Electrocatalytic CO$_2$ reduction at low overpotentials using iron(III) tetra(meso-thienyl)porphyrins

Josh D. B. Koenig, Janina Willkomm, Roland Roesler, Warren E. Piers, and Gregory C. Welch* 

Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, Alberta, T2N 1N4, Canada.

* Corresponding Author  
Email: gregory.welch@ucalgary.ca  
Phone Number: 1-403-210-7603

Abstract

The optical and electrochemical properties, as well as the CO$_2$ reduction capability of two different iron(III) thienyl-porphyrins, iron(III) tetra(meso-thien-2-yl)porphyrin (FeTThP) and iron(III) tetra(meso-5-methylthien-2-yl)porphyrin (FeTThMeP), are directly compared to those of iron(III) tetra(meso-phenyl)porphyrin (FeTPP). Through exploitation of mesomeric stabilization effects, FeTThP and FeTThMeP both reduced CO$_2$ to CO with comparable faradaic efficiencies and TON$_{CO}$ relative to FeTPP, with an overpotential 150 mV lower than the benchmark catalyst.
Introduction

The link between increased atmospheric CO$_2$-levels and climate change has inspired a variety of emission mitigation efforts.$^{[1,2]}$ To date, one of the more promising options for CO$_2$ removal is chemical feed-stocking, whereby CO$_2$ is electrochemically converted into value-added products.$^{[3–6]}$ One of the major issues with CO$_2$ conversion is the notoriously energy-intensive single electron reduction required for molecular activation, whereby CO$_2$ undergoes a kinetically unfavourable geometric rearrangement from linear to bent.$^{[7–9]}$ For this single-electron reduction of CO$_2$ to proceed, a high-energy electronic driving force is required. On the other hand, this high energy input for CO$_2$ reduction can be dramatically decreased by exploiting proton-coupled multi-electron chemical reductions.$^{[10]}$

Metal surfaces, nanoparticles, and alloys have all been used for proton-coupled multi-electron CO$_2$ reductions.$^{[11–13]}$ However, these electrocatalysts are frequently plagued by several drawbacks. Foremost, system efficiencies can be hindered by competitive surface processes such as dihydrogen (H$_2$) evolution.$^{[13,14]}$ Furthermore, these surfaces inherently lack the ability to control electron flow and surface-proximal protons.$^{[15,16]}$ Consequently, a variety of CO$_2$ reduction products (such as HCOO$^-$, CO, CH$_3$OH, and CH$_4$) can be simultaneously generated within a narrow redox window. Thus, to enhance system efficiency and product selectivity, molecular catalysts can be employed to mediate these electron-transfer processes.

Since the first reported molecular CO$_2$ reduction catalyst,$^{[17]}$ a variety of homogeneous catalyst classes have been developed to effectively enhance catalytic efficiency and product selectivity.$^{[18]}$ To date, some of the best CO$_2$ reduction catalysts are based on the iron(III) tetra(meso-phenyl)porphyrin (FeTPP) framework first reported by Savéant and co-workers.$^{[19–27]}$ By itself,
**FeTPP** was only capable of several CO₂ reduction cycles before it degraded through ring-saturation processes, such as carboxylation or hydrogenation. The catalytic activity of FeTPP can be enhanced upon the addition of either weak Lewis acids and/or weak Brønsted acids to the bulk solution. Moreover, the functionalization of the porphyrin’s *meso*-phenyl substituents can also improve catalytic performance. For example, the incorporation of positively-charged trimethylammonium-groups was found to not only stabilize the CO₂-bound intermediate, but their electron-withdrawing nature decreased the energy level of the lowest unoccupied molecular orbital (LUMO). By stabilizing the LUMO energy level, the molecule’s reduction potential was diminished, thus allowing CO₂ reduction to be achieved at lower overpotentials.

Another common method for stabilizing the LUMO energy level of a molecule is through extension of π-conjugation. Since the phenyl-substituents of TPP-derived catalysts lie out-of-plane with respect to the porphyrin-core, π-conjugation cannot be effectively extended across the molecule. However, molecular planarity can be encouraged by introducing smaller heterocycles at the *meso*-position of the porphyrin, such as thiophene. Remarkably, the LUMO-stabilizing resonance effects gained through extending π-conjugation in these thienyl-porphyrins appears to overcome the potentially detrimental LUMO destabilizing inductive effects associated with thiophene being more electron-rich than the phenyl groups. To the best of our knowledge, these synthetically diverse and potentially high-performing thienyl-porphyrins have yet to be explored as potential CO₂ reduction catalysts. Herein, we directly compare the optical and electronic properties, as well as the electrocatalytic CO₂ reduction proficiencies of two iron(III) thienyl-porphyrins, namely iron(III) tetra(*meso*-thien-2-yl)porphyrin chloride (FeTThP) and iron(III) tetra(*meso*-5-methylthien-2-yl)porphyrin chloride (FeTThMeP), relative to a benchmark compound, iron(III) tetra(*meso*-phenyl)porphyrin chloride (FeTPP).
Results and Discussion

