Synthesis and Characterization of *meso*-Substituted Cobalt Tetradehydrocorrin and Evaluation of Its Electrocatalytic Behavior Toward CO_2 Reduction and H_2 Evolution

Supporting Information

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Spectral information

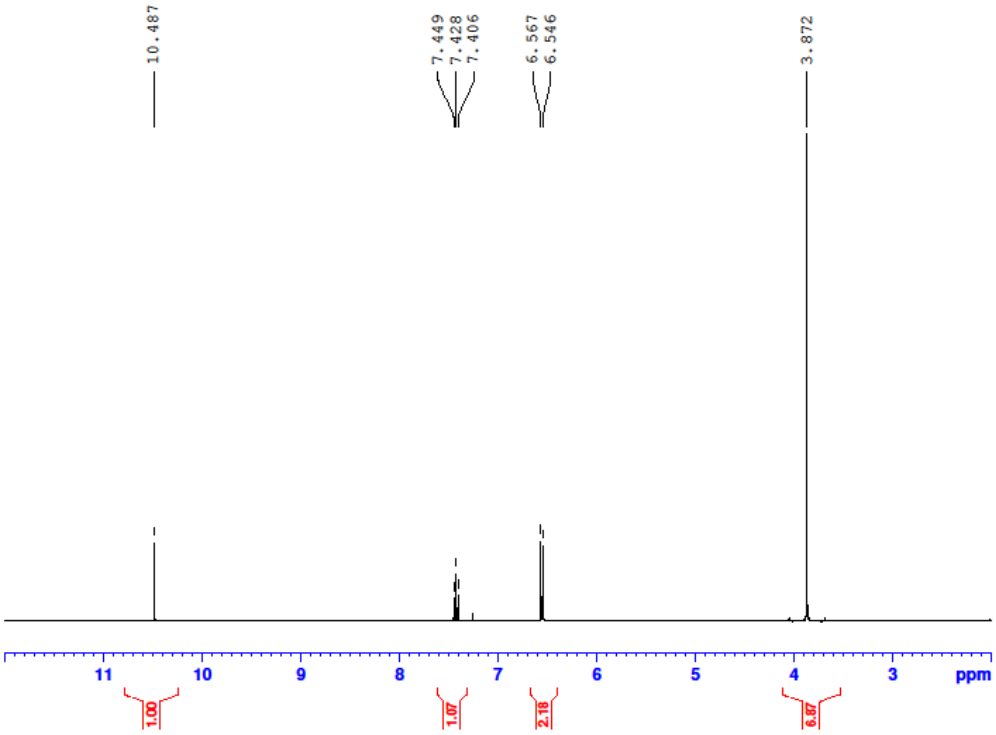

Figure S1. ^{1}H NMR spectrum of compound **1**.

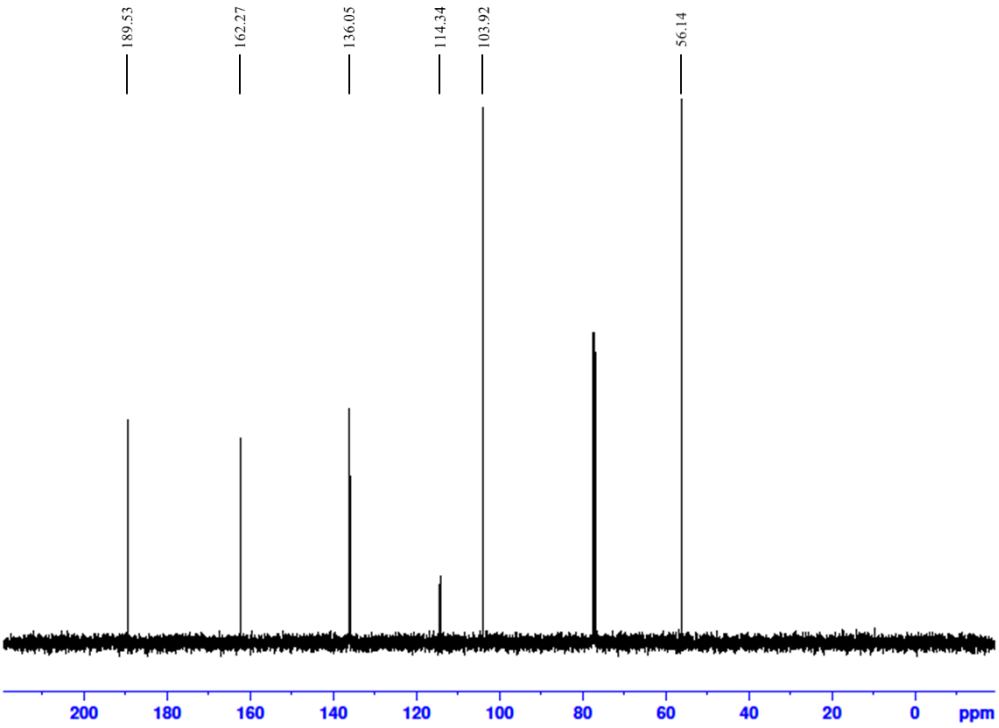

Figure S2. ^{13}C{^{1}H} NMR spectrum of compound **1**.

