

Metal-Organic Conjugated Microporous Polymer Containing a Carbon Dioxide Reduction Electrocatalyst

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A metal-organic conjugated microporous polymer (CMP) containing a manganese carbonyl electrocatalyst for CO₂ reduction has been synthesised and electrochemically characterised. Incorporation in a rigid framework changes the behavior of the catalyst, preventing reductive dimerization. These initial studies demonstrate the feasibility of CMP electrodes that can provide both high local CO₂ concentrations and well defined electrocatalytic sites.

The capture and electrocatalytic conversion of CO₂ into useful feedstocks and fuels is one of the most pressing challenges facing the chemistry community.¹ Historically electrocatalytic CO₂ reduction has been addressed *via* two main routes. Careful design has delivered molecular electrocatalysts with extremely high turnover frequencies, and in many cases low onset potentials, for C1 products such as CO and HCOOH.^{2–4} However, the majority of studies involve catalysts that are only soluble in organic solvents, an environment that also provides high CO₂ concentrations and suppresses the undesired hydrogen evolution reaction. In contrast, heterogeneous electrodes⁵ including metals such as Cu, Au and Ag have shown high current densities and stability in water, but rational design of the catalyst centre is challenging. Recently, a number of studies have demonstrated a third route using crystalline porous materials. High levels of activity for electrocatalytic CO₂ reduction have been reported for covalent organic frameworks (COFs)^{6,7} and metal organic frameworks (MOFs)^{8–10} that contain molecular electrocatalysts within the framework. Such an approach has significant advantages as it provides electrode materials with well-defined tuneable, catalytic in a stable heterogenised form. A range of porous organic polymers that lack long-range order are also known.¹¹ Amongst these are CMPs, materials formed by the polymerisation of rigid strut units with a high degree of π -conjugation across the network.¹² CMPs have excellent thermal stabilities and interesting electrical and photophysical properties. Furthermore,

many CMPs contain functionalities including porphyrins and bipyridines that can yield metal-organic CMPs through post-polymerization metalation.¹³ CMPs and metal-organic CMPs have been studied for a wide range of applications^{14,15} including catalysis, electrochemical energy storage and CO₂ capture.^{16,17} The high concentration of CO₂ achievable within the structure is potentially advantageous for CO₂ fixation¹⁷ and this has been exploited with materials for thermal catalysis including CO₂ hydrogenation¹⁸ and cycloaddition to epoxide.¹⁹ Metal-organic CMPs containing [Re(diimine)(CO)₃Cl] moieties have also been used as photocatalysts for CO₂ reduction.²⁰

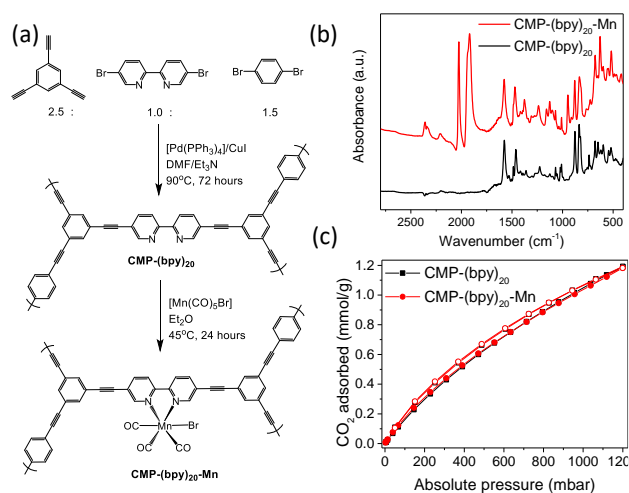


Figure 1. (a) Synthetic route to CMP-(bpy)₂₀-Mn. The notation for the bpy content of the polymer arises from the feed percentage of 5,5'-dibromo-2,2'-bipyridine in the polymerisation reaction. (b) FTIR spectra and (c) CO₂ adsorption-desorption isotherms measured at 298 K for CMP-(bpy)₂₀ (black) and CMP-(bpy)₂₀-Mn (red).

