Electronic Supplementary Material (ESI) for New Journal of Chemistry.

General information and materials

All solvents and starting materials were purchased from commercial sources and used without further purification. Salicylaldehyde was purchased from Energy Chemicals Shanghai China. Deionized water was used throughout the experimental work. The salts used as metal ions sources were $AlCl_3 \cdot 6H_2O$, $PbCl_2$, $Hg(OAc)_2$, $Cd(OAc)_2 \cdot 2H_2O$, LiCl, NaCl, KCl, $ZnCl_2$, $MgCl_2$, $CaCl_2$, $CuCl_2$, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $AgNO_3$, $FeCl_2$, $CrCl_3$, $MnCl_2$, $GaCl_3$ and $InCl_3$. The salts used as anion ions sources were KF, KBr, $KClO_4$, NH_4CN, KH_2PO_4, $KHSO_4$, KI, KNO_3, KOAc, KPF_6, K_2SO_4, KCl, K_3PO_4, and AlF_3.

Synthesis and characterization

Methyl 4-(pyridin-4-yl)benzoate: 4-(Pyridin-4-yl)benzoic acid (4.0 g, 20 mmol) was suspended in methanol (200 mL), concentrated sulfuric acid (5 mL) was added at room temperature, and the mixture was heated under reflux for 8 h. After completion of the reaction, the solvent was removed under vacuum, and water (100 mL) was added to the residue to precipitate it. The solid was filtered and further washed with water (50 mL × 3), the obtained solid was dried in air to a stable mass in 96% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (dd, *J* = 4.5, 1.6 Hz, 2H), 8.08 (d, *J* = 8.5 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.78 (dd, *J* = 4.5, 1.6 Hz, 2H), 3.89 (s, 3H).

4-(Pyridin-4-yl)benzohydrazide (**PBH**): Methyl 4-(pyridin-4-yl)benzoate (2.10 g, 10 mmol) was dissolved in methanol (30 mL), hydrazine hydrate (5 mL) was added at room temperature, and the mixture was heated under reflux overnight. After completion of the reaction, the solvent was removed under vacuum, and water (50 mL) was added to the residue to precipitate it. The solid was filtered and further washed with water (20 mL × 3), the obtained solid was dried in air to a stable mass in 90% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.90 (s, 1H), 8.65 (d, *J* = 5.1 Hz, 2H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 5.1 Hz, 2H), 4.55 (s, 2H).

***N'*-(2-hydroxybenzylidene)-4-(pyridin-4-yl)benzohydrazide** (**SPBH**): A mixture of **PBH** (213 mg, 1 mmol) and salicylaldehyde (122 mg, 1 mmol) in 10 mL of ethanol was mixed in a flask and then it was stirred at 50ºC for 6 h. When the reaction was completed (checked by TLC), the solvent was removed under vacuum. The solid obtained was suspended and shaken in ether, filtered and further washed with ether. It was recrystallized from *n*-hexane CH_2Cl_2 and dried in air to a stable mass. White flaky solid in 80% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.21 (s, 1H), 11.26 (s, 1H), 8.69 (d, *J* = 5.8 Hz, 2H), 8.67 (s, 1H), 8.08 (d, *J* = 8.2 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 5.8 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 6.95–6.88 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.6, 157.9, 150.8, 148.8, 146.4, 140.8, 133.6, 131.9, 129.9, 129.0, 127.5, 121.8, 119.8, 119.1, 116.9. HR-MS (ESI) calcd. for $C_{19}H_{16}N_3O_2$ $[M+1]^+$ m/z 318.1243, found 318.1247.

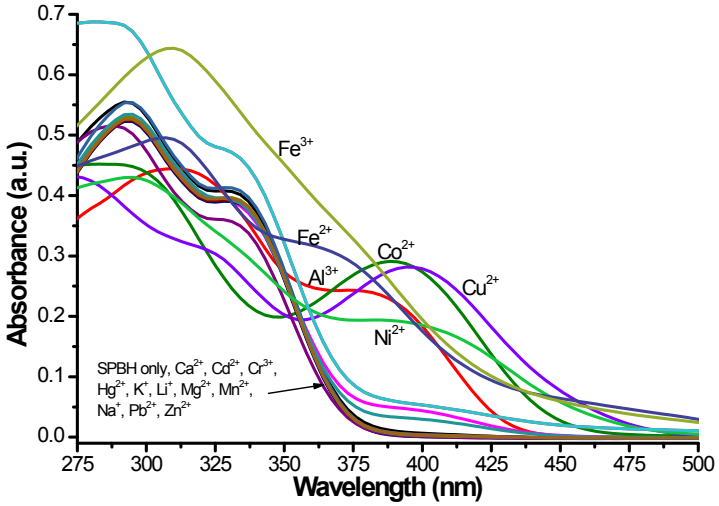

Fig. S1 UV-vis spectra of **SPBH** (25 µM) upon the addition of 75 µM of the respective metal ions (Ag^{+}, Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Hg^{2+}, K^{+}, Li^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+}) in DMF/H_2O (1:1).

Determination of binding constant from Fluorescence titration data:

Binding constant was calculated according to the Benesi-Hildebrand equation. K_a was calculated following the equation stated below.