The porphyrin frameworks of tetra(meso-phenyl)porphyrin (TPP), tetra(meso-thien-2-yl)porphyrin (TThP), and tetra(meso-5-methylthien-2-yl)porphyrin (TThMeP), were synthesized following literature procedure (see electronic supplementary information, ESI, pp. S4-S6). The identity of each porphyrin was confirmed by $^1$H-NMR spectroscopy and high-resolution MALDI-TOF mass spectrometry (Figures S1-S6 in ESI). The UV-Visible absorption spectra and cyclic voltammetry (CV) of these compounds were used to probe the optical and electrochemical properties. Regarding the optical properties of TPP (Figure S14), the Soret band wavelength of maximum absorption ($\lambda_{\text{max}}$) and the Q-band onset of absorption ($\lambda_{\text{Q1}}$) were observed at 417 nm and 644 nm, respectively. Relative to TPP, both optical absorption spectra of TThP ($\lambda_{\text{max}} = 426$ nm, $\lambda_{\text{Q1}} = 656$ nm) and TThMeP ($\lambda_{\text{max}} = 431$ nm, $\lambda_{\text{Q1}} = 662$ nm) have undergone a bathochromic shift. The origin of this red-shift may be attributed to either: i) LUMO stabilizing mesomeric effects caused by the meso-thienyl groups adopting a more co-planar arrangement; or ii) highest occupied molecular orbital (HOMO) destabilizing inductive effects caused by thiophene being more electron-donating than phenyl. CV analyses (Figure S15) revealed that the first oxidation events of TThP and TThMeP ($E_{1/2} = 0.41$ V and 0.28 V vs. Fc$^{+/0}$, respectively) have cathodically shifted relative to TPP ($E_{1/2} = 0.53$ V). The oxidation potential of TThMeP experienced the greatest cathodic shift, indicating that thienyl-porphyrins are susceptible to functional-group inductive effects. With respect to the reductions, TThP and TThMeP exhibited two identical reversible redox events (at $E_{1/2} = -1.59$ V and -1.94 V), both of which have anodically shifted relative to TPP ($E_{1/2} = -1.72$ V and -2.05 V). We therefore rationalized that the mesomeric effects overcome any inductive effects associated with the electron-rich thienyl moiety, thereby leading to LUMO stabilization and more facile reduction of the molecule.
Next, TPP was iron-metalated following literature procedure to afford FeTPP. The identity of FeTPP was confirmed by $^1$H-NMR spectroscopy, high-resolution MALDI-TOF mass spectrometry, CHN elemental analysis, UV-Vis absorption spectroscopy and CV (Figures S7, S8, and S13-S15). The same literature procedure was adapted to iron-metalate TThP and TThMeP, affording the previously unreported complexes FeTThP and FeTThMeP (see ESI pp. S8-S9). Despite the $^1$H-NMR spectra of FeTThP and FeTThMeP (Figures S9 and S11, respectively) being convoluted by the paramagnetic Fe$^{III}$ metal-center, both compounds displayed similar broad peak spectroscopic properties like FeTPP. Mass spectrometry of all three iron(III) porphyrins detected the [M-Cl]$^+$ peak, highlighting the lability of the axial chloride ligand. Compared to free-base TPP, the optical spectrum of FeTPP maintained its Soret band ($\lambda_{\text{max}} = 417$ nm), while the spectral fine-structure associated with the Q-bands (>500 nm) was greatly diminished and a new high-energy ICT-band ($\lambda_{\text{ict}}$) emerged at 376 nm (Figure 1). These same optical property
changes were also observed with both FeTThP ($\lambda_{\text{max}} = 425 \text{ nm}$, $\lambda_{\text{ict}} = 381 \text{ nm}$) and FeTThMeP ($\lambda_{\text{max}} = 431 \text{ nm}$, $\lambda_{\text{ict}} = 383 \text{ nm}$). The CV-determined electrochemical properties of FeTPP revealed three reversible redox events at $E_{1/2} = -0.68 \text{ V}$, -1.52 V, and -2.18 V. Comparable reversible redox events were observed for FeTThP and FeTThMeP ($E_{1/2} \approx -0.61 \text{ V}$, -1.47 V, and -2.03 V), but each event was anodically shifted relative to FeTPP. Crucially, the third reduction event of FeTThP and FeTThMeP (characteristic of CO$_2$ reduction onset)$^{[19-27]}$ has anodically shifted with respect to FeTPP by $\sim 150 \text{ mV}$, meaning CO$_2$ reduction can be performed using lower overpotentials ($\eta$).

**Figure 2.** CVs of FeTPP (A), FeTThP (B), and FeTThMeP (C) comparing catalytic current enhancement under CO$_2$ as a function of TFE concentration. All CV scans were recorded at 100 mV/s, with samples containing 1 mM catalyst and 0.1 M TBAPF$_6$ in CO$_2$-saturated DMF.

