Supporting Information

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

Muthaiah Shellaiah, Yen-Hsing Wu and Hong-Cheu Lin*

Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30049, Taiwan (ROC)

*Correspondence should be addressed to
E-mail: linhc@mail.nctu.edu.tw
Fax: +8863-5724727; Tel: +8863-5712121 ext.55305
Table contents:

Experimental section (S2-S3)

$^1$H NMR, $^{13}$C NMR and mass (FAB) scanned spectra of F1, F2 and F3 (S3-S8)

PL spectral responses of F1, F2 and F3 as a function of pH (S8)

Fluorescence and time resolved photoluminescence spectra (TRPL) of F1, F2 and F3 at acidic, neutral and basic pHs (2, 7 and 12) (S9-S10)

Computation analysis of HOMO-LUMO of F1, F2 and F3 (Semi empirical method) (S11)

Sensor responses, of F1, F2 and F3 in CH$_3$CN/H$_2$O (3/7) towards Al$^{3+}$ ions in H$_2$O (S12)

UV-Vis titrations of F1 and F2 towards Zn$^{2+}$ ions (S13)

UV-Vis titrations of F1, F2 and F3 in CH$_3$CN/H$_2$O (6/4 and 3/7) towards Al$^{3+}$ ions (S14)

Fluorescence spectra and histograms of sensor responses of F1, F2 and F3 CH$_3$CN/H$_2$O (3/7) towards Al$^{3+}$ ions in H$_2$O (S15-S16)

Comparison of relative fluorescence intensity changes of F1, F2, and F3 in CH$_3$CN/H$_2$O (6/4 and 3/7) towards Zn$^{2+}$, Al$^{3+}$ and OH$^-$ ions in H$_2$O (S17)

Fluorescence and UV-Vis titrations and histograms of F1, F2 and F3 towards OH$^-$ ions (S18-S20)

Stoichiometry calculation of F1, F2 and F3 to Zn$^{2+}$ and Al$^{3+}$ ions (S21)

$^{13}$C NMR spectral changes towards sensor responses of F1, F2 and F3 (S22-S29)

Mass (FAB) spectral changes towards sensor responses of F1, F2 and F3 (S30-S33)

Sensor reversibilities of F1+Zn$^{2+}$ and F2+Zn$^{2+}$ (S34)

Detection limits (LODs) calculations of F1, F2 and F3 towards Zn$^{2+}$, Al$^{3+}$ and OH$^-$ ions (S35-S36)

$^{13}$C NMR and mass (FAB) spectral changes of ratiometric displacements of F1+Zn$^{2+}$ and F2+Zn$^{2+}$ by Al$^{3+}$ ions (S37-S39)

Response parameter values ($\alpha$) of metal sensor complexes of F1, F2 and F3 (S40-S41)

TRPL spectra of sensor complexes of F1, F2 and F3 (S42)

Fluorescence spectral responses of F1, F2, F3 and their sensor complexes with respect to water concentration, pH and time/minutes (S43-S45)

$^1$H NMR, PL titrations LOD calculations and TRPL spectra of F1, F2 and F3 towards Ga$^{3+}$ ions (S46-S49)

TRPL and photophysical properties (Table S1 and S2) of F1, F2, F3 and their sensor responses (S50-S51)
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. \(^1\)H and \(^{13}\)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 \(^1\)H and \(^{13}\)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 \(^1\)H and \(^{13}\)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 \(F_1\), \(F_2\) and \(F_3\) were characterized by NMR (\(^1\)H & \(^{13}\)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 Timeharps 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.1

