Electronic Supplementary Information for RSC Advances

Supporting Information For

Highly selective colorimetric and fluroescent sensors for fluoride anion based on imidazo[4,5-f]-1,10-phenanthroline metal-complexes

Sisi Li, Zhang Chan, Shuyuan Huang, Fang Hu, Jun Yin,

Sheng Hua Liu*[a]

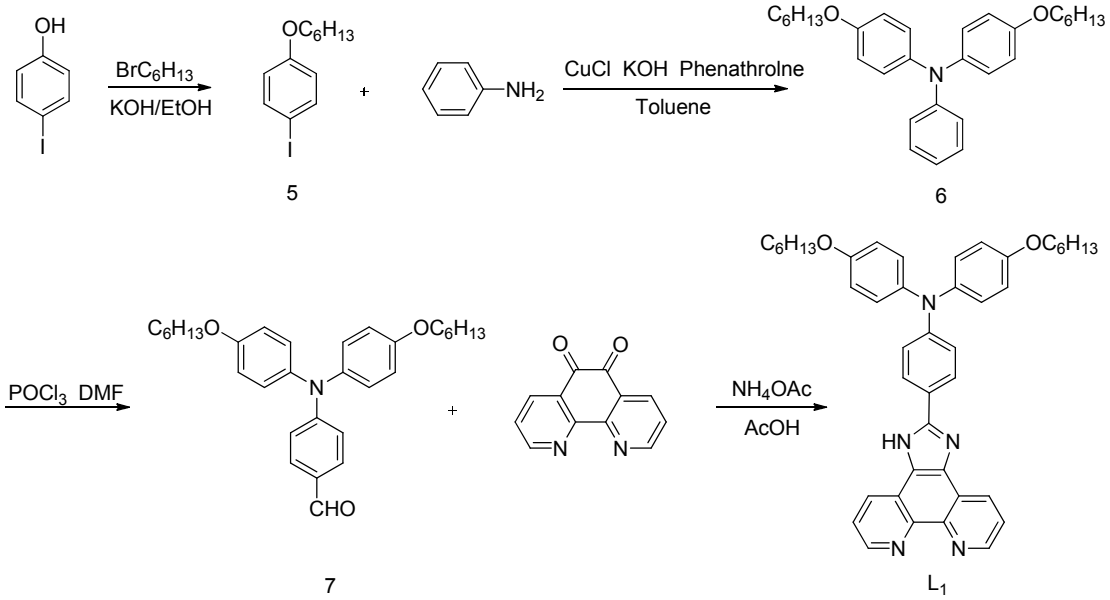
E-mail

chshliu@mail.ccnu.edu.cn

Electronic Supplementary Material (ESI) for RSC Advances

Content

1. Synthetic procedure and characterization of ligands L_1 and L_2



Scheme S1. Synthetic route of ligand L_1.

Hexyloxyl-4-iodobenzene (5) To a stirred mixture of 4-iodophenol (26.40g, 0.12 mol), hexylbromide (16.5 g, 0.1 mol), and dimethylformamide (100 mL) under argon was added K_2CO_3 (27.60 g, 0.20 mol). The reaction mixture was refluxed for 15h. After cooled to room temperature, the resulting mixture was filtered and then extracted with CH_2Cl_2. The organic layer was washed with a dilute solution of KOH and water and dried with $MgSO_4$. After filtration, removal of the solvents, purification with column chromatography, the compound was obtained. Yield, 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J_1 = 7.2 Hz, J_2 = 6.4 Hz 3H, CH_3), 1.31-1.34 (m, 4H, CH_2), 1.42-1.45 (m, 2H, CH_2), 1.72-1.78 (m, 2H, CH_2), 3.89 (t, J_1 = 6.8 Hz, J_2 = 6.4 Hz, 2H, OCH_2), 6.66 (d, J = 8.8 Hz, 2H, Ar-H), 7.52 (d, J = 8.8 H, 2H, Ar-H). MS(m/z): 304.03 $[M]^+$. Anal. Calcd for $C_{12}H_{17}IO$: C, 47.38; H, 5.63. Found: C, 47.42; H, 3.21.

