

Materials. Chemicals used in this work were purchased from Sigma-Aldrich Company and Wako Ltd, and were used without further purification, lithium diisobutyl-*t*-butoxyaluminum hydride (LDBBA),^{S1} **FeTPP** and 1,3-phenylene bridged iron tetraphenyl porphyrin dimer, ***m*-Fe₂DTPP** were prepared by literature methods.^{S2} Solvents were distilled from appropriate drying agents under nitrogen just prior to use. Mill-Q water (18 M Ω.cm) was used for solutions preparation.

Instruments. ¹H NMR spectra were recorded on a JEOL JMX-GX 400 (400 MHz) spectrometer. Chemical shifts are reported as parts per million (ppm) with respect to CHCl₃. Matrix Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-TOF) mass spectra were measured on a BRUKER Auto flex II LRF20 spectrometer using dithranol as a matrix. UV-vis spectra were recorded using a Shimadzu UV-3100PC spectrophotometer. Electrochemical measurements were performed with a Metrohm Autolab Potentiostat/Galvanostat model PGSTAT 302. Gas chromatographic analyses were done with a Shimadzu GC-8A equipped with a capillary column (0.53 mm ID x 15 m) with a Molecular Sieve 5A layer at 40 °C using Ar as a carrier gas. Capillary electrophoretic analyses were performed with Agilent model 7100 with use of a buffer (pH 6.0) consisting of quinolinic acid, hexadecyltrimethylammonium hydroxide, and 2- amino-2-hydroxymethyl-1,3-propandiol.

Cyclic voltammetry measurements. Cyclic voltammetric experiments were performed using a small three-electrode electrochemical cell. In a typical experiment, a total of 2.0 mL of DMF solution containing 0.1 M TBAPF₆ supporting electrolyte and 0.5 mM of the dimer was used. A glassy carbon (3 mm ø), a Pt wire and a Ag/AgCl (3M NaCl) were used as a working, a counter, and reference electrodes, respectively. All potentials reported in this work were referenced to normal hydrogen electrode (NHE) by addition of 0.198 V to the potential measured with respect to Ag/AgCl (3M NaCl) reference electrode. All measurements were made at room temperature 25°C.

Reduction of carbon dioxide using controlled potential electrolysis. The reduction of carbon dioxide was carried out under controlled-potential electrolysis in a CO₂-saturated DMF/10%H₂O solution containing 0.1 M TBAPF₆ as supporting electrolyte. This was performed in a gas tight one-compartment cell: The cell was filled with DMF/10% H₂O solution containing 0.1 M TBAPF₆ and 0.5 mM of the iron porphyrin dimer. The solution was substituted by Ar for 20 min, then saturated with CO₂ gas by bubbling the gas for 30 min. A glassy carbon (1 cm²) and Ag/AgCl (3 M NaCl) working and reference electrodes were inserted close to each other and a Pt foil (20 cm²) was used as a counter electrode.

***K*_{cat}, TON, and TOF calculations from bulk electrolysis experiment:**

0.5 mM (5 x 10⁻⁷ mole/cm³) ***o*-Fe₂TPP** catalyst was used. The net current density of 1.05 mA/cm² with 95% Faradic efficiency (*I* = 0.9975 mA/cm² is corresponding to CO formation) was obtained during 10 h-electrolysis at applied potential, *E* = -1.35 V. The catalyst standard potential obtained from the cyclic voltammogram under Ar atmosphere, *E*^o_{cat} is -1.45 V vs. NHE. By considering the diffusion coefficient of the catalyst, *D* = 5 x 10⁻⁶ mole•cm²•s⁻¹, and using the values of Faraday constant, *F* and the gas constant, *R*, *K*_{cat}, TON, and TOF were calculated from the reported equations (1) - (3),^{S3}

$$I/F = \frac{(K_{cat}D)^{1/2}C_{cat}^o}{(1 + \exp[(F/RT)(E-E_{cat}^o)])} \quad (1)$$

$$TOF = \frac{K_{cat}}{(1 + \exp[(F/RT)(E-E_{cat}^o)])} \quad (2)$$

$$TON = \frac{K_{cat} t}{(1 + \exp[(F/RT)(E-E_{cat}^o)])} \quad (3)$$

Product analysis.

