

SUPPLEMENTARY MATERIAL

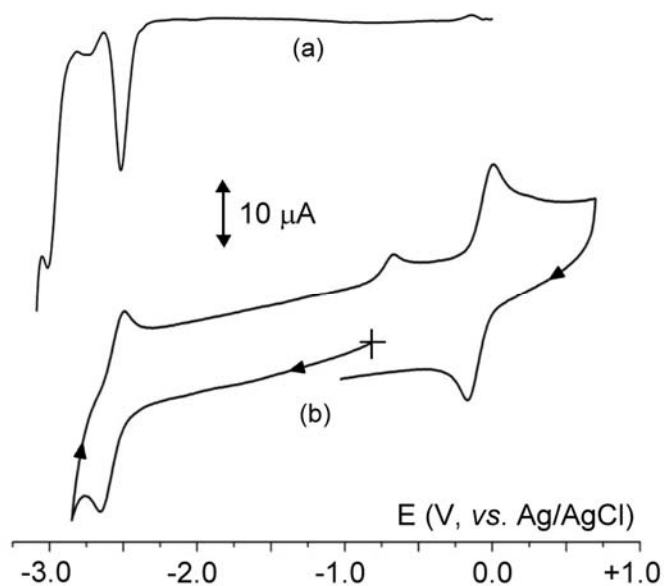


Figure S1. (a) Osteryoung square wave voltammogram recorded at a glassy-carbon electrode in DMF solution of C₂₁H₁₂ (1.0×10^{-3} mol dm⁻³); scan rate 0.1 Vs⁻¹. (b) Cyclic voltammogram recorded after the addition of an equimolar amount of (C₅Me₅)₂Fe; scan rate 0.2 Vs⁻¹. [NEt₄][PF₆] (0.1 mol dm⁻³) supporting electrolyte. T = 253 K.