One past study examined metal nanoparticle electrodes deposited onto a CMP membrane for CO₂ conversion²¹ but metal-organic CMPs with well-defined catalytic centres have not previously been explored as electrode materials for CO₂ reduction to the best of our knowledge. Such an approach has a number of potential benefits. Cobalt CMPs for electrocatalytic O₂ reduction²² and H₂O oxidation^{23,24} showed activities and stabilities exceeding the equivalent monomeric catalyst units, likely due to improved mass transport within the porous structure,²² prevention of catalyst agglomeration²³ and the conjugated nature of the structure allowing delocalization of charge between catalytic sites.²⁴ Furthermore, the ability of CMPs to

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concentrate CO₂ within the structure may provide a pathway with the ability for efficient conversion of dilute CO₂ sources.

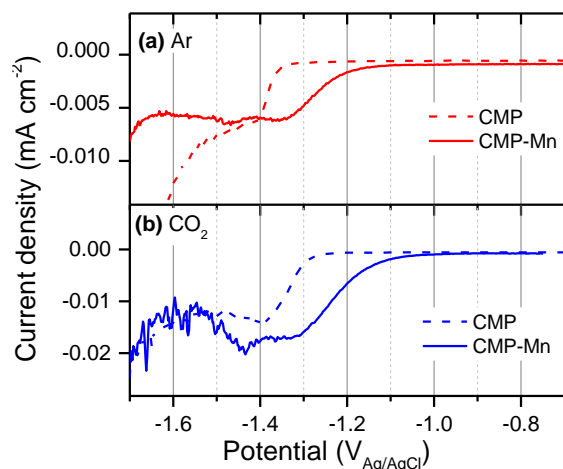


Figure 2. Square wave voltammograms (a,b) (10 mV s^{-1}) of CMP-(bpy)₂₀ (dashed) and CMP-(bpy)₂₀-Mn (solid) in pH 7 phosphate buffer under Ar (red) or CO₂ (blue). CMP-(bpy)₂₀-Mn shows an additional reduction (-1.35 V) assignable to [Mn(bpy)(CO)₃Br] moieties.

Here we report the electrochemistry of a *fac*-[Mn(bpy)(CO)₃Br] moiety incorporated into a CMP framework (the *fac*- notation is omitted from here on). [Mn(bpy)(CO)₃Br] and its derivatives have been shown to be effective electrocatalysts for the reduction of CO₂, principally to CO.^{25,26} However, in solution [Mn(bpy)(CO)₃Br] undergoes a reduction induced dimerisation prior to formation of the catalytically active species, making its study within the rigid electroactive CMP framework particularly interesting. The synthetic approach reported here is based on that previously reported for a related Re based CMP and a ratio of monomers that was previously identified to give an optimal balance between porosity and density of metal binding sites.¹³ Briefly, the amorphous polymer CMP-(bpy)₂₀ was prepared by Sonogashira–Hagihara cross-coupling reaction of 1,3,5-triethynylbenzene with 5,5'-dibromo-2,2'-bipyridine and 1,4-dibromobenzene, Figure 1a, S1. Following purification of CMP-(bpy)₂₀ the polymer and [Mn(CO)₅Br] are refluxed in Et₂O for 24 hours yielding a red/brown solid, CMP-(bpy)₂₀-Mn.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) demonstrates inclusion of 5.47% Mn by weight within CMP-(bpy)₂₀-Mn. This Mn loading is close to the calculated maximum (6.41%) based on 100% occupancy of all bpy units in the proposed structure in Figure 1. The presence of a tricarbonyl complex is confirmed by FTIR spectroscopy with CMP-(bpy)₂₀-Mn showing $\nu(\text{CO})$ bands at 2026, 1940 and 1919 cm^{-1} , and is in-line with the spectra of a similar Mn complex within a photoactive MOF,²⁷ Figure 1b. UV/Vis spectroscopy also supports the formation of CMP-(bpy)₂₀-Mn with the presence of a broad absorption from 400–550 nm, that is not seen with CMP-(bpy)₂₀, likely

due to a MLCT transition, Figure S2. Thermal gravimetric analysis shows a ~7% weight loss for CMP-(bpy)₂₀-Mn, due to the moderate thermal stability of [Mn(bpy)(CO)₃Br] (<100 °C), Figure S3.²⁶ By contrast, the underlying framework is stable to > 300 °C. We therefore conclude that the Mn is present as [Mn(bpy_{CMP})(CO)₃Br] moieties.

