Electronic Supplementary Information

Electrocatalytic proton reduction catalysed by the low-valent tetrairon-oxo cluster $[Fe_4(CO)_{10}(\kappa^2\text{-dppn})(\mu_4\text{-O})]^{2-}$ [dppn = 1,1′-bis(diphenylphosphino) naphthalene]

Shishir Ghosh,[a] Katherine B. Holt[a], Shariff E. Kabir[b], Michael G. Richmond[c] and Graeme Hogarth[a,d*]

[a] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ, UK*

[b] *Department of Chemistry, Jahangirnagar University, Savar, Dhaka-1342, Bangladesh*

[c] *Department of Chemistry, University of North Texas, 1155 Union Circle, Box 305070, Denton, TX 76203, USA*

[d] *Department of Chemistry, King's College London, Britannia House, 7 Trinity Street, London SE1 1DB, UK.*

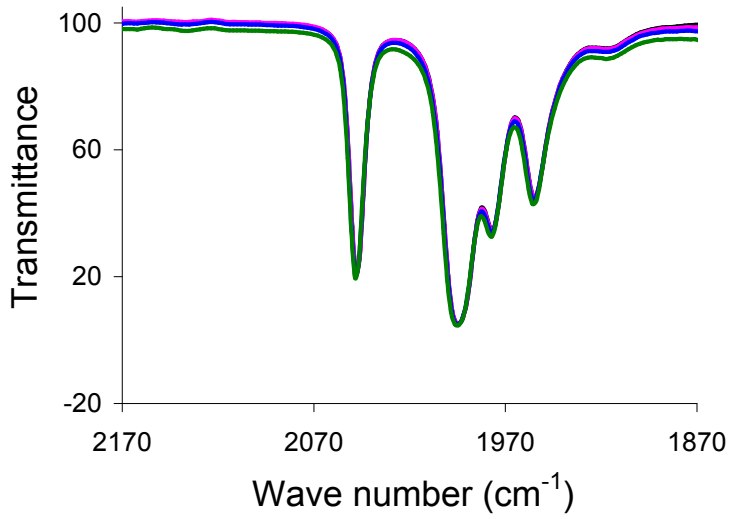


Fig. S1. IR spectra of $Fe_4(CO)_{10}(\kappa^2\text{-dppn})(\mu_4\text{-O})$ (**1**) in absence of (black) and in presence of 1 (pink), 3 (blue) and 5 (green) molar equivalents of Cl_2HCCO_2H in CH_2CL_2.

