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Enhanced Electrochemical Reduction of CO₂ Catalyzed by Cobalt and Iron Amino Porphyrin Complexes

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ABSTRACT: Metallo-porphyrin complexes such as cobalt and iron porphyrins (CoP and FeP) have shown potential as electrocatalysts for CO₂ reduction. Here we report that introducing amino substituents enhances the electro-catalytic activity of these systems toward CO₂ reduction through a dual active site approach. We developed a flexible synthesis of Co- and Fe-porphyrins having variable amino groups, and found that mono-amino FeP reduce CO₂ to carbon monoxide (CO) at ambient pressure and temperature with competitive turnover numbers (TONs). This efficiency enhancement approach opens a new path to designing and optimizing next generation homogeneous catalysts.

Anthropogenic climate change^{1,2} associated with increased carbon dioxide (CO₂) levels^{3,4} mandates, among other strategies, the electrochemical reduction of CO₂ to value-added chemicals. The goal is to upgrade CO₂ into a chemically stored form of energy source using renewable electricity.^{5–10} Homogeneous catalysts offer the potential for high catalytic activity and selectivity even under mild conditions. And although such systems may have limited industrial applications at this point,^{1–4,11–14} homogeneous systems offer tunability and allow a more systematic optimization and can then be converted to heterogeneous systems downstream.^{15–18}

A series of low-oxidation-state transition metal cyclams, porphyrins, and phthalocyanines, have been favored as homogeneous electrocatalysts for CO₂ reduction reactions in recent years.^{19–22} Structural changes of the porphyrin ligand have been shown to modulate the catalytic activity of the metal center, making the study of substituent effects a promising avenue of research.²² Cobalt and iron-based porphyrins are two of the most popular metallo-porphyrins for this purpose.^{20,23,24} Since interactions between the ligand, the metal center, the CO₂ adsorbate, and reduced products are critical,^{25–27} a judiciously-selected substitution pattern on the porphyrin is imperative as it allows influence over the electronic structure of the system, which in turn influences its catalytic activity.²²

The reactivity of amino groups and CO₂ to form carbamates has been well studied.^{27–30} Recent studies have built upon this

body of work and introduce N–H groups as substituents to enhance the activity of different metal ligands.^{31,32}

Savéant and coworkers explored the use of metallo-porphyrins for the electro-reduction of CO₂ to CO and demonstrated in an elegant study that it involves of proton coupled electron transfer (PCET).³³ Moreover, examples of amine-directed PCET have been demonstrated previously.³⁴

We hypothesized that the use of an amino group that is directly tethered to a porphyrin will essentially enable the system to function as a single unit, where the amino group captures CO₂, thereby enhancing the activity of the catalyst. Moreover, it was hypothesized that the activity of the catalyst is tunable,^{35,36} as a function of the number of amino substituents. Our goal was to investigate systematically the effect of amino substituents on the catalytic efficiency of metallated tetraphenylporphyrin (TPP) (**1a**) complexes for CO₂ reduction. We report the synthesis of Co and Fe-amino-porphyrin complexes and their catalytic activity for CO₂ reduction in DMF. To this end, we prepared a series of symmetrical and asymmetrical NH₂-substituted porphyrins (Scheme S1 **3a-3h** and **4a-5b**).^{37–39} We started our investigations with cobalt-porphyrin compounds and compared the catalytic activity of the most efficient cobalt-porphyrins **4a-4b** with that of similarly substituted iron-porphyrin complexes **5a-5b** as shown in Figure 1.

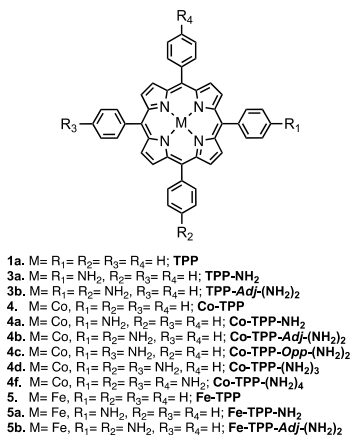


Figure 1. Molecular structure of metallated cobalt **4a-4f** and iron **5a-5b** amino phenyl-porphyrin complexes.