Nitrogen adsorption measurements at 77 K show that both CMP-(bpy)₂₀ and CMP-(bpy)₂₀-Mn have a type I and type IV physisorption isotherms with a H2-hysteresis loop, indicating the presence of mesopores and macropores within the 3D porous network, Figure S4. A slight decrease in surface area (CMP-(bpy)₂₀ = 637 $\text{m}^2 \text{g}^{-1}$) occurs following inclusion of the Mn catalyst (CMP-(bpy)₂₀-Mn = 549 $\text{m}^2 \text{g}^{-1}$) and this is also accompanied by a small decrease in pore volume from 0.24 to 0.21 $\text{cm}^3 \text{g}^{-1}$. Analysis of the differential pore volume suggests that all materials exhibit a broad range of pores from ultramicroporous (>1 nm) to macroporous (> 50 nm), Figure S5.

The decrease in the specific surface area is mostly due to the increased mass with the Mn present. At 298 K The CMP-(bpy)₂₀-Mn shows a moderate level of uptake of CO₂ (1.06 mmol g^{-1}) at 1 bar. At 273 K a heat of adsorption of 27 kJ mol^{-1} at low 0.1 mmol g^{-1} , dropping to values 22 kJ mol^{-1} 1 mmol g^{-1} , Figure S6. For reference BPL carbon, a common benchmark material, adsorbs 1.9 mmol g^{-1} at 298 K.²⁸ As a CO₂ capture material per se, CMP-(bpy)₂₀-Mn is not outstanding, but importantly it remains porous after metallation and able to uptake CO₂ within the polymer.

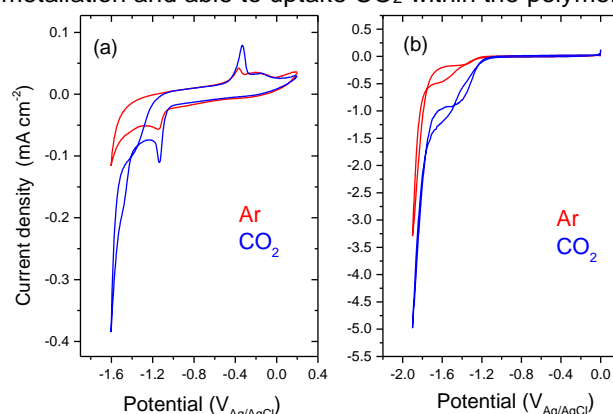


Figure 3. CVs of (a) [Mn(bpy)(CO)₃Br]/Nafion, (b) CMP-(bpy)₂₀-Mn/Nafion, both on a glassy carbon electrode in 0.06 M phosphate buffer pH 7, 10 mV s^{-1} recorded under CO₂ and Ar. The data in part (a) is reproduced with permission from reference [27].

To assess if the Mn centre remains electrochemically active, we carried out experiments in pH 7 aqueous phosphate buffer (0.06 M) under both CO₂ and Ar, Figures 2, 3. Electrodes were prepared by deposition of a suspension of either CMP-(bpy)₂₀ or CMP-(bpy)₂₀-Mn in an acetonitrile solution containing Nafion (0.5 wt. %) onto a glassy carbon electrode, which was left to dry in air. Square wave voltammetry of CMP-(bpy)₂₀ shows a single reduction at -1.46 V proposed to be due to reduction of the CMP framework, or residual Pd within the sample ($0.24 \pm 0.02\%$) that could not be removed, Figure 2b. CMP-

(bpy)₂-Mn shows the reduction at -1.46 V, and a new reduction at -1.35 V that is assigned to a CMP-Mn based process, Figure 2b. It is apparent that the catalyst remains electroactive within the CMP framework.

The electrochemical behaviour of [Mn(bpy)(CO)₃Br] in organic solution has been studied extensively^{25,30–33} and recently reviewed.³⁴ Following initial reduction, bromide

loss from the complex occurs, leading to rapid dimerization. Subsequent reduction of [Mn₂(bpy)₂(CO)₆], typically at potentials a further 0.3 V negative, leads to the formation of the primary catalytically-active species, [Mn(bpy)(CO)₃], which in the presence of a suitable weak Brønsted acid can bind to CO₂.

