In-Situ Study of The Low Overpotential "Dimer Pathway" for Electrocatalytic Carbon Dioxide Reduction By Manganese Carbonyl Complexes

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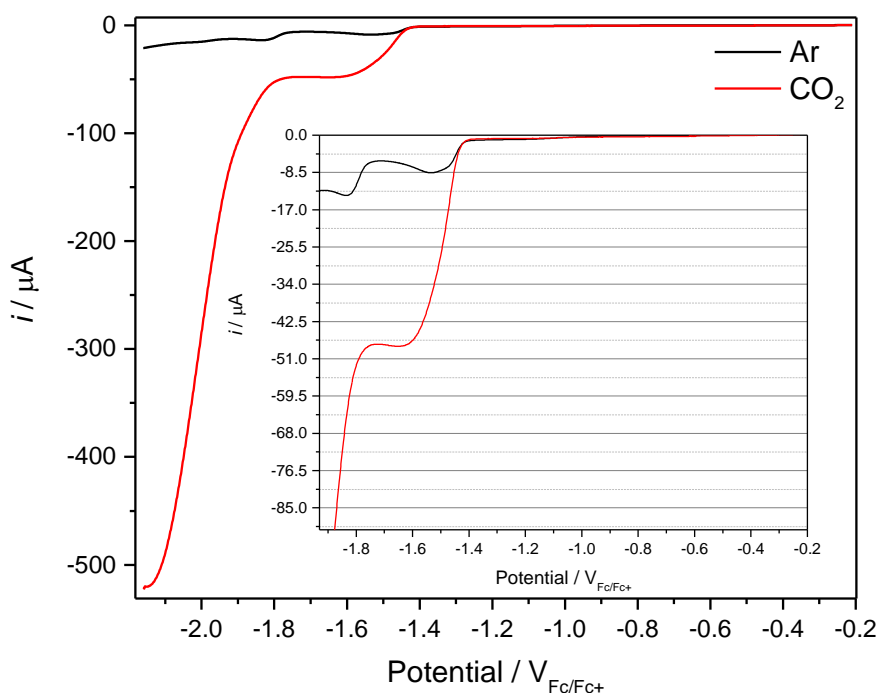
ELECTRONIC SUPPORTING INFORMATION