The CO$_2$ reduction capabilities of FeTThP and FeTThMeP were examined electrochemically (see ESI pp. S2-S3 for full experimental details). Under an atmosphere of CO$_2$, all three iron(III) porphyrins displayed only moderate current enhancement near the third reduction wave (at $E_{1/2} = -2.18 \text{ V}$ or -2.03 V vs. Fe$^{+/0}$). To enhance the catalytic activity, weak Brønsted acids such as water, phenol, and 2,2,2-trifluoroethanol (pKa = 31.5, 18.8, and 24.0, respectively)$^{[37]}$ were tested as viable proton sources (Figure S16). The proton source concentration was increased incrementally until a current plateau was observed (Figure 2). For all three catalysts, water provided only minor
current enhancement, while phenol and 2,2,2-trifluoroethanol (TFE) both caused significant current enhancements. Ultimately, TFE was chosen as the proton source for all subsequent tests because it induced the greatest current enhancement for all three catalysts.

The catalytic rate constants (k_cat) for FeTPP, FeTThP, and FeTThMeP were extracted using the plateau peak current under CO_2 with TFE-added (i_cat), relative to the peak current of the non-catalytic redox process under argon (i_p).[25,38] Determination of k_cat allowed the intrinsic CO_2 reduction catalysis properties of each catalyst to be directly compared using a catalytic Tafel plot (Figure 3A). Analyzing the k_cat and the catalytic Tafel plot emphasized two important features about FeTThP and FeTThMeP relative to FeTPP. First, the k_cat of FeTPP (8200 s\(^{-1}\)) was calculated to be slightly higher than those of FeTThP (6100 s\(^{-1}\)) and FeTThMeP (2800 s\(^{-1}\)) at large applied overpotentials. However, this undesirable decrease in k_cat has been frequently observed with compounds that exhibit lower reduction potentials.[25,39] Second, these thienyl-porphyrins can achieve significantly higher TOFs at lower applied overpotentials, suggesting that FeTThP and FeTThMeP can perform efficient CO_2 reduction with less energy input than FeTPP.

Figure 3. Catalytic Tafel Plot (A) comparing the intrinsic catalytic properties of FeTPP (red), FeTThP (purple), and FeTThMeP (blue). The average TON\(_{\text{CO}}\) (B) and Faradaic Efficiencies (C) obtained from the replicate controlled potential electrolysis experiments of each catalyst in the one-compartment cell (dashed lines) and two-compartment cell (solid lines).
To confirm this notion, the controlled potential electrolysis (CPE) of FeTPP, FeTThP, and FeTThMeP were performed in DMF using TFE as a proton source (Figure 3B and 3C). Catalytic performance was benchmarked with replicate trials of FeTPP (at E_{1/2} = -2.18 V vs. Fc^{+/0}). In the one-compartment cell, using a standard three-electrode setup (Figure S20A), FeTPP achieved a maximum Faradaic efficiency (F.E.) of 95 ± 4 %, with CO being the major product observed by GC over the 5-hour test period. The total turnover number of CO (TON_CO) for FeTPP was 40 ± 5, which is similar to the performance previously reported by Savéant and co-workers.[22] Any performance differences can most likely be attributed to the use of glassy carbon plate working electrode rather than a Hg-pool electrode.[40,41]

With an acceptable benchmark F.E. and TON_Co in hand, the CPE of FeTThP and FeTThMeP were also performed in the one-compartment cell (both at E_{1/2} = -2.03 V vs. Fc^{+/0}). Under these conditions, FeTThP was able to reduce CO_2 with a similar F.E. as FeTPP (92 ± 4 %), but only achieved a TON_Co of 10 ± 1. The catalyst was observed to decompose and precipitate out of the bulk solution over the course of the CPE trials. FeTThP degradation most likely resulted from the thiophene-substituents undergoing oxidative electropolymerization at the counter electrode.[42] This hypothesis was supported by the noticeable loss in reversibility of TThP’s oxidation event when the porphyrin framework was over-oxidized (Figure S17). While oxidative electropolymerization may be detrimental to solution-based CPE, it is possible to envision this process being used advantageously for electrode surface immobilization of the catalyst.[43] On the other hand, FeTThMeP performed CO_2 reduction with excellent F.E. (94 ± 9 %), and relative to FeTThP, the TON_Co of FeTThMeP increased three-fold (29 ± 4). This performance enhancement was likely caused by blocking thiophene’s highly reactive 5-position with a methyl group and successfully preventing these destructive oxidative electropolymerization processes.
Oxidative electropolymerization could also be avoided by performing CPE experiments in a two-compartment cell, whereby the counter electrode was placed in a compartment separated by a fine frit from the working and reference electrodes (Figure S20B). FeTPP was once again tested as the benchmark, obtaining a F.E. of 60 ± 7% and a TON_{CO} of 23 ± 2 after replicate 5-hour experiments (where the only gaseous product detected was CO). Now that FeTThP was no longer prone to decomposition during the 5-hour CPE tests in the two-compartment cell, it achieved a F.E. of 54 ± 1% and a TON_{CO} of 17 ± 1. FeTThMeP produced similar amounts of CO as FeTThP (TON_{CO} = 17 ± 3), while reaching a higher F.E. (63 ± 8%). Both thienyl-porphyrins, therefore, reduced CO_{2} to CO with a comparable F.E. and TON_{CO} relative to FeTPP, all while using an overpotential 150 mV lower than the benchmark catalyst. To confirm the catalyst, TFE, and CO_{2} were all necessary for CO_{2} reduction, control experiments omitting any one component were found to produce H_{2} as the major product, with only baseline levels of CO detected (Table S1).