$1/(F-F_o) = 1/\{K_a(F_{max}–F_o)[M^{n+}]\} + 1/[F_{max}-F_o]$

F_o represents the emission enhancement of **SPBH** at 480 nm in the absence of Al^{3+}, F_x is the emission intensity of **SPBH** in the presence of a particular concentration of Al^{3+}, F_{max} is the emission intensity of **SPBH** at final (maximum) concentration of Al^{3+}. K_a is the binding constant of **SPBH**/Al^{3+} interaction and $[M^{n+}]$ is the concentration of Al^{3+}. Plot of $(F_{max} – F_x)/(F_x - F_o)$ *vs* $1/[Al^{3+}]$ gives a straight line indicating 1:1 complexation between **SPBH** and Al^{3+}.

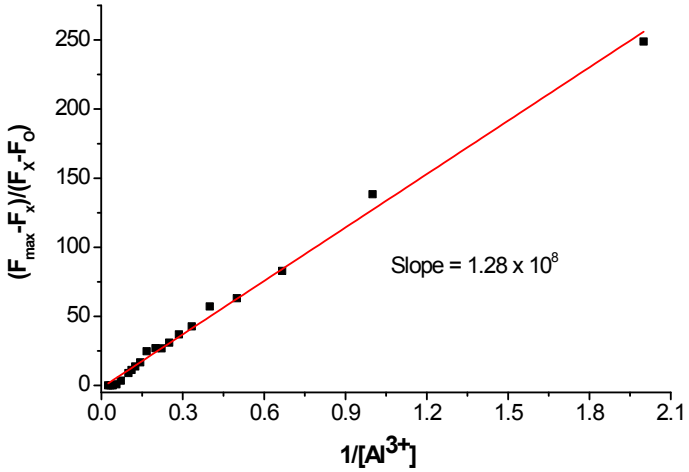

Fig. S2 Determination of association constant of **SPBH** for Al^{3+} from fluorescent titration data

Calculation of the limit of detection (LOD)

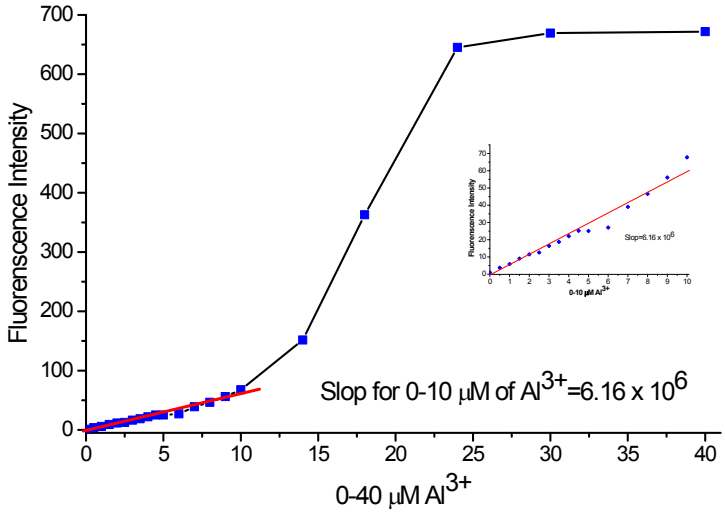

Fig. S3 Plot of emission intensity of titration of **SPBH** (10 μM) upon the addition of Al^{3+} (0–40 μM) in DMF/H_2O (1:1), λ_{ex} = 390 nm. Due to the instrumental figure of merit, slope value for 0–10 μM of Al^{3+} (6.16×10^6) was used for calculation of the detection limit (LOD).

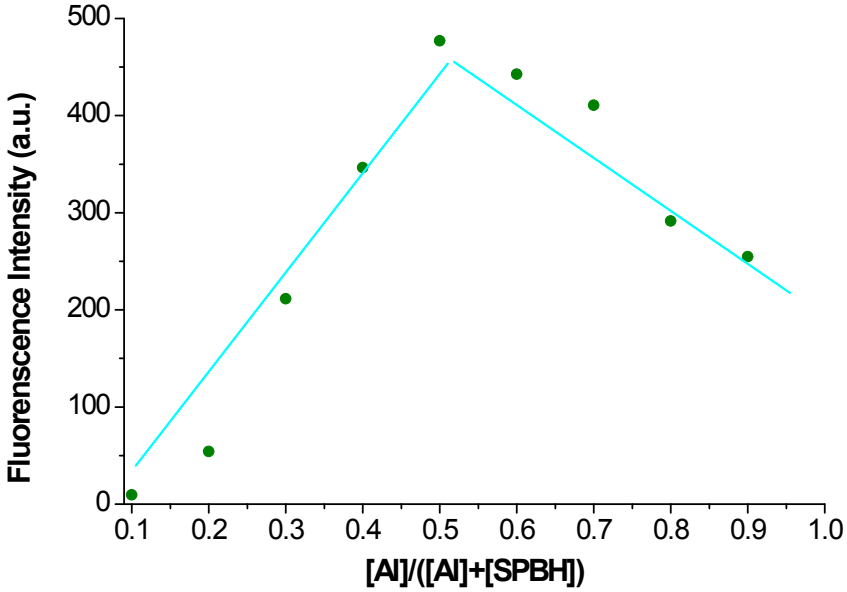

Fig. S4 Job's plot of **SPBH**/Al^{3+} interaction, changes in emission intensities were measured at 480 nm, λ_{ex} = 380 nm.

