Supplementary Material for PCCP

Supporting Information

For

Effects of *p*-Substituents on Electrochemical CO Oxidation by Rh Porphyrin-based Catalysts

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1. Experimental Details

1.1. Synthesis.

5, 10, 15, 20-tetrakis(4-carboxyphenyl)porphinato rhodium(III) carbonyl chloride ([Rh^{III}(TCPP)(CO)(Cl)]).

$Rh_2Cl_2(CO)_4$ (54.2 mg) and 5, 10, 15, 20-tetrakis(4-carboxyphenyl)porphine (TCPPH$_2$, 100.3 mg) were dissolved in ethanol (100 mL). After the suspension was refluxed for 5 h to produce a clear solution, the solvent was removed under reduced pressure to give a purple residue. The residue was washed with toluene (twice), diethylether, and hexane and then extracted with ethanol. Ethanol was removed to produce a crystalline powder. ESI-MS (in mixed solvent (water : ethanol = 1 : 1)): *m/z* 891.2 ([Rh^{III}(TCPP)]$^+$), *m/z* 919.2([Rh^{III}(TCPP)(CO)]$^+$). Anal. Calcd for [Rh^{III}(TCPP)(CO)(Cl)]·3H$_2$O: C, 58.31; H, 3.40; N, 5.55. Found: C, 58.30; H, 3.69; N, 5.14.

5, 10, 15, 20-tetrakis(4-methylcarboxyphenyl)porphinato rhodium(III) carbonyl chloride (rhodium 5, 10, 15, 20-tetrakis(4-carboxyphenyl)porphine tetramethyl ester carbonyl chloride) ([Rh^{III}(T(-COOCH$_3$)PP)(CO)(Cl)]).

$Rh_2Cl_2(CO)_4$ (45.4 mg) and 5, 10, 15, 20-tetrakis(4-carboxyphenyl)porphine tetramethyl ester (T(-COOCH$_3$)PPH$_2$, 178.5 mg) were dissolved in toluene (200 mL). After the suspension was refluxed for 5 h to produce a clear solution, the solvent was removed under reduced pressure to give a purple residue. The residue was washed twice with hexane, and extracted with ethanol. Ethanol was removed under reduced pressure to produce a purple crystalline powder. ESI-MS (in ethanol): *m/z* 947.4 ($[Rh^{III}(T(-COOCH_3)PP)]^+$), *m/z* 975.5($[Rh^{III}(T(-COOCH_3)PP)(CO)]^+$). Anal. Calcd for $[Rh^{III}(T(-COOCH_3)PP)(CO)(Cl)]\cdot H_2O$: C, 61.85; H, 3.72; N, 5.44. Found: C, 61.57; H, 3.98; N, 5.19.

5, 10, 15, 20-tetrakis(4-methoxyphenyl)porphinato rhodium(III) ethanol chloride ($[Rh^{III}(T(-OCH_3)PP)(C_2H_5OH)(Cl)]$).

$Rh_2Cl_2(CO)_4$ (13.4 mg) and 5, 10, 15, 20-tetrakis(4-methoxyphenyl)porphine ($T(-OCH_3)PPH_2$, 45.8 mg) were suspended in ethanol (170 mL). The suspension was refluxed for 5 hours and filtered. The filtrate was collected. The solvent was removed under reduced pressures. The resulting powder was washed with hexane (twice), diethylether, and a small amount of ethanol to produce a purple crystalline powder. ESI-MS (in ethanol solution): *m/z* 835.2 ($[Rh^{III}(T(-OCH_3)PP)]^+$). Anal. Calcd for $[Rh^{III}(T(-OCH_3)PP)(C_2H_5OH)(Cl)]\cdot H_2O$: C, 64.21; H, 4.74; N, 5.99. Found: C, 64.32; H, 4.25; N, 6.08.

5, 10, 15, 20-tetraphenylporphinato rhodium(III) chloride ($[Rh^{III}(TPP)(Cl)]$).

