Coordination-Driven Self-Assembly of Cofacial Porphyrin Prisms as Oxygen Reduction Catalysts

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Abstract

This thesis encompasses a suite of coordination-driven self-assembled porphyrin prisms differing in the molecular clips linking two porphyrin faces in a cofacial arrangement. The goal of this work was to apply the facile synthesis methods to rationally design cofacial catalysts and analyze the activity towards the oxygen reduction reaction (ORR). Specifically, we have explored how different molecular clips affected the prisms’ activity, selectivity, overpotential, and kinetics. High selectivity towards H₂O and low overpotential are key requirements of an oxygen reduction catalyst for applications in fuel cells.

We have demonstrated the first coordination-driven self-assembled porphyrin catalyst (Benzo-Co) used for small molecule activation, specifically ORR. The first report includes the characterization, along with catalytic chemical and electrochemical reduction studies. The selectivity and rate constants of this catalyst (H₂O vs. H₂O₂) were compared to the mononuclear CoTPyP. After these findings, the goal was to optimize the catalyst using alternative bridging ligands in the molecular clips that held the porphyrin subunits in a cofacial offset and analyze the selectivity towards H₂O. We hypothesized that if the metal centers of CoTPyP were held at a shorter distance, the selectivity of the catalyst would improve. The distance of the metals is critical to the O–O bond cleavage step. If there is not a secondary metal to interact with O₂, for example mononuclear CoTPyP, O–O cannot be cleaved. If the M–M distance is too large, the secondary metal may not interact with O₂ to participate in the bond cleavage step. The catalyst series were immobilized on the electrode surface and the selectivities of Ox-Co, Oxa-Co, and Benzo-Co prisms towards H₂O₂ as determined by rotating ring-disk electrode studies. Rotating disk electrode studies showed Levich current responses. Koutecký-Levich and Tafel analyses, were used to obtain kinetic information and estimation of rate constants. This thesis highlights how coordination-driven self-assembly can be used to address difficult multi-electron multi-proton transformations, like oxygen reduction, using cofacial polynuclear catalyst.
1 Introduction

1.1 Oxygen Reduction Reaction and Fuel Cells

The vastly growing global demand for energy necessitates innovations to energy conversion that are rooted in molecular chemistry. The ability to efficiently activate small molecule substrates, including the reduction of oxygen, is attractive due to the natural abundance and roles in carbon-neutral renewable energy applications.¹⁻⁶

Fuel cells are particularly attractive due to the high theoretical efficiency compared to that of heat or combustion engines.⁷ The thermodynamic efficiencies of combustion engines are

![General schematic of a fuel cell. The separator plate (yellow) is made out of graphite, which separates and distributes the reactant gases (H₂ and O₂). The catalyst layers (gray) are supported on graphite. H₂ oxidation occurs at the anode. The protons are transferred through the proton exchanged membrane (purple, typically Nafion) and the electrons are transferred through a current collector (represented as a wire). O₂ (from air) reduction occurs at the cathode.](image)

Figure 1.1. General schematic of a fuel cell. The separator plate (yellow) is made out of graphite, which separates and distributes the reactant gases (H₂ and O₂). The catalyst layers (gray) are supported on graphite. H₂ oxidation occurs at the anode. The protons are transferred through the proton exchanged membrane (purple, typically Nafion) and the electrons are transferred through a current collector (represented as a wire). O₂ (from air) reduction occurs at the cathode.
limited by the Carnot cycle laws. The internal combustion engines that are integrated into our transportation infrastructure have efficiencies of ≈ 20%.\(^7\)\(^8\) Since fuel cells are not combustion engines, they are not limited by the Carnot cycle and have a theoretical efficiency of ≈ 90%. Polymer electrolyte membrane fuel cells (Figure 1.1) convert chemical energy into usable electrical energy consuming molecule hydrogen (H\(_2\)) as fuel and molecular oxygen (O\(_2\)) as an oxidizing agent while emitting only water as a clean energy product. The reduction of oxygen to water is thermodynamically favorable (Scheme 1.1), but the difficult activation of the O\(_2\) is kinetically slow and can be attributed to the simultaneous management of multiple proton and electron inventories.\(^7\) Oxygen reduction is a multi-electron reaction that can occur through two main reduction pathways (Scheme 1.1). The four-proton, four-electron reduction of oxygen to water is the favorable reaction for use in a fuel cell because the products of this reaction are benign. Other oxygen reduction pathways have partially reduced oxygen products, for example H\(_2\)O\(_2\), can lead to catalyst fouling and low fuel cell efficiencies.\(^7\)\(^9\)

\[ \text{O}_2 + 4 \text{e}^- + 4 \text{H}^+ \rightarrow 2 \text{H}_2\text{O} \quad 1.23 \]

\[ \text{O}_2 + 2 \text{e}^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{O}_2 \quad 0.695 \]

**Scheme 1.1.** Molecule oxygen reduction pathways and thermodynamic potentials.

An electrocatalyst functions at an electrode surface and provides the ability to transfer electrons due to redox activity and participates in chemical reactions.\(^10\) Electrocatalysts lower the activation barrier needed to proceed with a reaction, such as the activation of small molecules like dioxygen. The current state-of-the-art electrocatalyst used in fuel cells is platinum, at both the anode and cathode. Although platinum favors the four-proton, four-electron reduction of oxygen to water, there are many of disadvantages to using this material; platinum is expensive ($5000-10,000) and the kinetics of the reaction are sluggish. The overpotential, additional driving force that is needed past the thermodynamic reduction potential to drive the reaction of interest at a
certain rate, associated with the reaction is large at sufficient current densities.\textsuperscript{11-12} Overpotential ($\eta$) is defined as the difference between the experimental potential ($E_{\text{exp}}$) and the equilibrium potential ($E_{\text{eq}}$) of the reaction (equation 1.1).

$$\eta = E_{\text{exp}} - E_{\text{eq}}$$ \hspace{1cm} (1.1)

Overpotential can be used to determine the efficiency of the reaction and also devices (i.e. fuel cells, equation 1.2). The overpotential of the oxygen reduction is what sets the limit of current fuel cell efficiency.\textsuperscript{13} In thermal reactions, to increase the rate of reaction you can increase the temperature, which occurs because the reactants in solution are moving faster and collide more frequently. To obtain a practical rate for electrochemical transformations, observing a sufficient current density, an overpotential is needed. If the overpotential is 0 V, you are at the thermodynamic potential and the system would be in equilibrium, and therefore no net reaction would be observed.

Efficiency of a fuel cell device can be defined as the following:

$$\zeta = 1 - \frac{\eta_a + \eta_c}{\Delta E^\circ}$$ \hspace{1cm} (1.2)

wherein $\zeta$ is the efficiency, $\eta_a$ and $\eta_c$ are the overpotentials associated with hydrogen oxidation and oxygen reduction, respectively, and $\Delta E^\circ$ is the total cell potential (i.e. 1.23 V vs. SHE).\textsuperscript{7} The Pt/C catalyst is very efficient for the hydrogen oxidation reaction with an $\eta_a$ of approximately 0.05 V, however, the $\eta_c$ for the oxygen reduction reaction is 0.6 V.\textsuperscript{13} Compared to the theoretical efficiencies ($\approx 90\%$) of fuel cells, where the overpotential of both oxidation and reduction are assumed to be 0.05 V ($\zeta = 1 - \frac{0.05 V + 0.05 V}{1.23 V} = 0.91$), the commercialized (Pt/C) catalyst have low efficiencies ($\approx 40\%$, $= 1 - \frac{0.05 V + 0.6 V}{1.23 V} = 0.47$), which can be improved upon.\textsuperscript{13-14} Therefore, studying alternative and more efficient catalysts for the oxygen reduction reaction is imperative to realize the benefits of clean energy fuel cells.
1.2 **Nature’s Oxygen Reduction Catalyst: Cytochrome c Oxidase**

