ELECTRONIC SUPPLEMENTARY INFORMATION

Nickel(II) macrocycles: highly efficient electrocatalysts for the selective reduction of CO_2 to CO

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I. SUPPLEMENTARY INFORMATION FOR CV AND LSV EXPERIMENTS

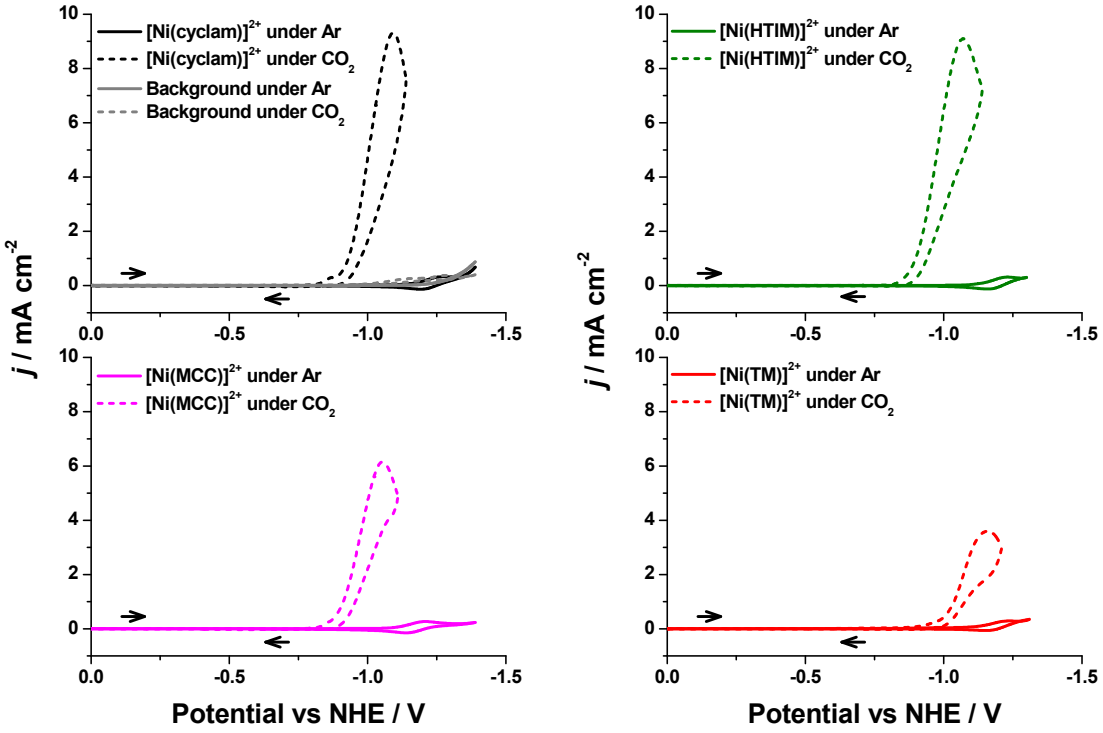


Figure S1. CVs of 1.6 mM solutions of $[Ni(L)]^{2+}$ in 0.1 M $NaClO_4$, pH 5, purged with Ar (solid lines) and CO_2 (dashed lines), scanning at 100 mV s^{-1}, SMDE working electrode (area = 0.0104 cm^2). Background scans are shown in the panel with $[Ni(cyclam)]^{2+}$ (top left). Arrows indicate the direction of the applied potential.