Figure S1 – LSVs of [Mn(bpy)(CO)₃Br] dissolved in CH₃CN in the presence of 1.5 M TFE, recorded at 10 mV s⁻¹ using a GCE working electrode under Ar (black) or CO₂ (red) sweeping from positive to negative potentials.
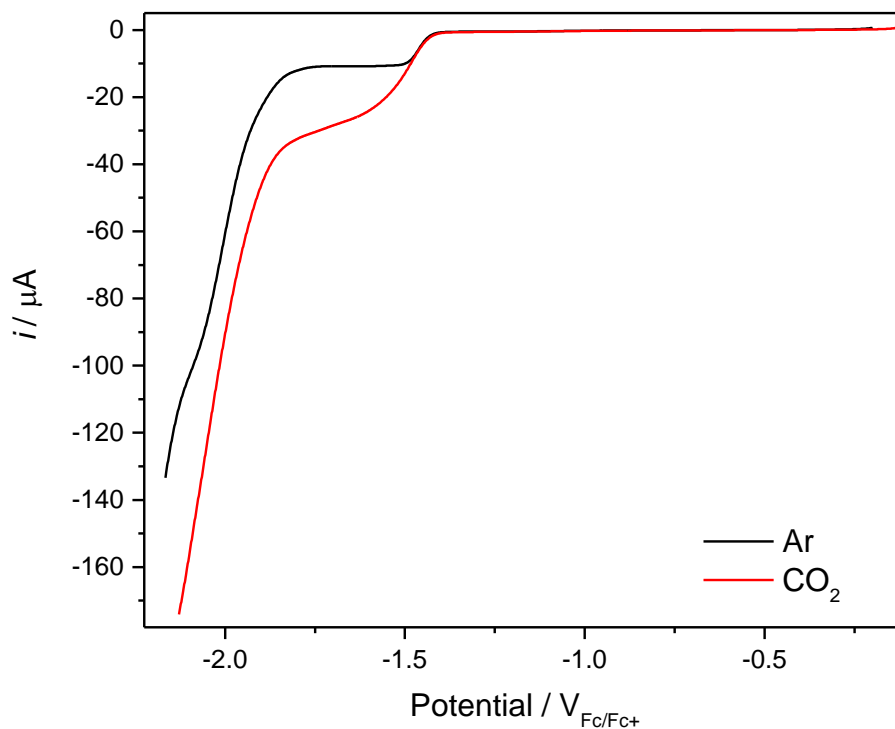
Figure S2 – LSVs of [Mn(bpy)(CO)₃Br] dissolved in CH₃CN in the presence of 1.5 M phenol, recorded at 10 mV s⁻¹ using a GCE working electrode under Ar (black) or CO₂ (red) sweeping from positive to negative potentials.
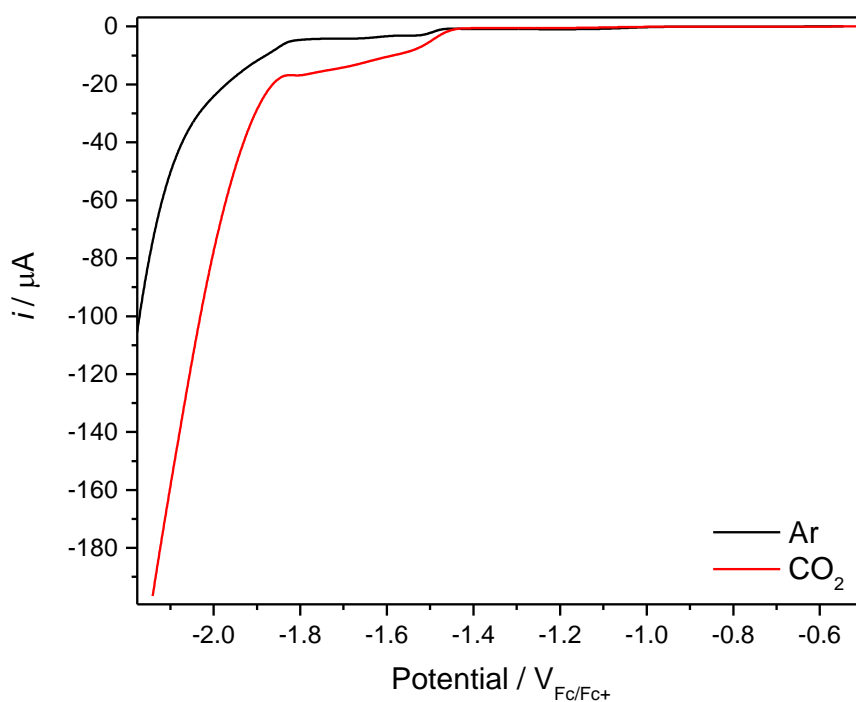

