Electronic Supplementary Material (ESI) for ChemComm.


# *Electronic Supplementary Information*

## ***meso*-Substituent electronic effect of Fe porphyrins on electrocatalytic $CO_2$ reduction reaction**

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**General Methods and Materials**.

Manipulations of air- and moisture-sensitive materials were performed under nitrogen gas using standard Schlenk line techniques. All reagents used in this work were purchased from commercial suppliers and were used without further purification unless otherwise noted. All solvents used in the experiments were reagent grades. Dry solvents, including acetonitrile, tetrahydrofuran, diethyl ether, dichloromethane, and chloroform were purified by passage through activated alumina. Dimethylformamide (DMF) was refluxed over $CaH_2$ and was distilled under reduced pressure. Fe porphyrins were synthesized according the reported procedures.[1-3] $^1H$ NMR spectra were recorded using a JEOL 400 MHz spectrometer. High-resolution mass spectrometry (HRMS) experiments were carried out by using a Brüker MAXIS. The samples were dissolved in methanol for mass spectrometry. UV-vis spectra were obtained using a Hitachi U-3900H spectrophotometer. The CO and $H_2$ gas generated during electrolysis was analyzed by Shimadzu gas chromatograph (GC-2014).

**Electrochemical Measurements**.

All electrochemical experiments were carried out using a CH Instruments (model CHI 660E Electrochemical Analyzer) at 20 °C. The solution was bubbled with argon or $CO_2$ for at least 30 min before analysis. Cyclic voltammograms (CVs) were acquired in 0.1 M $Bu_4N(PF_6)$ dry DMF or acetonitrile with a three-compartment cell using a 0.07 $cm^2$ glassy carbon (GC) electrode as the working electrode, $Ag/AgNO_3$ as the reference electrode (BASi, 10 mM $AgNO_3$, 0.1 M $Bu_4N(PF_6)$ in acetonitrile), and graphite rod as the auxiliary electrode. The GC electrode was polished with α-$Al_2O_3$ (50 nm) and washed with distilled $H_2O$ and absolute ethanol. Ferrocene was added at the end of the measurement as an external standard. All potentials reported in this work are referenced to ferrocene. Electrolysis was performed in a gas-tight electrochemical cell under $CO_2$ with stirring. The 7-mL DMF solution contains 0.1 M $Bu_4N(PF_6)$, and the headspace is approximately 14 mL. A graphite rod was used as the counter electrode, an Ag/$AgNO_3$ was used as the reference electrode, and a glassy carbon slice (1.0 $cm^2$ area) was used as the working electrode. Before electrolysis, the cell was degassed by bubbling $CO_2$ gas for at least 30 min. The glassy carbon slice was polished with α-$Al_2O_3$ powders (50 nm) and rinsed with deionized water and absolute ethanol. After electrolysis, 400 μL of gas in the cell headspace was sampled by a gas-tight syringe and then analyzed by gas chromatograph (GC-2014) equipped with a thermal conductivity detector.

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

in which *n* is the mole of product, *N* is the number of electrons transferred for a specific product (2 for CO and $H_2$), *F* is the Faraday constant, and *Q* is the total charges of passed during electrolysis.

**Details for the measurement of $CO_2$ binding constant ($K_{CO_2}$):**

CVs were recorded in 0.1 M $NBu_4(PF_6)$ in dry DMF, first under an atmosphere of argon and then upon saturation with $CO_2$. A fast scan rate (2 V/s) was necessary to achieve reversible $Fe^{I/0}$ couples under $CO_2$. Proton sources (other than adventitious water) were omitted to prevent subsequent catalytic turnover. $K_{CO_2}$ was calculated based on the difference between the standard potentials under argon and $CO_2$, ΔE, using the equation below:

$$K_{CO_2} = \frac{e^{(f*\Delta E)}-1}{[CO_2]}$$

in which $f$ = F/RT = 38.94 $V^{-1}$ and [$CO_2$] (for $CO_2$-saturated DMF) is 0.23 M.

**Computational Details**.

Density functional theory (DFT) calculations were conducted using the Gaussian 16 program.[4] Geometrical optimizations were performed employing the BP86 functional in conjunction with Grimme's D3 dispersion correction,[5-7] utilizing basis sets of 6-311G(d, p) (for C, N, H, F, O) and Lanl2dz (for Fe).[8,9] Vibrational analyses were carried out at the same level of theory to validate local minima and assess Gibbs free energy at room temperature. The polarizable continuum model (PCM) approach was applied to account for the solvent environment,[10,11] employing a dielectric constant of ε = 37.2 for the solution of DMF.

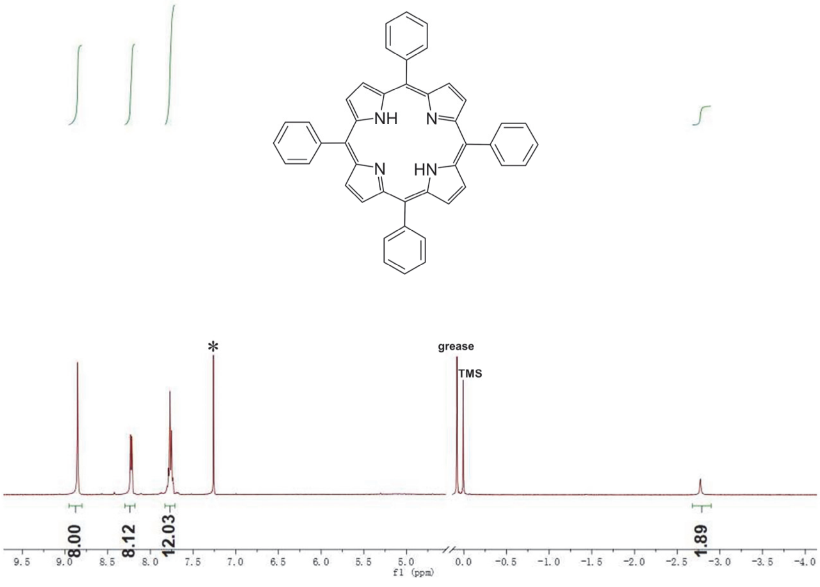


**Fig. S1** $^1$H NMR spectrum of the porphyrin ligand of **FeTPP** in $CDCl_3$. The solvent residue peak is labelled (*).

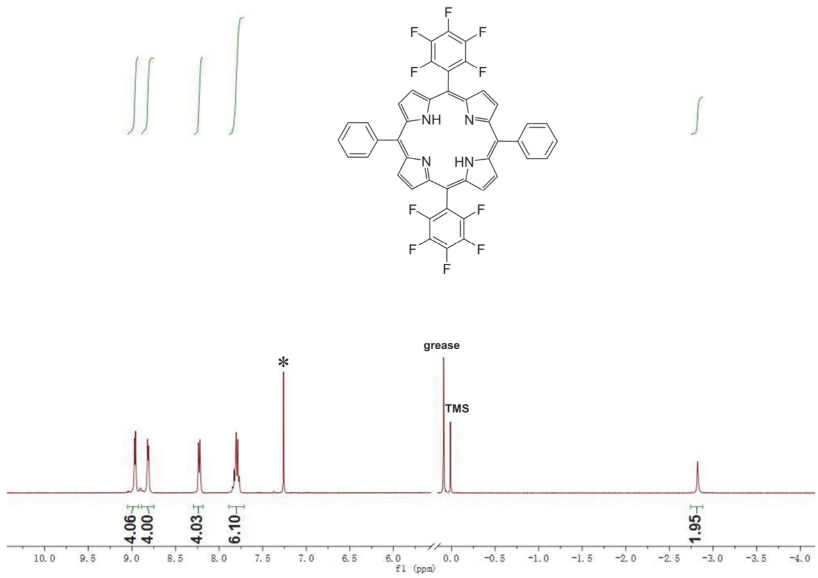


**Fig. S2** $^{1}H$ NMR spectrum of the porphyrin ligand of **$FeF_{10}TPP$** in $CDCl_3$. The solvent residue peak is labelled (*).