Sensor titrations

Compounds \(F_1\), \(F_2\), and \(F_3\) were dissolved in CH\(_3\)CN/H\(_2\)O (6/4 and 3/7) at 1 x 10\(^{-5}\) M concentration. Li\(^+\), Ag\(^+\), K\(^+\), Na\(^+\), Cs\(^+\), Fe\(^2+\), Co\(^2+\), Zn\(^{2+}\), Cd\(^{2+}\), Pb\(^{2+}\), In\(^3+\), Ga\(^{3+}\), Mg\(^{2+}\), Cu\(^{2+}\), Cr\(^3+\), Fe\(^3+\) and Al\(^{3+}\) metal cations were dissolved in water medium at 1x10\(^{-4}\) M concentration from their respective chloro compounds, and Ag\(^{3+}\), Mn\(^{2+}\), Eu\(^3+\), Hg\(^{2+}\) and Mg\(^{2+}\) were made from AgNO\(_3\), Mn(OAc)\(_2\), Eu(OAc)\(_3\), Hg(OAc)\(_2\) and MgSO\(_4\), respectively, in water medium at 1 x 10\(^{-4}\) M concentration. (Metal ion mixtures contained all above ions, except Zn\(^{2+}\) and Al\(^{3+}\) ions). Ethylene diamine tetra acetic acid (EDTA) was dissolved in H\(_2\)O at 1x10\(^{-5}\) M. All OH\(^-\), BH\(_4\)\(^-\), NO\(_3\)\(^-\), PO\(_4\)\(^-\), ClO\(_4\)\(^-\), F\(^-\), Cl\(^-\), Br\(^-\) and I\(^-\) anions were dissolved in water medium at 1x10\(^{-3}\) M from their respective tetra butyl ammonium salts. (Anion mixtures contained all above ions, except OH\(^-\) ion).

NMR titrations and mass spectra

1 equiv. of \(F_1\), \(F_2\) and \(F_3\) in CD\(_3\)CN were titrated with 1 equiv. of Zn\(^{2+}\) or Al\(^{3+}\) in D\(_2\)O and also titrated with 1:1 ratiometrically (each 3 equiv.) mixed with Zn\(^{2+}\) and Al\(^{3+}\) ions in D\(_2\)O and those NMR samples were stirred at 70°C for 2 days, after complete evaporation of the solvent it was dried in vacuum at 50°C for 3 hrs. The fine powders obtained were further investigated via Mass (FAB) spectra to confirm the complex formation. Similarly, OH\(^-\) anion was investigated by titrating 5 equiv. of tetra butyl ammonium hydroxide (TBAOH) in D\(_2\)O with 1 equiv. of \(F_1\) or \(F_2\) or \(F_3\) in CD\(_3\)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 \(F_1\), \(F_2\) and \(F_3\)

To 1 equiv. of 2-aminopyridyl derivatives [5 g; 53.13 mmol (\(F_1\)) and 46.24 mmol (\(F_2\) and \(F_3\))] in 50 ml of methanol, 1 equiv. of salicylaldehyde [6.5 g, 53.22 mmol (\(F_1\)) and 5.65 g, 46.26 mmol (\(F_2\) and \(F_3\))] 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; 1H NMR (300 MHz, CDCl3) 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)); 13C NMR (300 MHz, CDCl3) 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+, 100%). Anal. Calcd for C12H10N2O: 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; 1H NMR (300 MHz, CDCl3) 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)); 13C NMR (300 MHz, CDCl3) 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+, 100%). Anal. Calcd for C13H12N2O: 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; 1H NMR (300 MHz, CDCl3) 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)); 13C NMR (300 MHz, CDCl3) 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+, 100%). Anal. Calcd for C13H12N2O: 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
Figure S1 $^1$H NMR spectrum of F1.

Figure S2 $^{13}$C NMR spectrum of F1.
Fig. S3 Mass (FAB) spectrum of F1.

Fig. S4 $^1$H NMR spectrum of F2.
Fig. S5 $^{13}$C NMR spectrum of F2.

Fig. S6 Mass (FAB) spectrum of F2.
Fig. S7 \(^1\)H NMR spectrum of F3.

