Supporting Information

Evaluating the Role of Acidic, Basic, and Polar Amino Acids and Dipeptides on a Molecular Electrocatalyst for H_2 Oxidation

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1. ^{31}P NMR of the all six complexes
2. ^{31}P NMR to show the stability with time
3. Cyclic voltammetry of **CyGly** in methanol
4. Cyclic voltammetry of the Ni(II/I) only for **CyLys** and **CySer**
5. Cyclic voltammetry of **Cy(GlyPhe)** and **Cy(PheGly)** in THF
6. Cyclic voltammetry evaluating origin of H_2 production
7. Cyclic voltammetry in of **CyAsp** and **CyLys** in the presence of a base (triethyl amine)
8. Scan rate dependence for all six complexes
9. Proton-proton TOCSY of **Cy(GlyPhe)** and **Cy(PheGly)**

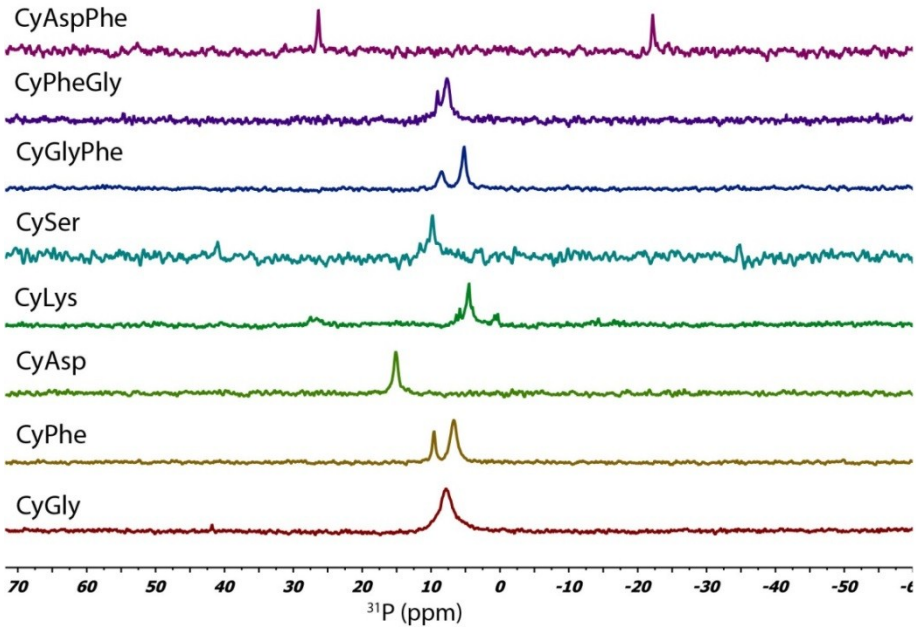

Figure S1. The ^{31}P NMR spectra of all of the complexes in methanol at 25 ^{o}C, collected at 500 MHz proton frequency.

