

Electrocatalytic Reduction of CO₂ to CO by Fe(III) Carbazole-porphyrin in Homogeneous Molecular Systems

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Electronic Supplementary Information

Experimental details

Materials. All chemical reagents and solvents were commercially available and used without further purification.

physical characterization: All ¹H NMR of the catalysts were carried out using a Bruker 300 Hz spectrometer. Catalysts were formulated into solutions of certain concentrations prior to testing. The solution was prepared by dissolving 6 mg catalyst in 600 μl d-chloroform (CDCl₃). All high-resolution mass spectrometry was characterized using Bruker Matrix Assisted Laser Desorption Time-of-Flight Mass Spectrometer. 1 mg catalyst was dissolved in 1 ml tetrahydrofuran (THF) to form solution prior to characterization. The UV-vis absorption spectrum of the catalyst was detected on Ocean Insight QE65pro High-sensitivity spectrometer.

Electrodes. All electrochemical experiments were tested with CH Instruments (CHI 660E). Before the test, the solution will be bubbled with Ar or CO₂ for 30 minutes to exhaust the air or form a CO₂-saturated solution. Cyclic voltammograms (CVs) were obtained in DMF solution containing 0.1 M tetrabutylammonium hexafluorophosphate ([Bu₄N]PF₆). All electrochemical characterizations were performed with three-electrode system using platinum wire as the counter electrode, saturated calomel electrode (SCE) as the reference electrode, and glassy carbon electrode (GC, 0.07 cm²) as the working electrode. In order to make the experimental results more accurate, the glassy carbon electrode was polished with alumina powder and cleaned with water and ethanol before testing. The reference electrode was calibrated with ferrocene.

Controlled potential electrolysis (CPE) was performed in a one-compartment cell with a three-electrode system using platinum sheet (1 × 1 cm) as the counter electrode, glassy carbon sheet (1 × 2 cm) as the working electrode, and saturated calomel electrode (SCE) as the reference electrode. During the electrolysis process, 200 ul gas was taken by syringe and analyzed by gas chromatograph, then the Faradaic efficiency of the gas product was calculated using the following formula.

$$FE (\%) = (nNF/Q) \times 100\%$$

In this formula, n is moles of product, which can be obtained by gas chromatography. N is the number of electrons transferred when reducing CO₂ to specific product, such as the number of electrons

transferred are 2 when forming H₂ or CO. F is Faraday constant (F=96485 C/mol). Q is the number of electrons transferred in the entire reduction reaction.

Details for Foot-of-the-Wave Analysis (FOWA)

FOWA is obtained by the following formula. The corresponding parameters in the formula are obtained by CV as described by Savéant and co-workers⁵¹⁻⁵³.

$$TOF = \frac{k_{cat}}{1 + \exp\left[\frac{F}{RT}(E_{CO_2/CO}^0 - E_{cat}^0 - \eta)\right]}$$

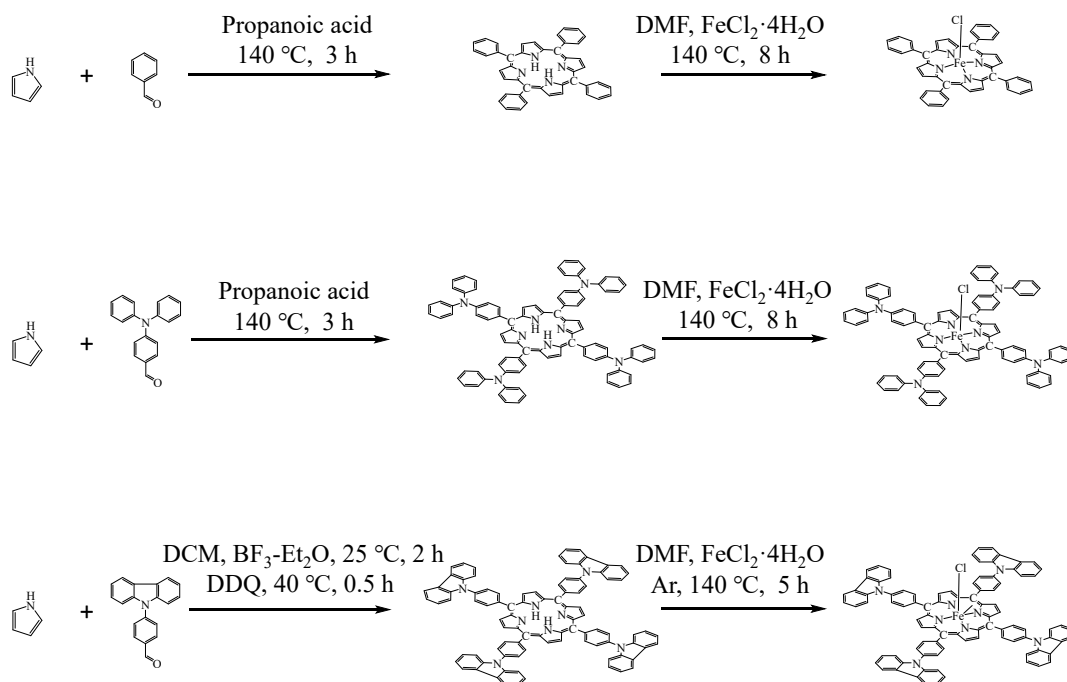
In this formula, F is Faraday constant (F=96485 C/mol), T is the absolute temperature, R is the gas constant (R=8.314). $\eta = E_{CO_2/CO}^0 - E$, $E_{CO_2/CO}^0$ is standard potential of the target reaction ($E_{CO_2/CO}^0 = -1.40$ V) versus ferrocene was used in DMF. E_{cat}^0 is catalyst standard potential. k_{cat} is catalytic rate constants and calculated by the following equation.

