An Iron Porphyrin Complex with Pendant Pyridine Substituents Facilitates Electrocatalytic CO₂ Reduction via Second Coordination Sphere Effects

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A bispyridylamine-based hanging unit within the ligand framework of a newly synthesized iron porphyrin complex (Py₂XPFe) can act, on the one hand, as a hydrogen bonding site to facilitate proton transfer in catalysis and, on the other hand, as coordination site for a second Lewis acidic metal center. The bispyridylamine group in close proximity of the iron porphyrin center is able to mediate electrocatalytic CO₂ reduction in anhydrous MeCN. The hydrogen bonding interactions within the hanging group affect the kinetics of catalysis likely through stabilization of the [Fe(CO₂H)]⁻ intermediate, increasing the overall rate of catalysis when compared to the non-functionalized analog, TMPFe (TMP = tetramesitylporphyrin). The rate constants (k_{app}) of the reduction reaction were calculated using the FOWA method which resulted in a higher TOF_{max} for the complex Py₂XPFe compared with TMPFe in neat MeCN (1.7 × 10³ vs. 1.1 × 10¹ s⁻¹). The addition of weak Brønsted acids to the reaction mixture (TFE or PhOH) shows an increase in the rate of catalysis for both complexes, yet the Py₂XPFe analog displays higher TOF_{max} at each relative acid concentration, suggesting the hanging group beneficially impacts the rate of catalysis in the presence of these proton sources. The addition of Lewis acidic Sc³⁺ to Py₂XPFe also results in an increase in current density of the CO₂ reduction reaction. Resonance Raman as well as 'H-NMR spectroscopy indicates coordination to the pyridine substituents.

Introduction

As the energy demands of the globe continue to increase, the use of petroleum-derived nonrenewable energy sources continue to be a less than ideal way forward. The sustainability of these nonrenewable sources is limited, and their significant detrimental impact environmentally poses immense dangers to the planet and its inhabitants. Combustion of these fuel sources contribute directly to environmental pollution from various carcinogenic byproducts as well as increasing atmospheric carbon dioxide (CO₂) levels.[3] Converting residual CO₂ into energy dense fuels sources represents an attractive avenue for attenuating the levels of CO₂ in the atmosphere. Electrocatalytic reduction of CO₂ to carbon monoxide (CO), which can in turn be used in the production of hydrocarbon fuels via the Fischer-Tropsch reaction is a viable route towards renewable and sustainable energy.[2] Electrochemically however, direct one electron reduction of CO₂ to generate the corresponding radical anion CO₂⁻ is thermodynamically demanding and energy intensive. Furthermore, product distribution after further reduction can be complicated as CO is not the only electrogenerated product formed, with molecular hydrogen and other reduction side products effecting selectivity.[5] These constraints stem from thermodynamic and kinetic factors governing electrochemical CO₂ reduction, which can be adjusted or mitigated through use of a molecular electrocatalyst.

Iron-based homogenous molecular electrocatalysts, specifically those bearing a porphyrin ligand system, have been thoroughly investigated in this reduction reaction with pioneering work by Savéant and coworkers helping to improve the electrochemical methodology for other molecular CO₂ reduction studies.[4] The ability to modify the surrounding ligand framework of these Fe–porphyrin catalysts synthetically allows a simple yet effective way to systematically adjust the thermodynamics and kinetics of the reduction reaction facilitated by these complexes.[5] These structural changes can influence the potential of the reduction or affect the catalytic mechanism via stabilization of intermediates. Of note, use of a modified ligand framework bearing proton donor moieties or hydrogen bonding motifs have shown enhancement in overall catalysis, likely due to a relative increase in proton concentration at the active site mediating proton transfer.[6]
In this vein, we have synthesized an iron porphyrin-based electrocatalyst bearing pyridine substituents within a functional group referred to as Py$_2$XPFe (5-[1-(N,N-bis(pyridin-2-yl)methyl)amino]-2,7-di-tert-butyl-9,9-dimethylxanthen-5-yl]-10, 20-bis(2,4,6-trimethylphenyl)-porphyrinato iron, Figure 1) to investigate the catalytic reduction of CO$_2$ in the presence of weak acids to initiate proton transfer with contribution from the functional group. This catalyst is compared directly with the more common structural analog TMPFe (TMP = 5, 10, 15, 20-tetramesitylporphyrin) to exemplify the structure-activity relationship of the hanging group in catalysis.

Results and Discussion

Synthesis

Ligand Py$_2$XPH$_2$ was synthesized via demetallation of known compound Py$_2$XPZn$^{[2]}$ followed by iron insertion according to established procedures.$^{[9]}$ The demetallation procedure was best achieved by using half-concentrated sulfuric acid, which led to quantitative conversion. Interestingly, using only dilute sulfuric or hydrochloric acid led to only partial demetallation. The metal-free ligand Py$_2$XPH$_2$ was characterized by NMR spectroscopy, mass spectrometry, UV/Vis spectroscopy as well as X-ray crystallography (details see SI) confirming the purity of the compound.

Reaction of Py$_2$XPH$_2$ with FeCl$_3$ in DMF, followed by aerobic acid work-up led to the formation of Py$_2$XPFeCl. Purification was achieved by, first, treating a DCM solution with aqueous EDTA solution to remove unwanted iron in the bispyridylamine coordination sphere and, second, column chromatography. The title compound was isolated in 79% yield (further descriptions and analytical data can be found in the experimental section and SI).

Electrochemistry

Initial CV experiments were conducted with Py$_2$XPFe and TMPFe under an argon atmosphere to observe the cathodic behavior in anhydrous MeCN (Figure S10) with the formal potential (E*) values for the respective reduction events reported in Table 1. Much like other iron porphyrin chloride complexes reported previously, an initial one electron reduction of the Fe$^{II}$ species results in chloride dissociation and formation of a neutral Fe$^{II}$ species. The subsequent second one electron reduction results in the formation of the [Fe$^{II}$] anion followed by the third one electron reduction to generate the dianion [Fe$^{II}$]$^{2-}$ which is then a sufficiently strong Lewis base to facilitate the coordination of CO$_2$.$^{[10]}$

Electrocatalysis

Previous studies have shown the main product of the electrochemical CO$_2$ reduction reaction catalyzed by iron porphyrins in the presence of a weak Brønsted acid with carbon electrodes to be CO and H$_2$O.$^{[11,12]}$ A general reaction scheme of the CO$_2$ reduction reaction facilitated by electrochemically generated porphyrinato [Fe$^{II}$]$^+$ is shown below (Scheme 1). Reversible binding of CO$_2$ to Lewis basic [Fe$^{II}$]$^+$ results in the formation of the [Fe($ \eta^1\text{-CO}_2$)$^+$]$^+$ intermediate. Protonation of this [Fe($ \eta^1\text{-CO}_2$)$^+$]$^+$ adduct leads to formation of a hydroxycarbonyl [Fe($ \text{CO}$)H]$^-$ species, which upon further protonation undergoes C–O bond breaking with subsequent liberation of water and CO.

