Supplementary Information

"Electrochemical CO_2 reduction in water at carbon cloth electrodes functionalized with a *fac*-Mn(apbpy)(CO)$_3$Br complex"

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Experimental:

Synthesis of the *fac*-Mn(apbpy)(CO)$_3$Br complex: The complex *fac*-Mn(apbpy)(CO)$_3$Br was synthesized reacting 4-(4-aminophenyl)-2,2'-bipyridine (apbpy) with the corresponding precursor Mn(CO)$_5$Br, following a similar synthetic approach as previously reported by some of us.[1]

Electrochemistry: Cyclic voltammetry experiments and diazonium salt reduction were performed using a Metrohm Autolab 302n potentiostat. 0.5–1.0 mM solutions of the compounds were used in dry MeCN, with tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte (0.1M). A single-compartment cell, with a carbon cloth (CC) as working electrode was employed, alongside a Pt counter electrode and a Ag/AgCl (KCl 3M) as reference electrode. Under our experimental conditions, the reference ferrocene/ferrocinium (Fc/Fc$^+$) redox is at $E_{1/2}$=0.40 V (ΔE_p=65 mV) *vs.* Ag/AgCl.

Cathode preparation on carbon cloth: The real electrochemical surface area (ECSA) was estimated by performing cyclic voltammetry on a 1.0 mM solution of ferrocene (Fc) at different scan rates (the diffusion coefficient of Fc is 2.24·10^{-5} cm^2/s[2]). The peak current was then plotted against the square of the scan rate (Figure S1) and the slope is used to determine the real surface area according to the Randles-Sevčik law:

$$i_p = 2.686 \cdot 10^5 \, n^{3/2} \, A \, D^{1/2} \, C \, v^{1/2}$$

Where A is electrochemical surface area ECSA (cm^2), i_p is peak current (A), n is the number of electrons exchanged, D is the diffusion coefficient (cm^2/s), C is the molar concentration of electroactive species (mol/cm^3) and v is the scan rate (V/s)
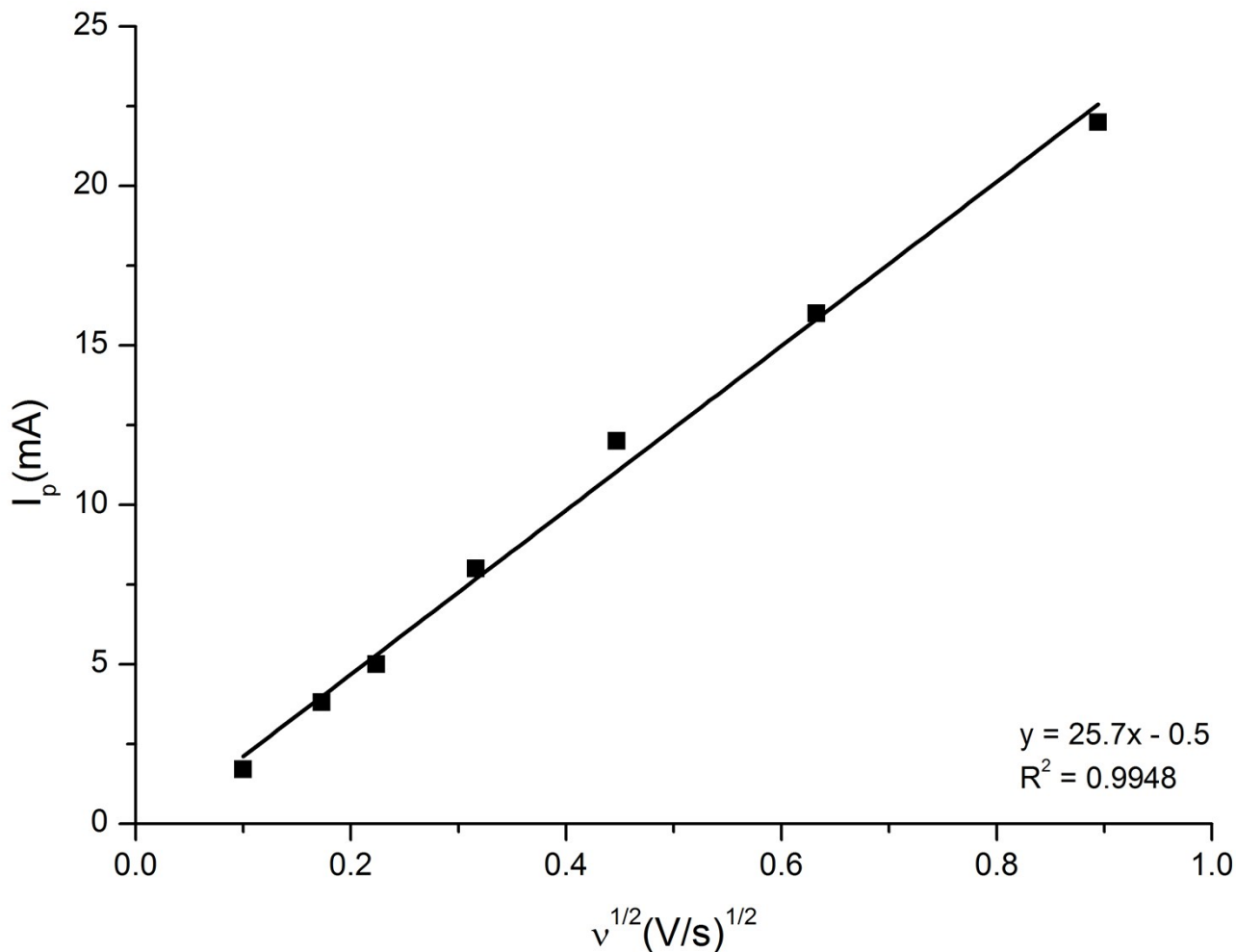

