

Supporting Information

Graphite-conjugation enhances porphyrin electrocatalysis

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Experimental Methods.

Chemicals and materials. Chloroform and methanol were obtained from BDH, dichloromethane and toluene were obtained from Macron Fine Chemicals, 200 proof ethanol was obtained from Koptec and all were used as received unless otherwise noted. Dry dichloromethane, dimethylsulfoxide and toluene were degassed and dried using a Glass Contour Solvent Purification System built by SG Water USA, LLC (New Hampshire, USA) and were stored under an atmosphere of N₂ over 4 Å molecular sieves. Dry ethanol (SeccoSolv) was obtained from EMD Millipore. All aqueous synthetic manipulations used deionized water while all aqueous electrochemical preparations and measurements used reagent grade water (Millipore Type 1, 18.2 MΩ-cm resistivity). Perchloric acid (Suprapur, 70%) was obtained from Sigma Aldrich. Sulfuric acid (OmniTrace, 95.5-96.5%,) and hydrochloric acid (OmniTrace, 34-37%) were obtained from EMD Millipore and were used as received. Glassy carbon disk electrodes were obtained from Pine Research Instrumentation, Inc. Vitreous carbon plates (VC000400) were obtained from Goodfellow. Hg/HgO and Hg/HgSO₄ reference electrodes were obtained from CH Instruments. Monarch 1300 was obtained from Cabot. Platinum wire (99.9%) and Platinum mesh (99.9%) were obtained from Alfa Aesar. All syntheses were performed in solvents of ACS grade or better. Sources and purities of other chemical reagents used in syntheses are included in the protocols below.

General electrochemical methods. All electrochemical experiments were performed under ambient conditions (21 ± 1 °C) using a Biologic VSP 16-channel potentiostat. Rotation experiments were performed using either a Metrohm Autolab RDE-2 or a Pine Research Instruments MSR. A Hg/HgO reference electrode (stored in 1 M NaOH, 99.999% semiconductor grade, Sigma Aldrich) was used for all experiments in pH > 10. All other aqueous experiments used a Hg/HgSO₄ reference electrode (stored in saturated K₂SO₄, 99.997% metals basis, Alfa Aesar). Both reference electrodes were periodically checked against pristine electrodes to ensure against potential drift. Electrode potentials for experiments conducted in aqueous media were plotted vs the reversible hydrogen electrode (RHE, $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.140 + \text{pH} \cdot 0.059 \text{ V}$ or $E_{\text{RHE}} = E_{\text{Hg/HgSO}_4} + 0.640 + \text{pH} \cdot 0.059 \text{ V}$). A Pt mesh counter electrode was used for all experiments unless otherwise noted. All electrochemical measurements were recorded in a custom 5-neck cell equipped with a sparge tube and counter compartment separated by a glass frit. All glassware used for electrochemical measurements was soaked in aqua regia for at least 30 minutes and thoroughly washed with water prior to use. The uncompensated resistances were determined to be ~40 Ω, which corresponds to a loss of 0.8 mV at 0.1 mA/cm². All electrochemical measurements were uncorrected for uncompensated Ohmic loss (iR_u loss).

Preparation of GCC-MTPP and Amide-MTPP.

Electrode cleaning and pre-treatment

Two types of glassy carbon electrodes were used: 5 mm diameter button electrodes (Pine Research Instruments) and glassy carbon plates (Goodfellow). Glassy carbon button electrodes were polished using a Buehler MetaServ 250 Grinder/Polisher equipped with a Buehler Vector LC 250 rotating head. The electrodes were placed in custom fabricated PTFE holders and polished against a rotating (350 rpm) ChemoMet (JH Technologies) surface with an alumina slurry for two minutes with 2 lbs of applied pressure, followed by rinsing with reagent grade water. This process was repeated in sequence using 1.0 μm , 0.3 μm , and 0.05 μm alumina slurries, each on a different ChemoMet plate. Finally, the electrodes were sonicated twice in reagent grade water. In order to increase the surface area and expose more quinone moieties, glassy carbon button electrodes were anodized via potentiostatic electrolysis at 3.5 V vs RHE for 10 seconds in 0.1 M H_2SO_4 . Electrodes were subsequently washed with copious amounts of reagent grade water and ethanol and dried in vacuo prior to electrochemical evaluation or further functionalization. Glassy carbon plates were each used only once and were used without polishing. Glassy carbon plates were anodized by potentiostatic electrolysis at 3.5 V vs RHE for 30 seconds in 0.1 M H_2SO_4 in order to clean the electrodes and increase the population of quinone moieties on the surface. The plates were then washed with copious amounts of reagent grade water and ethanol and dried in vacuo prior to functionalization. Electrodes that were anodized in this way are referred to as GCox.

Preparation of GCC-CoTPP and GCC- H_2 TPP electrodes

Under an inert atmosphere, a scintillation vial containing a 0.6 mM solution of either $\text{H}_2\text{TPPdNH}_2$ or CoTPPdNH_2 in dry 1:1 toluene/EtOH was charged with GCox electrodes. The vial was capped and heated to 100 $^\circ\text{C}$ for 12 hours. The vial was then cooled to room temperature. The electrodes were removed from the vial and washed with toluene, then were allowed to soak in toluene for 1 hour to remove physisorbed species. The electrodes were removed, rinsed with EtOH to remove residual toluene, rinsed with water and placed in electrochemical grade 0.1 M HCl to soak for an hour to cleave adventitious imine linkages. Finally, the electrodes were rinsed with water, ethanol and were dried in vacuo. This procedure generated GCC-MTPP electrodes.

Preparation of GCC-CoTPP on high surface area carbon

To a flask charged with a stir bar was added 125 mg of Monarch 1300 carbon powder and 9 ml EtOH. The mixture was sparged with Ar for 30 min to remove oxygen. A solution of 12.6 mg of CoTPPdNH_2 in 10 ml dry toluene was added via syringe. Against positive pressure of Ar, the flask was fit with a reflux condenser and the mixture was heated to 100 $^\circ\text{C}$ for 12 hours. Upon cooling to room temperature, the carbon powder was collected by filtration and washed with copious amounts of toluene and ethanol. The solid was transferred to a flask containing 15 ml of electrochemical grade 0.1 M HCl and stirred for 3 hours. The solid was collected by filtration,

washed with 3 by 20 ml reagent grade water and 3 by 20 ml EtOH. The carbon powder was transferred to a thimble and washed with toluene in a Soxhlet extractor for 14 hours. Yield: 50 mg. Elemental analysis: C, 90.26; H, 0.45; N, 0.69; Co, 0.26. Elemental analysis of unfunctionalized Monarch 1300 yields a native nitrogen percentage of 0.25%. Controlling for the native nitrogen content yields a N:Co ratio of 7:1, close to the expected 8:1 ratio.

Preparation of Amide-CoTPP and Amide-H₂TPP¹⁻³

Inside a nitrogen filled glovebox, a vial was charged with GCox electrodes and 10 ml dry toluene. The vial was removed from the glovebox and, via syringe, 1 ml of thionyl chloride was added and the vial were heated to 120 °C for 1 hour. Following cooling to room temperature, the solution was removed via syringe and the vials were brought back into the glovebox. Each electrode was washed by sequential submersion in two vials of dry toluene, and was then placed in a clean vial. To the electrodes was added 8 ml of dry toluene containing 2.3 mg of either cobalt or free-base 5-(*p*-aminophenyl)-10,15,20-triphenylporphine. The vial was sealed, removed from the glovebox and heated to 120 °C for 3 hours. Following cooling, the electrodes were washed with copious amounts of toluene, then sequentially submerged in methanol and dimethylformamide, rinsed with ethanol and dried in vacuo.

Determination of catalyst surface concentration.

General methods for inductively coupled plasma mass spectrometry (ICP-MS)

Spectra were collected using an Agilent 7900 ICP-MS. A calibration curve was generated from aqueous 2% nitric acid solutions containing known concentrations of Co. Erbium (Ricca Chemical Company, 1000 ppm in 3% HNO₃) was used as an internal standard in the calibration curve. The calibration solution series were prepared by serial dilution of a Co standard solution (Fluka, TraceCERT 1000 ppm in 2% HNO₃) with 2% nitric acid (EMD Millipore, OmniTrace Ultra). All volumetric flasks were soaked in aqua regia and rinsed with copious amounts of reagent grade water prior to use. Solutions, if not used immediately, were stored in air-tight plastic containers.