In an idealized electrochemical catalytic reaction, a molecular catalyst will consume substrate unperturbed without chemical side-phenomena and give rise to an S-shaped voltammogram represented in the zone diagram developed by Savéant and Su which represents "pure kinetic" conditions.$^{[12]}$ At a sufficiently fast scan rate, substrate depletion at the electrode

Table 1. Formal potentials (E*) determined via cyclic voltammetry for Py$_2$XPFe and TMPFe complexes recorded under argon atm. in MeCN/0.1 M Bu$_4$NBF$_4$ at a 3.0 mm glassy carbon electrode. All values are reported versus the non-aqueous Ferrocenium/Ferrocene (Fc$^{+}$/Fc) redox couple.

|          | Fe$^{II}$ | Fe$^0$ | Fe$^{III}$ |
|----------|----------|--------|-----------|
| Py$_2$XPFe | -0.71$^{[1]}$ | -1.63 | -2.24$^{[2]}$ |
| TMPFe    | -0.75$^{[2]}$ | -1.53 | -2.21$^{[2]}$ |

[a] Irreversible on the CV timescale at 0.2 V/s, Epa reported. (b) quasi reversible on the CV timescale at 0.2 V/s
The surface is suppressed and the resulting S-shaped CV response is proportional to the rate of the coupled chemical reaction proceeding at steady state. The calculation for the rate constant $k_{\text{app}}$ from an S-shaped voltammogram is shown in Equation (1).

The rate constant ($k_{\text{app}}$) is proportional to the ratio of $i_{\text{cat}}/i_p$ from the plateau current and dependent of the scan rate ($\nu$) at which the CV was conducted, where $i_{\text{cat}}$ is the current of the analyte in presence of substrate, $i_p$ is the current of the analyte in the absence of substrate, $n$ is number of electrons transferred in the redox event (here $n = 1$) $F$ is the Faraday constant and $R$ is the ideal gas constant.$^{[13]}$

$$\frac{i_{\text{cat}}}{i_p} = \frac{1}{0.446} \sqrt{\left(\frac{RT}{nFp}\right) k_{\text{app}} \cdot \nu}$$  \hspace{1cm} (1)

When unwanted side reactions hinder the possibility of observing an S-shaped voltammogram, application of Foot-off-the-wave analysis (FOWA) proposed by Savéant$^{[14]}$ and described in more detail by Dempsey$^{[15]}$ and Wang$^{[16]}$ has been shown to produce good approximate values for an apparent rate constant ($k_{\text{app-FOWA}}$) of the electrocatalytic reaction, assuming that no other electrochemical process takes place in this foot-of-the-wave regime and thus catalytic onset occurs under pure kinetic conditions.

The application of FOWA to evaluate the electrocatalytic response of the Py$_2$XPFe system in the presence of CO$_2$ was used to calculate the $k_{\text{app-FOWA}}$ of the reduction of CO$_2$ to CO$_2$ under the presumption that the Py$_2$XPFe and TMPFe systems follow an ECEC (E electrochemical, C chemical) mechanism.$^{[17]}$ The approximate rate constants calculated herein referred to as $k_{\text{app-FOWA}}$ are a composite of the steps involving the proton-coupled electron transfer activation process(es) of CO$_2$ (Scheme 1). Equation (2) describes the relationship between the $i_{\text{cat}}/i_p$, $E-E^0$ and $k_{\text{app-FOWA}}$ for the ECEC reaction mechanism with the reaction being first order with respect to CO$_2$ concentration.

$$i_{\text{cat}} = \frac{2.24 \sqrt{RT \cdot n \cdot k_{\text{app-FOWA}}}}{1 + \exp\left[i \cdot (E - E^0)\right]}$$ \hspace{1cm} (2)

Hereby $n'$ is the number of electrons required to complete a single catalytic cycle (in this case 2 for the reduction of CO$_2$ to CO), $E$ is the potential region scanned, $E^0$ is the formal potential of the reduction which initiates catalysis recorded under non-catalytic conditions, in this case the Fe$^{10}$ couple (Table 1). The rate constant $k_{\text{cat}}$ for the CO$_2$ reduction reaction in the presence of a proton source is related to the $k_{\text{app-FOWA}}$ via the following rate equation, where $k_{\text{cat}}$ (M$^{-2}$s$^{-1}$) is the intrinsic third order rate constant$^{[18]}$ [Eq. (3)].

$$\frac{[\text{dCO}_2]}{\text{dt}} = k_{\text{app-FOWA}} [\text{cat}] = k_{\text{cat}} [H^+] [\text{CO}_2] [\text{cat}] \hspace{1cm} (3)$$

The turn over frequency (TOF) of a molecular catalyst can be defined as the number of catalytic turnovers achieved in a unit of time, where catalytic decomposition remains negligible.$^{[17]}$ Under saturated CO$_2$ conditions, the maximum turnover frequency (TOF$_{\text{max}}$) is equal to the catalytic rate constant, defined here as $k_{\text{app}}$ via Equation (4).

$$\text{TOF}_{\text{max}} = k_{\text{app}}$$  \hspace{1cm} (4)

The Py$_2$XPFe complex under investigation demonstrates efficient CO$_2$ reduction catalysis under saturated CO$_2$ conditions (i.e. 0.23 M CO$_2$ in MeCN$^{[19]}$). Figure 2 displays an overlay of cyclic voltammograms of the Py$_2$XPFe complex under argon and CO$_2$ (blue and red trace respectively) with the catalytic onset observed in the region of the Fe$^{10}$ couple.

Under an argon atmosphere, the Fe$^{10}$ reduction in Py$_2$XPFe is observed at slightly more negative potentials compared to TMPFe (Table 1), possibly due to the removal of two mesityl substituents at meso positions on the porphyrin ring, with one substituted for the backbone/hanging group moiety which may result in coulombic differences at the iron center.$^{[19]}$ Alternatively, this more negative reduction may be attributed to a pyridine substituent within the hanging group binding weakly to the reduced four-coordinate Fe atom$^{[20]}$ thereby slightly increasing electron density at the metal center and shifting the reduction process to more cathodic potentials. In either case, although the Py$_2$XPFe displays a more negative reduction potential for the Fe$^{10}$ couple compared to the TMPFe, the onset potential for catalysis ($i_{\text{cat}}/i_p > 1$) is initiated at the same onset potentials, $-2.15 \pm 0.01$ V vs. Fe$^{1+}$. The difference in onset potential vs. respective Fe$^{10}$ couple can be observed qualitatively in the overlay traces in Figure 3 (left) and more quantitatively in Figure 3 (right). The latter presents an extrapolation of the linear portion of the onset potentials ($E-E^0_{\text{cat}}$) for Py$_2$XPFe and TMPFe and demonstrates a steeper slope of the linear region for the Py$_2$XPFe species which is the foundation for calculating the rate constant ($k_{\text{app-FOWA}}$). The earlier relative onset potential and thus larger $i_{\text{cat}}/i_p$ per unit $E$ ($E-E^0_{\text{cat}}$) indicates more current is passed per unit potential and correlates to a higher rate constant under identical conditions; from the FOWA method $k_{\text{app-FOWA}} = 1.7 \times 10^6$ for Py$_2$XPFe vs. TMPFe at $\nu = 0.2$ V/s. It should be noted however that the differences in current densities displayed in the plots between Py$_2$XPFe and TMPFe (Figure 3 (left)) are due, in part, to the limited solubility of TMPFe in MeCN and thus are not

**Figure 2.** Cyclic voltammograms of 1 mM Py$_2$XPFe under 1 atm argon (blue trace) and 1 atm CO$_2$ (red trace) vs. Fe$^{1+}$ recorded in MeCN/0.1 M Bu$_4$NPF$_6$ at a 3.0 mm glassy carbon electrode; scan rate ($\nu$) 0.2 V/s.
directly comparable to the current densities of the Py$_2$XPFe complex.

