

## Supporting Information

**Simple pyridyl-salicylimine-based fluorescence “turn-on” sensors for distinct detections of  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{OH}^-$  ions in mixed-aqueous media**

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## Experimental section

### General information

All anhydrous reactions were carried out by standard procedures under nitrogen atmosphere to avoid moisture. The solvents were dried by distillation over appropriate drying agents. Reactions were monitored by TLC plates and column chromatography was generally performed on silica gel.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR were recorded on a 300 MHz spectrometer. The chemical shifts ( $\delta$ ) are reported in ppm and coupling constants (J) in Hz and relative to TMS (0.00) for  $^1\text{H}$  and  $^{13}\text{C}$  R, (s, d, t, q, m, and br mean single, double, ternary, quadruple, multiple, and broad single, respectively), and d-chloroforms (7.26) & (77.0) were used as references for  $^1\text{H}$  and  $^{13}\text{C}$  NMR, respectively. Mass spectra (FAB) were obtained on the respective mass spectrometer. Elemental analysis was carried out by Elemental Vario EL. Absorption and fluorescence spectra were measured on V-670 spectrophotometer and F-4500 fluorescence spectrophotometer, respectively. Fargo Mp-2D melting point apparatus was used to measure the melting ranges of all solid compounds. Identification and purity of the compounds **F1**, **F2** and **F3** were characterized by NMR ( $^1\text{H}$  &  $^{13}\text{C}$ ), Mass (FAB), and melting point measurements. Time-resolved photoluminescence (TRPL) spectra were measured using a home-built single photon counting system. Excitation was performed using a 350 nm diode laser (Picoquant PDL-200, 50 ps fwhm, 2 MHz). The signals collected at the excitonic emissions of solutions were connected to a time-correlated single photon counting card (TCSPC, Picoquant Timeharp 200). The emission decay data were analyzed with the biexponential kinetics in which two decay components were derived. The lifetime values ( $\tau_1$  and  $\tau_2$ ) and pre-exponential factors ( $A_1$  and  $A_2$ ) were determined and summarized. 1-14 pH buffers were freshly prepared as per the literature.<sup>1</sup>

### Sensor titrations

Compounds **F1**, **F2**, and **F3** were dissolved in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (6/4 and 3/7) at  $1 \times 10^{-5}$  M concentration.  $\text{Li}^+$ ,  $\text{Ag}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Cs}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{In}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  metal cations were dissolved in water medium at  $1 \times 10^{-4}$  M concentration from their respective chloro compounds, and  $\text{Ag}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Hg}^{2+}$  and  $\text{Mg}^{2+}$  were made from  $\text{AgNO}_3$ ,  $\text{Mn}(\text{OAc})_2$ ,  $\text{Eu}(\text{OAc})_3$ ,  $\text{Hg}(\text{OAc})_2$  and  $\text{MgSO}_4$ , respectively, in water medium at  $1 \times 10^{-4}$  M concentration. (Metal ion mixtures contained all above ions, except  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$  ions). Ethylene diamine tetra acetic acid (EDTA) was dissolved in  $\text{H}_2\text{O}$  at  $1 \times 10^{-5}$  M. All  $\text{OH}^-$ ,  $\text{BH}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^-$ ,  $\text{ClO}_4^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  anions were dissolved in water medium at  $1 \times 10^{-3}$  M from their respective tetra butyl ammonium salts. (Anion mixtures contained all above ions, except  $\text{OH}^-$  ion).

### NMR titrations and mass spectra

1 equiv. of **F1**, **F2** and **F3** in  $\text{CD}_3\text{CN}$  were titrated with 1 equiv. of  $\text{Zn}^{2+}$  or  $\text{Al}^{3+}$  in  $\text{D}_2\text{O}$  and also titrated with 1:1 ratiometrically (each 3 equiv.) mixed with  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$  ions in  $\text{D}_2\text{O}$  and those NMR samples were stirred at  $70^\circ\text{C}$  for 2 days, after complete evaporation of the solvent it was dried in vacuum at  $50^\circ\text{C}$  for 3 hrs. The fine powders obtained were further investigated via Mass (FAB) spectra to confirm the complex formation. Similarly,  $\text{OH}^-$  anion was investigated by titrating 5 equiv. of tetra butyl ammonium hydroxide (TBAOH) in  $\text{D}_2\text{O}$  with 1 equiv. of **F1** or **F2** or **F3** in  $\text{CD}_3\text{CN}$ , and because of the hygroscopic nature of TBAOH, the NMR samples were immediately analyzed by mass (FAB) spectra without further drying.

### General procedure for the synthesis of **F1**, **F2** and **F3**

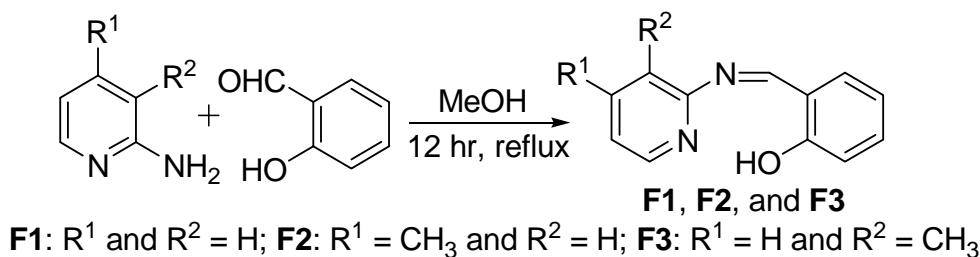
To 1 equiv. of 2-amino pyridyl derivatives [5 g; 53.13 mmol (**F1**) and 46.24 mmol (**F2** and **F3**)] in 50 ml of methanol, 1 equiv. of salicylaldehyde [6.5 g, 53.22 mmol (**F1**) and 5.65 g, 46.26 mmol (**F2** and **F3**)] was added with constant stirring under nitrogen and then refluxed for 12 hrs. The reaction was monitored by TLC. After completion, the reaction mixtures were cooled and the

solvent was evaporated to give the crude products, which were recrystallized from ethanol to afford pure compounds (**F1**, **F2** and **F3**).

*2-((pyridin-2-ylimino)methyl)phenol (F1)*: Dark yellow solid; 10.11 g; 96% yield; M.P = 65-67°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 6.90 – 7.18 (m, 2H), 7.20 – 7.48 (m, 4H), 7.71 (t, *J* = 9.0 Hz, 1H), 8.47 (d, *J* = 6.0 Hz, 1H), 9.40 (s, 1H), 13.44 (s, 1H (-OH)); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>) δ: 117.16, 118.89, 119.15, 120.50, 133.41, 133.77, 138.40, 148.86, 157.46, 161.77, 164.66; FAB: *m/z* = 198 (M<sup>+</sup>, 100%). Anal. Calcd for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O: C, 72.71; H, 5.08; N, 14.13. Found: C, 72.54; H, 5.06; N, 14.12.

*2-((4-methylpyridin-2-ylimino)methyl)phenol (F2)*: Bright yellow crystals; 9.62 g; 98% yield; M.P = 102-104°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 2.37 (s, 3H), 6.90 – 7.12 (m, 4H), 7.35 – 7.46 (m, 2H), 8.33 (d, *J* = 6.0 Hz, 1H), 9.40 (s, 1H), 13.49 (s, 1H (-OH)); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>) δ: 20.86, 117.13, 118.91, 119.07, 121.08, 123.55, 133.31, 133.63, 148.47, 149.80, 157.47, 161.77, 164.47; FAB: *m/z* = 212 (M<sup>+</sup>, 100%). Anal. Calcd for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.50; H, 5.67; N, 13.18.

*2-((3-methylpyridin-2-ylimino)methyl)phenol (F3)*: Bright yellow powder; 9.52 g; 97% yield; M.P = 81-83°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 2.49 (s, 3H), 6.96 – 7.19 (m, 3H), 7.53 – 7.61 (m, 3H), 8.36 (d, *J* = 6.0 Hz, 1H), 9.43 (s, 1H), 13.79 (s, 1H (-OH)); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>) δ: 17.65, 117.17, 119.14, 122.61, 124.71, 128.50, 133.38, 133.76, 139.48, 146.31, 155.79, 162.01, 163.87; FAB: *m/z* = 212 (M<sup>+</sup>, 100%). Anal. Calcd for C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.52; H, 5.68; N, 13.19.



**Scheme S1** Synthesis of **F1**, **F2** and **F3**.

## References

- (1) R. A. Robinson, R. H. Stokes, *"Electrolyte solutions"* 2nd ed., rev. 1968, London, Butterworth.
- (2) G. Gryniewicz, M. Poenie and R. Y. Tsein, *J. Biol. Chem.*, 1985, **260**, 3440.
- (3) D. Maity and T. Govindaraju, *Chem. Commun.*, 2012, **48**, 1039.

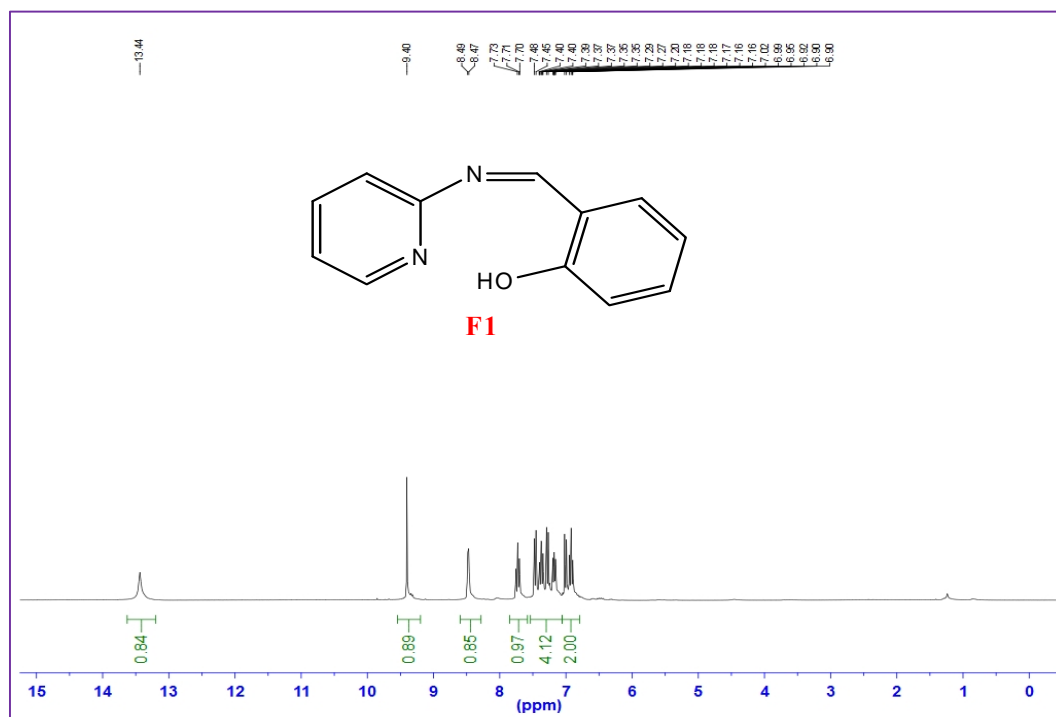


Figure S1 <sup>1</sup>H NMR spectrum of **F1**.

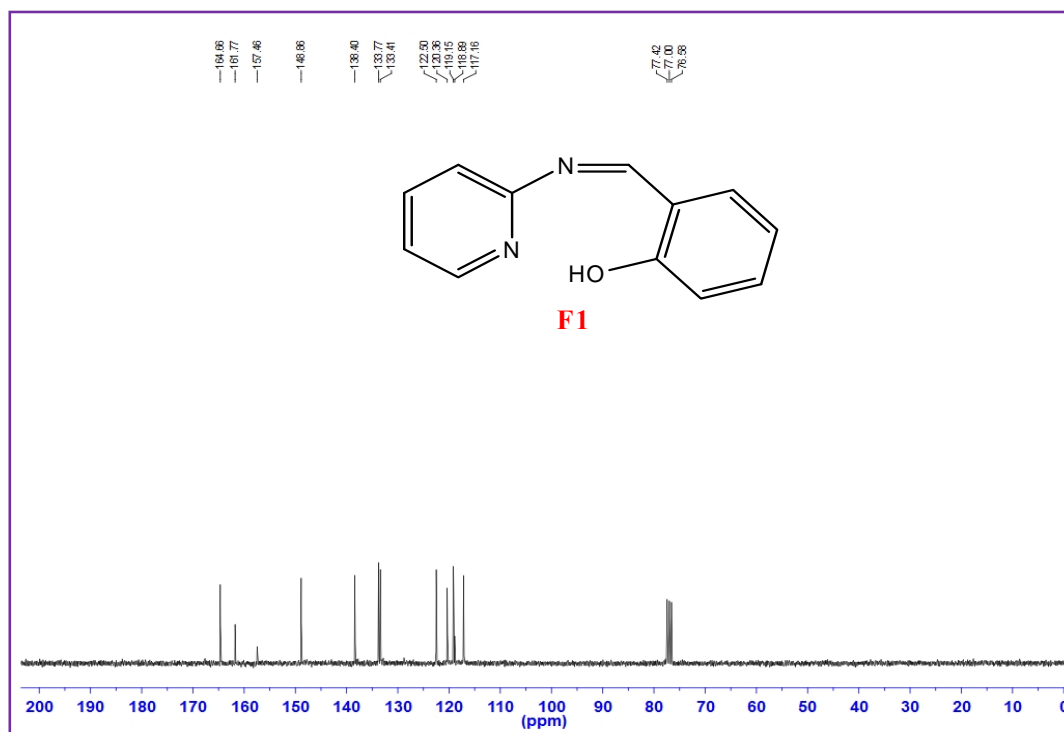


Figure S2 <sup>13</sup>C NMR spectrum of **F1**.

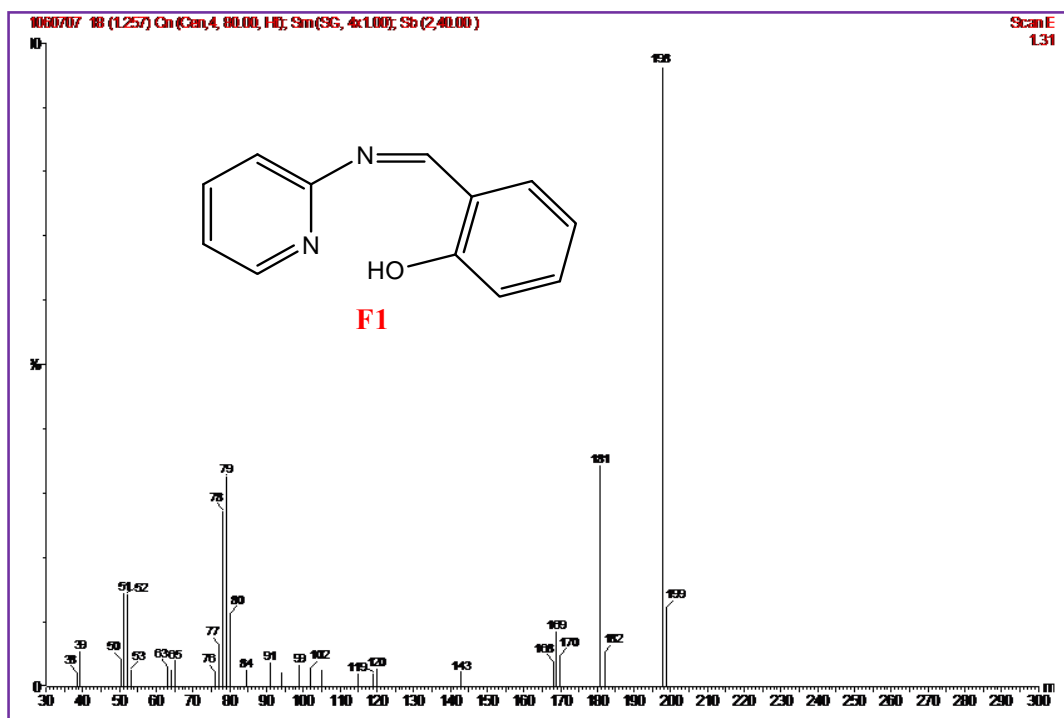


Fig. S3 Mass (FAB) spectrum of F1.

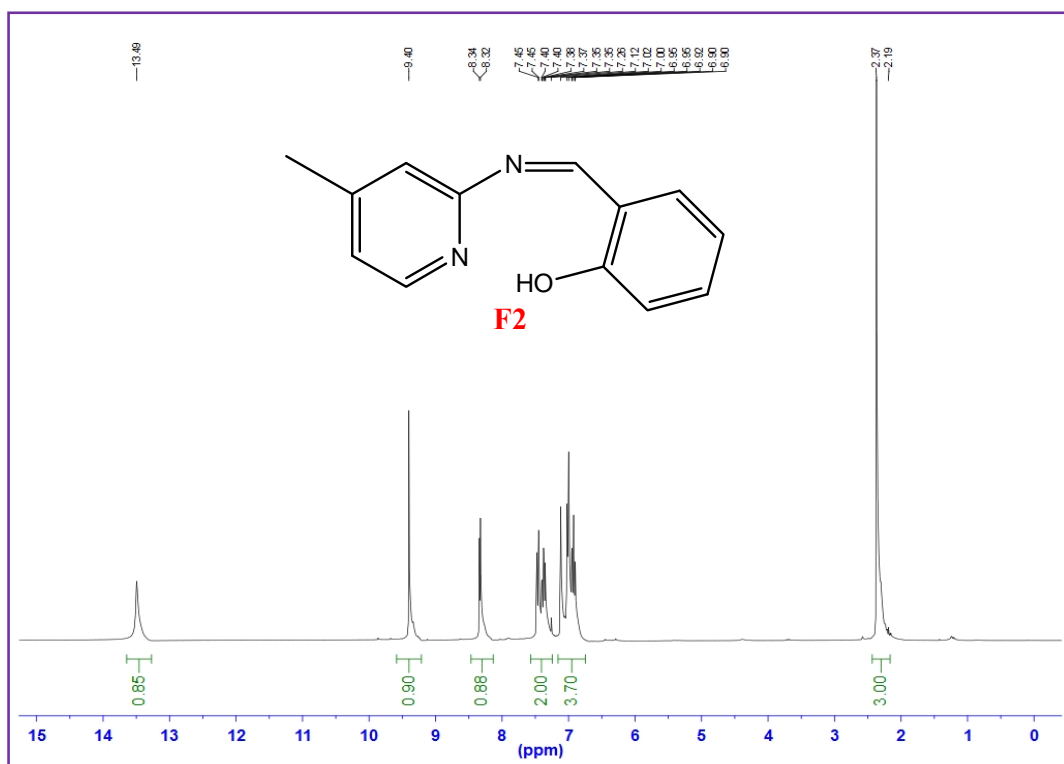


Fig. S4  $^1\text{H}$  NMR spectrum of F2.

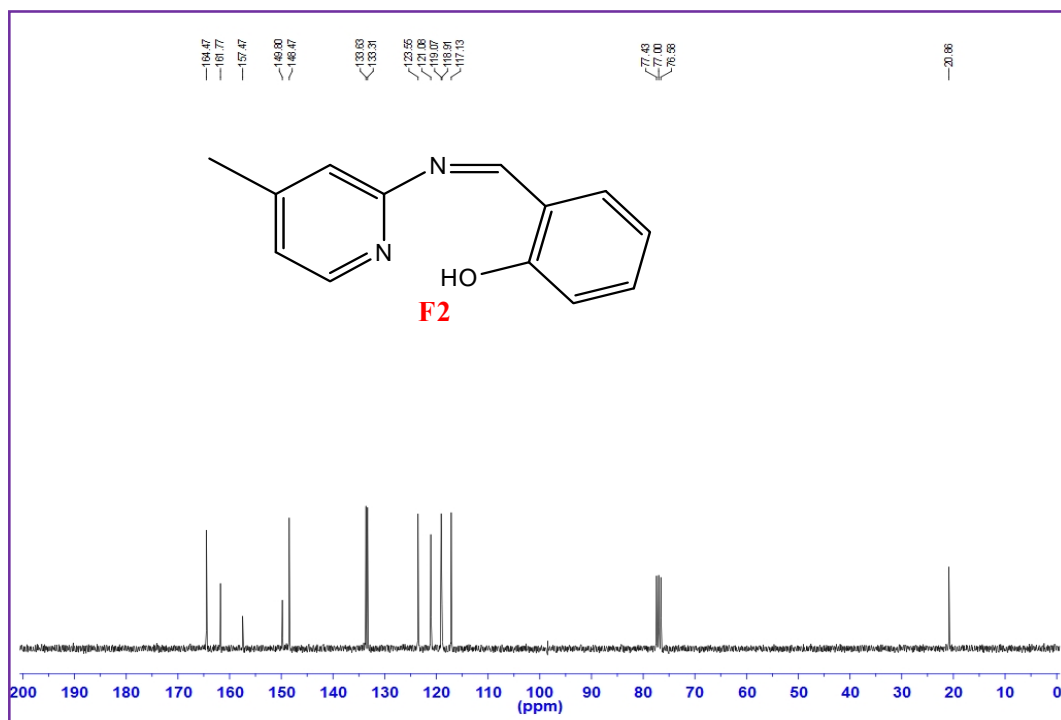


Fig. S5  $^{13}\text{C}$  NMR spectrum of F2.

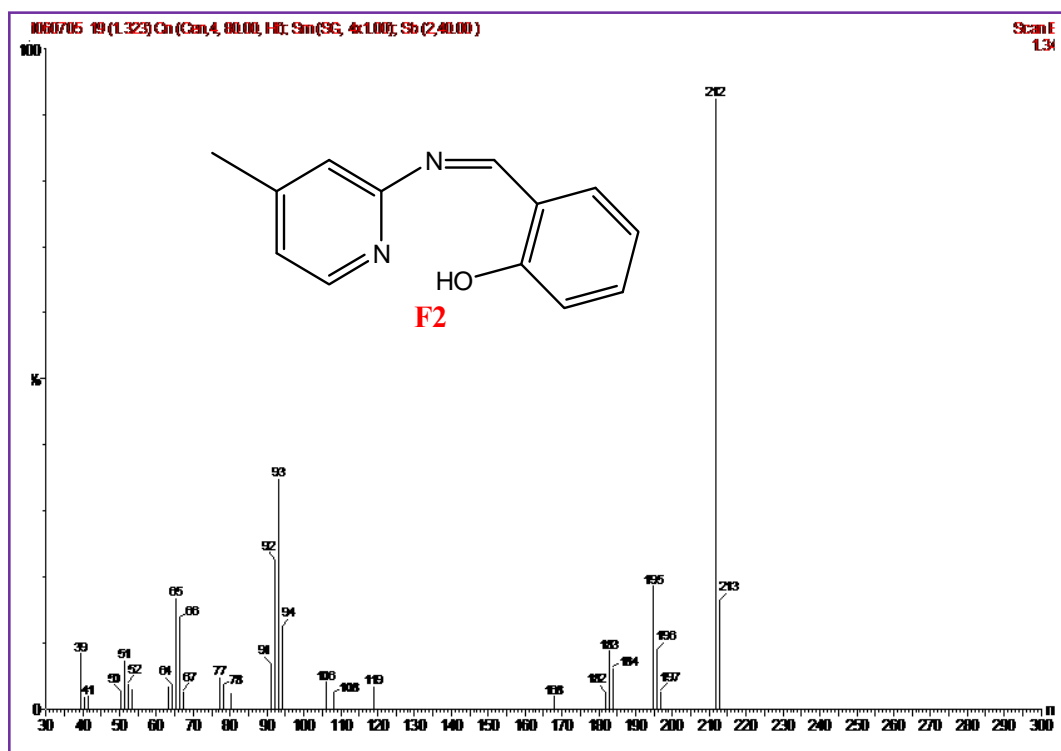


Fig. S6 Mass (FAB) spectrum of F2.