**Conclusion**

In summary, we have introduced a pair of new catalysts for CO_{2} reduction based on thienyl-porphyrins. Compared to phenyl-derived porphyrins, incorporating the smaller thiophene heterocycle has resulted in effective extension of π-conjugation, leading to stabilization of the LUMO energy level. This allowed FeTThP and FeTThMeP to achieve CO_{2} reduction performance comparable to FeTPP, but at a much lower overpotential. Functionalization of the 5-postion of thiophene effectively prevented any thienyl-based oxidative electropolymerization processes, which resulted in a three-fold increase in CO_{2} reduction performance. The synthetic-diversity of thiophene provides facile chemistry through which redox properties can be altered to further improve CO_{2} reduction performance. Efforts towards derivatization of the thienyl-
porphyrin framework, as well as the surface immobilization of FeTThP, are currently ongoing in our lab.

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References

Electrocatalytic CO$_2$ reduction at low overpotentials using iron(III) tetra(meso-thienyl)porphyrins

(Supporting Information)

Josh D. B. Koenig, Janina Willkomm, Roland Roesler, Warren E. Piers, and Gregory C. Welch$^{a,*}$

$^a$ Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, Alberta, T2N 1N4, Canada.

* Corresponding Author
Email: gregory.welch@ucalgary.ca
Phone Number: 1-403-210-7603

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1. Methods and Materials

Materials: All reactants, reagents, and catalysts were purchased from Sigma-Aldrich or VWR and used without further purification.

High-resolution MALDI-TOF (HR MALDI-TOF): All high-resolution MALDI-TOF mass spectrometry measurements were performed courtesy of Jian Jun (Johnson) Li in the Chemical Instrumentation Facility at the University of Calgary. The sample solution (~ 1 µg/ml in dichloromethane) was mixed with matrix trans2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) solution (~5 mg/ml in methanol). All spectra were acquired using a Bruker Autoflex III Smartbeam MALDI-TOF, set to the positive reflective mode (Na:YAG 355 nm laser settings: laser offset = 62-69; laser frequency = 200Hz; and number of shots = 300). The target used was Bruker MTP 384 ground steel plate target.

Nuclear Magnetic Resonance (NMR): All 1H NMR spectroscopy spectra were recorded using a Bruker Avance-500 MHz spectrometer at 295 K. All experiments were performed in deuterated chloroform (CDCl3) and chemical shifts (referenced to residual CHCl3) are reported in parts per million (ppm). Multiplicities are reported as follows: singlet (s), doublets (d), triplets (t), doublet of doublets (dd), and multiplets (m). No 13C-NMR spectra were recorded for the iron(III)-metalated porphyrins due to their paramagnetic properties.

CHN Elemental Analysis: All elemental analyses were performed by Johnson Li in the Chemical Instrumentation Facility at the University of Calgary. A Perkin Elmer 2400 Series II CHN Elemental Analyzer was used to obtain CHN data, using ~1.5 mg of sample (with particle sizes ranging between 0.2 and 0.5 mm in diameter).

UV-Visible Spectroscopy (UV-Vis): All optical absorption measurements were performed using Agilent Technologies Cary 60 UV-Vis spectrometer at room temperature. All solution UV-Vis spectra were measured with 2 mm quartz cuvettes, using either dichloromethane (DCM) or N,N-dimethylformamide (DMF) as solvent. Stock solutions (1.0 mg/mL) of each compound were prepared, serially diluted, and then used to construct calibration curves for determining molar absorptivity.

Cyclic Voltammetry (CV): All electrochemical measurements were performed using a CH Instruments Inc. Model 1200B Series Handheld Potentiostat. A standard 3-electrode setup was utilized, consisting of a freshly polished glassy carbon disk working electrode (WE), Pt-wire counter electrode (CE), and Ag-wire pseudo-reference electrode (RE). All measurements were referenced to a ferrocene (Fc+/0) as internal standard. All cyclic voltammetry experiments were performed at a scan rate of 100 mV/s. Sample solutions, with 1 mM compound and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) supporting electrolyte, were prepared in either anhydrous DCM or DMF. All electrochemical solutions were sparged with dry gas (either N2, Argon, or CO2) for 15 minutes prior to measurements.
Catalytic Tafel Plot: All experiments were performed using the same electrochemical setup previously described for CV (i.e. WE = glassy carbon disk, CE = Pt-wire, RE = Ag-wire). All CV scans were recorded at 100 mV/s, using DMF solutions comprised of 1 mM catalyst and 0.1 M TBAPF$_6$. The impact of proton source concentration on catalytic current enhancement was tested using three weak acids (namely water, phenol, and 2,2,2-trifluoroethanol). Two initial measurements were run, the first under argon and the second after the solution was sparged with CO$_2$. To the CO$_2$-saturated sample, the specified proton-source was added incrementally until a maximal current enhancement was achieved. To ensure system reversibility, one final CV was recorded after the sample was thoroughly purged with argon.