Bis(4-(2'-hexyloxyl)phenyl)amino)benzene (6) The mixture of **5** (9.73 g, 32 mmol), aniline (1.4 g, 15 mmol), CuCl (0.12 g, 1.2 mmol), phenanthroline (0.26 g, 1.44 mmol), KOH (14.7 g, 0.26 mol), and toluene (35 mL) was refluxed for 24 h and cooled to room temperature. The resulting mixture was poured into plenty of water and then extracted with CH_2Cl_2. The organic phase was washed several times with water, dried with $MgSO_4$. Then filtered, evaporated, and purified with

column chromatography. Yield, 73%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, J_1 = 7.2 Hz, J_2 = 7.6 Hz, 6H, CH_3), 1.32-1.35 (m, 8H, CH_2), 1.44-1.47 (m, 4H, CH_2), 1.75-1.78 (m, 4H, CH_2), 3.90 (t, J_1 = 6.8 Hz, J_2 = 6.4 Hz, 4H, OCH_2), 6.79 (d, J = 9.2 Hz, 4H, Ar-H), 6.92 (d, J = 8 Hz, 1H, Ar-H), 7.01 (d, J = 9.2 Hz, 4H, Ar-H), 7.13 (d, J = 8 Hz, 2H, Ar-H). MS(m/z): 445.30 $[M]^+$. Anal. Calcd for $C_{30}H_{39}NO_2$: C, 80.86; H, 8.82; N, 2.96. Found: C, 80.59; H, 8.76; N, 2.88.

4-(Bis(4'-(2"-hexyloxyl)phenyl)amino)benzaldehyde (7) Phosphorus oxychloride (2 mL, 21.6 mmol) was added dropwise to DMF (10 mL, 130 mmol) at 0 ℃. The mixture was stirred for 1 h at 0 ℃ and additionally stirred at room temperature for 1h. After the addition of **6** (1.43 g, 3.2 mmol) in 1,2-dichloroethane (10 mL), the mixture was stirred at 90 ℃ for 2 h. Atter cooling to room temperature, the solution was poured into plenty of water, the the resulting mixture was neutralized to pH7 with ammonia and then extracted with CH_2Cl_2. Then the extract was washed successively with water and brine. The organic extracts were dried with $MgSO_4$, then evaporated and purified with column chromatography. Yield, 66%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J_1 = 4.8 Hz, J_2 = 4.4 Hz, 6H, CH_3), 1.34-1.35 (m, 8H, CH_2), 1.44-1.47 (m, 4H, CH_2), 1.76-1.81 (m, 4H, CH_2), 3.93 (t, J_1 = 4.4 Hz, J_2 = 4.4 Hz, 4H, OCH_2), 6.83 (d, J = 6 Hz, 2H, Ar-H), 6.90 (d, J = 6 Hz, 4H, Ar-H), 7.10 (d, J = 6 Hz, 4H, Ar-H), 7.61 (d, J = 6 Hz, 2H, Ar-H), 9.75 (s, 1H, CHO). MS(m/z): 473.29 $[M]^+$. Anal. Calcd for $C_{31}H_{39}NO_3$: C, 78.61; H, 8.30; N, 2.96. Found: C, 78.68; H, 8.44; N, 2.74.

Ligand (L_1) A mixture of **7** (0.71 g, 1.5 mmol), 1,10-phenanthroline-5,6-dione (0.315 g, 1.5 mmol), ammonium acetate (2.31 g, 30 mmol) and glacial acetic (30 mL) was refluxed for 2 h, and then cooled to room temperature and diluted with water. The resulting mixture was neutralized to pH=7 with ammonia to get a yellow precipitate, which was collected and washed with water. The crude product in ethanol was purified with column chromatography. Yield, 94%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, J_1 = 7.2 Hz, J_2 = 6.4 Hz, 6H, CH_3), 1.27-1.31 (m, 8H, CH_2), 1.36-1.41 (m, 4H, CH_2), 1.67-1.73 (m, 4H, CH_2), 3.81 (t, J_1 = 7.6 Hz, J_2 = 6 Hz, 4H, OCH_2), 6.71 (d, J = 8.8 Hz, 6H, Ar-H), 6.91 (d, J = 8.4 Hz, 4H, Ar-H), 7.28 (m, 2H, pyridine-H), 8.03 (d, J = 8.8 Hz, 2H, Ar-H), 8.745 (m, 4H, pyridine-H). MS(m/z): 663.36 $[M]^+$. Anal. Calcd for $C_{43}H_{45}N_5O_2$: C, 77.80; H, 6.83; N, 10.56. Found: C, 77.87; H, 6.64; N, 10.34.

