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Quick and Easy Method for Dramatic Improvement of the Electrochemical CO_2 Reduction Activity of an Iron Porphyrin Complex

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Dedicated to the memory of Prof. Dr. Jean-Michel Savéant, who made a great contribution to this field.

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Abstract: The development of artificial molecular catalysts for CO_2 reduction is the key to solving energy and environmental problems. Although chemical modifications can generally improve the catalytic activity of this class of compounds, they often require complicated synthetic procedures. Here, we report a simple procedure that dramatically enhances electrochemical CO_2 reduction activity. A one-step counteranion exchange reaction increased the solubility of a commercially available catalyst, iron(III) tetraphenylporphyrin chloride, in a variety of solvents, allowing the investigation of its catalytic performance under various conditions. Surprisingly, the turnover frequency for CO evolution in acetonitrile (MeCN) reached 7,300,000 s^{-1}, which is the highest among those of current best-in-class molecular catalysts. This excellent catalytic activity originates from the unique reaction between the generated Fe(I) species and CO_2 in MeCN during catalysis. The present study offers a "quick and easy" method for obtaining an efficient catalytic system for electrochemical CO_2 reduction.

Introduction

The catalytic reduction of CO_2 into fuels or useful chemicals has attracted much attention because this technology can potentially solve both energy and environmental problems.[1] Therefore, in the past few decades, extensive efforts have been made to develop efficient molecular catalysts for the reduction of CO_2.[2–16] In general, the catalytic activity of this class of compounds can be improved by chemical modifications in the vicinity of the catalytic center. Among these compounds, iron(III) porphyrin complexes are one of the best catalytic centers because of their (i) high turnover frequency (TOF), (ii) high selectivity for CO_2 to CO conversion, and (iii) robustness (Figure 1a). Their catalytic activity can be further improved by introducing various substituents, such as acid/base groups, electron-donating/withdrawing moieties, and pendant amide at meso positions, that accelerate the CO_2 binding step (Figure 1b).[7,8,10,12] However, the introduction of functional substituents often requires complicated synthetic procedures and is expensive. Therefore, a more facile and low-cost method for

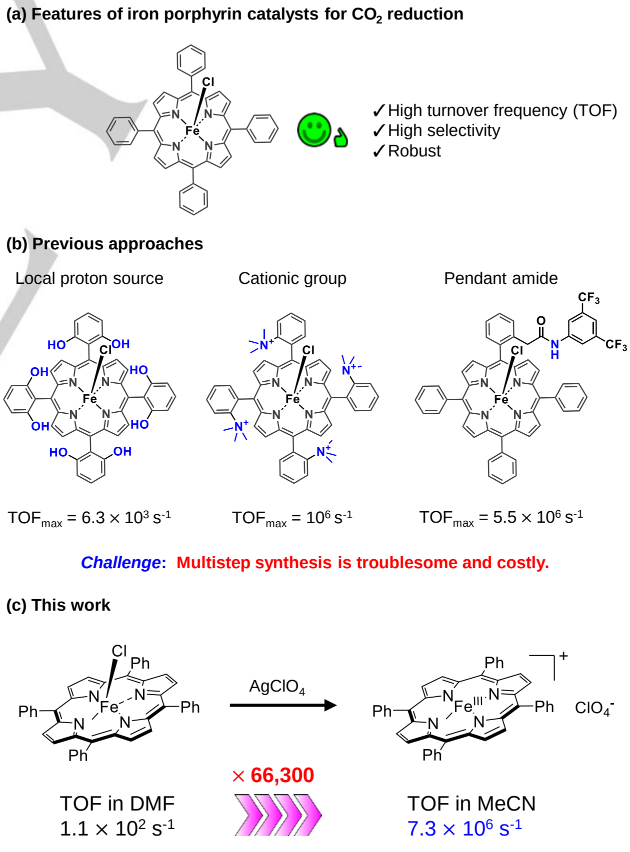

Figure 1. (a) Features of iron porphyrin catalysts for CO_2 reduction. (b) Previous approaches for improving catalytic activity. (c) Summary of this work.

