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# Tuning Product Selectivity for Aqueous CO<sub>2</sub> Reduction with a Mn(bipyridine)-pyrene Catalyst Immobilized on a Carbon Nanotube Electrode

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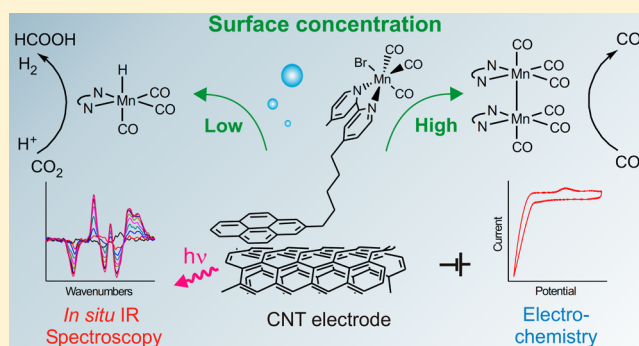
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## Supporting Information

**ABSTRACT:** The development of high-performance electrocatalytic systems for the controlled reduction of CO<sub>2</sub> to value-added chemicals is a key goal in emerging renewable energy technologies. The lack of selective and scalable catalysts in aqueous solution currently hampers the implementation of such a process. Here, the assembly of a [MnBr(2,2'-bipyridine)(CO)<sub>3</sub>] complex anchored to a carbon nanotube electrode via a pyrene unit is reported. Immobilization of the molecular catalyst allows electrocatalytic reduction of CO<sub>2</sub> under fully aqueous conditions with a catalytic onset overpotential of  $\eta = 360$  mV, and controlled potential electrolysis generated more than 1000 turnovers at  $\eta = 550$  mV. The product selectivity can be tuned by alteration of the catalyst loading on the nanotube surface. CO was observed as the main product at high catalyst loadings, whereas formate was the dominant CO<sub>2</sub> reduction product at low catalyst loadings.

Using UV–vis and surface-sensitive IR spectroelectrochemical techniques, two different intermediates were identified as responsible for the change in selectivity of the heterogenized Mn catalyst. The formation of a dimeric Mn<sup>0</sup> species at higher surface loading was shown to preferentially lead to CO formation, whereas at lower surface loading the electrochemical generation of a monomeric Mn-hydride is suggested to greatly enhance the production of formate. These results emphasize the advantages of integrating molecular catalysts onto electrode surfaces for enhancing catalytic activity while allowing excellent control and a deeper understanding of the catalytic mechanisms.



## INTRODUCTION

Efficient, low-cost, and scalable electrocatalytic reduction of CO<sub>2</sub> is currently under consideration as a viable means to produce useful chemicals while limiting the rise of CO<sub>2</sub> levels in the atmosphere.<sup>1–5</sup> During the past few years, transition metal complexes have been extensively studied for the electro- and photoreduction of CO<sub>2</sub>, mainly to carbon monoxide (CO) and formate (HCOO<sup>-</sup>).<sup>6–9</sup> The molecular nature of these complexes allows specific fine-tuning of their structure using synthetic chemistry to rationally control the activity,<sup>10</sup> selectivity,<sup>11</sup> and stability of the catalysts via a profound understanding of the catalytic mechanisms involved.<sup>12,13</sup> In order to replace expensive Re,<sup>14–17</sup> Ru,<sup>18,19</sup> and Ir<sup>20</sup> based catalysts, a range of different catalytic structures incorporating more abundant first-row transition metals such as Ni,<sup>21–23</sup> Co,<sup>24–27</sup> Fe,<sup>28,29</sup> and Mn<sup>30–32</sup> have been described for catalytic CO<sub>2</sub> reduction.

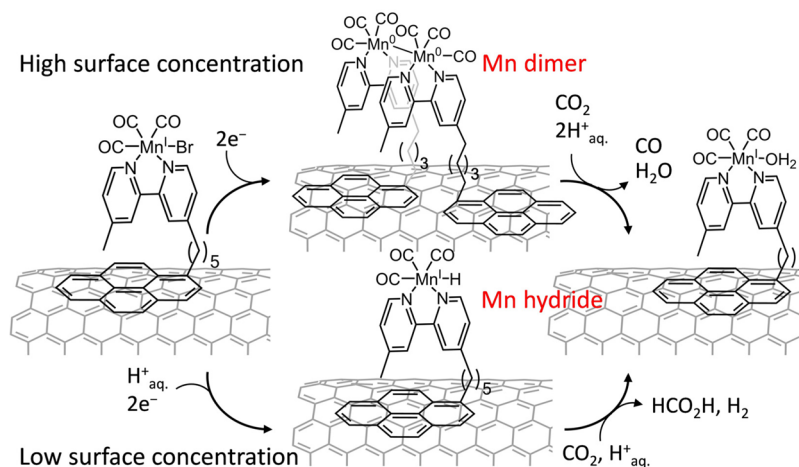
The integration of these molecular species onto electrodes in many cases gives an enhancement of the catalytic activity and

provides new insights into the involved mechanisms.<sup>33–36</sup> Immobilization also enables catalysts that would otherwise be insoluble to operate in water and overcomes limitations from diffusion-controlled electrocatalysis with catalysts in the bulk solution.<sup>37–41</sup> In this respect, carbon nanotubes (CNTs) are an established platform for the immobilization of molecular electrocatalysts.<sup>42–45</sup> Their high surface area and excellent conductivity allow grafting of large amounts of electrocatalytically active species while retaining good electron transfer properties.<sup>46</sup> The possibility to chemically modify CNTs using a variety of covalent or noncovalent techniques is another advantage of these nano-objects.<sup>47</sup> Specifically, the immobilization of pyrene-modified catalysts via  $\pi$ – $\pi$  interactions with the CNT sidewalls has emerged as a straightforward strategy.<sup>48–51</sup> Using this technique toward efficient electrochemical CO<sub>2</sub> reduction, recent examples have described the immobilization

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**Scheme 1. Schematic Representation of  $[\text{MnBr}(\text{bpy}_{\text{pyr}})(\text{CO})_3]$  ( $\text{Mn}_{\text{pyr}}$ ) Immobilized on a CNT Sidewall, Concentration-Dependent Dimerization or Mn–H Formation, and Intermediate-Dependent Reduction of  $\text{CO}_2$  to CO or  $\text{HCOOH}$**



of Re,<sup>52</sup> Ir,<sup>53</sup> and Fe<sup>54</sup> based catalysts onto CNT matrixes, the latter two examples affording catalytic activity in aqueous solution.

The complex  $[\text{MnBr}(\text{bpy})(\text{CO})_3]$  ( $\text{bpy} = 2,2'$ -bipyridine) has become a noble metal-free model catalyst for  $\text{CO}_2$  reduction thanks to the versatile and simple structure of the  $\text{bpy}$  ligand.<sup>30</sup> This catalyst exhibits high activity (turnover frequency up to  $480 \text{ s}^{-1}$ ) in MeCN, and its catalytic mechanism has been studied in depth by changing the nature of the substituents on the  $\text{bpy}$  ligand.<sup>12,13,55–61</sup> The Mn catalyst was previously integrated onto CNTs using Nafion,<sup>39,62</sup> onto p-Si via polymerization,<sup>63</sup> and onto  $\text{TiO}_2$  through a phosphonate anchoring group.<sup>33</sup> The latter system exhibited a record turnover number (TON) for the Mn catalyst of 112 in MeCN.<sup>33</sup> UV–vis spectroelectrochemistry (SEC) revealed that the grafted Mn catalyst dimerized on the electrode surface,<sup>33</sup> which has also been described in solution upon electrochemical reduction for this class of catalyst.<sup>12</sup> Although these studies showed enhancement of the catalytic properties of the Mn complex upon immobilization, the reported activity is still limited to organic solvents and low TONs (maximum of 101) in aqueous conditions.<sup>39,62</sup>

In this work, a novel *fac*- $[\text{MnBr}(\text{bpy})(\text{CO})_3]$ -type complex bearing a pyrene anchoring unit was synthesized ( $\text{Mn}_{\text{pyr}}$ , Schemes 1 and 2). The pyrene unit allowed stable immobilization onto CNTs. The electrocatalytic activity of

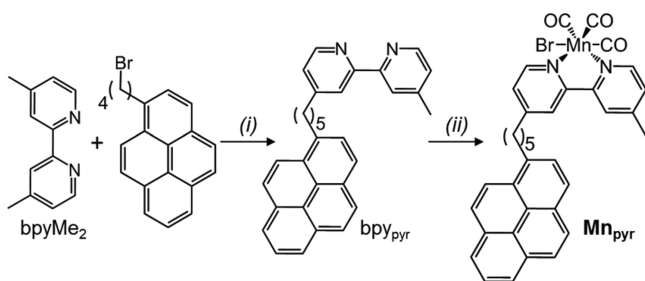
the compound was first studied toward the reduction of  $\text{CO}_2$  in homogeneous organic solution (MeCN + 5%  $\text{H}_2\text{O}$ ) and then in fully aqueous solutions after heterogenization on the CNT surface. The Mn catalyst modified electrodes were investigated using cyclic voltammetry (CV) and controlled-potential electrolysis (CPE). The surface loading of the Mn complex was found to have a distinct effect on the selectivity toward CO or  $\text{HCOO}^-$  production (Scheme 1). Using transmission UV–vis and surface-sensitive IR SEC in the attenuated total reflection (ATR) mode, the different catalytic intermediates involved were investigated in situ. Upon decreasing the surface loading, the previously described dimer formation was lowered. Instead, formation of a putative hydride species was detected. The formation of one or the other catalytic intermediate is assigned to be decisive for selectivity toward either CO or  $\text{HCOO}^-$  at different surface loadings.<sup>55,61,64</sup>

## RESULTS AND DISCUSSION

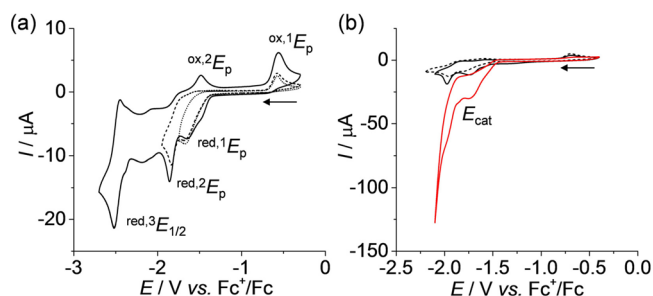
**Synthesis and Characterization of  $\text{Mn}_{\text{pyr}}$ .** 4-Methyl-4'-(5-(pyren-1-yl)pentyl)-2,2'-bipyridine ( $\text{bpy}_{\text{pyr}}$ ) was synthesized by reacting a lithiated 4,4'-dimethyl-bipyridine intermediate with 1-(4-bromobutyl)pyrene, as previously described (Scheme 2).<sup>65</sup> The ligand  $\text{bpy}_{\text{pyr}}$  was then refluxed with  $[\text{MnBr}(\text{CO})_5]$  in dry  $\text{Et}_2\text{O}$  for 4 h to yield *fac*- $[\text{MnBr}(\text{bpy}_{\text{pyr}})(\text{CO})_3]$  ( $\text{Mn}_{\text{pyr}}$ ) with an overall yield of 64% (Scheme 2). The composition and purity of  $\text{Mn}_{\text{pyr}}$  were confirmed by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, and FT-IR spectroscopy as well as mass spectrometry and elemental analysis (see the Experimental Section for details).