Ligand (L_2) A mixture of **L_1** (0.66 g, 1 mmol), indomethane (0.28 g, 2 mmol) and K_2CO_3 (0.28 g, 2 mmol) in anhydrous DMF (15 mL) was stirred over night. The solution was poured into plenty

of water, the solid precipitated was filtered and was washed with water and dried to give a yellow solid. The crude product in ethanol was purified with column chromatography. Yield, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J_1 = 6.4 Hz, J_2 = 6.4 Hz, 6H, CH_3), 1.25 (m, 8H, CH_2), 1.35-1.36 (m, 4H, CH_2), 1.76-1.83 (m, 4H, CH_2), 3.94 (t, J_1 = 6.4 Hz, J_2 = 6.4 Hz, 4H, OCH_2), 4.29 (s, 3H, CH_3), 6.87 (d, J = 8.8 Hz, 4H, Ar-H), 7.05 (d, J = 8.8 Hz, 2H, Ar-H), 7.12 (d, J = 8.8 Hz, 4H, Ar-H), 7.56 (d, J = 8.8 Hz, 2H, Ar-H), 7.66-7.72 (m, 2H, pyridine-H)8.75 (d, J = 8.4 Hz 1H, Ar-H), 9.05 (d, J = 8.4 Hz 1H, Ar-H),9.03 (d, J = 8.4 Hz 2H, pyridine-H). MS(m/z): 677.37 $[M]^+$. Anal. Calcd for $C_{44}H_{47}N_5O_2$: C, 77.96; H, 6.99; N, 10.33. Found: C, 77.79; H, 6.85; N, 10.21.

2. Supplementary spectra data (Fig. S1 – S6)

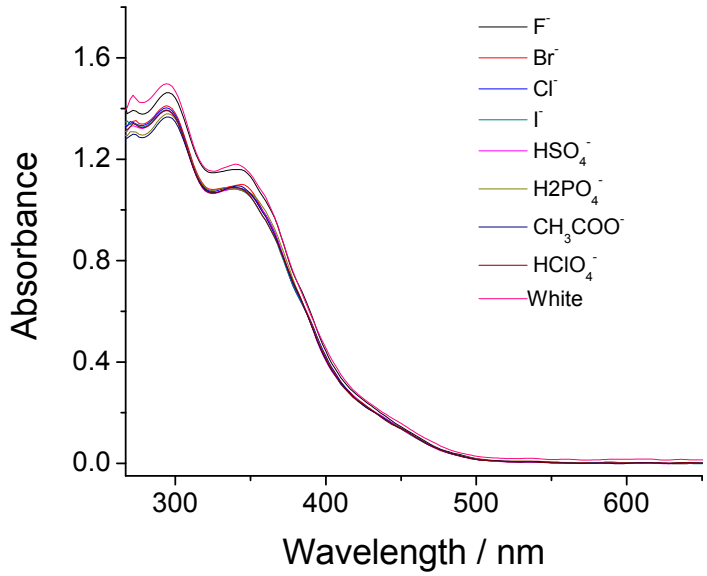


Fig. S1 Changes in the absorption spectra of complex **2** (2×10^{-5} mol/L in DMSO) upon addition of 10 equiv of several anions (2×10^{-4} mol/L in DMSO).

