

Supporting Information

for

**Electrocatalysis of Hydrogen Production by Active Site Analogues of the Iron
Hydrogenase Enzyme: Structure/Function Relationships**

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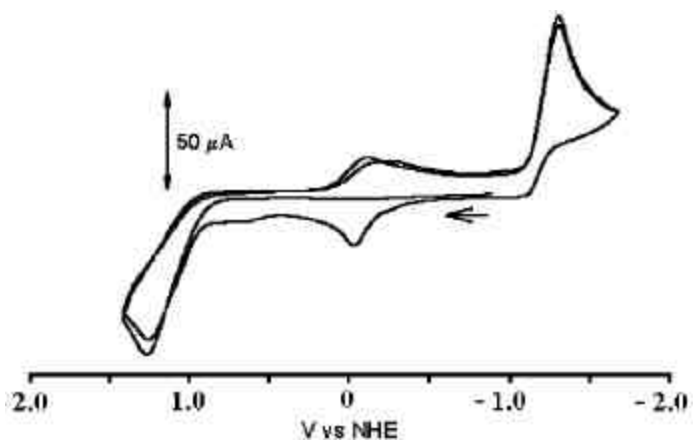


Fig. 1S Cyclic voltammogram of complex (μ-SEt)₂[Fe(CO)₃]₂ (**1**) to the anodic direction.

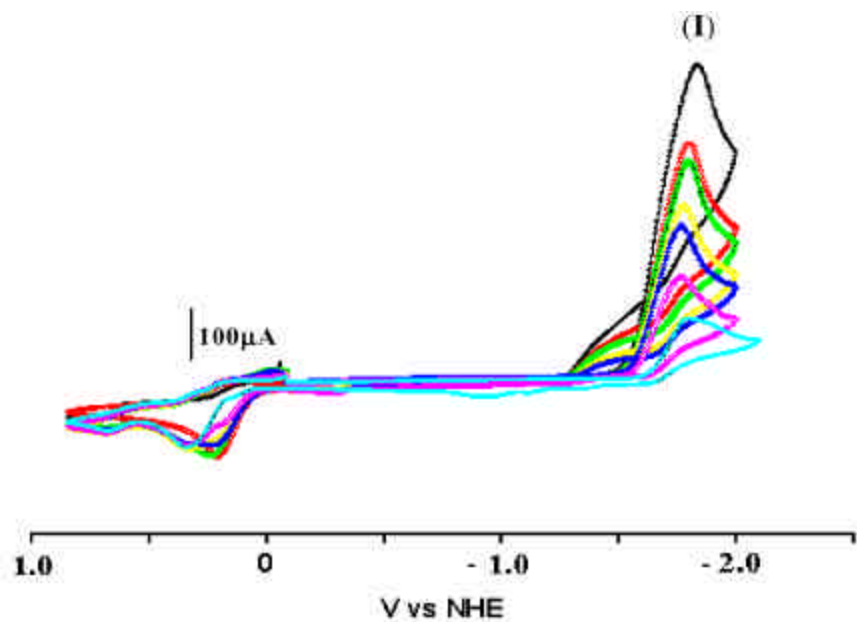


Fig. 2S Cyclic voltammograms of **4-P** (2.5 mM) with HOAc (0, 25, 50, 75, 100, 125 mM) in CH₃CN (0.1 M *n*-Bu₄NBF₄) with electrochemical parameters as described in Table 1. **(I)**: Fe^IFe^I/Fe⁰Fe^I, ca. -1.80 V.

