

Supported information

Pyrenyl-functionalized Ferrocenes for Multisignaling Recognition of Anions

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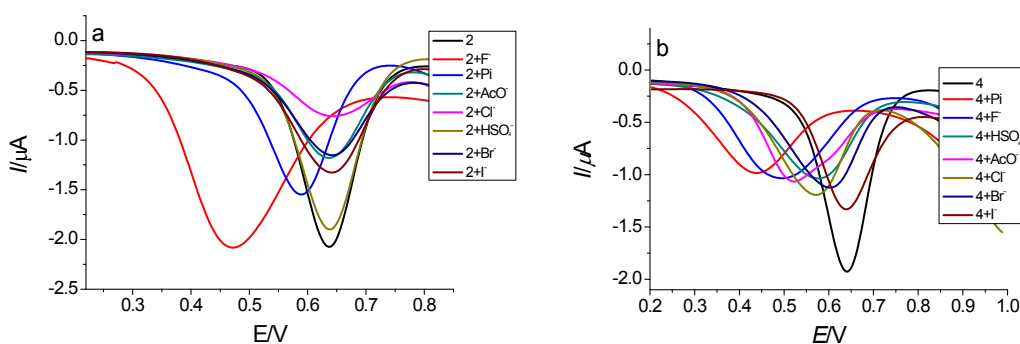


Fig. S1 DPV profile of **2** (a) and **4** (b) upon the addition of equal equiv of (5 equiv) anions in CH₃CN solution

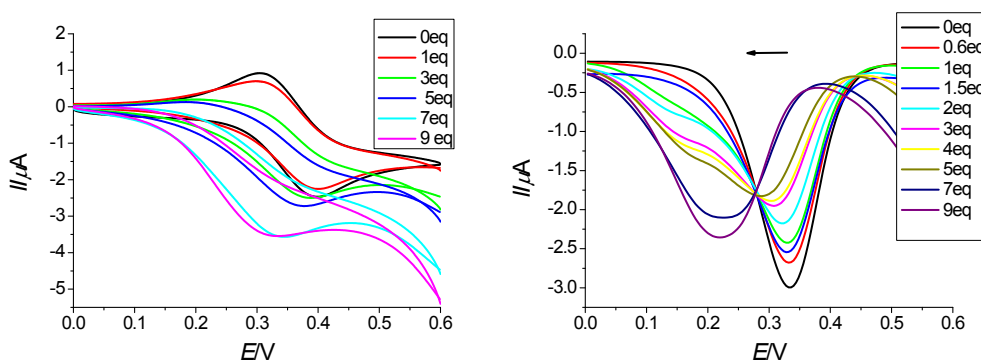


Fig. S2 CV and DPV titration profile of **1** (0.2 mM) upon addition of various amount of F⁻ in

CH₃CN solution. Reference electrode = Ag/AgNO₃; supporting electrolyte = [n-Bu₄N]PF₆ (0.1 M); scan rate = 100 mV S⁻¹.

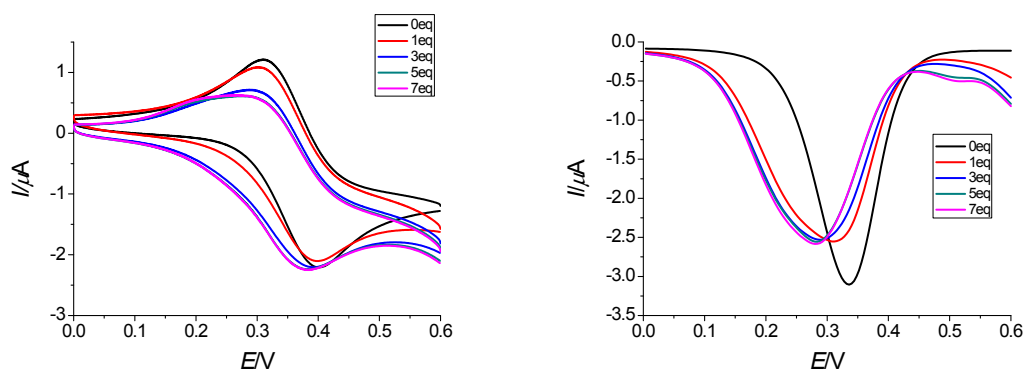


Fig. S3 CV and DPV titration profile of **1** (0.2 mM) upon addition of various amount of Pi in CH₃CN solution. Reference electrode = Ag/AgNO₃; supporting electrolyte = [n-Bu₄N]PF₆ (0.1 M); scan rate = 100 mV S⁻¹.

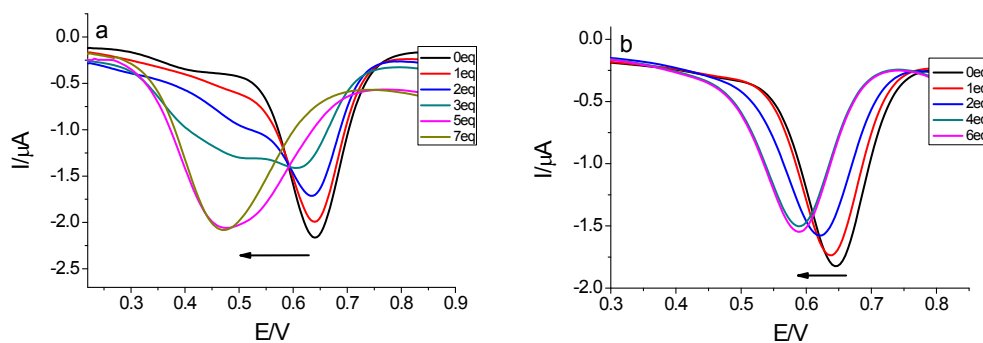


Fig. S4 DPV titration profile of **2** (0.2 mM) upon addition of various amount of F⁻ (a) and Pi (b) in CH₃CN solution. Reference electrode = Ag/AgNO₃; supporting electrolyte = [n-Bu₄N]PF₆ (0.1 M); scan rate = 100 mV S⁻¹.

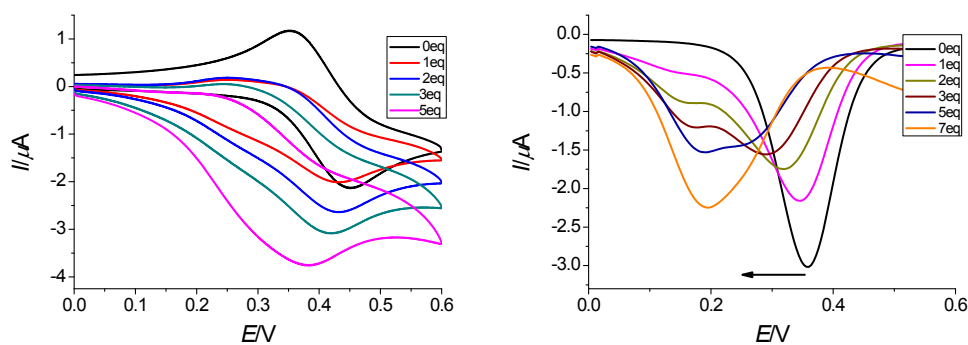


Fig. S5 CV and DPV titration profile of **3** (0.2 mM) upon addition of various amount of F⁻ in CH₃CN solution. Reference electrode = Ag/AgNO₃; supporting electrolyte = [n-Bu₄N]PF₆ (0.1 M); scan rate = 100 mV S⁻¹.

scan rate = 100 mV S⁻¹.

