

A Ferrocene-Based Heteroditopic Ligand for Electrochemical Sensing of Cations and Anions

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Electronic Supplementary Information (ESI)

General Electrochemistry

All electrochemical experiments were performed with a QUICELTRON potentiostat/galvanostat controlled by a personal computer and driven by dedicated software. Electrochemical experiments were conducted in a conventional three-electrode cell under a nitrogen atmosphere at 25 °C. The working electrode was a Pt disk (1 mm in diameter) polished before each recording. The auxiliary electrode was a platinum wire. The reference electrode was SCE . All potentials are quoted with respect to Fc^+/Fc . The experiments were carried out in dichloromethane solutions containing 0.1 M of Bu_4NClO_4 as supporting electrolyte and under these experimental conditions, the ferrocenium/ferrocene couple was observed at +0.405 V *vs* SCE. Deoxygenation of the solutions was achieved by bubbling nitrogen for at least 10 min and the working electrode was cleaned after each run. Cyclic voltammetry (CV) curves were recorded at a scan rate of 0.1 V s⁻¹ and the differential pulse voltammtery (DPV) curves were recorded at a 4 mV s⁻¹ scan rate with a pulse height of 50 mV and a step time of 50 ms¹.

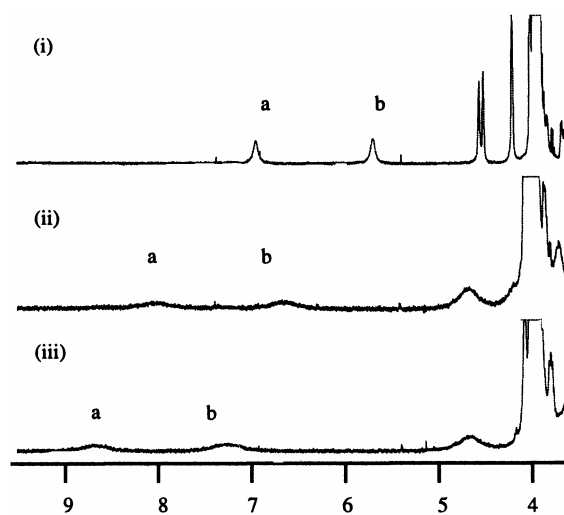


Fig. S1. Evolution of the ¹H-NMR spectra of **1** upon addition of increasing amounts of F⁻ anion: (i) **1**; (ii) **1**+0.5 eq F⁻; (iii) **1**+1 eq F⁻.