Determination of the ratio of integrated charge in the pyrazine wave to the surface Co concentration for GCC-CoTPP

Prior to digestion for ICP-MS, cyclic voltammetry of GCC-CoTPP modified glassy carbon plates was collected in 0.1 M NaOH under N₂. Voltammograms were initiated at the open circuit potential (OCP) and swept reductively, cycling three times between –0.48 V and 0.92 V vs RHE with a scan rate of 10 mV/s. The third cycle was used for integration. The same procedure performed on button electrodes was used to generate the data in Figure 1d. The redox features centered at 0.1 V vs RHE were assigned to the surface conjugated pyrazine linkages and were integrated to determine the charge passed in the pyrazine wave. Contact to the plate was made via copper wire and a copper flat-nose alligator clip which was then wrapped with parafilm to make a water-tight seal. The electrode was submerged in the electrolyte such that any carbon not covered with parafilm was in contact with the solution. Following cyclic voltammetry, the solution-exposed portion of the electrode was broken off. The severed electrode pieces were digested by complete submersion in ca. 1 ml of aqua regia (2:1 conc. HCl, OmniTraceUltra EMD Millipore; HNO₃ OmniTraceUltra EMD Millipore) for 12 hours followed by dilution to a final volume of 25.00 mL by addition of reagent grade water. The concentration of Co in the resulting solutions was measured by ICP-MS. The integrated charge in the pyrazine wave was converted to moles of electrons by dividing by Faraday's constant. The integrated charge quantities were divided by the corresponding Co surface concentration for each electrode to obtain the e[–]/Co ratio of 1.80 ± 0.11 reported in the main text.

Determination of Co surface concentration in GCC-CoTPP

The above e[–]/Co ratio was used along with the integrated charge in the pyrazine waves and the geometric surface area, to determine the area normalized Co surface concentration of all subsequent GCC-CoTPP electrodes using the following equation:

$$\Gamma_{Co} = \frac{Q_{pyr}}{R_{e^{-}/Co}FA}$$

where Γ_{Co} is the surface concentration of cobalt in mol/cm², Q_{pyr} is the integrated charge of the pyrazine wave, $R_{e-/Co}$ is the experimentally determined ratio of electrons to cobalt rounded to the nearest integer, F is Faraday's constant and A is the geometric area of the electrode.

Control for extraneous cobalt

To control for adventitious cobalt introduced from trace contaminants, glassy carbon plates were subjected to the GCC functionalization procedure without added CoTPPdNH₂ and then were digested in the same manner. The absolute amount of this adventitious Co in the digestate was determined to be less than 0.1 ppt Co, below the lowest value of the calibration curve. This corresponds to a value at least 100-fold lower than the amount of Co found for the digested GCC-CoTPP samples and was therefore not taken into account in the determination of the electron to Co ratio.

Determination of Amide-CoTPP surface coverage

No electrochemical handle for Amide-CoTPP is available to cross-correlate coverage on glassy carbon plates to glassy carbon button electrodes.³ Consequently, coverages were determined using three representative Amide-CoTPP electrodes that were prepared in the identically to those used for electrochemical evaluation. Three Amide-CoTPP glassy carbon button electrodes were pressed into the Teflon holders used for electrochemical measurements and only the exposed face of the electrode was submerged in conc. HNO₃ (OmniTraceUltra, EMD Millipore) for 12 hours. The electrode was rinsed with multiple changes of reagent grade water and these rinses were combined with the acid used for the digestion. The total volume was diluted up to 25.00 ml with reagent grade water. The concentration of Co in the resulting solutions was determined via ICP-MS then converted into a normalized surface coverage using the geometric surface area, 0.196 cm², of the electrode. This procedure results in relative large variability in Co surface coverage that contributes to the large error bars in TOF for the Amide-CoTPP in Figure 3.

X-ray photoelectron spectroscopy.

X-ray photoelectron spectra of GCC-MTPP and Amide-MTPP were recorded using a Physical Electronics PHI Versaprobe II with a monochromatic aluminum K α X-ray source (1486.6 eV) and a hemispherical energy analyzer. Spectra of the GCC-MTPP, Amide-MTPP and drop cast CoTPPdNH₂ were collected by fixing the glassy carbon button to the support platen with conductive carbon tape. Spectra of CoTPP were collected by tapping <0.1 mg CoTPP onto a gold-plated slide and rubbing with a Kimwipe until the molecule was smeared into a reflective film which is conductive.⁴ Contact of the platen to the gold-plated slide was made with a screw and washer. Data were collected at a base pressure of 5×10^{-9} torr using a 200 μ m, 50 W focused beam at a take-off angle of 45°. Survey spectra were collected using a pass energy of 187.85 eV and a step size of 0.8 eV. High energy resolution scans that were used for peak fitting were collected with a pass energy of 23.50 eV and a step size of 0.1 eV. Because of the low surface coverage of cobalt, quantification of GCC-CoTPP and Amide-CoTPP was performed on scans collected with a pass energy of 117.40 eV to maximize signal and a step size of 0.125 eV to minimize noise (Figure S11 & S12, respectively). All quantification was performed using MultiPak software. Each spectrum was smoothed with a 7-point Savitzky-Golay method prior to quantification.

Peak fitting was performed in CasaXPS. All scans were smoothed with a 5-point Savitzky-Golay method and referenced to the graphitic C 1s peak (284.3 eV) of glassy carbon or the Au 4f_{7/2} peak (84.0 eV). The N 1s peak manifolds of all compounds, excluding CoTPPdNH₂, were fit with a Shirley-type background and fit with Gaussian/Lorentzian line-shapes of 30% Gaussian shape. The N 1s peak manifold of CoTPPdNH₂ was fit with a linear background and Gaussian/Lorentzian peaks of 30% Gaussian shape. The GCC-CoTPP and Amide-CoTPP Co 2p peak manifolds were fit with a linear background and an asymmetric peak shape comprising a Gelius profile convoluted with a Gaussian/Lorentzian obtained in CasaXPS by inputting A(0.35,0.8,0)GL(30) in the entry for Line Shape in the peak fitting window. The Co 2p manifolds of CoTPP and CoTPPdNH₂ were not fit due to large background scattering and low signal intensity, respectively. The data referenced in this section are found in Figure 1a and 1b in the main text and in Figures S1-4 and S11-12 and relevant numerical values are summarized in Tables S1 and S2.

X-ray absorption spectroscopy.

X-ray absorption measurements of high surface area GCC-Co-TPP were conducted at the Co K-edge (7.708 keV) on the Insertion Device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. Quick scanning transmission mode was used to collect the data. Ionization chambers were set with inert N₂ gas to ensure repeatable measurements without concerns for arcing from monatomic gases. This yields a linear response in the voltage ranges and gain settings at 10⁵ V/A gain setting with an approximated flux of 10¹³ photons/sec. A silicon dioxide harmonic rejection mirror was used to filter out higher order harmonics at an angle of 0.16 degrees relative to the incident X-rays and ionization chambers were aligned at 0.32 degrees for the beam to pass through the central measurement region.

Samples were prepared via the tape method. Powder was collected and spread evenly over Kapton tape and sealed, then folded to achieve desired edge step. All spectra were obtained at room temperature in air. Both X-ray absorption near edge spectroscopy (XANES) and the extended X-ray absorption fine structure (EXAFS) measurements were collected simultaneously on the same loading with a desired edge step between 0.2 and 1, within the limit of linearity where the Beer-Lambert Law applies. Due to the nature of folding, uniform samples were achieved but precise edge steps with exact mass loadings were not possible. A uniform sample is more desirable than a specific edge step due to the small variations at high k regions. EXAFS and XANES data were processed using the Horae suite of analysis. EXAFS were processed using data within the range $k = 2$ to $k = 11$ due to convolution from the Ni K-edge near $k = 12$. The data were k^2 -weighted. The data referenced in this section are presented in Figure 1c and Figure S6.

Assessment of O₂ Reduction Activity.

Linear sweep voltammetry

Prior to collecting linear sweep voltammograms (LSVs) to assess ORR activity in acid, electrodes were cycled in base to verify the presence of the pyrazine linkage and quantify the surface coverage of Co. GCC-MTPP electrodes were cycled three times in 0.1 M NaOH under N₂ between –0.48 V and 0.92 V vs RHE at a scan rate of 10 mV/s. Cyclic voltammograms (CVs) were initiated at the open circuit potential (OCP) and swept in the negative direction. To make an equivalent comparison, Amide-MTPP electrodes were subjected to the same cyclic voltammetry procedure in 0.1 NaOH prior to analysis of their ORR activity. Following these CVs, ORR activity was assessed by collecting LSVs in 0.1 M HClO₄ in the presence of 1 atm of O₂. LSVs were initiated at OCP, sweeping in the negative direction at 5 mV/s while the electrode was rotated at 2000 rpm. The referenced data is presented in Figures 1d, 2 and S7.

Calculation of turnover frequencies

For determination of the turnover frequencies (TOFs), steady state data were collected via chronoamperometry at the series of potentials. Each chronoamperogram was continued for 30 seconds and the average current density over the last 5 seconds of data collection was used to determine the TOF at each potential. TOFs were calculated according to the following formula:

$$TOF = \frac{j}{1000Fn_{ORR}\Gamma_{Co}}$$

Where j is the current density in mA/cm², Γ_{Co} is the surface concentration of Co in mol/cm², F is Faraday's constant, n_{ORR} is the average number of electrons transferred per O₂ reduced (determined by K-L analysis, see below). The factor of 1000 is included to convert from mA to A for dimensional analysis to result in a TOF with a unit of s⁻¹. The data referenced in this section are presented in Figure 3.