Figure S3 – LSVs of [Mn(bpy)(CO)₃Br] dissolved in CH₃CN in the presence of 1.5 M TFE, recorded at 10 mV s⁻¹ using a Au working electrode under Ar (black) or CO₂ (red) sweeping from positive to negative potentials.
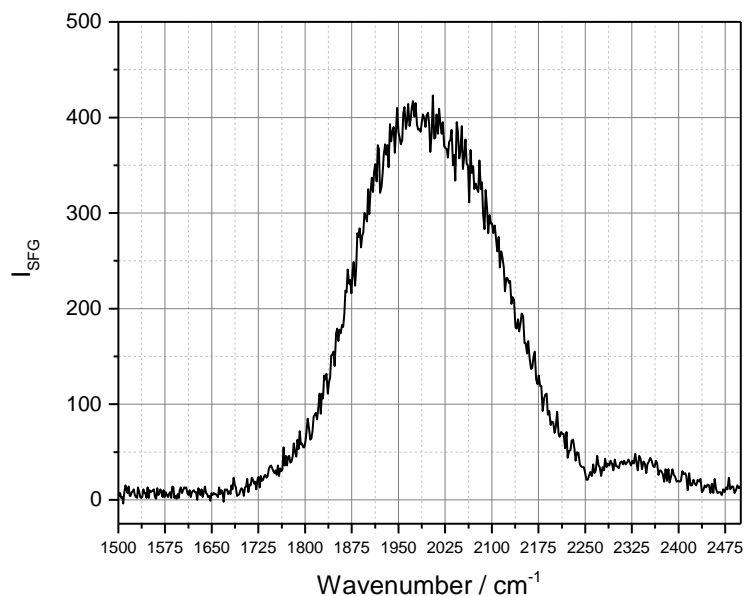
Figure S4 SFG spectrum recorded at -0.1 V during LSV's of [Mn(bpy)(CO)₃Br] dissolved in CH₃CN in the presence of 1.5 M PhOH, 50 mV s⁻¹, purged with Ar. The spectrum has been collected without a time delay between the broadband IR and the 800 nm lasers, to collect the non-resonant background, which can be used as a measure of the IR laser beam shape.
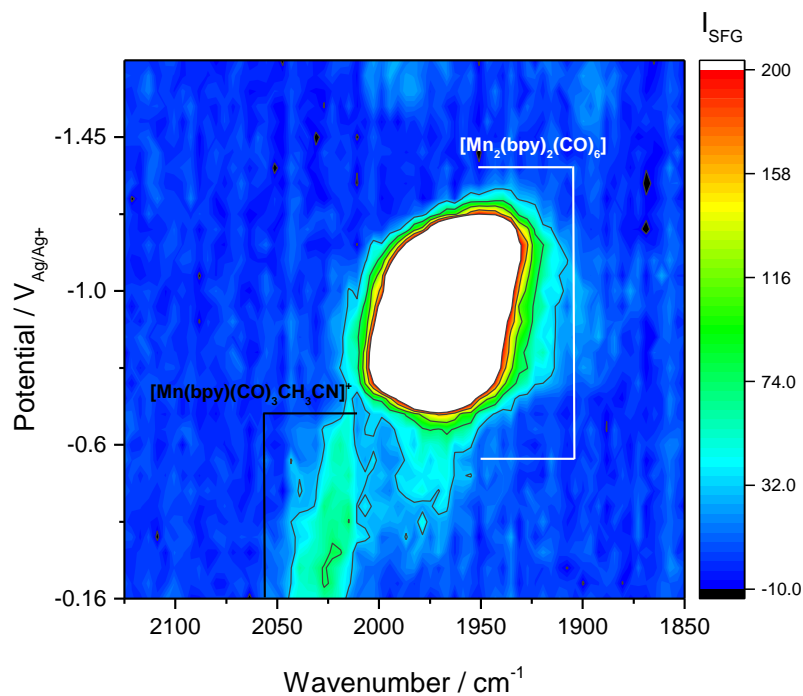

