

A water-soluble Mn polypyridyl complex for selective electrocatalytic CO₂ reduction

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Electronic Supplementary Information

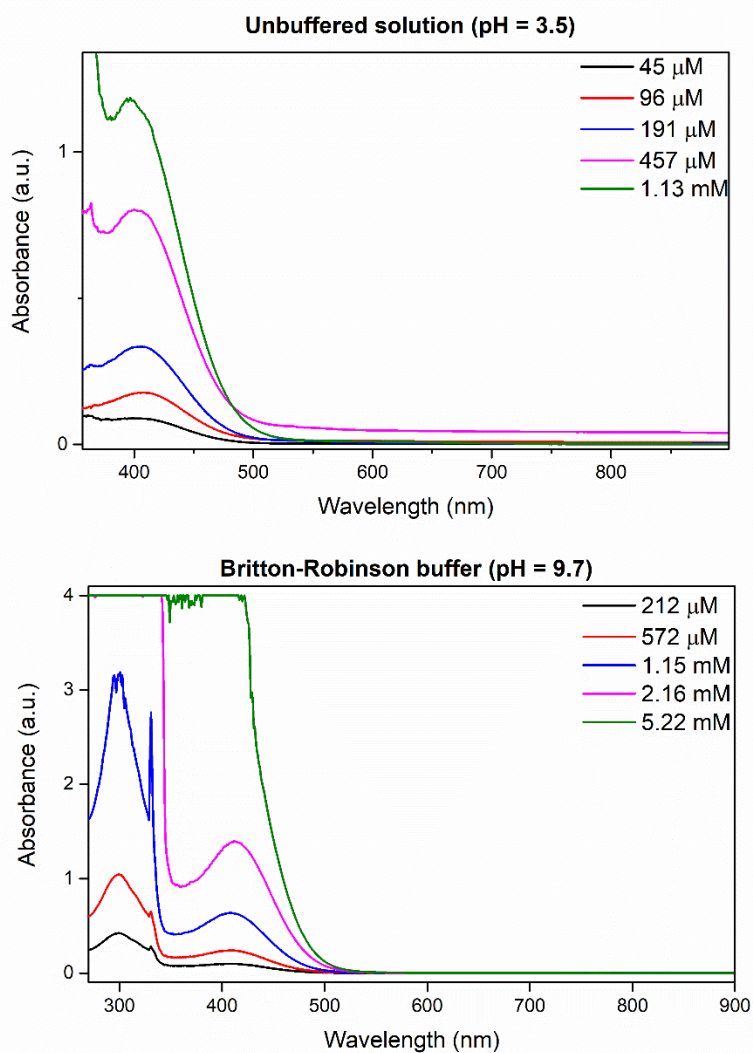


Figure S1 UV-Vis spectra of $[Mn^I(bpy)(COOH)_2(CO)_3Br]$ at various concentrations, carried out in water (top) or Britton Robinson buffer at pH = 9.7 (bottom), with at pathlength of 2 mm. The complex was dissolved in either Britton-Robinson buffer at pH 9.7 or in water, then centrifuged and the UV-vis spectrum was measured.

