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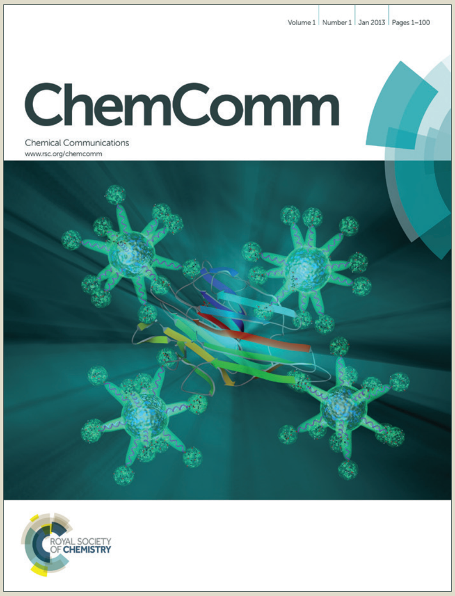
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Efficient Electrocatalytic CO_2 Reduction with a Molecular Cofacial Iron Porphyrin Dimer

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Abstract: **A cofacial iron tetraphenyl porphyrin dimer, *o*-Fe_2DTPP, bio-inspired from the Ni-Fe containing metalloenzyme, carbon monoxide dehydrogenase (CODH) efficiently and selectively catalyses the electrochemical reduction of CO_2 to CO in DMF/10% H_2O solution at the electro-generated Fe^0(por) species with high Faradic efficiency (95%) and TOF (4,300 s^{-1}) at a moderate overpotential, η = 0.66 V.**

Efficient electro- and/or photo-chemical reductions of CO_2 to provide useful carbon resources are promising approaches towards a sustainable society to overcoming the limited supply of fossil fuels and the resultant increase of greenhouse gas.[1] Selective CO_2 reduction at low activation energy, however, is one of the biggest challenges in chemistry, because of versatile product formation and single/multi-electron reactions.[2] Several $2e^-/2H^+$ coupled CO_2 electrochemical reduction molecular catalysts, that selectively reduce CO_2 to CO or HCOOH, have been reported. These include precious metal- (e.g. Re,[3] Ru,[4] Ir,[5] etc.) or non-precious base metal- (e.g. Fe,[6] Ni,[7] Mn,[8] etc.) based catalysts. In terms of practical applications, the development of base metal catalysts to replace the unsustainable rare and noble metal-based catalysts for CO_2 electrochemical reduction is essential.[9]

Among the non-precious metal-based $2e^-/2H^+$ coupled CO_2 electrochemical reduction catalysts, iron porphyrin monomers have been reported to catalyze the electrochemical CO_2 reduction to CO in DMF/tetraalkylammonium salts supporting electrolyte with high selectivity at the electro-generated $[Fe^{I}(por)^{\bullet}]^{2-}$ (conventionally described as $[Fe^{0}(por)]^{2-}$) species.[10] However, these catalysts decompose after only a few catalytic cycles.[6a] The presence of Lewis acids such as Mg^{2+} and Ca^{2+},[6b,c] or weak Brönsted acids[6d] such as trifluoroethanol and 1-propanol increases their catalytic efficiency and stability through a push-pull mechanism where the electro-generated electron-rich $[Fe^{0}(por)]^{2-}$ species pushes an electron pair to the CO_2 molecule and the electron-deficient synergist Lewis or Brönsted acid promotes the cleavage of one of C-O bonds.[6e] Modification of the iron tetraphenylporphyrin monomer, **FeTPP**, with phenolic hydroxy groups in all phenyl group *ortho* positions enhances its activity and stability for CO_2 electro-reduction to CO due to the high local concentration of protons associated with the phenolic hydroxy substituents.[6f]

The metalloenzyme, carbon monoxide dehydrogenese (CODH), has a Ni-Fe *dinuclear* complex at its active center which cooperatively promotes the selective conversion between CO_2 and CO.[11a] The CODH promoted electrochemical reaction achieves catalytic CO_2 reduction at an extremely low overpotential.[11b] Thus, dinuclear catalysts are promising candidates for catalytic CO_2 reduction. We previously reported the use of several cofacial porphyrin dimers as suitable ligands for holding two manganese ions with a suitable Mn-Mn separation distance (3.7~6.2 Å) to promote water oxidation to oxygen or H_2O_2 disproportionation.[12] Herein, we report for the first time the use of a dimer combination of two iron ions as bio-inspired catalysts. A cofacial iron tetraphenyl porphyrin dimer, ***o*-Fe_2DTPP** (Figure 1), efficiently and selectively catalyzes the electrochemical reduction of CO_2 to CO in DMF/10% H_2O solution. The activity is compared with the corresponding iron porphyrin monomer (**FeTPP**) and the 1,3-phenylene bridged iron porphyrin dimer (***m*-Fe_2DTPP**).