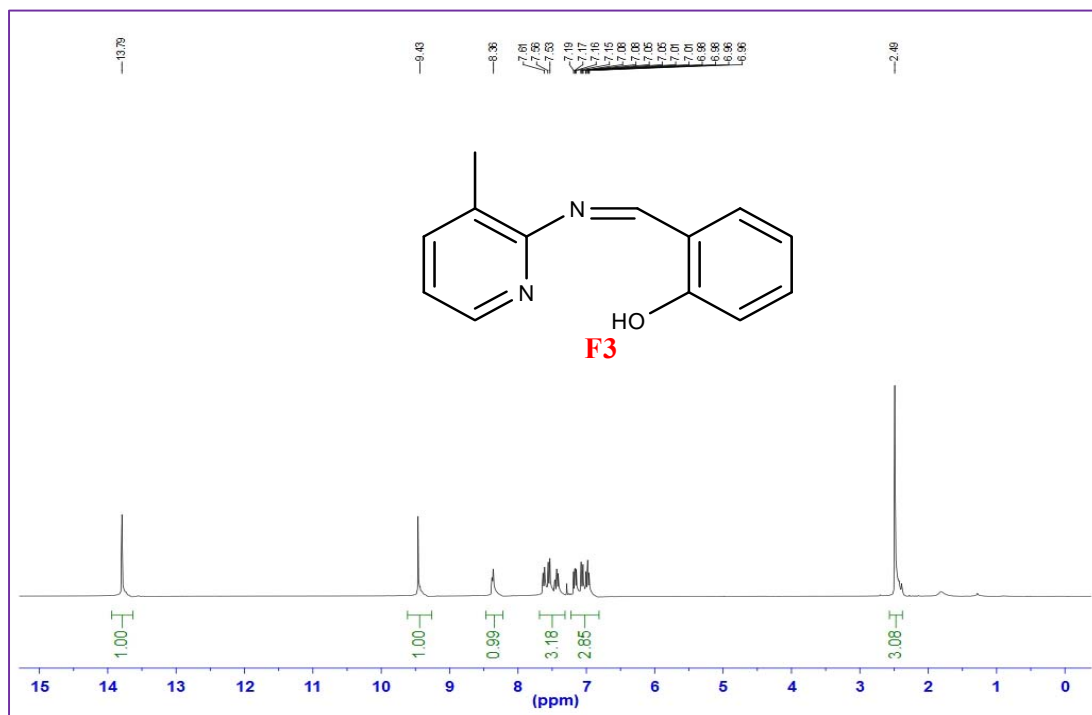


Fig. S7 <sup>1</sup>H NMR spectrum of F3.

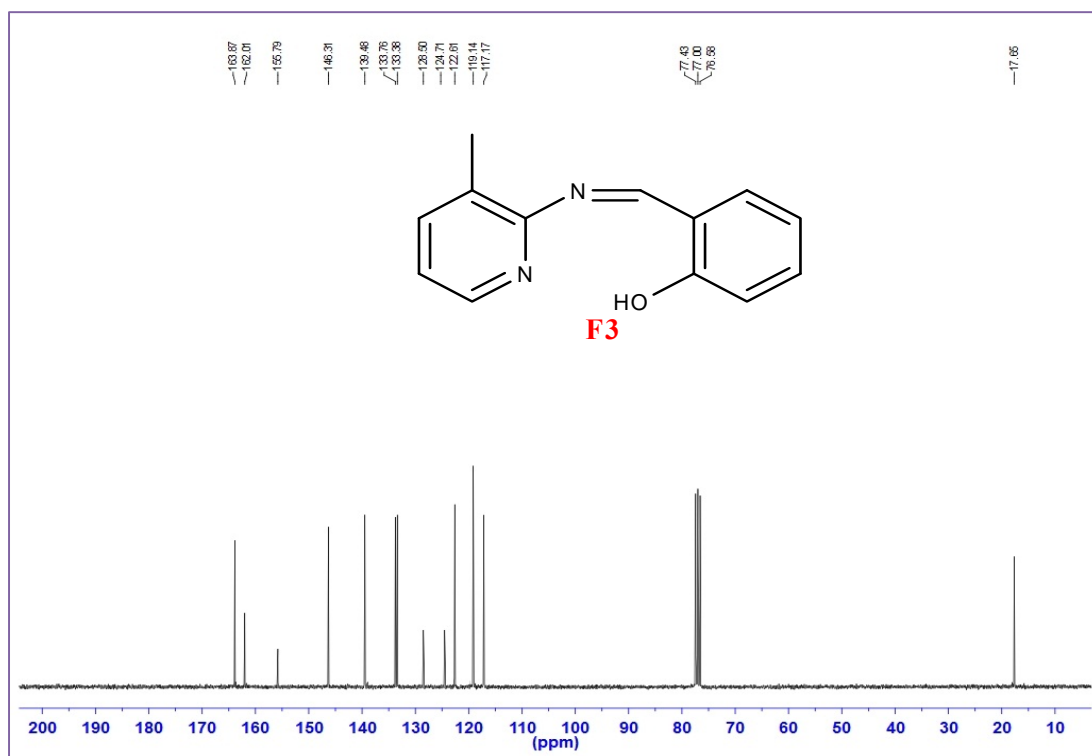


Fig. S8 <sup>13</sup>C NMR spectrum of F3.



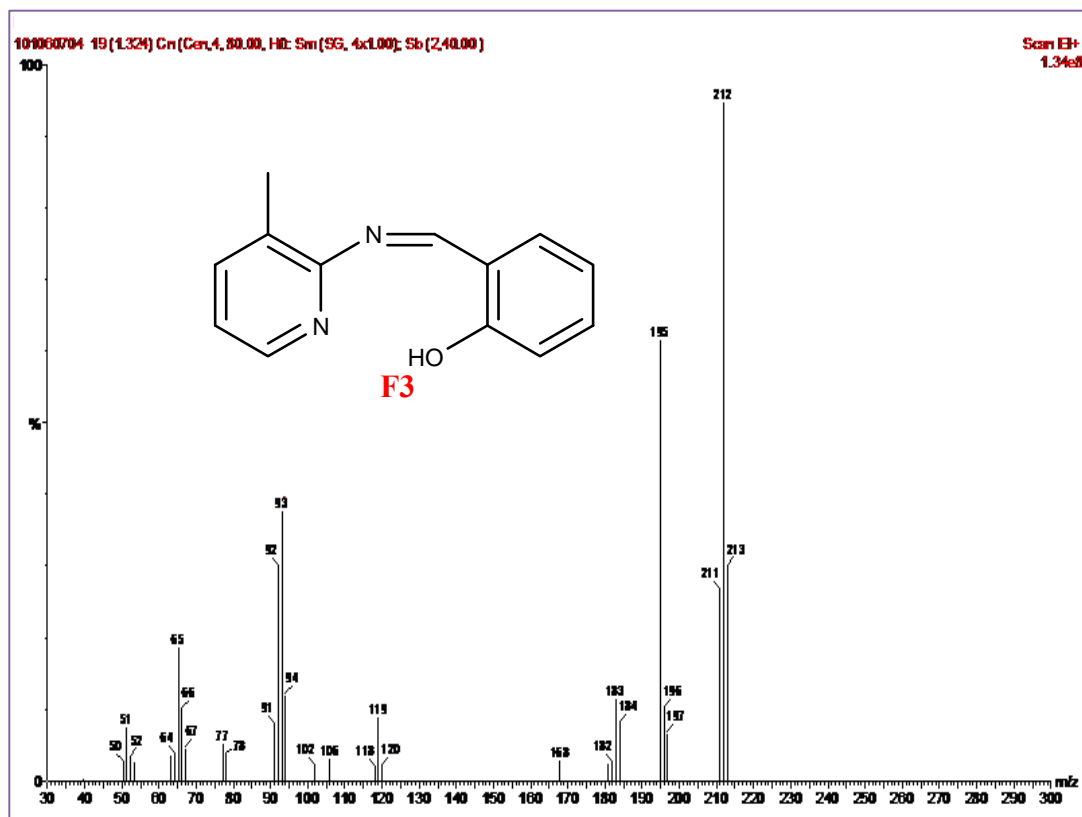


Fig. S9 Mass (FAB) spectrum of F3.

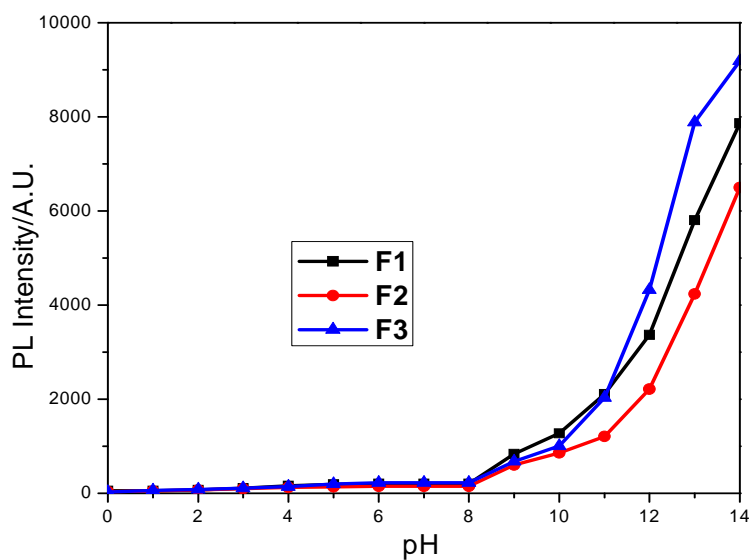
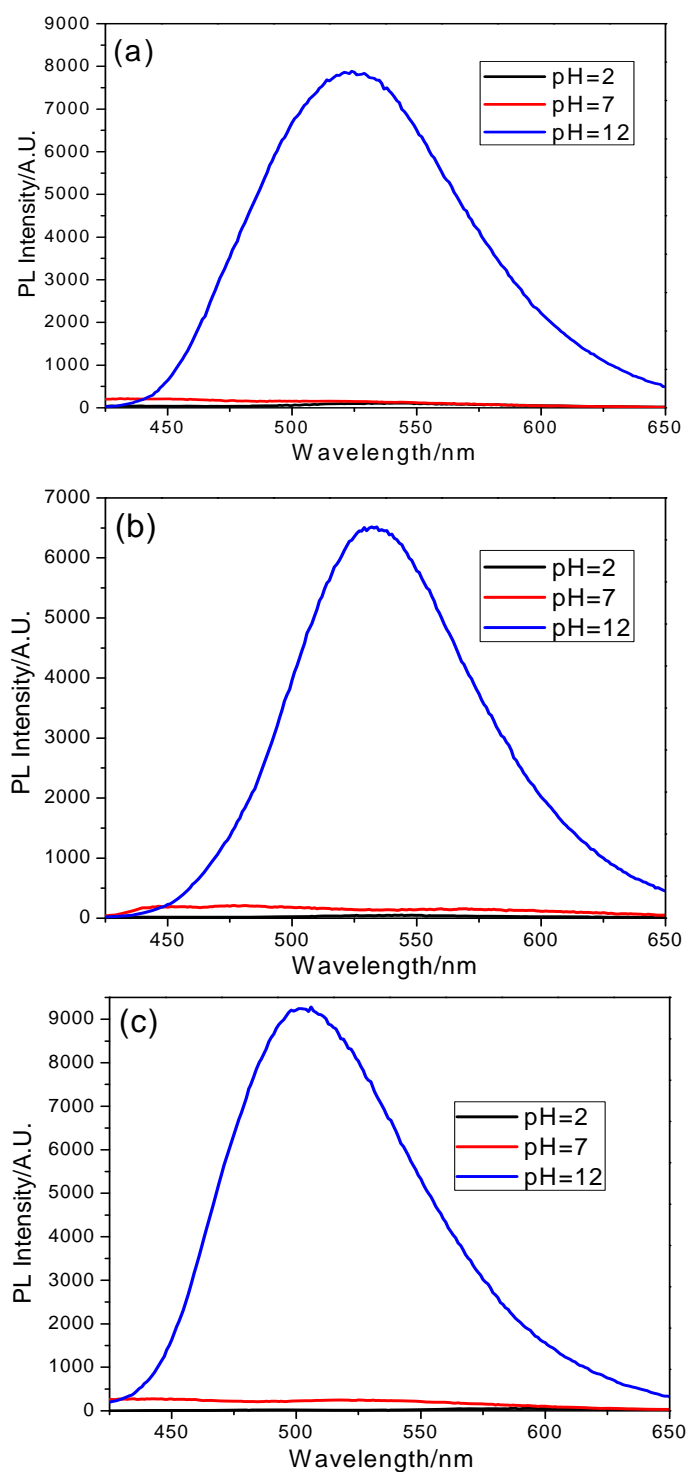
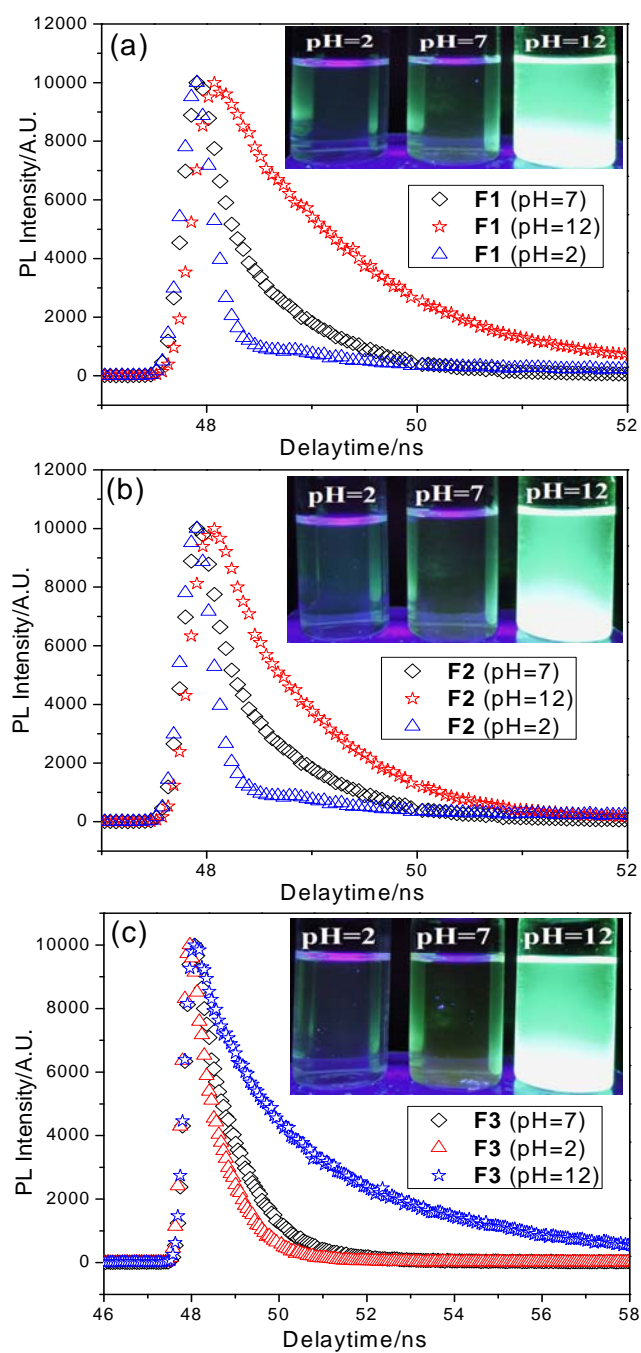


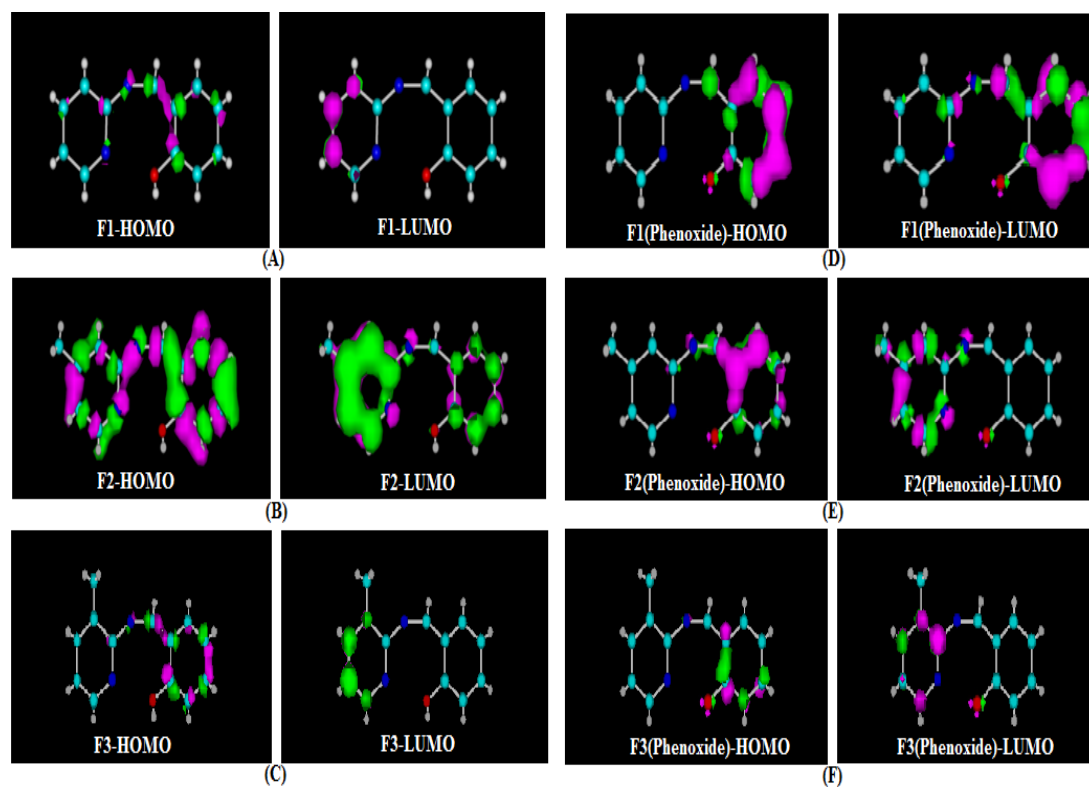
Fig. S10 PL spectral responses of (a) F1, (b) F2, and (c) F3 as function of pHs (0-14).



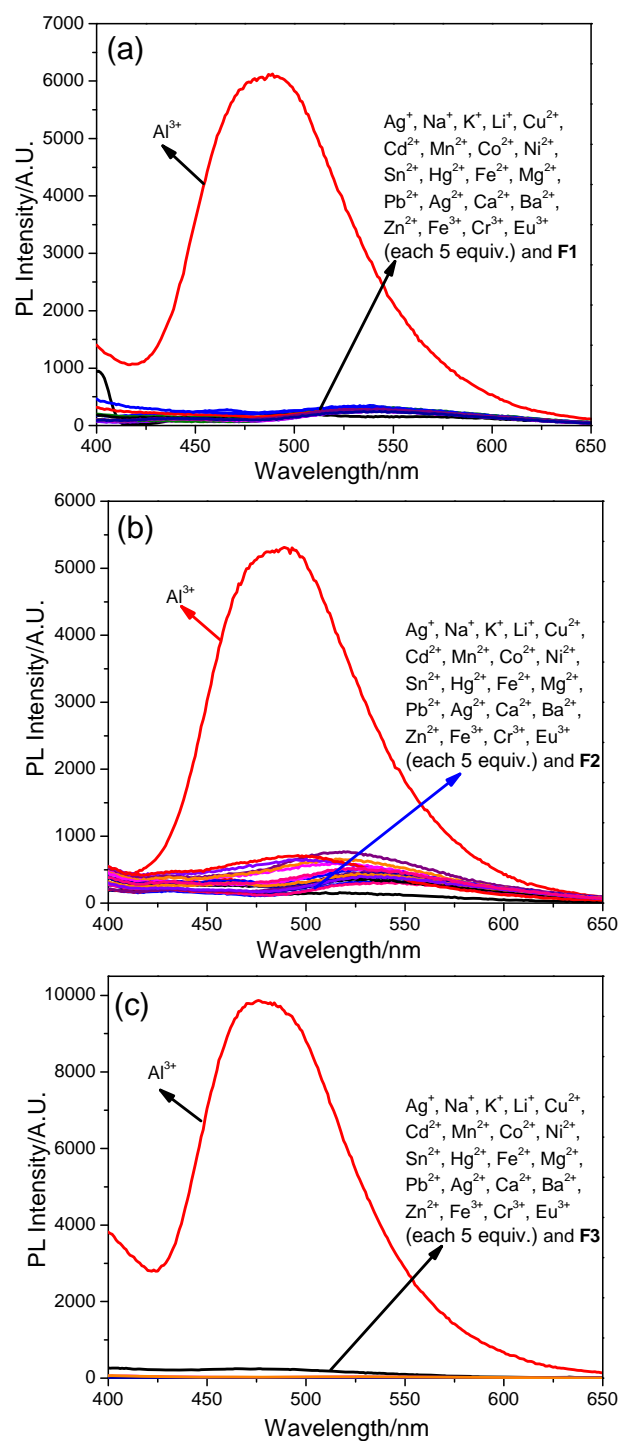
**Fig. S11** PL spectra of F1, F2 and F3 (a, b, and c) at acidic, neutral, and basic pHs (2, 7, and 12).



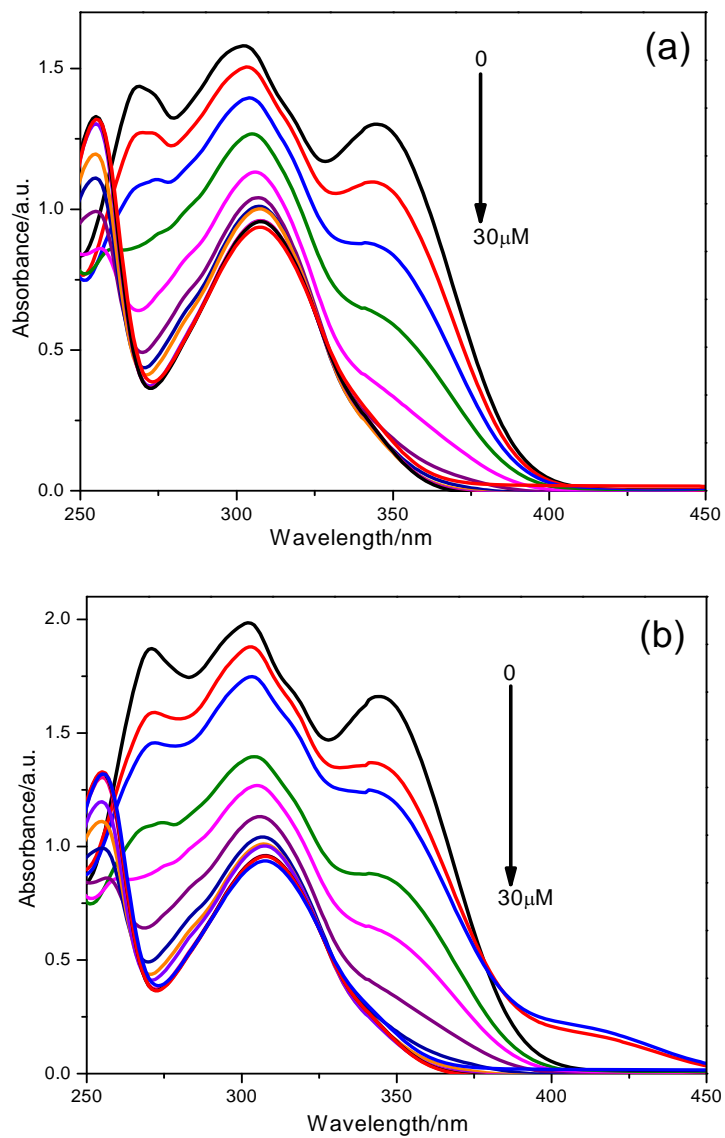
**Fig. S12** Time-resolved fluorescence spectra of F1, F2 and F3 (a, b, and c) at acidic, neutral, and basic pHs (2, 7, and 12); Inset: Photographs of F1, F2 and F3 at acidic, neutral, and basic pHs (2, 7, and 12).