Using these current enhancement CVs, the catalytic rate constants ($k_{\text{cat}}$) for each compound was extracted using: i) the plateau peak current under CO$_2$ with proton source added ($i_{\text{cat}}$); and ii) the peak current of the non-catalytic redox process under argon ($i_p$). The catalytic Tafel plot was therefore constructed using equation (1):

$$\text{TOF} = \frac{\text{TOF}_{\text{max}}}{\left( 1 + \exp \left( \frac{F}{RT} \left( E^0_{\text{tr}} - E^0_{\text{cat}} \right) \right) \right) \times \exp \left( - \frac{F}{RT} \eta \right)}$$

where $E^0_{\text{tr}}$: standard potential of CO$_2$/CO in DMF (-0.73 V vs. Fe$^{+}/0$); $E^0_{\text{cat}}$: catalyst standard potential of $E_{1/2}$ at R3; $\eta$: overpotential ($E^0_{\text{tr}} - E_{\text{electrode}}$); F: Faraday constant; R: Gas constant; T: temperature; and TOF$_{\text{max}}$: $k_{\text{cat}}$.

Controlled Potential Electrolysis (CPE): All CPE experiments were performed with a one-compartment heart-shaped flask or a customized two-compartment H-shaped cell, using a Princeton Applied Research VersaSTAT 3 potentiostat. A glassy carbon plate (20 mm x 8 mm x 2 mm) was used as the working electrode, along with a Pt-mesh counter electrode and a non-aqueous Ag/AgCl reference electrode. For experiments using the one-compartment flask, a single DMF solution containing 0.5 mM catalyst + 0.1 M TBAPF$_6$ + TFE was used. For experiments using the two-compartment cell, two solutions were prepared: an active solution (0.5 mM catalyst + 0.1 M TBAPF$_6$ + TFE), and a blank solution (0.1 M TBAPF$_6$ + TFE). The glassy carbon plate working electrode and reference electrode were immersed in the active solution in the cathodic compartment, while the counter electrode was immersed in the blank solution in the anodic compartment. The potentiostat, using the chronoamperometry setting, applied a constant voltage for the duration of testing. Small headspace aliquots (50 μL) were periodically removed from the flask/cell to analyze gaseous product distribution. Gas chromatography (GC) headspace analysis was performed using an Agilent Technologies 7890B GC, equipped with a VICI pulsed discharge detector. The system was calibrated using a customized gas mixture, containing known concentrations of: H$_2$, CO, CH$_4$, and ethylene.
2. Synthetic/Experimental Procedures

**Tetra(meso-phenyl)porphyrin (TPP)**
TPP was synthesized using slightly modified literature procedure \(^4\).

![Chemical Structure of TPP]

Freshly distilled pyrrole (2.25 mL, 32.5 mmol, 1 eq.) was added dropwise to a solution containing benzaldehyde (3.30 mL, 32.5 mmol, 1 eq.) and DCM (450 mL). The flask was covered in aluminum foil, placed into an ice-bath, and sparged with N\(_2\) for 15 minutes. Subsequently, catalytic BF\(_3\)-OEt\(_2\) (0.40 mL, 3.3 mmol, 0.1 eq.) was added and the mixture was left to stir for 2 hours, while slowly warming to room temperature. P-chloranil (4.06 g, 16.3 mmol, 0.5 eq.) was added in one-portion, then left to stir for another 2 hours. Next, the mixture was passed through an inch-thick silica plug (using DCM as eluent) and solvent was removed using rotary evaporation. The crude mixture was subsequently purified using silica-gel column chromatography (3:1 DCM:hexanes). After removing solvent under reduced pressure, the isolated purple product was precipitated from MeOH and collected by vacuum filtration (0.86 g, 1.4 mmol, 18% yield).

\(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.85 (s, 8H), 8.28 – 8.13 (m, 8H), 7.79 – 7.74 (m, 12H), -2.78 (s, 2H)

HRMS ([M+H]\(^+\)) calculated for M = C\(_{44}\)H\(_{30}\)N\(_4\): 615.2543; detected [M+H]\(^+\): 615.2556

UV-Vis \(\lambda (M^1 cm\(^{-1}\))\) 417 nm (480000), 515 nm (19000), 549 nm (7900), 590 nm (5800), 644 nm (4300)
Tetra(meso-thien-2-yl)porphyrin (TThP)
TThP was synthesized using slightly modified literature procedure \[^5\].