Figure S1. Plot of the **i_p** *vs* square root of the scan rate for carbon cloth sample of geometric surface area of 3.4 cm^2.

The 3.4 cm^2 geometric surface area of a carbon cloth electrode accounted for 19.95 cm^2 of ECSA (corresponding to a roughness factor of 5.87). The corresponding diazonium salt was synthesized *in situ* directly in the electrochemical cell under Ar atmosphere from a solution of the corresponding complex (5 mM) and trichloroacetic acid (30 μl) in acetonitrile (10 ml). The starting pale yellow solution was initially cooled in an ice water bath, and isoamyl nitrite (10 μl) was added; the solution became orange. TBAPF$_6$ (0.1M) was added as supporting electrolyte. The carbon cloth

functionalization was driven by CVs scans at reduction potential. In the first CV the peak at -0.3 V vs Ag/AgCl (KCl 3M) is attributed to the diazonium salt of Mn(apbpy)(CO)$_3$Br . The peak vanishes after following cycles indicating the grafting of covalently bounded layer. (Figure S2). This deposition in situ method has the advantage of avoiding isolation and purification of the diazonium salt.[3] To estimate the amount of electrocatalyst covalently bonded on ECSA, the electrochemical methods of charge integration of CV scan could be adopted.[1,4] However, the electrochemical reduction of 3/CC is chemically irreversible (as that of 3) and overlaps with the reduction of water. An indirect method for evaluating the surface coverage Γ (mol/cm^2) is via charge integration of CV data of CC bonded nitroaniline. This approach has the advantage of using an electrochemically reversible system in MeCN solutions, and it has Γ values about 10 times higher than those of bpy-type metal complexes, as previously reported.[1,5] The surface coverage of nitroaniline on CC (Figure S3) has been experimentally evaluated to be 1.4×10^{-8} mol cm$_{ECSA}^{-2}$. This value is comparable with that previously found for glassy carbon electrode (about 10^{-9} mol cm^{-2}), considering the much higher roughness of CC. Hence, we estimate that Γ of 3/CC is about 1.4×10^{-9} mol cm$_{ECSA}^{-2}$.