CO and H₂ gas calibration curve constrictions: The electrolysis cell was filled with the electrolysis solution (10 mL, DMF/10% H₂O containing 0.1 M TBAPF₆), the solution was then purged with CO₂ gas for 30 min then the cell was closed and different known amounts of CO and H₂ gases were introduced to the headspace at different intervals (each 2.0 h) then 500 µl of the headspace gas was taken with a gas-tight syringe at a fixed interval and analyzed the samples on a GC. The areas of the H₂ peak (at 0.9 min retention time) and that of CO (at 2.3 min retention time) were used for calibration of H₂ and CO, respectively.

The calibration curves for H₂ and CO were then used to determine the generated CO and H₂ gases produced during the bulk electrolysis experiments.

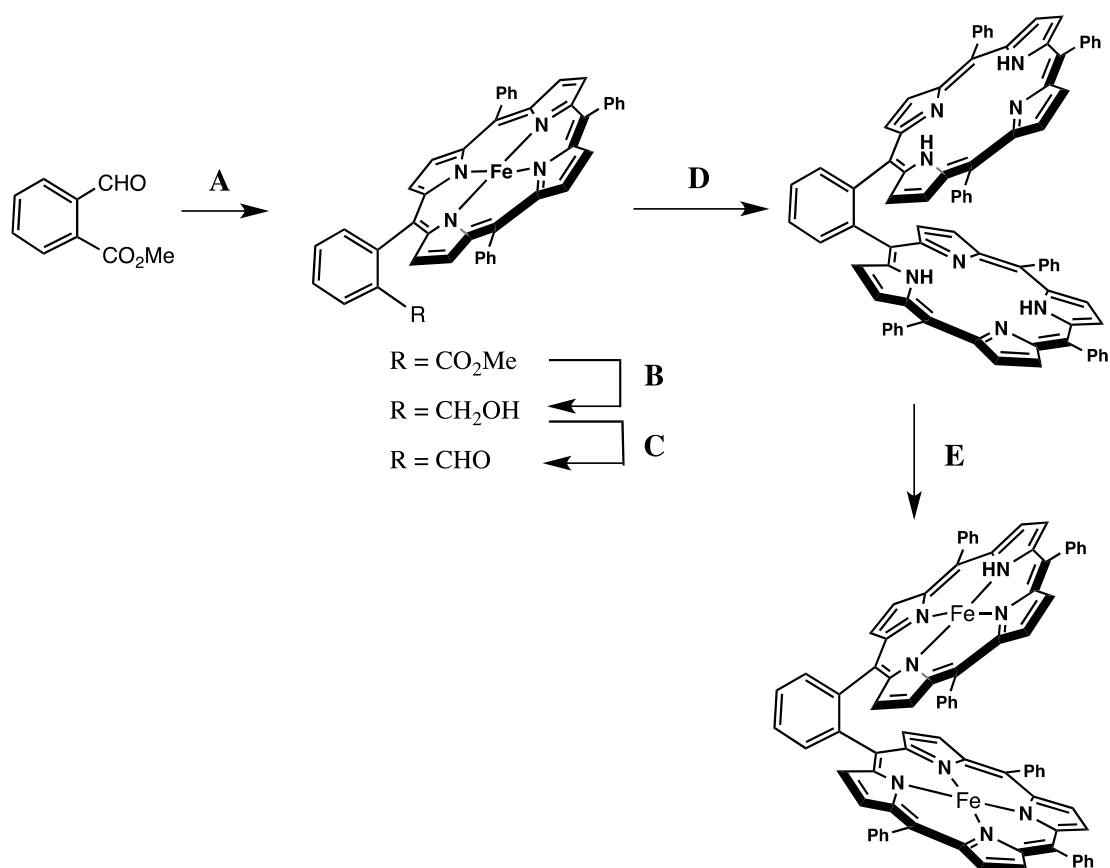
HCOOH calibration curve construction: HCOOH standard solutions were prepared in the same solution (DMF/10% H₂O) containing 0.1 M TBANPF₆, then 50 µl of the solution were transferred into 1 mL distilled water and a white precipitate of the supporting electrolyte was filtered off. The resultant clear solution was injected into a capillary electrophoresis instrument and eluted with buffer solution (pH 6.0). The area assigned for formic acid at 2.88 min retention time was used to make a calibration curve.