Product fractionation

Koutecký-Levich (K-L) data for GCC-CoTPP were collected by polarizing at 0.3 V at a given rotation rate until steady state current was obtained (~5 seconds). The rotation rate was then changed and the process was repeated. The range of rotation rates examined spanned 300 to 2000 rpm and were probed in a random order. K-L data for Amide-CoTPP was collected in the same manner as GCC-CoTPP but the electrodes were polarized at 0.2 V instead. Values for the kinematic viscosity, diffusion constant of O₂ and solubility of O₂ in 0.1 M HClO₄ were taken from the literature.⁵ The referenced data is presented in Figure S10.

Electrochemical assessment of CoTPP desorption from GCox and resulting ORR activity

GCox electrodes were pretreated according to the procedure described above. Following the oxidative treatment and subsequent drying, the electrodes were submerged in a solution of CoTPP (0.3 mM in CH₂Cl₂) for 10 seconds, removed, and then briefly submerged in fresh CH₂Cl₂ to dislodge loosely held material then dried in air. CVs were collected in 0.1 M NaOH (under N₂, no rotation) and LSVs were collected in 0.1 M HClO₄ (under O₂, with 2000 rpm rotation). These data are presented in Figure S8.

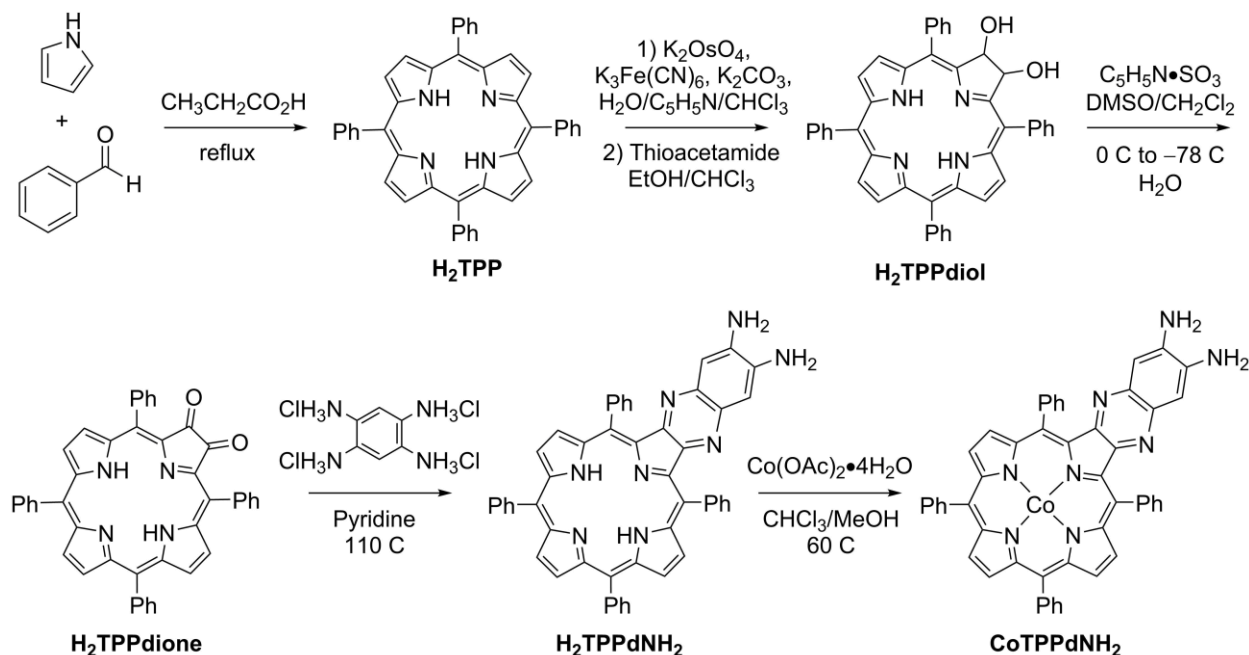
Chloride poisoning experiments on ORR activity of Amide-CoTPP

Prior to collecting linear sweep voltammograms (LSVs) to assess ORR activity in acid, Amide-CoTPP electrodes were cycled three times in 0.1 M NaOH under N₂ between -0.48 V and 0.92 V vs RHE at a scan rate of 10 mV/s. CV scans were initiated at the open circuit potential (OCP) and swept in the negative direction. Following these CVs, ORR activity was assessed by collecting LSVs in 50 ml of 0.1 M HClO₄ in the presence of 1 atm of O₂. LSVs were initiated at OCP, sweeping in the negative direction at 5 mV/s while the electrode was rotated at 2000 rpm. After the initial LSV, the total [Cl⁻] was brought to 1.5 mM by addition of 100 μ L of a stock solution of 0.75 M NaCl (Alfa Aesar, Puratronic 99.998%) in MilliQ water. The electrode was rotated at 2000 rpm in the solution for a few minutes to yield a homogeneous solution then LSVs were then recollected on the Amide-CoTPP electrodes in the presence of 1 atm of O₂. LSVs were initiated at OCP, sweeping in the negative direction at 5 mV/s while the electrode was rotated at 2000 rpm. The resulting data are presented in Figure S13.

Synthesis and characterization of molecular precursors and model complexes.

General synthetic methods

Chromatography was performed using either silica gel (60 Å, VWR high purity) or basic alumina (activated, Brockmann I, 58 Å, Sigma Aldrich). All ^1H and ^{13}C NMR spectra were recorded on a Varian 300 MHz, Bruker 400 MHz or a JEOL 500 MHz spectrometer. All chemical shifts are reported in ppm and are referenced to tetramethylsilane using the residual ^1H or ^{13}C signals of deuterated solvents (typically, $\text{CHCl}_3 = 7.26$ ppm) as internal standards. UV-Vis spectra were collected on a Cary 50 Scan spectrophotometer. Elemental analyses and ICP-MS on functionalized Monarch were carried out by Robertson Microlit Laboratories, Inc., Ledgewood, NJ. Mass spectrometry was measured on Bruker Omnisflex MALDI-TOF or Bruker Autoflex Speed instruments equipped with a reflectron accessory. Samples were loaded neat or mixed with tetraphenylporphine (H_2TPP) as an internal standard. Occasionally, the molecule required use of a matrix, in which case 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP, Alfa Aesar, 98%) was used, however, concurrent appearance of impurities in the spectrum resulted. These impurities were also present when POPOP was loaded on the target alone.



Scheme S1. Synthetic scheme for MTPPdNH₂.

meso-tetraphenylporphine (**H₂TPP**)⁶

Under ambient conditions, 500 ml of propionic acid (Alfa Aesar) was brought to reflux in a 1 L flask charged with a stir bar and equipped with a reflux condenser. To this was added 13.3 ml (0.13 mol) freshly opened benzaldehyde (Alfa Aesar) and 9.3 ml (0.13 mol) freshly opened pyrrole (Alfa Aesar). The mixture was refluxed for 30 minutes and then removed from heat. The mixture

was allowed to cool overnight. The mixture was sonicated to loosen the purple crystals from the side of the flask and the crystals were collected on a fritted glass funnel. The crystals were washed with hot water (ca. 90 °C) until the filtrate was colorless, followed by ca. 100 ml cold water. Finally, the crystals were washed with MeOH until the filtrate was colorless. The crystals were allowed to dry in air to yield 3.7509 g, 18.7 %. ¹H NMR (CDCl₃, 400 MHz, δ): 8.88 (s, 8H), 8.25 (m, 8H), 7.74-7.83 (m, 12H), -2.72 (br s, 2H). MALDI: 614.51 *m/z* found, 614.25 *m/z* expected. UV-Vis (CH₂Cl₂, λ_{max} in nm): Soret at 418, Q bands at 515, 551, 591, 648.

When used for preparation of standards for spectroscopic or electrochemical studies, further purification was performed. 1.0 g of the crude H₂TPP was taken up in 50 ml CHCl₃ and run through a column of dry, basic alumina (2.5 in by 7 in). The pink eluent was collected, concentrated to ca. 100 ml and 50 ml of MeOH was layered on top. The flask was wrapped with foil, let to sit at ambient conditions for 24 hrs, then was moved to a -35 °C fridge for a further 24 hours. 0.91 g of crystals were collected.

5,10,15,20-tetraphenyl-7,8-dihydroxychlorin (H₂TPPdiol)

This reaction is a modification of a literature procedure.⁷ It was adapted to avoid the direct use of OsO₄ and provide an alternative to H₂S gas.