Fig. S8 \(^{13}\)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 CH$_3$CN/H$_2$O (3/7; vol/vol), (b) F2 in CH$_3$CN/H$_2$O (3/7; vol/vol), and (c) F3 in CH$_3$CN/H$_2$O (3/7; vol/vol) towards metal ions in H$_2$O.
**Fig. S15** UV-Vis titrations of (a) **F1** (20 μM), and (b) **F2** (20 μM) in CH₃CN/H₂O (6/4; vol/vol) upon the addition of Zn²⁺ (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$_3$CN/H$_2$O (6/4 and 3/7; vol/vol ratios) upon the addition of Al$^{3+}$ (0, 2, 5, 10, 15, 20, 22, 24, 28, 32, 36 and 40 μM).
Fig. S17  Fluorescence spectral changes of (a) F1 (1x10⁻⁵ M) in CH₃CN/H₂O (3/7; vol/vol) (λₑₓ=344 nm), (b) F2 (1x10⁻⁵ M) in CH₃CN/H₂O (3/7; vol/vol) (λₑₓ=346 nm), and (c) F3 (1x10⁻⁵ M) in CH₃CN/H₂O (3/7; vol/vol) (λₑₓ=343 nm) titrated with 0-60 μM of Al³⁺ ions in H₂O (with an equal span of 3 μM). Insets show PL spectral responses of (a) F1, (b) F2 and (c) F3 as a function of Al³⁺.
Fig. S18  Relative fluorescence intensities of (a) F1 (20 μM), (b) F2 (20 μM) and (c) F2 (20 μM) in CH3CN/H2O (3/7; vol/vol) with 60 μM Al3+ in H2O in the presence of competing metal ions. Black bars; F1, F2, and F3 (20 μM) in CH3CN/H2O (3/7; vol/vol) with 60 μM of stated metal ions in H2O. Red bars; F1, F2, and F3 (20 μM) CH3CN/H2O (3/7; vol/vol) with 60 μM Al3+ + 60 μM of stated metal ions in H2O. (120 μM of Al3+ for Al3+ effect). (Mix = all metal ions except Zn2+ and Al3+).
**Fig. S19** Comparison of relative fluorescence intensity changes of (a) F1 in CH3CN/H2O (6/4 and 3/7; vol/vol ratios), (b) F2 in CH3CN/H2O (6/4 and 3/7; vol/vol ratios), and (c) F3 in CH3CN/H2O (6/4 and 3/7; vol/vol ratios) towards Zn2+, Al3+ and OH- ions in H2O.
Fig. S20 Fluorescence spectral changes of (a) F1 (20 μM) in CH3CN/H2O (6/4; vol/vol) (λex=346 nm), (b) F2 (20 μM) in CH3CN/H2O (6/4; vol/vol) (λex=344 nm) and (c) F3 (20 μM) in CH3CN/H2O (6/4; vol/vol) (λex=343 nm) titrated with 0-1000 μM of OH− ion in H2O (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− ion.
Fig. S21 Relative fluorescence intensities of (a) F1 (20 μM), (b) F2 (20 μM), and (c) F3 (20 μM) in CH₃CN/H₂O (6/4; vol/vol) with 1000 μM OH⁻ in H₂O in the presence of competing anions. Black bars; F1 or F2 (20 μM) in CH₃CN/H₂O (6/4; vol/vol) with 1000 μM of stated anions in H₂O. Red bars; F1 or F2 (20 μM) CH₃CN/H₂O (6/4; vol/vol) with 1000 μM OH⁻ + 1000 μM of stated anions in H₂O. (for OH⁻ effect 2000 μM of OH⁻). (Mix = all anions except OH⁻).
**Fig. S22** UV-Vis absorption spectral changes of (a) F1, (b) F2, and (c) F3, upon the addition of OH⁻ ions (0-1000 μM with an equal span of 100 μM).
**Fig. S23** Job plots for determination of stoichiometries of (a) $\text{F}_1 + \text{Zn}^{2+}$, (b) $\text{F}_2 + \text{Zn}^{2+}$, (c) $\text{F}_1 + \text{Al}^{3+}$, (d) $\text{F}_2 + \text{Al}^{3+}$, and (e) $\text{F}_3 + \text{Al}^{3+}$; $X_M = [\text{M}^{n+}] / ([\text{M}^{n+}] + [\text{F}_1 \text{ or } \text{F}_2 \text{ or } \text{F}_3])$; for (a), (b) $[\text{M}^{n+}] = \text{Zn}^{2+}$, and for (c), (d) and (e) $[\text{M}^{n+}] = \text{Al}^{3+}$. [Note: for (a), (b) stoichiometry calculations based on normalized PL spectral changes of $\text{F}_1$ and $\text{F}_2$ during the titration of $\text{Zn}^{2+}$, and for (c), (d) and (e) it was calculated from the UV-Vis spectral changes of $\text{Al}^{3+}$ titrations with $\text{F}_1$, $\text{F}_2$ and $\text{F}_3$]

