Supporting Information

Selective Electrocatalytic Conversion of CO_2 to HCOOH by a Cationic Rh_2(II,II) Complex

Hemanthi D. Manamperi, Suzanne E. Witt, and Claudia Turro*

Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH 43210

Corresponding author: C. Turro, turro.1@osu.edu

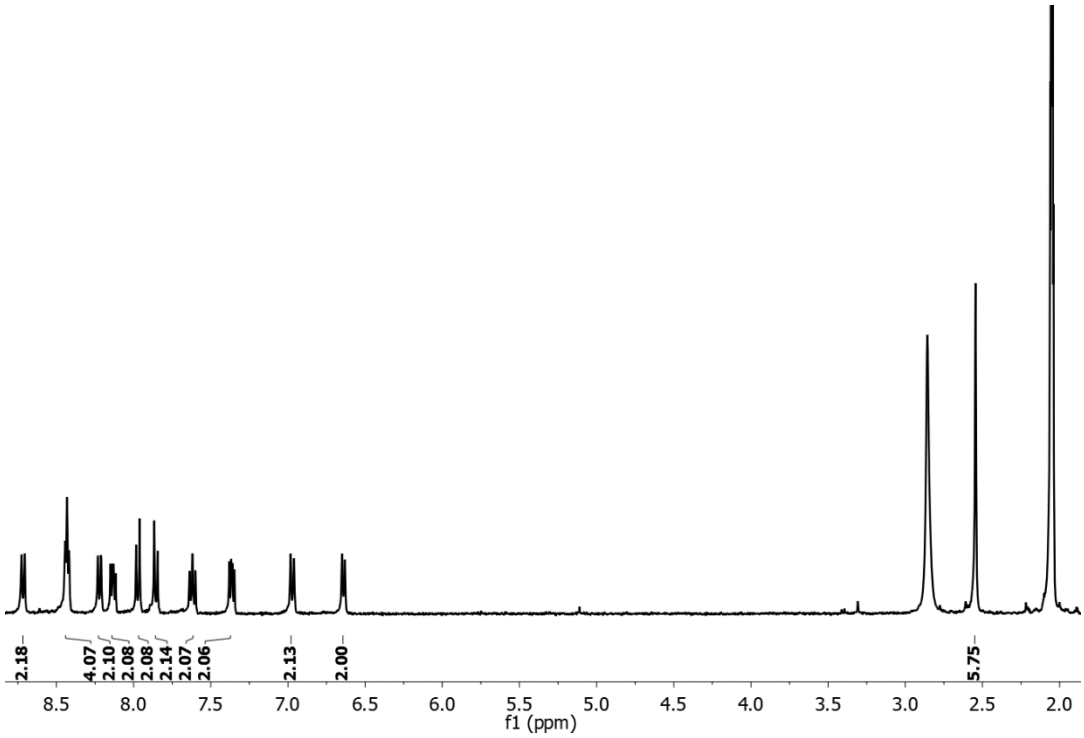

Figure S1. ^{1}H NMR spectrum of **Rh$_2$-phen$_2$** in $(CD_3)_2CO$, 400 MHz

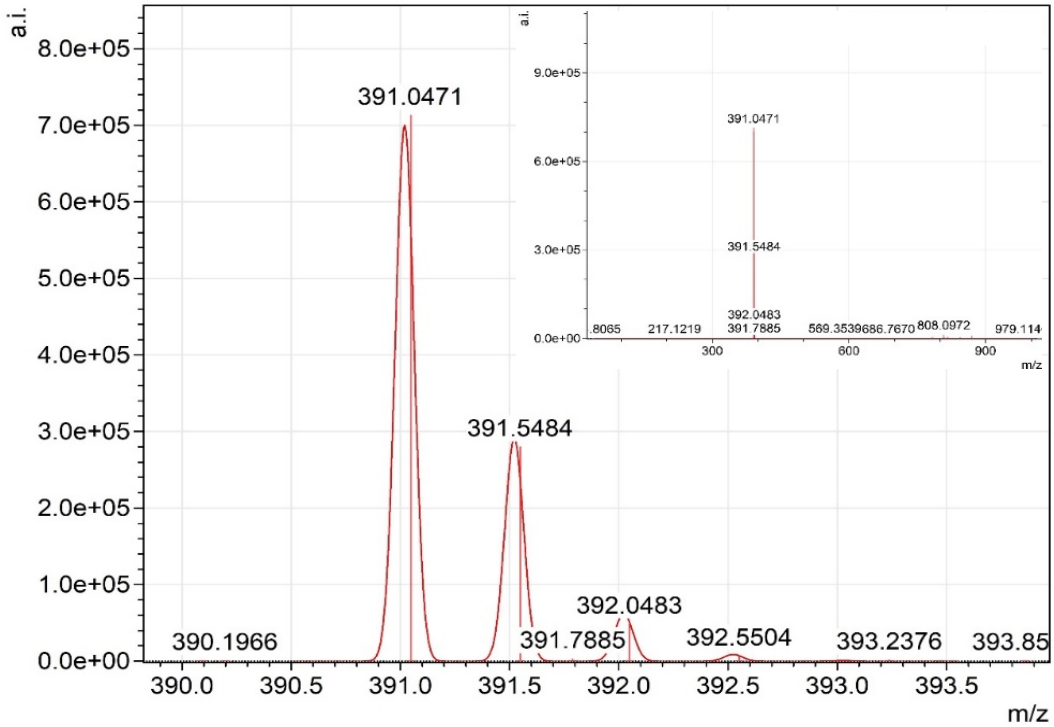

Figure S2. ESI-MS of **Rh$_2$-phen$_2$**

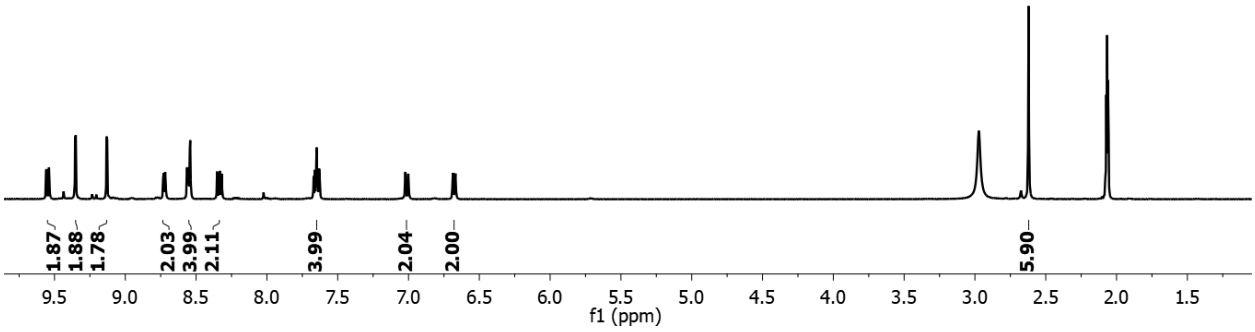

Figure S3. ^{1}H NMR spectrum of **Rh_2dpq$_2$** in $(CD_3)_2CO$, 400 MHz

