Supporting Information

Terpyridine-metal complexes of first row transition metals and electrochemical reduction of CO_2 to CO

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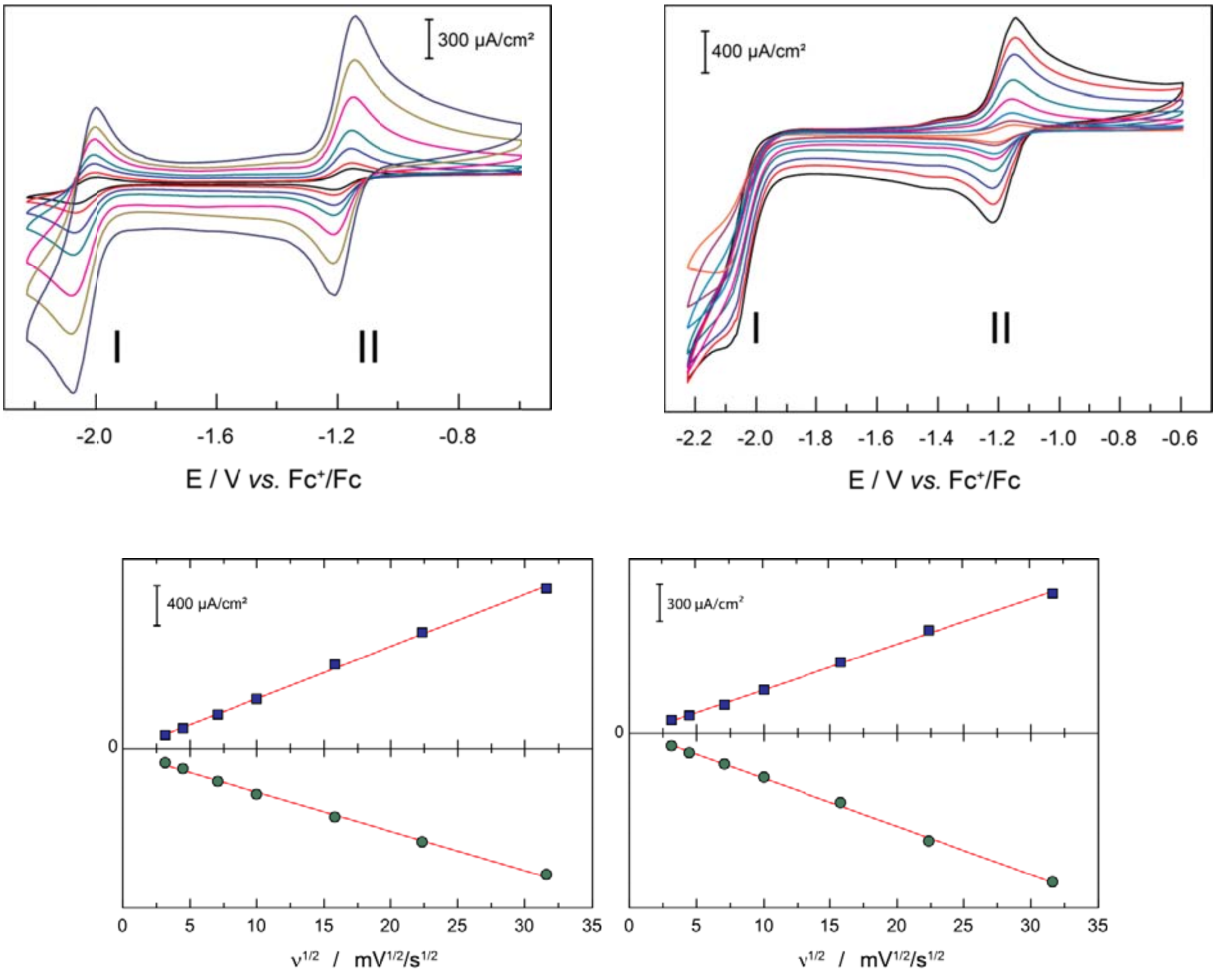


Figure S1. Top left: cyclic voltammograms of a 2 mM solution of **Co-tpy** under argon at 10 (black), 20 (red), 50 (blue), 100 (teal), 250 (pink), 500 (green) and 1000 (dark blue) mV/s. Top right : cyclic voltammograms of a 2 mM CO_2-saturated solution of **Co-tpy** at 10 (orange), 20 (purple), 50 (light blue), 100 (pink), 250 (teal), 500 (dark blue), 750 (red) and 1000 (black) mV/s. The working electrode used was 1 mm diameter glassy carbon electrode, the counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl, 3M KCl reference electrode. The solvent system used was DMF/H_2O (95:5, v:v), with 0.1M of TBAP as supporting electrolyte.

Bottom: i_{pc} (green circles) and i_{pa} (blue squares) curves *vs.* the square root of scan rate ($\nu^{1/2}$) for both of the electrochemical features (I: left; II: right) of **Co-tpy** under inert atmosphere.

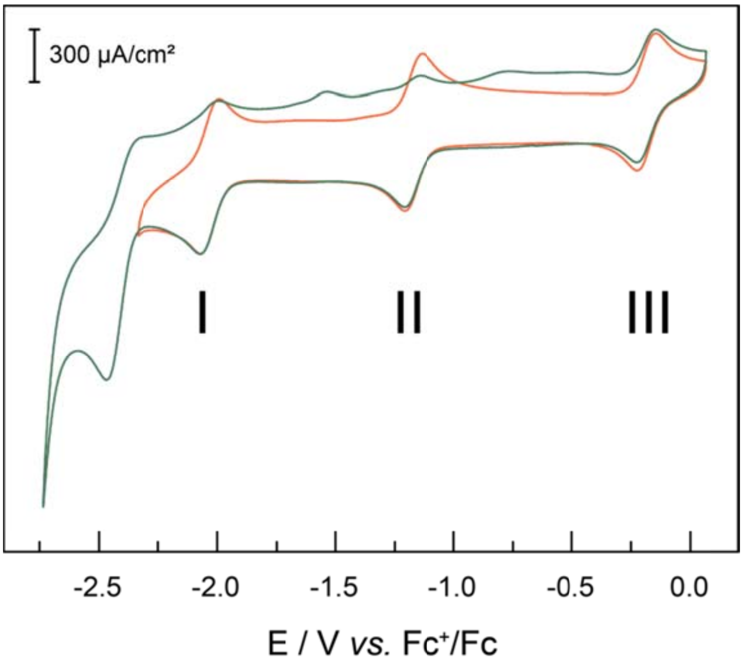


Figure S2. Cyclic voltammograms of a **Co-tpy** solution under N_2 atmosphere in the 0.06 to –2.33 V potential range (orange) and the same solution scanned to –2.73 V (green). Only the third scan is shown in the latter case, as more scans led to degradation. The working electrode used was 1 mm diameter glassy carbon electrode, the counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl, 3M KCl reference electrode. The solvent system used was DMF/H_2O (95:5, v:v), with 0.1M of TBAP as supporting electrolyte.