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improving the catalytic activity of iron(III) porphyrin complexes is required.

Herein, we report a “quick and easy” method for the dramatic enhancement of the electrochemical CO_2 reduction activity of iron porphyrin complexes. The simple one-pot counteranion exchange reaction of a commercially available catalyst, iron(III) tetraphenylporphyrin chloride (**FeTPP-Cl**), afforded a complex with improved solubility, iron (III) tetraphenylporphyrin (**FeTPP**). **FeTPP** exhibited the highest TOF for CO_2 reduction among the best-in-class molecular catalysts in appropriate reaction medium (Figure 1c). We have also clarified the effect of changing the reaction medium on the reaction mechanism.

Results and Discussion

We began by reinvestigating CO_2 reduction by **FeTPP-Cl** in DMF, a common solvent for iron porphyrin systems, as DMF can dissolve both the complex and CO_2 at high concentration.[4–11] The cyclic voltammogram of **FeTPP-Cl** was measured in a 0.1 M tetra-*n*-butyl ammonium perchlorate (TBAP)/DMF solution in the presence of 0.5 M trifluoroethanol (TFE) as a proton source. **FeTPP-Cl** indeed exhibited a large irreversible current approximately at –2.06 V [vs. ferrocene/ferrocenium (Fc/Fc^+)] under CO_2, corresponding to the electrocatalytic reduction of CO_2 (Figure 2a, red line). Unexpectedly, the intensity of the irreversible current increased when acetonitrile (MeCN) was added (Figure 2a, dashed lines). This observation prompted us to explore the influence of MeCN on catalysis. However, **FeTPP-Cl** does not dissolve in pure MeCN, which would hamper further investigation.

As a solution to this problem, we performed the counteranion exchange reaction of **FeTPP-Cl**[17] and prepared the perchlorate salt of **FeTPP** (**FeTPP-ClO₄**). **FeTPP-ClO₄** was characterized by elemental and single-crystal X-ray structural analyses[18] (see experimental section, Figure S1, and Table S1 in the Supporting Information (SI)). **FeTPP-ClO₄** was well soluble in various solvents, which enabled us to perform electrochemical measurements of the complex in MeCN.

Initially, the cyclic voltammogram of **FeTPP-ClO₄** was measured in a 0.1 M TBAP/MeCN solution. Under Ar, **FeTPP-ClO₄** in MeCN exhibited three redox waves. The potential of the first redox wave (–0.26 V, Figure 2b and Table S2), which is attributed to the Fe(III)/Fe(II) redox couple,[4–6] was shifted to more positive potential compared with that of **FeTPP-Cl** (–0.63 V). Note that the first reduction of **FeTPP-Cl** involves the dissociation of the coordinated chloride ligand;[19] thus, the observed difference between the first redox potentials of **FeTPP-ClO₄** in MeCN and **FeTPP-Cl** in DMF can be attributed to the difference in anion. The second [Fe(II)/Fe(I) redox couple] and third [Fe(I)/Fe(0) redox couple] redox waves were reversible for both **FeTPP-ClO₄** in MeCN and **FeTPP-Cl** in DMF (Figure S2). Moreover, the two catalysts have similar potentials for these redox waves. A CV of **FeTPP-ClO₄** in a 0.1 M TBAP/DMF solution under Ar also exhibited three reversible redox waves (Figure 2b, purple line, and Table S2), which is similar to **FeTPP-Cl** in DMF except for the first reduction wave. These results indicate that electronic structure of the porphyrin scaffold is not affected by counter anions. On the other hand, under CO_2 with 0.5 M TFE, there was a significant difference between the cyclic voltammograms in MeCN and DMF. The intensity of the irreversible reduction wave increased dramatically, and the onset potential shifted to more positive potential (ca. –1.91 V) in MeCN compared with that in DMF (Figure 2a, blue line). These results suggest that the catalytic activity is enhanced in MeCN.

