Supporting information for
Electroreduction of CO₂ Catalyzed by a Heterogenized Zn-Porphyrin Complex with a Redox-Innocent Metal Center

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Material Synthesis and Characterization

Materials. All chemicals and solvents were commercially available and used as obtained without further purification unless otherwise stated. The deionized water used throughout all experiments was purified through a Milli-Q reference water purification system to reach a resistivity of 18.2 MΩ cm (at 25 °C).

Synthesis of zinc(II)-5,10,15,20-tetramesitylporphyrin (PorZn). A solution of H₂Por (78.3 mg, 0.1 mmol) in CHCl₃ (150 mL) was added to a solution of zinc(II) acetate dehydrate (329 mg, 1.5 mmol) in CH₃OH (25 mL). The solution was refluxed for 18 h. After cooling down to room temperature, the solution was washed with brine, and extracted with CH₂Cl₂. The organic extract was dried (Na₂SO₄), concentrated and chromatographed [silica, hexanes/CH₂Cl₂(3:1)] to afford the title compound (72.8 mg, 86%). ¹H NMR (CDCl₃, 400 MHz)  δ 8.68 (s, 8H), 7.26 (s, 8H, overlapped with CHCl₃ from NMR solvent), 2.62 (s, 12H), 1.84 (s, 24H); MALDI-MS (M + H)⁺ = 843.9, calculated 844.3 (M = C₅₆H₅₂N₄Zn); λₘₐₓ (CH₂Cl₂) = 418, 548 nm.

Characterization. ¹H NMR spectra were recorded with an Agilent 400 MHz NMR instrument. UV-vis absorption spectra were recorded on a Varian Cary 50 Bio UV-visible spectrophotometer. Mass spectrometry was performed on a Matrix-Assisted Laser Desorption/Ionization (MALDI) Voyager DE Pro instrument using a positive mode with 1,4-bis(5-phenyl-2-oxaxol-2-yl)benzene as the matrix. SEM and EDS were taken on a Hitachi SU8230 field emission SEM. XPS measurements were performed on a PHI Versa Probe II system using a monochromatic 1486.7 eV Al Kα X-ray source. ICP-MS data were taken on a Perkin Elmer Optima 8000 inductively coupled plasma mass spectrometer.

Electrochemical Measurements
Electrochemical experiments were performed on a Bio-Logic VMP3 Multi Potentiostat using a custom-designed gas-tight H cell. The graphite rod counter electrodes were purchased from Sigma Aldrich and the Ag/AgCl reference electrodes were purchased from Pine Research Instrumentation. Carbon fiber paper (AvCarb GDS3250) was purchased from Fuel Cell Store. The working electrode was prepared by casting 125 µL of 1 mg mL\(^{-1}\) PorZn (or H\(_2\)Por)/dichloromethane solution onto a 2.5x1 cm\(^2\) carbon fiber paper to form a 1x1 cm\(^2\) area covered with the catalyst (corresponding to 0.125 mg cm\(^{-2}\)). The cathode compartment and the anode compartment were separated by an anion exchange membrane (Selemion DSV). Each compartment contained 12.5 mL of electrolyte and ~17.5 mL of gas headspace. For all experiments, 0.1 M TBAPF\(_6\) (recrystallized following a previously reported procedure\(^1\)) in a water/DMF solvent system (V\(_{H2O}\):V\(_{DMF}\) = 1:9) was used as the electrolyte. Before measurements, the electrolyte was pre-saturated with CO\(_2\) by bubbling CO\(_2\) for 15 min. During measurements, CO\(_2\) was continuously bubbled into the electrolyte at a flow rate of 10 sccm. Current densities were calculated based on the catalyst-covered geometric area of the working electrode. All potentials were referred to the standard hydrogen electrode (SHE) and were recorded with iR compensation.