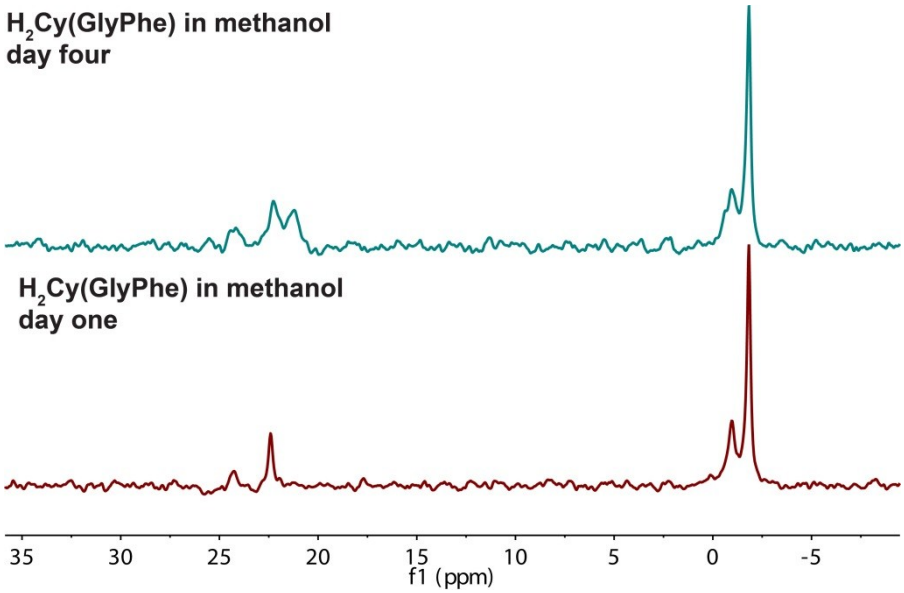

Figure S2. The stability of the complexes was demonstrated by comparing of the ^{31}P NMR spectra of the hydrogen addition product of **Cy(GlyPhe)**, **$(H)_2$Cy(GlyPhe)**, complex in methanol at 25 ^{o}C, collected at 500 MHz proton frequency immediately after preparation (bottom) and four days after preparation (top).

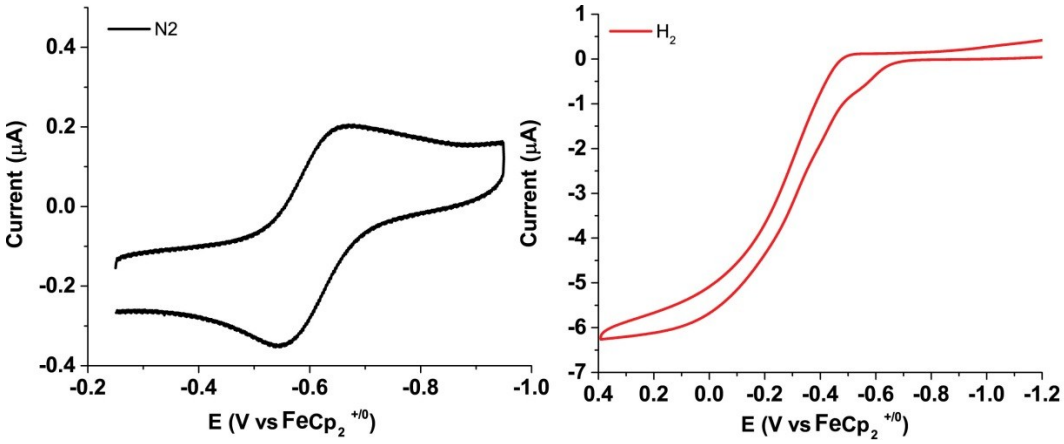

Figure S3. Cyclic voltammetry of **CyGly** (0.05 mM) in methanol. Black: under 1 atm N_2; red: under 1 atm of H_2. All data were collected using a glassy carbon electrode with a 0.2 Vs^{-1} scan rate at 25 ^oC.