The electrochemical properties of  $\text{Mn}_{\text{pyr}}$  were investigated by CV in MeCN containing  $\text{TBAPF}_6$  (0.1 M, TBA = tetrabutylammonium) at a glassy carbon working electrode (Figure 1a,b). In dry MeCN and under a  $\text{N}_2$  atmosphere, the  $\text{Mn}^{\text{I}}$  complex exhibits two successive irreversible reduction processes at  $^{\text{red}}E_p = -1.68$  and  $-1.86$  V vs  $\text{Fc}^+/\text{Fc}$  (see below for assignment of the reversible redox process at  $-2.48$  V). According to literature assignments,<sup>30</sup> the first cathodic wave ( $^{\text{red},1}E_p$ ) is attributed to the reduction to  $\text{Mn}^0$ , followed by dimerization and formation of a  $\text{Mn}^0\text{--Mn}^0$  species. The second cathodic process ( $^{\text{red},2}E_p$ ) is assigned to the one-electron reduction of the dimer to a mononuclear anionic species (Figure 1a).<sup>30</sup> The redox wave ( $^{\text{red},3}E_{1/2}$ ) observed at  $-2.48$  V vs  $\text{Fc}^+/\text{Fc}$  is attributed to the reversible redox response of the  $\text{bpy}$  ligand.<sup>30</sup> Two anodic waves were observed following scan

**Scheme 2. (a) Synthetic Route to *fac*- $[\text{MnBr}(\text{bpy}_{\text{pyr}})(\text{CO})_3]$  ( $\text{Mn}_{\text{pyr}}$ )<sup>a</sup>**



<sup>a</sup>Conditions: (i) Lithium diisopropylamide (LDA, 2 equiv), THF, 4 h,  $-10$  °C,  $\text{N}_2$  (77% yield); (ii)  $[\text{MnBr}(\text{CO})_5]$  (1.25 equiv),  $\text{Et}_2\text{O}$ , 4 h, reflux,  $\text{N}_2$  (83% yield).



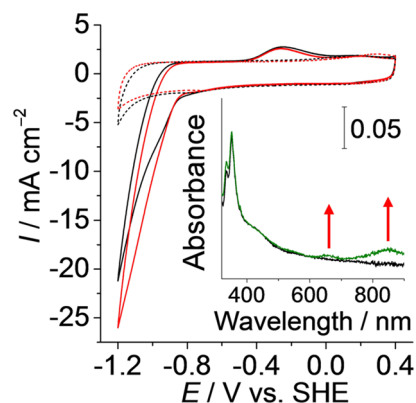
**Figure 1.** CV scans of  $\text{Mn}_{\text{pyr}}$  (1 mM) (a) in MeCN reversing the sweep at different potentials under  $\text{N}_2$ , (b) in MeCN under  $\text{N}_2$  (black solid trace), in MeCN containing 5%  $\text{H}_2\text{O}$  under  $\text{N}_2$  (black dashed trace), and in MeCN containing 5%  $\text{H}_2\text{O}$  under  $\text{CO}_2$  (red trace). All CV scans were recorded with  $\text{TBAPF}_6$  (0.1 M) as supporting electrolyte at a scan rate ( $\nu$ ) of  $100 \text{ mV s}^{-1}$  and room temperature with the scan start being indicated by an arrow.

reversal after  $\text{red.}^3E_p$  at  $-1.49$  and  $-0.57 \text{ V vs Fc}^+/\text{Fc}$ , assigned to one-electron processes corresponding to the reoxidation of the mononuclear anionic ( $\text{ox.}^2E_p$ ) and dimeric ( $\text{ox.}^1E_p$ ) species, respectively.<sup>30,56</sup> The latter assignment was confirmed by scan reversal after  $\text{red.}^1E_p$  and the observation of only the reoxidation of the dimer species at  $\text{ox.}^1E_p = -0.57 \text{ V vs Fc}^+/\text{Fc}$ .

Addition of 5%  $\text{H}_2\text{O}$  to the MeCN electrolyte solution does not show any significant increase in cathodic current, suggesting the limited ability of  $\text{Mn}_{\text{pyr}}$  to reduce protons under these conditions (Figure 1b). In contrast, purging this aqueous MeCN solution with  $\text{CO}_2$  gas results in a large catalytic wave for  $\text{CO}_2$  reduction with a catalytic onset potential ( $E_{\text{cat}}$ ) of  $-1.51 \text{ V vs Fc}^+/\text{Fc}$ , consistent with previous reports for the parent *fac*- $[\text{MnBr}(\text{bpy})(\text{CO})_3]$  under the same conditions.<sup>30</sup>

**Immobilization and Performance of  $\text{Mn}_{\text{pyr}}$ .** Immobilization of  $\text{Mn}_{\text{pyr}}$  onto a multiwalled carbon nanotube (MWCNT) electrode enabled the study of its electrocatalytic activity in fully aqueous solution. The Mn complex was anchored onto MWCNTs following an established two-step procedure:<sup>51,66</sup> First, a dispersion of MWCNTs in *N*-methylpyrrolidone ( $20 \mu\text{L}$ ,  $5 \text{ mg}_{\text{CNT}} \text{ mL}^{-1}$ ) was drop-cast and dried on a glassy carbon disk electrode (diameter  $\phi = 5 \text{ mm}$ ), giving a MWCNT electrode with  $5 \mu\text{m}$  thickness. The catalyst was subsequently immobilized by immersing the MWCNT electrode into an anhydrous DMF solution of  $\text{Mn}_{\text{pyr}}$  (10 mM) for 30 min in the dark and at room temperature. The resulting  $\text{CNT}|\text{Mn}_{\text{pyr}}$  electrode was subsequently rinsed successively with DMF and water before CV experiments were undertaken (see below for more characterization details of the Mn-loaded MWCNT electrode).

CV scans recorded with  $\text{CNT}|\text{Mn}_{\text{pyr}}$  in aqueous  $\text{KHCO}_3$  (0.5 M, pH 8.2) electrolyte solution under  $\text{N}_2$  show an irreversible cathodic wave at  $\text{red.}E_p = -1.0 \text{ V vs SHE}$  (“shoulder” of solid black trace in Figure 2), which was assigned to the one-electron reduction of  $\text{Mn}^{\text{I}}$  to  $\text{Mn}^0$ . This Mn reduction wave overlaps with a dominant cathodic current that is mainly attributed to proton reduction (Figure 2, see below for more details). Following scan reversal, an irreversible anodic process, assigned to the reoxidation of the  $\text{Mn}^0$  species,<sup>39</sup> can be observed at  $\text{ox.}E_p = -0.24 \text{ V vs SHE}$ . In the presence of  $\text{CO}_2$  (pH 7.4), the current observed at  $\text{red.}E_p$  is enhanced by a catalytic wave from reduction of  $\text{CO}_2$ . The observed onset potential ( $E_{\text{cat}} = -0.91 \text{ V vs SHE}$ ) with the immobilized  $\text{Mn}_{\text{pyr}}$  complex corresponds to a small overpotential ( $\eta = 360 \text{ mV}$  for CO and/or  $\eta = 390 \text{ mV}$



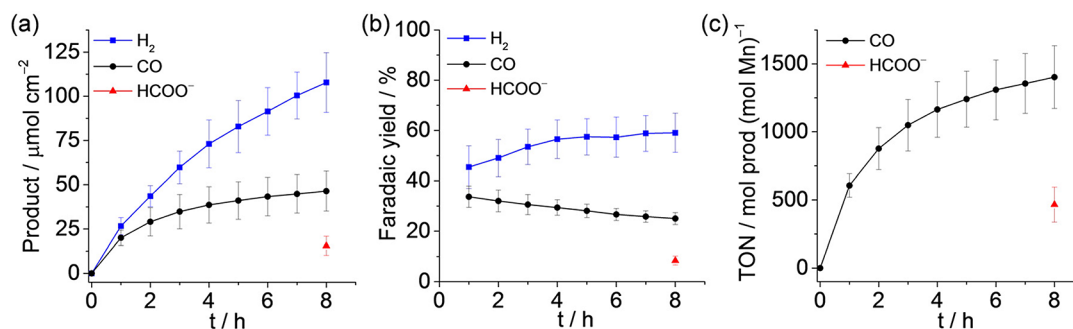
**Figure 2.** CV scans of the bare (unmodified) MWCNT electrodes (dashed traces) and  $\text{CNT}|\text{Mn}_{\text{pyr}}$  (solid traces) under  $\text{N}_2$  (pH 8.2) (black traces) and  $\text{CO}_2$  (pH 7.4) (red traces) in aqueous  $\text{KHCO}_3$  (0.5 M) electrolyte solution at  $\nu = 100 \text{ mV s}^{-1}$  and room temperature. Inset: UV-vis spectra of the  $\text{CNT}|\text{Mn}_{\text{pyr}}$  electrode without applied bias (black trace) and at  $E_{\text{app}} = -1.1 \text{ V vs SHE}$  (green trace) under  $\text{CO}_2$ .

for formate production).<sup>67</sup> It is noteworthy that the irreversible anodic process at  $\text{ox.}E_p$  is still present in the presence of  $\text{CO}_2$  but displays a decrease in peak current. This observation may highlight that some of the immobilized and electrochemically reduced  $\text{Mn}_{\text{pyr}}$  does not readily react with  $\text{CO}_2$  and is reoxidized at the electrode surface instead, which could possibly be due to limited diffusion of  $\text{CO}_2$  within the CNT film. The bare ( $\text{Mn}_{\text{pyr}}$ -free) MWCNT electrode does not show notable cathodic current enhancement in the presence of  $\text{CO}_2$ , confirming that the current enhancement observed with the  $\text{CNT}|\text{Mn}_{\text{pyr}}$  electrode solely arises from the presence of the catalyst on the electrode surface.