**In-situ and operando X-ray Absorption Spectroscopy (XAS) Measurements**

In-situ X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) experiments were carried out at beamline 5BM-D of DND-CAT, Advanced Photon Source (APS), Argonne National Laboratory (ANL). The working electrodes were prepared by casting PorZn on carbon fiber paper. The working electrode was mounted onto a custom-designed in-situ XAS backscattering fluorescence cell, as described in our previous study.\(^2\) The cell is designed for three-electrode measurements and can contain up to 30 mL of electrolyte. A graphite rod and a Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The same electrolyte as described in the Electrochemical Measurements section, namely 0.1 M TBAPF\(_6\) in a water/DMF solvent system (V\(_{H2O}\):V\(_{DMF}\) = 1:9), was used. Before measurements, the electrolyte was pre-saturated with CO\(_2\) by bubbling CO\(_2\) for 15 min. During the operando XAS measurements, CO\(_2\) was continuously bubbled at a flow rate of 30 sccm. Each XAS measurement was taken after maintaining a given potential for 30 min. All data were collected in fluorescence mode under an applied potential controlled by a Gamry Reference-600 electrochemistry workstation. A Lytle detector was used to collect the Zn K fluorescence signal while the Si(111) monochromator scanned the incident X-ray photon energy through the Zn K absorption edge. The monochromator was detuned to 80% of the maximum intensity at the Zn K edge to minimize the presence of higher harmonics. XAS measurements were done at different applied potentials. At each selected potential, the potential was held until enough data statistics of XAS were achieved. The X-ray beam was calibrated using a Zn metal foil. Data reduction and data analysis were performed with the Athena software packages. Standard procedures were used to extract the EXAFS data from the measured absorption spectra. The
pre-edge was linearly fitted and subtracted. The post-edge background was determined by using a cubic-spline-fit procedure and then subtracted. Normalization was performed by dividing the data by the height of the absorption edge at 50 eV.

TOF Calculation
CV measurements were conducted at various scan rates (10, 20, 40, 60, 80, and 100 mV/s) in 0.1 M TBAPF₆ solution saturated with CO₂ within the potential window from -0.100 to -0.400 V vs SHE where no Faradaic process takes place. The electrochemical double-layer (EDL) capacitance can be calculated by the equation: \[ C = \frac{i}{\nu}, \] where \( i \) is the current (mA) and \( \nu \) is the scan rate (mV s⁻¹). The EDL capacitance was derived from the slope of the linear regression in the current-scan rate plot (Figure S16). Since the EDL capacitance is proportional to the actual number of PorZn molecules exposed in the electrolyte, the TOF can be calculated by the equation: \[ TOF = \frac{j}{(n*e*m)} = \frac{j}{[ne*C*V/(k*e)]} = \frac{kJ}{nCV}, \] where \( j \) is the partial current (mA) resulting from CO production, \( n \) is the number of electrons transferred to produce one CO molecule \( (n=2) \), \( e \) is the elementary charge \( (1.602*10^{-19} \text{ C}) \), \( m \) is the actual number of exposed PorZn molecules, \( k \) is the number of elementary charges adsorbed on each molecule, \( C \) is the EDL capacitance (mF) and \( V \) is the potential window (V) of the CV measurements. Assuming one exposed PorZn molecule contributes to the EDL capacitance by adsorbing one elementary charge, we have \( k = 1 \) and the TOF for CO₂-to-CO conversion can then be calculated.

Chemical reduction experiments
General Considerations. The chemical reductions were performed under a N₂ atmosphere in an M. Braun glovebox maintained at or below 0.5 ppm of O₂ and H₂O. All glassware was dried at 160 °C under vacuum. THF was distilled under Ar from a potassium benzophenone ketyl solution and stored with 4 Å molecular sieves. THF-d₈ was dried over CaH₂ and then over K/benzophenone and vacuum transferred to a storage container containing 4 Å molecular sieves. Celite and 4Å molecular sieves were dried at 200 °C under vacuum overnight. Na sand was obtained through exhaustive pentane washing of a 25-35% dispersion in paraffin obtained from Sigma Aldrich followed by drying under a dynamic vacuum. Naphthalene was obtained from Sigma Aldrich and was sublimed before use. Sodium naphthalenide solutions were prepared in situ by stirring naphthalene with 4 equivalents of sodium sand for 45 minutes with subsequent filtration through a celite plug.

One-electron chemical reduction and subsequent reaction with CO₂. A solution of sodium naphthalenide \( (5.3 \mu\text{mol}, 1.05 \text{ eq}) \) in 0.5 mL THF was added dropwise to a pink suspension of PorZn \( (5.0 \mu\text{mol}, 1.00 \text{ eq}) \) in 3 mL THF. The resulting dark yellow green solution was stirred for 20 minutes after which all volatiles were evaporated. At this point an aliquot \( (0.5 \text{ mL}) \) was collected for UV-Vis and IR-ATR analysis. The purple residue was dissolved with THF-d₈ \( (0.6 \text{ mL}) \) to give a dark yellow-
green solution which was analyzed by $^1$H NMR spectroscopy in a J. Young NMR tube. The THF-$d_8$ solution was frozen, the headspace in the NMR tube was evacuated and the NMR tube was closed under vacuum. After thawing the tube was backfilled with an atmosphere of CO$_2$ and analyzed by $^1$H-NMR, UV-Vis and IR-ATR spectroscopy.

