

Supplementary Information

A local proton source from carboxylic acid functionalized metal porphyrins for enhanced electrocatalytic CO₂ reduction

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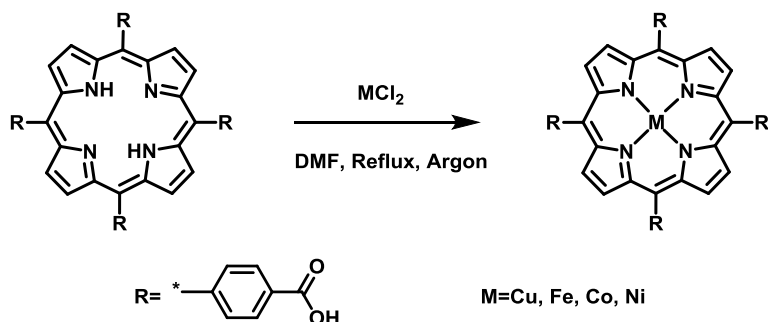
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Materials.

4,4',4'',4'''-(Porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid) (Dye content, 75%, Sigma-Aldrich LLC), Hematoporphyrin (Carbosynth, Ltd), NaOH (97%, Aladdin), HCl (36%-38%, Yongfei Chemical Reagent Co. Ltd.), ultrapure water (18.2 M Ω ·cm). CuCl₂·H₂O (98%), FeCl₂ (99.5%), CoCl₂ (98%), and NiCl₂ (98%) were purchased from Sun Chemical Technology (shanghai)Co., Ltd. All chemicals were used as received without further purification.

Preparation details.



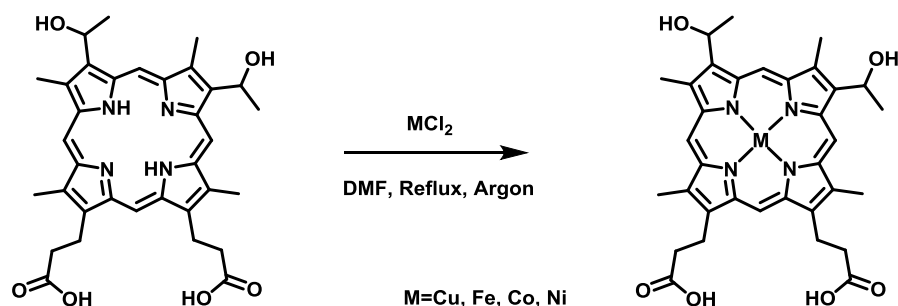
CuTPP_COOH (Cu^{II}AH): 70 ml anhydrous DMF was bubbled with argon for 0.5 h. 0.3103 g CuCl₂·H₂O was added and bubbled with argon for another 0.5 h. 0.2609g 4,4',4'',4'''-(Porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid) was added and bubbled for another 1 h. The mixture solution was refluxed at 160-170 °C overnight. After cooling and DMF removal by distillation, the obtained electrocatalysts CuTPP_COOH were precipitated by adding water. The precipitate was then dissolved in 0.1 M NaOH solution and re-precipitated by adding 1 M HCl solution. Finally, the metal porphyrin was dissolved in ethanol and recrystallized by solvent evaporation (0.278g). UV-vis (DMF): $\lambda_{\text{max}} = 417 \text{ nm}$ (Soret), 540 nm (Q₁).

FeTPP_COOH (Fe^{II}AH): 70 ml anhydrous DMF was bubbled with argon for 0.5 h. 0.2307 g FeCl₂ was added and bubbled with argon for another 0.5 h. 0.2609g 4,4',4'',4'''-(Porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid) was added and bubbled for another 1 h. The mixture solution was refluxed at 160-170 °C overnight. After cooling and DMF removal by distillation, the obtained electrocatalysts FeTPP_COOH were precipitated by adding water. The precipitate was then dissolved in 0.1 M NaOH solution and re-precipitated by adding 1 M HCl solution. Finally, the metal porphyrin was dissolved in ethanol and recrystallized by solvent evaporation (0.32g). UV-vis (DMF): $\lambda_{\text{max}} = 420 \text{ nm}$ (Soret), 508 nm (Q₁), 574 nm (Q₂).

CoTPP_COOH (Co^{II}AH): 70 ml anhydrous DMF was bubbled with argon for 0.5 h. 0.2363 g FeCl₂ was added and bubbled with argon for another 0.5 h. 0.2609g 4,4',4'',4'''-(Porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid) was added and bubbled for another 1 h. The mixture solution was refluxed at 160-170 °C overnight. After cooling and DMF removal by distillation, the obtained electrocatalysts CoTPP_COOH were precipitated by adding water. The precipitate was then dissolved in 0.1 M NaOH solution and re-precipitated by adding 1 M HCl solution. Finally, the metal porphyrin was dissolved in ethanol and recrystallized by solvent evaporation (0.33g). UV-vis (DMF): $\lambda_{\text{max}} = 435 \text{ nm}$ (Soret), 550 nm (Q₁), 590 nm (Q₂).