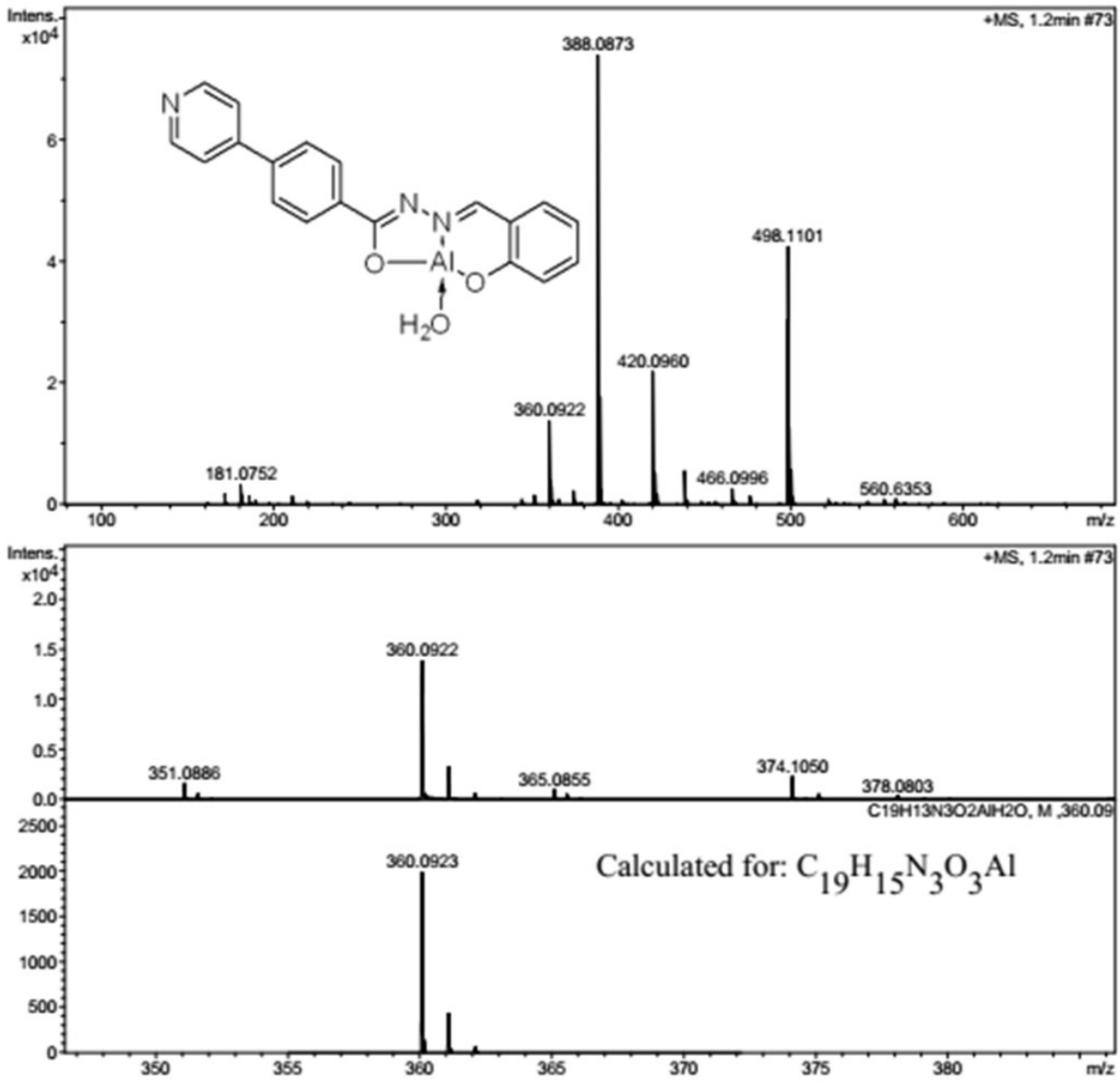

Fig. S5 HRMS-ESI spectrum of **SPBH** in the presence of 3 equivalents of Al^{3+} in DMF/H_2O (1:1). Expanding peak at m/z 360.0922.

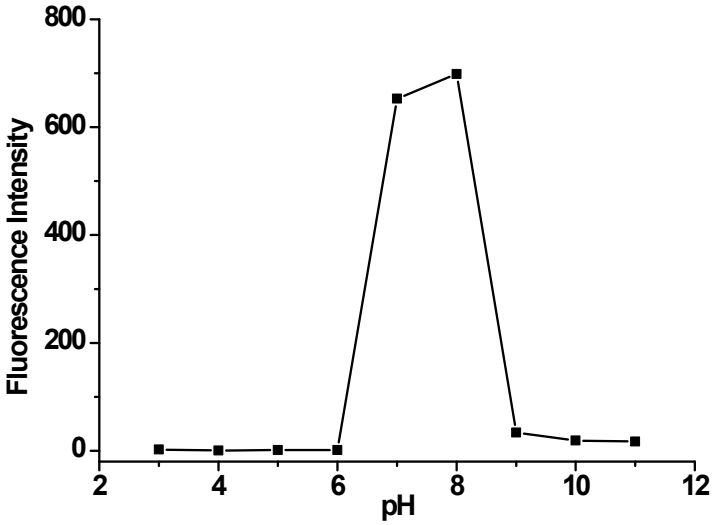

Fig. S6 Fluorescence intensity plot (at 480 nm) of 10 μM of **SPBH** and 30 μM of Al^{3+} in DMF/H_2O (1:1, v/v) mixture at different pH, λ_{ex} = 380 nm.