To confirm the formation of the dimeric  $\text{Mn}^0$  species on the electrode surface upon reduction at  $\text{red.}E_p$ , transmission UV-vis SEC was carried out using  $\text{Mn}_{\text{pyr}}$  deposited onto MWCNT films on a transparent FTO glass substrate (see the Experimental Section for details). CV of  $\text{CNT}|\text{Mn}_{\text{pyr}}$  on FTO-coated glass was carried out to confirm the immobilization of the complex (Figure S1), and UV-vis absorption spectra of the electrodes without and with applied potential ( $E_{\text{appl}} = -1.1 \text{ V vs SHE}$ ) were compared in aqueous electrolyte solution (Figure 2, inset). Two bands appear at 655 and 850 nm under negative applied bias, which are comparable to the bands described previously for the dimer in solution and on a  $\text{TiO}_2$  electrode in MeCN.<sup>30,33</sup> The UV-vis SEC analysis therefore supports generation of the  $\text{Mn}^0$ - $\text{Mn}^0$  dimer at the surface of the MWCNT electrode upon reduction at  $\text{red.}E_p$ .

To gain more insight into the overall activity, selectivity, and stability of the  $\text{CNT}|\text{Mn}_{\text{pyr}}$  electrode, CPE was performed at  $E_{\text{appl}} = -1.1 \text{ V vs SHE}$  under  $\text{CO}_2$  and the electroreduction products were analyzed using gas and ion chromatography (Figure 3). The  $\text{CNT}|\text{Mn}_{\text{pyr}}$  electrodes showed high current densities between  $-5$  and  $-1.5 \text{ mA cm}^{-2}$  during the first hour of CPE before stabilizing at approximately  $-0.5 \text{ mA cm}^{-2}$  after 8 h (Figure S2), which coincides with a decrease in CO production activity (Figure 3a). Indeed, the electrodes showed good activity for CO production during the first hour, before stabilizing at  $46 \pm 11 \mu\text{mol cm}^{-2} \text{ CO}$ . This decrease in CO production can be attributed to deactivation of the immobilized catalyst as it is commonly observed for molecular catalysts.<sup>68</sup> On the other hand,  $\text{H}_2$  evolution remained stable over time and





**Figure 3.** (a) Quantification and (b) cumulative Faradaic yields of  $\text{H}_2$  (blue squares),  $\text{CO}$  (black circles), and formate (red triangle) production and (c) their corresponding TONs for  $\text{CO}$  and formate production as a function of CPE time at  $E_{\text{appl}} = -1.1$  V vs SHE under  $\text{CO}_2$  in aqueous  $\text{KHCO}_3$  (0.5 M, pH 7.4) at room temperature.

reached a value of  $108 \pm 17 \mu\text{mol cm}^{-2}$  after 8 h. Some  $\text{HCOO}^-$  was also detected at the end of CPE measurements ( $16 \pm 5 \mu\text{mol cm}^{-2}$ ).

Control CPE measurements on a bare (Mn-free) MWCNT electrode under  $\text{CO}_2$  showed only small current densities of  $-0.3 \text{ mA cm}^{-2}$ , with linear production of  $\text{H}_2$  ( $26 \mu\text{mol cm}^{-2}$  after 8 h) and only traces of  $\text{CO}$  (Figure S3a). In addition, no  $\text{CO}$  was observed for a  $\text{CNT}|\text{Mn}_{\text{pyr}}$  electrode under  $\text{N}_2$ , whereas  $\text{H}_2$  production was higher than that with the bare MWCNT electrode ( $47.2 \mu\text{mol cm}^{-2}$  after 8 h; Figure S3b). This observation confirms that the  $\text{CO}$  production solely arises from  $\text{Mn}_{\text{pyr}}$  on the electrode and in the presence of dissolved  $\text{CO}_2$  in the electrolyte solution, whereas some  $\text{H}_2$  is produced by the MWCNT scaffold under reductive conditions as well as by  $\text{Mn}_{\text{pyr}}$ . The high current densities and  $\text{CO}$  evolution rates during the first hours of CPE translated into a reasonable Faradaic yield for  $\text{CO}$  (Figure 3c), with a maximum yield of ( $34 \pm 4$ )% being obtained after 1 h of CPE, before decaying to ( $25 \pm 2$ )% cumulated after 8 h. In contrast, the efficiency for  $\text{H}_2$  slightly increases over time and Faradaic yields of ( $45 \pm 8$ ) and ( $59 \pm 8$ )% were observed after 1 and 8 h, respectively. For formate, a Faradaic yield of ( $8 \pm 2$ )% was determined after 8 h, which results in a close-to-quantitative overall yield of ( $93 \pm 4$ )% for all detected products.

The carbon source for the generated  $\text{CO}$  and  $\text{HCOO}^-$  was confirmed by gas-phase IR spectroscopy and  $^1\text{H}$  NMR spectroscopy, respectively. CPE under  $^{13}\text{CO}_2$  resulted exclusively in  $^{13}\text{CO}$  and  $\text{H}^{13}\text{COO}^-$  (Figure S4). A  $\text{TON}_{\text{Mn}}$  of  $1400 \pm 230$  was obtained for  $\text{CO}$  (Figure 3d), which is more than 10 times higher than previous results obtained electrochemically<sup>30</sup> or photochemically<sup>59</sup> using Mn(bpy)-type catalysts in organic<sup>33</sup> or aqueous<sup>39,62</sup> solution. Thus, the  $\text{CNT}|\text{Mn}_{\text{pyr}}$  electrode displays high activity for catalytic  $\text{CO}_2$  to  $\text{CO}$  reduction in aqueous solution and compares well with noble metal-free solid-state electrocatalysts in terms of the TON at a low overpotential.<sup>37,38,54,69,70</sup> A respectable  $\text{TON}_{\text{Mn}}$  of  $460 \pm 120$  was obtained for  $\text{HCOO}^-$  production.

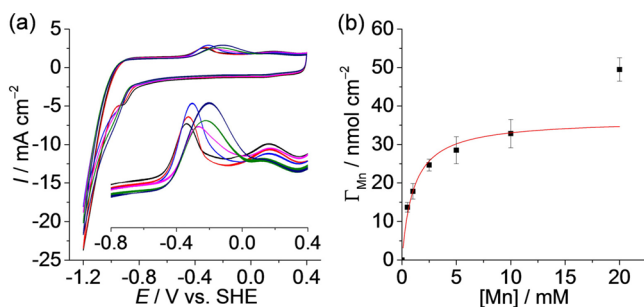
In order to verify the importance of immobilization and the molecular nature of the catalytically active species, a series of control experiments were carried out using anchor-free *fac*- $[\text{MnBr}(\text{bpyMe}_2)(\text{CO})_3]$  ( $\text{bpyMe}_2 = 4,4'$ -dimethyl-2,2'-bipyridine),<sup>30</sup> the precursors of  $\text{Mn}_{\text{pyr}}$  and Mn salts drop-cast (10 mM in DMF) onto the MWCNT electrode or in solution (Figure S5). CV of *fac*- $[\text{MnBr}(\text{bpyMe}_2)(\text{CO})_3]$  on the electrode shows the appearance of a catalytic feature when  $\text{CO}_2$  is added to the fully aqueous electrolyte solution (Figure S5a). CPE performed on  $\text{CNT}|\text{fac}-[\text{MnBr}(\text{bpyMe}_2)(\text{CO})_3]$

resulted in  $\text{CO}$  production with a  $\text{TON}_{\text{Mn}}$  of 237 after 8 h, which is approximately 6 times less than that obtained by using  $\text{Mn}_{\text{pyr}}$ . CV scans performed on the MWCNT electrode modified with  $[\text{MnBr}(\text{CO})_5]$  or  $\text{bpy}_{\text{pyr}}$  with  $\text{MnCl}_2$  (1 mM) in solution did not display a distinguishable catalytic wave under  $\text{CO}_2$  (Figure S5b,c), and only traces of  $\text{CO}$  could be detected after 8 h of CPE ( $1.1$  and  $2.4 \mu\text{mol cm}^{-2}$  for  $[\text{MnBr}(\text{CO})_5]$  and  $\text{bpy}_{\text{pyr}}/\text{MnCl}_2$ , respectively; Figure S5d). These results support that the high activity observed for  $\text{CNT}|\text{Mn}_{\text{pyr}}$  is not caused by possible degradation products of the molecular Mn catalyst. In addition, CV scans performed on  $\text{CNT}|\text{Mn}_{\text{pyr}}$  after CPE showed the appearance (although at reduced intensity) of identical redox behavior compared to pre-electrolysis measurements (Figure S6). The presence of the irreversible peak at  $^{\text{ox}}E_p$  at  $-0.24$  V vs SHE (due to dimer reoxidation in aqueous conditions<sup>39</sup>) and the catalytic wave at  $E_{\text{cat}} = -0.91$  V vs SHE confirm that at least some of the molecular species remains on the surface throughout the CPE experiment without clearly observable degradation.

#### Tuning of Selectivity by Varying the Surface Loading.

To study the dimerization of the heterogenized  $\text{Mn}_{\text{pyr}}$  catalyst in more detail, the influence of catalyst surface loading was investigated by incubating the MWCNT electrodes in solutions containing different concentrations of  $\text{Mn}_{\text{pyr}}$ . The electrochemical behavior of the electrodes with different surface loadings of  $\text{Mn}_{\text{pyr}}$  was subsequently examined. From integration of the oxidation wave in CV, the amount of electroactive  $\text{Mn}_{\text{pyr}}$  immobilized on the electrode can be estimated. The surface loading and the position of the oxidation peak of  $\text{Mn}_{\text{pyr}}$  immobilized onto MWCNTs was shown to be dependent on the  $\text{Mn}_{\text{pyr}}$  incubation concentration (Figure 4).