This compound was synthesized as described in the literature,[1] with some modifications. The UV/vis spectrum coincided with that reported in the literature.[1] ESI-MS (in CH_3CN solution): *m/z* 715.5 ($[Rh^{III}(TPP)]^+$), *m/z* 773.4 ($[Rh^{III}(TPP)(CH_3CN)(OH)]^+$, *m/z* 797.4 ($[Rh^{III}(TPP)(CH_3CN)_2]^+$). Anal. Calcd for $[Rh^{III}(TPP)]Cl\cdot 2H_2O$: C, 67.14; H, 4.10; N, 7.12. Found: C, 67.91; H, 4.24; N, 6.70.

5, 10, 15, 20-tetra(4-methylphenyl)porphinato rhodium(III) carbonyl chloride ([$\mathbf{Rh^{III}(T(-CH_3)PP)(CO)(Cl)}$]).

$Rh_2Cl_2(CO)_4$ (9.7 mg) and 5, 10, 15, 20-tetra(4-methylphenyl)porphine ($T(-CH_3)PPH_2$, 30.3 mg) were suspended in toluene. The suspension was refluxed for 5 hours. The solvent was removed under reduced pressure. The residue was washed with hexane (twice) and water (twice). The powder was recrystallized in ethanol. ESI-MS (in ethanol solution): *m/z* 771.1 ($[Rh^{III}(T(-CH_3)PP)]^+$), *m/z* 799.1 ($[Rh^{III}(T(-CH_3)PP)(CO)]^+$). Anal. Calcd for $[Rh^{III}(T(-CH_3)PP)(CO)(Cl)]\cdot 0.5\ H_2O$: C, 69.71; H, 4.42; N, 6.63 Found: C, 69.41; H, 4.66; N, 6.56.

5, 10, 15, 20-tetrakis(4-fluorophenyl)porphinato rhodium(III) carbonyl chloride ([$\mathbf{Rh^{III}(TFPP)(CO)(Cl)}$]).

$Rh_2Cl_2(CO)_4$ (15.8 mg) and 5, 10, 15, 20-tetrakis(4-fluorophenyl)porphine ($TFPPH_2$, 49.5 mg) were dissolved in toluene (190 mL). The suspension was refluxed for 9 hours. The suspension after reflux was filtered and the filtrate was collected. The solvent of the filtrate was removed under reduced pressure. The residue was washed with distilled water (three times) and hexane (three times). ESI-MS (in $CHCl_3$ solution): *m/z* 769.1 ($[Rh^{III}(TFPP)\text{-}F\text{+}H]^+$), *m/z* 787.1 ($[Rh^{III}(TFPP)]^+$), *m/z* 815.1 ($[Rh^{III}(TFPP)(CO)]^+$). Anal. Calcd for $[Rh^{III}(TFPP)(CO)(Cl)]\ \cdot H_2O$: C, 62.19; H, 3.02; N, 6.45 Found: C, 62.40; H, 3.20; N, 6.30.

5, 10, 15, 20-tetrakis(4-bromophenyl)porphinato rhodium(III) carbonyl chloride ([$\mathbf{Rh^{III}(TBPP)(CO)(Cl)}$]).

$Rh_2Cl_2(CO)_4$ (11.8 mg) and 5, 10, 15, 20-tetrakis(4-bromophenyl)porphine ($TBPPH_2$, 51.4 mg) were dissolved in toluene (170 mL). The suspension was refluxed for 14 hours. The suspension after reflux was filtered and the filtrate was collected. The solvent of the filtrate was removed under reduced pressure. The residue was washed with distilled water (twice) and hexane (three times). ESI-MS (in $CHCl_3$ solution): *m/z* 952.9 ($[Rh^{III}(TBPP)\text{-}Br+H]^+$), *m/z* 1030.8 ($[Rh^{III}(TBPP)]^+$) , *m/z* 1058.7 ($[Rh^{III}(TBPP)(CO)]^+$). Anal. Calcd for $[Rh^{III}(TBPP)(CO)(Cl)]\cdot 0.5\ H_2O$: C, 48.97; H, 2.28; N, 5.08 Found: C, 48.99; H, 2.35; N, 5.01.

1.2. Calculation of electrons transferred to the electrode in CO oxidation.

The number of electrons transferred to the electrode (n) was determined from the slope of the Koutecky-Levich plot based on the following equation.