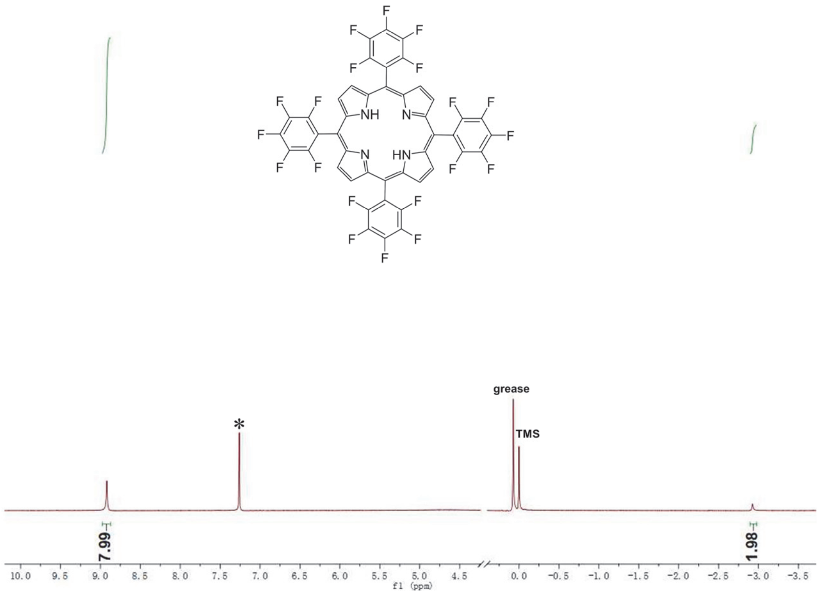


**Fig. S3** [1]H NMR spectrum of the porphyrin ligand of **$FeF_{20}TPP$** in $CDCl_3$. The solvent residue peak is labelled (*).