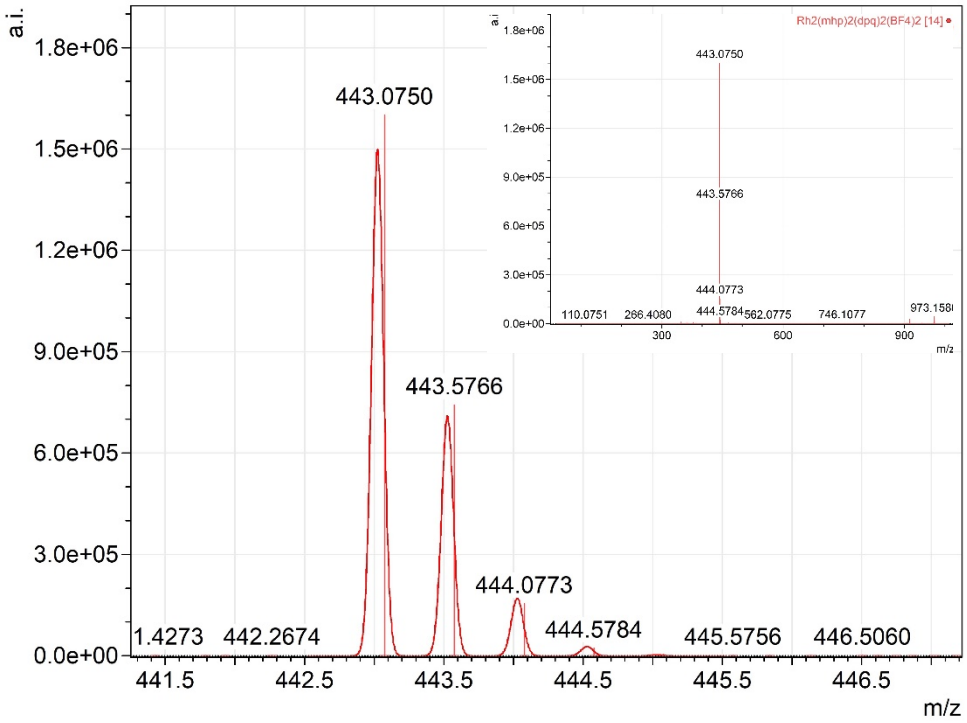

Figure S4. ESI-MS of **Rh_2-dpq$_2$**

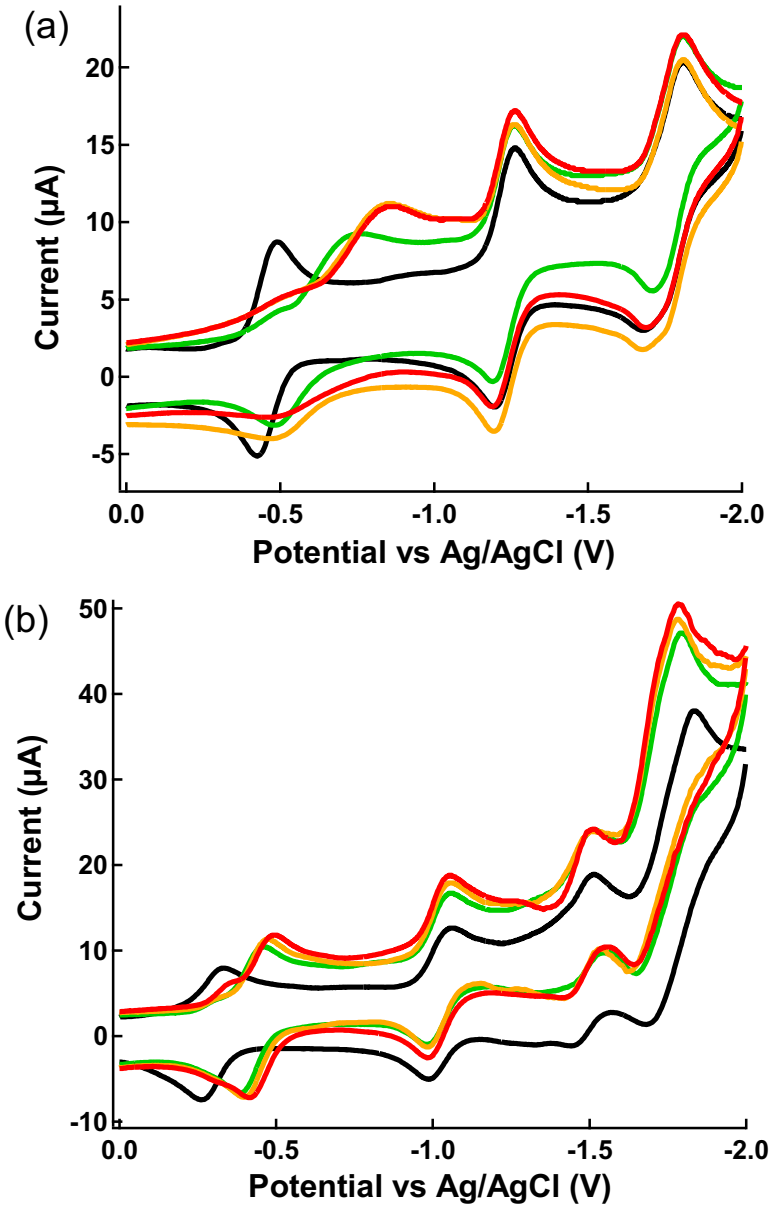

Figure S5. Cyclic voltammograms of (a) **Rh_2-$phen_2$** and (b) **Rh_2-dpq_2** collected with added pyridine 0 mM (black), 5 mM (green), 10 mM (yellow) and 20 mM (red).