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_m} + \frac{1}{0.620 nFAD_{CO}^{\frac{2}{3}} \omega^{\frac{1}{2}} \nu^{-\frac{1}{6}} C^{*}_{CO}}$$

where $A = 0.0707\ \mathrm{cm}^2$, $D_{\mathrm{CO}} = 2.1 \times 10^{-5}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$, $\nu = 0.01\ \mathrm{cm}^2\ \mathrm{s}^{-1}$, and $C_{\mathrm{CO}} = 1.0 \times 10^{-6}\ \mathrm{mol\ cm}^{-3}$. I_{k} indicates the current controlled by the kinetics of the catalysts. I_{m} is the current limited by the diffusion across the Nafion membrane. The diffusion coefficient and concentration of CO were taken from the literature.[2]

1.3. Differences in potential between reference electrodes.

The difference in potential between Ag|AgCl|KCl(sat.) and RHE was determined by the following experiment. Ag|AgCl|KCl(sat.) and platinum electrodes were immersed in 0.1 M H_2SO_4. The solution was purged with hydrogen, and the difference in potential between a Ag|AgCl|KCl(sat.) electrode and a platinum electrode was measured using a potentiometer under a hydrogen atmosphere. Ag|AgCl|KCl(sat.) was shown to be 263 mV more positive than RHE in 0.1 M H_2SO_4. In the experiments at 60 °C, the difference in the potential of RHE between room temperature and cell temperature was determined by the same method. RHE (60 ºC) was 11 mV higher than RHE (r. t.).

1.4. Analysis of the electron transfer process.

In Scheme 2, the electron transfer from Rh(por)-COOH complex to electrode can be analyzed based on a model of a multistep electron transfer as follows:

$$\text{Rh(por)-COOH} \rightarrow \text{X} + r\text{e}^- \qquad (1)$$

$$\text{X} \rightarrow \text{Y} + m\text{e}^- \qquad (2)$$

$$\text{Y} \rightarrow \text{Rh(por)} + (n\text{-}r\text{-}m)\text{e}^- \qquad (3)$$

where X and Y are possible intermediates before and after the electron transfer process, respectively. r, and m denote numbers of electron transferred in the processes (1) and (2), respectively. n denotes the overall number of electron transferred. Neglecting the reverse reaction and assuming the equilibrium for the reaction (1), Tafel slope (b) is expressed in the following equation.

$$b = 2.303\frac{RT}{F(r + (1-\alpha)m)} \qquad (4)$$

The Tafel slope obtained indicates that $r + (1-\alpha)m$ is 1. Assuming that α is 0.5, r and m are 0 and 2, respectively. Thus, the electron transfer from Rh(por)-COOH is an apparent 2-electron transfer process.

References

[1] V. Grass, D. Lexa, M. Momenteau, J.-M. Savéant, *J. Am. Chem. Soc.* 1997, **119,** 3536–3542.

[2] C. Shi, F. C. Anson, *Inorg. Chem.* 2001, **40,** 5829–5833.

Table S1. Summary of X-ray Crystallographic of [Rh^{III}(TCPP)(C_3H_7OH)(Cl)]

Compound	[Rh^{III}(TCPP)(C_3H_7OH)(Cl)](H_2O)(C_3H_7OH)$_2$
Empirical formula	C57H54N4O12RhCl
Formula weight	1125.5
Crystal system	Triclinic
Space group	P-1
a, Å	10.014(3)
b, Å	17.880(6)
c, Å	18.207(6)
α, deg	101.013(7)
β, deg	97.413(7)
γ, deg	96.628(6)
V, $Å^3$	3140.2(18)
Z	2
$F(000)$	1164.0
D_{calc}, Mg/m^3	1.190
T, K	183(2)
Crystal size, mm^3	0.20 × 0.20 × 0.03
Absorption coefficient, cm^{-1}	3.75
Reflections collected	14529
Independent reflections	10696 [R(int) = 0.0863]
Final R indices [I>2sigma(I)]	R1 = 0.0940, wR2 = 0.2082
Goodness of fit on F^2	0.776