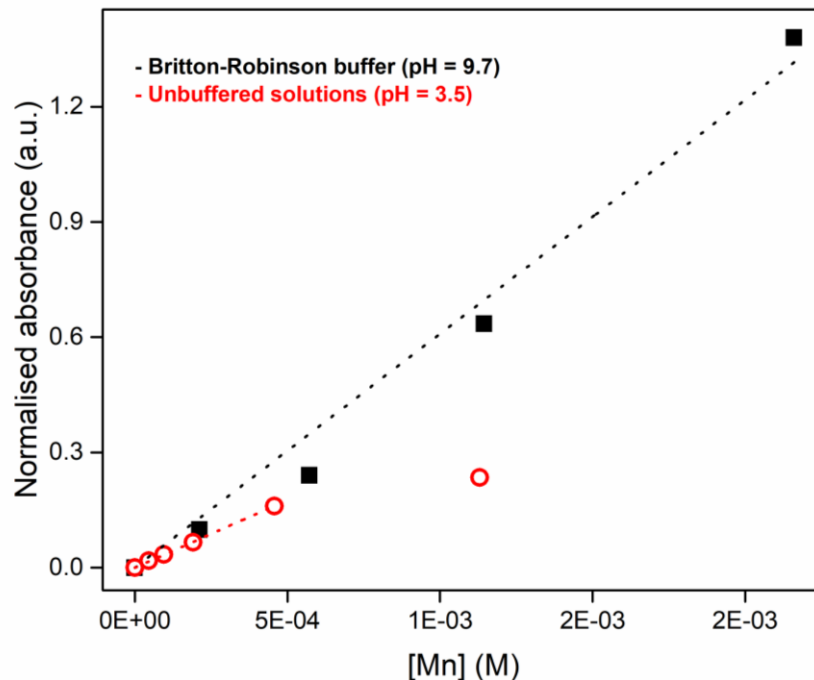


Figure S2 Normalised absorbance (at 408 nm) plotted versus the concentration of $[Mn^I(bpy)(COOH)_2(CO)_3Br]$ in the solutions indicated, taken from **Figure S1**. The complex was dissolved in either Britton-Robinson buffer at pH 9.7 or in water, then centrifuged and the UV-vis spectrum was measured. While at high pH the trend is linear throughout the concentrations measured, in unbuffered solutions (pH 3.5) the concentration shows a plateau, indicating the solution is saturated.

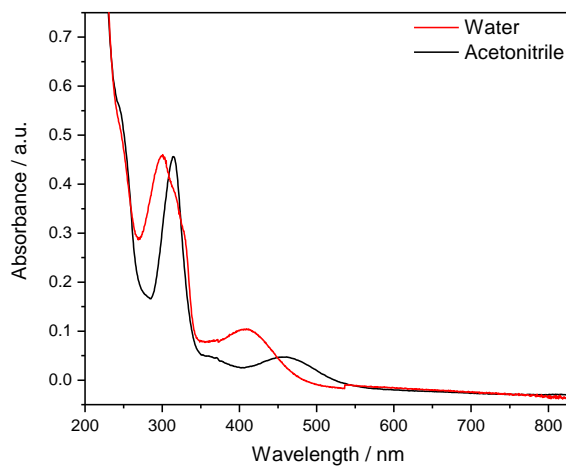


Figure S3 UV-Vis spectra of $[Mn^I(bpy)(COOH)_2(CO)_3Br]$ (0.25 mM) in water (pH 3.5, red) or acetonitrile (black), under argon, pathlength 1 mm. Solutions were made up in volumetric flasks covered with aluminium foil to protect from photodecomposition and measured within 5 minutes of dissolution. The λ_{max} of both the 1MLCT and $\pi-\pi^*$ absorptions blue shift in H_2O , relative to in CH_3CN , primarily due to ligand exchange (see below).