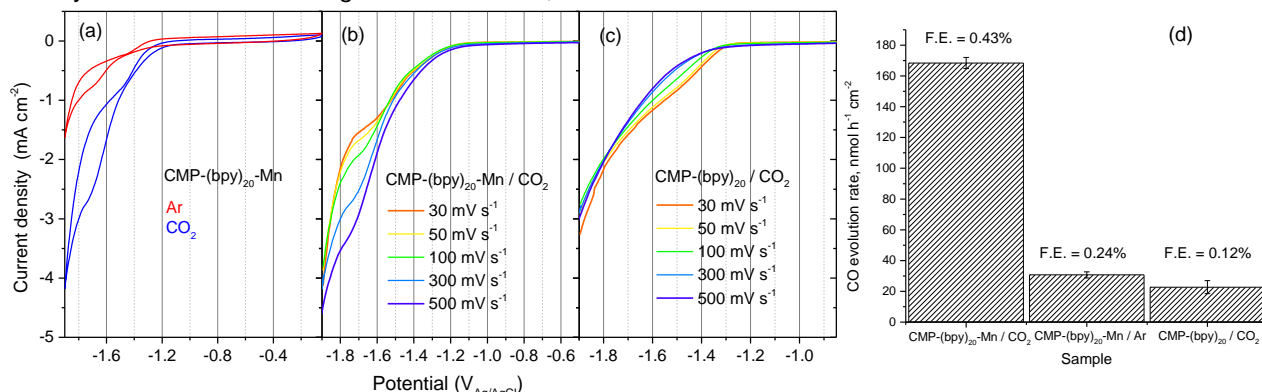


Figure 4. (a) CV of CMP-(bpy)₂₀-Mn in pH 7 phosphate buffer under Ar (red) and CO₂ (blue) (300 mV s⁻¹). Linear sweep scan rate dependence of (b) CMP-(bpy)₂₀-Mn and (c) CMP-(bpy)₂₀ under CO₂. The CMP-(bpy)₂₀-Mn shows a scan-rate dependent plateau current between -1.6 and -1.8 V not observed in the unmodified framework. (d) CO evolution rate during bulk electrolysis experiments at -1.6 V_{Ag/AgCl} for 3 hours. The Faradic efficiencies are for CO. H₂ was the only other product detected.

Although CO₂ reduction can occur *via* the dimer complex in solution the turn-over frequency (TOF) is significantly lower.^{32,35} The observation of a single reduction assignable to the Mn site at -1.35 V for CMP-(bpy)₂₀-Mn indicates that the incorporation of the catalytic centre within the rigid CMP prevents dimerisation. Previously, [Mn(bpy)(CO)₃Br] has been immobilised using a range of methods including; casting the unmodified complex in Nafion,²⁹ the non-covalent immobilization of a pyrene modified complex³⁶ and by binding of phosphonated and carboxylated derivatives^{37,38} to oxide supports. Remarkably in these past studies dimerisation still occurred due to the use of flexible linkers or formation of catalyst aggregates. Comparison between the previously recorded CVs of [Mn(bpy)(CO)₃Br] in Nafion²⁹ and CMP-(bpy)₂₀-Mn (Figure 3) further supports the conclusion that the rigid framework prevents dimerisation. For [Mn(bpy)(CO)₃Br] in Nafion, reductions at -1.15 and -1.47 V are assignable to [Mn(bpy)(CO)₃Br] and [Mn₂(bpy)₂(CO)₆] and an oxidation peak at -0.35 V is due to the dimer.²⁹ In contrast with CMP-(bpy)₂₀-Mn we see no evidence of the dimer oxidation, figure 3(b). The shift in the reduction potential of the Mn centre in CMP-(bpy)₂₀-Mn (-1.35 V) compared to [Mn(bpy)(CO)₃Br] (-1.15 V) is due to the modification of the bpy ligand and the presence of the Mn centre within the conjugated framework of the CMP.³⁴

Dimer formation has been prevented previously in acetonitrile solutions through addition of sterically bulky groups to the bpy ligand.^{4,39} There, the monomer anion ([Mn(bpy-R)(CO)₃]⁻) was formed by an initial one electron reduction and ligand loss step, followed by a second reduction with a formal potential positive of the first, giving rise to the observation of a single reduction (-1.55 V vs.