The activation of small molecules is oftentimes kinetically hindered due to the inventory of protons and electrons needed for the transformations. Most enzymes in nature have circumvented this issue with the use of multiple metal centers that act in concert to affect key catalytic steps. Cytochrome c Oxidase (CcO), also known as complex IV, is an integral membrane enzyme located in the mitochondrial electron transport chain and is responsible for the reduction of oxygen to water without the release of partially reduced oxygen species, like \( \text{H}_2\text{O}_2 \). The enzyme also “pumps” protons against the electrochemical proton gradient to drive the final step in the electron transport chain, ATP (adenosine triphosphate) synthesis. The CcO crystal structure has been reported in literature and showed that the active site is dinuclear and includes an iron porphyrin. The mechanism of CcO is still under discussion in the literature. The dinuclear CcO active site, as shown in Figure 1.2, in the fully reduced form (A) has three redox active groups: an iron (II) heme, a copper (I) bound by three histidine ligands (not shown), and a mechanistically relevant tyrosine that is bound to one of the histidine ligands. Oxygen binds in the “pocket” of the fully reduced form CcO (B) to the Fe(II) porphyrin and is subsequently reduced to superoxide (\( \text{O}_2^- \)), while iron is oxidized from Fe(II) to Fe(III), then enters the catalytic cycle shown in Figure 1.2. Superoxide is further reduced by three electrons and protonated to form a Cu(II) hydroxo and an Fe(IV) oxo porphyrin; this is a key step that is mentioned in many proposed mechanisms for synthesized catalysts (C) where the mechanism diverges to peroxide formation if the O–O bond is not broken. The electrons in this step are coming from Fe(III) (oxidized to Fe(IV)), Cu(I) (oxidized to Cu(II)), and tyrosine (oxidized to a neutral radical and the proton is transferred to the oxygen bound to the Cu site). The Cu(II) is reduced to Cu(I) and the hydroxo ligand bound is protonated to form an aquo ligand (D). The aquo ligand leaves as water (E) and the oxo ligand bound to the Fe(IV), is protonated to a bridging hydroxo ligand, while the Fe(IV) is reduced to Fe(III). There are other mechanisms in the literature that invoke an Fe(V) oxo intermediate, but this is apart of the electron “bookkeeping” and the overall mechanistic scheme.
is quite similar. The hydroxo ligand bound to the Fe(III) is protonated to form an aquo ligand that leaves as the second water and the tyrosyl radical is reduced by one electron (F). The active site is returned to the fully reduced form; the tyrosine is prontronated and Fe(III) is reduced to Fe(II). It should also be noted that the distance between the Fe porphyrin and the Cu histidine.

Figure 1.2. Simplified catalytic oxygen reduction cycle of Cytochrome c Oxidase active site.
sites varies from ≈ 4.9 Å to 5.3 Å. This range in M—M distances indicates the enzyme has conformational flexibility that allows the binding and activation of oxygen.

1.3 **A Brief Overview of Oxygen Reduction Catalysts**

1.3.1 **Mononuclear Porphyrinoid Catalysts for Oxygen Reduction Reaction**

Metalloporphyrins have been largely studied as oxygen reduction catalysts to mimic the metalloenzyme cytochrome-c oxidase (Figure 1.3). The mononuclear iron tetra-(4-N-methylpyridyl)porphyrin pentachloride (FeTMPyP) has been extensively studied as both a homogeneous and heterogeneous catalyst with a high conversion of the two-electron, two-proton reduction of oxygen to hydrogen peroxide and large overpotentials were associated with the catalyst. Some of the earliest work by Kuwana, investigated FeTMPyP and showed that porphyrin catalyzed the reduction of oxygen to exclusively peroxide (95% H₂O₂) at large

![Figure 1.3. Metalloporphyrinoids used as catalysts for the oxygen reduction reaction.](Image)
overpotentials (onset potential of \(-0.11\) V vs. SCE) where appreciable currents were drawn.\(^\text{32}\) Savéant and coworkers reported an onset potential of 0.2 V vs SCE and 40-60\% \(\text{H}_2\text{O}_2\) for \(\text{FeTMPyP}\) under both homogeneous and heterogeneous conditions.\(^\text{27}\) It has been reported in literature that pyrolysis of porphyrin structures at high temperatures (>700 °C) that can lead to both nitrogen and metal sites bonded together with a structure similar to tetra-azamacrocycles. The pyrolysis of these compounds stabilizes the active site in acidic conditions and can have higher activity than non-pyrolyzed materials. Uchida and coworkers pyrolyzed \(\text{FeTMPyP}\) on to Vulcan XC-72 and reported 65\% \(\text{H}_2\text{O}_2\) faradaic yield.\(^\text{33}\)

The catalysts studied included cobalt porphyrins because of the lower overpotentials associated with the oxygen reduction reaction.\(^\text{34-40}\) Guilard and coworkers reported Cobalt 5-(4-pyridyl)-10,15,20-triphenylporphyrin (\(\text{TriPCo}\)) with a more positive onset potential than iron porphyrins (0.2 V vs. Ag/AgCl) and with high selectivity towards the two-electron, two-proton conversion (76\% \(\text{H}_2\text{O}_2\)).\(^\text{35}\) Anson reported \(\text{CoTPP}\) with a positive catalytic onset potential of 0.2 V vs SCE but, exclusively catalyzed oxygen to peroxide.\(^\text{36}\) \(\text{CoOEP}\) was reported as an oxygen reduction catalyst that almost exclusively produced \(\text{H}_2\text{O}_2\) with a 94\% faradaic yield.\(^\text{41}\)

Porphyridoid oxygen reduction catalysts were attractive due to the possibility of shifting onset of catalysis to more positive potentials and decreasing the amount of peroxide produced compared to the porphyrin counterparts.\(^\text{42}\) One of the first porphyridoid macrocycles investigated for oxygen reduction activity was cobalt phthalocyanine (\(\text{CoPc}\)) and was reported in 1964.\(^\text{43}\) Jasinski studied \(\text{CoPc}\) as a heterogeneous catalyst that was immobilized on a Ni plug. The catalyst was also pyrolyzed and the current densities were noted at different potentials. The pyrolyzed \(\text{CoPc}\) had a moderate change to potential needed to reach a current density of 110 A/sq. ft. (\(-0.50\) V vs. SCE) compared to that of the not pyrolyzed \(\text{CoPc}\) (108 A/sq. ft. at \(-0.57\) V vs. SCE).\(^\text{43}\) \(\text{CoPc}\) was revisited in 1992 by Linkous, who reported an onset of potential at 0 V vs. SCE and \(\text{H}_2\text{O}_2\) as a major reduction product.\(^\text{44}\) Fukuzumi and coworkers reported various cobalt
corroles, like (TFPCor)Co, which had an onset potential of 0.3 V vs SCE (more positive than other mononuclear porphyrinoids) but, exclusively catalyzed the two-electron reduction to H₂O₂.⁴⁵ These studies demonstrated that most mononuclear porphyrinoid catalysts favor O₂ reduction to H₂O₂.⁴⁶

1.3.2 Synthetic Models of Cytochrome C Oxidase

The synthesis and oxygen reactivity studies of biomimetic CcO catalysts was initiated in the 1980s with a binuclear Fe(II)/Cu(I) complex (CcO Model 1, Figure 1.4).⁴⁷ Over the past few decades, many variations of the nature-inspired model complexes were synthesized and analyzed for oxygen reduction activity.²⁴, ⁴⁸ Collman has described a synthetic analogue to the iron heme and proximal copper site as a mimic of CcO that enforces the complete four-electron reduction of O₂ while avoiding the need for an external electron shuttle and circumventing the release of partially reduced oxygen intermediates (FeCuPhOH).⁴⁹-⁵⁰ Karlin has synthesized a variety of biomimetic analogs, including (F₆)Fe³⁺-O-Cu²⁺(TMPA), as µ-oxo and µ-peroxo complexes.⁴⁸ These synthetic mimics allow for the study of oxygen interaction with the dinuclear metal centers and the reduction of oxygen. Although the mechanism of oxygen reduction by the enzyme CcO can be studied it is difficult to tune the natural system to probe structure-activity

![CcO Model 1](image1)

![FeCuPhOH](image2)

![F₆)Fe³⁺-O-Cu²⁺(TMPA)](image3)

**Figure 1.4.** Synthetic analogs to cytochrome c oxidase
relationships. Synthetic analogs can be used to systematically study how changes to the catalyst can affect the activity. Small changes in the catalyst, however, would result in a total synthetic redesign that would not be very effective towards rapid studies of structure-function relationships.

1.3.3 Polynuclear Cofacial Porphyrin Catalysts for Oxygen Reduction

Over the past few decades, covalently tethered “pacman” structures were of interest because they have the ability for two metals to participate in the binding event of oxygen due to a cofacial offset offered by a rigid ligand scaffold. Additionally polynuclear catalysts are inherently effective owing to their ability to spread the coordination and redox demand between the metal sites and offers selectivity of substrate.

