

A new fluoride selective electrochemical and fluorescent chemosensor based on a ferrocene-naphthalene dyad.

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Electronic Supplementary Information (ESI)

Spectroscopic data of compound 1.

IR (CH₂Cl₂) ν_{\max} 3360, 3263, 1665, 1600, 1493, 1374, 1067, 1035, 852, 804, 750 cm⁻¹.
¹H NMR (DMSO-d₆): δ = 8.48 (s, 2H, *NH*-napht.), 7.72 (m, 4H, *NH*-Fc + *H*₄ napht.), 7.43 (t, 2H, *J* = 7.0 Hz, *H*₃ napht.), 7.25 (d, 2H, *J* = 7.0 Hz, *H*₂ napht.), 4.89 (bs, 2H, *Fc*), 4.08 (bs, 2H, *Fc*), 3.81 (bs, 4H, *Fc*). ¹³C NMR (DMSO-d₆): δ 153.80 (C=O), 135.68 (q), 134.00 (q), 125.68 (CH), 125.17 (CH), 124.41 (CH), 97.74 (q, *Fc*), 63.27 (CH, *Fc*), 62.15 (CH, *Fc*), 60.95 (CH, *Fc*), 57.94 (CH, *Fc*). MS (EI): *m/z* (%): 426 (M⁺, 100), 399 (3), 268 (100), 158 (54). Anal Calcd for C₂₂H₁₈FeN₄O₂: C, 61.99; H, 4.26; N, 13.14. Found: C, 61.74; H, 4.30; N, 13.38.

Computational details.- Calculations were performed at the DFT level of theory, which has been widely recommended as a practical and effective tool for organometallic compounds, especially for reproducing experimental ground-state geometries and rotational barriers for ferrocenes¹, and were based on the Spartan'02 (build 119, Wavefunction Inc., Irvine, CA) program system. Prior to the final DFT *ab initio*

calculation, a full conformational search was performed at the semiempirical PM3(d) level until local minima (all real frequencies) were found, as verified by harmonic frequency calculations. The obtained geometry for the $1 \cdot 2F^-$ complex was thereafter fully optimized (Figure I) by using the B3LYP functional and the all-electron moderate size 3-21G(d) basis set.

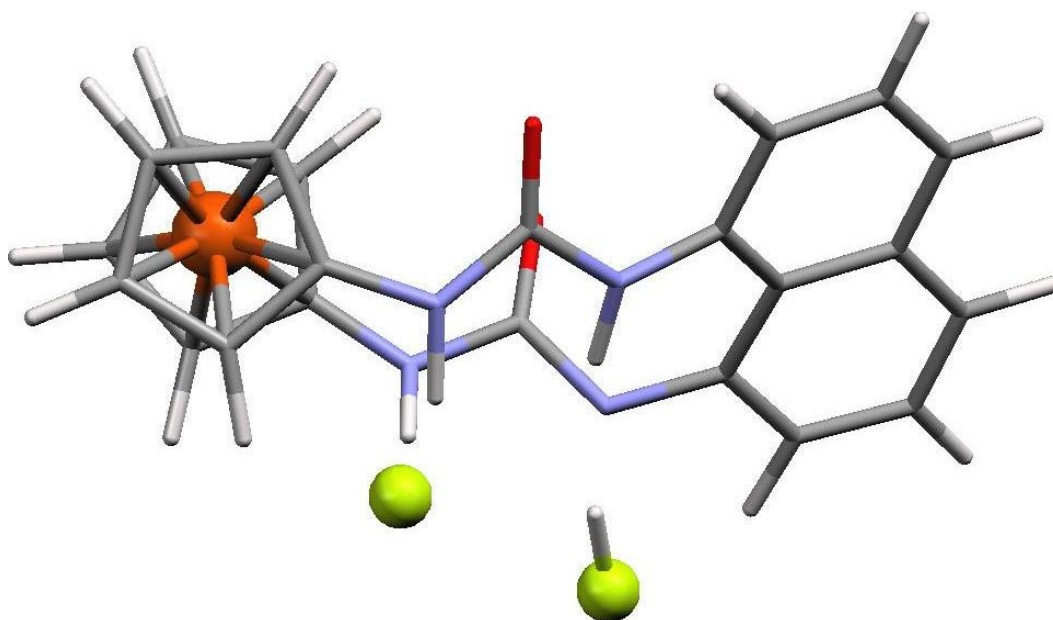


Figure S1. Calculated structure (B3LYP/3-21G*) for the complex $1 \cdot 2F^-$. Fluorine atoms are represented as green-yellow balls.

