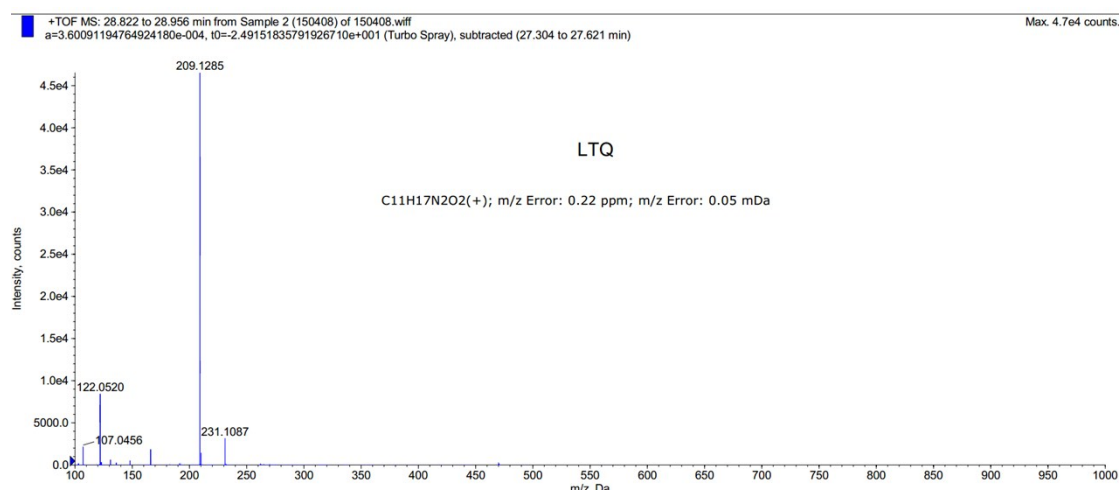


Fig. S3 High-resolution mass spectrum of SA. HRMS (ESI): calcd for C₁₁H₁₇N₂O₂ [SA+H⁺]⁺: 209.1285; found: 209.1285.

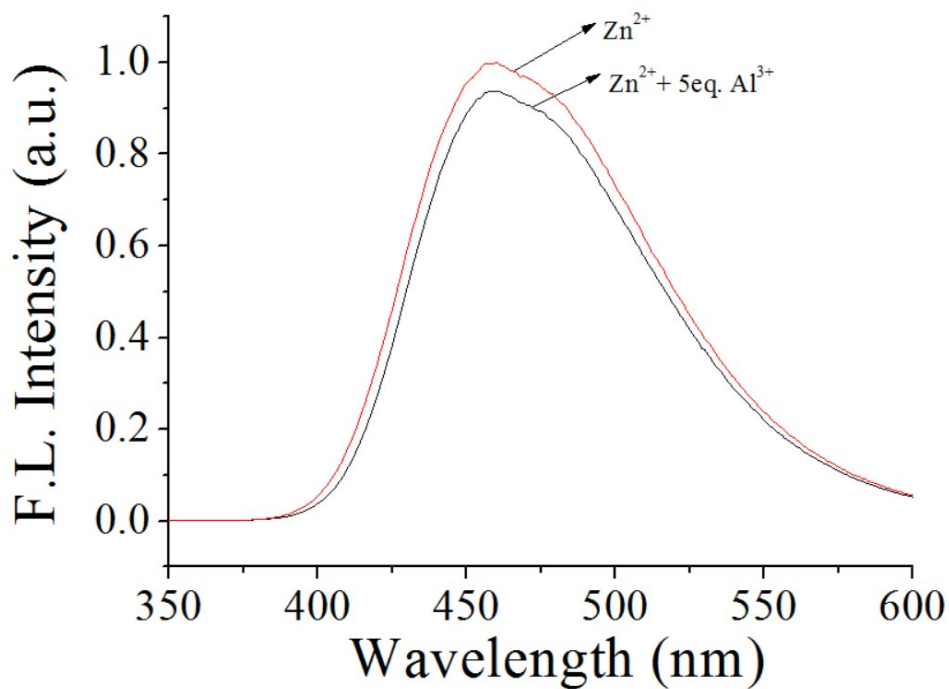


Fig. S4 Fluorescence spectra of SA (50 μ M) in HAC-NaAc buffer (60 mM, pH=6, ω_{NH_4F} =0.02, $\omega_{tartaric\ acid}$ =0.07). The red line represents the fluorescence spectra in the presence of Zn^{2+} ; the black line represents the fluorescence spectra in the presence of Zn^{2+} and 5eq. Al^{3+} .