Covalent cofacial porphyrins can be divided into two classes: strapped complexes, where the macrocycles are linked together at two or more β or meso porphyrin positions, and Pacman porphyrins, which contains a rigid-pillar (examples: anthracene, dibenzofuran, xanthene) at a single meso position forcing the porphyrins in a stacked geometry (Figure 1.5). A strapped porphyrin complex linked at two positions, \( \text{Co}_2\text{FTF4} \), catalyzed oxygen reduction at an onset potential at 0.7 V vs NHE with no peroxide detection until 0.55 V vs NHE, but the amide linkages are vulnerable to hydrolyzation in strong acidic conditions.

Starting in the 1980s, Anson, Collman, and co-workers synthesized various first-generation cofacial pacman porphyrin catalysts and probed the activity for oxygen reduction. The covalently tethered \( \text{Co}_2\text{DPA} \) (anthracene backbone) complex was reported by Anson with an onset potential of 0.45 V vs SCE and almost exclusively provided the four-electron pathway towards \( \text{H}_2\text{O} \).

Second generation flexible pacman porphyrin catalysts, established by Nocera and coworkers, enabled mechanistic insight to the ORR. This class of cofacial covalent porphyrins architectures catalyzed oxygen reduction at \( \approx 0.4 \) V vs Ag/AgCl with 20-40% \( \text{H}_2\text{O}_2 \).
faradaic yield. An example of the tedious 18 step total synthesis scheme is shown in Figure 1.6. Although each step has a moderate to high yield, the overall yield of a covalent cofacial

**Figure 1.5.** Cofacial “strapped” and “pacman” porphyrins exemplifying traditional covalent tethering approaches.
Figure 1.6. Example of synthetic scheme of covalent cofacial bisporphyrins architectures.
bisporphyrin complex is \(\approx 0.01\%\) and the purification of these molecules requires four columns in total and multiple recrystallizations.\(^{25, 63}\)

These pioneering examples confirms that cofacial porphyrins are excellent catalysts in terms of efficiency in favoring the four-electron reduction and as scaffolds for mechanistic study. The complex, multi-step covalent syntheses required to link two porphyrin macrocycles together and the time consuming purification steps that yield very little product have limited the practicality of these designs. As such, systematic investigations of covalent cofacial catalyst activities have been hindered. Hence, the imposing total syntheses of cofacial catalysts encumbers systematic variations and is the primary bottleneck in forward progress. To this end, the strategy of facile coordination-driven self-assembly circumvents the synthetic challenges allowing rapid progress.

The covalent, cofacial porphyrin catalysts are more selective than the mononuclear porphyrin counterparts, but the arduous syntheses renders these platforms useless. Thus, there is a critical need for a rational catalyst design with facile techniques to realize the benefits of polynuclear porphyrin catalysts.

1.4 Rational Catalyst Design and Coordination-Driven Self-Assembly

As described in section 1.3.3, cofacial platforms are rare due to the complex multi-step covalent syntheses that are required to access them. Synthesis of these elaborate structures can be greatly simplified with the use of one-pot, coordination-driven self-assembly techniques, wherein metal-ligand bond formation drives the reaction.\(^{66-68}\) The key to this strategy is the formation of complementary building blocks with Lewis-acid acceptors and basic donors with controllable orientations that exploit the coordination environment of the Lewis-acid acceptor.\(^{69}\) Lewis-basic donors, organic ligands, and metal-containing precursors, Lewis-acid acceptors, can be rationally designed to make discrete 2D shapes and 3D polyhedra. Figure 1.7 shows the two main approaches towards self-assembling intricate structures. When a self-assembled metallacage has ligands that occupy the edges and vertices of the final architecture, it is referred to as edge-directed self-assembly. Polyhedra and metallacages can also include ligands that
occupy the faces of the shape, this is called face-directed self-assembly.\textsuperscript{68} The directional-bonding approach of coordination-driven self-assembly, along with the vast library of donors/acceptors with different angles and number of coordination sites has allowed for a rapid population of metallacages and metallacycles of various shapes and sizes.\textsuperscript{67-68}

Each component can be synthesized independently, isolated, and characterized prior to self-assembly, and then unified via self-assembly reactions, which furnish products in near quantitative yields.\textsuperscript{66, 70-71} Synthetic efforts of final complex architectures are typically not demanding due to the purification steps minimized to monomer synthesis. The final product oftentimes does not need purification methods, like column chromatography.

\textbf{Figure 1.7.} Edge- and face-directed self-assembled metallacages and metallacycles use capping ligands to enforce discrete structures.
Some of the applications of coordination-driven self-assembled complexes include biomedical applications,\textsuperscript{72-74} host-guest systems,\textsuperscript{75-78} and catalysis.\textsuperscript{79-84} The literature is rich with discrete self-assembled cages that provide a well-defined cavity in which reactions can occur. It should be noted that the cages, oftentimes, do not catalyze the reaction itself. Despite the rich chemistry associated with coordination-driven self-assembly, very little work has been done wherein a metallacycle or cage directly acts as a catalyst. Fujita and coworkers reported an octahedral cage that was synthesized with the 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt) ligand as the Lewis-basic donor and N,N,N’,N’-tetramethylethylenediamine Pd(II) node as the Lewis-acid

\textbf{Figure 1.8.} 2D rectangular metallacycles and 3D prismatic metallacages synthesized using self-assembly methods, where A is the acceptor ligand and D is the donor ligand.
acceptor that was used in a host-mediated Diels-Alder reaction. The authors found that the Diels-Alder reaction favored the syn-1,4-regioselective product (Figure 1.9) which was due to the favorable π-stacking interaction between the substrates.\cite{85} It is important to note that most reactions that have been studied in molecular cages include, Diels-Alder, Michael addition, and Knoevenagel condensation reactions.\cite{86}

Molecular clips that are used in self-assembly methods serve the same purpose as the covalently linked rigid pillar groups by offering a cofacial offset between the Lewis-base donor. Clips containing two parallel coordination sites have been extensively used in the synthesis of 2D rectangular metallacycles and 3D wedge and prismatic metalla cages, affording cofacial components (Figure 1.8).\cite{87} [D\textsubscript{2}A\textsubscript{n}] prisms, where D is the donor building block and A is the acceptor building block, are well-established self-assembly designs in literature.\cite{66,83} For example, when 4,4′-bipyridine is used as a Lewis-basic ligand, the final product is a 2D rectangular metallacycle. The combination of a tripyridyl planar ligand, like tpt, with three molecular clips

![Figure 1.9. A host-mediated Diels-Alder reaction that occurs inside a self-assembled octahedral cage using substituted anthracenes and maleimides as substrates.](image.png)
furnishes trigonal prisms. When a tetrapyridyl porphyrin is used, a tetragonal prism is obtained. This specific construct is particularly motivating to the proposed work, as it represents a four-strapped cofacial design. Whereas the rich structural chemistry of [D$_2$A$_n$] prisms has primarily centered on the formation of novel metallacages and host-guest assemblies, this chemistry can be expanded to exploit the potential to quickly generate suites of polynuclear catalysts. Pyridyl-functionalized metalloporphyrins can be assembled into a cofacial conformation using a η$_6$-arene Ruthenium clip that forces an offset between the two porphyrins similar to that of the covalent metalloporphyrin system. The syntheses of the cofacial porphyrin prisms have been well established by the Therrien group and literature methods were used to synthesize the suite of prisms in this work.

1.5 Electrochemical Techniques Used to Analyze Catalysts

Hydrodynamic voltammetry is one of the most common techniques that is used to investigate oxygen reduction activities of catalysts, which includes rotating disk and rotating ring-disk electrode studies. A wealth of information can be gathered from hydrodynamic voltammetry and used to evaluate electrocatalysts, like mass activity, overpotential, and faradaic efficiency. Rotating disk voltammetry includes a three electrode set-up: one reference, one counter, and one

![Figure 1.10. Ideal voltammograms showing mixed diffusion-kinetic controlled (left) and complete kinetic controlled (right) current responses at four different rotation rates.](image)
working electrode. The working disk electrode is rotated at various rates to obtain steady state current responses, examples are shown in Figure 1.10. If the plateau current response increases when the electrode rotation rate is increased, also called Levich current, the analyte is diffusion controlled. The analyte concentration at the electrode surface is depleted and diffusion is relied on to replenish the double layer instead of convection from the rotation of the electrode.\(^{10}\) If the current response remains the same when the rotation rate of the electrode is increased, the catalyst is under kinetic control and the substrate at the electrode double layer is equal to the bulk solution.\(^{89}\) Kinetic information can be obtained from both responses.

