NJC

A novel ratiometric and reversible fluorescence probe based naphthalimide for detection of Al^{3+} and pH with excellent selectivity

Zhuo Li[a,d], Weihong Chen[b], Liuyan Dong[c], Yan Song[a,d], Ronghang Li[e], Qiang Li[a], Dehui Qu[a,d] , Hao Zhang[b], Qingbiao Yang[a*] and Yaoxian Li[a]

Published in NEW JOURNAL OF CHEMISTRY

[a] *College of Chemistry, Jilin University, Changchun 130021, PR China*
[b] *Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun, 130023, PR China*
[c] *School of Chemistry and Environmental Engineering, Changchun University of Science and Technology, Changchun 130022, PR China*
[d] *College of Materials Science and Engineering, Jilin University of Chemical Technology, Jilin 132022, PR China*
[e] *Orthopaedic Medical Center, the Second Hospital of Jilin University, Changchun, 130041, PR China*

目录

Synthesis of compound *1*

A mixture of N-butyl-4-hydroxy-1,8-naphthalimide (270 mg, 1.0 mmol) and 5 hexamethylenetetramine (420 mg, 3.0 mmol) was dissolved in TFA (20 mL). The mixture was stirred and refluxed at 80 ° C for 6 hours. After the reaction was completed, the mixture solution was poured into ice water (200 mL), and the precipitate was filtered and washed with water. The crude product was purified on silica gel (DCM / MeOH = 50: 1) to give a yellow solid with a yield of 70%.

Fluorescence spectra and UV-vis of probe L to pH

The probe L consisted of a naphthalimides fluorophore moiety and a 2-(methylthio)aniline moiety. Naphthalimides functional moieties have specific binding sites for H^+ and OH^- ions (Scheme 1). When the pH value of the solution was increased from pH 8.00 to pH 10.00, the maximum absorption band of probe L was under 450nm (Figure S1a). With the increase of pH, the fluorescence intensity of the probe at 518 gradually increased (Figure S1b). The responding model for probe detection of pH is Turn ON. These results demonstrate probe L could serve as an alkaline pH probe. Results of these studies revealed that the fluorometric response of L toward pH changes from pH 8.00 to 10.00 was mainly based on ICT effect of probe L through the reversible phenol and phenolate change. The linear range for the ratiometric response of probe L was a pH of 8.00 - 10.00, indicating its suitability to practically track pH.

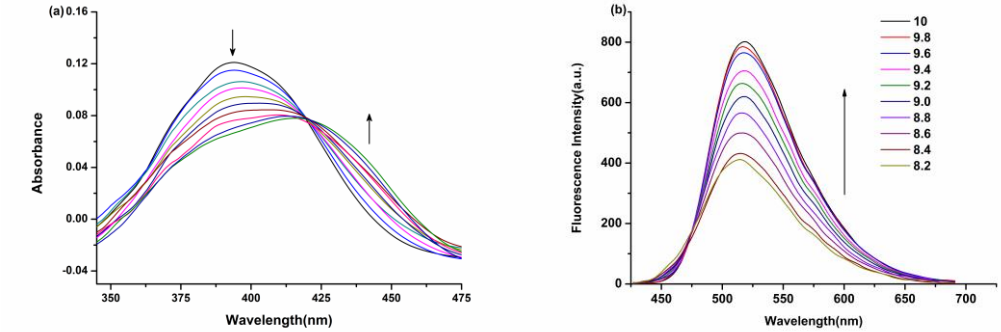


Figure S1. (a) Absorption spectrum of probe L in response to pH value; (b) Fluorescence spectra of probe L in response to pH value (λ_{ex} = 365 nm, slit=5 nm/5 nm, DMSO/Tris = 2/8).

NMR titration of probe L

In order to further verify the recognition mechanism of the probe, we used the probe to carry out the experiment of nuclear magnetic titration of Al^{3+} (figure S2). From the NMR spectra before and after adding Al^{3+}, it could be seen that the hydrogen on carbon 25, 26, 27 and 28 moves to high field after adding Al^{3+}, which indicates that the coordination between the probe and Al^{3+} destroys the original large conjugation of the probe.