In an attempt to achieve an S-shaped voltammogram from which $k_{app-S}$ could be calculated via Equation (1), the scan rate was incrementally increased for both complexes. At faster scan rates, the catalytic wave begins to adopt a “non-ideal” catalytic wave character for both species (Figure 4) from which the respective rate constants were approximated.

The $k_{app-S}$ Calculated from this method at E-values of $-2.75$ and $-2.70$ V vs FC$^{+/0}$ is $4.8 \times 10^3$ s$^{-1}$ and $4.6 \times 10^3$ s$^{-1}$ for the Py$_2$XPFe and TMPFe complexes respectively. These values should be taken with great care, as they are just an approximation due to the ambiguity of this “non-ideal” wave shape. The rate constants calculated from these traces indicate that these catalysts function at approximately the same rate assuming pure kinetic conditions in anhydrous MeCN. Notably however, there is a large discrepancy between the $k_{app}$ calculated from the S-shaped curves ($k_{app-S}$) and from the FOWA method ($k_{app-FOWA}$) for the Py$_2$XPFe species ($4.8 \times 10^3$ s$^{-1}$ vs. $1.7 \times 10^4$ s$^{-1}$). Although described previously by Dempsey and Johnson that the $k_{app-FOWA}$ approximates the $k_i$ within the ECCE mechanism (in this case CO$_2$ binding, see Scheme 1), the subtleties affecting the mechanism of the Py$_2$XPFe and the $k_{app-FOWA}$’s propensity to change upon the addition of a proton source (vide infra) suggest that the $k_{app-FOWA}$ represents an amalgamation of multiple rate constants within the catalytic cycle and may not define the slowest step of the reduction of CO$_2$ to CO for this system.

Influence of Protons

The hanging group’s impact on the rate of catalysis was investigated further through titrations of trifluoroethanol (TFE) and phenol (PhOH) as proton sources. The influence of weak Bronsted acids on the enhancement of iron porphyrins to facilitate CO$_2$ reduction in DMF is well documented,[4c,10,21] however there are much fewer investigations on this system in MeCN.[22] This report focuses on the reduction of CO$_2$ in MeCN in the presence of TFE ($pK_a = 35.4$ in MeCN) and PhOH ($pK_a = 29.1$ in MeCN)[18] to quantify the effects of these proton sources at varying concentrations for the systems investigated. The experiments were conducted in triplicate, with the reported catalytic rate constant values being an average of three measurements. The catalytic current responses of a CO$_2$ reduction reaction conducted by Py$_2$XPFe and TMPFe at increasing TFE concentrations are shown in Figure 5 with the corresponding rate constants listed in Table 2.

The addition of TFE to the reaction mixture under saturated CO$_2$ conditions results in an increase in current density for both the Py$_2$XPFe and TMPFe complexes. Rate constants calculated via the S-shaped curve equation were approximated from CV

![Figure 3](image_url) Overlay of normalized cyclic voltammograms of Py$_2$XPFe and TMPFe (forward traces only), under 1 atm CO$_2$ (red and green traces, respectively); Fe$^{II}$ couple omitted for clarity. Highlighted box displays portion of the wave extrapolated with FOWA. Recorded in MeCN/0.1 M Bu$_4$NPF$_6$ at a 3.0 mm glassy carbon electrode and scan rate $v = 0.2$ V/s; (right) Overlay of the linear extrapolated FOWA area where the onset of catalysis takes places; red trace Py$_2$XPFe, green trace TMPFe.

![Figure 4](image_url) Overlay of normalized cyclic voltammograms of (left) Py$_2$XPFe and (right) TMPFe at increasing scan rates under 1 atm CO$_2$ recorded in MeCN/0.1 M Bu$_4$NPF$_6$, at a 3.0 mm glassy carbon electrode with scan rates (v) 0.1 V/s black trace, 0.2 V/s red trace, 0.4 V/s blue trace, 0.8 V/s green trace, 1.6 V/s purple trace, 2.0 V/s gold trace.

![Figure 5](image_url) Overlay of cyclic voltammograms of (left) 1 mM Py$_2$XPFe or (right) 1 mM TMPFe at increasing TFE concentrations in MeCN/0.1 M Bu$_4$NPF$_6$ recorded at $v = 0.2$ V/s, forward traces only under CO$_2$ atm (red trace): 1 (blue) 2 (green) 4 (purple) 8 (orange) 16 (yellow) 32 (magenta) 64 (pink) 128 (gray) mM concentration.

| TFE [mM] | Py$_2$XPFe | TMPFe | Py$_2$XPFe | TMPFe |
|----------|------------|-------|------------|-------|
|          | $k_{app-FOWA}$ | $k_{app-FOWA}$ | $k_{app-FOWA}$ | $k_{app-FOWA}$ |
| 1        | $8.8 \times 10^3$ | $6.0 \times 10^3$ | $8.7 \times 10^3$ | $4.6 \times 10^3$ |
| 2        | $5.8 \times 10^3$ | $1.5 \times 10^3$ | $1.4 \times 10^3$ | $1.2 \times 10^3$ |
| 4        | $7.0 \times 10^3$ | $1.0 \times 10^3$ | $4.6 \times 10^3$ | $2.4 \times 10^3$ |
| 8        | $2.1 \times 10^4$ | $1.6 \times 10^3$ | $1.0 \times 10^3$ | $6.3 \times 10^3$ |
| 16       | $1.6 \times 10^4$ | $6.1 \times 10^3$ | $2.6 \times 10^3$ | $1.3 \times 10^3$ |
| 32       | $5.2 \times 10^4$ | $1.7 \times 10^3$ | $4.6 \times 10^3$ | $3.7 \times 10^3$ |
| 64       | $2.4 \times 10^4$ | $1.3 \times 10^3$ | $7.9 \times 10^3$ | $6.1 \times 10^3$ |
| 128      | $7.4 \times 10^4$ | $3.1 \times 10^3$ | $1.5 \times 10^3$ | $1.1 \times 10^3$ |

(a) Calculated from the FOWA method, reported in s$^{-1}$. [b] Approximated from the S-shaped wave equation, reported in s$^{-1}$. All values reported herein are a cumulative average between three separate trials.
curves obtained at a scan rate of 0.2 V/s, as successive scans at increasing scan rates resulted in electrode fouling and inconsistencies between replication attempts, not unlike work with GC electrodes in acidic MeCN medium for H₂ reduction.\textsuperscript{[23]} It is absolutely clear that this system does not proceed at steady state under the conditions reported, however we thought it insightful to compare the rate constants from the FOWA and S-shaped calculation, if only approximations (Table 2 and S3).