In a homogeneous solution where kinetic control is observed, equation 1.3 can be used to obtain \(k_{\text{obs}}\), the apparent rate constant \(^{27}\)

\[
i_{pl} = n_{ap}FAC_{cat}^0\sqrt{D_{cat}k_{obs}}
\]

in which \(i_{pl}\) is the plateau current, \(n_{ap}\) is the apparent number of electrons transferred, \(F\) is the Faraday constant, \(A\) is the surface area of the electrode (0.95 cm\(^2\)), \(C_{cat}^0\) is the bulk concentration of the catalyst, \(D_{cat}\) is the diffusion coefficient of the catalysts, and \(k_{obs}\) is the apparent rate constant.\(^{89-90}\) \(k_{obs}\) corresponds to a combination of elementary rate constants in a catalytic cycle or to a rate determining step.

Levich current can be observed in either homogeneous or heterogeneous solutions and the equation (1.4)\(^{10}\) that applies to the diffusion limited condition is

\[
i_{lim} = 0.62nFAC_{cat}^0D^{2/3\omega}v^{-1/6}
\]

in which \(i_{lim}\) is the limiting plateau current, \(n\) is the number of electrons transfer, \(F\) is Faraday’s constant, \(A\) is the surface area of the electrode, \(C_{cat}^0\) is the bulk concentration of the catalyst, \(D\) is the diffusion coefficient, \(\omega\) is the rotation rate of the electrode, and \(v\) is the kinematic viscosity. For a heterogeneous catalyst, kinetic information can be obtained from the Koutecký-Levich equation (1.5)\(^{91-94}\)
\[ \frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_{lim}} = \frac{1}{nFAk_{het}[O_2]\Gamma_{cat}} + \frac{1}{B \omega^2} \]  

5) 

in which \( i \) is the current that is observed, \( i_K \) is the current that is under kinetic control (the concentration of analyte in the double layer is equal to the concentration in the bulk solution), \( k_{het} \) is the heterogeneous electron transfer rate constant, \([O_2]\) is the bulk concentration of oxygen in solution, and \( \Gamma_{cat} \) is the electrochemically active surface area of the catalyst. When the reaction is under mixed diffusion-kinetic control, the Koutecký-Levich plots (\( i^{-1} \) vs. \( \omega^{-1/2} \)) yield straight lines and the y-int can be used to find \( k_{het} \).95 We can use the set values of \( k_{het} \) at set overpotentials to find \( k_0 \), the standard rate constant with the following equation (1.6)95 

\[ k_{het} = k_0 \exp \left[ -\frac{\alpha F \eta}{RT} \right] \]  

Reactions with large \( k_0 \) will be fast and systems with small \( k_0 \) will be sluggish.10 

Mass activity is used as a measure of a catalyst’s activity, which is reported as a current density, instead of current response.96-100 Mass activity is simply ratio of the disk current response, in mA, and the mass of the catalyst used, in mg (equation 1.7). 

\[ \text{Mass activity} = \frac{i_{disk}}{mg_{catalyst}} \]  

1.7) 

A typical rotating ring-disk voltammetry experiment involves four electrodes; one reference, one counter, and two working electrodes (a disk and ring). For the purpose of analyzing oxygen reduction catalysts faradaic efficiency, the rotating ring-disk working electrode is rotated at various speeds. The oxygen-saturated solution is drawn up to the disk electrode, where the potential is scanned from the open circuit to a set vertex potential. At this electrode, the current response associated with catalytic oxygen reduction (to either water or hydrogen peroxide) is recorded. The solution is then swept towards the ring electrode that is held at a potential to oxidize any hydrogen peroxide generated at the disk (Figure 1.11). Not all the \( \text{H}_2\text{O}_2 \) that is generated at the disk is detected at the ring electrode. The collection efficiency of the electrode is
experimentally determined to measure the percent of analyte that was reduced at the disk and detected at the ring and is accounted for when calculate the faradic efficiency of an electrochemical reaction.\textsuperscript{10} Faradaic efficiency is used to report the selectivity of the catalyst (H\textsubscript{2}O vs. H\textsubscript{2}O\textsubscript{2}).\textsuperscript{42,101}

\begin{equation}
\%H_2O_2 = \frac{2i_{\text{ring}}}{i_{\text{disk}} + i_{\text{ring}}} N (100) \tag{8}
\end{equation}

in which \(i_{\text{ring}}\) is the current response from the Pt ring, \(i_{\text{disk}}\) is the current response from the glassy carbon disk, and \(N\) is collection efficiency of the RRDE. The selectivity of the catalyst is important because if hydrogen peroxide is produced, it can lead to fouling and oxidation of the catalyst, which lowers device efficiencies.\textsuperscript{7,9}

Mass activity, overpotential, rate constants, and faradaic efficiency are metrics used to benchmark catalysts and allows for comparisons of catalysts in difference conditions.\textsuperscript{90,102} To improve upon the current commercial catalysts, it is important to develop catalysts that operate at low overpotentials, have high activity towards the oxygen reduction reaction, and have high selectivity towards water.

\textbf{Figure 1.11.} Rotating ring-disk working electrode (left), the half reactions that are occurring at the disk and ring (center), and an example current response (right).
1.6 **Scope and Outline of Thesis**

The overarching goal of this work was to synthesize cofacial porphyrin architectures with facile coordination-driven self-assembly techniques and probe the activity of the catalysts towards the oxygen reduction reaction using chemical and electrochemical methods. Unlike the conventional step-wise synthetic method of the existing porphyrin catalysts, a number of different prisms can be rapidly generated by selecting an alternative molecular clip. Owing to the modularity of our approach it is possible to predictably alter the separation distance between the cofacial moieties. The metalation of the porphyrin can also be modified which can change the reactivity of the scaffold. Since the bridging clip and porphyrin platforms are independently synthesized, these pre-self-assembly modifications will not significantly affect self-assembly.\(^{66}\) The facile ability to tune the angles and distances between metal sites would be a great advantage for small molecule catalysis.\(^{79}\)

Specific aims of this work were underscored by three working hypotheses.

1) Coordination-driven self-assembly of cofacial porphyrin prisms will occur in substantially higher overall yields relative to the covalent cofacial pacman porphyrins due to the one-pot convergent nature of the process.

2) Cofacial porphyrin prisms will have a higher selectivity towards the four-electron, four-proton pathway over the mononuclear counterpart, CoTPyP, when appropriate M–M distances are encoded.

3) Shortening the M–M distance between the porphyrin subunits by using an alternative molecular clip will enhance the selectivity of H\(_2\)O over H\(_2\)O\(_2\). When the M–M distance is too large, the secondary metal may not interact with oxygen to enforce the critical O–O bond breaking step of the mechanism.
Herein we demonstrate that with this rational catalyst design and facile synthetic technique, we can rapidly populate a library of catalysts and analyze the activity towards the oxygen reduction reaction.

In chapter two, we report the first study of the oxygen reduction reaction (ORR) catalyzed by a cofacial porphyrin scaffold accessed in high yield (overall 53%) using coordination-driven self-assembly with no chromatographic purification steps. The ORR activity was investigated using chemical and electrochemical techniques on the monomeric CoTPyP and its cofacial analogue, [Ru₈(η⁶-iPrC₆H₄Me)₈(dh bq)₄(CoTPyP)₂][OTf]₈ (Benzo-Co; dh bq = 2,5-dihydroxy-1,4-benzoquinato, OTf = triflate) as homogeneous oxygen reduction catalysts. The Benzo-Co is obtained in one self-assembly step that organizes six total building blocks, two CoTPyP and four arene-Ru clips, into a cofacial motif previously demonstrated with free base, Zn(II) and Ni(II) porphyrins. Turnover frequencies (TOF) from chemical reduction and rate constants of overall homogenous catalysis (kobs) determined from rotating ring-disk experiments establish a cofacial enhancement when comparing the activity of Benzo-Co to CoTPyP, respectively. Cyclic voltammetry was used to initially probe the electrochemical catalytic behavior. Rotating ring-disk electrode studies were completed to probe faradaic efficiency and obtain an estimation of the rate constant associated with the ORR.