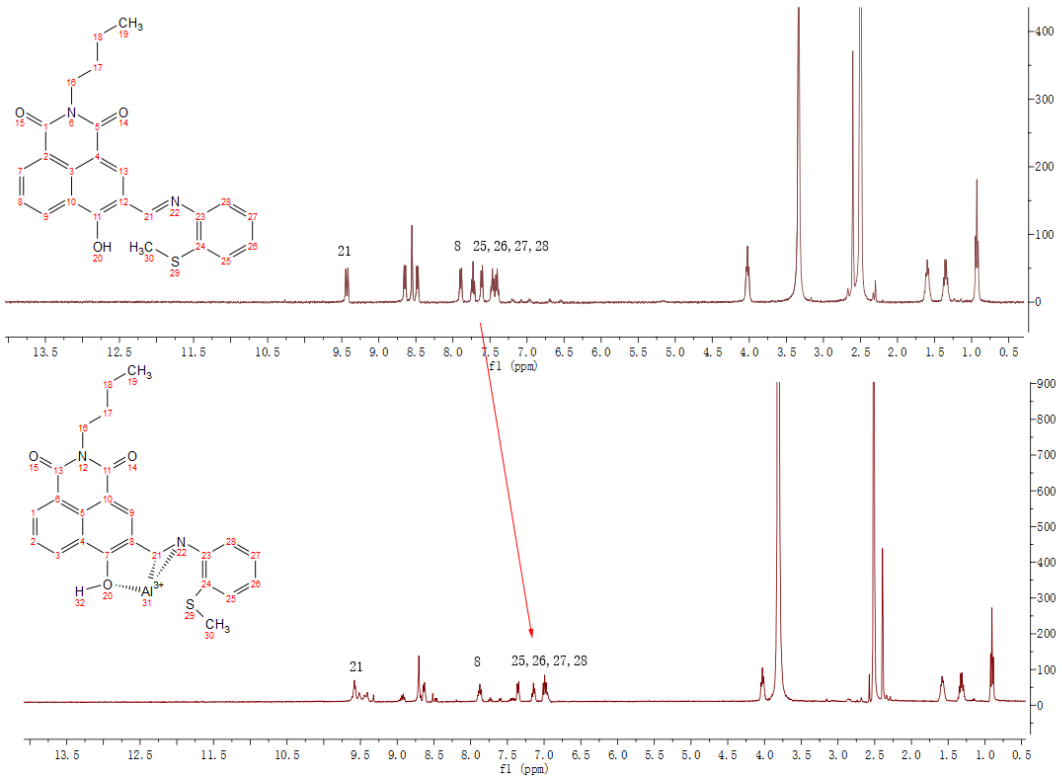


Figure S2. ^{1}H NMR spectra of L, and L-Al^{3+} in DMSO:D_2O = 10:1.

Job's plot

Job-plot for calculating the stoichiometry between probe L with Al^{3+} in DMSO/TRIS buffer solution (2/8, v/v, pH=7.4), the total concentration of L and Al^{3+} was 20 μM. (λ_{ex} = 365 nm).

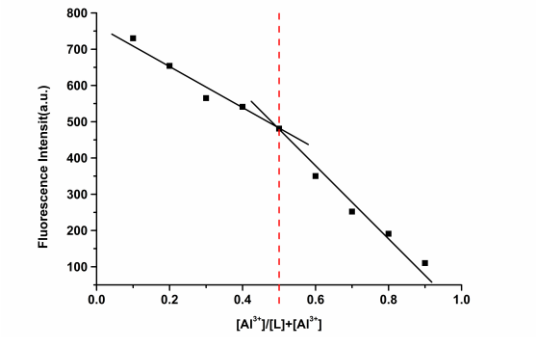


Figure S3. Job-plot for calculating the stoichiometry between probe L with Al^{3+}.

Calculation of the association constant (K_a)

The association constant K_a is determined from the emission intensity data following the Benesi–Hildebrand equation:

$$log\frac{F-F_0}{F_{max}-F}=nlog[M]+logK_a$$

Herein, F_0 is the fluorescence intensity (at 518 nm) of the probe L, F and F_{max} are the fluorescence intensity (at 518 nm) upon addition of Al^{3+} at the intermediate, and at saturation point, respectively. [M] stands for the metal ion concentration. The plot of the linear regression of log[(F − F_0)/(F_{max} − F)] *versus* log[M] yielded the intercept as $logK_a$ and the binding constant K_a = 8.34 × 10^7.