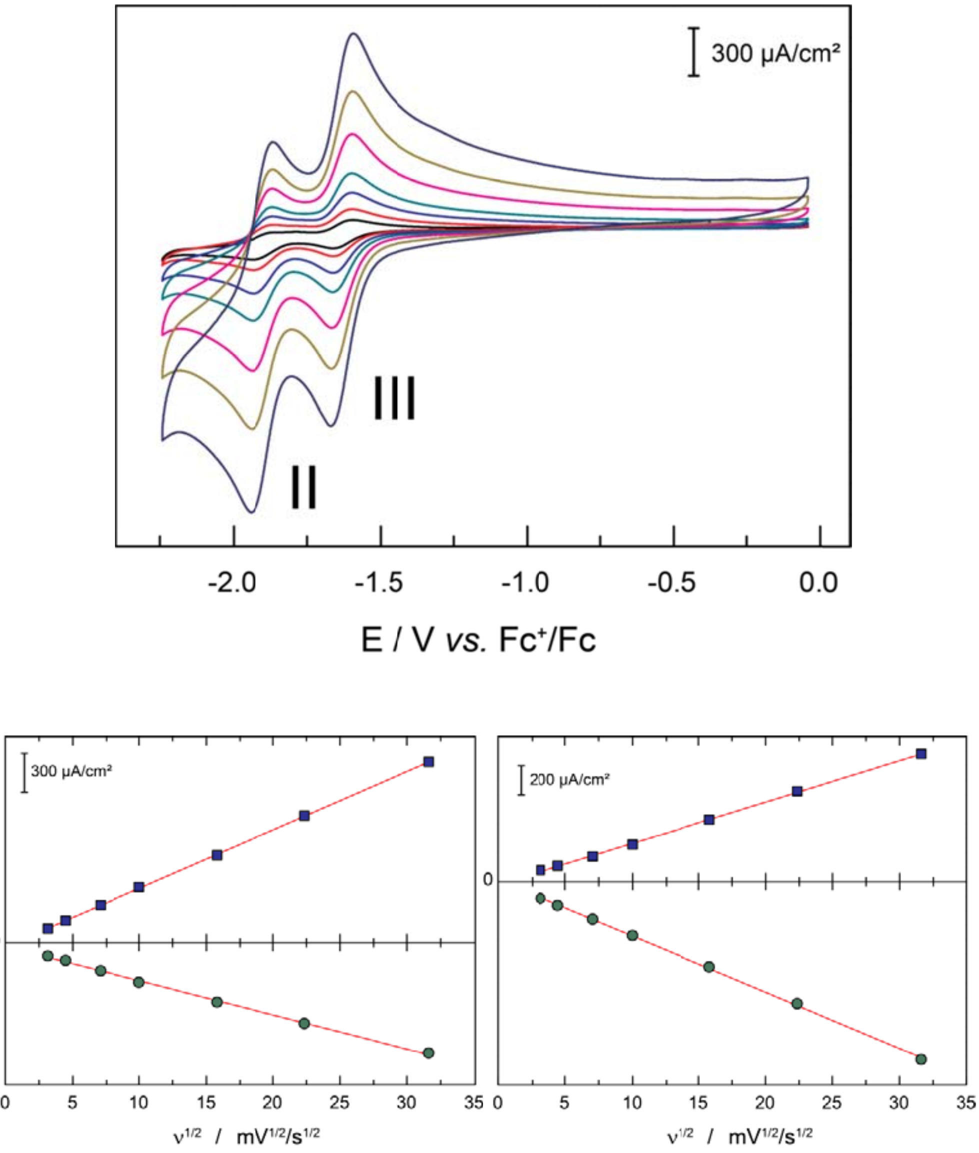


Figure S3. Top: cyclic voltammograms of a 2 mM N_2-saturated solution of **Ni-tpy** at 10 (black), 20 (red), 50 (blue), 100 (teal), 250 (pink), 500 (green) and 1000 (dark blue) mV/s. Bottom: i_{pc} (green circles) and i_{pa} (blue squares) curves *vs.* the square root of scan rate for the ($\nu^{1/2}$) for both of the electrochemical features (II: left; III: right). The working electrode used was 1 mm diameter glassy carbon electrode, the counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl, 3M KCl reference electrode. The solvent system used was DMF/H_2O (95:5, v:v), with 0.1M of TBAP as supporting electrolyte.

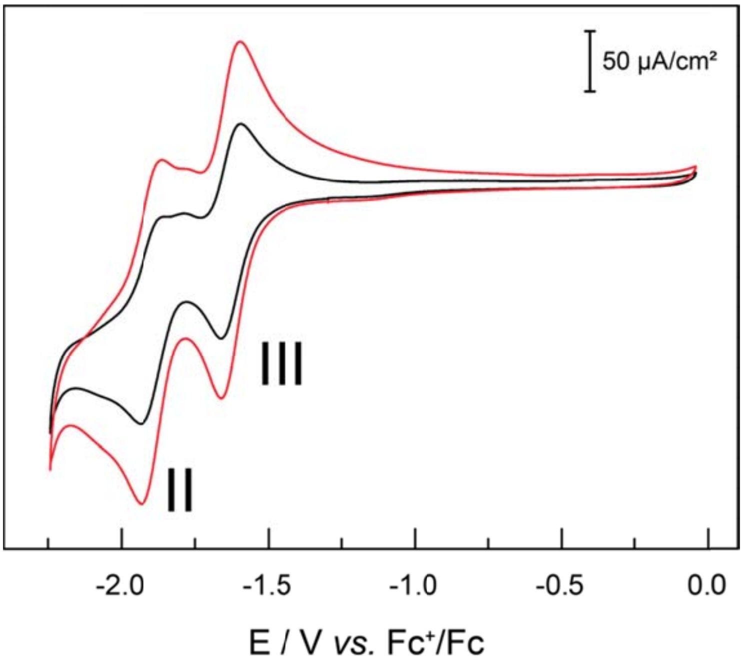


Figure S4. Cyclic voltammograms of a 2 mM N_2-saturated solution of **Ni-tpy** at slow scan rates (10 mV/s, black; 20 mV/s, red). The working electrode used was 1 mm diameter glassy carbon electrode, the counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl, 3M KCl reference electrode. The solvent system used was DMF/H_2O (95:5, v:v), with 0.1M of TBAP as supporting electrolyte.

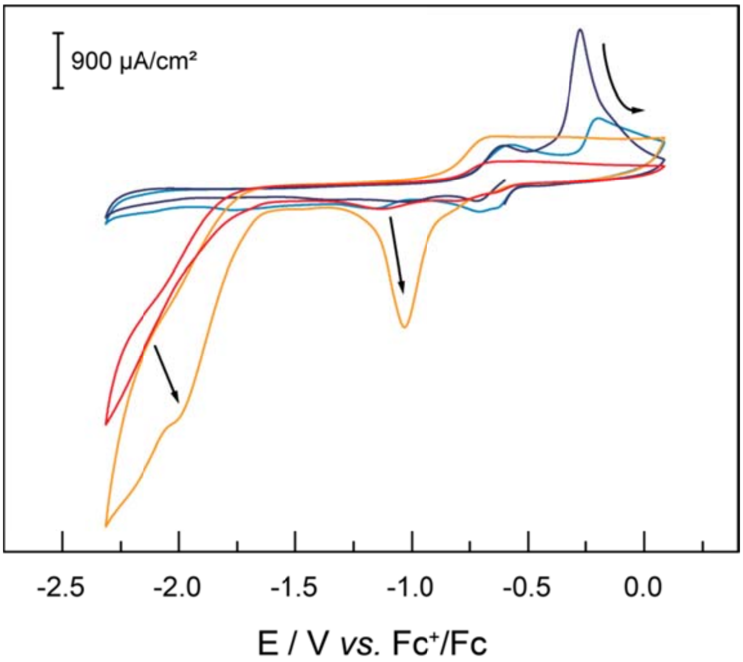


Figure S5. Cyclic voltammograms of a 2 mM solution of **Cu-tpy** at 100 mV/s under argon (light blue: scan 1; dark blue: scan 38) and under a CO_2 atmosphere (red: scan 1; orange: scan 38). The working electrode used was 1 mm diameter glassy carbon electrode, the counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl, 3M KCl reference electrode. The solvent system used was DMF/H_2O (95:5, v:v), with 0.1M of TBAP as supporting electrolyte.

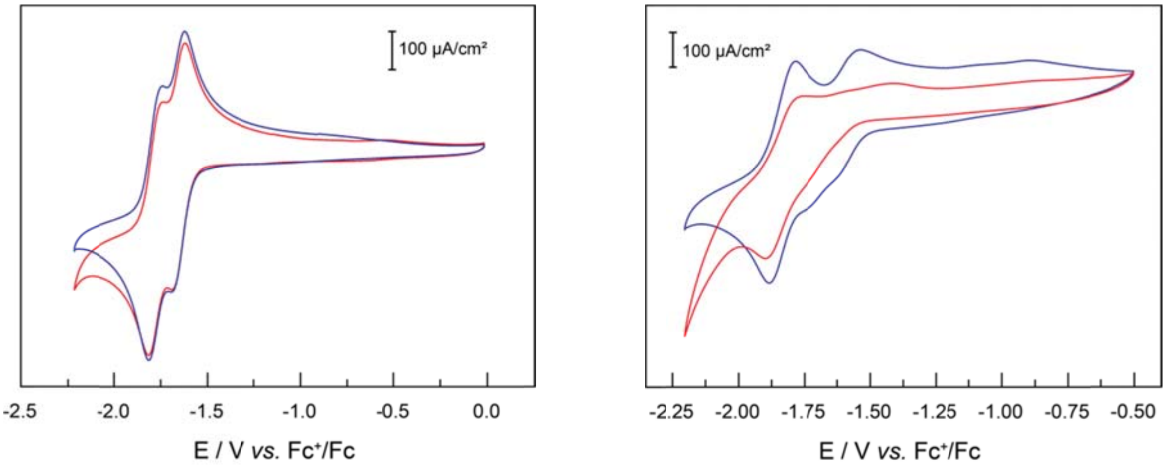


Figure S6. Cyclic voltammograms under argon of 2 mM solutions of **Fe-tpy** (left) and **Mn-tpy** (right) at 100 mV/s (blue) and CO_2 (red) atmospheres. The working electrode used was 1 mm diameter glassy carbon electrode, the counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl, 3M KCl reference electrode. The solvent system used was DMF/H_2O (95:5, v:v), with 0.1M of TBAP as supporting electrolyte.