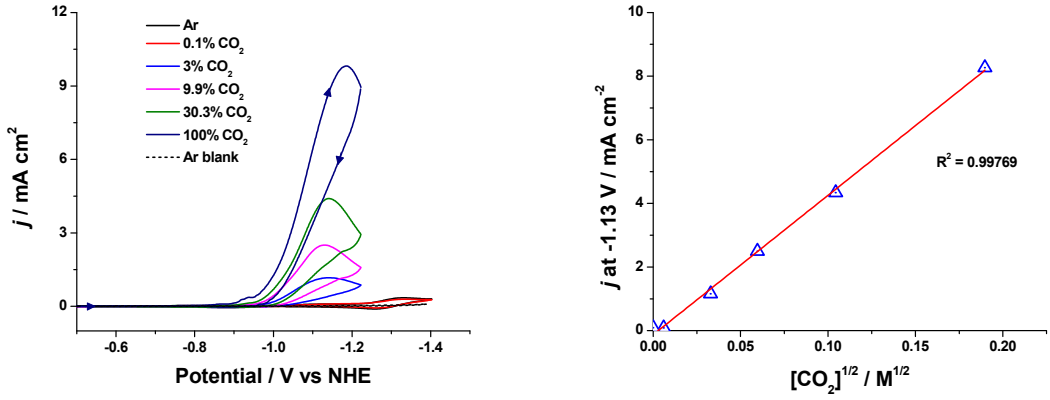


Figure S2. CVs of $[Ni(MTC)]^{2+}$ under different concentrations of CO_2 (left panel); 0.1% (0.036 mM), 3% (1.08 mM), 9.9% (3.56 mM), 30.3% (10.9 mM), and 100% CO_2 (36 mM). The right panel shows the linear correlation between the current densities at –1.13 V versus the square root of the concentration of CO_2. Conditions: *ca*. 1 mM [Ni] in 0.1 M $NaClO_4$, pH 4-5; SMDE working (area = 0.0104 cm^2), Pt wire auxiliary, and Ag/AgCl (satd KCl) reference electrodes; 100 mV s^{-1} scan rate. Nitrogen is the gas balance for CO_2 at different concentrations.

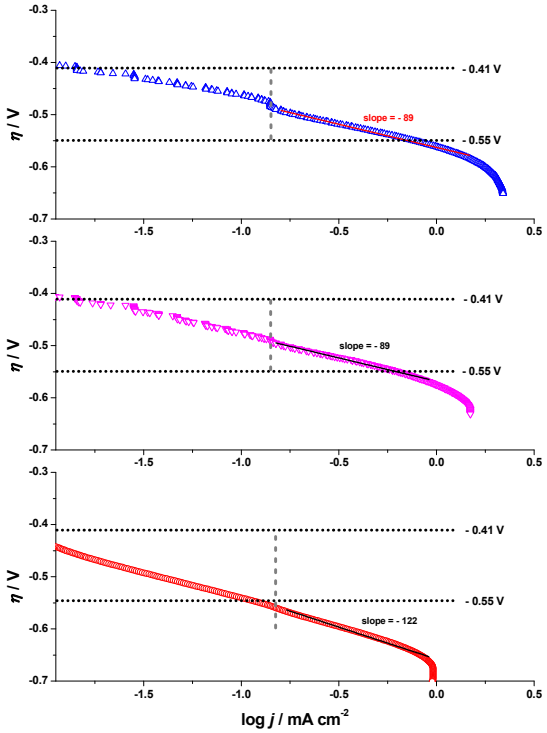


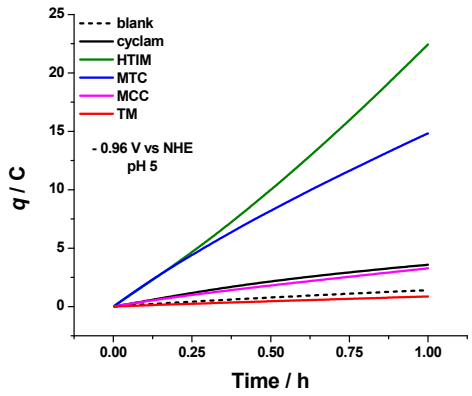
Figure S3. Plots of the overpotential (η) for CO_2 reduction at pH 5 versus the log of the current density (j) for $[Ni(MTC)]^{2+}$ (top), $[Ni(MCC)]^{2+}$ (middle) and $[Ni(TM)]^{2+}$ (bottom). LSVs run in CO_2 saturated solutions containing 1 mM $[Ni(L)]^{2+}$ in 0.1 M $NaClO_4$, 2 mV s^{-1} scan rate, SMDE working electrode (area = 0.0104 cm^2). Here, η is calculated from the thermodynamic potential for CO_2 reduction to CO at pH 5 (–0.41 V vs NHE). The horizontal dotted lines correspond to potentials used in bulk electrolysis experiments (see Bulk electrolysis section in manuscript). The vertical dashed lines correspond to the pre-wave due to $[Ni(L)]^{+}$ adsorption and geometric rearrangement.

Table S1. Selected data from the LSV slow scan analysis[a].