The calibration curve was used to determine the concentration of the formic acid generated from the bulk electrolysis experiments.

Preparation of cofacial iron porphyrin dimer (*o*-Fe₂TPP). The cofacial tetraphenyl porphyrin ligand^{S2} was prepared by stepwise procedures developed in our group according to Scheme S1. Iron was inserted into the free-base porphyrin dimer by refluxing a solution of the porphyrin dimer (200 mg, 0.13 mmol) in dry DMF (20 ml,) with excess FeBr₂ (150 mg, 0.69 mmol) overnight. The solvent was then removed and the desired compound was extracted with CHCl₃/HCl (1M in H₂O) three times then with CHCl₃/NaHCO₃ (saturated) three times and finally with the CHCl₃/H₂O three times. The organic layer containing the desired compound was dried

over anhydrous sodium sulfate. The compound was further purified with silica gel column using CH_2Cl_2 containing 5% MeOH as an eluent. The reddish brown band was collected to give a reddish brown powder (197 mg, 88.3 % yield). MALDI-TOF-MS of the *o*- Fe_2TPP dimer shows peaks at m/z values of 1294.2 corresponding to *o*- $\text{Fe}_2\text{TPP}\text{Cl}$ (calc. 1294.47) and 1259.0 corresponding to *o*- Fe_2TPP (calc. 1259.02).

Scheme S1. Synthetic route of the cofacial iron porphyrin dimer catalyst, *o*- Fe_2DTPP . Reaction conditions, **A**: pyrrole, benzaldehyde, $\text{BF}_3\cdot\text{Et}_2\text{O}$, CHCl_3 , DDQ, **B**: LDBBA, **C**: MnO_2 , **D**: pyrrole, benzaldehyde, $\text{BF}_3\cdot\text{Et}_2\text{O}$, CHCl_3 , DDQ, **E**: FeBr_2 , DMF.



Details of the CV behavior of *o*- Fe_2DTPP_2 :

In a DMF/TBAPF₆ (TBAPF₆ = tetra-*n*-butylammonium hexafluorophosphate, 0.1M) solution saturated with Ar gas, ***o*-Fe₂DTPP₂** (0.5 mM), shows cyclic voltammetric (CV) behavior as depicted in Figure 2 (black dotted line) and in Figure S1a. The dimer shows a reversible redox couple with a reduction peak potential, $E_p(\text{Red}) = -0.64$ V and a corresponding return oxidation peak potential, $E_p(\text{Ox}) = -0.58$ V vs. NHE upon scanning to -0.8 V vs. NHE. The reduction peak current, $i_p(\text{red})$ increases linearly with the square root of the scan rate indicating a diffusion-controlled process (Figure S2). This redox couple is attributed to two successive electrons reductions/oxidations of the two iron centers of the dimer, *i.e.*, $2\text{Fe}^{3+}/2\text{Fe}^{2+}$. The significant negative shift in the reduction/oxidation reversible couple of the $2\text{Fe}^{3+}/2\text{Fe}^{2+}$ in the dimer relative to that in the monomer (FeTPP monomer shows 1e⁻ reversible $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple at 0.013/0.066 V, Figure S1b) is tentatively attributed to strong Cl⁻ binding/association to the two iron centers between the two cofacial porphyrin bi-layers. Scanning to further negative potential, -1.1 V resulted in partial dissociation of Cl⁻ as indicated from the return oxidation peaks at -0.58 V, -0.15 V, and 0.10 V (Figure S1a). Scanning to a more negative potential of -1.4 V or more (to -2.0 V) resulted in complete removal of the Cl⁻ as indicated from the complete disappearance of the return oxidation peak at -0.58 V and the enhancement of the oxidation peaks at -0.15 V and 0.10 V (Figure S1a). The cofacial iron porphyrin dimer undergoes two further irreversible reductions of the two iron centers, *i.e.*, $2\text{Fe}^{2+}/2\text{Fe}^+$ at -1.22 V with two corresponding return oxidation peaks at -1.09 V and -0.82 V. This indicates that EC mechanism is operating. Finally, two stepwise reversible redox couples attributed to the further reduction of the two iron centers, *i.e.*, $2\text{Fe}^+/2\text{Fe}^0$ was observed at $-1.48/-1.42$ V and $-1.58/-1.52$ V (Figure S1a). Under the same conditions and as previously reported,³ the **FeTPP** in DMF with a glassy carbon or a mercury electrode shows three reversible redox couples corresponding to $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Fe}^{2+}/\text{Fe}^+$, and Fe^+/Fe^0 at 0.013/0.07, $-0.081/-0.75$ V, and $-1.45/-1.38$ V, respectively (Figure S1b).