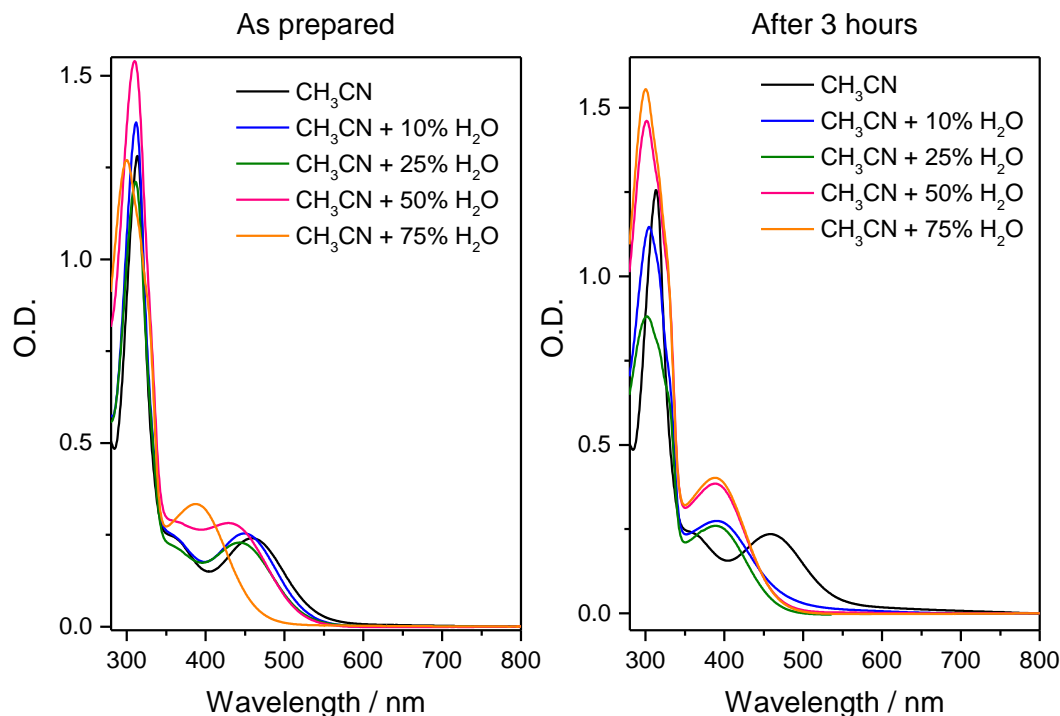
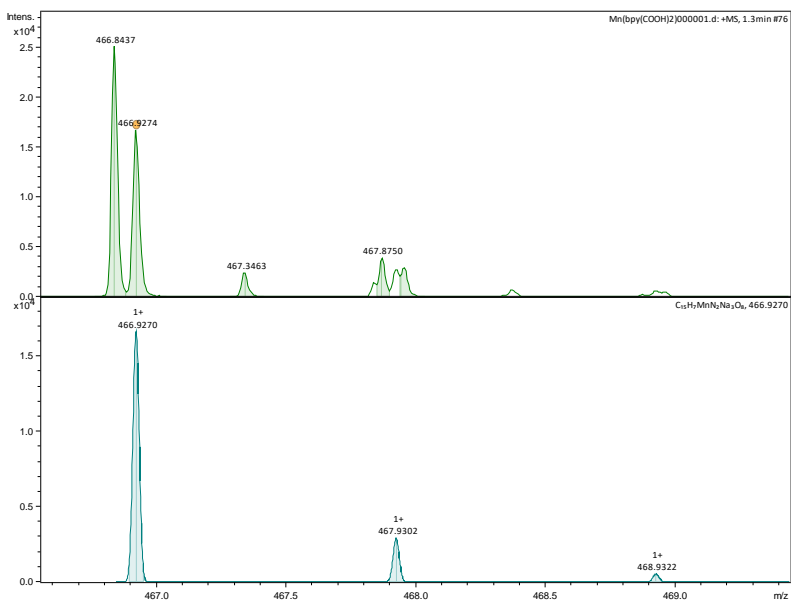


Figure S4 UV-Vis spectra of $[Mn^I(bpy)(COOH)_2(CO)_3Br]$ in acetonitrile- water mixtures both immediately after preparation and after 3 hours at room temperature in the dark.

Figure S4 shows UV/Vis spectra of the complex in water, acetonitrile and acetonitrile/water mixes recorded immediately after preparation of the sample and then again after 3 hours shows the relative contributions from solvatochromism and ligand exchange. The as prepared samples show a slight shift in the UV/Vis maxima of the MLCT as the water content is increased (100% CH_3CN $\lambda_{max} = 460$ nm, 75% CH_3CN 25% H_2O $\lambda_{max} = 453$ nm, 50% CH_3CN 50% H_2O $\lambda_{max} = 444$ nm) which is assigned to solvatochromic effects. The sample prepared with 75% water has $\lambda_{max} = 393$ nm as prepared, similar to that observed at low pH for a sample prepared in solely aqueous solvent. The large shift in UV/Vis maxima in 75% water indicates that ligand displacement takes place rapidly at higher water concentrations. After 3 hours all water containing samples have very similar UV/Vis spectra with $\lambda_{max} \sim 393$ nm, markedly different from the initially prepared samples. This larger change in UV/Vis spectrum cannot be assigned to solvatochromism – such behaviour would be immediately apparent. Instead it is apparent that the large shift in MLCT maxima when the complex is studied in water is primarily due to the exchange of the halide ligand with water and the solvatochromic contribution, although present, is significantly smaller.