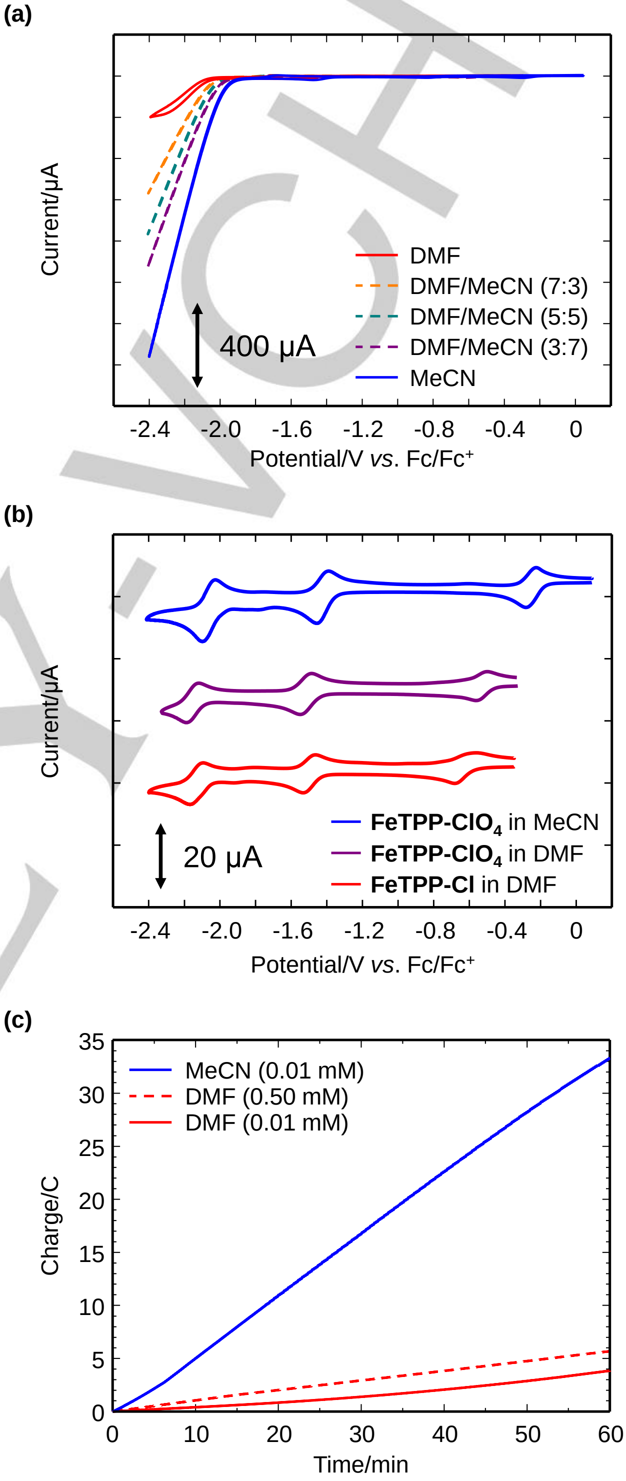
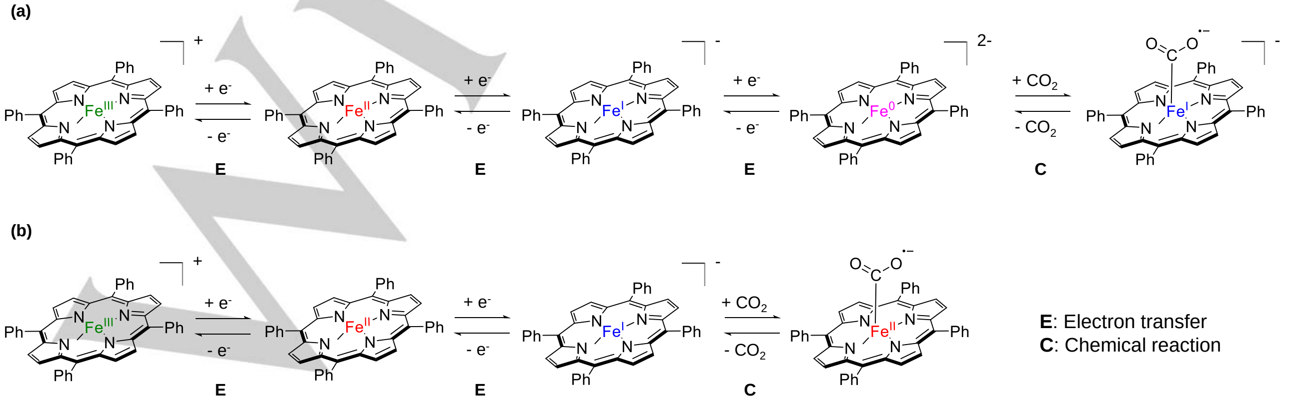