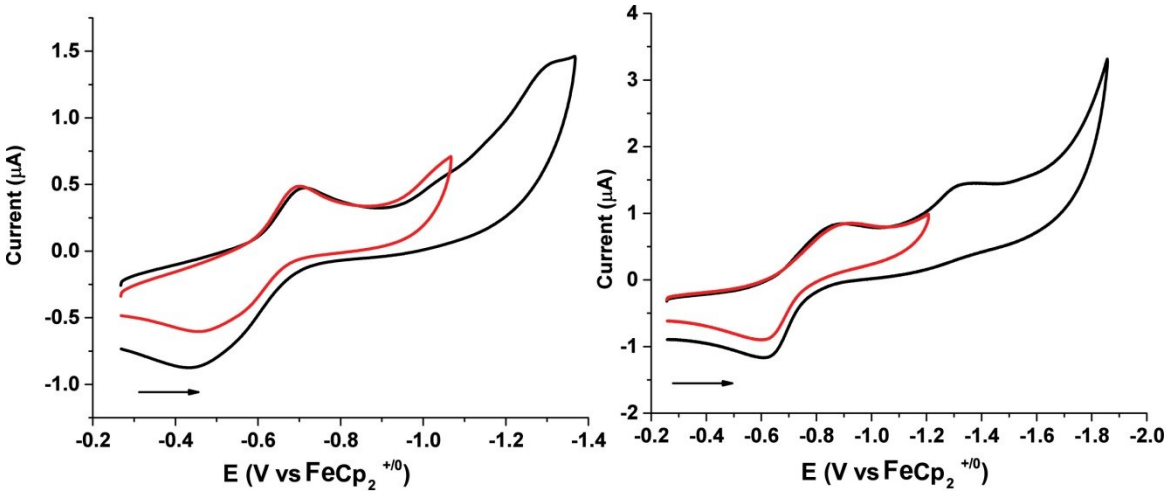

Figure S4. Left, **CyLys** (0.02 mM) and right, **CySer** (0.05 mM) in methanol showing full (black) and partial (red) scans of cyclic voltammetry to result in a more reversible Ni(II/I) wave. All data collected were collected using a glassy carbon electrode at a scan rate of 0.2 Vs^{-1}.

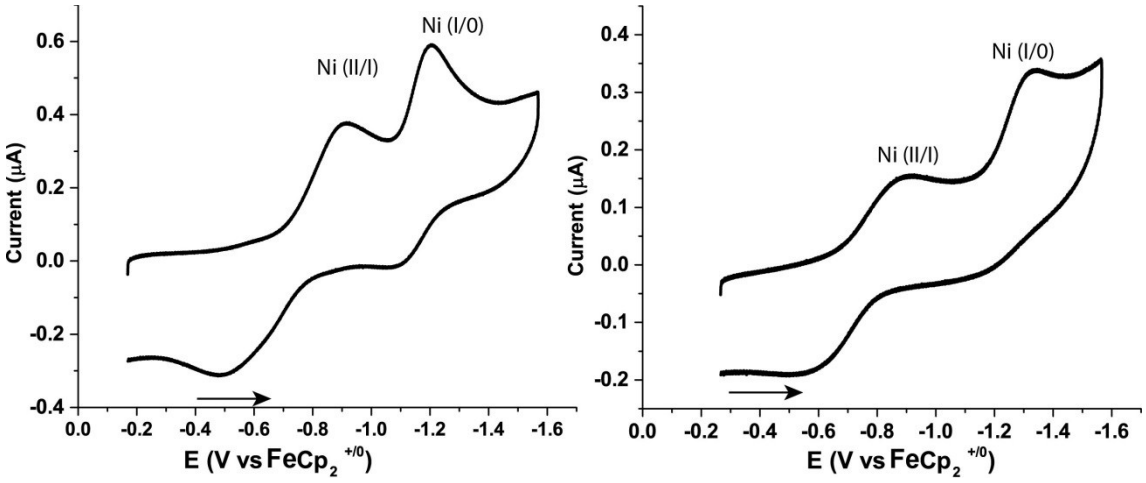

Figure S5. Cyclic voltammetry of **Cy(GlyPhe)** (left) and **Cy(PheGly)** (right) in THF showing more reversible Ni(I/0) couples due to increased solubility of the Ni(0) species in THF.