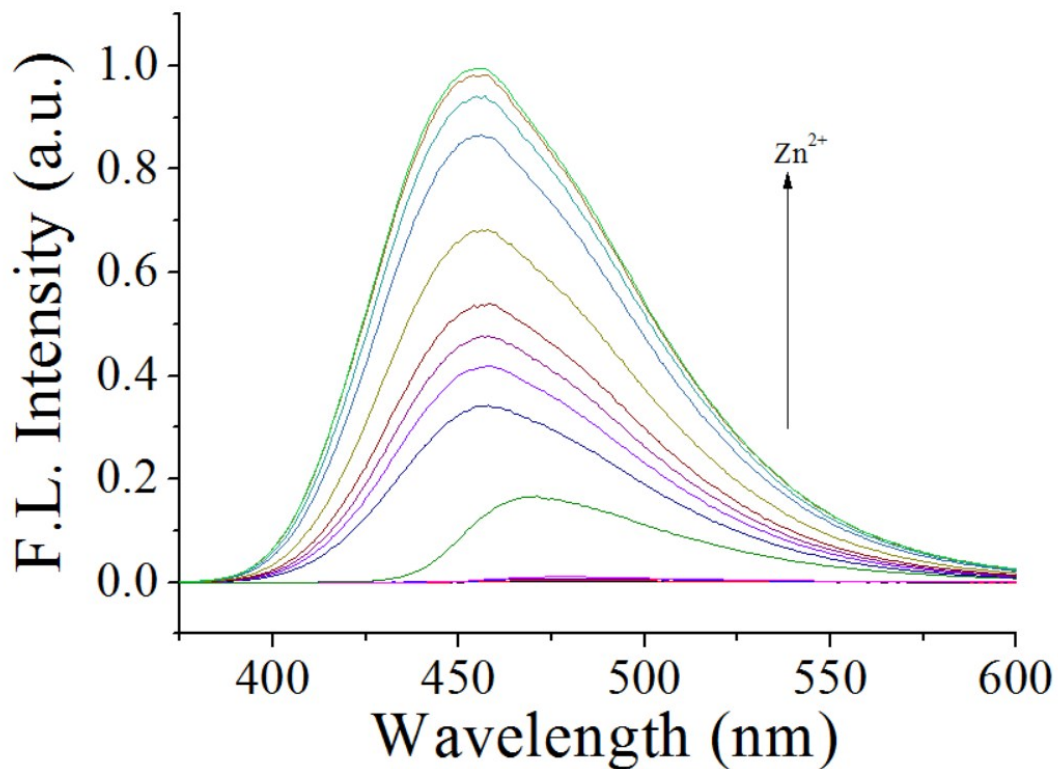


Fig. S5 Fluorescence spectra of SA (50 μ M) in the presence of increasing concentrations of Zn^{2+} in HAC-NaAc buffer (60 mM, pH=6, ω_{NH_4F} =0.02, $\omega_{tartaric\ acid}$ =0.07).