General Electrochemistry

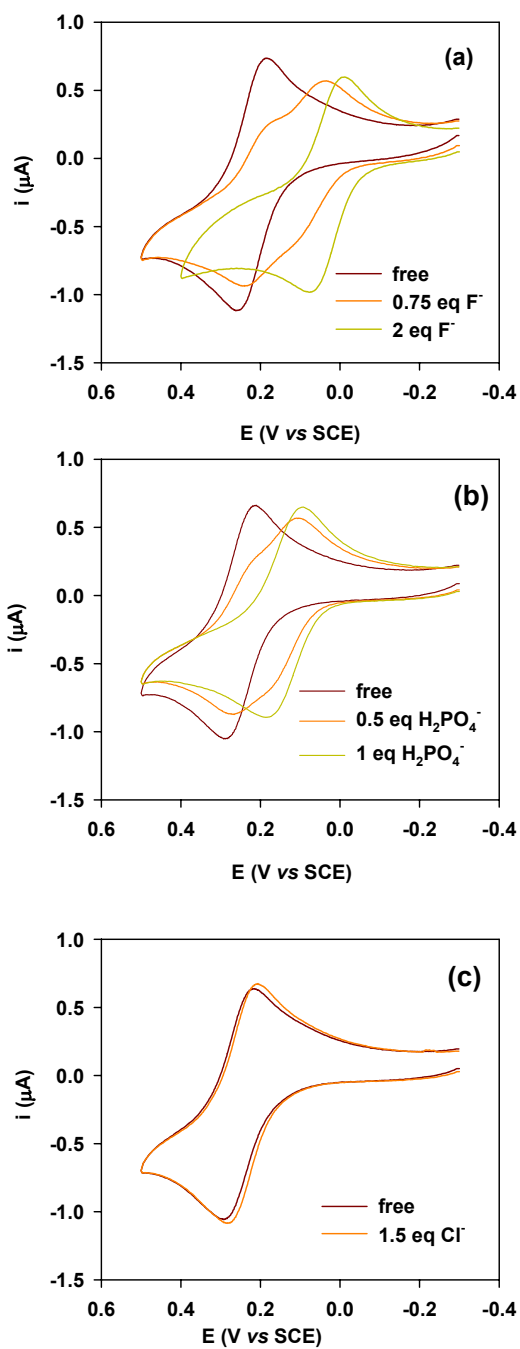


Figure S2. Cyclic voltammograms for the recognition of anions: Solvent : DMSO ; reference electrode : aqueous SCE; working and counter electrode: Pt; supporting electrolyte: 0.1 M [*n*-Bu₄N][PF₆] ; scan rate: 100 mVs⁻¹. Samples 1 mM of **1** : (a) with [*n*-Bu₄N][F] ; (b) with [*n*-Bu₄N][H₂PO₄] and (c) with [*n*-Bu₄N][Cl]

Fluorescence:

