Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Biomimetic peptide-based models of [FeFe]-hydrogenases: Utilization of phosphine containing peptides

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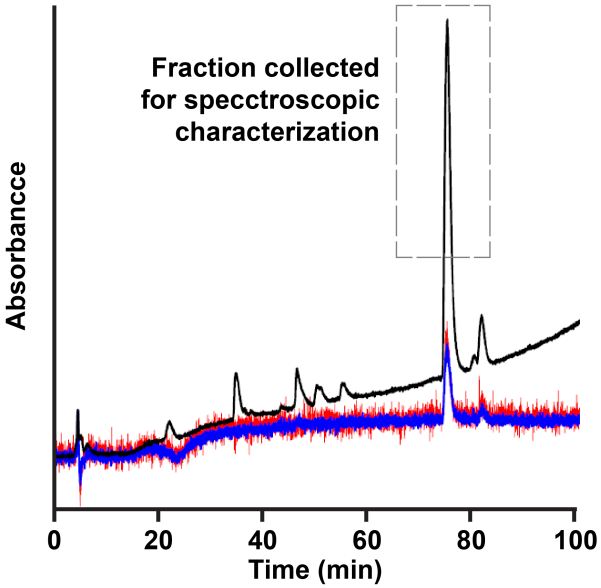

Figure S1. Analytical HPLC trace for **1**. Absorbances are shown at 220 nm (black), 280 nm (blue), and 350 nm (red).

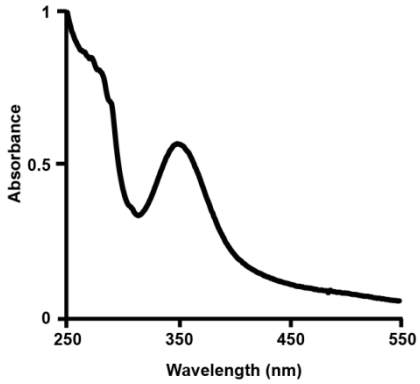

Figure S2. UV-vis spectrum of **1** (0.05 mM) in acetonitrile.

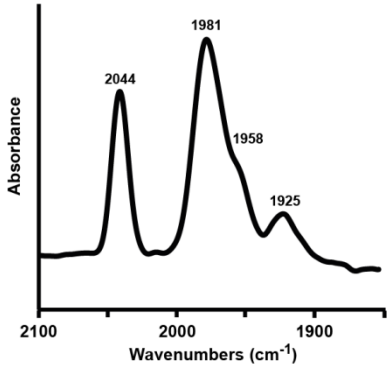

Figure S3. FTIR spectrum of **1** recorded in a KBr pellet.

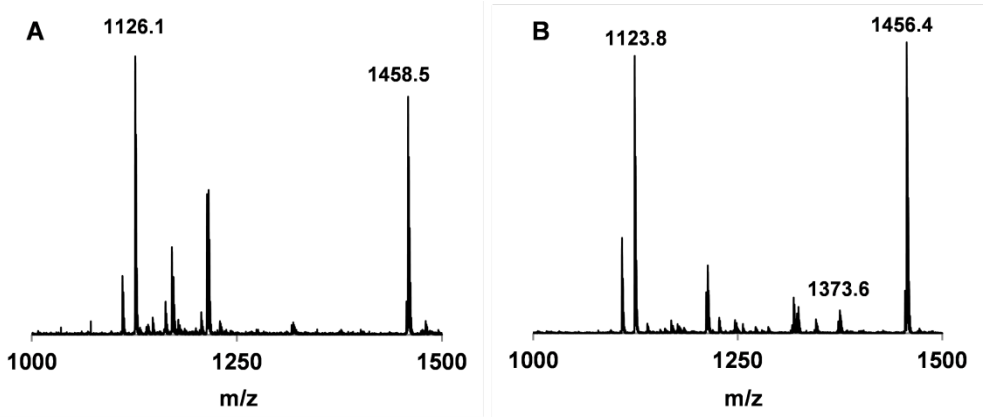

Figure S4. ESI-MS spectra for **1** in (A) positive mode and (B) negative mode.

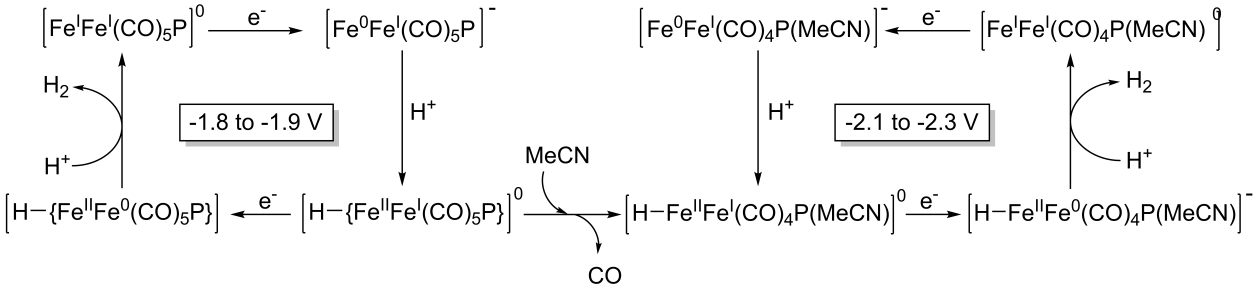

Figure S5. Hypothetical ECEC pathways for electrocatalytic H^+ reduction by **2-4** in the presence of acetic acid. Since the catalysis mostly occurs at -2.1 to -2.3 V, the active electrocatalyst is likely to be the solvent coordinated species $\{Fe^IFe^I(CO)_4P(MeCN)\}$ shown on the right. P denotes the phosphine-peptide, and the dithiolate ligand is not shown for clarity.