To a round bottom flask charged with a stir bar was added 1.0 g potassium carbonate (Fisher Scientific) and 300 mg potassium osmate dihydrate (0.8 mmol, Alfa Aesar) followed by 10 ml water. The mixture was stirred to fully dissolve all solids and to this solution was added 500 mg H₂TPP (0.8 mmol) dissolved in 100 ml of 20% pyridine in chloroform. Finally, 540 mg of potassium ferricyanide (1.6 mmol, Aldrich) dissolved in 10 ml water was added and the flask immediately stoppered. The flask was wrapped with foil to shield from light and allowed to stir for 4 days at room temperature at which point 50 ml of water containing ca. 5 g sodium thiosulfate was added and the mixture stirred to quench any residual aqueous osmium salts. This step did not cleave the stable porphyrin osmate ester, even after stirring overnight. After an hour of stirring in the presence of sodium thiosulfate, the aqueous layer was removed and 0.9 g thioacetamide (11.9 mmol, Alfa Aesar) dissolved in 30 ml ethanol was added to the organic layer and the mixture was stirred. Full cleavage of the porphyrin osmate ester typically proceeded within 3 hours, however, the mixture was usually stirred overnight. The solution was then filtered through a plug of celite to remove the insoluble OsS, washing with ca. 30 ml CHCl₃ to elute all porphyrin material. The eluent was washed with 3 by 100 ml water, dried over sodium sulfate, filtered and the solvent removed in vacuo. The residue was taken up in minimal dichloromethane and chromatographed over silica (1 in. by 6 in.). The unreacted H₂TPP was eluted with dichloromethane and a gradient to 1.5 % methanol in dichloromethane eluted the product as a deep pink band. Removal of the solvent in vacuo yields 300 mg, 57%. ¹H NMR (500 MHz, CDCl₃, δ): 8.65 (d, 2H, *J*=4.84 Hz), 8.49 (s, 2H), 8.34 (d, 2H, *J*=4.84 Hz), 8.19-8.07 (m, 6H), 7.94 (br. d, 2H, *J*=6.29), 7.78-7.65 (m, 12H), 6.38 (s, 2H), -1.76, (br. s, 2H). MALDI: 647.50 *m/z* (found), 648.25 *m/z* (expected). UV-Vis (CH₂Cl₂, λ_{max} in nm): Soret at 412, Q-bands at 522, 546, 594, 645, 708.

5,10,15,20-tetraphenyl-7,8-dioxoporphyrin (H₂TPPdione)⁸

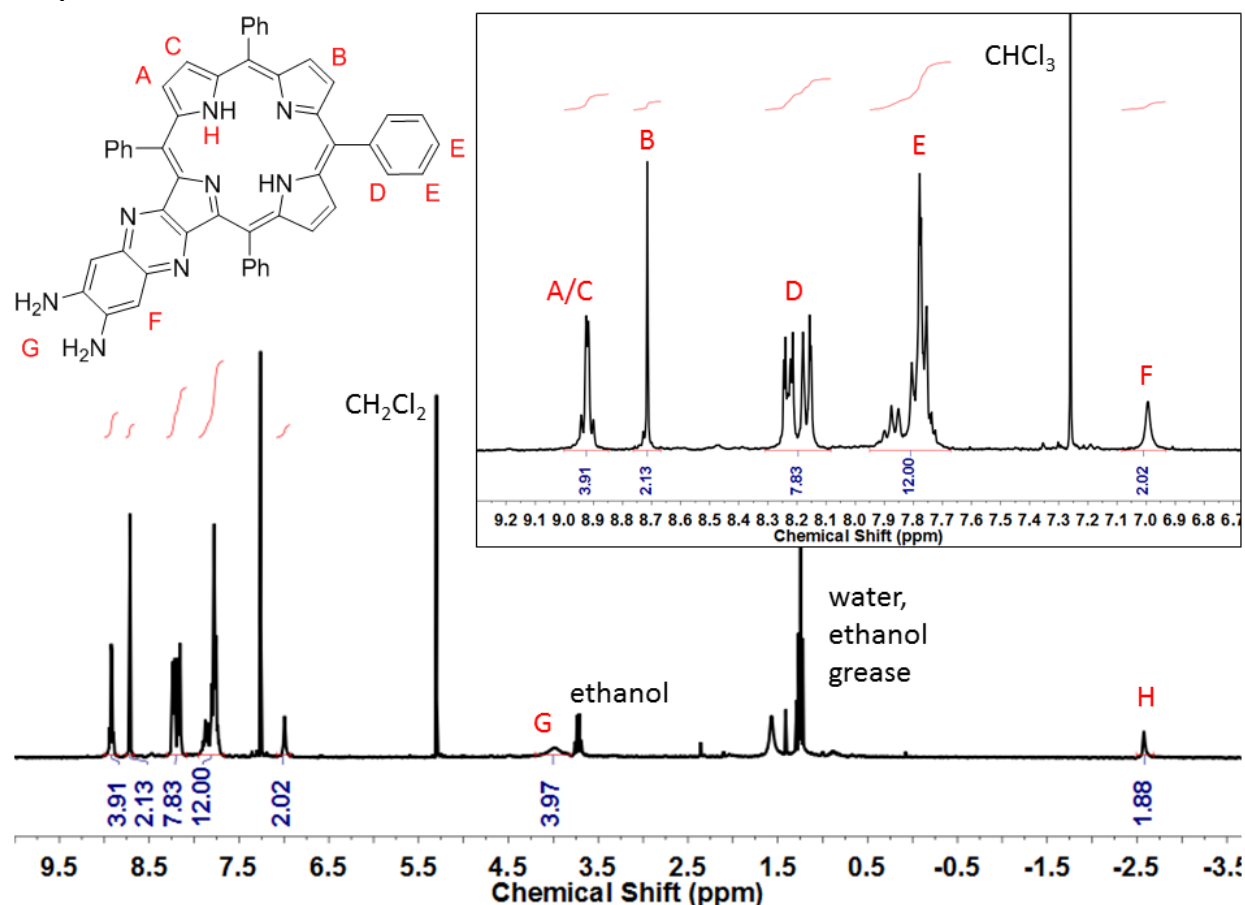
Under an inert atmosphere, three vials were each charged with a stir bar and 30 mg of H₂TPPdione for a total of 90 mg (0.14 mmol). To each of these vials was added 8 ml dry dichloromethane and 300 μ l dry diisopropylethylamine (1.8 mmol, Sigma-Aldrich, 99.5%). To a fourth vial was added 100 mg pyridine sulfur trioxide complex (0.63 mmol, Alfa Aesar) followed by 4.5 ml dry dimethylsulfoxide. The vials were sealed and the first three vials were cooled to 0 °C in an ice-water bath. Via syringe, 1.2 ml (4 equivs.) of the oxidant solution was added to each vial and the mixtures stirred for 30 seconds at which point the solution had turned a deep brown. The vials were then transferred to a dry ice-acetone bath. To each vial was added 0.5 ml water to quench the reaction and the mixtures combined, diluted with 50 ml dichloromethane and washed with 2 by 50 ml water. The organic layer was collected, dried over sodium sulfate, filtered and the solvent removed in vacuo. The residue was chromatographed over silica (1 in. by 9 in.), eluting with dichloromethane. The initial red-purple bands were discarded and the major brown band was collected. The fractions were combined and the solvent removed in vacuo to yield 49 mg, 54% of a purple solid. ¹H NMR (500 MHz, CDCl₃, δ): 8.75 (d, 2H, *J*=4.61 Hz), 8.60 (d, 2H, *J*=4.64 Hz), 8.56 (s, 2H), 8.13 (d, 4H, *J*=6.96), 7.90 (d, 4H, *J*=7.01), 7.80-7.67 (m, 12H), -2.03 (br. s, 2H). This compound is fairly unstable and was used for the next reaction within 24-36 hours.

5,10,15,20-Tetraphenyl-6',7'-diaminoquinoxalino[2,3-*b'*]porphyrin (H₂TPPdNH₂)

This reaction follows a slight modification of the literature methods.^{9,10}

Inside a glovebox, a 100 ml Schlenk flask was charged with 100 mg of 1,2,4,5-tetraaminobenzene tetrahydrochloride (0.3 mmol, ArkPharm or Matrix Scientific), a stir bar and 10 ml dry pyridine. The flask was sealed and brought out of the box, placed under Ar and heated to 110 °C, at which point the mixture was hot pink. 40 mg of H₂TPPdione (0.06 mmol) in 10 ml dry pyridine were cannula transferred over the course of 10 to 15 minutes. Once the addition was complete, the mixture was stirred at 110 °C for a further 30 minutes then cooled to room temperature. The mixture was diluted up with 100 ml toluene, washed with 4 by 100 ml water and the organic layer was collected, dried over sodium sulfate, filtered and the solvent removed in vacuo. The residue was taken up in minimal dichloromethane and chromatographed (alumina, 1 in. by 5 in.). The dichondensed by-product was washed off with dichloromethane and a gradient to 0.5 % ethanol in dichloromethane eluted the product as a long, broad yellow smear. Removal of solvent yielded 37 mg, 89%, as a dark blue solid. ¹H NMR (300 MHz, CDCl₃, δ): 8.94 (ABq, 4H, *J*=5.01 Hz), 8.73 (s, 2H), 8.28-8.15 (m, 8H), 7.92-7.72 (m, 12H), 7.01 (s, 2H), 4.00 (br. s, 4H), -2.03 (br. s, 2H). MALDI: 747.47 *m/z* found, 747.30 *m/z* expected for [M+H]⁺. UV-Vis (CH₂Cl₂, λ_{max} in nm): Soret at 439, Q bands at 525, 560, 600, 651. This compound protonates easily resulting in a loss of symmetry in the NMR spectrum. Shaking an organic solution of the compound with 1 M NaOH recovered the symmetry without perturbing the mass spectrum.