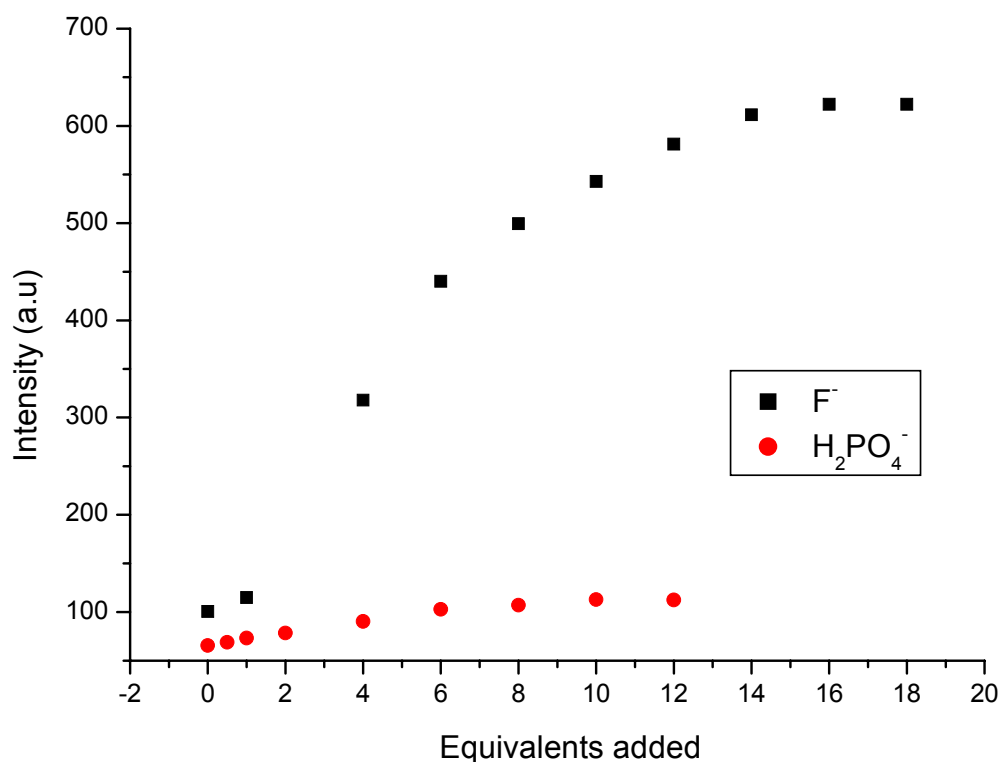


Figure S3. Changes in the emission spectra of **1** in the region 362-380 nm as a function of equivalents of anion added

Evolution of the ^1H -NMR spectra upon addition of the appropriate anion

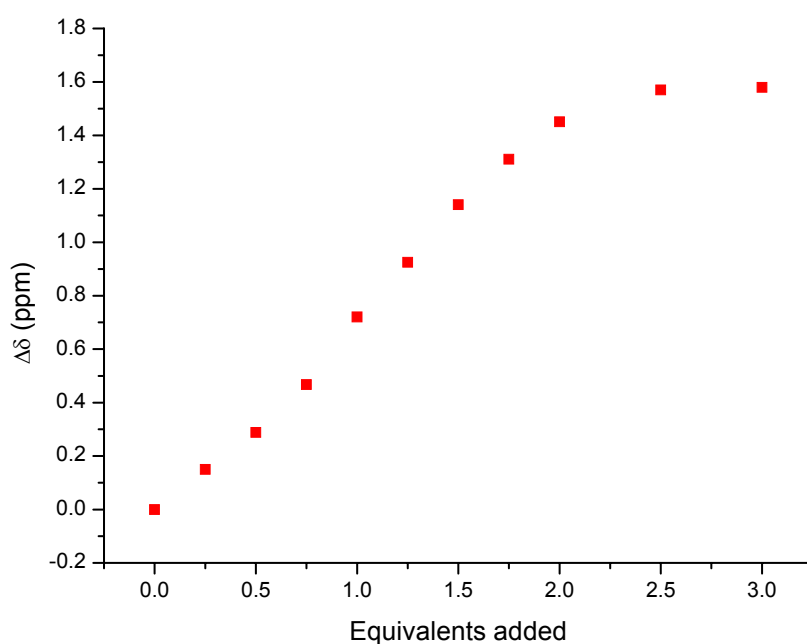


Figure S4. The changes ^1H NMR (300 MHz, $\text{DMSO-}d_6$) in NH-naphtalene protons of **1** upon titration with F^- .

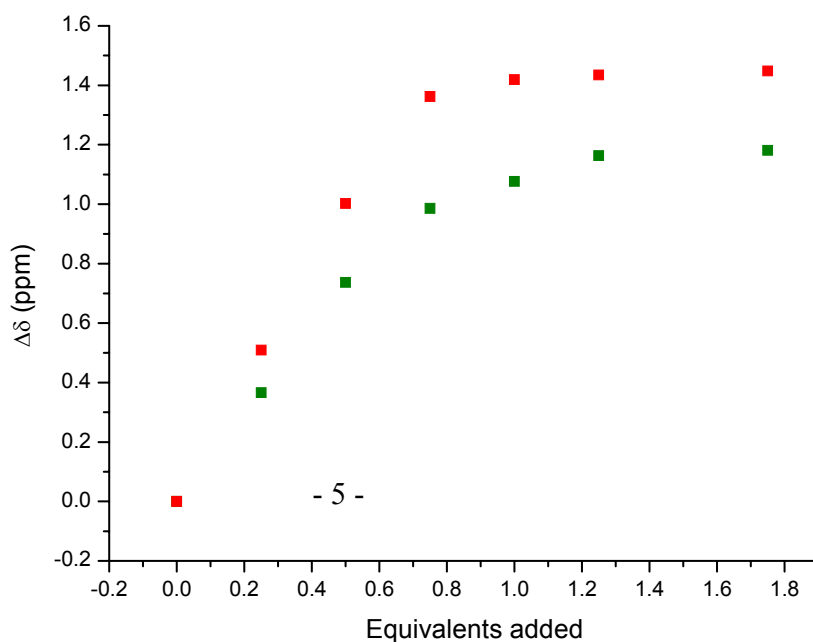


Figure S5. The changes ^1H NMR (300 MHz, $\text{DMSO-}d_6$) in NH protons of **1** upon titration with H_2PO_4^- : NH-naphtalene (red square); NH-ferrocene (green square)