Figure 2. (a) Cyclic voltammograms of **FeTPP-Cl** (0.50 mM) in DMF/MeCN (10:0, 7:3, 5:5, and 3:7) and **FeTPP-ClO₄** (0.50 mM) in MeCN with TBAP (0.1 M) in the presence of TFE (0.5 M) under CO_2 (scan rate: 100 mV s^{-1}). (b) Cyclic voltammograms of **FeTPP-ClO₄** (0.50 mM) in MeCN (blue line) and DMF (purple line) and **FeTPP-Cl** (0.50 mM) in DMF (red line) with TBAP (0.1 M) under Ar (scan rate: 100 mV s^{-1}). (c) Electrolysis data of **FeTPP-ClO₄** (0.01 mM) in MeCN and **FeTPP-Cl** (0.50 and 0.01 mM) in DMF with TBAP (0.1 M) in the presence of 1.0 M TFE under CO_2 at a potential of –2.35 V vs. Fc/Fc^+.

To quantify the catalytic product, controlled potential electrolysis (CPE) experiments were then performed both in DMF and MeCN with 1.0 M TFE and 0.1 M TBAP under CO_2 at –2.35 V vs. Fc/Fc^+. In CPE experiments, tetra-*n*-butylammonium acetate (TBAA) was added in the anodic chamber (for details of the experimental setup, see Figure S3) to promote an oxidation process on the Pt counter electrode. TBAA reacts at anode to consume the holes and to produce CO_2 and ethane via Kolbe reaction[20]. In the CPE of **FeTPP-Cl** in DMF, the total amount of charge passed over a period of 60 min was 3.9 C when 0.01 mM of catalyst was used (Figure 2c, red line), and CO (4.5 μmol) was formed with a Faradaic efficiency (FE) of 23%. The similar catalytic performance was also obtained in the CPE of **FeTPP-ClO₄** in DMF; 2.6 C of charge has passed, and the formation of CO (FE: 21.9%), H_2 (FE: 17.4%) was detected (Figure S4, No.11 and Table S4, No.11), indicating that catalytic performance is not affected by counter anions. Upon increasing the catalyst concentration to 0.50 mM, CO (27.0 μmol) was formed with a total charge and FE of 5.7 C and 92%, respectively. On the other hand, in the CPE of **FeTPP-ClO₄** in MeCN, the total amount of charge was 33.3 C and the FE was 98% (170.0 μmol), even at a low catalyst concentration (0.01 mM). These results clearly demonstrate that the electrocatalytic activity of **FeTPP** for CO_2 reduction is significantly enhanced in MeCN. Note that the CPE of **FeTPP-ClO₄** in MeCN using 0.5 mM of catalyst afforded the similar amounts of products (Table S4, No.10), indicating that the catalytic process is deaccelerated when higher concentration (0.5 mM) of catalyst is used in MeCN.