Under a CO₂ atmosphere, ***o*-Fe₂DTPP** (0.5 mM) shows the CV behavior depicted in Figure 2 (blue line) and Figure S3. The reversible $2\text{Fe}^{3+}/2\text{Fe}^{2+}$ redox couple

observed at $\square 0.64/\square 0.58$ V upon scanning to $\square 0.80$ V under an Ar atmosphere disappeared. A new reduction peak appeared at $\square 0.61$ V upon negative scanning to $\square 0.8$ V. We tentatively propose that this new reduction peak is due to the dissociation of the Cl^\square and the coordination of the CO_2 molecule to the electro-generated 2Fe^{2+} species inside the cofacial porphyrin cavity within the time scale of CV. This proposed dissociation of the Cl^\square and coordination of CO_2 is supported by the irreversibility of the reduction peak at $\square 0.61$ V and the appearance of a new return oxidation peak at 0.07 V that is coupled with the reduction peak at $\square 0.033$ V upon successive cycling under a CO_2 atmosphere. The UV-vis spectra of the chemically reduced $o\text{-Fe}_2^{2+}\text{DTTPP}$ shows the remarkable change of its Soret and the Q-bands upon purging of CO_2 gas at -30°C , indicating the binding of CO_2 to the Fe^{2+} porphyrin species (Figure S6). Upon further scanning to more negative potential ($\square 1.3$ V) the electro-generated CO_2 -coordinated 2Fe^{2+} species showed a reversible $2e^\square$ redox couple at $\square 0.86/\square 0.75$ V corresponding to the generation of CO_2 coordinated $2\text{Fe}^{2+}/2\text{Fe}^+$ species. This couple is completely different from that observed under Ar atmosphere (under Ar, the $2\text{Fe}^{2+}/2\text{Fe}^+$ is observed at $\square 1.22$ V and is irreversible). Indeed, the ability of CO_2 to coordinate transition metal complexes is well documented.^{S4} However, the coordination of CO_2 to the electro-generated Fe^{2+} species is not observed in the corresponding iron porphyrin monomer under similar experimental conditions.

The effect of water content on the catalytic CO_2/CO reduction with ***o*-Fe₂DTTPP** is shown in Figure S4. In the water-free DMF solution, a large catalytic current started at $\square 1.32$ V and reached to a plateau current of $60 \mu\text{A}$ at $\square 1.8$ V in a CO_2 -saturated solution. Increasing the H_2O content to 10% in the medium induces the positive shift of the starting potential and increases the catalytic peak current, where the catalytic peak starts at $\square 1.22$ V and reaches to $235 \mu\text{A}$ at $\square 1.8$. Further addition of H_2O above 10% decreases the catalytic peak current due to the decreasing solubility of the dimer.