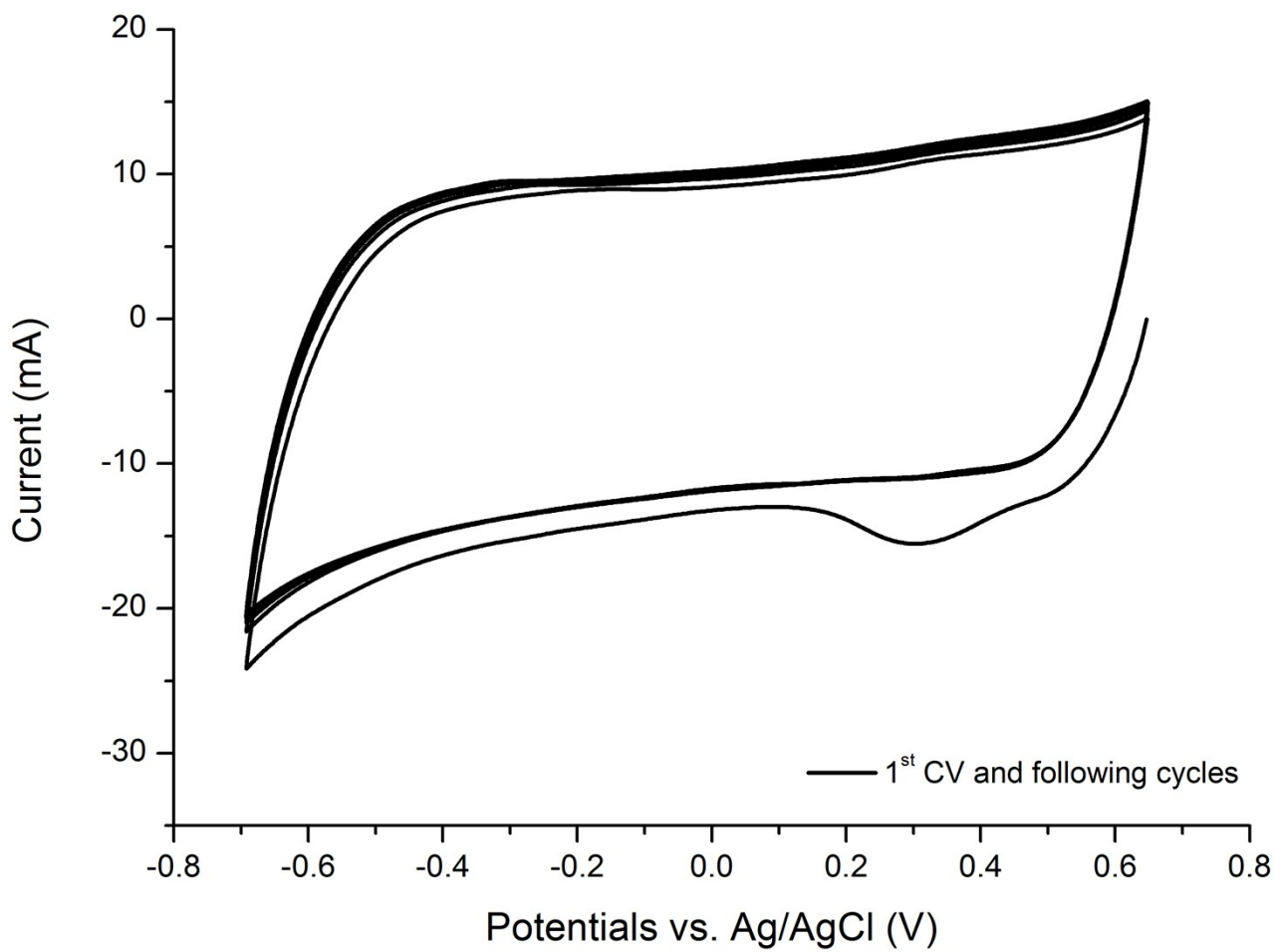**Figure S2.** First and steady state CVs of carbon cloth modified with diazonium salt of Mn(apbpy)(CO)$_3$Br. Scan rate of 50 mV/s.
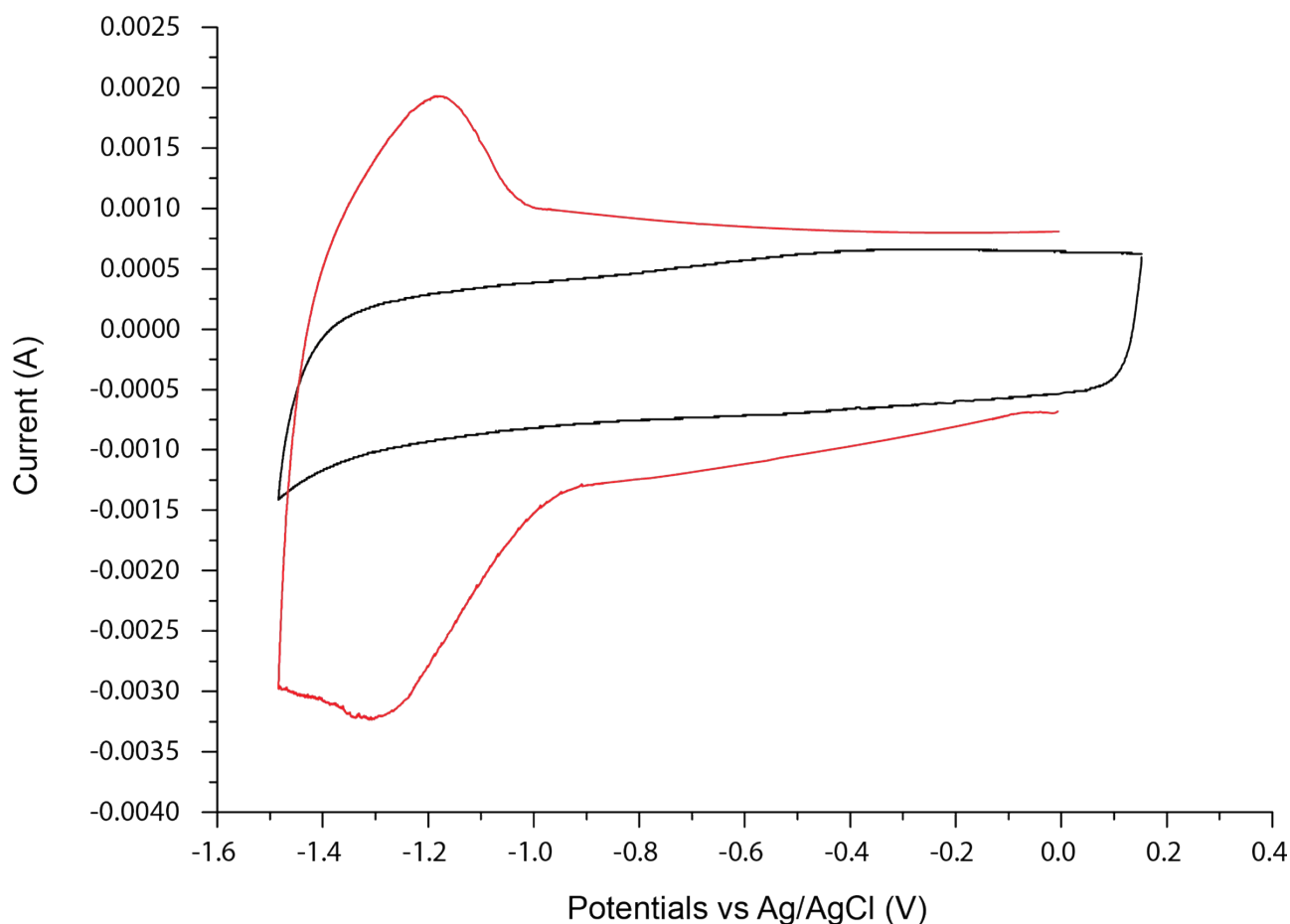
Figure S3. CV (red line) of nitroaniline/CC in MeCN solution used for the evaluation of surface coverage. Scan rate 10 mV/s. The black line is the background in MeCN under Ar of the CC before functionalization.