At higher surface loading, above  $30 \text{ nmol cm}^{-2}$  from incubation with 10 and 20 mM  $\text{Mn}_{\text{pyr}}$ , the dimer reoxidation peak was detected at  $^{\text{ox}}E_p = -0.24$  V vs SHE, close to the previously reported value.<sup>39</sup> At lower loading, below  $20 \text{ nmol cm}^{-2}$  from incubation with 0.5 and 1 mM  $\text{Mn}_{\text{pyr}}$ , a small irreversible reduction wave was observed at  $^{\text{red}}E_p = -1.0$  V vs SHE and the corresponding reoxidation wave was shifted considerably to  $^{\text{ox}}E_p = -0.34$  V vs SHE (100 mV more cathodic than the response at higher surface loadings). At intermediate surface loadings, between 20 and  $30 \text{ nmol cm}^{-2}$  from incubation with 2.5 and 5 mM  $\text{Mn}_{\text{pyr}}$ , a broadened oxidation wave was attributed to a convoluted response from both anodic processes. For all  $\text{Mn}_{\text{pyr}}$  surface loadings, a strong reduction wave followed the reduction of the  $\text{Mn}^{\text{I}}$  to  $\text{Mn}^{\text{0}}$  ( $^{\text{red}}E_p = -1.0$  V vs SHE), which is assigned to the reduction of protons to  $\text{H}_2$  under a  $\text{N}_2$  atmosphere (see above). This catalytic reduction



**Figure 4.** (a) CV scans of CNT|Mn<sub>pyr</sub> loaded from incubation of the MWCNT electrode in Mn<sub>pyr</sub> solutions at different concentrations: 0.5 (black); 1 (red); 2.5 (blue); 5 (purple); 10 (green); and 20 mM (navy) in aqueous KHCO<sub>3</sub> (0.5 M) electrolyte solution under N<sub>2</sub> at pH 8.2 ( $\nu = 100 \text{ mV s}^{-1}$ ) at room temperature. (b) Variation of Mn<sub>pyr</sub> surface loadings depending on incubation of the MWCNT electrode in different Mn<sub>pyr</sub> concentrations (0.5, 1, 2.5, 5, 10, and 20 mM), experimental data (black squares), and fitted adsorption isotherm (red trace).

wave becomes more dominant at lower surface loadings of Mn<sub>pyr</sub> ( $\Gamma_{\text{Mn}}$ ).

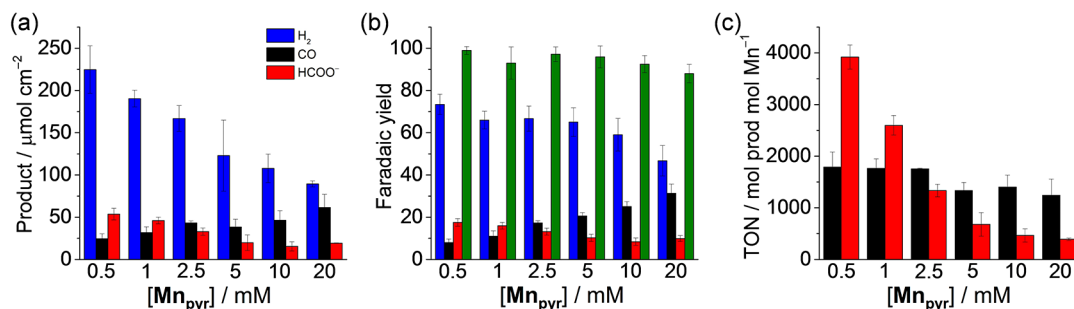
$\Gamma_{\text{Mn}}$  increased with the concentration of the incubation solution until reaching a plateau between 5 and 10 mM, following a Langmuir isotherm (see the Experimental Section and Figure 4b).<sup>66,71</sup> The best fit (using Mn concentrations, [Mn], up to 10 mM) was obtained with a saturation surface concentration,  $\Gamma_{\text{Mn,max}}$  of  $36.5 \text{ nmol cm}^{-2}$  and with a  $K_{\text{Mn}}$  of  $950 \text{ L mol}^{-1}$ , in line with previously reported values for pyrene-bearing coordination complexes.<sup>66</sup> The surface loading after incubation with the highest Mn<sub>pyr</sub> concentration (20 mM) does not align with the fit, which can be rationalized by oversaturation of the surface at higher incubation concentrations. At  $\Gamma_{\text{Mn,max}}$  the probability for Mn<sub>pyr</sub> to dimerize on the surface during electroreduction is high. On the other hand, for lower  $\Gamma_{\text{Mn}}$ , the probability of two Mn<sub>pyr</sub> units being close enough to each other to form a dimer is substantially decreased. The altered surface loading therefore gives a possible explanation for the different electrochemical response of Mn<sub>pyr</sub>. At lower surface concentration, impeded dimerization would lead to the formation of another reduced species and the oxidation peak observed at  $^{\text{ox}}E_p = -0.33 \text{ V vs SHE}$  could possibly be attributed to the one-electron oxidation of a single Mn<sup>0</sup> complex back to the Mn<sup>I</sup> complex.

As the CV response of Mn<sub>pyr</sub> changed as a function of catalyst loading, the possible impact of  $\Gamma_{\text{Mn}}$  on the catalytic activity and selectivity was studied by CPE coupled to H<sub>2</sub>, CO,

and formate analysis. Figure 5 summarizes the results and shows clear trends (see Figures S7 and S8 for the complete data set). Lowering the surface loading of Mn<sub>pyr</sub> on MWCNTs resulted in a decrease in overall CO production from  $62 \pm 15 \mu\text{mol cm}^{-2}$  at high  $\Gamma_{\text{Mn}}$  ( $50 \pm 3 \text{ nmol cm}^{-2}$ ) to  $26 \pm 5 \mu\text{mol cm}^{-2}$  at low  $\Gamma_{\text{Mn}}$  ( $14 \pm 1 \text{ nmol cm}^{-2}$ ), which is consistent with less Mn dimer available for CO<sub>2</sub> reduction (Figure 5c). The TON<sub>Mn</sub> for CO remained between 1500 and 2000 independent of the surface loading. However, the production of HCOO<sup>-</sup> increased substantially, from  $19 \pm 1 \mu\text{mol cm}^{-2}$  at high  $\Gamma_{\text{Mn}}$  ( $50 \pm 3 \text{ nmol cm}^{-2}$ ) to  $54 \pm 7 \mu\text{mol cm}^{-2}$  at low  $\Gamma_{\text{Mn}}$  ( $14 \pm 1 \text{ nmol cm}^{-2}$ ), thus leading to a high TON<sub>Mn</sub> for HCOO<sup>-</sup> generation of  $3920 \pm 230$  (Figure S9). This increase of HCOO<sup>-</sup> production appears to be inversely correlated to the surface loading of the catalyst and starts to become predominant when  $\Gamma_{\text{Mn}}$  reaches values lower than  $25 \text{ nmol cm}^{-2}$  (Figures 4b and S8), which is significantly lower than  $\Gamma_{\text{Mn,max}}$  estimated from the Langmuir isotherm. In addition to the increased production of HCOO<sup>-</sup>, the production of H<sub>2</sub> is also greatly enhanced at lower catalyst loading, from  $90 \pm 4 \mu\text{mol cm}^{-2}$  at high  $\Gamma_{\text{Mn}}$  ( $50 \pm 3 \text{ nmol cm}^{-2}$ ) to  $225 \pm 27 \mu\text{mol cm}^{-2}$  at low  $\Gamma_{\text{Mn}}$  ( $14 \pm 1 \text{ nmol cm}^{-2}$ ).

Several *fac*-[MnBr(bpy)(CO)<sub>3</sub>] systems have already been described for the photocatalytic<sup>57,59,64</sup> or electrocatalytic<sup>55,61</sup> reduction of CO<sub>2</sub> to HCOO<sup>-</sup>, and for this transformation, a Mn-hydride is thought to be the active catalytic intermediate. This Mn–H intermediate was recently characterized using IR-SEC in solution, and it was shown that the HCOO<sup>-</sup> production is greatly enhanced by the addition of strong Brønsted acids through more favorable formation of the transient Mn–H species.<sup>61</sup> In agreement, at low surface loadings of Mn<sub>pyr</sub>, dimerization is less likely, giving rise to a monomeric reduced Mn<sup>0</sup> species that is suggested to form a transient Mn–H upon further reduction in aqueous solution (below the  $^{\text{red}}E_p$  of  $-1.0 \text{ V vs SHE}$ ). The Mn–H can then preferentially produce H<sub>2</sub> and HCOO<sup>-</sup> over CO (Scheme 1).

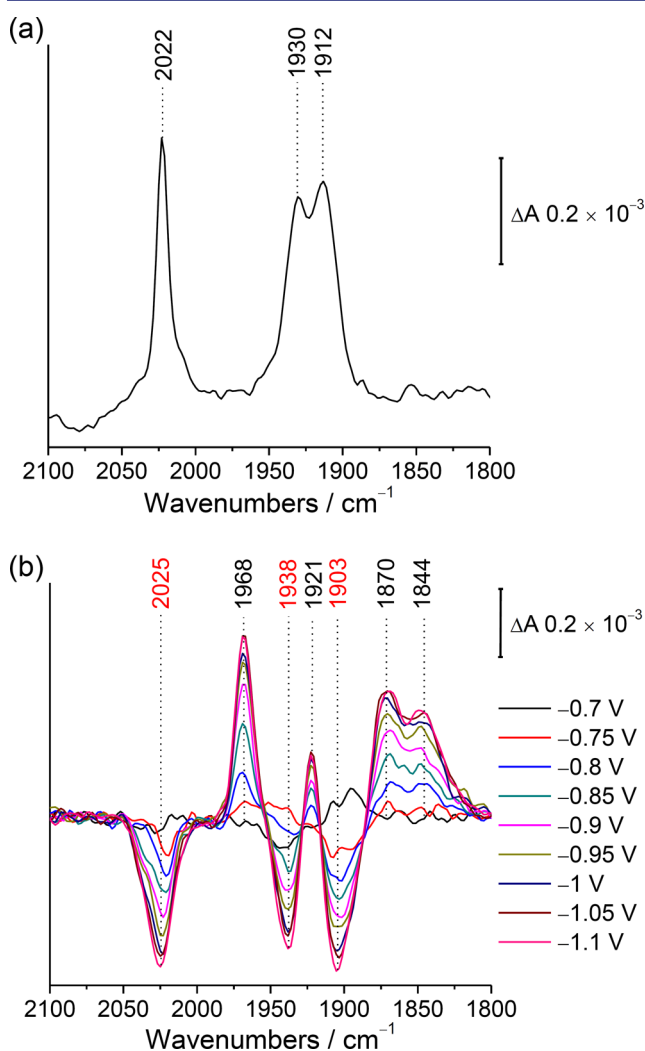
**Spectroelectrochemistry of Mn<sub>pyr</sub> Dimerization.** IR SEC was employed to obtain structural information on the catalytically relevant states of the immobilized Mn<sub>pyr</sub> at different surface loadings. Specifically, the CO stretching vibrations,  $\nu(\text{CO})$ , were monitored as their frequencies strongly depend on the electronic properties (i.e., oxidation state and coordination environment) of the metal atom.<sup>72,73</sup> Although ATR IR SEC has previously been used for the in situ study of active sites of adsorbed enzymes (on graphite nanoparticles<sup>74</sup> and Au-modified surfaces<sup>75,76</sup>) as well as for probing bulk catalytic reactions,<sup>77,78</sup> only a few examples applied this method