$\text{F}_1+\text{Zn}^{2+} = 1:1$ stoichiometry (ca. 0.506); $\text{F}_1+\text{Al}^{3+} = 1:1$ stoichiometry (ca. 0.500)

$\text{F}_2+\text{Zn}^{2+} = 1:1$ stoichiometry (ca. 0.503); $\text{F}_2+\text{Al}^{3+} = 1:1$ stoichiometry (ca. 0.507) and

$\text{F}_3+\text{Al}^{3+} = 1:1$ stoichiometry (ca. 0.508)
Fig. S24 $^{13}$C NMR spectral changes of F1 (1 equiv.) in CD$_3$CN with Zn$^{2+}$ (1 equiv.) in D$_2$O.
Fig. S25 $^{13}$C NMR spectral changes of F1 (1 equiv.) in CD$_3$CN with Al$^{3+}$ (1 equiv.) in D$_2$O.
Fig. S26 $^{13}$C NMR spectral changes of F2 (1 equiv.) in CD$_3$CN with Zn$^{2+}$ (1 equiv.) in D$_2$O.
Fig. S27 $^{13}$C NMR spectral changes of F2 (1 equiv.) in CD$_3$CN with Al$^{3+}$ (1 equiv.) in D$_2$O.
Fig. S28 $^{13}$C NMR spectral changes of F3 (1 equiv.) in CD$_3$CN with Al$^{3+}$ (1 equiv.) in D$_2$O.
Fig. S29 $^{13}$C NMR spectral changes of F1 (1 equiv.) in CD$_3$CN with OH$^-$ (5 equiv.) in D$_2$O.
Fig. S30 $^{13}$C NMR spectral changes of F2 (1 equiv.) in CD$_3$CN with OH$^-$ (5 equiv.) in D$_2$O.
Fig. S31 $^{13}$C NMR spectral changes of F3 (1 equiv.) in CD$_3$CN with OH$^-$ (5 equiv.) in D$_2$O.
Fig. S32  Mass (FAB) spectral changes of F1 (1 equiv.) + Zn$^{2+}$ (1 equiv.).

Fig. S33  Mass (FAB) spectral changes of F1 (1 equiv.) + Al$^{3+}$ (1 equiv.).
Fig. S34. Mass (FAB) spectral changes of F2 (1 equiv.) + Zn²⁺ (1 equiv.).

Fig. S35. Mass (FAB) spectral changes of F2 (1 equiv.) + Al³⁺ (1 equiv.).
Fig. S36  Mass (FAB) spectral changes of F3 (1 equiv.) + Al$^{3+}$ (1 equiv.).

Fig. S37  Mass (FAB) spectral changes of F1 (1 equiv.) + OH$^-$ (5 equiv.).
Fig. S38  Mass (FAB) spectral changes of F2 (1 equiv.) + OH⁻ (5 equiv.).

Fig. S39  Mass (FAB) spectral changes of F3 (1 equiv.) + OH⁻ (5 equiv.).
Fig. S40  UV-Vis absorption spectra (a, b), fluorescence spectra (c, d), and reversible cycles (e, f) for sensor reversibilities of $F_1 + Zn^{2+}$ and $F_2 + Zn^{2+}$, 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⁻, (b) F2+OH⁻, and (c) F3+OH⁻, respectively, by standard deviations and linear fit equations.
Fig. S43  $^{13}$C NMR spectral changes of F1 (1 equiv.) in CD$_3$CN with (Al$^{3+}$ + Zn$^{2+}$) [(1:1) (each 3 equiv.)] in D$_2$O.
Fig. S44 $^{13}$C NMR spectral changes of F2 (1 equiv.) in CD$_3$CN with (Al$^{3+}$ + Zn$^{2+}$) [ (1:1) (each 3 equiv.)] in D$_2$O.
Fig. S45  Mass (FAB) spectral changes of F1 (1 equiv.) + (Al$^{3+}$+Zn$^{2+}$) [(1:1) (each 3 equiv.)].