L	mA cm^{-2} at η = –0.41 V	mA cm^{-2} at η = –0.55 V
cyclam	0.014	0.766
HTIM	0.009	0.971
MTC	0.014	0.764
MCC	0.014	0.639
TM	0.007	0.125

[a] The thermodynamic overpotential (η) for the reduction of CO_2 to CO is taken to be –0.41 V vs NHE at pH 5.

II. Supplementary Information for Bulk Electrolysis Experiments



L	q / C	F.E. (%)	CO:H_2
cyclam	3.6 ± 0.1	84 ± 4	Trace H_2
HTIM	22 ± 3	88 ± 7	No H_2
MTC	15 ± 0	88 ± 7	No H_2
MCC	3.3 ± 0.1	92 ± 2	No H_2
TM	0.87 ± 0.22	42 ± 4	Trace H_2
blank	1.4 ± 0.3	64 ± 12	0.4 ± 0.3

Figure S4. Bulk electrolysis at –0.96 V vs NHE (η = –0.55 V) for 50 μM $[Ni(L)]^{2+}$ in 0.1 M $NaClO_4$, pH 5; CO:H_2 is the ratio (mol CO / mol H_2), as quantified by GC analysis after 1 h electrolysis.

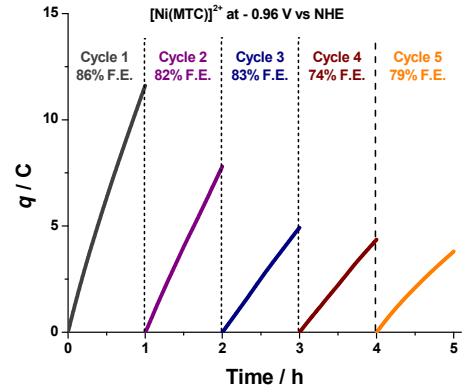


Figure S5. Bulk electrolysis of 50 μM $[Ni(MTC)]^{2+}$ in 0.1 M $NaClO_4$, pH 5, at –0.96 V vs NHE cycled five times with the same solution; 1 h each cycle. After Cycle 4, the mercury pool electrode was cleaned and the $[Ni(MTC)]^{2+}$ solution kept overnight in a vial before use in Cycle 5.

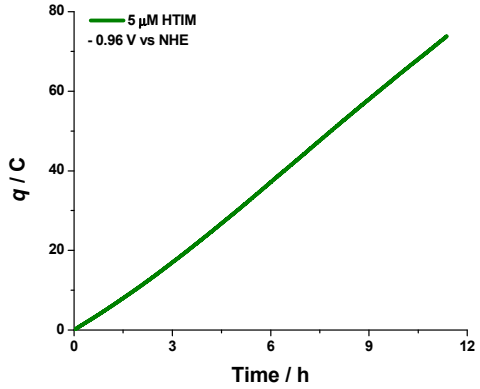
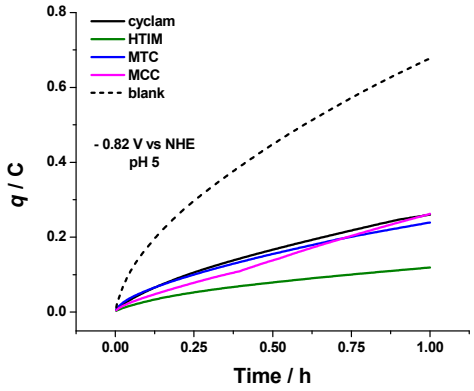
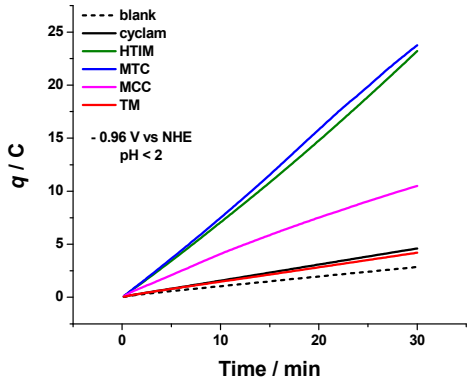


Figure S6. Bulk electrolysis data for a 5 μM solution of $[Ni(HTIM)]^{2+}$ in 0.1 M $NaClO_4$, pH 5, electrolysing at –0.96 V for *ca.* 12 h.