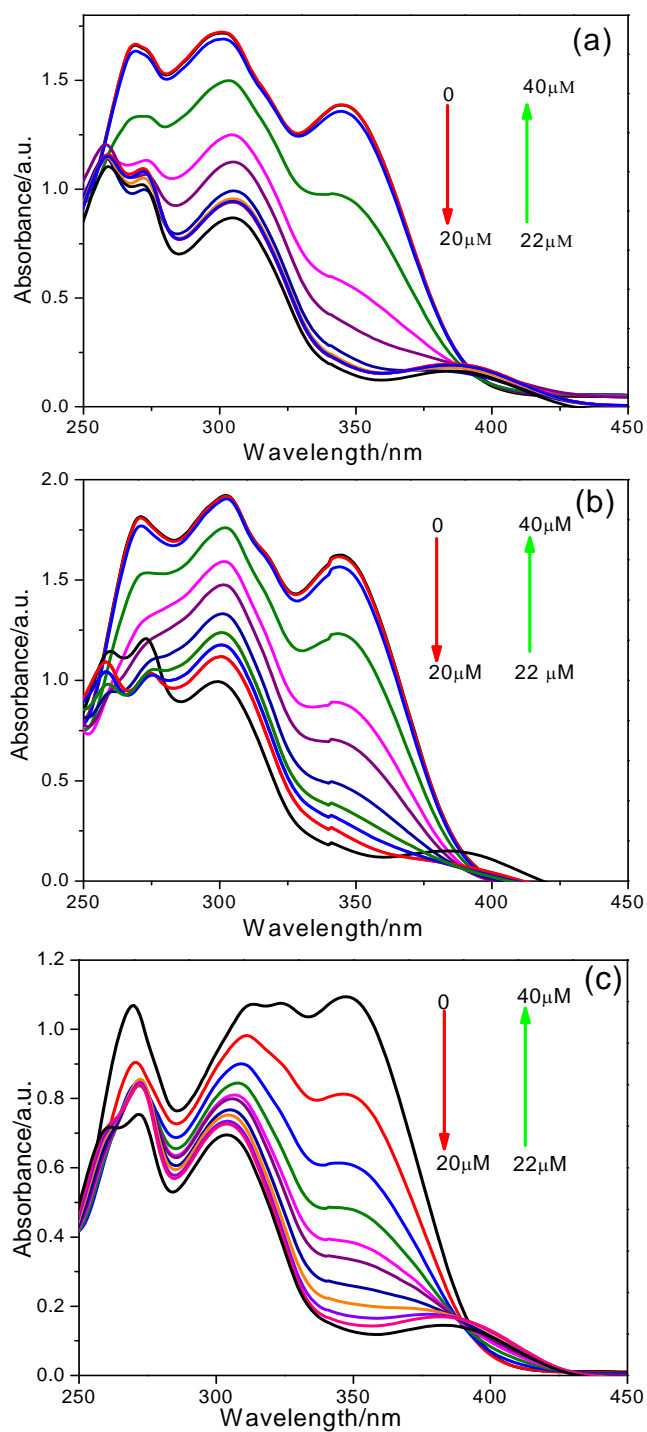
**Fig. S13** Computational analysis of HOMO and LUMO levels of F1, F2, F3, F1-phenoxide, F2-phenoxide, and F3-phenoxide ions. (Semi-empirical AM1 method).



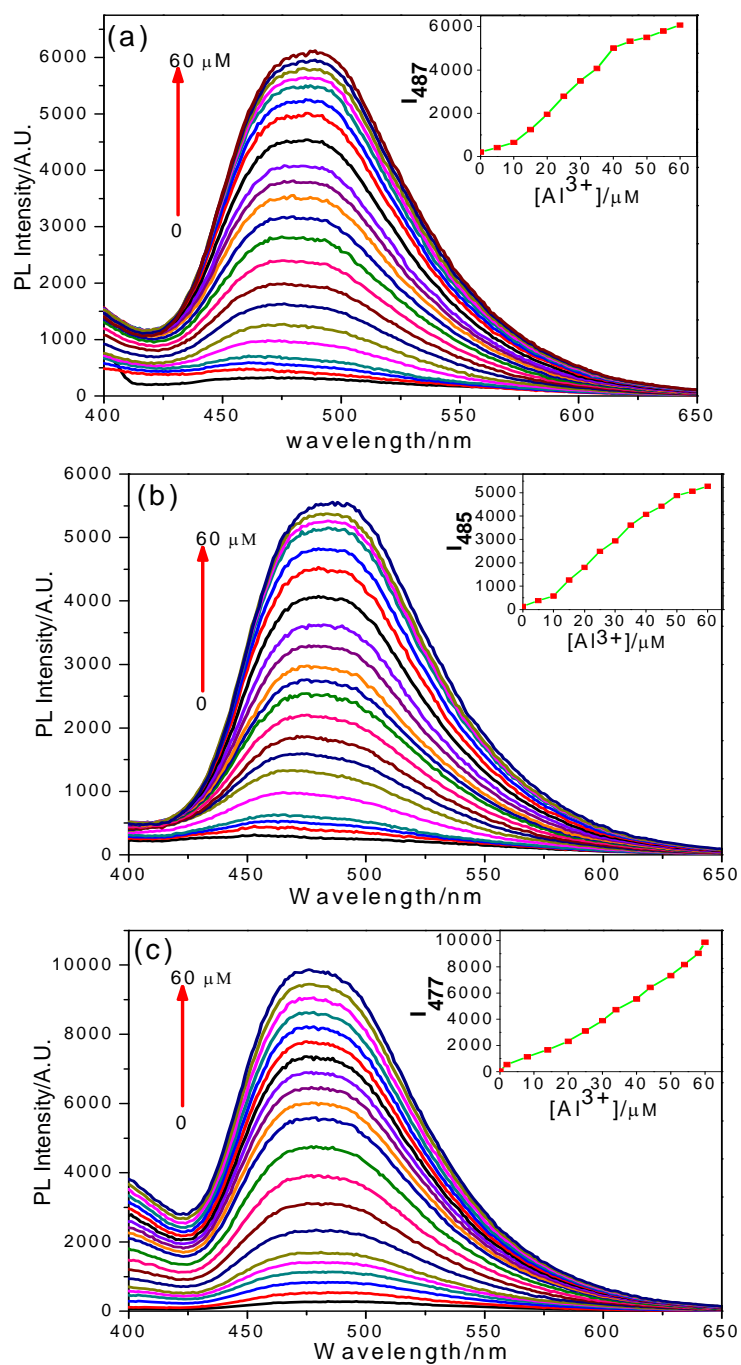
**Fig. S14** Sensor responses of (a) **F1** in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (3/7; vol/vol), (b) **F2** in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (3/7; vol/vol), and (c) **F3** in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (3/7; vol/vol) towards metal ions in  $\text{H}_2\text{O}$ .



**Fig. S15** UV-Vis titrations of (a) **F1** (20 μM), and (b) **F2** (20 μM) in CH<sub>3</sub>CN/H<sub>2</sub>O (6/4; vol/vol) upon the addition of Zn<sup>2+</sup> (0, 5, 10, 15, 20, 22, 24, 28 and 30 μM).

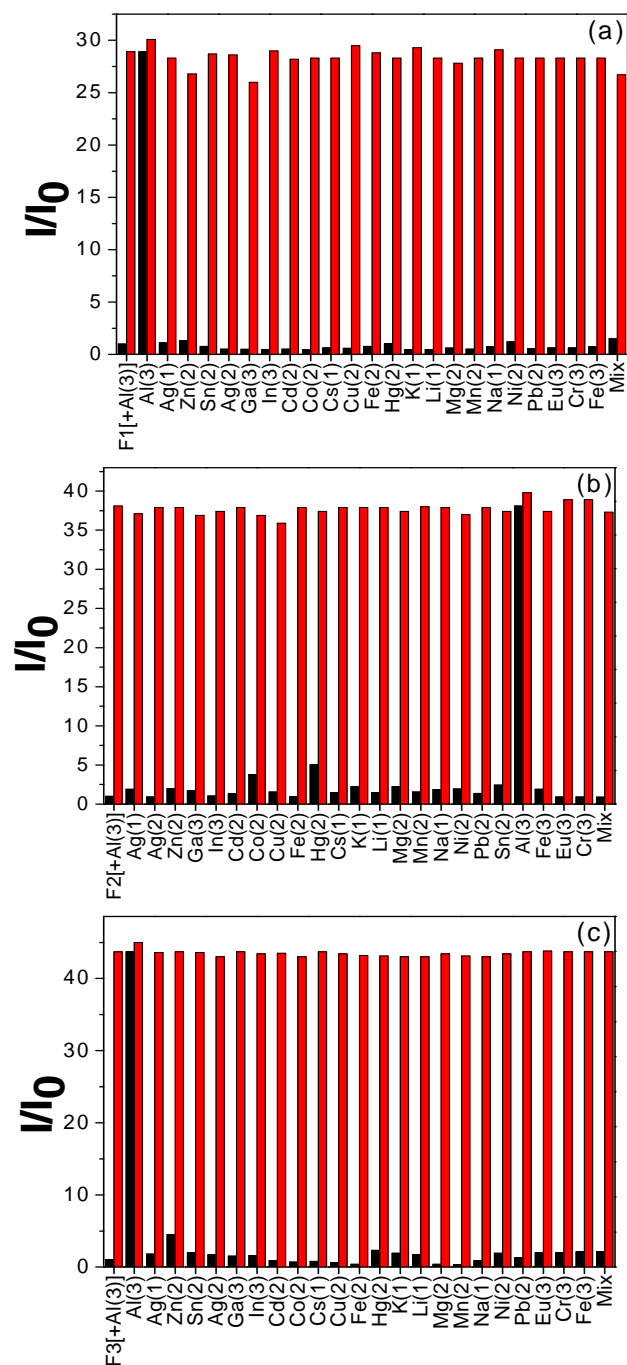


**Fig. S16** UV-Vis titrations of (a) **F1** (20 μM), (b) **F2** (20 μM), and (c) **F3** (20 μM) in CH<sub>3</sub>CN/H<sub>2</sub>O (6/4 and 3/7; vol/vol ratios) upon the addition of Al<sup>3+</sup> (0, 2, 5, 10, 15, 20, 22, 24, 28, 32, 36 and 40 μM).

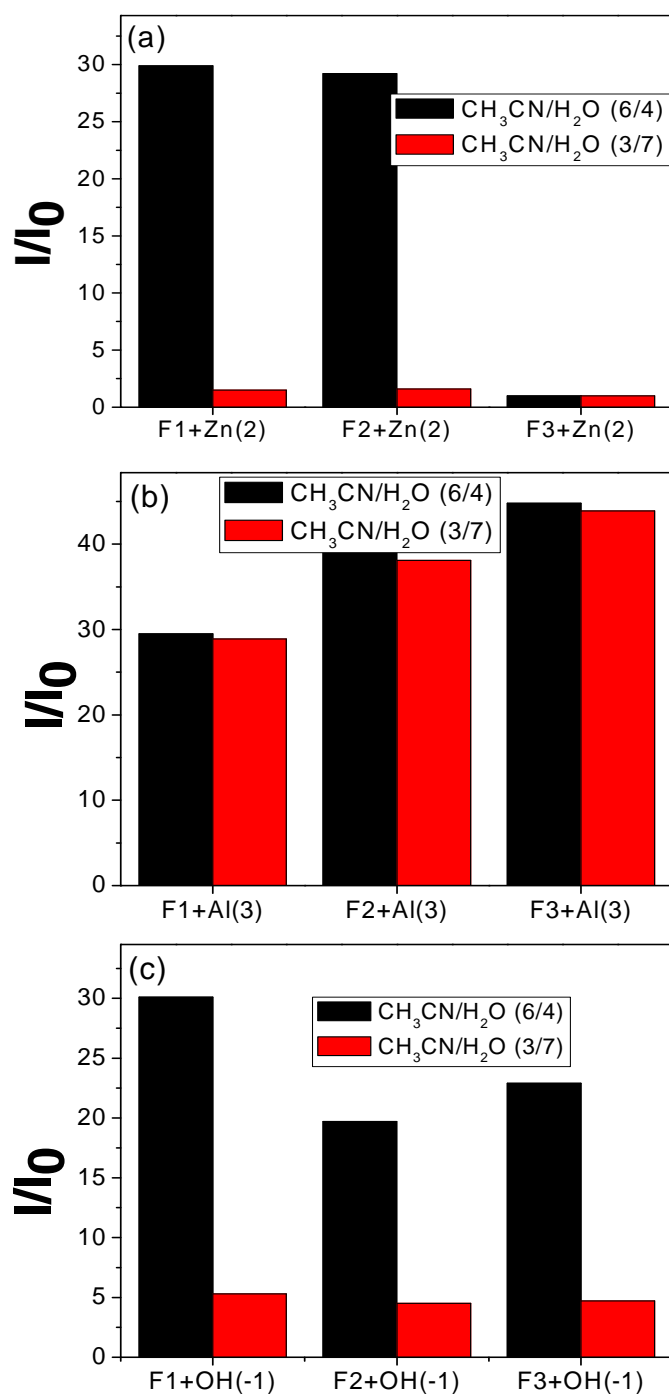


**Fig. S17** Fluorescence spectral changes of (a) **F1** ( $1 \times 10^{-5}$  M) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (3/7; vol/vol) ( $\lambda_{\text{ex}}=344$  nm), (b) **F2** ( $1 \times 10^{-5}$  M) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (3/7; vol/vol) ( $\lambda_{\text{ex}}=346$  nm), and (c) **F3** ( $1 \times 10^{-5}$  M) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (3/7; vol/vol) ( $\lambda_{\text{ex}}=343$  nm) titrated with 0-60  $\mu\text{M}$  of  $\text{Al}^{3+}$  ions in  $\text{H}_2\text{O}$  (with an equal span of 3  $\mu\text{M}$ ). Insets show PL spectral responses of (a) **F1**, (b) **F2** and (c) **F3** as a function of  $\text{Al}^{3+}$ .

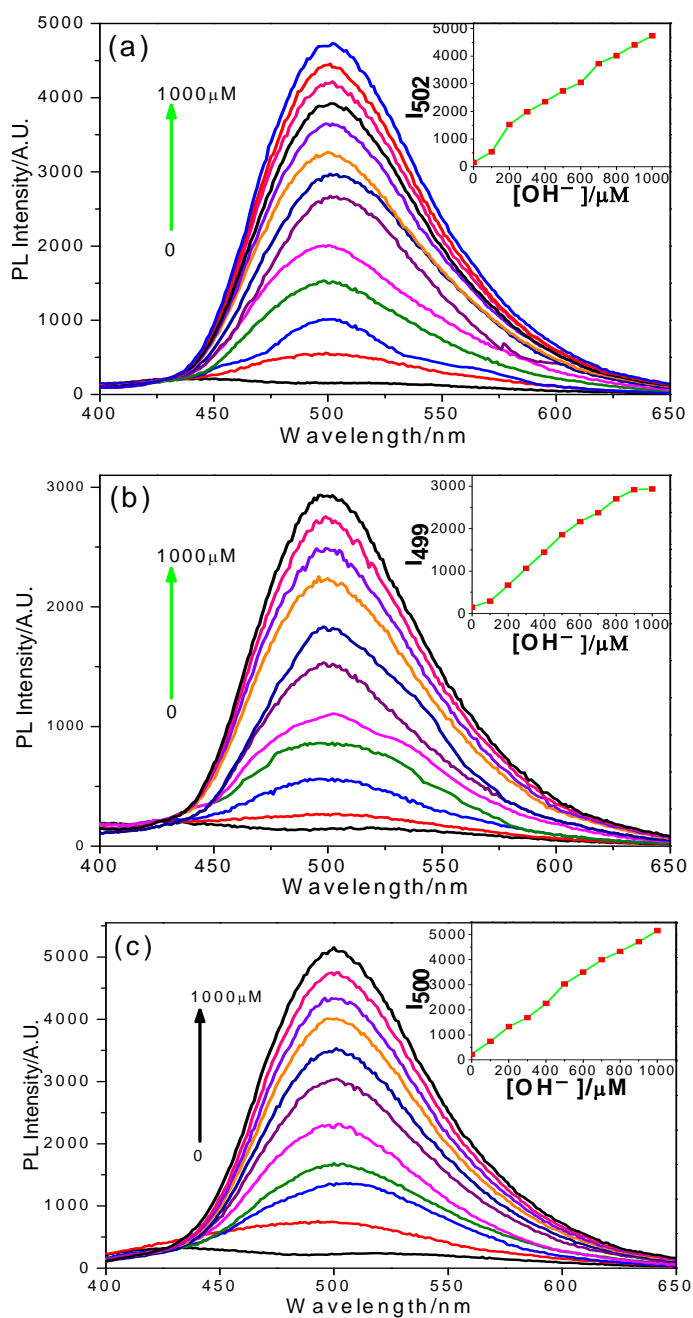




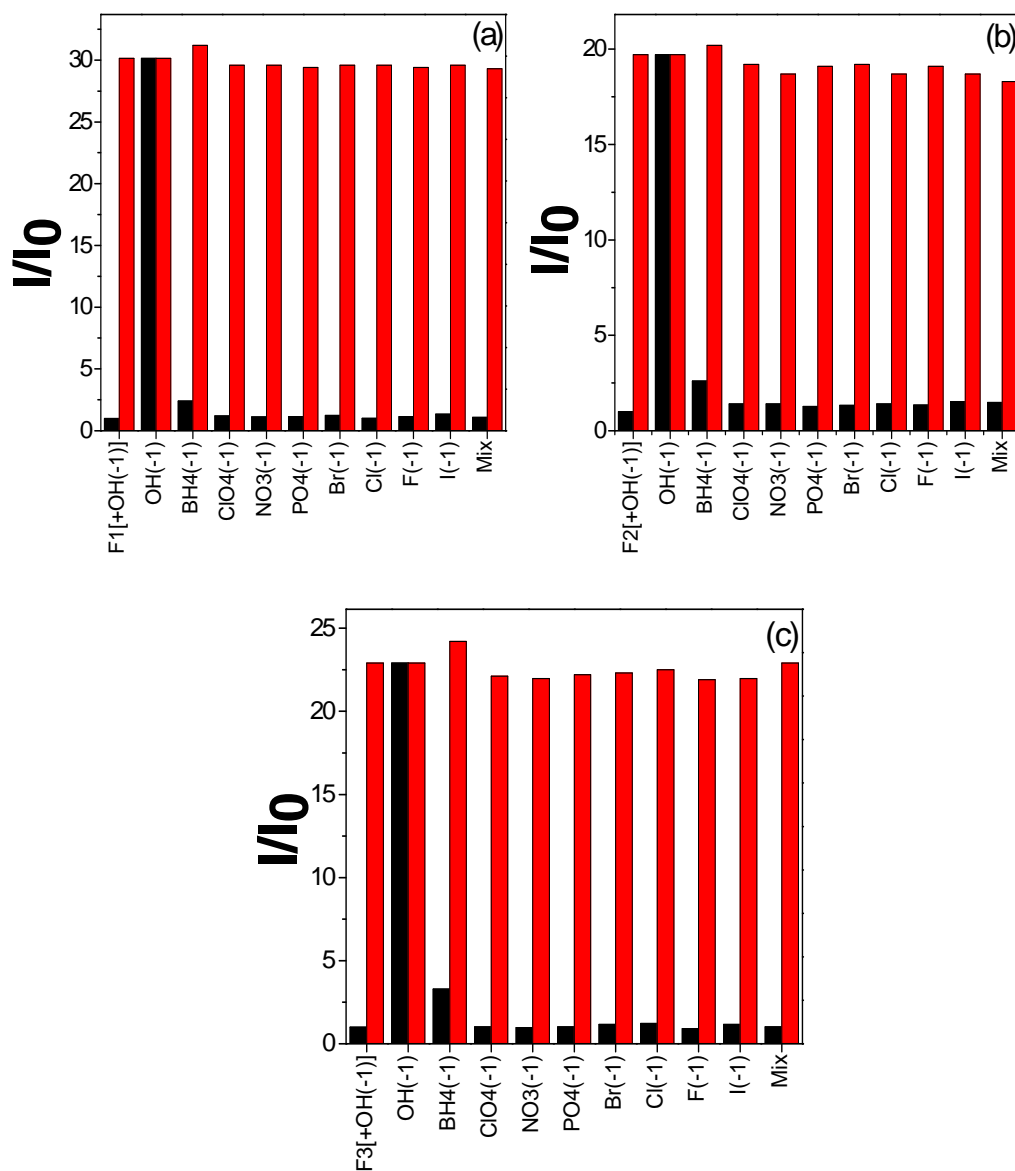
**Fig. S18** Relative fluorescence intensities of (a) F1 (20  $\mu\text{M}$ ), (b) F2 (20  $\mu\text{M}$ ) and (c) F2 (20  $\mu\text{M}$ ) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (3/7; vol/vol) with 60  $\mu\text{M}$   $\text{Al}^{3+}$  in  $\text{H}_2\text{O}$  in the presence of competing metal ions. Black bars; F1, F2, and F3 (20  $\mu\text{M}$ ) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (3/7; vol/vol) with 60  $\mu\text{M}$  of stated metal ions in  $\text{H}_2\text{O}$ . Red bars; F1, F2, and F3 (20  $\mu\text{M}$ )  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (3/7; vol/vol) with 60  $\mu\text{M}$   $\text{Al}^{3+}$  + 60  $\mu\text{M}$  of stated metal ions in  $\text{H}_2\text{O}$ . (120  $\mu\text{M}$  of  $\text{Al}^{3+}$  for  $\text{Al}^{3+}$  effect). (Mix = all metal ions except  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$ ).



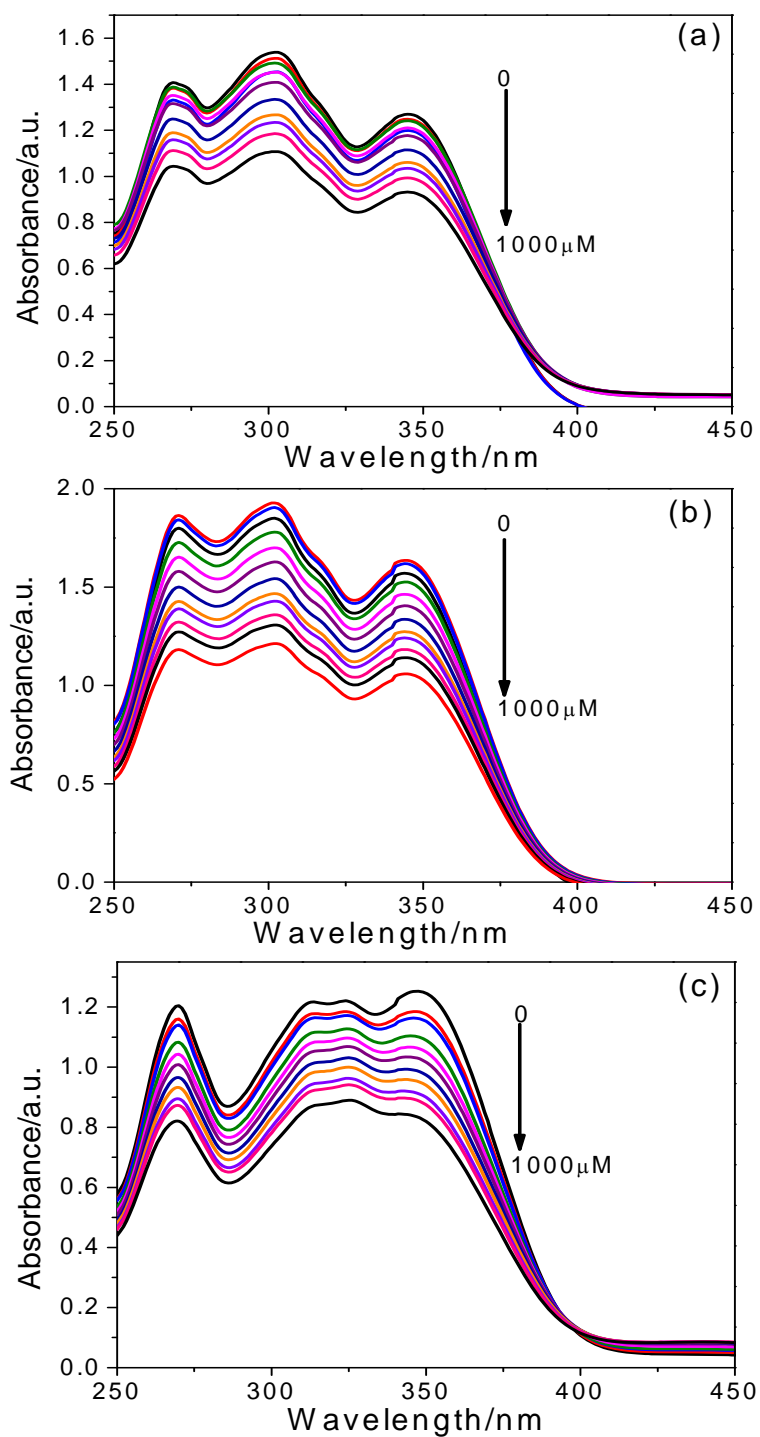
**Fig. S19** Comparison of relative fluorescence intensity changes of (a) **F1** in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (6/4 and 3/7; vol/vol ratios), (b) **F2** in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (6/4 and 3/7; vol/vol ratios), and (c) **F3** in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (6/4 and 3/7; vol/vol ratios) towards  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{OH}^-$  ions in  $\text{H}_2\text{O}$ .