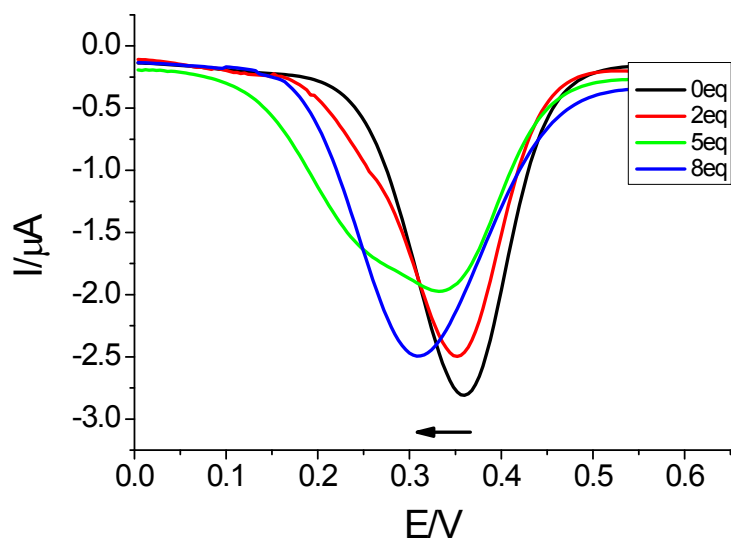


Fig. S6 DPVs titration profile of **3** (0.2 mM) upon addition of various amount of AcO⁻ in CH₃CN solution. Reference electrode = Ag/AgNO₃; supporting electrolyte = [n-Bu₄N]PF₆ (0.1 M); scan rate = 100 mV S⁻¹.

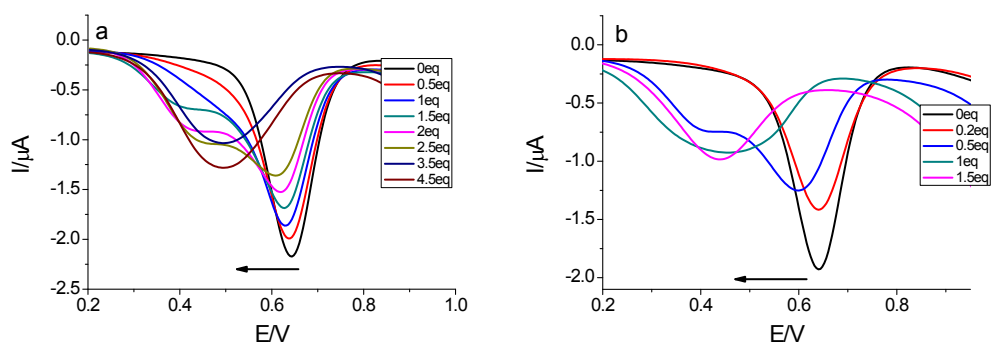


Fig. S7 DPV titration profile of **4** (0.2 mM) upon addition of various amount of F⁻ (left) and Pi (right) in CH₃CN/DMF (9:1, V/V) solution. Reference electrode = Ag/AgNO₃; supporting electrolyte = [n-Bu₄N]PF₆ (0.1 M); scan rate = 100 mV S⁻¹

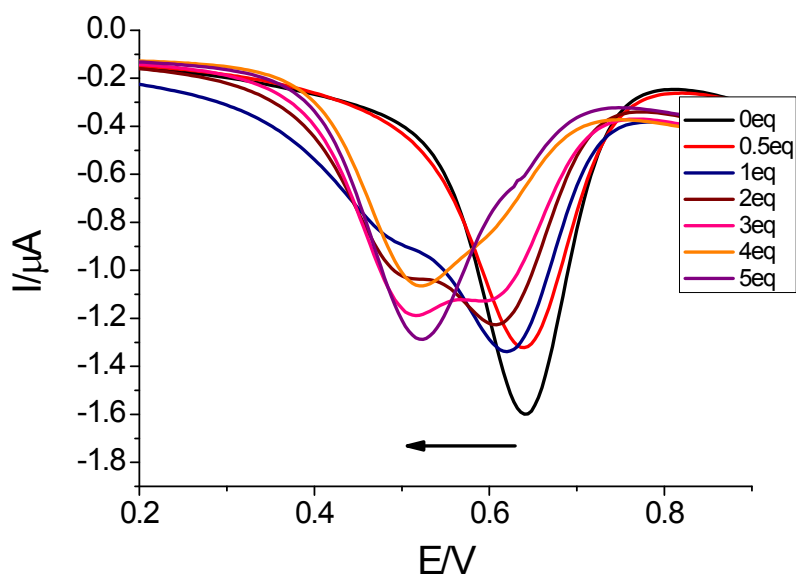


Fig. S8 DPV titration profile of **4** (0.2 mM) upon addition of various amount of AcO^- in $\text{CH}_3\text{CN}/\text{DMF}$ (9:1, V/V) solution. Reference electrode = Ag/AgNO_3 ; supporting electrolyte = $[\text{n-Bu}_4\text{N}]\text{PF}_6$ (0.1 M); scan rate = 100 mV S^{-1}

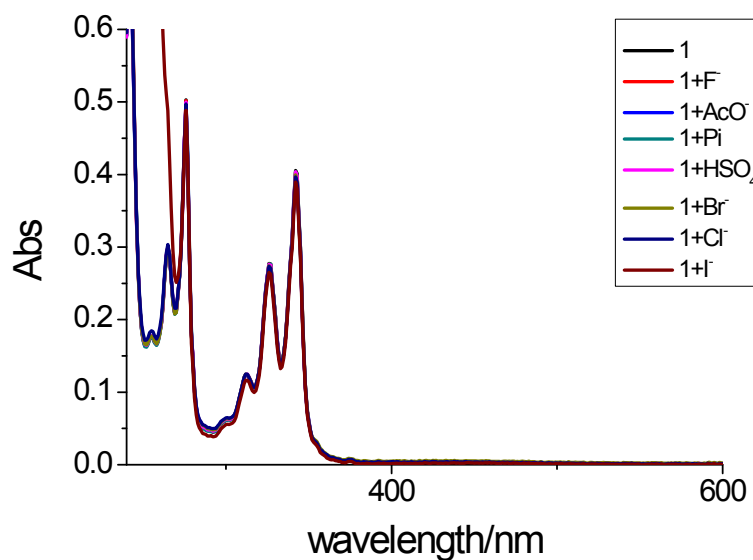


Fig. S9 The absorption spectra of **1** upon addition various anions (30 equiv) in CH_3CN solution.