$$\frac{i}{i_p^0} = \frac{2.24 \sqrt{\frac{RT}{Fv}} k_{cat}}{1 + \exp\left[\frac{F}{RT}(E - E_{cat}^0)\right]}$$

In this formula, v is the scan rate (0.1 V/s), i_p^0 is the reduction peak current of the Fe^{III/I} redox couple under argon.

Experimental Procedures

The synthesis diagram of porphyrins and iron porphyrins were shown in Scheme S1. The detailed synthesis steps are shown below.



Scheme S1. synthetic pathways of porphyrins and iron porphyrins

Tetra(meso-phenyl)porphyrin (TPP)

The synthesis route of TPP is based on the previous report by Harapriya Rath and co-workers⁵⁴. Benzaldehyde (1 eq.) was added to propionic acid and stirred at 90 °C for 30 minutes, then pyrrole (1 eq.) was added to the above mixture. Adjust the temperature to 140 °C and reflux for 3 h. After the reaction was completed, it was cooled to room temperature, and the solvent was removed by filtration to obtain a purple product. The porphyrin was washed with propionic acid and acetone, dried in vacuo and purified by silica gel chromatography. Yield: 23 %.

UV-Vis (CH₂Cl₂): 416 nm, 515 nm, 549 nm, 590 nm, 546 nm.

¹H-NMR (300 MHz, CDCl₃): δ 8.86 (s, 8H), 8.26 – 8.20 (m, 8H), 7.80 – 7.72 (m, 12H), -2.76 (s, 2H).

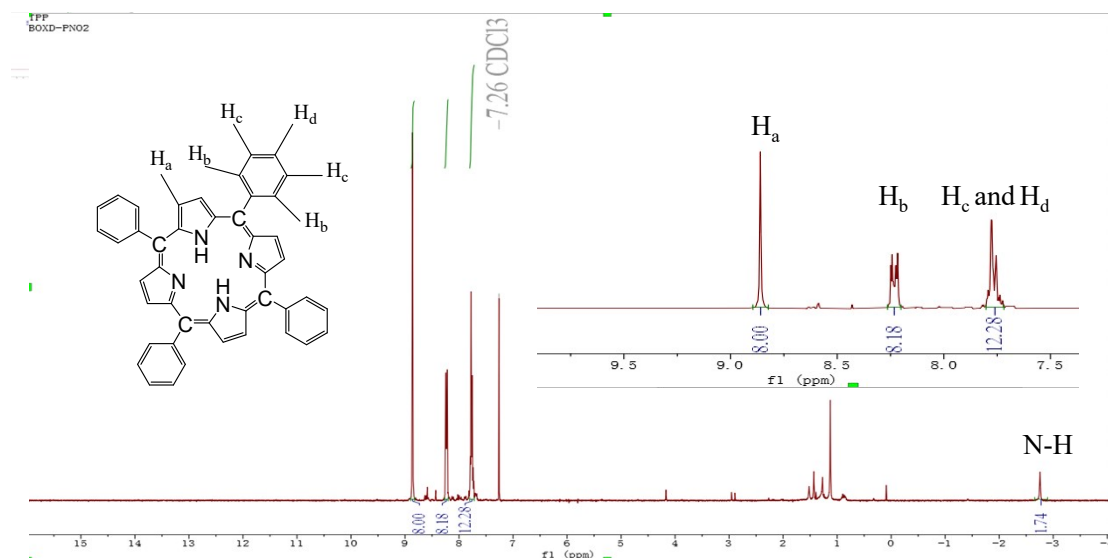


Figure S1. ¹H-NMR spectrum of TPP

Synthesis of FeTPP

TPP (1 eq.) and FeCl₂·4H₂O (2 eq.) were added to DMF and stirred, then the temperature was adjusted to 140 °C and refluxed for 8 h. After the reaction was completed and cooled to room temperature, water is added to the above solution, and the solid will precipitate out rapidly. The solvent was removed by vacuum filtration, the solid product was collected and dried at 80 °C. The solid product was purified by silica gel column chromatography using dichloromethane as eluent. The solvent is removed by spin evaporation and the product is dried at 80 °C. Yield: 92 %.

UV-Vis (CH₂Cl₂): 376 nm, 416 nm, 509 nm.

HRMS of [M-Cl]⁺ : calculated for [C₄₄H₂₈FeN₄]⁺: 668.580, found: 667.986.