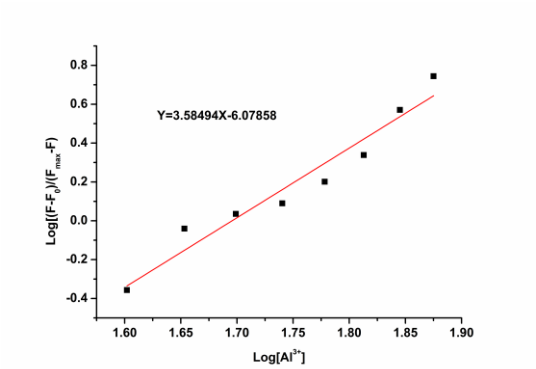


Figure S4. Benesi-Hildebrand plots (λ_{ex} = 365 nm) of Log[(F-F_0)/(F_{max}-F)] versus log [Al^{3+}] for the association base on a 1:1 between probe L and Al^{3+}.

Cytotoxicity of probe L

The results are shown in Figure S5. When the probe reaches 15 μm, the cell survival rate is still above 90%, indicating that the probe L is generally less toxic to cells, and the sensor can be used for intracellular detection.

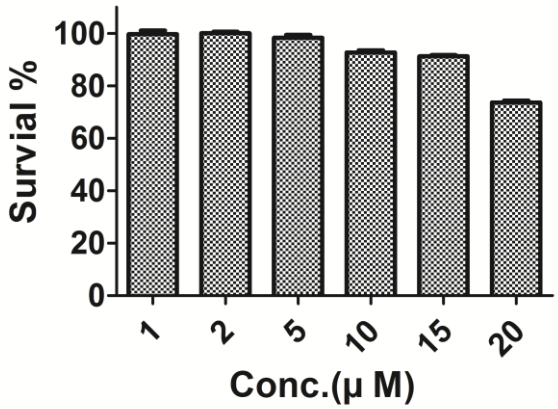


Figure S5. Cytotoxicity of probe L in Hela cells.

Figures:

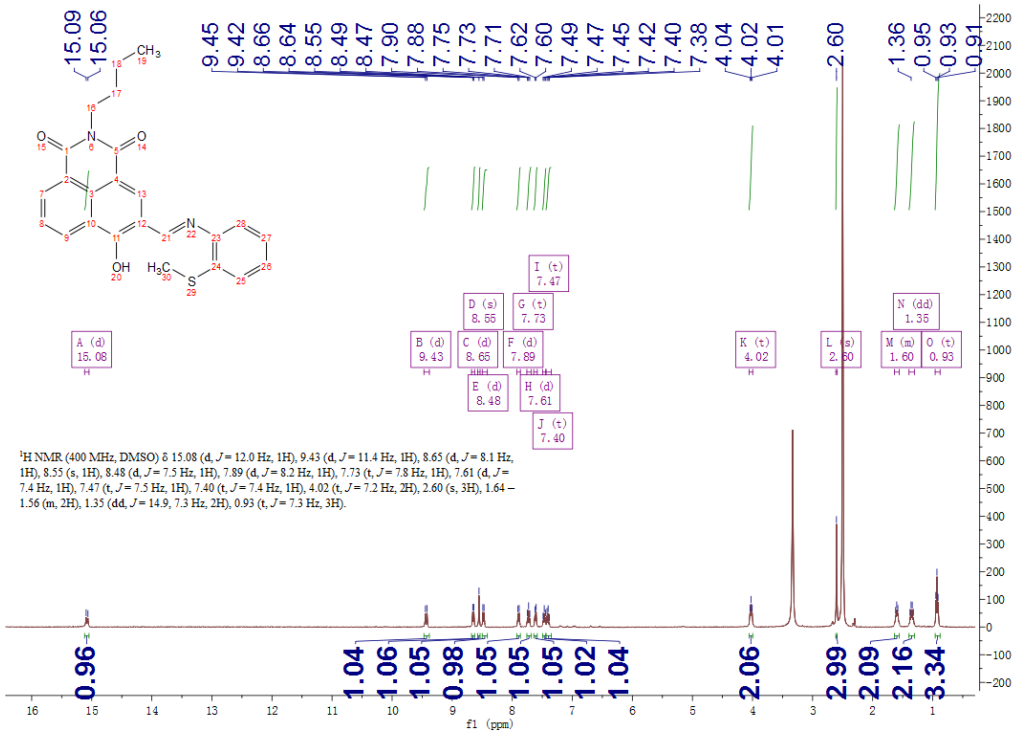


Figure S6. ^{1}H NMR spectra of L in DMSO-d_6.