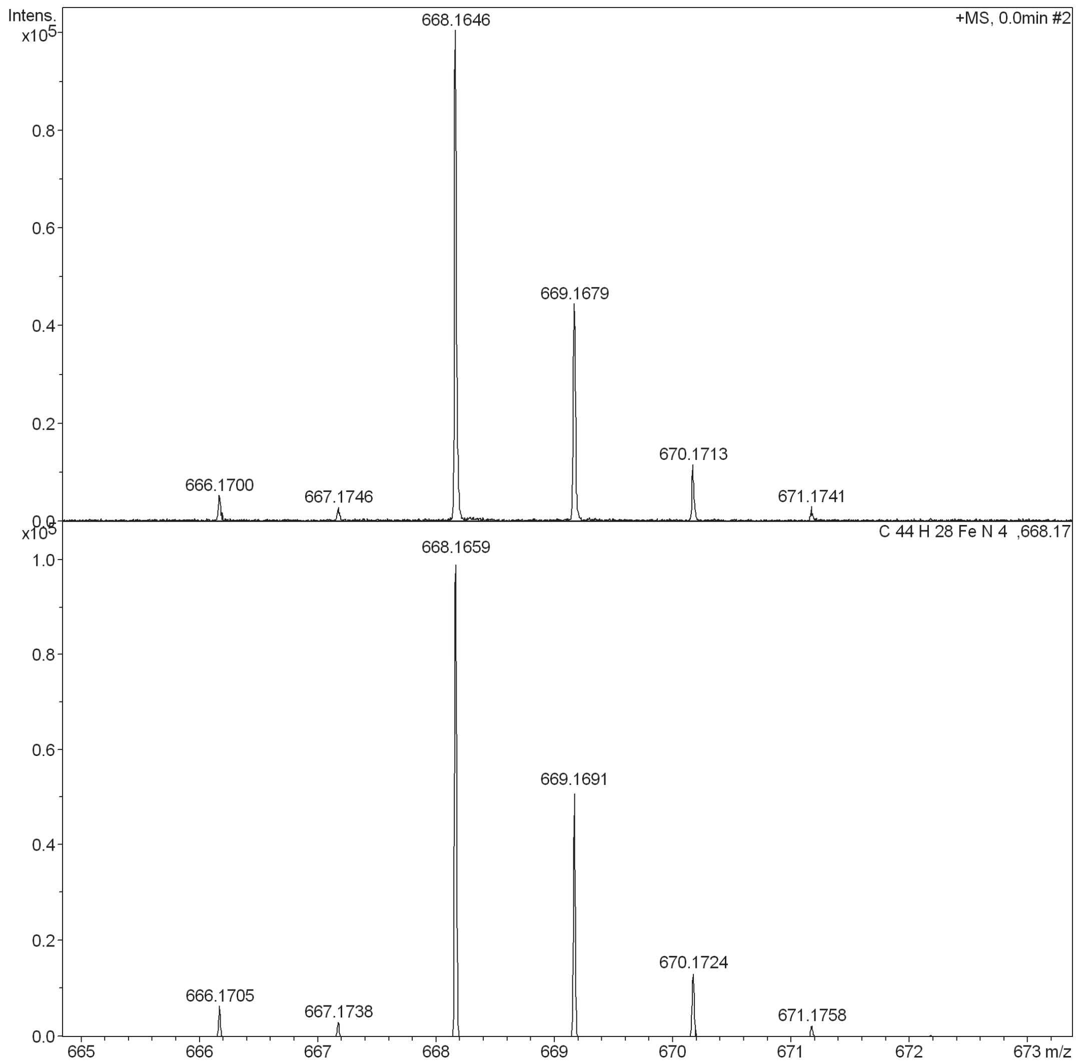


**Fig. S4** HRMS of **FeTPP** in methanol, showing a peak at 668.1646.

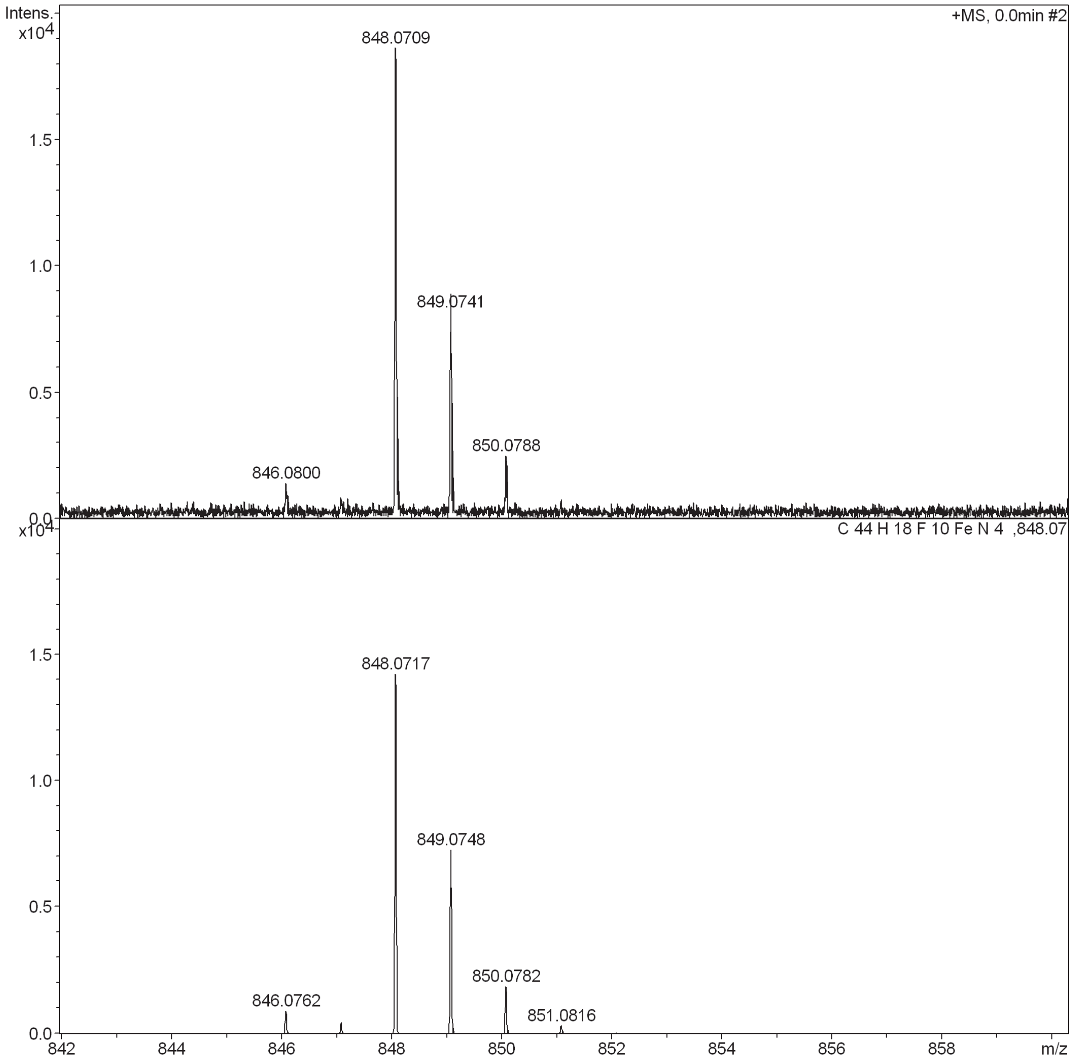


**Fig. S5** HRMS of **$FeF_{10}TPP$** in methanol, showing a peak at 848.0709.

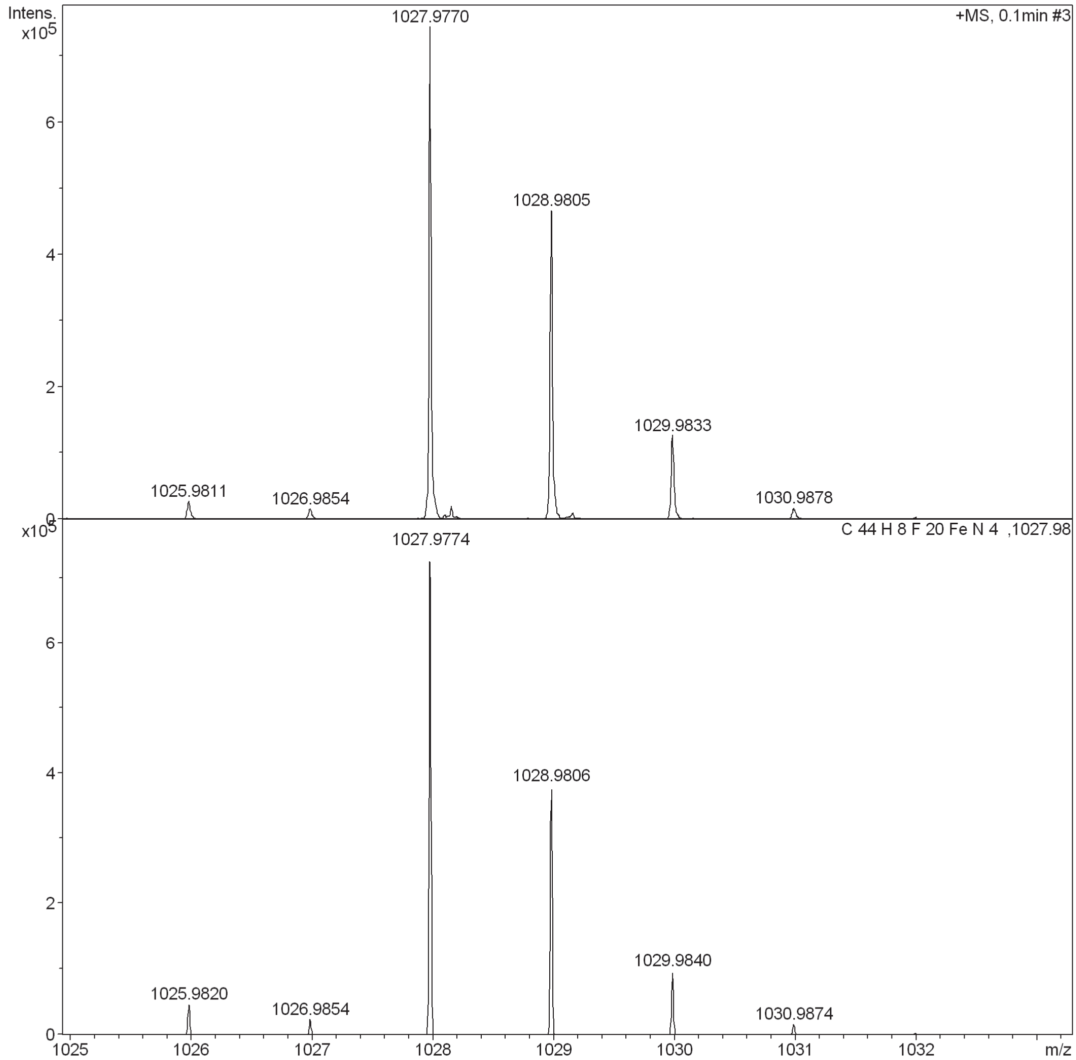


**Fig. S6** HRMS of **$FeF_{20}TPP$** in methanol, showing a peak at 1027.9770.

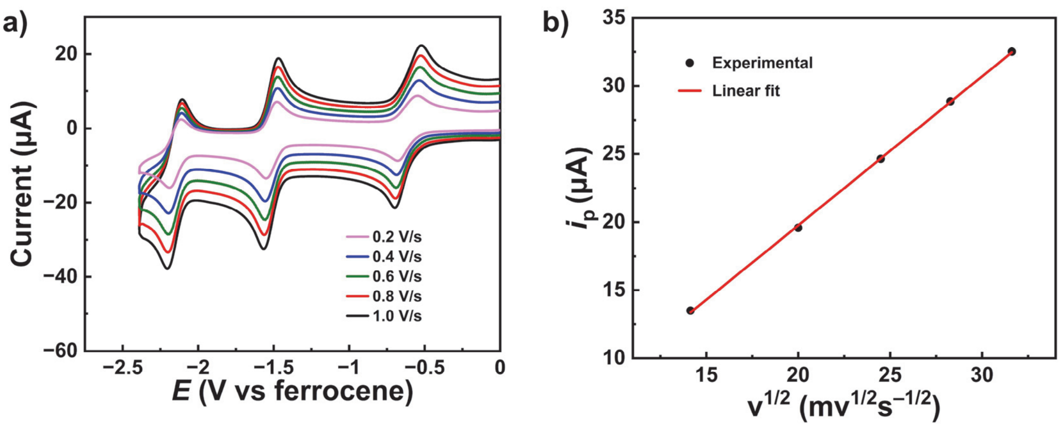


**Fig. S7** (a) CVs of 0.5 mM **FeTPP** under argon with different scan rates in DMF. (b) Plot of the $Fe^{II/I}$ reduction peak current of **FeTPP** versus the square root of scan rates. Conditions: 0.1 M $Bu_4N(PF_6)$, GC working electrode, 20°C.

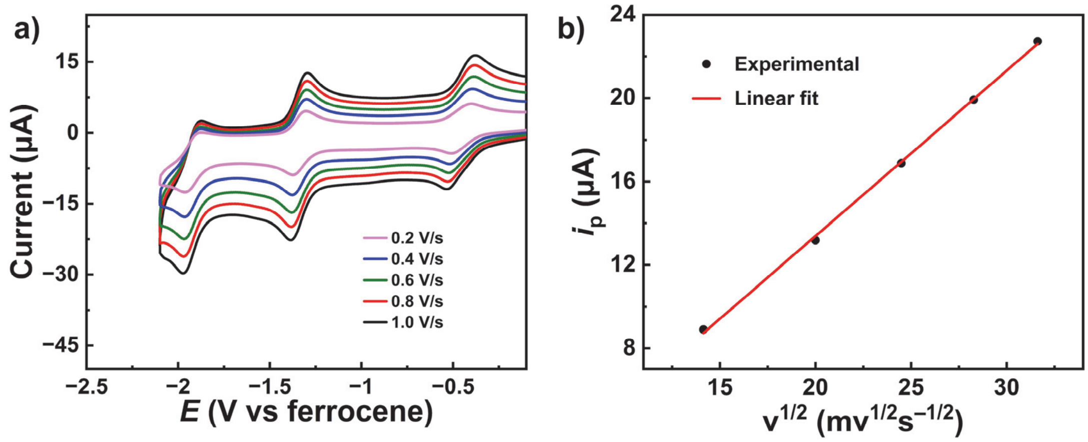


**Fig. S8** (a) CVs of 0.5 mM **FeF$_{10}$TPP** under argon with different scan rates in DMF. (b) Plot of the Fe$^{II/I}$ reduction peak current of **FeF$_{10}$TPP** versus the square root of scan rates. Conditions: 0.1 M $Bu_4N(PF_6)$, GC working electrode, 20°C.