Meas. m/z #	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e ⁻ Conf	N-Rule
466.9274 1	C ₁₅ H ₇ MnN ₂ Na ₃ O ₈	466.9270	-0.8	n.a.	1	100.00	12.5	odd	-

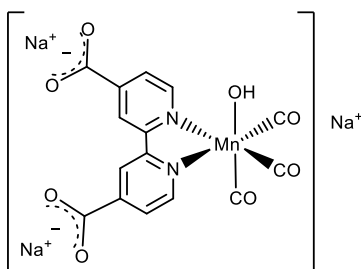


Figure S5 High resolution mass spectrometry following the dissolution of $[Mn^I(bpy)(COOH)_2](CO)_3Br$ (0.2 mM) in 0.1 M Na_2CO_3 . The peak at $m/z = 466.9270$ and its isotopic distribution corresponds to $C_{15}H_7MnN_2Na_3O_8$. A proposed structure for this mass is given.

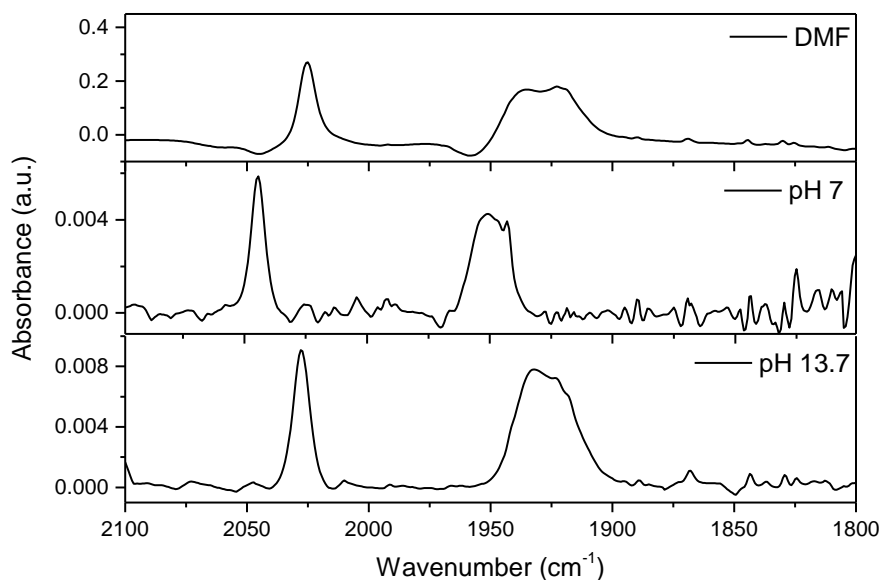


Figure S6 FTIR spectra of solutions of $[Mn^I(bpy)(COOH)_2(CO)_3Br]$ (0.2 mM). The highlighted vibrational modes are assigned to the carbonyl groups of the complexes: $[Mn^I(bpy)(COOH)_2(CO)_3DMF]$ (top), $[Mn^I(bpy)(COO)_2(CO)_3H_2O]^{2-}$ (middle) and $[Mn(bpy)(COO)_2(CO)_3OH]^{3-}$ (bottom).

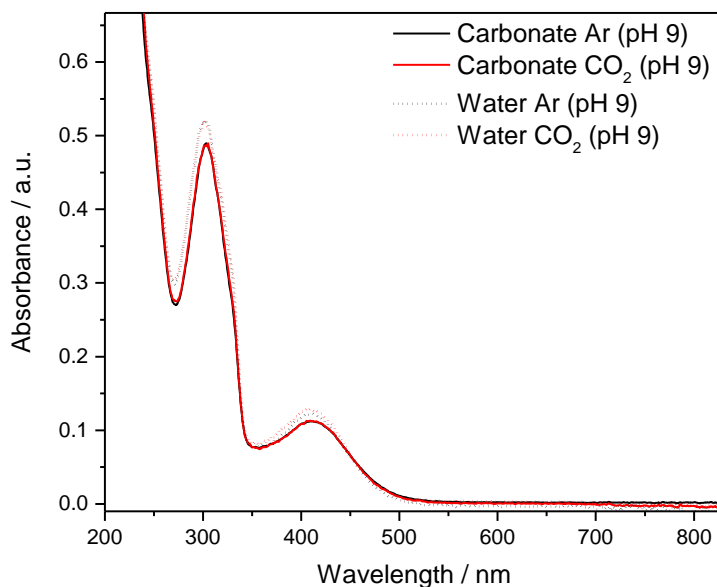


Figure S7 UV-Vis spectra of $[Mn^I(bpy)(COOH)_2(CO)_3Br]$ (0.25 mM) in water (dotted lines) or carbonate solution (0.5 M K_2CO_3 , solid lines) under argon or CO_2 . The absence of changes in the spectra in the different solutions suggests that the carbonate complex does not form at high concentrations.