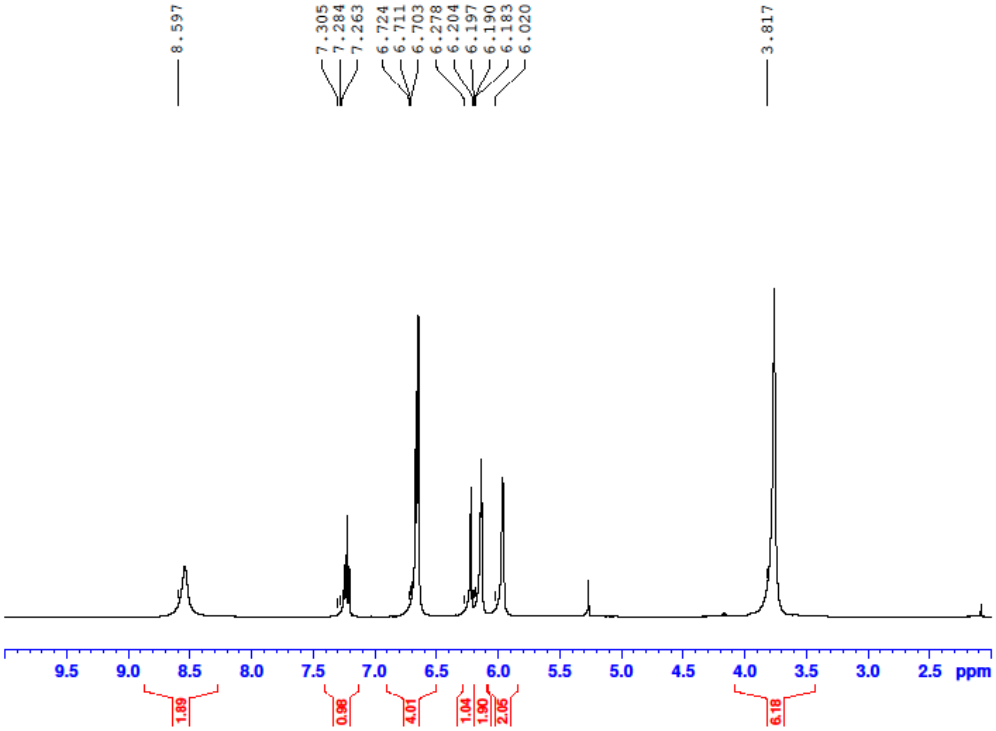

Figure S3. ^{1}H NMR spectrum of compound **2**.

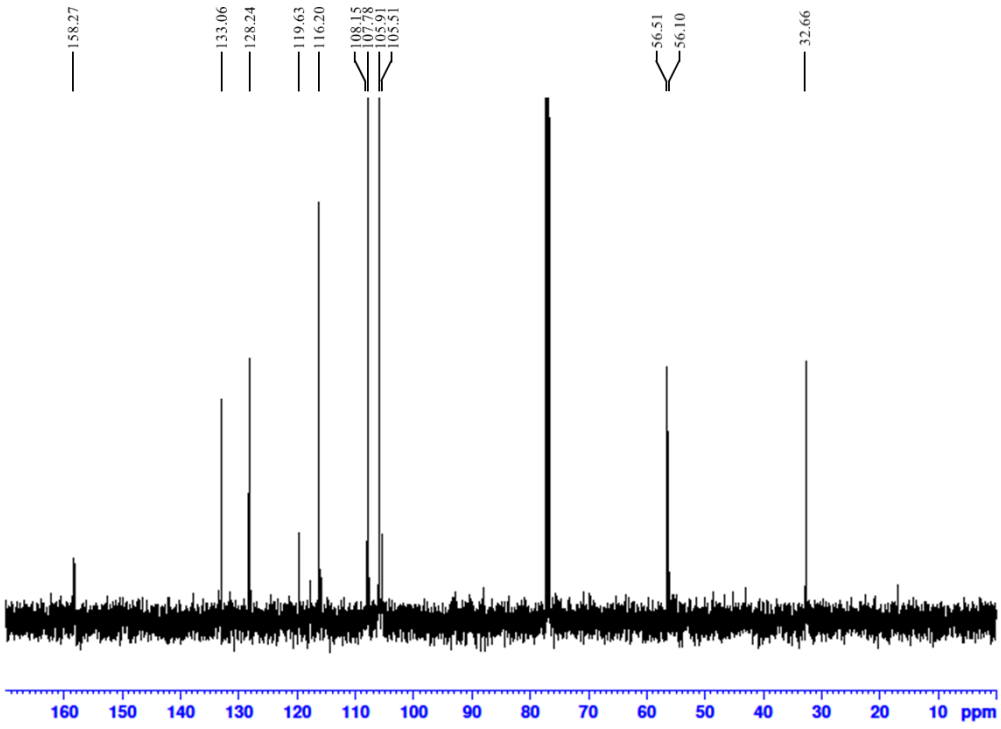

Figure S4. ^{13}C{^{1}H} NMR spectrum of compound **2**.

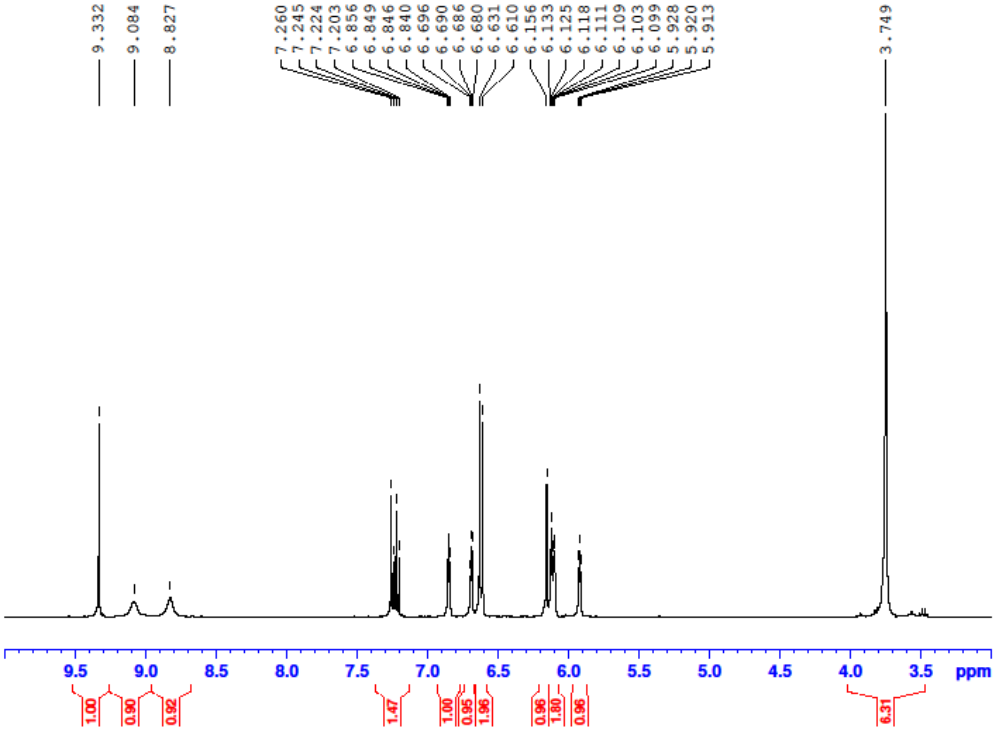

Figure S5. ^{1}H NMR spectrum of compound **3**.