To further verify the effect of MeCN, the reaction mechanism of CO_2 reduction was investigated. Initially, the cyclic voltammograms of **FeTPP-Cl** in DMF and **FeTPP-ClO₄** in MeCN were measured in the absence of a proton source under both Ar and CO_2. As shown in Figure S5a, the cyclic voltammograms of **FeTPP-Cl** in DMF displayed almost identical redox peaks at −1.51 V for the Fe(II)/Fe(I) redox couple, indicating the lack of reaction between the Fe(I) species and CO_2 in DMF. In contrast, the cyclic voltammograms of **FeTPP-ClO₄** in MeCN exhibited distinct features when measured under different conditions: under Ar, there was a reversible redox wave at −1.43 V attributed to the Fe(II)/Fe(I) redox couple (Figure S5b, red line), while under CO_2, there was an increase in the cathodic current (Figure S5b, blue line). The same phenomenon was also observed in the cyclic voltammograms measured in the MeCN-DMF mixed solvent system (Figure S5c). These results suggest that **FeTPP** reacts with CO_2 as Fe(I) in MeCN. As reported previously,[4–6] in DMF, **FeTPP** undergoes one-electron reduction thrice to form the three-electron-reduced species, **Fe(0)TPP**, which reacts with CO_2 (Scheme 1a, EEEC mechanism). In contrast, our results indicate that the two-electron-reduced species, **Fe(I)TPP**, reacts with CO_2 in MeCN (Scheme 1b, EEC mechanism). The binding constant of CO_2 to **Fe(I)TPP** in MeCN (K_{CO2}) was calculated to be 2.58 M^{-1} (see the SI (P.S27) for details of the calculation).

Subsequently, UV-visible absorption spectroelectrochemistry (SEC) measurements were performed to further clarify the reaction of **Fe(I)TPP** with CO_2 in the presence of MeCN. Figure S7a shows the UV-visible absorption spectra of the **Fe(II)TPP** species generated in DMF by applying a potential at $E = -1.20$ V. The spectra measured under Ar and CO_2 were almost identical, and two Q-bands were observed at 569 and 609 nm. A scan to the negative potential region showed changes in the UV-visible absorption spectra with the occurrence of isosbestic points, and three Q-bands (538, 569, and 609 nm) were observed when $E = -1.70$ V. Notably, the features of the reduction-induced spectral change measured under Ar and CO_2 were identical (Figures 3a and 3b). These results indicate that **Fe(I)TPP** does not react with CO_2 in DMF, which is consistent with the cyclic voltammetry (CV) results. Similarly, **Fe(II)TPP** was also generated by applying a potential at $E = -1.20$ V in the presence of MeCN,[21] and UV-visible absorption spectra with two Q-bands (569 and 609 nm) were obtained under both Ar and CO_2 (Figure S7b). However, the changes in the UV-visible spectra under Ar and CO_2 upon scanning the potential to the negative potential region were quite different (Figures 3c and 3d). While two Q-bands (569 and 609 nm) were observed at $E = -1.70$ V under Ar, only one Q-band (538 nm) was observed under CO_2. These results strongly indicate that in the presence of MeCN, **Fe(I)TPP** rapidly reacts with CO_2 to form **Fe(II)TPP-CO₂⁻**. It should be also noted that the comparison of the CVs of **FeTPP-ClO₄** in MeCN and **FeTPP-Cl** in DMF also indicate the interaction of **Fe(I)TPP** with CO_2 in MeCN. Under Ar, the difference in redox potentials attributed to Fe(I)/Fe(0) process is 0.08 V (–2.06 V in MeCN and –2.14 V in DMF). On the other hand, under CO_2 in the presence of TFE, the difference in the onset potentials for catalytic current is 0.15 V (–1.91 V in MeCN and –2.06 V in DMF), which is significantly larger than that observed under Ar. These results support our proposed catalytic cycle that the reduction of **Fe(II)TPP-CO₂⁻** triggers the catalysis in MeCN whereas the reduction of **Fe(I)TPP** triggers the catalysis in DMF (for detailed discussion, see the SI (P.S15)). Based on the aforementioned results, a plausible catalytic cycle in MeCN was proposed, as shown in Scheme S1.