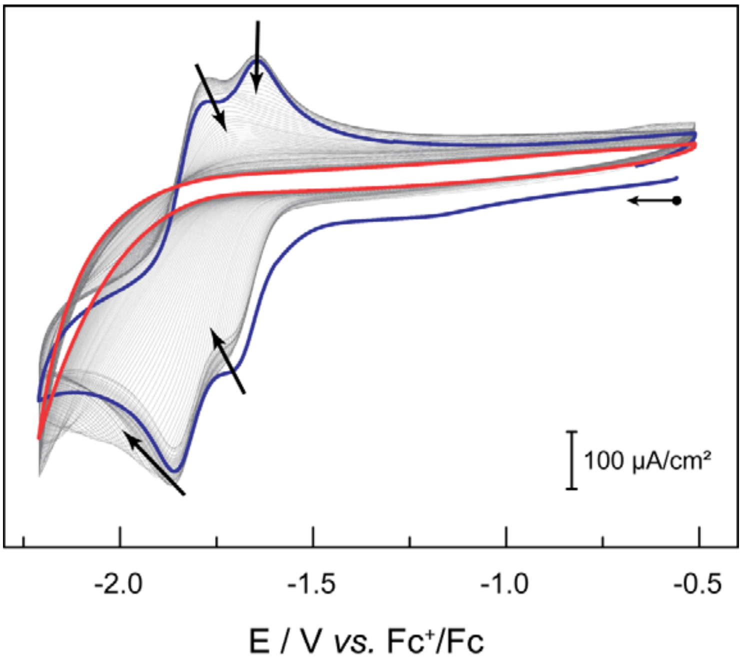


Figure S7. Cyclic voltammograms of a 2 mM N_2-saturated solution of **Zn-tpy** and its evolution as the number of scans is increased. The working electrode used was 1 mm diameter glassy carbon electrode, the counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl, 3M KCl reference electrode. The solvent system used was DMF/H_2O (95:5, v:v), with 0.1M of TBAP as supporting electrolyte. The first scan is represented in blue and the last scan in red. Arrows indicate the evolution of the electrochemical features.

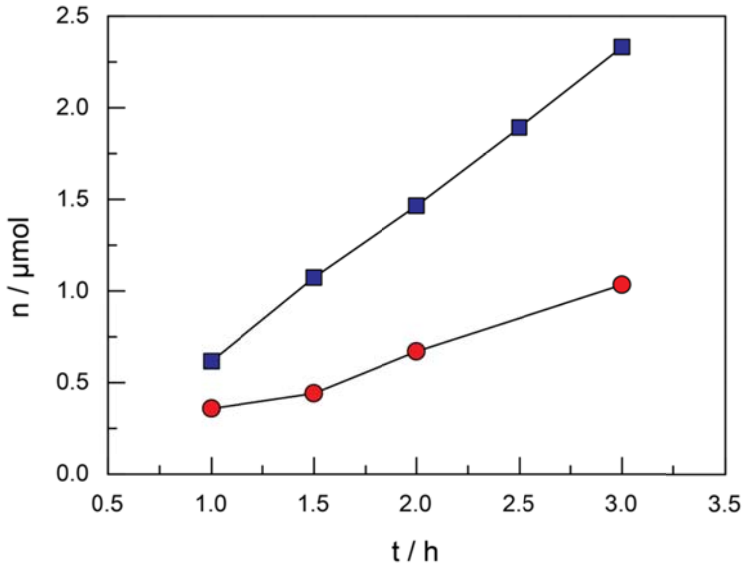


Figure S8. Total moles of H_2 (red circles) and CO (blue squares) measured in the headspace during the electrolysis of a 2 mM solution of **Co-tpy** at –2.03 V *vs.* Fc^+/Fc under a CO_2 atmosphere. The working compartment of the bulk electrolysis consisted of 10 mL of DMF/H_2O (95:5, v:v), with 0.1M TBAP as supporting electrolyte and a 1.5 cm diameter pool of mercury as the working electrode. The cell used is described in Figure S20.

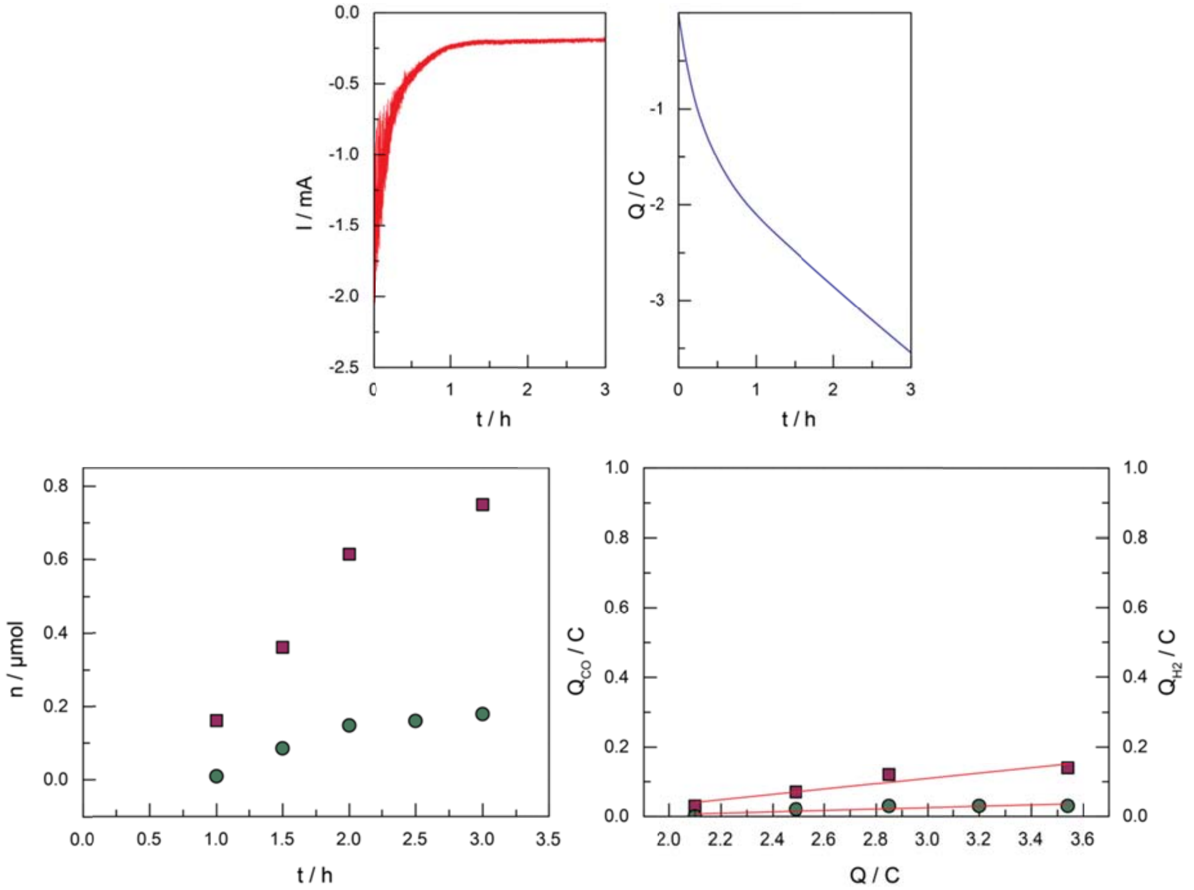
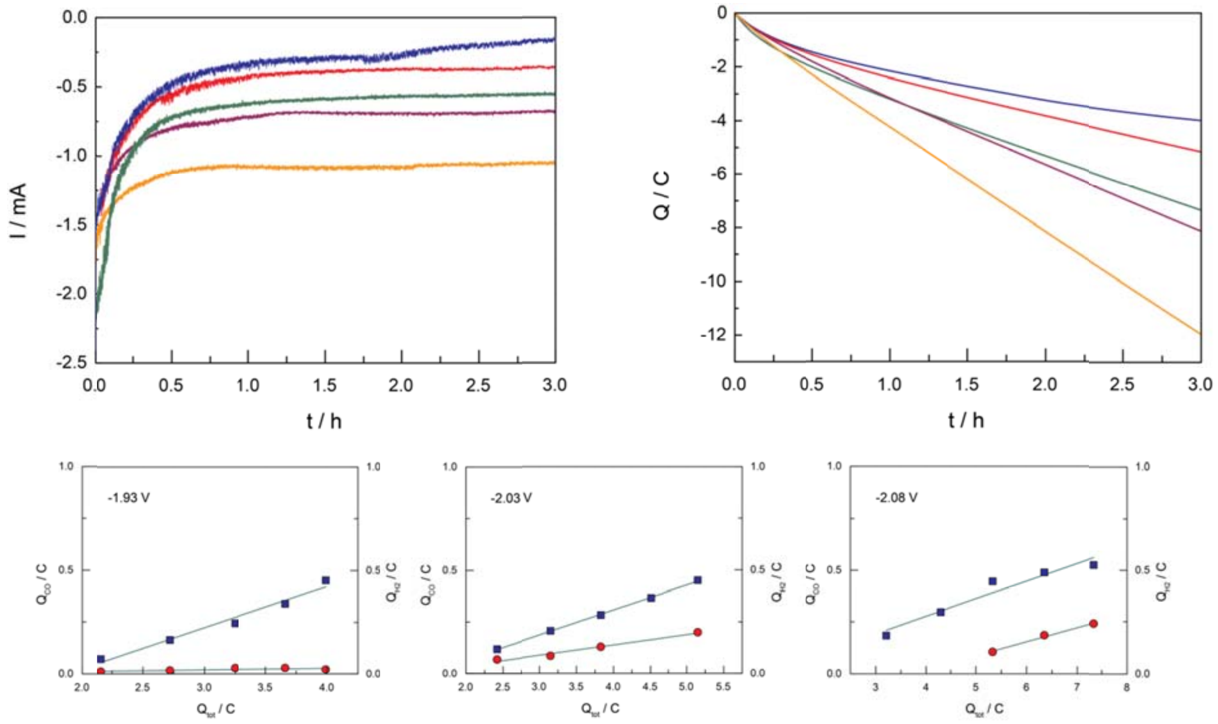
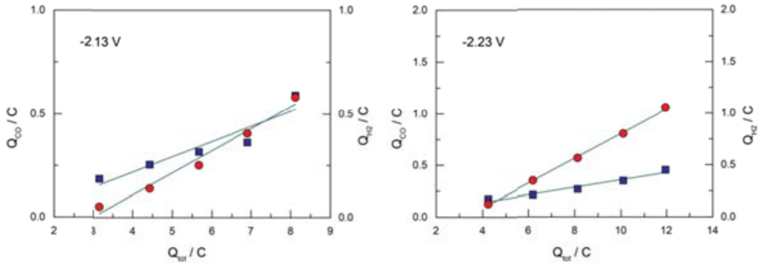