**Figure 5.** Product analysis following 8 h of CPE at  $E_{\text{app}} = -1.1 \text{ V vs SHE}$  in aqueous KHCO<sub>3</sub> (0.5 M, pH 7.4) under CO<sub>2</sub> at room temperature: (a) Total amounts, (b) Faradaic yields, and (c) TON<sub>Mn</sub> for CNT|Mn<sub>pyr</sub> electrodes prepared from different Mn<sub>pyr</sub> incubation concentrations. Color-coding: H<sub>2</sub> (blue), CO (black), HCOO<sup>-</sup> (red), and total (green).

to investigate heterogenized synthetic molecular catalysts.<sup>79,80</sup> An IR signal enhancing Au layer is usually required to obtain the necessary signal intensity to analyze a surface-attached cocatalyst. To tackle the limitations of established approaches, we employed a modified ATR IR SEC setup to allow an in-depth study of the immobilized molecular Mn catalyst on the MWCNT-coated Si prism as the working electrode under in situ conditions (Figure S10).

Incubation of the MWCNT electrode with  $\text{Mn}_{\text{pyr}}$  (10 mM in dry DMF) afforded intense IR signals of the catalyst. In particular, well-resolved  $\nu(\text{CO})$  bands in the region from 1800 to 2050  $\text{cm}^{-1}$  were observed (Figure 6a). As the evanescent IR wave exhibits a penetration depth of about 0.5  $\mu\text{m}$  in this experimental configuration,<sup>81</sup> this spectral feature should exclusively result from immobilized  $\text{Mn}_{\text{pyr}}$  molecules with  $\nu(\text{CO})$  frequencies at 2022, 1930, and 1912  $\text{cm}^{-1}$  for the



**Figure 6.** ATR IR spectra of a CNT/ $\text{Mn}_{\text{pyr}}$  electrode. (a) Absorbance spectra showing the  $\nu(\text{CO})$  bands of  $\text{Mn}_{\text{pyr}}$  on a MWCNT electrode in DMF (incubated from a 10 mM solution of  $\text{Mn}_{\text{pyr}}$ ). The  $\nu(\text{CO})$  modes are observed at 2022, 1930, and 1912  $\text{cm}^{-1}$ . (b) Potential-dependent (vs SHE) difference spectra of  $\text{Mn}_{\text{pyr}}$  in aqueous  $\text{KHCO}_3$  (0.5 M) under argon and at room temperature with the reference spectrum recorded at 0 V (fully oxidized conditions) prior to each measurement. Reduction causes an increase of  $\nu(\text{CO})$  located at 1968, 1921, 1870, and 1844  $\text{cm}^{-1}$  (black numbers) and the disappearance of the bands at 2025, 1938, and 1903  $\text{cm}^{-1}$  (red numbers).

facially coordinated tricarbonyl metal complex.<sup>73</sup> These frequencies match well those of unmodified  $[\text{MnBr}(\text{bpy})(\text{CO})_3]$  in MeCN solution,<sup>73</sup> indicating once again that introduction of the pyrene linker does not significantly influence the electronic properties of the Mn center (Table 1). The observation of intense and distinctly resolved  $\nu(\text{CO})$  bands demonstrates that ATR IR is sufficiently sensitive to probe  $\text{Mn}_{\text{pyr}}$  on the MWCNT electrode in this experimental configuration.

Negative potentials were applied in aqueous  $\text{KHCO}_3$  solution (0.5 M, pH 8.2) to monitor the reduction of the immobilized  $\text{Mn}_{\text{pyr}}$  catalyst through the surface-sensitive ATR IR SEC approach. Figure 6b displays IR difference spectra at increasingly negative electrode potentials (a spectrum at 0 V vs SHE was used prior to each potential step as a reference spectrum). Major spectral differences were only observed at potentials more negative than  $-0.7$  V vs SHE, upon which the appearance of bands located at 1968, 1921, 1870, and 1844  $\text{cm}^{-1}$  was accompanied by a decrease of bands at 2025, 1938, and 1903  $\text{cm}^{-1}$  (Table 1). Note that the absolute frequencies of the latter two bands are difficult to determine as the band at 1921  $\text{cm}^{-1}$  increases upon reduction. Accordingly, the stated frequencies are estimated. Plotting the intensity of the positive bands at 1968 and 1870  $\text{cm}^{-1}$  as the function of poised electrode potential yielded sigmoidal curves that could be fitted with the Nernst equation affording matching midpoint potentials at  $-0.84 \pm 0.05$  V vs SHE for both redox transitions (see the Experimental Section and Figure S11). The concomitant rise and the matching midpoint potentials indicate that these bands belong to the same redox species.

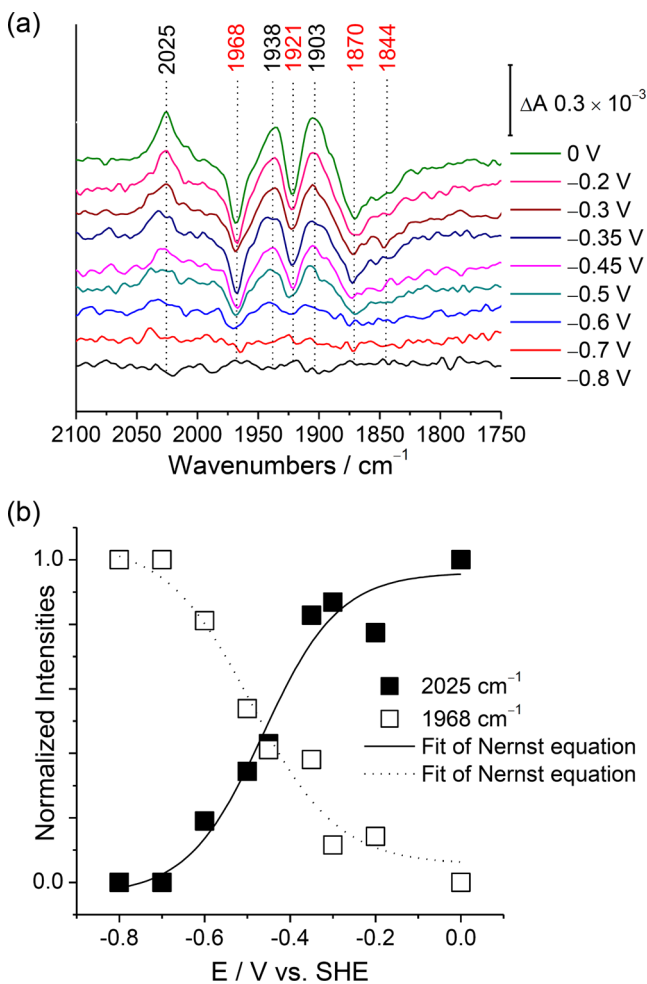
The band at 1921  $\text{cm}^{-1}$  was not considered because two neighboring negative bands at 1938 and 1902  $\text{cm}^{-1}$  masked its intensity (see above). The appearance of the four  $\nu(\text{CO})$  bands upon applying reductive conditions is indicative of the formation of a  $\text{Mn}^0$  dimer species, as previously reported.<sup>56,73</sup> A fifth band (predicted at around 1963  $\text{cm}^{-1}$  from previous measurements in THF<sup>73</sup>) is known to exhibit only weak IR absorption; therefore, it is most likely masked by the more intense adjacent 1968  $\text{cm}^{-1}$  absorption.<sup>56,73</sup> A frequency downshift (up to  $-15$   $\text{cm}^{-1}$  compared to literature values in organic solvents listed in Table 1) is observed in this work, which may be attributed to decreased electron density at the CO bond resulting from hydrogen bonding to the carbonyl oxygen atoms in aqueous electrolyte solution.<sup>82</sup> The assignment of these bands to a  $\text{Mn}^0$  dimer is also supported by the UV-vis SEC experiments above (Figure 2, inset). No indication for the presence of another reduced species was found by IR SEC under the applied conditions.

Reoxidation of the dimer was monitored with IR SEC by a stepwise increase of the potential from  $-0.8$  to 0 V (fully oxidized state) vs SHE. Figure 7a shows the resulting difference spectra (a reference spectrum was recorded under fully reduced conditions,  $E_{\text{appl}} = -1.1$  V vs SHE, prior to each potential step). The previously observed set of bands located at 2025, 1938, and 1903  $\text{cm}^{-1}$  re-emerges upon applying  $E_{\text{appl}} > -0.5$  V vs SHE at the expense of bands assigned to the dimer species (see above). Upon comparison with literature reports, the emerging  $\nu(\text{CO})$  bands are assigned to formation of a (monomolecular)  $\text{Mn}^{\text{I}}$  complex upon reoxidation of the dimer. As the initial generation of the dimer complex involves removal of the bromide ligand, the state formed at more positive potentials most likely represents a  $\text{Mn}^{\text{I}}$  complex with the bromido ligand being replaced by the solvent water (Table 1).<sup>13,73</sup> Thus, the