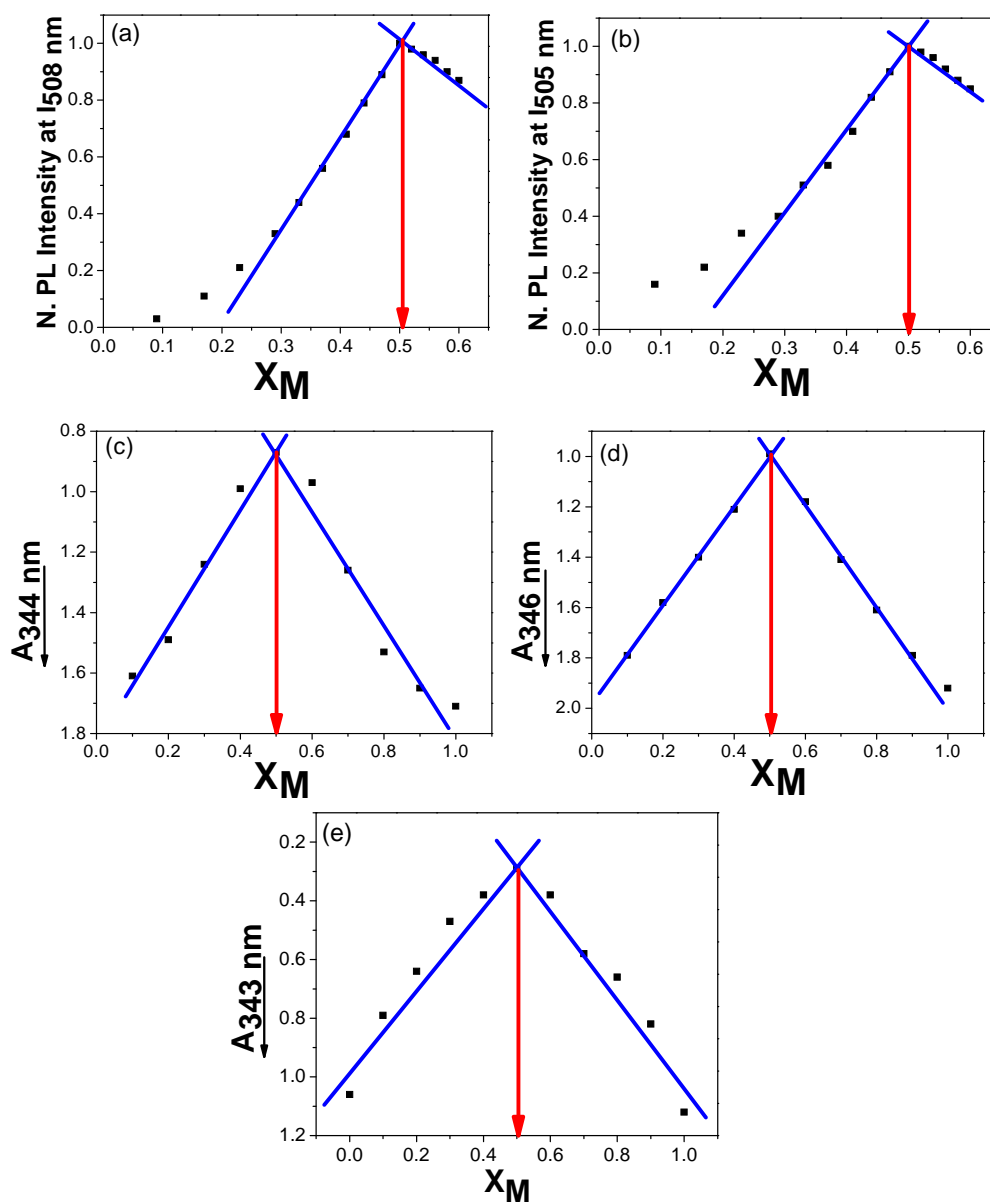
**Fig. S20** Fluorescence spectral changes of (a) **F1** (20 μM) in CH<sub>3</sub>CN/H<sub>2</sub>O (6/4; vol/vol) (λ<sub>ex</sub>=346 nm), (b) **F2** (20 μM) in CH<sub>3</sub>CN/H<sub>2</sub>O (6/4; vol/vol) (λ<sub>ex</sub>=344 nm) and (c) **F3**(20 μM) in CH<sub>3</sub>CN/H<sub>2</sub>O (6/4; vol/vol) (λ<sub>ex</sub>=343 nm) titrated with 0-1000 μM of OH<sup>-</sup> ion in H<sub>2</sub>O (0, 100, 200, 300, 400, 500, 600, 700, 800, 850, 900, 950 and 1000 μM) were plotted for **F1**, and **F2** was plotted with an equal span of 100 μM). Insets showed PL spectral responses of (a) **F1** and (b) **F2** as a function of OH<sup>-</sup> ion.



**Fig. S21** Relative fluorescence intensities of (a) **F1** (20  $\mu\text{M}$ ), (b) **F2** (20  $\mu\text{M}$ ), and (c) **F3** (20  $\mu\text{M}$ ) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (6/4; vol/vol) with 1000  $\mu\text{M}$   $\text{OH}^-$  in  $\text{H}_2\text{O}$  in the presence of competing anions. Black bars; **F1** or **F2** (20  $\mu\text{M}$ ) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (6/4; vol/vol) with 1000  $\mu\text{M}$  of stated anions in  $\text{H}_2\text{O}$ . Red bars; **F1** or **F2** (20  $\mu\text{M}$ )  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (6/4; vol/vol) with 1000  $\mu\text{M}$   $\text{OH}^-$  + 1000  $\mu\text{M}$  of stated anions in  $\text{H}_2\text{O}$ . (for  $\text{OH}^-$  effect 2000  $\mu\text{M}$  of  $\text{OH}^-$ ). (Mix = all anions except  $\text{OH}^-$ ).



**Fig. S22** UV-Vis absorption spectral changes of (a) **F1** (b) **F2**, and (c) **F3**, upon the addition of OH<sup>-</sup> ions (0-1000 μM with an equal span of 100 μM).



**Fig. S23** Job plots for determination of stoichiometries of (a) **F1** + Zn<sup>2+</sup>, (b) **F2** + Zn<sup>2+</sup>, (c) **F1** + Al<sup>3+</sup>, (d) **F2** + Al<sup>3+</sup>, and (e) **F3** + Al<sup>3+</sup>;  $X_M = [M^{n+}] / [M^{n+}] + [F1 \text{ or } F2 \text{ or } F3]$ ; for (a), (b)  $[M^{n+}] = Zn^{2+}$ , and for (c), (d) and (e)  $[M^{n+}] = Al^{3+}$ . [Note: for (a), (b) stoichiometry calculations based on normalized PL spectral changes of **F1** and **F2** during the titration of Zn<sup>2+</sup>, and for (c), (d) and (e) it was calculated from the UV-Vis spectral changes of Al<sup>3+</sup> titrations with **F1**, **F2** and **F3**]

**F1**+Zn<sup>2+</sup> = 1:1 stoichiometry (ca. 0.506); **F1**+Al<sup>3+</sup> = 1:1 stoichiometry (ca. 0.500)

**F2**+Zn<sup>2+</sup> = 1:1 stoichiometry (ca. 0.503); **F2**+Al<sup>3+</sup> = 1:1 stoichiometry (ca. 0.507) and

**F3**+Al<sup>3+</sup> = 1:1 stoichiometry (ca. 0.508)

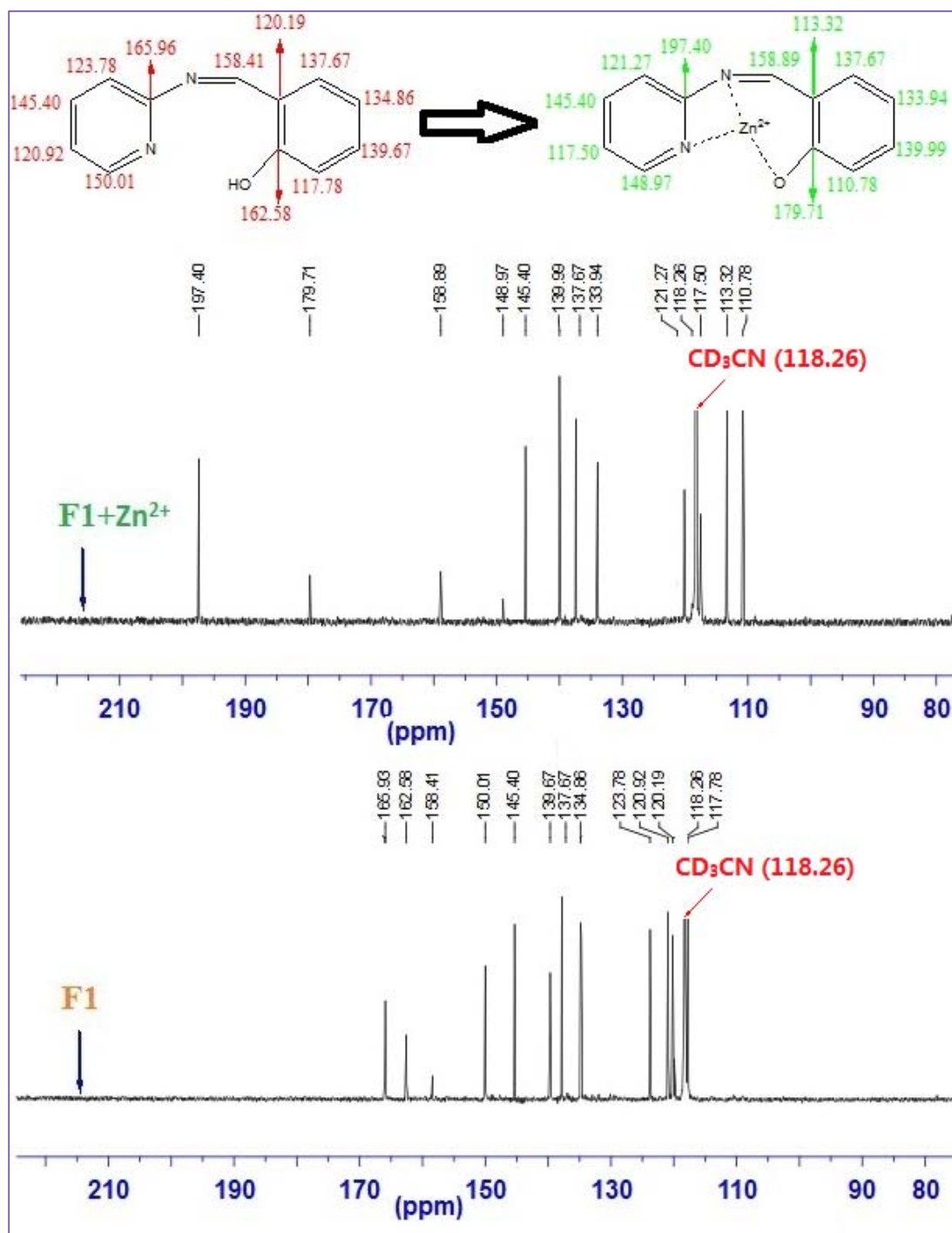
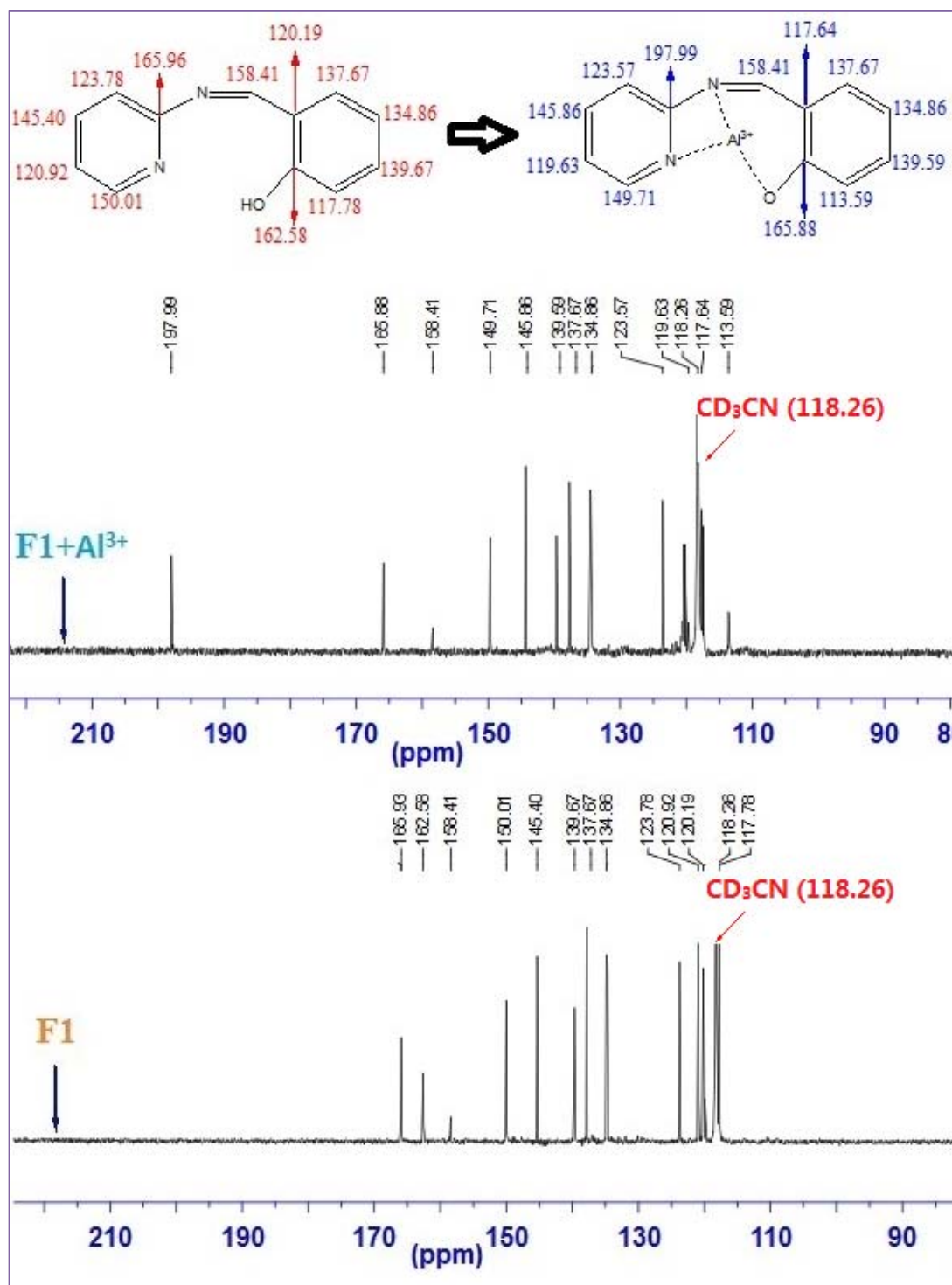


Fig. S24 <sup>13</sup>C NMR spectral changes of F1 (1 equiv.) in CD<sub>3</sub>CN with Zn<sup>2+</sup> (1 equiv.) in D<sub>2</sub>O.



**Fig. S25** <sup>13</sup>C NMR spectral changes of **F1** (1 equiv.) in CD<sub>3</sub>CN with Al<sup>3+</sup> (1 equiv.) in D<sub>2</sub>O.



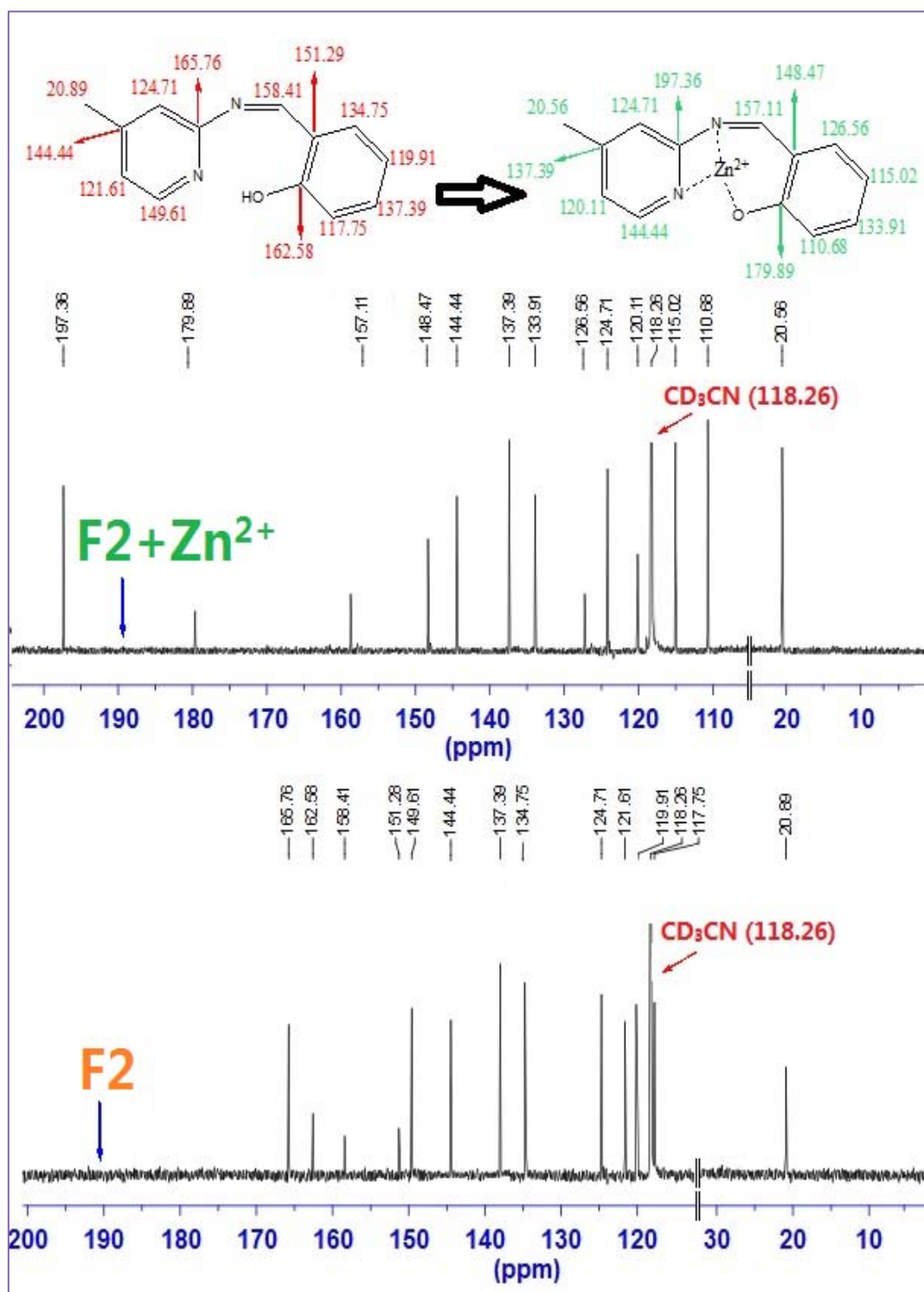


Fig. S26 <sup>13</sup>C NMR spectral changes of F2 (1 equiv.) in CD<sub>3</sub>CN with Zn<sup>2+</sup> (1 equiv.) in D<sub>2</sub>O.

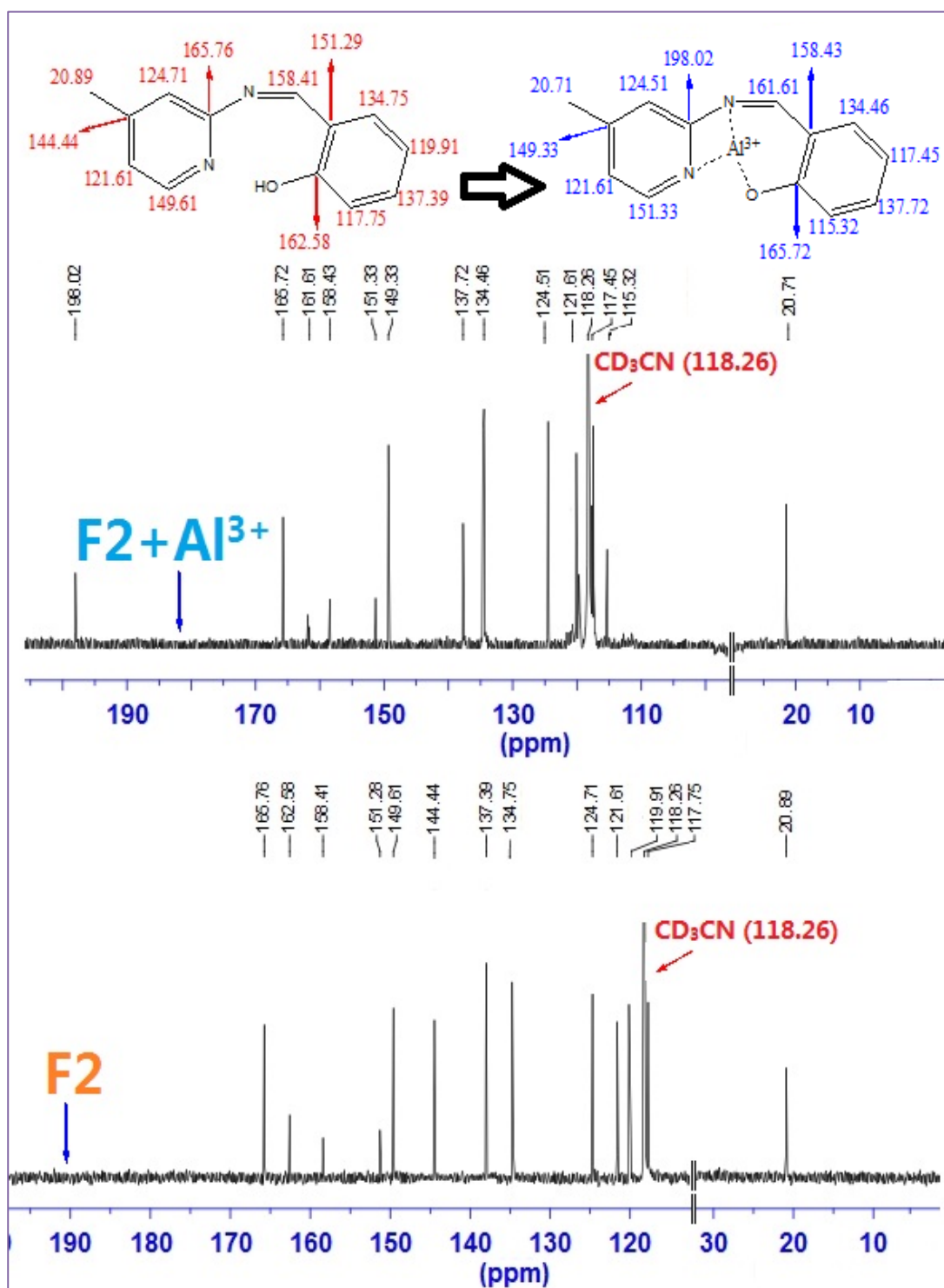


Fig. S27 <sup>13</sup>C NMR spectral changes of F2 (1 equiv.) in CD<sub>3</sub>CN with Al<sup>3+</sup> (1 equiv.) in D<sub>2</sub>O.