pH	$V_{\text{Ag/AgCl}}$ of 1 st reduction	$V_{\text{Ag/AgCl}}$ of 2 nd reduction
2.5	-0.90	-1.40
3.5	-0.95	-1.38
4	-1.00	-1.37
6	-1.05	-1.37
7.5	1.05	-1.37
9	-1.04	-1.37
11.5	-1.07	-1.32

Table S1 Peak potentials for the two irreversible reductions showed by $[\text{Mn}^{\text{I}}(\text{bpy}(\text{COOH})_2)(\text{CO})_3\text{Br}]$ at the pH values indicated, taken from the CVs Fig. 1 in the main paper. CVs were recorded with argon purged 0.5 mM solutions of $[\text{Mn}^{\text{I}}(\text{bpy}(\text{COOH})_2)(\text{CO})_3\text{Br}]$ (K_2CO_3 (0.5 M) + KCl (0.1 M) electrolyte for pH 11.5-7.5, 0.1 M KCl for pH 3.5-6) at a scan rate of 100 mV s^{-1} on a Hg/Au working electrode. The pH was adjusted by adding aliquots of either HCl or KOH solutions at various concentrations, while purging the solution with Ar .

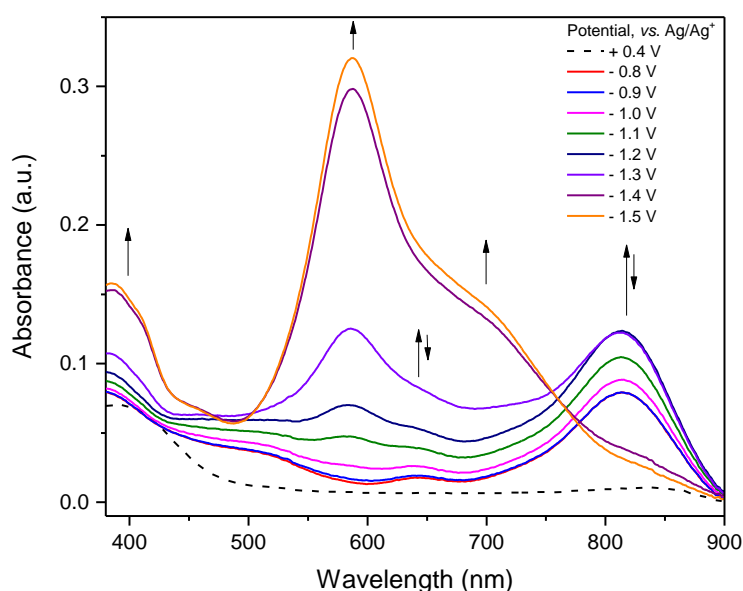


Figure S8 UV/Vis spectroelectrochemistry of 1 mM complex in $\text{DMF}/0.1 \text{ M } (\text{n}\text{But}_4\text{N})_4\text{ClO}_4$. Spectra were recorded using an OTTLE cell with Pt mesh working and counter electrodes, and a silver wire pseudo-reference electrode.

Complex	Solvent	λ (nm)	Reference
[Mn(bpy)(CO) ₃ Br]	CH ₃ CN	366 (sh.), 416	Angew. Chem. Int. Ed. 2011, 50, 9903
[Mn(bpy)(CO) ₃] ₂	CH ₃ CN	394, 461, 633, 806	Angew. Chem. Int. Ed. 2011, 50, 9903
[Mn(bpy)(CO) ₃] ⁻	CH ₃ CN	370, 560, 626 (sh.)	Angew. Chem. Int. Ed. 2011, 50, 9903
[Mn(bpy(COO) ₂)(CO) ₃ (C ₃ H ₇ NO)] ⁻	C ₃ H ₇ NO	386	This work
[Mn(bpy(COO) ₂)(CO) ₃] ₂ ⁴⁻	C ₃ H ₇ NO	380, 499, 644, 810	This work
[Mn(bpy(COO) ₂)(CO) ₃] ³⁻	C ₃ H ₇ NO	385, 410, 587, 703	This work
[Mn(bpy(COO) ₂)(CO) ₃ (OH ₂)] ⁻	H ₂ O	306, 413	This work
[Mn(bpy(COO) ₂)(CO) ₃] ₂ ⁴⁻	H ₂ O	393, 536, 641, 824	This work

Table S2 UV/Vis spectroelectrochemical data summarised from this work (figure S8, figure3) and published literature.