NiTPP_COOH (Ni^{II}AH): 70 ml anhydrous DMF was bubbled with argon for 0.5 h. 0.2359 g FeCl₂ was added and bubbled with argon for another 0.5 h. 0.2609g 4,4',4'',4'''-(Porphine-

5,10,15,20-tetra(2-hydroxyethyl)tetraakis(benzoic acid) was added and bubbled for another 1 h. The mixture solution was refluxed at 160-170 °C overnight. After cooling and DMF removal by distillation, the obtained electrocatalysts NiTPP~COOH were precipitated by adding water. The precipitate was then dissolved in 0.1 M NaOH solution and re-precipitated by adding 1 M HCl solution. Finally, the metal porphyrin was dissolved in ethanol and recrystallized by solvent evaporation (0.35g). UV-vis (DMF): $\lambda_{\text{max}} = 415 \text{ nm}$ (Soret), 526 nm (Q_1).



CuTPP~COOH ($\text{Cu}^{\text{II}}\sim\text{AH}$): 70 ml anhydrous DMF was bubbled with argon for 0.5 h. 0.3103 g $\text{CuCl}_2\cdot\text{H}_2\text{O}$ was added and bubbled with argon for another 0.5 h. 0.1976g hematoporphyrin was added and bubbled for another 1 h. The mixture solution was refluxed at 160-170 °C overnight. After cooling and DMF removal by distillation, the obtained electrocatalysts CuTPP~COOH were precipitated by adding water. The precipitate was then dissolved in 0.1 M NaOH solution and re-precipitated by adding 1 M HCl solution. Finally, the metal porphyrin was dissolved in ethanol and recrystallized by solvent evaporation (0.265g). UV-vis (DMF): $\lambda_{\text{max}} = 406 \text{ nm}$ (Soret), 535 nm (Q_1), 573 nm (Q_2).

FeTPP~COOH ($\text{Fe}^{\text{II}}\sim\text{AH}$): 70 ml anhydrous DMF was bubbled with argon for 0.5 h. 0.2307 g FeCl_2 was added and bubbled with argon for another 0.5 h. 0.1976g hematoporphyrin was added and bubbled for another 1 h. The mixture solution was refluxed at 160-170 °C overnight. After cooling and DMF removal by distillation, the obtained electrocatalysts FeTPP~COOH were precipitated by adding water. The precipitate was then dissolved in 0.1 M NaOH solution and re-precipitated by adding 1 M HCl solution. Finally, the metal porphyrin was dissolved in ethanol and recrystallized by solvent evaporation (0.3g). UV-vis (DMF): $\lambda_{\text{max}} = 382 \text{ nm}$ (Soret), 508 nm (Q_1), 542 nm (Q_2).

CoTPP~COOH ($\text{Co}^{\text{II}}\sim\text{AH}$): 70 ml anhydrous DMF was bubbled with argon for 0.5 h. 0.2363 g FeCl_2 was added and bubbled with argon for another 0.5 h. 0.1976g hematoporphyrin was added and bubbled for another 1 h. The mixture solution was refluxed at 160-170 °C overnight. After cooling and DMF removal by distillation, the obtained electrocatalysts CoTPP~COOH were precipitated by adding water. The precipitate was then dissolved in 0.1 M NaOH solution and re-precipitated by adding 1 M HCl solution. Finally, the metal porphyrin was dissolved in ethanol and recrystallized by solvent evaporation (0.25g). UV-vis (DMF): $\lambda_{\text{max}} = 421 \text{ nm}$ (Soret), 537 nm (Q_1), 572 nm (Q_2).

NiTPP~COOH ($\text{Ni}^{\text{II}}\sim\text{AH}$): 70 ml anhydrous DMF was bubbled with argon for 0.5 h. 0.2359 g FeCl_2 was added and bubbled with argon for another 0.5 h. 0.1976g hematoporphyrin was added and bubbled for another 1 h. The mixture solution was refluxed at 160-170 °C overnight. After cooling and DMF removal by distillation, the obtained electrocatalysts NiTPP~COOH were precipitated by adding water. The precipitate was then dissolved in 0.1 M NaOH solution and re-precipitated by adding 1 M HCl solution. Finally, the metal porphyrin was dissolved in ethanol and recrystallized by solvent evaporation (0.28g). UV-vis (DMF): $\lambda_{\text{max}} = 396 \text{ nm}$ (Soret), 522 nm (Q_1), 559 nm (Q_2).