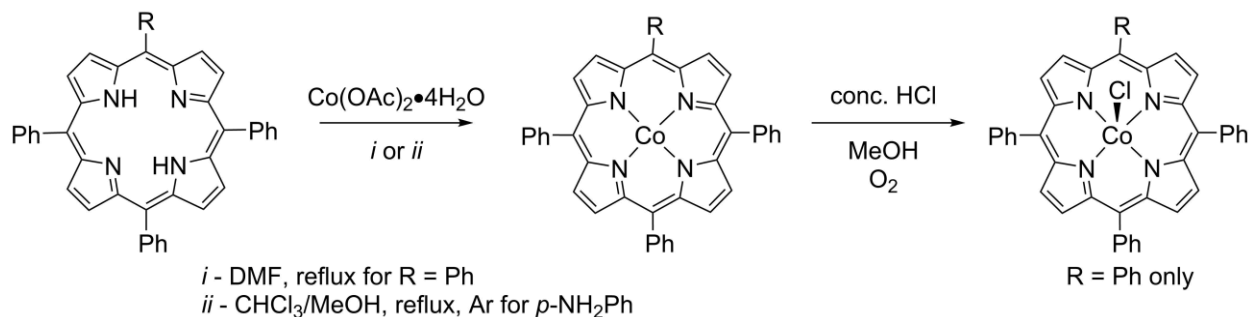
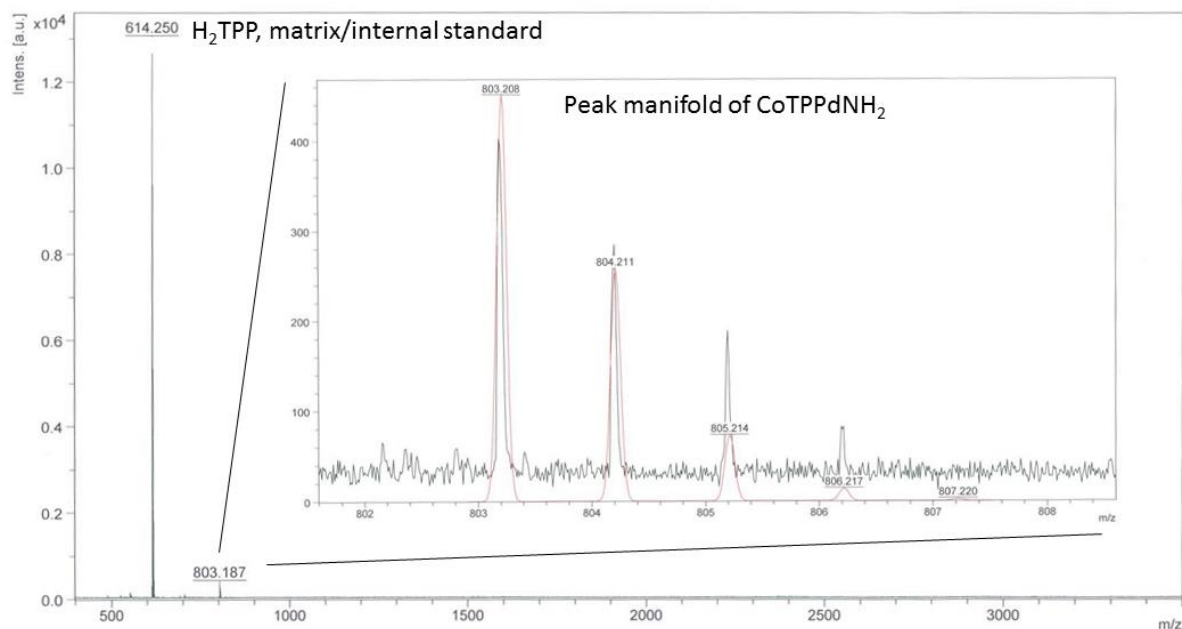
^1H spectrum of $\text{H}_2\text{TPPcond}$:



Cobalt 5,10,15,20-Tetraphenyl-6',7'-diaminoquinoxalino[2,3-*b'*]porphyrin (CoTPPdNH_2)

To a vial charged with a stir bar was added 10 mg $\text{H}_2\text{TPPdNH}_2$ (0.01 mmol) and 6 ml CHCl_3 and the solution was sparged with Ar for 15 minutes. In a separate vial, 12 mg of cobalt (II) acetate tetrahydrate (0.05 mmol, Alfa Aesar, 99.999%) and 2 ml methanol were mixed, sonicated to aid dissolution and the mixture sparged with Ar for 15 min. Once thoroughly de-aerated, the chloroform solution was heated to 60 °C and the methanolic solution was transferred via syringe to the vial containing $\text{H}_2\text{TPPdNH}_2$ and the mixture was stirred at temperature under static Ar overnight. The mixture was cooled to room temperature, diluted with 10 ml dichloromethane and washed with 10 ml water, 10 ml of aqueous 50 mM EDTA, and 10 ml water. The organic layer was collected, dried over sodium sulfate, decanted and the solvent removed in vacuo to yield a purple-brown solid. The residue was taken up in minimal dichloromethane and chromatographed over silica (1 in. by 4 in.) and eluted with a gradient from 0.5% ethanol in dichloromethane to 5% ethanol in dichloromethane. Yield variable (16% to 40%). The ^1H NMR spectrum shows broad peaks characteristic of a paramagnetic species. MALDI: 803.187 m/z found, 803.207 m/z expected for M^+ . UV-Vis (CH_2Cl_2 , λ_{max} in nm): Soret (broad) at 425, Q bands at 555 and 595. Satisfactory elemental analysis could not be obtained, likely due to the protonation of the peripheral amines.

The MALDI spectrum of CoTPPdNH₂ shows the isotopic manifold with the modelled spectrum given in red:



Scheme 2. Synthetic scheme for standards and surface amide functionalization precursors.

Cobalt *meso*-tetraphenylporphyrin¹¹

To a flask charged with a stir bar was added 80 ml N,N-dimethylformamide and 0.8 g H₂TPP (1.3 mmol) and the mixture was brought to reflux. To the solution was added 0.1 g cobalt acetate tetrahydrate (Alfa Aesar, 99.999%) and the mixture allowed to reflux for 5 minutes. A small aliquot was removed and checked for fluorescence under UV light. When observed, further portions of 0.02 to 0.04 g of cobalt acetate tetrahydrate were added, refluxing for 5 minutes and checking until no fluorescence was observed under UV light irradiation. The mixture was cooled to room temperature then placed in an ice bath to cool. 80 ml of water was added and the precipitate collected on a frit and washed with water until the eluent was colorless. The solid was eluted from the frit with chloroform and chromatographed (dry, basic alumina). The red-orange

band was collected and the solvent allowed to evaporate to yield 0.41 g, 47%. Anal. Calcd. for $C_{44}H_{28}N_4Co$: C, 78.68; H, 4.20; N, 8.34. Found: C, 78.20; H, 3.91; N, 8.29. UV-Vis (C_6H_6 , λ_{max} in nm): Soret at 415, Q bands at 529, 615, 654.

Cobalt (III) *meso*-tetraphenylporphine chloride (CoCITPP)¹²

100 mg of cobalt *meso*-tetraphenylporphyrin was added to a flask charged with a stir bar. To this flask was added a mixture of 99 ml methanol and 1 ml concentrated hydrochloric acid. The mixture was allowed to stir open to air for 12 hours. The mixture was filtered and the eluent concentrated in vacuo at 50 °C until a precipitate formed. The solid was collected on a frit and washed with water. Recrystallization from chloroform-diethyl ether yielded 60 mg, 57% of a dark purple solid. Anal. Calcd: C, 74.74; H, 3.99; N, 7.92. Found: C, 73.24; H, 3.55; N, 7.68. UV-Vis (CH_3OH , λ_{max} in nm): N band at 314, Soret at 426, Q-band at 540 with shoulders at 501 and 576.