The amino- and nitro- derivatives were characterized using ¹H NMR spectroscopy (see Figures S1-S12). Metallations of the porphyrins were monitored by UV-vis spectroscopy and the products were confirmed by mass spectrometry.⁴⁰⁻⁴³ Figure S14 and Table S2 provide an overview of the UV-vis spectroscopic data of the various amino-porphyrins, while Table S3 provides an overview of the corresponding Co and Fe complexes. The presence of NH₂ substituents at the *meso* position resulted in a slight red shift of the Soret band compared to TPP. As the number of NH₂ groups increased, the Soret bands are increasingly red-shifted, demonstrating a greater distribution of charge towards the porphyrin core.

Addition of CO₂ to a solution of amino-porphyrins **4a-4f** may proceed via carbamate formation involving the amino substituent or direct CO₂ coordination to the metal center. Organocarbamate formation was originally reported by Caplow⁴⁴ in 1968 and studied in more detail by Danckwerts⁴⁵ and Kortunov.^{29,46} The mechanisms of CO₂ reduction in aqueous and non-aqueous solvents has been widely studied, suggesting an interaction between the carbon atom of CO₂ and the metal centers of cobalt and iron. It was also found that more negative potentials (*i.e.* larger overpotential) are needed in aqueous environments compared to that of non-aqueous solutions.^{36,23,33,47-50}

As depicted in Figure 2, protonation of the free amine to produce molecules (I) and (II) results in a stronger electron-withdrawing ability, which in turn causes more positive applied potential (the formation of the carbamate is indicated in Figure S13 using Fourier-transform infrared spectroscopy (FT-IR)).

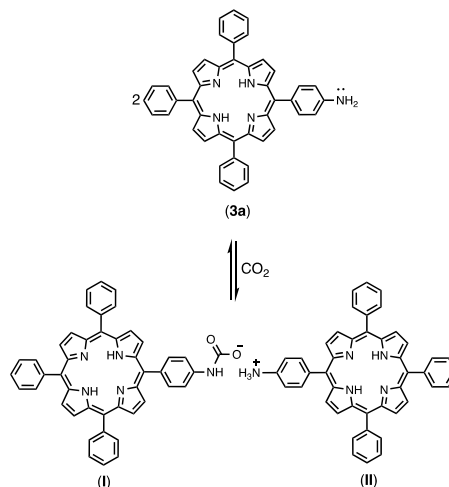


Figure 2. The formation of carbamic salt after purging **3a** with CO₂

Cyclic voltammetry (CV) experiments of TPP (**1a**) and TPP-NH₂ (**3a**) were performed in the presence and absence of CO₂ (Figure S15) to uncover the effects of the amino group in the formation of the carbamic salt complex (I+II) in Figure 2. Comparison of the total charge of **1a** (-0.05 μC) and **3a** (-0.58 μC) shown in Figure S16 and Table 1 with the saturated **4a** (-1.00 μC) with CO₂ in DMF solution show an increase in the reductive current of the cobalt-porphyrin system. The current enhancement in the presence of CO₂ could be due to hydrogen evolution or the reduction of CO₂ itself.

To clarify mechanism and discern if hydrogen evolves, we ran these studies in a non-aqueous (Figure 3A and 3B) as well as aqueous environment (Figure 3C). By adding water the starting material, **4a**, is regenerated (Figure 2), a more negative potential and higher efficiency was observed, a finding we attribute to the electron donating nature of the NH₂. Adding water as a proton source to the electrolyte solution enhances the catalytic current and confirms the catalytic peak at -2.04 V is related to CO₂ reduction, and not the competitive hydrogen evolution peak observed at much more negative potential of -2.42 V (Figure S17 and Table S4). To a 5 mL electrolyte solution, adding 0.25 mL of water shifts the catalytic peak potential from -2.35 V to -2.42 V, which arises from hydrogen evolution.