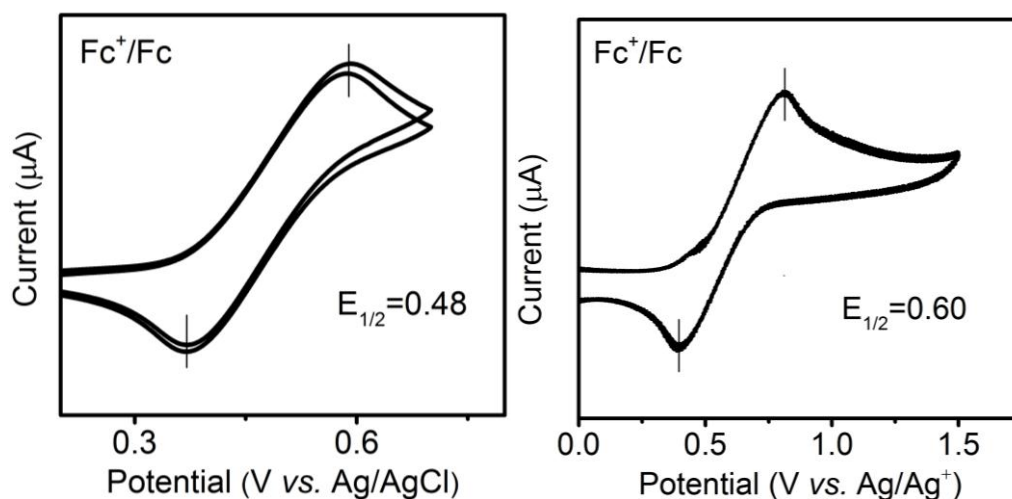


Figure S1. CV curves of Fc^+/Fc in anhydrous DMF (0.1 M TBATFB) at 100 mV/s with different reference electrodes.

According to Figure S1, +1.0 V to -2.0 V vs. Ag/AgCl for the cyclic voltammetry (CV) test is calculated to be +1.48 V to -1.52 V vs. Fc^+/Fc .

According to Figure S1, -1.8 V to -2.3 V vs. Ag/Ag⁺ for the electrocatalytic CO₂ test is calculated to be -1.2 V to -1.7 V vs. Fc^+/Fc .