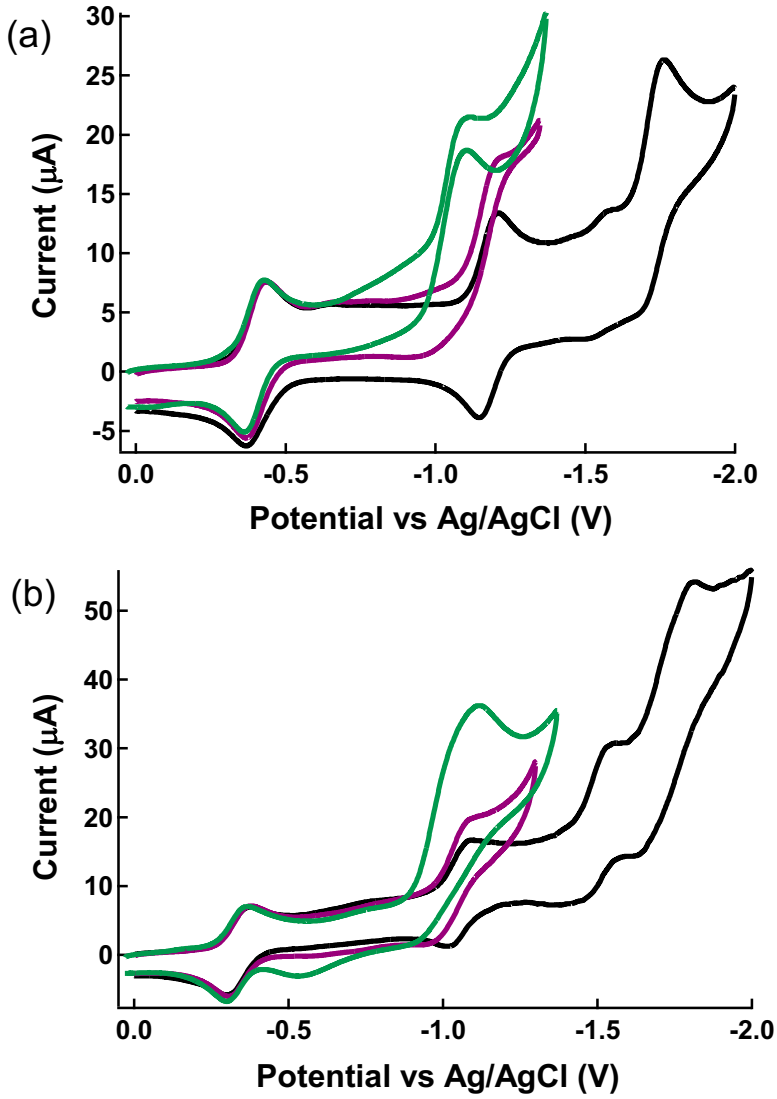

Figure S6. Cyclic voltammograms of 0.5 mM (a) **Rh_2-phen$_2$** and (b) **Rh_2-dpq$_2$** purged with N_2 (solid lines), CO_2 (purple) and CO_2/3M H_2O (green) in CH_3CN/0.1 M $TBAPF_6$ (scan rate of 0.1 V/s).

