Supporting Information

Electrochemical CO₂ reduction by a cobalt bipyricorrole complex: Decrease of an overpotential value derived from monoanionic ligand character of the porphyrinoid species

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Materials and methods.

NMR spectra of compounds 1-4 and Zn(II) bipyricorrole (Zn(II)BIPC) were recorded on a Bruker Avance III HD (400 MHz) spectrometer at 298 K and Bruker Avance III (600 MHz) spectrometer at 305 K, respectively. Chemical shifts are reported in ppm relative to the residual solvent resonances. ESI-TOF MS analyses were performed on a Bruker micrOTOF-II mass spectrometer. UV-vis spectral measurements were carried out with a Shimadzu UV-3600 Plus double-beam spectrophotometer with a thermostated cell holder. EPR spectra were measured with a Bruker EMXmicro spectrometer at the X-band (9.61 GHz) microwave frequency with 20.0 mW microwave power and 10.0 G of modulation amplitude. During EPR measurements, the sample temperature was maintained at 100 K using liquid N₂ vapor. Co(II) tetraphenylporphyrin (Co(II)TPP) was prepared from the freebase tetraphenylporphyrin according to our previous buffer acid method.1 As components, 2-(*N*-morpholino)ethanesulfonic (MES), Ntris(hydroxymethyl)methyl-3-aminopropanesulfonic acid (HEPES) and N-cyclohexyl-2aminoethanesulfonic acid (CHES) were obtained from Dojindo Molecular Technologies, Inc. and 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (TAPS) was purchased from Nacalai Tesque, Inc. Tetrabutylammonium hexafluorophosphate (TBAPF₆, >98%) from Tokyo Chemical Industry Co., Ltd. was recrystallized in heated ethanol and dried in vacuo before use. Distilled water was demineralized using a Merck Millipore Integral 3 apparatus. All other reagents of the highest guaranteed grade available were obtained from commercial sources and used as received unless otherwise indicated.

X-ray Crystallography.

The single crystal X-ray diffraction study was carried out with Rigaku XtaLAB synergy. The structure was refined on F^2 by full-matrix least-squares method using Olex2. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms.

Electrochemistry.

Electrochemical studies were performed using a potentiostat (CompactStat, Ivium Technologies). A single-compartment cell with a custom silicon top was used for all cyclic voltammetry (CV) experiments with a polished glassy carbon working electrode (3 mm in diameter from ALS Co., Ltd. unless otherwise indicated), a Pt wire counter electrode, and an Ag|AgCl reference electrode (3 M NaCl_{aq.}, from ALS Co., Ltd.). All experiments were referenced relative to the Fe^{III/II} couple at 0.00 V using ferrocene (Fc) as an internal standard. All electrochemical experiments were conducted with 0.1 M TBAPF₆ as a supporting electrolyte. All solutions were purged with N₂ or CO₂ gas before CVs were measured. Pseudo-pH values were measured with an F-72 Horiba pH meter equipped with a 9615-10D Horiba electrode.

Controlled-potential electrolysis.

Controlled-potential electrolysis (CPE) experiments were carried out in a custom-made single compartment cell designed in our laboratory with a custom silicon top to hold each electrode and a joint for sealing with septa and gas sampling. This apparatus included a glassy carbon plate (5.8 cm²) surface area, from ALS Co., Ltd.) as a working electrode, a Pt wire counter electrode separated from the bulk solution by a porous glass frit (from EC FRONTIER Co., Ltd.), and an Ag|AgCl reference electrode (3 M NaCl_{aq.}) separated from the solution by a Vycor tip (from ALS Co., Ltd.). A potentiostat (CompactStat, Ivium Technologies) was used to apply potentials and record currents. The CPE experiments were performed in DMF with various amounts of proton sources and 0.1 M TBAPF₆. The CPE solutions were purged with N₂ or CO₂ gas for 20 min before the electrolysis. Gaseous products after the CPE experiments were analyzed using 50 µL sample aliquots taken from the headspace of the electrochemical cell and injected on a Shimadzu BID-2010 plus series gas chromatography with a 250 m \times 0.5 mm ID micropacked column using helium as a carrier gas at a flow rate of 3.0 mL/min. For the liquid products, a 1 mL sample solution was diluted twice with H₂O, filtered and analyzed with a Shimadzu ion chromatography system equipped with a Shodex IC SI-35 4D column equilibrated with a 1.8 mM Na₂CO₃ aqueous solution as eluent at a flow rate of 0.3 mL/min. Faradaic efficiencies were determined by dividing the measured amount of H₂ and CO by the expected amount of H₂ and CO calculated based on the charge passed during the CPE experiments. The CPE experiments were performed at least twice, and the reported Faradaic efficiencies are average values. As a rinse test, the glassy carbon electrode was removed from the bulk solution after CPE and rinsed carefully with DMF. Then the working electrode was immersed in a catalyst-free CO₂-saturated DMF/H₂O co-solution with 0.1 M TBAPF₆ and CV measurements were conducted.