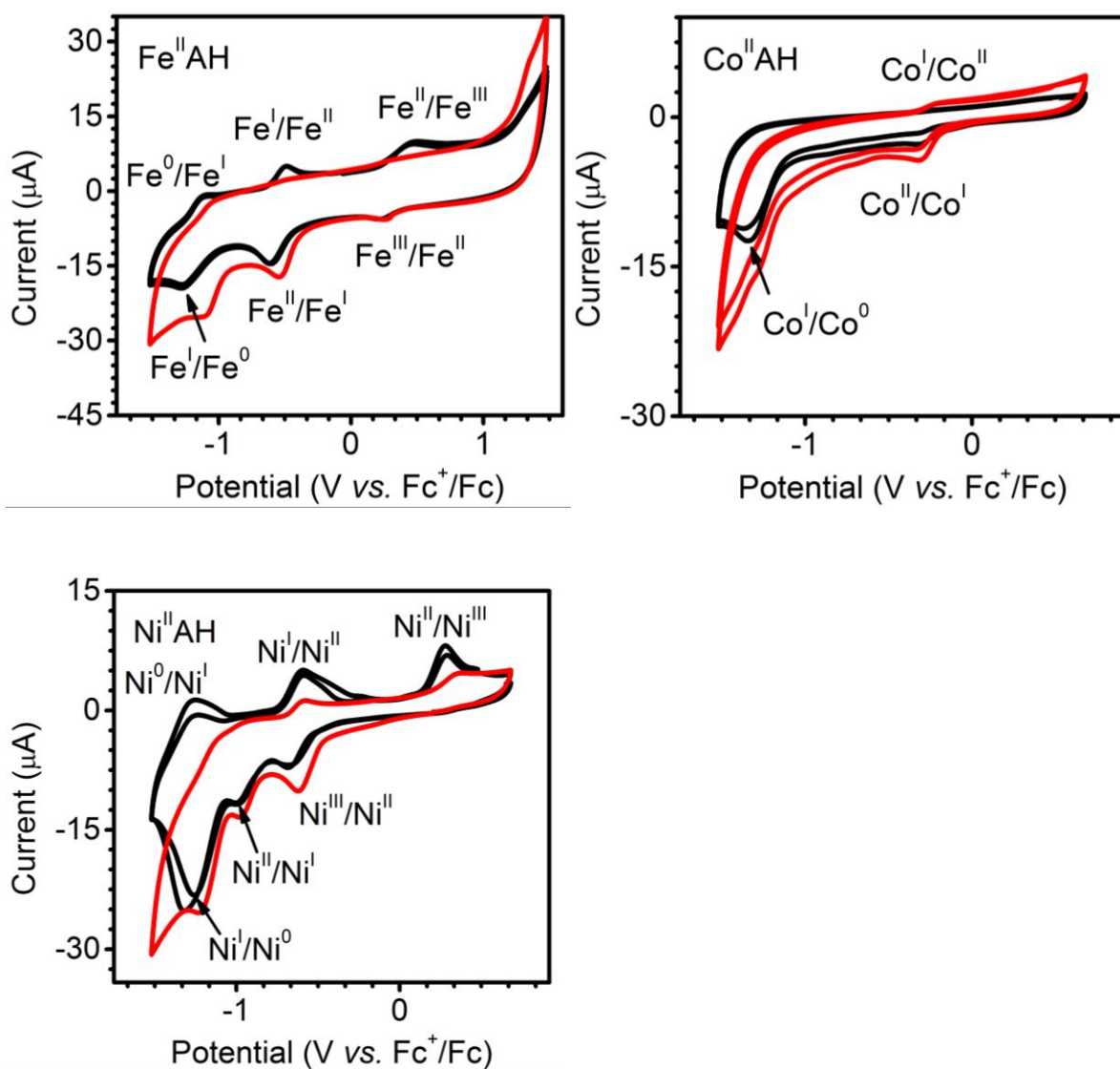


Figure S2. CV curves of 1 mM $\text{Fe}^{\text{II}}\text{AH}$, $\text{Co}^{\text{II}}\text{AH}$ and $\text{Ni}^{\text{II}}\text{AH}$ under argon (black) and CO_2 (red) in anhydrous DMF (0.1 M TBATFB) at 100 mV/s.

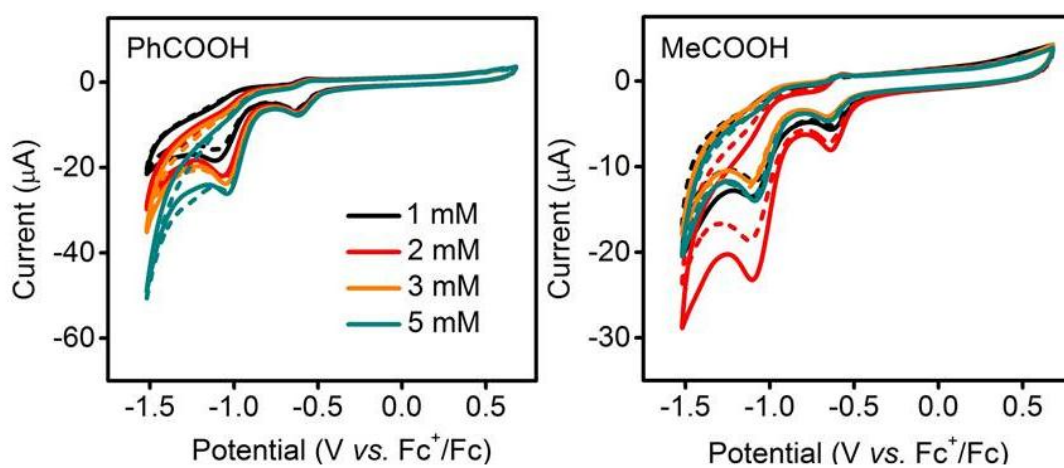


Figure S3. Cyclic voltammetry of 1 mM Cu^{II}AH under argon (dash) and CO₂ (solid) in anhydrous DMF (0.1 M TBATFB) at 100 mV/s, variations with concentration of added PhCOOH and MeCOOH

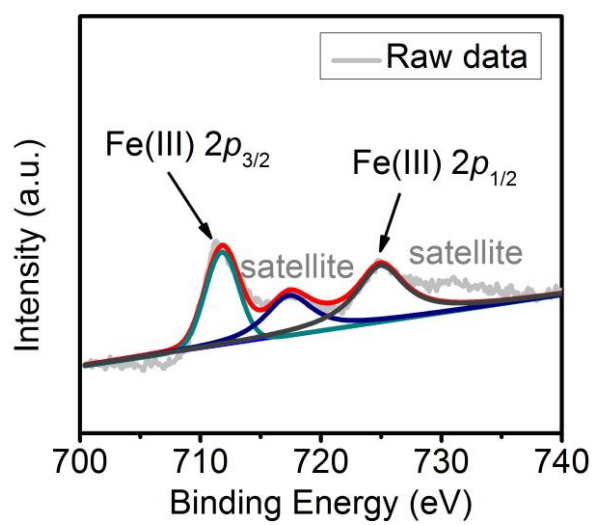


Figure S4. XPS spectra of FeTPP_COOH (Fe^{II}AH).

