Electrochemically Triggered Dynamics Within a Hybrid Metal-Organic Electro catalyst

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Abstract:

A wide array of systems, ranging from enzymes to synthetic catalysts, exert adaptive motifs to maximize their functionality. In a related manner, select metal-organic frameworks (MOFs) and related systems exhibit structural modulations under stimuli such as the infiltration of guest species. Probing their responsive behavior \textit{in-situ} is a challenging but important step towards understanding their function and subsequently building from there. In this report, we investigate the dynamic behavior of an electrocatalytic Mn-porphyrin containing MOF system (Mn-MOF). We discover, using a combination of electrochemistry and \textit{in-situ} probes of UV-Vis absorption, resonance Raman and infrared spectroscopy, a restructuring of this system via a reversible cleavage of the porphyrin carboxylate ligands under an applied voltage. We further show, by combining experimental data and DFT calculations, as a proof of concept, the capacity to utilize the Mn-MOF for electrochemical \textit{CO\textsubscript{2}} fixation and to spectroscopically capture the reaction intermediates in its catalytic cycle. The findings of this work and methodology developed opens opportunities in the application of MOFs as dynamic, enzyme-inspired electrocatalytic systems.
Introduction:

From enzymes to zeolites and metal-organic frameworks (MOFs), three-dimensional catalysts possess key inherent attributes that endow them unique functionalities. In the context of chemical catalysis, operating in three dimensions allows for precise controls of both reactant binding and the immediate environment around the catalytic site. For example, enzyme catalytic pockets feature not only binding sites, but also amino acid residues that stabilize high-energy intermediates through hydrogen bonding or electrostatics. Local hydrophobicity modulates reorganization energies, substrate channels precisely control rates of reactant delivery and reactant concentration, and an adaptable structure is responsive to stimuli. Amorphous catalysts similarly feature structural rearrangement to yield a catalytically active state upon the application of a voltage, though they lack the well-defined hierarchical structure of enzymes.2-3

To this end, chemical tunability and three-dimensional structure of MOFs and related porous has drawn great interest in designing functional materials with predetermined, precisely controlled crystallinity, pore dimensions and internal chemistry.4 These attributes gave rise to the applications of MOFs in the areas of gas storage,5-6 and gas separation,7 cargo delivery,8 and catalysis.9 In addition, the chemical nature of several MOFs leads to structural dynamics upon a stimulus: MOF and coordination-polymers have been shown to exhibit lattice deformations,10-11 rotation about internal bonds,12 and cooperative adsorption.13 However, investigations of MOF dynamics under electrochemical stimuli are just emerging.

In the context of electrochemistry, MOFs and covalent organic frameworks (COFs) have been used as supercapacitors,14 battery electrodes,15 and catalysts for fuel cells16 and fuel forming reactions.17-19 Their inherent porosity is advantageous for ionic charging in the case of supercapacitors and batteries, and for accommodating a high density of catalytically active sites, beneficial for electrocatalysis. While the area of MOF electrochemistry is rather nascent, the use of in-situ techniques to investigate their function as they operate is newer still.

In the case when MOF linkers exhibited an oxidation state-dependent absorption profile, UV-Vis absorption has been successfully utilized to probe MOF linker redox processes in both steady state and time-dependent conditions.20-22 A combination of electroanalytical experiments and modelling has recently elucidated diffusion kinetics of electrons and electrolyte ions in metallocene-doped MOF films.23 Within the context of catalysis, electrochemical reduction of Co(II) active sites to Co(I) of a Co-porphyrin-bearing COF-367 under the conditions where it was active for CO2 reduction was studied with x-ray absorption spectroscopy.24 Co(II/I) reduction in a Co-porphyrin containing MOF was also probed with UV-vis absorption spectroscopy to link Co(I) formation to the onset of CO2 reduction catalysis.25 Active sites and adsorbed *OOH intermediates were detected in a series of lattice-strained MOFs with infrared spectroscopy
as they performed electrochemical water oxidation and oxygen reduction.\textsuperscript{16} However, reaction intermediates of CO\textsubscript{2} reduction, while being increasingly probed in heterogeneous catalysts,\textsuperscript{26-27} have not yet been captured within a MOF.

In this work, we have developed an electrocatalytic metal-organic system, bearing Mn-porphyrin units as its catalytic unit and spectroscopically addressable component (labelled Mn-MOF for simplicity). The Mn-MOF was grown in the form of thin layers atop a conductive mesoporous TiO\textsubscript{2} scaffold that facilitated charge transfer from the electrode and reactant transfer from the bulk solution while simultaneously being transparent to enable its investigation with spectroscopic techniques (Fig. 1a).

To fabricate the composite system, we first deposited a thin film of mesoporous TiO\textsubscript{2} onto a fluorine-doped tin oxide (FTO) coated glass slide (Fig. 1b). The film was briefly annealed to improve conductivity, cleaned with a UV-ozone treatment, and soaked overnight in an ethanolic solution of 2-aminoethylphosphonic acid. The Mn-MOF was grown through an adaptation of a previously established recipe by subsequently dipping the electrodes in ethanolic solutions containing zinc nitrate, the Mn porphyrin, and 4,4’-bypiridine for typically three cycles.\textsuperscript{28} After deposition, the film was visibly brownish-green in color. Scanning and transmission electron microscopy (SEM and TEM) imaging revealed that the electrode featured a ~3 µm mesoporous thick film of 20 nm TiO\textsubscript{2} nanoparticles, coated with a ~3 nm shell of the MOF (Fig. 1c,d). The Mn-MOF exhibited very weak crystallinity, as evidenced by the broad peaks at ~3.6 and 6.5° in the powder x-ray diffraction (XRD) spectrum. As expected from the nature of the synthetic route and nanoscopic film thickness, there was no long-range periodicity that would lead to intense, well-defined diffraction peaks and likely the metal-organic layer on the TiO\textsubscript{2} has a large amount of amorphous character. We thus use the term MOF very liberally in this work, as our synthesized material does not possess the idealized long-range crystallinity and well-defined ordering as with conventional MOF materials. The TiO\textsubscript{2} scaffold, featuring a mixture of rutile and anatase phases, contributed the remainder of the visible peaks.
Figure 1: Concept and synthesis of the catalytic MOF composite system (a). The TiO$_2$ nanoparticles were drop-cast onto a conductive FTO substrate, then coated with a MOF thin-film through layer-by-layer deposition (b). A porous ~3 µm thick film of 20 nm TiO$_2$ particles (c) was covered with 2 nm of the MOF layer (d). The weak-crystallinity of the Mn-MOF was evidenced by broad peaks in the low-angle portion (inset) of the XRD spectrum (e). The remainder of the peaks match those of the simulated patterns for TiO$_2$ in the anatase and rutile phases.

Following the synthesis, we moved to probe the Mn-MOFs behavior under electrochemical bias. First, to monitor the oxidation state of the Mn-porphyrin under electrochemical conditions, we turned to UV-Vis spectroelectrochemistry (Fig. 2a). The absorbance spectrum of the Mn-MOF exhibited features characteristic of porphyrins: a strong Soret band at 476 nm and two weaker Q-bands in the 550-650 nm range (Fig. 2b). A red-shift and a broadening of the Soret band relative to that of the free porphyrin indicates both a change in coordination and a distribution of coordination environments of the porphyrin unit within the framework, respectively. The Mn-MOF grown on a planar FTO surface exhibited a similar absorbance
spectrum to that on the TiO$_2$ surface (Fig. S2). Next, the Mn-MOF’s absorbance was monitored \textit{in-situ} in a N$_2$-purged electrochemical cell with an acetonitrile solvent and 0.1 M tetrabutylammonium hexafluorophosphate supporting electrolyte. At $-1.0\,\text{V vs. Ag/Ag}^+$ the Mn(III), present at open circuit conditions, was completely converted Mn(II), evidenced by the shift of the Soret band to 442 nm (Fig. 2c).

Ligand-based reductions in porphyrins are typically accompanied by changes at longer wavelengths indicating that the reduction was solely metal-centered.

Tracking the ratio of the Mn(III) to Mn(II) Soret bands revealed the redox potential of the Mn to be centered at $-0.8\,\text{V}$ (Fig. 2d).

