A Sc-3-HF Complex as a Fluorescent Chemsensors for the Selective Detection of Dihydrogen Phosphate

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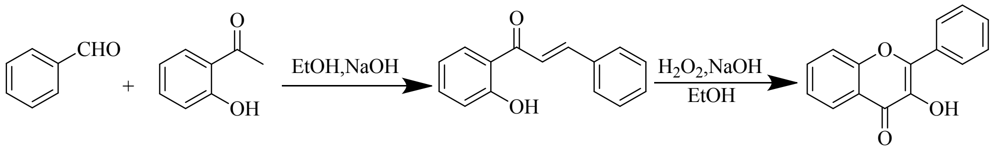
Supporting Information

Table of contents

1. General procedure for the synthesis of compound 3-HF S2
2. References S2
3. ^{1}H NMR and ^{13}C NMR data S2
4. UV-vis absorption data of 3-HF S4
5. Fluorescence spectra dataand HRMS data of Sc-3-HF S4
6. FTIR spectra data S4
7. Fluorescence spectra dataand HRMS data of Al-3-HF S4
8. PH response of Sc-3-HF complex for $H_2PO_4^-$ ion S5
9. Fluorescence sensing datas and UV-vis absorption datas for F^- ion S6
10. Fluorescence reversibility data...S7
11. The data of practical application S8

1. General procedure for the synthesis of compound 3-HF



3-HF

Scheme S1 The synthesis of compound 3-HF

3-HFwas synthesized according to previous report[1]. In a 250mL three-necked flask, 2-hydroxyacetophenone (12 mmol) and benzaldehyde (12 mmol) was dissolved in ethanol (30 mL) and warmed to 50℃, then aqueous NaOH (50%, 5.4 mL) was dropwise to the reaction mixture during 15 min. The mixture was stirred at 50℃ for 4 h and then kept at room temperature for 24 h. The yellow precipitate was formed and the reaction mixure was duiled with ice-cold water (80mL) until yellow precipitate was dissolved. The reaction mixture was neutralized with 1M HCl,mataining the temperature at 0°C.The precipitate was collected by filtration. Recrystallization from ethanol afforded the product 2'-hydroxychalcones, m=2.2874g, Yield=85%. And then in a 250mL round-bottom flask, 2'-hydroxychalcones (6mmol) was dissolved in ethanol (30mL) and aqueous NaOH (1.2 g in 5 mL water),the reaction mixture was placed in an ice-water bath and 4mL of 30% H_2O_2 solution was slowly added.The reaction mixture was stirred at room temperature for 6 h. The reaction mixture was neutralized with 1M HCl, mataining the temperature at 0°C. The yellow precipitate was gradually formed and collected by filtration.The precipitation was dried and the crude product was recrystallized from ethanol afforded the product 3-Hydroxyflavone (3-HF), m=1.0434g,Yield=73%.

2. References

1)B. Liu, J. Wang, G. Zhang, R. Bai, and Y.Pang, *ACS Appl. Mater. Interfaces* 2014, 6,4402-4407.