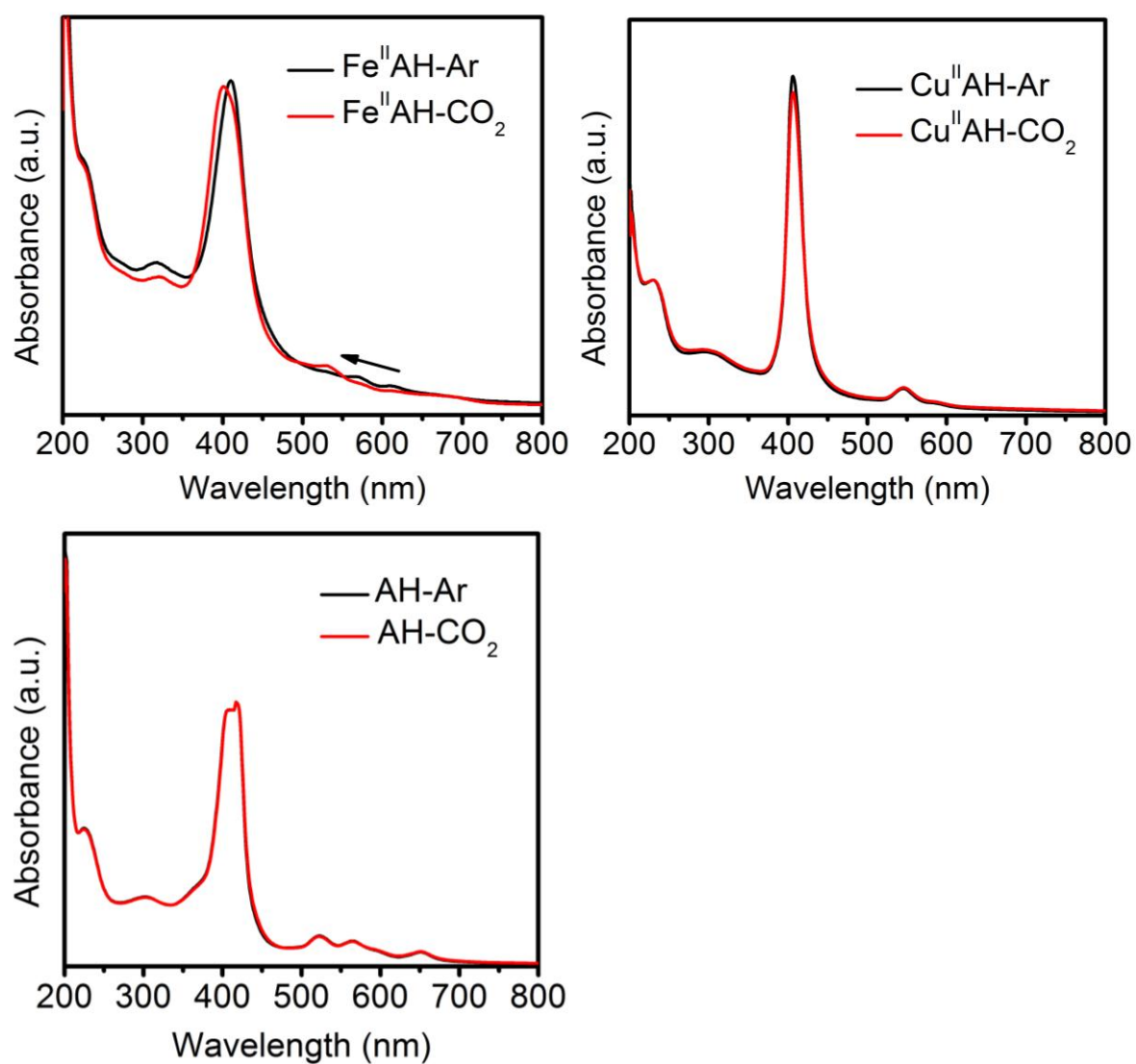


Figure S5. UV-Vis spectra of FeTPP_COOH, CuTPP_COOH and pure TPP_COOH ligand under argon and CO₂ in 0.1 M KPi pH=7.