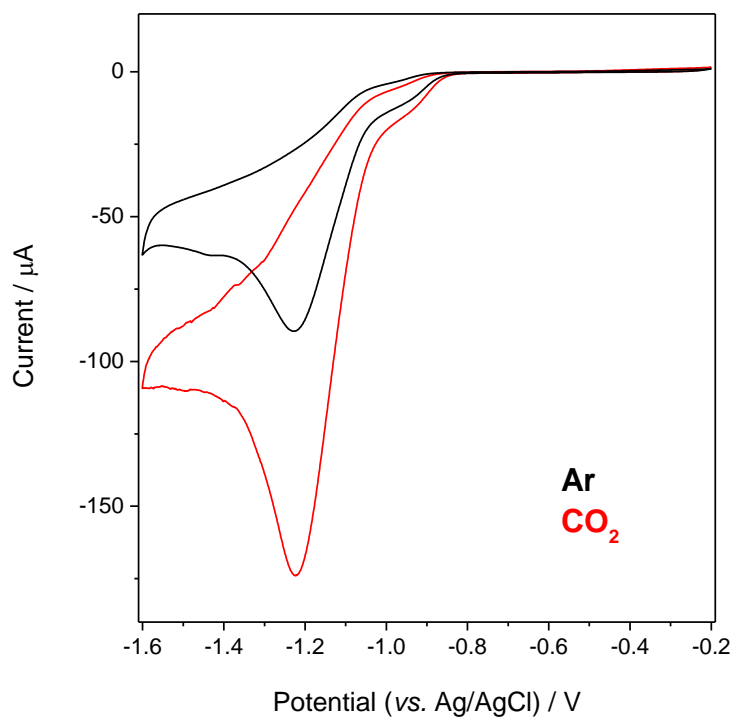


Figure S9 CVs of [Mn^I(bpy)(COOH)₂(CO)₃Br] (0.5 mM), under argon (black) and CO₂ (red), carried out at a scan rate of 100 mV s⁻¹, Hg/Au WE at pH 2.5. The electrolyte was 0.1 M KCl adjusted to the desired value by adding aliquots of HCl.

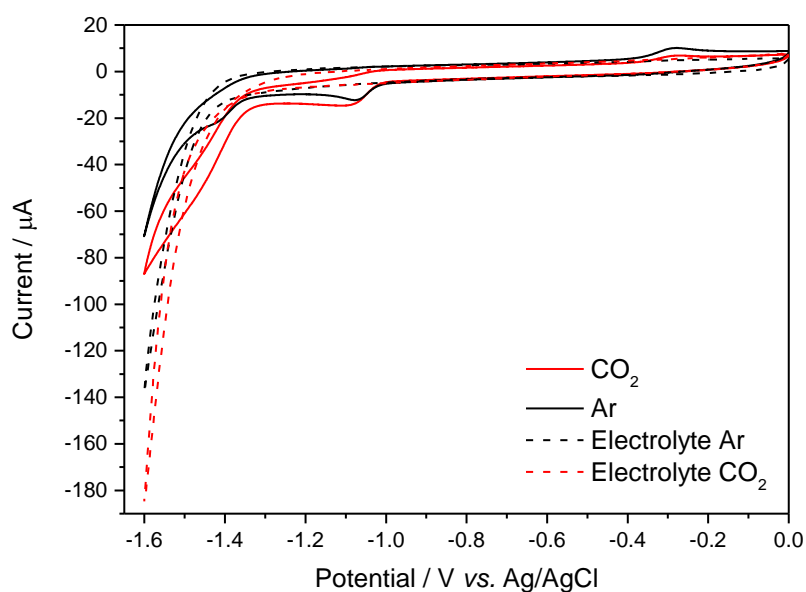


Figure S10 CVs of $[Mn^I(bpy)(COOH)_2(CO)_3Br]$ (0.5 mM) in a 0.1 M KCl + 0.5 M K_2CO_3 electrolyte at pH = 9, under argon (black) and CO_2 (red), recorded on a GC working electrode, Pt counter electrode and Ag/AgCl reference working electrode. The scan rate was 100 mV s^{-1} . The dashed lines are the CV of the blank electrolyte recorded at the same scan rate, showing the solvent potential window on this electrode.