Figure S9. Top: current (left, red) and charge (right, blue) measured during a controlled-potential electrolysis of a 2 mM **Co-tpy** CO_2-saturated solution in 10 mL of anhydrous DMF, with 0.1 M of TBAP as supporting electrolyte. The bulk electrolysis cell, described in Figure S20, uses a 1.5 cm diameter pool of mercury as the working electrode. Data was recorded every 0.2 s and the current intensity data was smoothed using an adjacent-averaging method over 4 s. Bottom: total moles of CO (purple squares) and H_2 (green circles) measured in the headspace during the electrolysis (left) and charge corresponding to the products measured *vs.* the total charge passed during the electrolysis (right). The slope of the linear fit, corresponding to the faradic efficiency, is 8% for CO and 2% for H_2.





	CO	H_2
−1.93 V	20%	1%
−2.03 V	12%	5%
−2.08 V	9%	7%
−2.13 V	7%	11%
−2.23 V	3%	12%

Figure S10. Current (Top left) and charge (Top right) measured during controlled-potential electrolyses of 2 mM **Co-tpy** CO_2-saturated solutions at different applied potentials (blue: −1.93 V, red: −2.03 V, green: −2.08 V, purple: −2.13 V and orange: −2.23 V). Bulk electrolyses were performed in 10 mL of DMF/H_2O (95:5, v:v), with 0.1M TBAP, using a 1.5 cm diameter pool of mercury as the working electrode. The cell used is described in Figure S20. Data was recorded every 0.2 s and the current intensity data was smoothed using an adjacent-averaging method over 4 s. Bottom: Charge corresponding to the products measured (CO: blue squares, H_2: red circle) *vs.* the total charge passed during the electrolyses. The slopes of the linear fits, corresponding to the faradic efficiencies, are given in the table.

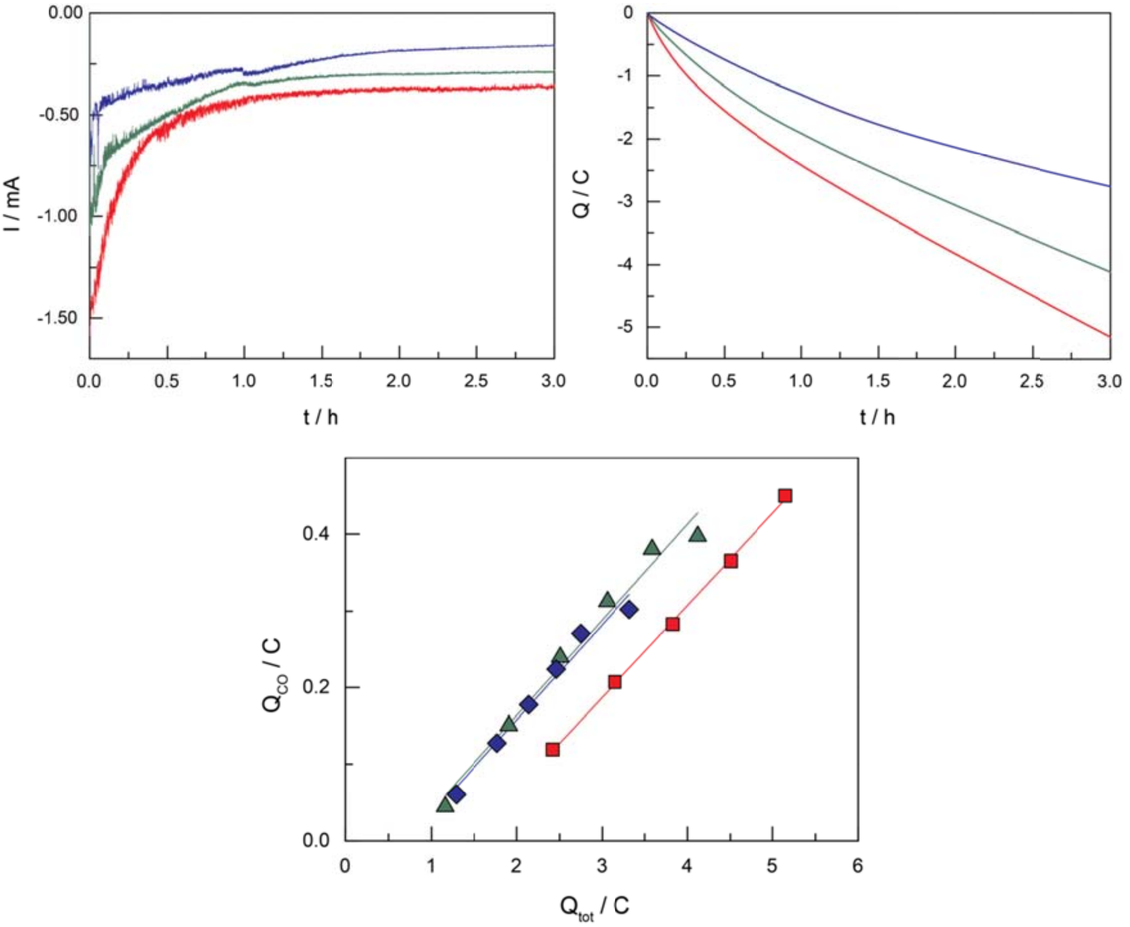
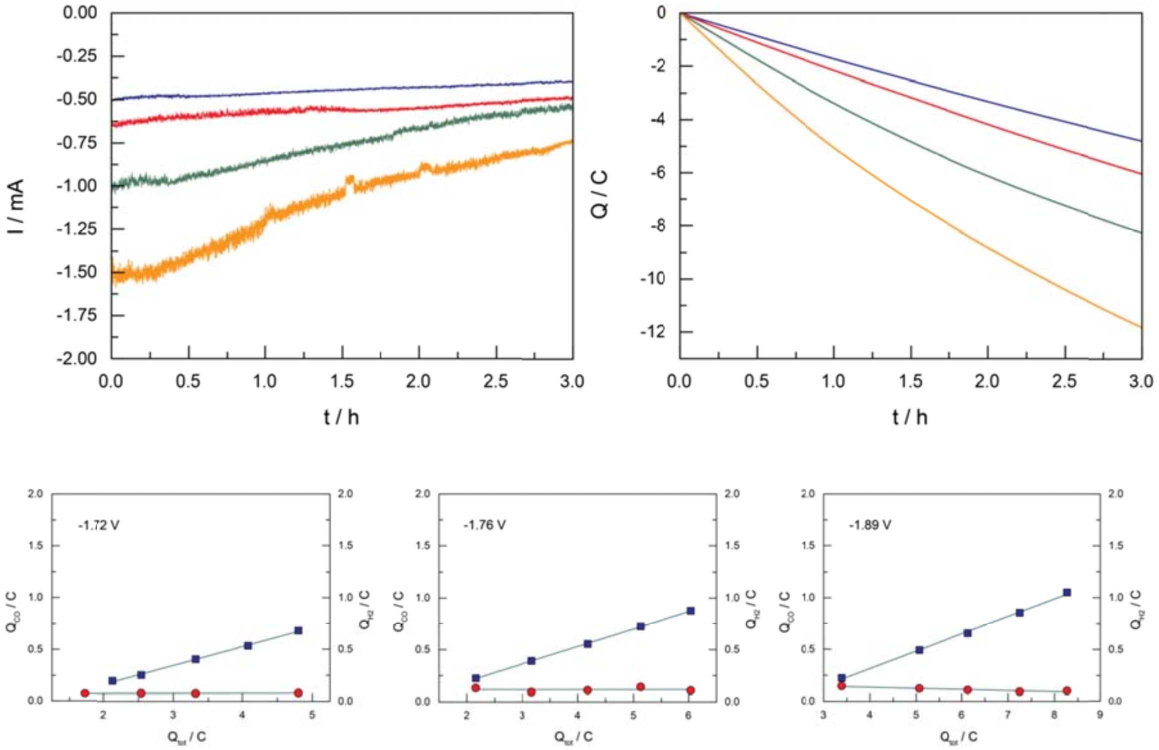
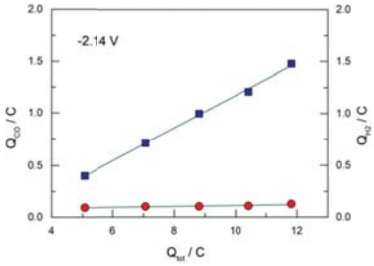