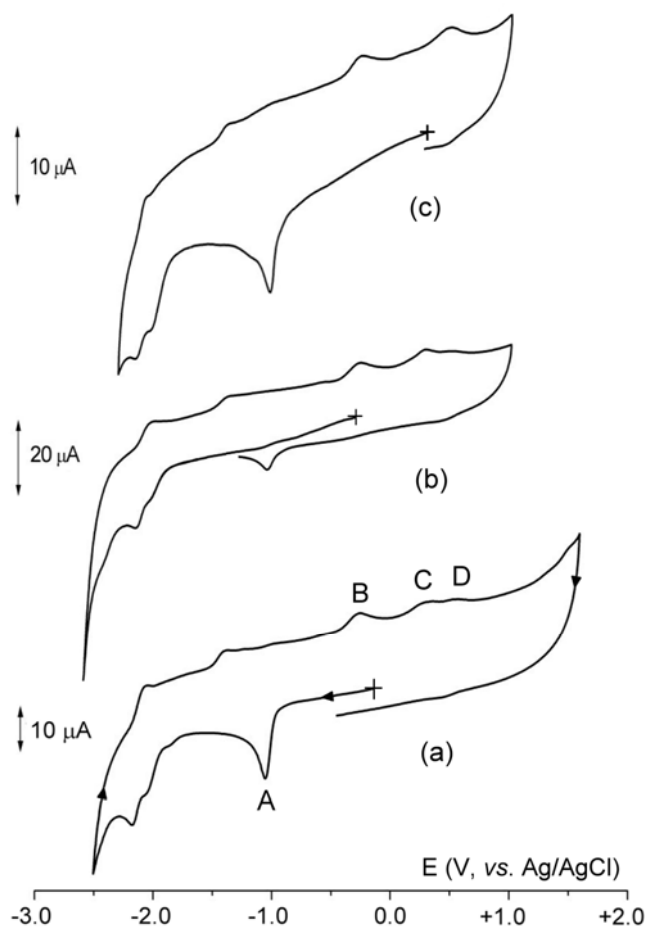


Figure S2. Cyclic voltammetric responses recorded at a glassy carbon electrode in DMF solution of $\mathbf{1}^+\text{PF}_6^-$ ($0.7 \times 10^{-3} \text{ mol dm}^{-3}$) containing $[\text{NEt}_4][\text{PF}_6]$ (0.1 mol dm^{-3}) as supporting electrolyte. (a) Original solution; (b) after exhaustive one-electron reduction at a platinum gauge macroelectrode ($E_w = -1.4 \text{ V}$); (c) after the subsequent exhaustive re-oxidation in correspondence of peak D ($E_w = +0.6 \text{ V}$) (which required the consumption of about 0.8 electrons/molecule). Scan rates 0.2 Vs^{-1} . $T = 293 \text{ K}$.

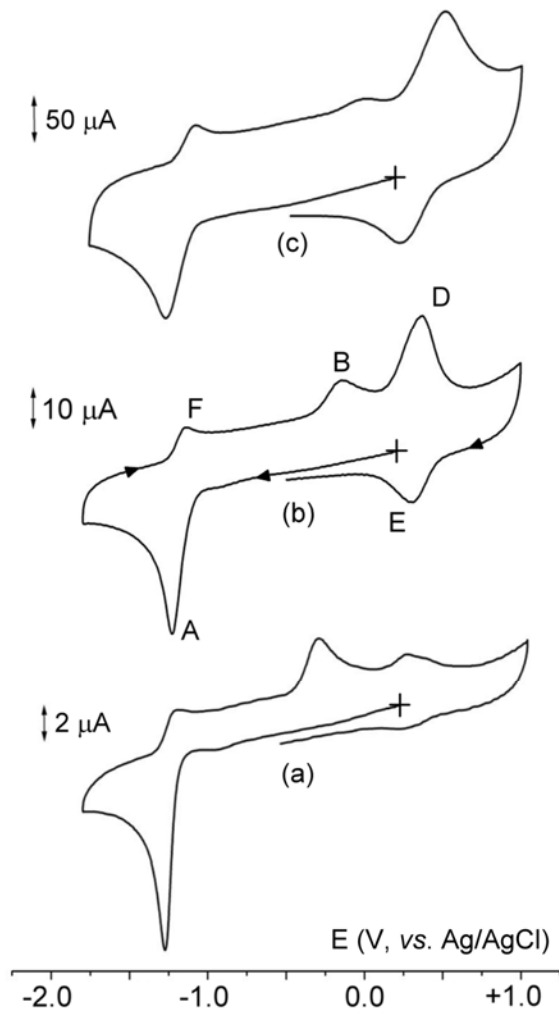


Figure S3. Cyclic voltammetric responses recorded at a platinum electrode in DMF solution of $\mathbf{1}^+\text{PF}_6^-$ ($0.8 \times 10^{-3} \text{ mol dm}^{-3}$). $[\text{NEt}_4][\text{PF}_6]$ (0.1 mol dm^{-3}) supporting electrolyte. Scan rates: (a) 0.2 Vs^{-1} ; (b) 2.0 Vs^{-1} ; (c) 20.5 Vs^{-1} . $T = 253 \text{ K}$.