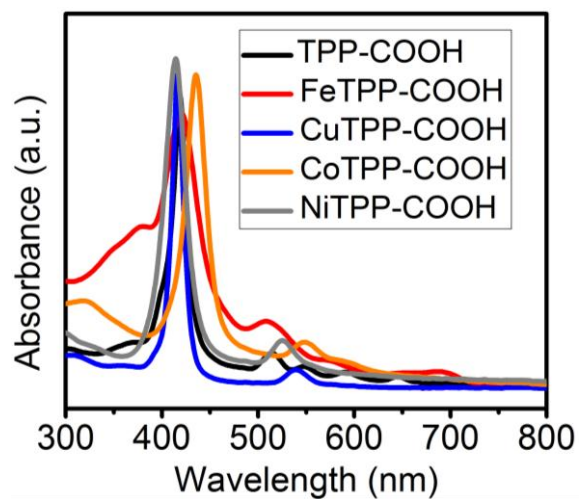


Figure S6. UV-Vis spectra of FeTPP-COOH, CuTPP-COOH, CoTPP-COOH, NiTPP-COOH and pure TPP-COOH ligand in DMF.

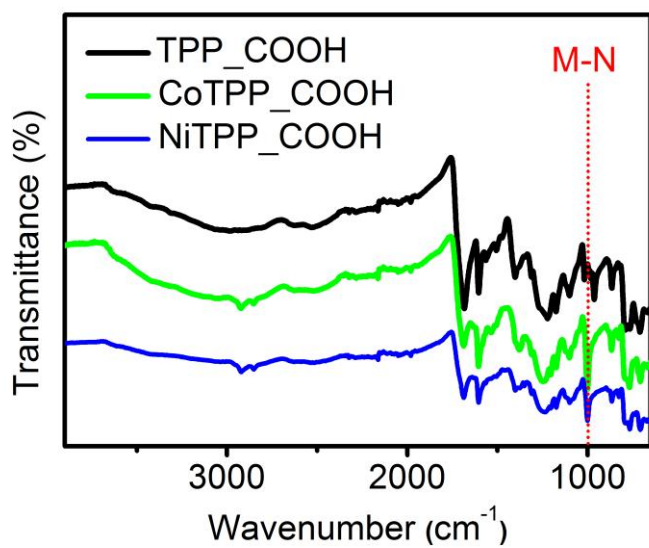


Figure S7. ATR-FTIR spectra of CoTPP_COOH, NiTPP_COOH and pure TPP_COOH ligand.

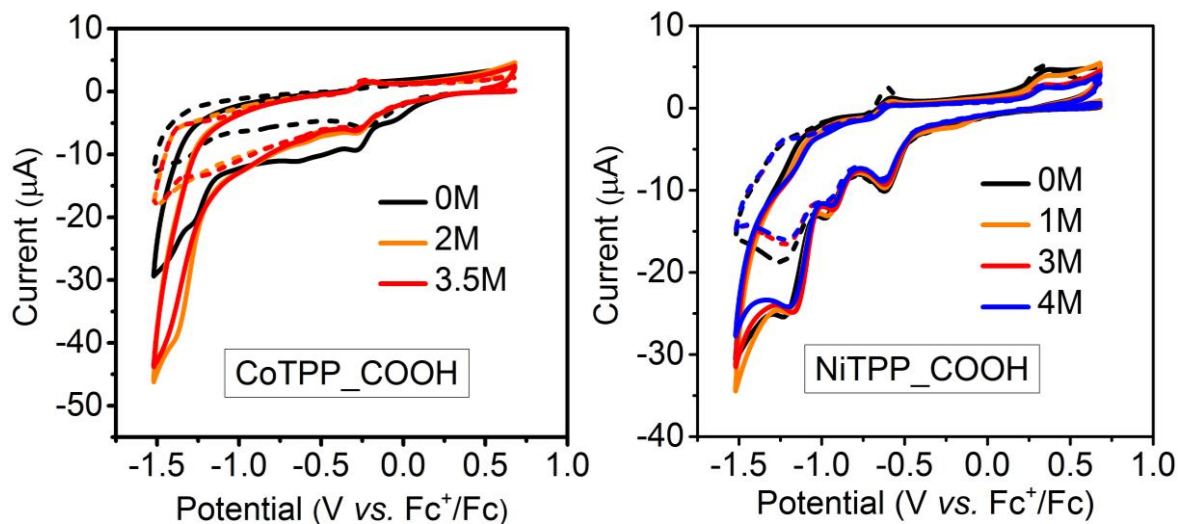


Figure S8. Cyclic voltammetry of 1 mM CoTPP-COOH and NiTPP-COOH under argon (dash) and CO₂ (solid) in anhydrous DMF (0.1 M TBATFB) at 100 mV/s, variations with concentration of added H₂O.

