

# Metal-Organic Conjugated Microporous Polymer Containing A Carbon Dioxide Reduction Electrocatalyst

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## Supporting information

**Materials:** Milli-Q water (18.2 M $\Omega$ ) was used throughout (Millipore Corp). All chemicals were purchased from Sigma Aldrich except for 5,5'-dibromo-2,2'-bipyridyl which was purchased from TCI Chemicals. 3 mm GCE were purchased from IJ Cambrian Scientific Ltd. Argon and helium N6 grade, and CO<sub>2</sub> CP grade were purchased from BOC. Calibrant gas for the GC was a custom order of 500 ppm H<sub>2</sub> and 200 ppm CO in helium.

**Synthesis of CMP-(bpy)<sub>20</sub>:** Under an argon atmosphere 1,4-dibromobenzene (0.35 g, 0.75 mmol), 5,5-dibromo-2,2'-bipyridine (0.34 g, 0.50 mmol) and 1,3,5-triphenylbenzene (0.375 g, 1.25 mmol) were stirred under reflux at 90 °C for 3 days in DMF (8 mL) and NEt<sub>3</sub> (8 mL) with CuI (20 mg) and [Pd(PPh<sub>3</sub>)<sub>4</sub>] (40 mg). Over the 3-day period the mixture had turned from a brown suspension to a brown solid. The polymer was then ball milled for 30 minutes, to obtain a powder which was then washed and purified *via* Soxhlet extraction with methanol at 90 °C for 3 days. Yield: 322 mg (81%). Elemental combustion analysis (%) calculated for C<sub>24.5</sub>H<sub>9.75</sub>N: C 92.52, H 3.06, N 4.40; Found: C 82.17, H 3.42, N 4.14. Please note: The elemental composition was calculated ignoring defects within the material, molecular weight distribution and the presence of end-groups whose nature is unclear.

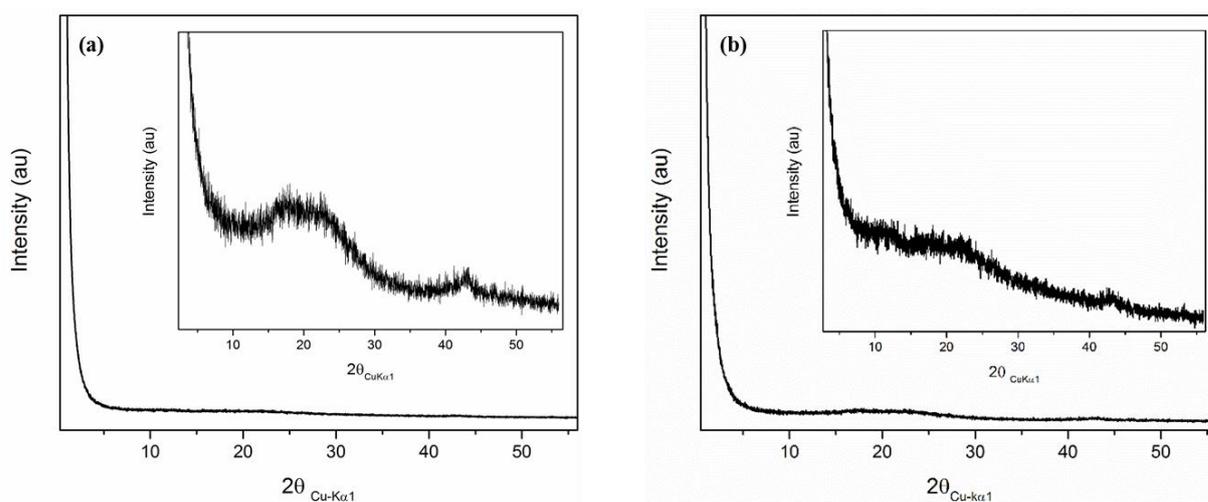
**Synthesis of CMP-(bpy)<sub>20</sub>-Mn:** CMP-(bpy)<sub>20</sub> (0.25 g, 0.39 mmol) was suspended in diethyl ether with [Mn(CO)<sub>5</sub>Br] (0.25 g, 0.9 mmol) and heated to 45 °C for 24 hours. The obtained red/brown solid was washed with methanol, water and chloroform (50 mL each) and a Soxhlet extraction was carried out with DCM at 75 °C. Yield: 300 mg, (67%). Elemental combustion analysis (%) calculated for C<sub>26</sub>H<sub>9.75</sub>NO<sub>1.5</sub>Mn<sub>0.5</sub>Br<sub>0.5</sub>: C 73.11, H 2.28, N 3.28; Found: C 61.10, H 3.58, N 2.98. Pd content determined by ICP-OES: 0.24 ± 0.02%. Mn content determined by ICP-OES: 5.47 ± 0.21%.