To investigated the kinetics of the Mn(III/II) redox process, the 442 nm band corresponding to Mn(II) was monitored following a voltage step from 0V to $-1.0\,\text{V}$. Temporally tracking the band intensity indicated that the Mn was mostly reduced within 1 minute (Fig. 2e). However, the oxidation of the Mn-MOF, facilitated by switching the applied potential to 0V, only occurred within 30 minutes (Fig. 2f). Slow kinetics, despite a large applied overpotential, suggests that the oxidation is likely linked to a rate-limiting chemical process rather than an electronic one. The Mn-MOF grown on a planar FTO surface exhibited slightly slower reduction, likely due to a slower rate of charge transport through larger crystals (Fig. S2). The oxidation process, on the other hand, occurred at the same timescale as for the Mn-MOF on TiO$_2$. The band intensity and position completely returned to its original position, indicating that this process was reversible (Fig. S3).
Figure 2: Schematic illustration UV-Vis absorption spectroelectrochemistry (a). The Mn-MOF features a red-shifted and broadened Soret band, reflecting its coordination within the MOF network and distribution of bonding motifs (b). Under a negative applied bias, the same band shifts completely from 476 nm (ox.) to 442 nm (red.), indicating that the porphyrin units are all in electrical contact with the electrode (c). Tracking the oxidized vs reduced Soret band ratios indicates a mid-point redox potential of approximately \(-0.8\) V vs. Ag/Ag\(^+\) (d). The reduction of the Mn-MOF is mostly complete within 0.5 minutes (e). In contrast, the oxidation occurs at a timescale of tens of minutes (f).

To obtain insights of the redox process at a molecular level, we utilized in-situ vibrational spectroscopy in a parallel set of experiments by developing spectroelectrochemical cells that enable the application of an electrochemical bias coupled with spectroscopic probing (Fig. 3a). First, Raman spectroscopy, utilizing a 473 nm laser in resonance with the Mn(III) porphyrin’s Soret band, selectively tracked this unit’s electrochemical reduction (Fig. 3b). When moving from \(-0.3\)V to \(-1.2\)V, significant changes to bands in the 300-1800 cm\(^{-1}\) region were noted. At positive potentials, the spectra were dominated by bands located at 389 cm\(^{-1}\) and 1004 cm\(^{-1}\) band that can be assigned to the \(A_{1g}\) \(\upsilon_8\) (Mn-N) and \(\phi_8\) mode, respectively.\(^3^2\) Reducing the potential resulted in a shift of these bands to 378 cm\(^{-1}\) and 991 cm\(^{-1}\) along with a notable decrease in overall intensity resulting from moving off-resonance.

The high frequency region from 1200 cm\(^{-1}\) to 1700 cm\(^{-1}\) features porphyrin marker bands that are specifically sensitive to the oxidation and spin state of the metal atom. At positive potentials, bands at 1453
cm\(^{-1}\), 1497 cm\(^{-1}\), and 1556 cm\(^{-1}\) were noted that can be assigned to the \(\nu_3\), \(\nu_{12}\), and \(\nu_2\) mode, respectively, and most likely suggest the presence of a five-coordinated high spin Mn(III).\(^{32-33}\) The \(\nu_4\) mode is heavily overlapped by the strong acetonitrile band at 1375 cm\(^{-1}\) and was identified at 1366 cm\(^{-1}\) by component fit analysis (Fig. S6). At this point, the nature of a possible 5\(^{th}\) ligand is not unambiguously determined, but is likely represented by a coordinating acetonitrile molecule. Shifting the potential more negative than \(-0.7\) V lead to a low-frequency shift of these bands in line with a metal centered reduction from Mn(III) to Mn(II). A \(\nu_4\) band at 1339 cm\(^{-1}\) was noted, which usually found above 1345 cm\(^{-1}\).\(^{33}\) The \(\nu_3\) mode of the Mn(II) porphyrin was found at 1446 cm\(^{-1}\), while a \(\nu_2\) could not be clearly assigned due to its lower intensity in the Mn(II) state. A possible candidate is a band at 1530 cm\(^{-1}\), which however would correspond to a heavily low-shifted \(\nu_2\) (expected around 1540-1550 cm\(^{-1}\)). In contrary, the \(\nu_3\) mode was found at 378 cm\(^{-1}\) and matches well with the frequency expected for Mn(II) porphyrin in the absence of axial coordination. Thus, the Mn(III) to Mn(II) transition could potentially involve the loss of an axial ligand.\(^{34-35}\) Component fit analysis\(^{36}\) of the spectral series revealed that there were indeed two species present in the spectra that interconverted at \(-0.8\) V, matching the observations from UV-Vis absorbance (Fig. 3c).

Complementary attenuated total reflection infrared (ATR-IR) spectroscopy was then applied to further bolster our understanding of the changes occurring \textit{in-situ}. The Mn-MOF was grown in an identical fashion on a mesoporous TiO\(_2\)-coated silicon prism and subjected to electrochemical reduction/oxidation. Upon the application of \(-1.2\) V, positive bands rapidly appeared in the 1400-1700 cm\(^{-1}\) range (Fig. 5d), which can be assigned to the symmetric and asymmetric COO\(^{-}\) modes of deprotonated and in small moiety a band around 1730 cm\(^{-1}\) representing the protonated carboxyl functional groups.\(^{37}\) The DFT calculated IR spectrum on porphyrins predict the presence of strong intense band features for the four carboxylic functional groups, while bands arising from vibrational modes of the porphyrin structure are relatively weak due to their D\(_{4h}\) symmetry. Furthermore, band feature changes for porphyrins upon reduction have been reported to be small in case of a metal-centered reduction but large and discrete in case of ligand-based reduction.\(^{38}\) Here, our observations of the spectral feature changes within the porphyrin region matches well a metal-centered reduction, in line with UV-Vis data which shows the Soret band shift caused by metal reduction. Most of the changes upon reduction occurred within 1.5 minutes, while the oxidation process shows a much slower reversion of the spectra. By applying a negative voltage, a broad region which are here assigned to blue-shifted \(\nu_{as}\) and red-shifted \(\nu_s\) modes of the four carboxylate ligands increase, while strong negative bands can be observed between 1600 cm\(^{-1}\) and 1500 cm\(^{-1}\). This latter region overlaps with the weak vibrational modes of the porphyrin structure, but also represents the decrease of the Zn\(^{2+}\) -coordinated carboxylate groups of the porous framework.\(^{39-41}\) Most likely, these changes arise from the restructuring of the Mn-MOF through the porphyrin carboxylate linkages. This is shown to be a reversible process as previously demonstrated with electrochemical testing and indicated by the fact that the difference
spectrum in Fig. 3d demonstrates an inverse spectrum for the reduction and oxidation process. We believe that the porphyrin units do not completely detach, rather they experience dissociation from the Zn atoms at a fraction of their carboxylate ligands. The IR spectrum shows an ensemble average of all of the carboxylate ligands detaching/reattaching. This change occurs in parallel to the (de)ligation of the Mn and these two processes are likely to be the root of the sluggish oxidation (Fig. 3d). We speculate that the Zn unit may be reduced after the Mn and this triggers the porphyrin carboxylate group detachment. The re-oxidation of the Mn would then have to take place after the re-oxidation of the Zn, thus leading to the slow reaction rate. To the best of our knowledge, this is the first example of electrochemically-triggered reversible restructuration of a MOF or porous organic-inorganic hybrid system.
**Figure 3:** Potential-dependent RR spectra and ATR-IR difference spectra of the Mn-MOF in N₂-purged electrolyte under applied potentials using a custom-designed setup (a). The Raman spectra exhibit a number of potential-dependent changes that are ascribed to the transition from a 5-coordinate Mn(III) to a 4-coordinate Mn(II) (b). Component fit analysis indicates that this occurs at potentials similar to those as extracted from UV-Vis absorbance (c). ATR-IR difference spectra shows increasing and decreasing band features in the spectral region of carboxylate functional groups (highlighted in grey), which suggest that the redox and ligation change at the Mn is coupled to reversible de-binding of the carboxylate ligands of the porphyrin (d). ATR-IR difference spectra for reduction process (at $E_{\text{app}} = -1.2\,\text{V vs Ag/AgNO}_3$; red) have been all referenced to ATR-IR spectrum prior the reduction step ($E_{\text{app}} = 0\,\text{V}$) and spectra for reverse oxidation process (at $E_{\text{app}} = 0\,\text{V}$; blue) are referenced to the last recorded reduction spectrum (at $E_{\text{app}} = -1.2\,\text{V}$; dark red. A simplified illustration is presented in (e).