In chapter three, we report a suite of coordination-driven self-assembled prisms for heterogeneous electrocatalytic oxygen reduction differing in the molecular clips linking two porphyrin faces in a cofacial arrangement. The catalytically active Co(II) containing prisms were obtained in high yields (50%-79%) and without the need for any column chromatography. ORR activities and selectivities of monomeric CoTPyP along with cofacial prisms [Ru₈(η⁶-iPrC₆H₄Me)₈(Ox)₄(CoTPyP)₂][OTf]₈ (Ox-Co; Ox = oxalato, OTf = triflate), [Ru₈(η⁶-iPrC₆H₄)₈(Oxa)₄(CoTPyP)₂][OTf]₈ (Oxa-Co; Oxa = N,N′dimethyloxamido), and Benzo-Co were probed using cyclic voltammetry and rotating ring-disk techniques (RRDE). All species were
immobilized as heterogeneous catalysts on glassy carbon electrodes using a Nafion ink method. The selectivities of Ox-Co, Oxa-Co, and Benzo-Co Prisms towards H₂O₂ as determined by RRDE. Koutecký-Levich and Tafel analyses were used to obtain kinetic information and estimation of rate constants. Zn prism variants, CoTPyP, and 10% platinum-on-carbon (Pt/C) were used as controls and benchmarks. The current density of the Oxa-Co prism plateaus at five times that of Pt/C when normalized per Co/Pt. The high synthetic yield (79%), moderate overpotential (η ~ 660 mV) and high selectivity (%H₂O₂ ~3%) of the Oxa-Co prism highlights how self-assembly can be used to address difficult multi-electron multi-proton transformations using polynuclear catalysts.

In chapter four, the major conclusions from this work are discussed. The later sections of chapter four include proposed future steps of this work. Since the coordination-driven self-assembly is a modular approach, we can rapidly populate a cofacial porphyrin catalyst library differing in the molecular clips. We are interested in tuning the core oxamido bridging ligand of the ruthenium clips and preliminary data for characterization of the new clips is shown. We propose that the bridging ligand with electron-withdrawing groups will allow for the catalyst to be easily reduced and push the onset potential more positive and closer to that of 10% Pt/C, while still maintaining the preferred Co–Co to favor the four-electron, four-proton pathway.

Despite the rich chemistry of cofacial porphyrin catalysts in literature, polypyrrole macrocycles held in cofacial architectures have been absent, especially given interesting electrochemical properties.²⁻⁻³ We have proposed several porphyriniod macrocycles: corroles, diazaporphyrins, and phlorins. These porphyrinoids can be adapted for use in self-assembly schemes similar to that of the tetrapyridyl porphyrin that is shown in this body of work. Initial designs will focus on the molecular clips used in this work and described above and pyridyl-functionalized porphyrinoids. We will establish a library of molecular clip acceptors and
mononuclear catalysts that will be combined to deliver cofacial catalysts with selectable M–M separations and tunable electronic properties.

We also propose that salens can be adapted for self-assembly and used as oxygen reduction catalysts. Salens and metallated derivatives are known to catalyze a suite of chemical reactions involving small molecules, including the use of molecular oxygen in epoxidation reactions and for polymerizations. Mononuclear salen platforms have shown mediate the electrocatalytic reduction of O₂ via the two-electron, two-proton pathway. We hypothesized that the self-assembled salen complexes will attenuate the two-electron, two-proton pathway due to the interaction of multiple metal centers with oxygen that will enforce the critical O–O bond breaking step.

1.1 References


2 Homogeneous Self-Assembled Cofacial Cobalt Porphyrin Prism for Oxygen Reduction Catalysis


2.1 Introduction

The ability to efficiently activate small molecules, such as oxygen, is important due to the role that these substrates play in carbon neutral energy schemes, for example within hydrogen fuel cells.\(^1\) Efforts to mimic naturally occurring catalysts for the oxygen reduction reaction (ORR) have motivated the study of metalloporphyrin architectures.\(^2\) Among these, cofacial systems have unique advantages over their monomeric analogues. The presence of two metals distributes redox and coordination number demands across two sites, a useful feature for multi-electron reactions. Furthermore, a preorganization of the transition state of activation may occur, which manifests in enhanced rates of catalysis and selectivity over monomeric porphyrins.\(^3\) Due to these advantages, a small number of *covalently* tethered structures have been reported that demonstrate reactivity of relevance to the ORR.\(^3\)-\(^7\) Cofacial platforms are rare, in part due to the

![Figure 2.1](image.png)

**Figure 2.1.** ORR catalysts, Cobalt meso-tetra(4-pyridyl)porphine (CoTPyP) and [Ru\(_8\)(η\(^6\)-\(\text{PrC}_6\text{H}_4\text{Me})_6\text{dhbq})_4\text{(CoTPyP)}_2\])\([\text{OTf}]_8\) (Benzo Co)
complex, multi-step covalent syntheses required to link two porphyrin macrocycles together, typically resulting in low yields and time consuming purifications. The synthesis of these functionally promising structures can be greatly simplified with the use of one-pot, coordination driven self-assembly techniques, wherein metal-ligand bond formation drives formation. Coordination-driven self-assembled complexes have been broadly applied towards biomedical applications,10-12 host-guest systems,13-16 and for catalysis.17-22 Pyridyl-functionalized metalloporphyrins can be assembled into a cofacial conformation using an arene ruthenium clip that forces a coplanar arrangement between the two macrocycles by bridging the pendant pyridyl sites. The synthesis of cofacial Ni(II) and Zn(II) porphyrin prisms has been established by Therrien and coworkers,12, 23 and related self-assembled prisms are known.21, 24-26 Since the arene ruthenium and porphyrin subunits are independently synthesized, resultant cofacial complexes can be readily tuned without a total synthetic redesign, for example by altering the Ru—Ru distance within the clip or selecting an alternative metal in the porphyrin.27 Herein, we provide the

![Figure 2.2. ESI-FTMS (red) and simulated (black) peaks corresponding to [Benzo-Co – 4 OTf]$^{4+}$ (left) and [Benzo-Co – 3 OTf]$^{3+}$ (right).](image)
first report of discrete self-assembled prisms that show catalytic activity for the ORR using a monomeric Co(II) porphyrin as a benchmark (Figure 2.1).

2.2 Synthesis and Characterization

The arene ruthenium clip used for self-assembly is readily synthesized from the \{Ru(\eta^6-PrC_6H_4Me)(Cl)_2\}Cl_2 dimer and 2,5-dihydroxy-1,4-benzoquinone.\(^{21}\) The chlorides of the clip are removed prior to self-assembly by a pre-treatment with AgOTf, after which the appropriate porphyrin is added to the reaction vessel, as previously described in the literature for the Zn porphyrin used as a control in the current work.\(^{23}\) The unreported Co(II) variant was obtained by first forming CoTPyP from a literature route, followed by analogous self-assembly conditions to the Zn prism.\(^{26}\) The metalation of TPyP with Co(II) was monitored by diagnostic changes to the

![Figure 2.3](image)

**Figure 2.3.** ORR catalysis by CoTPyP (0.04 mM, black), and Benzo-Co (0.02 mM, open purple) monitored by ferrocenium formation (\(\lambda_{max} = 620\) nm) in oxygen-saturated PhCN and 100 mM TFA. Inset isolates the Benzo-Co data.
Q-bands (collapsing to two bands from four) in the electronic absorption spectrum (Figure 2.14, Figure 2.15). Evidence for the [2+4] stoichiometry of self-assembly was obtained from electrospray ionization mass spectrometry (ESI-FTMS). Two strong ion peaks were observed that correspond to intact Benzo-Co with a loss of three (m/z = 1510.74109) and four (m/z = 1095.56331) triflate counterions (Figure 2.2). The isotopic spacing of these peaks match the simulated spectrum, providing strong evidence for the proposed structural assignment.

