Electronic Supporting Information

Strong Impact of Intramolecular Hydrogen Bonding on the Cathodic Path of [Re (3,3′-dihydroxy-2,2′-bipyridine)$(CO)_3Cl$] and Catalytic Reduction of Carbon Dioxide

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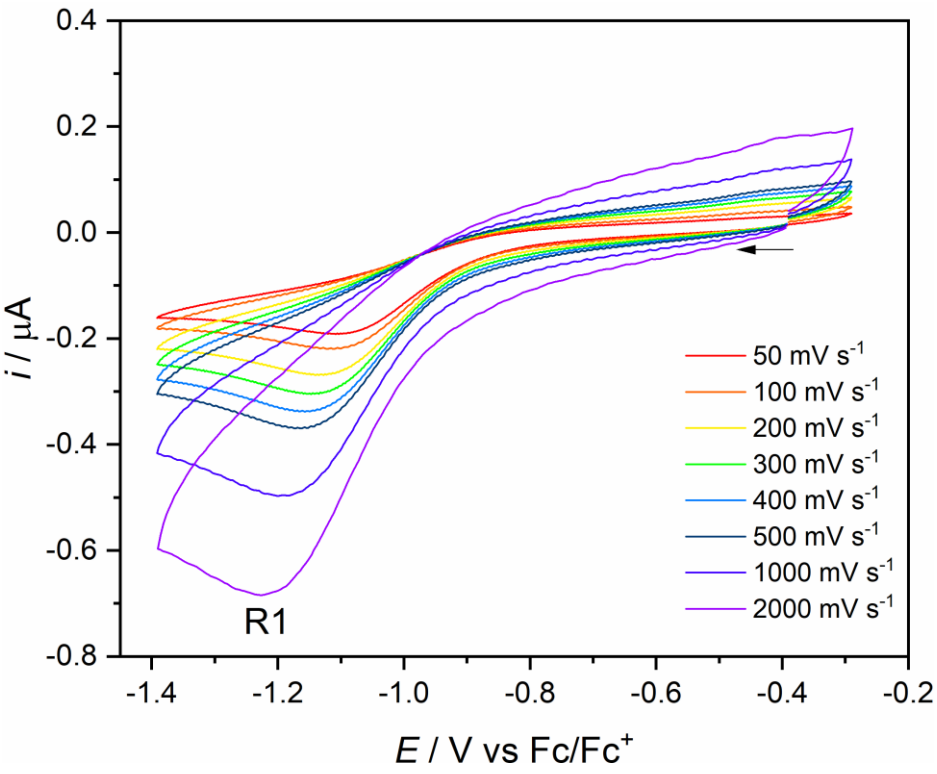

Figure S1: Cyclic voltammograms of [Re(3,3′-DHBPY)$(CO)_3$Cl] in THF/Bu_4NPF_6 in the region of R1. Experimental conditions: Pt microdisc, T = 298 K, scan rates v = 50 - 2000 mV s^{-1}.