![Chemical structure of TThP]

Freshly distilled pyrrole (2.15 mL, 31.3 mmol, 1 eq.) was added dropwise to a solution containing 2-thiophenecarboxaldehyde (2.90 mL, 31.3 mmol, 1 eq.) and DCM (500 mL). The flask was covered in aluminum foil, placed into an ice-bath, and sparged with N\(_2\) for 15 minutes. Next, catalytic BF\(_3\)•OEt\(_2\) (0.38 mL, 3.1 mmol, 0.1 eq.) was added and the mixture was left to stir for 3 hours, while slowly warming to room temperature. Once thin-layer chromatography (TLC) confirmed no further reaction progress, the mixture was heated in a bead bath. To the refluxing mixture, p-chloranil (3.88g, 15.7 mmol, 0.5 eq.) was added in one portion. The mixture was left to stir at reflux for 2 hours. The crude mixture was poured through an inch-thick silica plug (using DCM as eluent) and solvent was subsequently removed using rotary evaporation. The resulting crude solid was purified by silica-gel column chromatography (gradient DCM:hexanes from 2:3 \(\rightarrow\) 9:1). After removing solvent under reduced pressure, the isolated purple solid was precipitated into MeOH and collected by vacuum filtration (0.41 g, 0.64 mmol, 8% yield).

\(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 9.05 (s, 8H), 7.93 (dd, \(J = 3.4\) Hz & 1.3 Hz, 4H), 7.87 (dd, \(J = 5.4\) Hz & 1.2 Hz, 4H), 7.52 (dd, \(J = 5.4\) Hz & 3.3 Hz, 4H), -2.64 (s, 2H)

HRMS ([M+H]\(^+\)) calculated for M = C\(_{36}\)H\(_{22}\)N\(_4\)S\(_4\): 639.0800; detected [M+H]\(^+\): 639.0779

UV-Vis \(\lambda\) (M\(^{-1}\) cm\(^{-1}\)) 426 nm (290000), 522 nm (14000), 560 nm (7300), 597 nm (5600), 656 nm (2500)
**Tetra(meso-5-methylthien-2-yl)porphyrin (TThMeP)**

TThMeP was synthesized using slightly modified literature procedure \[6\].

Freshly distilled pyrrole (3.86 g, 57.5 mmol, 1 eq.) and 5-methyl-2-thiophenecarboxaldehyde (7.25 g, 57.5 mmol, 1 eq.) were each dissolved in 50 mL of glacial acetic acid and placed in separate addition funnels. Both compounds were added dropwise over the course of 15 minutes to refluxing glacial acetic acid (200 mL). After addition was completed, the mixture was left to stir for 45 minutes, then cooled to room temperature. Solvent was removed under reduced pressure and the residual solid was collected by vacuum filtration (using MeOH). The resulting crude brown solid was dissolved in DCM, adhered to silica, and then purified by silica-gel column chromatography (gradient 1:1 CH\(_2\)Cl\(_2\):hexanes to CH\(_2\)Cl\(_2\) + 1% acetone). After removing solvent under reduced pressure, the isolated purple solid was precipitated into MeOH and collected by vacuum filtration (0.41 g, 0.59 mmol, 4% yield).

\(^1\)H-NMR (500 MHz, CDCl\(_3\)) \(\delta\) 9.10 (s, 8H), 7.68 (d, \(J = 3.3\) Hz, 4H), 7.16 (s, 4H), 2.83 (d, \(J = 1.1\) Hz, 12H), -2.63 (s, 2H)

HRMS ([M+H]\(^+\)) calculated for \(M = C_{40}H_{30}N_4S_4\): 695.1426; detected [M+H]\(^+\): 695.1408

UV-Vis \(\lambda (M^1 \text{ cm}^{-1})\) 431 nm (270000), 525 nm (12000), 567 nm (9000), 599 nm (5800), 662 nm (4600)
Iron(III) tetra(meso-phenyl)porphyrin chloride (FeTPP)
FeTPP was synthesized using slightly modified literature procedure \[7,8\].

TPP (316mg, 0.51 mmol, 1 eq.) and FeCl$_2$•4H$_2$O (121 mg, 0.61 mmol, 1.2 eq.) were combined in a glass pressure-tube, along with a stir-bar and anhydrous DMF (10 mL). The vessel was sealed, sparged with N$_2$ for 15 minutes, and then placed into a bead bath (170 °C). The mixture was left to stir at reflux for 4 hours, then slowly cooled to room temperature. The dark brown mixture was poured into water and the resulting solid was collected by vacuum filtration. This isolated solid was dissolved in DCM (30 mL) and transferred to a round-bottom flask. Some dilute 1 M HCl (20 mL) was added to the solution, then vigorously stirred overnight (14 hours) at room temperature. The contents of the flask were poured into a separatory funnel and the organic phase was washed with water (3 x 30 mL). The collected organic phase was dried over Na$_2$SO$_4$, filtered through a glass frit, and then solvent was removed by rotary evaporator. The crude solid was adhered to silica and purified by silica-gel column chromatography (CH$_2$Cl$_2$ + 1% acetone). After removing solvent under reduced pressure, the resulting dark purple solid was precipitated from water and collected by vacuum filtration (296 mg, 0.42 mmol, 86% yield).