Fig. S46  Mass (FAB) spectral changes of F2 (1 equiv.) + (Al$^{3+}$+Zn$^{2+}$) [(1:1) (each 3 equiv.)].
Response parameter and determination of binding constant\textsuperscript{2,3}

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\textsubscript{T}]:

$$\alpha = \frac{[L]}{[L\textsubscript{T}]}$$

$\alpha$ can be determined from the emission changes in the presence of different concentrations of M\textsuperscript{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\textsuperscript{n+}) and $\alpha = 0$ (probe is completely complexes with M\textsuperscript{n+}), respectively.

Tsein equation\textsuperscript{3} to the following equations that can be used in any stoichiometric ratio between the ligand and analyte.

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

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

The stoichiometric ratio of the Zn\textsuperscript{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\textsuperscript{3+}: fluoroionophore is 1:1. So, this equation can be written as

$$[Al^{3+}] = \frac{1}{3KL^2} \cdot \frac{1 - \alpha}{\alpha^3}$$
Fig. S47  Response parameter values ($\alpha$) of (a) F1 and (b) F2 as a function of the logarithm of [Zn$^{2+}$]; (c) F1, (d) F2, and (e) F3 as a function of the logarithm of [Al$^{3+}$]. $\alpha$ is defined as the ratio between the free ligand concentration [L] and the initial concentration [L$_0$] of ligand.
Fig. S48  Time-resolved fluorescence spectra of [F1 and F2 (1 equiv.) + Zn$^{2+}$ (1 equiv.)] (a, b); [F1, F2 and F3 (1 equiv.) + Al$^{3+}$ (3 equiv.)] (c, d, and e); [F1 or F2 (1 equiv.) + (Al$^{3+}$+Zn$^{2+}$) [(1:1) (each 3 equiv.)] (f, g); and [F1, F2 and F3 (1 equiv.) + OH$^{-}$ (50 equiv.)] (h, i, and j)
Fig. S49  PL spectral responses of (a) F1+Zn^{2+}, F2+Zn^{2+} and F3+Zn^{2+}, (b) F1+Al^{3+}, F2+Al^{3+} and F3+Al^{3+}, and (c) F1+OH^-, F2+OH^- and F3+OH^- as a function of time (0-60 minutes).
Fig. S50  PL spectral responses of (a) F1, F2 and F3, (b) F1+Zn$^{2+}$, F2+Zn$^{2+}$ and F3+Zn$^{2+}$, (c) F1+Al$^{3+}$, F2+Al$^{3+}$ and F3+Al$^{3+}$, (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+Zn²⁺, F2+Zn²⁺ and F3+Zn²⁺, (b) F1+Al³⁺, F2+Al³⁺ and F3+Al³⁺, (c) F1+OH⁻, F2+OH⁻ and F3+OH⁻ as a function of pH (0-14).
Fig. S52 $^1$H NMR spectral changes of (a) F1 (1 equiv.) in CD$_3$CN (b) F2 (1 equiv.) in CD$_3$CN with Ga$^{3+}$ ions (5 equiv.) in D$_2$O.
Fig. S53  Fluorescence spectral changes of (a) F1 (1x10^{-5} M) in CH$_3$CN/H$_2$O (6/4; vol/vol) ($\lambda_{ex}$=344 nm), (b) F2 (1x10^{-5} M) in CH$_3$CN/H$_2$O (6/4; vol/vol) ($\lambda_{ex}$=346 nm), and (c) F3 (1x10^{-5} M) in CH$_3$CN/H$_2$O (6/4; vol/vol) ($\lambda_{ex}$=343 nm) titrated with 0-60 $\mu$M of Al$^{3+}$ ions in H$_2$O (0, 20, 40, 60, 80, 100 and 200 $\mu$M were plotted). Insets show PL spectral responses of (a) F1, (b) F2 and (c) F3 as a function of Ga$^{3+}$. 