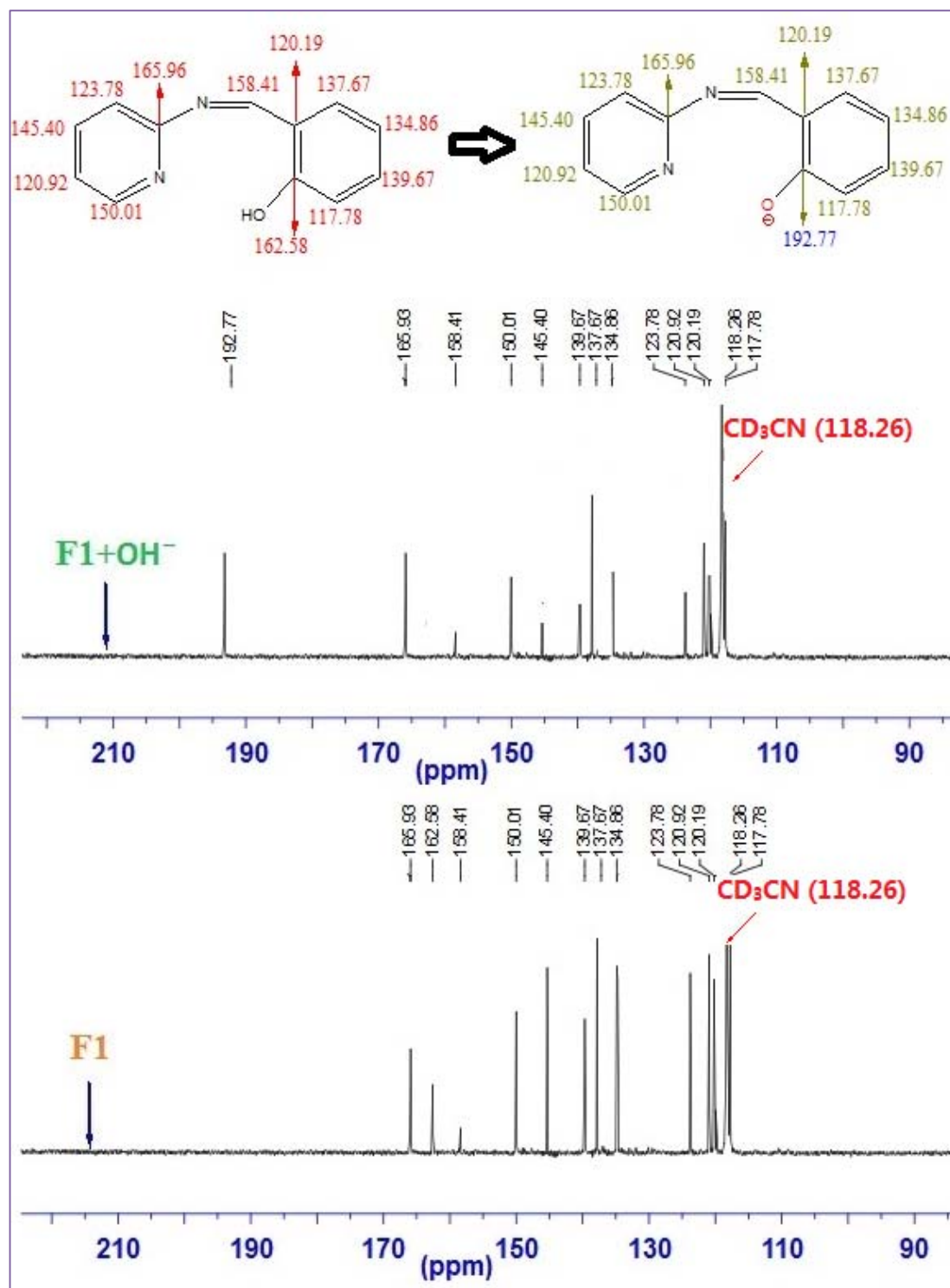


Fig. S29 <sup>13</sup>C NMR spectral changes of F1 (1 equiv.) in CD<sub>3</sub>CN with OH<sup>-</sup> (5 equiv.) in D<sub>2</sub>O.

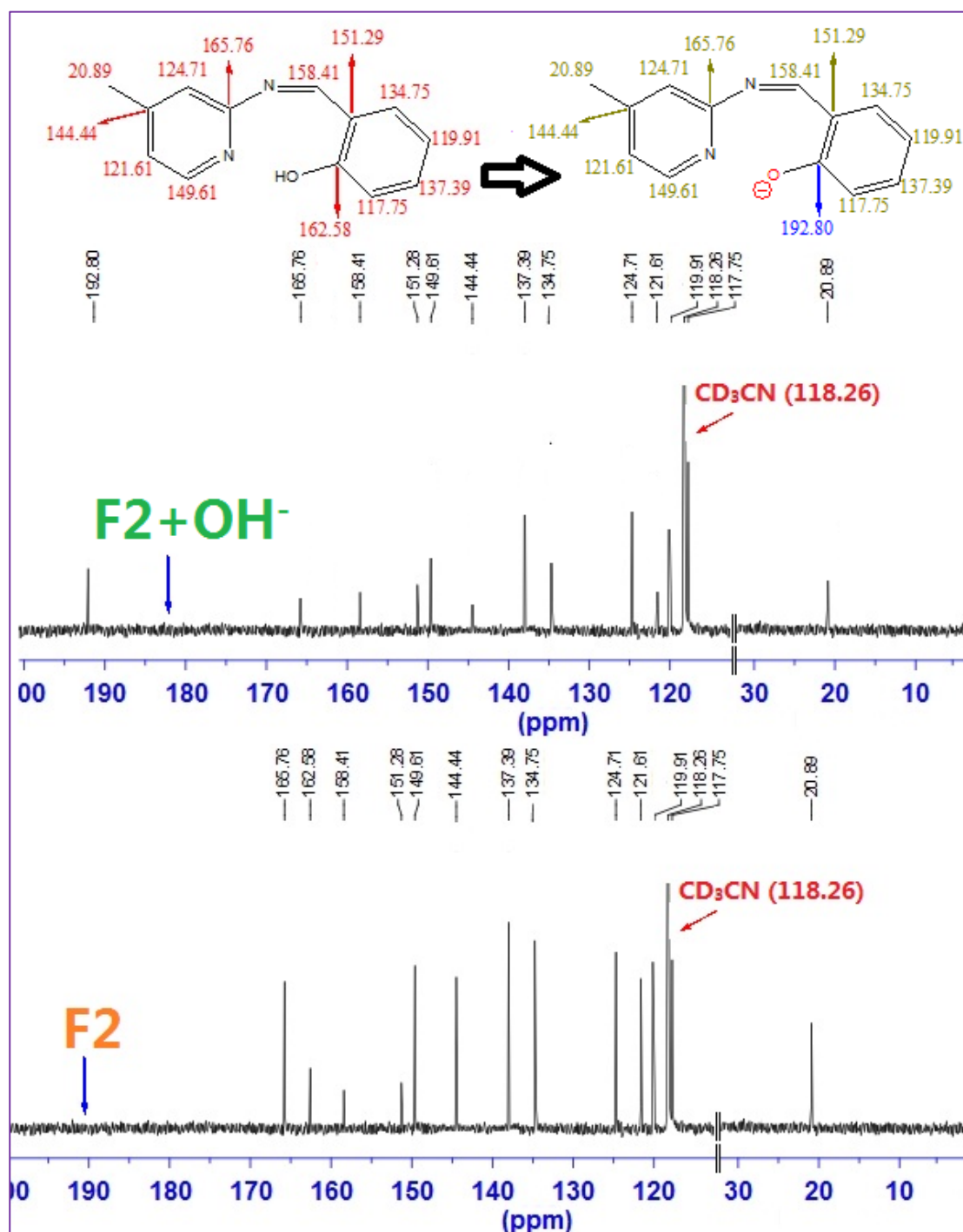


Fig. S30 <sup>13</sup>C NMR spectral changes of F2 (1 equiv.) in CD<sub>3</sub>CN with OH<sup>-</sup> (5 equiv.) in D<sub>2</sub>O.

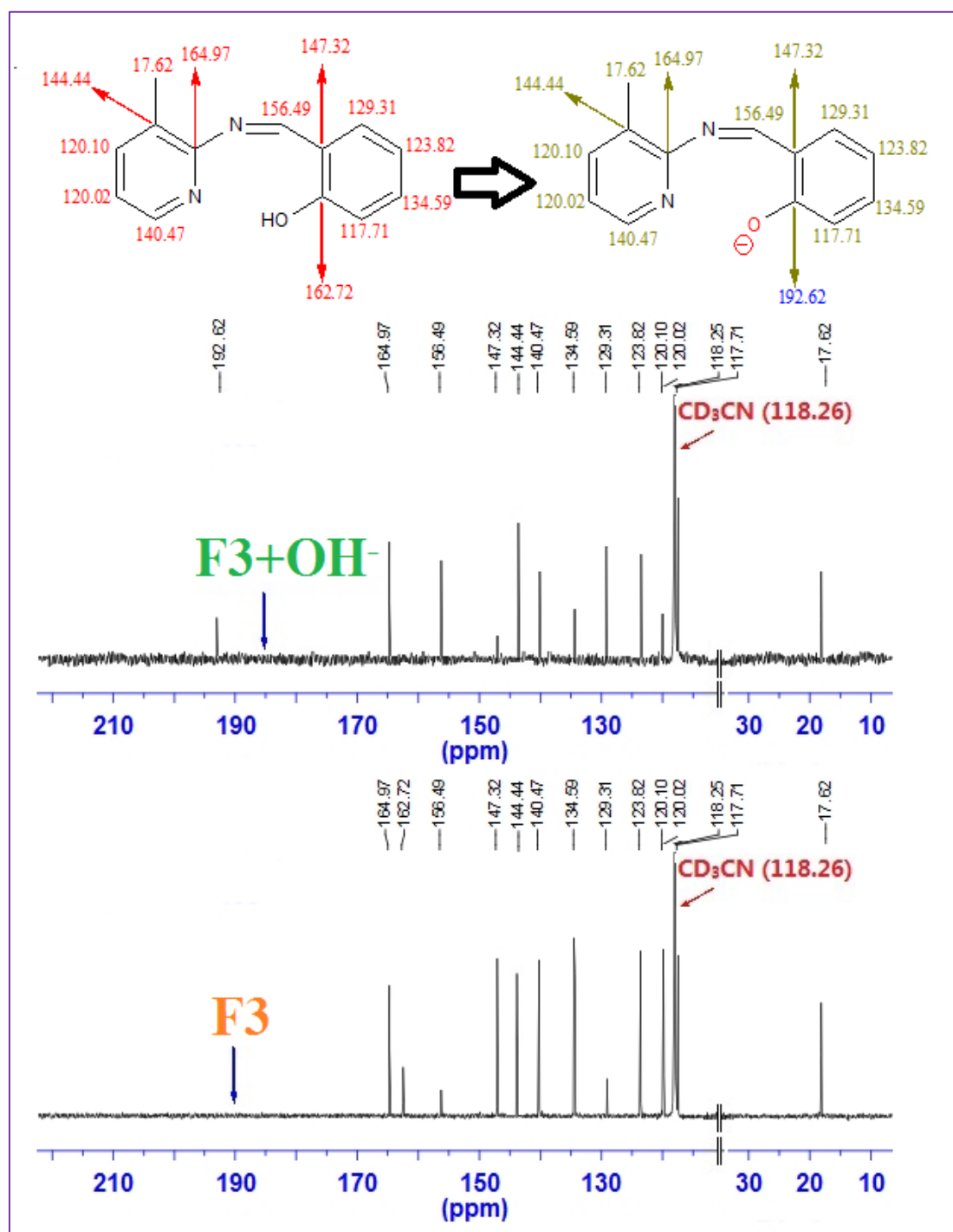


Fig. S31 <sup>13</sup>C NMR spectral changes of F3 (1 equiv.) in CD<sub>3</sub>CN with OH<sup>-</sup> (5 equiv.) in D<sub>2</sub>O.

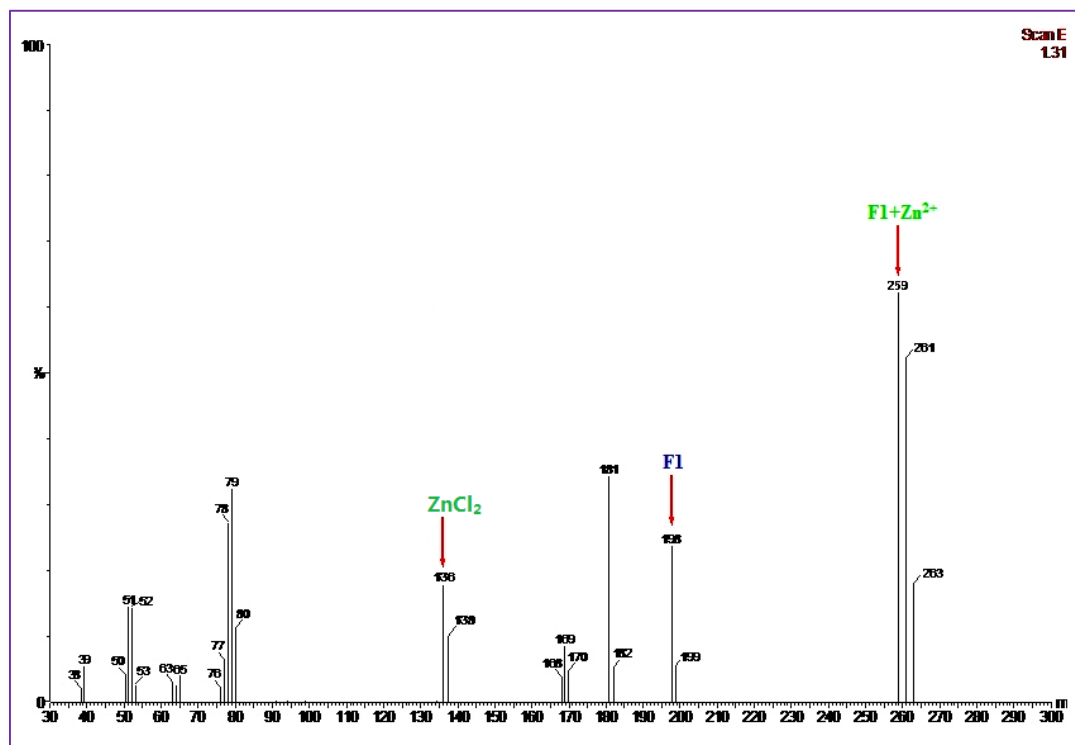


Fig. S32 Mass (FAB) spectral changes of **F1** (1 equiv.) + **Zn<sup>2+</sup>** (1 equiv.).

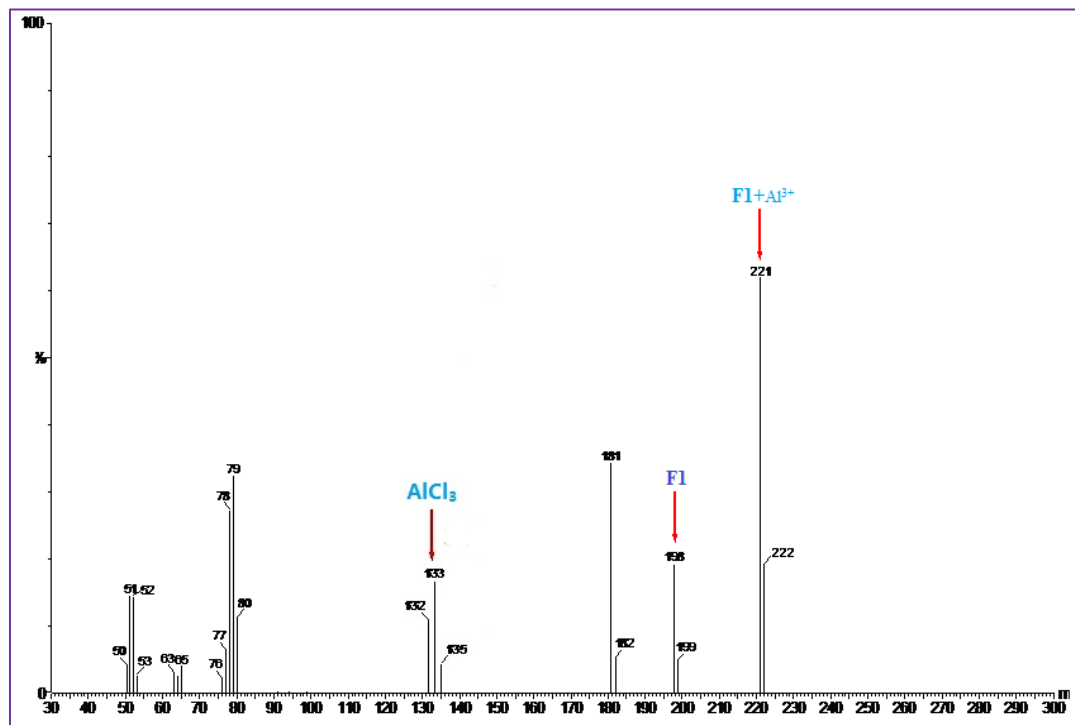


Fig. S33 Mass (FAB) spectral changes of **F1** (1 equiv.) + **Al<sup>3+</sup>** (1 equiv.).

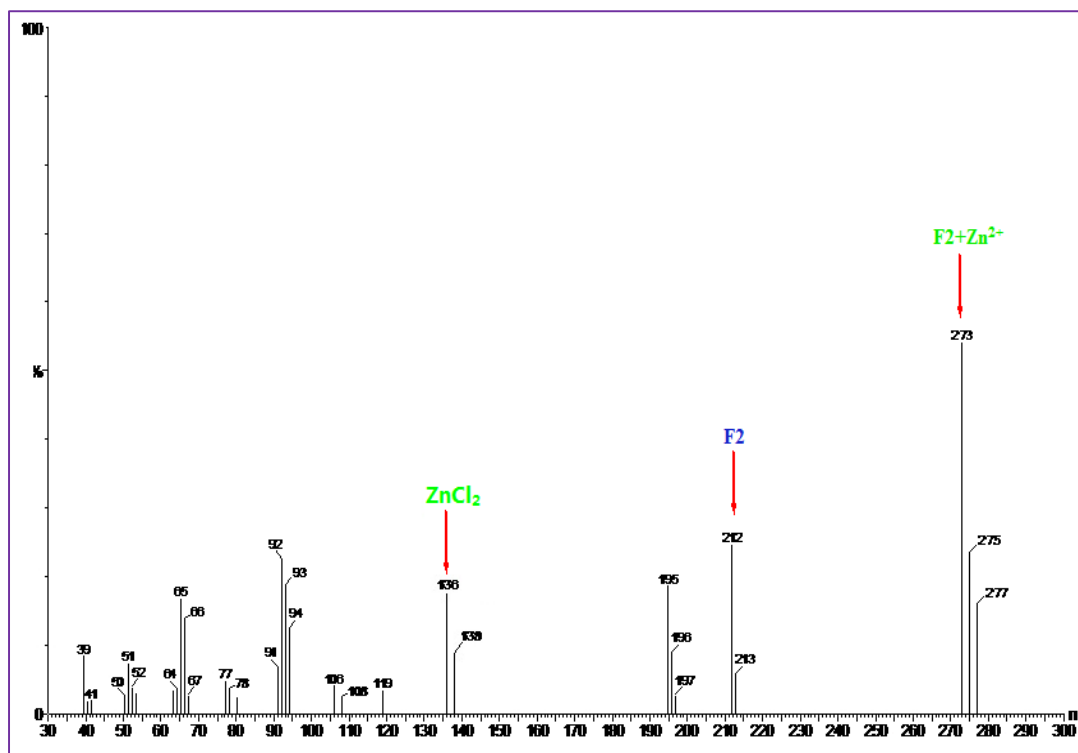


Fig. S34. Mass (FAB) spectral changes of F2 (1 equiv.) + Zn<sup>2+</sup> (1 equiv.).

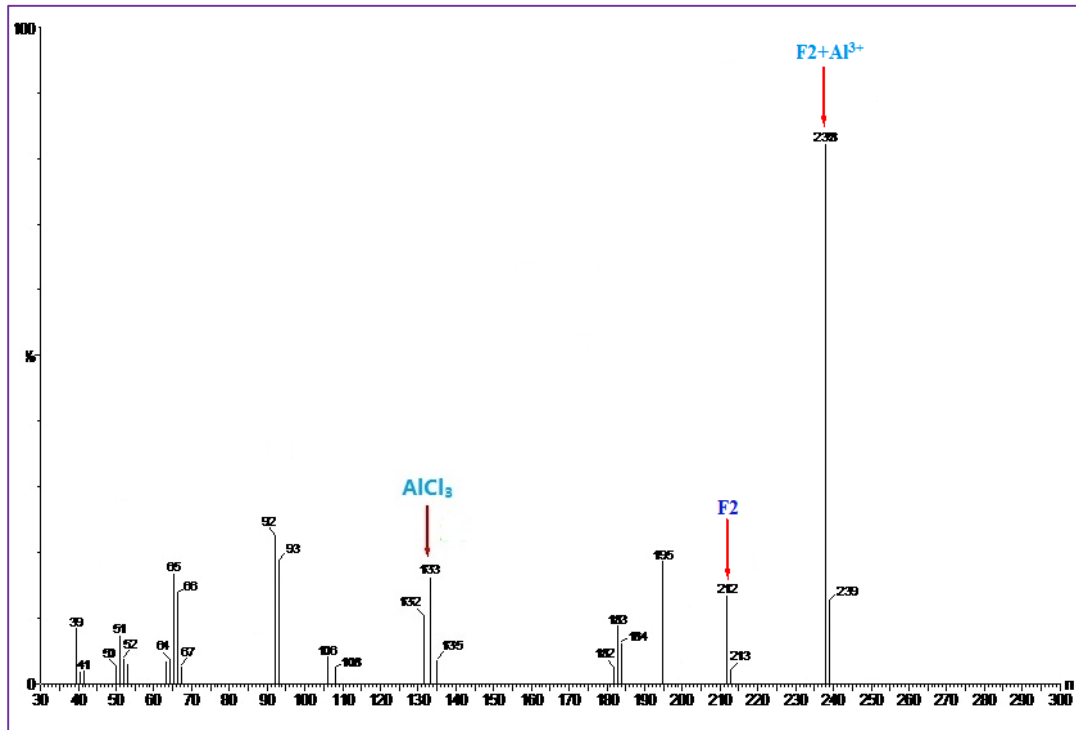


Fig. S35 Mass (FAB) spectral changes of F2 (1 equiv.) + Al<sup>3+</sup> (1 equiv.).



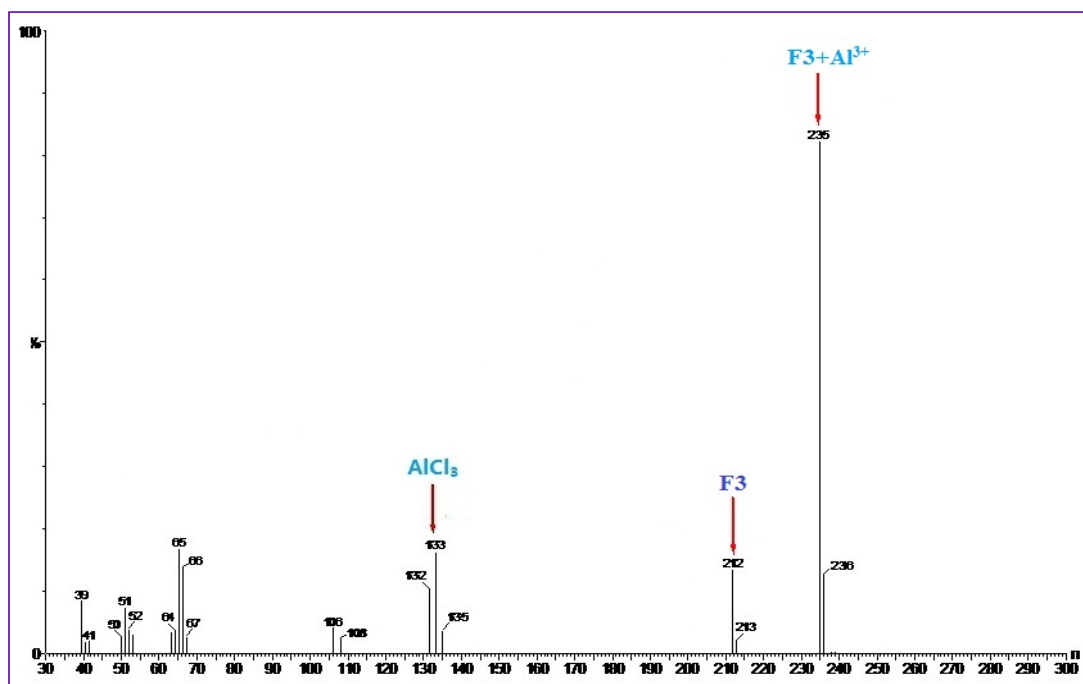


Fig. S36 Mass (FAB) spectral changes of F3 (1 equiv.) + Al<sup>3+</sup> (1 equiv.).