Calculation of the limit of detection (LOD)

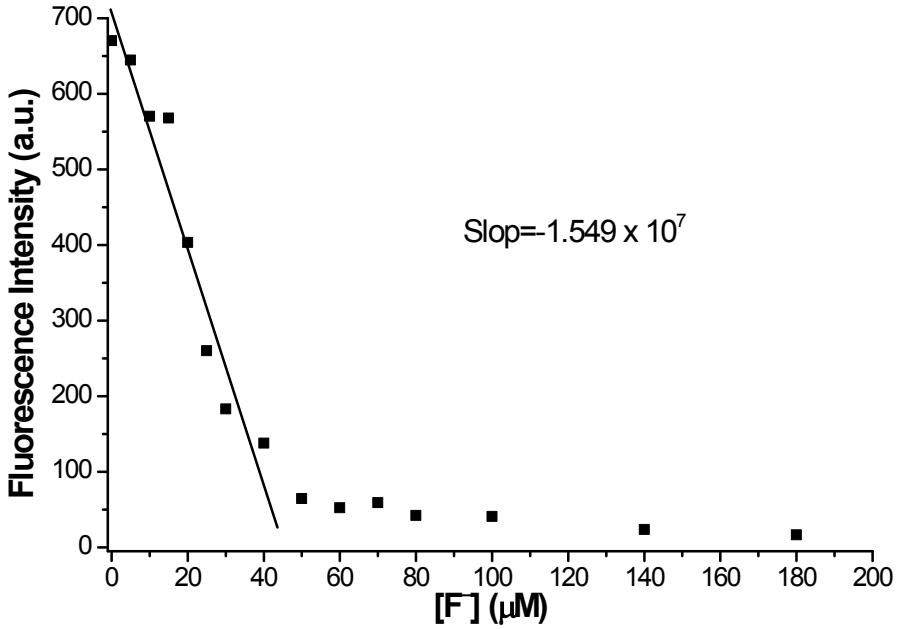

Fig. S7 Plot of emission intensity of titration of complex of **SPBH** (10 μM) and Al^{3+} (30 μM) upon the addition of F^- (0–180 μM) in DMF/H_2O (1:1), λ_{ex} = 390 nm. Slope value for 0–50 μM of F^-= -1.549×10^7. Thus using the formula we get the LOD = 1.47×10^{-6} M.

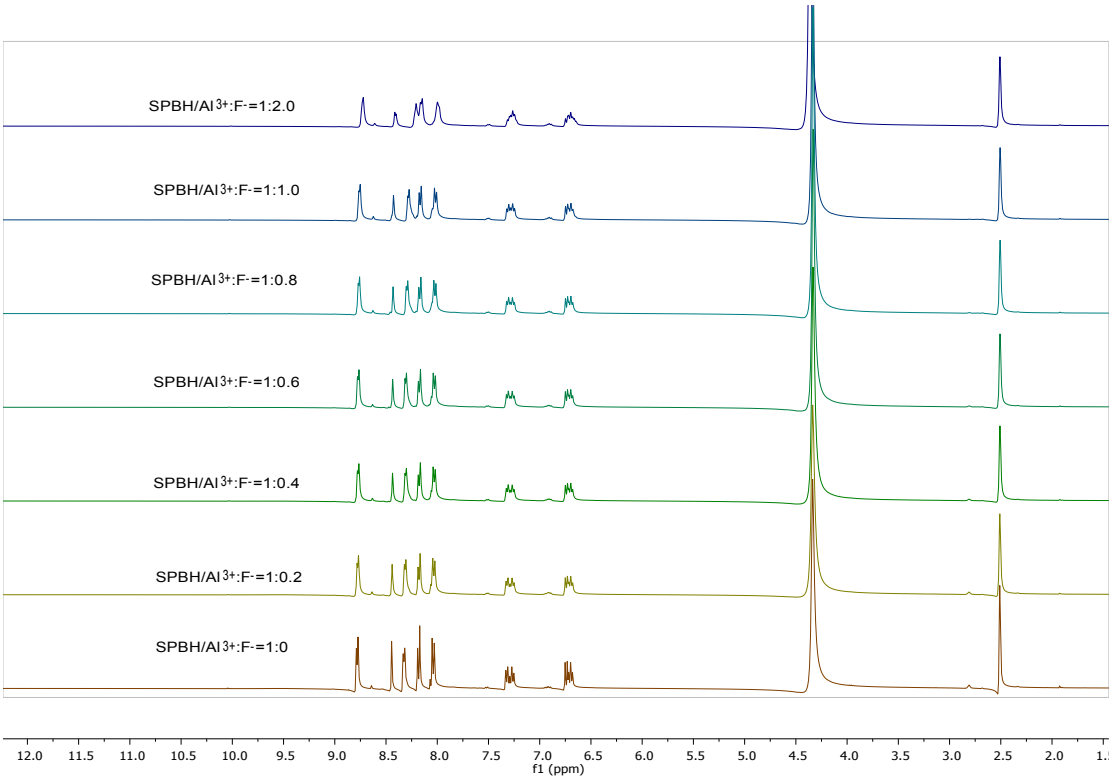

Fig. S8 ^{1}H NMR Spectra of **SPBH**/Al^{3+} complex (bottom) and titration studies with 0-1.2 eq. of F^{-}(KF) in DMSO-d_6.