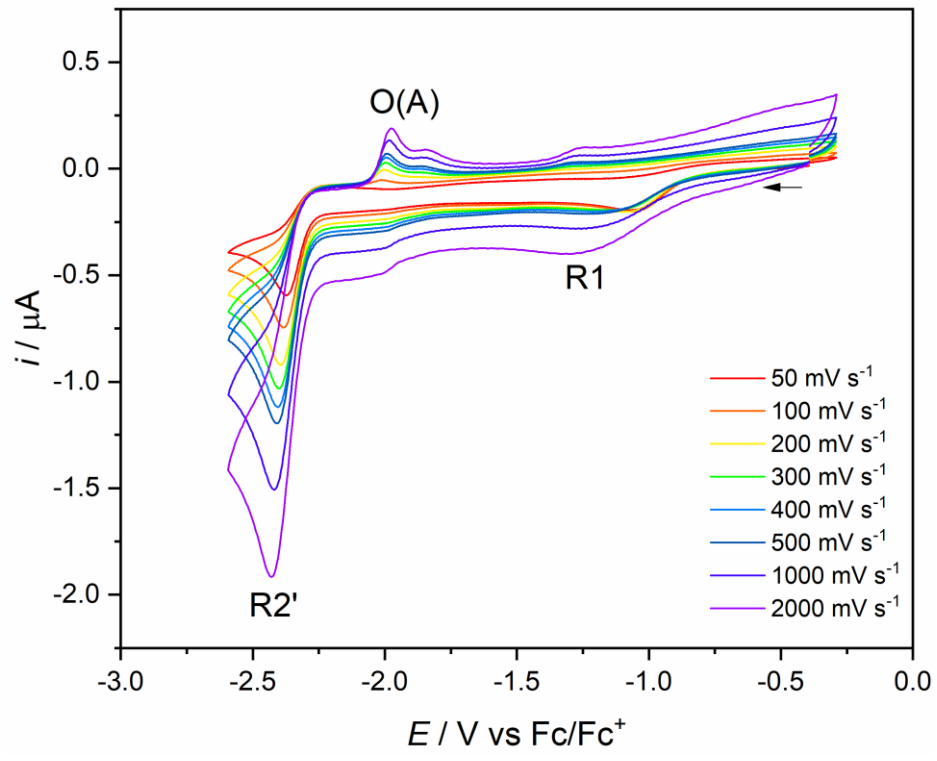

Figure S2: Cyclic voltammograms of [Re(3,3′-DHBPY)$(CO)_3$Cl] in THF/Bu_4NPF_6 across the full cathodic region. Experimental conditions: Pt microdisc, T = 298 K, scan rates v = 50 - 2000 mV s^{-1}.

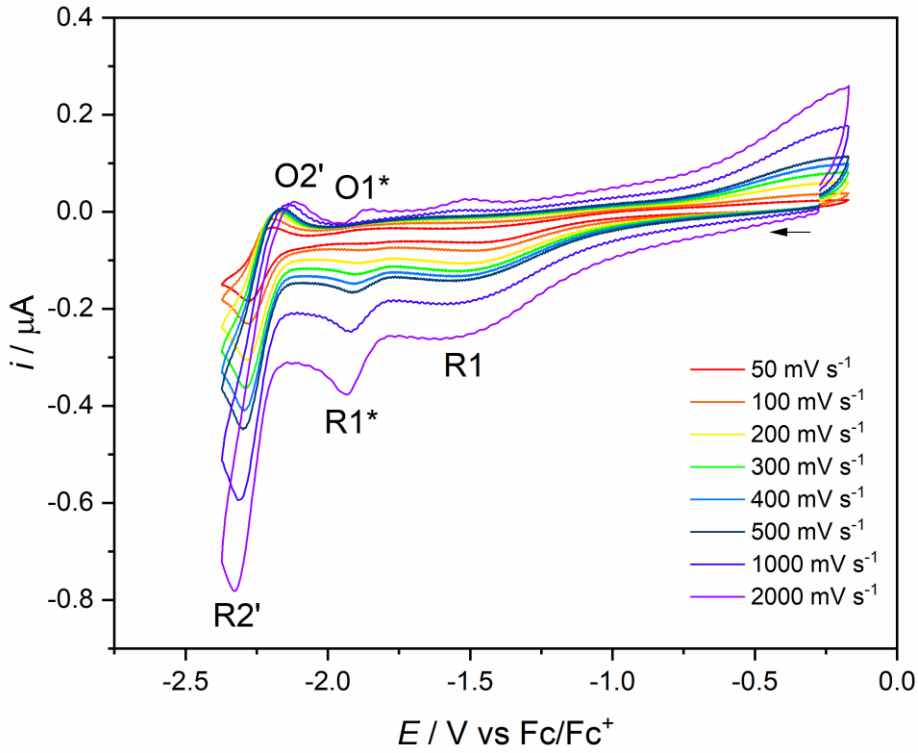

Figure S3: Cyclic voltammograms of [Re(3,3′-DHBPY)$(CO)_3$Cl] in THF/Bu_4NPF_6 across the cathodic potential region. Experimental conditions: Pt microdisc, T = 195 K, scan rates v = 50 - 2000 mV s^{-1}.