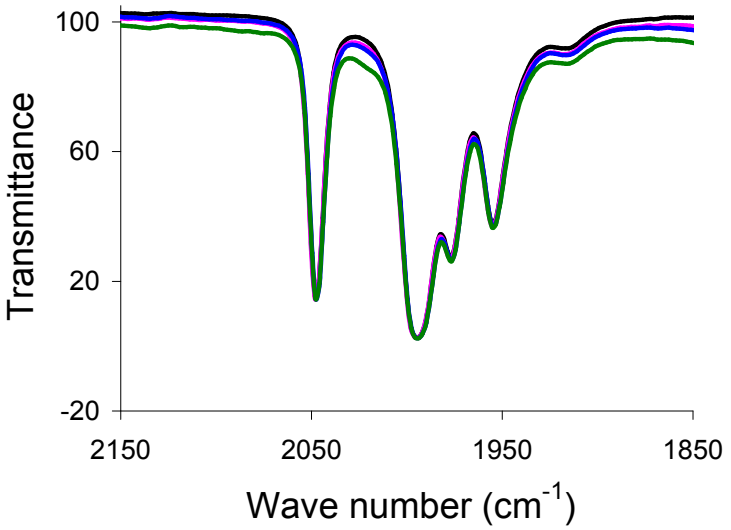
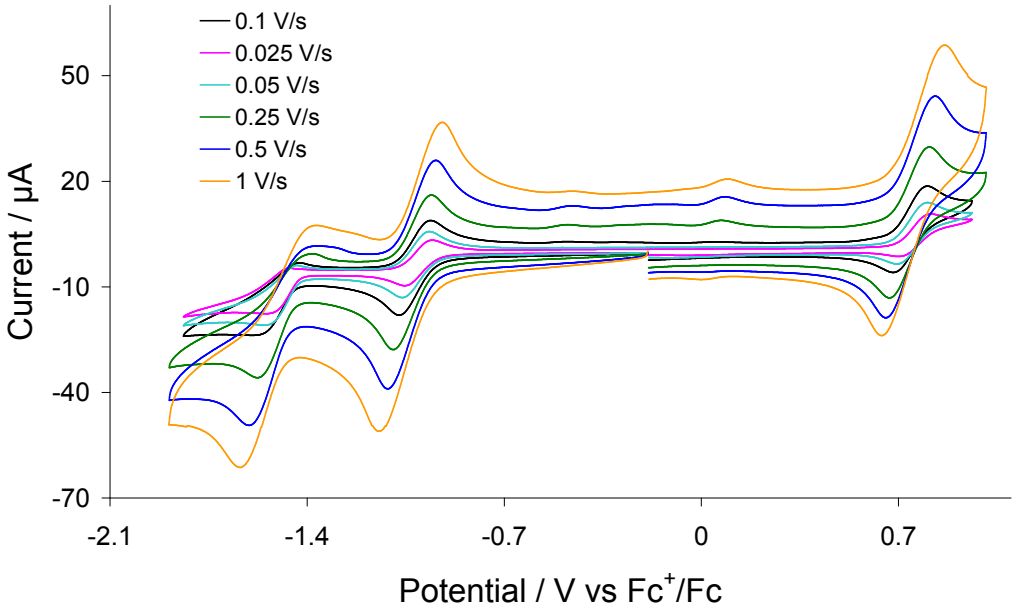
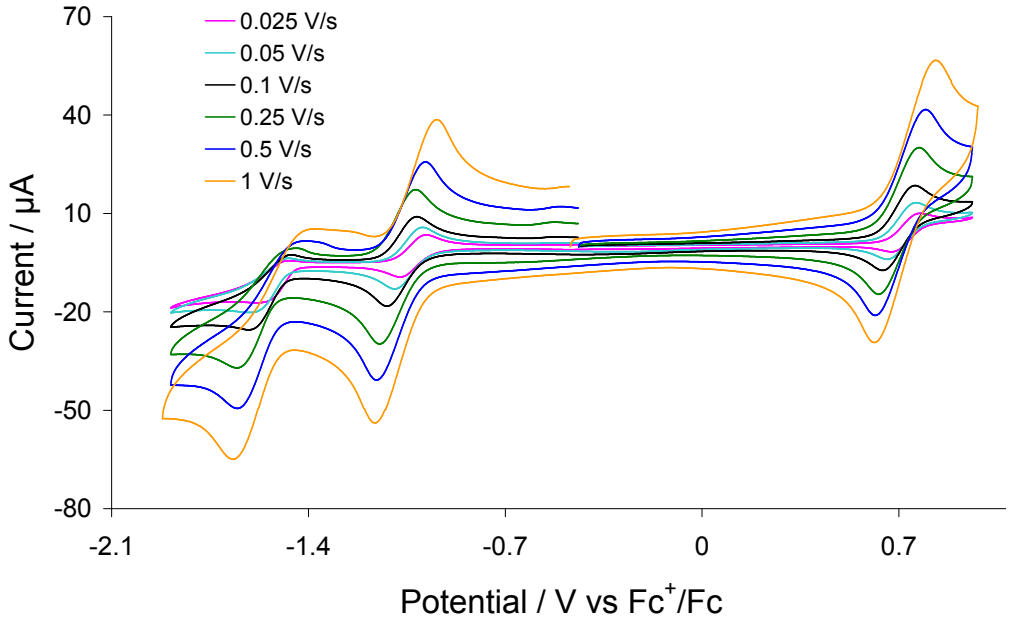


Fig. S2. IR spectra of $Fe_4(CO)_{10}(\kappa^2\text{-dppn})(\mu_4\text{-O})$ (**1**) in absence of (black) and in presence of 1 (pink), 3 (blue) and 5 (green) molar equivalents of CF_3CO_2H in CH_2CL_2.

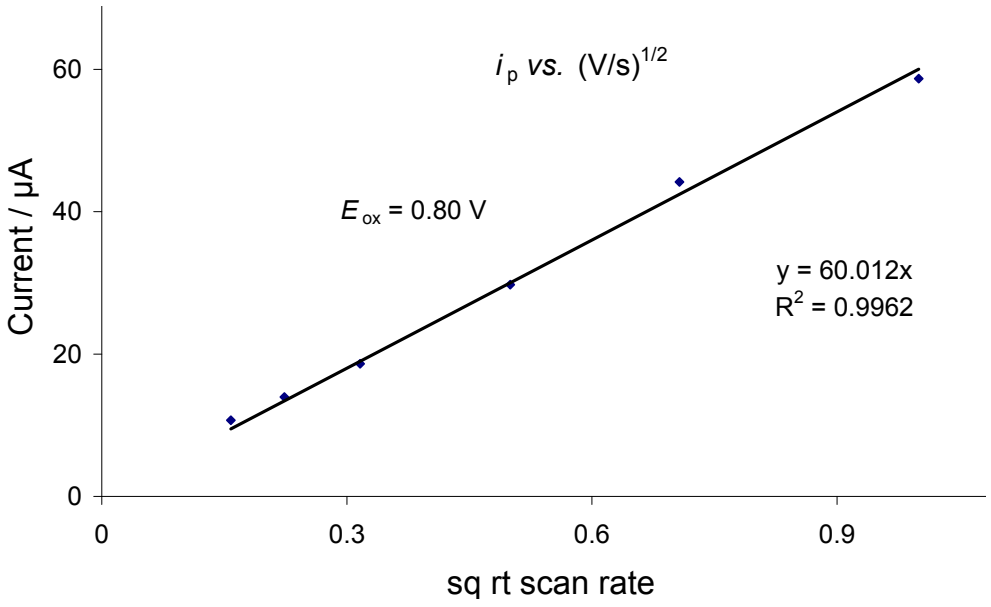


(a)