3.^{1}H NMR and ^{13}C NMR data

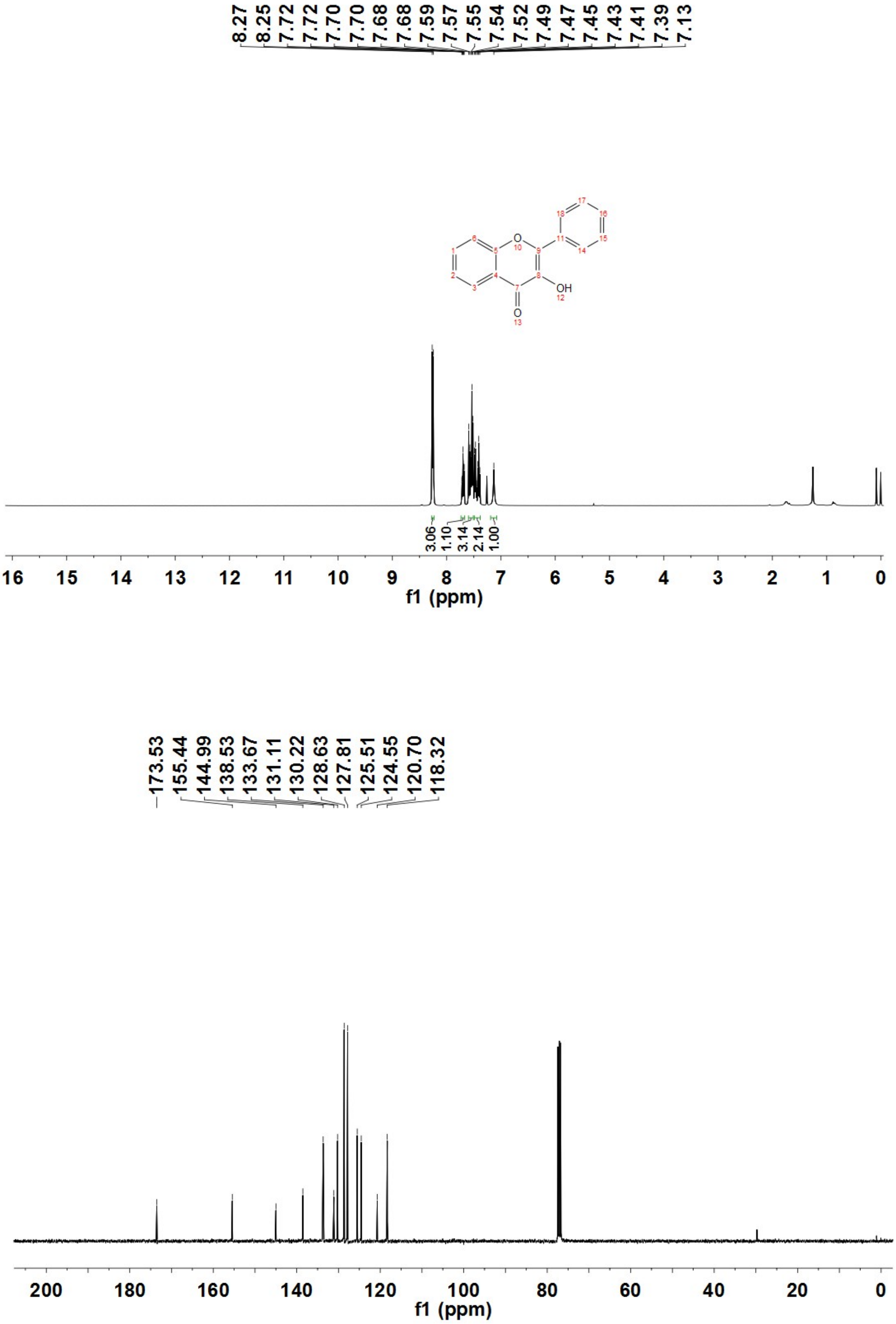


Fig. S1 ^{1}H NMR and ^{13}C NMR of 3-HF

4.UV-vis absorption data of 3-HF

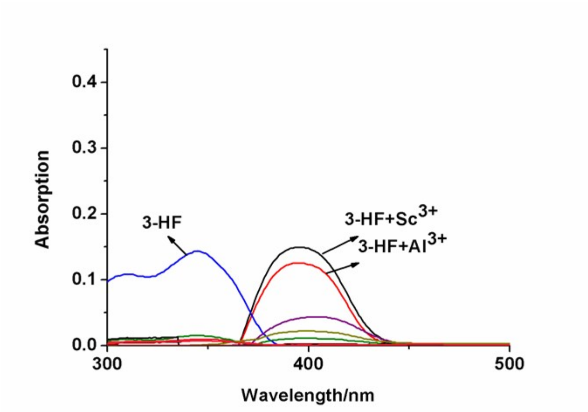


Fig.S2 The UV-vis absorption of 3-HF (10 μM, in CH_3CN) in a CH_3CN–H_2O (1 : 4, v/v) solution upon addition of various metal ions (10 μM, in H_2O).