Figure S11. Current (Top left) and charge (Top right) measured during controlled-potential electrolyses of **Co-tpy** CO_2-saturated solutions at –2.03 V using *N,N*-diethylformamide (DEF) (green, 1 mM **Co-tpy**), 1-methyl-2-pyrrolidinone (NMP) (blue, 1 mM **Co-tpy**) and DMF (red, 2 mM **Co-tpy**) as primary solvent. Bulk electrolyses were performed in 10 mL of a mixture of DEF, NMP or DMF respectively with 5% of H_2O, with 0.1M TBAP as supporting electrolyte, using a 1.5 cm diameter pool of mercury as the working electrode. The cell used is described in Figure S20. Data was recorded every 0.2 s and the current intensity data was smoothed using an adjacent-averaging method over 4 s. Bottom: Charge corresponding to the CO produced (in DMF: red squares, DEF: green triangles and NMP: blue diamonds) *vs.* the total charge passed during the electrolyses. The slope of the linear fits, corresponding to the faradic efficiency, is 12% in the three cases.





	CO	H_2
−1.72 V	18%	0%
−1.76 V	17%	0%
−1.89 V	17%	0%
−2.14 V	16%	0%

Figure S12. Current (Top left) and charge (Top right) measured during controlled-potential electrolyses of 2 mM **Ni-tpy** CO_2-saturated solutions at different applied potentials (blue: −1.72 V, red: −1.76 V, green: −1.89 V and orange: −2.14 V). Bulk electrolyses were performed in 10 mL of DMF/H_2O (95:5, v:v), with 0.1M TBAP, using a 1.5 cm diameter pool of mercury as the working electrode. The cell used is described in Figure S20. Data was recorded every 0.2 s and the current intensity data was smoothed using an adjacent-averaging method over 4 s. Bottom: Charge corresponding to the products measured (CO: blue squares, H_2: red circle) *vs.* the total charge passed during the electrolyses. The slopes of the linear fits, corresponding to the faradic efficiencies, are given in the table.

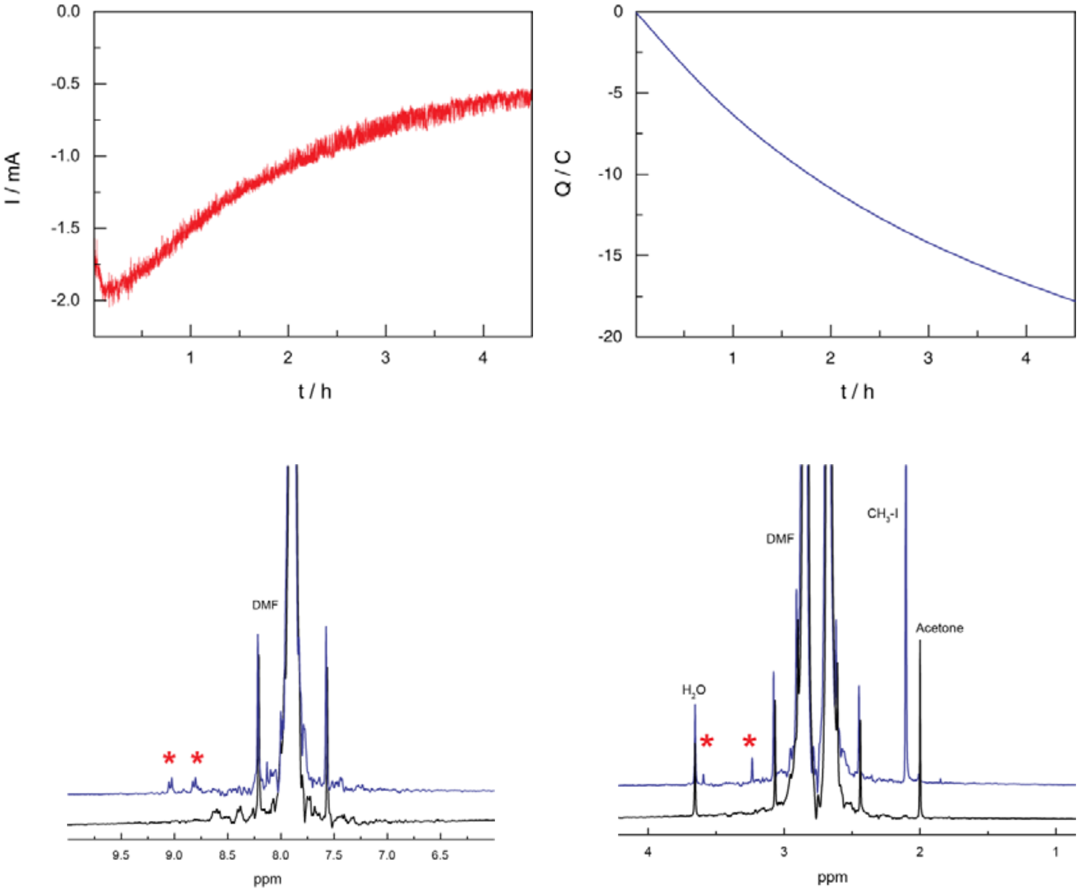


Figure S13. Current (Top left) and charge (Top right) measured during controlled-potential electrolyses of 5 mM **Zn-tpy** CO_2-saturated solutions at –2.15 V. Bulk electrolyses were performed in 10 mL of DMF/D_2O (95:5, v:v), with 0.1M $LiClO_4$, using a 1.5 cm diameter pool of mercury as the working electrode. The cell used is described in Figure S20. Data was recorded every 0.2 s and the current intensity data was smoothed using an adjacent-averaging method over 4 s.

Bottom: At the end of the bulk electrolysis, 200 μL of iodomethane (3.2 mmol) was added trough the septum of the electrochemical cell and the solution was stirred at room temperature for 1h30min. The aliphatic (right) and aromatic (left) regions of ^1H NMR spectra before the addition of CH_3I (black) and after reaction with CH_3I (blue) are presented here. The spectra have been referenced to the aldehyde proton of DMF (7.9 ppm). The Red stars mark the appearance of new peaks after reaction with CH_3I.