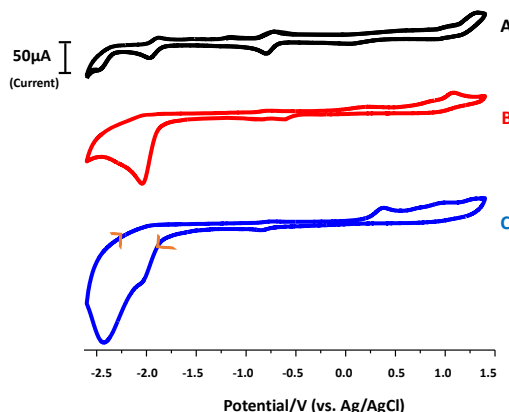


Figure 3. Cyclic voltammograms (CV) of 0.01 mM of: A) **4b** B) **4a** C) **4a** with 5% H₂O; under CO₂ in 0.1M NBu₄PF₆ and DMF solutions; conditions: scan rate: 100 mV s⁻¹; working electrode:

glassy carbon; reference electrode: Ag/AgCl; counter electrode: platinum

After observing higher reductive currents for compound **4a** in comparison to **4** and **3a**, experiments were performed on porphyrins having more than one amino substituent. Our studies show that an increased number of amino substituents significantly decreases the catalytic current (**4a**: -1.00 μC ; **4f**: -0.02 μC ; see Table S5 and Figure S18).

Substituent effects on FePs complexes for reduction of CO_2 to CO have been well studied.^{22,26,33,34} To expand on this research, we chose to compare the reductive capabilities of the iron-porphyrins **5a** and the Fe-*adj*-amino-porphyrin **5b**, which demonstrated the best efficiency with cobalt **4a** and **4b**. Our results show that higher catalytic efficiencies were observed for Fe versus Co catalysis (Figure S20).

Table 1 provides an overview of our electro-catalytic reduction experiments. It is evident that significant differences between the electrochemical characteristics and the electronic spectra of the cobalt-amino-porphyrin, iron-amino-porphyrin and free amino-porphyrin compounds were observed. We found that a small amount of cobalt-amino porphyrin complexes in parallel undertook an alternative electrocatalytic CO_2 reduction pathway different to that of their iron analogues that led to formation of small amount of methanol. No methanol was observed in the absence of the amino substituent (Co-TPP, **4**), nor for the Fe systems **5**, **5a**, and **5b**, demonstrating the necessity of both cobalt and $-\text{NH}_2$ substituent in the formation of methanol. Although GC-MS supports the formation of methanol (see Figure S22) and further confirmed by D_2O addition to DMF solutions (see Figure S24), the experiments conducted to confirm the production of methanol were not sufficient to unequivocally satisfy this claim. Further experiments involving $^{13}\text{CO}_2$ would be necessary to remove any doubt of methanol impurities, which will be investigated in future works.

The TONs and TOFs for CO formation were higher than those observed for the corresponding Co analogues. It has been shown that CoTPP perform poorly in DMF with a slow reaction for CO_2 electroreduction since $[\text{Co}^{\text{I}}\text{TPP}]^-$ reacts slowly with CO_2 in DMF,²⁴ which will be much faster in case of iron porphyrin compounds. In the case of iron porphyrin compounds, the Fe- CO_2 interaction is weaker which cause a less energy to cleave the C-O bond, therefore having a higher efficiency.⁵¹

TOFs were calculated using the catalyst concentration in the solution, an approach that underestimates the activity of the catalyst.⁵² The TOF and TON comparison of different catalysts is more meaningful when all reaction conditions, including the type of solvent, electrolyte, and electrodes, are the same. The TOF and TON of a variety of homogeneous catalysts have been compared,⁵³ introducing FeTDHPP and $\text{Re}(\text{bpy})(\text{CO})_3$ with the highest TOF of 0.5/s and 0.3/s respectively.^{26,54} A later study by Savéant involving fluorinated porphyrin catalysis recorded TOFs of as high as 170/s; however, these findings were reported in the presence of phenol or acetic acid which act as an additional proton source.²⁶ In another comparative study between CoTPP (1mM) and FeTPP (1mM) using a glassy carbon plate with an area of 3 cm^2 in 0.1 M $\text{Bu}_4\text{NBF}_4/\text{DMF}$, CoTPP TONs of 3.8/h and TOFs of 0.95/h over a 4 hour time period were recorded.²⁴ The significant difference in electrochemical CO_2 reduction ability of CoTPP compared to that of FeTPP (TON of 60/h and TOF of 30/h)⁵¹ was attributed to the relative poor product selectivity and slow reaction rates observed in CoTPP.^{24,55,56} Similarly, we observed higher TONs and TOFs for the Fe-porphyrin systems compared to the Co-porphyrin systems.