5.Fluorescence spectra data and HRMS data of Sc-3-HF

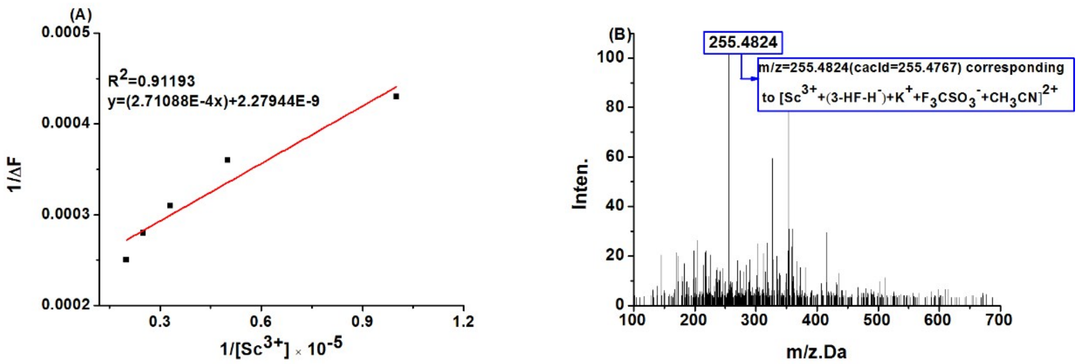


Fig. S3 (A)A linear plot of1/ΔF versus 1/[Sc^{3+}]. (B) ESI mass spectrum of Sc-3-HF.

6.FTIR spectra data

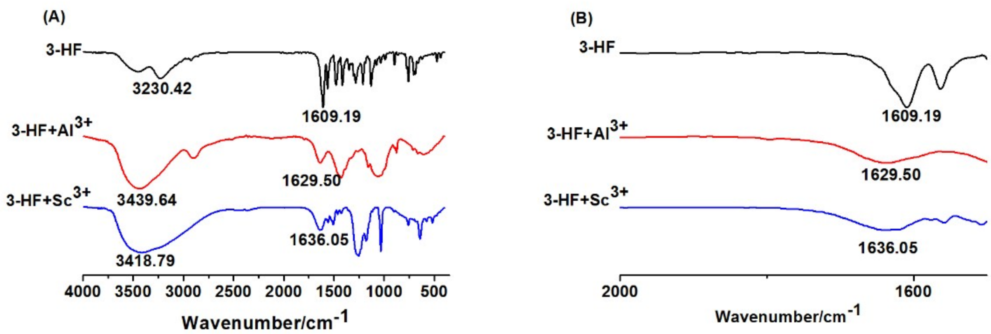


Fig. S4(A) The whole FTIR spectra of 3-HF, 3-HF–Sc^{3+} and 3-HF–Al^{3+} complex. (B) The 1600 region of spectra of 3-HF, 3-HF–Sc^{3+} and 3-HF–Al^{3+} complex.