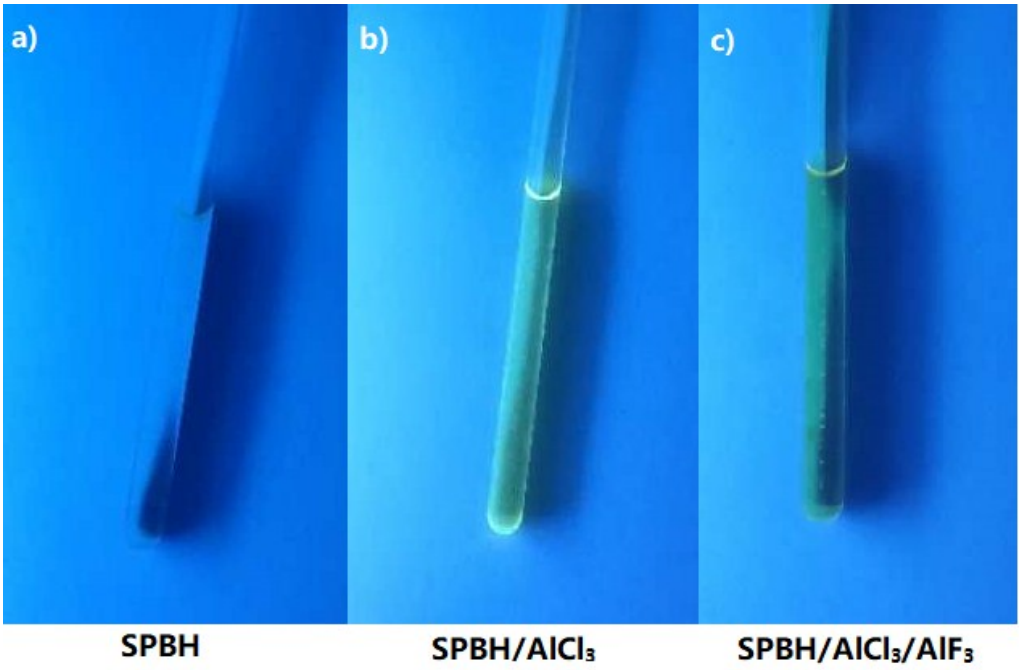

Fig. S9 Naked eyes color response of a) **SPBH** (0.5 mM), b) **SPBH**/Al^{3+} (1:3) and c) the mixture of sensor and F^{-} (1:3:3) under 365 nm UV light.

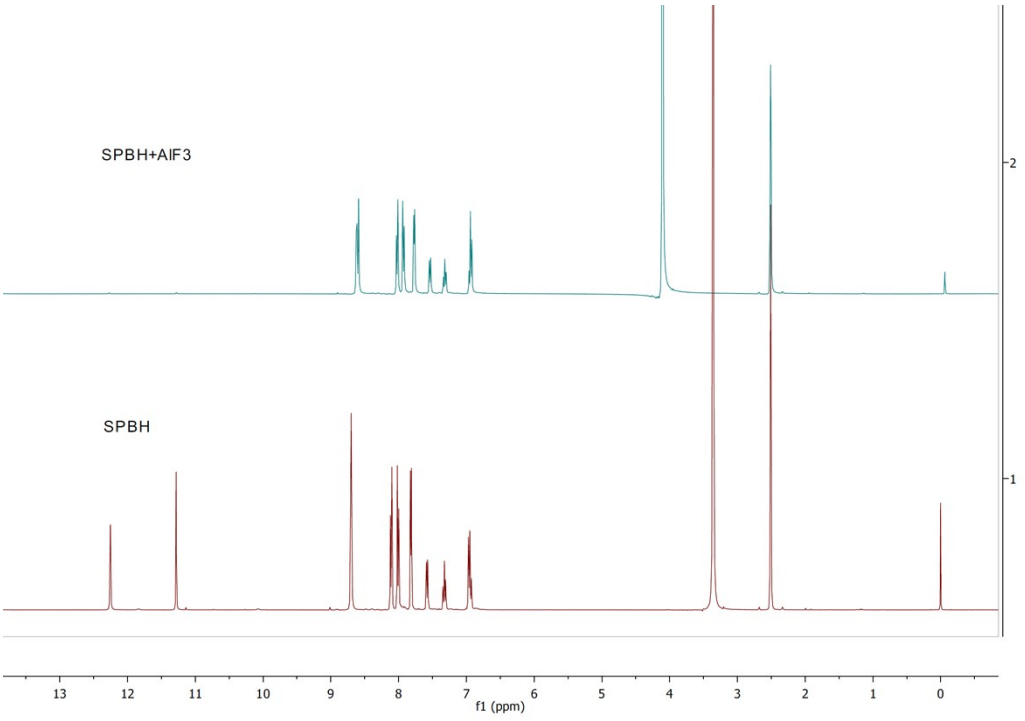

Fig. S10 ^{1}H NMR Spectra of 1 mM of **SPBH** (bottom) and **SPBH**/AlF_3 (1:1) in DMSO-d_6.