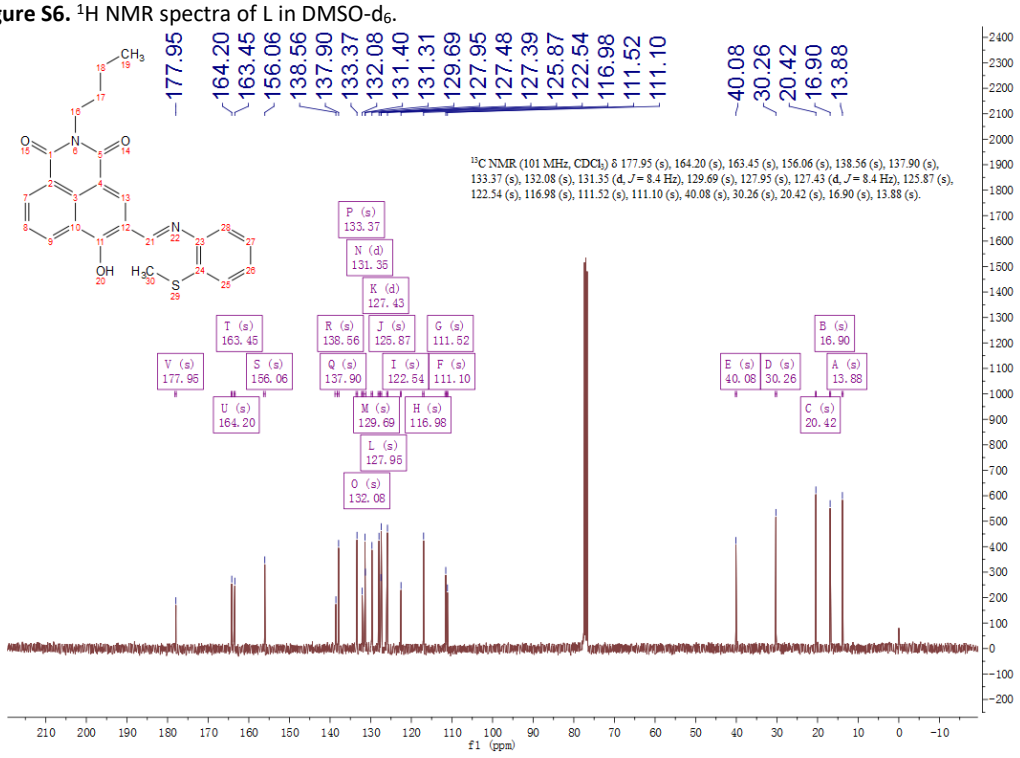
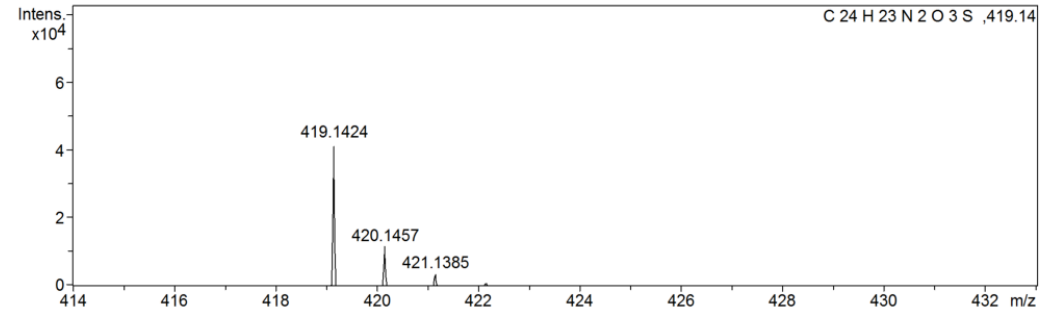


Figure S7. ^{13}C NMR spectra of L in $CDCl_3$.

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e¡¥ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
419.1424	1	C 24 H 23 N 2 O 3 S	419.1424	0.0	-0.0	14.5	ok	even	2.44	0.0048	0.0000	0.0020	0.0000	0.8427

Figure S8. HRMS spectra of probe L.

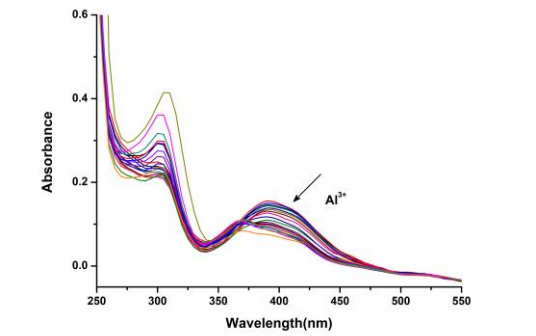


Figure S9. Absorption spectrum of probe L in response to Al^{3+}.