**ICP-OES and CHN analysis:** Carried out by the University of Liverpool analytical services. ICP-OES samples were prepared *via* microwave digestion using a PerkinElmer titan. Digestion was carried out in concentrated nitric acid, and the temperature was ramped to 170 °C over a ramp time of 5 minutes at 30 bar and held for 5 minutes, then increased to 210 °C over 3 minutes at 30 bar and held for 45 minutes. Finally, the temperature was lowered to 50 °C over 1 minute at 30 bar and held for 15 minutes. The sample was diluted with water to 14% nitric acid content before ICP-OES analysis.

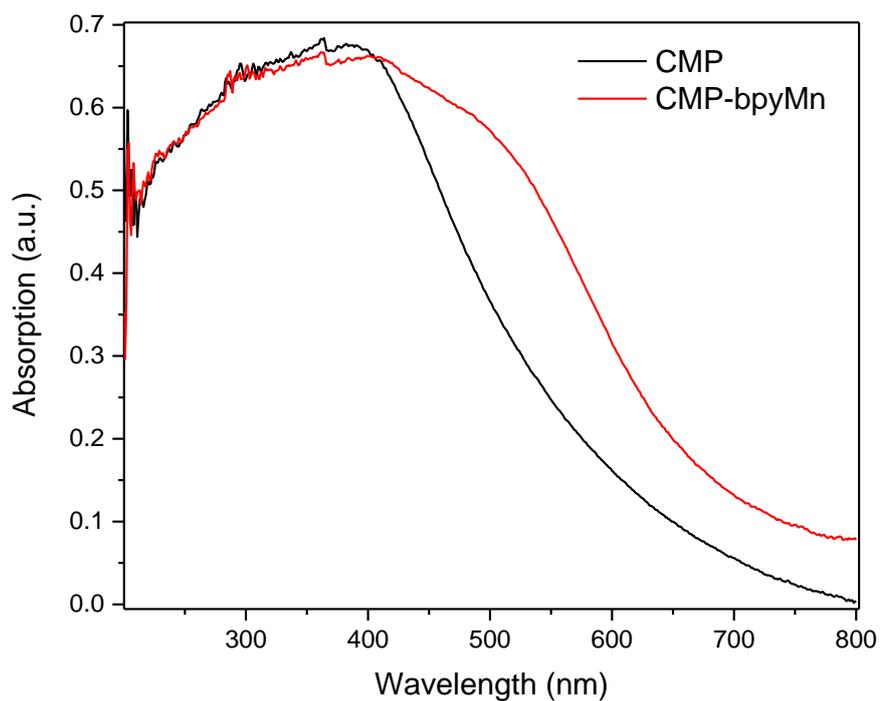
**Materials characterisation:** UV/Vis absorption spectra were recorded on a Shimadzu UV-2550 UV-VisNIR spectrometer as powders. Fourier-transform infrared (FTIR) spectra were recorded using a JASCO 4000 FTIR in an ATR geometry (resolution, 4 cm<sup>-1</sup>). Powder x-ray-diffraction (PXRD) measurements were performed on a PANalytical X'Pert PRO MPD, with a Cu X-ray source, used in high throughput transmission mode with K $\alpha$  focusing mirror and PIXCEL 1D detector. Thermogravimetric analysis (TGA) measurements were performed on an EXSTAR6000 by heating samples at rate of 5 °C min<sup>-1</sup> under an air flow of 25 mL min<sup>-1</sup> and nitrogen flow of 10 mL min<sup>-1</sup>, in open aluminium pans from 40 to 600 °C and holding at 600 °C for 30 minutes.