L	q / C	F.E.(%)	CO:H_2
cyclam	0.26	Trace CO and H_2	
HTIM	0.12	No CO or H_2	
MTC	0.24	Trace CO and H_2	
MCC	0.26	Trace CO and H_2	
TM	-	-	-
blank	0.68 ± 0.01	87 ± 10	No CO

Figure S7. Bulk electrolysis at –0.82 V vs NHE (η = –0.41 V) for 50 µM $[Ni(L)]^{2+}$ in 0.1 M $NaClO_4$, pH 5; CO:H_2 is the ratio (mol CO / mol H_2), as quantified by GC analysis after 1 h electrolysis.



L	q / C	F.E.(%)	CO:H_2
cyclam	4.60	80	0.4
HTIM	23.2	88	0.8
MTC	23.7	82	0.6
MCC	10.5	83	0.1
TM	4.20	79	0.04
blank	2.85	64	No CO

Figure S8. Bulk electrolysis at –0.96 V vs NHE for 5 μM $[Ni(L)]^{2+}$ in 0.1 M $NaClO_4$, pH < 2; CO:H_2 is the ratio (mol CO / mol H_2), as quantified by GC analysis after 0.5 h electrolysis.

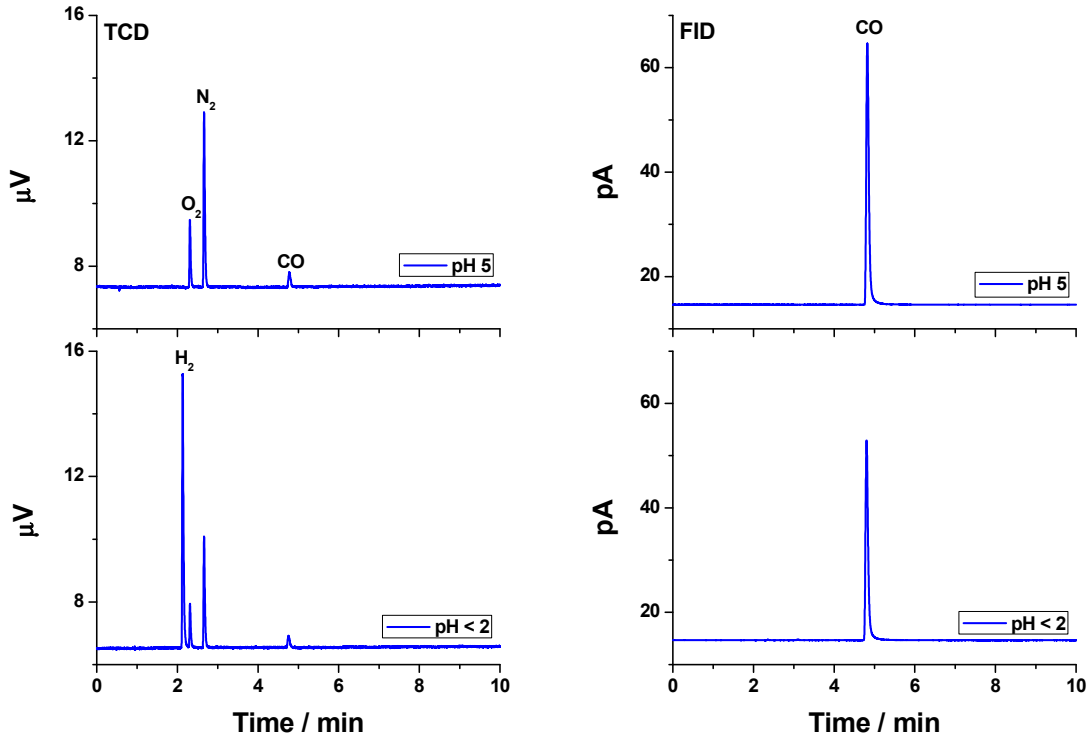


Figure S9. Chromatograms (TCD at left, FID at right) corresponding to gaseous product analysis after bulk electrolysis (–0.96 V vs NHE) at pH 5, 50 uM $[Ni(MTC)]^{2+}$ after 1 h electrolysis (top panels), and at pH < 2, 5 uM $[Ni(MTC)]^{2+}$ after 0.5 h electrolysis (bottom panels).