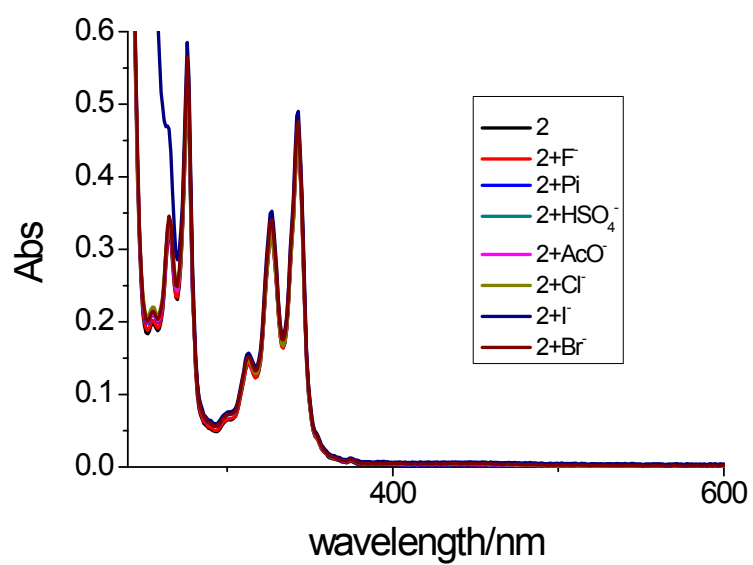


Fig. S10 The absorption spectra of **2** upon addition various anions (20 equiv) in CH₃CN solution.

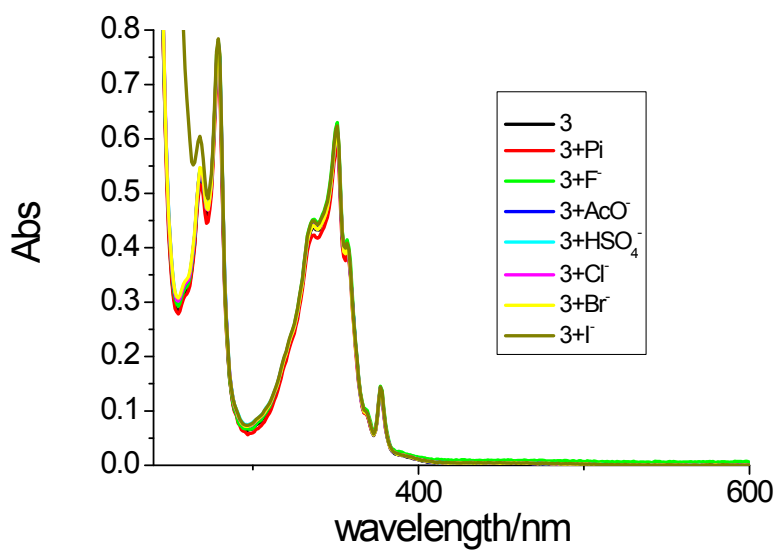


Fig. S11 The absorption spectra of **3** upon addition various anions (30 equiv) in CH₃CN solution.

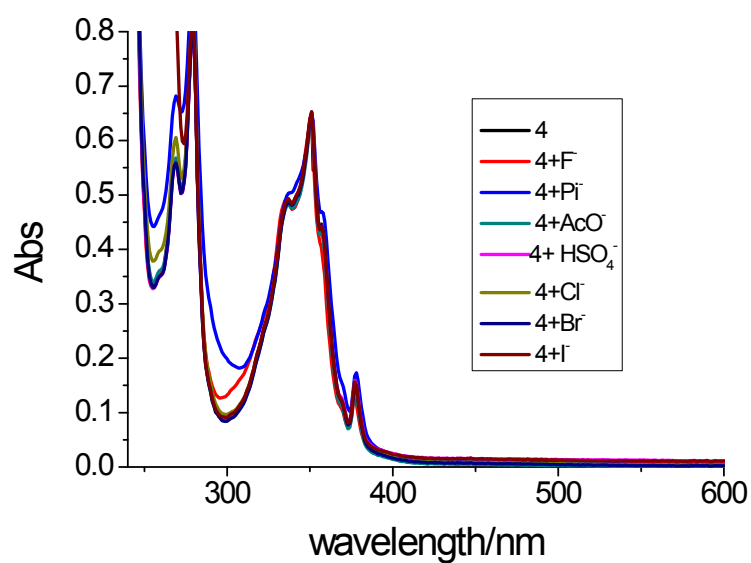


Fig. S12 The absorption spectra of **4** upon addition various anions (20 equiv) in CH₃CN solution.

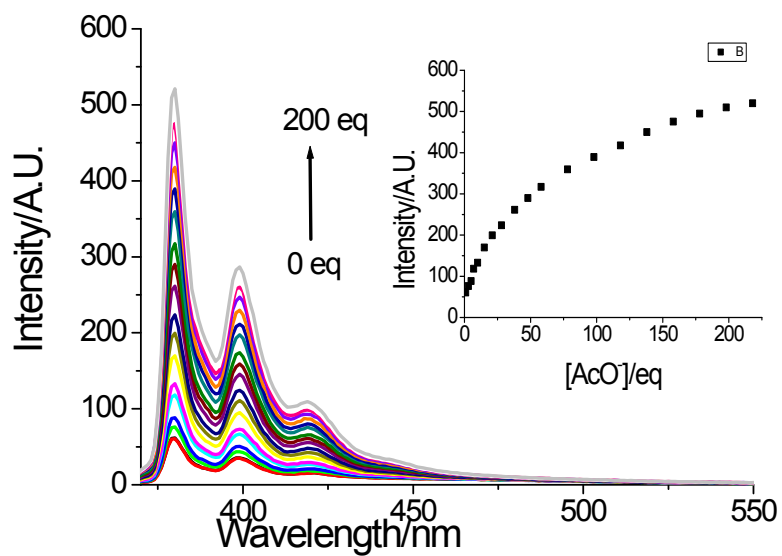


Fig. S13 Emission titration spectra of **3** (20 μM) in CH₃CN solution upon addition AcO⁻ (1-200eq). Inset : Fluorescence spectra changes of **3** at 380 nm upon the addition of various amount of AcO⁻ in CH₃CN solution.

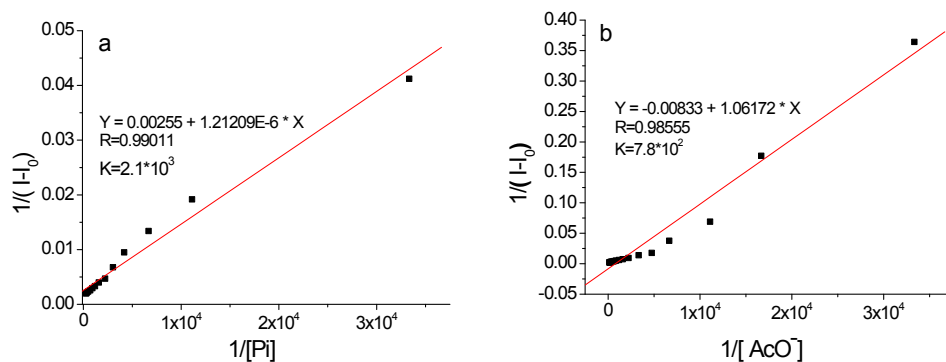


Fig. S14 the Benesi-Hildebrand plot for 1:1 complexation of **3** with Pi (a) and AcO⁻ (b) in CH₃CN solution

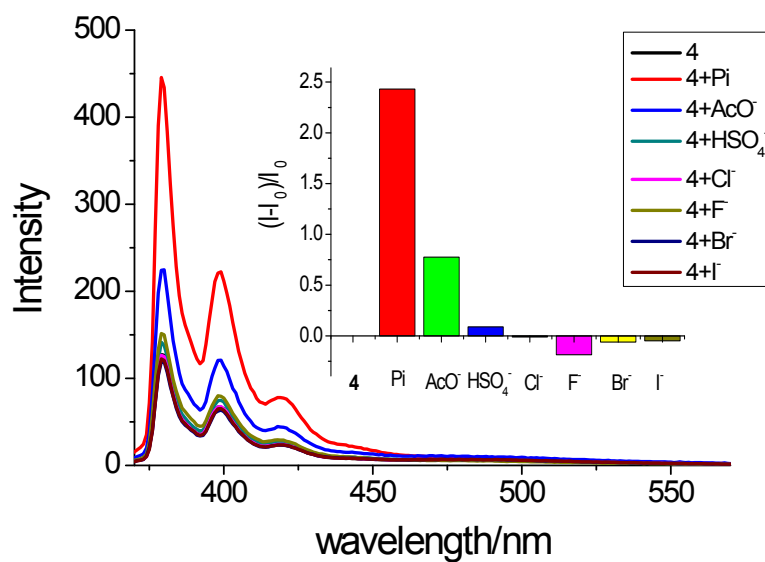


Fig. S15 The emission spectra of **4** upon addition various anions (20 equiv) in CH₃CN solution ($\lambda_{exc} = 360$ nm). Inset: shows the emission intensity at 380 nm upon the addition of various anions.