We next moved to demonstrate the applicability of this MOF as an electrocatalyst for CO₂ fixation and to investigate its catalytic mechanism with in-situ ATR-IR spectroscopy. Structurally similar catalysts featuring a Mn-N₄ coordination were recently found and were predicted to be active for electrochemical CO₂ reduction.⁴²-⁴⁶ Mn bipyridine-based catalysts are also well-established systems for this reaction.⁴⁷-⁴⁹ We first compared through cyclic voltammetry (CV) under non-turnover conditions (N₂ purged system) the Mn-MOF to that of the uncoated mesoporous TiO₂ and to an equivalent MOF electrode coated onto mesoporous TiO₂ substrate featuring an un-metallized center (H₂-MOF). At negative potentials, the Mn-MOF exhibits a reductive current, the onset of which coincides with the Mn(III/II) redox potential. Noticeably absent is the reverse oxidation process (Fig.4a, dashed line). This falls in line with the previous observation that the oxidation of the MOF is too slow to be captured with a CV performed at 50 mV/s. This is further confirmed by the observation that the reductive current returns after allowing the system to oxidatively equilibrate for 30 minutes at open circuit (Fig. S8). Furthermore, the slow oxidation is not due to the porphyrin unit itself as it shows reversible redox behavior when either solubilized in the electrolyte or adsorbed onto an electrode (Fig. S9, 10). In terms of electrochemical performance in the context of CO₂ reduction, the advantages here of employing the MOF framework are 1) stability 2) a higher density of catalytic units can be achieved, and 3) the further modulation possible through tuning the three-dimensional pocket chemistry.⁵⁰

After purging with CO₂, the Mn-MOF exhibited significantly increased currents in the CV relative to the CV taken under N₂ purged conditions (Fig.4a, solid line). In contrast to the Mn-MOF, the bare TiO₂ substrate and H₂-MOF do not show such an increased current. The currents in the Mn-MOF now likely stem from electrons directed towards CO₂ reduction electrocatalysis. The products of the reaction when the potential was held at −1.5V were subsequently measured with gas chromatography (GC) and NMR. After
6 hours of electrolysis, with 0.25% vol. acetic acid added as a proton donor, 0.027 µMols of CH₄ and 0.173 µMols of CO were the only detectable reaction CO₂ reduction products. The turnover number for the CO production, based on the quantity of electroactive Mn centers was estimated to be 21. In comparison, under an N₂ environment under otherwise identical conditions, only ~0.1 nMols of CO could be detected.

Figure 4: The catalytic activity was probed for the Mn-MOF as well as the underlying TiO₂ substrate and an un-metallated H₂-MOF with CV scans in an N₂ atmosphere (dashed lines) and CO₂-purged system (solid lines) (a). Potential-dependent ATR-IR difference spectra of Mn-MOF in N₂-purged (red) and CO₂-purged (violet) electrolyte provided possible evidence for the COO⁻ binding under steady state conditions (b). ATR-IR difference spectra of N₂-purged spectrum in red (at \( E_{\text{app}} = -1.2 \text{V vs Ag/AgNO}_3 \)) represents changes of the Mn-MOF framework during its reduction process under N₂ and the ATR-IR difference spectra of CO₂-purged spectrum in violet (at \( E_{\text{app}} = -1.2 \text{V vs Ag/Ag}^+ \)) shows additional changes occurring when CO₂ is present. Additional bands are highlighted in violet numbers (b). Upon the addition of CO₂ to a N₂-purged solution, the final CO intermediate was observed (c).

ATR-IR spectroelectrochemistry was next applied to elucidate the catalytic cycle that generated CO from the Mn-MOF. IR spectroscopy was preferentially used due to its high sensitivity to CO₂ intermediates based on the IR selection rule. Spectra acquired under CO₂ reduction conditions at −1.2V revealed new bands within the 1300-1700 cm⁻¹ region at 1598 cm⁻¹, 1489 cm⁻¹ and 1334 cm⁻¹ (Fig. 4b). These bands appeared only in a CO₂ environment and, from their positions, and the combination of the former and latter could correspond to the first COO⁻ intermediate of the catalytic cycle. Similar band positions have been ascribed to asymmetric and symmetric vibrational modes of a deprotonated carboxylic functional group in molecules such as metal-bound formic acids, carbonate ions and surface-bound carboxylate groups. CO, also a common intermediate observed on heterogeneous catalysts, was not detected under steady-state conditions, likely because it rapidly desorbs as soon as it is generated. However, we were able to detect a band at 1970 cm⁻¹, tentatively assigned to CO under certain conditions. When the
MOF is reduced first under N\textsubscript{2}, then the system was switched to open circuit and CO\textsubscript{2} was subsequently purged through the system, the CO band appeared (Fig. 4c). In these conditions, the MOF contained Mn(II) but likely not enough driving force and/or reducing equivalents to rapidly complete the catalytic cycle, trapping the CO at open circuit conditions. We were also able to see this bound CO when the MOF was re-oxidized after acquiring steady-state spectra under CO\textsubscript{2}. This suggests that CO, the final intermediate is weakly bound and readily desorbs once it is formed, hampering its detection under steady state conditions. The unique slow oxidation process of this system enables the probing of transient intermediates such as CO. Free CO was not detected, likely because of its low solubility and production rate. To the best of our knowledge, this work represents the first time that the CO\textsubscript{2} reduction intermediates in an electrochemical MOF system were observed. This is especially important as this can now be translated into more complex MOF-based systems such as those that generate more complex intermediates and function through more complex catalytic pocket chemistry.

Density functional theory (DFT\textsuperscript{54-55}) calculations with the B3LYP functional\textsuperscript{56-57} implemented in the Gaussian16 software\textsuperscript{58} were subsequently utilized to grant a further level of insight into the spectroelectrochemical data. The model employed in our electronic structure calculations was PCM(MeCN)-[B3LYP/6-31+G(d,p)/LANL2DZ]\textsuperscript{59-62}. This method was used in a previous study\textsuperscript{63} without the PCM solvation model to evaluate the binding properties of different metalloporphyrins with several ligands. The comparison between the theoretical results and the experimental data was very good, suggesting that the electronic structure model is appropriate. Moreover, the comparison between the calculated and experimental IR and Raman spectra obtained in the present work is very good, thus confirming the reliability of the method (Fig. S11, S12).

The theoretical results associated with the mechanism of the catalytic process are resumed in Fig. 5. The approximations that were made in order to obtain those results are the following:

1. The Mn-MOF is modeled by the [Mn-porphyrin] complex where the catalytic reduction takes place. Hence, the electronic structure investigation of the possible intermediates describing the electrochemical reduction was made on a [Mn\textsuperscript{III}-porphyrin]\textsuperscript{+} starting complex.

2. The chemical potential of the electron (\(\mu_e\)) was determined by combining DFT with spectroelectrochemical data. More precisely, we based our model on the experimental observation indicating that, at \(E_{\text{app}} = -0.8\text{V vs Ag}^+/\text{Ag}_\text{ele} \), the Mn\textsuperscript{III} and Mn\textsuperscript{II} species are in equilibrium with each other. It was then straightforward to combine this information with DFT calculations to obtain \(\mu_e\).
at any value of $E_{\text{app}}$ (see details in section 3 of SI), thus allowing us to compute the free energies for all intermediates shown in group A of Fig. 5.

3. The energy of the transition state at $E_{\text{app}} = -1.5$ V vs Ag$^+/Ag_{(s)}$ was calculated combining the transition state theory with the experimentally determined rate constant at which CO was produced form CO$_2$.

4. The energy difference between the transition state and the highest intermediate at $E_{\text{app}} = -1.5$V (see Fig. 5) is denoted by $\delta$ and remains unknown. Using this notation, the free energies of the remaining intermediates in group C of Fig. 5 were calculated via DFT as a function of $\delta$.

5. The lower limits for the free energies of the transition states at $E_{\text{app}} = -0.8$V and 0 V (group B$_2$ Fig.5) were deduced from DFT in conjunction with Marcus theory for electron and proton transfer reactions (see SI for more details).