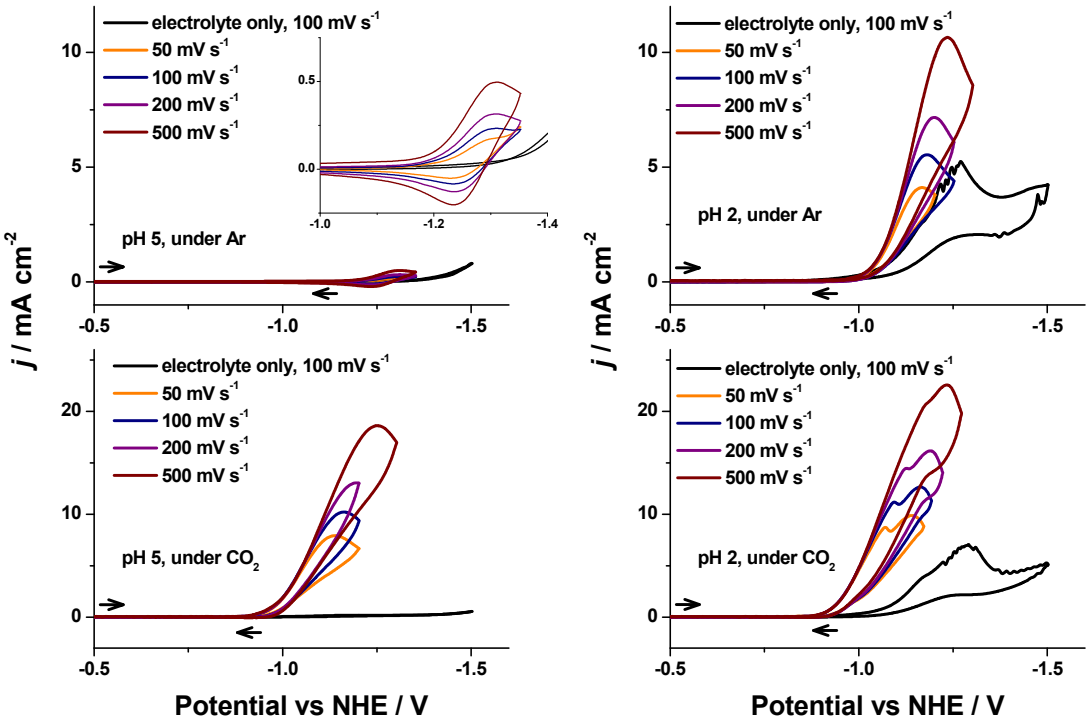


Figure S10. Scan rate dependence of the current density (j) vs applied potential for 1 mM solutions of $[Ni(HTIM)]^{2+}$ in 0.1 M $NaClO_4$ under Ar and CO_2, pH 5 (left panel) and pH 2 (right panel), with SMDE working electrode (area = 0.0104 cm^2); 10 mM phosphate buffer added to pH 2 study, pH adjusted with concentrated $HClO_4$. Notice that when the system is under Ar, the peak current densities are significantly higher and are shifted to more positive potential at pH 2 compared to at pH 5. When the system is under CO_2, however, the peak current densities and their respective potentials are comparable at either pH.

III. SUPPLEMENTARY INFORMATION FOR PULSE RADIOLYSIS EXPERIMENTS

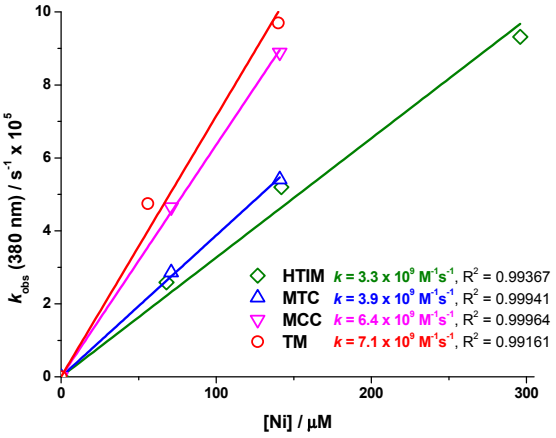


Figure S11. Determination of the bimolecular rate constants, k, for the reduction of $[Ni(L)]^{2+}$ (L = HTIM, MTC, MCC, TM) by $CO_2^{\bullet-}$, measured in 50 mM formate, pH 7, $G([Ni(L)]^{+}) = G(e_{aq}^{-}) + G(H^{\bullet}) + G(CO_2^{\bullet-}) = 6$.