Cobalt (II) 5-(*p*-aminophenyl)-10,15,20-triphenylporphine¹³

To a round bottom flask charged with a stir bar was added 50 mg 5-(*p*-aminophenyl)-10,15,20-triphenylporphine (0.08 mmol, Frontier Scientific) followed by 25 ml of chloroform. To a separate flask was added 195 mg of cobalt acetate tetrahydrate (0.8 mmol) followed by 5 ml of methanol. Both mixtures were sparged with Ar for 30 minutes and combined. The reaction was placed under Ar and refluxed for 14 hours. Upon cooling to room temperature, the solvent was removed in vacuo and the residue chromatographed over silica (1 in. by 6 in.), eluting with a gradient of dichloromethane to 8% MeOH in dichloromethane to 33% MeOH in dichloromethane. The product eluted as a long, red-orange smear. Removal of solvent in vacuo yielded 32 mg, 59%, of a purple solid. MALDI: 686.168 m/z found, 686.175 m/z expected for M^+ . UV-Vis (CH_2Cl_2 , λ_{max} in nm): N band at 325, Soret at 438, Q-bands at 549 and 584.

Table S1. Surface atomic concentrations derived from high energy resolution XPS scans

Sample	% C (1s)	% N (1s)	% Co (2p)	% Cl (2p)
GCC-H ₂ TPP	92.43 ± 0.41	7.56 ± 0.41	-	-
GCC-CoTPP	94.74 ± 0.77	4.43 ± 0.72	0.54 ± 0.04	0.29 ± 0.14
Amide-H ₂ TPP	95.07 ± 0.53	3.57 ± 0.49	-	1.36 ± 0.03
Amide-CoTPP (freshly prepared)	96.21 ± 0.56	3.12 ± 0.32	0.51 ± 0.02	1.35 ± 0.23
Amide-CoTPP (post base CVs)	96.31 ± 0.01	2.86 ± 0.06	0.41 ± 0.04	0.42 ± 0.03

Table S2. Peak binding energies (in eV) of GCC-MTPP, Amide-CoTPP and model complexes obtained from XPS measurements

Sample	N 1 _{Sp} pyrazinic	N 1 _{Sp} pyrrolic	N 1 _{Sam} monium	N 1 _{Sam} ide	Co 2p _{3/2}	Co 2p _{1/2}
GCC-H ₂ TPP	399.5	398.6	-	-	-	-
GCC-CoTPP	399.8	398.4	-	-	779.9	795.2
Amide-CoTPP (post base CVs)	-	399.5	-	398.2	780.1	795.4
CoTPP (measured)	-	398.8	-	-	-	-
CoTPP (literature)	-	398.1	-	-	779.8	Not reported
CoTPPdNH ₂	399.7	398.4	401.3	-	-	-

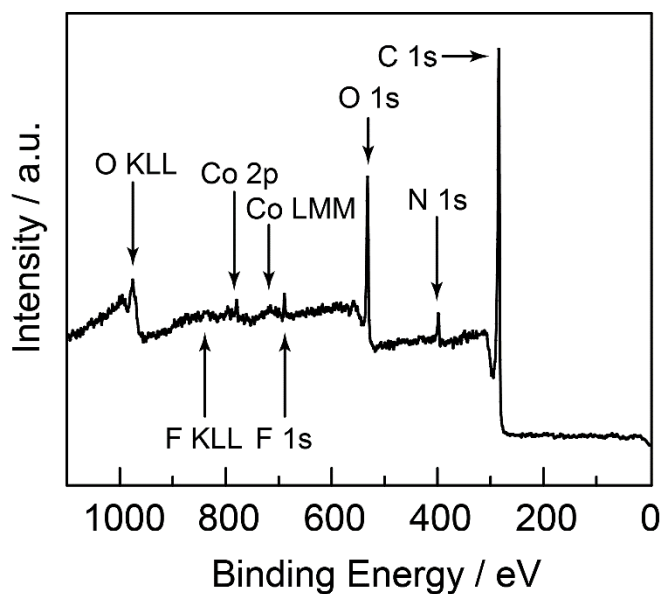


Figure S1. Representative XPS survey spectrum of GCC-CoTPP. Adventitious fluorine arises from the Teflon holder used for electrode polishing.

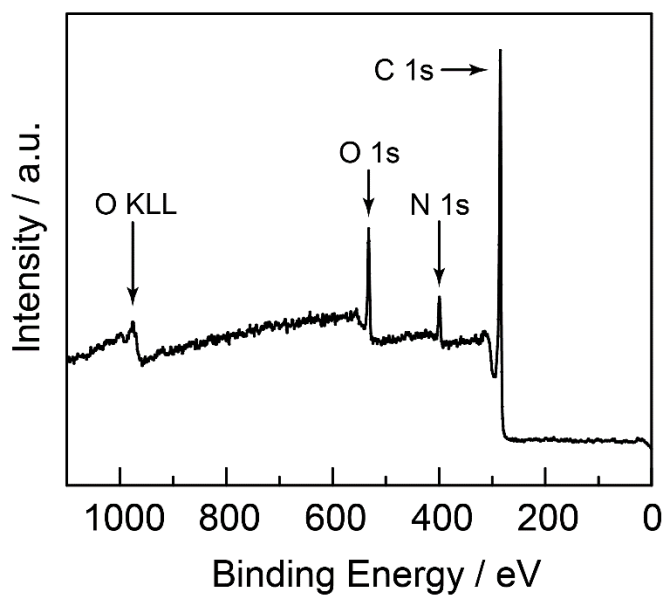


Figure S2. Representative XPS survey spectrum of GCC-H₂TPP.

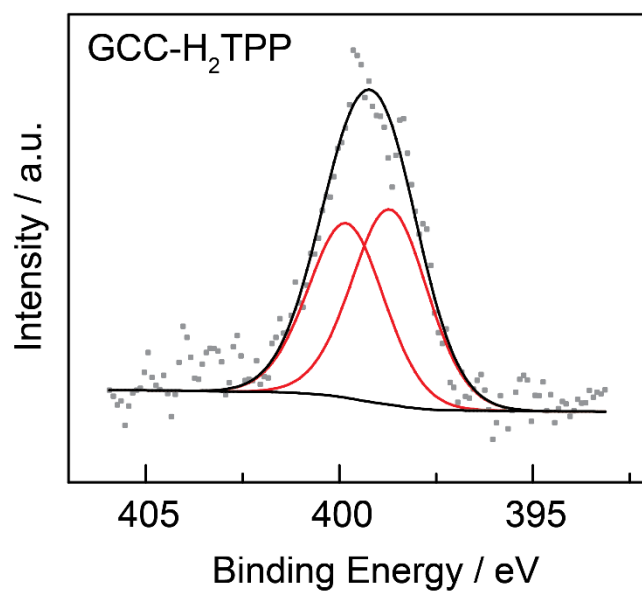


Figure S3. High energy resolution XPS spectrum of the N 1s region of GCC-H₂TPP.

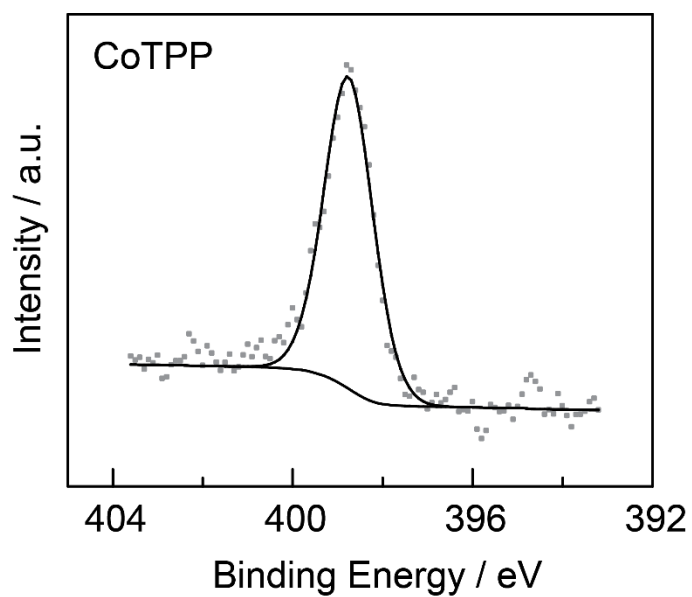


Figure S4. High energy resolution XPS spectrum of the N 1s region of CoTPP.