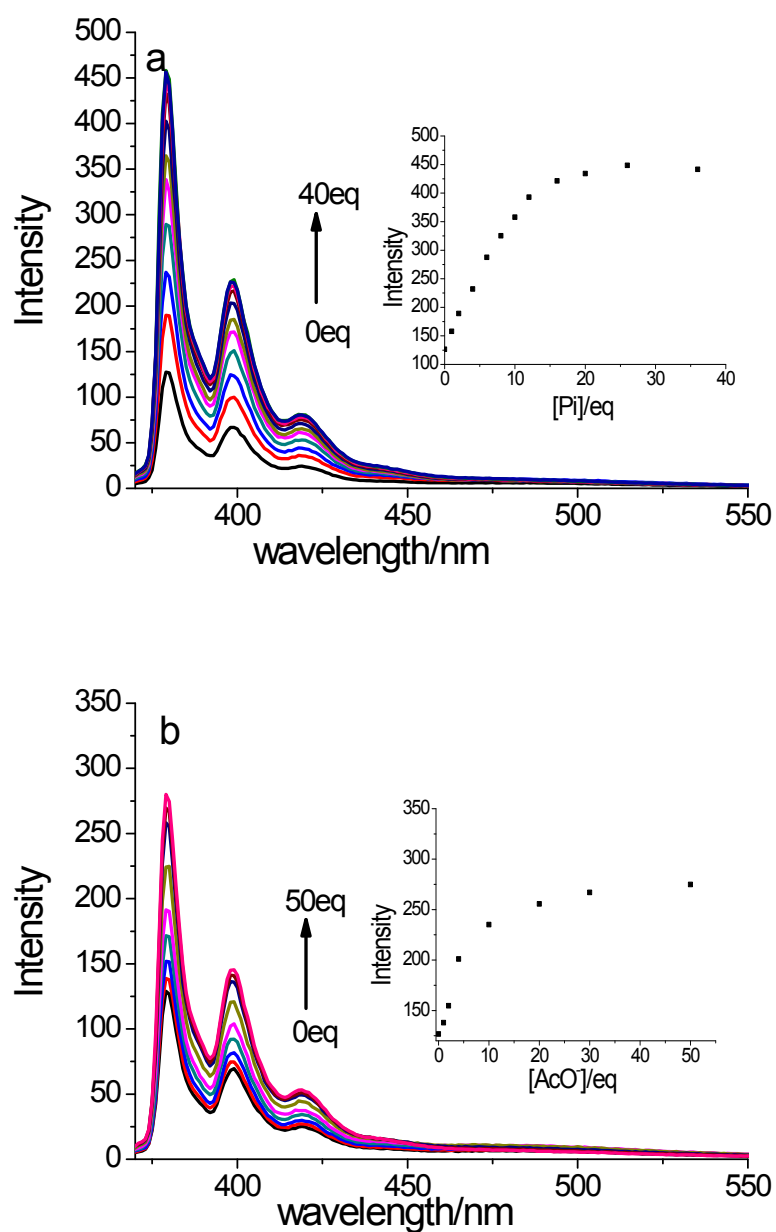


Fig. S16 (a) Emission titration spectra of **4** (20 μM) in CH_3CN solution upon addition H_2PO_4^- (0–40 eq) with excitation at 360 nm. Inset: Fluorescence spectra changes of **4** at 380 nm upon the addition of various amount of H_2PO_4^- in CH_3CN solution; (b) Emission titration spectra of **4** (20 μM) in CH_3CN solution upon addition AcO^- (1–50 eq). Inset: Fluorescence spectra changes of **4** at 380 nm upon the addition of various amount of AcO^- in CH_3CN solution.

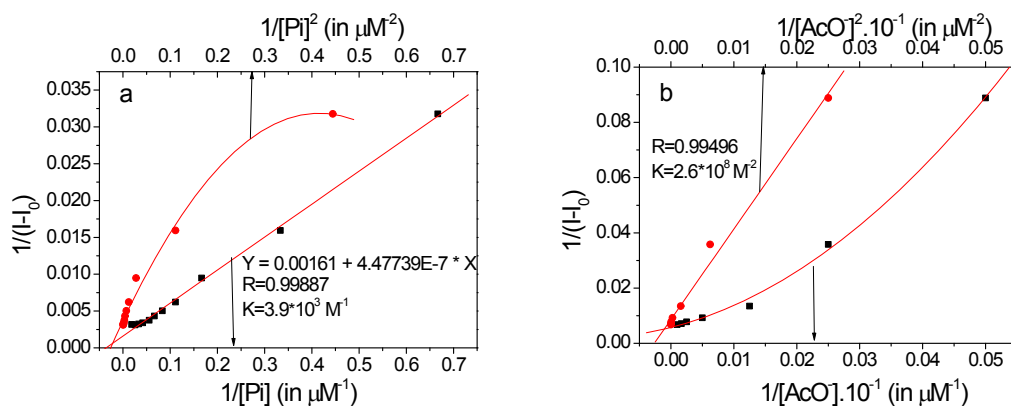


Fig. S17. (a) Benesi-Hildebrand plots using fluorescence data for the complexation of **4** with Pi in CH₃CN. solid line (●) is for for 1:2 complexation; solid line (■) is for for 1:1 complexation. I and I_0 are the fluorescence intensity of **4** in the presence and absence of Pi, respectively in CH₃CN solution; **(b)** Benesi-Hildebrand plots using fluorescence data for the complexation of **4** with AcO⁻ in CH₃CN. solid line (●) is for for 1:2 complexation; solid line (■) is for for 1:1 complexation. I and I_0 are the fluorescence intensity of **4** in the presence and absence of AcO⁻, respectively in CH₃CN solution.