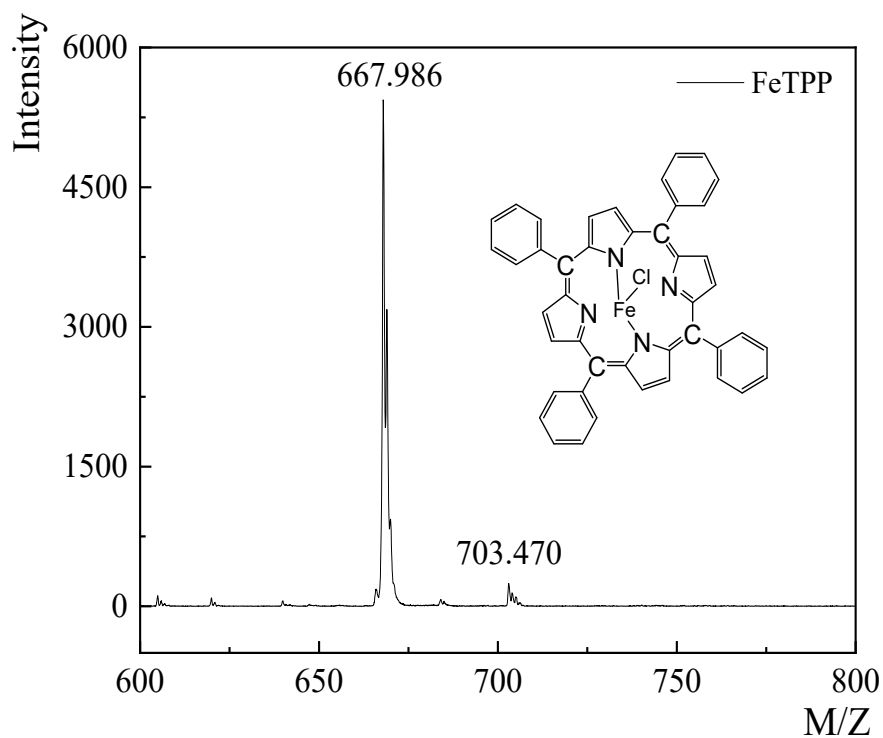


Figure S2. HRMS of FeTPP

Tetrakis(4-(diphenylamino)phenyl)porphyrin (TDPP)

4-(N,N-Diphenylamino)benzaldehyde (1 eq.) was added to propionic acid and stirred at 90 °C for 30 minutes. Pyrrole (1 eq.) was added to the above mixture. Adjust the temperature to 140 °C and reflux for 3 h. After the reaction was completed, it was cooled to room temperature. The solvent was removed by filtration to obtain a purple product. The porphyrin was washed with propionic acid and acetone, dried in vacuo and purified by silica gel chromatography. Yield: 20 %.

UV-Vis (CH₂Cl₂): 302 nm, 435 nm, 524 nm, 568 nm, 657 nm.

¹H-NMR (300 MHz, CDCl₃): δ 9.00 (s, 8H), 8.09 (d, J = 8.4 Hz, 8H), 7.50 – 7.39 (m, 40H), 7.15 (td, 8H), -2.66 (s, 2H).

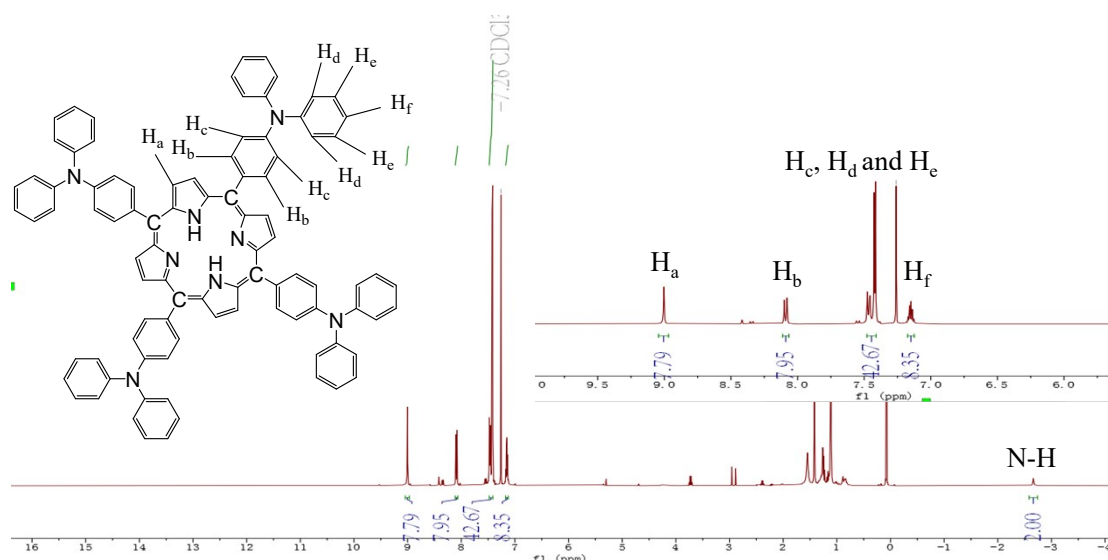


Figure S3. $^1\text{H-NMR}$ spectrum of TDPP

Synthesis of FeTDPP

TDPP (1 eq.) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2 eq.) were added to DMF and stirred, then the temperature was adjusted to $140\text{ }^\circ\text{C}$ and refluxed for 8 h. After the reaction was completed and cooled to room temperature, water was added to the above solution, solids would precipitate out rapidly at this time. The solvent was removed by vacuum filtration, the solid product was collected and dried at $80\text{ }^\circ\text{C}$. The solid product was purified by silica gel column chromatography using dichloromethane as eluent. The solvent is removed by spin evaporation and the product is dried at $80\text{ }^\circ\text{C}$. Yield: 94 %.