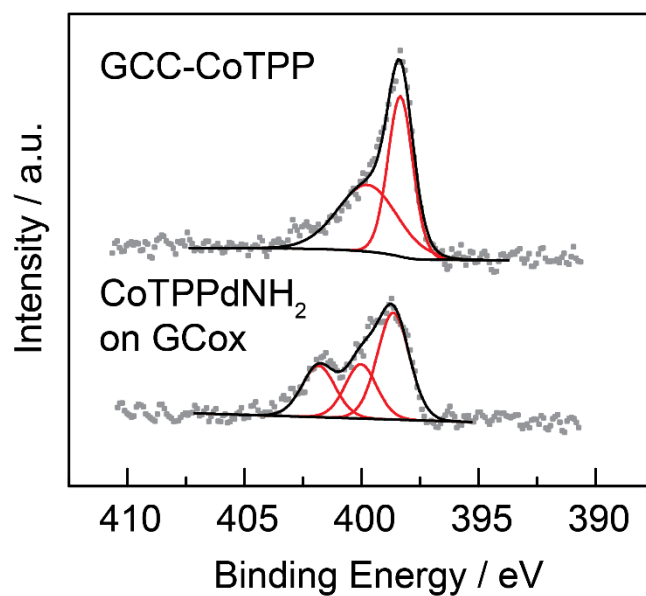


Figure S5. High energy resolution XPS spectra of the N 1s regions of GCC-CoTPP and CoTPPdNH₂.

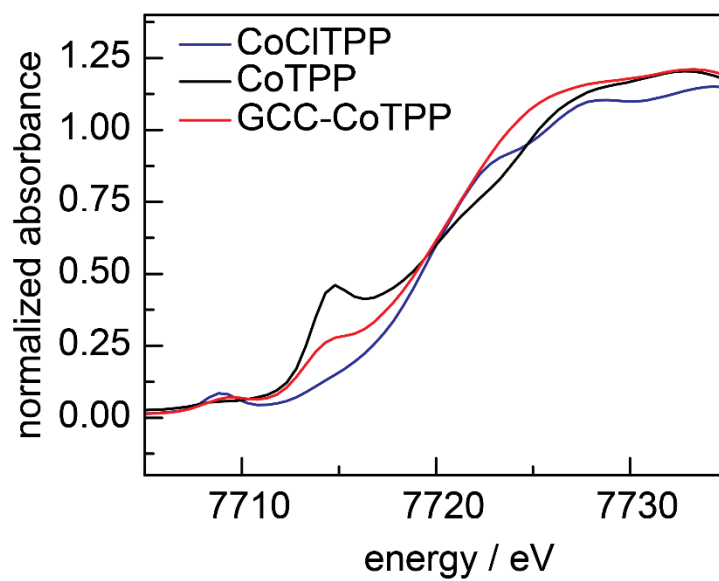


Figure S6. X-ray absorption near-edge spectra of GCC-CoTPP (red), CoTPP (black), and CoCITPP (blue).

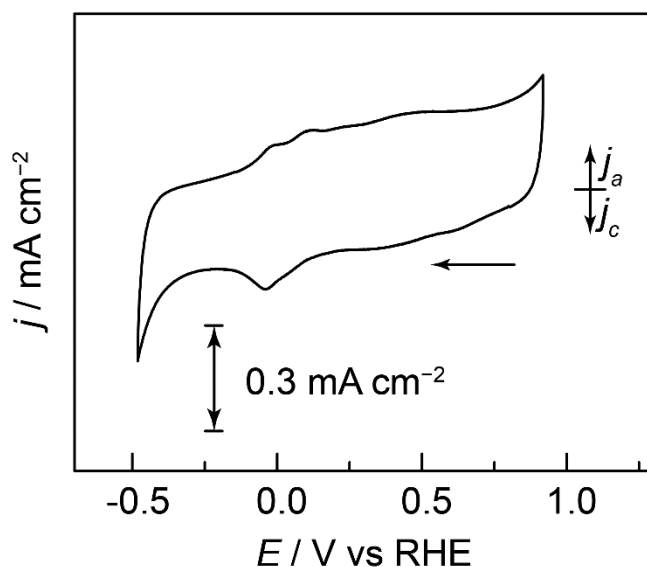


Figure S7. CV of GCC-H₂TPP recorded in 0.1 M NaOH under a N₂ atmosphere at a scan rate of 10 mV/s. Initial direction of scan indicated on plot.

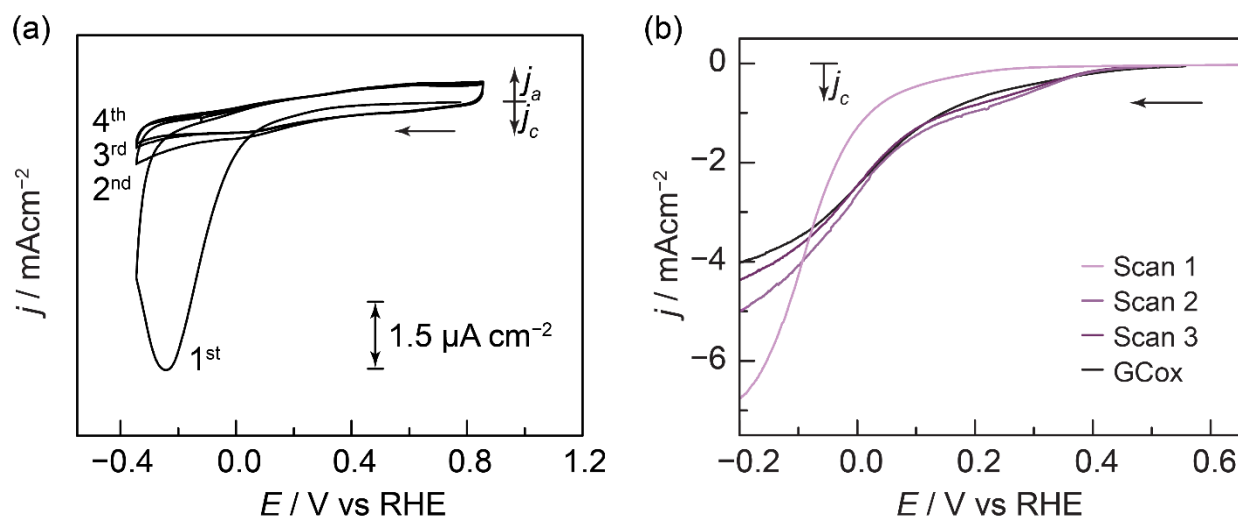


Figure S8. Representative CVs and LSVs of the desorption of CoTPP from the GCox substrate. **a** – CV under a N₂ atmosphere showing the reductive stripping feature on the first scan and the absence of this feature on subsequent scans. The data were recorded in 0.1 M NaOH at a scan rate of 10 mV/s without electrode rotation. **b** – LSVs collected under 1 atmosphere O₂ showing the large reductive stripping feature on the first scan (light purple) and the subsequent scans (purple and dark purple) that show good agreement with background activity of GCox (black). Data were recorded in 0.1 M HClO₄ at a scan rate of 5 mV/s with the electrode rotated at 2000 rpm. Initial direction of scan indicated on plots.

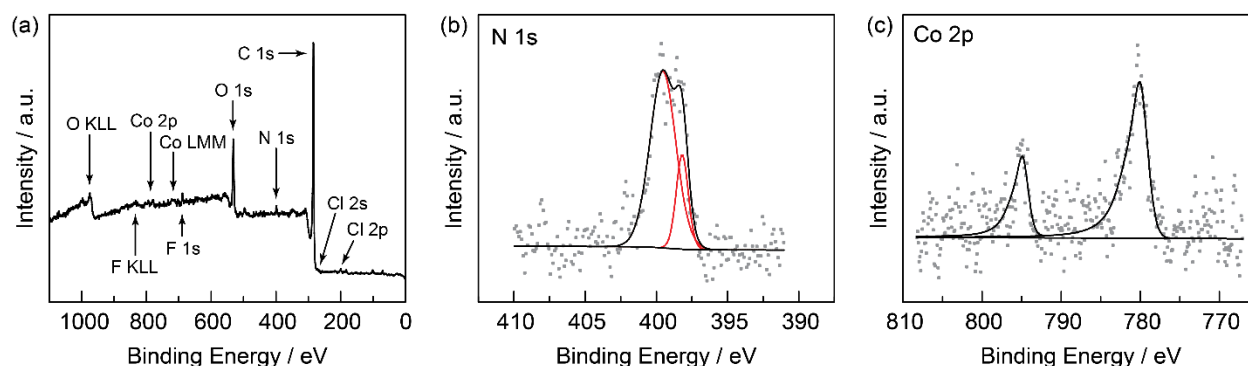


Figure S9. XPS characterization of Amide-CoTPP after electrochemical cycling in base. **a** – Survey spectrum., **b** – High energy resolution spectrum of N 1s region. **c** – High energy resolution spectrum of Co 2p region. The N:Co ratio is 7.1:1 (expected is 5:1).