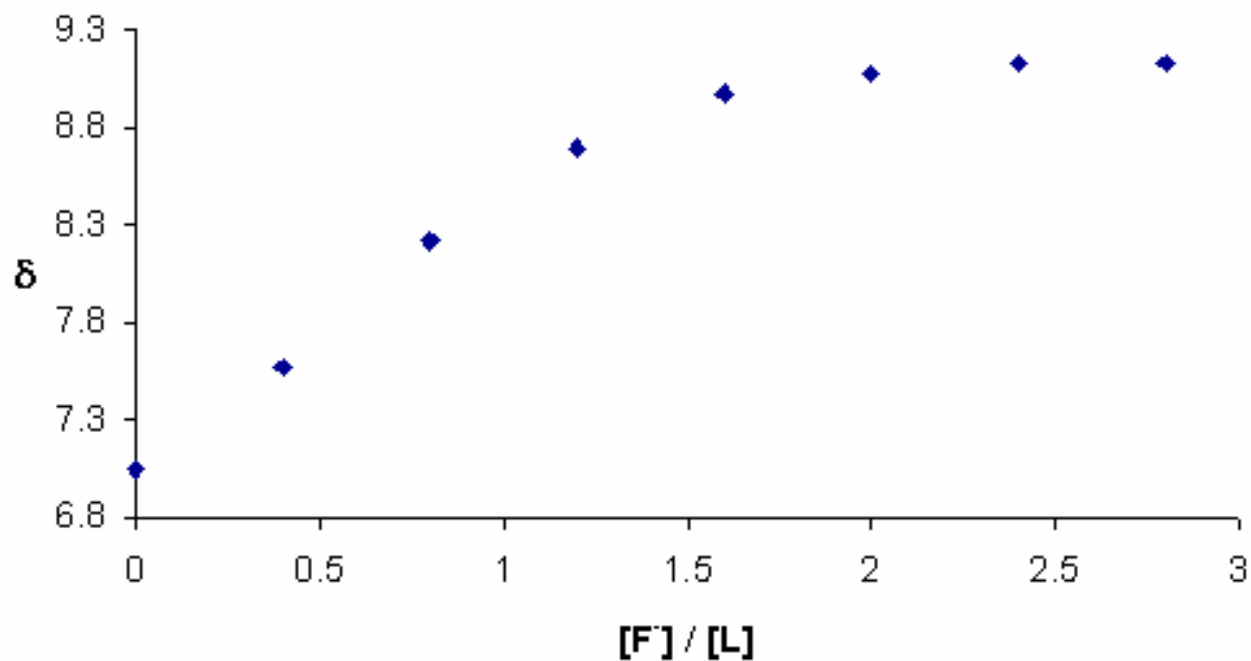


Fig. S2: Changes in the chemical shifts of the NH protons of **1** upon addition of $n\text{Bu}_4\text{NF}$.

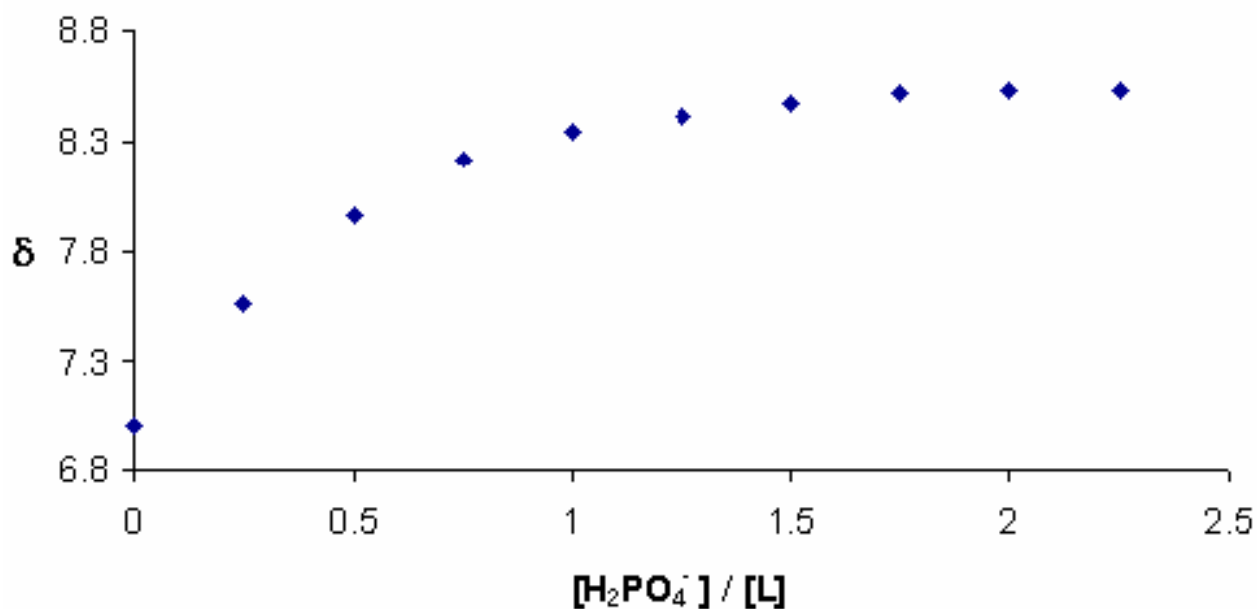


Fig. S3: Changes in the chemical shifts of the NH protons of **1** upon addition of $n\text{Bu}_4\text{NH}_2\text{PO}_4$.