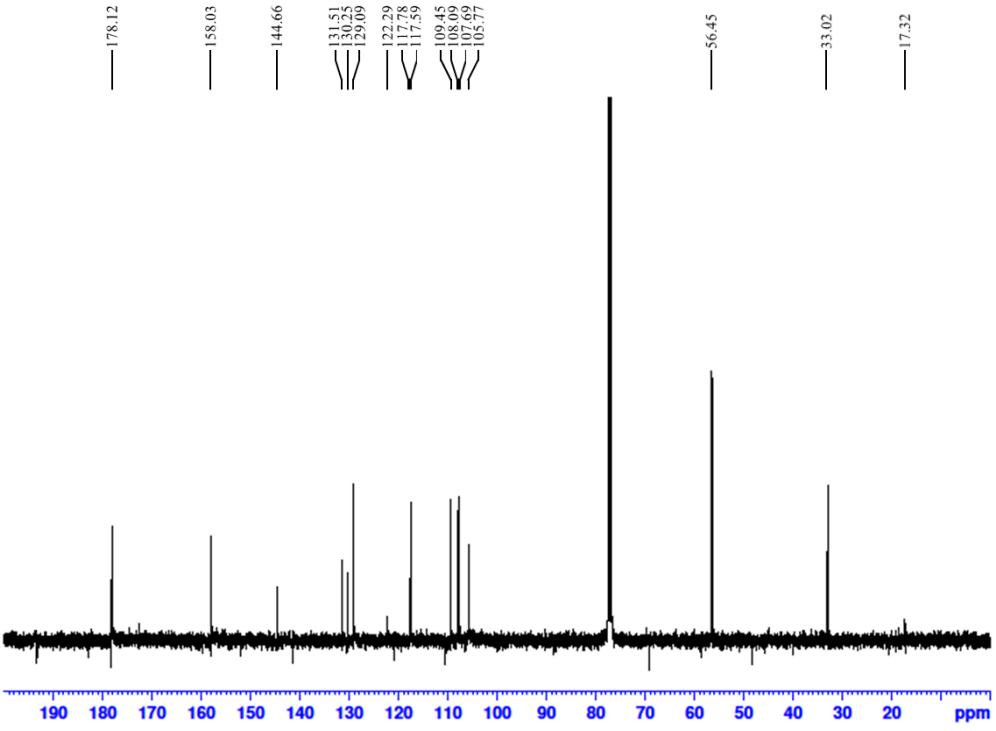

Figure S6. ^{13}C{^{1}H} NMR spectrum of compound **3**.

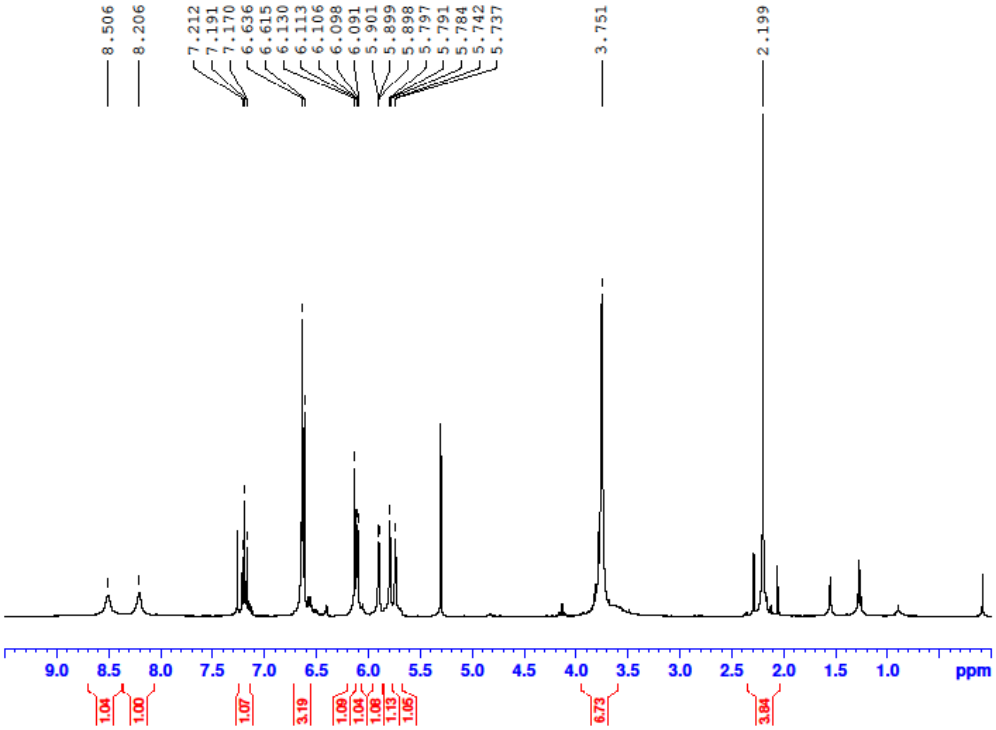

Figure S7. ^{1}H NMR spectrum of compound **4**.