Electronic Supplementary Material (ESI) for Analyst
This journal is © The Royal Society of Chemistry 2013
Fig. S54 Standard deviations and linear fit equations for detection limit calculations of (a) F1 + Ga³⁺, (b) F2 + Ga³⁺ and (c) F3 + Ga³⁺. [Note: Detection limit calculations were based on relative fluorescence intensity changes versus respective metal ion concentrations].
Fig. S55  TRPL spectra of (a) F1 + Ga^{3+}, (b) F2 + Ga^{3+} and (c) F3 + Ga^{3+}.
Table S1 Photophysical properties of sensor complexes.

<table>
<thead>
<tr>
<th>Sensor Complexes</th>
<th>Φa</th>
<th>Association Constants (log K_a)</th>
<th>Detection Limits (LODs/M)</th>
<th>Fluorescence lifetimes (τ (ns))</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1+Zn²⁺</td>
<td>0.281&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.92</td>
<td>4.22x10⁻⁷</td>
<td>4.15</td>
</tr>
<tr>
<td>F1+Al³⁺</td>
<td>0.291&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>10.96</td>
<td>1.69x10⁻⁶</td>
<td>11.97</td>
</tr>
<tr>
<td>[F1+Al³⁺] + Zn²⁺</td>
<td>0.286&lt;sup&gt;a&lt;/sup&gt;</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>F1+OH⁻</td>
<td>0.220&lt;sup&gt;a&lt;/sup&gt;</td>
<td>NA</td>
<td>2.79x10⁻⁵</td>
<td>3.95</td>
</tr>
<tr>
<td>F1+Ga³⁺</td>
<td>0.072</td>
<td>NA</td>
<td>4.73x10⁻⁶</td>
<td>2.65</td>
</tr>
<tr>
<td>F2+Zn²⁺</td>
<td>0.196&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.76</td>
<td>4.89x10⁻⁷</td>
<td>3.83</td>
</tr>
<tr>
<td>F2+Al³⁺</td>
<td>0.221&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>11.64</td>
<td>1.42x10⁻⁶</td>
<td>11.52</td>
</tr>
<tr>
<td>[F2+Al³⁺] + Zn²⁺</td>
<td>0.214&lt;sup&gt;a&lt;/sup&gt;</td>
<td>NA</td>
<td>NA</td>
<td>11.47</td>
</tr>
<tr>
<td>F2+OH⁻</td>
<td>0.122&lt;sup&gt;a&lt;/sup&gt;</td>
<td>NA</td>
<td>2.89x10⁻⁵</td>
<td>2.28</td>
</tr>
<tr>
<td>F2+Ga³⁺</td>
<td>0.064</td>
<td>NA</td>
<td>5.82x10⁻⁶</td>
<td>1.76</td>
</tr>
<tr>
<td>F3+Al³⁺</td>
<td>0.307&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>12.38</td>
<td>1.27x10⁻⁶</td>
<td>12.16</td>
</tr>
<tr>
<td>F3+OH⁻</td>
<td>0.171&lt;sup&gt;a&lt;/sup&gt;</td>
<td>NA</td>
<td>2.78x10⁻⁵</td>
<td>2.18</td>
</tr>
<tr>
<td>F3+Ga³⁺</td>
<td>0.076</td>
<td>NA</td>
<td>4.65x10⁻⁶</td>
<td>1.54</td>
</tr>
</tbody>
</table>