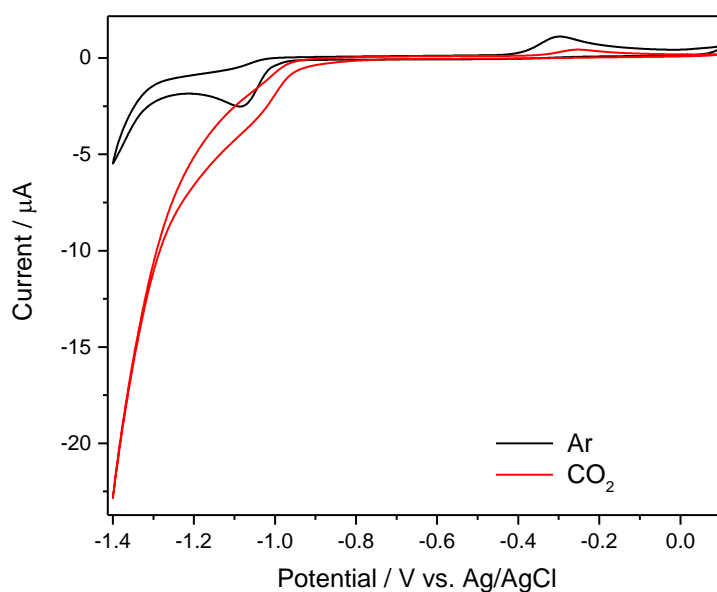


Figure S11 CVs of $[Mn^I(bpy)(COOH)_2(CO)_3Br]$ (0.5 mM) in a 0.1 M KCl, 0.5 M K_2CO_3 electrolyte at pH = 7, under argon and CO_2 , recorded on a BDD working electrode, Pt counter electrode and Ag/AgCl reference working electrode. The scan rate was 10 mV s^{-1} .

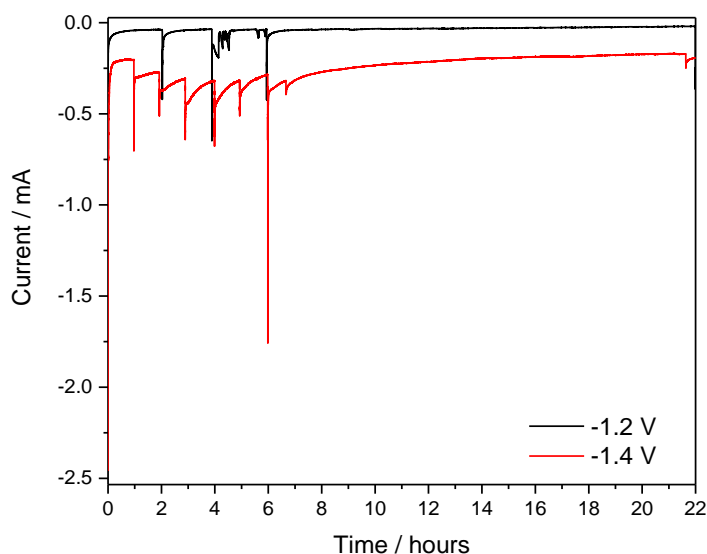


Figure S12 Bulk electrolysis of $[Mn^I(bpy)(COOH)_2(CO)_3Br]$ (0.2 mM) in a 0.1 M KCl, 0.5 M K_2CO_3 electrolyte (pH =9) under CO_2 at the potentials indicated. The working electrode was a Hg pool, with a Pt mesh as the counter electrode and a Ag/AgCl reference electrode. The spikes in the traces are due to the sampling of the headspace for GC analysis.