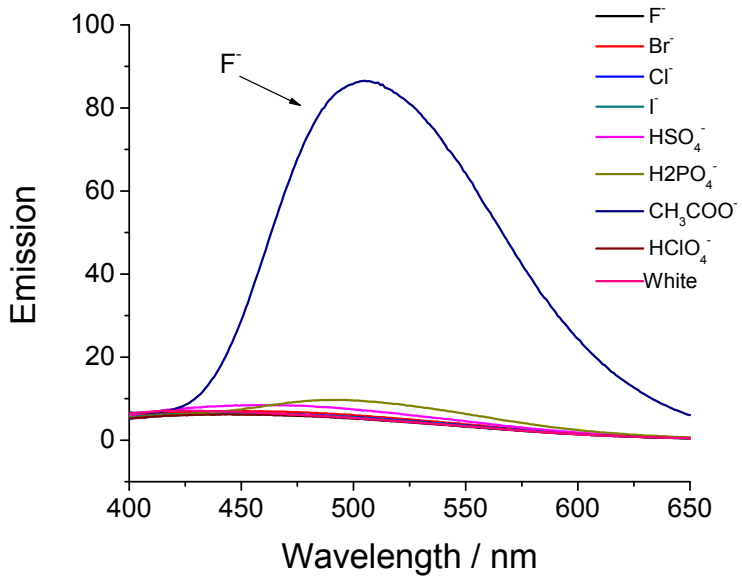


Fig. S2 Fluorescence spectra of complex **4** (2×10^{-5} mol/L in DMSO) upon addition of 10 equiv of several anions (2×10^{-4} mol/L in DMSO) excited at 364nm.

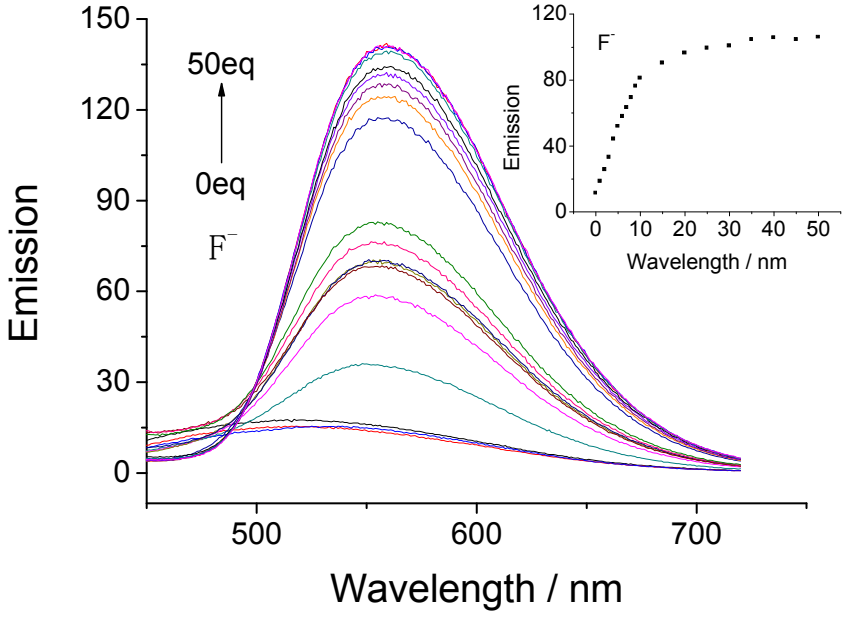


Fig. S3 Changes in the fluorescence emission of complex **4** (2×10^{-5} mol/L in DMSO) upon addition of F^- (equiv = 0, 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50.) excited at 364nm