**Gas sorption properties:** Surface area and pore size distributions were performed on a Micromeritics ASAP 2020 volumetric adsorption analyzer under nitrogen or CO<sub>2</sub> at 77.4 K. Samples were degassed at 120 °C or 60 °C for 15 hours under vacuum (10<sup>-5</sup> bar) prior to analysis.

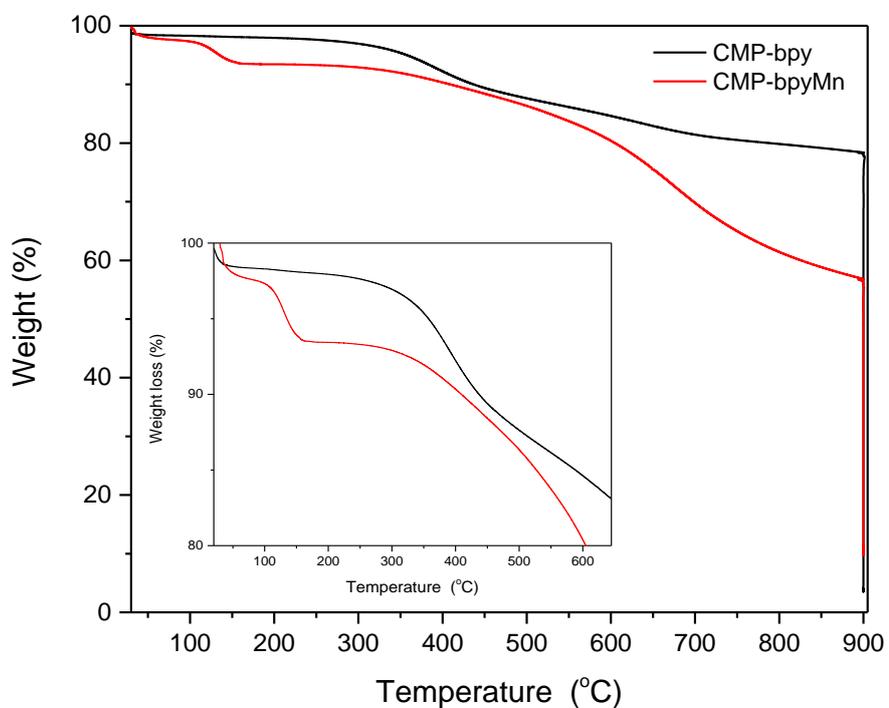
**Electrochemical analysis:** Experiments were carried out in a 3-neck flask containing a Ag/AgCl reference electrode, Pt counter electrode and glassy carbon working electrode. Working electrodes were prepared by casting 10  $\mu\text{L}$  of a sample containing a suspension of either CMP-(bpy)<sub>20</sub> or CMP-(bpy)<sub>20</sub>-Mn (5.5 mg mL<sup>-1</sup>) in a Nafion (at 0.5% weight) acetonitrile/alcohol solution onto a GCE (0.07 cm<sup>2</sup>). The Nafion acetonitrile/alcohol solution is prepared by dilution of a 5% weight Nafion in mixed lower aliphatic alcohol solution (Sigma Aldrich, used as supplied) in acetonitrile. All samples were dried in air. The electrolyte used was either 60 mM buffer. The cell was kept in the dark using aluminium foil for the entire experiment. The cell was purged with argon or CO<sub>2</sub> for 20-30 minutes before starting the experiment. PalmSens or emstat potentiostats were used. During bulk electrolysis experiments the Pt counter electrode was kept being a Vycor tip containing ferrocene carboxylic acid in 0.1 M KOH. The electrolyte was stirred through the experiment. Samples were purged with CO<sub>2</sub> and then sealed. 100  $\mu\text{L}$  injections were recorded of the cell headspace periodically and analysed using an Agilent 6890N with N6 helium as the carrier gas (5 mL min<sup>-1</sup>). A 5 Å molecular sieve column (ValcoPLOT, 30 m length, 0.53 mm ID) and a pulsed discharge detector (D-3-I-HP, Valco Vici) were employed. At the end of the experiment the electrolyte was also examined for formate production by ion chromatography using an Eco IC (Metrohm) instrument with a sup 5-150/4 column.