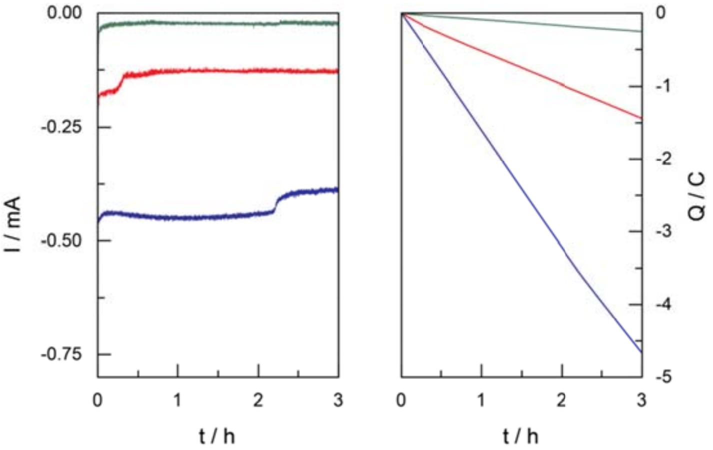


Figure S14. Current (left) and charge (right) measured during controlled-potential electrolyses of 4 mM terpyridine solutions. Electrolyses carried out at –2.03 V under Ar (green) and CO_2 (red) and at –2.23 V under CO_2 (blue). Bulk electrolyses were performed in 10 mL of DMF/H_2O (95:5, v:v), with 0.1M TBAP, using a 1.5 cm diameter pool of mercury as the working electrode. The cell used is described in Figure S20. Data was recorded every 0.2 s and the current intensity data was smoothed using an adjacent-averaging method over 4 s.

Steady State Photolysis Details. Photochemical Reactions were performed using a 300 W, high pressure Hg/Xe arc lamp (Oriel Instruments). The beam was passed through an infrared filter, a collimating lens, a filter holder equipped with a 415 nm band pass filter, and an iris. Samples were prepared in a 1 cm path length quartz cuvette (Starna) which was placed in a temperature controlled cuvette holder (Quantum Northwest) maintained at 20°C with a circulated water bath.

Sample preparation involved the use of a 5:1 volumetric ratio of acetonitrile-d_3 to triethanolamine. This solvent system was chosen due to practical considerations regarding deuterated solvent accessibility. The solvent mixture was used to prepare a 4.0 mM stock solution of $Ru(bpy)_3Cl_2(H_2O)_6$ and a 2.0 mM stock solution of **Zn-tpy**. For photolysis including **Zn-tpy**, two samples were made in tandem, each of which included 0.4 mL of the **Zn-tpy** stock solution mixed with 0.4 mL of the $Ru(bpy)_3Cl_2(H_2O)_6$ stock solution within the quartz cuvette. The resulting 0.8 mL solution (2.0 mM $Ru(bpy)_3Cl_2(H_2O)_6$ and 1.0 mM **Zn-tpy**) was saturated with CO_2 via vigorous bubbling of CO_2 through the solution for 15 minutes through a cuvette cap with a septum. One of the samples prepared was then photolyzed for 6 hours while the other was placed in the dark for the same length of time. Upon completion the reaction mixtures were pipetted from the quartz cuvette into an NMR tube for analysis via ^1H NMR. Photolysis samples including only $Ru(bpy)_3Cl_2(H_2O)_6$ were prepared and treated in an analogous manner with the 0.4 mL of **Zn-tpy** stock solution being replaced by 0.4 mL of the solvent mixture.

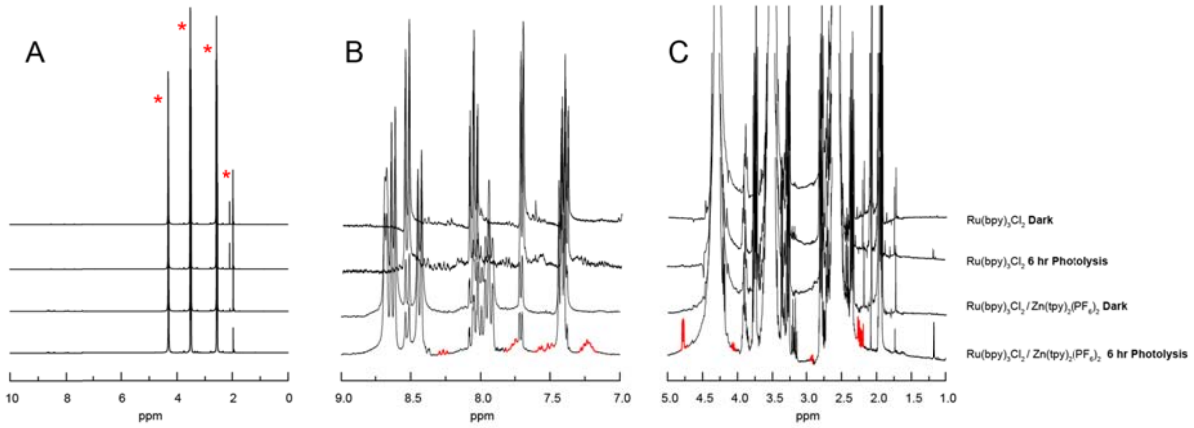


Figure S15. ^1H NMR spectra for the photolysis of experiments of 1.0 mM **Zn-tpy** in the presence of 2.0 mM $Ru(bpy)_3Cl_2(H_2O)_6$ in a CO_2-saturated 5:1 volumetric ratio of acetonitrile-d_3 to triethanolamine. (a-c) From top to bottom, the spectra represent $Ru(bpy)_3Cl_2(H_2O)_6$ in the dark; $Ru(bpy)_3Cl_2(H_2O)_6$ photolyzed; both $Ru(bpy)_3Cl_2(H_2O)_6$ and **Zn-tpy** in the dark; and both $Ru(bpy)_3Cl_2(H_2O)_6$ and **Zn-tpy** photolyzed. (a) The full spectra are shown with the intense peaks associated with TEOA marked by *. (b) Aromatic resonances are shown with peaks only observed post-photolysis of **Zn-tpy** presented in red. (c) Aliphatic resonances are shown with peaks only observed post-photolysis of **Zn-tpy** presented in red.

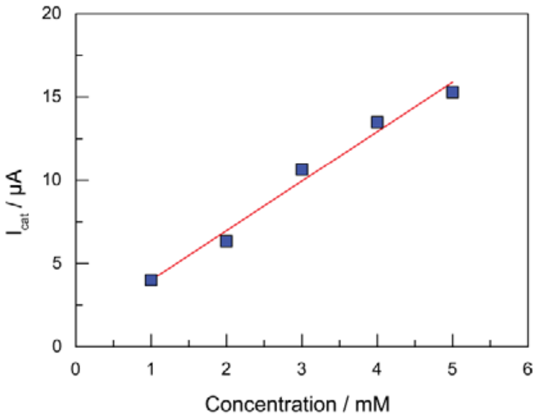
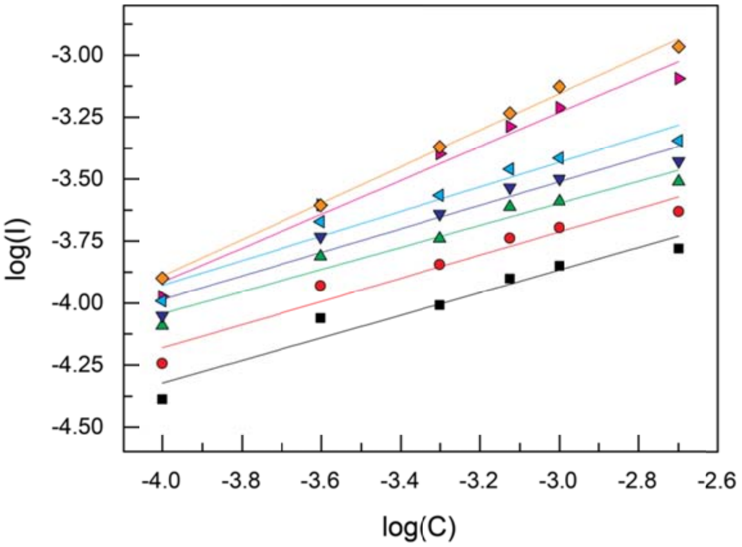


Figure S16. Variation of I_{cat} with the concentration of **Co-tpy** in CO_2-saturated solutions during cyclic voltammetry experiments at 50 mV/s. The working electrode used was 1 mm diameter glassy carbon electrode, the counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl, 3M KCl reference electrode. The solvent system used was DMF/H_2O (95:5, v:v), with 0.1M of TBAP as supporting electrolyte. The correlation coefficient of the linear fit (red) is 0.98.