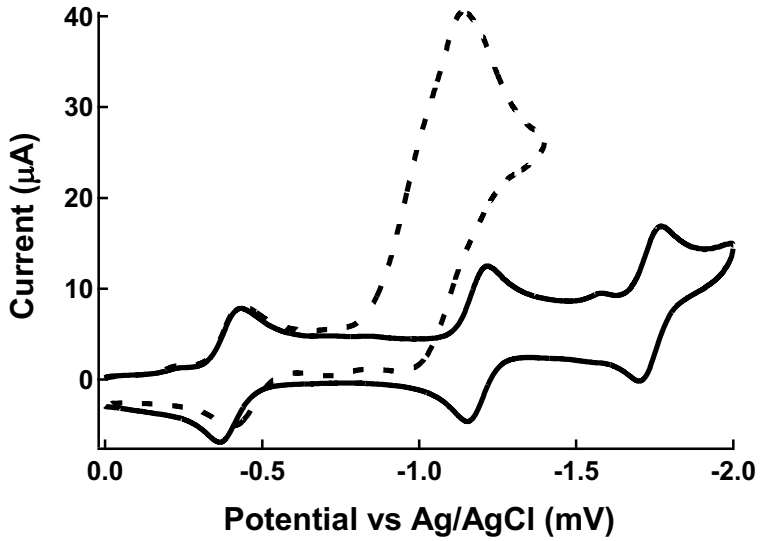

Figure S7. Cyclic voltammograms of **Rh_2-phen$_2$** with 0 mM (black), 0.5 mM (dashed line) of CH_3COOH at a scan rate of 0.1 V/s (0.1 M $TBAPF_6$) collected under N_2.

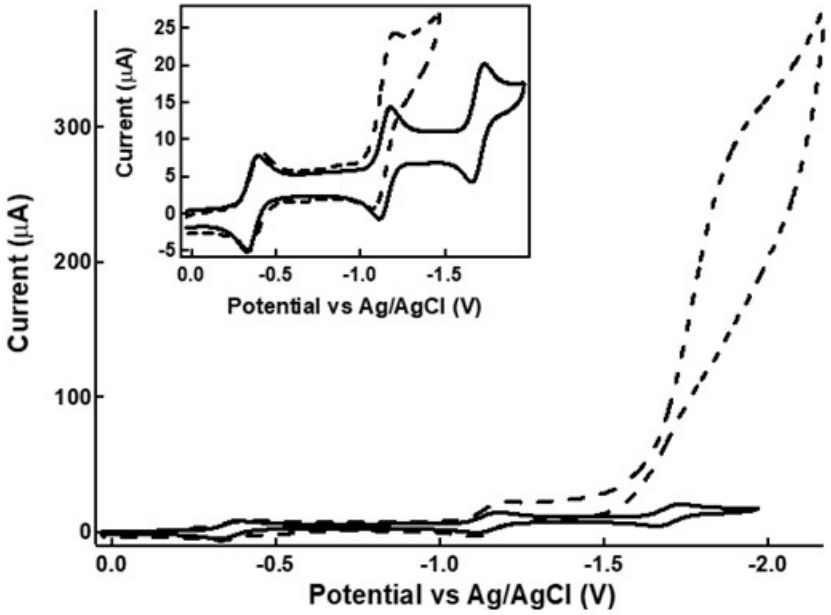

Figure S8. Cyclic voltammograms of **Rh_2-phen$_2$** with 0 mM (black), 10 mM (dashed line) of CF_3CH_2OH at a scan rate of 0.1 V/s (0.1 M $TBAPF_6$) collected under N_2. Inset shows the CV reversed followed by the second reduction.