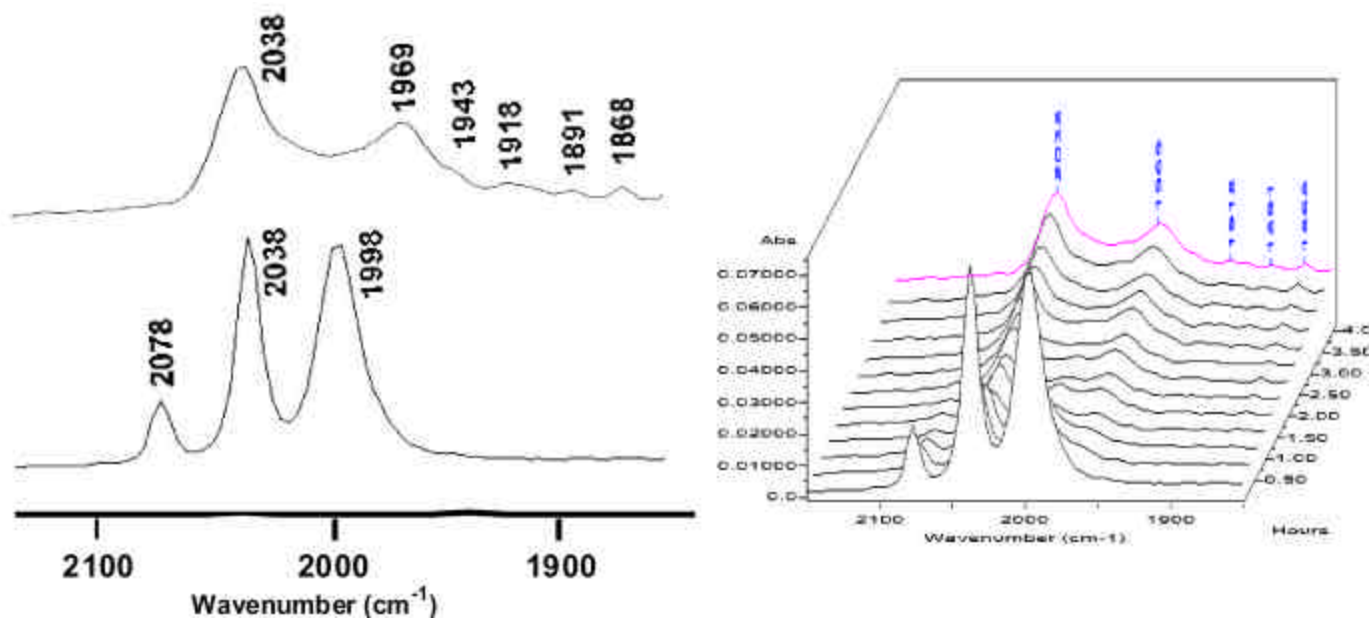


Fig. 3S *In situ* IR spectra during bulk electrolysis for **2** (7.5 mM) in the presence acid (HOAc, 150 mM) at -1.34 V in CH₃CN solution (0.1 M *n*-Bu₄NBF₄) with electrochemical parameters as described in Table 1.

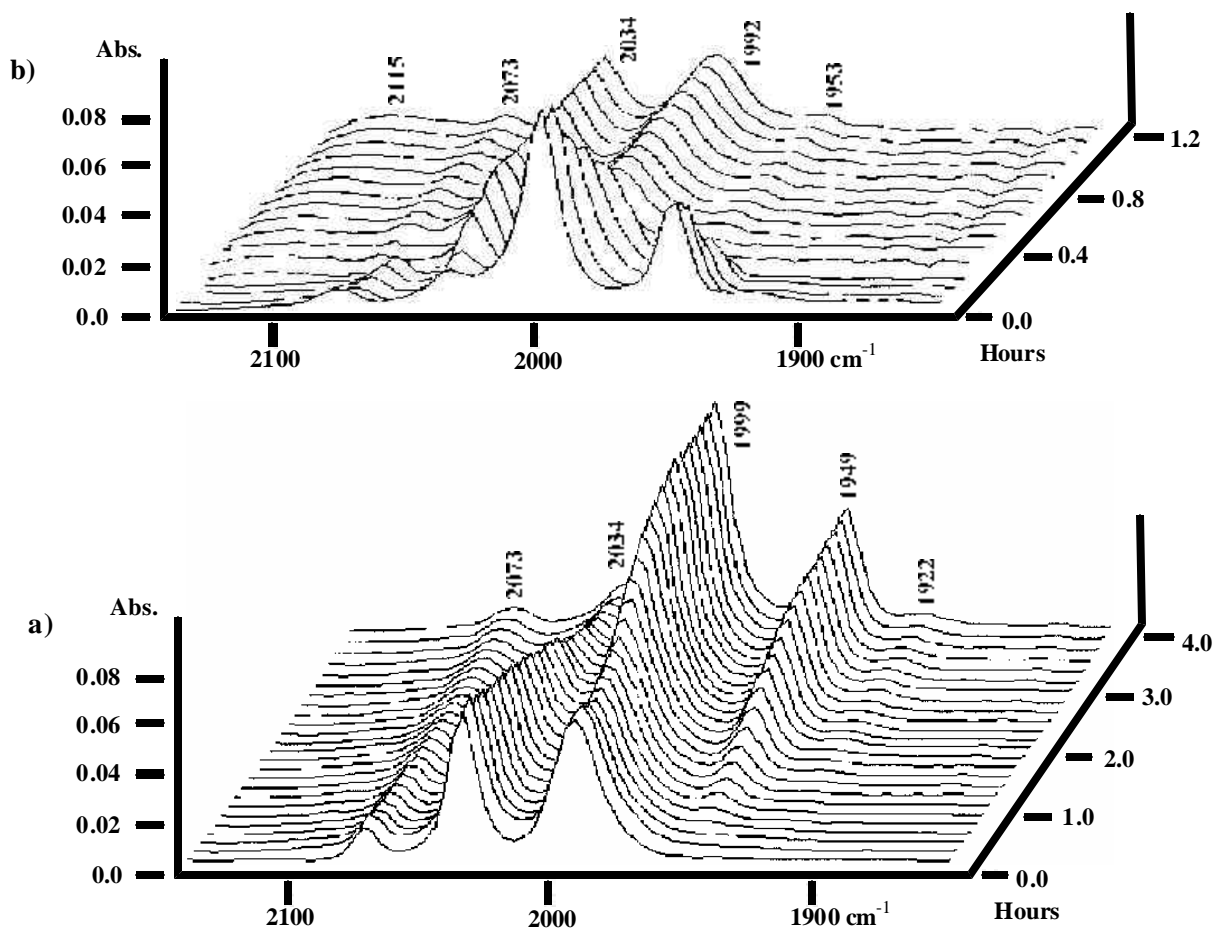


Fig. 4S *In situ* IR spectra during bulk electrolysis for **1** (7.5 mM) a) reduction process at -1.34 V and b) re-oxidation process at -0.95 V in CH₃CN solution (0.1 M *n*-Bu₄NBF₄) with electrochemical parameters as described in Table 1.