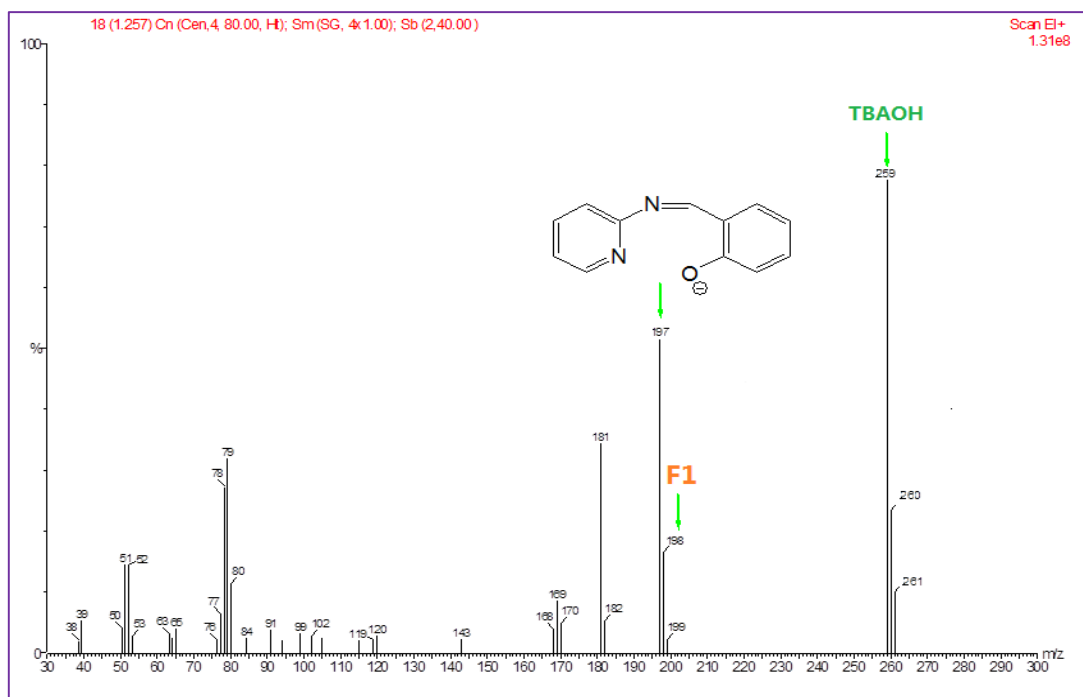
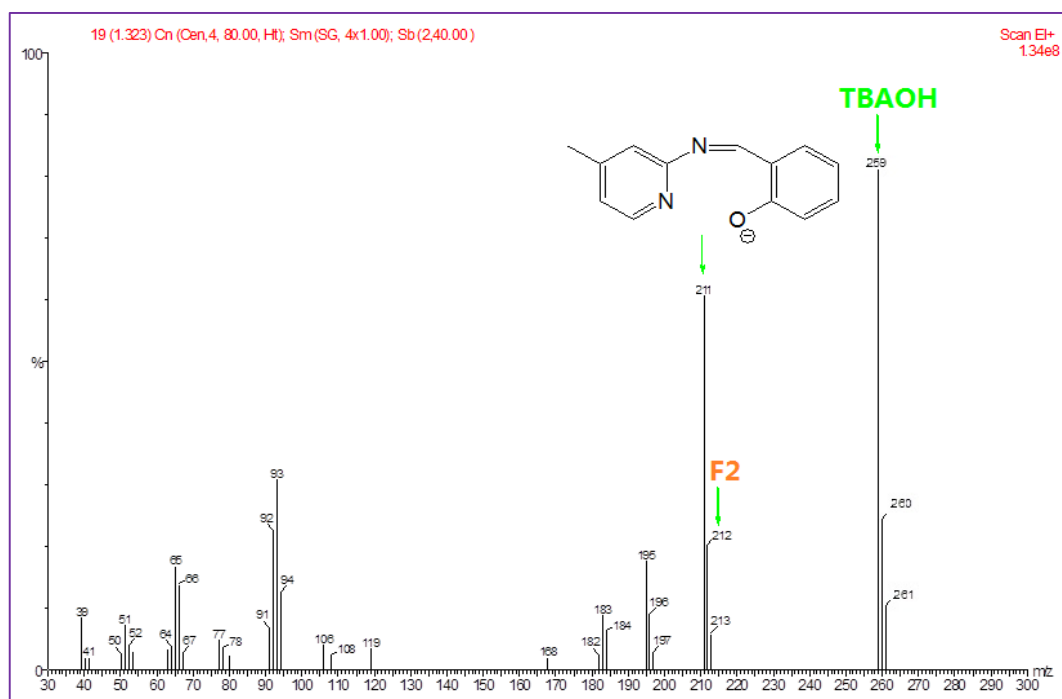
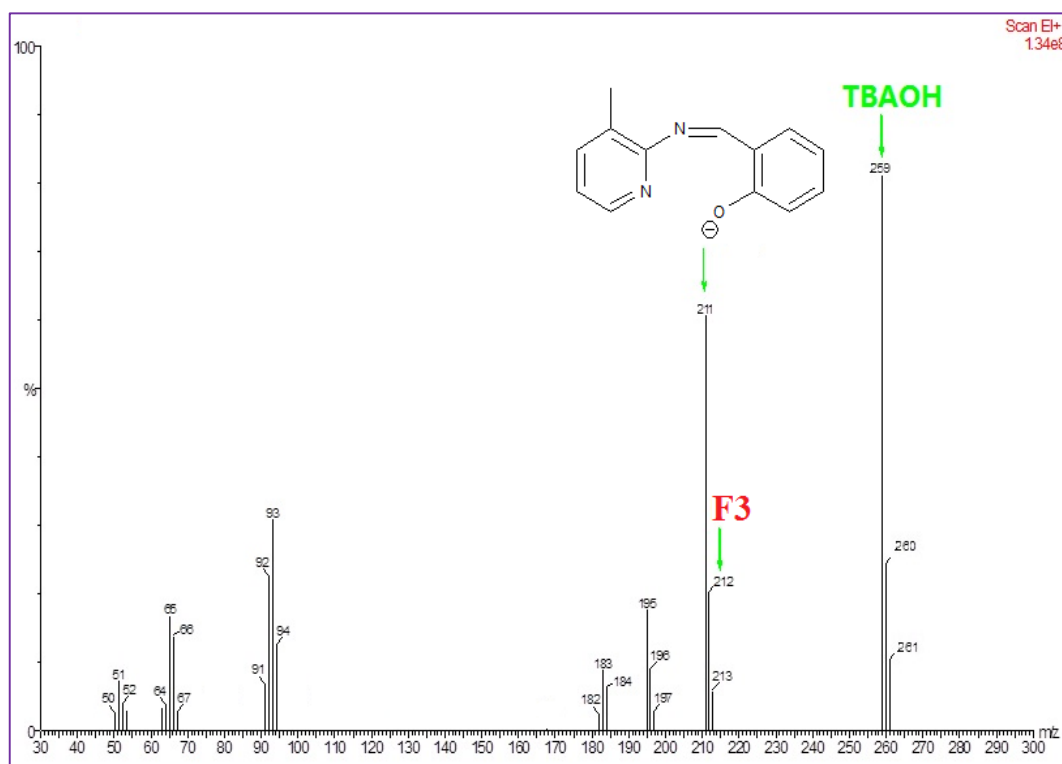


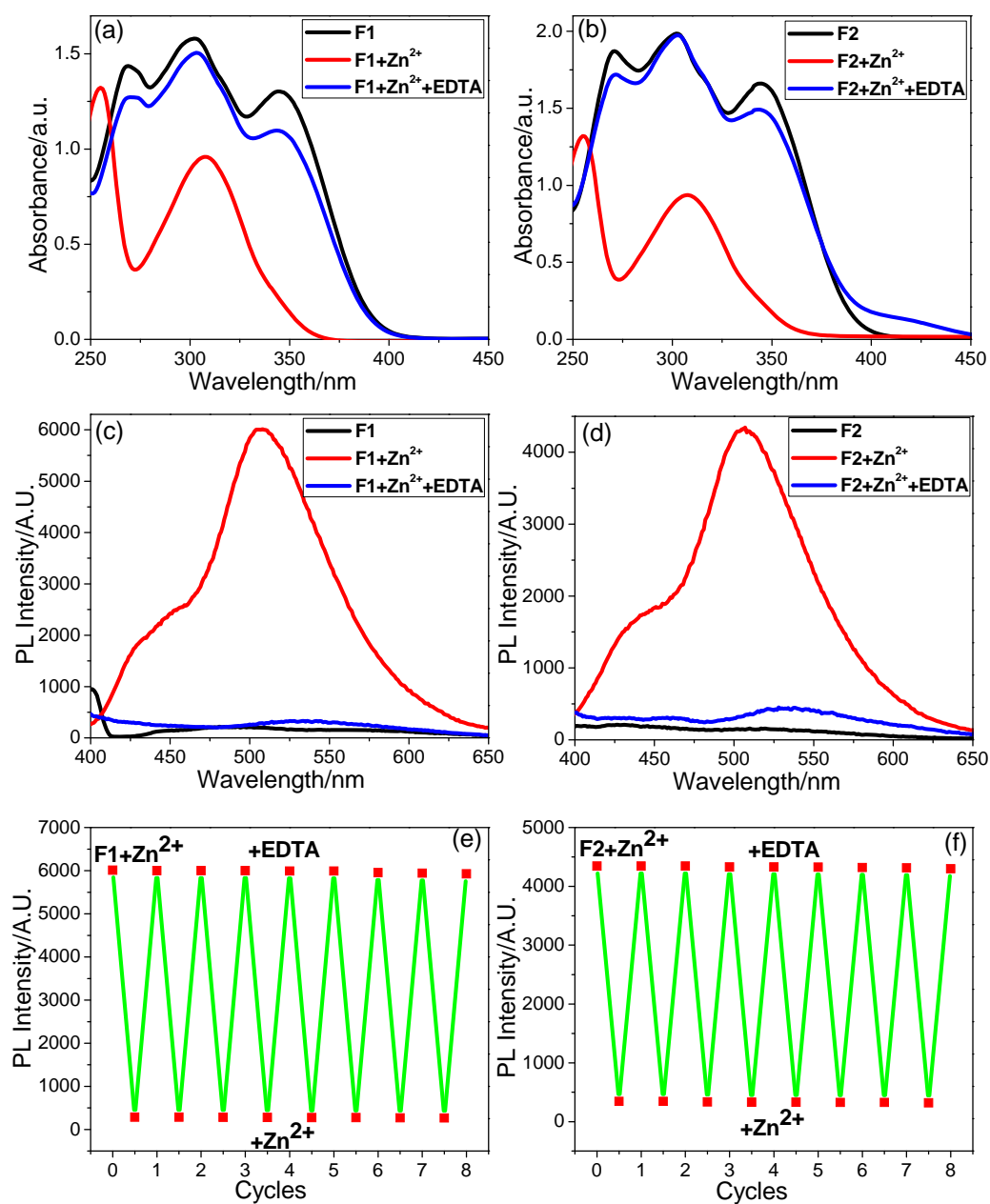
Fig. S37 Mass (FAB) spectral changes of F1 (1 equiv.) + OH<sup>-</sup> (5 equiv.).



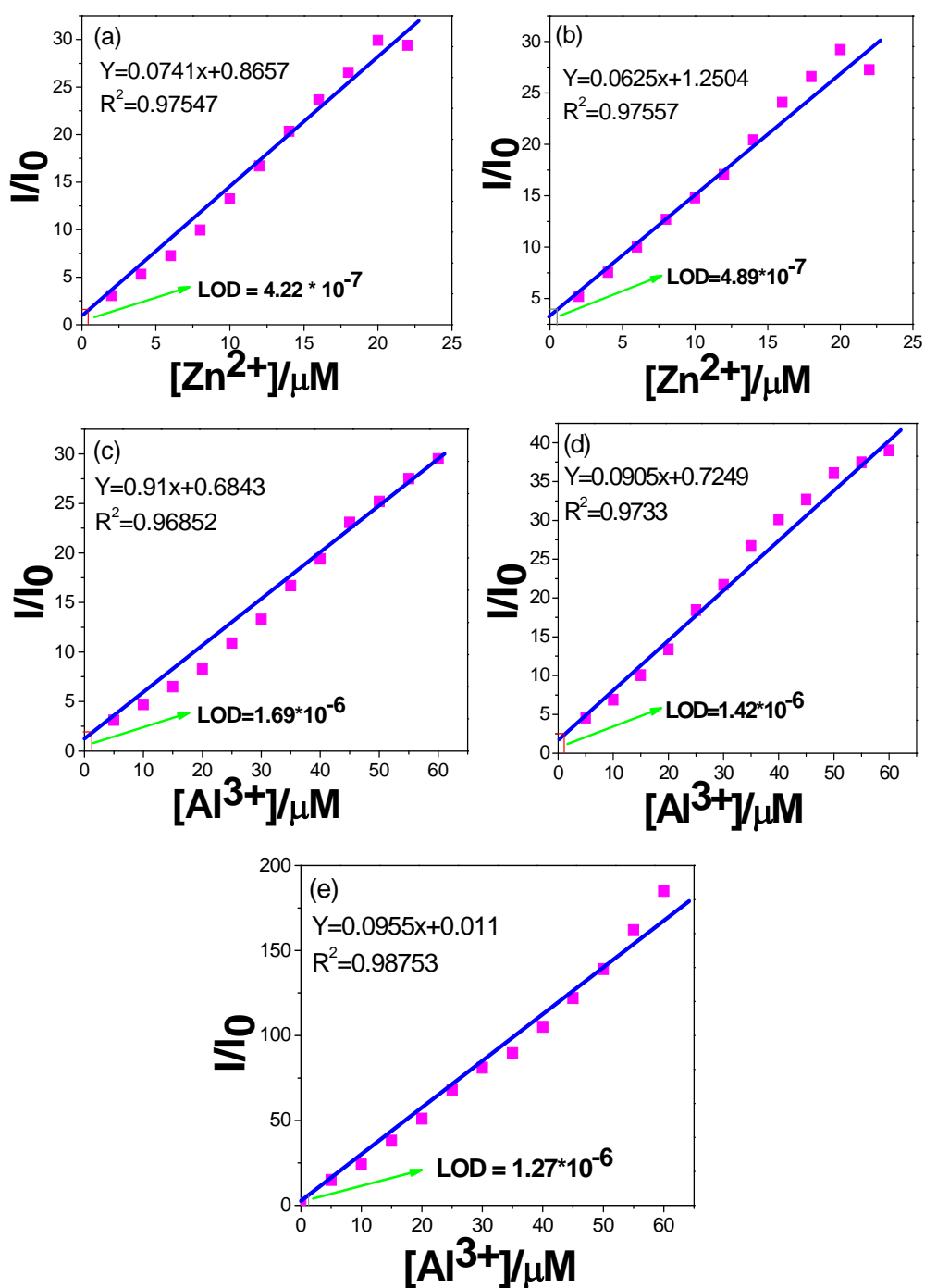
**Fig. S38** Mass (FAB) spectral changes of **F2** (1 equiv.) + OH<sup>-</sup> (5 equiv.).



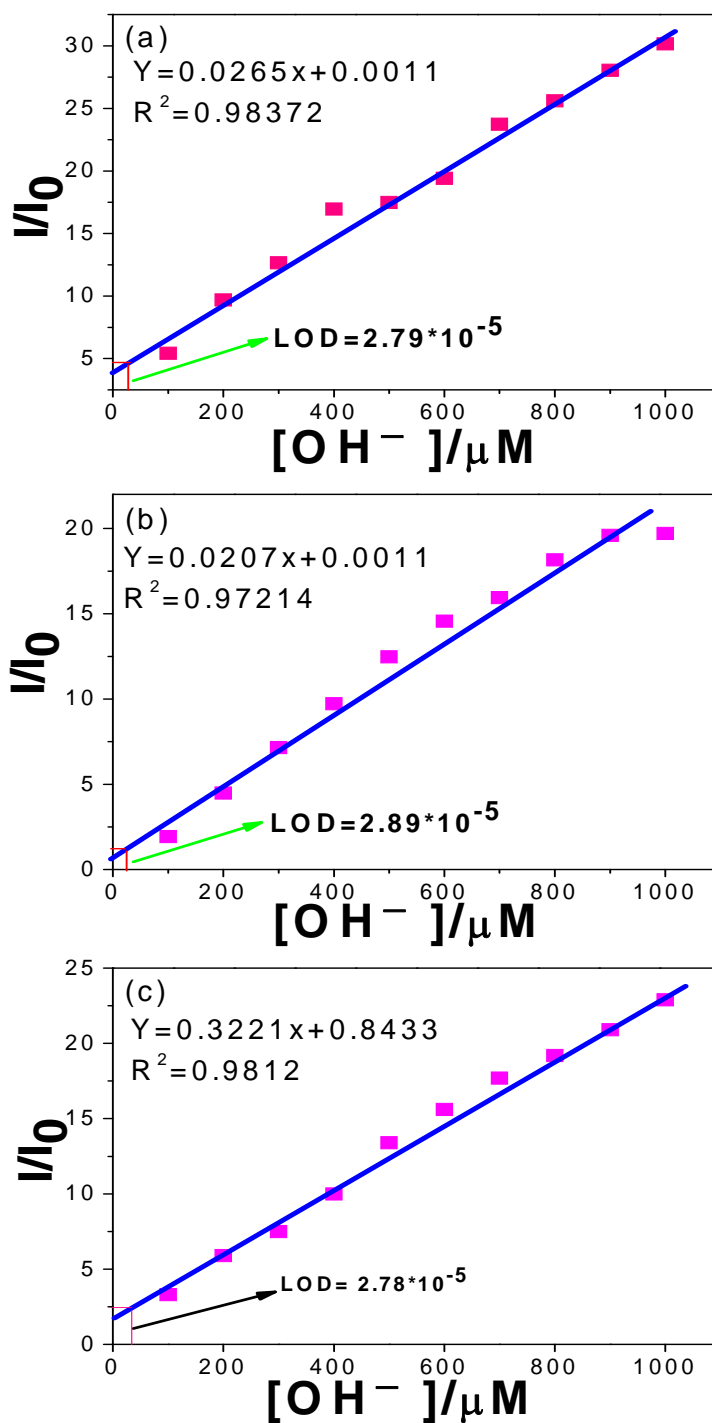
**Fig. S39** Mass (FAB) spectral changes of **F3** (1 equiv.) + OH<sup>-</sup> (5 equiv.).



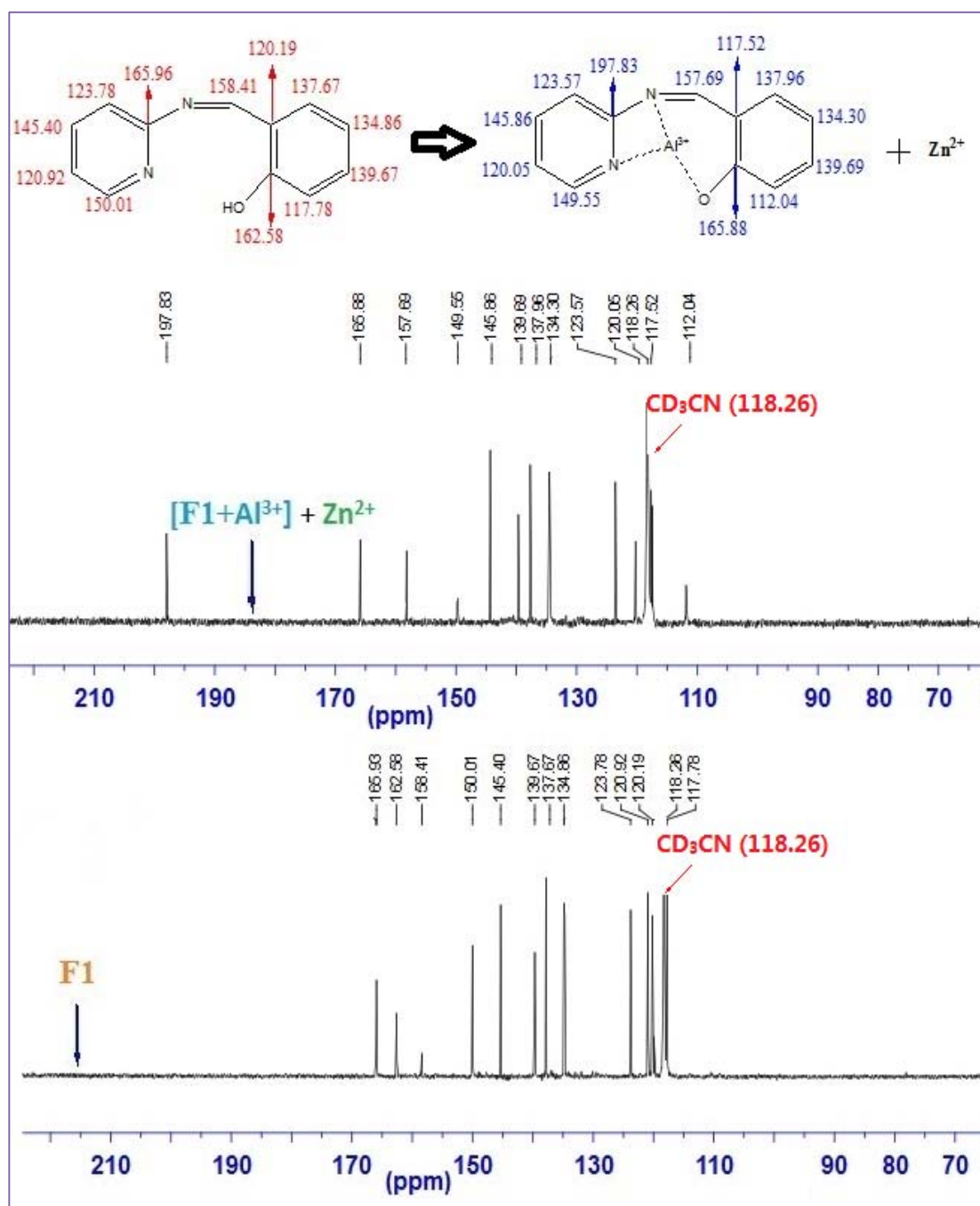
**Fig. S40** UV-Vis absorption spectra (a, b), fluorescence spectra (c, d), and reversible cycles (e, f) for sensor reversibilities of F1+ Zn<sup>2+</sup> and F2+ Zn<sup>2+</sup>, respectively.



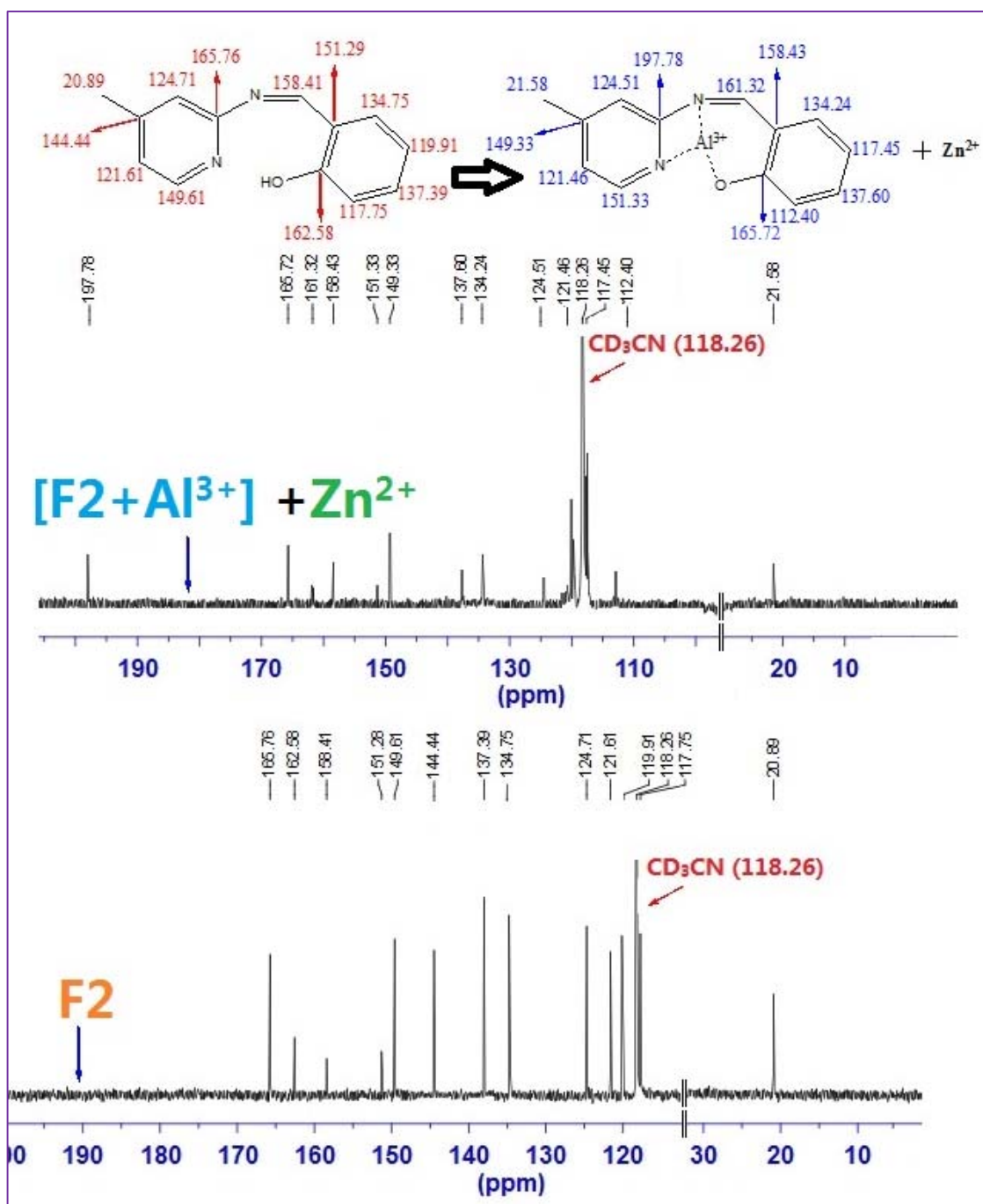
**Fig. S41** Standard deviations and linear fit equations for detection limit calculations of (a) **F1** +  $Zn^{2+}$ , (b) **F2** +  $Zn^{2+}$ , (c) **F1** +  $Al^{3+}$ , (d) **F2** +  $Al^{3+}$  and (e) **F3** +  $Al^{3+}$ . [Note: Detection limit calculations were based on relative fluorescence intensity changes versus respective metal ion concentrations].