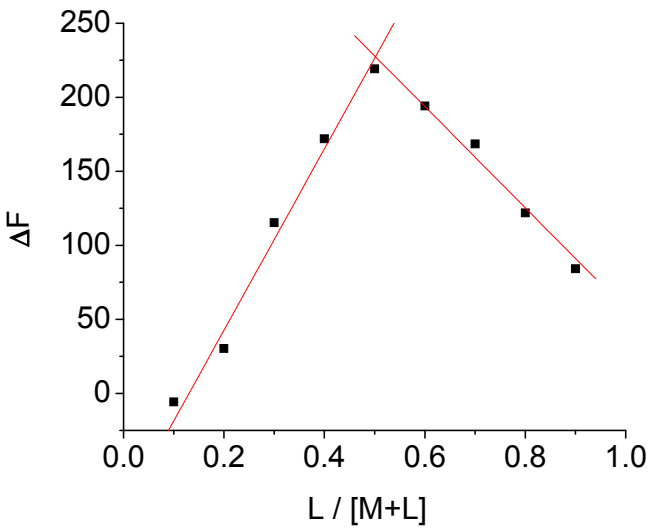
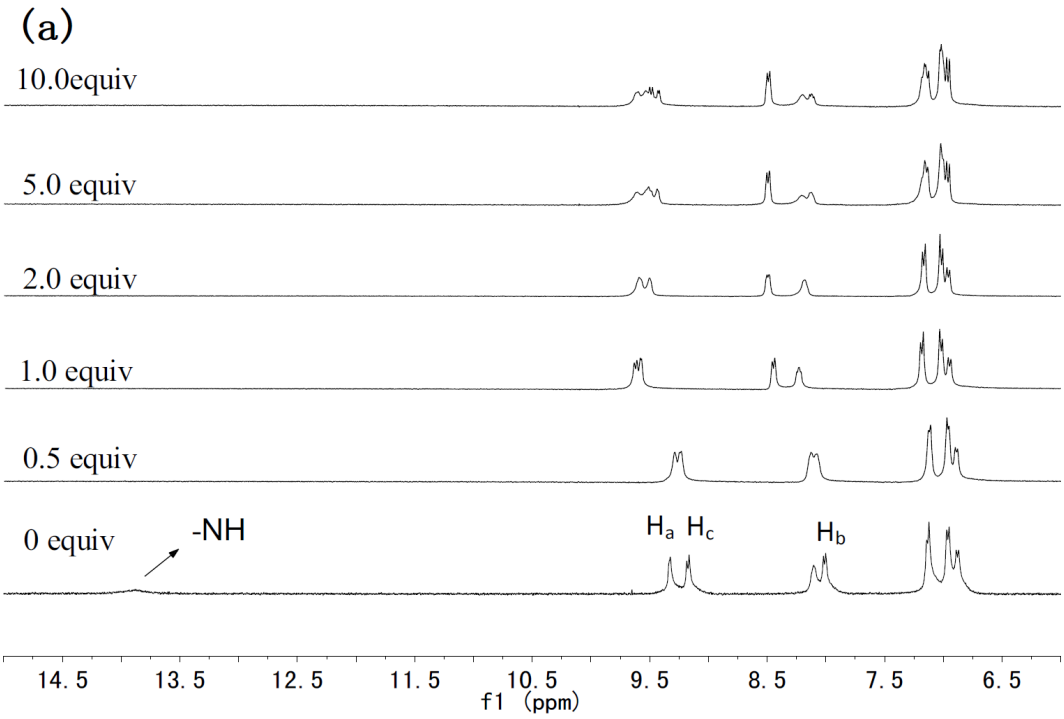