Table S2. Dihedral angles between porphyrin ring and *meso*-phenyl groups (deg of [Rh^{III}(TCPP)(C_3H_7OH)(Cl)]

Group 1: C(21)-C(22)-C(23)-C(24)-C(25)-C(26)	94.3(4)
Group 2: C(28)-C(29)-C(30)-C(31)-C(32)-C(33)	61.4(4)
Group 3: C(35)-C(36)-C(37)-C(38)-C(39)-C(40)	127.1(3)
Group 4: C(42)-C(43)-C(44)-C(45)-C(46)-C(47)	82.1(3)

Table S3. Summary of X-ray Crystallographic Data of [$Rh^{III}(T(-OCH_3)PP)(C_2H_5OH)Cl$]

Compound	[$Rh^{III}(T(-OCH_3)PP)(C_2H_5OH)Cl$]
Empirical formula	C50H42N4O5RhCl
Formula weight	917.24
Crystal system	Monoclinic
Space group	C2/c
a, Å	23.601(6)
b, Å	9.222(2)
c, Å	39.715(9)
α, deg	90
β, deg	91.825(5)
γ, deg	90
V, $Å^3$	8640(3)
Z	8
$F(000)$	3776
D_{calc}, Mg/m^3	1.410
T, K	183(2)
Crystal size, mm^3	0.30 x 0.10 x 0.05
Absorption coefficient, cm^{-1}	5.10
Reflections collected	21132
Independent reflections	7535 [R(int) = 0.0900]
Final R indices [I>2sigma(I)]	R1 = 0.0811, wR2 = 0.1687
Goodness of fit on F^2	1.026

Table S4. Dihedral angles between porphyrin ring and *meso*-phenyl groups of $[Rh^{III}(T(-OCH_3)PP)(C_2H_5OH)Cl]$ (deg)

Group 1: C(21)-C(22)-C(23)-C(24)-C(25)-C(26)	66.5(2)
Group 2: C(28)-C(29)-C(30)-C(31)-C(32)-C(33)	63.5(2)
Group 3: C(35)-C(36)-C(37)-C(38)-C(39)-C(40)	71.4(2)
Group 4: C(42)-C(43)-C(44)-C(45)-C(46)-C(47)	73.6(2)