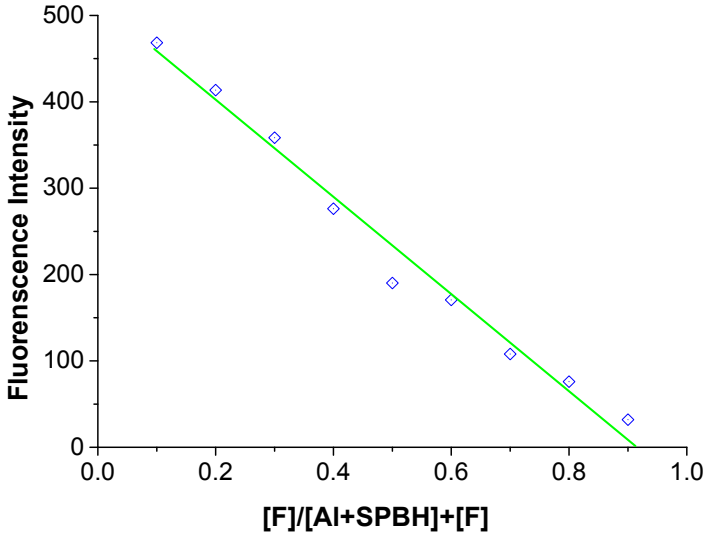

Fig. S11 Job's plot of **SPBH**/Al^{3+} with F^- interaction, changes in emission intensities were measured at 480 nm, λ_{ex} = 380 nm (ex slit=10 nm; em slit =5 nm).

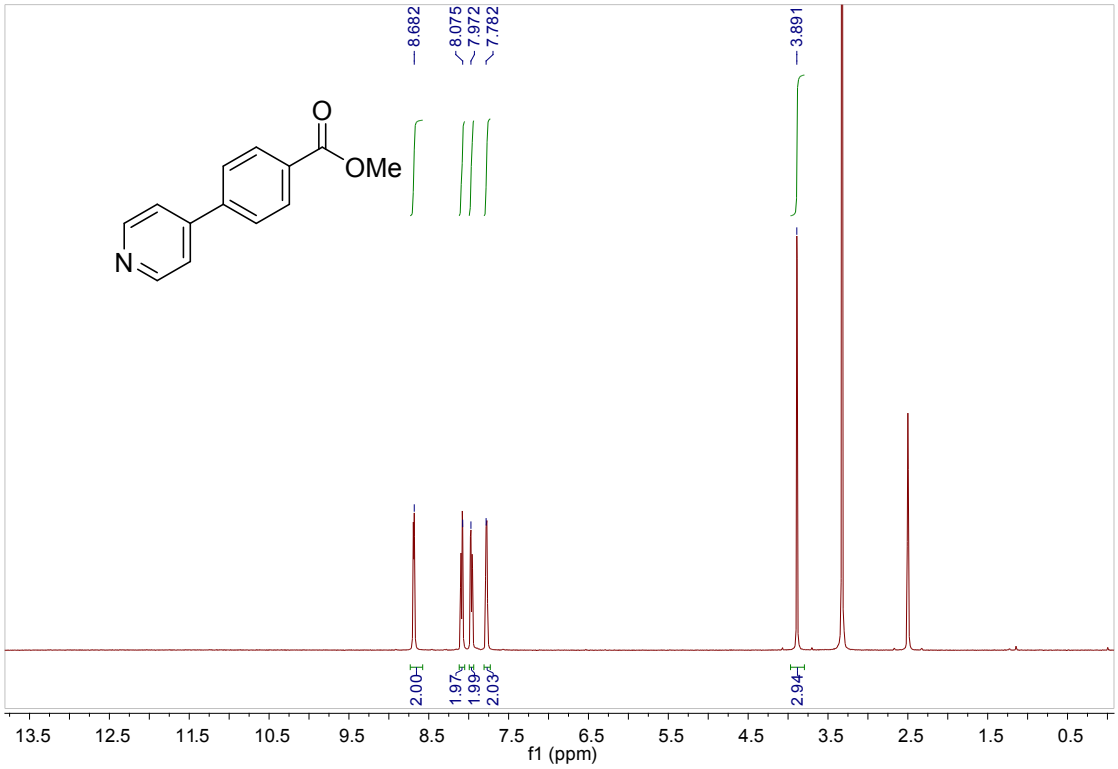

Fig. S12 ^{1}H NMR spectrum of methyl 4-(pyridin-4-yl)benzoate in DMSO-d_6 at room temperature