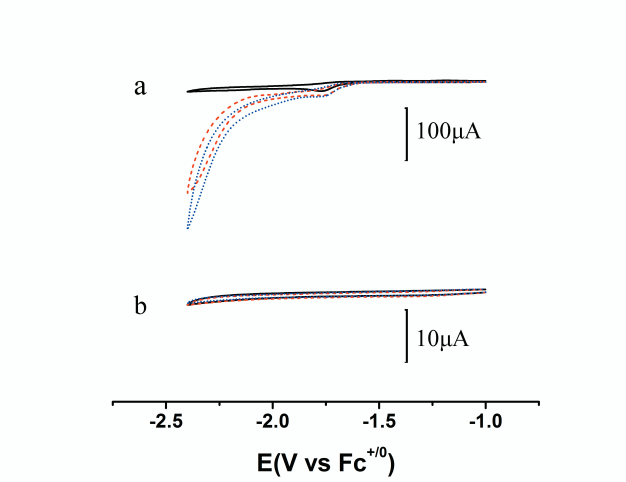

Figure S6. Rinse test to confirm the homogeneous nature of the catalysis. (a) Cyclic voltammograms of **4** (1.1 mM) were recorded in acetonitrile with increasing amount of acetic acid. Then the working glassy carbon electrode was removed from the solution and rinsed thoroughly with acetonitrile. (b) This electrode was then placed in a fresh electrolyte solution and cyclic voltammograms were recorded with increasing acetic acid concentration. Black solid line: 0 mM AcOH; red dashed line: 25 mM AcOH; blue dashed line: 125 mM AcOH. Conditions: 0.1 M $[NBu_4][PF_6]$ as supporting electrolyte, scan rate 100 mV s^{-1}.

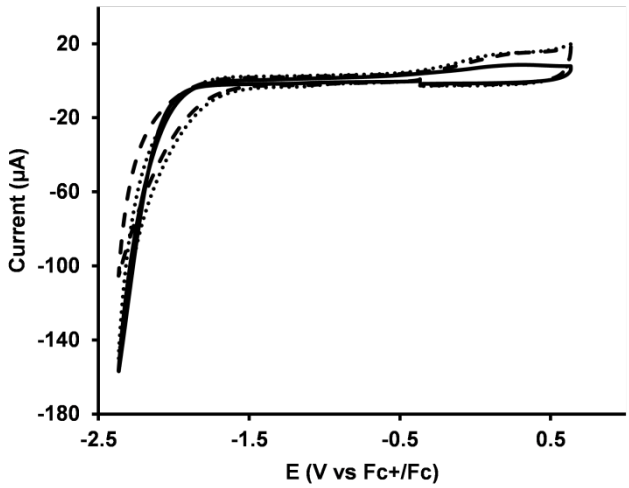

Figure S7. Cyclic voltammograms of 50 mM acetic acid in acetonitrile (solid line), 3:1 acetonitrile/water (dotted line), 3:2 acetonitrile/water (dashed line) using a glassy carbon working electrode at scan rate of 0.2 V s^{-1}.

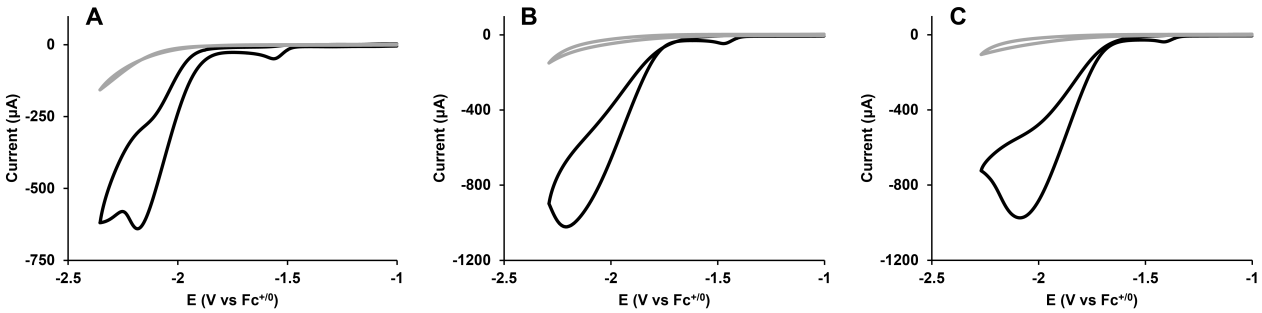

Figure S8. Cyclic voltammograms of 50 mM acetic acid without any catalyst (grey line) and in the presence of **5** (black line) under different solvent conditions: (A) acetonitrile, (B) 3:1 acetonitrile/water, and (C) 3:2 acetonitrile/water. A glassy carbon working electrode was used at a scan rate of 0.2 V s^{-1}.