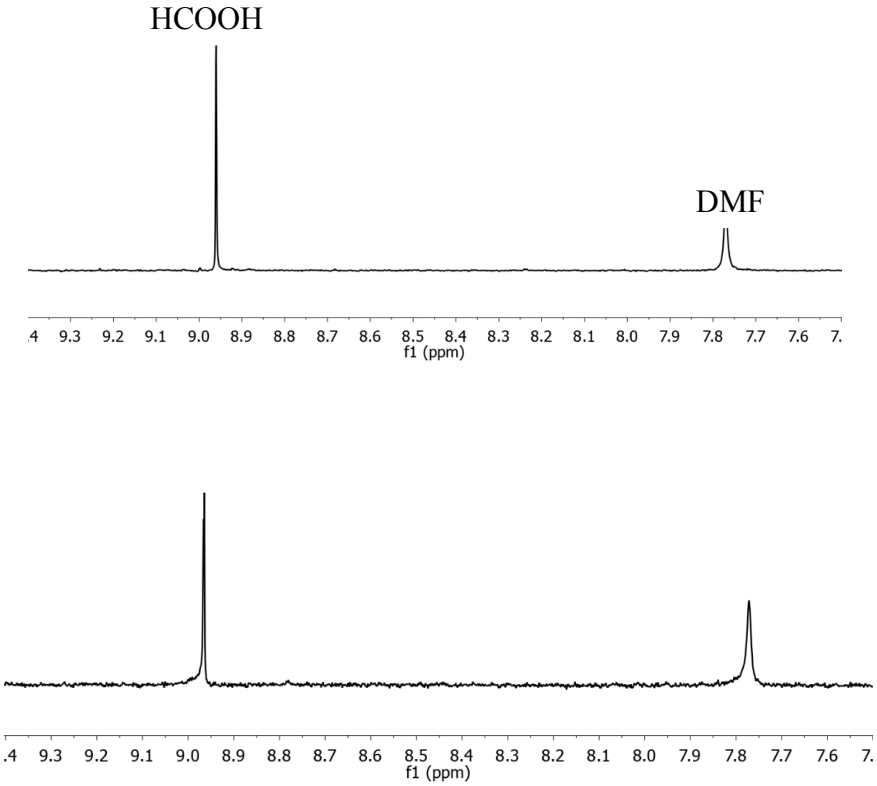

Figure S9. ^{1}H NMR spectra of HCOOH in 3 M H_2O / 0.1 M $TBAPF_6$ in CH_3CN (top) and reaction mixture of **Rh_2-phen$_2$** after one hour electrolysis at – 1.5 V in 3 M H_2O / 0.1 M $TBAPF_6$ in CH_3CN under CO_2 (bottom).

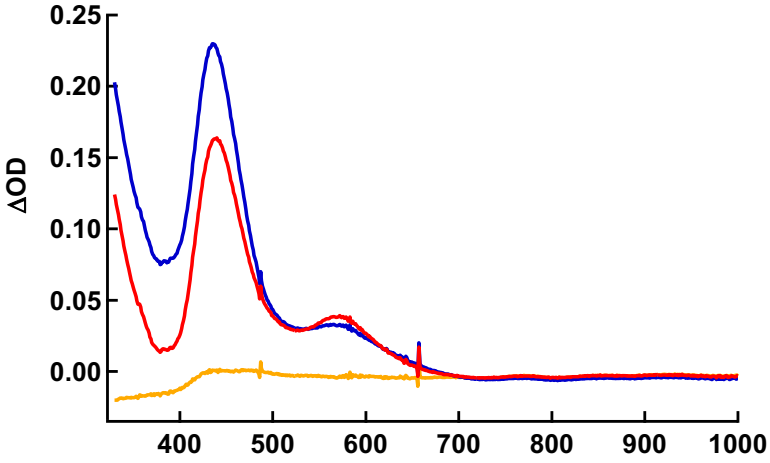

Figure S10. Difference spectra for the electrolysis of **Rh_2-phen$_2$** at –0.8 V (**yellow**), –1.5 V (**blue**), and –2.0 V (**red**) in 3 M H_2O/CH_3CN/0.1 M $TBAPF_6$ under N_2.

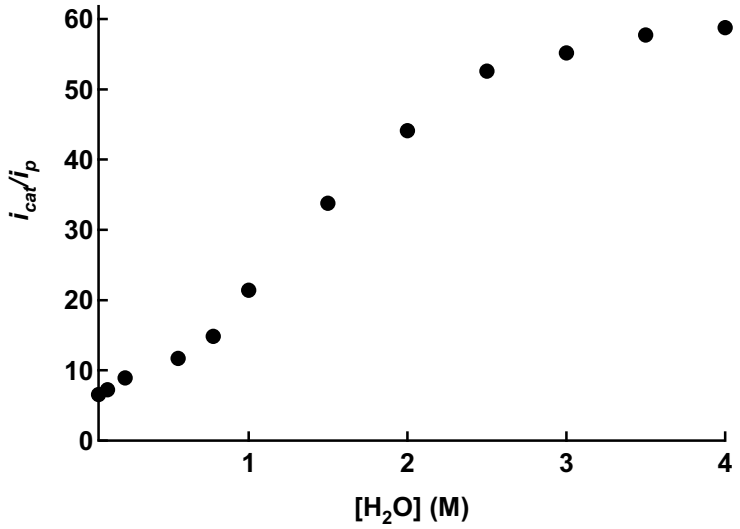

Figure S11. Dependence of icat/ip on [H_2O] for **Rh_2-phen$_2$** in CH_3CN (0.1 M $TBAPF_6$) under CO_2 at 0.1 V/s.