**Two-electron chemical reduction and subsequent reaction with CO$_2$.** The two-electron reduction was performed analogous to the one-electron reduction but with 2.1 equivalents of sodium naphthalenide (10.5 μmol, 2.1 eq) in 1 mL THF. The color changed from pink to dark forest-green.
Figure S1. (A) Mass spectrometry spectrum and (B) $^1$H NMR spectrum of PorZn in CDCl$_3$ with peaks assigned.
Table S1. Elemental analysis results of PorZn (C_{56}H_{52}N_{4}Zn).

| Mass percentage (%) | C   | H   | N   |
|---------------------|-----|-----|-----|
| **Calculated**      | 79.46 | 6.19 | 6.62 |
| **Found**           | 79.43 | 6.25 | 6.31 |

Table S2. ICP-MS results for the supernatant from PorZn dispersed in water, PorZn digested in nitric acid, and the blank nitric acid. *

* Note that the results for the acid-digested PorZn are obtained after correction for the contribution from the blank nitric acid. The low concentration signals of other metal elements are likely due to instrumental fluctuation, as the nitric acid (99.999% trace metal basis) we used to digest the PorZn sample still contains impurities in itself.
**Figure S2.** Photo of the electrochemical setup for CO\textsubscript{2} electroreduction.

**Figure S3.** Sample \textsuperscript{1}H NMR spectra of (A) a mixture of formic acid (a typical CO\textsubscript{2} reduction product in the liquid phase) and working electrolyte, and (B) electrolyte solution after 4 h of electrolysis at -1.7 V vs SHE. Both spectra were recorded in D\textsubscript{2}O. No peaks attributed to liquid-phase products were detected.
Figure S4. (A) A representative GC-MS spectrum for gas-product analysis during electrolysis. (B) Calibration curve for CO concentration in 200 µL of sample gas vs CO peak area calculated from the GC-MS spectrum.

Figure S5. Normalized UV-vis spectra of pure PorZn in CH$_2$Cl$_2$, pure PorH in CH$_2$Cl$_2$ and the CH$_2$Cl$_2$ solution obtained from rinsing the PorZn electrode after 1 h of electrolysis at -1.7 V vs SHE.
Figure S6. Chronoamperometry at -1.7 V vs SHE under reaction conditions. The PorZn working electrode was taken out after 1 h of electrolysis and a blank carbon fiber paper was used as the new working electrode under the same operating conditions. The blue dotted trace corresponds to the current response of a blank carbon fiber paper electrode in a fresh electrolyte solution at -1.7 V vs SHE.

Figure S7. SEM images of a PorZn electrode (A, B) before and (C, D) after 1 h of electrolysis at -1.7 V vs SHE.
Table S3. Current density and Faradaic efficiency* of a blank carbon paper electrode at -1.7 V vs SHE in a fresh electrolyte solution compared with the data in a used electrolyte.

| Electrolyte solution | Current Density (mA cm⁻²) | H₂ FE% | CO FE% | Formic Acid FE% |
|----------------------|---------------------------|--------|--------|-----------------|
| Fresh                | 0.46                      | 33%    | <1%    | trace           |
| Used                 | 0.48                      | 38%    | 3%     | trace           |

*The fact that the Faradaic efficiencies do not add up to unity might be due to non-Faradaic current and the larger error in the measurement when the current density is small.

Figure S8. (A) SEM image and (B) EDS mapping of a PorZn electrode after 1 h of electrolysis at -1.7 V vs SHE.

Figure S9. Zn 2p core level XPS spectra of a PorZn electrode before (lower, black) and after (upper, blue) electrolysis, with the peaks assigned according to the literature (red).³
Figure S10. (A) Operando Zn K-edge X-ray absorption spectra of the PorZn catalyst electrode at all examined potentials. (B) Fourier transforms of the EXAFS spectra. (C) The k-space plots of the EXAFS spectra. (D) Derivatives of the XANES spectra. Spectra of Zn and ZnO are collected as references.

| Potential (V vs NHE) | Current Density (mA cm⁻²) | H₂ FE% | CO FE% | Formic Acid FE% |
|----------------------|----------------------------|--------|--------|-----------------|
| -1.4                 | 0.27                       | 40%    | 0%     | Trace           |
| -1.5                 | 0.32                       | 59%    | 0%     | Trace           |
| -1.6                 | 0.44                       | 70%    | 0%     | Trace           |
| -1.7                 | 0.64                       | 62%    | 1%     | Trace           |

Table S4. Current densities and Faradaic efficiency* of H₂Por electrode.