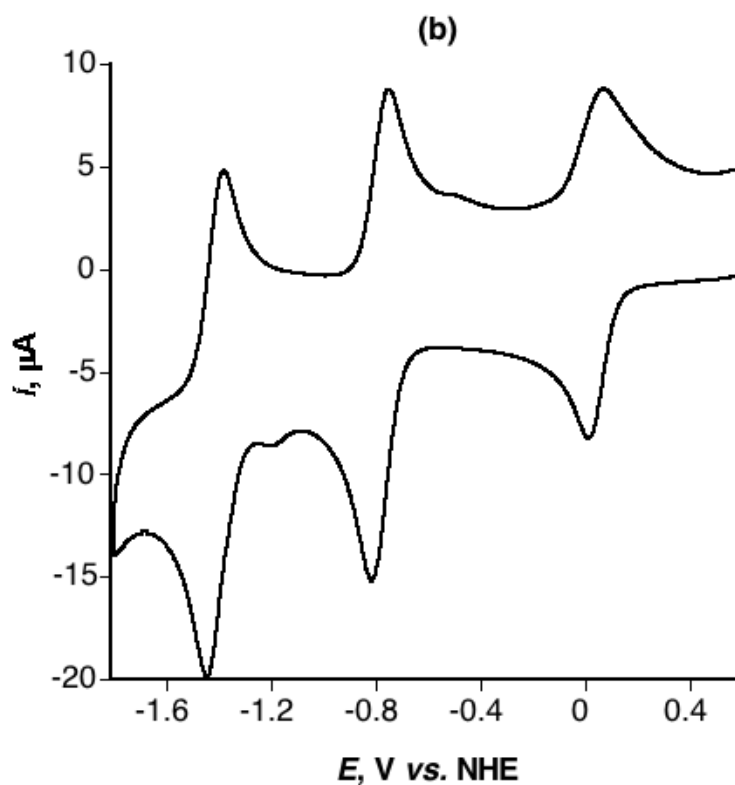
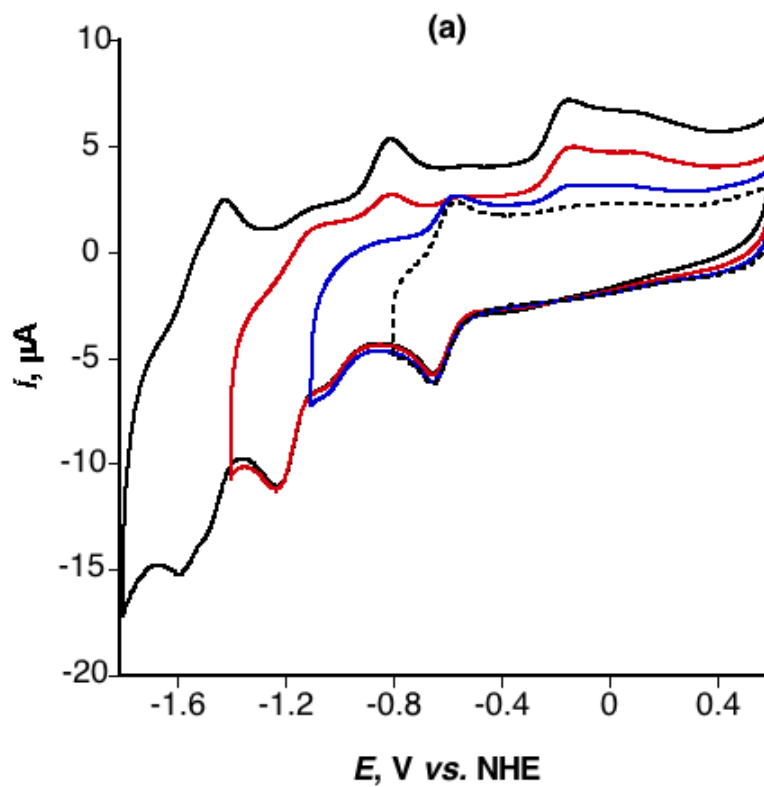