2.3 Chemical Reduction Experiments

Oxygen reduction can deliver either H\textsubscript{2}O or H\textsubscript{2}O\textsubscript{2} via four electron/four proton or two electron/two proton pathways, respectively. Chemical reduction experiments may be used to determine the product distribution of homogenous ORR catalysts using ferrocene (Fc) as an electron source, a method developed Fukuzumi and Guilard.\textsuperscript{5} In the absence of catalyst, no ferrocenium was observed (\(\lambda = 620 \text{ nm}\)) using oxygen-saturated PhCN, and 100 mM TFA (TFA = trifluoroacetic acid (Figure 2.17). Figure 2.3 shows the concentration of ferrocenium (Fc\textsuperscript{+}) formed over time in the presence of CoTPyP or Benzo-Co. No Fc\textsuperscript{+} is formed using the Zn analogue of the prism (Figure 2.19). Under Fc-limiting conditions, the products of ORR can be quantified. In the presence of CoTPyP, O\textsubscript{2}, and TFA, Fc is completely oxidized to Fc\textsuperscript{+} over the course of 7.5 hours. A NaI titration was used to determine that 1.8 \(\pm\) 0.064 mM H\textsubscript{2}O\textsubscript{2} was produced over the course of the reaction.\textsuperscript{5} In the presence of Benzo-Co, O\textsubscript{2}, and TFA, Fc oxidation to Fc\textsuperscript{+} occurs over 1.5 hours and the NaI titration confirmed the production of 2.1 \(\pm\) 0.083 mM of H\textsubscript{2}O\textsubscript{2}. Under chemical reduction conditions, the selectivity (H\textsubscript{2}O vs H\textsubscript{2}O\textsubscript{2}) and turnover frequency of CoTPyP and CoTPyP are significantly different. The cobalt loading in each trial was normalized to 0.04 mM, therefore the Benzo-Co displayed markedly increased kinetics over its monomeric counterpart, akin to previously observed cofacial enhancement.\textsuperscript{3, 28} However, the Benzo-Co showed enhanced selectivity for H\textsubscript{2}O\textsubscript{2} (90%) versus CoTPyP (70%). The apparent turnover frequency for a given product\textsuperscript{29} is defined as:
\[ TOF = \frac{\text{moles of product}}{\text{moles of catalyst}(t)} \]  

in which H$_2$O$_2$ is the product and time (t) is in hours. The turnover frequency for H$_2$O$_2$ of Benzo-Co (66 hr$^{-1}$) is an order of magnitude greater than that of CoTPyP (6 hr$^{-1}$).

### 2.4 Electrochemical Reduction Experiments

The onset of catalysis for both CoTPyP and Benzo-Co occurs with a high overpotential, no current response is observed until 0 V vs Ag/AgNO$_3$ is reached. Glassy carbon (GC) electrodes introduce background current past −0.6 V vs Ag/AgNO$_3$ and therefore obscure catalysis at very reducing potentials. In previous reports it was shown that covalently bridged Co(II) porphyrin catalysts do not interact with O$_2$ in their neutral form and require pre-oxidation to enter ORR cycles, in stark contrast to monomeric systems wherein no pre-oxidation was needed.$^6,30$ As such, the effect of pre-oxidation on the activity of CoTPyP and Benzo-Co was investigated. The CoTPyP monomer interacts with O$_2$ and catalyzes oxygen reduction with no need for pre-oxidation (Figure 2.30). No significant change to the current response is observed when initially scanning oxidizing versus reducing.
The same experiments were used to probe the effects of pre-oxidation on Benzo-Co. Figure 2.4 shows current responses that are dependent on the direction of the initial potential sweep. Although a strong oxidation feature is not observed when scanning towards anodic potentials, a significant change in current response occurs. The current response observed when the reducing potentials are applied first does not match that of CoTPyP, indicating that when reducing potentials are applied first, the activity is not due to each porphyrin simply acting like a monomeric site. Nonetheless, overpotentials were attenuated when pre-oxidation was performed.

Since catalysis by CoTPyP and Benzo-Co occurs with high overpotentials, it is possible for background current from the GC electrode to compete. Previous studies of CoTPyP indicate that it does not adsorb strongly on GC electrodes.\(^{31}\) As such, the current response associated with catalysis by CoTPyP and Benzo-Co can be corrected using porphyrin-free solutions (Figure2.38). The corrected current responses show plateau currents that can be used to estimate \(k_{\text{obs}}\), associated with the overall rate of homogenous catalysis,\(^{32}\) using the methods of Savèant and coworkers.\(^{33}\) From the RRDE voltammograms, we can obtain product distributions (\(\text{H}_2\text{O}_2\) vs. \(\text{H}_2\text{O}\)) using the equation for faradaic yield (equation 2.2)\(^{30, 34}\)

Figure 2.5. Corrected RRDE (left) and faradaic efficiency (right) of 0.2 mM CoTPyP, 100 mM TBAPF\(_6\), 100 mM TFA, and oxygen-saturated acetonitrile. The Pt ring was held at 1.5 V vs. Ag/AgNO\(_3\). Rotation rate: 2500 rpm \(i_{pl} = 6.86 \times 10^{-4}\) A
\[
\%H_2O_2 = \frac{2i_{\text{ring}}}{i_{\text{disk}} + i_{\text{ring}}} \times N (100) \tag{2.2}
\]

in which \(i_{\text{ring}}\) is the current response from the Pt ring, \(i_{\text{disk}}\) is the current response from the GC disk, and \(N\) is collection efficiency of the RRDE. The collection efficiency was experimentally determined to be 0.35 (Figure 2.7).\(^{30}\) Figure 2.5 shows the corrected RRDE current response of CoTPyP and its faradaic efficiency. A plateau current (\(i_{pl}\)) is obtained at \(-0.6\) V vs. Ag/AgNO\(_3\) and can be used to estimate \(k_{\text{obs}}\) only if the catalyst is not limited by mass transport.\(^{33}\) \(k_{\text{obs}}\) can be estimated using equation 2.3:

\[
i_{pl} = n_{ap} F A C_{cat}^0 \sqrt{D_{cat} k_{\text{obs}}} \tag{2.3}
\]

in which \(i_{pl}\) is the plateau current, \(n_{ap}\) is the apparent number of electrons transferred, \(F\) is the Faraday constant, \(A\) is the surface area of the electrode (0.95 cm\(^2\)), \(C_{cat}^0\) is the bulk concentration of the catalyst, \(D_{cat}\) is the diffusion coefficient of the catalysts, and \(k_{\text{obs}}\) is the apparent rate constant.\(^{32-33}\) A \(D_{cat}\) of \(1.1 \times 10^{-5}\) cm\(^2\)/s was used with the assumption that the hydrodynamic radii

![Figure 2.6](image)

**Figure 2.6.** Corrected RRDE (left) and faradaic efficiency (right) of 0.1 mM Benzo-Co, 100 mM TBAPF\(_6\), 100 mM TFA, and oxygen-saturated acetonitrile. The Pt ring was held at 1.5 V vs. Ag/AgNO\(_3\). Rotation rate: 2500 rpm \(i_{pl} = 1.03 \times 10^{-3}\) A
of CoTPyP and ZnTPyP do not substantially differ. The diamagnetic nature of ZnTPyP enabled the determination of $D_{\text{cat}}$ using DOSY NMR methods. The n_{ap} (3.12) can be calculated from equation 2.4.

$$n_{ap} = 4 - 2 \left( \frac{\%H_2O_2}{100} \right) \quad (2.4)$$

The $k_{obs}$ associated with catalysis by CoTPyP was calculated to be 0.05 hr$^{-1}$.

Figure 2.6 shows the corrected RRDE current response of Benzo-Co and its faradaic efficiency. A plateau current is obtained at $-0.7$ V vs. Ag/AgNO$_3$. Equation 2 can also be applied to the Co Prism data using a $D_{\text{cat}} (4.1 \times 10^{-6}$ cm$^2$/s) and n_{ap} (3.22), revealing a $k_{obs}$ of 1.1 hr$^{-1}$. The $D_{\text{cat}}$ used here was determined using a DOSY NMR measurement of the diamagnetic Zn Prism and an assumption that the paramagnetic Benzo-Co would have a similar hydrodynamic radius (Figure 2.10). Since the concentration of Co sites was the same in both experiments, the increase of $k_{obs}$ is attributed to a cofacial enhancement. The selectivity of both CoTPyP and Benzo-Co are similar in the electrochemical studies, with an average faradaic efficiency of 44% and 39%, respectively.

2.5 Proposed Mechanism of Oxygen Reduction Reaction

The mechanism shown in Scheme 2.1 was proposed for Benzo-Co and is based off of previous proposed mechanisms (Scheme 2.1, black arrows). Literature reports of pacman porphyrins have suggested a pre-oxidation event of Co(II) to Co(III) with a sacrificial O$_2$ molecule, which provides a mixed-valent Co(II,III) before O$_2$ binds with the catalyst. When oxygen binds, the Co(II) is oxidized to Co(III) and oxygen is reduced by one electron. At this point, the mechanism can diverge to reduce via two-electron, two-proton method to peroxide (green arrows) or the superoxide ligand is subsequently protonated. The bridging hydroperoxyl ligand is then reduced by two electrons, which breaks the O–O bond to a Co(IV) oxo and Co(III) hydroxo. The
Co(IV) oxo is then reduced and protonated to a Co(III) hydroxo. Both hydroxo ligands are then protonated and leave as two waters. One of the Co(III) centers is then reduced to Co(II) to the active form of the catalyst.