UV-Vis (CH_2Cl_2): 302 nm, 435 nm.

HRMS of $[\text{M-Cl}]^+$: calculated for $[\text{C}_{92}\text{H}_{64}\text{FeN}_8]^+$: 1337.430, found:1335.921.

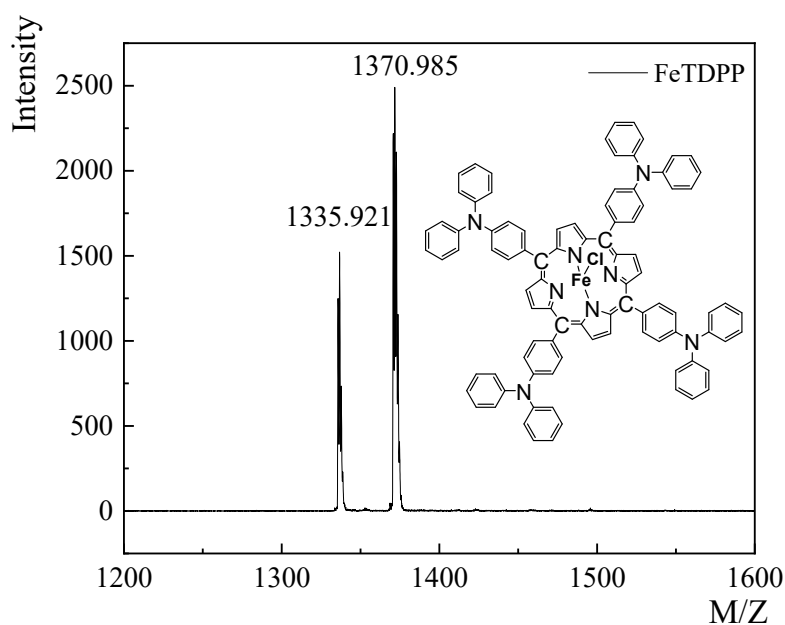


Figure S4. HRMS of FeTDPP

Tetrakis(carbazol-9-ylphenyl)porphyrin (TCPP)

TCPP was synthesized by previous literature reports and slight modifications⁵⁵. Pyrrole (1 eq.) and 4-(9-carbazolyl)benzaldehyde (1 eq.) were added to dichloromethane and covered with tin foil. Boron trifluoride ether (0.4 eq.) was added under Ar conditions and stirred for 2 h at room temperature. P-chloranil (0.9 eq.) was added to the above solution and stirred for 0.5 h at room temperature. After the reaction was completed, the solvent was removed under vacuum to obtain the black product. The black product was purified on a silica gel chromatography column using dichloromethane as the eluent. The obtained product was recrystallized using methanol and dichloromethane to obtain purple porphyrin. Yield: 18 %.

UV-Vis (CH₂Cl₂): 289 nm, 422 nm, 518 nm, 554 nm, 590 nm, 646 nm.

¹H-NMR (300 MHz, CDCl₃): δ 8.95-8.86 (d, 8H), 8.80 (s, 8H), 8.38-8.25 (dd, J = 15.4, 8.0 Hz, 16H), 7.98-7.89 (d, J = 8.2 Hz, 8H), 7.68-7.56 (t, J = 7.6 Hz, 8H), 7.51-7.40 (d, J = 14.8 Hz, 8H).