7. Fluorescence spectra data and HRMS data of Al-3-HF

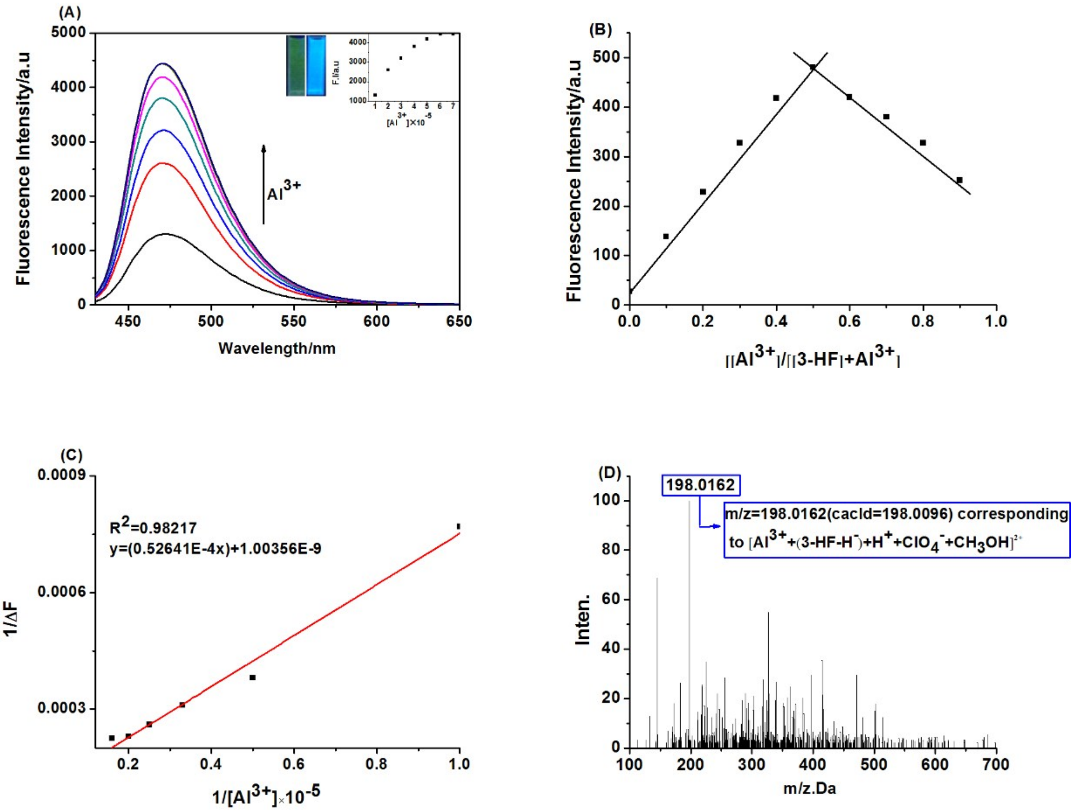


Fig. S5 (A) Titration curves of 3-HF (10 μM, in CH_3CN) in CH_3CN-H_2O (1 : 4, v/v) solution upon addition of $Al(ClO_4)_3{\cdot}9H_2O$ (0 ~ 70 μM, in H_2O). Inset (left) shows the color change of the solution before (left) and after (right) the addition of Al^{3+}; Inset (right) : plot of the fluorescence intensity at 470 nm vs. [Al^{3+}]. (B) Job's plot of the Al-3-HF complex in CH_3CN-H_2O (1 : 4, v/v) solution. The total concentration of 3-HF and Al^{3+} was 10 μM. The fluorescence intensity was monitored at 470 nm. (C) A linear plot of$1/\Delta F$ versus $1/[Al^{3+}]$ and association constant of the Al-3-HF complex was 1.9×10^5 M^{-1}. (D) ESI mass spectrum of Al-3-HF.

8. PH response of Sc-3-HF complex for $H_2PO_4^-$ ion

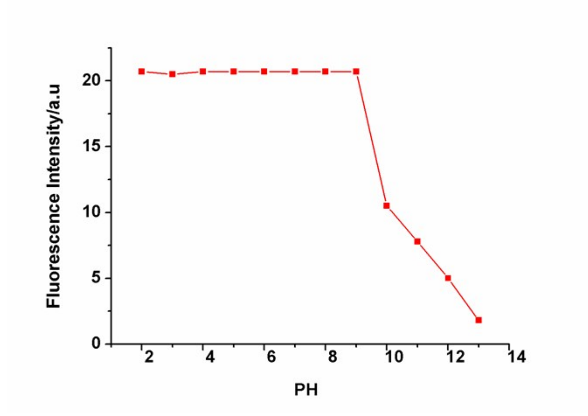


Fig.S6 pH response of the fluorescent chemsensor at the range of pH 2.0 -13.0.