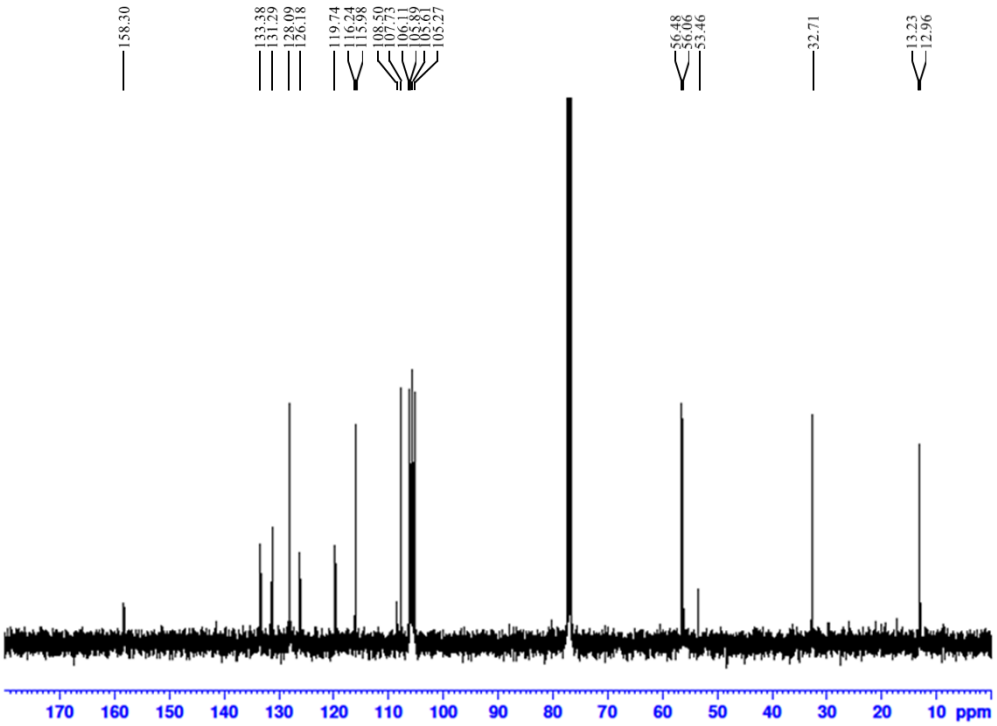

Figure S8. ^{13}C{^{1}H} NMR spectrum of compound **4**.

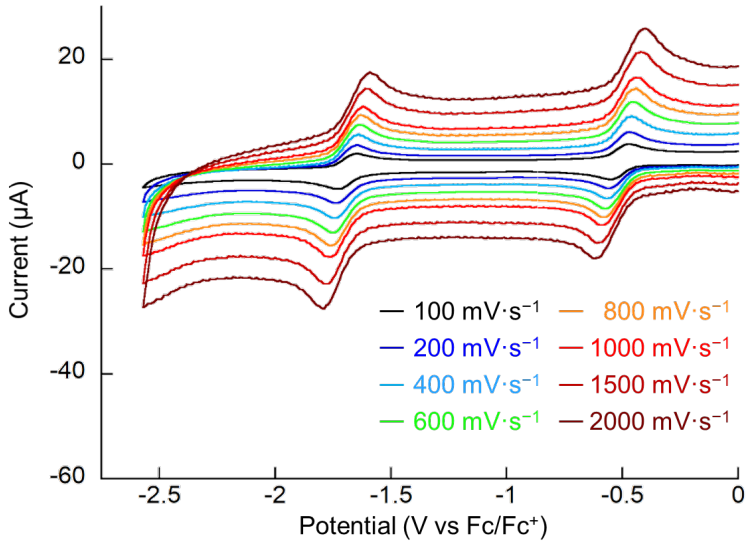

Figure S9. Cyclic voltammograms of **Co(II)TDHC** (0.5 mM) in anhydrous DMF with 0.1 M $TBAPF_6$ under an N_2 atmosphere. Scan rate varies from 100 to 2000 $mV \cdot s^{-1}$.

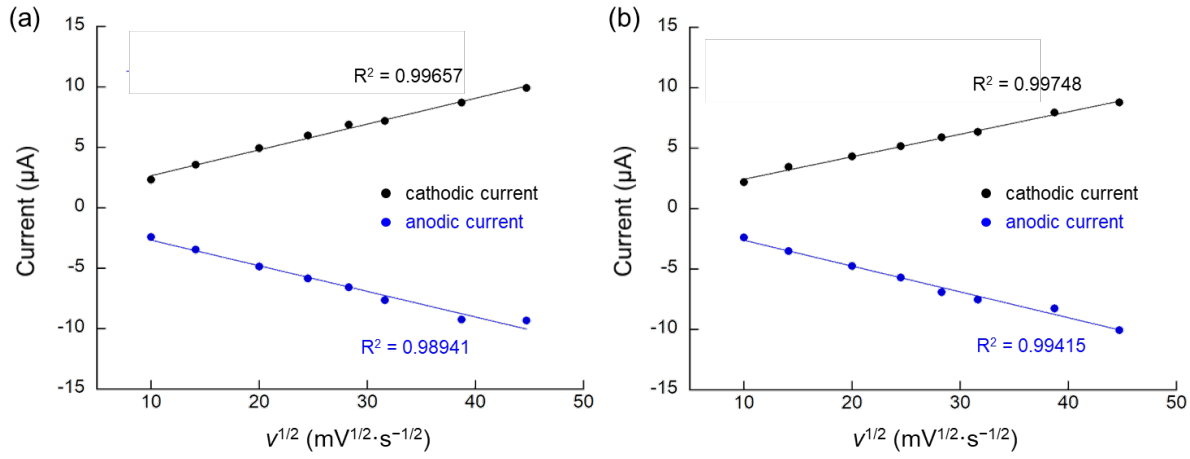

Figure S10. Plots of (a) first and (b) second redox peak currents against $v^{1/2}$ in the cyclic voltammograms in anhydrous DMF with 0.1 M $TBAPF_6$ under an N_2 atmosphere.

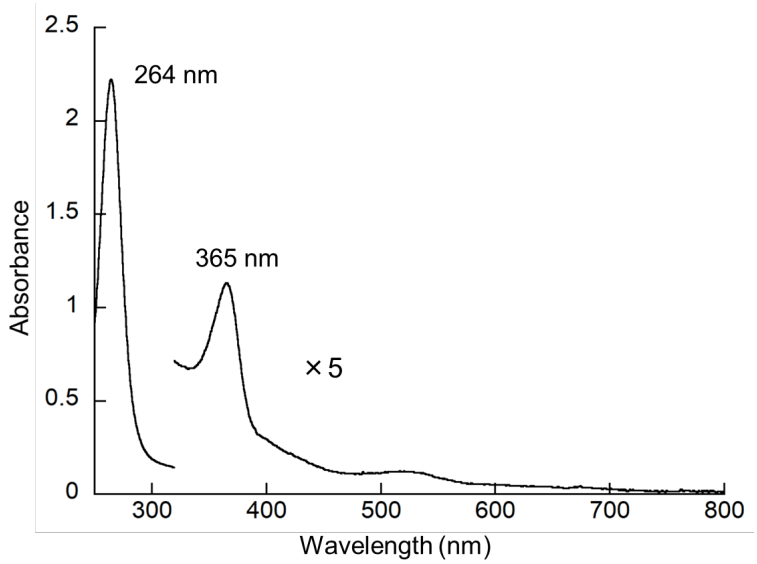

Figure S11. UV-vis absorption spectrum of cobaltocene under an N_2 atmosphere in CH_2Cl_2.