Figure S1. CV's of cofacial iron tetraphenyl porphyrin dimer, *o*-Fe₂TPP (0.5mM) (a) and FeTPP (1 mM) (b) at 100 mV/s scan rate in DMF containing 0.1 M TBANPF₆ supporting electrolyte under Ar. In (a), black dotted, blue, red, and black solid lines are CVs scanned to -0.8, -1.1, -1.4, □□□ -1.8 V □□□□□□□□□□□□□□□□

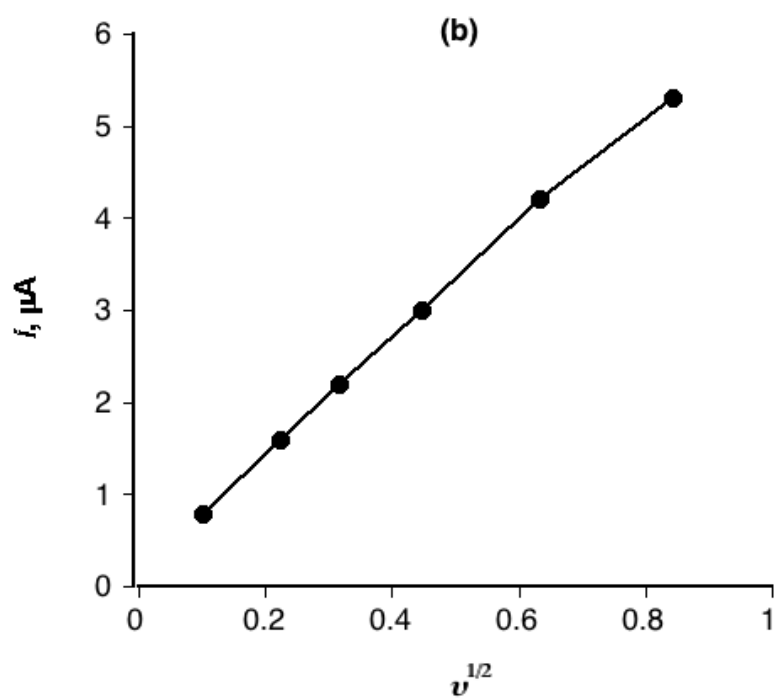
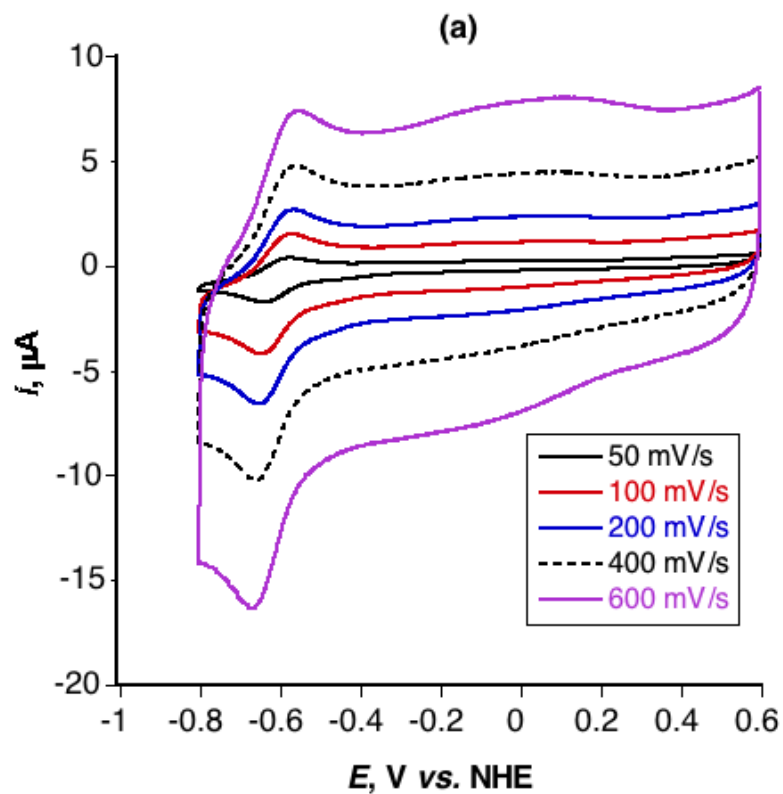


Figure S2. CV's of cofacial iron tetraphenyl porphyrin dimer, *o*- Fe_2TPP (0.5mM) at different scan rates (a) and the diffusion current peak-(scan rate)^{1/2} relationship (b), in DMF containing 0.1 M TBANPF₆ supporting electrolyte under Ar.