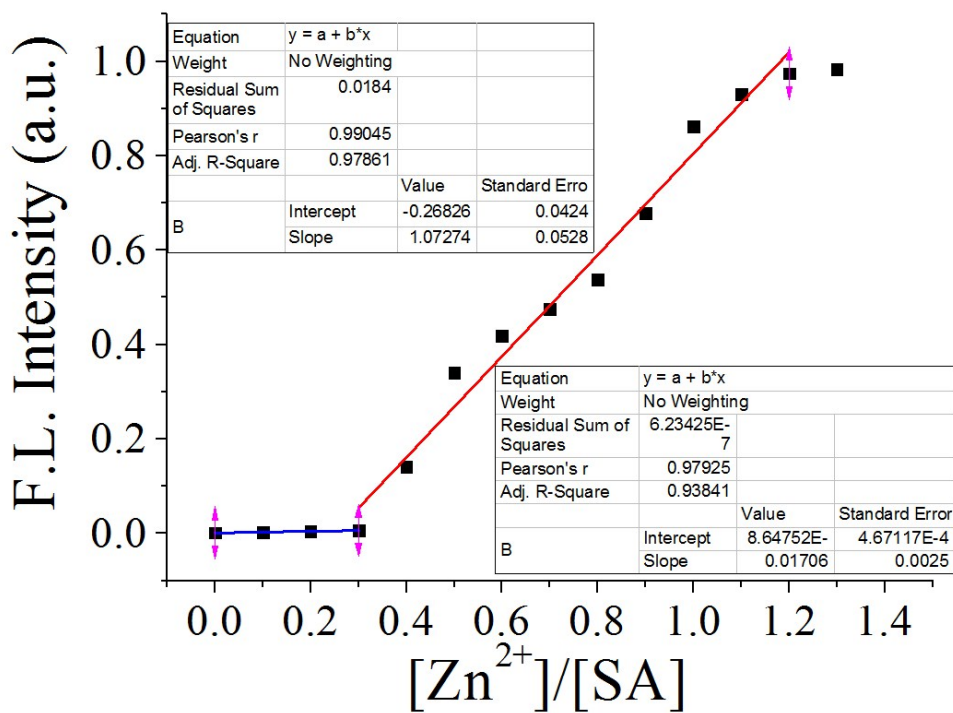


Fig. S6 Fluorescence intensity at 458 nm as a function of $[Zn^{2+}]/[SA]$.

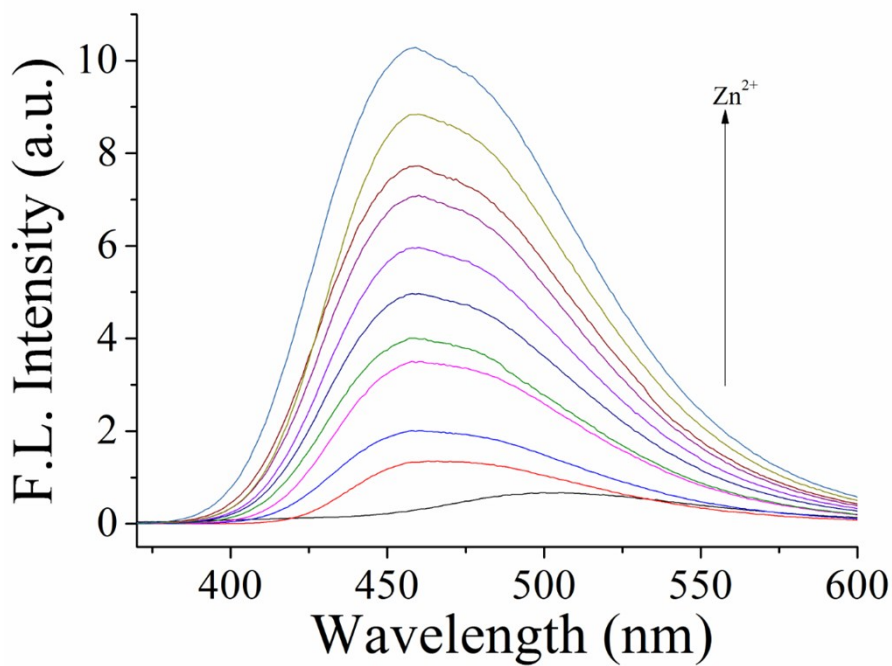


Fig. S7 Fluorescence spectra of SA (50 μ M) in the presence of increasing concentrations of Zn^{2+} in tap water.