Although both species display relatively large \(k_{app-FOWA}\) for the reduction of CO₂ to CO in MeCN in the presence of TFE, the PyₓXPFe complex displays a higher \(k_{app-FOWA}\) at each added TFE aliquot compared with TMPFe and an order of magnitude difference at 0.128 M TFE (7.4 × 10⁻⁶ vs. 3.1 × 10⁻⁸ s⁻¹ for PyₓXPFe and TMPFe respectively at \(ν = 0.2\) V/s). This difference in \(k_{app-FOWA}\) of the PyₓXPFe indicates that the hanging group contributes beneficially to catalysis in the presence of a proton source as compared to the unsubstituted analog.

The catalytic current responses of PyₓXPFe and TMPFe with increasing PhOH concentrations are shown in Figure 6 and the corresponding rate constants are listed in Table 3. The current densities and \(I_{cat}/I_{p}\) values for the PyₓXPFe complex are larger per concentration of PhOH compared to TFE (Table S3 and S4), highlighting the improvement in overall catalysis per PhOH aliquot, due to its stronger acidity than TFE in MeCN. The calculated rate constants display an order of magnitude difference between the PyₓXPFe and TMPFe complexes with added PhOH, with \(k_{app-FOWA}\) values for the PyₓXPFe complex to be as large as 2.1 × 10⁸ s⁻¹ at 128 mM PhOH, compared with 7.1 × 10⁶ s⁻¹ for TMPFe; i.e. ~ 30 times faster rate for PyₓXPFe.

This difference in overall reactivity between PyₓXPFe and TMPFe particularly in the presence of a proton source is likely due to the hanging group acting as a hydrogen bonding acceptor to facilitate proton transfer to the reduced CO₂ adduct \([\text{Fe}(\text{n}^2-\text{CO}_2)^+\text{]}^2\) or stabilization of the \([\text{Fe}^+(\text{CO}_2\text{H})]^+)\) intermediate (Scheme 1). The functional group thus influences the reaction kinetics of the reduction process, affecting the onset potential of catalysis and the apparent rate constant. Although the precise mechanism of protonation of the reduced CO₂ adduct is not yet clear, the current moment is evident, that the hanging group positively influences the kinetics of catalysis and increases the overall \(k_{app-FOWA}\) compared to TMPFe with both added TFE and PhOH. The \(k_{app}\) remains within the same order of magnitude for both complexes throughout both sets of titrations and reach a maximum for PhOH at 2.3 ± 0.2 × 10⁸ for both species, suggesting a current maximum is limited by side-phenomena taking place.

The relationship between Log[TOF\(_{max}\)] and Log[TFE or PhOH] concentration for PyₓXPFe and TMPFe is shown in Figure 7. As observable from the plot, the PyₓXPFe complex functions at higher Log[TOF\(_{max-FOWA}\)] with both TFE and PhOH compared with TMPFe at the acid concentrations investigated. Both catalysts display a near linear correlation between TOF\(_{max}\) from FOWA and acid concentration on a logarithmic scale, with slopes of 2.0 ± 0.5 (Figures S17, S18) for each line, suggesting the rate constant calculated from FOWA follows a second-order type rate reaction. The TOF\(_{max}\) calculated from the steady state

*Figure 6. (left) Overlay of cyclic voltammograms of 1 mM PyₓXPFe at increasing PhOH concentrations in MeCN/0.1 M Bu₄NPF₆ recorded at \(ν = 0.2\) V/s, forward traces only. (right) Overlay of cyclic voltammograms of 1 mM TMPFe at \(ν = 0.2\) V/s, forward traces only. CO₂ atm (red trace): 1 (blue) 2 (green) 4 (purple) 8 (orange) 16 (yellow) 32 (magenta) 64 (pink) 128 (gray) mM PhOH concentration.*

| Table 3. Rate constants calculated for PyₓXPFe and TMPFe with increasing PhOH concentrations in MeCN/0.1 M Bu₄NPF₆ recorded at \(ν = 0.2\) V/s |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| PhOH [mM]      | PyₓXPFe \(k_{app-FOWA}\) | TMPFe \(k_{app-FOWA}\) | PyₓXPFe \(k_{app-FOWA}\) | TMPFe \(k_{app-FOWA}\) |
| 1               | 1.1 × 10⁷       | 2.2 × 10⁶       | 3.3 × 10⁶       | 1.7 × 10⁷       |
| 2               | 1.7 × 10⁷       | 3.6 × 10⁶       | 1.2 × 10⁷       | 9.2 × 10⁷       |
| 4               | 3.5 × 10⁷       | 1.1 × 10⁷       | 2.2 × 10⁷       | 2.1 × 10⁷       |
| 8               | 2.3 × 10⁷       | 1.1 × 10⁷       | 3.4 × 10⁷       | 2.8 × 10⁷       |
| 16              | 2.9 × 10⁷       | 5.4 × 10⁶       | 6.5 × 10⁶       | 6.1 × 10⁷       |
| 32              | 1.7 × 10⁷       | 1.3 × 10⁷       | 1.0 × 10⁷       | 9.9 × 10⁶       |
| 64              | 6.0 × 10⁷       | 2.3 × 10⁷       | 1.4 × 10⁷       | 1.5 × 10⁷       |
| 128             | 2.1 × 10⁸       | 7.1 × 10⁶       | 2.4 × 10⁷       | 2.2 × 10⁷       |

[a] Calculated from the FOWA method, reported in s⁻¹ [b] Approximated from the S-shaped wave equation, reported in s⁻¹. All values reported herein are a cumulative average between three separate trials.

*Figure 7. Log[TOF\(_{max}\)] vs. Log(acid) for each catalyst with TOF\(_{max}\) calculated via FOWA and the S-shaped wave approximation as a cumulative average of three separate trials.*
approximation for both Py,XPFe and TMPFe are lower compared to the rate constants calculated via FOWA, particularly at higher acid concentrations. The TOF max for both compounds reaches a Log[TOF max] at around 4.0 ± 0.4 for the S-shaped approximation, compared with Log[TOF max] for FOWA which are as large as 8.3 for the Py,XPFe complex at high phenol concentrations. The TOF max from the S-shaped steady state approximation scales proportionally with acid concentration on the logarithmic scale, displaying a linear correlation vs. [TFE or PhOH] with slopes of 1.0 ± 0.2 (Figures S17, S18) indicating a first order rate or pseudo first order rate dependence on the acid concentration, in agreement with Nocera et al.’s work with iron hangman porphyrin complexes in the presence of acid where pure kinetic conditions (steady-state) were achieved.[24] The catalytic currents of the reaction (i) fit linearly to the function \[\frac{1}{1-e^{[\text{inf}/\text{RT}](\text{E}^-\text{cat})]} \] for both Py,XPFe and TMPFe, which occurs when first order dependence on catalyst is observed, whereas a second order dependence results in a linear fit for the function \[\frac{1}{1-e^{[\text{inf}/\text{RT}](\text{E}^-\text{cat})]} \] (FOWA traces, Figure S15, S16). Although the hanging group contributes beneficially to the CO2 reduction reaction through hydrogen bonding, the correlation between Log[TOF max] and Log[TFE or PhOH] for the Py,XPFe remains linear even at higher acid concentrations, suggesting that the catalytic mechanism is the same for both proton sources and the pyridine substituents are not protonated within the acid concentrations investigated (pyridine pK\text{a} is 14.5 in MeCN).[26] NMR and CV experiments incorporating excess PhOH or TFE (Figures S4, S13) also indicate the tertiary amine situated within the hanging group is not protonated within the concentrations of acids investigated. As a consequence, the pyridine and tertiary amine substituents likely act as hydrogen bonding promoters throughout the titrations rather than proton relays to the active site.[27]