Calculation of catalytic rate constant from the results of cyclic voltammetry.²

The catalytic current i_{cat} is given by eq (1) when the catalysis proceeds via a two-electron transfer pathway:

$$i_{cat} = 2FA[cat]_0 \sqrt{Dk_{cat}}$$
(1)

where *F* is Faraday's constant, *A* is the surface area of the electrode, $[cat]_0$ is the concentration of catalyst, and *D* is the diffusion coefficient of the catalyst. The one-electron diffusion current of the catalyst i_p is determined from eq (2),

$$i_p = 0.446FA[cat]_0 \sqrt{\frac{FD\nu}{RT}}$$
(2)

where v is the scan rate in the cyclic voltammetry measurements, R is the universal gas constant, and T is temperature.

Dividing eq (1) by eq (2) avoids determining A and D, and leads to eq (3).

$$k_{cat} = \left(\frac{i_{cat}}{i_p}\right)^2 \times \frac{1}{(2 \times 2.24)^2} \times \frac{Fv}{RT}$$
(3)

Eq (3) is converted to eq (4),

$$\left(\frac{i_{cat}}{i_p}\right)^2 = \frac{(2 \times 2.24)^2 RT}{F} \times k_{cat} \times \frac{1}{\nu}$$
(4)

where $(i_{\text{cat}}/i_{\text{p}})^2$ is obtained as a function of $1/\nu$.

The k_{cat} values in this work were determined as apparent catalytic rate constants using eq (3) with the plateau current in Fig. S25, and eq (4) with the plots in Fig. S22 and Fig. S23.

According to ref 2, Tafel plots that relate the turnover frequency (TOF) toward the overpotential η applied at the electrode were obtained using the following eq (5). In this equation,

$$\text{TOF} = \frac{k_{cat}}{1 + \exp\left[\frac{F}{RT} \left(E^0_{\text{CO}_2/\text{CO}} - E_{1/2}\right)\right] \times \exp\left(-\frac{F}{RT}\eta\right)]}$$
(5)

where, $E_{CO2/CO}^0$ is the standard potential for the conversion of CO₂ to CO (-0.69 V vs NHE),³ $E_{1/2}$ is the half-plateau wave potential in the CV measurement, where the potential measured in our conditions is converted to the NHE referenced value by adding 0.22 V for catalytic Tafel plot.

Synthesis of Co(II)BIPC and Zn(II)BIPC.

The targets **Co(II)BIPC** and **Zn(II)BIPC** were synthesized through Scheme S1. Ethyl 3,4diethyl-1*H*-pyrrole-2-carboxylate was prepared according to our previous report.⁴



Scheme S1. Synthesis of Co(II)BIPC and Zn(II)BIPC.