Applied potential	Apparent order in Cobalt	correlation coefficient
−1.97 V	0.46	0.93
−1.99 V	0.47	0.93
−2.02 V	0.44	0.95
−2.04 V	0.47	0.93
−2.07 V	0.50	0.94
−2.17 V	0.68	0.97
−2.27 V	0.74	0.99

Figure S17. Plot of the log(current(A)) *vs.* the log(concentration(mol/L)) obtained in 6 controlled-potential electrolyses of **Co-tpy** CO_2-saturated solutions at different concentrations of **Co-tpy** where the potential was first held at –2.03 V until the current reached the plateau region and then varied in a step manner every 30 min and the plateau current at each potential was recorded (yellow diamonds: –2.27 V, pink triangles: –2.17 V, light blue triangles: –2.07 V, dark blue triangles: –2.04 V, green triangles: –2.02 V, red circles: –1.99 V, black squares: –1.97 V). Bulk electrolyses were performed in 10 mL of DMF/H_2O (95:5, v:v), with 0.1M TBAP, using a 1.5 cm diameter pool of mercury as the working electrode. In an effort to obtain activation controlled conditions, the solution above the pool of mercury was stirred as vigorously as possible without disrupting the surface of the mercury electrode. The cell used is described in Figure S20. Current values were corrected for the values observed in a solution without **Co-tpy**, at each given potential. The slope of the linear fits, corresponding to the apparent order in Cobalt under bulk electrolyses conditions, is given in the table.

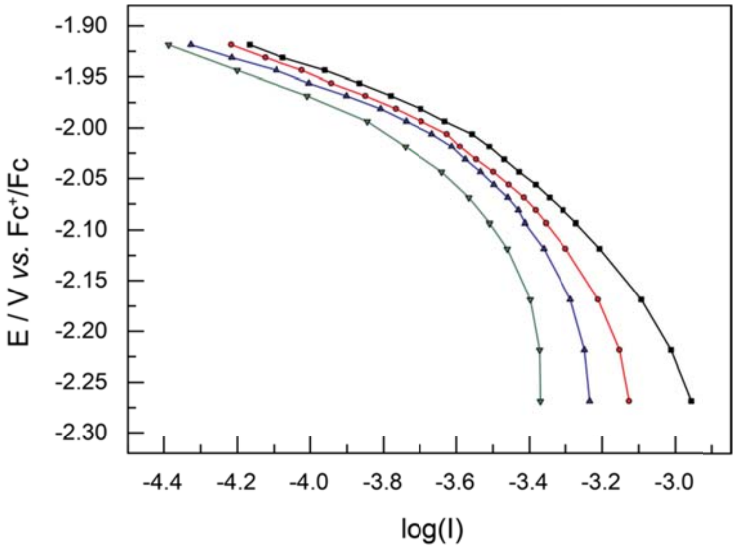


Figure S18. Plot of applied potential *vs.* log(current(A)) extracted from the experiments described in Figure S17 (black squares: 2 mM, red circles: 1 mM, blue triangles: 0.75 mM and green triangles: 0.5 mM of **Co-tpy**). At all **Co-tpy** concentrations, the slope of the linear fit (not represented) of the –1.9 V to –2.1 V region is ~135 mV/dec).

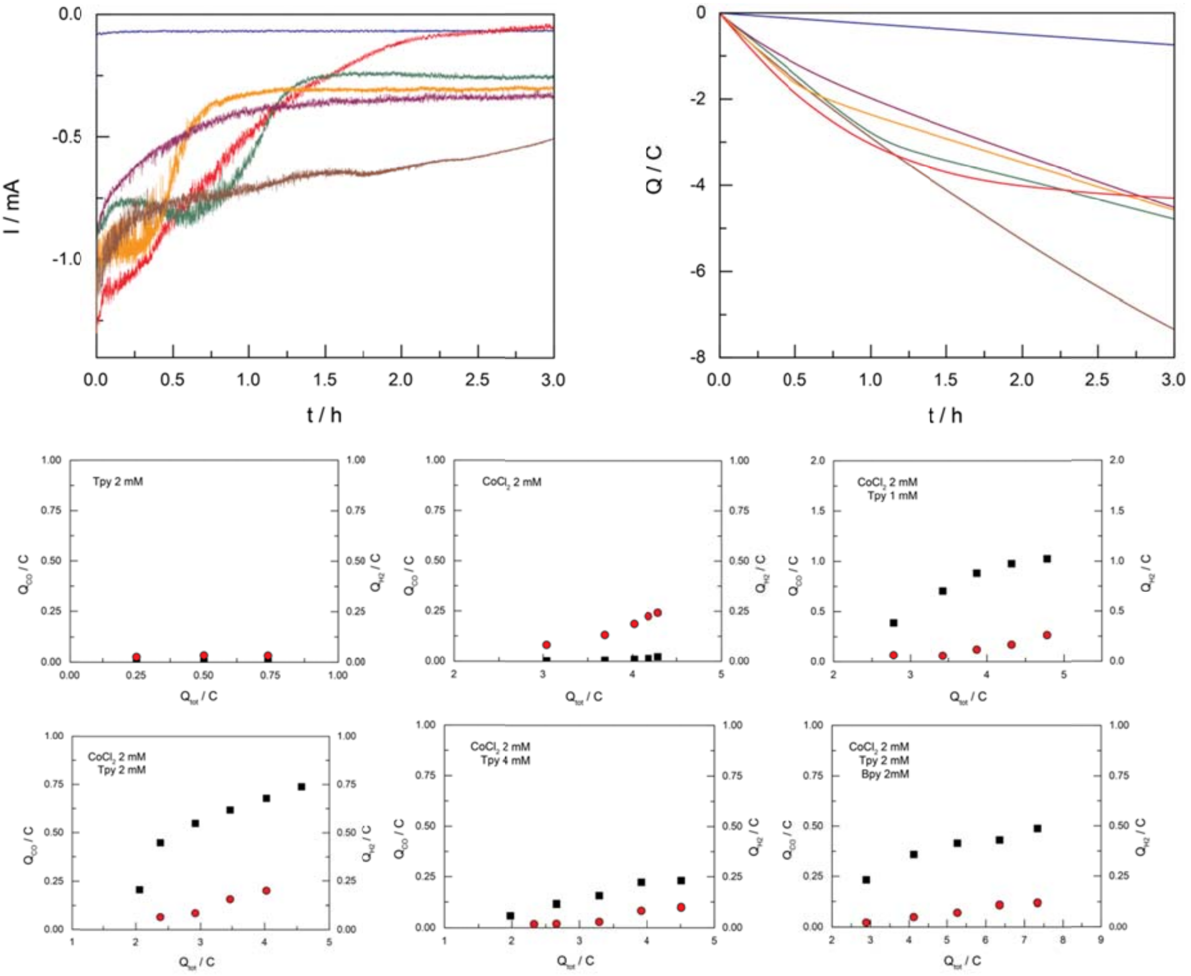


Figure S19. Top: current (left) and charge (right) measured during controlled-potential electrolyses of CO_2-saturated solutions at –2.03 V of: 2 mM tpy (blue), 2 mM $CoCl_2$ (red), 2 mM tpy and 2 mM $CoCl_2$ (yellow), 4 mM tpy and 2 mM $CoCl_2$ (purple), 1 mM tpy and 2 mM $CoCl_2$ (green) and a mixture of 2 mM $CoCl_2$, 2 mM tpy and 2mM bpy (brown). Data was recorded every 0.2 s and the current intensity data was smoothed using an adjacent-averaging method over 4 s. Bulk electrolyses were performed in 10 mL of DMF/H_2O (95:5, v:v), with 0.1M TBAP, using a 1.5 cm diameter pool of mercury as the working electrode. The cell used is described in Figure S20. Bottom: charge corresponding to the products measured (CO: black squares, H_2: red circle) *vs.* the total charge passed during the electrolyses.

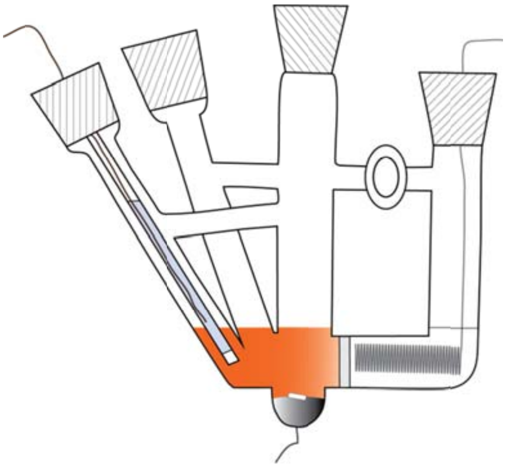


Figure S20. Schematic representation of the electrochemical cell used for bulk electrolyses. The working compartment (10 mL, orange), on the left, contains the 1.5 cm diameter pool of mercury used as working electrode and the Ag/AgCl, 3M KCl reference electrode. The working and reference electrodes are separated from the coiled platinum wire counter electrode by a porous glass frit. The solution is constantly stirred with a small stir bar floating over the pool of mercury. The electrochemical cell is gas tight, and the headspace can be sampled through rubber septa using gas tight syringes for gaseous products analyses. An additional glassy carbon electrode can be fitted through one of the septa for direct cyclic voltammetry experiments of the bulk solution.