Overpotential Required for Catalysis

The overpotential required for catalysis (\(\eta\)) is a thermodynamic property of the molecular catalyst which quantifies the additional driving force necessary to conduct catalysis at a specific rate at standard potential.[28] The standard reduction potential of the two-electron two-proton reduction of CO2 to CO (\(E_{\text{CO2/CO}}\)) in MeCN reported by Mayer and coworkers at \(-0.12\) V vs FC \(-1\) defines the reaction at pH 0.[29] However, the equilibrium potential for the reduction of CO2 to CO (\(E_{\text{CO2/CO}}\)) is a pH dependent value, therefore \(E_{\text{CO2/CO}}\) should change as a function of solution pH. There is a significant amount of discrepancy in the literature regarding what values are used for this \(E_{\text{CO2/CO}}\) particularly in the presence of proton sources. Bullock and coworkers have devised an effective method for the determination of this equilibrium potential value for the hydrogen evolution reaction through open circuit measurements[30] and Mastubara and coworkers have done substantial work in determining these potential values at various MeCN:H2O mixtures through isothermal titration calorimetry and density functional theory.[31] Ideally, a buffer system should be utilized to ensure that the pH of the solution is equal to the respective acid’s pK\text{a}, thus allowing the application of the pH dependent Nernst equation.[32] However, calculating \(E_{\text{CO2/CO}}\) at a given pH is not necessarily straight-forward, as the analytical concentrations of the acids may not be equal to their respective activities in solution particularly when acid-base pairs aggregate resulting in homoconjugation.[33] Under the conditions investigated in this report in the absence of a buffered system, we have chosen to use the value of \(-1.36\) V vs FC \(-1\) reported by Kubiak et al.[18] for \(E_{\text{CO2/CO}}\) in the presence of an acid source in MeCN for the calculation of catalytic overpotential at 128 mM PhOH and TFE. This value is sufficiently more positive than those reported by Mastubara at low H2O concentrations in MeCN, in agreement with the trend in which lowering the pH shifts the equilibrium potential more positive, yet far more negative than the reported \(E_{\text{CO2/CO}}\) in dry MeCN.[31b]

The overpotential (\(\eta\)) required for catalysis is then defined as the difference between the equilibrium potential \(E_{\text{CO2/CO}}\) at a given pH and the catalytic peak half-wave potential (\(E_{\text{r/2}}\)) ([Eq. (5)]).

\[
\eta = |E_{\text{CO2/CO}} - E_{\text{r/2}}| \tag{5}
\]

These overpotential values don’t take into account the interaction of the respective acid with CO2 in solution which typically results in a lower pH of the MeCN/acid/CO2 mixture.[34] The \(E_{\text{CO2/CO}}\) and thus \(\eta\) are approximations for the current system and should be viewed as such. From equation 5, the overpotentials at which catalysis is most efficient with both acids (128 mM) are 0.95 V vs FC \(-1\) and 0.89 V vs FC \(-1\) for Py,XPFe and 0.86 V and 0.85 V for TMPFe (PhOH and TFE respectively). Although the overpotential is an intrinsic property of the catalyst and should not change with pH, these differences in overpotential values between the same catalysts are within the error deviation particularly when measuring \(E_{\text{r/2}}\).[33] The TMPFe species displays a lower overpotential compared with the Py,XPFe species, likely due to the Fe\text{II} down reduction being slightly more negative for the Py,XPFe complex compared to the TMPFe (Table 1).

Catalytic Tafel plots are useful diagrams which allow the comparison of homogenous catalysts and their efficiencies amongst one another.[35] Catalytic Tafel plots relate a catalyst’s thermodynamic parameter for catalysis (\(\eta\)) with its kinetic parameter (TOF), with effective catalysts situated in the upper left portion of the plot having large TOF max at low \(\eta\).[46] Equation (6) relates TOF with \(\eta\) and allows for the comparison between molecular catalysts investigated in this study as well as other reported iron porphyrin-based CO2 reduction catalysts reported previously (for which TOF max or \(k_{\text{cat}}\) has been reported; Table S5).[5d,6e,18,22,27,36] The catalytic Tafel plot comparing the present system is shown in Figure 8 with a more detailed plot incorporating other relevant catalysts for the literature in Figure S19.

\[
\text{TOF} = \frac{\text{TOF max}}{1 + \exp\left[\frac{1}{RT}\left(E_{\text{CO2/CO}} - E_{\text{r/2}}\right)\exp\left(\frac{\eta}{RT}\right)\right]} \tag{6}
\]
Interestingly, both the TMPFe and Py,XPFe complex reported here have relatively large TOF max values calculated via the FOWA method compared with other CO2 reduction catalysts. What seems to be a contributing factor to this catalytic enhancement is the solvent effects in MeCN compared with DMF. Although the exact effects appear to be not yet completely understood, Warren et al. have reported on this phenomenon with iron porphyrin CO2 reduction catalysts previously[22] where even small aliquots of acid result in a large enhancement of TOF max in MeCN. This is contrary to what is observed in DMF and suggests the hydrogen bonding properties of the solvent drastically affect catalysis. Indeed preliminary experiments of the Py,XPFe species in DMF display a lower current density increase and lower \( \text{current} / \text{voltage} \) values per PhOH or TFE aliquot compared to work in MeCN (Figure S14, Table S5, S6). This difference in catalytic activity due to solvent dependence requires a more in-depth investigation to determine to what extent the solvent affects catalysis and the possible mechanism therein, which at the moment, is beyond the scope of the current manuscript. Jiang et al. recently reported on an iron porphyrin complex containing a poly(ethylene glycol) hanging group which is shown to promote hydrogen bonding in MeCN, and reports TOF max as high as \( 1.4 \times 10^8 \text{ s}^{-1} \) in acetonitrile with only 2.0 M H2O as the proton source (teal trace, Figure 8).[18] Chang and coworkers reported on a series of iron porphyrin catalysts containing amide pendant, with the most efficient catalyst displaying a TOF max of \( 5.5 \times 10^8 \text{ s}^{-1} \) in DMF with 0.1 M PhOH (Fe-ortho-2amide, brown/gold trace in Figure 8).[19] The rate constants for the Py,XPFe complex under similar conditions (128 mM PhOH) yet in MeCN display a calculated TOF max two orders of magnitude greater than reported for the Fe-ortho-2amide. It is unclear whether this difference is due to a particular system dependent improvement in catalysis or rather a result of solvent enhancement, although it is likely the latter. Despite the Py,XPFe displaying large TOF max values under the conditions investigated, the overpotential required for catalysis is slightly larger than other complexes reported previously. As a result, this enhanced catalysis comes at the cost of a larger potential (E) driving force necessary for catalysis. The overpotential however is again only an approximation of the \( E_{\text{CO2/CO}} \) couple under the given conditions and may not necessarily define the true overpotential of the Py,XPFe complex.