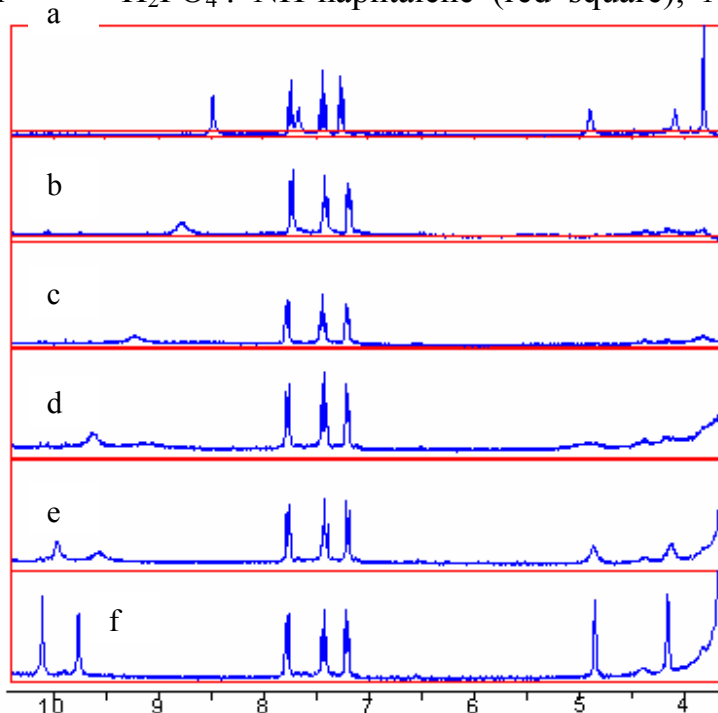
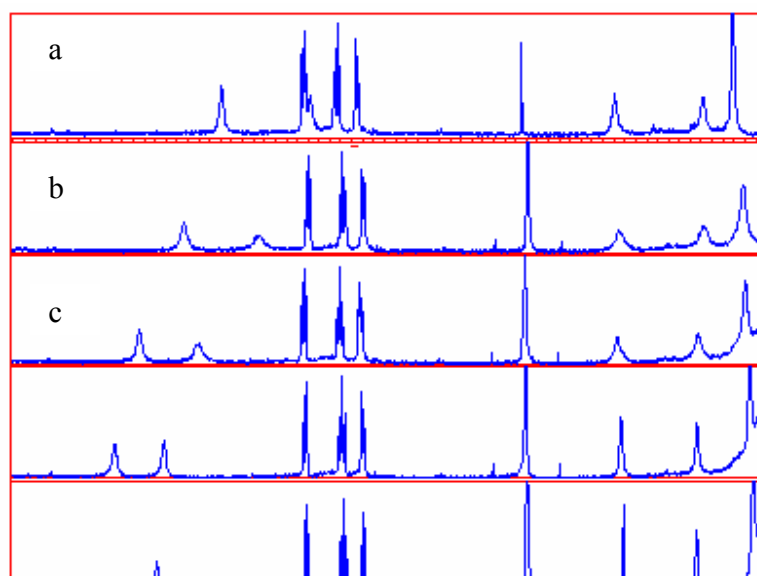


Figure S6. Evolution of the ^1H NMR spectra of **1** upon addition of increasing amounts of F^- anion: (a) **1**; (b) **1** + 0.5 eq F^- ; (c) **1** + 1 eq F^- ; (d) **1** + 1.5 eq F^- ; (e) **1** + 2 eq F^- ; (f) **1** + 2.5 eq F^- .



d

e

Figure S7. Evolution of the ^1H NMR spectra of **1** upon addition of increasing amounts of H_2PO_4^- anion: (a) **1**; (b) **1** + 0.25 eq H_2PO_4^- ; (c) **1** + 0.5 eq H_2PO_4^- ; (d) **1** + 0.75 eq H_2PO_4^- ; (e) **1** + 1 eq H_2PO_4^- .

References.-

- 1.- For instance see: A. Tárraga, F. Otón, A. Espinosa, M.D. Velasco, P. Molina, D.J. Evans; *Chem. Commun.*, **2004**, 458-459.