**Figure 5.** Computed Gibbs energy profile ($\Delta_G$ and $\Delta_G'$ in kcal/mol at 298.15 K) for the electrochemical reduction of CO$_2$ to CO catalyzed by a Mn-porphyrin complex (LMn), at three different potentials vs Ag$^+/Ag_{(s)}$: 0V (black), $-0.8$V (orange) and $-1.5$V (green). All calculations were performed at the PCM(MeCN)-[B3LYP/6-31+G(d,p)/LANL2DZ] level of theory. The transition state energies are shown inside the blue brackets and the transition state structures are unknown. The free energies were computed using DFT calculations, experimentally-determined kinetic data and several assumptions as detailed in the text and SI.
It is shown in the SI that $\delta$ and $\mu_{H^+}$ are related. Since $\delta > 0$ one can deduce a lower limit for $\mu_{H^+}$ and an upper limit for the local pH close to the catalytic core (see SI). While there is trace water in the electrolyte which may act as the proton source (or acetic acid added for bulk electrolysis), various functionalities within the framework could act as a proton shuttle and Brønsted acid during catalysis (see SI). Possibilities are that the Zn and bipyridine species play a role in this regard. Nevertheless, the theoretical modelling points to an oxygen-bound $\text{CO}_2$ as the first intermediate in the catalytic process and its reduction/protonation to a $\text{CO}_2H$ as the rate-limiting step. This is in line with our IR experiments which show a buildup of adsorbed $\text{CO}_2$. Furthermore, as the CO formation and release is exergonic, it is reasonable that this species does not appear under steady-state conditions.

Concluding Remarks:

Taking full advantage of the unique aspects of MOFs and porous materials in electrochemical applications requires in-situ investigations of their behavior at the molecular level. Here, we present a multifaceted investigation, employing electrochemistry coupled with UV-Vis, Raman and infrared spectroscopies, of a Mn-MOF system that reveals a unique redox cycle and catalytic behavior. Rapid electrochemical reduction and slow oxidation of the Mn porphyrin is coupled to a reversible restructuring of the framework through the carboxylate linkages connecting the porphyrin. Such physical changes are evidenced for the first time under these conditions and point to the potential of MOFs to function as structurally dynamic catalytic systems. Furthermore, we developed the methodology to detect $\text{CO}_2$ reduction intermediates in the MOF catalytic cycle for the first time and used the resultant insights in conjunction with DFT modeling to build up a proposed mechanism that generates CO as the principal product. This study paves the way to understanding the complex reactivity within MOFs and porous structures to enable rational design of next generation functional devices.

Experimental

MOF Growth

FTO substrates were first cleaned with water and acetone, then dried in ambient conditions. Next, a slurry of 20% wt. TiO$_2$ nanoparticles (Sigma Aldrich) in ethanol + 5M Acetic acid was drop-cast onto the FTO glass and annealed at 400 °C for 30 min (ramp rate of 5 °C min$^{-1}$). The FTO/TiO$_2$ was next soaked overnight in an ethanolic solution of 2-aminoethylphosphonic acid at room temperature, then rinsed with ethanol and dried under ambient conditions. Finally, the MOF was grown overtop by dipping into heated (40° C) ethanolic solutions of 0.1 mM zinc nitrate, the Mn porphyrin, and 4,4’-bypiridine for 15 minutes each. Between each step, the films were thoroughly rinsed with ethanol. Typically, three complete cycles were
utilized. Following the synthesis, the substrates were dried under ambient conditions and no further modifications were made prior to use.

**Electrochemistry**

Electrochemistry experiments were performed in a two-compartment glass electrochemical cell, with the counter electrode separated by a medium-porosity glass frit. Typically, a graphite rod was used as the counter electrode and an Ag/Ag⁺ reference electrode that featured the Ag/AgNO₃ redox couple saturated in CH₂CN was employed. The electrode potential was determined to be -0.1V vs. Fc/Fc⁺ (Fig. S14). Electrochemistry experiments were performed after bubbling the 0.1M Tetrabutylammonium hexafluorophosphate in CH₃N electrolyte solution for at least 15 minutes with either N₂ or CO₂, then flowing the gas over the reactor headspace. For product analysis, the openings of the reactor were sealed with septa that were pierced only to inject the headspace gas into the GC. In the case of electrochemical measurements in aqueous conditions, an Ag/AgCl in saturated KCl solution was used as the reference electrode.

**UV-Vis**

*In-situ* UV-Vis absorption experiments were conducted with a two-compartment, sealed glass-cell in transmission mode. All electrochemical parameters, including solvent and electrodes were identical as listed above. Spectra were acquired under steady state conditions after the working electrode was held for at least 5 minutes at each potential. Kinetic experiments were performed by monitoring the intensity at a particular wavelength over time as a particular voltage was applied in a stepped chronoamperometric mode to the Mn-MOF working electrode. For UV-Vis experiments, an Agilent Cary 400 UV-Vis spectrometer was employed.

**Raman Spectroscopy and Component Fit Analysis.**

Raman spectra were acquired with a Horiba Labram Evolution spectrometer. The excitation wavelength was selected to be 473 nm (laser power ~0.5mW), in line with the Soret band of the porphyrin unit of the Mn-MOF. Spectroelectrochemical measurements were conducted at steady-state conditions and the Mn-MOF was allowed to equilibrate at each potential for at least 5 minutes prior to spectral acquisition. Electrochemical parameters were the same as described above. The stability of the Mn-MOF and reversibility of the spectra was confirmed by acquiring and comparing spectra of the Mn-MOF before and after testing.

Component fit analysis was performed to reveal insights into the distribution of redox and conformational species in the potential window from −0.3 V to −1.2 V. Briefly, the spectra at the opposing potentials, *i.e.*
0.3 V and −1.2 V were fitted first using Lorentzian bands. The resulting set of bands for the two potentials were grouped to two component fit spectra. These two component spectra were iteratively refined by fitting the RR spectra recorded at intermediate potentials. To simplify the process, the RR spectra were divided in three frequency regions, \textit{i.e.} low (200-550 cm\(^{-1}\)), mid (550-1150 cm\(^{-1}\)) and high (1150-1650 cm\(^{-1}\)) frequency region respectively. Satisfying fitting of the experimental spectra was achieved using two component spectra (excluding contributions from the TiO\(_2\) and MeCN background) (Fig. S6). This indicates the presence of two Mn porphyrin species in the investigated potential window. Plotting the relative intensities of the two species with respect to each other against the applied potentials yielded sigmoidal curves indicating a redox transition with an apparent redox potential at around −0.8 V (Fig. S7) in line with the UV-vis data. Considering the marker band frequencies, it is reasonable to assume that potential dependent RR spectra under non-turnover conditions shows the redox transition from Mn(III) to Mn(II) which potentially involves a loss of axial ligand. No significant indication for contribution of other Mn species (\textit{e.g.} Mn(I)) was found in the RR at 473 nm excitation. This however does not exclude the presence of Mn(I) as the electronic absorption of this species may be strongly shifted affording no RR enhancement at the employed laser excitation as well as may require a lower potential to be stabilized.

**Spectro-electrochemical Attenuated Total Reflectance Infrared Studies.** Spectro-electrochemical ATR-IR measurements were carried out on the Mn-MOF prepared on a Si ATR prism. A TiO\(_2\) suspension consisting of 20 wt % of TiO\(_2\) nanopowder in 5 M acetic acid in ethanol was prepared and sonicated well. This was spin-coated onto the flat surface of the Si ATR-prism over the complete area of 3 cm\(^2\), using a volume of 20 \(\mu\)L and a spin speed of 1000 rpm for 1 minute. The solution was left to dry completely in air before annealing at 400 °C for 30 min (ramp rate of 5 °C min\(^{-1}\)) under atmospheric conditions. The MOF was assembled onto the TiO\(_2\) as described above. After the MOF assembly procedure was completed, residual solution and weakly bound ligands were removed from the ATR cell and the TiO\(_2\)MOF electrode rinsed several times with acetonitrile.

Spectro-electrochemical ATR-IR measurements were performed in a single-reflection PIKE ATR-IR setup and a customized ATR -IR spectro-electrochemical cell using an angle of incidence of 60°. The electrochemical studies were carried out in a three-electrode system with the Mn-MOF film as working electrode, a Ag/AgCl electrode (in acetonitrile – same solution as the electrolyte) as reference electrode, and a Pt mesh as counter electrode. Potentials were applied using a Biologic VMP300 or an Ivium CompactStat potentiostat. The ATR-IR spectra were recorded in a spectral range from 4000 to 900 cm\(^{-1}\) (note that the range below 900 cm\(^{-1}\) is inaccessible due to strong absorption by the Si ATR prism) with a spectral resolution of 4 cm\(^{-1}\) on a Bruker Vertex 70 spectrometer equipped with a photovoltaic MCT detector. A total of 200 scans were co-added for one spectrum, requiring an accumulation time of 1.5 min.
All measurements were carried out at room temperature, and were carried out under either N\textsubscript{2} or CO\textsubscript{2} atmosphere.