Incorporation of Lewis Acidic Sc(III)

Seminal work by Savéant et al. has shown that the addition of Lewis acidic metals to the electrochemical reaction mixture of iron porphyrins improves overall catalytic performance facilitating the CO2 reduction reaction.[37] As well as acting as hydrogen bonding residues to promote catalysis, the bispyridylamine-based hanging group of the Py,XPFe complex can function as an additional coordination sphere for a second metal.[20] Kojima et al. have also reported on a NiII complex bearing an S2N2-type ligand with peripheral pyridine substituents, which has shown to coordinate Mg2+ in solution and display improved CO2 to CO reduction reactivity compared with the parent complex.[21] With this in mind, we sought to investigate the introduction of a second Lewis acidic metal coordinating in-situ in the vacant site of the Py,XPFe complex to improve catalytic performance. Initially, Mg2+ was tried as a possible second metal, however attempts to add Mg(OTf)2 to the reaction mixture resulted in electrode fouling after cathodic scanning, presumably due to Mg2+ reduction as a result of the slightly larger overpotential required for this catalyst compared to Mn and Ni-based CO2 reduction catalysts.[39] or effects from the solvent. Therefore, Sc(OTf)3 was chosen as a catalysis promoter as its Lewis acidic quality would likely allow for incorporation into the pyridine residues while it’s reduction is observed at a more negative potential (\( -2.53 \text{ V vs. } \text{Fc}^{0/1} \)) versus the onset potential of the Py,XPFe system catalyzing CO2 reduction. An initial titration of increasing amounts of Sc(OTf)3 to a solution of Py,XPFe in anhydrous MeCN was conducted under saturated CO2 conditions, with CV responses for the titration shown in Figure 9. As evident from the figure, incremental addition of

Figure 8. Catalytic Tafel plot comparing the Py,XPFe and TMPFe complexes at 128 mM PhOH and TFE with other iron porphyrin catalysts. Please be aware that different solvents as well as proton sources have been used.

Figure 9. Overlay of normalized cyclic voltammograms of 1 mM Py,XPFe under 1 atm CO2 in MeCN/0.1 M Bu4NPF6 at increasing Sc(OTf)3 equivalents recorded at \( v = 0.2 \text{ V/s} \), forward traces only.
Sc$^{3+}$ to the reaction mixture results in catalytic current enhancement compared to Py$_2$XPFe alone.

The catalytic current enhancement is observed at increasing Sc$^{3+}$ concentrations, which reaches a maximum at approximately 1.2 equivalents of Sc$^{3+}$. The FOWA analysis of these curves was unable to be calculated due to an early onset in the catalytic wave, however the corresponding rate constants were approximated again using the steady state curve equation and are shown along with other catalytic descriptors in Table 4.

The very similar current maxima at 1.2 equivalents and at 1.0 equivalents suggest stabilization of the [Fe(η¹-CO$_2^*$)]$^{3-}$ adduct in terms of a 1:1 type interaction. Further addition of Sc$^{3+}$ leads to a slight decrease in overall current (1.4 equiv., brown trace in Figure 9) indicating that more equivalents hinder optimum performance of the reduction reaction possibly due to unwanted side-phenomena taking place. Resonance Raman optimum performance of the reduction reaction possibly due to brown trace in Figure 9) indicating that more equivalents hinder optimum performance of the reduction reaction possibly due to unwanted side-phenomena taking place. Resonance Raman spectrum of Sc$^{3+}$ upon the addition of the Lewis-acidic Sc$^{3+}$ enhances compared to Py$_2$XPFe complex in dry MeCN excited at 405 nm before and after the addition of Sc$^{3+}$ shows a distinct intensity change in the peaks at 1005 and 1025 cm$^{-1}$ (Figure 10, Figure S20). These bands correspond to the pyridine substituents ring stretching modes which change in relative intensity upon the addition of the Lewis-acidic Sc$^{3+}$, similar to what is observed with pyridine protonation indicating some degree of pyridine–Sc$^{3+}$ interaction. $^3$H NMR spectroscopic titration studies also confirm the in-situ formation of an adduct between Sc$^{3+}$ and Py$_2$XPZn (Figure S3).

To summarize, NMR as well as Raman spectra confirm that Lewis-acidic Sc$^{3+}$ added to the reaction mixture interacts with the pyridine substituents of the hanging group, generating a bi-metallic species in-situ in solution, similar to that of Kojima’s catalyst with Mg$^{2+}$ and enhances the catalytic reduction of CO$_2$.$^{[38]}$

**Mechanism**

Scheme 2 depicts the proposed mechanism for the reduction of CO$_2$ catalyzed by the Py$_2$XPFe complex. Initially, two one electron transfers from the electrode to the Py$_2$XPFe complex generates the formal [Fe]$^0$ species [Py$_2$XPFe]$^{2-}$. This dianion then binds CO$_2$ reversibly to generate the [Fe(η¹-CO$_2^*$)]$^{3-}$ intermediate. The equilibrium binding constants of CO$_2$ ($K_{CO_2}$) were estimated from CVs at fast scan rates ($^{[40]}$ (Figure S21) and were approximately 42 M$^{-1}$ and 27 M$^{-1}$ for Py$_2$XPFe and TMPFe. These values are much larger than those reported previously for amide supported iron porphyrins (14–17 M$^{-1}$) and unsupported iron porphyrins (2–4 M$^{-1}$) in DMF, likely due to the solvent enhancement observed in MeCN. The larger equilibrium constant for the Py$_2$XPFe compared to TMPFe suggests a greater extent of favorable interaction within [Fe(η¹-CO$_2^*$)]$^{3-}$ stabilizing the adduct of the Py$_2$XPFe complex due to second-coordination sphere interactions.$^{[10]}$ In the presence of a proton

**Table 4.** Catalytic descriptors of Py$_2$XPFe with increasing Sc(OTf)$_3$ equivalents at 0.2 V/s in anhydrous MeCN under 1 atm CO$_2$ in MeCN/0.1 M Bu$_4$NPF$_6$ recorded at $\nu$ = 0.2 V/s.