Figure S5 VSFG spectra recorded between -0.3 and -1.6 V during LSV's of [Mn(bpy)(CO)₃Br] dissolved in CH₃CN in the presence of 1.5 M TFE, 10 mV s⁻¹, purged with Ar. The contour plot has been magnified to allow the identification of species less intense than the dominating dimer band.
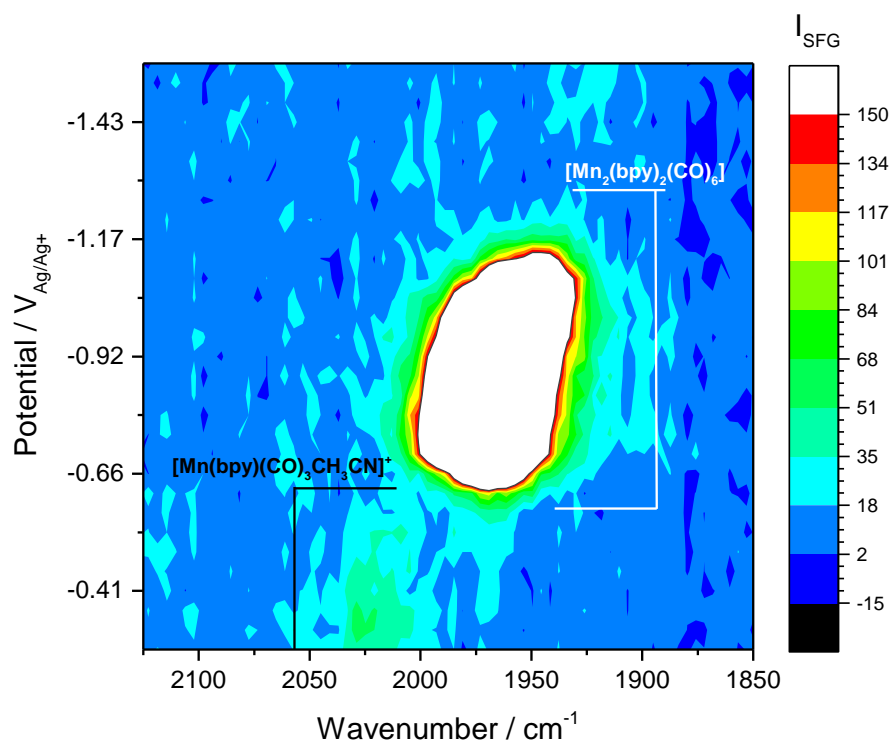
Figure S6 VSFG spectra recorded between -0.3 and -1.6 V during LSV's of [Mn(bpy)(CO)₃Br] dissolved in CH₃CN in the presence of 1.5 M phenol, 10 mV s⁻¹, purged with Ar. The contour plot has been magnified to allow the identification of species less intense than the dominating dimer band.
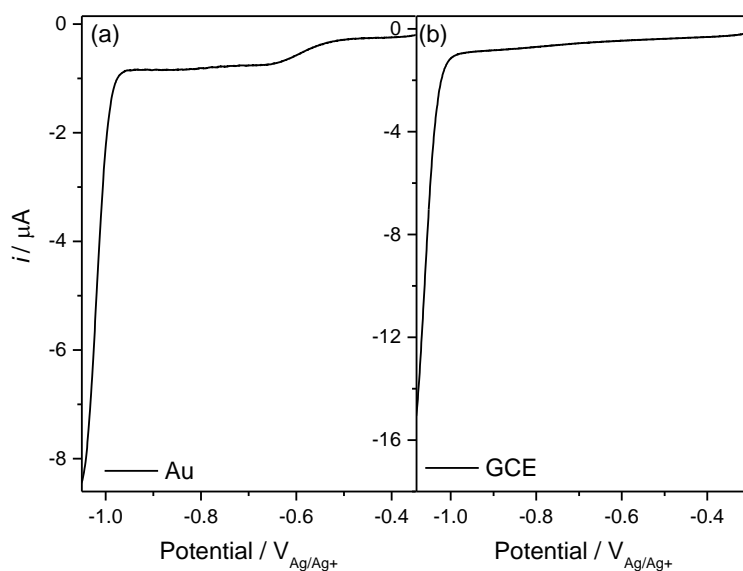