**Fig. S42** Detection limits calculations of (a) **F1+OH<sup>-</sup>**, (b) **F2+OH<sup>-</sup>**, and (c) **F3+OH<sup>-</sup>**, respectively, by standard deviations and linear fit equations.



**Fig. S43** <sup>13</sup>C NMR spectral changes of **F1** (1 equiv.) in CD<sub>3</sub>CN with (Al<sup>3+</sup> + Zn<sup>2+</sup>) [(1:1) (each 3 equiv.)] in D<sub>2</sub>O.



**Fig. S44** <sup>13</sup>C NMR spectral changes of F2 (1 equiv.) in CD<sub>3</sub>CN with (Al<sup>3+</sup> + Zn<sup>2+</sup>) [(1:1) (each 3 equiv.)] in D<sub>2</sub>O.

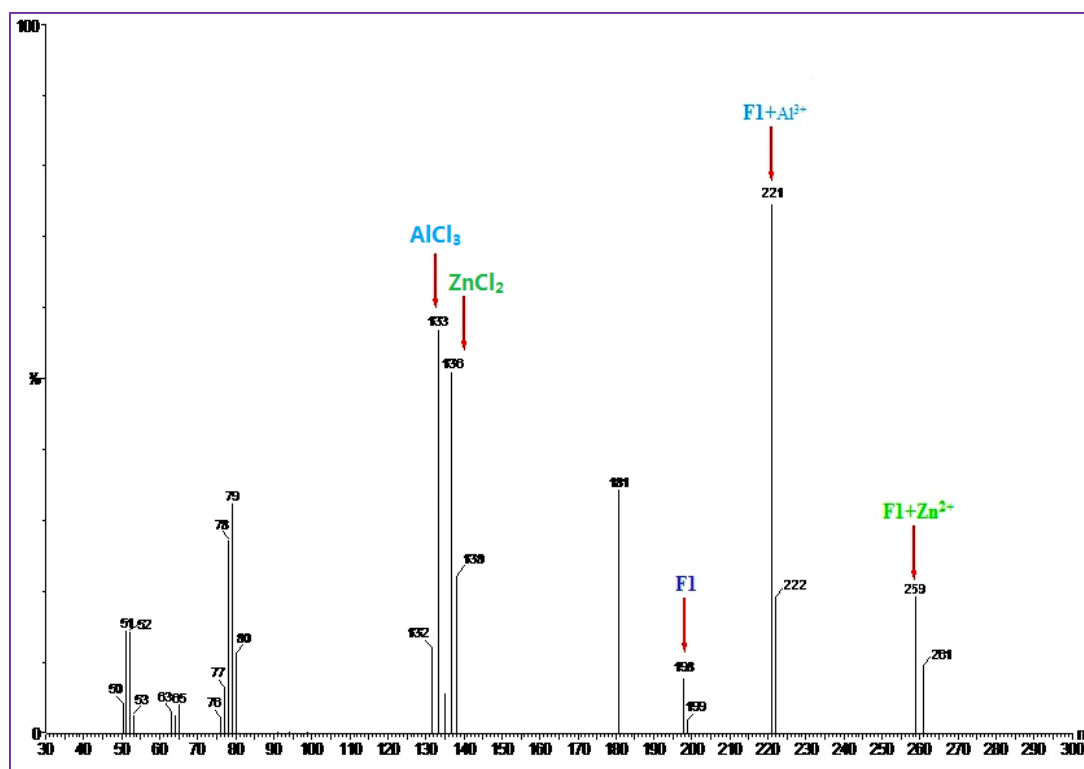


Fig. S45 Mass (FAB) spectral changes of F1 (1 equiv.) + (Al<sup>3+</sup>+Zn<sup>2+</sup>) [(1:1) (each 3 equiv.)].

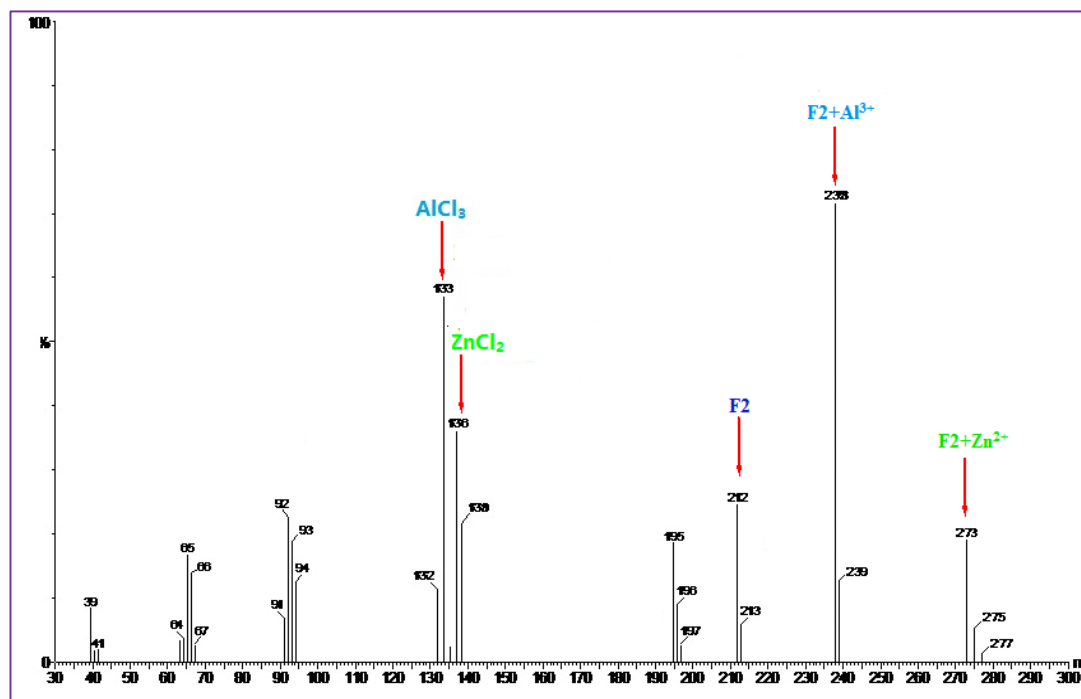


Fig. S46 Mass (FAB) spectral changes of F2 (1 equiv.) + (Al<sup>3+</sup> + Zn<sup>2+</sup>) [(1:1) (each 3 equiv.)].



## Response parameter and determination of binding constant<sup>2, 3</sup>

The response parameter  $\alpha$  is defined as the ratio of the free ligand concentration to the initial concentration of the ligand.  $\alpha$  defined as the ratio between the free ligand concentration ( $[L]$ ) and the total concentration of ligand  $[L_T]$ :

$$\alpha = \frac{[L]}{[L_T]}$$

$\alpha$  can be determined from the emission changes in the presence of different concentrations of  $M^{n+}$ :

$$\alpha = \frac{[I - I_0]}{[I_1 - I_0]}$$

where  $I_1$  and  $I_0$  are the limiting emission values for  $\alpha = 1$  (in the absence of  $M^{n+}$ ) and  $\alpha = 0$  (probe is completely complexes with  $M^{n+}$ ), respectively.

Tsein equation<sup>2</sup> to the following equations that can be used in any stoichiometric ratio between the ligand and analyte.

$$[M^{n+}]^m = \frac{1}{n.K} \cdot \frac{1}{[L]_T^{n-1}} \cdot \frac{1-\alpha}{\alpha^n}$$

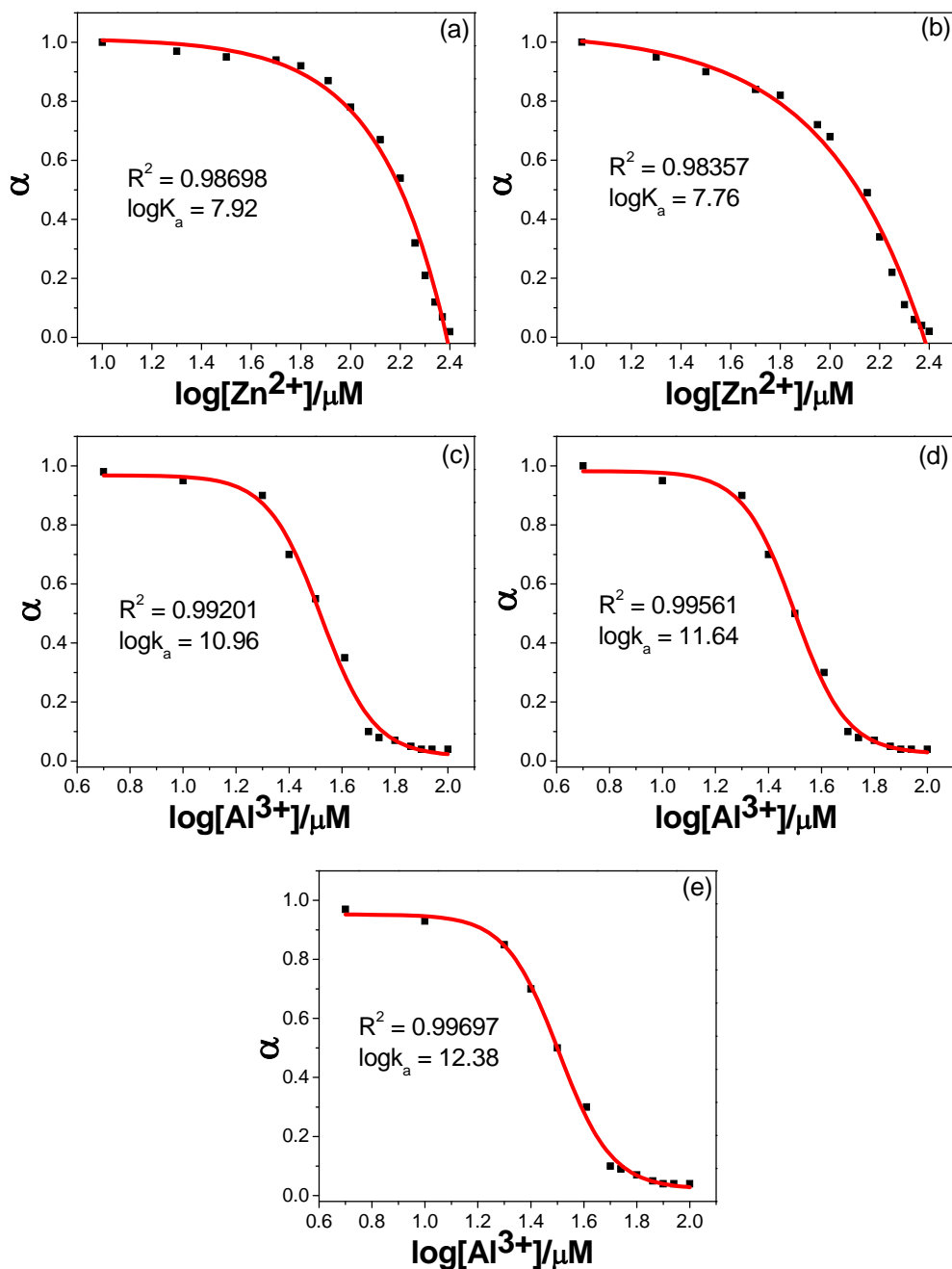
Where  $K$  is complex equilibrium constant,  $M_mL_n$  is metal-ligand,  $L$  is ligand,  $[L]$ ,  $[M^{n+}]$ , and  $[M_mL_n]$  are the concentrations of respective species.

The stoichiometric ratio of the  $Zn^{2+}$ : fluoroionophore is 1:1. So, this equation can be written as

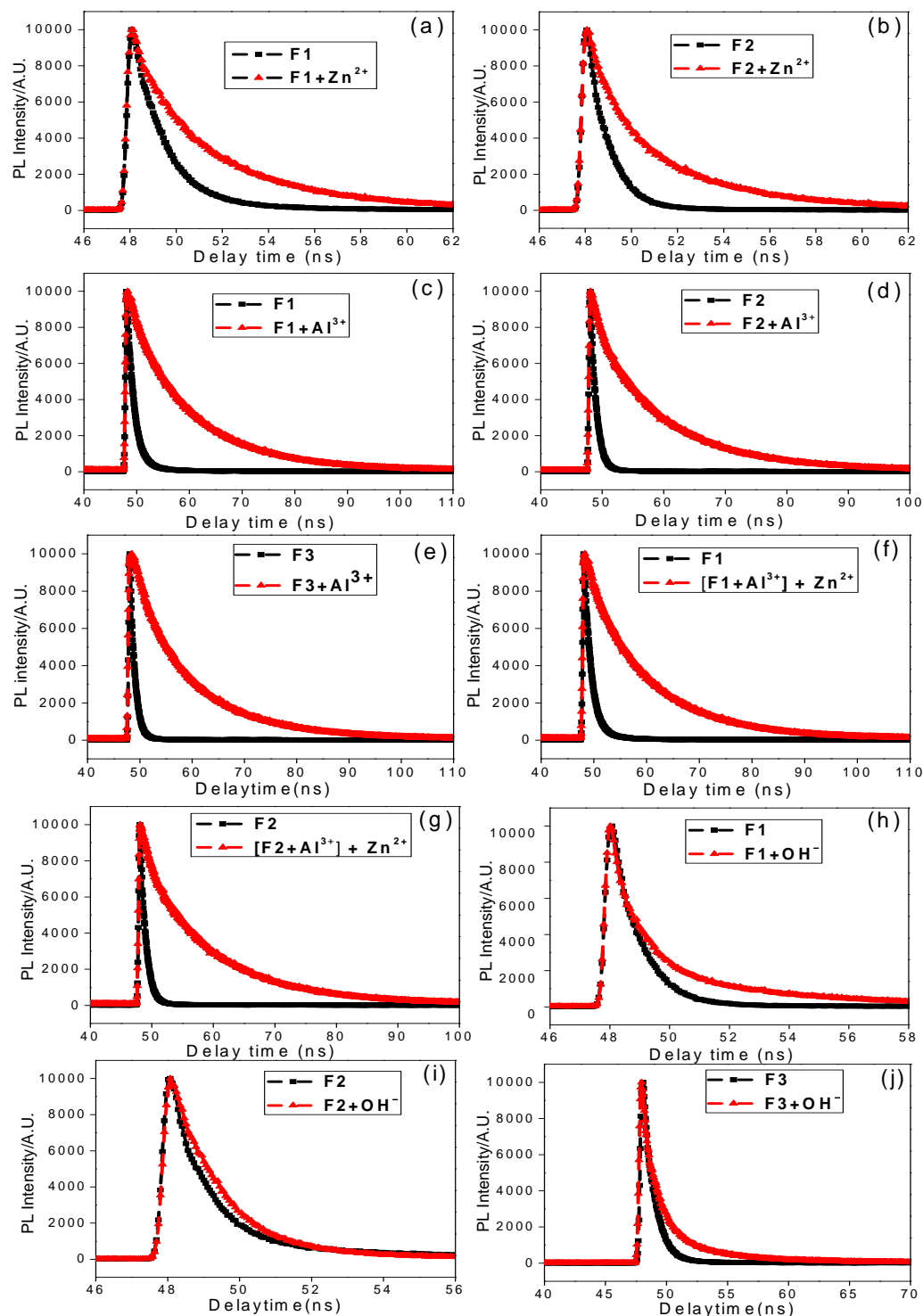
$$[Zn^{2+}] = \frac{1}{2KL} \cdot \frac{1-\alpha}{\alpha^2}$$

The stoichiometric ratio of the  $Al^{3+}$ : fluoroionophore is 1:1. So, this equation can be written as

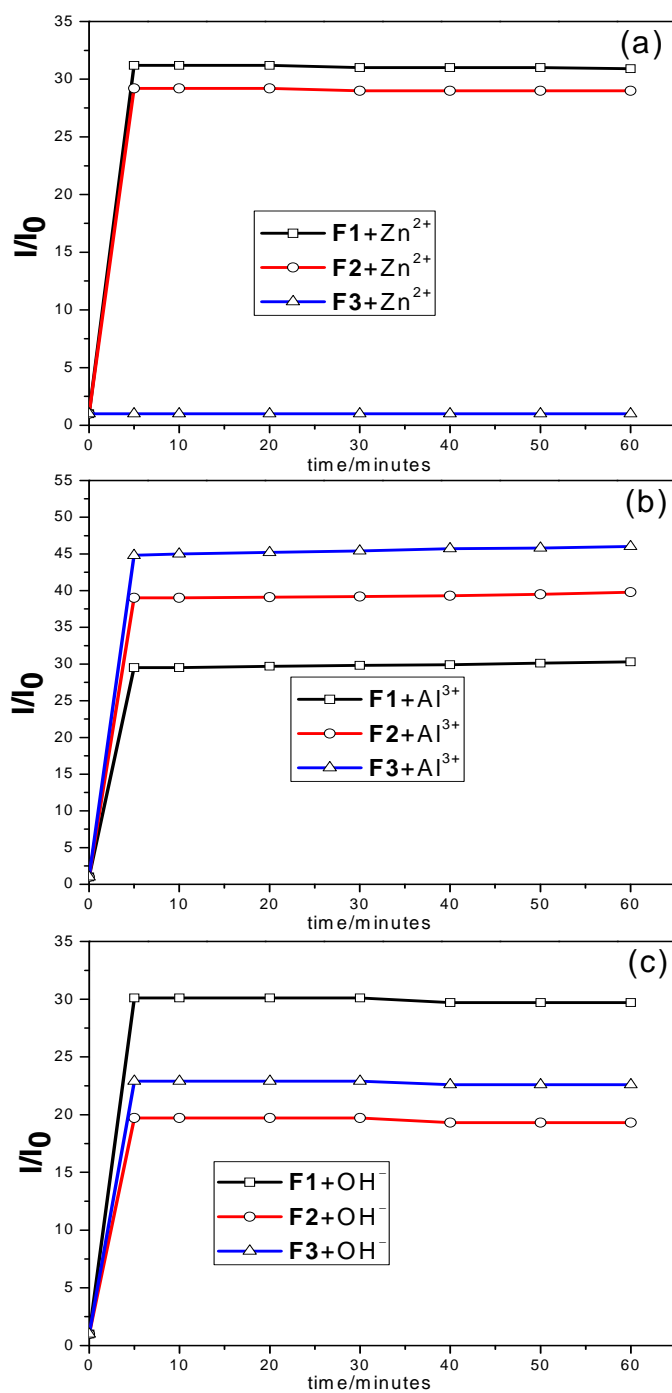
$$[Al^{3+}] = \frac{1}{3KL^2} \cdot \frac{1-\alpha}{\alpha^2}$$



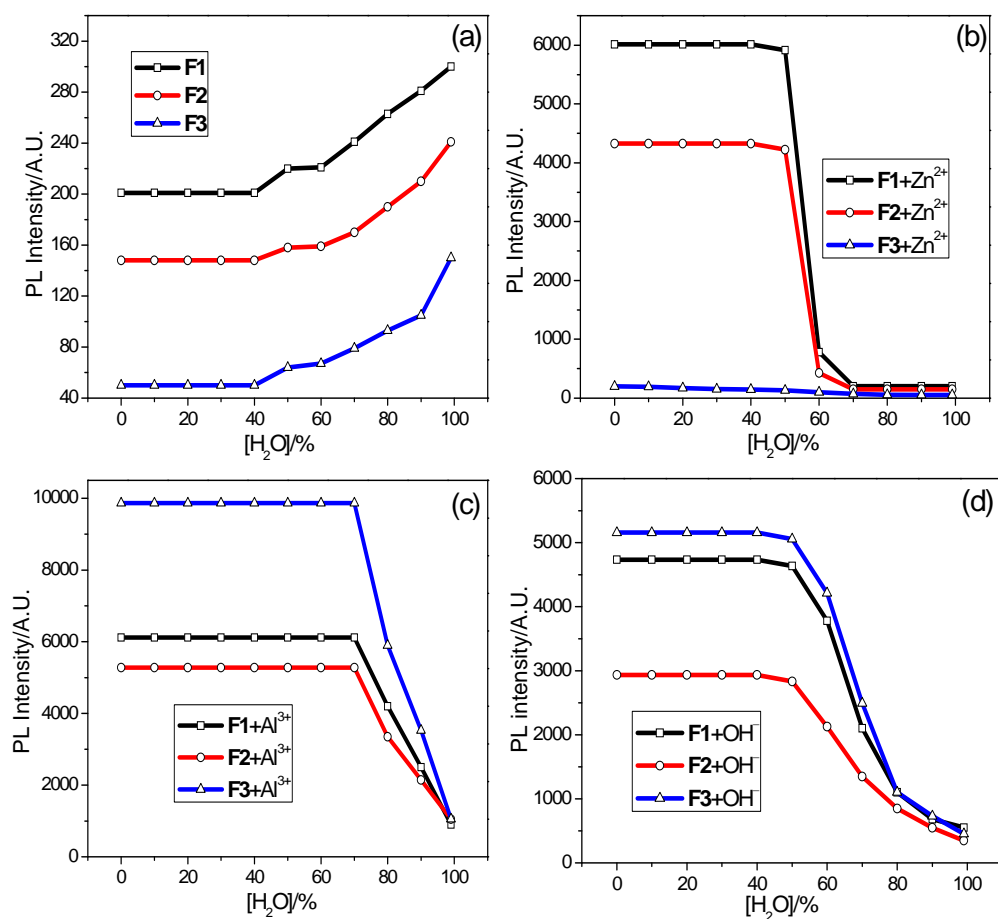
**Fig. S47** Response parameter values ( $\alpha$ ) of (a) **F1** and (b) **F2** as a function of the logarithm of  $[\text{Zn}^{2+}]$ ; (c) **F1**, (d) **F2**, and (e) **F3** as a function of the logarithm of  $[\text{Al}^{3+}]$ .  $\alpha$  is defined as the ratio between the free ligand concentration  $[\text{L}]$  and the initial concentration  $[\text{L}_0]$  of ligand.