*The fact that the Faradaic efficiencies do not add up to unity might be due to non-Faradaic current and the larger error in the measurement when the current density is small.
Detailed Discussion on Chemical Reduction of PorZn and Subsequent Reactions with CO₂

The reaction of PorZn with NaNap was confirmed by 1H NMR and UV-Vis spectroscopies. The 1H NMR spectrum of PorZn in THF-d₅ shows extra peaks due to PorZn aggregates in THF (Figure S13a). After reduction to PorZn₁, the characteristic proton peaks of PorZn at 8.58 and 7.26 ppm disappeared and broad paramagnetic features appeared at 13 and 7 ppm (Figure S13b), indicating successful reduction of PorZn. Note that the spectrum of PorZn₂ also shows similar paramagnetic features (Figure S13d), probably because the two-electron reduction is incomplete and the solution thus contains one-electron reduced species. The UV-Vis spectra of the reduced species show new peaks at 710, 820 and 920 nm (Figure S14) that match well with the reported data of a singly reduced tetraphenylporphyrin, where the authors claim that “the excess electrons appear to be distributed in the π-system of the organic ligand”. DFT calculations have also shown that a ligand-reduced zinc-porphyrin complex in aprotic solvent can give absorption peaks in the near-infrared region. The observed absorption features thus support our conclusion that the metal center of the PorZn is redox-innocent and the ligand mediates redox during electrocatalytic CO₂ reduction. The absorption features of PorZn₂ are similar to those of PorZn₁, possibly due to incomplete two-electron reduction. Both reduced species are immediately oxidized back to PorZn after being exposed to air (Figure S12, S14).

To study the reactions of the reduced PorZn species with CO₂, the PorZn₁ and PorZn₂ THF solutions were then exposed to dry CO₂. Clear color changes were observed (Figure S12). The redox reaction with CO₂ was confirmed by 1H NMR, as the PorZn peaks at 8.58 and 7.26 ppm that disappeared upon reduction re-appeared after addition of CO₂ (Figure S13), indicating that the electrons were transferred to CO₂. Similar spectral changes were observed for PorZn₁ and PorZn₂. The PorZn absorption features in the UV-Vis spectra also recovered after addition of CO₂ (Figure S14). The extra

Figure S11. CVs of H₂Por on a glassy carbon electrode in Ar- and CO₂-saturated electrolyte.
features present in the NMR and UV-Vis spectra imply that additional species are formed during the process. These species may not be present in the electrocatalysis case because the electrocatalysis is heterogeneous and happens in the presence of proton donors, and the redox transformation sequence takes place on a much shorter timescale. Upon reaction with \( \text{CO}_2 \), PorZn reduced by two equivalents of NaNap shows a new IR absorption band at \( \approx 1580 \text{ cm}^{-1} \) (Figure S15), which could be inherent to an incorporated \( \text{CO}_2 \) molecule.

\[
\text{PorZn} \quad \text{PorZn}^{1-} \quad \text{PorZn}^{2-} \quad \text{PorZn}^{1-} + \text{CO}_2 \quad \text{PorZn}^{2-} + \text{CO}_2
\]

\[\downarrow \text{All exposed to air}\]

\[
\text{PorZn} \quad \text{PorZn}^{1-} \quad \text{PorZn}^{2-} \quad \text{PorZn}^{1-} + \text{CO}_2 \quad \text{PorZn}^{2-} + \text{CO}_2
\]

**Figure S12.** Photographs of PorZn solutions under anaerobic atmosphere (top) and after brief exposure to air (bottom).
Figure S13. $^1$H NMR spectra of (a) PorZn, (b) PorZn$^{1-}$, (c) PorZn$^{1-}$ after exposure to CO$_2$, (d) PorZn$^{2-}$, and (e) PorZn$^{2-}$ after exposure to CO$_2$ in THF-d$_8$. $@$ indicates porphyrin aggregates due to poor solubility in THF; $#$ shows the neutral porphyrin features; $^*$ indicates naphthalene peaks.

Figure S14. Absorption spectra of PorZn, its reduced species with and without CO$_2$, as well as its reduced species after exposure to air in THF.
Figure S15. Stacked IR spectra of neutral PorZn (black), PorZn reduced with two equivalents of sodium naphthalenide (green), and reduced PorZn after reacting with CO$_2$ (blue).

Figure S16. The linear regression of the current-scan rate plot as described in the method section to determine the electrochemical double-layer (EDL) capacitance.

Reference
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