9.Fluorescence sensing datas for F^- ion

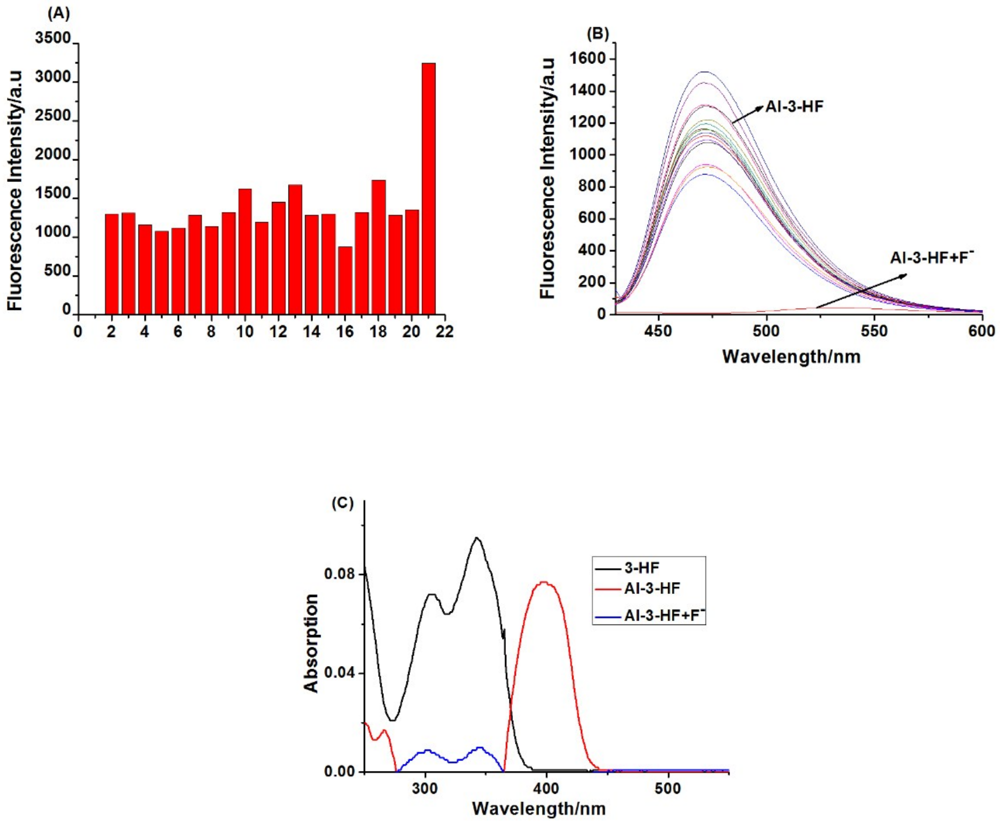


Fig. S7 (A)Fluorescence response of 3-HF (10 μM, in CH_3CN) in the presence of Al^{3+} (10μM, in H_2O) or Al^{3+} (10μM, in H_2O) with other metal ions (M^{n+}, 50 μM, in H_2O) in a CH_3CN-H_2O (1 : 4, v/v) solution. (1) Blank; (2) Al^{3+}; (3) Al^{3+}+Co^{2+}; (4) Al^{3+}+ Zn^{2+}; (5) Al^{3+}+Pb^{2+}; (6) Al^{3+}+Ag^{+}; (7) Al^{3+} +Ni^{2+}; (8) Al^{3+}+La^{3+}; (9) Al^{3+}+Fe^{3+}; (10) Al^{3+} +Hg^{2+}; (11) Al^{3+}+Mn^{2+}; (12) Al^{3+}+Fe^{2+}; (13) Al^{3+}+Cd^{2+}; (14) Al^{3+}+Ca^{2+}; (15) Al^{3+}+Cr^{3+}; (16) Al^{3+}+Na^{+}; (17) Al^{3+} +K^{+}; (18) Al^{3+}+Mg^{2+}; (19) Al^{3+}+Cu^{2+}; (20) Al^{3+}+ Pd^{2+}; (21) Al^{3+}+Sc^{3+}.The fluorescence intensity was monitored at 470 nm. (B)Fluorescence spectra of the Al-3-HF complex (10 μM, Al^{3+} : 1 equiv.) in CH_3CN-H_2O (1 : 4, v/v) solution upon addition of various anions (50 μM, in H_2O). (C)The UV-vis absorption of 3-HF (10 μM), Al-3-HF complex (10 μM), Al-3-HF complex (10 μM) + F^- (1.0 equiv.).