Fig. S4 Job's plots for the reactions of complex **4** with F^- in DMSO



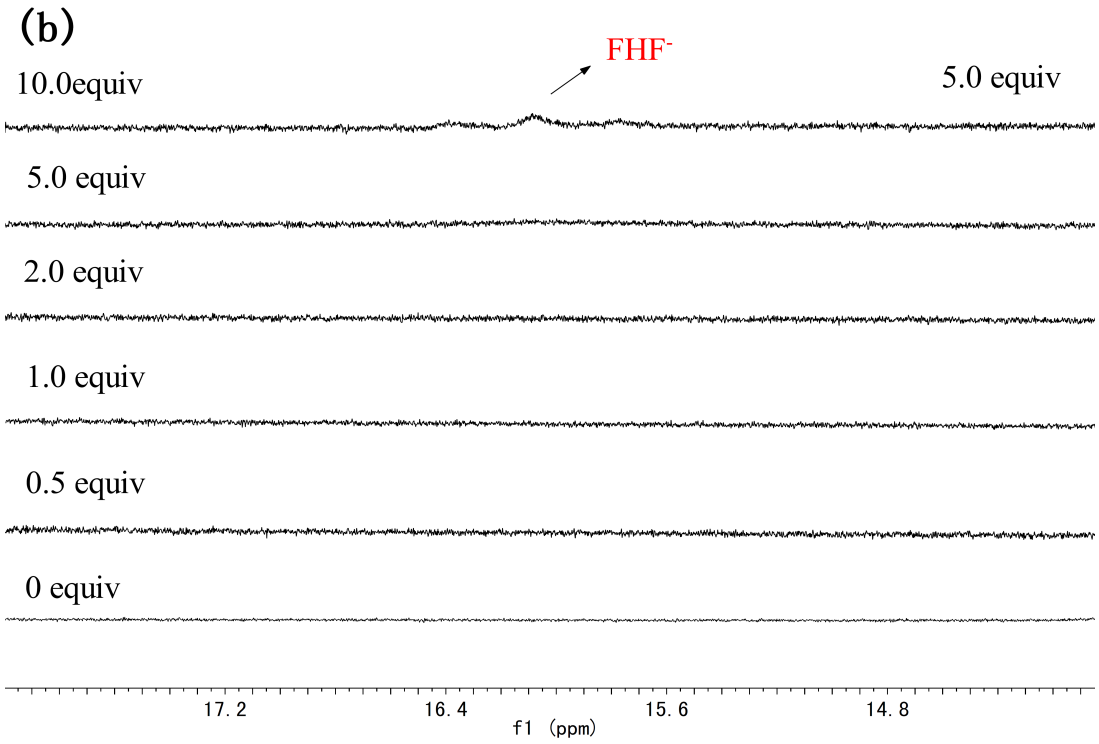
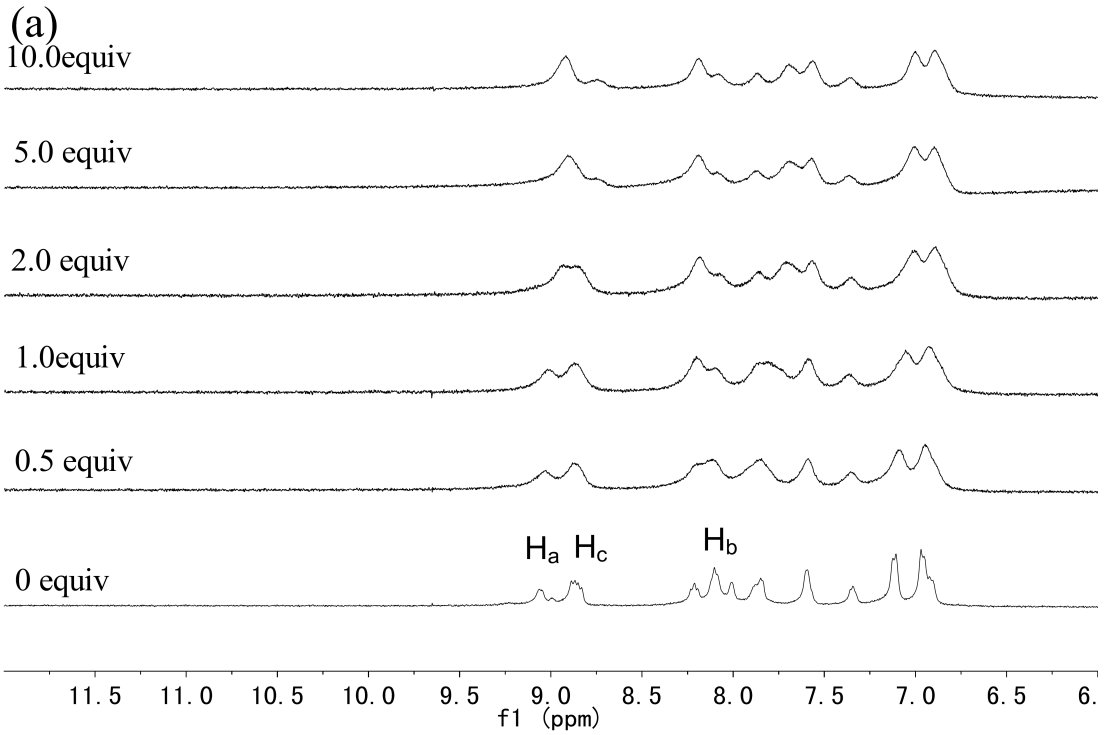


Fig. S5 Partial ^{1}H NMR spectra (400 MHz in d^{6}-DMSO at 298 K) of **1** upon addition of 0-10 equiv of TBAF.