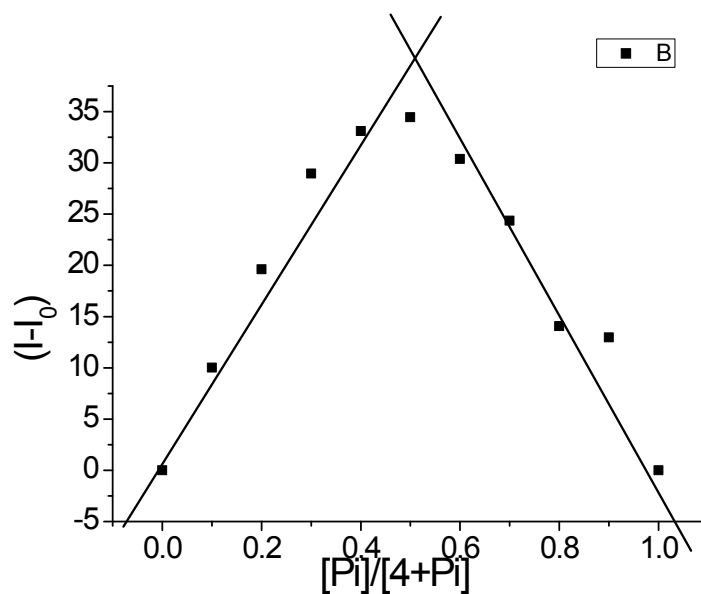


Fig. S18 Job-plot of **4**-Pi.

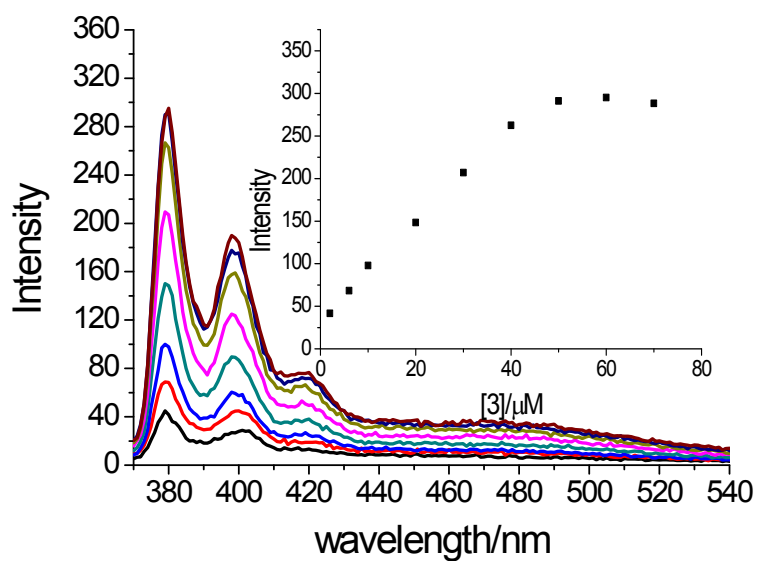


Fig. S19 Fluorescence spectra changes of **3** upon the addition of various amount of **3** in CH₃CN solution. Inset: Fluorescence spectra changes of **3** at 380 nm upon the addition of various amount of **3** in CH₃CN solution.

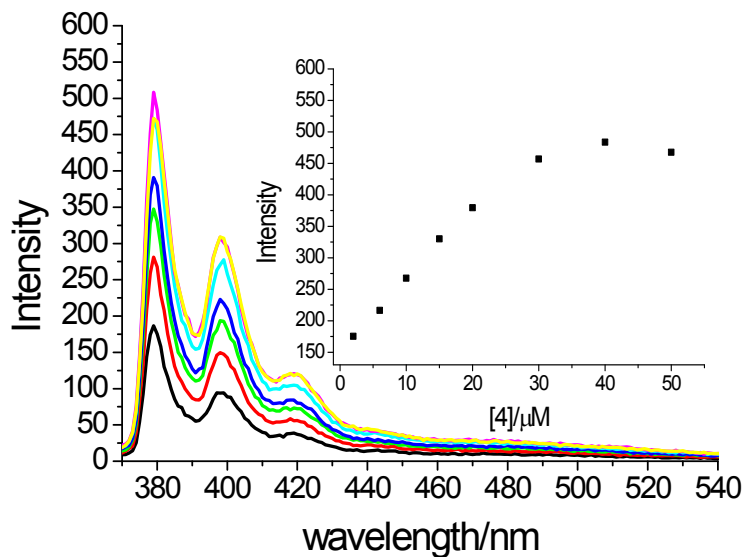


Fig. S20 Fluorescence spectra changes of **4** upon the addition of various amount of **4** in CH₃CN solution. Inset: Fluorescence spectra changes of **4** at 380 nm upon the addition of various amount of **4** in CH₃CN solution.

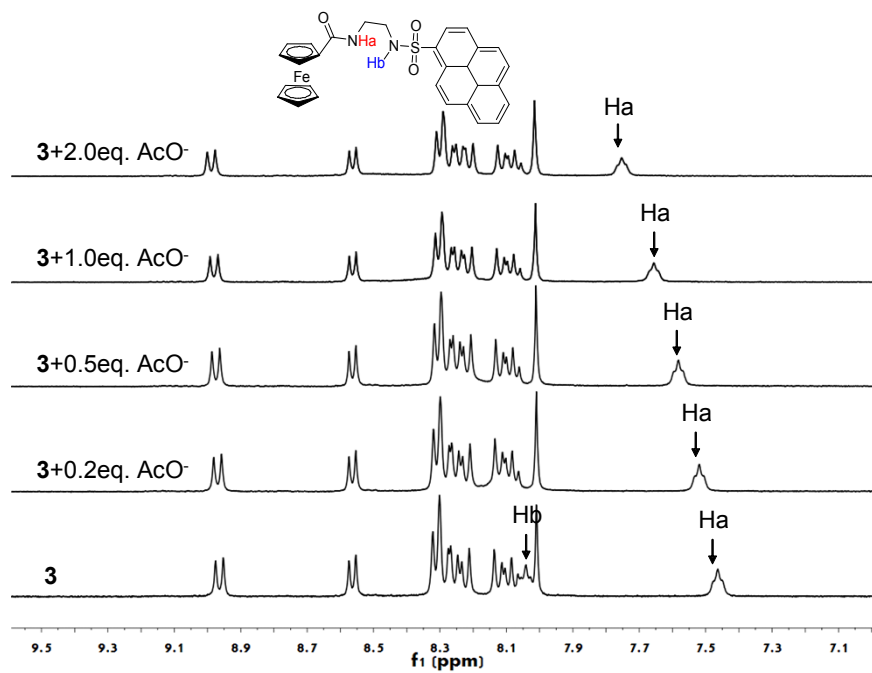


Fig. S21 ¹H NMR spectra of **3** upon addition various amount of AcO⁻ in DMSO-d₆ solution

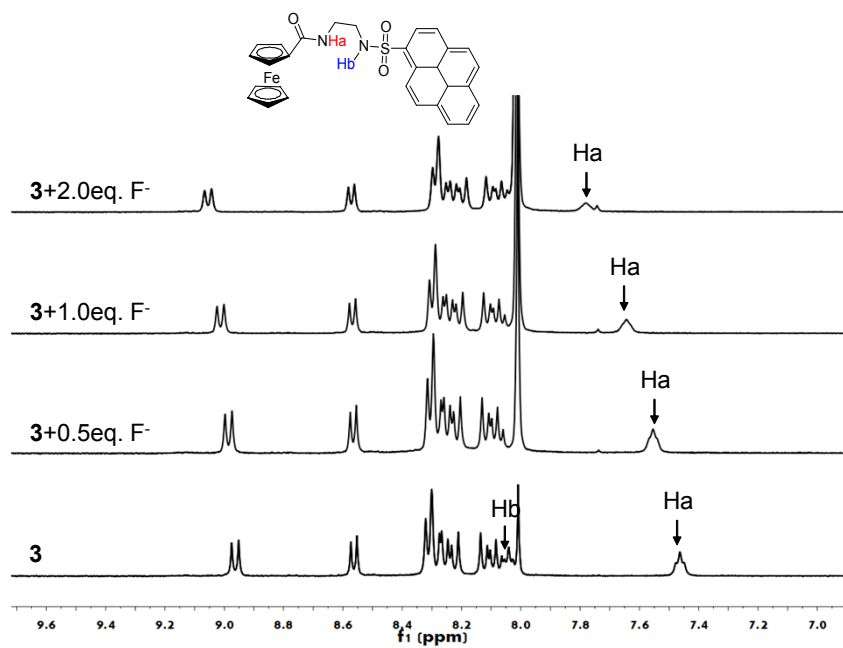


Fig. S22 ¹H NMR spectra of **3** upon addition various amount of F⁻ in DMSO-d₆ solution