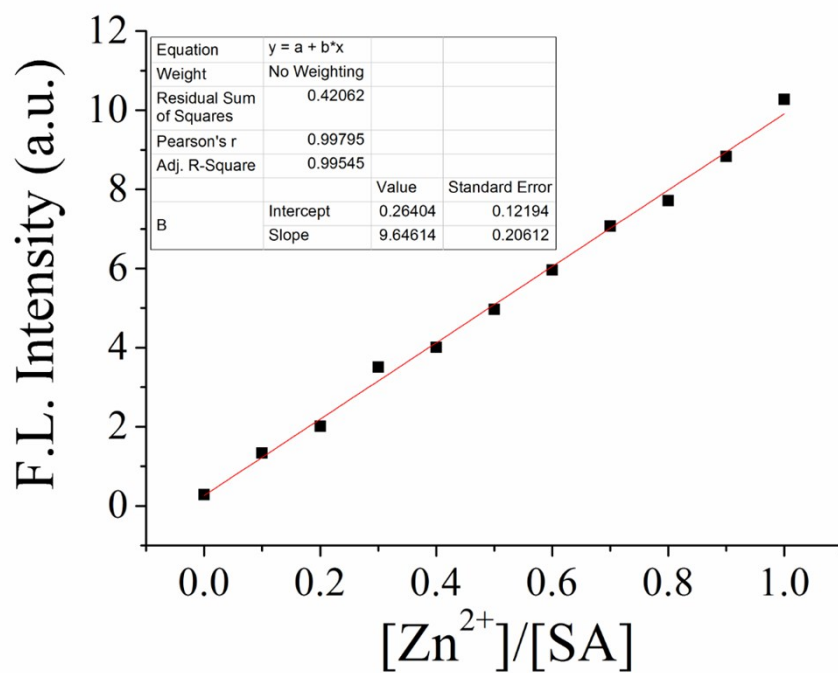


Fig. S8 Fluorescence intensity at 458 nm as a function of $[Zn^{2+}]/[SA]$.

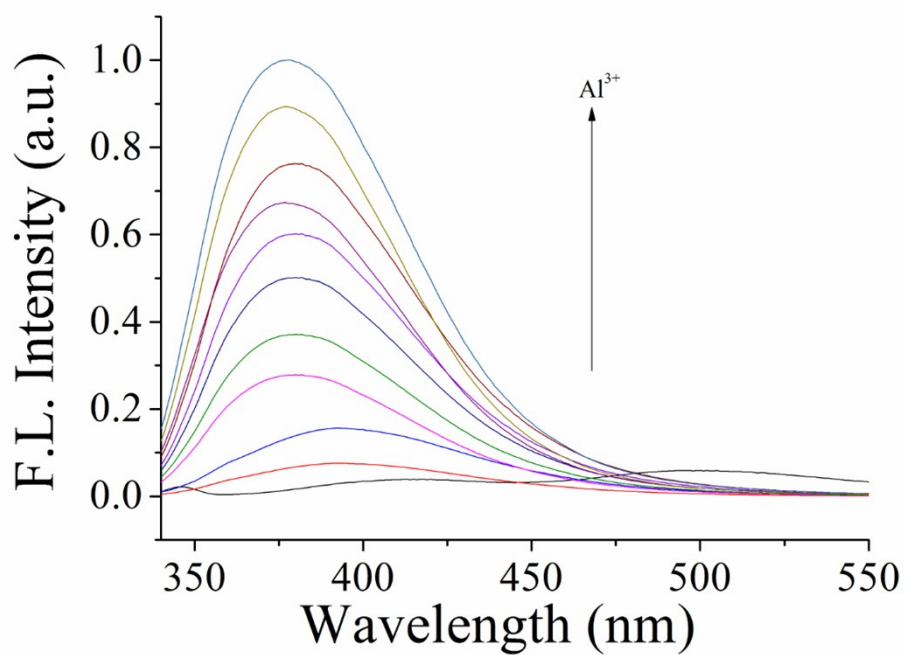


Fig. S9 Fluorescence spectra of SA (50 μ M) in the presence of increasing concentrations of Al^{3+} in tap water.