ATR-IR spectra were evaluated using the OPUS 5.5 software. Absorbance and difference spectra (A) were generated according to the Lambert–Beer equation:

\[
A = -\log \frac{I_{\text{sample}}}{I_{\text{reference}}}
\]

\(I_{\text{sample}}\) denotes the sample spectrum and \(I_{\text{reference}}\) denotes the respective reference spectrum for either absorbance or difference spectra. Baseline corrections of the absorbance spectra and second derivative spectra were generated by means of the OPUS 5.5 software data analysis tools.

**Computational details**

The calculations were performed using DFT\textsuperscript{54-55} with the B3LYP functional\textsuperscript{56-57} implemented in the Gaussian16 software\textsuperscript{58}. The geometry optimization were performed using the 6-31+G(d,p) basis set for the C H N O atoms and LANL2DZ as a pseudopotential and basis set for the Mn. We used the default temperature and pressure given by the software, which are 298.15 K and 1 atm. The minima were confirmed by doing frequency calculations on each optimized structure using the same method. We also optimized each complex with every possible spin state allowed by the d valence electrons of the Mn. The most stable spin state was then used for our theoretical investigation of the catalytic process. A stability test of the wave function was also performed on each of them. To simulate the acetonitrile solvent environment, we used the integral equation formalism polarized continuum model (IEFPCM).\textsuperscript{61-62} Only the electrostatic stabilization part of the solvation model (\(G_{\text{es,MeCN}}\)) was used in our study in order to approximate the solvation energy. Since the gas phase standard state is different from the liquid phase standard state (1 mol of gas at 1 atm vs 1 mol/L), a correction of 1.89 kcal/mol (\(\text{corr}_{\text{gas/liq}}\)) was added to the total Gibbs free energy (\(G_{\text{tot}}\) eq. 1.\textsuperscript{64}

\[
G_{\text{tot}} = G_{\text{gas}} + G_{\text{es,MeCN}} + \text{corr}_{\text{gas/liq}}
\]
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Supporting Information

Electrochemically Triggered Dynamics Within a Hybrid Metal-Organic Electro catalyst

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Theoretical Study

1. Computational details

The calculations were performed using DFT\textsuperscript{1-2} with the B3LYP\textsuperscript{3-4} functional implemented in the Gaussian16\textsuperscript{5} software. The geometry optimization were performed using the 6-31+G(d,p) basis set\textsuperscript{6} for the C H N O atoms and LANL2DZ\textsuperscript{7} as a pseudopotential and basis set for the Mn. We used the default temperature and pressure given by the software, which are 298.15 K and 1 atm. The minima were confirmed by doing frequency calculations on each optimized structure using the same method. We also optimized each complex with every possible spin state allowed by the $d$ valence electrons of the Mn. The most stable spin state was then used for our theoretical investigation of the catalytic process. A stability test of the wave function was also performed on each of them. To simulate the acetonitrile solvent environment, we used the integral equation formalism polarized continuum model (IEFPCM).\textsuperscript{8-9} Only the electrostatic stabilization part of the solvation model ($G_{\text{es,MeCN}}$) was used in our study in order to approximate the solvation energy. Since the gas phase standard state is different from the liquid phase standard state (1 mol of gas at 1 atm vs 1 mol/L), a correction of 1.89 kcal/mol ($corr_{\text{gas/liquid}}$) was added to the total Gibbs free energy ($G_{\text{tot}}$) Eq. (1).\textsuperscript{10}

\begin{equation}
G_{\text{tot}} = G_{\text{gas}} + G_{\text{es,MeCN}} + corr_{\text{gas/liquid}}
\end{equation}

2. Model used for the theoretical study and proposed catalytic cycle

The computational method employed in our electronic structure calculations was PCM(MeCN)-[B3LYP/6-31+G(d,p)/LANL2DZ]. This method was successfully used in a previous study\textsuperscript{11} without the PCM solvation model to evaluate the binding properties of different metalloporphyrin with some ligands. Moreover, as shown in Fig. S11-S12, the predicted Raman and IR spectra of the Mn(II)-TBAP complex found in the MOF are in good agreement with the experimental ones, which suggests that the theoretical model is appropriate for our study. The theoretical results for the catalytic process are resumed in Fig. S1.
Figure S1. Computed Gibbs energy profile ($\Delta G$ and $\Delta G'$ in kcal/mol at 298.15 K) for the electrochemical reduction of CO$_2$ to CO catalyzed by a Mn-porphyrin complex (LMn), at three different potentials vs Ag$^+/Ag$: 0V (black), -0.8V (orange) and -1.5V (green). All calculations were performed at the PCM(MeCN)-[B3LYP/6-31+G(d,p)/LANL2DZ] level of theory. The transition state energies are shown inside the blue brackets and the transition state structures are unknown. The free energies were computed using DFT calculations, experimentally-determined kinetic data and several assumptions (*vide infra*).

The approximations that were made in order to study the catalytic process are represented in scheme 1 and are going to be explain in detail in section 3. The challenge of this theoretical study was to model the complex behavior of the Mn-MOF using reasonably accurate electronic structure calculations while retaining the chemistry of the catalytic core. The electronic structure investigation on the possible intermediates describing the process was made on a [Mn$^{III}$-porphyrin]$^+$ starting complex. Our model assumes that the carboxylate groups of the benzoic acid (BZA) moieties are too far from the metal center to have a significant impact on the outcome of the electronic structure calculations. The catalytic cycle proposed in this work is represented in scheme 2.
We didn’t try to model the transition state structures associated with steps A to E since we have no information about the way in which the proton and electron can be transferred through the framework.

3. Finding of $\mu_e$ and $\mu_H^+$ and construction of the potential energy diagram

In order to calculate the free energies of the steps A, C and D, one needs to model the electrochemical potential of the electron ($\mu_e$) and the chemical potential of the proton ($\mu_H^+$).
The strategy to obtain $\mu_e$ is depicted in scheme 3. It was based on the experimental observation indicating that, at $E_{app} = -0.8V$ vs Ag$^+/Ag(s)$, the Mn$^{III}$ and Mn$^{II}$ species were in equilibrium at equal concentration. It was then straightforward to combine this information with DFT calculations to obtain $\mu_e$ at $E_{app} = -0.8V$.

![Scheme 3. Strategy to find $\mu_e$](image)

Eq. (2) was then used in order to find $\mu_e$ for other values of $E_{app}$ vs Ag$^+/Ag(s)$.

$$ (2) \quad \mu_{e,E_{app}} = \mu_{e,0V} - E_{app} \cdot F $$

The catalytic cycle of scheme 2 suggests that the MOF would somehow act as a proton source. In order to be able to find some insight about this hypothesis, we first had to determine what would be the value of $\mu_H^+$ that would allow the reaction to take place. Since we don’t have any proposed transition states, it was only possible to calculate a lower limit for the chemical potential of the proton. To do so, we used the following information concerning the experimental starting conditions: $V_{CO_2} = 15$ ml, $P_{CO_2} = 1$ atm, $T = 298.15K$, $E_{app} = -1.5V$ vs Ag$^+/Ag(s)$. Based on this information and on the experimentally-measured CO$_2$ to CO conversion timescale, we then used transition state theory$^{12}$ to calculate the activation energy barrier associated with the catalytic cycle.

The CO$_2$ to CO conversion detected by gas chromatography after 6 hours indicates that this energy barrier is approximately 28.2 kcal/mol. Scheme 4 shows the logical steps of the approach used to derive the following lower bound for $\mu_H^+$:

$$ (3) \quad \mu_{H^+} > \mu_{L_{Mn}^{III}COOH}^\mu - \mu_{L_{Mn}^{II}CO_2(g)}^\mu - \mu_{e,-1.5V} - \Delta G^\mu $$
where the chemical potentials are defined in scheme 4, and $\Delta G^\circ = 28.2$ kcal/mol represents the activation free energy of the catalytic cycle shown in Fig. S1 at $E_{app} = -1.5V$ vs Ag$^+/Ag$ (s), and which was estimated from experimental kinetic measurements. In order to obtain the final equations shown in scheme 4, we assumed that the experimental ratio of the activities of complexes 1 and 3 is close to one and that the partial pressure of CO$_2$ is 1 atm. If the chemical potential of the activated state is denoted by $\mu = \mu_{Lmn}^{ii} + \mu_{CO_2(g)} + \mu_{H^+} + \mu_{e,-1.5V} + \Delta G^\circ$ then one can verify that the quantity $\delta > 0$ defined in scheme 4 is identical to the quantity $\delta$ shown in Fig. S1 and in the main article:

\[
\delta = \mu_{H^+} - (\mu_{Lmn}^{iii} - \mu_{Lmn}^i - \mu_{CO_2(g)} - \mu_{e,-1.5V} - \Delta G^\circ) \\
= (\mu_{Lmn}^{ii} + \mu_{CO_2(g)} + \mu_{H^+} + \mu_{e,-1.5V} + \Delta G^\circ) - (\mu_{Lmn}^{iii} - \mu_{Lmn}^{ii} - COOH) \\
= \mu^* - \mu_{Lmn}^{iii} - COOH
\]