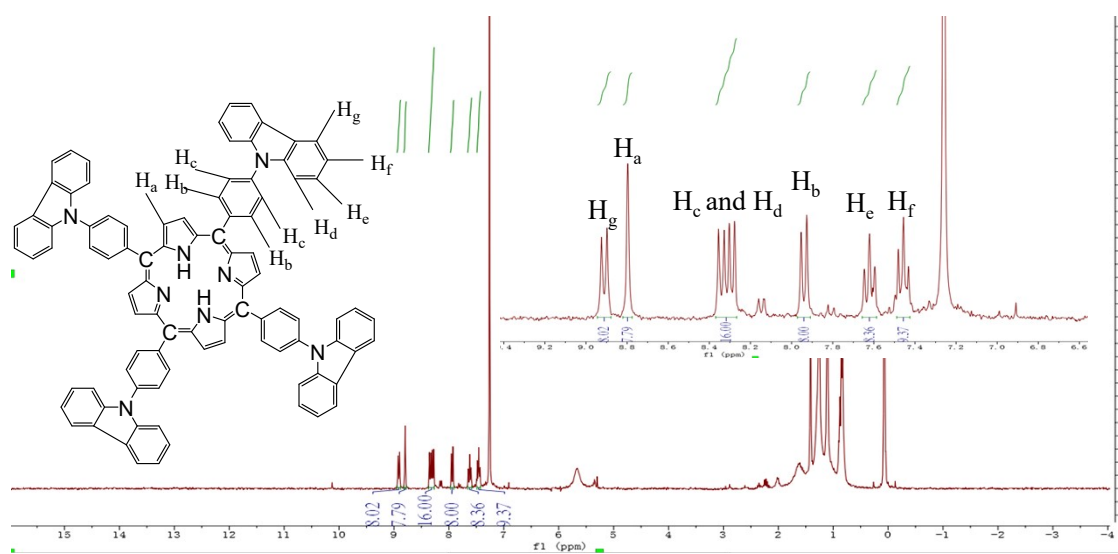


Figure S5. ¹H-NMR spectrum of TCPP

Synthesis of FeTCPP

DMF was bubbled with Ar for 15 min, TCPP (1 eq.) and FeCl₂·4H₂O (2 eq.) were added to the above DMF and stirred. The mixed solution was heated to 140 °C and refluxed for 5 hours. The mixed solution was cooled to room temperature under Ar condition, then exposed to the air and stirred for 2 h. Water was added to the above solution, and the solid precipitated out rapidly. The solid was collected by centrifugation and washed several times with water. The product is purified by silica gel chromatography. Yield: 95 %.

UV-Vis (CH₂Cl₂): 289 nm, 422 nm, 511 nm.

HRMS of $[M-Cl]^+$: calculated for $[C_{92}H_{56}FeN_8]^+$: 1329.360, found:1328.654.

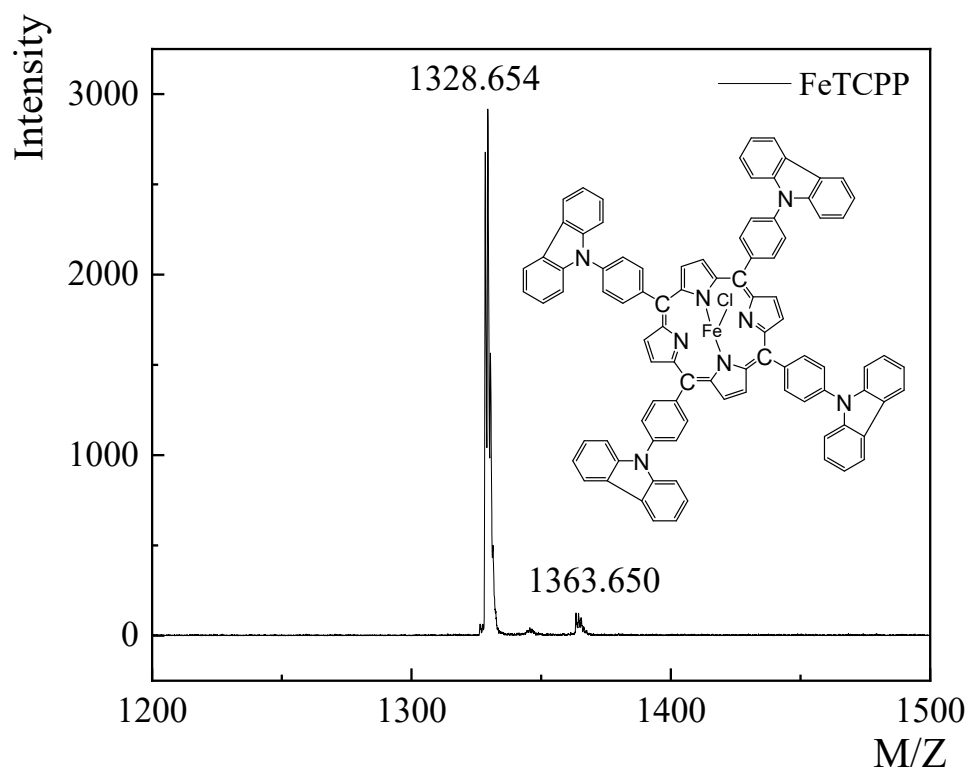


Figure S6. HRMS of FeTCPP

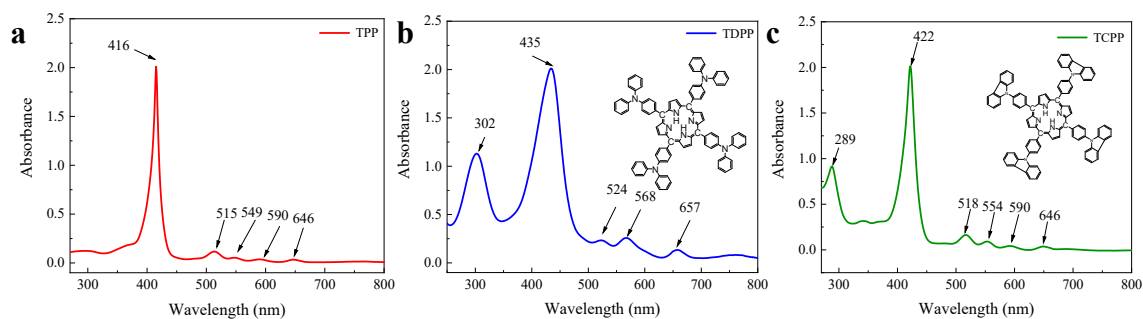


Figure S7. UV-vis absorption spectra of TPP (a), TDPP (b) and TCPP (c)