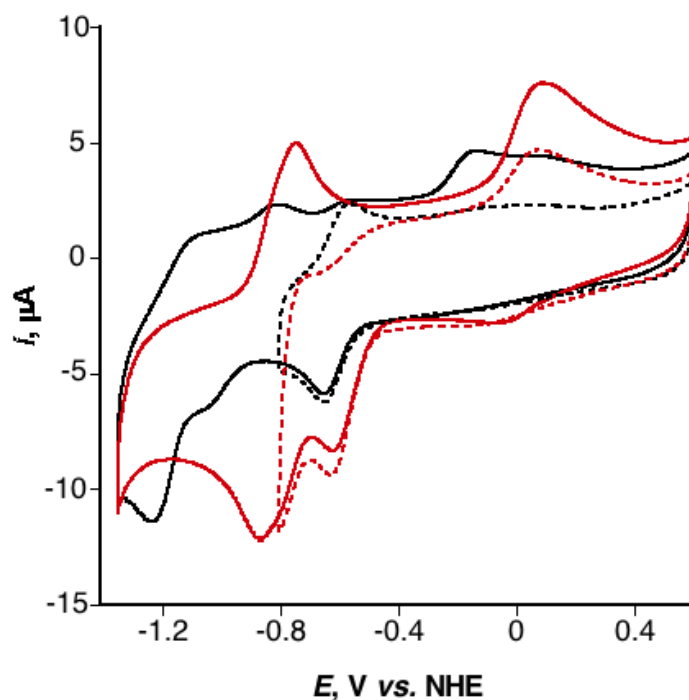


Figure S3. CV's of *o*-Fe₂TPP (0.5mM) at 100 mV/s scan rate in DMF containing 0.1 M TBANPF₆ supporting electrolyte under Ar (black dotted and solid lines) and under CO₂ (red dotted and solid lines). Dotted red and black lines are CVs scanned to -0.8 V and solid red and black lines are CVs scanned to -1.4 V.

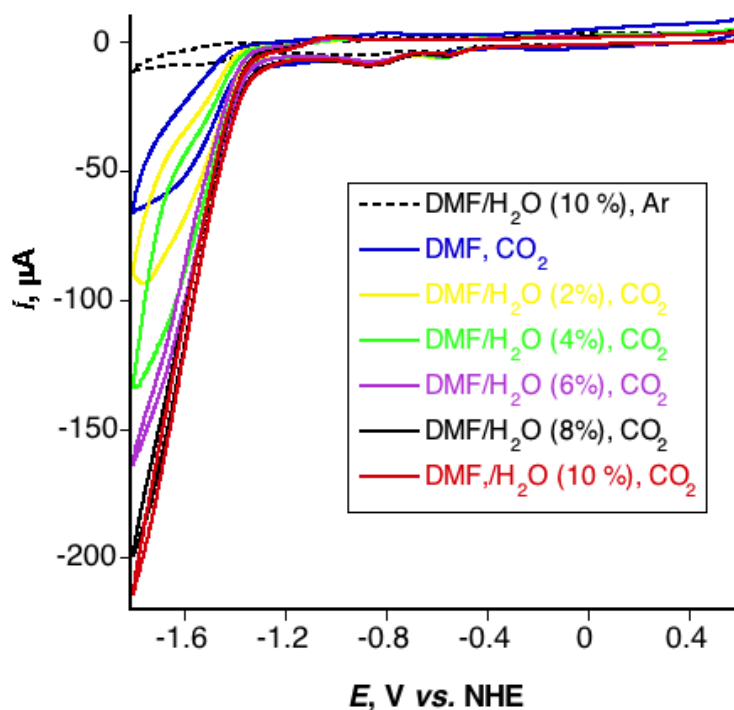


Figure S4. CVs of *o*-Fe₂TPP (0.5 mM) at 100 mV/s scan rate in DMF containing 0.1 M TBANPF₆ supporting electrolyte in the presence of different amounts of H₂O under Ar or CO₂.