Figure S7 LSVs of [Mn(bpy)(CO)₃Br] dissolved in CH₃CN in the presence of 1.5 M TFE under Ar, recorded at 10 mV s⁻¹ using a Au (left) or GCE (right) working electrode sweeping from positive to negative potentials.
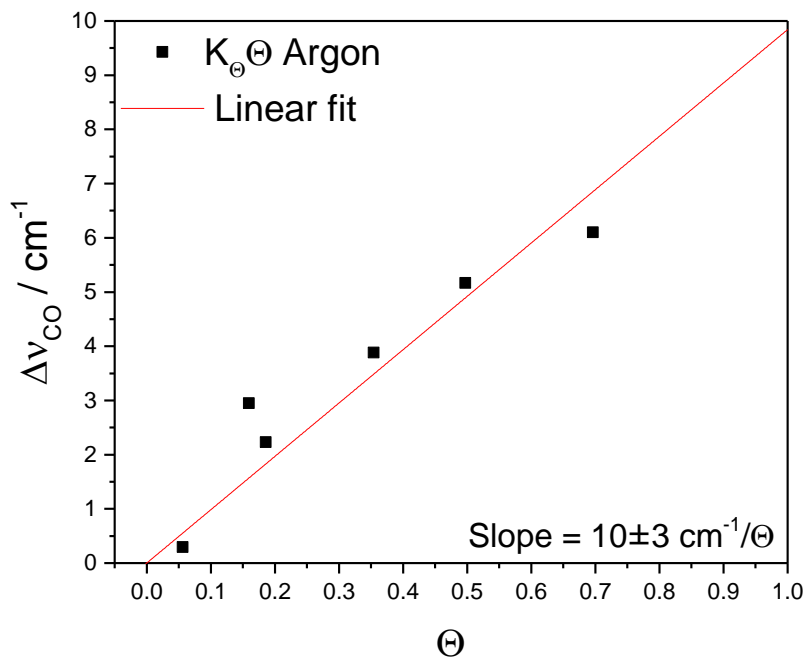
Figure S8 Deviation between experimentally measured peak maxima and $[K_\phi(\phi - \phi_0) + v_0]$ (see equation 1) plotted against the square root of the dominating VSFG signal assigned to $[Mn_2(bpy)_2(CO)_6]$ at potentials where incomplete coverage occurs (between -0.70 and -0.81 V and between -1.1 and -1.2 V). The red line shows the linear fit.
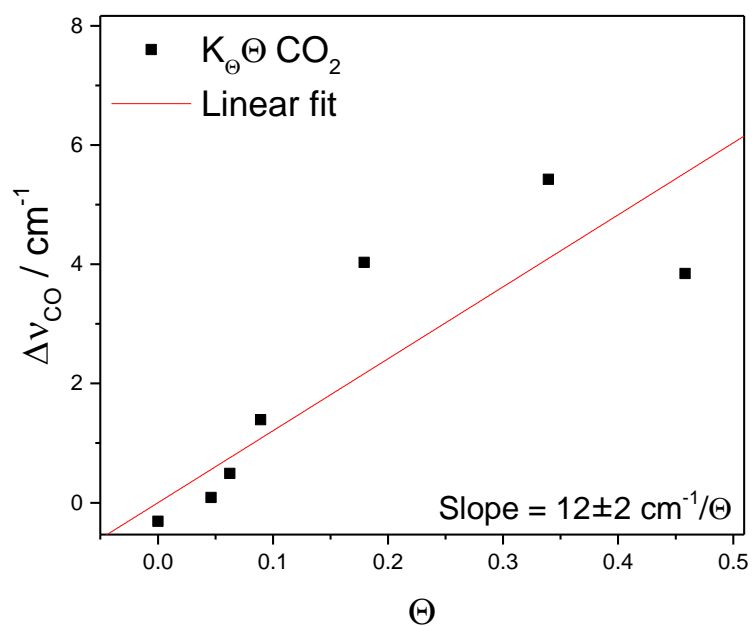

Figure S9 Deviation between experimentally measured peak maxima and $[K_\phi(\phi - \phi_0) + v_0]$ (see equation 1) plotted against the square root of the dominating VSFG signal assigned to $[Mn_2(bpy)_2(CO)_6]$ at potentials where incomplete coverage occurs (between -0.70 and -0.81 V). The red line shows the linear fit.