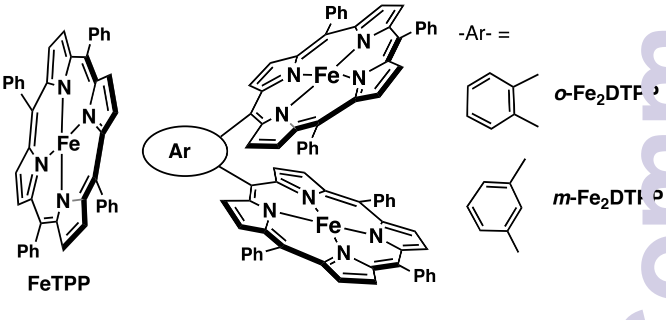

Figure 1. Chemical structures of the iron porphyrin monomer, **FeTPP** and iron porphyrin dimers, ***o*-Fe_2DTPP** and ***m*-Fe_2DPP.**

The iron porphyrin dimers, ***o*-Fe_2TPP** and ***m*-Fe_2DTPP**[13] were prepared according to stepwise methods outlined in Scheme S (supporting information).

Figure 2 shows the CVs ***o*-Fe_2DTPP$_2$** (0.5 mM) In a DMF/10% H_2O containing $TBAPF_6$ ($TBAPF_6$ = tetra-*n*-butylammonium hexafluorophosphate, 0.1M) solution saturated with Ar gas (blue line) and CO_2 gas (red line). The most interesting finding is the observation of a strong catalytic current in the presence of CO_2 gas indicating electro-catalytic reduction of CO_2 promoted by ***o*-Fe₂DTPP**. The appearance of the catalytic peak over the Fe^+-Fe^+/Fe^+-Fe^0 redox couple under Ar at −1.48/−1.46 V *vs.* NHE (hereafter, all potentials are indicated against NHE except as noted) indicates the starting of the catalytic process once the Fe^+-Fe^0 porphyrin species is electro-generated. Details of the CV behavior are presented in the supporting information (Figures S1~S4).

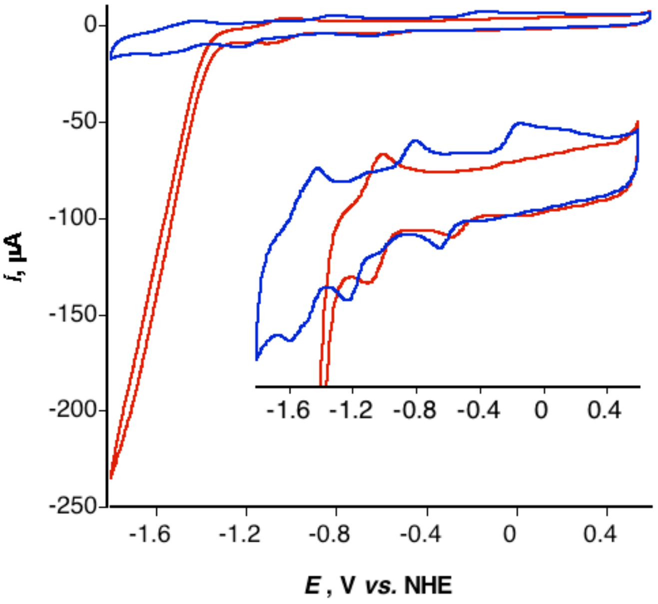

Figure 2. CVs of ***o*-Fe₂DTPP** (0.5 mM) at a 100 mV scan rate in DMF/10% H_2O containing 0.1 M $TBAPF_6$ supporting electrolyte under Ar (blue line) or CO_2 (red line). Insert: magnified trace of CVs.

To evaluate the electro-catalytic CO_2 reduction activity, stability, and selectivity of ***o*-Fe₂DTPP**, a chronoamperometric experiments were performed at −1.35 V (−1.55 V *vs.* Ag/AgCl) for 10-h in the absence and presence of ***o*-Fe₂DTPP** (0.5 mM). Figure 3 shows the time course of appearance of the products. Without the catalyst, H_2 is the sole product obtained with 99% Faradic efficiency and a small average current density of 0.1 mA/cm². On the other hand, in the presence of ***o*-Fe₂DTPP** (0.5 mM), a significant charge, $Q = 41.4$ C was consumed at an average current density of 1.15 mA/cm² over 10-h electrolysis reaction, with concomitant formation of CO (88% Faradic efficiency) and H_2 (12% Faradic efficiency). Subtracting the amount of H_2 produced during the control experiment, the dimer catalyzes the CO_2 reduction to CO with 95% Faradic efficiency. The current density-time profile showed no decrease for the 10-h.