Sample Foot of the Wave Calculation

Constants

R = Gas Constant = 8.31446 (C V)/(mol K)

T = Temperature = 297 K

F = Faradays Constant = 96485.34 C/mol

Variables

i^o_p = peak current in the absence of substrate (CO_2)

i = current measured under catalytic conditions

v = scan rate of CV in V/s

C^o_A = Concentration of substrate (CO_2) in the bulk solution in mol/L

E = applied potential in V

E^o_{PQ} = $(E_{pa}+E_{pc})/2$ measured for reaction couple ($Co(tpy)_2^+/Co(tpy)_2$) in the absence of CO_2 in V

E^o_{AB} = potential for CO_2 reduction to CO under conditions used in V

η = overpotential in V

k_2 = second order rate constant

k_{ap} = pseudo-first order rate constant under excess of CO_2

TOF_0 = Turnover Frequency at 0 applied overpotential

TOF = Turnover Frequency at a specified overpotential

Values of Variables set by Experiment or Estimated from Literature

v = 0.250 V/s

C^o_A = 0.23 mol/L → Estimated from Reference 1

E^o_{AB} = –1.41 V *vs.* Fc^+/Fc → Estimated from Reference 1 which reports the potential as –0.690 V *vs.* NHE with the Fc^+/Fc potential taken to be 0.720 V *vs.* NHE[4]

Values of Variables Measured by Experiments in absence of CO_2

i^o_p = peak current in the absence of substrate (CO_2)

E^o_{PQ} = –2.03 V *vs.* Fc^+/Fc

Values Recorded during Catalytic CVs

i, *E*

Calculations of Rate Constant and Turnover Frequency[2,3]

The following relationship from Reference 2 (bottom of first column on page 11238) is utilized:

$$\frac{i}{i_p^o} = \frac{2.24\sqrt{\frac{RT}{Fv}2k_2C_A^o}}{1+e^{\frac{F}{RT}(E-E_{PQ}^0)}}$$

Plotting the following relationship $\frac{i}{i_p^o} = \frac{1}{1+e^{\frac{F}{RT}(E-E_{PQ}^0)}}$

transforms a typical CV (a current *vs.* Potential plot) into a form wherein the slope of the of the linear region of the low potential values provides access to the rate constant k:

$$Slope = 2.24\sqrt{\frac{RT}{Fv}2k_2C_A^o}$$

or

$$k_2 = \frac{Slope^2Fv}{(10.0352)RTC_A^o}$$

The CV found in Figure S1 can be transformed into the black trace shown below in Figure S19.

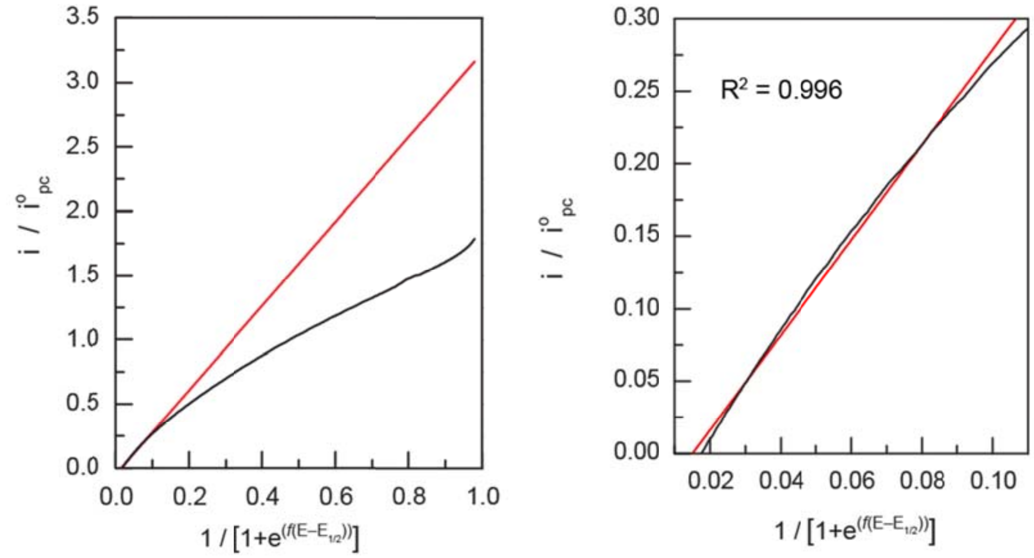


Figure S21. Foot of the Wave Analysis plots for Co(tpy)$_2$(PF$_6$)$_2$ catalytic reduction in the presence of CO$_2$. The black trace represents the transformed electrochemical data. The red trace represents the tangent line to the data at low potentials. The variable *f* equals F/(RT). The left plot includes the entire catalytic region of the cathodic scan, while the right plot includes only the linearized region at low overpotentials.

The red trace represents the linear trend line for the low overpotential region. It was determined by eliminating higher potentials until a trend with an $R^2=0.99$ was achieved. The slope of the above trend line is found to equal 3.2791. Therefore the second order rate constant can be calculated as follows:

$$k_2 = \frac{Slope^2Fv}{(10.0352)RTC_A^o} = \frac{3.2791^2(96485.34\ \mathrm{C/mol})(0.250\ \mathrm{V/s})}{(10.0352)\left(8.31446\frac{\mathrm{C\,V}}{[\mathrm{mol\ K}]}\right)(297\ \mathrm{K})(0.23\frac{mol}{L})} =$$

$$\frac{259{,}364.5776\frac{C\,V}{[mol\,s]}}{5{,}699.6013\frac{C\,V}{L}} = 45.5\ M^{-1}s^{-1}$$

The second order rate constant is thus calculated to be 45.5 $M^{-1}\ s^{-1}$. The pseudo-first order rate constant can be obtain by multiplying by 45.5 $M^{-1}\ s^{-1}$ by the concentration of CO$_2$ (assumed to be 0.23 M) and is found to be 10.5 s^{-1}.

$$k_{ap} = k_2 \times C_A = 45.5M^{-1}s^{-1} \times 0.23\ M = 10.5\ s^{-1}$$

This pseudo first order rate constant can be transformed into a turnover frequency via the following relationship found in reference 2, based off of equation 4 within said reference, which was slightly amended within reference 3.

$$\log(TOF) = \log\left(k_{ap}\right) - \frac{F}{RT\ln(10)}\left(E_{AC}^{0} - E_{PQ}^{0} - \eta\right)$$

In an effort to compare the activity to other values reported in the literature, of particular interest is the activity of the catalyst at zero overpotential. Using the pseudo-first order rate constant derived above, the TOF_0 can be calculated as such:

$$\log(TOF_0) = \log\left(k_{ap}\right) - \frac{F}{RT\ln(10)}\left(E_{AC}^{0} - E_{PQ}^{0} - \eta\right) =$$

$$\log(10.5\ M^{-1}s^{-1}) - \frac{96485.34\frac{C}{mol}}{\left(8.31446\frac{C\,V}{mol\,K}\right)(297K)(\ln[10])}(-1.41V - -2.03V - 0V) =$$

$$1.0212 - 16.96895\ V^{-1}(0.62V) = -9.5$$

Thus, the $\log(TOF_0)$ at zero overpotential is calculated to be −9.5 . This corresponds to an intrinsic TOF equal to $3.2\times10^{-10}\ M^{-1}\ s^{-1}$.

The above procedure was followed for all of the different scan rates analyzed within this manuscript.

Practically, within the catalytic wave that is observed experimentally, there is an applied overpotential of 0.670 V. This can be be included in the calculation of TOF as shown below:

$$\log(TOF) = \log\left(k_{ap}\right) - \frac{F}{RT\ln(10)}\left(E_{AC}^{0} - E_{PQ}^{0} - \eta\right) =$$

$$\log(10.5\ M^{-1}s^{-1}) - \frac{96485.34\frac{C}{mol}}{\left(8.31446\frac{C\,V}{mol\,K}\right)(297K)(\ln[10])}(-1.41V - -2.03V - 0.67V) =$$

$$1.0212 - 16.96895\ V^{-1}\left(-0.05V\right) = 1.9$$

Thus, the log(TOF) with an applied overpotential of 0.670 V, representing conditions within the catalytic wave found experimentally, is calculated to be 1.9. This corresponds to a TOF equal to $7.4\times10^{1}\ s^{-1}$.

References

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