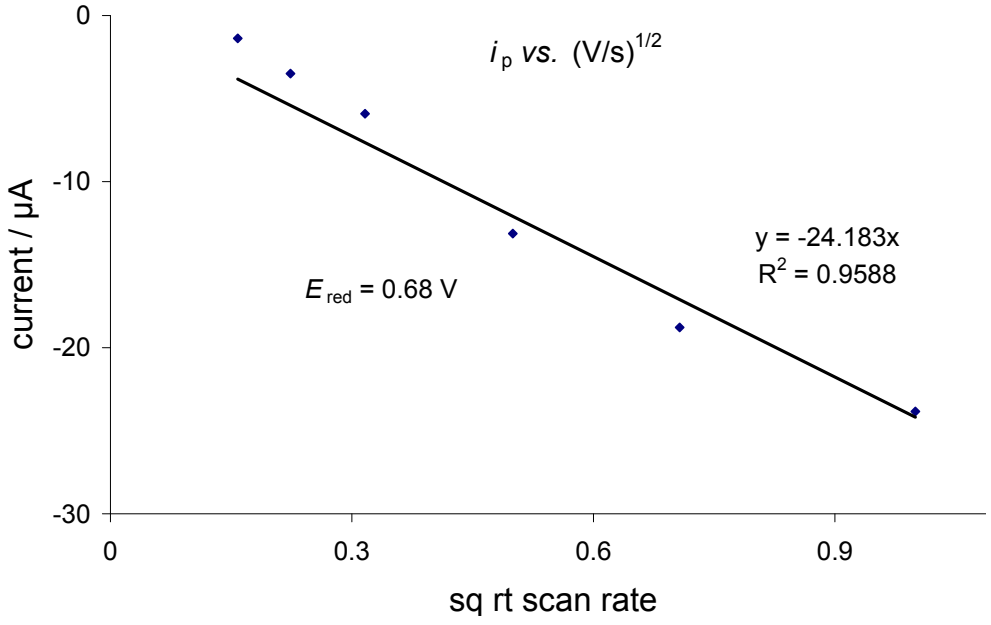


(b)

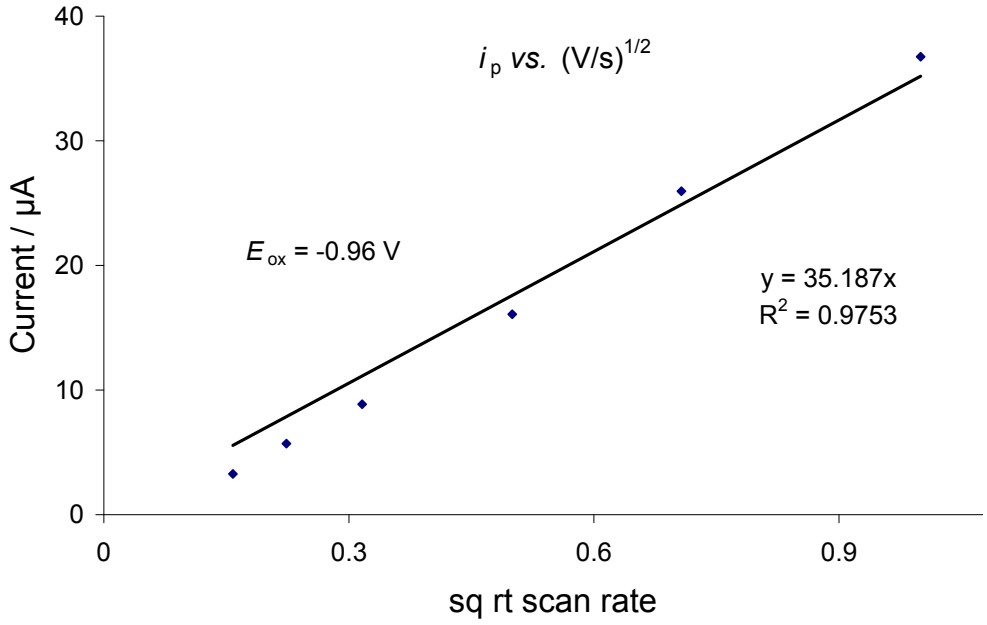
Fig. S3. CVs of $Fe_4(CO)_{10}(\kappa^2\text{-dppn})(\mu_4\text{-O})$ (**1**) at various scan rates as shown in the legend (in CH_2Cl_2, 1 mM solution, supporting electrolyte $[NBu_4][PF_6]$, scan rate 0.1 Vs^{-1}, glassy carbon electrode, potential vs Fc^+/Fc) – (a) CVs recorded scanning negative potential window first; (b) CVs recorded scanning positive potential window first.