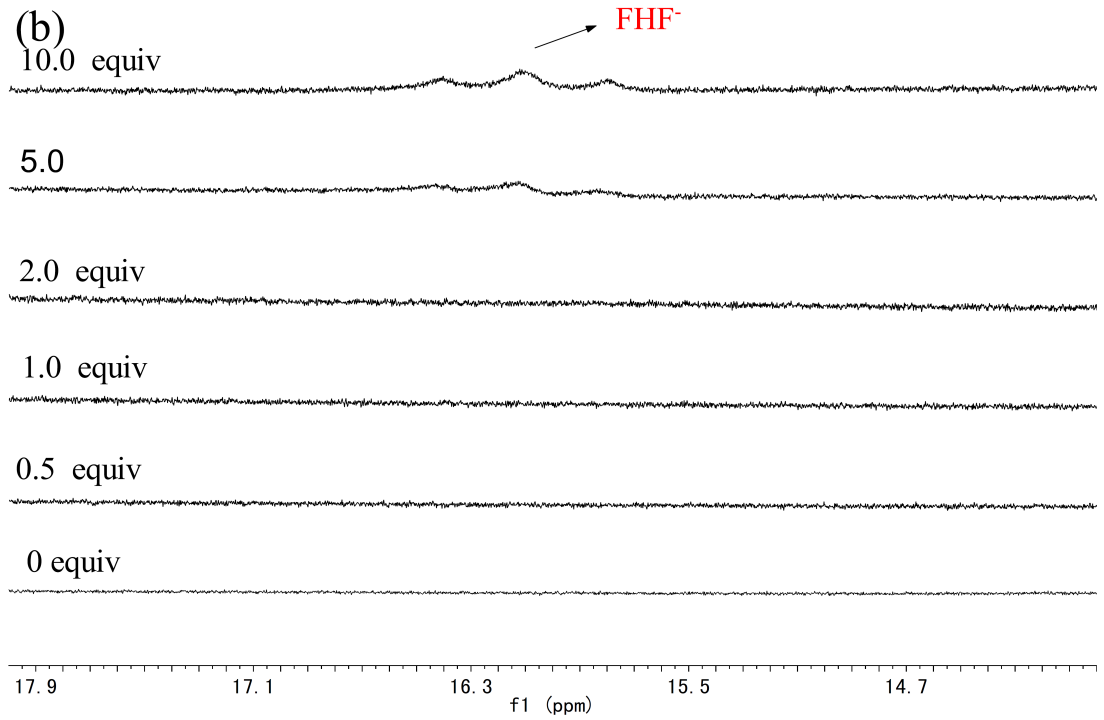
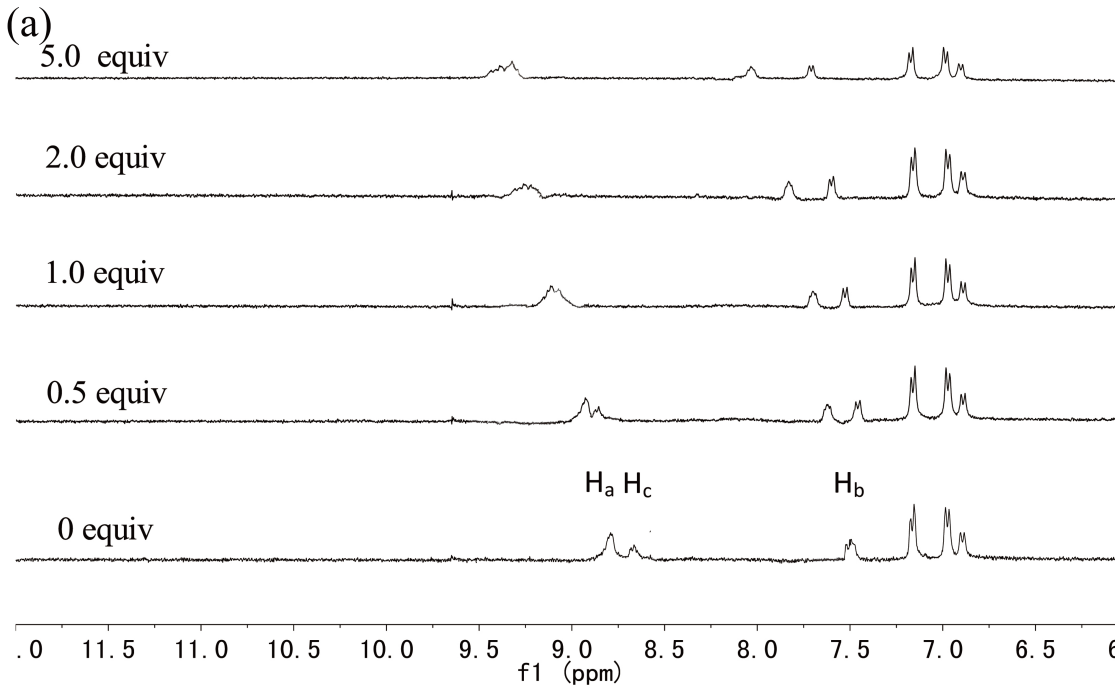