Table 1. Product Analysis of the Constant Potential Electrolysis for the CO_2 reduction

Compound	Coulomb (C)	[CO] ppm	[H ₂] ppm	[MeOH] ppm	FE% (CO)	FE% (MeOH)	FE% (H ₂)	TON	TOF/h ⁻¹
1a	5×10^{-5}	0	737	0	0	0	100	0	0
3a	5×10^{-4}	0	1774	0	0	0	100	0	0
4	2×10^{-4}	299	1476	0	1	0	98	17 (CO)	6
4a	1×10^{-3}	1233	7498	4	0.4	0.03	99	0.5 (MeOH) 196 (CO)	0.18 (MeOH) 65 (CO)
4b	3×10^{-4}	826	10496	2	8	0.4	99	0.3 (MeOH) 134 (CO)	0.09 (MeOH) 45 (CO)
4c	3×10^{-5}	418	9867	1	0.3	0.008	99	0.06 (MeOH) 23 (CO)	0.02 (MeOH) 7 (CO)
4d	1×10^{-5}	537	16793	1	0.4	0.006	99	0.04 (MeOH) 30 (CO)	0.01 (MeOH) 10 (CO)
4f	2×10^{-5}	329	18304	0	0.2	0	99	0 (MeOH)	0 (MeOH)

								18 (CO)	6 (CO)
5	5×10^{-4}	8572	1594	0	27	0	72	663 (CO)	332
5a	2×10^{-3}	34997	2500	0	49	0	50	2267 (CO)	945
5b	3×10^{-4}	30870	2771	0	36	0	63	1663 (CO)	554

The TOFs were calculated based on the charge transfer considering the catalysts' concentration in solution (see ESI). After applying a constant potential, both liquid and gas phases were analyzed using gas chromatography-mass spectrometry (GC-MS) and gas chromatography (GC), respectively.

In conclusion the effect of different numbers of amino substituents on several metalloporphyrins was investigated for their effect on the electrocatalytic reduction of CO₂. Here, a series of amino substituted Fe- and Co-porphyrins were designed and synthesized as new electrochemical catalysts for CO₂ reduction and their catalytic efficiencies were systematically examined. In contrast to previous works performed with homogeneous metallo-porphyrin catalysts,^{16,21,50,57-63} we sought to investigate the potential effects of amino group functionalization on the catalytic activity of both Fe- and Co systems. It was observed that mono-substituted amino-porphyrins had the greatest efficiency amongst both the Fe or Co group in terms of TON and TOF improvement.

The cobalt-amino-porphyrin complexes were found to be more active for the hydrogen evolution reaction (HER) compared to their iron analogues, which could explain their lower reductive efficiencies. Electrochemical reduction of CO₂ is a multi-step PCET process, which involves both electron transfer and proton transfer to the catalytic site at multiple intermediate stages with different oxidation states. Each micro-step requires a different electronic microenvironment in order to achieve an optimal yield. In general, electron-withdrawing groups decrease the electron density and facilitate the transfer electrons to the catalytic center, but may concertedly impede the proton transfer step. Vice versa, an electron donating group helps the proton transfer but disfavors the electron transfer. An optimal catalyst therefore, would require a balance between electron-donating and withdrawing ability, and ideally, would be able to controllably alternate between the two to match the requirement at each micro-step. The amino-group shows potential for such tunability. Even though -NH₂ is a classic electron-donating group due to its lone pair, protonation and/or conversion of -NH₂ to a carbamate will reverse its electron-donating effect. It is possible that the electron-donating and withdrawing effect of mono-amino substituted porphyrins is better balanced for CO₂ reduction than that of the other amino-porphyrin derivatives, accounting for its higher relative catalytic activity. Whether and how this dynamic electronic interaction plays a role in CO₂ reduction is among the most interesting questions for future study.

Ongoing work exploring the mechanism of metallo-porphyrin catalysts for the reduction of CO₂ will further increase understanding of the roles of amino substituents and their relationship with catalytic activity. This discovery provides a new approach to the design and optimization of next generation catalysts for electrochemical CO₂ reduction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

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