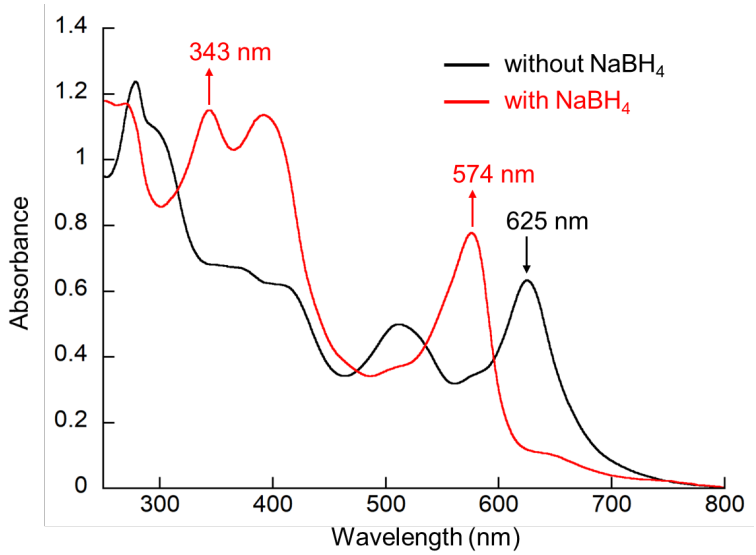

Figure S12. UV-vis absorption spectra of **Co(II)TDHC** in the absence (black) and presence (red) of $NaBH_4$ in THF.

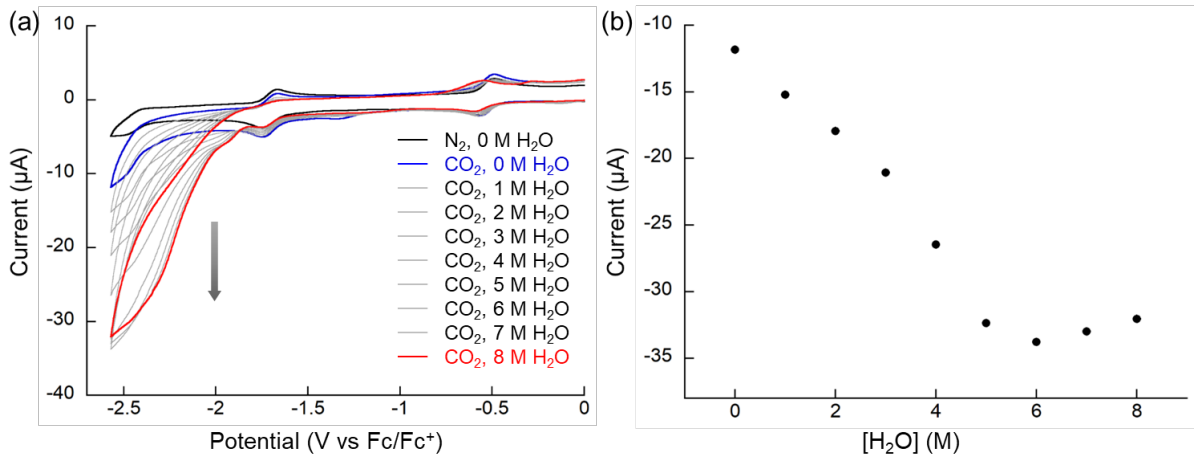

Figure S13. (a) Cyclic voltammograms of **Co(II)TDHC** (0.5 mM) in dry DMF with 0.1 M $TBAPF_6$ at a scan rate of 100 $mV \cdot s^{-1}$ under an N_2 atmosphere (black). Addition of H_2O under a CO_2 atmosphere (from blue to red): $[H_2O]$ = 0, 1, 2, 3, 4, 5, 6, 7 and 8 M. (b) Relationship between the concentration of H_2O and current at −2.57 V in cyclic voltammetry.

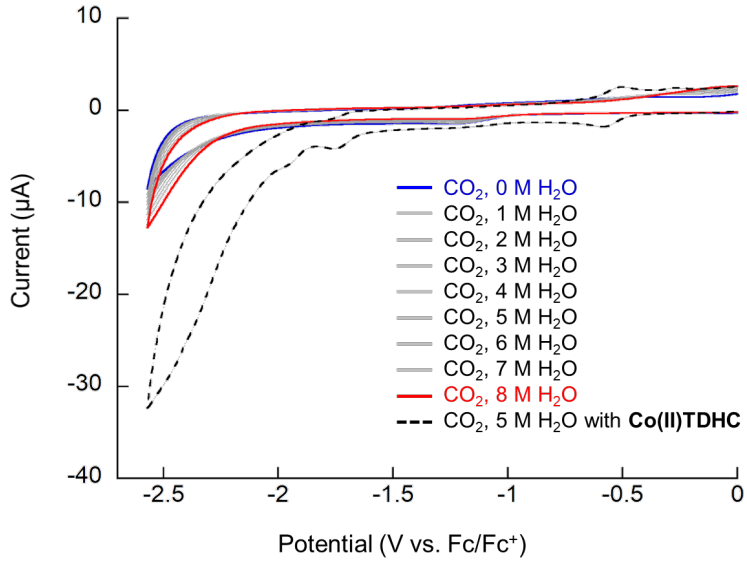

Figure S14. Cyclic voltammograms without catalyst in DMF with 0.1 M $TBAPF_6$ at a scan rate of 100 $mV \cdot s^{-1}$ under a CO_2 atmosphere upon addition of H_2O ranging from 0 M (blue) to 8 M (red). Black dotted line shows the redox behavior of **Co(II)TDHC** (0.5 mM) in the presence of 5 M H_2O under a CO_2 atmosphere.