Moreover, the inequality shown in Eq. (3) allows one to derive an upper limit to the value of the $pH$ that the environment has to provide in order to enable the catalytic cycle to proceed. This calculation was undertaken in two steps: first, as detailed in scheme 5, the standard chemical potential of the proton ($\mu_{H^+}^o$) in MeCN was estimated using DFT calculations combined with the experimental pKa of the acetic acid in MeCN.$^{13}$

Scheme 4. Strategy to find the lower limit of $\mu_{H^+}$. 
Next, using the inequality shown in Eq. (3) and the newly found value of $\mu^o_{H^+}$, the following inequalities were found:

$$\mu_{H^+} = \mu^o + RT \ln a_{H^+} \Rightarrow$$

$$pH = -\log a_{H^+} = \frac{\mu^o - \mu_{H^+}}{2.303RT} \Rightarrow$$

$$pH < \frac{\mu^o + \Delta G^o + \mu_{Lmn^{II}} + \mu_{CO_{2g}} + \mu_{e,-1.5V} - \mu_{Lmn^{III}COOH}}{2.303RT}$$

$$pH < 9.4$$
The value $pH = 9.4$ represents the upper pH limit that the Mn-MOF environment needs to provide in order to proceed with the catalytic cycle shown in scheme 2 and Fig. S1. The inequalities associated with the transition states of group B2 in Fig. S1 were determined using Marcus theory\textsuperscript{12} which relates the $\Delta G^\ddagger$ with the $\Delta_G$ of Eq. (6), where $\lambda_0$ represents $\Delta G^\ddagger$ when $\Delta_G = 0$:

\begin{equation}
\Delta G^\ddagger = \frac{(\lambda_0 + \Delta_G)^2}{4\lambda_0}
\end{equation}

Marcus theory was demonstrated to provide an appropriate model for several electron\textsuperscript{14} and proton\textsuperscript{15} transfer reactions and was used in the present investigation to obtain lower limits for the free energies of the transition states represented in the group B2 in Fig. S1. The strategy for obtaining these inequalities is shown below in scheme 5. Using the approach indicated in scheme 5 allows one to conclude that the activation free energies for the catalytic cycle depicted in Fig. S1 are higher than 36.3 and 63.5 kcal/mol, at $E_{app} = -0.8\text{V}$ and 0.0 V vs Ag$^+/Ag(s)$, respectively. According to transition state theory, these values are too high to be able to expect any product formation in the experimental conditions, which agrees with experimental observations. Indeed, at $E_{app} = -0.8\text{ V}$, only the reduction of Mn$^{III}$ to Mn$^{II}$ took place and no CO was detected.

Scheme 5. Inequalities for the transition state energies of group B2
4. The proton source

A pH value of 9.4 in MeCN indicates the presence of a relatively strong Brønsted acid which should act as a source of protons. Several Brønsted acids and Brønsted bases were employed to build the MOF framework, all of which could potentially serve as a proton source for the catalytic cycle depicted in scheme 2. Among these species, the benzoic acid (BZA) is a particularly appealing candidate given its proximity in space to the Mn catalytic core. In order to test if the BZA moiety can potentially serve as a proton source to the catalytic cycle depicted in scheme 2, we performed DFT calculations on a [Zn-BZA]$^{2+}$ complex which served as a model proton source. Indeed, it is known from the literature that the Zn$^{2+}$/carboxylate interaction is very stable as it is found in a variety of metalloenzymes$^{16}$. This interaction is also used to stabilized polyvinyl chloride$^{17}$. The [Zn-BZA]$^{2+}$ modeling strategy is detailed in scheme 6.

Scheme 6. [Zn-BZA]$^{2+}$ modeled as a proton source
The validity of this computational strategy was first tested on phenol, a molecule whose experimental pKa value in MeCN can be found in the literature\textsuperscript{13}. The pKa of the phenol obtained by DFT was of 30.2 while the experimental value is 29.1, indicating that the DFT can predict pKa values in MeCN with an uncertainty of ± 1 pKa unit. Next, the pKa of the \([\text{Zn-BZA}]^{2+}\) complex was calculated by DFT. A value of -0.1 was found, indicating that most of the \([\text{Zn-BZA}]^{2+}\) complexes would be deprotonated. If one assumes that the BZA moieties are indeed the source of protons during the catalytic cycle as suggested by the present DFT calculations, one can deduce a lower \(pH\) limit of the environment in the experimental conditions. As mentioned in the main paper, the turnover number was deduced by cyclic voltammetry analysis. Combining this information with the number of CO molecules produced, it was then possible to estimate the total number of BZA moieties found in the MOF. This would correspond to a concentration of 2.1 µM. Since we determined that the \([\text{Zn-BZA}]^{2+}\) complex was highly acidic, the concentration of the proton in solution would also be of 2.1 µM but considering all deprotonation would induce a dramatic change in the MOF structure. So, in order to preserve the MOF structure and effectiveness we considered only half deprotonation of all the BZA moieties. This assumption leads to a \(pH = 6.0\), a value that is consistent with the upper \(pH\) limit found in the previous section.

Moreover, Costentin et al.\textsuperscript{18} found that the catalytic conversion of CO\(_2\) to CO on a Fe(II) core of tetraphenylporphyrin was significantly enhanced by adding two hydroxyl substituents on the phenyl group of the tetraphenylporphyrin moiety, an effect which was attributed to a local increase in acidity. If such non-equilibrium, but long-lived environments in which the local \(pH\) is significantly smaller than the bulk \(pH\) are also relevant in the present experiment, one should expect that the catalytic cycle is taking place at \(pH\) values that may be significantly lower than 6.0.

5. Conclusion and future work

By combining DFT calculations and experimental observations we were able to propose a catalytic cycle for the CO\(_2\) reduction process. Experimentally and computationally derived information concerning the kinetics of the reaction allowed us to estimate that \(pH < 9.4\) in the neighborhood of the catalytic core.
Moreover, considering the Zn$^{2+}$/BZA interaction in the MOF frameworks acting as a proton source, we estimated that the internal $pH$ supplied by the MOF is approximately $pH = 6.0$ and possibly even lower if the local concentration of protons is significantly larger than the bulk concentration during the catalytic cycle. Recent works have been done on energy cells involving proton transfer through a metal-organic framework\textsuperscript{19} i.e.: proton exchange membrane fuel cells (PEMFC). The proton dependence of the MOF catalytic system investigated in the present work maybe use to make further progress in this field.

Figure S2: SEM image (a) and UV-Vis absorbance (b) of the Mn-MOF grown on ITO. The MOF was grown under identical conditions as that on the mesoporous ITO but because of the different surface morphology and chemistry the MOF grew as larger crystals rather than thin conformal layers.
Figure S3: UV-Vis spectroelectrochemistry in N\textsubscript{2}-purged acetonitrile electrolyte of the Mn-MOF grown on mesoporous TiO\textsubscript{2} and planar FTO substrates. The reduction is shown in a linear (a) and square-root (b) time scale and the oxidation is shown in (c).

Figure S4: Complete spectroelectrochemical kinetic trace of the Mn-MOF under a stepped chronoamperometric scan that features the reduction and oxidation of the Mn on mesoporous TiO\textsubscript{2} (a) and planar FTO (b).
Figure S5: Raman spectra of the Mn-MOF before and after spectroelectrochemical analysis. Over the course of 1 hr of stepped chronoamperometric testing in a N$_2$ purged acetonitrile electrolyte, the spectrum indicates that significant changes within the porphyrin unit of the Mn-MOF did not occur.
Figure S6: Component spectra of the Mn(II) and Mn(III) redox species in low, medium, and high frequency regimes (a-c). Proper fitting of the RR experimental spectrum was achieved throughout the complete potential window (-0.3 V to -1.2 V) using the two component spectra (excluding background contributions from TiO2 and MeCN). Experimental spectra recorded at the intermediate potential -0.8 V and their fits for the three frequency windows are shown (d-f).
Figure S7: Relative intensities for Mn(III) (black squares) and Mn(II) (hollow squares) derived from component fit analysis in figure S6 in a potential window from -0.3 V to -1.2 V for the three frequency regions 200-550 cm\(^{-1}\) (a), 550-1150 cm\(^{-1}\) (b), and 1150-1650 cm\(^{-1}\) (c).