Cell assembly: the experiments were conducted in a base-resistant 3d-printed ABS cell (Figure S4) designed with a gas collector cone housed on the top of the cell. The cell, oriented vertically, was assembled in two halves, one housing the cathodic compartment and the other the anodic one, separated by a Nafion 117 membrane in the middle, hold by a Teflon gasket. The cathode composed by the functionalized carbon cloth working electrode was secured by an insulated screw-terminal connected to the outside of the cell with enamelled copper wire; the reference was of an Ag|AgCl|KCl$_{sat}$ electrode placed in close proximity with the working electrode. The counter electrode, a platinum wire, was housed into the anodic compartment. Both compartments were filled with 0.1M $KHCO_3$ and sealed with rubber gaslock® plugs. Prior to each electrolysis

experiment, the cathodic compartment electrolyte was saturated by bubbling 99.99% purity CO_2 and the collector cone gas headspace was completely evacuated and filled with electrolyte.
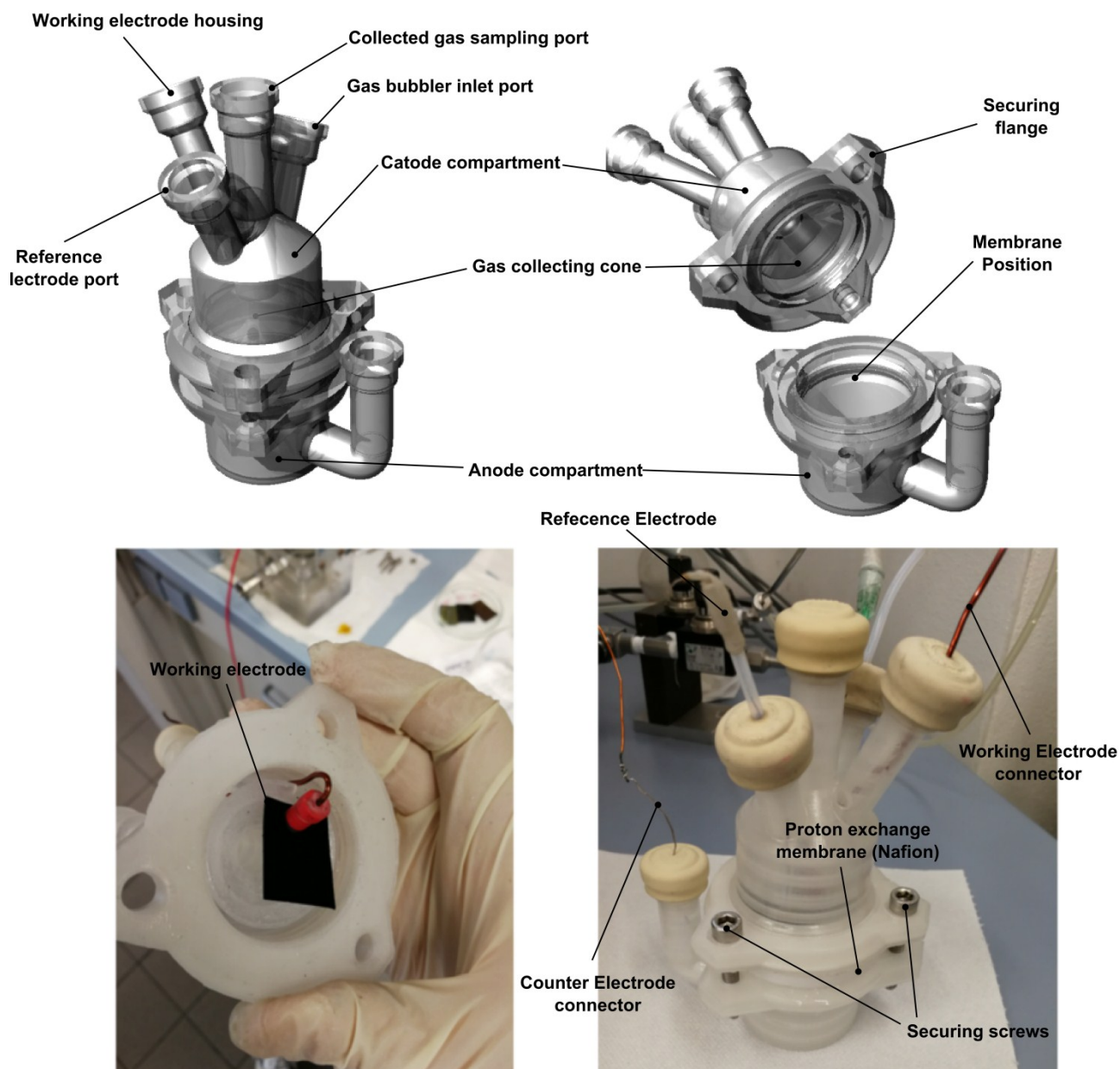

Figure S4. 3D-printed ABS electrochemical cell used for CO_2RR experiments.