i_p *vs.* $(V/s)^{1/2}$
E_{ox} = 0.80 V
y = 60.012x
R^2 = 0.9962
Current / µA
sq rt scan rate
0
20
40
60
0
0.3
0.6
0.9

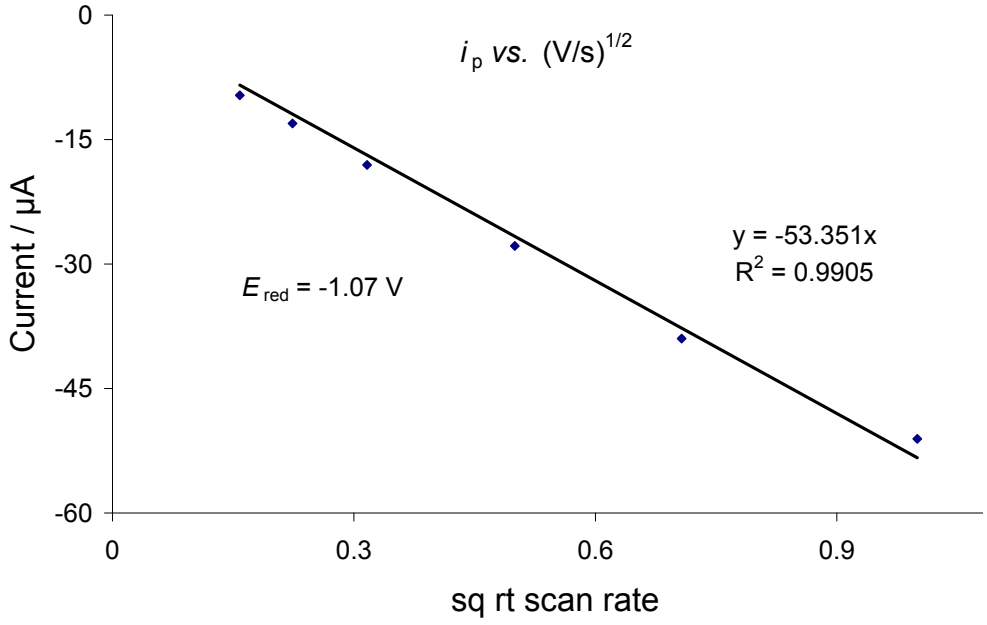
(a)


i_p *vs.* $(V/s)^{1/2}$
E_{red} = 0.68 V
y = -24.183x
R^2 = 0.9588
current / µA
sq rt scan rate
0
-10
-20
-30
0
0.3
0.6
0.9

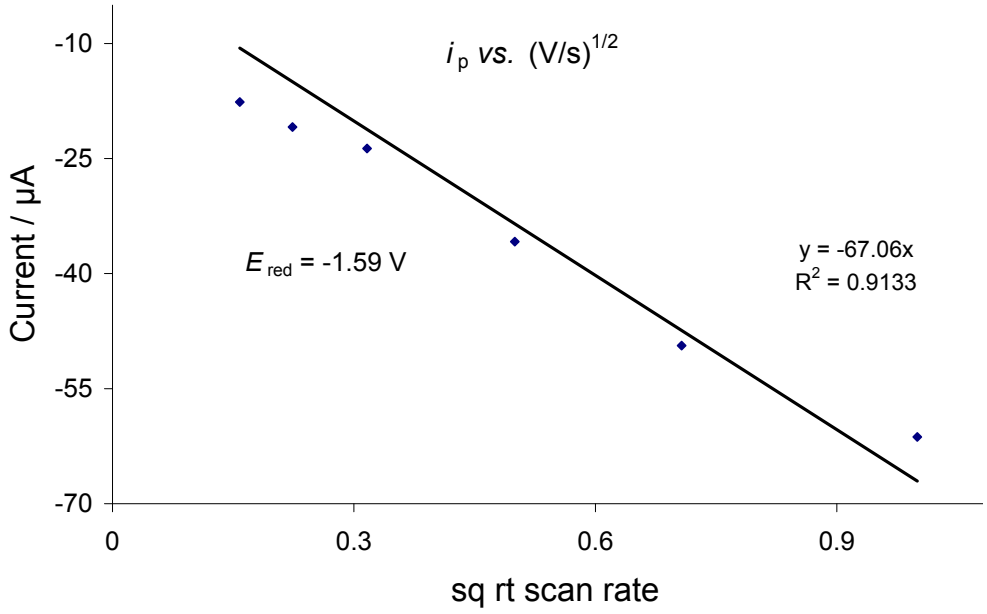
(b)


i_p *vs.* $(V/s)^{1/2}$
E_{ox} = -0.96 V
y = 35.187x
R^2 = 0.9753
Current / µA
sq rt scan rate
0
10
20
30
40
0
0.3
0.6
0.9

