

Synthesis and Characterisation of Halide, Separated Ion Pair, and Hydride Cyclopentadienyl Iron *Bis*(Diphenylphosphino)ethane Derivatives

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Electrochemistry

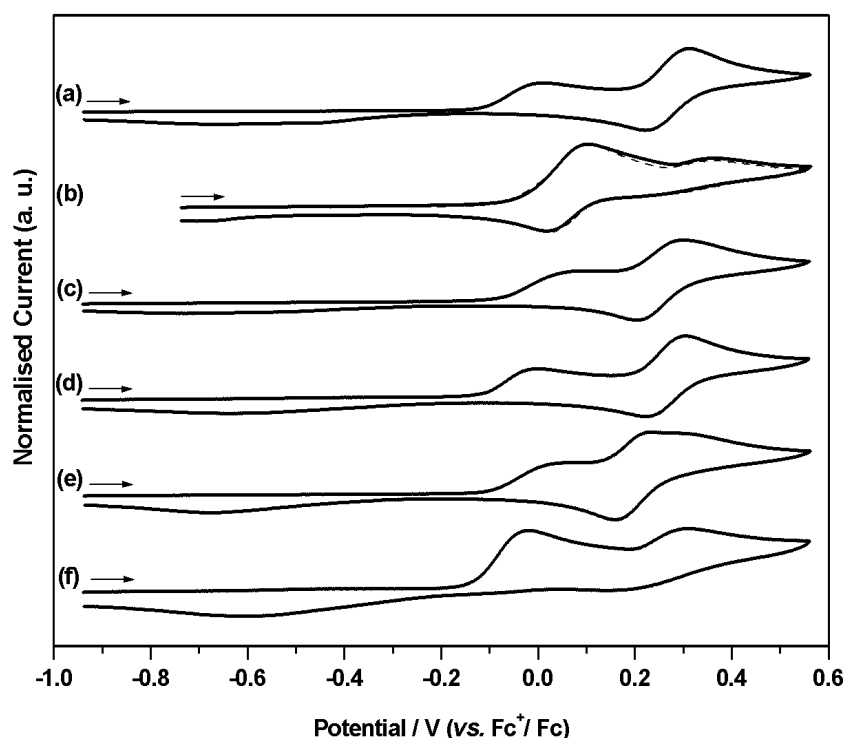


Figure S1: Cyclic voltammograms for (a) $[\text{Fe}(\text{Cp})(\text{I})(\text{dppe})]$, (b) $[\text{Fe}(\text{Cp}^*)(\text{I})(\text{dppe})]$ (solid line) and **2SIP** (dashed line), (c) $[\text{Fe}(\text{Cp}')(\text{I})(\text{dppe})]$, (d) $[\text{Fe}(\text{Cp}'')(\text{I})(\text{dppe})]$, (e) $[\text{Fe}(\text{Cp}''')(\text{I})(\text{dppe})]$ and (f) $[\text{nBu}_4\text{N}][\text{I}]$ in MeCN containing $[\text{nBu}_4][\text{BF}_4]$ (0.1 M) as supporting electrolyte at 0.1 Vs^{-1} . Currents are normalised to I_p^a for clarity. Typical currents obtained from CV experiments for the separated ion pairs in MeCN are shown in Figure S13 for **2SIP**, as are designations of OX, OX', OX'' and RED for **1SIP-5SIP** used in Table S11.