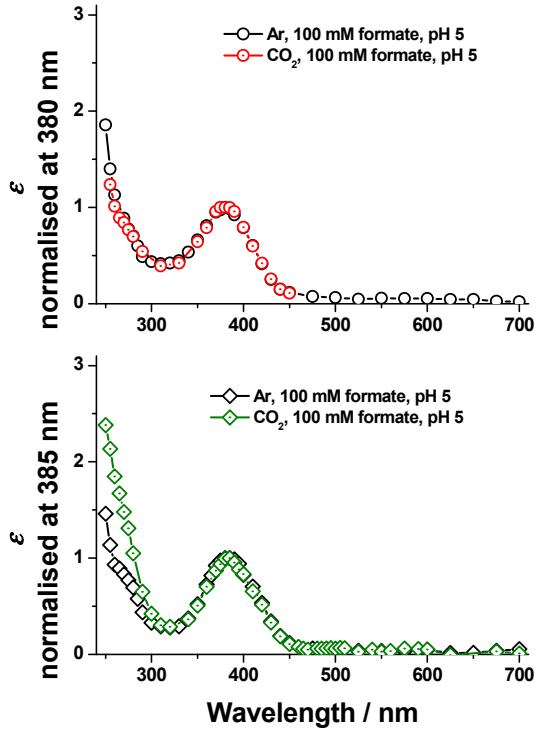
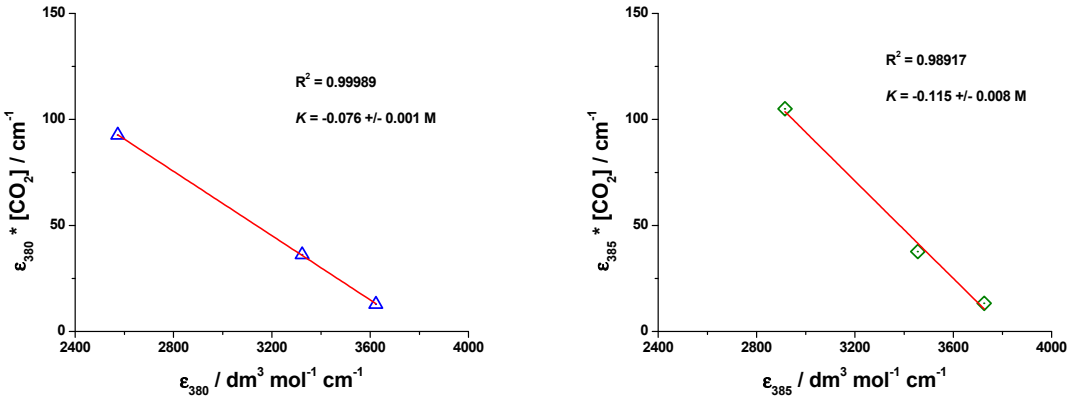


Figure S12. Transient spectra of $[Ni(TM)]^+$ (top panel) and $[Ni(HTIM)]^+$ (bottom panel) obtained by pulse radiolysis in 0.1 M formate under Ar and CO_2.

(A)



(B)

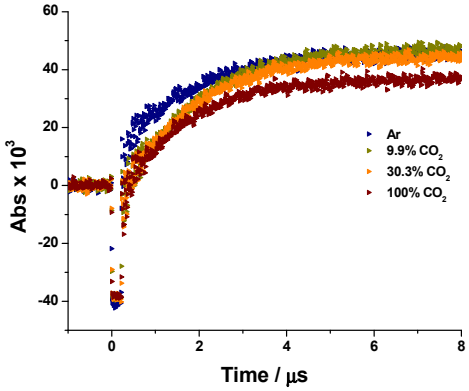


Figure S13. **(A)** Plots of the extinction coefficient (ε) at *ca.* 380 nm times $[CO_2]$, versus ε at *ca.* 380 nm, for $[Ni(MTC)]^+$ (blue triangles) and $[Ni(HTIM)]^+$ (green diamonds). The linear fits allow for the determination of the CO_2 binding constant, K_{CO2}. The ε at *ca.* 380 nm for complexes $[Ni(MCC)]^+$ and $[Ni(TM)]^+$ show no dependence on $[CO_2]$ (not shown). **(B)** Kinetic traces for pulse radiolysis experiments with $[Ni(HTIM)]^+$ in solutions saturated with different concentrations of CO_2 and monitoring at 380 nm; 150 µM Ni, 100 mM formate, pH 5, 200 ns pulses of electrons (1.13 µM radicals). Notice the fast component under Ar, from e_{aq}^-, disappears when CO_2 is present, even at only 9.9%.