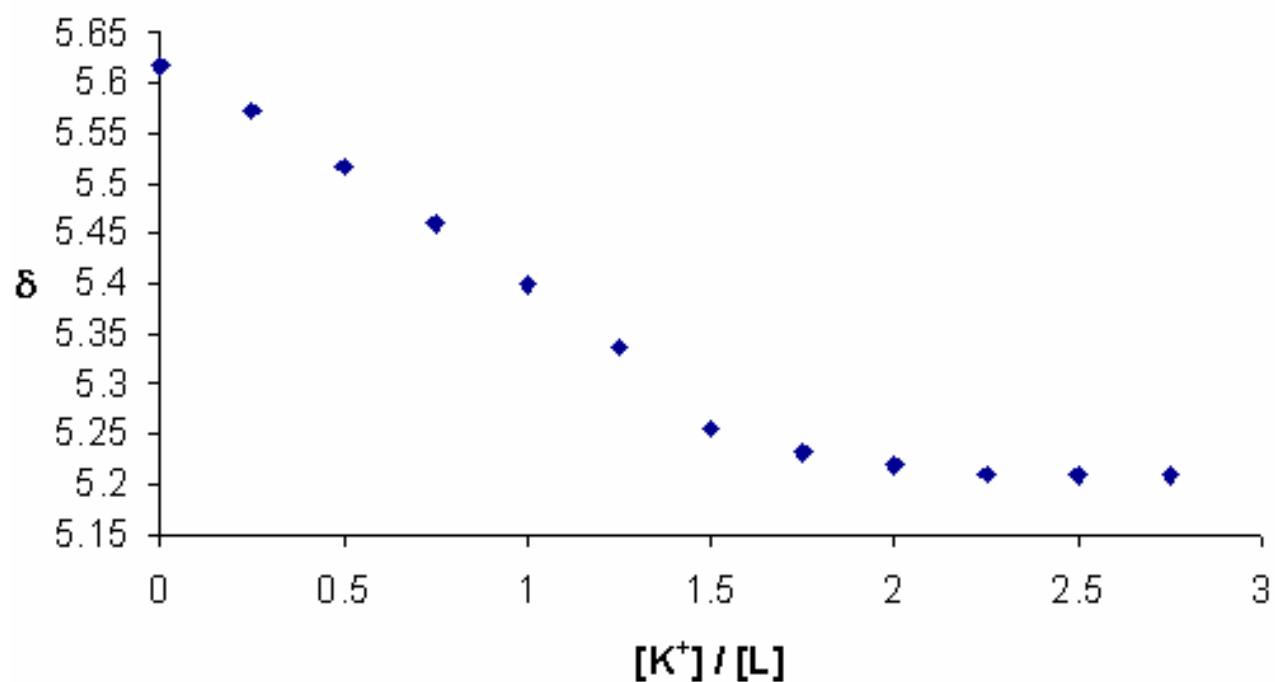


Fig. S4: Changes in the chemical shifts of the NH protons of **1** upon addition of KClO₄.