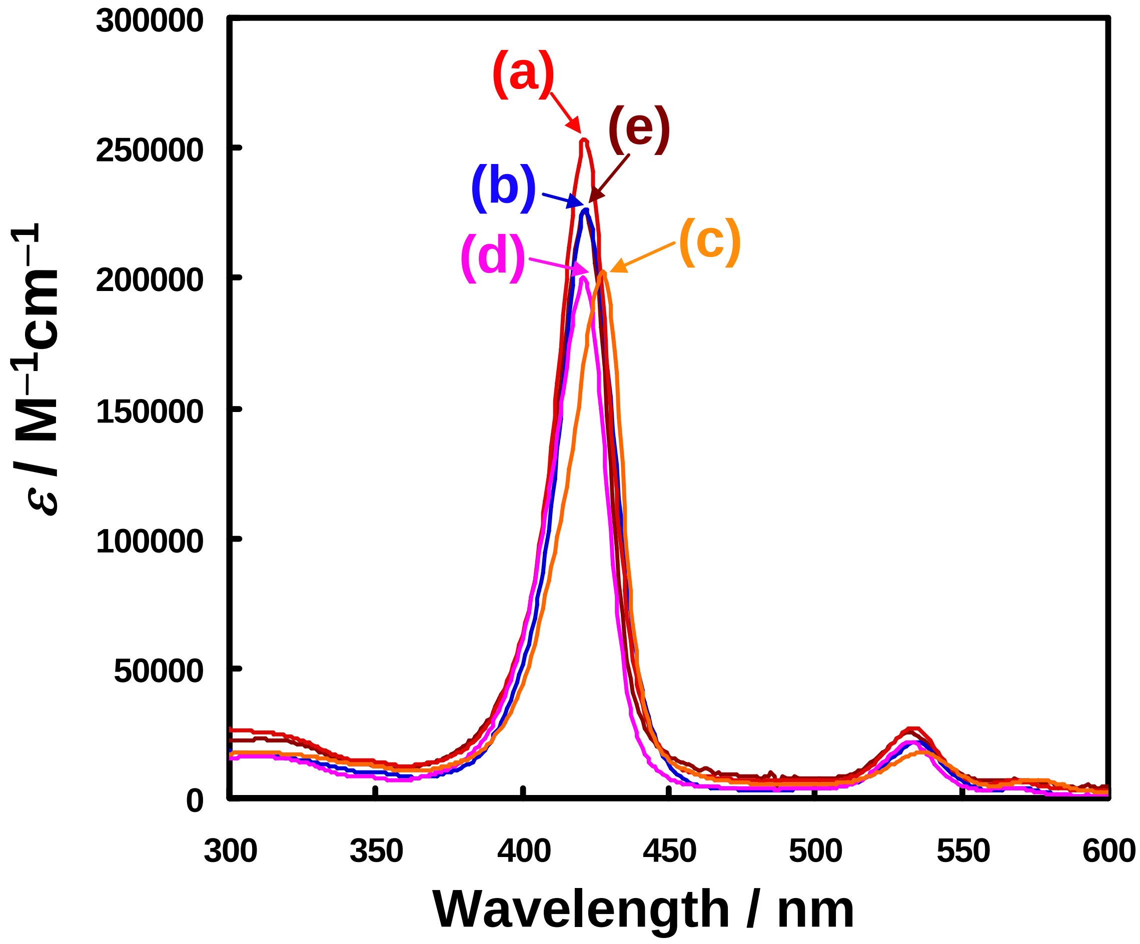


Figure S1. UV spectra of Rh porphyrins: (a) [Rh^{III}(TCPP)(Cl)], (b) [Rh^{III}(T(-COOCH$_3$)PP)(Cl)], (c) [Rh^{III}(T(-OCH$_3$)PP)(Cl)], (d) [Rh^{III}(TPP)(Cl)] and (e) [Rh^{III}(TFPP)(Cl)]. CH_2Cl_2 is used as a solvent, except that [Rh^{III}(TCPP)(Cl)] is dissolved in ethanol.