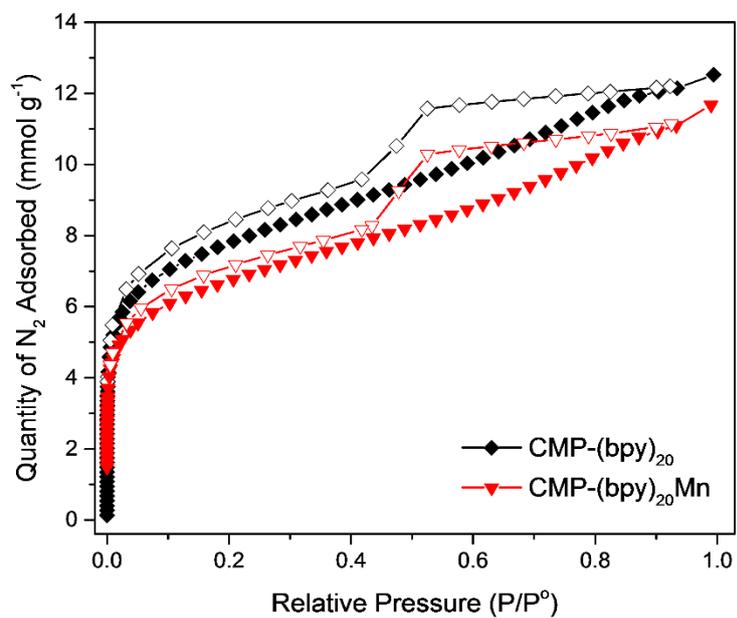
**Figure S1:** PXRD patterns of a) CMP and b) CMP-bpyMn, both of which can be seen to be amorphous materials.



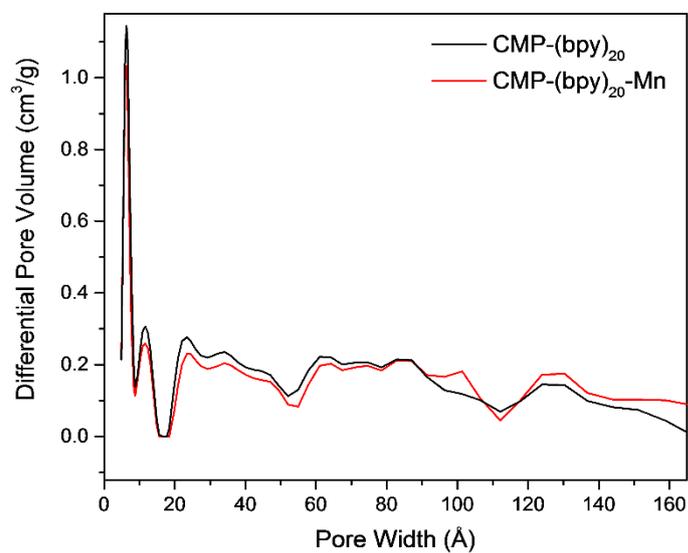
**Figure S2.** UV/Vis spectra of CMP-(bpy)<sub>20</sub> (black) and CMP-(bpy)<sub>20</sub>-Mn (red).