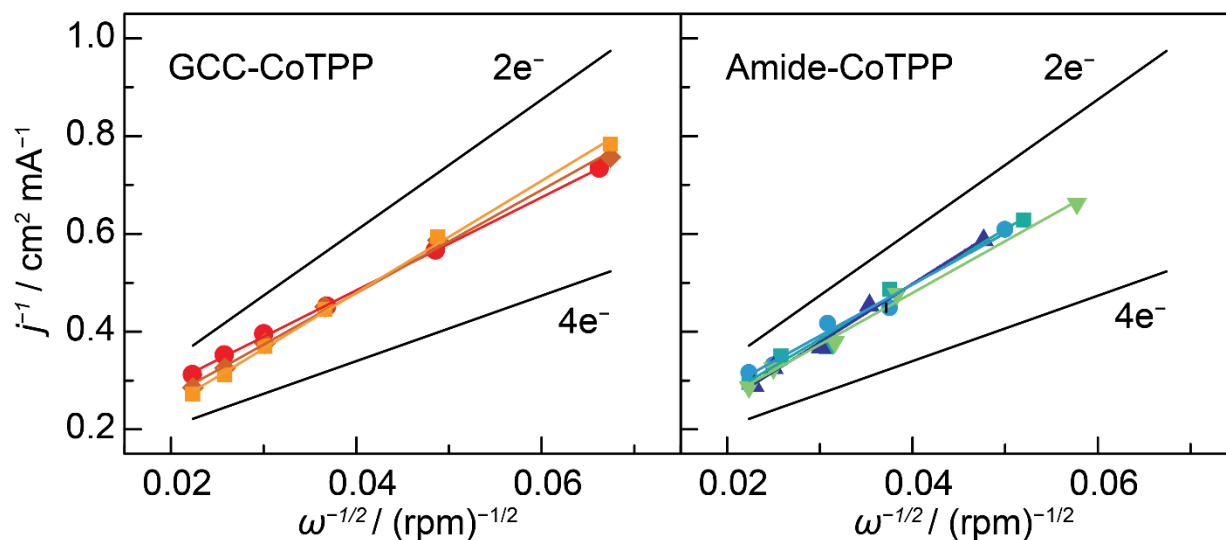


Figure S10. Koutecký-Levich data for GCC-CoTPP (left) and Amide-CoTPP (right). Black lines represent calculated responses for the pure two- and four-electron reduction pathways and these lines are offset from the data by arbitrary values for clarity. The data were collected in 0.1 M HClO₄.

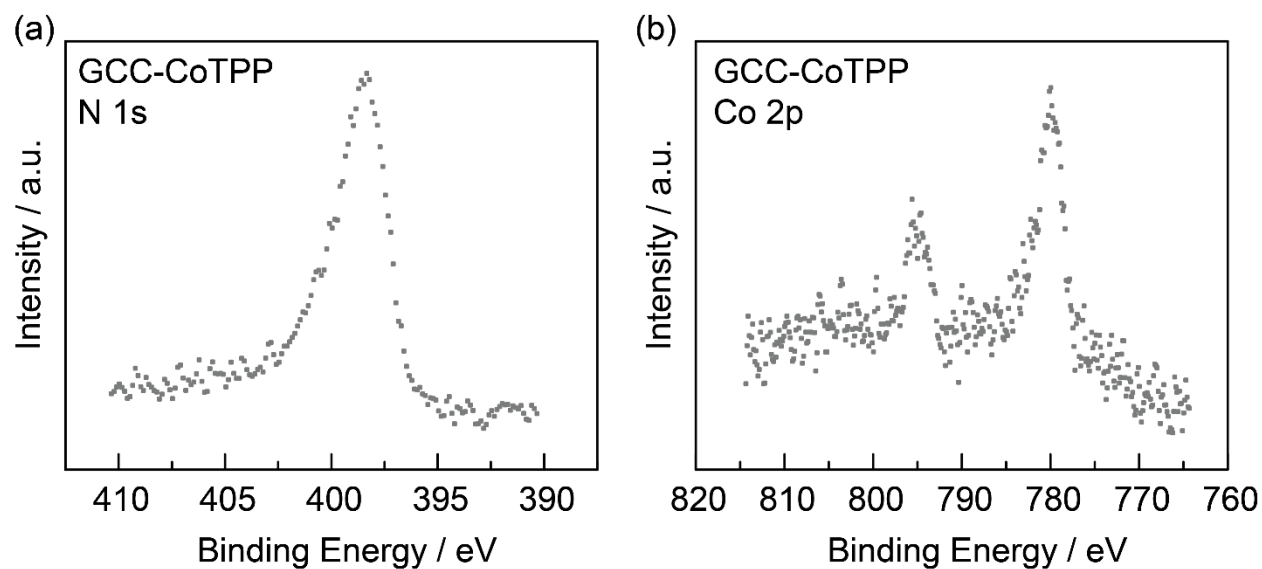


Figure S11. Representative XPS spectra of GCC-CoTPP used for quantification. **a** – Spectrum of the N 1s region. **b** – Spectrum of the Co 2p region.

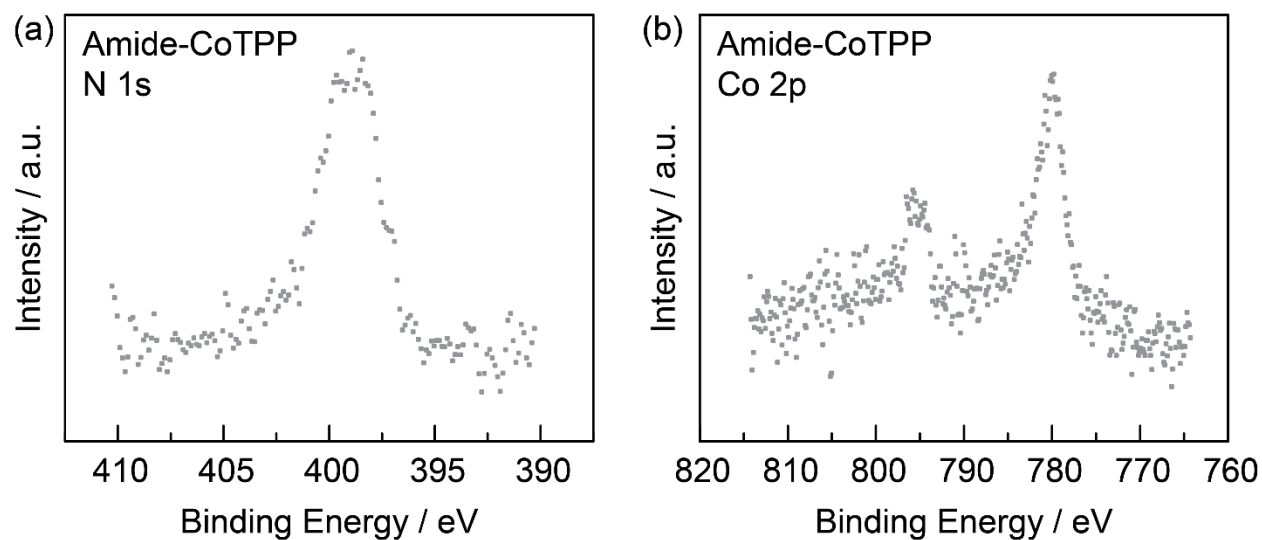


Figure S12. Representative XPS spectra of Amide-CoTPP used for quantification after electrochemical cycling in base. **a** – Spectrum of the N 1s region. **b** – Spectrum of the Co 2p region.

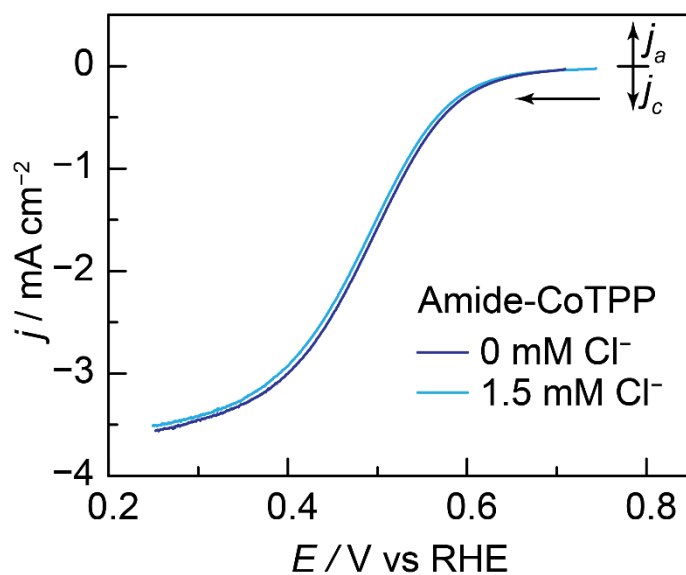


Figure S13. Representative LSVs showing the ORR activity of Amide-CoTPP in 0.1 M HClO₄ without additional chloride (dark blue) and in the presence of 1.5 mM chloride (sky blue). Data were recorded at a scan rate of 5 mV/s with the electrode rotated at 2000 rpm. Initial direction of scans indicated on the plot.

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