Electrolysis experiment, electrochemical characterization and product analysis: the electrolysis experiments were conducted at different potentials, ranging from -1.0V to -1.6V *vs* Ag|AgCl|KCl$_{sat}$ for an appropriate electrolysis time, in order to collect enough gas for GC analysis, ranging from 15 minutes (high currents) to 1 hour (low currents). After the electrolysis time is

elapsed, the current is integrated to obtain the charge and the gas is collected by a syringe, measured and injected (100 µl) into a gas cromatograph (Carboxen Column, designed to separate hydrogen, O_2, N_2, CO, CO_2 and c1-c3 gases) with a 140°C 9 minute isotherm, followed by a 30 °C/min ramp to 225°C and a holding time of 25 minutes. The cell was saturated again with CO_2 prior each experiment. The liquid catholyte sample was collected in order to detect any trace soluble product present at the end of the experiment cycle. The stability experiments were conducted by subsequent electrolysis cycles at fixed potential, -1.3V in this case, each elapsing 1 hour time; the products were analysed following the same protocol of the potential variation test. The potential was chosen accordingly to the activity test, as a tradeoff between electrolysis current and faradaic efficiency.

ATR measurements: IR-ATR spectra were collected on a Fourier transform Equinox 55 (Bruker) spectrophotometer equipped with an ATR device; resolution was set at 2 cm^{-1} for all spectra. A spectral range of 400–4000 cm^{-1} was scanned, using KBr as a beam splitter.

