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

Wei Du, a Chunman Jia, a,b Yinfeng Zhang, a,c Qing Chen, a Yile Wang, a Yan Huang, d Qi Zhang a,b

a Hainan Provincial Key Lab of Fine Chemistry, Hainan University, Haikou, Hainan 570228, China. Email: zhangqi@hainu.edu.cn; jiachunman@hainu.edu.cn.

b Key Study Center of the National Ministry of Education for Tropical Resources Utilization, Hainan University, Haikou, Hainan 570228, China.

c Department of Pathology, Johns Hopkins University School of Medicine, Baltimore, Maryland, USA. E-mail: yzhan249@jhmi.edu.

d School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China.

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

\[
\text{CH}_2\text{CHO} + \text{O} \xrightarrow{\text{EtOH, NaOH}} \text{O} \xrightarrow{\text{H}_2\text{O}_2, \text{NaOH}} \text{O} \xrightarrow{\text{EtOH}} \text{HO}
\]

Scheme S1 The synthesis of compound 3-HF

3-HF was 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°C, then aqueous NaOH (50%, 5.4 mL) was dropwise to the reaction mixture during 15 min. The mixture was stirred at 50°C for 4 h and then kept at room temperature for 24 h. The yellow precipitate was formed and the reaction mixture was diluted with ice-cold water (80 mL) until yellow precipitate was dissolved. The reaction mixture was neutralized with 1M HCl maintaining the temperature at 0°C. The precipitate was collected by filtration. Recrystallization from ethanol afforded the product 2'-hydroxychalcones, \(m=2.2874\)g, Yield=85%. And then in a 250mL round-bottom flask, 2'-hydroxychalcones (6 mmol) was dissolved in ethanol (30 mL) 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\(_2\)O\(_2\) solution was slowly added. The reaction mixture was stirred at room temperature for 6 h. The reaction mixture was neutralized with 1M HCl, maintaining 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), \(m=1.0434\)g, Yield=73%.

2. References


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$_3$CN) in a CH$_3$CN–H$_2$O (1 : 4, v/v) solution upon addition of various metal ions (10 μM, in H$_2$O).

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

Fig. S3 (A) A linear plot of 1/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$_3$CN) in CH$_3$CN-H$_2$O (1 : 4, v/v) solution upon addition of Al(ClO$_4$)$_3$·9H$_2$O (0 ~ 70 µM, in H$_2$O). 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$_3$CN-H$_2$O (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/∆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$_2$PO$_4^-$ ion

Fig. S6 pH response of the fluorescent chemsensor at the range of pH 2.0 -13.0.
9. Fluorescence sensing data for F⁻ ion

Fig. S7 (A) Fluorescence response of 3-HF (10 µM, in CH₃CN) in the presence of Al³⁺ (10 µM, in H₂O) or Al³⁺ (10 µM, in H₂O) with other metal ions (Mⁿ⁺, 50 µM, in H₂O) in a CH₃CN-H₂O (1 : 4, v/v) solution. (1) Blank; (2) Al³⁺; (3) Al³⁺+Co²⁺; (4) Al³⁺+Zn²⁺; (5) Al³⁺+Pb²⁺; (6) Al³⁺+Ag⁺; (7) Al³⁺+Ni²⁺; (8) Al³⁺+La³⁺; (9) Al³⁺+Fe³⁺; (10) Al³⁺+Hg²⁺; (11) Al³⁺+Mn²⁺; (12) Al³⁺+Fe²⁺; (13) Al³⁺+Cd²⁺; (14) Al³⁺+Ca²⁺; (15) Al³⁺+Cr³⁺; (16) Al³⁺+Na⁺; (17) Al³⁺+K⁺; (18) Al³⁺+Mg²⁺; (19) Al³⁺+Cu²⁺; (20) Al³⁺+Pd²⁺; (21) Al³⁺+Sc³⁺. The fluorescence intensity was monitored at 470 nm. (B) Fluorescence spectra of the Al-3-HF complex (10 µM, Al³⁺ : 1 equiv.) in CH₃CN-H₂O (1 : 4, v/v) solution upon addition of various anions (50 µM, in H₂O). (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 (10 µM, in CH₃CN) in the presence of Sc³⁺.
(10µM, in H₂O) and Al³⁺ (10µM, in H₂O) with H₂PO₄⁻, F⁻ (in H₂O) in CH₃CN-H₂O (1 : 4, v/v) solution. Left: (1,1) 3-HF+Sc³⁺+Al³⁺+F⁻ (2.0equiv.)+ H₂PO₄⁻ (1.0equiv.); (1,2)3-HF+Sc³⁺+Al³⁺+F⁻ (2.0equiv.); (1,3)3-HF+Sc³⁺+Al³⁺+F⁻ (1.0 equiv);(1,4)3-HF+Sc³⁺+Al³⁺. Right:(2, 1) 3-HF+Sc³⁺+Al³⁺+H₂PO₄⁻ (2.0equiv.) +F⁻(1.0 equiv.);(2, 2)3-HF+Sc³⁺+Al³⁺+H₂PO₄⁻ (2.0equiv.);(2,3)3-HF+Sc³⁺+Al³⁺+ H₂PO₄⁻ (1.0equiv.);(2,4)3-HF+Sc³⁺+Al³⁺. The fluorescence intensity was monitored around 480 nm.

Fig. S9 (A) Titration curves of the Al-3-HF complex (10 µM, 1 equiv. Al³⁺) in CH₃CN-H₂O (1 : 4, v/v) solution upon addition of KH₂PO₄ (0 ~ 9 µM, in H₂O) solution. (B) A plot of I₀/I versus [F⁻]. (C) A linear plot of I₀/(I₀-I) versus 1/[F⁻] and the binding constant was calculated to be 8.7 × 10⁶ M⁻¹.

10. Fluorescence reversibility data
Fig. S10 Reversibility study of probe 3-HF (10 μM) in CH$_3$CN-H$_2$O (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$_2$PO$_4^-$, Sc-3-HF + H$_2$PO$_4^- +$ Al$^{3+}$, Sc-3-HF + H$_2$PO$_4^- +$ Al$^{3+} +$ F$^-$, Sc-3-HF + H$_2$PO$_4^- +$ 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$_2$PO$_4^-$, Al-3-HF + F$^- +$ Sc$^{3+} +$ H$_2$PO$_4^- +$ Al$^{3+}$. 