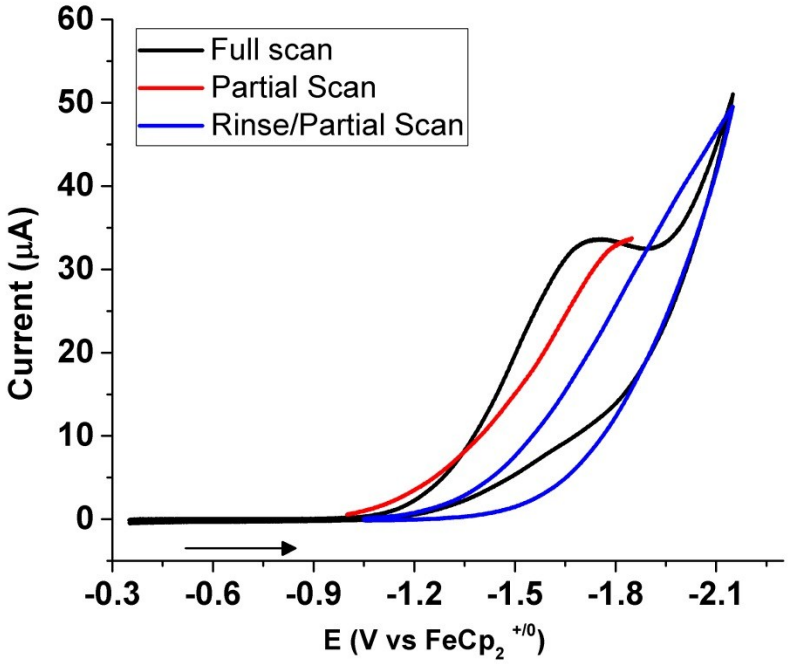

Figure S6. The nature of the H_2 production catalysis (heterogeneous vs homogeneous) was determined using a series of cyclic voltammetry experiments. Black: A full scan of 0.05 mM **CyAsp** in (0.5mM) HTFSI solution in 0.1 M tetrabutyl ammonium tetrafluoroborate ($TBABF_4$) electrolyte in methanol at a 0.5 Vs^{-1} scan rate. Red: A partial scan of the same solution, stopping at the wave maximum. Blue: A partial scan of the glassy carbon electrode after the previous scan after rinsing (not polishing) the electrode in 0.5 mM HTFSI in methanol at a 0.5 Vs^{-1} scan rate. Based on this data it is not definitive whether the H_2 production wave is due to a heterogeneous wave, or a mechanism catalytic at the Ni(0), though the significant wave remaining upon running in the absence of any complex is most consistent with a heterogeneous process.

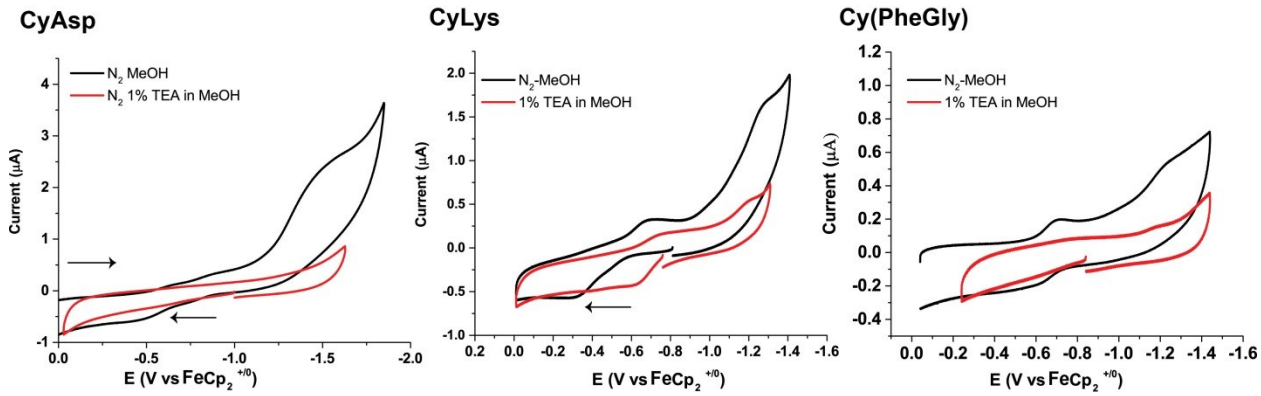

Figure S7. Cyclic voltammetry in of **CyAsp** (0.01 mM), **CyLys** (0.01 mM), and **Cy(PheGly)** (0.01 mM) under N_2 in methanol as a function of added base. For **CyLys**, the H_2 production wave reduces as acid is neutralized and a wave attributed to the Ni(I/0) is more prominent. Adding more base to fully remove the H_2 production resulted in dissolution of the **CyLys** complex and a concomitant loss of all of the electrochemical waves. Both **CyAsp** and **Cy(PheGly)** lose all signal due to reduced solubility upon the addition of base. All data were collected with a glassy carbon electrode at a scan rate of 0.2 Vs^{-1} at 25 °C.