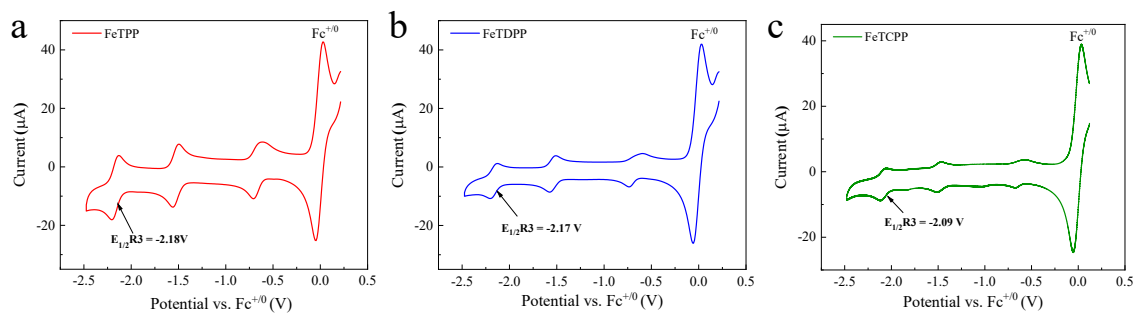


Figure S8. CVs of FeTPP (a), FeTDPP (b), and FeTCPP (c) in DMF containing 0.1 M $[Bu_4N]PF_6$ under argon, corrected by ferrocene

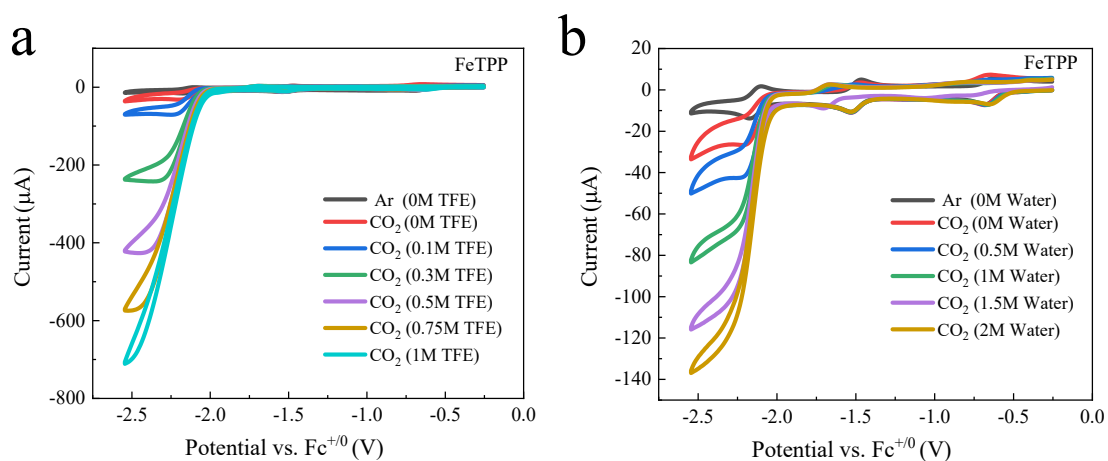


Figure S9. CVs of FeTPP in CO₂-saturated DMF with increasing trifluoroethanol (a) or water (b). Conditions: 0.5 mM catalyst, 0.1 M [Bu₄N]PF₆, 100 mV/s scan rate, GC working electrode (0.07 cm²)

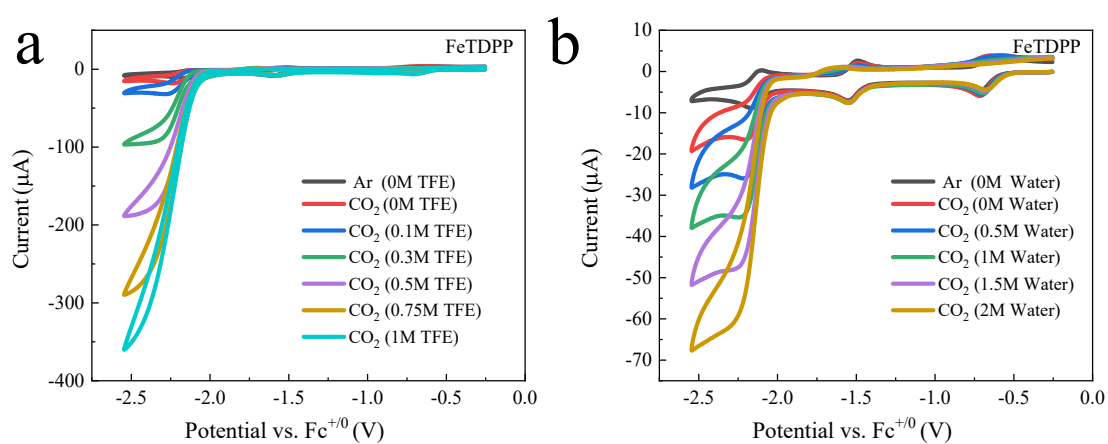


Figure S10. CVs of FeTDPP in CO₂-saturated DMF with increasing trifluoroethanol (a) or water (b). Conditions: 0.5 mM catalyst, 0.1 M [Bu₄N]PF₆, 100 mV/s scan rate, GC working electrode (0.07 cm²)