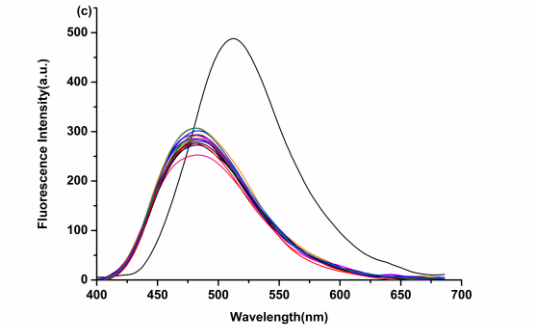


Figure S10. Fluorescence intensity change of probe L upon adding with aluminum ions (475 μM) and other metal ions (1 mM).

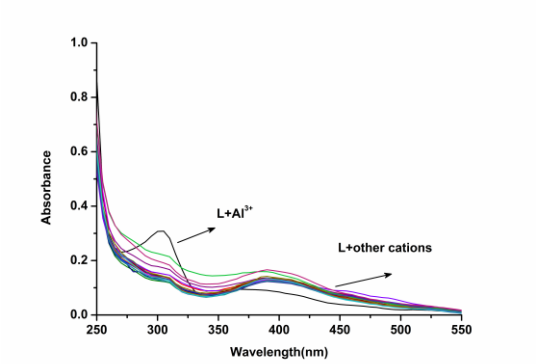


Figure S11. Absorption spectrum of different metal ions after adding the probe L.

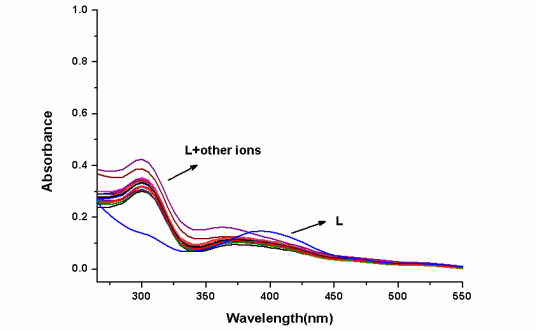


Figure S12. Absorption spectrum of probe L upon adding with aluminum ions (475 μM) and other metal ions (1 mM).

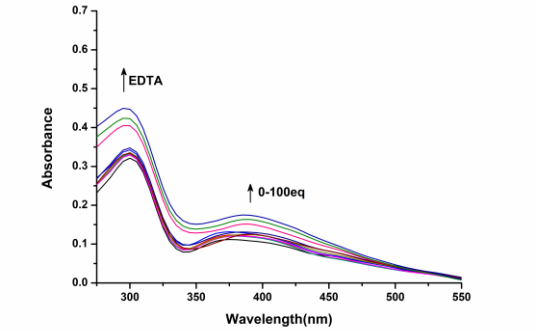


Figure S13. Absorption spectrum of L-Al^{3+} varying concentrations of EDTA were presented in TRIS buffer solutions (pH = 7.4).

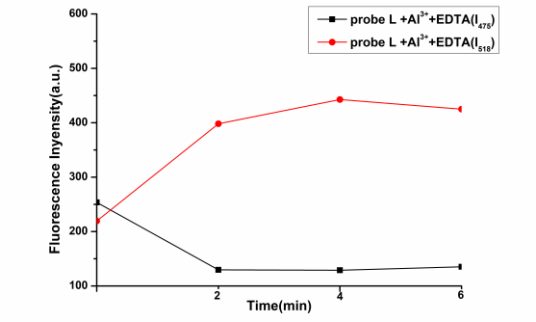


Figure S14. The time required for complete reaction with EDTA after the reaction of probe L and Al^{3+}.

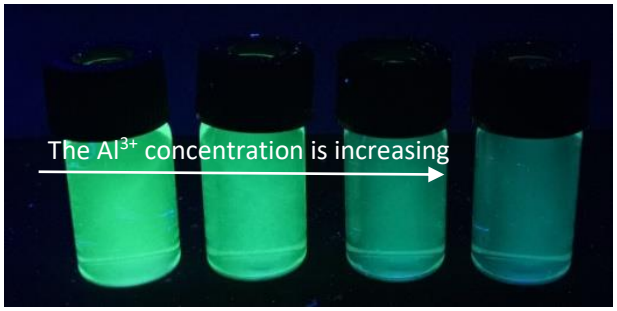


Figure S15. The fluorescence of the probe increased with Al^{3+}.