Scheme 1. Proposed mechanism for the formation of the metallocarboxylate intermediate of **FeTPP** (a) in DMF via the EEEC mechanism (b) in MeCN via the EEC mechanism.

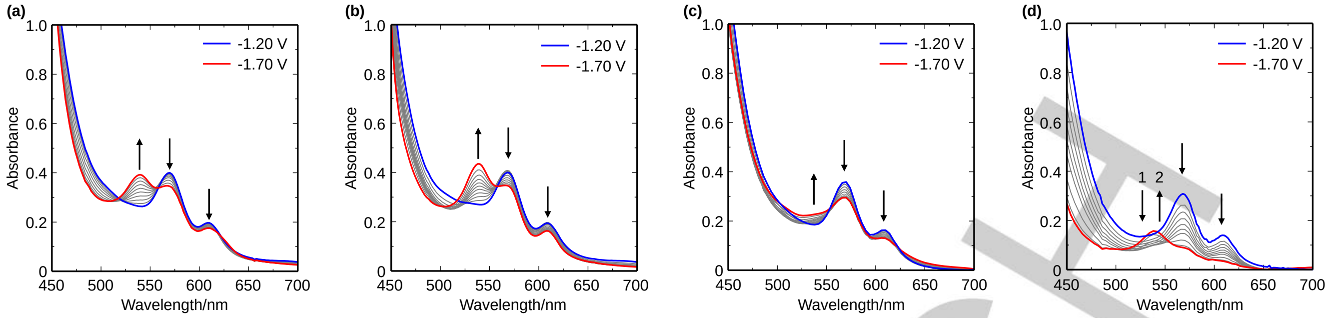


Figure 3. UV-visible absorption SEC measurements of **FeTPP-Cl** (0.50 mM) in DMF with TBAP (0.1 M) under (a) Ar and (b) CO_2 and in DMF/MeCN (3:7) with TBAP (0.1 M) under (c) Ar and (d) CO_2. Potential is corrected by Fc/Fc^+.

Table 1. Calculated turnover frequencies (TOFs) of iron porphyrin catalysts.

No.	Catalyst	Medium	[cat]/mM	TOF_{max} (CV)/s^{-1} [a]	TOF (CPE)/s^{-1} [b]
1	**FeTPP-Cl**	0.1 M TBAP/DMF, 1.0 M TFE	0.50	3,200	112
2	**FeTPP-ClO₄**	0.1 M TBAP/MeCN, 1.0 M TFE	0.01	650,000	1,400,000[c]
3	**FeTPP-ClO₄**	0.1 M TBAP/MeCN, 1.0 M TFE	0.01		7,300,000[d]

[a] calculated from CV data. [b] calculated from CPE data. [c] using 0.04 M tetra-*n*-butylammonium acetate (TBAA) in the second compartment. [d] using 0.40 M TBAA in the second compartment.