Diethyl 5,5'-((2,6-dimethoxyphenyl)methylene)bis(3,4-diethyl-1*H***-pyrrole-2-carboxylate) (1). To a stirred solution of ethyl 3,4-diethyl-1***H***-pyrrole-2-carboxylate (2.55 g, 15.4 mmol) and 2,6-dimethoxybenzaldehyde (6.00 g, 30.7 mmol) in ethanol (76.5 mL), conc. HCl_{aq.} (1.3 mL) was added and the mixture was refluxed for 1.5 h. After cooling to 0 °C, precipitant was filtered and washed with cold methanol to give compound 1 as a white solid (4.24 g, 51%). ¹H NMR (400 MHz, CDCl₃) \delta: 9.17 (s, 2H, N***H***); 7.19 (t,** *J* **= 8.4 Hz, 1H,** *p***-C₆***H***₃(OMe)₂); 6.61 (d,** *J* **= 8.0 Hz, 2H,** *m***-C₆***H***₃(OMe)₂); 6.25 (s, 1H,** *meso-H***); 4.27 (q,** *J* **= 6.0 Hz, 4H, -CO₂CH₂CH₃); 3.80 (s, 6H, -OCH₃); 2.68 (q,** *J* **= 7.2 Hz, 4H, -CH₂CH₃); 2.31 (q,** *J* **= 7.6 Hz, 4H, -CH₂CH₃); 1.33 (t,** *J* **= 7.2 Hz, 6H, -CO₂CH₂CH₃); 1.12 (t,** *J* **= 7.2 Hz, 6H, -CH₂CH₃); 0.88 (t,** *J* **= 7.2 Hz, 6H, -CH₂CH₃). ¹³C NMR (100 MHz, CDCl₃) \delta: 161.58, 157.87, 133.35, 132.50, 128.77, 123.34, 118.14, 116.63, 105.74, 59.62, 56.30, 29.16, 18.49, 17.20, 16.02, 15.81, 14.61. ESI-TOF MS:** *m***/***z* **= 561.2955 [M + Na]⁺, calculated for C₃₁H₄₂N₂O₆Na 561.2935.**

5,5'-((2,6-dimethoxyphenyl)methylene)bis(3,4-diethyl-1*H***-pyrrole-2-carboxylic acid) (2). A mixture of compound 1** (2.00 g, 3.72 mmol) and NaOH (1.25 g, 31.4 mmol) in ethanol (40 mL) was refluxed for 1 h. After cooling to room temperature, glacial acetic acid (20 mL) was added and the mixture was extracted with CH₂Cl₂, washed with sat. NaCl_{aq.}, dried over Na₂SO₄ and the solvent was evaporated. The target compound **2** was obtained by re-precipitation in a hexane/CH₂Cl₂ solution as a white powder (1.45 g, 81%). ¹H NMR (400 MHz, DMSO-*d*₆) δ : 12.09 (s, 2H, -COO*H*); 9.48 (s, 2H, N*H*); 7.25 (t, *J* = 8.4 Hz, 1H, *p*-C₆*H*₃(OMe)₂); 6.76 (d, *J* = 8.4 Hz, 2H, *m*-C₆*H*₃(OMe)₂); 6.18 (s, 1H, *meso-H*); 3.77 (s, 6H, -OC*H*₃); 2.60 (q, *J* = 7.2 Hz, 4H, -CH₂CH₃); 2.27 (q, *J* = 7.2 Hz, 4H, -CH₂CH₃); 1.04 (t, *J* = 7.2 Hz, 6H, -CH₂CH₃); 0.84 (t, *J* = 7.2 Hz, 6H, -CH₂CH₃). ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 161.86, 157.20, 131.68, 131.57, 128.88, 122.33, 117.42, 116.66, 105.94, 56.33, 28.24, 17.67, 16.60, 16.07, 15.76. ESI-TOF MS: *m*/*z* = 505.2300 [M + Na]⁺, calculated for C₂₇H₃₄N₂O₄Na 505.2309.

6,6'-dibromo-2,2'-bipyridine (3). A solution of 2,6-dibromopyridine (10.0 g, 50.6 mmol) in diethyl ether (39 mL) was cooled to -78 °C and 1.6 M ^{*n*}BuLi hexane solution (29.0 mL, 55.8 mmol) was added dropwise. After stirring for 1 h at -78 °C, CuCl₂ (2.84 g, 25.4 mmol) was added and the mixture was further stirred for 1 h at -78 °C. The equipment was then substituted and the mixture was stirred for 2 h under an O₂ atmosphere. After the reaction, the flask was substituted with N₂, and the reaction was quenched with 6 M HCl_{aq}. (33 mL). The organic layer was separated with CH₂Cl₂, washed with sat. citric acid_{aq}, dried over Na₂SO₄ and the solvent was evaporated. The resulting precipitant was washed with CH₃OH and subsequent filtration afforded compound **3** as a white powder (3.85 g, 24%).