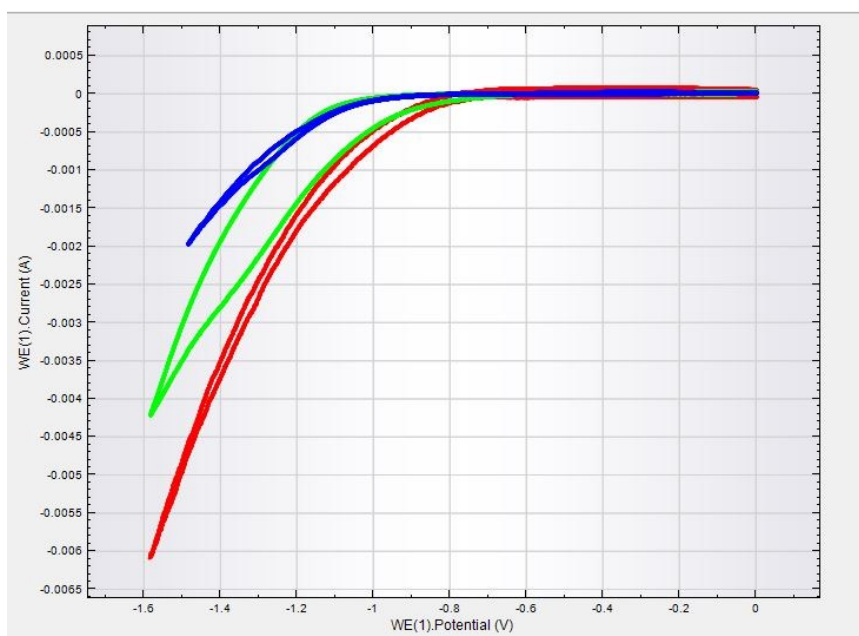**Figure S5:** CVs in $KHCO_3$ 0.1 M in water. Scan rate 10 mV/s, A= 2.5 cm^2. Blue: Pristine Carbon Cloth (CC) under Ar; Red: Mn-functionalized CC (3/CC) under Ar; Green: Mn- functionalized CC (3/CC) under CO_2.
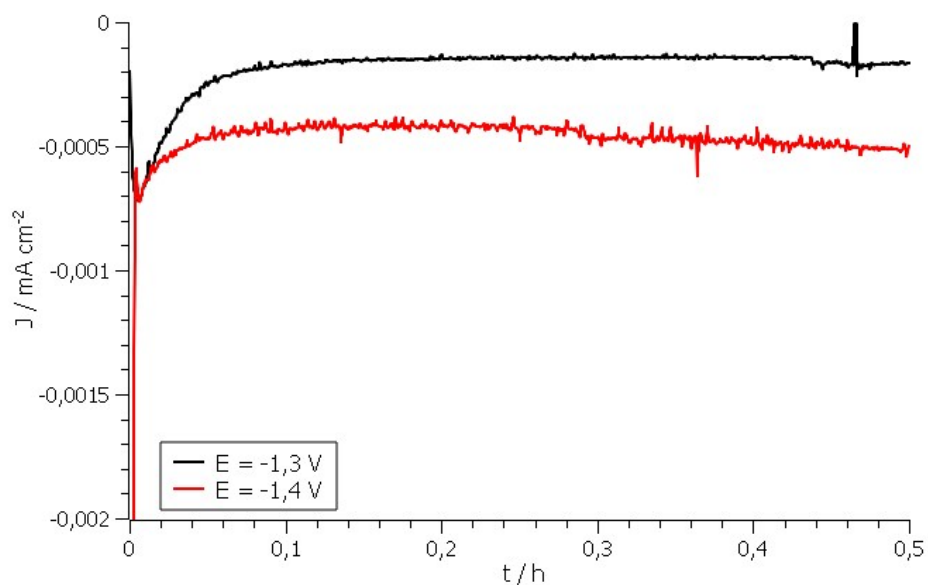
Figure S6. Background current density profile of carbon cloth support in CO_2-saturated 0.1M $KHCO_3$ measured in the same potential window of the CO_2 electrolysis
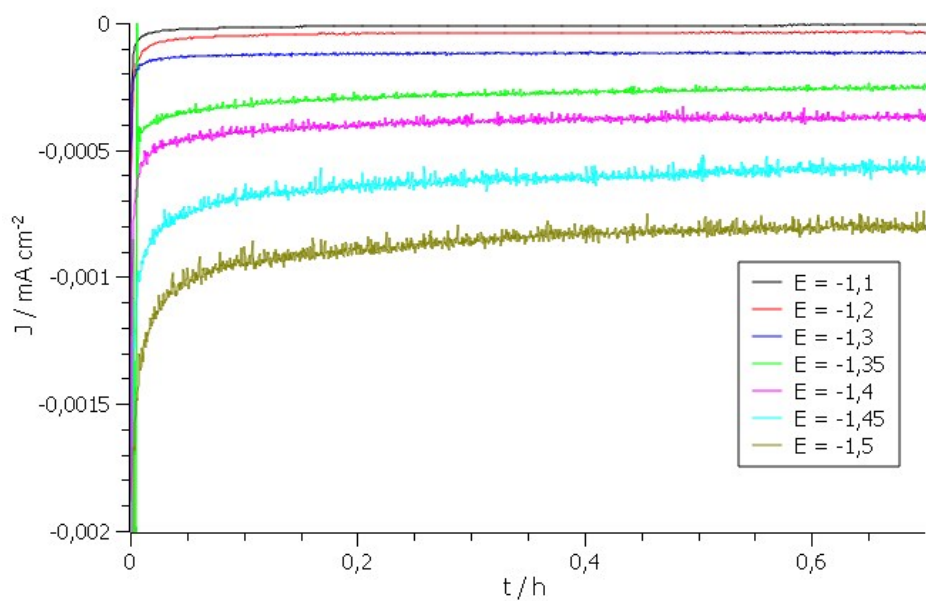

Figure S7. Background current density profile of carbon cloth support functionalized with 4-(4-aminophenyl)-2,2'-bipyridine ligand in CO_2-saturated 0.1M $KHCO_3$ measured in the same potential window of the CO_2 electrolysis

Supporting References:

[1]   C. Sun, L. Rotundo, C. Garino, L. Nencini, S. S. Yoon, R. Gobetto and C. Nervi, *ChemPhysChem*, 2017, **18**, 3219–3229.

[2]   Y. Wang, E. I. Rogers, R. G. Compton, *J. Electroanal. Chem.* , 2010, **648**, 15–19.

[3]   S. Baranton and D. Bélanger, *J. Phys. Chem. B*, 2005, **109**, 24401–24410.

[4]   M. Sandroni, G.Volpi, J. Fiedler, R. Buscaino, G. Viscardi, L. Milone, R. Gobetto, C. Nervi, *Cat. Today*, 2010, **158**, 22–28.

[5]   A. Adenier, M.M. Chehimi, I. Gallardo, J. Pinson, N. Vila, *Langmuir*, 2004, **20,** 8243–8253.