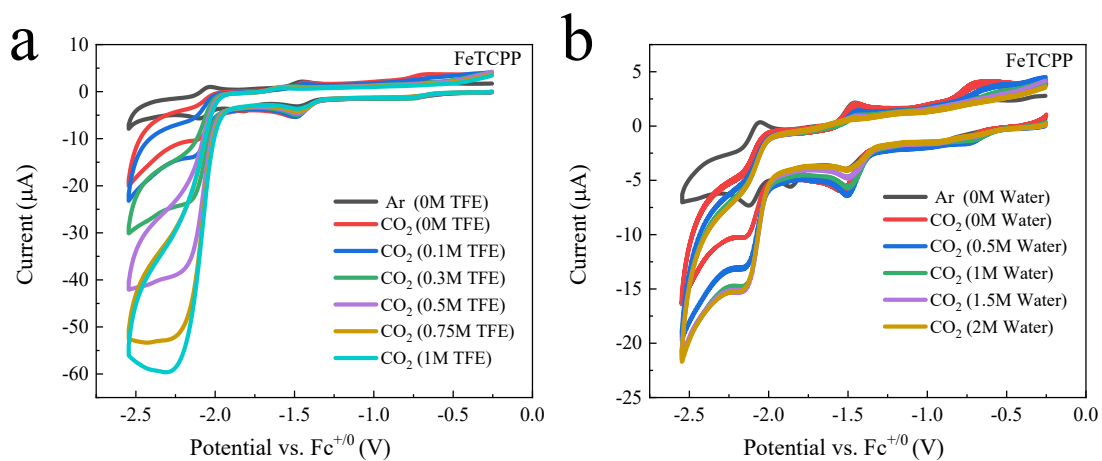


Figure S11. CVs of FeTCPP in CO₂-saturated DMF with increasing trifluoroethanol (a) or water (b). Conditions: 0.5 mM catalyst, 0.1 M [Bu₄N]PF₆, 100 mV/s scan rate, GC working electrode (0.07 cm²)

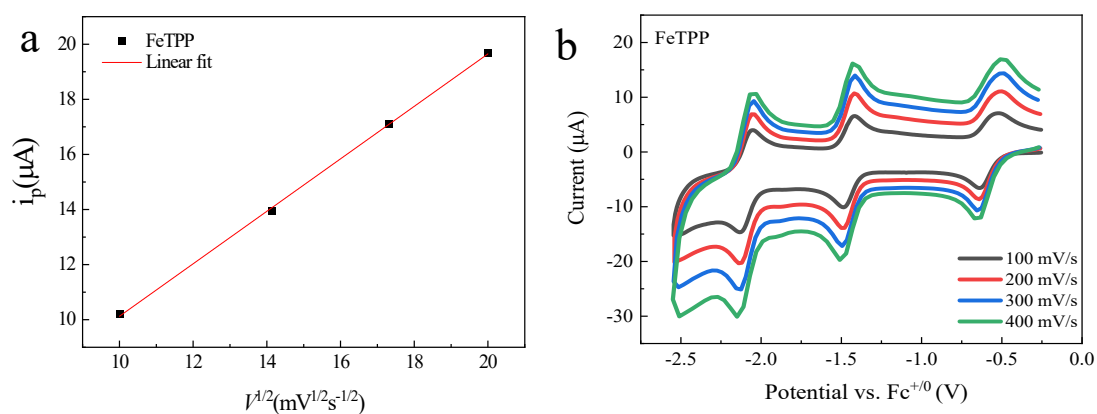


Figure S12. Plot of the Fe^{II/I} reduction peak current of FeTPP on the square root of scan rates in Ar-saturated DMF (a). CVs of 0.5 mM FeTPP with different scan rates in DMF under argon (b).