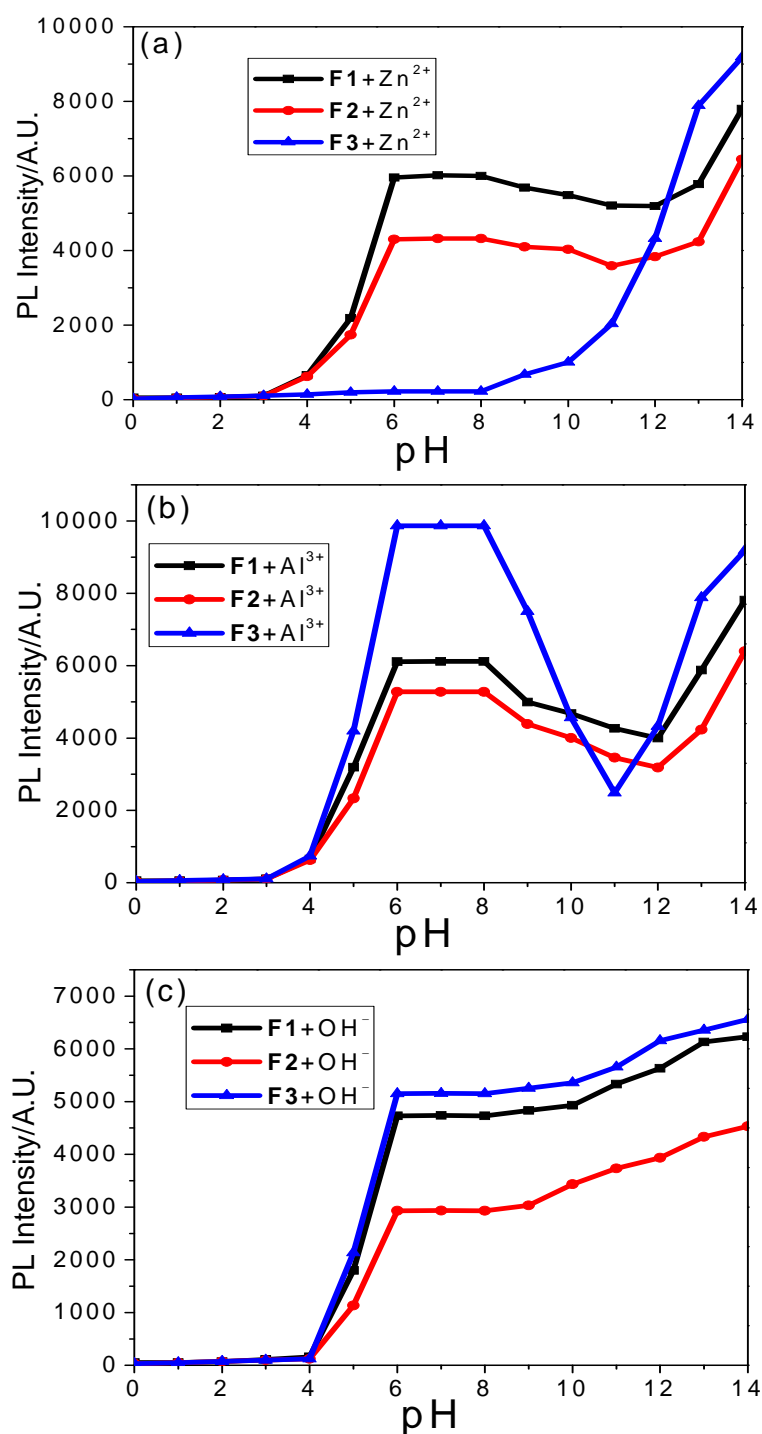
**Fig. S48** Time-resolved fluorescence spectra of [F1 and F2 (1 equiv.) + Zn<sup>2+</sup> (1 equiv.)] (a, b); [F1, F2 and F3 (1 equiv.) + Al<sup>3+</sup> (3 equiv.)] (c, d, and e); [F1 or F2 (1 equiv.) + (Al<sup>3+</sup>+Zn<sup>2+</sup>) [(1:1) (each 3 equiv.)] (f, g); and [F1, F2 and F3 (1 equiv.) + OH<sup>-</sup> (50 equiv.)] (h, i, and j)



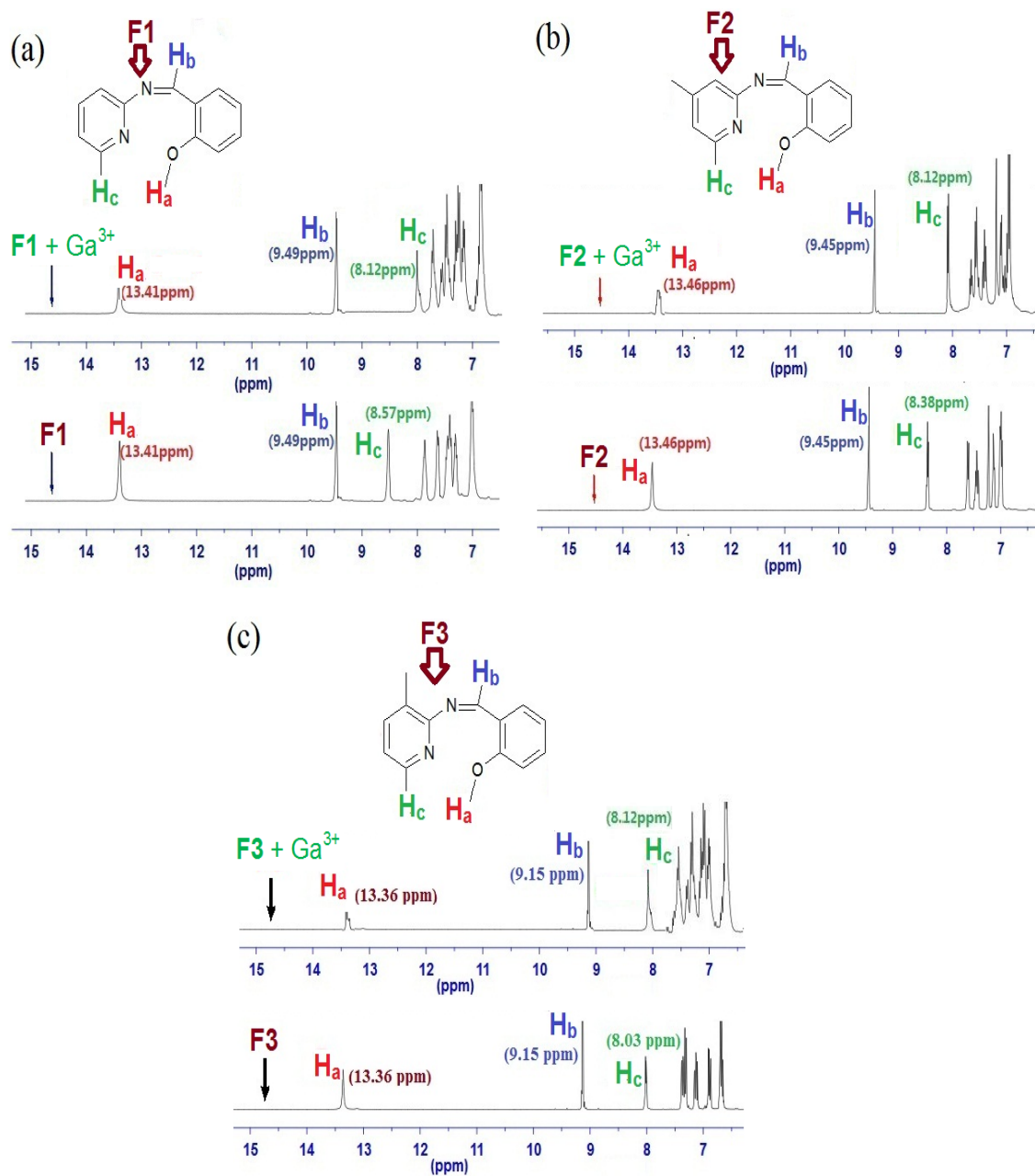
**Fig. S49** PL spectral responses of (a) **F1+Zn<sup>2+</sup>**, **F2+Zn<sup>2+</sup>** and **F3+Zn<sup>2+</sup>**, (b) **F1+Al<sup>3+</sup>**, **F2+Al<sup>3+</sup>** and **F3+Al<sup>3+</sup>**, and (c) **F1+OH<sup>-</sup>**, **F2+OH<sup>-</sup>** and **F3+OH<sup>-</sup>** as a function of time (0-60 minutes).



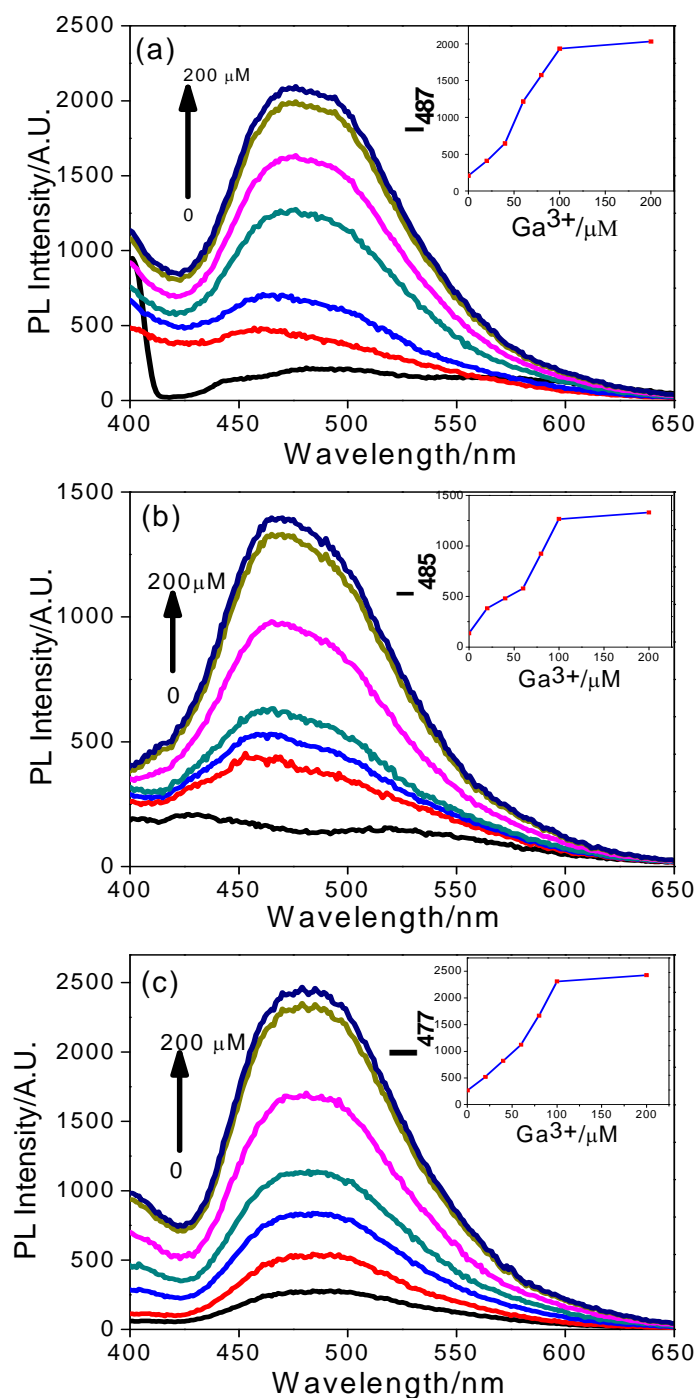
**Fig. S50** PL spectral responses of (a) F1, F2 and F3, (b) F1+Zn<sup>2+</sup>, F2+Zn<sup>2+</sup> and F3+Zn<sup>2+</sup>, (c) F1+Al<sup>3+</sup>, F2+Al<sup>3+</sup> and F3+Al<sup>3+</sup>, (d) F1+OH, F2+OH and F3+OH as a function of increasing water concentration (0-99%).



**Fig. S51** PL spectral responses of (a) F1+Zn<sup>2+</sup>, F2+Zn<sup>2+</sup> and F3+Zn<sup>2+</sup>, (b) F1+Al<sup>3+</sup>, F2+Al<sup>3+</sup> and F3+Al<sup>3+</sup>, (c) F1+OH<sup>-</sup>, F2+OH<sup>-</sup> and F3+OH<sup>-</sup> as a function of pH (0-14).

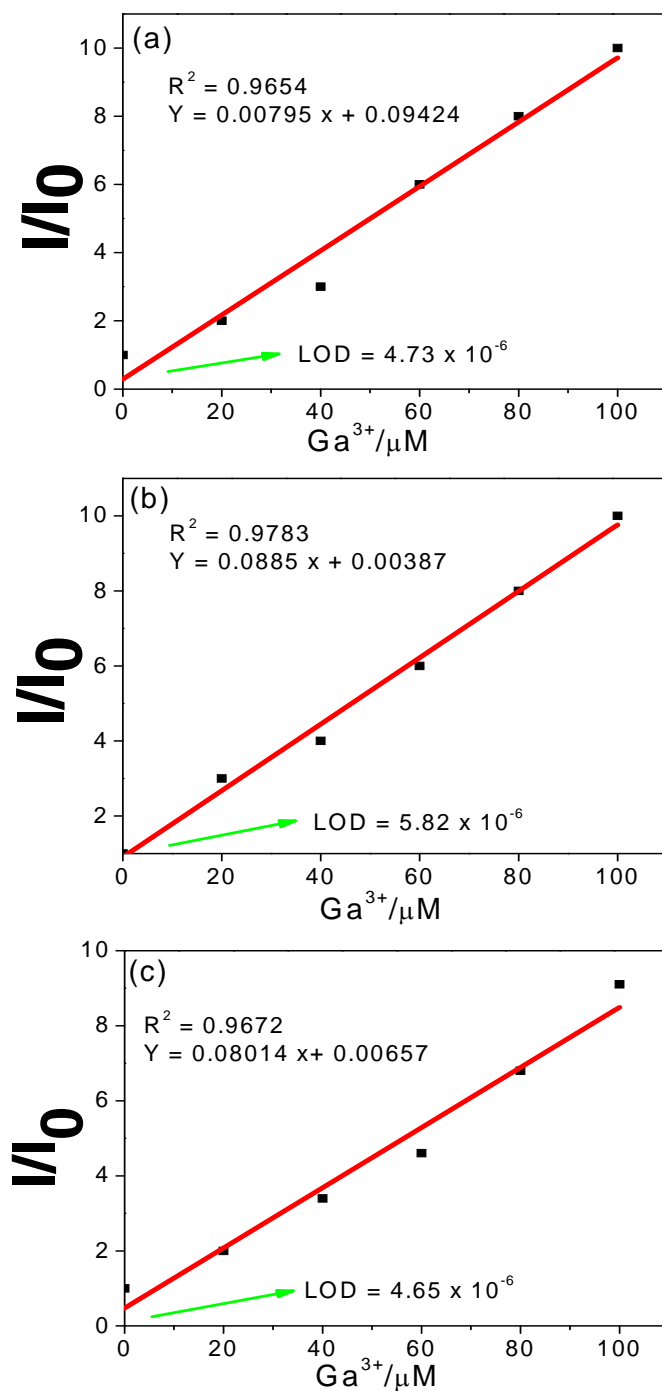


**Fig. S52**  $^1\text{H}$  NMR spectral changes of (a) **F1** (1 equiv.) in  $\text{CD}_3\text{CN}$  (b) **F2** (1 equiv.) in  $\text{CD}_3\text{CN}$  with  $\text{Ga}^{3+}$  ions (5 equiv.) in  $\text{D}_2\text{O}$ .



**Fig. S53** Fluorescence spectral changes of (a) **F1** ( $1 \times 10^{-5}$  M) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (6/4; vol/vol) ( $\lambda_{\text{ex}}=344$  nm), (b) **F2** ( $1 \times 10^{-5}$  M) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (6/4; vol/vol) ( $\lambda_{\text{ex}}=346$  nm), and (c) **F3** ( $1 \times 10^{-5}$  M) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (6/4; vol/vol) ( $\lambda_{\text{ex}}=343$  nm) titrated with 0-60  $\mu\text{M}$  of  $\text{Al}^{3+}$  ions in  $\text{H}_2\text{O}$  (0, 20, 40, 60, 80, 100 and 200  $\mu\text{M}$  were plotted). Insets show PL spectral responses of (a) **F1**, (b) **F2** and (c) **F3** as a function of  $\text{Ga}^{3+}$ .





**Fig. S54** Standard deviations and linear fit equations for detection limit calculations of (a) **F1** + Ga<sup>3+</sup>, (b) **F2** + Ga<sup>3+</sup> and (c) **F3** + Ga<sup>3+</sup>. [Note: Detection limit calculations were based on relative fluorescence intensity changes versus respective metal ion concentrations].

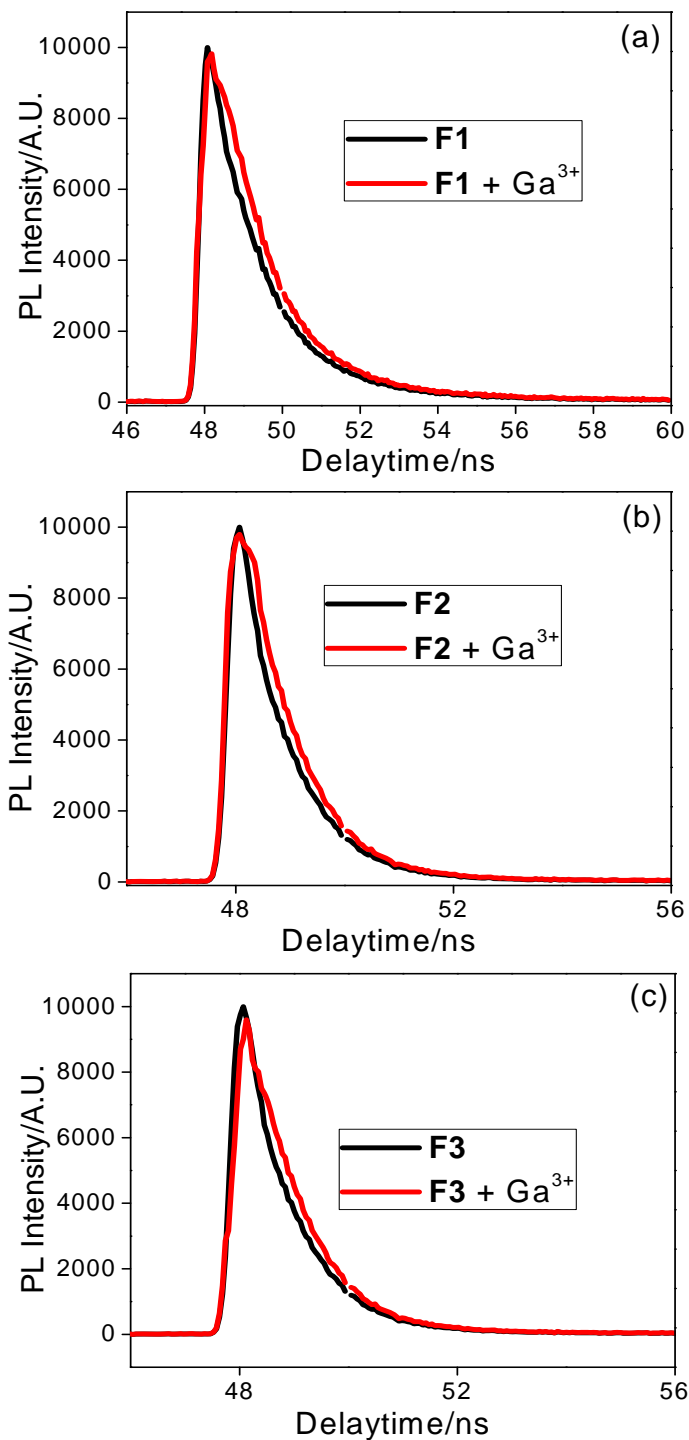


Fig. S55 TRPL spectra of (a) **F1** +  $\text{Ga}^{3+}$ , (b) **F2** +  $\text{Ga}^{3+}$  and (c) **F3** +  $\text{Ga}^{3+}$ .

**Table S1** Photophysical properties of sensor complexes.

Sensor	$\Phi$	<sup>a, c</sup> Association	<sup>a</sup> Detection	
Complexes		Constants	Limits	<sup>a, d</sup> $\tau$ (ns)
		(log $K_a$ )	(LODs/M)	
<b>F1</b> +Zn <sup>2+</sup>	0.281 <sup>a</sup>	7.92	4.22x10 <sup>-7</sup>	4.15
<b>F1</b> +Al <sup>3+</sup>	0.291 <sup>a, b</sup>	10.96	1.69x10 <sup>-6</sup>	11.97
[ <b>F1</b> +Al <sup>3+</sup> ] + Zn <sup>2+</sup>	0.286 <sup>a</sup>	NA	NA	11.78
<b>F1</b> +OH <sup>-</sup>	0.220 <sup>a</sup>	NA	2.79x10 <sup>-5</sup>	3.95
<b>F1</b> +Ga <sup>3+</sup>	0.072	NA	4.73x10 <sup>-6</sup>	2.65
<b>F2</b> +Zn <sup>2+</sup>	0.196 <sup>a</sup>	7.76	4.89x10 <sup>-7</sup>	3.83
<b>F2</b> +Al <sup>3+</sup>	0.221 <sup>a, b</sup>	11.64	1.42x10 <sup>-6</sup>	11.52
[ <b>F2</b> +Al <sup>3+</sup> ] + Zn <sup>2+</sup>	0.214 <sup>a</sup>	NA	NA	11.47
<b>F2</b> +OH <sup>-</sup>	0.122 <sup>a</sup>	NA	2.89x10 <sup>-5</sup>	2.28
<b>F2</b> +Ga <sup>3+</sup>	0.064	NA	5.82x10 <sup>-6</sup>	1.76
<b>F3</b> +Al <sup>3+</sup>	0.307 <sup>a, b</sup>	12.38	1.27x10 <sup>-6</sup>	12.16
<b>F3</b> +OH <sup>-</sup>	0.171 <sup>a</sup>	NA	2.78x10 <sup>-5</sup>	2.18
<b>F3</b> +Ga <sup>3+</sup>	0.076	NA	4.65x10 <sup>-6</sup>	1.54

<sup>a</sup>CH<sub>3</sub>CN/H<sub>2</sub>O (6/4), <sup>b</sup>CH<sub>3</sub>CN/H<sub>2</sub>O (3/7), 9-10 DPA in CH<sub>3</sub>CN as a reference standard ( $\Phi = 0.9$ ) and <sup>c</sup>[Zn<sup>2+</sup>] = 1/2K<sub>a</sub>L (1- $\alpha$  /  $\alpha^2$ ) and [Al<sup>3+</sup>] = 1/3K<sub>a</sub>L<sup>2</sup> (1- $\alpha$  /  $\alpha^3$ ); where L is the ligand and  $\alpha$  = ratio between the free ligand concentration [L] and the initial concentration of ligand [L<sub>0</sub>], <sup>d</sup>Fluorescence lifetimes.

**Table S2** TRPL decay constants of **F1**, **F2**, and **F3** in the presence of  $Zn^{2+}$ ,  $Al^{3+}$  and  $OH^-$  ions.

Compound	$\tau_1$ (ns)	$\tau_2$ (ns)	$A_1$ (%)	$A_2$ (%)	$\tau_{Avg}$ (ns)
<b>F1</b>	1.38 <sup>a</sup>	8.93 <sup>a</sup>	89.2 <sup>a</sup>	10.8 <sup>a</sup>	2.19 <sup>a</sup>
	0.67 <sup>b</sup>	6.18 <sup>b</sup>	93.58 <sup>b</sup>	6.42 <sup>b</sup>	1.02 <sup>b</sup>
	1.55 <sup>c</sup>	5.91 <sup>c</sup>	27.6 <sup>c</sup>	72.4 <sup>c</sup>	3.85 <sup>c</sup>
<b>F1+Zn<sup>2+</sup></b>	2.59	5.58	27.5	72.5	4.15
<b>F1+Al<sup>3+</sup></b>	12.44	3.73	5.4	96.6	11.97
<b>[F1+Al<sup>3+</sup>] + Zn<sup>2+</sup></b>	11.68	3.71	6.8	93.2	11.78
<b>F1+OH<sup>-</sup></b>	1.49	4.90	37.2	62.8	3.95
<b>F1+Ga<sup>3+</sup></b>	1.67	6.72	76.2	23.8	2.65
<b>F2</b>	0.91 <sup>a</sup>	13.09 <sup>a</sup>	95.1 <sup>a</sup>	4.9 <sup>a</sup>	1.51 <sup>a</sup>
	0.71 <sup>b</sup>	7.66 <sup>b</sup>	95.25 <sup>b</sup>	4.75 <sup>b</sup>	1.04 <sup>b</sup>
	0.29 <sup>c</sup>	6.95 <sup>c</sup>	30.40 <sup>c</sup>	69.6 <sup>c</sup>	4.12 <sup>c</sup>
<b>F2+Zn<sup>2+</sup></b>	1.55	4.71	27.6	72.4	3.83
<b>F2+Al<sup>3+</sup></b>	12.08	2.28	5.1	94.9	11.52
<b>[F2+Al<sup>3+</sup>] + Zn<sup>2+</sup></b>	12.00	2.04	4.9	95.1	11.47
<b>F2+OH<sup>-</sup></b>	0.99	5.74	44.6	55.4	2.28
<b>F2+Ga<sup>3+</sup></b>	0.78	12.67	87.3	12.7	1.76
<b>F3</b>	0.88 <sup>a</sup>	13.48 <sup>a</sup>	98.1 <sup>a</sup>	1.9 <sup>a</sup>	1.35 <sup>a</sup>
	0.70 <sup>b</sup>	9.65 <sup>b</sup>	97.01 <sup>b</sup>	2.92 <sup>b</sup>	0.96 <sup>b</sup>
	0.51 <sup>c</sup>	6.68 <sup>c</sup>	27.72 <sup>c</sup>	72.28 <sup>c</sup>	3.59 <sup>c</sup>
<b>F3+Al<sup>3+</sup></b>	14.07	5.95	4.1	95.9	12.16
<b>F3+OH<sup>-</sup></b>	1.39	4.24	34.6	65.4	2.18
<b>F3+Ga<sup>3+</sup></b>	0.92	11.56	85.6	14.4	1.54

<sup>a</sup>pH=7, <sup>b</sup>pH=2 and <sup>c</sup>pH=12.