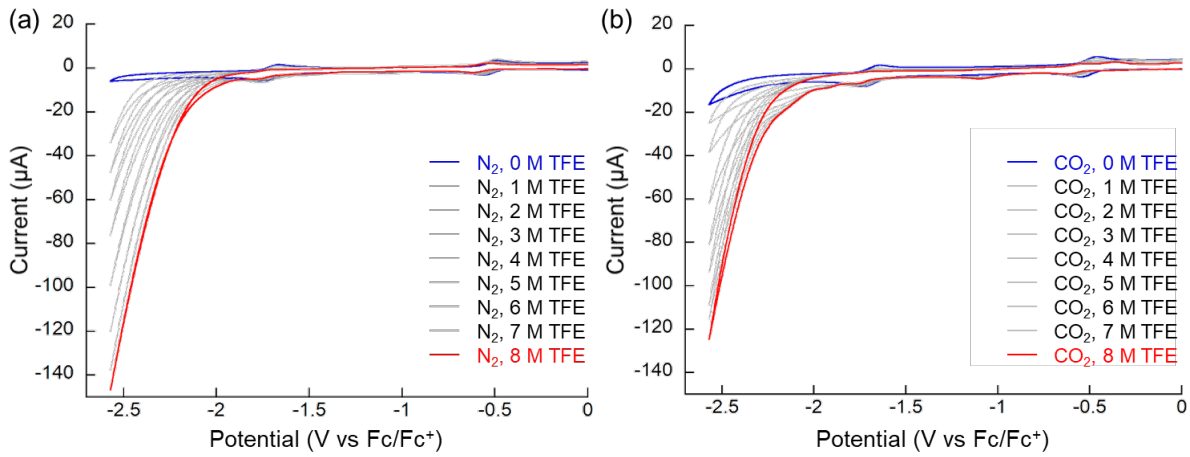

Figure S15. Cyclic voltammograms of **Co(II)TDHC** (0.5 mM) in DMF with 0.1 M $TBAPF_6$ at a scan rate of 100 $mV \cdot s^{-1}$ under (a) an N_2 atmosphere and (b) a CO_2 atmosphere upon addition of 2,2,2-trifluoroethanol (TFE) ranging from 0 M (blue) to 8 M (red).

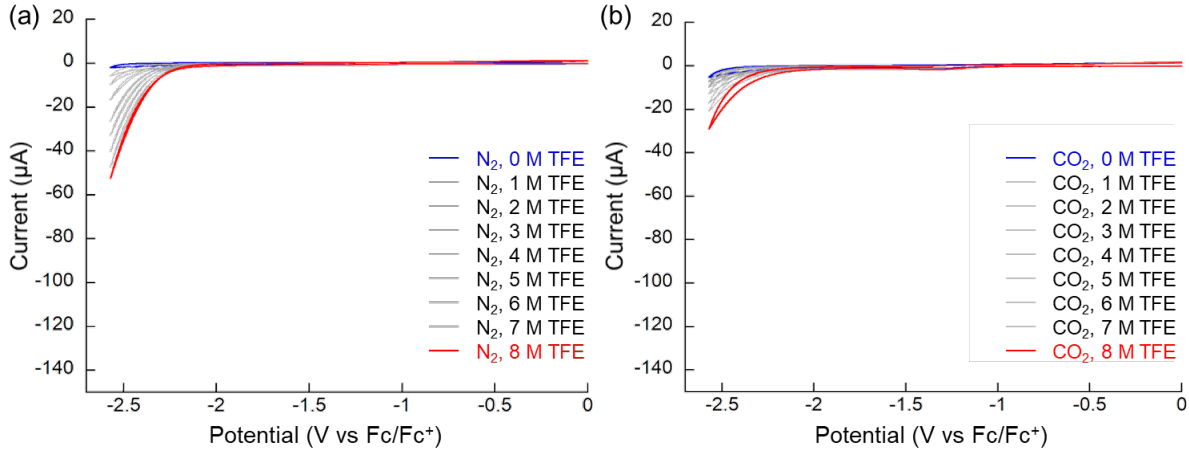

Figure S16. Cyclic voltammograms without catalyst in DMF with 0.1 M $TBAPF_6$ at a scan rate of 100 $mV \cdot s^{-1}$ under (a) an N_2 atmosphere and (b) a CO_2 atmosphere upon addition of TFE ranging from 0 M (blue) to 8 M (red).

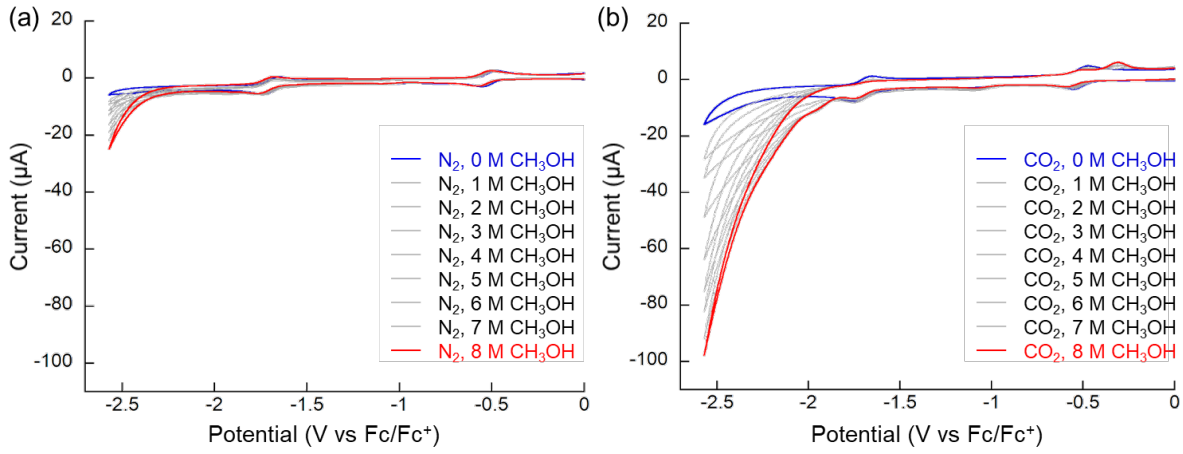

Figure S17. Cyclic voltammograms of **Co(II)TDHC** (0.5 mM) in DMF with 0.1 M $TBAPF_6$ at a scan rate of 100 $mV \cdot s^{-1}$ under (a) an N_2 atmosphere and (b) a CO_2 atmosphere upon addition of CH_3OH ranging from 0 M (blue) to 8 M (red).