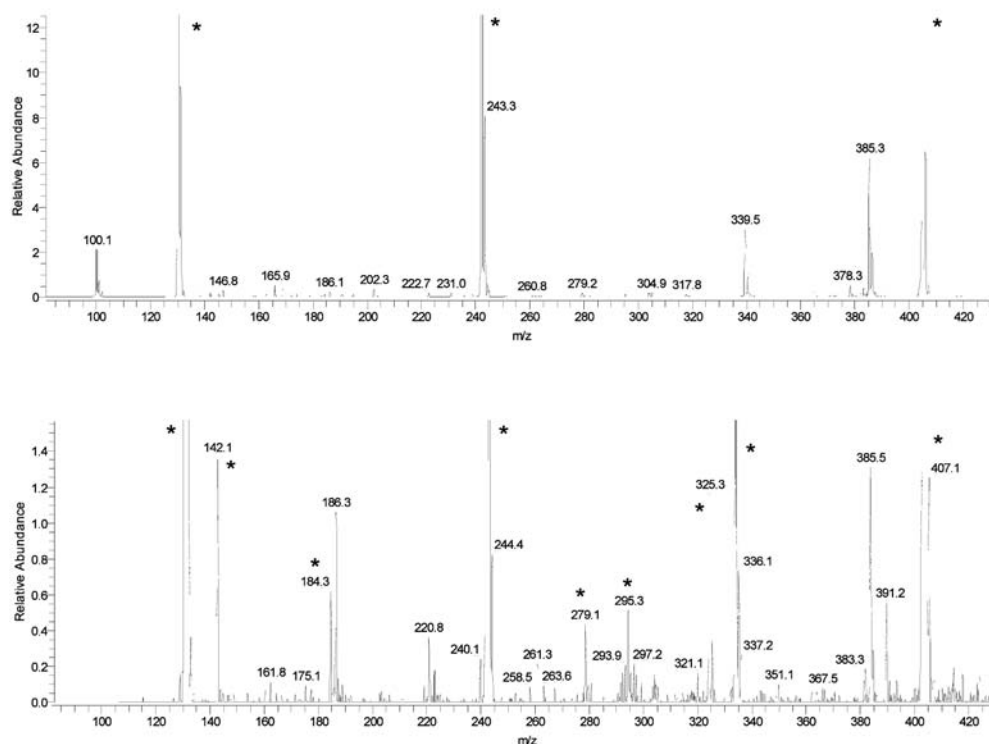


Figure S4. ESI(+) mass spectra of the original DMF solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^6\text{-C}_{21}\text{H}_{12})]^+$ (top) and after exhaustive one-electron reduction (bottom). The asterisked peaks indicate ions arising from the $[\text{NEt}_4][\text{PF}_6]$ supporting electrolyte.

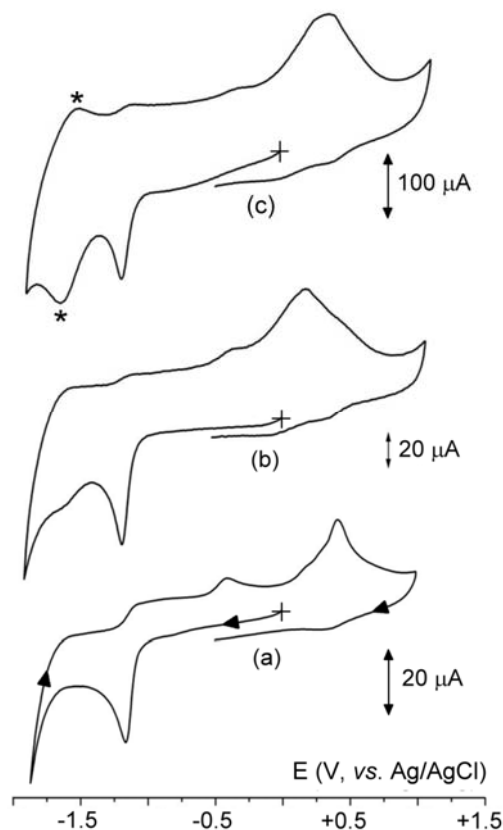


Figure S5. Cyclic voltammetric responses recorded at a platinum electrode in MeCN solution of $\mathbf{1}^+\text{PF}_6^-$ ($0.8 \times 10^{-3} \text{ mol dm}^{-3}$). $[\text{NEt}_4][\text{PF}_6]$ (0.1 mol dm^{-3}) supporting electrolyte. Scan rates: (a) 0.2 V s^{-1} ; (b) 0.5 V s^{-1} ; (c) 2.00 V s^{-1} . $T = 293 \text{ K}$.