Scheme 2.1. Proposed mechanism of oxygen reduction catalyzed by Benzo-Co.
The mechanism proposed is modeled after the previously proposed mechanisms, however, both chemical and electrochemical data suggests an alternative pathway (purple arrow). The NaI assay from chemical reduction studies confirmed 90% H₂O₂ formed, which would follow the pathway highlighted as green in Scheme 2.1. The RRDE electrochemical data corresponds to 39% H₂O₂ formed. The chemical reduction studies occur at one cell potential and additional overpotential cannot be applied to further reduce O₂²⁻ to water if a peroxo intermediate is formed during the course of the reaction. During the electrochemical studies, the potential is scanned towards more cathodic potentials, which allows for a larger overpotential to be applied to the system and peroxo intermediates to be further reduced to water.

2.6 Conclusions

The first discrete self-assembled catalyst for oxygen reduction was synthesized in two facile steps, using coordination-driven self-assembly with an overall yield of 53% without any need for purification by chromatography. This is a substantial improvement over traditional step-wise routes that are associated with overall yields of ~3% or lower. The Benzo-Co (66 hr⁻¹) showed an enhanced turnover frequency over CoTPyP (6 hr⁻¹) and catalyzed oxygen reduction to hydrogen peroxide almost exclusively (90%) in the chemical reduction studies. Electrochemical studies provided rate constants for ORR using both the cofacial and monomeric catalysts. The selectivities of CoTPyP and Benzo-Co were similar in the electrochemical studies, with an average faradaic efficiency of hydrogen peroxide of 44% and 39%, respectively. The cofacial enhancement is quite strong in this system, with the rate constant for Benzo-Co (k_{obs} ≈ 1.1 hr⁻¹) exceeding that of CoTPyP (k_{obs} ≈ 0.05 hr⁻¹) by over an order of magnitude. We have demonstrated herein that it is possible to realize the benefits of polynuclear catalysis using simple synthetic methods. Because the resulting molecules are obtained in high yields and without tedious purification steps, we envision that a library of such catalysts may now be rapidly populated. Towards this end, efforts are underway to exploit the modular nature of self-assembly using
alternative building blocks that optimize metal-metal separation, redox properties, and scaffold rigidity.

2.7 Supporting Information

General Methods

All chemicals were used as purchased unless otherwise noted. *meso*-tetra(4-pyridyl)porphine (*H*₂TPyP) and zinc *meso*-tetra(4-pyridyl)porphine (*ZnTPyP) were purchased from Frontier Scientific. Dichloro(p-cymene)ruthenium(II) dimer was purchased from Alfa Asar. All solvents used were reagent grade or better. Acetonitrile used in electrochemical experiments was purified from a Pure Process Technology free standing solvent purification system. UV–Vis absorption spectra were acquired with a Cary 8454 UV-Vis Diode Array System. All NMR experiments were carried out on Varian Mercury-300 (broadband) and Varian Inova-500 (broadband) instruments. Evans Method was used to obtain effective magnetic moment. Mass spectra were acquired with Bruker Daltonics SolariX 12T Fourier Transform Ion Cyclotron Resonance Mass Spectrometer and calibrated with > 90% Angiotensin I purchased from Sigma Aldrich. Infrared spectra were acquired with Perkin Elmer 1760 FTIR spectrometer with horizontal attenuated total reflectance (HATR). Elemental analysis was obtained from Midwest Microlab, Inc. All experiments were carried out at room temperature, unless otherwise noted.

Synthetic Procedure

CoTPyP²⁶, [Ru₂(η⁶-iPr₆C₆H₄Me)₂(benzo)Cl₂]²¹, and [Ru₆(η⁶-iPr₆C₆H₄Me)₈(dhbq)₄(ZnTPyP)₂][CF₃SO₃]₈ (Benzo-Zn)²³ were prepared according to literature procedures.

Metalation of CoTPyP A mixture of H₂TPyP (220 mg, 0.36 mmol) and Co(OAc)₂· 4 H₂O (360 mg, 1.4 mmol) in DMF was refluxed for 5 hours. The reaction mixture was poured into water to precipitate a dark crystalline product, which was filtered, and washed with (3 × 10 mL) water, (3
× 10 mL) ethanol, and (2 × 25 mL) chloroform. Yield 98% (240 mg, 0.35 mmol), UV-Vis (PhCN, TFA): Soret band: $\lambda_{\text{max}} = 437$ nm, $\varepsilon = 156,000 \, \text{M}^{-1} \text{cm}^{-1}$ Q band: $\lambda_{\text{max}} = 552$ nm, $\varepsilon = 9,600 \, \text{M}^{-1} \text{cm}^{-1}$

**Synthesis of [Ru$_2$(η$^6$-iPrC$_6$H$_4$Me)$_2$(dhbq)Cl$_2$] (Ru-Benzo clip)** A mixture of dichloro($p$-cymene) ruthenium (II) dimer (300 mg, 0.489 mmol) and 2,5-dihydroxy-1,4-benzoquinone (70 mg, 0.49 mmol) was stirred at room temperature in methanol (50 mL) for 2 hours and a red precipitate formed. The reaction mixture was filtered and washed with (3 × 10 mL) diethyl ether to afford the product as a red solid. Yield 70% (240 mg, 0.40 mmol) 

$^1$H NMR (300 MHz, CDCl$_3$) δ (ppm) = 5.80 (s, 2H), 5.62 (d, 4H $J = 10$ Hz), 5.38 (d, 4H $J = 10$ Hz), 2.92 (m, 2H), 2.29 (s, 6H), 1.34 (d, 12 H $J = 10$ Hz), UV-Vis (PhCN): $\lambda_{\text{max}} = 300$ nm, $\varepsilon = 23,000 \, \text{M}^{-1} \text{cm}^{-1}$ $\lambda_{\text{max}} = 508$ nm, $\varepsilon = 28,000 \, \text{M}^{-1} \text{cm}^{-1}$

**Synthesis of [Ru$_6$(η$^6$-iPrC$_6$H$_4$)$_6$(benzo)$_4$(ZnTPyP)$_2$][OTf]$_8$ (Benzo-Zn)**

A mixture of AgOTf (38 mg, 0.15 mmol) and [Ru$_2$(η$^6$-iPrC$_6$H$_4$Me)$_2$(benzo)Cl$_2$] (50 mg, 0.07 mol) in methanol (10 mL) was stirred at room temperature for 3 hr. A white precipitate was formed and was filtered out with a glass fiber disc. The red filtrate was added to ZnTPyP (25 mg, 0.037 mmol) and refluxed for 24 hours. The solvent was removed under vacuum, remaining solid was dissolved in dichloromethane and filtered with a glass fiber disc. Ether was added to precipitate the product as a dark red solid. Yield 47% (40 mg, 0.009 mmol) 

$^1$H NMR (500 MHz, CD$_3$CN) of Benzo-Zn δ (ppm) = 8.95 (d, 8H, $H_{\text{pyr}}$ $J = 5$ Hz), 8.88 (d, 8H, $H'_\alpha$ $J = 5$ Hz), 8.81 (d, 8H, $H_\beta$ $J = 5$ Hz), 8.56 (d, 8H, $H_\alpha$ $J = 5$ Hz), 8.18 (d, 8H, $H'_{\text{pyr}}$ $J = 5$ Hz), 7.41 (d, 8H, $H'_{\beta}$ $J = 5$ Hz), 6.26 (d, 8H, $H_{\text{ar}}$ $J = 5$ Hz), 6.22 (s, 8H, $H_\delta$), 6.06 (dd, 16H, $H_{\text{ar}}$ $J = 7.5$ Hz, 12.5 Hz), 5.92 (d, 8H, $H_{\text{ar}}$ $J = 5$ Hz), 3.07 (m, 8H,
H_c), 2.37 (s, 24H, H_b), 1.42, (d, 24 H, H_a J = 7.5 Hz), 1.52 (d, 24 H, H_a J = 7.5 Hz), UV-Vis (PhCN): Soret band: λ_{max} = 438 nm, ε = 501,000 M^{-1}cm^{-1} Q band 1: λ_{max} = 518 nm, ε = 49,000 M^{-1}cm^{-1} Q band 2: λ_{max} = 565 nm, ε = 53,000 M^{-1}cm^{-1}