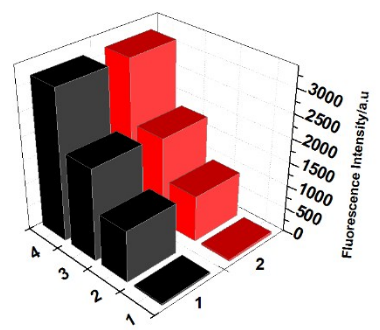
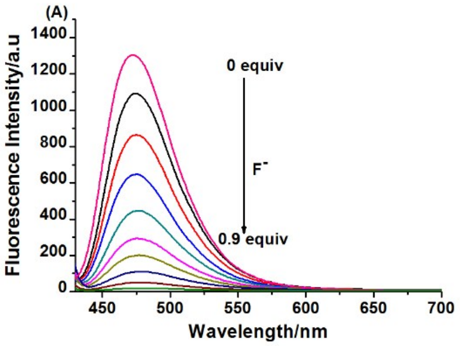
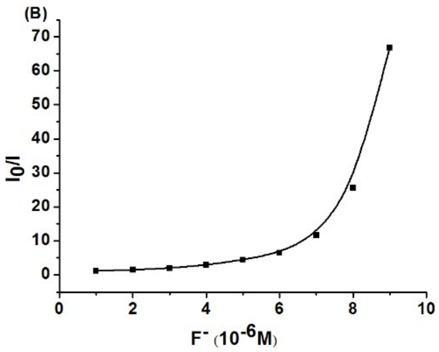


Fig. S8 Fluorescence intensity change profiles of 3-HF (10μM, in CH_3CN) in the presence of Sc^{3+}

(10μM, in H_2O) and Al^{3+} (10μM, in H_2O) with $H_2PO_4^-$, F^- (in H_2O) in CH_3CN-H_2O (1 : 4, v/v) solution.Left: (1,1) 3-HF+Sc^{3+}+Al^{3+}+F^- (2.0equiv.)+ $H_2PO_4^-$ (1.0equiv.); (1,2)3-HF+Sc^{3+}+Al^{3+}+F^- (2.0equiv.); (1,3)3-HF+Sc^{3+}+Al^{3+}+F^- (1.0 equiv);(1,4)3-HF+Sc^{3+}+Al^{3+}. Right:(2, 1) 3-HF+Sc^{3+}+Al^{3+}+$H_2PO_4^-$ (2.0equiv.) +F^-(1.0 equiv.);(2, 2)3-HF+Sc^{3+}+Al^{3+}+$H_2PO_4^-$ (2.0equiv.);(2,3)3-HF+Sc^{3+}+Al^{3+}+ $H_2PO_4^-$ (1.0equiv.);(2,4)3-HF+Sc^{3+}+Al^{3+}.The fluorescence intensity was monitored around 480 nm.





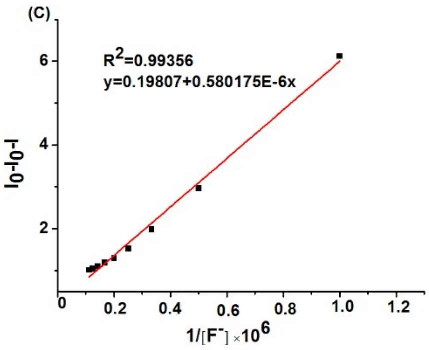


Fig. S9 (A) Titration curves oftheAl-3-HFcomplex (10 μM, 1 equiv. Al^{3+}) in CH_3CN-H_2O (1 : 4, v/v) solution upon addition of KH_2PO_4 (0 ~ 9 μM, in H_2O) solution. (B) A plot of I_0/Iversus [F^-]. (C) A linear plot of $I_0/(I_0$-I) versus 1/[F^-] and the binding constant was calculated to be 8.7 × 10^6 M^{-1}.