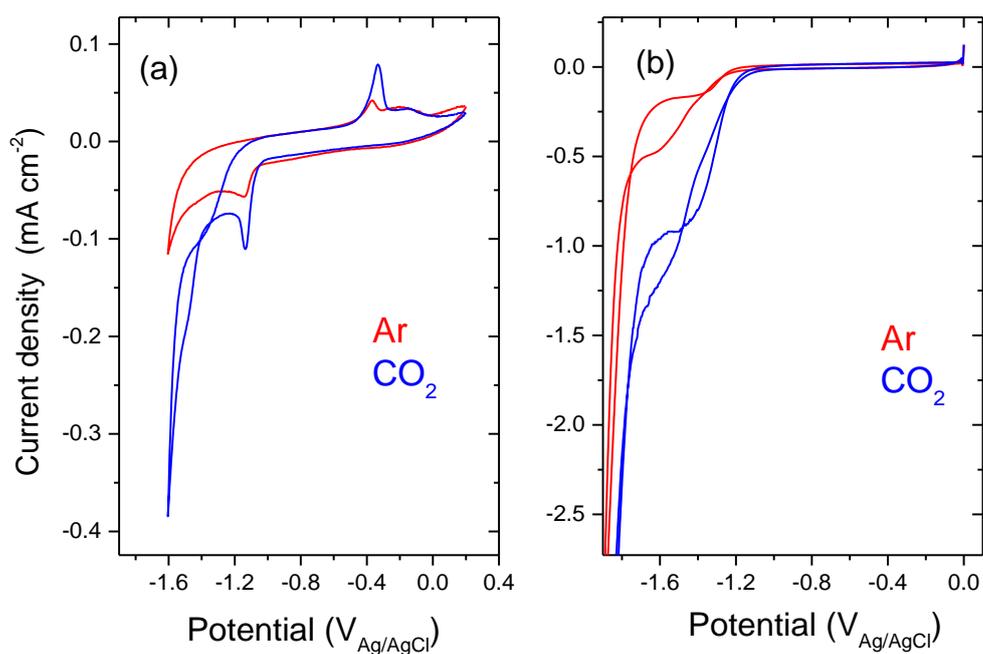
**Figure S3.** Thermal gravimetric analysis of CMP-(bpy)<sub>20</sub> (black) and CMP-(bpy)<sub>20</sub>-Mn (red) under a nitrogen atmosphere. The inset shows the mass loss at ~150 °C for CMP-(bpy)<sub>20</sub>-Mn that is not observed with CMP-(bpy)<sub>20</sub>.



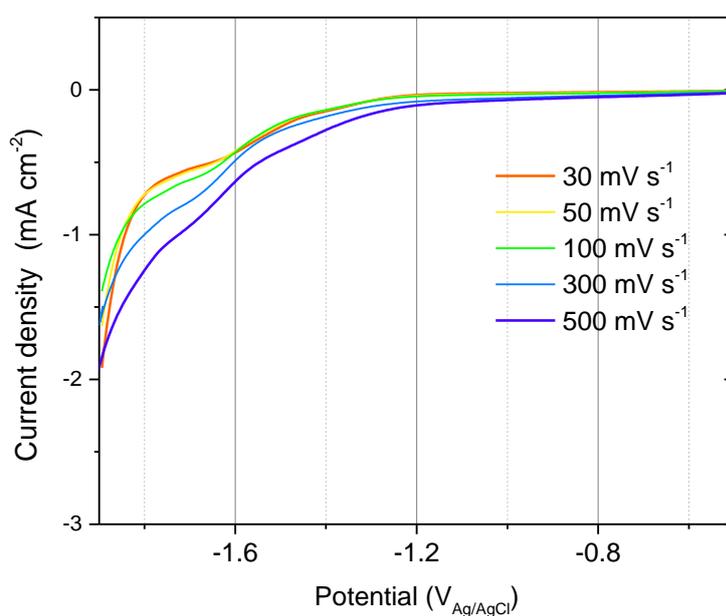
**Figure S4.** N<sub>2</sub> adsorption-desorption isotherms measured at 77.4 K for CMP-(bpy)<sub>20</sub> (black) and CMP-(bpy)<sub>20</sub>-Mn (red).