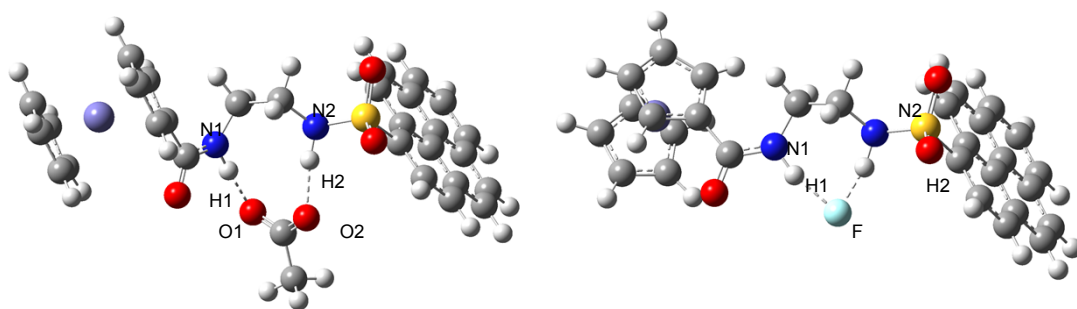


Fig. S23 Calculated structure (B3LYP/6-31G^{*}) of **3**•CH₃COO⁻ (left) and **3**•F⁻ (right) complexes. Nitrogen, oxygen, sulfur, carbon and hydrogen atoms are represented as blue, red, yellow, gray and white balls respectively. Selected bond and angles: N1–H1···O1, 1.853 Å, 173.15 °; N2–H2···O2, 1.782 Å, 172.23 °; N1–H1···F, 1.567 Å, 166.34 °; N2–H2···F, 1.713 Å, 165.71 °.