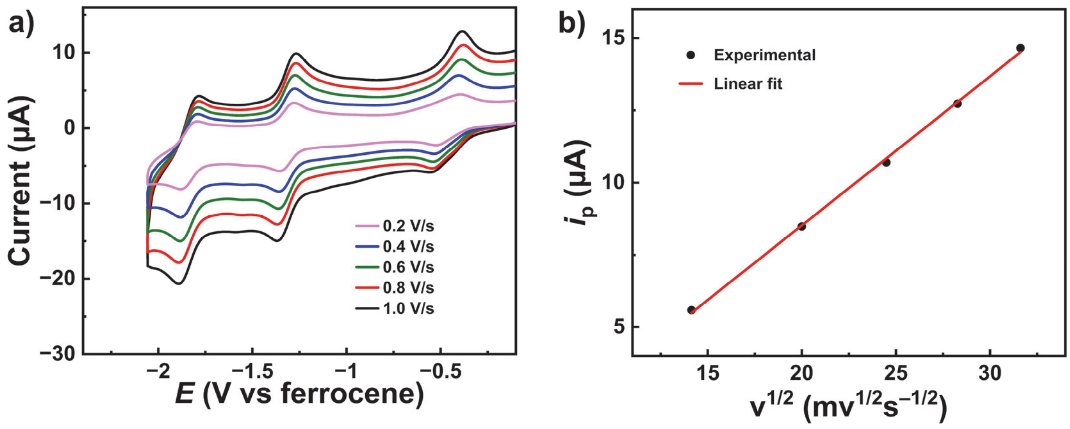


**Fig. S9** (a) CVs of 0.5 mM **$FeF_{20}TPP$** under argon with different scan rates in DMF. (b) Plot of the $Fe^{II/I}$ reduction peak current of **$FeF_{20}TPP$** versus the square root of scan rates. Conditions: 0.1 M $Bu_4N(PF_6)$, GC working electrode, 20 °C.

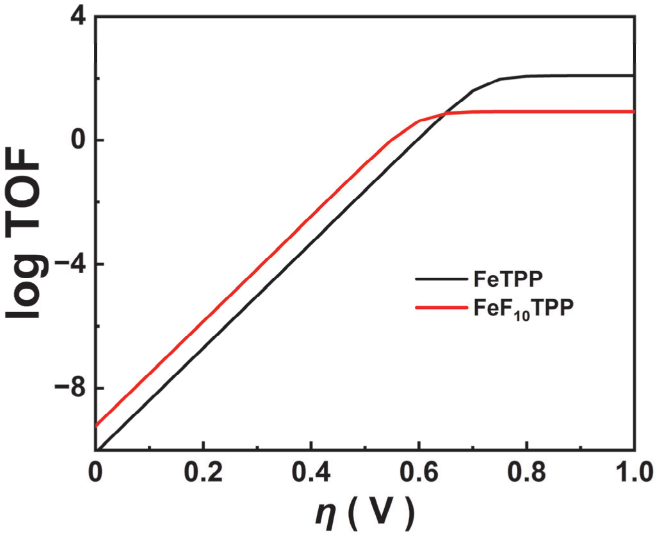


**Fig. S10** TOF plots of **FeTPP** and **$FeF_{10}TPP$** for $CO_2RR$ as determined using the foot-of-the-wave analysis.

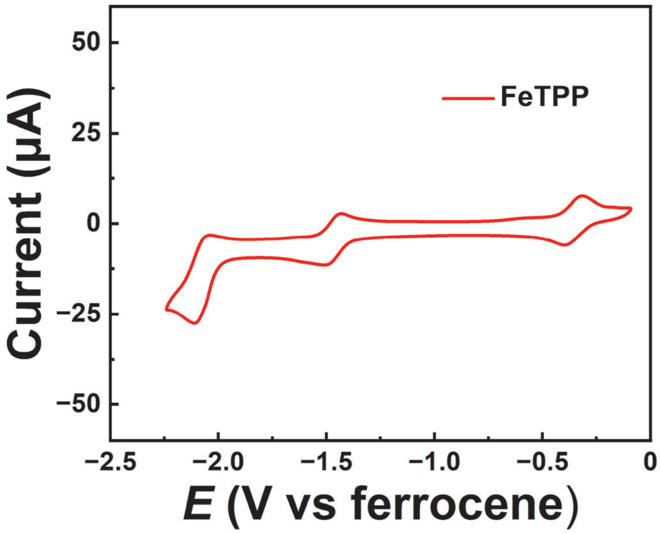


**Fig. S11** CV of 0.5 mM **FeTPP** in acetonitrile. Conditions: 0.1 M $Bu_4N(PF_6)$, 100 mV $s^{-1}$ scan rate.

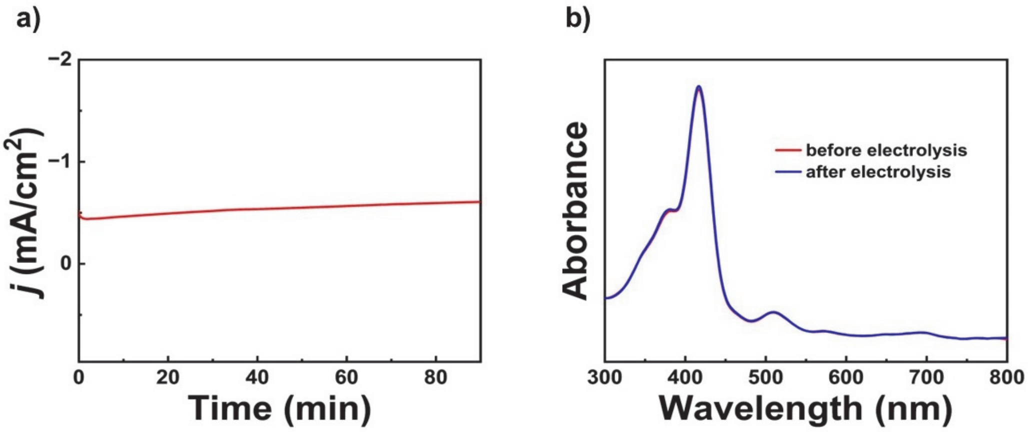


**Fig. S12** (a) Electrolysis of 0.5 mM **FeTPP** at –2.10 V with 10 mM phenol under $CO_2$ in DMF. (b) UV-vis spectra of **FeTPP** before and after electrolysis in DMF.

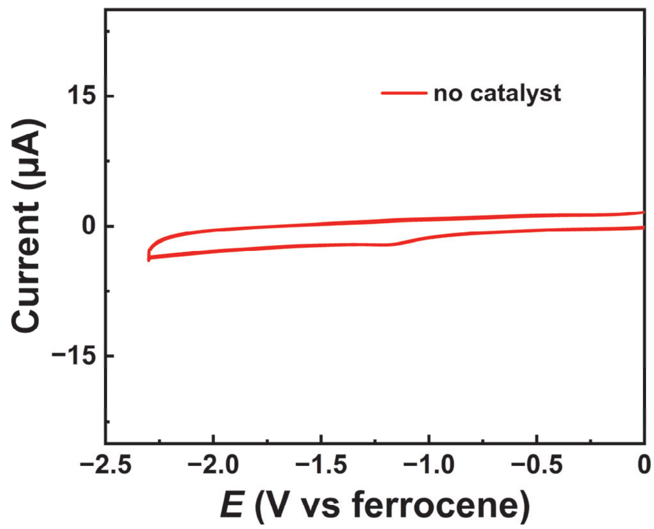


**Fig. S13** CV of the GC electrode after electrolysis measured in a $CO_2$-saturated DMF with phenol but without catalysts. Conditions: 0.1 M $Bu_4N(PF_6)$, 100 mV $s^{-1}$ scan rate.

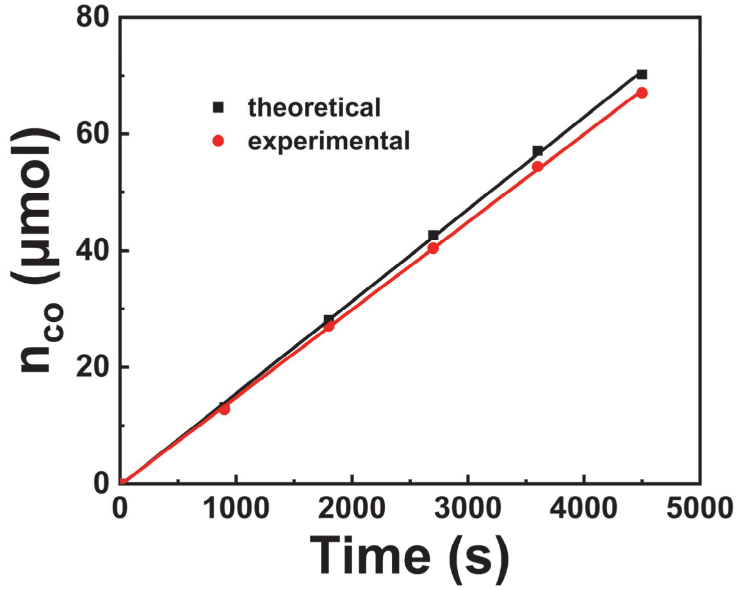


**Fig. S14** Gas chromatography detection of evolved CO during the electrolysis with **FeTPP**, giving a Faradaic efficiency of 98% for the CO production.