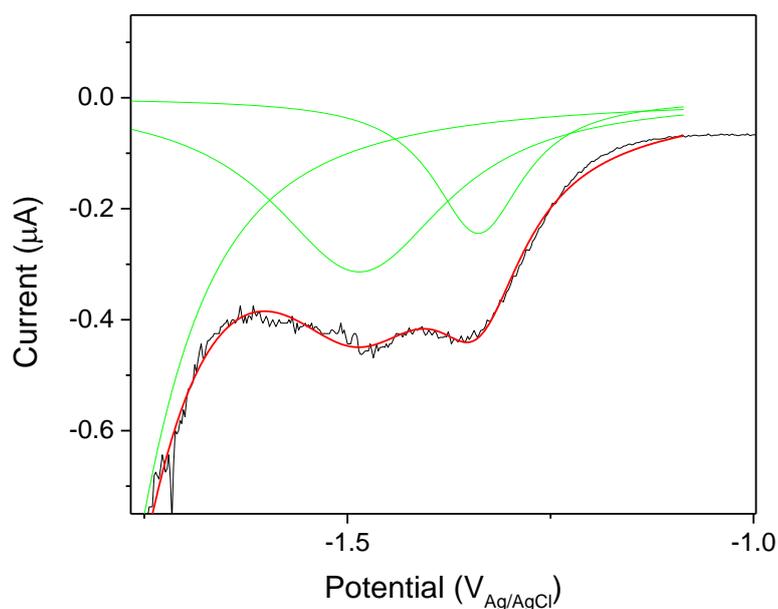
**Figure S5.** Differential pore volume of CMP-(bpy)<sub>20</sub> (black) and CMP-(bpy)<sub>20</sub>-Mn (red) measured under N<sub>2</sub> (77.4 K) showing the pore distribution is maintained following addition of the Mn centre.



**Figure S6.** CVs of (a)  $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]/\text{Nafion}$ , (b)  $\text{CMP}-(\text{bpy})_{20}\text{-Mn}/\text{Nafion}$ , both on a glassy carbon electrode in 0.06 M phosphate buffer pH 7,  $10 \text{ mV s}^{-1}$  recorded under  $\text{CO}_2$  and Ar. The data in part (a) is replotted from reference [1]. Electrodes are prepared using  $10 \mu\text{l}$  of a solution containing of either  $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$  or  $\text{CMP}-(\text{bpy})_{20}\text{-Mn}$  on a  $0.07 \text{ cm}^2$  electrode.



**Figure S7.** Linear sweep voltammetry of  $\text{CMP}-(\text{bpy})_{20}\text{-Mn}$  in 0.06 M phosphate buffer pH 7,  $10 \text{ mV s}^{-1}$  recorded under Ar atmosphere.



**Figure S8.** Square wave voltammetry of CMP-(bpy)<sub>20</sub>-Mn in 0.06 M phosphate buffer pH 7, 10 mV s<sup>-1</sup> recorded under Ar atmosphere. Integration of the reductive feature in the SWV assigned to the Mn centre indicates  $5.2 \times 10^{-6}$  C is passed, corresponding to an estimated  $2.7 \times 10^{-11}$  mol of electroactive Mn on a 0.07 cm<sup>2</sup> GCE assuming a two-electron reduction. Using this estimate of the electroactive content it is possible to arrive at an approximate TON over 4 hours of 1296. However great caution should be taken when interpreting the square-wave voltammograms of polymer thin films quantitatively,<sup>2</sup> and we highlight this value to be a best estimate. Regardless of the absolute value it is clear that the electroactive content is low. This is likely due to the fact that only the CMP-(bpy)<sub>20</sub>-Mn particles in direct contact with the GCE will be active and this represent a small fraction of the overall material deposited. Furthermore structural distortions of the CMP structure can lead to a loss of conjugation which will make regions of each polymer particle insulating.

#### References:

- [1] J. J. Walsh, G. Neri, C. L. Smith and A. J. Cowan, *Chem. Commun.*, 2014, **50**, 12698–12701  
 [2] V. Mirčeski, R. Gulaboski and F. Scholz, *J. Electroanal. Chem.*, 2004, **566**, 351–360.