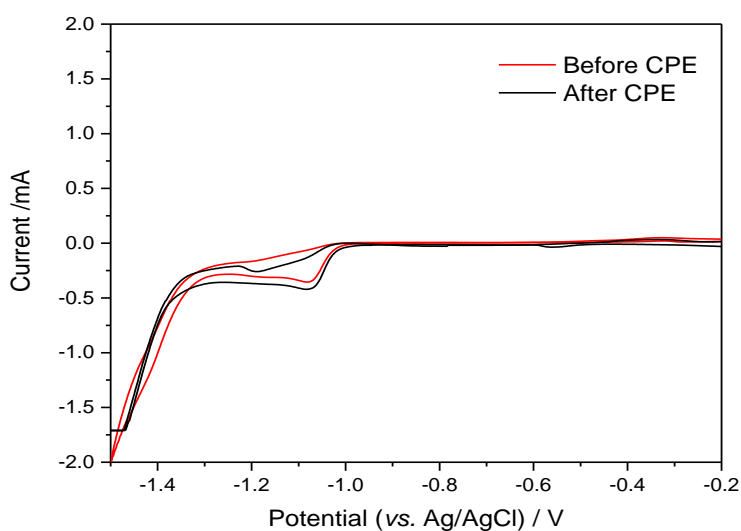


Figure S13 CVs of $[Mn^I(bpy)(COOH)_2(CO)_3Br]$ (0.2 mM) in a 0.1 M KCl, 0.5 M K_2CO_3 electrolyte (pH 9) under CO_2 recorded before and after bulk electrolysis, showing minimal degradation of the catalyst. CVs were recorded on a Hg pool as the working electrode, Pt mesh counter electrode and Ag/AgCl reference electrode, at a scan rate of 50 mV s^{-1} .

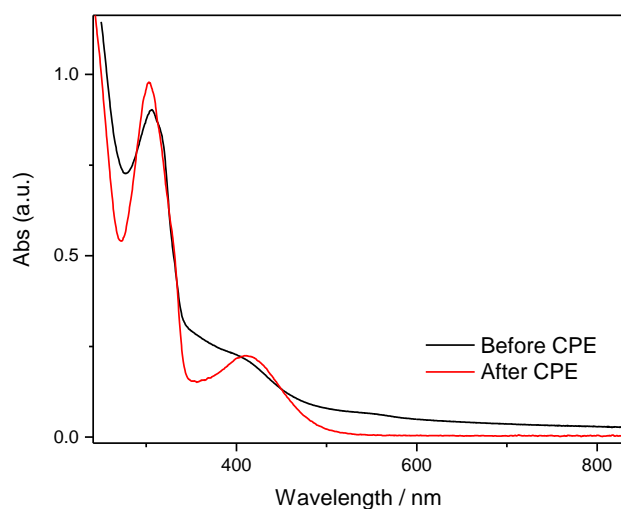


Figure S14 UV-vis spectra of $[Mn^I(bpy(COOH)_2)(CO)_3Br]$ (0.2 mM, 0.1 M KCl, 0.5 M K_2CO_3) under CO_2 recorded before and after the bulk electrolysis experiment.

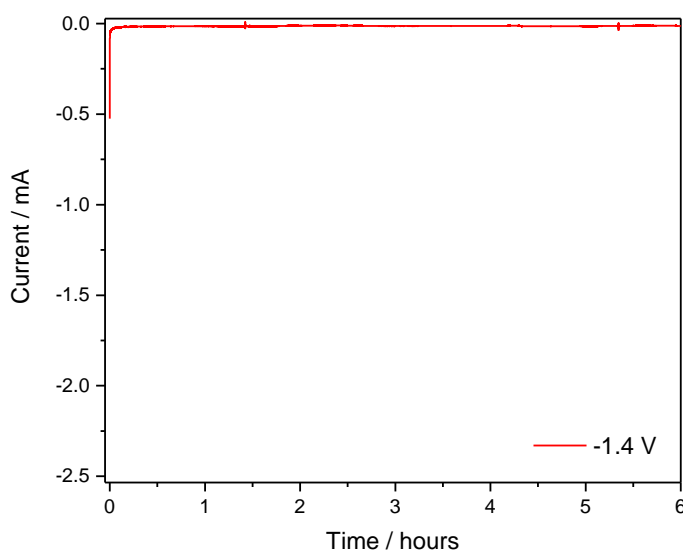


Figure S15 Bulk electrolysis in the absence of $[Mn^I(bpy)(COOH)_2(CO)_3Br]$. 0.1 M KCl, 0.5 M K_2CO_3 electrolyte (pH =9) under CO_2 at the potential indicated. The working electrode was a Hg pool, with a Pt mesh as the counter electrode and a Ag/AgCl reference electrode. GC analysis of the headspace at the end of the experiment showed only H_2 being produced, with only traces of CO in the chromatogram.