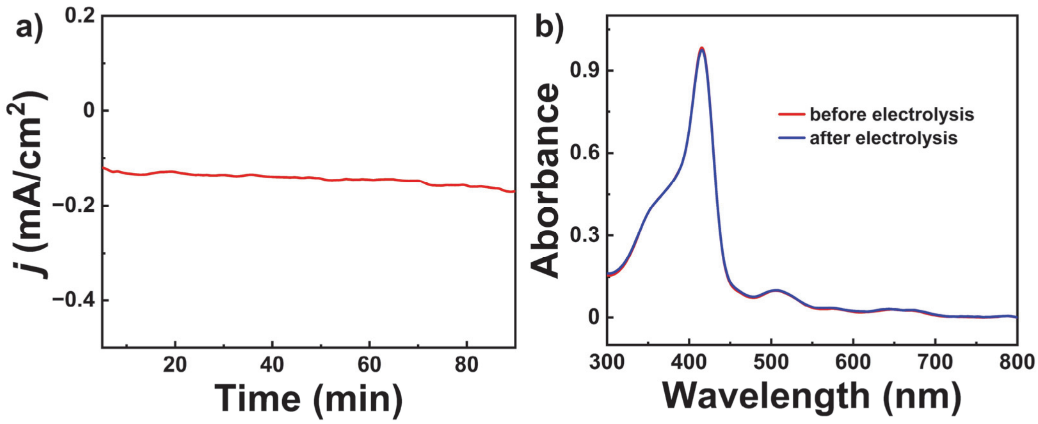


**Fig. S15** (a) Electrolysis of 0.5 mM **FeF$_{10}$TPP** at –1.90 V with 10 mM phenol under $CO_2$ in DMF. (b) UV-vis spectra of **FeF$_{10}$TPP** before and after electrolysis in DMF.

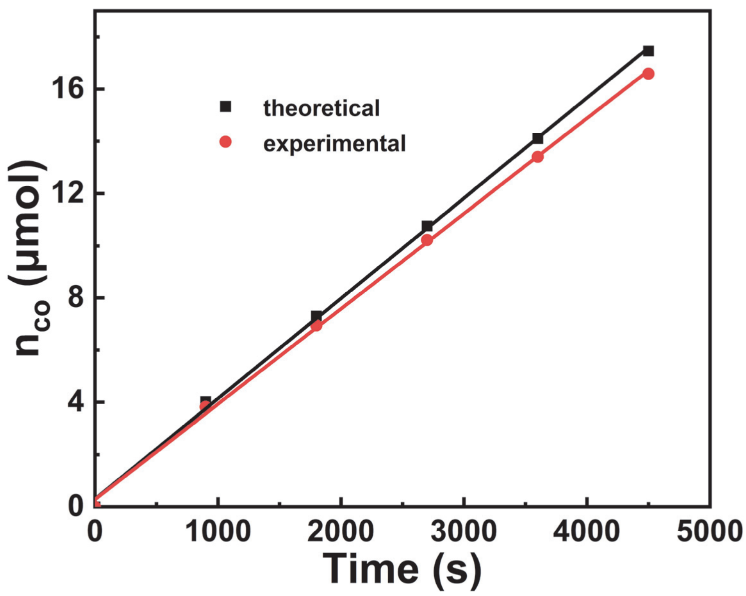


**Fig. S16** Gas chromatography detection of evolved CO during the electrolysis with **$FeF_{10}TPP$**, giving a Faradaic efficiency of 94% for the CO production.

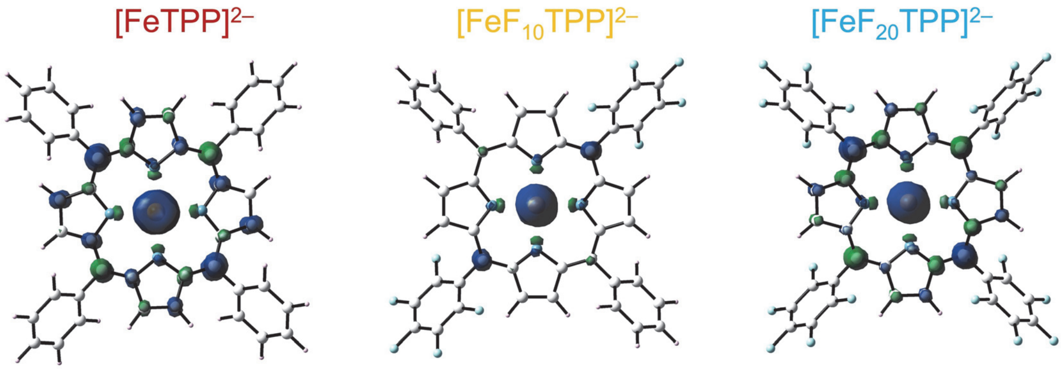


**Fig. S17** Spin density map of [**FeTPP**]$^{2-}$, [**FeF$_{10}$TPP**]$^{2-}$, and [**FeF$_{20}$TPP**]$^{2-}$.

**Table S1** Reduction potentials of **FeTPP**, **FeF$_{10}$TPP**, and **FeF$_{20}$TPP** in DMF.

| complex | $E_{1/2}$ (V *vs* ferrocene) | | |
|---|---|---|---|
| | **Fe$^{III/II}$** | **Fe$^{II/I}$** | **Fe$^{I/0}$** |
| **FeTPP** | –0.59 | –1.51 | –2.13 |
| **FeF$_{10}$TPP** | –0.49 | –1.38 | –1.94 |
| **FeF$_{20}$TPP** | –0.42 | –1.24 | –1.81 |

**Table S2** Summary of the electrochemical properties of **FeTPP**, **FeF$_{10}$TPP**, and **FeF$_{20}$TPP** in DMF.

| **complex** | **TOF$_{max}$ (s$^{-1}$)** | ***K*$_{CO2}$ (M$^{-1}$)** | **FE$_{CO}$(%)** |
|---|---|---|---|
| **FeTPP** | 124 | 2.07 | 98 |
| **FeF$_{10}$TPP** | 8.38 | 1.14 | 94 |
| **FeF$_{20}$TPP** | – | 0.26 | 3 |

**Table S3** The electronic energies of the singlet and triplet spin states ($E_S$ and $E_T$) and the singlet-triplet splitting energies ($\Delta E_{S\text{-}T} = E_S - E_T$) at the $Fe^0$ state of **FeTPP**, **FeF$_{10}$TPP**, and **FeF$_{20}$TPP**.

| Catalysts (at $Fe^0$ state) | $E_S$ (a.u.) | $E_T$ (a.u.) | $\Delta E_{S\text{-}T}$ (kcal mol$^{-1}$) |
|---|---|---|---|
| **FeTPP** | –2036.4535 | –2036.4599 | 4.0 |
| **FeF$_{10}$TPP** | –3029.1611 | –3029.1672 | 3.8 |
| **FeF$_{20}$TPP** | –4021.8656 | –4021.8731 | 4.7 |

**Table S4** The free energy change of $CO_2$-binding at the $Fe^0$ state ($\Delta G_{*CO_2}$) of **FeTPP**, **FeF$_{10}$TPP**, and **FeF$_{20}$TPP**.

| Catalysts | **FeTPP** | **FeF$_{10}$TPP** | **FeF$_{20}$TPP** |
|---|---|---|---|
| $\Delta G_{*CO_2}$ (kcal mol$^{-1}$) | –5.6 | –4.3 | –2.0 |