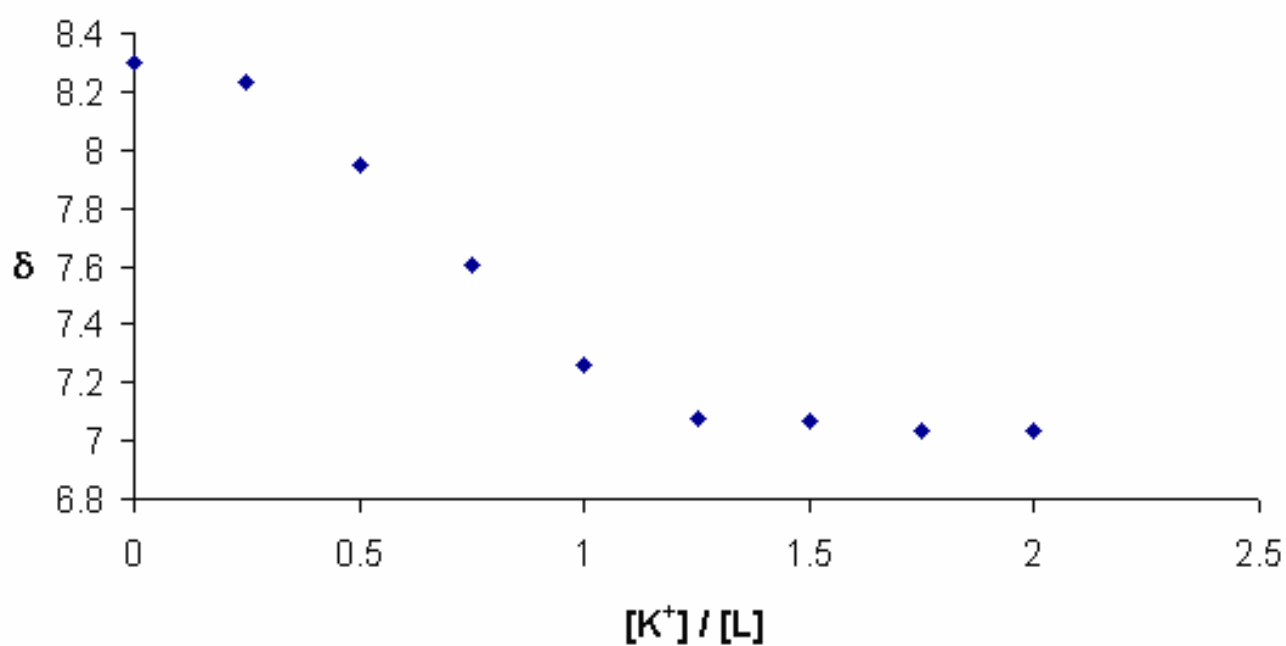


Fig. S5: Changes in the chemical shifts of the NH protons of [**1**•H₂PO₄⁻] upon addition of KClO₄.