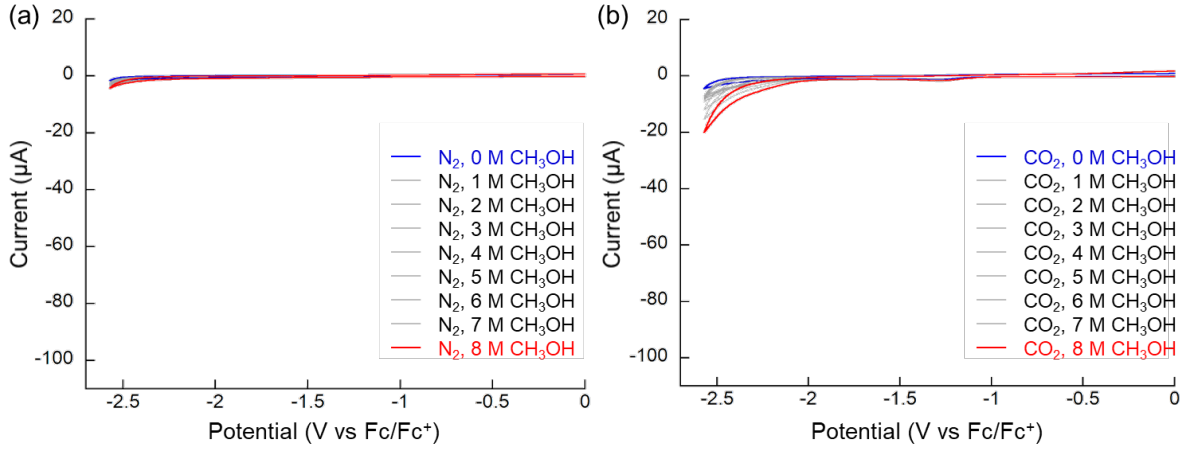

Figure S18. Cyclic voltammograms without catalyst in DMF with 0.1 M $TBAPF_6$ at a scan rate of 100 $mV \cdot s^{-1}$ under (a) an N_2 atmosphere and (b) a CO_2 atmosphere upon addition of CH_3OH ranging from 0 M (blue) to 8 M (red).

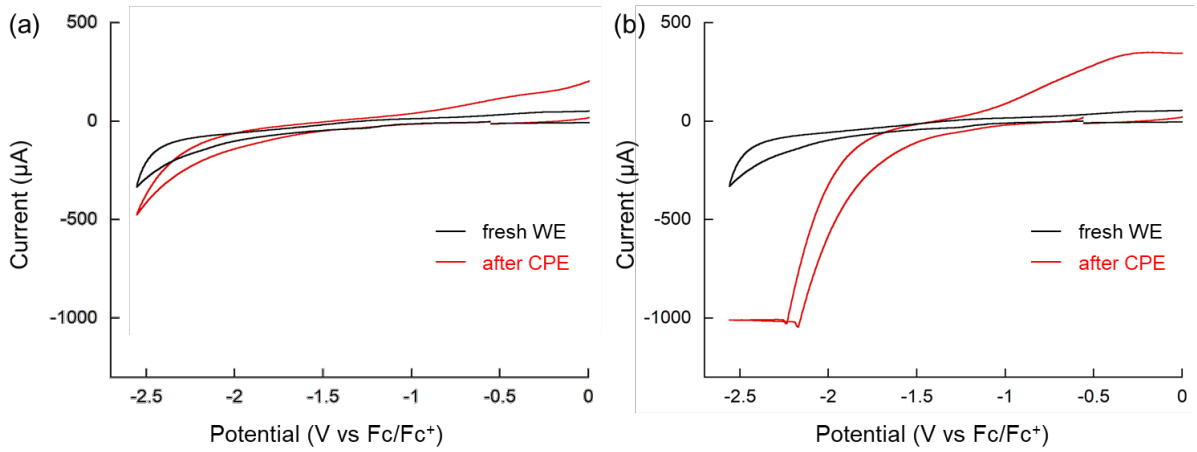

Figure S19. Cyclic voltammograms of the glassy carbon plate electrode (5.8 cm^2 surface area) without catalyst before (black) and after (red) a controlled-potential electrolysis with (a) 2 M H_2O and (b) 3 M H_2O in wet DMF + 0.1 M $TBAPF_6$ solution at a scan rate of 100 $mV \cdot s^{-1}$ under a CO_2 atomosphere. A plateau current in (b) is caused by the limitation of the potentiostat.