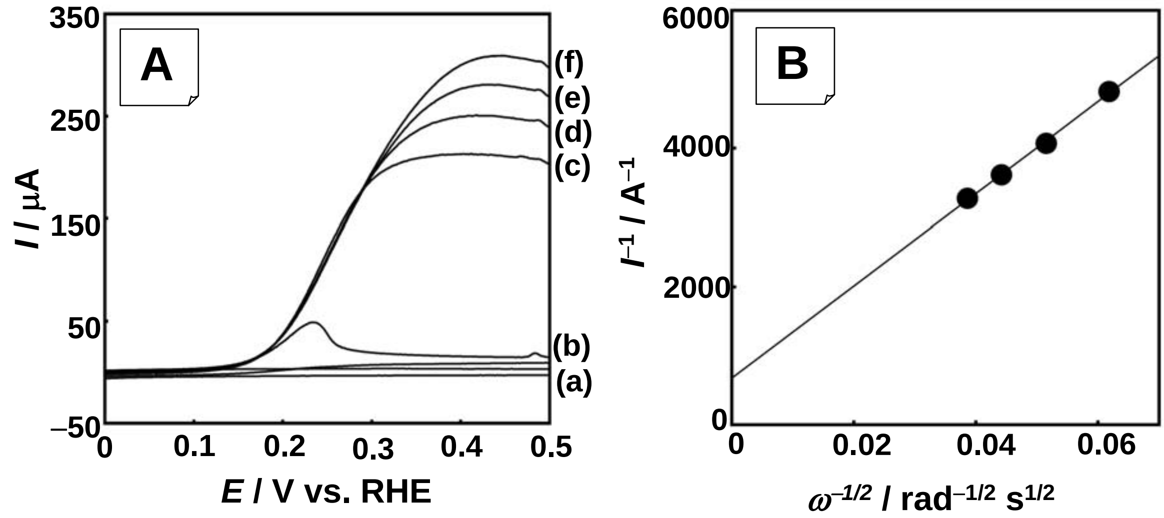
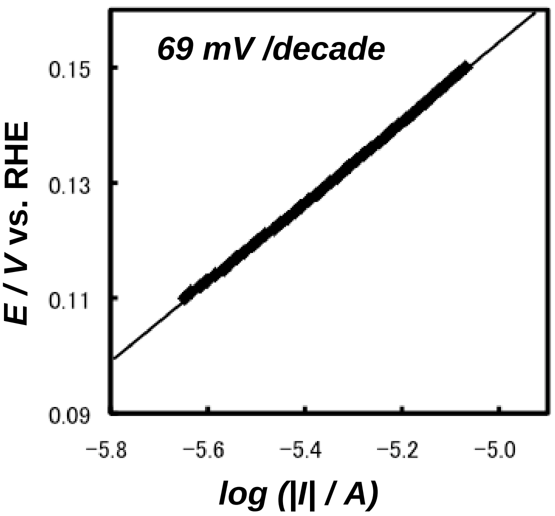
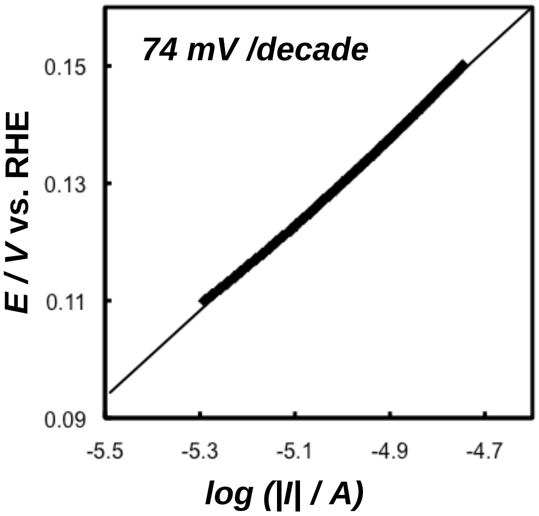


Figure S2. (A) Cyclic and linear sweep voltammograms of Rh(TCPP)/C under (a) an argon atmosphere, (b) a CO atmosphere without electrode rotation, and a CO atmosphere with electrode rotation at (c) 2500 rpm (262 rad s^{-1}) , (d) 3600 rpm (377 rad s^{-1}), (e) 4900 (513 rad s^{-1}), and (f) 6400 rpm (670 rad s^{-1}) (scan rate = 10 mV/s). The measurements were performed at a scan rate of 10 mV/s in 0.1 M H_2SO_4 at 25 °C. (B) Koutecky-Levich plot of the current at 0.45 V.


Rh(T(-COOCH$_3$)PP)/C


Rh(T(-OCH$_3$)PP)/C

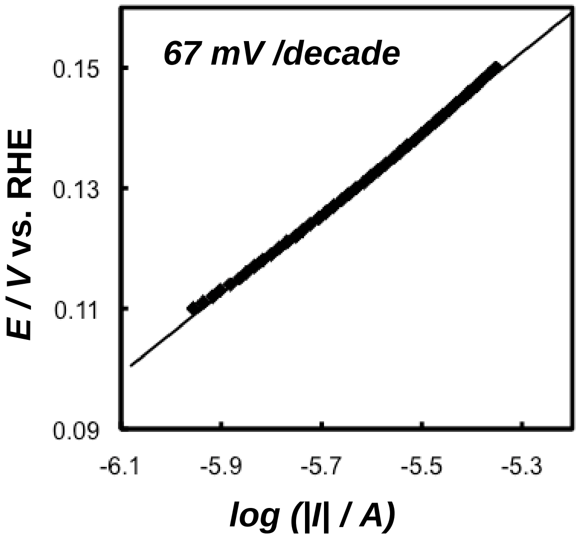

Rh(TPP)/C

Figure S3. Logarithmic plots of potential vs. current of CO oxidation by Rh(T(-COOCH$_3$)PP)/C, Rh(T(-OCH$_3$)PP)/C, and Rh(TPP)/C.