## Cartesian coordinates of calculated structures

## [FeTPP]$^{2-}$

| | | | |
|---|---|---|---|
| N | 1.809 | 0.867 | -0.097 |
| N | -0.860 | 1.793 | 0.016 |
| C | -1.643 | -4.682 | -0.042 |
| C | -2.229 | 2.075 | 0.161 |
| C | -3.440 | -2.424 | -0.638 |
| H | -3.903 | -3.383 | -0.861 |
| C | 1.145 | 5.653 | -0.940 |
| H | 0.385 | 5.355 | -1.667 |
| C | -2.592 | -7.358 | 0.014 |
| C | -1.145 | -5.652 | -0.940 |
| H | -0.385 | -5.354 | -1.667 |
| C | -1.139 | -3.281 | -0.064 |
| C | -1.610 | -6.975 | -0.911 |
| C | -0.215 | 3.042 | 0.142 |
| C | 3.043 | 0.226 | -0.252 |
| C | 1.180 | -4.065 | 0.483 |
| H | 0.937 | -5.106 | 0.689 |
| C | -2.080 | -2.232 | -0.285 |
| C | -4.045 | -1.164 | -0.618 |
| H | -5.085 | -0.923 | -0.829 |
| C | 6.467 | -3.141 | -0.732 |
| C | 4.680 | -1.644 | 0.042 |
| C | -2.412 | 3.472 | 0.499 |
| H | -3.370 | 3.937 | 0.725 |
| C | 3.274 | -1.167 | -0.016 |
| C | 2.229 | -2.075 | 0.161 |
| C | 7.372 | -2.561 | 0.168 |
| H | 8.406 | -2.913 | 0.218 |
| C | 5.143 | -2.685 | -0.798 |
| C | 1.610 | 6.975 | -0.910 |
| C | -3.105 | -6.404 | 0.909 |
| C | 2.638 | 5.084 | 0.878 |
| H | 3.037 | 4.344 | 1.576 |
| C | 6.935 | -1.518 | 1.003 |
| H | 7.628 | -1.061 | 1.715 |
| N | 0.860 | -1.793 | 0.016 |
| N | -1.809 | -0.867 | -0.097 |
| C | 3.105 | 6.403 | 0.909 |
| C | 2.592 | 7.357 | 0.014 |
| C | -1.180 | 4.065 | 0.484 |
| H | -0.937 | 5.106 | 0.690 |
| C | 2.080 | 2.232 | -0.285 |
| C | -3.274 | 1.166 | -0.016 |
| C | 4.045 | 1.164 | -0.618 |
| H | 5.085 | 0.923 | -0.829 |
| C | 3.440 | 2.424 | -0.638 |
| H | 3.903 | 3.383 | -0.861 |
| C | 2.412 | -3.472 | 0.499 |
| H | 3.370 | -3.937 | 0.724 |
| C | 5.612 | -1.068 | 0.938 |
| H | 5.277 | -0.260 | 1.594 |
| C | 0.215 | -3.042 | 0.142 |
| C | -3.043 | -0.226 | -0.252 |
| C | 1.643 | 4.682 | -0.042 |
| C | -2.637 | -5.084 | 0.877 |
| H | -3.037 | -4.344 | 1.576 |
| C | 1.139 | 3.281 | -0.064 |
| Fe | 0.000 | 0.000 | -0.042 |
| C | -6.935 | 1.518 | 1.003 |
| C | -4.680 | 1.644 | 0.042 |
| C | -7.372 | 2.561 | 0.168 |
| H | -8.406 | 2.913 | 0.218 |
| C | -5.612 | 1.068 | 0.938 |
| C | -6.466 | 3.141 | -0.732 |
| H | -6.795 | 3.946 | -1.396 |
| C | -5.143 | 2.685 | -0.798 |
| H | -4.447 | 3.132 | -1.513 |
| H | 1.209 | 7.707 | -1.617 |
| H | 2.958 | 8.388 | 0.038 |
| H | 3.867 | 6.692 | 1.639 |
| H | -5.277 | 0.260 | 1.594 |
| H | -7.628 | 1.061 | 1.715 |
| H | -3.867 | -6.692 | 1.639 |
| H | -2.957 | -8.388 | 0.037 |
| H | -1.209 | -7.706 | -1.619 |
| H | 4.447 | -3.132 | -1.513 |
| H | 6.795 | -3.946 | -1.396 |

## [$FeF_{10}TPP$]$^{2-}$

| | | | |
|---|---|---|---|
| N | 1.408 | 1.415 | 0.066 |
| N | 1.408 | -1.415 | -0.066 |
| C | -4.959 | 0.000 | 0.000 |
| C | 1.229 | -2.792 | -0.175 |
| C | -3.457 | -2.469 | 0.451 |
| H | -4.526 | -2.592 | 0.613 |
| C | 5.681 | -0.665 | 1.011 |
| H | 5.128 | -1.183 | 1.800 |
| C | -7.788 | 0.000 | 0.000 |
| C | -5.681 | 0.665 | 1.011 |
| H | -5.128 | 1.183 | 1.800 |
| C | -3.464 | 0.000 | 0.000 |
| C | -7.083 | 0.665 | 1.014 |
| C | 2.805 | -1.222 | -0.183 |
| C | 1.229 | 2.792 | 0.175 |
| C | -3.457 | 2.469 | -0.451 |
| H | -4.526 | 2.592 | -0.613 |
| C | -2.805 | -1.222 | 0.183 |
| C | -2.482 | -3.444 | 0.454 |
| H | -2.608 | -4.512 | 0.628 |
| C | -0.748 | 7.095 | 0.948 |
| C | 0.000 | 4.944 | 0.000 |
| C | 2.482 | -3.444 | -0.454 |
| H | 2.608 | -4.512 | -0.628 |
| C | 0.000 | 3.467 | 0.000 |
| C | -1.229 | 2.792 | -0.175 |
| C | 0.000 | 7.803 | 0.000 |
| C | -0.728 | 5.699 | 0.945 |
| C | 7.083 | -0.665 | 1.014 |
| C | -7.083 | -0.665 | -1.014 |
| C | 5.681 | 0.665 | -1.011 |
| H | 5.128 | 1.183 | -1.800 |
| C | 0.748 | 7.095 | -0.948 |
| N | -1.408 | 1.415 | -0.066 |
| N | -1.408 | -1.415 | 0.066 |
| C | 7.083 | 0.665 | -1.014 |
| C | 7.788 | 0.000 | 0.000 |
| C | 3.457 | -2.469 | -0.451 |
| H | 4.526 | -2.592 | -0.613 |
| C | 2.805 | 1.222 | 0.183 |
| C | 0.000 | -3.467 | 0.000 |
| C | 2.482 | 3.444 | 0.454 |
| H | 2.608 | 4.512 | 0.628 |
| C | 3.457 | 2.469 | 0.451 |
| H | 4.526 | 2.592 | 0.613 |
| C | -2.482 | 3.444 | -0.454 |
| H | -2.608 | 4.512 | -0.628 |
| C | 0.728 | 5.699 | -0.945 |
| C | -2.805 | 1.222 | -0.183 |
| C | -1.229 | -2.792 | 0.175 |
| C | 4.959 | 0.000 | 0.000 |
| C | -5.681 | -0.665 | -1.011 |
| H | -5.128 | -1.183 | -1.800 |
| C | 3.464 | 0.000 | 0.000 |
| Fe | 0.000 | 0.000 | 0.000 |
| C | -0.748 | -7.095 | -0.948 |
| C | 0.000 | -4.944 | 0.000 |
| C | 0.000 | -7.803 | 0.000 |
| C | -0.727 | -5.699 | -0.945 |
| C | 0.748 | -7.095 | 0.948 |
| C | 0.727 | -5.699 | 0.945 |
| H | 7.625 | -1.182 | 1.810 |
| H | 8.882 | 0.000 | 0.000 |
| H | 7.625 | 1.182 | -1.811 |
| H | -7.625 | -1.182 | -1.810 |
| H | -8.882 | 0.000 | 0.000 |
| H | -7.625 | 1.182 | 1.811 |
| F | 0.000 | 9.156 | 0.000 |
| F | -1.454 | 7.775 | 1.883 |
| F | 1.454 | 7.775 | -1.883 |
| F | 1.430 | 5.068 | -1.919 |
| F | -1.430 | 5.068 | 1.919 |
| F | 1.429 | -5.068 | 1.919 |
| F | 1.454 | -7.775 | 1.884 |
| F | 0.000 | -9.156 | 0.000 |
| F | -1.454 | -7.775 | -1.884 |
| F | -1.429 | -5.068 | -1.919 |