**Table 1. Frequencies of  $\nu(\text{CO})$  for  $\text{Mn}_{\text{pyr}}$  Adsorbed on MWCNT Electrodes under Different Conditions and Respective Assignment to Different  $\text{Mn}_{\text{pyr}}$  Species Based on Comparison to Literature Values Obtained in Solution<sup>a</sup>**

this work		comparison to literature	
$\nu(\text{CO})/\text{cm}^{-1}$	assignment	$\nu(\text{CO})/\text{cm}^{-1}$	assignment
2022, 1930, 1912	$[\text{Mn}^{\text{I}}\text{Br}(\text{bpy}_{\text{pyr}})(\text{CO})_3]$	2023, 1935, 1914 (THF) <sup>73</sup>	$[\text{Mn}^{\text{I}}\text{Br}(\text{bpy})(\text{CO})_3]$
2025, 1938*, 1903*	$[\text{Mn}^{\text{I}}(\text{H}_2\text{O})(\text{bpy}_{\text{pyr}})(\text{CO})_3]^+$	2019, 1933, 1919 (MeCN) <sup>73</sup>	$[\text{Mn}^{\text{I}}(\text{solvent})(\text{bpy})(\text{CO})_3]^+$
1968, 1921, 1870, 1844	$[\text{Mn}^{\text{0}}(\text{bpy}_{\text{pyr}})(\text{CO})_3]_2$	1973, 1928, 1878, 1858 (MeCN) <sup>56</sup> 1975, 1963 (weak), 1936, 1886, 1866 (THF) <sup>73</sup>	$[\text{Mn}^{\text{0}}(\text{bpy})(\text{CO})_3]_2$
not detected	$[\text{Mn}(\text{bpy}_{\text{pyr}})(\text{CO})_3]^-$	1909, 1811 (THF) <sup>73</sup>	$[\text{Mn}(\text{bpy})(\text{CO})_3]^-$
1991, 1880	$[\text{Mn}^{\text{I}}(\text{H})(\text{bpy}_{\text{pyr}})(\text{CO})_3]$	1991, 1888 (MeCN) <sup>61</sup>	$[\text{Mn}^{\text{I}}(\text{H})(\text{bpy})(\text{CO})_3]$

<sup>a</sup>The asterisk assigns estimated frequencies.**Figure 7.** Reoxidation of the  $\text{Mn}^{\text{0}}$  dimer species at positive potentials in aqueous  $\text{KHCO}_3$  solution (0.5 M, pH 8.2) under Ar at room temperature. (a) ATR IR difference spectra of the reoxidation of  $\text{Mn}_{\text{pyr}}$  at different potentials (vs SHE; reference spectrum recorded at  $E_{\text{appl}} = -1.0$  V).  $\nu(\text{CO})$  bands located at 2025, 1983, and 1903  $\text{cm}^{-1}$  (black numbers) increase at the expense of the prior observed marker bands (for the dimer state) at 1968, 1921, 1870, and 1844  $\text{cm}^{-1}$  (red numbers). (b) Intensity of the bands at 2025 (black squares) and 1968  $\text{cm}^{-1}$  (hollow squares) as a function of electrode potential. Lines correspond to a fit of the Nernst equation to the data set.

observed  $\nu(\text{CO})$  frequencies are slightly shifted compared to those found for the bromide-bound  $\text{Mn}_{\text{pyr}}$  complex (Figure 6a, Table 1).<sup>64</sup> Figure 7b shows the normalized intensity of the bands at 2025 and 1968  $\text{cm}^{-1}$ , representing the two different redox species (i.e.,  $\text{Mn}^{\text{0}}\text{--Mn}^{\text{0}}$  dimer vs monomolecular  $\text{Mn}^{\text{I}}$  species) as a function of electrode potential. Both intensities

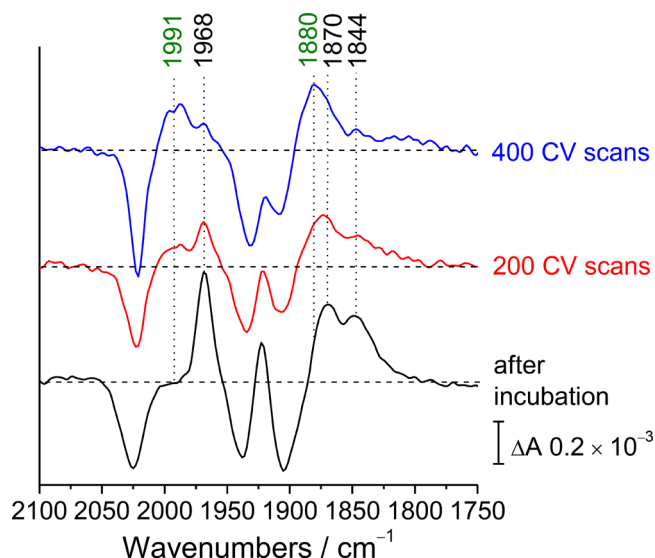
follow the same trend with opposite signs, and the data sets can be fitted satisfactorily using the Nernst equation with matching apparent midpoint potentials (Figure 7b). This observation points to a coupled redox events, in which dimer oxidation directly affords formation of the  $\text{Mn}^{\text{I}}$  species with marker bands identified at 2025, 1938, and 1903  $\text{cm}^{-1}$ .

**Spectroelectrochemistry at Low  $\text{Mn}_{\text{pyr}}$  Loading.** The change in selectivity of product formation from high to low loading of adsorbed  $\text{Mn}_{\text{pyr}}$  and the suggested change in mechanism for  $\text{CO}_2$  reduction were also probed by IR SEC. An obvious challenge in this SEC analysis was associated with the monitoring of very low concentrations of  $\text{Mn}_{\text{pyr}}$  and the resulting weak  $\nu(\text{CO})$  frequencies, which made a reliable evaluation difficult. We have therefore incubated from a relatively high concentration of  $\text{Mn}_{\text{pyr}}$  (10 mM in DMF) and followed the decreasing  $\text{Mn}_{\text{pyr}}$  surface loading over time by performing repetitive CV scans (scanning between  $-1.1$  and  $0$  V vs SHE at  $\nu = 50$   $\text{mV s}^{-1}$ ) of the  $\text{CNT}|\text{Mn}_{\text{pyr}}$  electrode in aqueous  $\text{KHCO}_3$  solution (0.5 M, pH 8.2). The progress of slow  $\text{Mn}_{\text{pyr}}$  loss from the MWCNT electrode can be analyzed by following the decreasing anodic wave ( $^{\text{ox}}E_p$ ; see above), and the catalytic intermediates are monitored through IR SEC by tracking the intensity of the strongest dimer band at 1968  $\text{cm}^{-1}$  formed upon reduction ( $E_{\text{appl}} = -1.0$  V vs SHE, reference spectrum recorded at  $0$  V vs SHE). The electroactive  $\text{Mn}_{\text{pyr}}$  surface concentration was reduced by approximately 50% after 400 CV scans (Figure S12). The  $\text{Mn}_{\text{pyr}}$  film loss may be due to desorption or decomposition of the immobilized  $\text{Mn}_{\text{pyr}}$  complex. Only two reduced Mn species carrying CO ligands were observed, which can be consistently assigned to reduced species of the intact  $\text{Mn}_{\text{pyr}}$  catalyst on the surface (see below). Possible decomposition of the molecular  $\text{Mn}_{\text{pyr}}$  would not interfere with the IR SEC experiment as  $\nu(\text{CO})$  frequencies were selectively monitored.

Figure 8 shows the surface-sensitive IR difference spectra after incubation as a reference and after 200 and 400 CV scans. After incubation, reduction of  $\text{Mn}_{\text{pyr}}$  at  $E_{\text{appl}} = -1.0$  V vs SHE afforded the spectral pattern as discussed above (Figure 6b), indicating the formation of the  $\text{Mn}^{\text{0}}\text{--Mn}^{\text{0}}$  dimer species. Lowering of the concentration of  $\text{Mn}_{\text{pyr}}$  is consistent with a decrease in the overall signal intensity of the dimer bands (at 1968, 1870, and 1844  $\text{cm}^{-1}$ ) and the appearance of spectral features at 1991 and 1880  $\text{cm}^{-1}$ . Stepwise reduction by applying potentials from  $-0.7$  to  $-1.0$  V vs SHE revealed that the new spectral features in the spectrum in Figure 8 were almost reversibly formed only upon reduction of the catalyst (Figure S13). Further decrease of  $\Gamma_{\text{Mn}}$  afforded the increase of the latter bands, which dominate the spectrum upon reduction.

To verify that these two bands belong to the same redox species, band analysis for the spectra recorded after 200 and





**Figure 8.** ATR IR difference spectra monitoring the reduced species of  $\text{Mn}_{\text{pyr}}$  at  $E_{\text{appl}} = -1.0$  V vs SHE (reference spectrum recorded at 0 V vs SHE at fully oxidized conditions) as a function of decreasing surface concentration (0.5 M aqueous  $\text{KHCO}_3$ , pH 7.4). Successive lowering of the surface concentration was achieved by performing CV scans at a scan rate of  $50 \text{ mV s}^{-1}$ . The band intensity at  $1968 \text{ cm}^{-1}$  is used to monitor the overall decrease in concentration (black numbers indicate the  $\text{Mn}^0$  dimer). At lowered surface concentrations, bands at  $1991$  and  $1880 \text{ cm}^{-1}$  (green numbers) arise that are assigned to  $\nu(\text{CO})$  stretching vibrations of a Mn-hydride species (Table 1).

400 CV scans was performed (Figure 8). Lorentzian band profiles were chosen for the positive bands, and their intensity and half-width iteratively varied until full reconstruction of the (positive parts of the) experimental spectra (Figure S14a). The bands at  $1991$  and  $1880 \text{ cm}^{-1}$  do not alter in relative intensity in the red and blue spectra in Figure 8, indicating that they belong to the same spectral component, that is, redox species. For comparison, such behavior is also observed for the bands at  $1968$  and  $1844 \text{ cm}^{-1}$  (Figure S14), which is expected as these bands are assigned to the dimer species, as demonstrated above (see Figure S11). The bands at  $1991$  and  $1880 \text{ cm}^{-1}$  likely represent a Mn-hydride complex that is formed upon reduction under these conditions, which is supported by the striking match between observed and literature-reported band frequencies for measured and calculated Mn-hydride complexes (Table 1).<sup>61</sup> Furthermore, the species is reversibly formed only upon reduction, and the presence of an anionic species (i.e., the  $[\text{Mn}(\text{bpy}_{\text{pyr}})(\text{CO})_3]^-$  species) can be ruled out as this species would be indicated by two strong  $\nu(\text{CO})$  bands located at approximately  $1910$  and  $1811 \text{ cm}^{-1}$ .<sup>73</sup> While the first band may be masked by the negative bands of the oxidized  $\text{Mn}_{\text{pyr}}$ , no indication for the latter is observed in any of the recorded spectra upon reduction at potentials down to  $-1.1$  V vs SHE. Finally, the assignment of a Mn-hydride species is also in accordance with preferential formation of formate and  $\text{H}_2$  upon CPE experiments using lowered  $\text{Mn}_{\text{pyr}}$  surface concentrations, providing thereby an explanation for the switch in reactivity. Accordingly, the SEC IR experiments demonstrate that low concentrations of  $\text{Mn}_{\text{pyr}}$  favor formation of the hydride over the dimer species, and the long-term CPE measurements reflect the catalytic consequences of this change in mechanism.