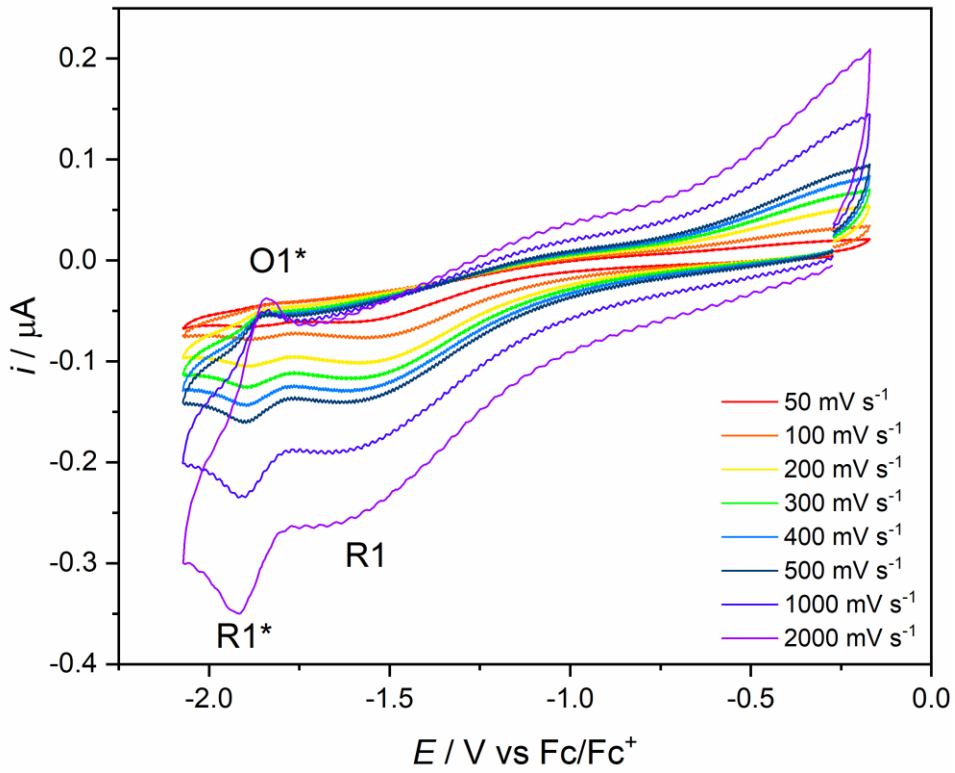

Figure S4: Cyclic voltammograms of [Re(3,3′-DHBPY)$(CO)_3$Cl] in THF/Bu_4NPF_6 up to R1*. Experimental conditions: Pt microdisc, T = 195 K, scan rates v = 50 - 2000 mV s^{-1}.

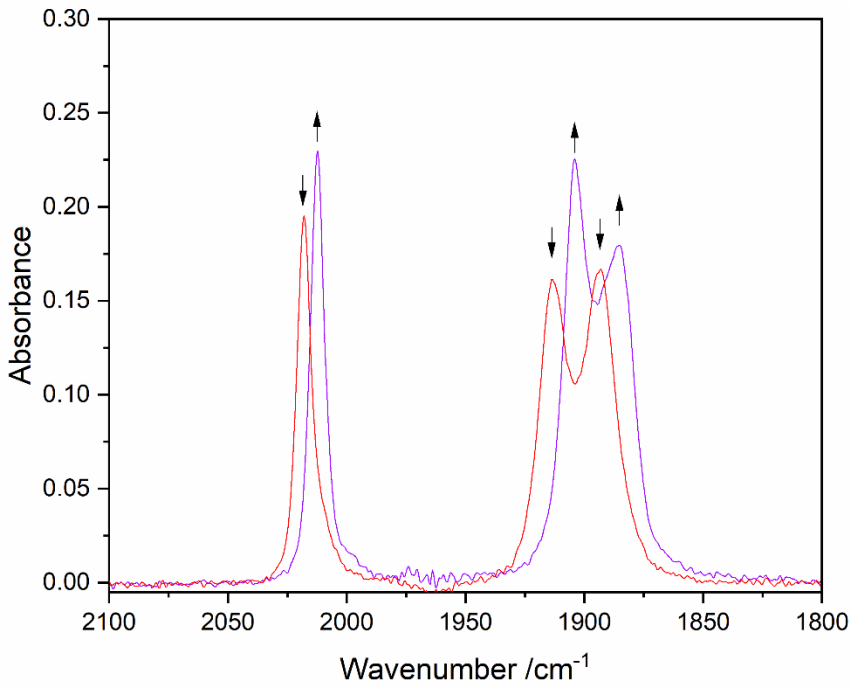

Figure S5. Chemical deprotonation of [Re(3,3′-DHBPY)$(CO)_3$Cl] to [Re(3,3′-DHBPY-H^+)$(CO)_3$Cl]$^-$ in THF caused by the addition of 1 equiv. NaHMDS.