Fc/Fc⁺, *ca.* -1.17 V vs. Ag/AgCl). Here, we propose that the reduction at -1.35 V in Figure 2a is the two-electron reduction to generate a [Mn(bpy_{CMP})(CO)₃] moiety within the CMP framework. Past reports in solution using bulky ligands, CO₂ binding led to a positive shift in reduction potential and the formation of a Mn^I-CO₂H intermediate.³⁹ We also find that under CO₂, the CMP-Mn based reduction shifts by 30 mV to more positive values, indicating CO₂ binding to the reduced Mn centre within the CMP framework can also occur, Figure 2b.

Under CO₂ using CMP-(bpy)₂₀-Mn we observe a small increase (*ca.* × 2.5 at -1.35 V, Figure 2a, 3a) in current density between -1.2 V and -1.4 V. Over this potential region, increasing the scan rate of the CV does not lead to a significant increase in current density suggesting that substrate (CO₂, H⁺) diffusion is not limiting catalysis, Figure 3b.¹ By contrast, between -1.6 and -1.8 V, the plateau current under CO₂ increases with scan rate. This indicates the presence of a second higher TOF catalytic pathway that is substrate limited. Interestingly, the current-density for CMP-(bpy)₂₀ under CO₂ does not increase with scan rate between -1.6 and -1.8 V demonstrating that the second higher TOF pathway is CMP-Mn based, Figure 3c. The observation of a fast catalytic pathway, 0.25 V negative of the potential where CO₂ binding initially occurs, mirrors that reported when Mn dimerisation was prevented in solution.³⁹ In that study, at potentials positive of the reduction potential of Mn-CO₂H, catalysis proceeded by a slow pathway, reliant on the rate limiting formation of a [Mn(bpy)(CO)₄]⁴⁺ complex. In contrast, at very negative potentials Mn-CO₂H reduction occurred and the fast catalysis pathway dominated.

The focus of this initial communication is to demonstrate the viability of the approach by showing that the Mn centre remains electrochemically active within the CMP framework. No attempts have been made to optimise the electrode for catalysis. Nonetheless, we have also carried out a preliminary bulk electrolysis study to confirm that the Mn complex remains catalytically active. For CMP-(bpy)₂₀-Mn under CO₂ at -1.6 V, CO is the sole carbon-based product formed, Figure S8, 9. Control experiments using CMP-(bpy)₂₀ show a CO evolution rate that is approximately 7 times less than when the Mn catalyst is present and 5 times less under Ar, Figure 3d. This confirms that the Mn centre is acting as the catalytic site (Figure S8) and indicates that CO is primarily produced from CO₂ reduction although isotopic labelling is required to definitively confirm this. The small amount of CO produced under Ar may be due to either reduction of CO₂ captured from air by the CMP, ligand loss or organic degradation pathways. Unfortunately Faradic efficiencies for CO are low (0.43%) with H₂ production dominating. Kubiak *et al.* have shown⁴ that the presence of Mg²⁺ can greatly accelerate the “slow catalysis” pathway in solution, allowing for activity at reduced overpotentials which will be explored in future studies as a route to improving the Faradic efficiency for CO₂ reduction here also. Furthermore, structural distortions of the CMP framework can lead to a loss of conjugation, leading to insulating regions within the polymer and low electroactive contents (Figure S8) making it likely that gains in electrocatalytic activity can be made by optimising the CMP-supporting electrode interface.

Conclusions

We report the inclusion and electrochemical behaviour of the well-known [Mn(bpy)(CO)₃Br] CO₂ reduction catalyst into a CMP framework. This is significant because the CMP is able to act as both a CO₂ uptake material and an electroactive support for the Mn catalytic centres. We prevent catalyst dimerization, a target of previous studies,^{4,39} because the catalyst is held in a rigid framework. Although Faradic efficiencies are extremely low, CV measurements show the catalytic centre remains active, and this first study represents an important step towards the use of metal-organic CMP materials for the conversion of dilute CO₂ sources. Future studies will be focused on the engineering the CMP-(bpy)₂₀-Mn electrode structure, as it is likely that the porous CMP structure can be best exploited through the development of a three-phase (gas diffusion) electrodes.

Conflicts of interest

There are no conflicts to declare

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