10.Fluorescence reversibility data

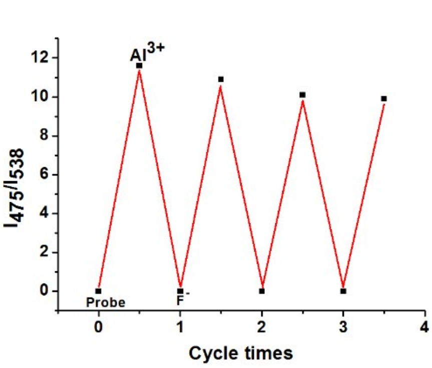
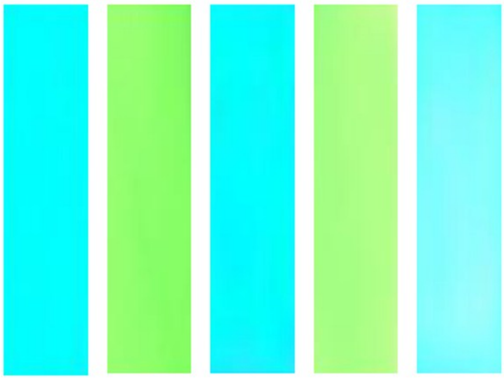


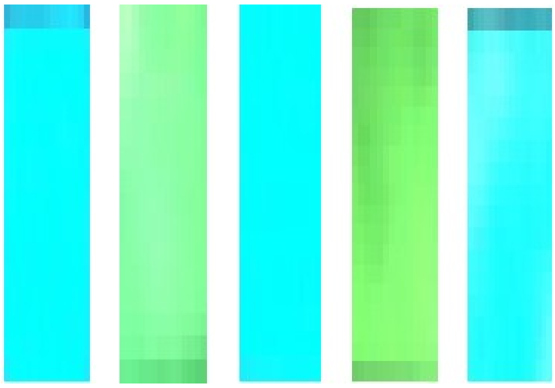
Fig. S10 Reversibility study of probe 3-HF (10 μM) in CH_3CN-H_2O (1 : 4, v/v) toward Al^{3+} (40 μM) upon addition of F^- (40 μM).

11.The data of practical application

(A)



(B)



(C)

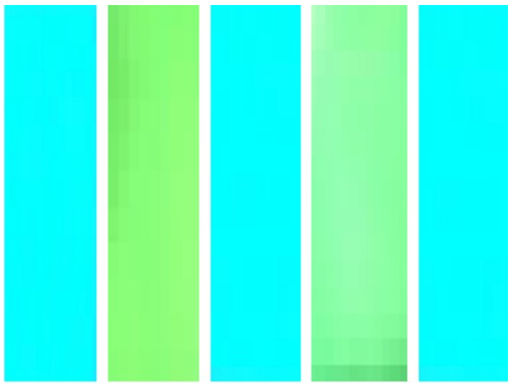


Fig.S11(A)Images of the test strips coated with Sc-3-HF for transformation among these ions. Left to right:Sc-3-HF, Sc-3-HF + $H_2PO_4^-$, Sc-3-HF + $H_2PO_4^-$ + Al^{3+}, Sc-3-HF + $H_2PO_4^-$ + Al^{3+} + F^-, Sc-3-HF + $H_2PO_4^-$ + Al^{3+} + F^- + Sc^{3+}.(B) Images of the test strips coated with Al-3-HF for transformation between F^- and Al^{3+}.Left to right: Al-3-HF,Al-3-HF + F^-, Al-3-HF + F^-+ Al^{3+}, Al-3-HF + F^-+Al^{3+} + F^-, Al-3-HF + F^-+ Al^{3+} + F^- + Al^{3+}. (C) Images of the test strips coated with Al-3-HF for transformation among these ions. Left to right: Al-3-HF, Al-3-HF + F^-, Al-3-HF + F^- + Sc^{3+}, Al-3-HF + F^- + Sc^{3+}+ $H_2PO_4^-$, Al-3-HF + F^- + Sc^{3+}+ $H_2PO_4^-$ + Al^{3+}.