Figure S8: CVs in N\(_2\) saturated acetonitrile electrolyte of the Mn-MOF grown with 3 cycles on ITO (a) and consecutive CVs as compared with a CV after allowing 30 minutes to equilibrate at open circuit (b). The current mostly returns after 30 minutes of equilibration indicating kinetically limited oxidation of the Mn-MOF.
**Figure S9:** CV of the Mn-TBAP species in aqueous electrolyte (0.1 M pH7 phosphate buffer) (a). The peak height scales with the square root of the scan rate (b), indicating diffusion-limited kinetics and an absence of the slow oxidation as observed in the Mn-MOF. The peak separation increases slightly (c). An aqueous electrolyte and Ag/AgCl reference electrode was used because the Mn-TBAP is more soluble in these conditions.

**Figure S10:** CVs of the Mn-TBAP in solution and adsorbed (through soaking for 3 hours in a Mn-TBAP 10 mM ethanolic solution) onto a mesoporous ITO surface in aqueous phosphate buffer. The redox peaks occur in a similar potential range and the redox of the Mn is reversible.
Figure S11: Comparison of the ATR-IR spectra of Mn(III)-TBAP and Bipyridine powder samples vs the calculated DFT IR spectra of Mn(II)-TBAP with protonated carboxylic functional groups. Band accordance between experimental and calculated spectrum agrees with a systematic offset of 50 cm$^{-1}$. 
**Figure S12:** Comparison of the RR spectrum of Mn-MOF at -1.2V under N₂ in acetonitrile electrolyte vs the calculated DFT Raman spectrum of Mn(II)-TBAP with protonated carboxylic functional groups for different multiplicities of the species. A 50 cm⁻¹ offset is evident between theory and experiment.
Figure S13: Comparison of ATR-IR spectra of Mn(III)-TBAP powder samples vs ATR-IR difference spectra for reduction process (at $E_{\text{app}} = -1.2V$ vs Ag/Ag$^+$; red) have been all referenced to ATR-IR spectrum prior the reduction step ($E_{\text{app}} = 0V$) and spectra for reverse oxidation process (at $E_{\text{app}} = 0V$; blue) are referenced to last recorded reduction spectrum (at $E_{\text{app}} = -1.2V$; dark red).

Figure S14: A CV of 1mM ferrocene in an acetonitrile solvent and 0.1 M tetrabutylammonium hexafluorophosphate supporting electrolyte shows the Ag/AgNO$_3$ reference electrode potential to be at -0.1V relative to the Fc/Fc$^+$ redox couple. Carbon rod electrodes were employed as both the working and counter electrode in this experiment.
Cartesian coordinates and energies (au).

\[ \text{[Mn}^{II}\text{-porphyrin]}^{+} \]

Gibbs Energy PCM(MeCN)-[B3LYP/6-31+G(d,p)/ LANL2DZ] = -1092.053047

\[
\begin{array}{ccc}
1 & 5 \\
C & -2.88215200 & 1.01834800 & -0.00002100 \\
C & -3.64509500 & 2.23585200 & -0.00001600 \\
C & -2.75228700 & 3.27035600 & 0.00000600 \\
C & -1.43641800 & 2.69433300 & 0.00001500 \\
N & -1.53022200 & 1.31266500 & -0.00000200 \\
H & -4.72577800 & 2.28103500 & -0.00002800 \\
H & -2.95353600 & 4.33321200 & 0.00001600 \\
C & 2.69433300 & 1.43641800 & 0.00000500 \\
C & 2.23585200 & 3.64509500 & 0.00000060 \\
C & 1.01834800 & 2.88215200 & 0.00004700 \\
N & 1.31266400 & 1.53022200 & 0.00000370 \\
H & 2.28103500 & 4.72577800 & 0.00000800 \\
C & 1.43641800 & -2.69433300 & -0.00001600 \\
C & 2.75228700 & -3.27035500 & -0.00000800 \\
C & 3.64509500 & -2.23585200 & 0.00001500 \\
C & 2.88215100 & -1.01834800 & 0.00002100 \\
N & 1.53022200 & -1.31266400 & 0.000000100 \\
H & 2.95353500 & -4.33321200 & -0.00001800 \\
H & 4.72577800 & -2.28103500 & 0.000002700 \\
C & 1.01834800 & -2.88215100 & -0.000004700 \\
C & -2.23585200 & -3.64509500 & -0.000006800 \\
C & -3.27035600 & -2.75228700 & -0.000006900 \\
C & -2.69433300 & -1.43641800 & -0.000004900 \\
N & -1.31266500 & -1.53022100 & -0.000003600 \\
H & -2.28103500 & -4.72577800 & -0.000007900 \\
H & -4.33321200 & -2.95353500 & -0.000008100 \\
C & 3.42803400 & 0.25772200 & 0.000004400 \\
\end{array}
\]
C  -3.42803400  -0.25772200  -0.00004300
C   0.25772200  -3.42803400  -0.00003800
C  -0.25772200  3.42803400   0.00003700
H  -0.34049400  4.50919200   0.00004800
H   4.50919200  -0.34049400  -0.00005500
H  -4.50919200  -0.34049400  -0.00005500
H   0.34049400  -4.50919200  -0.00004900
Mn   0.00000000   0.00000000   0.00000000
C   3.27035500   2.75228700   0.00007100
H   4.33321200   2.95353600   0.00008400

[Mn^{II}-porphyrin]

Gibbs Energy PCM(MeCN)-[B3LYP/6-31+G(d,p)/ LANL2DZ] = -1092.219471

C  -2.89628400   1.13195500   0.00001800
C  -4.28743700   0.71547300   0.00001200
C  -4.29702500  -0.65500100  -0.00000800
C  -2.91185600  -1.09093000  -0.00001300
N  -2.10202300   0.01492700   0.00000200
H  -5.13995200   1.38322200   0.00002100
H  -5.15878500  -1.31077600  -0.00001700
C   1.09092900  -2.91185500  -0.00003900
C  -0.71547400  -4.28743600  -0.00006200
C  -1.13195600  -2.89628300  -0.00003800
N  -0.01492800  -2.10202200  -0.00002400
H  -1.38322300  -5.13995100  -0.00007700
C   2.91185500   1.09092900   0.00001600
C   4.29702400   0.65500100   0.00001000
C   4.28743500  -0.71547400  -0.00009000
C   2.89628300  -1.13195600  -0.00001500
N   2.10202200  -0.01492700   0.00000100
[(CO$_2$)-Mn$^{II}$-porphyrin]

Gibbs Energy PCM(MeCN)-[B3LYP/6-31+G(d,p)/ LANL2DZ] = -1280.811156
C  -2.72276600  -1.12375500  -0.94881400
C  -4.09957400   0.66977500  -1.15541800
C  -2.72903200   1.09904200  -0.94077000
N  -1.93312600   -0.01056400  -0.82102400
H  -4.94840200   1.32964900  -1.28476500
C  1.24970600  -2.90846000  -0.34321400
C  0.83274500  -4.29762300  -0.41565800
C  -0.52163000  -4.30056800  -0.62529100
C  -0.94693100  -2.91323200  -0.68295000
N  0.14899600  -2.10879200  -0.50879900
H  1.48928900  -5.15338000  -0.31915800
H  -1.17295600  -5.15918300  -0.73129200
C  3.01511900  -1.11115400  -0.06213100
C  4.38612800  -0.68188400   0.14947800
C  4.38226300   0.68854800   0.15449000
C  3.00887000   1.11162000  -0.05408700
N  2.21877900  -0.00156200  -0.17925200
H  5.23533200  -1.34175400   0.27634700
H  5.22772400   1.35227200   0.28617500
C  -2.26340700  -2.45398000  -0.88434500
C  2.54984600   2.44186400  -0.12019800
C  2.56352900  -2.44341600  -0.13794500
C  -2.27710900   2.43130100  -0.86658300
H  -3.03902900   3.19758700  -0.98192100
H  -3.02103100  -3.22358200  -1.00576100
H  3.30773400   3.21144300  -0.00029100
H  3.32571900  -3.20965500  -0.02410100
Mn  0.14195200  -0.00613200  -0.49407400
C  -1.05136200   0.07475400   4.34413200
O  -0.57532600  -0.02276600   3.28043200
O  -1.52728900   0.17223800   5.40810100
\[(\text{CO}_2\text{H})\text{-Mn}^{\text{III}}\text{-porphyrin}]\]