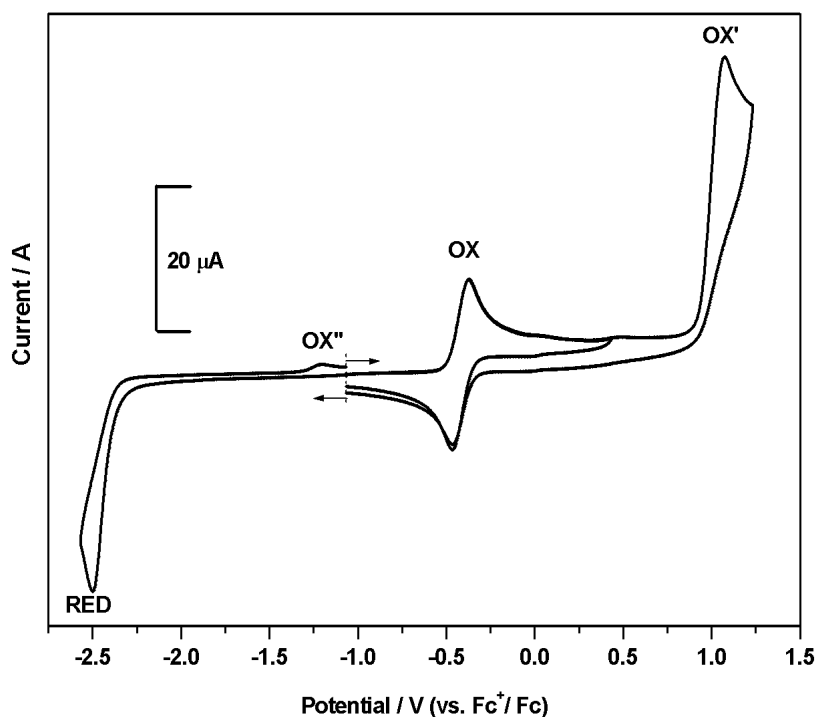


Figure S2a: Cyclic voltammetry for $[\text{Fe}(\text{Cp}^*)(\text{Cl})(\text{dppe})]$ in THF containing $[\text{NBu}_4][\text{BF}_4]$ (0.5 M) as supporting electrolyte, at 0.1 Vs^{-1} , showing designations of OX, OX', OX'' and RED for **1Cl-5Cl**, **1Br-5Br**, **1I-5I** and **1H-5H** compounds used in Table SII.

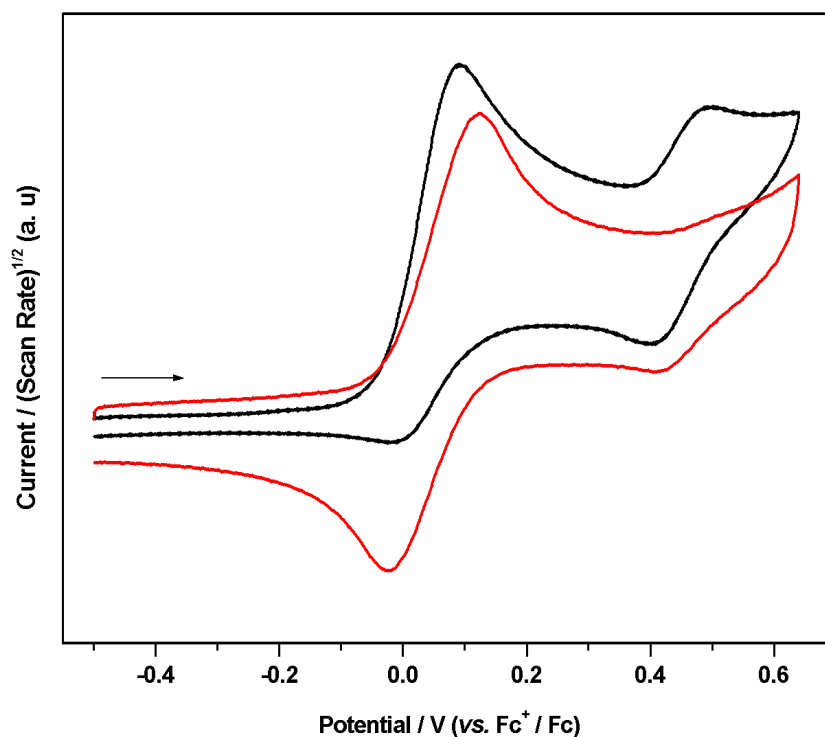


Figure S2b: Cyclic voltammetry for compound **4H** in THF containing $[\text{NBu}_4][\text{BF}_4]$ (0.5 M) as supporting electrolyte, at 0.1 Vs^{-1} (black line) and 1.0 Vs^{-1} (red line). Note that the oxidation process at $E_p^a + 0.49 \text{ V}$ is scan rate dependent, and is diminished as OX becomes reversible at faster scan rate.