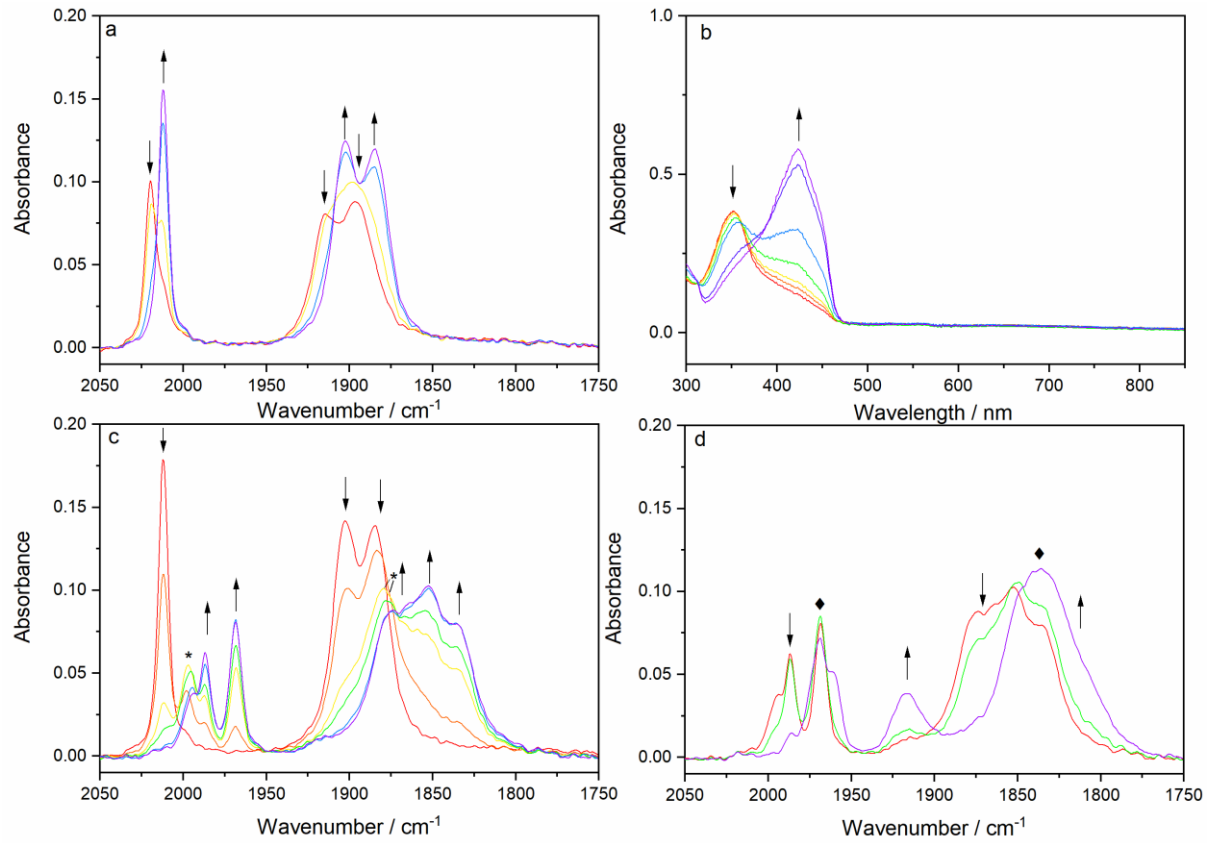

Figure S6. (a) IR and (b) UV-VIS spectroelectrochemistry of [Re(3,3′-DHBPY)$(CO)_3$Cl] (↓) in PrCN/Bu_4NPF_6 at 298 K as it is converted by reductive deprotonation at R1 to [Re(3,3′-DHBPY-H^+)$(CO)_3$Cl]$^-$ (↑) in an OTTLE cell. (c) IR spectroelectrochemistry of [Re(3,3′-DHBPY-H^+)$(CO)_3$Cl]$^-$ (↓) as it undergoes, 1e$^-$ reduction at the onset of R2' and ETC conversion to [Re(3,3′-DHBPY)$(CO)_3$Cl]$^{\bullet-}$ (*). The latter radical anion is further reduced on scanning through R2′, forming the 6-coordinate redox couple [Re(3,3′-DHBPY-2H^+)$(CO)_3$(PrCN)]$^{n-}$ (n = 2, 3) (↑) existing in redox equilibrium (cf. Figure 11). (d) Re(3,3′-DHBPY-2H^+)$(CO)_3$(PrCN)]$^{2-}$ (↓) continues to reduce by a small negative potential shift, generating mainly 5-coordinate [Re(3,3′-DHBPY-2H^+)$(CO)_3$]$^{3-}$ (↑) in equilibrium with 6-coordinate [Re(3,3′-DHBPY-2H^+)$(CO)_3$(PrCN)]$^{3-}$ (♦).