In the CO_2 saturated solution, the CV of ***o*-Fe₂DTPP** shows a CO_2 to CO catalytic peak current at an onset potential of −1.22 V (overpotential, $\eta = 0.53$ V, $E^0(CO_2/CO) = -0.69$ V[6f]). At $\eta = 0.66$ V ($E = -1.35$ V), ***o*-Fe₂DTPP** shows a net current density of 1.05 mA/cm² (the difference between 1.15 mA/cm² for the overall reaction and 0.1 mA/cm² obtained in the control experiment) corresponding to CO_2 reduction to CO with 95% Faradic efficiency. Based on the results of the chronoamperometric experiment, the rate constant of the catalysis, k_{cat}, TON, and TOF are 2.15 x 10^5 s^{-1}, 1.54 x 10^8, and 4,300 s^{-1} (log TOF = 3.6), respectively, based on the catalyst molecules in the diffusion layer at the cathode. These values are higher than those of two typical molecular catalysts for CO_2/CO electrochemical reduction, $Re(bpy)(CO)_3$ (bpy = 2,2'-bipyridine)[14] and Fe(TDHPP)Cl (TDHPP= 5,10,15,20-tetrakis(2',6'-dihydroxylphenyl)porphyrin) tested under same conditions.[6f] The precious metal based $Re(bipy)(CO)_3$ catalyst has a TOF = 2,000 s^{-1} (log TOF = 3.3) at −1.25 V ($\eta = 0.56$ V) based on a bulk electrolysis experiment conducted at −1.25 V for 14 h. in DMF/10% H_2O solution containing 0.075 mM of the $Re(bipy)(CO)_3$ catalyst. The Fe(TDHPP)Cl catalyst showed TOF = 1,750 s^{-1} (log TOF = 3.24) at −1.16 V ($\eta = 0.47$ V) based on a bulk electrolysis experiment conducted at −1.16 V for 2 h. in DMF/H_2O (2M) solution saturated with CO_2 gas. Thus, ***o*-Fe₂DTPP** has the highest TOF value. However, it is obtained at a higher overpotential, $\eta = 0.66$ V. Correlation between log TOF and η for the CO_2/CO electroreduction ***o*-Fe₂DTPP** catalyst is presented in Figure S5 (supporting information).

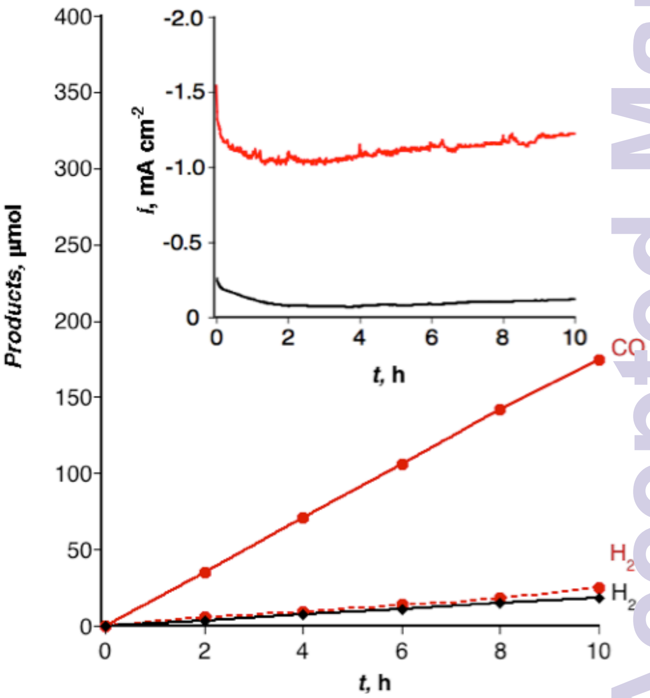

Figure. 3 CO_2 reduction products with time and the current density-time profile (inset) produced during the 10-h chronoamperometry experiment at −1.35 V *vs.* NHE in a DMF/10% H_2O/ 0.1 M $TBAPF_6$ solution saturated with CO_2 without (black lines) and with 0.5 mM ***o*-Fe₂DTPP** (red lines).