| Sc$^{3+}$ equiv. | $i_{\text{cat}}$ [A] | $i_{\text{cat}}/i_p$ | $J$ [mA/cm$^2$] | $k_{\text{app}}$ [s$^{-1}$] | Log[TOF$_{\text{max}}$] |
|-----------------|-------------------|-----------------|----------------|----------------|----------------|
| 0               | $-1.3 \times 10^{-4}$ | 1.8             | 7.1            | $2.0 \times 10^7$ | 1.3            |
| 0.2             | $-1.5 \times 10^{-4}$ | 2.1             | 8.4            | $2.7 \times 10^7$ | 1.4            |
| 0.4             | $-1.9 \times 10^{-4}$ | 2.7             | 10.8           | $4.5 \times 10^7$ | 1.7            |
| 0.8             | $-2.9 \times 10^{-4}$ | 4.2             | 16.4           | $1.0 \times 10^8$ | 2.0            |
| 1.0             | $-3.9 \times 10^{-4}$ | 5.5             | 21.5           | $1.8 \times 10^8$ | 2.3            |
| 1.2             | $-4.0 \times 10^{-4}$ | 5.6             | 22.1           | $1.9 \times 10^8$ | 2.3            |
| 1.4             | $-3.6 \times 10^{-4}$ | 5.1             | 20.2           | $1.6 \times 10^8$ | 2.2            |

$^[a]$ Approximated from the S-shaped wave equation, reported in s$^{-1}$.

Figure 10. Resonance Raman spectrum of Py$_2$XPFe in neat MeCN at 405 nm excitation before and after the addition of 1.2 equivalents of Sc(OTf)$_3$.

Scheme 2. Proposed CO$_2$ reduction mechanism catalyzed by Py$_2$XPFe (mesityl groups on the porphyrin ligand have been omitted for clarity).
source, the \([\text{Fe}(\eta^1\text{-CO}^\cdot)^\pm]^-\) species is prone to generate the singly protonated anion \([\text{Fe}(\text{CO})\text{H}]^-\). This protonation is likely a concerted proton-coupled electron transfer event\(^{[44]}\) and constitutes the rate determining step of the reaction, as the reaction is first order or pseudo-first order with respect to \(\text{H}^+\) (from \(k_{\text{app}}\)) at the concentrations investigated. This again suggests the \(k_{\text{app-FOA}}\) defines a global rate constant for the overall reduction reaction rather than \(k_i\) or \(k_{\text{app}}\), as the rate constants calculated with the FOWA method are influenced by an increase in proton concentration and are closer to second order with respect to the proton concentration. The \([\text{Fe}(\text{CO})\text{H}]^-\) adduct is stabilized by hydrogen bonding from pyridine substituents of the hanging group, resulting in a cooperative effect and improvement in catalysis compared to that of the unsubstituted TMPFe. The pyridine substituents are suggested to increase the local concentration of the added acid by fortuitous generation of a hydrogen bonding network. A subsequent (second) protonation event takes places to generate the doubly protonated adduct, after which \(\text{H}_2\text{O}\) is lost to form the \([\text{Fe}^\text{II}\text{CO}]^-\) neutral species. In the presence of \(\text{Sc}^{3+}\), the pyridine substituents likely act to coordinate the \(\text{Sc}^{3+}\) ion and stabilize a \([\text{Fe}(\eta^1\text{-CO}^\cdot)^\pm\text{M}]^2^-\) type-species. After protonation of the \([\text{Fe}(\eta^1\text{-CO}^\cdot)^\pm\text{M}]^2^-\) adduct from adventitious water present in the electrochemical reaction mixture, \(\text{H}_2\text{O}\) is lost to generate the \([\text{Fe}^\text{II}\text{CO}]^-\) neutral species. The exact rate of the \(\text{Sc}^{3+}\) within the catalytic cycle is still uncertain and will be the point of investigation of future work.

In either scenario, the resulting \([\text{Fe}^\text{II}\text{CO}]^-\) neutral species is then reduced homogenously to the \([\text{Fe}^\text{II}\text{CO}]^-\) complex, mediated by a comproportionation reaction with a \([\text{Py}_2\text{XPF}^\text{II}]^2^-\) molecule in solution resulting in CO dissociation and re-generation of the pre-catalyst \([\text{Py}_2\text{XPF}]^-\). The CO dissociation however can be considered somewhat reversible, as the re-oxidation of the \([\text{Fe}^\text{II}\text{CO}]^-\) to \([\text{Fe}^\text{II}\text{CO}]^-\) is observed electrochemically on the CV timescale (Figure S12). It should be noted however that the exact oxidation states of the \([\text{Fe}]\) complex throughout the catalytic mechanism are probably more nuanced than denoted here numerically, as more in-depth theoretical analysis of such systems has shown much of the electron density may reside on the porphyrin ligand throughout catalysis.\(^{[10]}\)

### Conclusion

The \([\text{Py}_2\text{XPF}]^-\) complex shows a larger rate of catalysis for the reduction of \(\text{CO}_2\) to \(\text{CO}\) \((k_{\text{app-FOA}})\) when compared to its unfunctionalized structural analog TMPFe in neat anhydrous MeCN as well as in the presence of weak Brønsted acids. This enhancement likely stems from the hydrogen bonding interactions of the pyridine substituents aiding in the transfer of protons to the one electron reduced \(\text{CO}_2\) adduct \([\text{Fe}(\eta^1\text{-CO}^\cdot)^\pm\text{M}]^2^-\) or stabilization of the singly protonated intermediate \([\text{Fe}(\text{CO})\text{H}]^-\). The rate of \(\text{CO}_2\) reduction mediated by the \([\text{Py}_2\text{XPF}]^-\) complex was calculated with FOWA to be as fast as \(2.1 \times 10^8 \text{ s}^{-1}\) at 128 mM phenol concentrations compared to \(1.7 \times 10^7 \text{ s}^{-1}\) in the absence of a proton source in anhydrous MeCN. This significant increase in rate upon addition of small amounts (< 0.2 M) of Bronsted acids has only rarely been observed and is much more pronounced in MeCN than in DMF.\(^{[22]}\) Catalytic enhancement observed by the \([\text{Py}_2\text{XPF}]^-\) compared with its counterpart TMPFe underlines the utility of the hanging group to improve catalysis. Here, we utilized a hydrogen bond acceptor functionality in contrast to the more widely used proton donor functionalities, such as phenolic or amide substituents. The pyridine-based hanging group also acts as a second coordination sphere for Lewis acidic \(\text{Sc}^{3+}\); the addition of which results in an increase in current density for the \(\text{CO}_2\) reduction reaction facilitated by the \([\text{Py}_2\text{XPF}]^-\) complex. In general, the rate constants \((k_{\text{app}})\) and equilibrium constants \((K_{\text{CO2}})\) for the electrocatalytic reduction of \(\text{CO}_2\) to \(\text{CO}\) promoted by both \([\text{Py}_2\text{XPF}]^-\) and TMPFe in MeCN are substantially higher than other iron porphyrin systems reported in DMF.\(^{[14,15]}\) The differences between the reactivity in DMF compared with MeCN is still not completely understood, partly due to insolubility of iron porphyrins, such as TPPFe (TPP = 5, 10, 15, 20-tetraphenylporphyrin) in MeCN. Further investigations into this reactivity difference are currently under investigation as well as the introduction of different Lewis acidic metal ions into the bispyridylamine moiety.