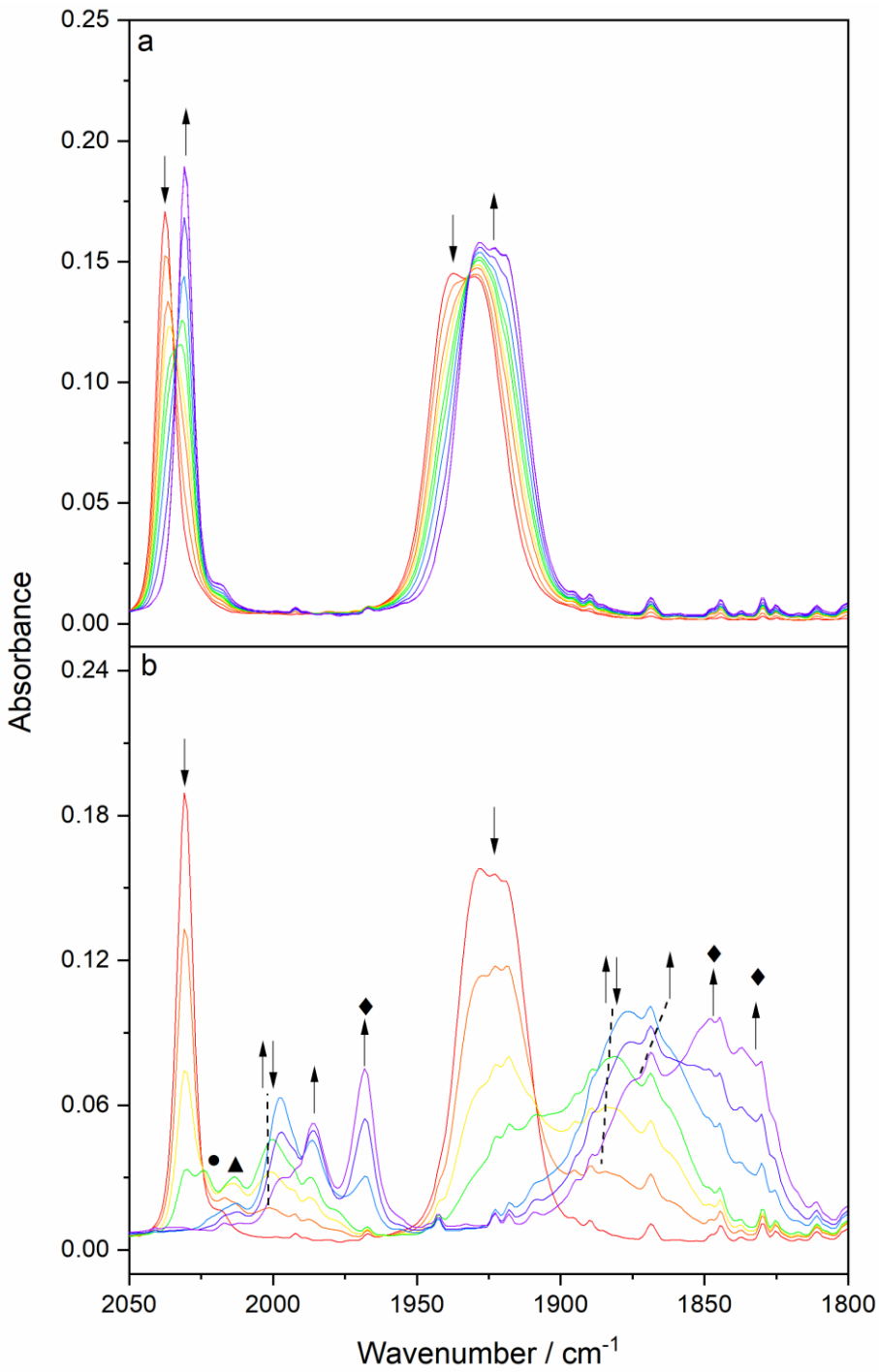

Figure S7. Cathodic IR spectroelectrochemistry of $[Re(3,3'\text{-DHBPY})(CO)_3(PrCN)]^+$ in $PrCN/Bu_4NPF_6$ at 223 K. (a) $1e^-$ reduction of the parent complex (↓) at R1 producing deprotonated $[Re(3,3'\text{-DHBPY-H}^+)(CO)_3(PrCN)]$ (↑). (b) Subsequent reduction of $[Re(3,3'\text{-DHBPY-H}^+)(CO)_3(PrCN)]$ (↓) at R2' to give a mixture of products with dominating $[Re(3,3'\text{-DHBPY})(CO)_3(PrCN)]$ (↑↓) formed in an ETC step. The small band labelled with ● may belong to marginal reductively double-deprotonated $[Re(3,3'\text{-DHBPY-2H}^+)(CO)_3(PrCN)]^-$. Its $1e^-$ and $2e^-$ reduced forms, $[Re(3,3'\text{-DHBPY}^{\bullet-}\text{-2H}^+)(CO)_3(PrCN)]^{2-}$ (↑) and $[Re(3,3'\text{-DHBPY}^{2-}\text{-2H}^+)(CO)_3(PrCN)]^{3-}$ (♦), terminate the cathodic path. The label ▲ denotes an unassigned reduced intermediate (see also Figure 11b).

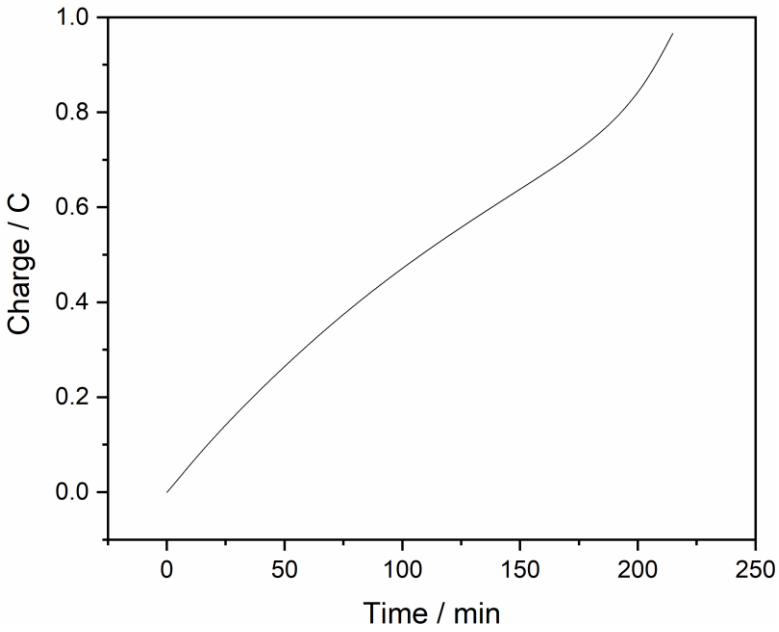

Figure S8. Charge vs time plot following the CPE of 3 mM [Re(3,3′-DHBPY)$(CO)_3$Cl] in CO_2-saturated 0.5 M THF/Bu_4NPF_6. The catalytic electrode potential was held at - 2.6 V vs Fc/Fc^+ for 3 h, using a Pt microdisc electrode (diameter of 2 mm).