**$[FeF_{20}TPP]^{2-}$**

| | | | |
|---|---|---|---|
| N | -1.284 | 1.536 | -0.036 |
| N | -1.542 | -1.277 | 0.044 |
| C | 4.932 | -0.451 | -0.002 |
| C | -1.485 | -2.681 | 0.123 |
| C | 3.223 | -2.806 | -0.290 |
| H | 4.281 | -3.038 | -0.409 |
| C | -5.726 | -0.082 | -1.036 |
| C | 7.770 | -0.704 | -0.014 |
| C | 5.726 | 0.082 | -1.036 |
| C | 3.456 | -0.317 | 0.003 |
| C | 7.119 | -0.025 | -1.049 |
| C | -2.906 | -0.976 | 0.117 |
| C | -0.973 | 2.906 | -0.114 |
| C | 3.680 | 2.173 | 0.300 |
| H | 4.761 | 2.208 | 0.418 |
| C | 2.680 | -1.488 | -0.108 |
| C | 2.162 | -3.687 | -0.289 |
| H | 2.191 | -4.769 | -0.401 |
| C | 1.136 | 7.007 | -1.099 |
| C | 0.451 | 4.925 | 0.005 |
| C | -2.796 | -3.232 | 0.298 |
| H | -3.021 | -4.291 | 0.411 |
| C | 0.315 | 3.442 | 0.004 |
| C | 1.485 | 2.681 | 0.123 |
| C | 0.709 | 7.750 | 0.006 |
| C | 0.998 | 5.616 | -1.088 |
| C | -7.119 | 0.025 | -1.049 |
| C | 7.017 | -1.257 | 1.027 |
| C | -5.627 | 1.116 | 1.025 |
| C | 0.155 | 7.096 | 1.111 |
| N | 1.542 | 1.277 | 0.044 |
| N | 1.284 | -1.536 | -0.036 |
| C | -7.017 | 1.257 | 1.027 |
| C | -7.770 | 0.704 | -0.014 |
| C | -3.680 | -2.173 | 0.300 |
| H | -4.761 | -2.208 | 0.418 |
| C | -2.680 | 1.488 | -0.108 |
| C | -0.315 | -3.442 | 0.004 |
| C | -2.162 | 3.687 | -0.289 |
| H | -2.191 | 4.769 | -0.401 |
| C | -3.223 | 2.806 | -0.290 |
| H | -4.281 | 3.038 | -0.409 |
| C | 2.796 | 3.232 | 0.298 |
| H | 3.021 | 4.291 | 0.411 |
| C | 0.038 | 5.702 | 1.098 |
| C | 2.906 | 0.976 | 0.117 |
| C | 0.973 | -2.906 | -0.114 |
| C | -4.932 | 0.451 | -0.002 |
| C | 5.627 | -1.116 | 1.025 |
| C | -3.456 | 0.317 | 0.003 |
| Fe | 0.000 | 0.000 | 0.004 |
| C | -0.155 | -7.096 | 1.111 |
| C | -0.451 | -4.925 | 0.005 |
| C | -0.709 | -7.750 | 0.006 |
| C | -0.038 | -5.702 | 1.098 |
| C | -1.136 | -7.007 | -1.099 |
| C | -0.998 | -5.616 | -1.088 |
| F | 0.832 | 9.094 | 0.007 |
| F | 1.664 | 7.642 | -2.169 |
| F | -0.251 | 7.814 | 2.182 |
| F | -0.486 | 5.105 | 2.194 |
| F | 1.406 | 4.935 | -2.184 |
| F | -1.406 | -4.935 | -2.184 |
| F | -1.664 | -7.642 | -2.169 |
| F | -0.832 | -9.094 | 0.007 |
| F | 0.251 | -7.814 | 2.182 |
| F | 0.486 | -5.105 | 2.194 |
| F | -4.946 | 1.637 | 2.075 |
| F | -7.646 | 1.898 | 2.040 |
| F | -9.116 | 0.824 | -0.020 |
| F | -7.843 | -0.496 | -2.067 |
| F | -5.139 | -0.717 | -2.080 |
| F | 4.946 | -1.637 | 2.075 |
| F | 7.646 | -1.898 | 2.040 |
| F | 9.116 | -0.824 | -0.020 |
| F | 7.843 | 0.496 | -2.067 |
| F | 5.139 | 0.717 | -2.080 |

$CO_2$-[**FeTPP**]$^{2-}$

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| N | 1.762 | 0.854 | -0.115 | H | 8.370 | -2.880 | 0.078 | C | -2.618 | -5.084 | 0.911 |
| N | -0.846 | 1.779 | 0.141 | C | 5.104 | -2.576 | -0.898 | H | -3.000 | -4.366 | 1.642 |
| C | -1.642 | -4.657 | -0.014 | C | 1.628 | 6.917 | -0.967 | C | 1.142 | 3.255 | -0.005 |
| C | -2.209 | 2.059 | 0.271 | C | -3.091 | -6.402 | 0.903 | Fe | 0.001 | 0.002 | 0.139 |
| C | -3.435 | -2.406 | -0.611 | C | 2.621 | 5.088 | 0.905 | C | -6.897 | 1.580 | 1.013 |
| H | -3.896 | -3.368 | -0.827 | H | 3.004 | 4.371 | 1.636 | C | -4.652 | 1.623 | 0.042 |
| C | 1.156 | 5.598 | -0.954 | C | 6.901 | -1.576 | 1.000 | C | -7.333 | 2.533 | 0.080 |
| H | 0.401 | 5.277 | -1.677 | H | 7.597 | -1.184 | 1.747 | H | -8.368 | 2.884 | 0.095 |
| C | -2.598 | -7.323 | -0.034 | N | 0.848 | -1.774 | 0.140 | C | -5.570 | 1.130 | 0.993 |
| C | -1.156 | -5.594 | -0.950 | N | -1.760 | -0.850 | -0.113 | C | -6.431 | 3.032 | -0.872 |
| H | -0.403 | -5.273 | -1.675 | C | 3.094 | 6.407 | 0.895 | H | -6.763 | 3.770 | -1.606 |
| C | -1.141 | -3.250 | -0.003 | C | 2.600 | 7.327 | -0.041 | C | -5.104 | 2.580 | -0.889 |
| C | -1.629 | -6.913 | -0.961 | C | -1.178 | 4.052 | 0.575 | H | -4.402 | 2.967 | -1.632 |
| C | -0.216 | 3.024 | 0.254 | H | -0.938 | 5.098 | 0.751 | H | 1.240 | 7.625 | -1.704 |
| C | 3.000 | 0.220 | -0.248 | C | 2.048 | 2.216 | -0.263 | H | 2.968 | 8.356 | -0.050 |
| C | 1.180 | -4.047 | 0.573 | C | -3.239 | 1.139 | 0.026 | H | 3.848 | 6.719 | 1.624 |
| H | 0.941 | -5.094 | 0.750 | C | 4.026 | 1.173 | -0.607 | H | -5.228 | 0.389 | 1.720 |
| C | -2.046 | -2.211 | -0.260 | H | 5.064 | 0.923 | -0.816 | H | -7.591 | 1.188 | 1.762 |
| C | -4.026 | -1.168 | -0.600 | C | 3.436 | 2.410 | -0.617 | H | -3.844 | -6.713 | 1.633 |
| H | -5.064 | -0.919 | -0.807 | H | 3.896 | 3.372 | -0.834 | H | -2.967 | -8.352 | -0.042 |
| C | 6.430 | -3.028 | -0.884 | C | 2.416 | -3.449 | 0.582 | H | -1.242 | -7.621 | -1.699 |
| C | 4.653 | -1.619 | 0.034 | H | 3.383 | -3.913 | 0.765 | H | 4.399 | -2.963 | -1.639 |
| C | -2.414 | 3.454 | 0.585 | C | 5.574 | -1.126 | 0.982 | H | 6.761 | -3.767 | -1.619 |
| H | -3.380 | 3.917 | 0.770 | H | 5.234 | -0.385 | 1.710 | C | 0.002 | 0.002 | 2.169 |
| C | 3.240 | -1.135 | 0.021 | C | 0.218 | -3.020 | 0.254 | O | -1.137 | -0.086 | 2.671 |
| C | 2.211 | -2.055 | 0.268 | C | -2.999 | -0.215 | -0.244 | O | 1.142 | 0.091 | 2.669 |
| C | 7.334 | -2.529 | 0.066 | C | 1.644 | 4.661 | -0.018 | | | | |