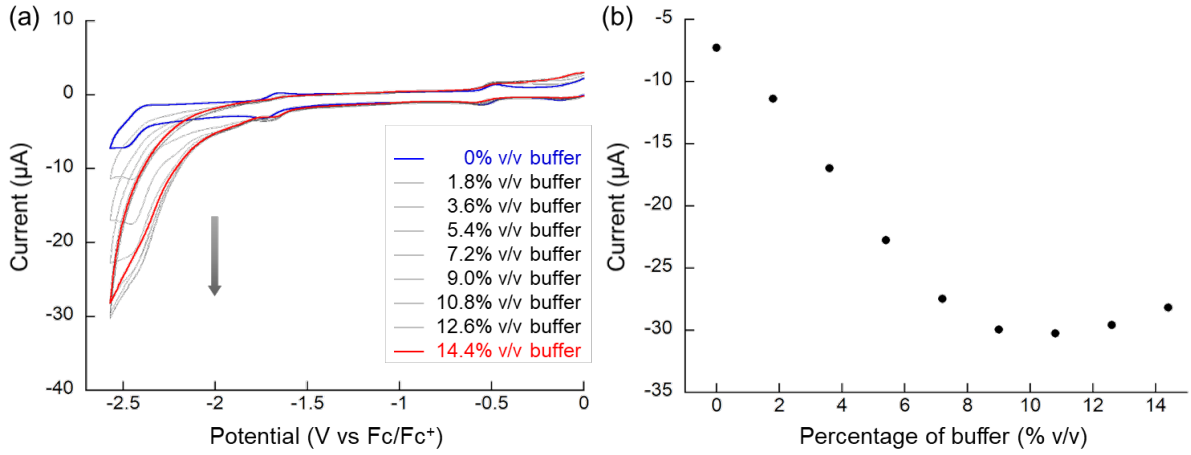

Figure S20. (a) Cyclic voltammograms of **Co(II)TDHC** (0.5 mM) in DMF with 0.1 M $TBAPF_6$ at a scan rate of 100 $mV \cdot s^{-1}$ upon addition of buffer solution under an N_2 atmosphere ranging from 0% v/v (blue) to 14.4% v/v (red). (b) Relationship between the percentage of buffer solution and current at –2.57 V in cyclic voltammetry.

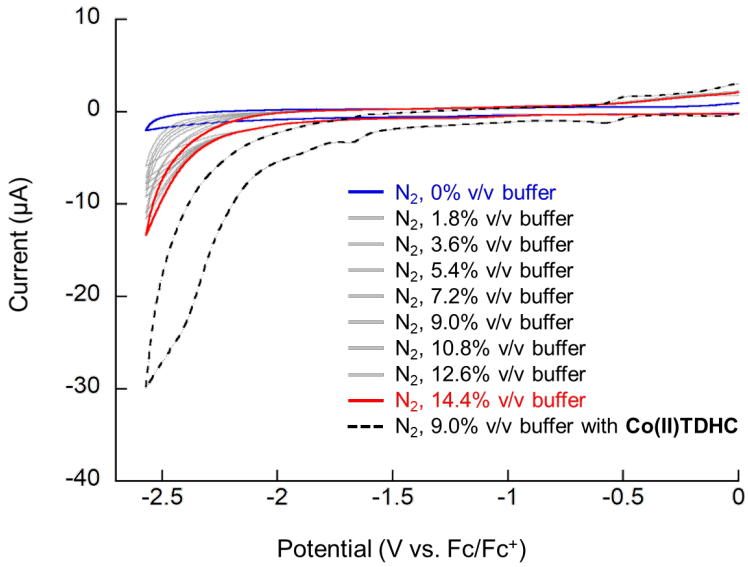

Figure S21. Cyclic voltammograms without catalyst in DMF with 0.1 M $TBAPF_6$ at a scan rate of 100 $mV \cdot s^{-1}$ upon addition of buffer solution under an N_2 atmosphere ranging from 0% v/v (blue) to 14.4% v/v (red). Black dotted line shows the redox behavior of **Co(II)TDHC** (0.5 mM) in the presence of 9.0% v/v buffer solution under an N_2 atmosphere.

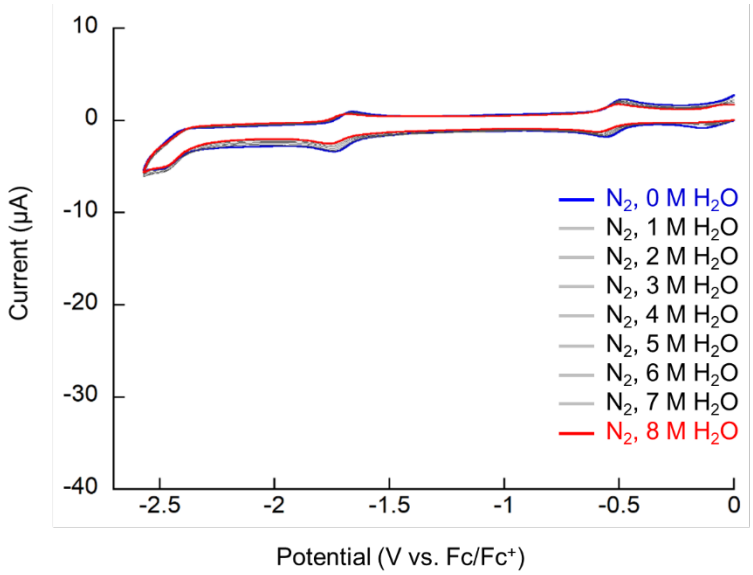

Figure S22. Cyclic voltammograms of **Co(II)TDHC** (0.5 mM) in dry DMF with 0.1 M $TBAPF_6$ at a scan rate of 100 $mV \cdot s^{-1}$ under an N_2 atmosphere upon addition of H_2O ranging from 0 M (blue) to 8 M (red).

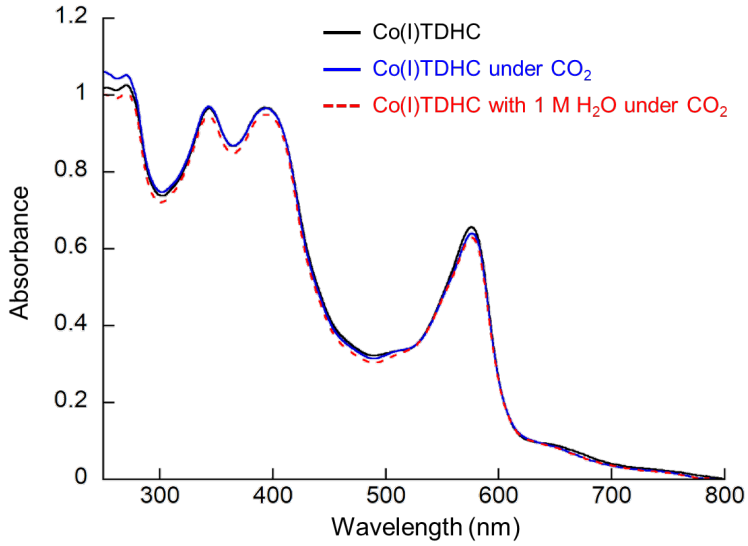

Figure S23. UV-vis absorption spectra of **Co(I)TDHC** generated by $NaBH_4$ reduction under an N_2 atmosphere (black solid), under a CO_2 atmosphere (blue solid) and with 1 M H_2O under a CO_2 atmosphere (red dotted) in THF.