¹H NMR (400 MHz, CDCl₃) δ : 8.40 (dd, J = 0.8 Hz, 7.6 Hz, 2H, m-NC₅ H_3); 7.69 (t, J = 7.4 Hz, 2H, p-NC₅ H_3); 7.53 (dd, J = 0.4 Hz, 7.8 Hz, 2H, m-NC₅ H_3). ¹³C NMR (100 MHz, CDCl₃) δ : 155.75, 141.74, 139.45, 128.74, 120.30. ESI-TOF MS: m/z = 334.8798 [M + Na]⁺, calculated for C₁₀H₆Br₂N₂Na 334.8790.

6,6'-diformyl-2,2'-bipyridine (4). To a THF solution of *ⁿ*BuLi (9.60 mmol, 66 mL) at -78 °C was added compound **3** (500 mg, 1.59 mmol) in THF (50 mL) and stirred for 45 min at -78 °C. The mixture was then treated with DMF (0.8 mL, 9.55 mmol) and allowed to warm to room temperature. After stirring for 3 h, the reaction was quenched with 4 M HCl_{aq.} (20 mL) and the organic layer was separated with ethyl acetate. The water layer was treated with K₂CO₃ to increase the pH to 10 and then extracted with ethyl acetate. The organic layers were combined and dried over Na₂SO₄. After removal of solvent, cold CH₃OH was added and the precipitant was filtered to yield compound **4** as a white powder (140 mg, 41%). ¹H NMR (400 MHz, CDCl₃) δ : 10.19 (s, 2H, -CHO); 8.83 (d, *J* =7.2 Hz, 2H, *m*-NC₅H₃); 8.03-8.09 (m, 4H, *m*-NC₅H₃, *p*-NC₅H₃). ¹³C NMR (100 MHz, CDCl₃) δ : 193.41, 155.52, 152.42, 138.21, 125.34, 122.03. ESI-TOF MS: *m/z* = 235.0472 [M + Na]⁺, calculated for C₁₂H₈N₂O₂Na 235.0478.

11-(2,6-dimethoxyphenyl)bipyricorrole (BIPC). To a mixture of compound **2** (1.36 g, 2.83 mmol) and compound **4** (600 mg, 2.83 mmol) in THF (960 mL), trifluoroacetic acid (65 mL) was added and the mixture was stirred for 14 h at room temperature. After removal of solvent, toluene was added and residual trifluoroacetic acid was removed by evaporation. After addition of triethylamine (6 mL) to a CH₂Cl₂ (20 mL) solution of the crude product, the mixture was washed with sat. NaCl_{aq.}, dried over Na₂SO₄ and the solvent was evaporated. Re-precipitation in a solution of hexane/CH₂Cl₂ afforded **BIPC** as a red powder and the crude product was used in the next step without further purification. ESI-TOF MS: m/z = 571.3042 [M + H]⁺, calculated for C₃₇H₃₉N₄O₂ 571.3068.

11-(2,6-dimethoxyphenyl)bipyricorrolatocobalt(II) perchlorate (Co(II)BIPC). A solution of **BIPC** (500 mg) in CH₂Cl₂ (150 mL) and CH₃OH (150 mL) was treated with Co(OAc)₂·4H₂O (1.09 g, 4.38 mmol) for 5 h at room temperature. After stirring, the mixture was washed with sat. NaCl_{aq}, dried over Na₂SO₄ and the solvent was evaporated. To a solution of the crude product in CH₃OH (10 mL), NaClO₄·H₂O (1.23 g, 8.76 mmol) in H₂O (30 mL) was added and stirred for 30 min at room temperature. The organic layer was separated with CH₂Cl₂, washed with H₂O, dried over Na₂SO₄ and the solvent was evaporated out by SiO₂ column chromatography (CH₂Cl₂/acetone = 3/2) followed by re-precipitation in a diethyl ether/CH₂Cl₂ solution to give **Co(II)BIPC** as a green solid (49 mg, 25% from compound **2**). ESI-TOF MS: m/z = 628.2249 [M]⁺, calculated for C₃₇H₃₇CoN₄O₂ 628.2243. UV-vis (CH₃OH) λ_{max}/nm (absorbance) = 367 (0.481), 639 (0.138). Elemental analysis: C 59.21, H 5.06, N 7.31, calculated for C₃₇H₃₉ClCoN₄O₇ C 59.56, H 5.27, N 7.51.