$CO_2$-[**$FeF_{10}$TPP**]$^{2-}$

| | | | |
|---|---|---|---|
| N | 1.389 | 1.394 | 0.160 |
| N | 1.386 | -1.378 | -0.097 |
| C | -4.938 | 0.005 | 0.029 |
| C | 1.207 | -2.755 | -0.235 |
| C | -3.432 | -2.472 | 0.529 |
| H | -4.502 | -2.598 | 0.679 |
| C | 5.648 | -0.726 | 1.008 |
| H | 5.087 | -1.279 | 1.766 |
| C | -7.767 | 0.031 | 0.034 |
| C | -5.652 | 0.731 | 1.004 |
| H | -5.092 | 1.285 | 1.762 |
| C | -3.444 | -0.003 | 0.028 |
| C | -7.053 | 0.745 | 1.009 |
| C | 2.767 | -1.195 | -0.217 |
| C | 1.206 | 2.777 | 0.255 |
| C | -3.426 | 2.448 | -0.544 |
| H | -4.491 | 2.562 | -0.731 |
| C | -2.777 | -1.213 | 0.261 |
| C | -2.459 | -3.439 | 0.522 |
| H | -2.578 | -4.512 | 0.667 |
| C | -0.648 | 7.061 | 0.998 |
| C | -0.013 | 4.919 | -0.013 |
| C | 2.454 | -3.412 | -0.550 |
| H | 2.569 | -4.477 | -0.745 |
| C | -0.006 | 3.429 | 0.006 |
| C | -1.210 | 2.760 | -0.237 |
| C | -0.031 | 7.753 | -0.049 |
| C | -0.628 | 5.663 | 1.005 |
| C | 7.049 | -0.739 | 1.014 |
| C | -7.070 | -0.695 | -0.943 |
| C | 5.666 | 0.712 | -0.940 |
| H | 5.122 | 1.275 | -1.703 |
| C | 0.594 | 7.042 | -1.079 |
| N | -1.389 | 1.383 | -0.099 |
| N | -1.392 | -1.389 | 0.160 |
| C | 7.068 | 0.699 | -0.938 |
| C | 7.764 | -0.027 | 0.040 |
| C | 3.423 | -2.443 | -0.540 |
| H | 4.489 | -2.557 | -0.726 |
| C | 2.773 | 1.218 | 0.262 |
| C | 0.003 | -3.424 | 0.008 |
| C | 2.456 | 3.444 | 0.522 |
| H | 2.574 | 4.517 | 0.666 |
| C | 3.429 | 2.477 | 0.530 |
| H | 4.498 | 2.603 | 0.681 |
| C | -2.457 | 3.417 | -0.554 |
| H | -2.572 | 4.482 | -0.749 |
| C | 0.592 | 5.645 | -1.050 |
| C | -2.770 | 1.200 | -0.220 |
| C | -1.210 | -2.772 | 0.256 |
| C | 4.935 | 0.000 | 0.032 |
| C | -5.669 | -0.708 | -0.944 |
| H | -5.124 | -1.271 | -1.706 |
| C | 3.441 | 0.008 | 0.030 |
| Fe | -0.002 | 0.002 | 0.160 |
| C | -0.597 | -7.038 | -1.074 |
| C | 0.010 | -4.914 | -0.010 |
| C | 0.028 | -7.748 | -0.044 |
| C | -0.594 | -5.641 | -1.047 |
| C | 0.644 | -7.055 | 1.004 |
| C | 0.624 | -5.657 | 1.009 |
| H | 7.583 | -1.304 | 1.783 |
| H | 8.857 | -0.037 | 0.043 |
| H | 7.617 | 1.253 | -1.704 |
| H | -7.619 | -1.250 | -1.709 |
| H | -8.860 | 0.042 | 0.037 |
| H | -7.588 | 1.310 | 1.776 |
| F | -0.040 | 9.101 | -0.067 |
| F | -1.247 | 7.749 | 1.995 |
| F | 1.184 | 7.712 | -2.093 |
| F | 1.192 | 4.991 | -2.071 |
| F | -1.223 | 5.028 | 2.041 |
| F | 1.218 | -5.022 | 2.045 |
| F | 1.242 | -7.743 | 2.001 |
| F | 0.037 | -9.096 | -0.060 |
| F | -1.186 | -7.709 | -2.088 |
| F | -1.194 | -4.988 | -2.069 |
| C | -0.002 | 0.003 | 2.209 |
| O | -0.971 | 0.611 | 2.702 |
| O | 0.966 | -0.605 | 2.703 |

$CO_2$-[**$FeF_{20}$TPP**]$^{2-}$

| | | | |
|---|---|---|---|
| N | -1.260 | 1.516 | -0.068 |
| N | -1.508 | -1.279 | 0.071 |
| C | 4.894 | -0.444 | 0.186 |
| C | -1.462 | -2.676 | 0.069 |
| C | 3.230 | -2.769 | -0.285 |
| H | 4.295 | -2.981 | -0.362 |
| C | -5.733 | 0.078 | -0.872 |
| C | 7.706 | -0.729 | 0.361 |
| C | 5.735 | -0.077 | -0.874 |
| C | 3.413 | -0.300 | 0.101 |
| C | 7.126 | -0.208 | -0.800 |
| C | -2.867 | -0.983 | 0.188 |
| C | -0.974 | 2.878 | -0.201 |
| C | 3.655 | 2.187 | 0.317 |
| H | 4.736 | 2.220 | 0.439 |
| C | 2.656 | -1.459 | -0.084 |
| C | 2.184 | -3.650 | -0.366 |
| H | 2.223 | -4.728 | -0.518 |
| C | 1.100 | 6.940 | -1.386 |
| C | 0.435 | 4.916 | -0.173 |
| C | -2.780 | -3.240 | 0.236 |
| H | -3.004 | -4.304 | 0.283 |
| C | 0.303 | 3.434 | -0.103 |
| C | 1.465 | 2.677 | 0.069 |
| C | 0.693 | 7.733 | -0.308 |
| C | 0.964 | 5.551 | -1.307 |
| C | -7.123 | 0.209 | -0.798 |
| C | 6.895 | -1.110 | 1.435 |
| C | -5.506 | 0.961 | 1.338 |
| C | 0.160 | 7.133 | 0.837 |
| N | 1.511 | 1.280 | 0.071 |
| N | 1.263 | -1.515 | -0.069 |
| C | -6.892 | 1.110 | 1.437 |
| C | -7.703 | 0.729 | 0.363 |
| C | -3.653 | -2.187 | 0.318 |
| H | -4.734 | -2.220 | 0.441 |
| C | -2.654 | 1.459 | -0.083 |
| C | -0.301 | -3.433 | -0.103 |
| C | -2.182 | 3.651 | -0.365 |
| H | -2.221 | 4.728 | -0.517 |
| C | -3.228 | 2.770 | -0.284 |
| H | -4.292 | 2.982 | -0.360 |
| C | 2.783 | 3.241 | 0.235 |
| H | 3.007 | 4.305 | 0.282 |
| C | 0.042 | 5.740 | 0.891 |
| C | 2.869 | 0.984 | 0.187 |
| C | 0.976 | -2.877 | -0.201 |
| C | -4.892 | 0.444 | 0.188 |
| C | 5.508 | -0.961 | 1.336 |
| C | -3.410 | 0.300 | 0.102 |
| Fe | 0.001 | 0.000 | 0.120 |
| C | -0.157 | -7.132 | 0.838 |
| C | -0.433 | -4.916 | -0.173 |
| C | -0.691 | -7.733 | -0.307 |
| C | -0.039 | -5.740 | 0.892 |
| C | -1.098 | -6.940 | -1.385 |
| C | -0.962 | -5.551 | -1.306 |
| F | 0.816 | 9.074 | -0.372 |
| F | 1.611 | 7.523 | -2.491 |
| F | -0.228 | 7.900 | 1.878 |
| F | -0.468 | 5.191 | 2.017 |
| F | 1.359 | 4.814 | -2.370 |
| F | -1.357 | -4.814 | -2.369 |
| F | -1.609 | -7.523 | -2.490 |
| F | -0.813 | -9.074 | -0.371 |
| F | 0.231 | -7.900 | 1.879 |
| F | 0.472 | -5.190 | 2.017 |
| F | -4.751 | 1.332 | 2.396 |
| F | -7.456 | 1.609 | 2.558 |
| F | -9.042 | 0.865 | 0.447 |
| F | -7.908 | -0.153 | -1.836 |
| F | -5.203 | -0.420 | -2.013 |
| F | 4.754 | -1.332 | 2.395 |
| F | 7.459 | -1.609 | 2.556 |
| F | 9.044 | -0.865 | 0.444 |
| F | 7.910 | 0.153 | -1.838 |
| F | 5.205 | 0.420 | -2.015 |
| C | 0.001 | 0.000 | 2.172 |
| O | 1.102 | -0.320 | 2.654 |
| O | -1.099 | 0.320 | 2.655 |

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