(c)


i_p *vs.* $(V/s)^{1/2}$
E_{red} = -1.07 V
y = -53.351x
R^2 = 0.9905
Current / µA
sq rt scan rate
0
-15
-30
-45
-60
0
0.3
0.6
0.9

(d)



(e)

Fig. S4. Scan rate dependence of the oxidative and reductive features in cyclic voltamograms of $Fe_4(CO)_{10}(\kappa^2\text{-dppn})(\mu_4\text{-O})$ (**1**) in CH_2Cl_2 (1 mM solution, supporting electrolyte $[NBu_4][PF_6]$, glassy carbon electrode, potential vs Fc^+/Fc). Line shows best linear fit of data through the origin.

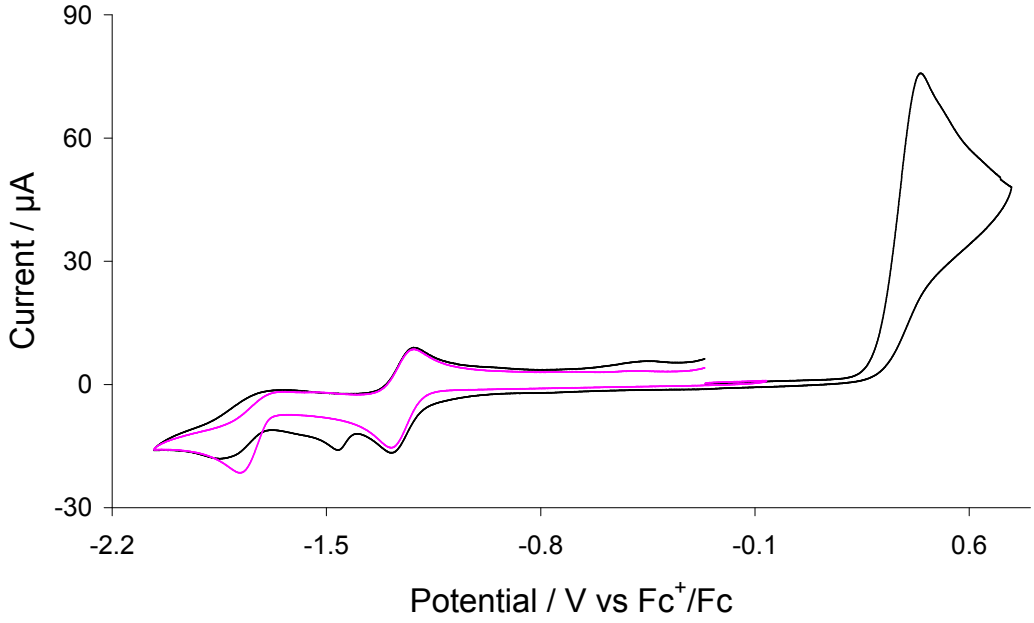
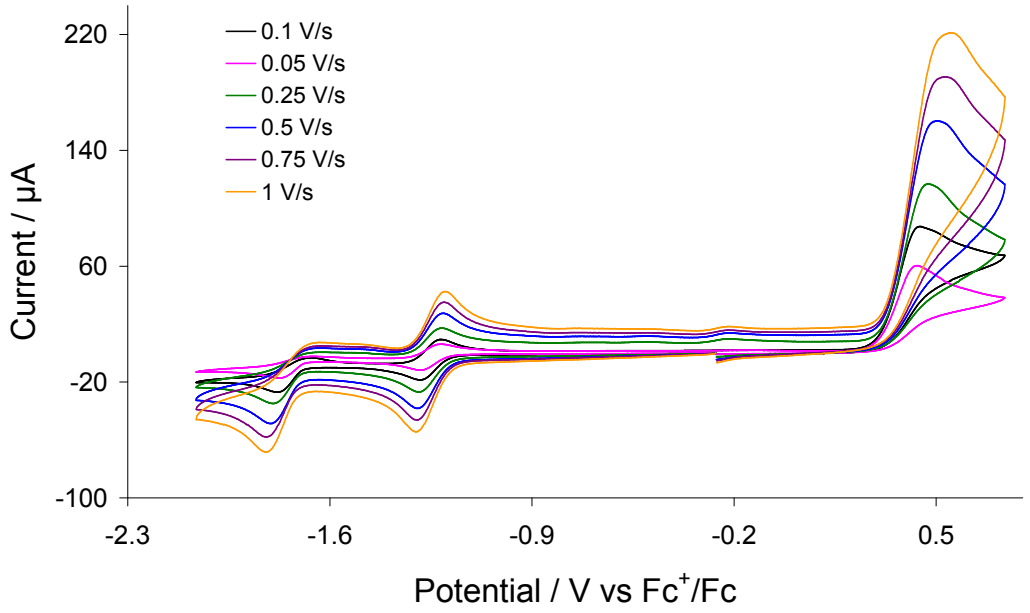
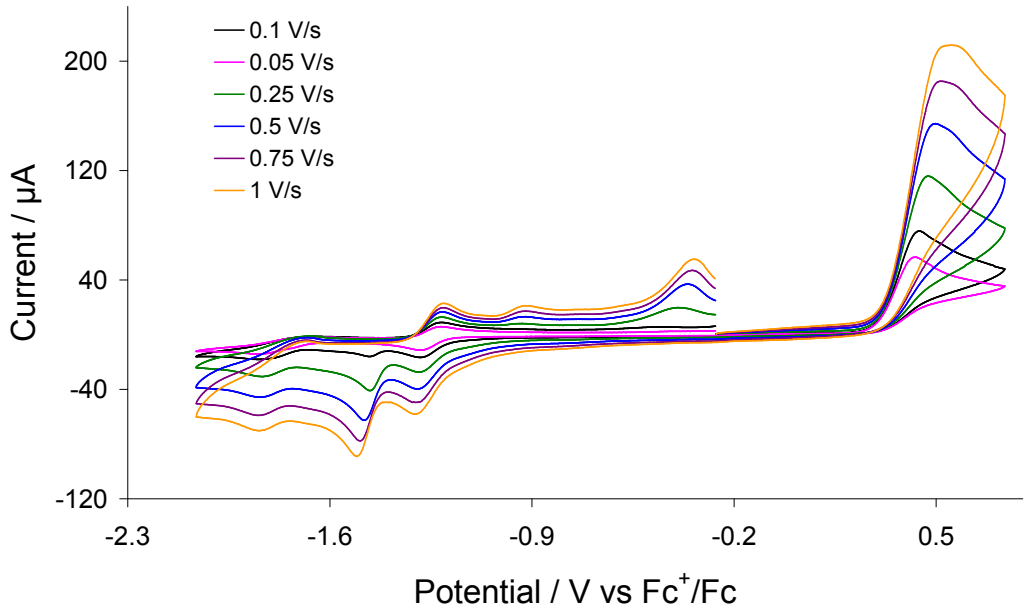