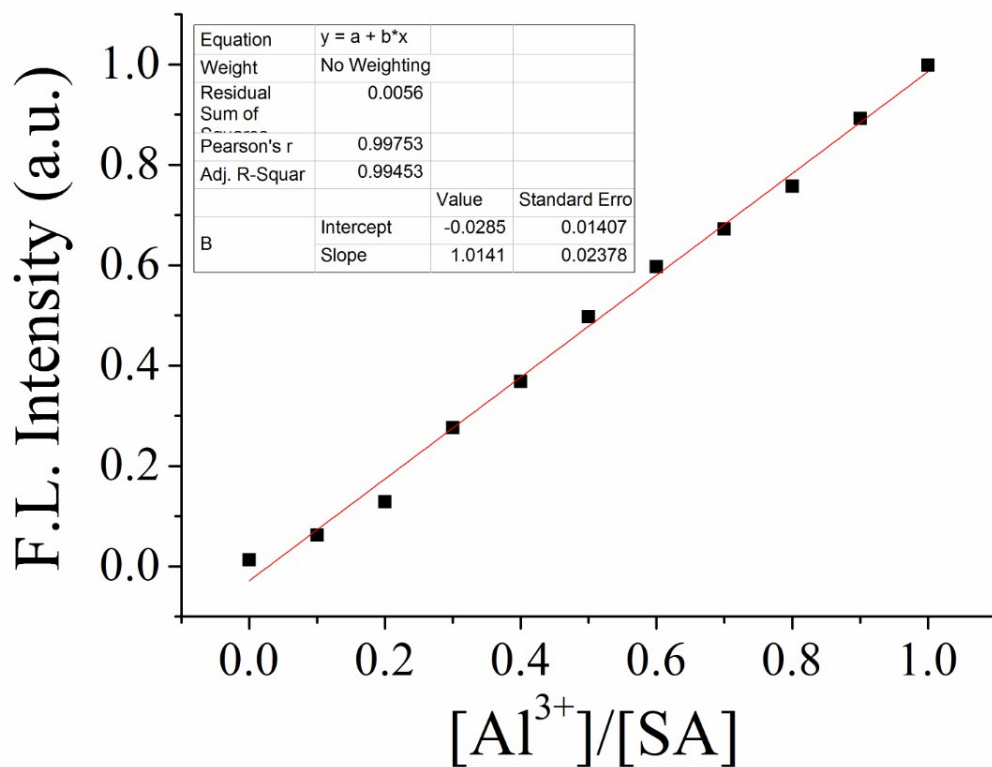


Fig. S10 Fluorescence intensity at 376 nm as a function of $[Al^{3+}] / [SA]$.

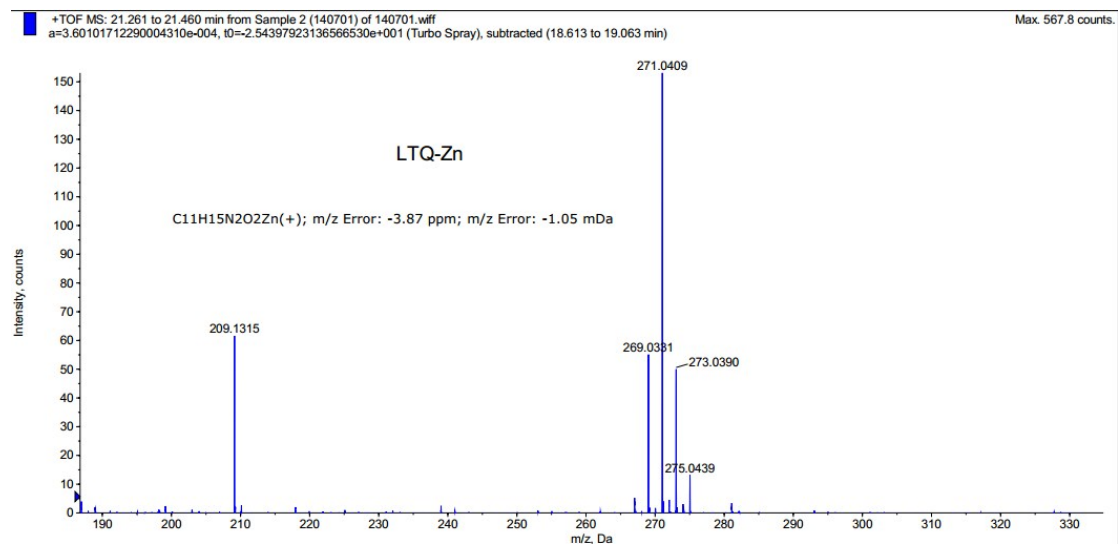


Fig. S11 High-resolution mass spectrum of SA-Zn²⁺ complex. HRMS (ESI): calcd for C₁₁H₁₅N₂O₂Zn [SA+Zn²⁺-H⁺]⁺: 271.0420; found: 271.0409.