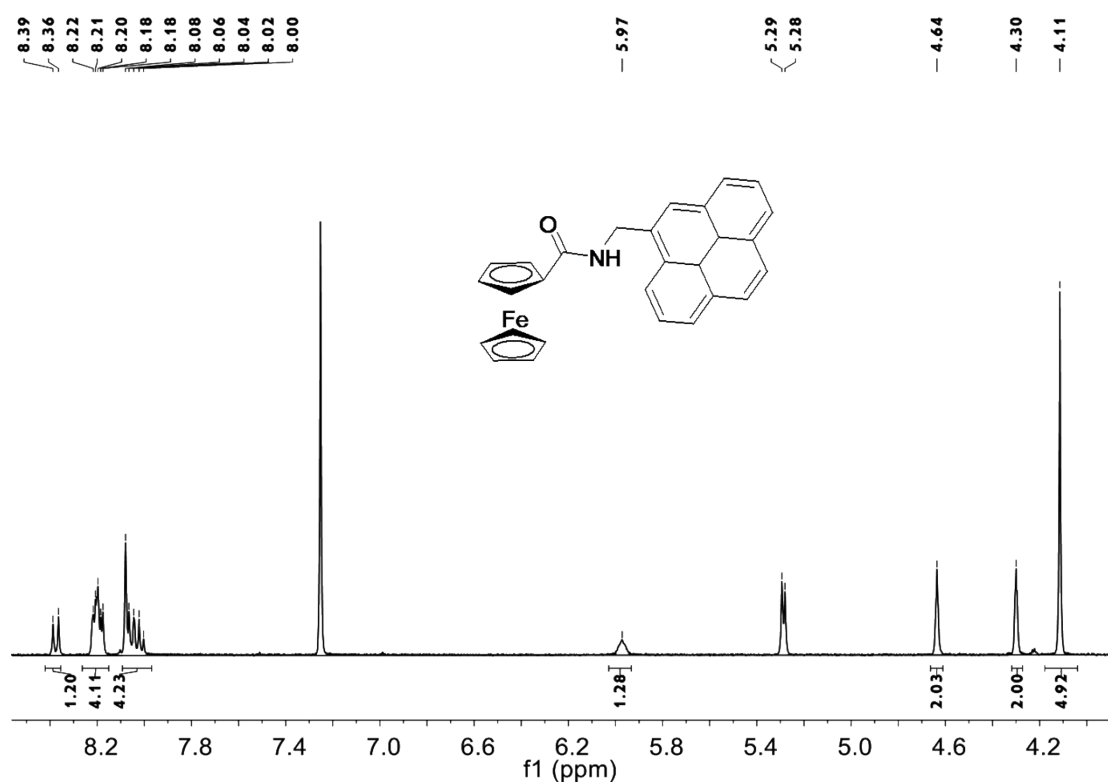


Fig. S24 ¹H NMR spectrum of **1** in CDCl₃ solution

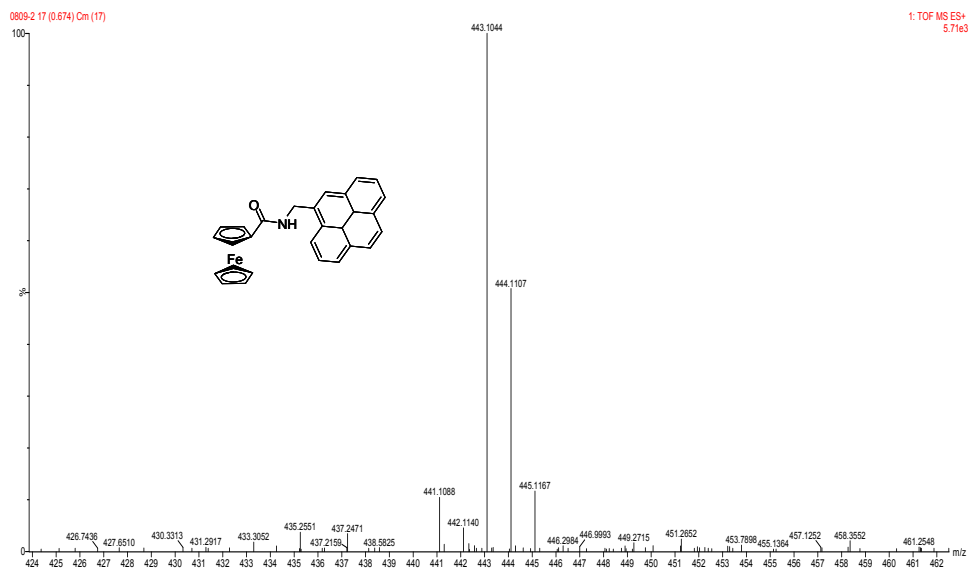


Fig. S25 ESI-MS (ES⁺) spectrum of **1**

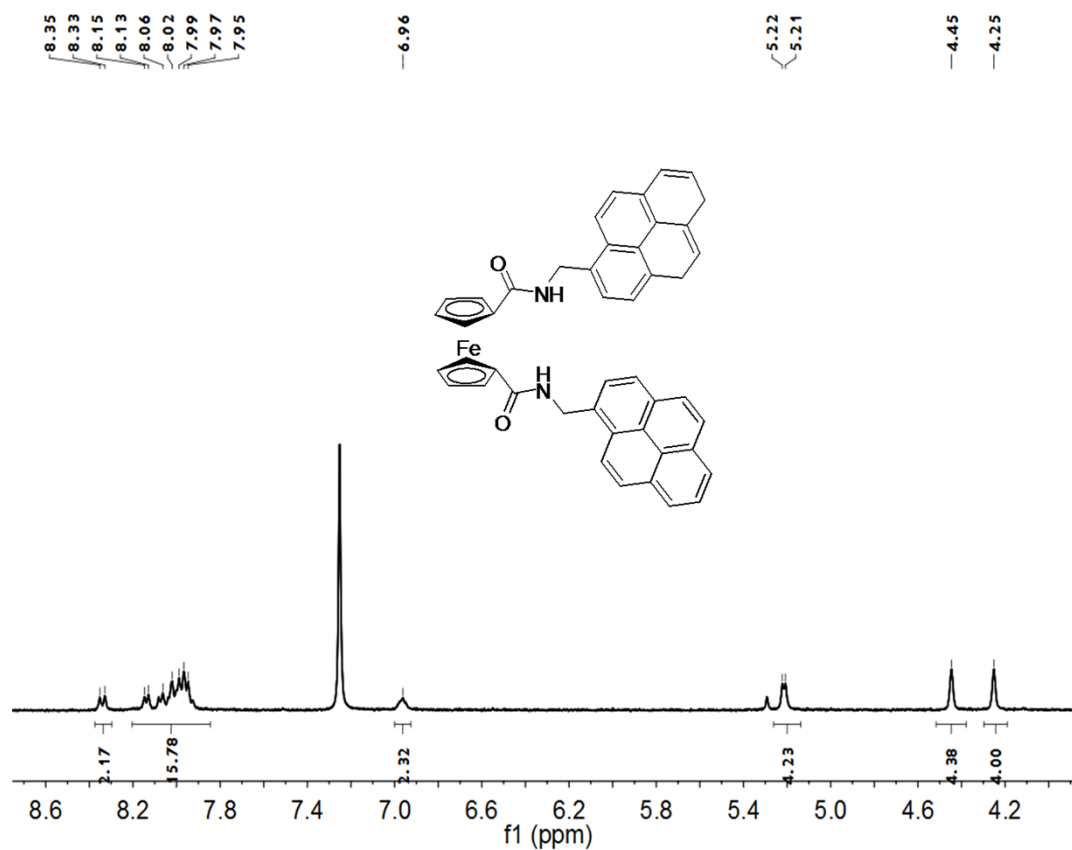


Fig. S26 ¹H NMR spectrum of **2** in CDCl₃ solution

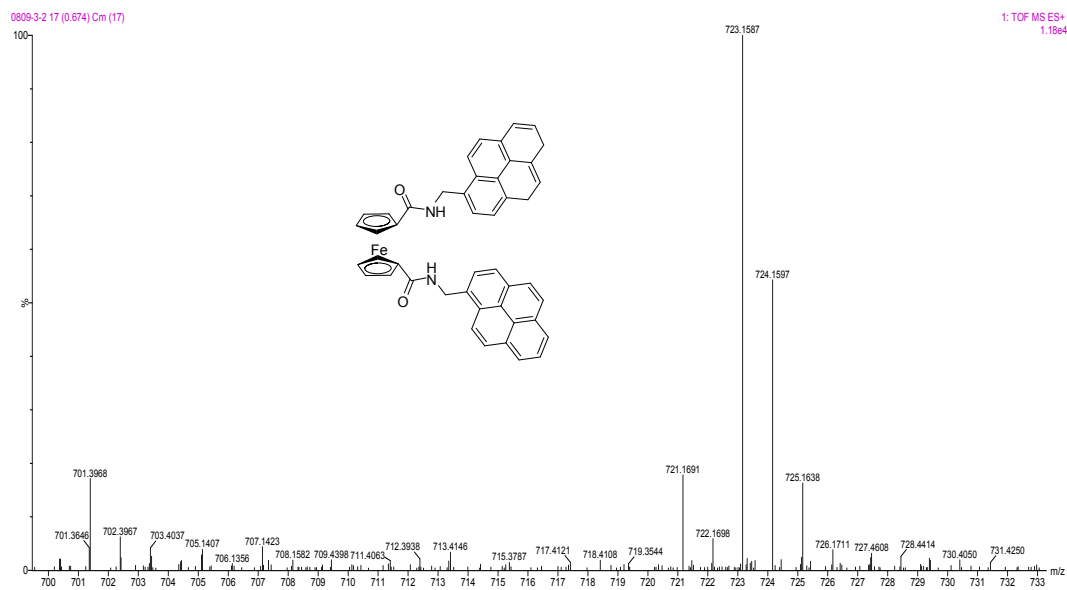


Fig. S27 ESI-MS (ES⁺) spectrum of **2**

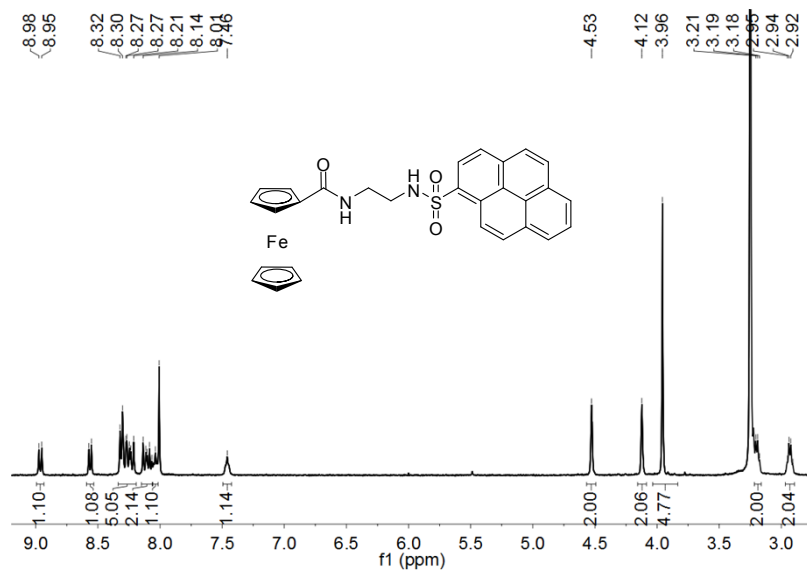