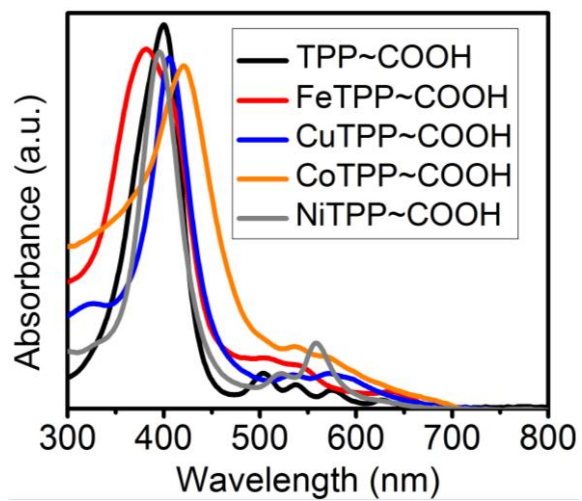


Figure S9. UV-Vis spectra of FeTPP~COOH, CuTPP~COOH, CoTPP~COOH, NiTPP~COOH and pure TPP~COOH ligand in DMF.

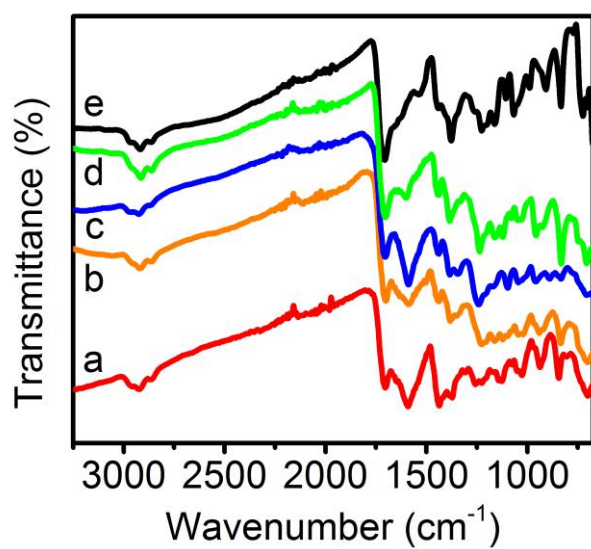


Figure S10. ATR-FTIR spectra of a) FeTPP~COOH, b) CuTPP~COOH, c) CoTPP~COOH, d) NiTPP~COOH and e) pure TPP~COOH ligand.

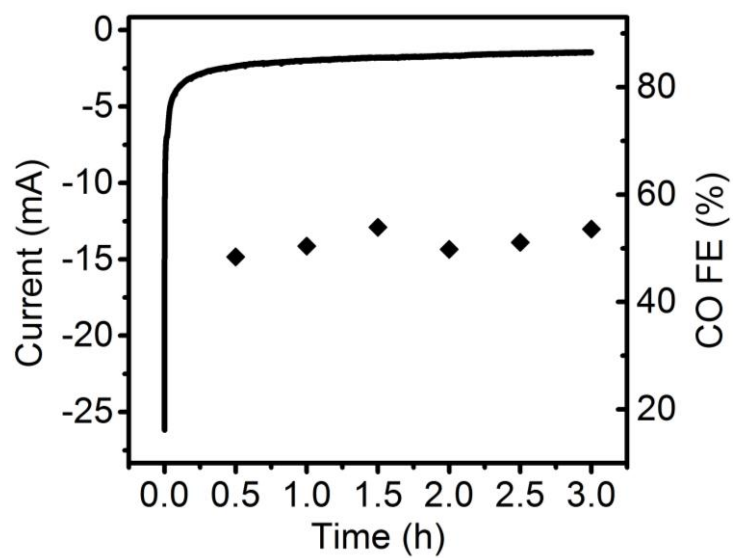


Figure S11. The prolonged electrolysis at -1.5 V vs. Fc^+/Fc with $\text{Fe}^{\text{II}}\sim\text{AH}$.