Gibbs Energy PCM(MeCN)-[B3LYP/6-31+G(d,p)/ LANL2DZ] = -1281.338134

| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | -4.09569500 | -0.70067800 | -1.16044000 |
| H       | -4.94077000  | -1.36439500  | -1.29461200  |

| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | -4.94077000  | -1.36439500  | -1.29461200  |
| H       | -5.16065100  | -1.12098100  | -0.57701000  |
| C       | 0.98878700   | -2.87071200  | -0.27749200  |
| C       | -0.86411700  | -4.16316500  | -0.28475200  |
| C       | -1.22737500  | -2.77052200  | -0.29689800  |
| N       | -0.08202300  | -1.99390500  | -0.27641300  |
| H       | -1.57241700  | -4.98102500  | -0.30148800  |
| C       | 2.93993900   | 0.97112000   | -0.41882500  |
| C       | 4.30127000   | 0.49161000   | -0.48686700  |
| C       | 4.23968600   | -0.87349400  | -0.48189600  |
| C       | 2.84080200   | -1.22811200  | -0.41172100  |
| N       | 2.07184300   | -0.09148700  | -0.39520500  |
| H       | 5.17875400   | 1.12377100   | -0.52504800  |
| H       | 5.05638800   | -1.58268900  | -0.51552200  |
| C       | 1.24251400   | 2.77280600   | -0.28042500  |
| C       | 0.87942600   | 4.16550400   | -0.26815600  |
| C       | -0.48598500  | 4.22753200   | -0.27007300  |
| C       | -0.97363900  | 2.87337500   | -0.28419800  |
| N       | 0.09688300   | 1.99638900   | -0.27411700  |
[(CO)-Mn$^{III}$-porphyrin]$^+$

Gibbs Energy PCM(MeCN)-[B3LYP/6-31+G(d,p)/ LANL2DZ] = -1205.365670
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| N       | 2.01195300 | 0.09381700 | -0.24261300 |
| H       | 5.12444200 | -1.11756000 | -0.26506800 |
| C       | -1.23783200 | 2.79197900 | -0.24874000 |
| C       | -0.87934800 | 4.18259400 | -0.25895200 |
| C       | 0.48581900 | 4.24643800 | -0.25836200 |
| C       | 0.97252900 | 2.89523600 | -0.24788600 |
| N       | -0.09380600 | 2.01189800 | -0.24303000 |
| H       | -1.59050000 | 4.99766900 | -0.26738300 |
| H       | 1.11757100 | 5.12438200 | -0.26626700 |
| C       | -2.89522800 | 0.97247600 | -0.24817500 |
| C       | -4.24642900 | 0.48576200 | -0.25858000 |
| C       | -4.18258400 | -0.87940500 | -0.25885600 |
| C       | -2.79196900 | -1.23788500 | -0.24852600 |
| N       | -2.01188900 | -0.09385600 | -0.24305300 |
| H       | -5.12437400 | 1.11751100 | -0.26665300 |
| H       | -4.99765700 | -1.59055900 | -0.26714800 |
| C       | 2.31470200 | 2.54119800 | -0.24675400 |
| C       | -2.31463900 | -2.54124100 | -0.24681800 |
| C       | -2.54118800 | 2.31464900 | -0.24733900 |
| C       | 2.54125100 | -2.31469200 | -0.24623100 |
| H       | 3.34245300 | -3.04518600 | -0.24915700 |
| H       | 3.04519600 | 3.34240000 | -0.24986100 |
| H       | -3.04513400 | -3.34244200 | -0.24994600 |
| H       | -3.34238800 | 3.04514400 | -0.25064700 |
| Mn      | 0.00002300 | -0.00001700 | -0.19473200 |
| C       | -0.00029900 | 0.00019900 | 2.42866300 |
| O       | -0.00047700 | 0.00030400 | 3.56143300 |
| C       | 4.18265300 | 0.87935800 | -0.25795400 |
| H       | 4.99773000 | 1.59051000 | -0.26615000 |
CO
Gibbs Energy PCM(MeCN)-[B3LYP/6-31+G(d,p)/ LANL2DZ] = -113.332228
0 1
C    0.00000000 0.00000000 -0.64984000
O    0.00000000 0.00000000  0.48738000

CO₂
Gibbs Energy PCM(MeCN)-[B3LYP/6-31+G(d,p)/ LANL2DZ] = -188.602465
0 1
C    0.00000000 0.00000000  0.00000000
O    0.00000000 0.00000000  1.16915000
O    0.00000000 0.00000000 -1.16915000

H₂O
Gibbs Energy PCM(MeCN)-[B3LYP/6-31+G(d,p)/ LANL2DZ] = -76.438556
0 1
O    0.00000000 0.00000000  0.11773200
H    0.00000000 0.76688000 -0.47092700
H    0.00000000 -0.76688000 -0.47092700

CH₃COOH
Gibbs Energy PCM(MeCN)-[B3LYP/6-31+G(d,p)/ LANL2DZ] = -229.079497
0 1
C    0.08731100 0.11994100  0.00000000
O    0.63322500 1.20985500  0.00000000
O    0.79086400 -1.03499000  0.00000000
H    1.73930400 -0.81527300 -0.00002000
C   -1.39609400 -0.12096100  0.00000000
H   -1.67670500 -0.70406100 -0.88222600
H   -1.67670200 -0.70409200  0.88220600
H   -1.92591300  0.83062500  0.00017000
\[ \text{CH}_3\text{COO}^- \]

Gibbs Energy PCM(MeCN)-[B3LYP/6-31+G(d,p)/ LANL2DZ] = -228.625427

-1 1
C 0.18591800 0.00000000 -0.01066300
O 0.76363800 1.12863700 0.00201700
O 0.76363800 -1.12863700 0.00201700
C -1.35371800 0.00000000 -0.00436800
H -1.75430700 -0.89467700 -0.48904300
H -1.70279800 -0.00001700 1.03597000
H -1.75430600 0.89469500 -0.48901400

\[ \text{Phenol} \]

Gibbs Energy PCM(MeCN)-[B3LYP/6-31+G(d,p)/ LANL2DZ] = -307.425359

0 1
C -0.24999800 0.00538400 0.14134800
C 1.14404900 -0.04206100 0.03966500
C 1.89205200 1.13559900 -0.05415900
C 1.23064100 2.36965800 -0.04540200
C -0.16065400 2.43120200 0.05590800
C -0.89967400 1.24563500 0.14939800
H -0.82742800 -0.91303600 0.21323300
H 1.64241600 -1.00717900 0.03404100
H 2.97383700 1.09341300 -0.13300800
H 1.79921500 3.29237200 -0.11789500
H -0.68132900 3.38376700 0.06344000
O -2.26444200 1.36161700 0.24642000
H -2.67184800 0.48566300 0.30491000
Phenolate

Gibbs Energy PCM(MeCN)-[B3LYP/6-31+G(d,p)/ LANL2DZ] = -306.956821

-1 1
C -0.20576200 -0.06996800 0.00497300
C 1.18913300 -0.06206400 0.00025400
C 1.91246200 1.14160000 -0.00299200
C 1.18921700 2.34531800 -0.00127500
C -0.20567700 2.35332500 0.00343200
C -0.97886500 1.14170700 0.00639200
H -0.74527100 -1.01587900 0.00738000
H 1.72424300 -1.01091600 -0.00083200
H 2.99878800 1.14156000 -0.00660200
H 1.72439300 3.29413000 -0.00354300
H -0.74512100 3.29927500 0.00467300
O -2.27558700 1.14175500 0.01027100

[Zn-BZA]^{2+}

Gibbs Energy PCM(MeCN)-[B3LYP/6-31+G(d,p)/ LANL2DZ] = -486.094527

2 1
C 1.22366600 0.25923200 0.44366600
C 2.61088400 0.14186900 0.47681400
C 3.41316300 1.19613400 0.02268100
C 2.82922100 2.36976700 -0.46932800
C 1.44226000 2.49370400 -0.51393100
C 0.63498000 1.43597800 -0.05463700
H 0.59135800 -0.54938300 0.79250900
H 3.06754800 -0.76714300 0.85461400
H 4.49458300 1.10294700 0.05206600
H 3.45455500 3.18549100 -0.81736700
H 0.98621800 3.40017500 -0.89463200
C -0.82907800 1.53817100 -0.08543400
\[ \text{[Zn-BZA]}^+ \]

Gibbs Energy PCM(MeCN)-[B3LYP/6-31+G(d,p)/LANL2DZ] = -485.691869
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