$^1$H-NMR (500 MHz, CDCl$_3$) δ 80.7 (s), 13.5 (s), 12.3 (s), 7.8 – 7.6 (m), 6.4 (s), 5.1 (s)

HRMS ([M-Cl]$^+$) calculated for M = C$_{44}$H$_{28}$N$_4$FeCl: 668.1658; detected [M-Cl]$^+$: 668.1663

CHN Analysis Theoretical % C (75.07), H (4.01), N (7.96); found % C (75.82), H (4.24), N (7.94)

UV-Vis λ (M$^{-1}$ cm$^{-1}$) 376 nm (45000), 417 nm (86000), 509 nm (13000), 582 nm (5600)
Iron(III) tetra(meso-thien-2-yl)porphyrin chloride (FeTThP)

TThP (231 mg, 0.36 mmol, 1 eq.) and FeCl$_2$ • 4H$_2$O (288 mg, 1.45 mmol, 4 eq.) were combined in a glass pressure-tube, along with a stir-bar and anhydrous DMF (10 mL). The vessel was sealed, sparged with N$_2$ for 15 minutes, and then placed into a bead bath (170 °C). The mixture was left to stir at reflux overnight (14 hours), then slowly cooled to room temperature. The dark brown mixture was poured into water and the resulting solid was collected by vacuum filtration. This isolated solid was dissolved in DCM (60 mL) and transferred to a round-bottom flask. Some dilute 1 M HCl (40 mL) was added to the solution, then vigorously stirred for 24 hours at room temperature. The contents of the flask were poured into a separatory funnel and the organic phase was washed with water (3 x 30 mL). The collected organic phase was dried over Na$_2$SO$_4$, filtered through a glass frit, and then solvent was removed by rotary evaporator. The crude solid was adhered to silica and purified by silica-gel column chromatography (CH$_2$Cl$_2$ + 1% acetone). After removing solvent under reduced pressure, the resulting dark purple solid was precipitated from water and collected by vacuum filtration (231 mg, 0.32 mmol, 80% yield).

$^1$H-NMR (500 MHz, CDCl$_3$) $\delta$ 79.0 (s), 16.4 (s), 13.5 (d), 8.0 (s), 7.6 – 7.4 (m), 4.6 (s)

HRMS ([M-Cl]$^+$) calculated for M = C$_{36}$H$_{20}$N$_4$S$_4$FeCl: 691.9915; detected [M-Cl]$^+$: 691.9939

CHN Analysis Theoretical % C (59.39), H (2.77), N (7.69); found % C (60.23), H (2.91), N (7.59)

UV-Vis $\lambda$ (M$^{-1}$ cm$^{-1}$) 381 nm (38000), 425 nm (82000), 516 nm (11000), 593 nm (3700)
Iron(III) tetra(meso-5-methylthien-2-yl)porphyrin chloride (FeTThMeP)

TThMeP (249mg, 0.36 mmol, 1 eq.) and FeCl₂ • 4H₂O (429 mg, 2.16 mmol, 6 eq.) were combined in a glass pressure-tube, along with a stir-bar and anhydrous DMF (20 mL). The vessel was sealed, sparged with N₂ for 15 minutes, and then placed into a bead bath (170 ºC). The mixture was left to stir at reflux overnight (14 hours), then slowly cooled to room temperature. The dark brown mixture was poured into water and the resulting solid was collected by vacuum filtration. This isolated solid was dissolved in DCM (100 mL) and transferred to a round-bottom flask. Some dilute 1 M HCl (40 mL) was added to the solution, then vigorously stirred for 24 hours at room temperature. The contents of the flask were poured into a separatory funnel and the organic phase was washed with water (3 x 30 mL). The collected organic phase was dried over Na₂SO₄, filtered through a glass frit, and then solvent was removed by rotary evaporator. The crude solid was adhered to silica and purified by silica-gel column chromatography (CH₂Cl₂ + 1% acetone). After removing solvent under reduced pressure, the resulting dark purple solid was precipitated from water and collected by vacuum filtration (248 mg, 0.32 mmol, 88% yield).

¹H-NMR (500 MHz, CDCl₃) δ 79.6 (s), 12.7 (s), 7.7 (s), 3.5 (s)

HRMS ([M-Cl]⁺) calculated for M = C₄₀H₂₈N₄S₄FeCl: 748.0541; detected [M-Cl]⁺: 748.0521

CHN Analysis Theoretical % C (62.26), H (3.60), N (7.14); found % C (61.29), H (3.91), N (7.07)

UV-Vis λ (M⁻¹ cm⁻¹) 332 nm (26000), 383 nm (37000), 431 nm (84000), 522 nm (12000)
3. $^1$H-NMR Spectra and HS MALDI-TOF

Figure S1. $^1$H-NMR spectrum of TPP (500 MHz, CDCl$_3$).

Figure S2. HR MALDI-TOF MS of TPP.
**Figure S3.** $^1$H-NMR spectrum of TThP (500 MHz, CDCl$_3$).