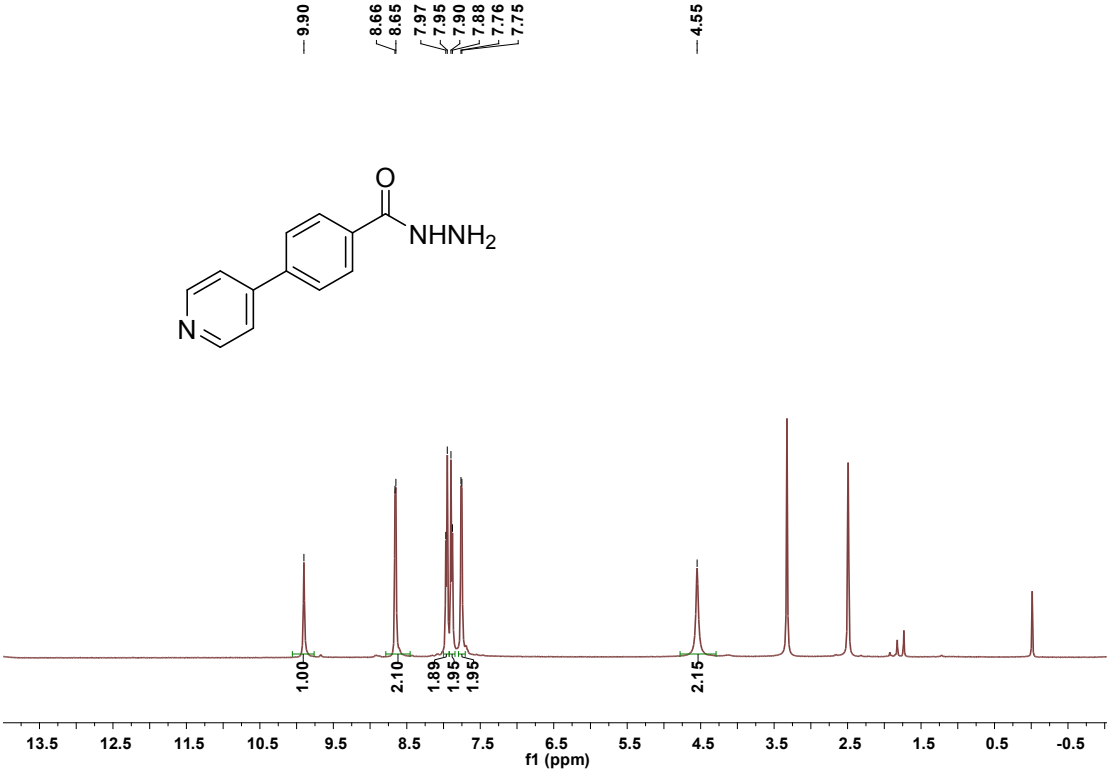

Fig. S13 ^{1}H NMR spectrum of 4-(pyridin-4-yl)benzohydrazide in DMSO-d_6 at room temperature