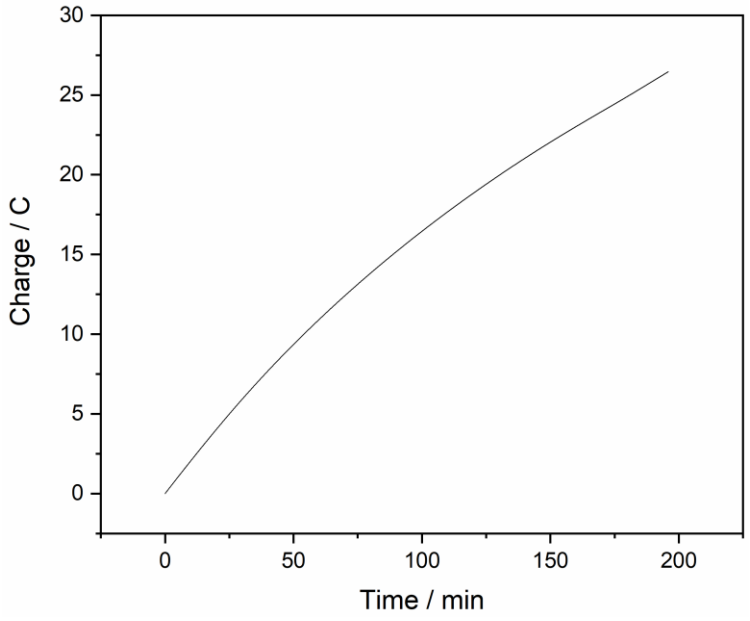

Figure S9. Charge vs time plot following the CPE of 3 mM [Re(3,3′-DHBPY)$(CO)_3$Cl] in CO_2-saturated 0.5 M THF/Bu_4NPF_6. The catalytic electrode potential was held at - 2.6 V vs Fc/Fc^+ for 3 h, using a Pt foil electrode (surface area of 2× 0.96 cm^2).

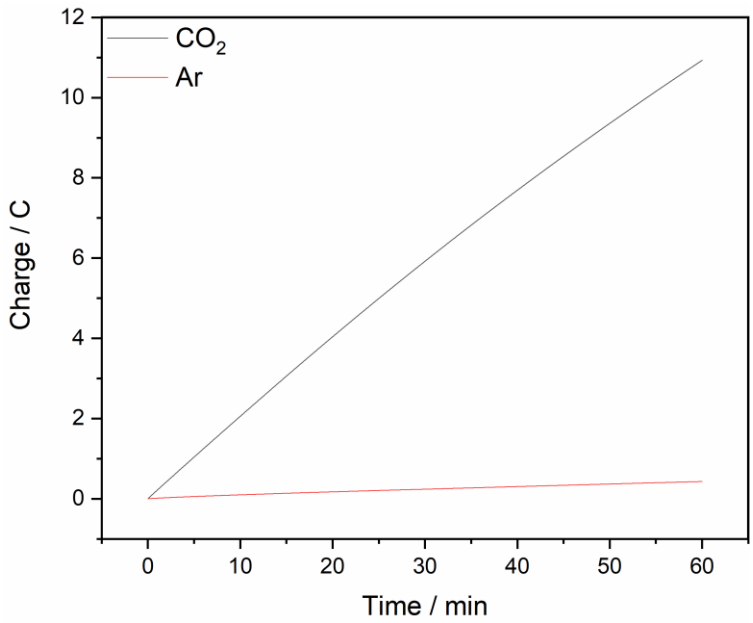

Figure S10. Charge vs time plot following the CPE of 3 mM [Re(3,3′-DHBPY)$(CO)_3$Cl] in CO_2-saturated (black) and Ar-saturated (red) 0.5 M THF/Bu_4NPF_6. The catalytic electrode potential was held at - 2.6 V vs Fc/Fc^+ for 1 h, using a Pt foil electrode (surface area of 2× 0.96 cm^2).