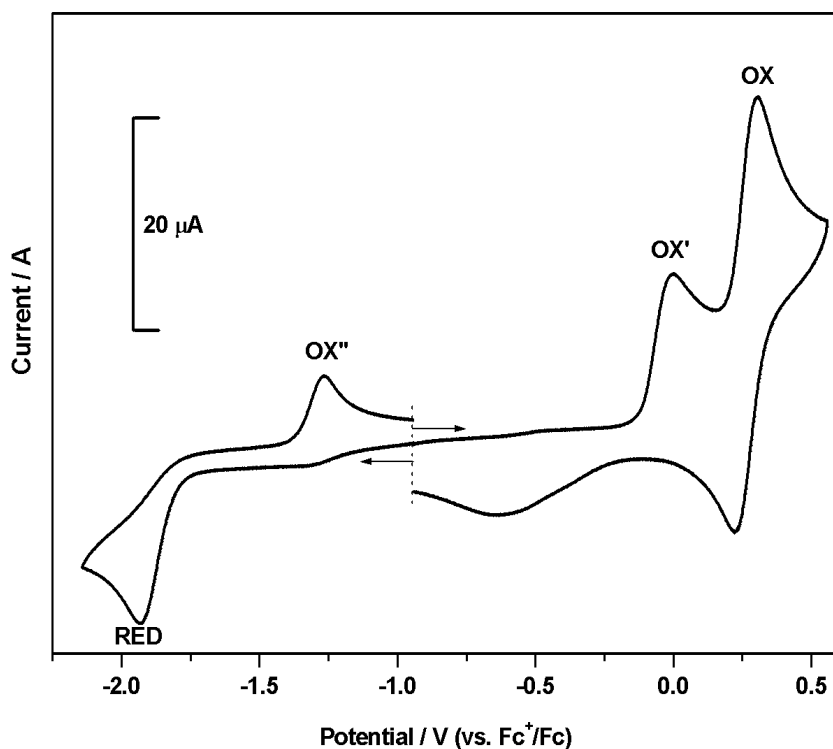


Figure S3: Cyclic voltammetry for $[Fe(Cp^\dagger)(I)(dppe)]$ in MeCN containing $[NBu^*_4][BF_4]$ (0.1 M) as supporting electrolyte, at 0.1 Vs^{-1} , showing designations of OX, OX', OX'' and RED for 1SIP-5SIP compounds used in Table S11.

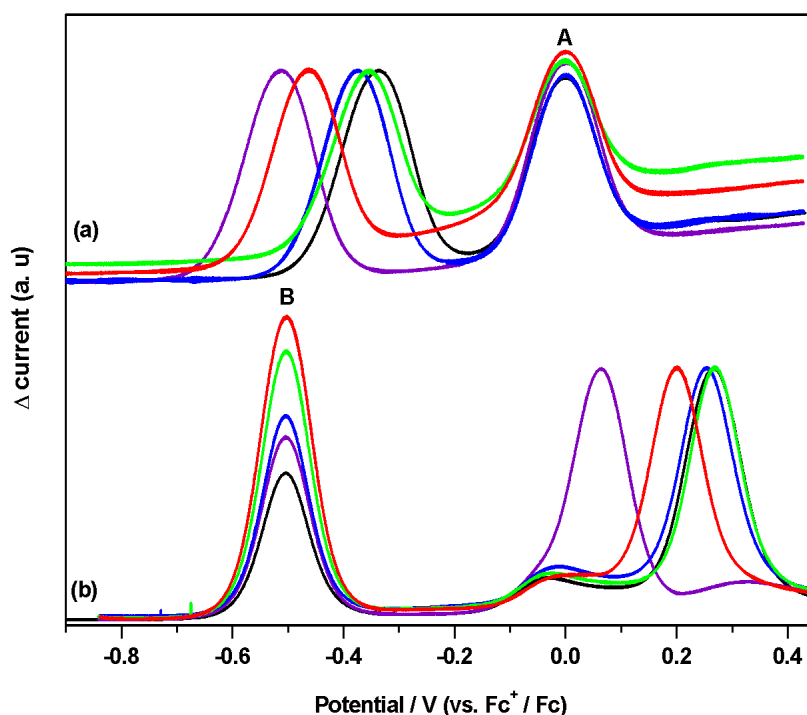


Figure S4: Square wave voltammetry showing OX for (a) $[Fe(Cp^\dagger)(Cl)(dppe)]$ in THF containing $[NBu^*_4][BF_4]$ (0.5 M) as supporting electrolyte and (b) $[Fe(Cp^\dagger)(I)(dppe)]$ in MeCN containing $[NBu^*_4][BF_4]$ (0.1 M) as supporting electrolyte ($Cp^\dagger = Cp$ (black), Cp^* (violet), Cp' (blue), Cp'' (green), Cp^{tt} (red)). The peaks labelled A and B are ferrocene and decamethylferrocene, respectively used as the internal standards.