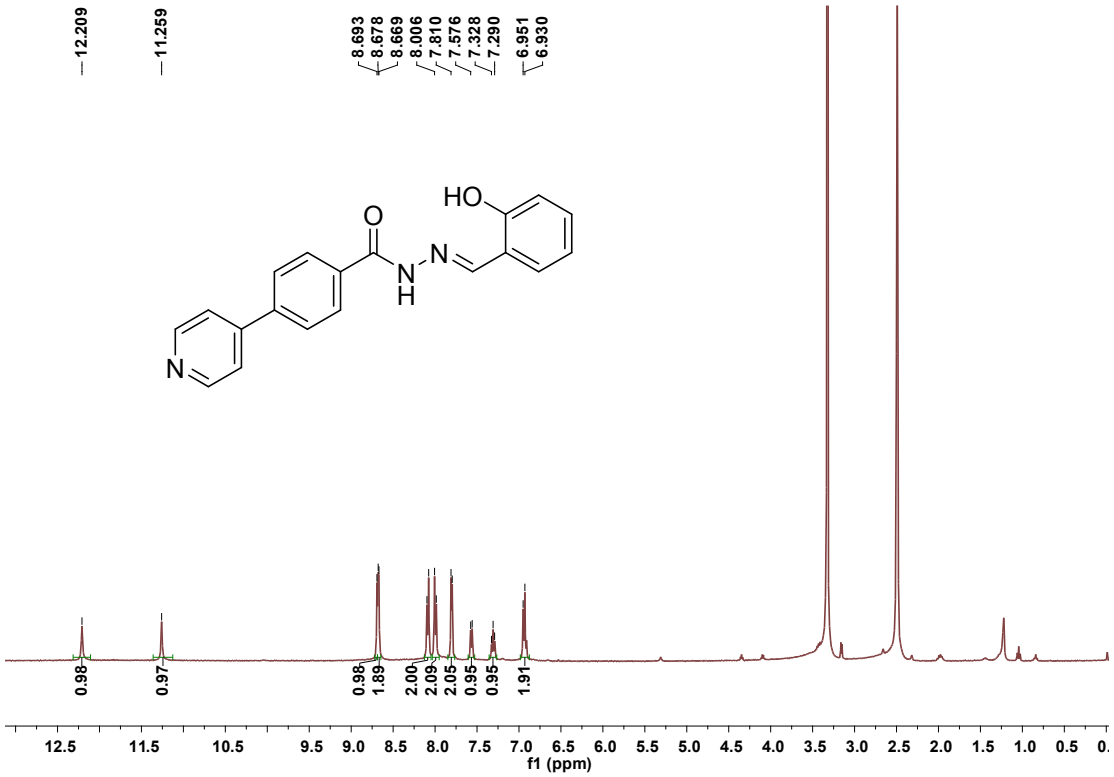

Fig. S14 ^{1}H NMR spectrum of **SPBH** in DMSO-d_6 at room temperature

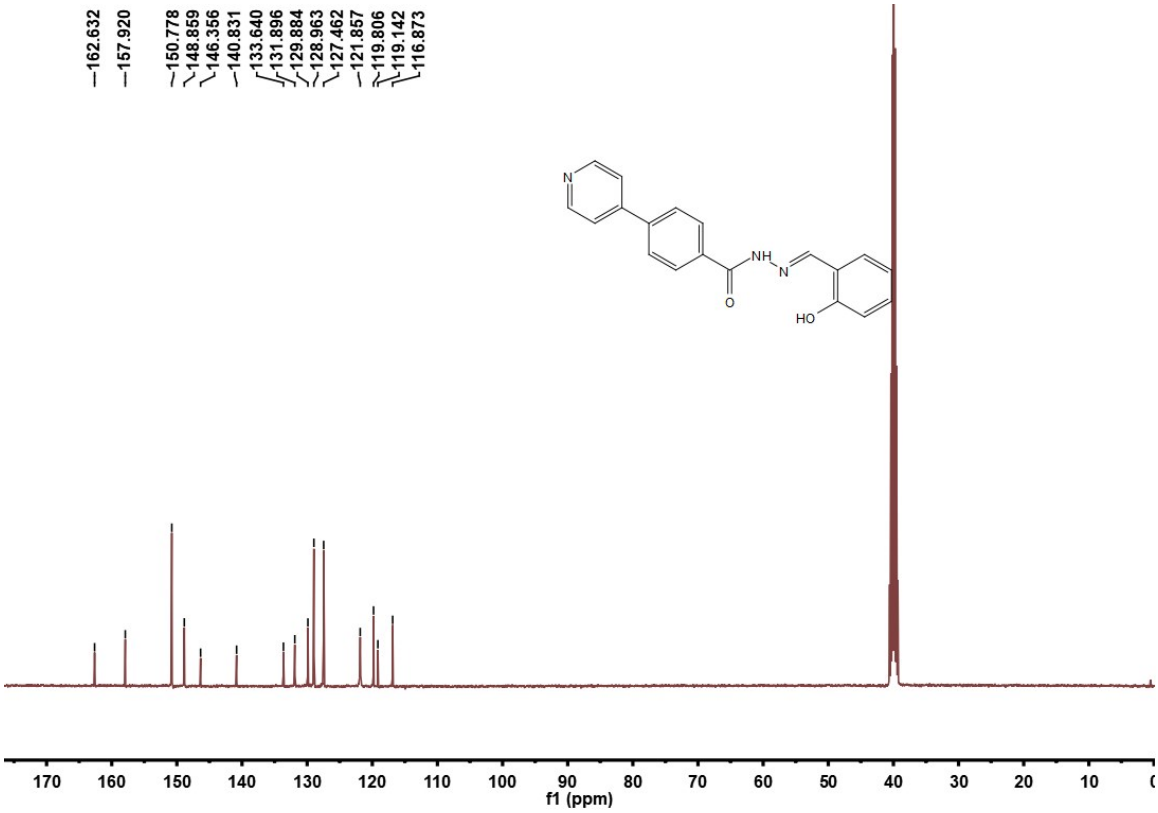

Fig. S15 ^{13}C NMR spectrum of **SPBH** in DMSO-d_6 at room temperature.

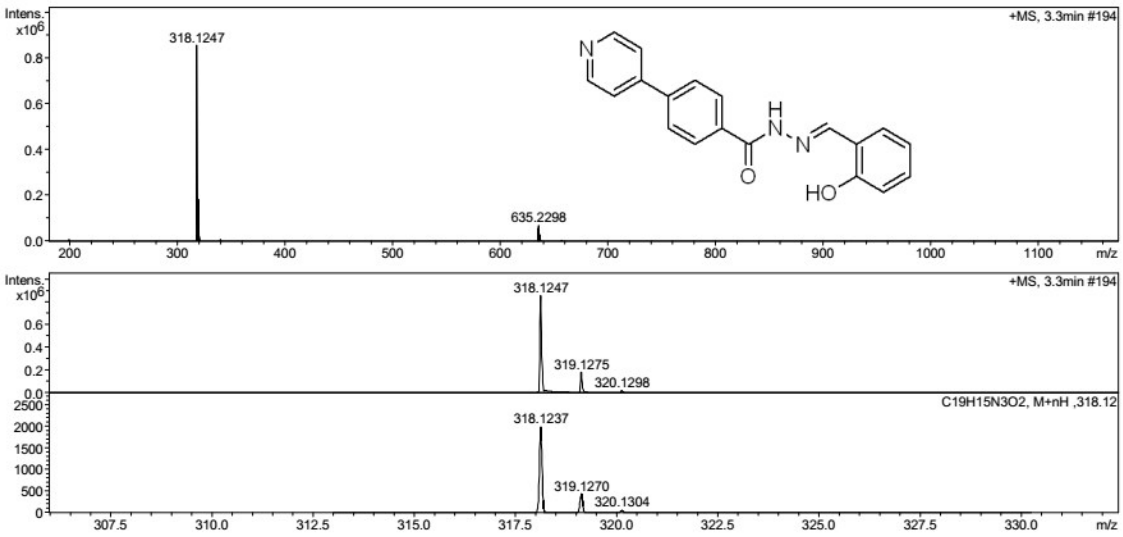

Fig. S16 HRMS-ESI spectrum of **SPBH**