The potential dependence of the VSFG peak maxima observed in figures 2 and 5 can be interpreted within the model developed by Pfisterer et al.[1], Eq 1.

$$\nu_{CO}(\phi, \Theta) = K_{\phi}(\phi - \phi_0) + K_{\Theta}\Theta + \nu_0 \qquad \text{Eq. 1.}$$

Where ϕ refers to the applied potential, K_{ϕ} the Stark tuning constant, $\Theta(\phi)$ the coverage at an applied potential, K_{Θ} the coverage tuning constant, and ν_0 the vibrational mode frequency at the potential of initial adsorption. The surface coverage of the complex was estimated from the square root of the VSFG amplitude. For experiments under Ar the surface coverage was found to reach a stable constant value between -0.9 and -1.1 V, figure 3 main text. Therefore in this region it is possible to find K_{ϕ} from a linear regression of the potential – peak maxima plot. ν_0 represents the frequency of an idealised isolated molecule at the electrode surface and this value was estimated to occur at the potential where the complex is first identifiable by VSFG spectroscopy and found through the application of K_{ϕ}. A plot of $1-\Theta$ against deviation between the experimentally determined peak maxima and $[K_{\phi}(\phi - \phi_0) + \nu_0]$ is shown in figure S6 and S7 for argon and CO_2 respectively. We find a reasonable fit to a linear correlation which yields the value of K_{Θ} given in the main text.
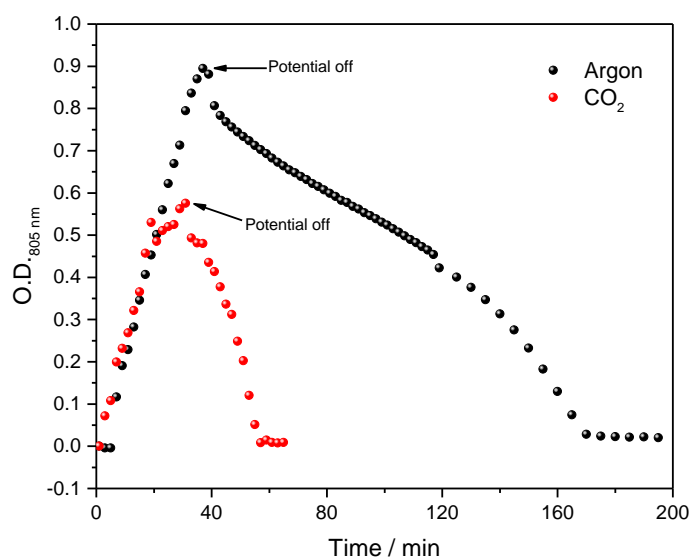

Figure S10 UV-vis absorbance at 805 nm with time during controlled potential electrolysis (CPE, -1.05 V$_{Ag/Ag+}$) of a 0.5 mM solution of [Mn(bpy)(CO)$_3$]Br in CH$_3$CN with 1.5 M TFE to generate [Mn$_2$(bpy)$_2$(CO)$_6$] under Argon (black) and CO$_2$ (red). The SEC experiment was carried out using a Pt mesh working electrode, a Ag wire pseudo reference electrode and a Pt mesh counter electrode which was separated from the main cell compartment using a Vycor® double junction.

The concentration of the dimer complex grows steadily during CPE, and slowly decreases when the potential control is removed. Under CO_2, we find that about 60% of the dimer forms, compared to the argon solution. When the potential is turned off, the depletion of the dimer is much faster under CO_2. These two observations indicate that the dimer reacts with CO_2 in the presence an acid (such as TFE used here).

REFERENCES

1.   J. H. K. Pfisterer, U. E. Zhumaev, W. Cheuquepan, J. M. Feliu, and K. F. Domke, *J. Chem. Phys.*, 2019, **150**, 41709.