Fig. S5. CVs of $Fe_4(CO)_{10}(\kappa^2\text{-dppn})(\mu_4\text{-O})$ (**1**) in a 1:1 mixture of CH_2Cl_2/MeCN recorded by scanning the anodic region first (1 mM solution, supporting electrolyte $[NBu_4][PF_6]$, scan rate 0.1 Vs^{-1}, glassy carbon electrode, potential vs Fc^+/Fc)



(a)



(b)

Fig. S6. CVs of $Fe_4(CO)_{10}(\kappa^2\text{-dppn})(\mu_4\text{-O})$ (**1**) at various scan rates as shown in the legend (in a 1:1 mixture of CH_2Cl_2/MeCN, 1 mM solution, supporting electrolyte $[NBu_4][PF_6]$, scan rate 0.1 Vs^{-1}, glassy carbon electrode, potential vs Fc^+/Fc) – (a) CVs recorded scanning negative potential window first; (b) CVs recorded scanning positive potential window first.

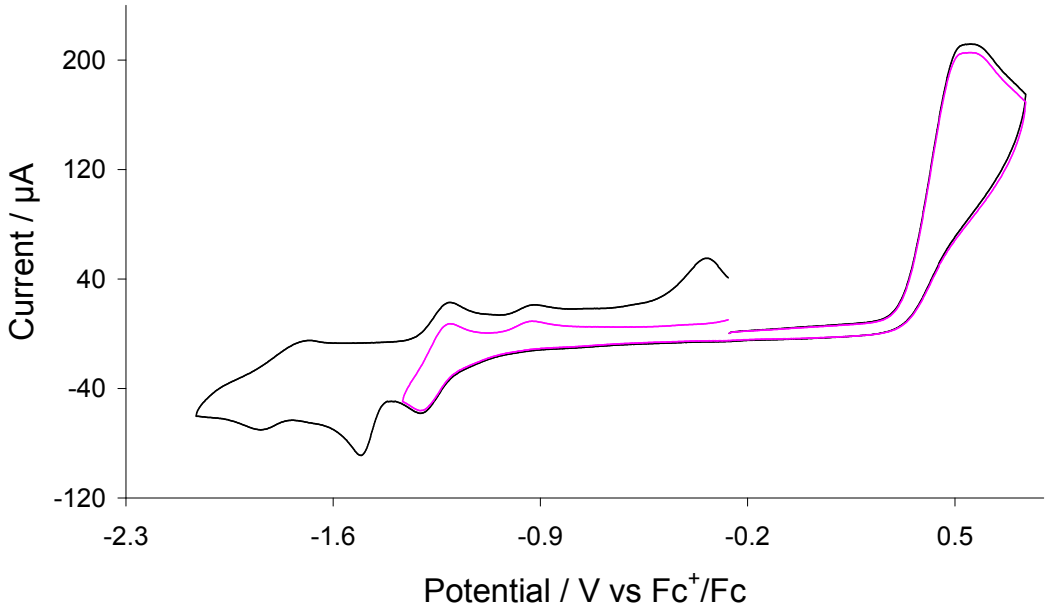
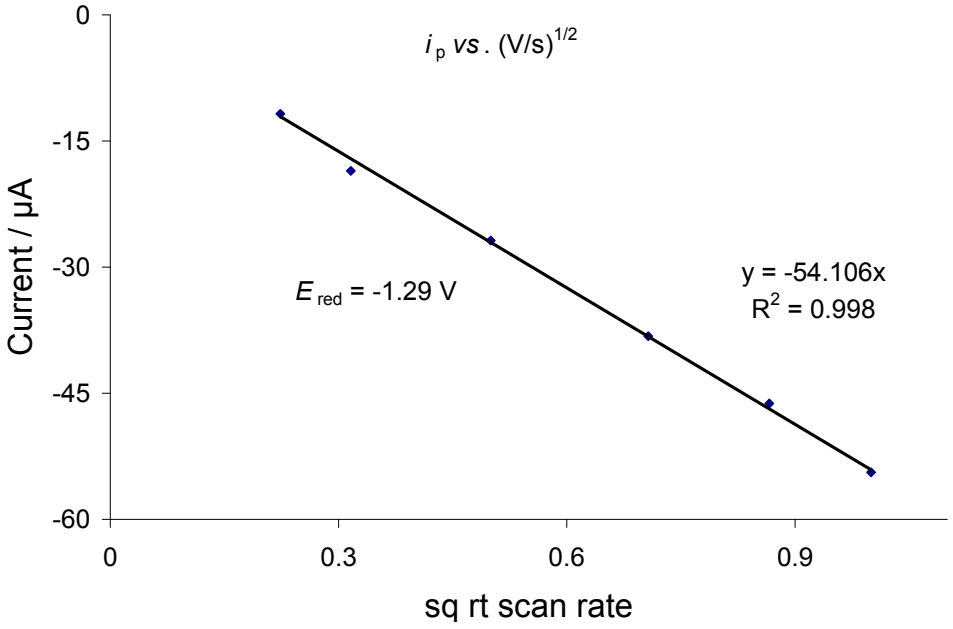
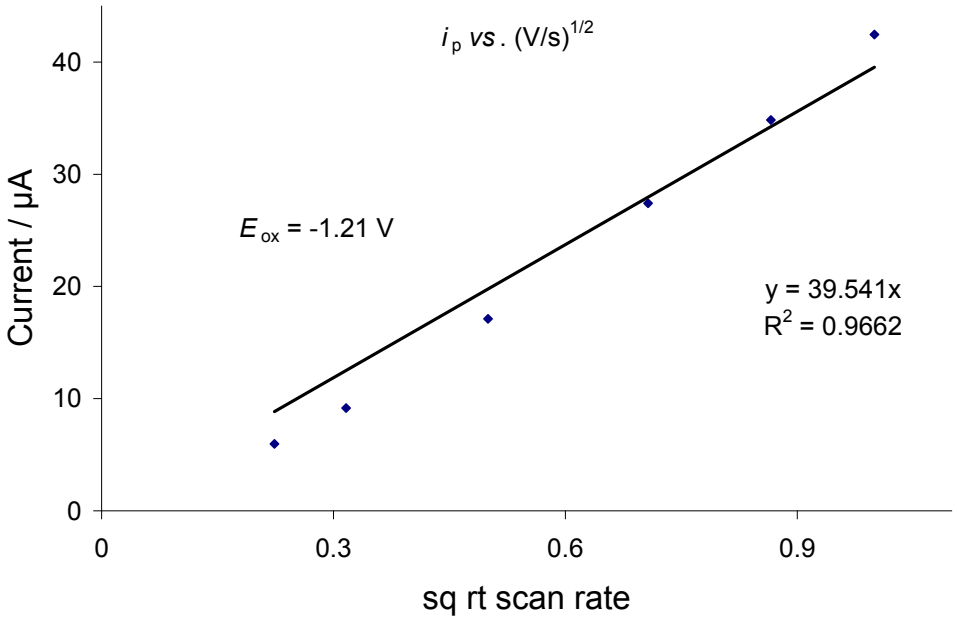