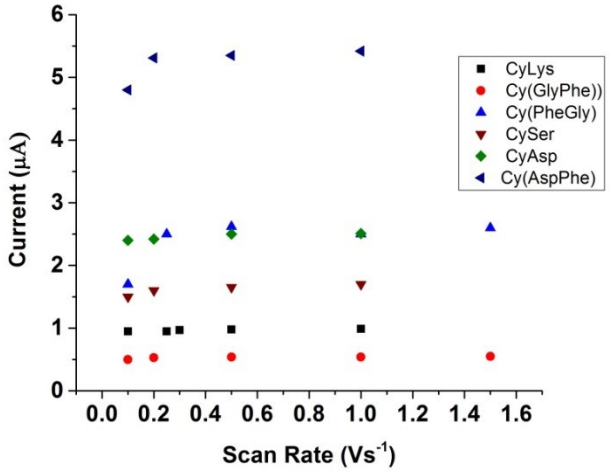

Figure S8. Scan rate dependence of H_2 oxidation catalytic current for **CyAsp** (0.02 mM), **CyLys** (0.02 mM), **CySer** (0.09mM), **Cy(GlyPhe)** (0.06 mM), **Cy(PheGly)** (0.05 mM) and **Cy(AspPhe)** (0.06mM) in methanol under 1 atm H_2. Scan rate independence was observed at 0.2 Vs^{-1} for all complexes.

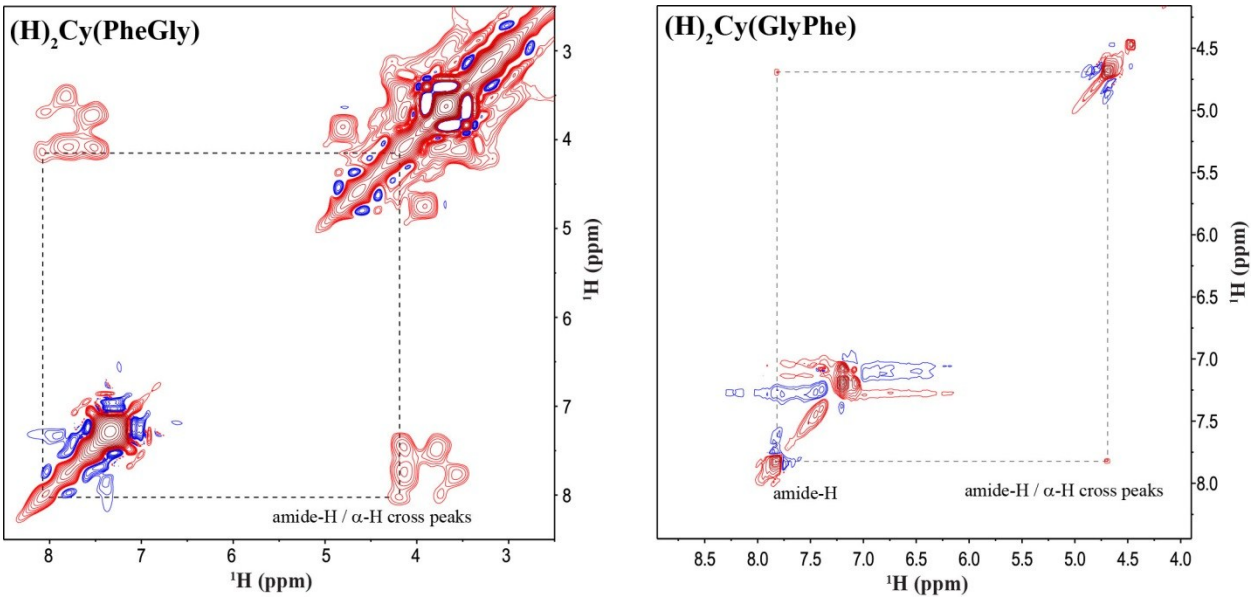

Figure S9. TOCSY spectra of **$(H)_2$Cy(PheGly)** and **$(H)_2$Cy(GlyPhe)** in *d8*-THF at 25°C collected at 500 MHz at mixing period of 80 ms.