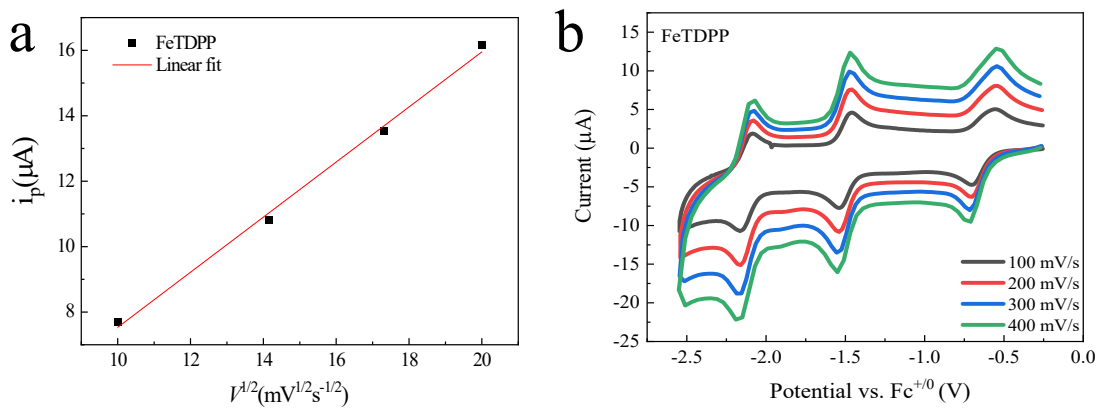


Figure S13. Plot of the $\text{Fe}^{\text{II/I}}$ reduction peak current of FeTDPP on the square root of scan rates in Ar-saturated DMF (a). CVs of 0.5 mM FeTDPP with different scan rates in DMF under argon (b).

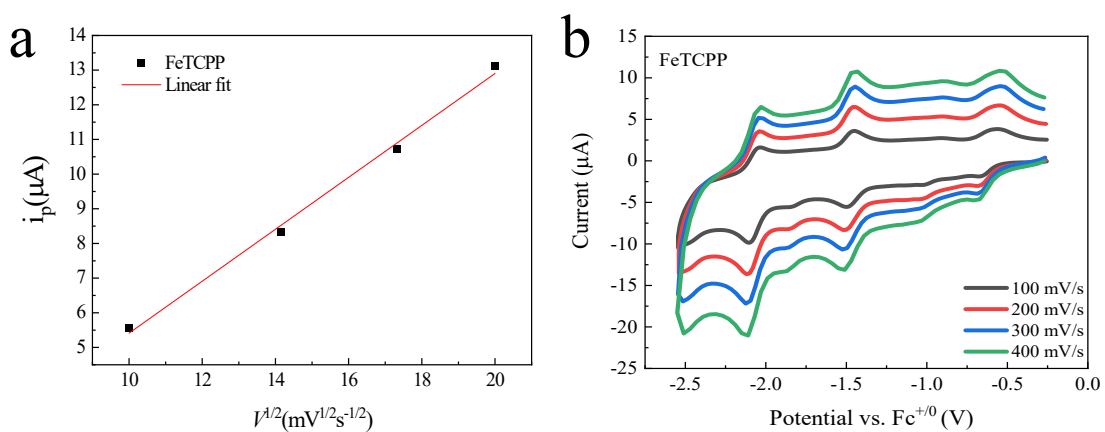


Figure S14. Plot of the $\text{Fe}^{\text{II/I}}$ reduction peak current of FeTCPP on the square root of scan rates in Ar-saturated DMF (a). CVs of 0.5 mM FeTCPP with different scan rates in DMF under argon (b).

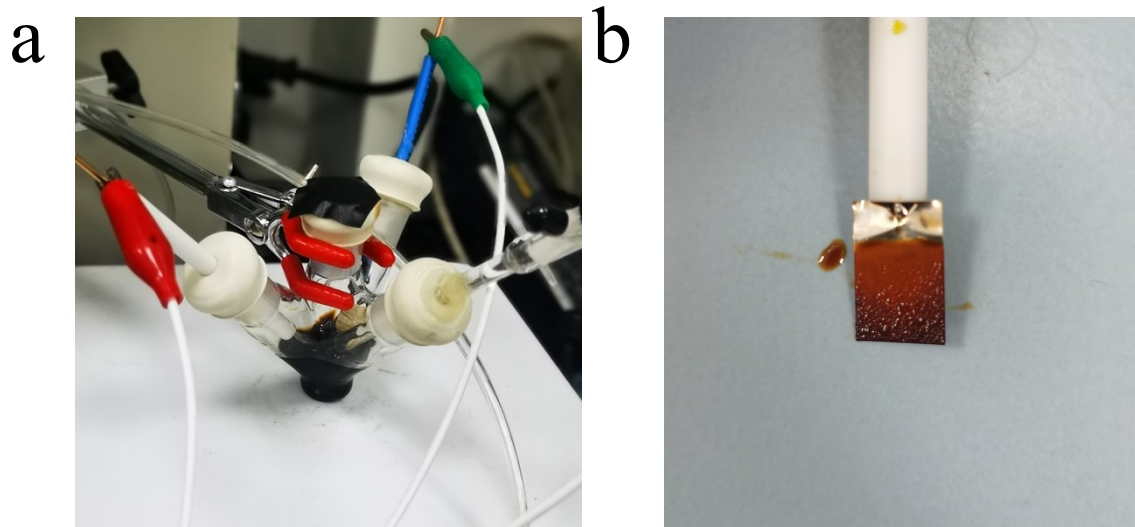


Figure S15. One-compartment electrolytic cell (a). Film electropolymerized on the counter electrode (b).

Additional references

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