Fig. S6 Partial ^{1}H NMR spectra (400 MHz in d^{6}-DMSO at 298 K) of **3** upon addition of 0-10 equiv of TBAF.



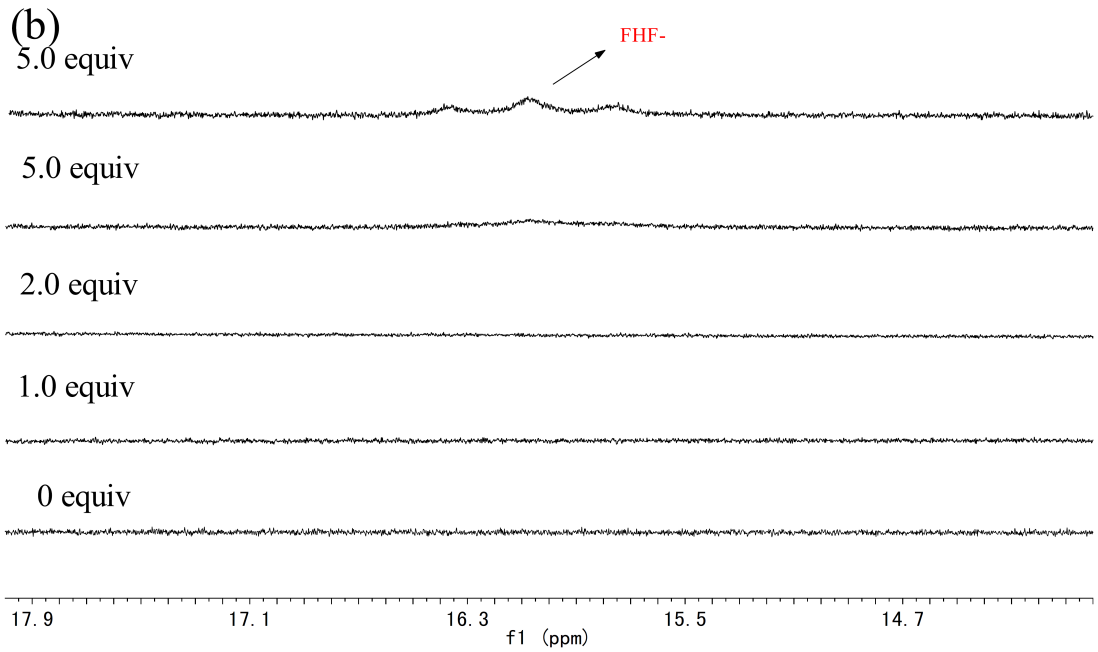


Fig. S7 Partial ^{1}H NMR spectra (400 MHz in d^{6}-DMSO at 298 K) of **4** upon addition of 0-10 equiv of TBAF.