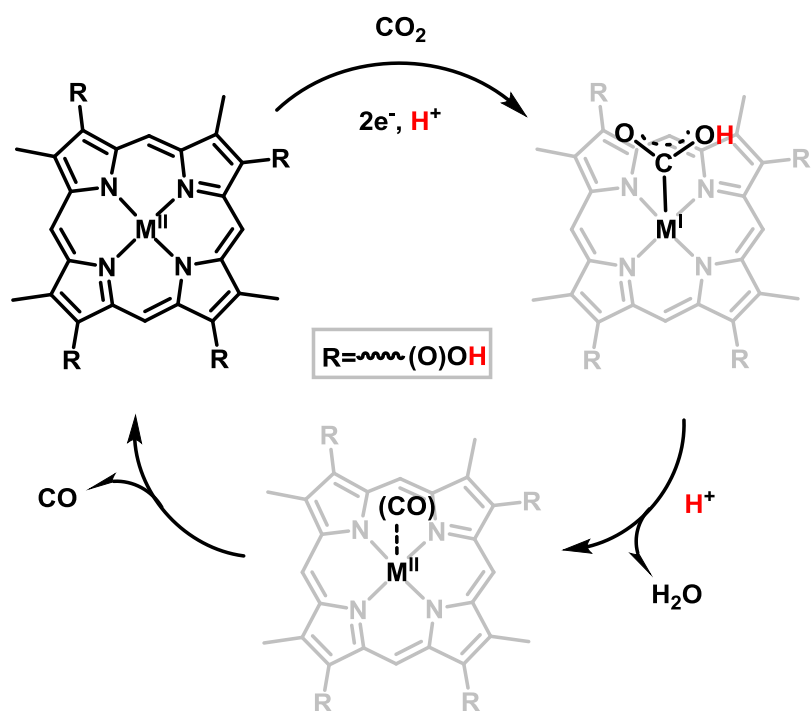


Figure S12. The proposed possible mechanism for promoting CO₂ reduction to CO with aliphatic carboxylic acid as local proton source (compound 5).

Table S1. Comparison of various metal complexes for electrochemical CO₂ reduction.

Electrocatalysts	Onset potential (V)	jCO ₂ /jH ₂	FE of CO	Electrolyte
FeTPP~COOH	-1.02 vs. Fc ⁺ /Fc	6.0 at -1.52 V vs. Fc ⁺ /Fc	53% CO at -1.5 V vs. Fc ⁺ /Fc	DMF, this work
Compound 1	-1.35 V vs. NHE	4.7 at -1.46 V vs. NHE	100% CO at -1.46 V vs. NHE with 1 M PhOH	DMF+ 10mM PhOH ^[1]
Compound 2	-1.2 V vs. NHE	26.5 at -1.33 V vs. NHE	94% CO at -1.16 V vs. NHE	DMF+ 2M H₂O ^[2]
	-1.35 V vs. NHE	5.57 at -1.6 V vs. NHE	100% CO at -1.14 V vs. NHE	DMF+ 1M PhOH ^[3]
Compound 3	-1.4 V vs. SCE	4.8 at -2.0 V vs. SCE	70% CO at -1.8 V vs. SCE	Acetonitrile ^[4]
[Mn(bpy-R)(CO) ₃ X] (bpy-R=2,2'-bipyridine; X=Cl, Br)	-2.8 V vs. Ag/Ag ⁺	3.0 at -3.0 V vs. Ag/Ag ⁺	N.A.	Acetonitrile ^[5]
[Ni(tpy) ₂] ²⁺ tpy=terpyridine	-1.6 V vs. Fc ⁺ /Fc	N.A.	100% CO at -1.72 V vs. Fc ⁺ /Fc	DMF+ H₂O(90:10 v:v) ^[6]
Fe-amide-functionalized tetraphenylporphyrin	-2.0~-2.1 V vs. Fc ⁺ /Fc	30~85 at -2.2 V vs. Fc ⁺ /Fc	74~92% CO at -2.15 V vs. Fc ⁺ /Fc with 1 M PhOH	DMF+ 100mM PhOH ^[7]
ReCl(α-diimine)(CO) ₃	-1.75 V vs. Fc ⁺ /Fc	12 at -2.11 V vs. Fc ⁺ /Fc	70% CO at -2.11 V vs. Fc ⁺ /Fc	Acetonitrile+ 0.3M H₂O ^[8]
[Co ^{II} (L)](ClO ₄) ₂ L=pentadentate N5 ligand	-1.7 V vs. SCE	3.1 at -2.0 V vs. SCE	75%~80% CO at -1.25 V vs. SCE	DMF ^[9]
Re[bpyMe(ImMe)]- (CO) ₃ Cl}PF ₆	-1.77 V vs. Fc ⁺ /Fc	3.9 at -1.9 V vs. Fc ⁺ /Fc	N.A.	Acetonitrile ^[10]
	-1.55 V vs. Fc ⁺ /Fc	12 at -1.9 V vs. Fc ⁺ /Fc	60% CO at -1.77 V vs. Fc ⁺ /Fc	Acetonitrile+ 2.8M H₂O ^[10]
Co-TPP-NH ₂	-2.04 V vs. Ag/AgCl	N.A.	0.4% CO, 0.03% MeOH at -2.04 V vs. Ag/AgCl	DMF+ 5% H₂O ^[11]
Fe porphyrin-pyridine	-0.8 V vs. RHE	N.A.	56% CO, 20% CH ₄ at -1.4 V vs. RHE	DMF ^[12]
Fe-TPP-Dimer	-0.8 V vs. RHE	10.6 at -1.3 V vs. RHE	48% CO at -1.3 V vs. RHE	DMF ^[13]
cobalt meso-tetraphenylporphyrin	-1.85 V vs. SCE	5.2 at -2.05 V vs. SCE	50% CO at -2.05 V vs. SCE	DMF ^[14]

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