The application of our surface-sensitive ATR IR SEC configuration allowed the effective in situ detection of

catalytically relevant states of the immobilized  $\text{Mn}_{\text{pyr}}$  complex. Formation of the  $\text{Mn}^0$ – $\text{Mn}^0$  dimer species as well as the monomeric reduced Mn–H complex could be characterized on a MWCNT electrode surface. Notably, the presence of the two species could be directly linked to the electrocatalytic product selectivity ( $\text{CO}$  via the dimer and  $\text{HCOO}^-$  and  $\text{H}_2$  via the Mn-hydride).

## CONCLUSIONS

This work describes the synthesis, electrochemistry and SEC characterization of a Mn  $\text{CO}_2$  reduction catalyst immobilized through a pyrene anchoring group on a MWCNT electrode. Despite the low Faradaic yield for  $\text{CO}$  and formate, the hybrid electrode displays high activity for electrocatalytic reduction of aqueous  $\text{CO}_2$  with TONs of up to  $1790 \pm 290$  for  $\text{CO}$  and up to  $3920 \pm 230$  for formate at  $E_{\text{appl}} = -1.1$  V vs SHE (corresponding to overpotentials of  $\eta = 550$  mV for  $\text{CO}$  and  $\eta = 590$  mV for formate production). Product selectivity can be fine-tuned by controlling the surface loading of the catalyst on the CNT sidewalls. Low Mn catalyst loadings afford selectivity for the generation of dissolved formate, whereas high loading result in higher selectivity for gaseous  $\text{CO}$ . Control over product selectivity is a first step to rationally synthesize desired high-value products from  $\text{CO}_2$  on demand.

In situ ATR IR and UV–vis SEC characterization of the molecular catalyst on the electrode surface allowed distinguishing between two different catalytic pathways by detecting the involved intermediates. The identified Mn dimer and Mn-hydride species formed on the electrode surface could be directly linked to the occurrence of distinct catalytic products. The implementation of such surface-sensitive in situ spectroscopy therefore proves to be of importance for understanding catalytic reactions of surface-bound molecular catalysts, stimulating future interdisciplinary research also beyond  $\text{CO}_2$  reduction and MWCNT electrodes.

Overall, the present study highlights the benefits of rational incorporation of molecular catalysts onto electrode surfaces. Our strategy allowed enhancement of the catalytic activity and stability, as well as tuning of the selectivity of the immobilized catalyst, while enabling a detailed understanding of the catalytic mechanisms involved through the use of a powerful SEC approach.

## EXPERIMENTAL SECTION

**Materials and Reagents.** Dry tetrahydrofuran (THF), diethyl ether ( $\text{Et}_2\text{O}$ ), and acetonitrile (MeCN) were used for the synthesis and electrochemistry of the compounds. 4,4'-Dimethyl-2,2'-bipyridine ( $\text{bpyMe}_2$ ),  $[\text{MnBr}(\text{CO})_5]$ , *n*-BuLi (1.6 M in hexane), diisopropylamine, *N*-methyl-2-pyrrolidone, dimethylformamide (DMF), fluorine-doped tin oxide (FTO), tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ),  $\text{KHCO}_3$  (99.95% purity), and MWCNTs (thin and short, 755117 Aldrich, purity 95%) were purchased from Sigma-Aldrich. Column chromatography was carried out using silica gel 60 (0.040–0.063 mm mesh) from Merck. Other chemicals and solvents were purchased from commercial suppliers and used as received. 1-(4-Bromobutyl)pyrene<sup>83</sup> and the complex  $[\text{MnBr}(\text{bpyMe}_2)(\text{CO})_3]$ <sup>30</sup> were synthesized and characterized as previously described.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DPX-400 MHz spectrometer at room temperature. High-resolution mass spectra were recorded using a ThermoScientific Orbitrap Classic mass spectrometer. The ATR FT-IR spectrum of  $\text{Mn}_{\text{pyr}}$  was recorded on a Nicolet iS50 spectrometer. Elemental analysis was carried out by the Microanalysis Service of the Department of Chemistry, University of Cambridge, using a PerkinElmer 240 Elemental Analyzer.

**Synthesis of  $\text{bpy}_{\text{pyr}}$ .** Diisopropyl amine (0.33 mL, 2.35 mmol) was added to THF (10 mL). The mixture was cooled to  $-10\text{ }^{\circ}\text{C}$  with an ice/acetone bath. A solution of *n*-BuLi (1.6 M, 1.5 mL, 2.4 mmol) was slowly added to the reaction mixture and stirred for another 5 min at  $-10\text{ }^{\circ}\text{C}$  under a  $\text{N}_2$  atmosphere. Then,  $\text{bpyMe}_2$  (230 mg, 1.25 mmol) in THF (40 mL) was added dropwise to the mixture (over 15 min) and further stirred for 10 min at  $-10\text{ }^{\circ}\text{C}$  under a  $\text{N}_2$  atmosphere. Then, 1-(4-bromobutyl)pyrene (400 mg, 1.2 mmol) in THF (40 mL) was added slowly to the mixture (over approximately 30 min), and stirred for another 30 min at  $-10\text{ }^{\circ}\text{C}$  under  $\text{N}_2$  atmosphere. Cold water (60 mL) was slowly added, followed by  $\text{CH}_2\text{Cl}_2$  (80 mL). The product was extracted twice with  $\text{CH}_2\text{Cl}_2$  (80 mL), dried over  $\text{MgSO}_4$ , and the solvent evaporated to dryness. The crude product was purified by column chromatography on silica gel using  $\text{CH}_2\text{Cl}_2/\text{MeCN}$  (9:1), yielding the product as an off-white solid. Yield: 410 mg, 77%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta_{\text{H}}$  (ppm) = 1.50–1.60 (m, 2H), 1.80 (q,  $J$  = 7.8 Hz, 2H), 1.91 (q,  $J$  = 7.7 Hz, 2H), 2.44 (s, 3H), 2.72 (t,  $J$  = 7.8 Hz, 2H), 3.34 (t,  $J$  = 7.8 Hz, 2H), 7.08–7.15 (m, 2H), 7.84 (d,  $J$  = 7.7 Hz, 1H), 7.95–8 (m, 1H), 8–8.04 (m, 2H), 8.06–8.12 (m, 2H), 8.12–8.18 (m, 2H), 8.22–8.28 (m, 3H), 8.52 (d,  $J$  = 4.9 Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta_{\text{C}}$  (ppm) = 21.3, 29.4, 30.4, 31.6, 33.5, 35.5, 121.5, 122.2, 123.4, 124.1, 124.7, 124.8, 124.9, 125.1, 125.2, 126.6, 127.2, 127.3, 128.6, 129.8, 130.9, 131.5, 136.9, 148.8. MS (+ESI,  $m/z$ ): calcd. for  $\text{C}_{32}\text{H}_{28}\text{N}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 441.23; found, 441.25.

**Synthesis of  $\text{Mn}_{\text{pyr}}$ .** [ $\text{MnBr}(\text{CO})_5$ ] (57 mg, 0.21 mmol) was added to  $\text{Et}_2\text{O}$  (15 mL) under a  $\text{N}_2$  atmosphere. Then,  $\text{bpy}_{\text{pyr}}$  (75 mg, 0.17 mmol) was added, and the mixture was refluxed for 4 h in the dark. The mixture was then cooled to room temperature, and the orange precipitate was filtered off and washed with  $\text{Et}_2\text{O}$  (50 mL) and dried under high vacuum at room temperature to give the product as an orange solid. Yield: 93 mg, 83%. The light-sensitive compound was stored in the dark, and all electrochemical experiments were executed in the absence of light.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta_{\text{H}}$  (ppm) = 1.5–1.65 (br, 2H), 1.68–1.8 (m, 2H), 1.86–1.96 (m, 2H), 2.45–2.55 (m, 3H), 2.66–2.78 (2H), 3.30–3.40 (m, 2H), 7.20–7.30 (m, 2H), 7.75–7.95 (m, 3H), 7.95–8.05 (m, 3H), 8.05–8.20 (m, 4H), 8.20–8.30 (m, 1H), 8.95–9.10 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta_{\text{C}}$  (ppm) = 21.3, 29.1, 30.1, 31.5, 33.3, 35.3, 122.1, 122.9, 123.3, 124.8, 125.0, 125.9, 126.4, 126.7, 127.3, 127.5, 128.6, 129.8, 130.8, 131.5, 150.2, 153.1, 154.6, 155.3, 221.8. FT-IR ATR ( $\nu/\text{cm}^{-1}$ ): 2016 (CO), 1900 (CO) (br). MS (+ESI,  $m/z$ ): calcd. for  $\text{C}_{35}\text{H}_{28}\text{BrMnN}_2\text{O}_3$  [ $\text{M} - \text{Br}$ ] $^+$ : 579.15; found, 579.19. Elemental analysis: calcd. for  $\text{C}_{35}\text{H}_{28}\text{BrMnN}_2\text{O}_3$ : C, 63.8; H, 4.3; N, 4.3; Br, 12.1; found: C, 64.2; H, 4.4; N, 3.9; Br, 12.1.

**Electrodes for CV and CPE.** MWCNT/glassy carbon electrodes were drop-cast by adding 20  $\mu\text{L}$  of a 5 mg  $\text{mL}^{-1}$  dispersion of MWCNTs in *N*-methylpyrrolidone onto a glassy carbon electrode, and the deposit was dried under high vacuum before use. A 5  $\mu\text{m}$  thick homogeneous MWCNT film was obtained as reported previously (0.2  $\text{cm}^2$  geometrical surface,  $\phi$  = 5 mm).<sup>66</sup> The MWCNT/glassy carbon electrodes were soaked in a solution of  $\text{Mn}_{\text{pyr}}$  in dry DMF for 30 min in the dark. The modified electrode was subsequently rinsed with DMF and deionized water. Control experiments were performed with [ $\text{MnBr}(\text{bpyMe}_2)(\text{CO})_3$ ],  $\text{MnCl}_2/\text{bpy}_{\text{pyr}}$  and [ $\text{MnBr}(\text{CO})_5$ ] instead of  $\text{Mn}_{\text{pyr}}$ .