11-(2,6-dimethoxyphenyl)bipyricorrolatozinc(II) perchlorate (Zn(II)BIPC). To a stirred solution of **BIPC** (200 mg) in CH_2Cl_2 (50 mL) and CH_3OH (50 mL) was added $Zn(OAc)_2$ (0.32 g, 1.74 mmol) and the mixture was then stirred for 30 min at room temperature. After stirring, the solution was washed with sat. Na Cl_{aq} , dried over Na₂SO₄ and the solvent was evaporated. To a solution of crude product in CH_3OH (10 mL), Na $ClO_4 \cdot H_2O$ (0.49 g, 3.49 mmol) in H_2O (20 mL) was added and the

mixture was further stirred for 30 min at room temperature. The organic layer was separated with CH₂Cl₂, washed with H₂O, dried over Na₂SO₄ and the solvent was evaporated. The crude product was purified by SiO₂ column chromatography (CH₂Cl₂/acetone = 3/2) followed by further purification by SiO₂ column chromatography (CH₂Cl₂/CH₃OH = 5/1) and the blue fraction was collected. **Zn(II)BIPC** was obtained by re-precipitation in a diethyl ether/CH₃OH solution as a green powder (10 mg, 5% from compound **2**). ¹H NMR (600 MHz, DMSO-*d*₆, 305 K) δ : 9.20 (d, *J* = 7.8 Hz, 2H, *m*-NC₅*H*₃); 8.72 (t, *J* = 7.8 Hz, 2H, *p*-NC₅*H*₃); 7.66 (s, 2H, *meso-H*); 7.61 (t, *J* = 9.0 Hz, 1H, *p*-C₆*H*₃(OMe)₂); 6.87 (d, *J* = 9.0 Hz, 2H, *m*-C₆*H*₃(OMe)₂); 3.64 (s, 6H, -OCH₃); 2.93 (q, *J* = 7.8 Hz, 6H, -CH₂CH₃); 1.99 (q, *J* = 7.8 Hz, 4H, -CH₂CH₃); 1.36 (t, *J* = 7.8 Hz, 6H, -CH₂CH₃); 0.76 (t, *J* = 7.8 Hz, 6H, -CH₂CH₃). ¹³C NMR (150 MHz, DMSO-*d*₆, 305 K) δ : 164.08, 160.04, 153.55, 150.98, 148.54, 144.85, 144.69, 138.47, 130.77, 130.44, 119.28, 115.43, 106.26, 104.15, 55.33, 19.03, 17.62, 16.91, 15.20. ESI-TOF MS: *m/z* = 633.2188 [M]⁺, calculated for C₃₇H₃₇N₄O₂Zn 633.2202. UV-vis (CH₃OH) λ_{max} /nm (absorbance) = 367 (0.911), 635 (0.138), 690 (0.383). Elemental analysis: C 58.49, H 5.35, N 7.51, calculated for C₃₇H₃₉CIN₄O₇Zn C 59.05, H 5.22, N 7.44.

11-(2,6-dihydroxyphenyl)bipyricorrolatocobalt(II) perchlorate (demethylated Co(II)BIPC: Fig. S27(a)). To a solution of Co(II)BIPC (16 mg, 22.0 μ mol) in CH₂Cl₂ (4.2 mL), 1 M BBr₃/CH₂Cl₂ solution (1.12 mL, 1.12 mmol) was added at room temperature, and the mixture was refluxed for 24 h. After quenching with sat. NaHCO_{3aq}, the organic layer was washed with H₂O, dried over Na₂SO₄ and the solvent was evaporated. Purification was carried out by SiO₂ column chromatography (CH₂Cl₂/acetone/CH₃OH = 20/20/3) to afford demethylated Co(II)BIPC as a green solid (8 mg, 52%). ESI-TOF MS: m/z = 600.1914 [M]⁺, calculated for C₃₅H₃₃CoN₄O₂ 600.1930.