Finally, the kinetic parameters of the catalysts were evaluated to determine the effect of MeCN on the catalytic performance of **FeTPP**. In this study, the TOF values were extracted from the results of both the CV and CPE experiments. Both methods of TOF calculation were established by Savéant et al.[21,22] and are frequently used to evaluate the catalytic performance of molecular electrocatalysts for CO_2 reduction.[6–16] Note that we modified the previously reported methods[22,23] (see pp. S18–S23 of the SI for details) because the reaction mechanism of our system is distinct from that of conventional catalytic systems (vide supra). The TOF_{max} of **FeTPP-ClO₄** in MeCN, calculated from the CV data shown in Figures S8 and S10, was 650,000 s^{-1}. This value is significantly higher than that of **FeTPP-Cl** in DMF (3,200 s^{-1}), demonstrating the positive effect of the MeCN medium on catalytic activity. Then, TOF was extracted directly from the results of our CPE experiments, where the products (CO and H_2) were detected and quantified by gas chromatography. The results and conditions are presented in Tables 1 and S4 and Figure S4. For **FeTPP-Cl** in DMF in the presence of 1.0 M TFE, the estimated TOF was 112 s^{-1} at –2.35 V (Table 1, No. 1). On the other hand, for **FeTPP-ClO₄** in MeCN in the presence of 1.0 M TFE, the estimated TOF was 1,400,000 s^{-1} (Table 1, No. 2). Furthermore, under the optimized conditions (Table 1, No. 3), the TOF reached 7,300,000 s^{-1}, which is approximately 66,300 times higher than that in DMF. The performance of **FeTPP-ClO₄** in MeCN is superior to those of current best-in-class molecular catalysts for electrochemical CO_2 reduction[6–16] (Figure S11 and Table S5). The catalytic Tafel plot (Figure S12) also indicates the enhancement of catalytic perforemance in MeCN. It is also worth noting that in most previous works,[6–8,10–15] the TOF_{max} values predicted from CV data were very high (10^3–10^6 s^{-1}), while the actual TOF determined from CPE data was relatively low (~10^2 s^{-1}). In this work, the TOF_{max} predicted from the CV data is consistent with the TOF determined from the CPE data (Table 1), which reflects the excellent performance of our system.

Conclusion

In conclusion, we have shown a dramatic improvement in the electrochemical CO_2 reduction activity of **FeTPP** simply by changing the reaction medium. The simple counteranion exchange reaction of **FeTPP-Cl** successfully provided a well-soluble complex, **FeTPP-ClO₄**. Importantly, the use of MeCN as the solvent significantly enhanced the catalytic activity. The results of the CV and UV-visible absorption SEC measurements suggested that this reaction medium changes the reaction mechanism: in MeCN, CO_2 and **FeTPP** react at the redox potential of Fe(I)/Fe(II), while in DMF, they react at the redox potential of Fe(0)/Fe(I). It should be noted that although there are a few reports on the high CO_2 reduction activity of several specific iron porphyrin complexes in MeCN,[12,13] the influence of this solvent on the reaction mechanism has not been clarified. Thus, the present study is the first to disclose the origin of the positive effect of MeCN on the catalytic activity of iron porphyrin complexes. Furthermore, under the optimized conditions, **FeTPP-ClO₄** in MeCN exhibited the highest TOF (7,300,000 s^{-1}) among the current best-in-class molecular catalysts. Our “quick and easy” method is a new approach for improving the electrochemical CO_2 reduction activity of iron porphyrin complexes.

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Conflict of Interest

The authors declare no competing financial interest.

Keywords: CO_2 reduction • electrocatalysis • iron porphyrin • solvation effect

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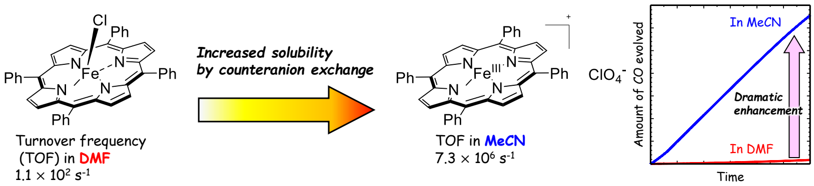

Facile strategy for the dramatic enhancement of electrochemical CO_2 reduction activity is reported. Simple one-step counteranion exchange reaction of a commercially available catalyst, iron(III) tetraphenylporphyrin chloride, afforded a complex with improved solubility (**FeTPP**). We revealed that turnover frequency for CO evolution of **FeTPP** in acetonitrile is 7.3×10^6 s^{-1}, which is the highest among those of the relevant molecular catalysts.