**Electrodes for UV–Vis SEC.** A MWCNT film was prepared as previously described.<sup>84</sup> Briefly, 2 mg of MWCNTs were sonicated in 500 mL of deionized water for 30 min and left to settle overnight. Then 200 mL of the supernatant were filtered over a cellulose nitrate filter (Millipore, 0.45  $\mu\text{m}$  pore size, overall diameter of  $\phi$  = 3.5 cm), leading to the homogeneous MWCNT film. The MWCNT film was subsequently deposited on a 2  $\times$  1 cm glass slide with the top 1  $\times$  1 cm coated with FTO (so that the MWCNT film covered both FTO-coated and bare glass areas) by carefully dissolving the cellulose filter with several washings of acetone, leading to the MWCNT film on FTO glass. The  $\text{Mn}_{\text{pyr}}$  modified electrode was obtained by drop-casting 10  $\mu\text{L}$  of a 10 mM solution of  $\text{Mn}_{\text{pyr}}$  onto the MWCNT/FTO electrode (geometrical surface area of 0.25  $\text{cm}^2$ ) in the dark. After 10 min, the electrode was rinsed with deionized water and the FTO-coated portions of the electrode were not exposed to the electrolyte

solution to prevent reductive degradation of FTO from influencing the spectra.

**Electrodes for ATR IR SEC.** The MWCNT films were deposited onto the Si substrate by carefully dissolving the cellulose filter with several washings of acetone, leading to the MWCNT film. The  $\text{Mn}_{\text{pyr}}$  modified electrode was obtained by drop-casting 10  $\mu\text{L}$  of a 10 mM solution of  $\text{Mn}_{\text{pyr}}$  onto the CNT surface in the dark. After 10 min, the electrode was rinsed with DMF and with deionized water.

**Electrochemistry.** All electrochemical measurements were performed on a PalmSens EmStat or MultiEmStat<sup>3+</sup> potentiostat in the dark. Electrochemistry in organic media was performed in MeCN containing 0.1 M TBAPF<sub>6</sub> in a three-electrode configuration using a Ag/AgCl wire as the reference electrode and a platinum mesh as the counter electrode. Ferrocene was used as the internal reference at the end of the measurements.

Aqueous electrochemistry was performed in  $\text{KHCO}_3$  (99.95%, 0.5 M) electrolyte solution using a three-electrode configuration using a Ag/AgCl (sat. KCl) reference electrode and platinum mesh as the counter electrode. The potentials were converted from Ag/AgCl to standard hydrogen electrode (SHE) by adding +0.199 V. The CV and CPE measurements were carried out in a three-necked two-compartment cell separated by a Nafion membrane under  $\text{N}_2$  or  $\text{CO}_2$ . The working electrode compartment was stirred during the CPE measurement. All experiments were carried out at room temperature ( $\sim 22\text{ }^{\circ}\text{C}$ ).

The surface loading of the catalyst was calculated through the integration of the reoxidation wave in the CV scans

$$\Gamma_{\text{Mn}} = \frac{q}{nFA}$$

where  $\Gamma_{\text{Mn}}$  is the surface loading ( $\text{mol cm}^{-2}$ ),  $q$  is the charge (C) obtained from integration of the oxidation wave,  $n$  the number of electrons in the redox process per Mn center ( $n = 1$ ),  $F$  is the Faraday constant (96485 C  $\text{mol}^{-1}$ ), and  $A$  is the geometrical electrode area (0.2  $\text{cm}^2$ ).

To model the impact of the  $\text{Mn}_{\text{pyr}}$  solution concentration over the surface loading, a single Langmuir isotherm was used

$$\Gamma_{\text{Mn,eq}} = \frac{\Gamma_{\text{Mn,max}} K_{\text{Mn}} [\text{Mn}_{\text{pyr}}]}{1 + K_{\text{Mn}} [\text{Mn}_{\text{pyr}}]}$$

where  $\Gamma_{\text{Mn,eq}}$  is the equilibrium surface coverage of  $\text{Mn}_{\text{pyr}}$  ( $\text{mol cm}^{-2}$ ),  $\Gamma_{\text{Mn,max}}$  is the saturation surface coverage ( $\text{mol cm}^{-2}$ ), and  $K_{\text{Mn}}$  ( $\text{L mol}^{-1}$ ) the association constant of  $\text{Mn}_{\text{pyr}}$  with the MWCNT surface in DMF at room temperature.

**UV–Vis SEC.** Measurements were carried out using a Varian Cary 50 Bio UV–visible spectrometer. The measurements were performed using a three-electrode configuration using a Ag/AgCl (sat. KCl) reference electrode and platinum mesh as a counter electrode in a flat custom-designed three-necked electrochemical cell suited for UV–vis measurements. The working MWCNT-FTO electrode was placed between the beam source (FTO was not in contact with the solution to prevent degradation) and the collector to measure UV–vis spectra of the immobilized catalyst at different potentials.

**ATR IR SEC.** Surface-sensitive IR measurements were carried out in 60° single-reflection ATR configuration using an ATR-active Si prism and an IFS66v/s FT-IR spectrometer (Bruker Instruments) equipped with a photoconductive nitrogen-cooled MCT detector. A total of 400 scans were co-added for a spectrum. The spectral region was set to a range from 400 to 4000  $\text{cm}^{-1}$ . The resolution of the spectra was 4  $\text{cm}^{-1}$ . The MWCNT membrane film-coated Si prism was mounted into a homemade ATR IR spectroelectrochemical cell (fill volume of 5 mL).<sup>85</sup> The solvent-accessible electrode surface had a geometrical area of 0.9  $\text{cm}^2$ . A Ag/AgCl 3 M KCl (DriRef, WPI) and a hydrogen flame-cleaned Pt wire (99%, Goodfellow) were used as reference and counter electrodes, respectively. All measurements were carried about at room temperature. Potentials were applied using an Autolab PGSTAT 12 (Metrohm) potentiostat. All measurements were carried out with either Ar or  $\text{CO}_2$  overpressure. Absorbance ( $A$ ) spectra were generated according to Lambert–Beer's equation

$$-\log \frac{I_{\text{sample}}}{I_{\text{ref}}} = A$$

$I_{\text{sample}}$  denotes the relevant sample spectrum and  $I_{\text{ref}}$  the respective reference spectrum.

The normalized band intensities  $I_{\text{band}}$  as a function of applied electrode potential  $E$  were fitted using a transformed Nernst equation

$$I_{\text{band}} = \frac{1}{1 + e^{[(nF/RT)(E-E^{0'})]}} + C$$

$I_{\text{band}}$  denotes the (normalized) intensity of the respective band.  $F$ ,  $R$ , and  $T$  denote the Faraday constant, the ideal gas constant, and room temperature, respectively.  $n$  and  $E^{0'}$  represent the number of transferred electrons and the apparent midpoint potential of the redox transition, respectively. Both values are varied in the fits.  $C$  is a dimensionless parameter, accounting for possible offsets to obtain better fits of the equation to the data set. Band fitting of the difference IR spectra was performed using a homemade software (Qpipisi).

**Isotopic Labeling.** CPE experiments were performed in a gastight single-compartment (for  $^{13}\text{CO}$  detection) or two-compartment (for  $^{13}\text{C}$  formate detection) electrochemical cell equipped with a CNT1 Mn<sub>pyr</sub> working electrode, Pt counter electrode, and Ag/AgCl (sat. KCl) reference electrode in phosphate buffer (0.1 M, pH 7). The solution was purged with  $\text{N}_2$  for 10 min before the headspace gas was replaced with  $^{12}\text{CO}_2$  or  $^{13}\text{CO}_2$  (>99 atom %  $^{13}\text{C}$ , Sigma-Aldrich) by evacuating three times and refilling with the respective  $\text{CO}_2$  isotopologue. CPE was performed at  $E_{\text{appl}} = -1.1$  V vs SHE for 3 and 12 h for CO and  $\text{HCOO}^-$  detection, respectively. Subsequently, the headspace gas was transferred to an evacuated gas IR cell (SpecAc, 10 cm path length, equipped with KBr windows), and a high-resolution transmission FT-IR spectrum was collected on a Thermo Scientific Nicolet iS50 FT-IR spectrometer. For  $\text{H}^{13}\text{COO}^-$  or  $\text{H}^{12}\text{COO}^-$  detection, 35  $\mu\text{L}$  of  $\text{D}_2\text{O}$  were added to 700  $\mu\text{L}$  of the electrolyte solution in an NMR tube. The spectra were recorded on a Bruker DPX-400 MHz spectrometer at room temperature, and water suppression was applied.

**Product Analysis.** The amount of  $\text{H}_2$  and CO produced during CPE measurements under  $\text{N}_2$  or  $\text{CO}_2$  (with 2%  $\text{CH}_4$  as an internal standard) was quantified by gas chromatography by analyzing a 50  $\mu\text{L}$  volume of the working electrode headspace compartment with a Shimadzu Tracera GC-2010 Plus using a barrier discharge ionization detector (BID). The gas chromatograph was equipped with a ShinCarbon micro ST column (0.53 mm diameter) kept at 40  $^\circ\text{C}$ , using helium carrier gas.  $\text{HCOO}^-$  was analyzed by ion chromatography (Metrohm 882 compact IC plus ion chromatography system) with carbonate buffer (4 mM, pH 7.4) eluent containing acetone (50 mL  $\text{L}^{-1}$ ). The Faradaic yield for  $\text{H}_2$  and CO was calculated using

$$\text{Faradaic yield product (\%)} = 100 \times \frac{(2F \times n_{\text{prod}})}{Q}$$

where  $F$  is the Faraday constant ( $\text{C mol}^{-1}$ ),  $n_{\text{prod}}$  (mol) is the amount of  $\text{H}_2/\text{CO}$  measured in the headspace,  $\text{HCOO}^-$  in the electrolyte solution, and  $Q$  (C) is the charged passed during electrolysis.

The surface loading (from CV) and product quantification (from CPE) were determined from separate sets of experiments in triplicate. The error bars shown in the graphs are the standard deviation calculated as previously described.<sup>36</sup>

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b06269.

Supporting figures (PDF)

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## Notes

The authors declare no competing financial interest.

Additional data related to this publication are available at the University of Cambridge data repository (<https://doi.org/10.17863/CAM.13194>).

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