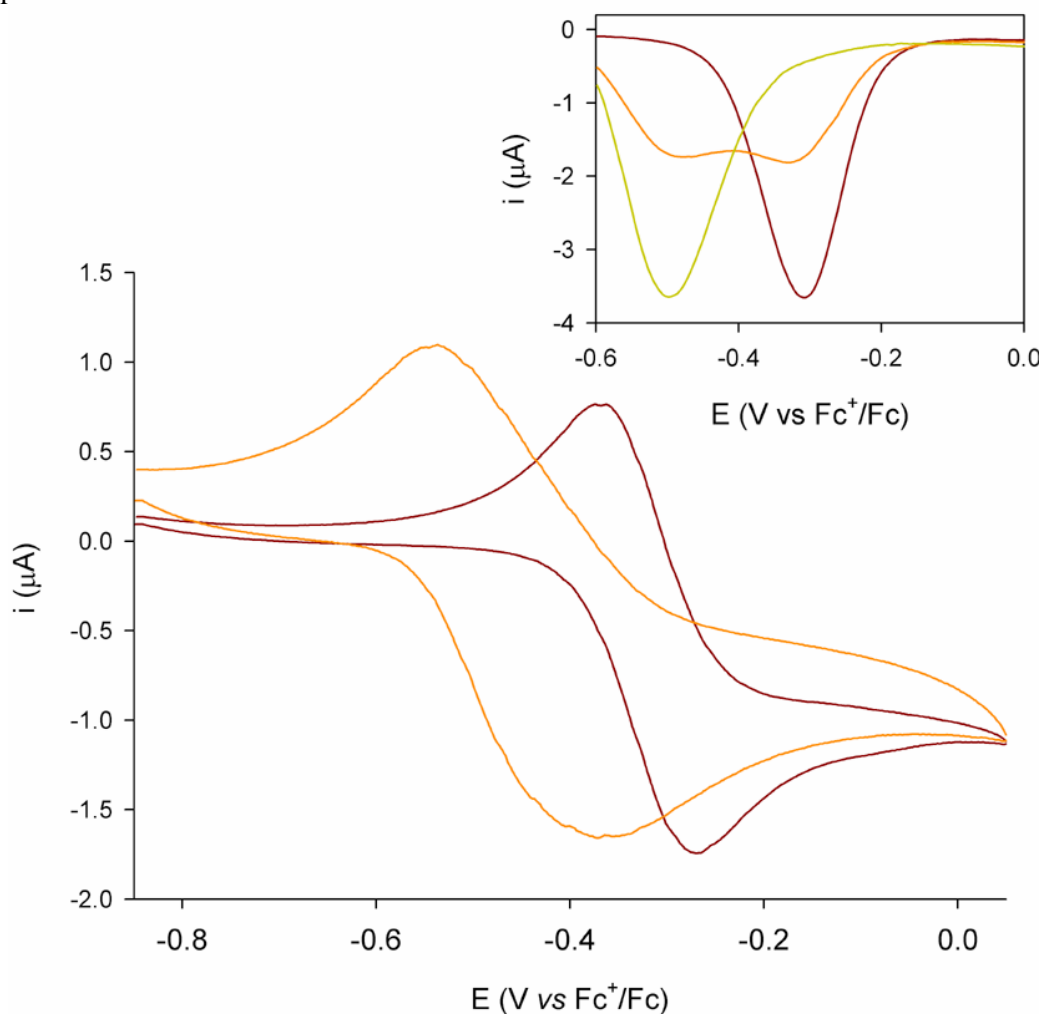


Fig. S6: CV response of compound **1** (1mM) in CH_2Cl_2 before (brown) and after addition of 2 equivalents of H_2PO_4^- (orange). Scan rate: 0.1 V s^{-1} . Upper inset DPV response : **1** (brown); **1** + 1 equivalents of H_2PO_4^- (orange); **1** + 2 equivalents of H_2PO_4^- (green); Scan rate: 0.004 V s^{-1} , pulse width: 50 ms, amplitude: 50 mV

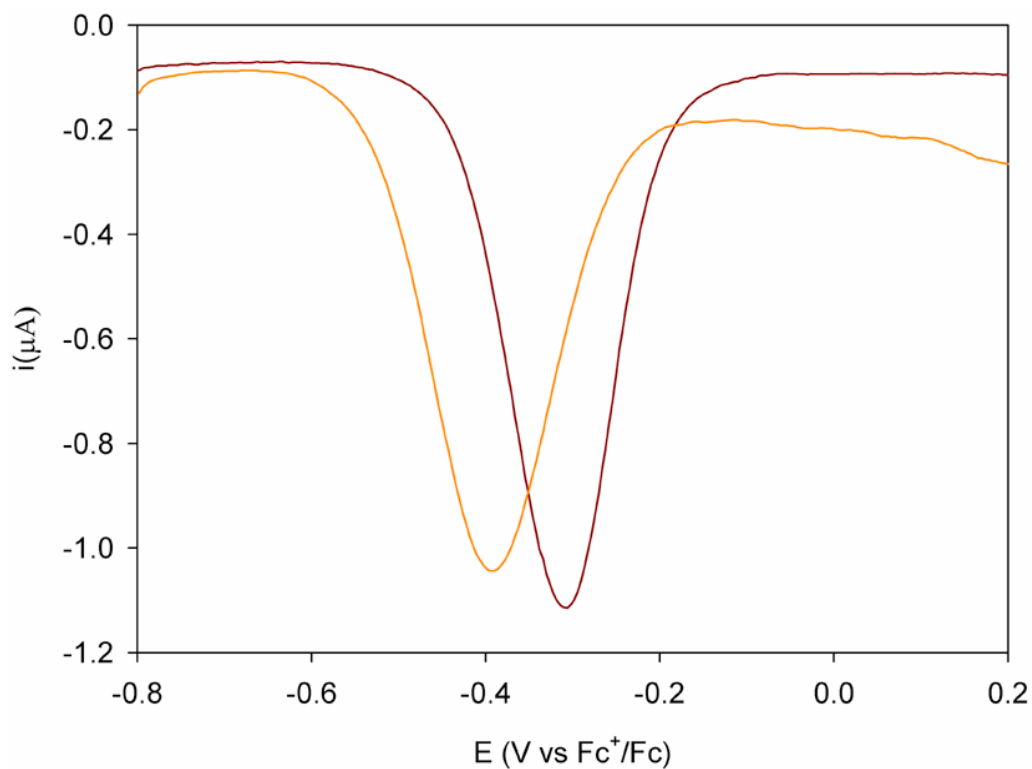


Fig. S7: Voltammetric response of compound **1** (1mM) in CH_2Cl_2 before (brown) and after addition of 1.5 equivalents of F^- (orange). Scan rate: 0.004 V s^{-1} , pulse width: 50 ms, amplitude: 50 mV