Fig. S1. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 1.



Fig. S2. ¹³C NMR spectrum (100 MHz, CDCl₃) of compound 1.



Fig. S3. ¹H NMR spectrum (400 MHz, DMSO- d_6) of compound **2**.



Fig. S4. ¹³C NMR spectrum (100 MHz, DMSO- d_6) of compound 2.



Fig. S5. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 3.



Fig. S6. ¹³C NMR spectrum (100 MHz, CDCl₃) of compound **3**.



Fig. S7. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 4.



Fig. S8. ¹³C NMR spectrum (100 MHz, CDCl₃) of compound 4.



Fig. S9. ¹H NMR spectrum (600 MHz, DMSO- d_6) of **Zn(II)BIPC**.



Fig. S10. ¹³C NMR spectrum (150 MHz, DMSO- d_6) of **Zn(II)BIPC**.



Fig. S11. UV-vis absorption spectrum of Co(II)BIPC in CH₃OH.



Fig. S12. UV-vis absorption spectrum of Zn(II)BIPC in CH₃OH.



Fig. S13. (a) EPR spectrum of **Co(II)BIPC** in THF at 100 K. (b) EPR spectrum of **Co(II)BIPC** in THF at 100 K with an excess amount of NaBH₄.



Fig. S14. (a) UV-vis spectral changes of **Co(II)BIPC** (50 μ M in CH₂Cl₂) upon addition of cobaltocene (from blue to red). Asterisk (*) shows an absorption peak of cobaltocene. (b) Absorbance changes of **Co(II)BIPC** upon addition of cobaltocene.



Fig. S15. (a) Cyclic voltammograms of **Co(II)BIPC** (0.5 mM, red solid line) and **Zn(II)BIPC** (0.5 mM, black dashed line) in anhydrous DMF with 0.1 M TBAPF₆ at a scan rate of 100 mV·s⁻¹ under an N₂ atmosphere. Since Zn(II) is redox-innocent due to its fully occupied *d* orbitals, two reversible peaks of **Zn(II)BIPC** at -1.24 V and -1.75 V in the CV are both attributed to ligand-based reductions. The enhanced Coulomb repulsion between the additional electron and the neutral **Co(I)BIPC** complex relative to that between the electron and cationic **Zn(II)BIPC** seems to induce the negative shift of the first reduction potential of the macrocycle. The value of the potential shift is 0.51 V, which is similar to the previously reported value of 0.56 V observed in Zn(II) and Co(II) tetraphenylporphyrins.⁵



Fig. S16. (a) Cyclic voltammograms of **Co(II)BIPC** (0.5 mM) in dry DMF with 0.1 M TBAPF₆ at a scan rate of 100 mV·s⁻¹ under an N₂ atmosphere (black). Addition of H₂O under a CO₂ atmosphere (from blue to red): [H₂O] = 0, 1, 2, 3, 4, 5, 6, 7 and 8 M. (b) Relationship between the concentration of H₂O and current at -2.17 V in cyclic voltammetry.



Fig. S17. Cyclic voltammograms of **Co(II)BIPC** (0.5 mM) in dry DMF with 0.1 M TBAPF6 at a scan rate of 100 mV·s⁻¹ under an N₂ atmosphere upon addition of H₂O ranging from 0 M (blue) to 8 M (red).



Fig. S18. Cyclic voltammograms of a fresh glassy carbon plate electrode (black) and the glassy carbon plate electrode after a controlled-potential electrolysis with 5 M H₂O (red) without catalyst in DMF with 0.1 M TBAPF₆ and 5 M H₂O at a scan rate of 100 mV·s⁻¹ under a CO₂ atmosphere.



Fig. S19. Normalized UV-vis absorption spectra of an aliquot of the electrochemical solution of Co(II)BIPC before (black) and after (red) a controlled-potential electrolysis with 5 M H₂O in DMF.



Fig. S20. (a) Cyclic voltammograms of **Co(II)BIPC** (0.5 mM) in DMF with 0.1 M TBAPF₆ at a scan rate of 100 mV·s⁻¹ upon addition of 2,2,2-trifluoroethanol (TFE) under a CO₂ atmosphere (from blue to red): [TFE] = 0, 1, 2, 3, 4 and 5 M. (b) Relationship between the concentration of TFE and current at -2.28 V in cyclic voltammetry.