### Experimental Section

All chemicals were purchased from commercial suppliers (e.g. Sigma-Aldrich, VWR, Acros Organics or ABCR) and, unless otherwise noted, used as received. Metalloligand \([\text{Py}_2\text{XPF}]^\text{II}\) was synthesized according to a recently published procedure.\(^{[5]}\) Solvents were purified and dried according to standard procedures or directly taken from a MBraun solvent purification system (e.g. THF, acetonitrile or toluene). Unless otherwise stated, all reactions which are sensitive towards air or moisture were carried out under dry argon by using Schlenk techniques. For thin layer chromatography (TLC) TLC Silicagel 60 F254 plates from Merck were used. Column chromatography was performed with silica gel purchased from Acros Organics (Silica Gel 60, 0.035–0.070 mm).

NMR spectra were recorded on a Bruker Avance I 400 or Avance II 300 at 293 K and processed with the software TopSpin or MestReNova (Version 12.0.0). The chemical shifts \(\delta\) are reported in parts per million (ppm). 1H and 13C NMR shifts are referenced according to the applied deuterated solvent as internal standard. Coupling constants \(\text{J}\) are presented as absolute values in Hz, without considering the kind of the coupling. For the characterization of the NMR signals the following abbreviations are used: \(s = \text{singlet}\), \(d = \text{doublet}\), \(t = \text{triplet}\), \(q = \text{quartet}\), \(m = \text{multiplet}\), \(dd = \text{doublet of doublets}\) and \(br = \text{broad}\). Signal assignment was possible by using different 2D NMR techniques, such as COSY, HSQC, HMBC and NOESY. All of these experiments were measured using standard Bruker pulse sequences and parameters.

Elemental analysis was performed by the microanalytical laboratory of the institute of chemistry at the Humboldt-Universität zu Berlin using a HEKAttech EURO 3000.

Mass spectrometry. High resolution mass spectra were measured using electrospray ionization (ESI) on a Thermo Finnigan LTQ FT instrument or an Agilent Technologies 6210 TOF in the positive as well as negative mode. MS values are given as m/z.

X-Ray crystallographic data collection was performed with a Bruker D8 Venture area detector with Mo–Kα radiation (\(\lambda = 0.71073\) Å).
Multi-scan absorption corrections implemented in Sadabs[43] were applied to the data. The structure was solved by intrinsic phasing method (Sheldrick-2014)[44] and refined by full matrix least square procedures based on \( F^2 \) with all measured reflections (Sheldrick-2018)[44–46] with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model.

CCDC number 2077924 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Steady-state absorption spectroscopy. Steady-state UV/vis absorption spectra were recorded with a Cary 100 UV/Vis-NIR spectrometer. All samples were measured in solution in a standard 10 mm fluorescence quartz glass cuvette.

Resonance Raman spectroscopy was conducted using a confocal Raman microscope (S&I Monovista CRS+) with laser excitation by a Topctica Top mode single frequency 405 nm diode laser. The laser was aligned and then focused on the sample using a Nikon 10 × objective at a laser power of 1.2 mW. Spectra were calibrated with respect to mercury lines and the Raman spectrum of toluene.

Electrochemistry: Electrochemical experiments were conducted using an Ivium Vertex One EIS potentiostat with Ivium electrolytical software. Experiments were performed in 0.1 M TBAPF\(_6\) in 5 mL of acetonitrile with 1 mM catalyst unless otherwise stated. Ferrocene (~1 mM) was used as an internal standard through all scans and oriented at 0 V throughout data analysis. A custom-made electrochemical cell was constructed using a 20 mL scintillation vial and rubber-sealed Teflon top, with fittings designed for 3 mm diameter glasses. Argon and CO\(_2\) gas was first purged through a Drierite column, with CO\(_2\) gas subsequently bubbled through their own gas for at least 5 minutes and kept under a blanket of the respective gas throughout the course of the data collection. The counter electrode and an Ag/AgCl wire was used as a pseudo-reference electrode, with all E values reported against the Fe/C couple. CO\(_2\) gas was first purged through a Drierite column, with both argon and CO\(_2\) gas subsequently bubbled through their own sealed bubbler apparatus containing acetonitrile and activated 3 Å molecular sieves to prevent solvent loss through sparging of the electrochemical cell. Electrochemical solutions were sparged with either argon or CO\(_2\) gas for at least 5 minutes and kept under a blanket of the respective gas throughout the course of the data collection. Ommic drop of the cell was compensated for using the Ivium software iR compensation tool, resulting in ferrocene peak-peak separation of approximately 63–73 mV depending on the experiment correlating to an 80–90% correction of the measured resistance.

HR ESI-MS in m/z ([M + H\(^+\)]\(^{+}\)): found 1064.5947, calc. for \( \text{C}_{39}\text{H}_{35}\text{N}_{10}\text{O}_{3} \): 1064.5949.

EA: found C: 81.87 H: 7.01 N: 9.20; calc. for \( \text{C}_{39}\text{H}_{35}\text{N}_{10}\text{O}_{3} \): 82.87 H: 6.91 N: 9.21.

Synthesis of the Py\(\text{XPFeCl} \): Following known procedures[27] the ligand Py\(\text{XP} \) (59 mg, 0.055 mmol) and FeCl\(_3\) (28 mg, 0.22 mmol) were dissolved in 15 mL dry DMF and heated at 110°C overnight. After cooling, 0.1 mL of a 1 M hydrochloric acid solution was added and stirred for one hour at room temperature. The precipitate was collected and washed with water. The crude product was taken up in 15 mL CH\(_3\)Cl and 10 mL of a saturated aqueous EDTA solution was added, followed by stirring for 20 hours at room temperature. Then, the organic phase was separated, washed first with aqueous 5% NaHCO\(_3\) solution and then with water and dried over sodium sulfate. After removal of the drying agent and the solvent, the product was purified by column chromatography on silica starting with ethylacetate:CH\(_3\)Cl: 1:1 to recover some of the porphyrinic starting material. Changing the eluent to CH\(_3\)Cl:methanol:CH\(_3\)Cl: 95:5 and then 9:1 gives, after evaporation, the product that is taken up in 30 mL CH\(_3\)Cl and washed once with 1 M HCl and twice with water. Removal of the organic solvent leads to the isolation of Py\(\text{XPFeCl} \) as dark brown solid (50 mg, 79% yield).

HR ESI-MS m/z ([M + H\(^+\)]\(^{+}\)): found 1153.4858, calc. for \( \text{C}_{39}\text{H}_{35}\text{FeN}_{10}\text{O}_{3} \): 1153.4831; ([M–Cl\(^-\)]\(^{+}\)): found 1053.4858, calc. for \( \text{C}_{39}\text{H}_{35}\text{FeN}_{10}\text{O}_{3} \): 1053.4831.

EA: found C: 76.23 H: 6.57N: 8.01; calc. for \( \text{C}_{39}\text{H}_{35}\text{FeN}_{10}\text{O}_{3} \): 76.00 H: 6.20 N: 8.50.

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Conflict of Interest

The authors declare no conflict of interest.