To emphasize the importance of ***o*-Fe₂DTPP** on the catalytic activity for CO_2 electrochemical reduction to CO, we compared the CV behavior of the corresponding **FeTPP**, 1mM, normalized on the concentration of Fe ion under the same experimental conditions. The catalytic peak current (i) obtained under CO_2 reduction was normalized to the first reduction peak current (i_p) of the reversible redox couple in the case of the dimer and to the second reduction peak current (i_p) of the reversible redox couple in case of the monomer under Ar. Figure 4 shows the i/i_p of ***o*-Fe₂DTPP** (0.5 mM) and that of **FeTPP** (1 mM) with the applied potential. **FeTPP** has an i/i_p value of 35 and ***o*-Fe₂DTPP** has an i/i_p value of 200 at −1.8 V. The i/i_p for the dimer is 5.7 times higher than that of the monomer. Indeed, in a CO_2-saturated solution of DMF/$TBAClO_4$, the reported value for **FeTPP** = ~ 1.5 suggests that the monomer has low activity in this solution.[6] This value increases to 35 at a 0.1 V/s scan rate by introducing 10% H_2O to the DMF/0.1 M $TBAPF_6$ solution

Introducing 2M phenol to the solution increases the i/i_p value to 100.[15]

The importance of the separation between the two Fe ions in the porphyrin dimers on the catalytic activity for CO_2 reduction was also emphasized by comparing i/i_p values of ***o*-Fe$_2$DTPP** (0.5 mM) and ***m*-Fe$_2$DTPP** (0.5 mM) (Figure 4). ***m*-Fe$_2$DTPP** has $i/i_p = 36$, which is similar to that of **FeTPP**, while ***o*-Fe$_2$DTPP** has $i/i_p = 200$ at −1.8 V. Thus, the metal-metal separation is very sensitive for the catalytic activity.

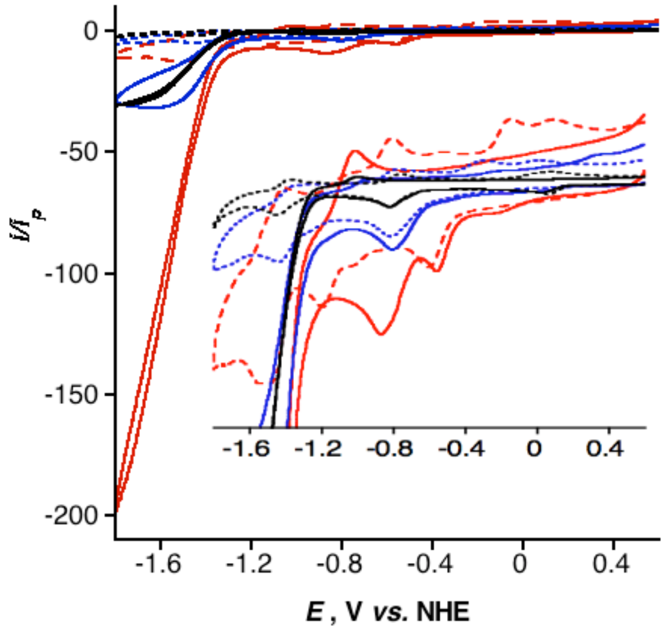

Figure 4. i/i_p-applied potential curves of **FeTPP** monomer (1 mM, black lines), ***m*-Fe$_2$DTPP** (0.5 mM, blue lines), and ***o*-Fe$_2$DTPP** (0.5 mM, red lines) in DMF/10% H_2O/ 0.1 M $TBAPF_6$ solution saturated with Ar (dotted lines) and CO_2 (solid lines) gases. Insert: magnified trace of CVs.

The high activity, selectivity, and stability of ***o*-Fe$_2$DTPP** is tentatively attributed to the suitable separation of the two iron ions. Such a structure facilitates the holding of CO_2 molecules inside the cavity, where CO_2 binds to the iron centers once the Fe^{2+} species is electro-generated as indicated by the CVs. This does not occur for **FeTPP** or ***m*-Fe$_2$DTPP**. Moreover, the presence of two Fe centers at a suitable separation distance provides a local push-pull mechanism where one Fe center acts as a Lewis base to push an electron pair to the coordinated CO_2 molecules and the second Fe center acts as a Lewis acid to promote C-O bond cleavage and the formation of CO. The molecular structure of the analogous cofacial zinc porphyrin dimer showed an average interplanar separation between the two rings of 3.43 Å[16] and the modeling of the analogous manganese porphyrin dimers showed a calculated interplanar separation of 3.7 Å that increases to 6.2 Å by introducing bulk substituents at the peripheral porphyrin rings for the cofacial dimer and 10.5 Å for the 1,3-phenylene bridged dimer.[12c] The dimer with Mn-Mn separation of 4.0 showed the highest catalase activity for H_2O_2 disproportionation. The ***o*-Fe$_2$DTPP** is expected to have Fe-Fe separation in the range 3.4-4.0 Å that is suitable to hold the linear CO_2 molecules of 2.32 Å length.

Conclusions

We report for the first time that a cofacial iron porphyrin dimer bearing a shorter metal-metal separation works as an efficient catalyst for reduction of CO_2 to CO with high selectivity and stability without the use of any external Lewis or Brönsted acids. Since the electronic character of the porphyrin ring can be fine-tuned by substitution of various functional groups, efforts are underway to reduce the overpotential required for catalytic reduction.

Notes and references

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