<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 (Φ = 0.9) and <sup>c</sup>[Zn²⁺] = 1/2K_aL (1-α / α²) and [Al³⁺] = 1/3K_aL² (1-α / α³); where L is the ligand and α = ratio between the free ligand concentration [L] and the initial concentration of ligand [L₀]. <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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\tau_1$(ns)</th>
<th>$\tau_2$(ns)</th>
<th>A$_1$(%)</th>
<th>A$_2$(%)</th>
<th>$\tau_{avg}$(ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>1.38$^a$</td>
<td>8.93$^a$</td>
<td>89.2$^a$</td>
<td>10.8$^a$</td>
<td>2.19$^a$</td>
</tr>
<tr>
<td></td>
<td>0.67$^b$</td>
<td>6.18$^b$</td>
<td>93.58$^b$</td>
<td>6.42$^b$</td>
<td>1.02$^b$</td>
</tr>
<tr>
<td></td>
<td>1.55$^c$</td>
<td>5.91$^c$</td>
<td>27.6$^c$</td>
<td>72.4$^c$</td>
<td>3.85$^c$</td>
</tr>
<tr>
<td>F1+Zn$^{2+}$</td>
<td>2.59</td>
<td>5.58</td>
<td>27.5</td>
<td>72.5</td>
<td>4.15</td>
</tr>
<tr>
<td>F1+Al$^{3+}$</td>
<td>12.44</td>
<td>3.73</td>
<td>5.4</td>
<td>96.6</td>
<td>11.97</td>
</tr>
<tr>
<td>[F1+Al$^{3+}$]+Zn$^{2+}$</td>
<td>11.68</td>
<td>3.71</td>
<td>6.8</td>
<td>93.2</td>
<td>11.78</td>
</tr>
<tr>
<td>F1+OH$^-$</td>
<td>1.49</td>
<td>4.90</td>
<td>37.2</td>
<td>62.8</td>
<td>3.95</td>
</tr>
<tr>
<td>F1+Ga$^{3+}$</td>
<td>1.67</td>
<td>6.72</td>
<td>76.2</td>
<td>23.8</td>
<td>2.65</td>
</tr>
<tr>
<td>F2</td>
<td>0.91$^a$</td>
<td>13.09$^a$</td>
<td>95.1$^a$</td>
<td>4.9$^a$</td>
<td>1.51$^a$</td>
</tr>
<tr>
<td></td>
<td>0.71$^b$</td>
<td>7.66$^b$</td>
<td>95.25$^b$</td>
<td>4.75$^b$</td>
<td>1.04$^b$</td>
</tr>
<tr>
<td></td>
<td>0.29$^c$</td>
<td>6.95$^c$</td>
<td>30.40$^c$</td>
<td>69.6$^c$</td>
<td>4.12$^c$</td>
</tr>
<tr>
<td>F2+Zn$^{2+}$</td>
<td>1.55</td>
<td>4.71</td>
<td>27.6</td>
<td>72.4</td>
<td>3.83</td>
</tr>
<tr>
<td>F2+Al$^{3+}$</td>
<td>12.08</td>
<td>2.28</td>
<td>5.1</td>
<td>94.9</td>
<td>11.52</td>
</tr>
<tr>
<td>[F2+Al$^{3+}$]+Zn$^{2+}$</td>
<td>12.00</td>
<td>2.04</td>
<td>4.9</td>
<td>95.1</td>
<td>11.47</td>
</tr>
<tr>
<td>F2+OH$^-$</td>
<td>0.99</td>
<td>5.74</td>
<td>44.6</td>
<td>55.4</td>
<td>2.28</td>
</tr>
<tr>
<td>F2+Ga$^{3+}$</td>
<td>0.78</td>
<td>12.67</td>
<td>87.3</td>
<td>12.7</td>
<td>1.76</td>
</tr>
<tr>
<td>F3</td>
<td>0.88$^a$</td>
<td>13.48$^a$</td>
<td>98.1$^a$</td>
<td>1.9$^a$</td>
<td>1.35$^a$</td>
</tr>
<tr>
<td></td>
<td>0.70$^b$</td>
<td>9.65$^b$</td>
<td>97.01$^b$</td>
<td>2.92$^b$</td>
<td>0.96$^b$</td>
</tr>
<tr>
<td></td>
<td>0.51$^c$</td>
<td>6.68$^c$</td>
<td>27.72$^c$</td>
<td>72.28$^c$</td>
<td>3.59$^c$</td>
</tr>
<tr>
<td>F3+Al$^{3+}$</td>
<td>14.07</td>
<td>5.95</td>
<td>4.1</td>
<td>95.9</td>
<td>12.16</td>
</tr>
<tr>
<td>F3+OH$^-$</td>
<td>1.39</td>
<td>4.24</td>
<td>34.6</td>
<td>65.4</td>
<td>2.18</td>
</tr>
<tr>
<td>F3+Ga$^{3+}$</td>
<td>0.92</td>
<td>11.56</td>
<td>85.6</td>
<td>14.4</td>
<td>1.54</td>
</tr>
</tbody>
</table>

$^a$pH=7, $^b$pH=2 and $^c$pH=12.