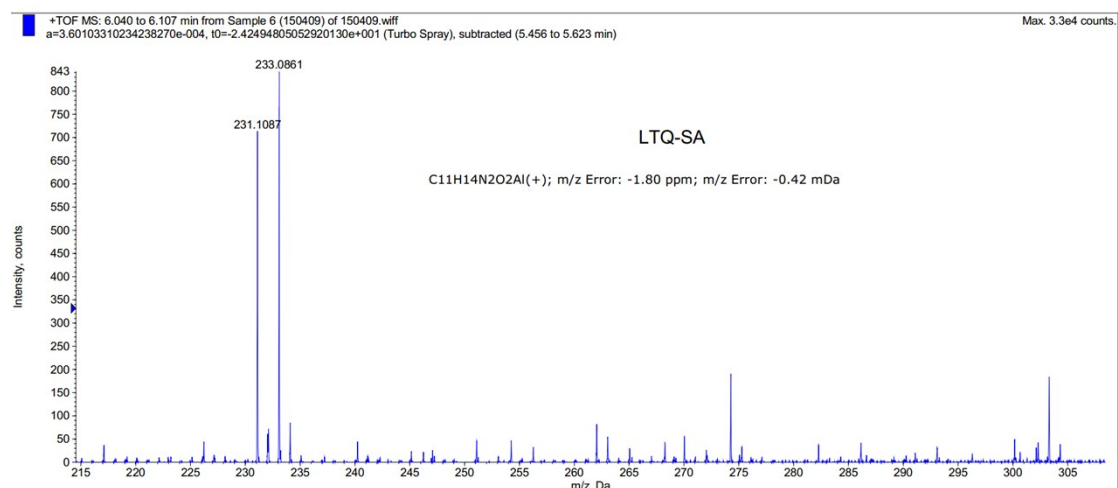


Fig. S12 High-resolution mass spectrum of SA- Al^{3+} complex. HRMS (ESI): calcd for $C_{11}H_{14}N_2O_2Al [SA+Al^{3+}-2H^+]^+$: 233.0865; found: 233.0861.

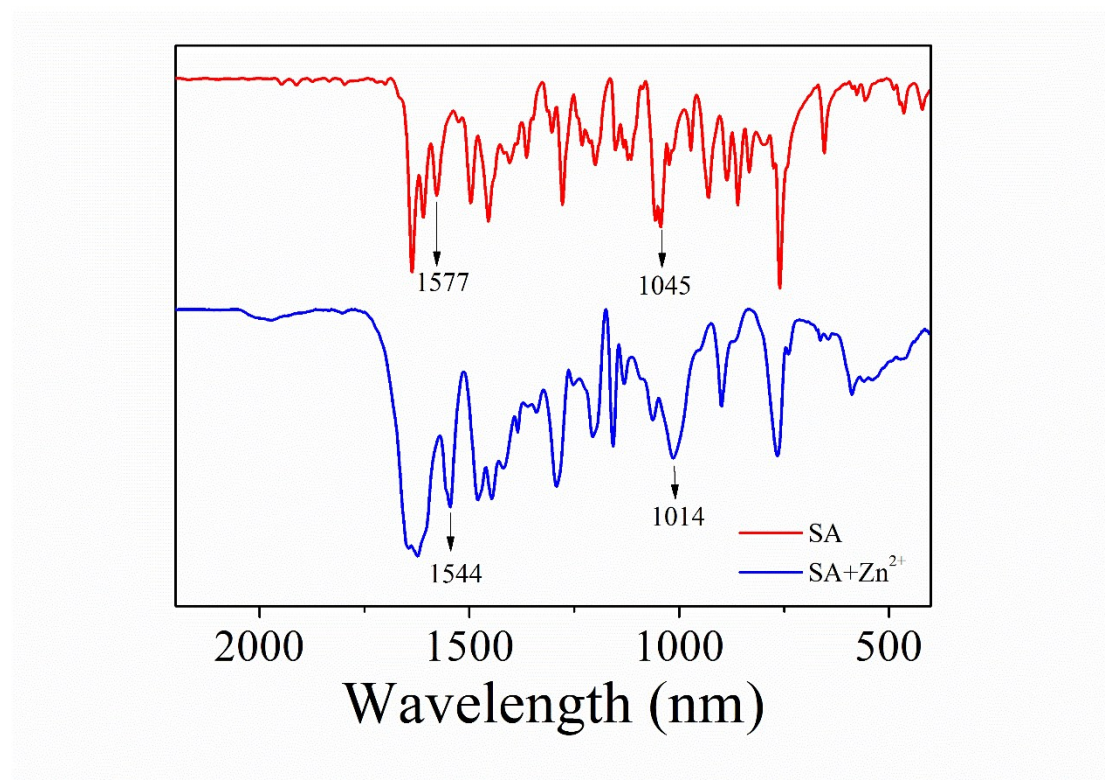
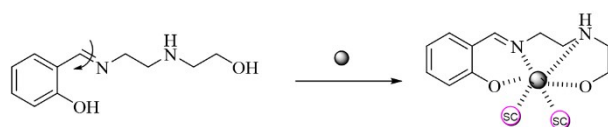




Fig. S13 FT-IR spectra of SA and SA- Zn^{2+} complex.



 Denotes: Zn^{2+} or Al^{3+}

 Denotes: Solution Circumstance

..... Denotes: Interaction between metal ions and other particles, which could provide lone pair electrons, such as anion, solvent molecules, ect.

Fig. S14 Probable binding mode of SA with metal ion