**Figure S4.** HR MALDI-TOF MS of TThP.
Figure S5. $^1$H-NMR spectrum of TThMeP (500 MHz, CDCl$_3$).

Figure S6. HR MALDI-TOF MS of TThMeP.
Figure S7. $^1$H-NMR spectrum of FeTPP (500 MHz, CDCl$_3$).

Figure S8. HR MALDI-TOF MS of FeTPP.
**Figure S9.** $^1$H-NMR spectrum of FeTTThP (500 MHz, CDCl$_3$).

**Figure S10.** HR MALDI-TOF MS of FeTTThP.
Figure S11. $^1$H-NMR spectrum of FeTThMeP (500 MHz, CDCl$_3$).

Figure S12. HR MALDI-TOF MS of FeTThMeP.
4. CHN Elemental Analysis

![Table](image-url)

**Figure S13.** CHN elemental analyses of FeTPP, FeTThP, and FeTThMeP.
5. UV-Visible Spectroscopy

Figure S14. The UV-Visible absorption spectra of TPP (A), FeTPP (B), TThP (C), FeTThP (D), TThMeP (E) and FeTThMeP (F) in DCM.
6. Cyclic Voltammetry

Figure S15. Cyclic voltammograms of TPP (A), TThP (C), and TThMeP (E) in DCM, as well as FeTPP (B), FeTThP (D), and FeTThMeP (F) in DMF. TPP, TThP, and TThMeP were measured in DCM to observe oxidation events. FeTPP, FeTThP, and FeTThMeP were measured in DMF to accurately determine controlled potential electrolysis conditions.
Figure S16. Cyclic voltammograms of FeTPP, FeTThP, and FeTThMeP, comparing catalytic current enhancement under CO$_2$ as a function of proton source concentration for water (A, C, and E, respectively) and phenol (B, D, and F, respectively). All samples contained ~1 mM catalyst and 0.1 M TBAPF$_6$ in CO$_2$-saturated DMF. All CV scans were recorded at 100 mV/s.
Figure S17. Over-oxidizing TThP leads to irreversible oxidation events on the CV return sweep.
7. Controlled Potential Electrolysis

Figure S18. Controlled potential electrolysis (CPE) determined TON\textsubscript{CO} and faradaic efficiency for FeTPP (A and B, respectively), FeTThP (C and D, respectively), and FeTThMeP (E and F, respectively). Full experimental details of each trial are described in Table S1.
Figure S19. Averaged controlled potential electrolysis TON$_{\text{CO}}$ (A) and Faradaic efficiency (B) for FeTPP (red), FeTThP (purple), and FeTThMeP (light blue) in a two-compartment cell.

Figure S20. One-compartment heart-shaped flask (A) and two-compartment H-shaped cell (B) for CPE. The standard 3-electrode setup consisted of a glassy carbon plate working electrode (WE), Pt-mesh counter electrode (CE), and non-aqueous Ag/AgCl reference electrode (RE).
Table S1. Replicate controlled potential electrolyses of FeTPP, FeTThP and FeTThMeP. All experiments were completed in the specified cell type using 0.5 mM catalyst and 0.1 M TBAPF$_6$ in CO$_2$ saturated DMF, with 2 M TFE as a proton source. Turnovers of CO (TON$_{CO}$) were measured by GC and calculated based on bulk catalyst concentration. Reported faradaic efficiencies represent the highest value obtained over the 5-hour controlled potential electrolysis.

<table>
<thead>
<tr>
<th>Entry</th>
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<th>TON$_{CO}$</th>
<th>F.E. (%)</th>
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$^+$ = control experiment under argon; $^*$ = control experiment under CO$_2$ with no TFE added.
Table S2. UV-Vis absorption spectra of TPP, TThP, TThMeP, FeTPP, FeTThP, and FeTThMeP.

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<thead>
<tr>
<th>Compound</th>
<th>ICT band, nm</th>
<th>Soret Band, nm</th>
<th>Q-band(s), nm</th>
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<td>$\times 10^3$ cm$^{-1}$ M$^{-1}$</td>
<td>$\times 10^3$ cm$^{-1}$ M$^{-1}$</td>
<td>$\times 10^3$ cm$^{-1}$ M$^{-1}$</td>
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<td>TPP</td>
<td>-</td>
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<td>525 (12), 567 (9.0), 599 (5.8), 662 (4.6)</td>
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<td>FeTPP</td>
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<td>417 (0.86)</td>
<td>509 (13), 582 (5.6)</td>
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<td>425 (0.82)</td>
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<td>FeTThMeP</td>
<td>383 (37)</td>
<td>431 (0.84)</td>
<td>522 (12)</td>
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</table>

Table S3. Electrochemical data of TPP, TThP, TThMeP, FeTPP, FeTThP, and FeTThMeP.

<table>
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<tr>
<th>Compounds</th>
<th>Solvent</th>
<th>Oxidations (V vs. Fc$^{+/0}$)</th>
<th>Reductions (V vs. Fc$^{+/0}$)</th>
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<td>-0.61, -1.46, -2.03</td>
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8. References