Fig. S28 ¹H NMR spectrum of **3** in CDCl₃/DMSO solution

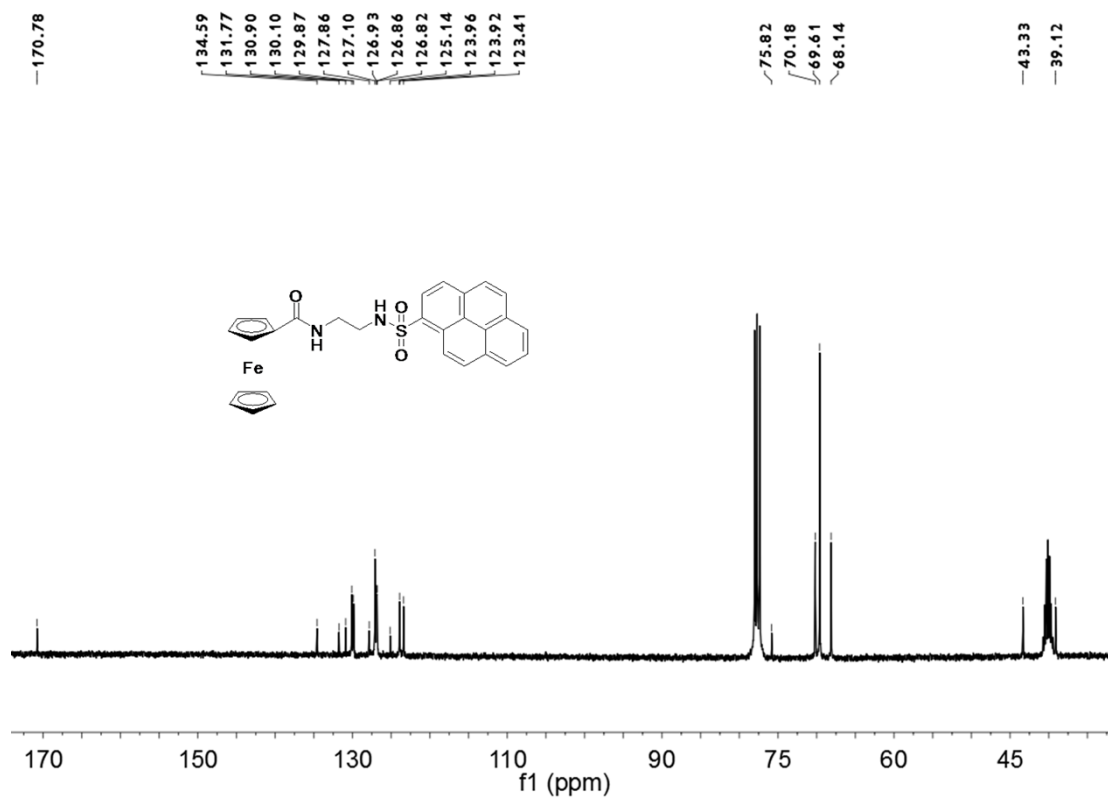


Fig. S29 ¹³C NMR spectrum of **3** in CDCl₃/DMSO solution

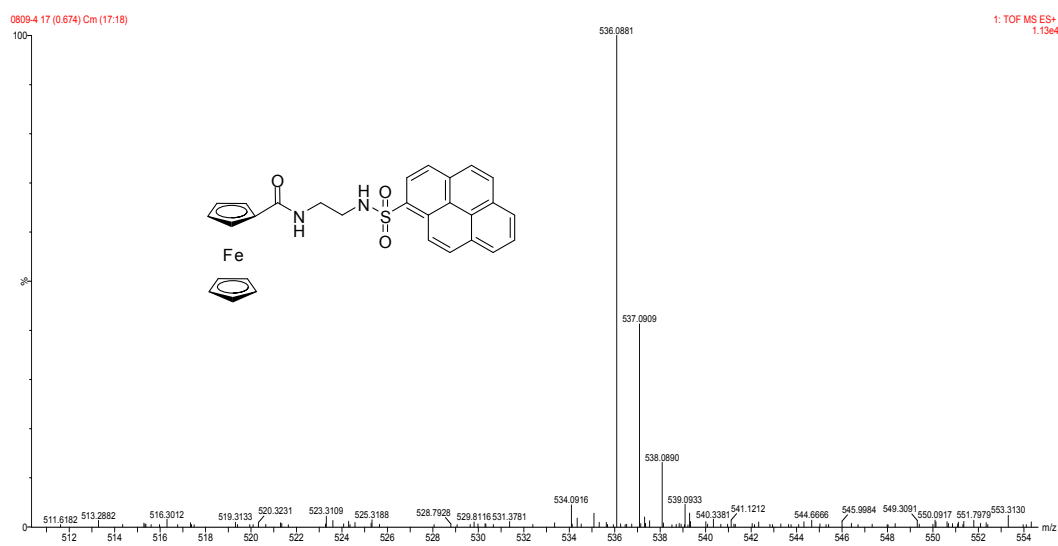


Fig. S30 ESI-MS (ES⁺) spectrum of **3**

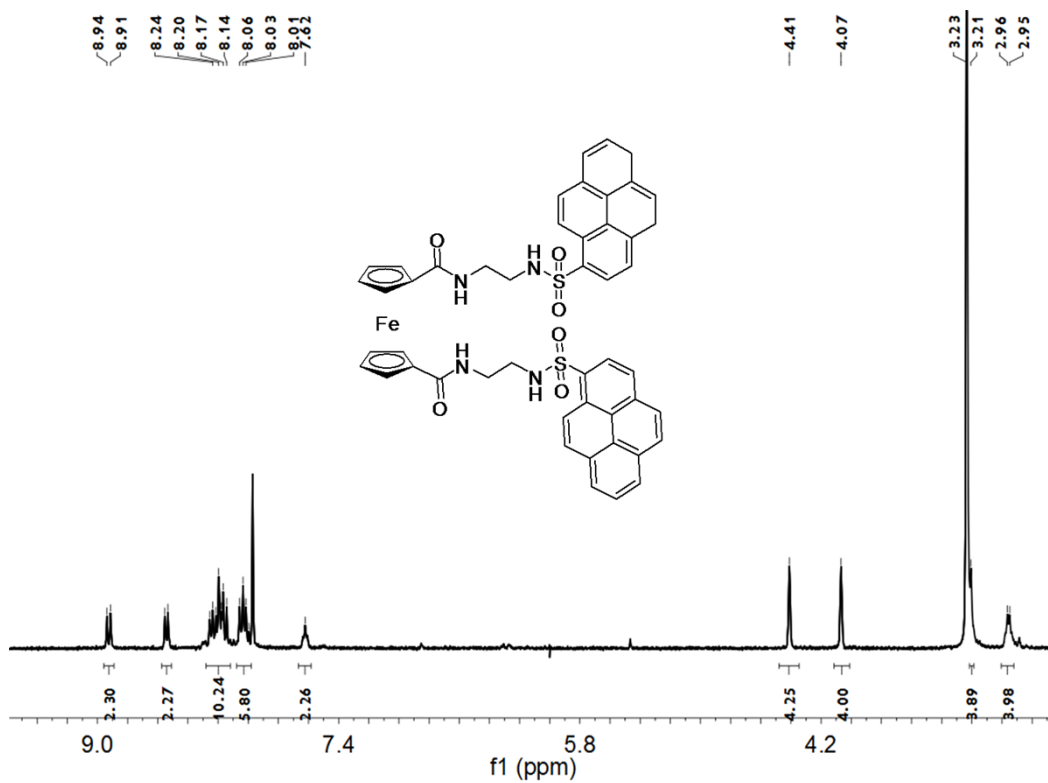


Fig. S31 ^1H NMR spectrum of 4 in $\text{CDCl}_3/\text{DMSO}(1:1)$ solution



Fig. S32 ESI-MS (ES^+) spectrum of 4