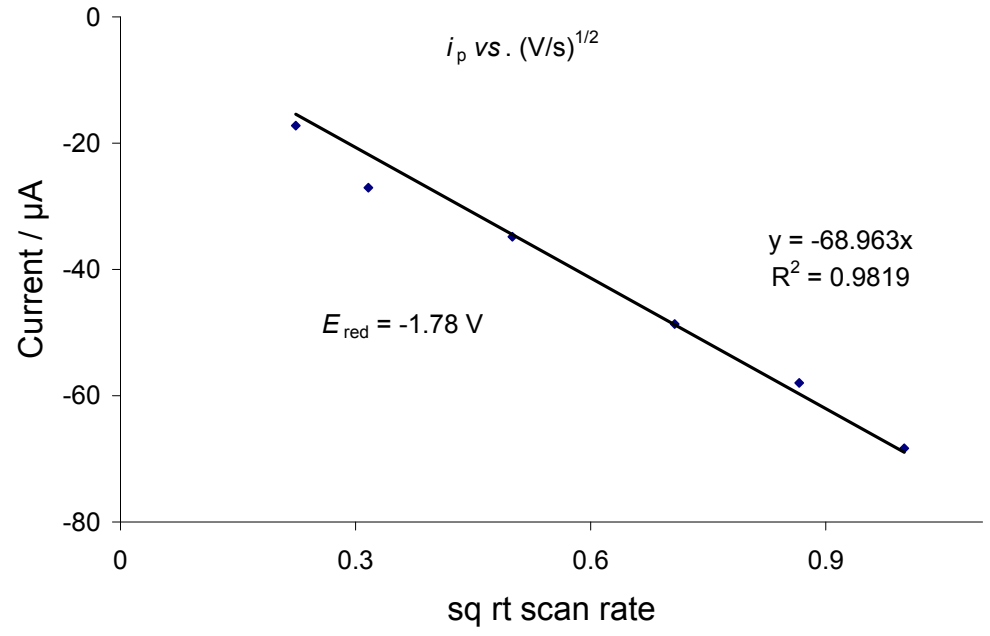
Fig. S7. CVs of $Fe_4(CO)_{10}(\kappa^2\text{-dppn})(\mu_4\text{-O})$ (**1**) in a 1:1 mixture of CH_2Cl_2/MeCN recorded by scanning the anodic region first (1 mM solution, supporting electrolyte $[NBu_4][PF_6]$, scan rate 1 Vs^{-1}, glassy carbon electrode, potential vs Fc^+/Fc)


i_p *vs*. $(V/s)^{1/2}$
Current / µA
0
-15
-30
-45
-60
0
0.3
0.6
0.9
sq rt scan rate
E_{red} = -1.29 V
y = -54.106x
R^2 = 0.998

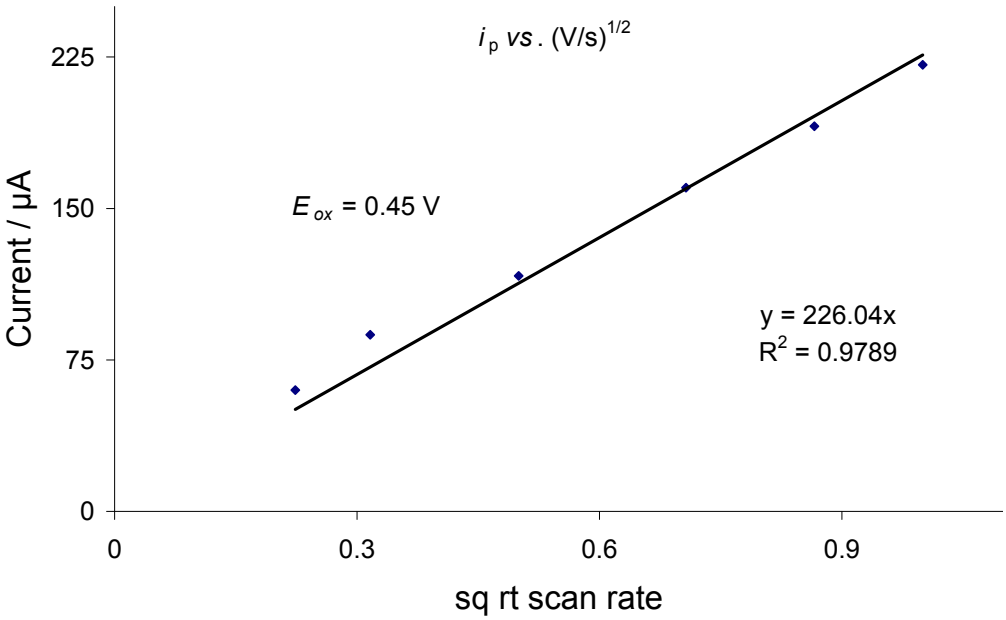
(a)


i_p *vs*. $(V/s)^{1/2}$
Current / µA
40
30
20
10
0
0
0.3
0.6
0.9
sq rt scan rate
E_{ox} = -1.21 V
y = 39.541x
R^2 = 0.9662

(b)



(c)



(d)

Fig. S8. Scan rate dependence of the oxidative and reductive features in cyclic voltamograms of $Fe_4(CO)_{10}(\kappa^2\text{-dppn})(\mu_4\text{-O})$ (**1**) in a 1:1 mixture of CH_2Cl_2/MeCN (1 mM solution, supporting electrolyte $[NBu_4][PF_6]$, glassy carbon electrode, potential vs Fc^+/Fc). Line shows best linear fit of data through the origin.