IV. Supplementary Information for Calculations, Calibrations, etc.

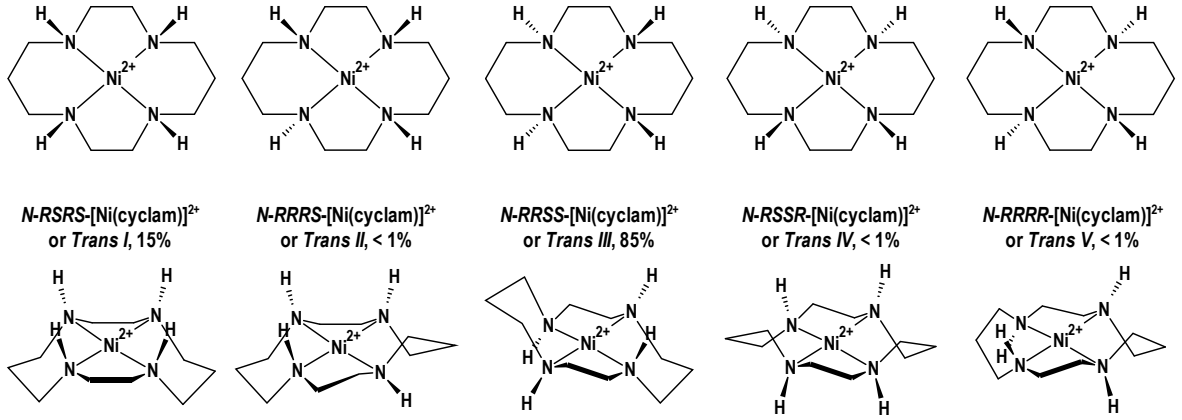


Figure S14. Conformational isomers of $[Ni(cyclam)]^{2+}$ present in solution and their relative abundance at equilibrium.