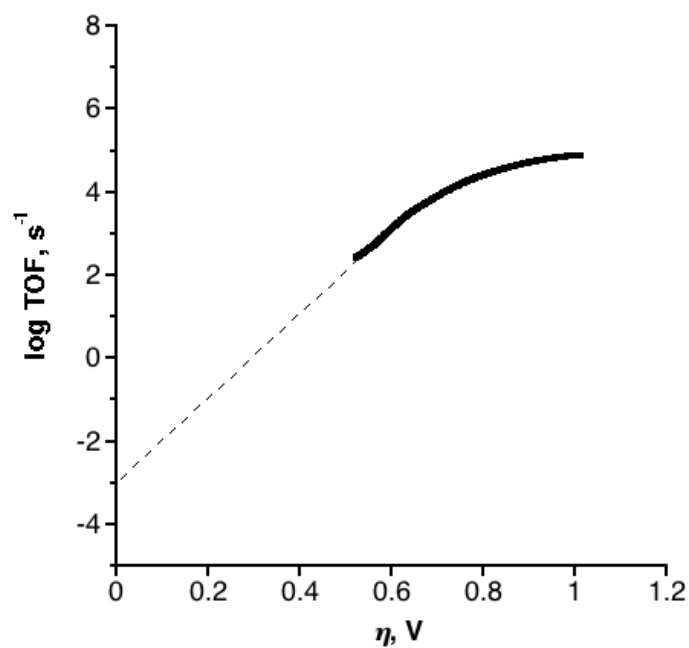


Figure S5. Log TOF- η relationship of *o*-Fe₂TPP (0.5mM) in DMF/10% H₂O containing 0.1 M TBAPF₆ supporting electrolyte saturated with CO₂.

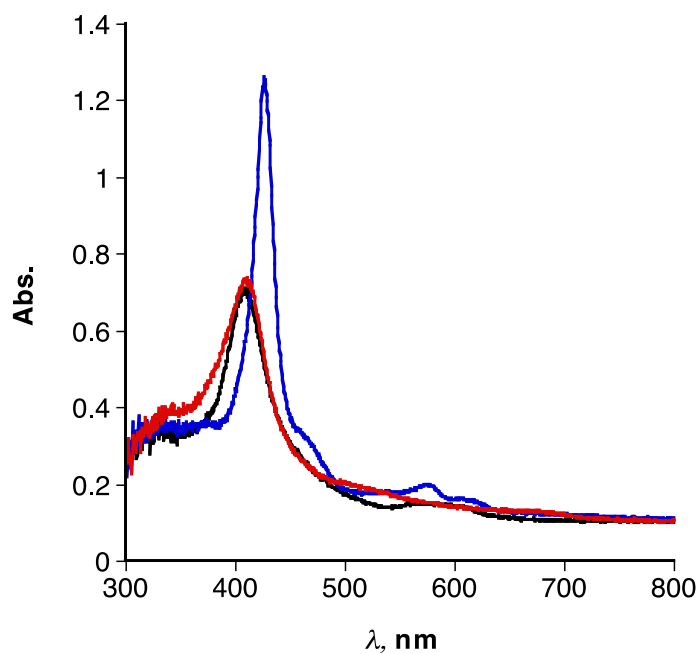


Figure S6. UV-vis spectra of *o*-Fe₂³⁺TPP (black line, 38 μM) and chemically reduced *o*-Fe₂²⁺TPP under Ar (blue line) and CO₂ (red line) in dry DMF at -30 °C indicating the binding of CO₂ to the Fe²⁺por species.

References

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