Fig. S21. A proposed reaction mechanism of the catalytic CO₂ reduction by **Co(II)BIPC**. (i) Oneelectron reduction of [**Co(II)BIPC**]⁺ proceeds to generate [**Co(I)BIPC**] followed by (ii) further oneelectron reduction to afford [**Co(I)BIPC**]⁻. (iii) CO₂ is bound to [**Co(I)BIPC**]⁻ to form [**Co(II)BIPC**(CO₂H)] coupled with protonation, which is supported by the slight increase in current at the second reduction process of **Co(II)BIPC** under a CO₂ atmosphere relative to the current under an N₂ atmosphere. (iv) At the potential of *ca*. –1.98 V, which is consistent with the observed onset potential of the catalytic current, one-electron reduction occurs to produce [**Co(I)BIPC**(CO₂H)]⁻ and (v) the subsequent C–OH bond cleavage by protonation affords [**Co(I)BIPC**(CO)]. (vi) Spontaneous dissociation of CO regenerates the starting complex [**Co(I)BIPC**] in the catalytic cycle. The proposed mechanism by **Co(II)BIPC** is slightly different from that performed by **Co(II)TPP**,⁶ whereas it is similar to that performed by a Mn complex reported by Kubiak.⁷



Fig. S22. (a) Cyclic voltammograms of **Co(II)BIPC** in dry DMF with 0.1 M TBAPF₆ under an N₂ atmosphere. The scan rate varies from 100 to 2000 mV·s⁻¹. (b) Plots of second redox peak current against $v^{1/2}$. The proportional dependence of the current on the square root of the scan rates indicates that the redox event is a diffusion-controlled process.



Fig. S23. (a) Cyclic voltammograms of **Co(II)BIPC** in CO₂-saturated DMF with 0.1 M TBAPF₆ and 5 M H₂O. The scan rate varies from 100 to 2000 mV·s⁻¹. (b) Plots of $(i_{cat}/i_p)^2$ values against 1/v. The apparent catalytic rate constant of **Co(II)BIPC** with 5 M H₂O was calculated from the slope using eq (4).



Fig. S24. (a) Cyclic voltammograms of **Co(II)BIPC** in CO₂-saturated DMF with 0.1 M TBAPF₆ and 5 M TFE. The scan rate varies from 100 to 2000 mV·s⁻¹. The catalytic current was independent of the scan rates in the range of 400 mV·s⁻¹ to 2000 mV·s⁻¹. (b) Plots of $(i_{cat}/i_p)^2$ values against 1/v with the scan rates ranging from 400 to 2000 mV·s⁻¹. The apparent catalytic rate constant of **Co(II)BIPC** with 5 M TFE was calculated from the slope using eq (4).



Fig. S25. (a) Cyclic voltammograms of **Co(II)TPP** in dry DMF with 0.1 M TBAPF₆ under an N₂ atmosphere. The scan rate varies from 100 to 800 mV·s⁻¹. (b) Plots of second redox peak current against $v^{1/2}$. The proportional dependence of the current on the square root of the scan rates indicates that the redox event is diffusion-controlled process



Fig. S26. (a) Cyclic voltammograms of **Co(II)TPP** in dry CO₂-saturated DMF with 0.1 M TBAPF₆. The scan rate varies from 100 to 800 mV·s⁻¹. The apparent catalytic rate constant of **Co(II)TPP** under CO₂-saturated conditions was calculated using the plateau current at a scan rate of 800 mV·s⁻¹ using eq (3).



Fig. S27. (a) Cyclic voltammogram of demethylated **Co(II)BIPC** (0.5 mM) in dry DMF with 0.1 M TBAPF₆ under an N₂ atmosphere. (b) Normalized cyclic voltammograms of **Co(II)BIPC** (0.5 mM, black) and demethylated **Co(II)BIPC** (0.5 mM, red) in DMF containing 0.1 M TBAPF₆ with 5 M H₂O under a CO₂ atmosphere. Scan rate: 100 mV·s⁻¹.

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