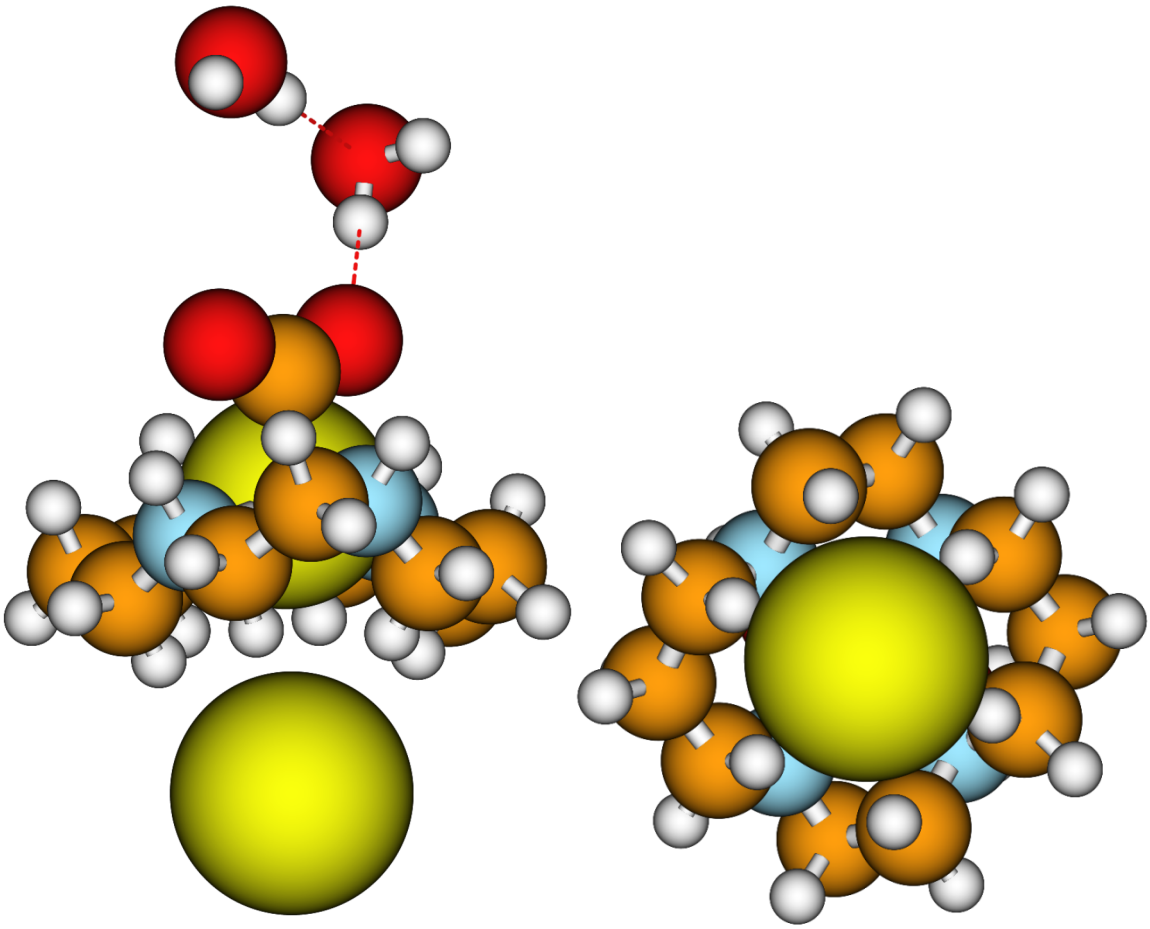


Figure S15. Side view (left) and bottom view from the 'mercury surface' looking up (right) of *N-RSRS*-$[Ni(cyclam)(CO_2)]^{+}$ adduct adsorbed to 'mercury surface' in CPCM of water solvent, where the 'mercury surface' is represented by a single Hg atom in the sixth coordination position of Ni. Atom colors: Ni (yellow), C (orange), H (white), N (cyan), O (red), Hg (yellow). Quite similar results were obtained using the B3LYP and the LC-ωPBE functionals with the 6-31+G(d,p) basis for Ni, C, N, O and H, and the SBKJC ECP basis for Hg.

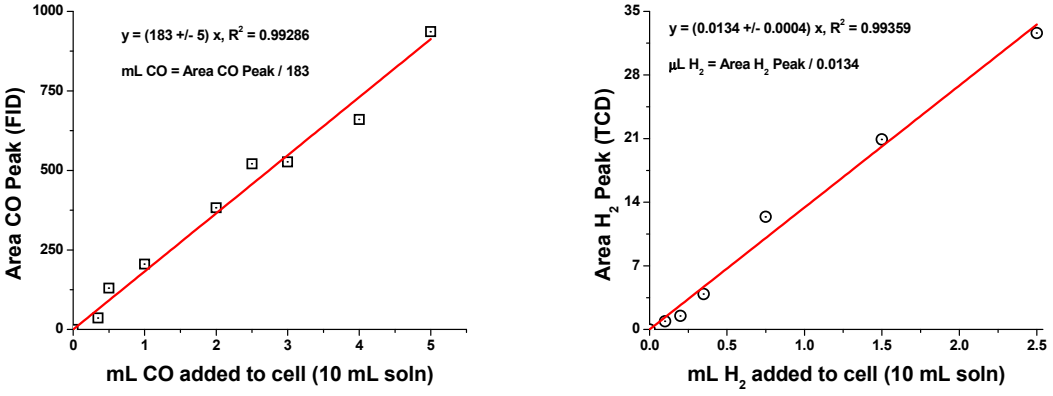


Figure S16. Calibration plots for measuring CO and H_2 produced during bulk electrolysis experiments, the gases were quantified by FID and TCD detectors, respectively. Calibration is for 10 mL solution present in the electrolysis cell.

Faradaic efficiency: example calculation

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9.79 C passed after 1 h; A_{H_2} (TCD) = 0.8; A_{CO} (FID) = 180.9; **F.E. = 86%**

µL H_2 = A_{H_2} / 0.0134 = 60 µL H_2
60 µL H_2 / 24.4 L mol^{-1} = **2.5 µmol H_2**

mL CO = A_{CO} / 183 = 0.99 mL CO
0.99 mL CO / 24.4 L mol^{-1} = 0.0405 mmol or **41 µmol CO**

2.5 + 41 = **43.5 µmol total product (H_2 and CO)**

9.79 C passed / 96485 C mol e^{-} $^{-1}$ = **101 µmol e^{-} passed**

F.E. = µmol total product* / µmol e^{-} passed = **86%**

*quantity doubled because two e^{-} process for water reduction to H_2 *or* CO_2 reduction to CO

Figure S17. Example calculation for determining the Faradaic efficiency (F.E.) of a typical bulk electrolysis experiment.