**Synthesis of [Ru_8(η^6-iPrC_6H_4Me)_6(benzo)_4(CoTPyP)_2][OTf]_8 (Benzo-Co)**

A mixture of AgOTf (38 mg, 0.15 mmol) and [Ru_2(η^6-iPrC_6H_4Me)_2(benzo)Cl_2] (50. mg, 0.074 mol) in methanol (10 mL) was stirred at room temperature for 3 hr. A white precipitate was formed and filtered out with a glass fiber disc. The red filtrate was added to CoTPyP (25 mg, 0.037 mmol) and refluxed for 48 hours. The solvent was removed under vacuum, remaining solid was dissolved in dichloromethane and filtered with a glass fiber disc. Ether was added to precipitate the product as a dark red solid. Yield 75% (86 mg, 0.014 mmol), ESI-FTICR-MS experimental (calc.) m/z: 1510.79035 (1510.71698) [Benzo-Co – 3 CF_3SO_3]^3+, 1095.58687 (1095.55200) [Benzo-Co – 4 CF_3SO_3]^4+, UV-Vis (PhCN): Soret band: λ_{max} = 436 nm, ε = 216,000 M^{-1}cm^{-1} Q band: λ_{max} = 550 nm, ε = 25,400 M^{-1}cm^{-1}, IR (cm^{-1}): 3070 (w, CH_aryl), 1515 (s, C=O), 1255 (s,CF_3), Magnetic moment (300 MHz): μ_{eff} = 2.59, Elemental Analysis for C_{192}H_{168}Co_2F_{24}N_{15}O_{40}Ru_8S_8 with two CH_2Cl_2 calc: C, 45.26; H, 3.37; N, 4.35; found: C, 44.71; H, 3.44; N, 4.63

**Chemical Reduction**

Chemical oxygen reduction experiments were modified from a procedure developed by Fukuzumi and Guilard. These experiments were used to probe product distribution (H_2O vs. H_2O_2) of the catalysts. The appearance of ferrocenium absorbance band (λ_{max} = 620 nm, ε = 330
M$^{-1}$ cm$^{-1}$) was monitored in the presence of 0.02 – 0.04 mM of catalyst, 100 mM Trifluoroacetic acid (TFA), O$_2$ saturated benzonitrile (PhCN), and 5 mM ferrocene (Fc). Oxygen was bubbled into the solution between spectral acquisitions.

To test the ruthenium clip for ORR activity, a mixture of AgOTf (10.3 mg, 40.1 µmol) and [Ru$_2$(η$^6$-iPrC$_6$H$_4$Me)$_2$(benzo)Cl$_2$] (13.5 mg, 20.0 µmol) in PhCN (3 mL) was stirred at room temperature for 3 h, then filtered with a glass fibre disk to remove the solid AgCl formed. This solution was used as a stock solution for the chemical reduction studies of the Ru Clip. In this control study, 0.1 M [Ru$_2$(η$^6$-iPrC$_6$H$_4$Me)$_2$(benzo)Cl$_2$], 0.1 M TFA, and 0.1 M Fc was used in O$_2$ saturated PhCN.

To determine the amount of H$_2$O$_2$ produced, an excess amount of NaI (≈ 25 mg) was added to a solution of PhCN and a 30 µL aliquot of the ORR solution. The appearance of the absorbance band corresponding to I$_3^-$ ($\lambda_{\text{max}}$ = 365 nm, $\varepsilon$ = 28,000 M$^{-1}$ cm$^{-1}$) was observed to determine the amount of I$_3^-$ formed, which corresponds to the amount of H$_2$O$_2$ produced.

**Prism Stability Experiments**

The absorbance spectra of Benzo-Co and Benzo-Zn was monitored before and after the addition of TFA. A stock solution of 0.1 mM Prism was used. An aliquot (10 µL) of stock solution was diluted in 3 mL of acetonitrile and UV-Vis spectra were acquired. 0.1 M TFA was added to the stock solution and stirred for 10 mins. An aliquot (10 µL) of stock solution with TFA was diluted in 3 mL of acetonitrile and UV-Vis spectra were acquired.

Additional chemical reduction experiments were utilized to monitor the stability of Benzo-Zn and Benzo-Co in acidic environments. UV-Vis spectra of 0.02 mM Benzo-Zn and 0.1 M TFA in acetonitrile (20 mL) were acquired initially with 100 µL aliquot in 3 mL acetonitrile. At $t = 0$ mins, 18.6 mg of ferrocene was added to the O$_2$ saturated reaction solution. UV-Vis spectra were acquired every 5 mins (100 µL aliquot in 3 mL acetonitrile) for 30 mins and then every 10 mins for
an additional 30 mins, with O₂ bubbling between spectral acquisitions. The soret band was monitored throughout the experiment.

UV-Vis spectra of 0.02 mM Benzo-Co and 0.1 M TFA in acetonitrile (20 mL) were acquired initially with 100 µL aliquot in 1 mL acetonitrile. At t = 0 mins, 2 mg of ferrocene was added to the O₂ saturated reaction solution. UV-Vis spectra were acquired every minute (100 µL aliquot in 1 mL acetonitrile) for 30 mins, with O₂ bubbling between spectral acquisitions. Every 5 mins, an additional 2 mg of ferrocene is added to the reaction solution. The soret band was monitored throughout the experiment. The UV-Vis spectra were baseline corrected.

Cyclic Voltammetry Experiments

All electrochemical experiments (cyclic voltammetry and rotating ring-disk experiments) were acquired with a Bio-Logic SP-300 bipotentiostat/galvanostat. All voltammograms are reported versus Ag/AgNO₃ reference electrode (BASi, West Lafayette, IN). Glassy carbon was used for the working electrode and platinum wire was used for the counter electrode (CH Instruments, Austin, TX). The working electrodes were carefully polished with 0.05 µM alumina powder/water slurry, rinsed with water, sonicated for 30 seconds, rinsed with acetone, and allow to air dry. Tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte and was recrystallized from ethanol three times and dried under vacuum prior to use.

Rotation Ring-Disk Electrode Experiments

A Pine MSR rotator (PINE Research, Durham, NC) was used for all rotating ring-disk electrode (RRDE) voltammetry. A glassy carbon fixed-disk/platinum ring PEEK shroud working electrode (PINE Research, Durham, NC) and a platinum mesh counter electrode were used for RRDE experiments. The electrodes were prepared in the same way as the electrodes used for cyclic voltammetry. The glassy carbon (GC) disk was scanned from the E_OC (open circuit potential) to −1.5 V vs. Ag/AgNO₃ at a scan rate of 50 mV/s. The Pt ring was held at 1.5 V vs. Ag/AgNO₃ to
oxidize H₂O₂ formed during the course of the experiment. The working electrode was rotated at rates of 1600 rpm and 2500 rpm.

**Collection Efficiency of Rotating Ring-Disk Electrode**

Due to the reversible redox chemistry of ferrocene (Fc⁺/0), it was used in the determination of RRDE collection efficiency (Figure 2.7). The glassy carbon disk electrode under different rotation rates (ω = 700, 900, 1100, 1600, 2000, and 2500 rpm) was scanned from E° to 0.7 V vs. Ag/AgNO₃ at a scan rate of 50 mV/s. The Pt ring electrode was held at 0.02 V. Equation S2.1 was used for determining collection efficiency:

\[
N = \frac{i_{disk}}{i_{ring}} \tag{S2.1}
\]

in which \( N \) is collection efficiency, \( i_{disk} \) is disk current, and \( i_{ring} \) is ring current. The collection efficiency was experimentally determined to be 0.35, using published methods.34,38
Figure 2.7. Collection Efficiency of RRDE using 10 mM ferrocene and 100 mM TBAPF$_6$ in acetonitrile under different rotation rates ($\omega = 700, 900, 1100, 1600, 2000, \text{ and } 2500 \text{ rpm}$).
$^{1}$H NMR of $[\text{Ru}_2(\eta^5\text{-iPrC}_5\text{H}_4\text{Me})_2(\text{dhbq})\text{Cl}_2]$}

**Figure 2.8.** $^{1}$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) = 5.80 (s, 2H), 5.62 (d, 4H $J$ = 10 Hz), 5.38 (d, 4H $J$ = 10 Hz), 2.92 (m, 2H), 2.29 (s, 6H), 1.34 (d, 12 H $J$ = 10 Hz),
$^1$H NMR of Benzo-Zn

**Figure 2.9.** $^1$H NMR (500 MHz, CD$_3$CN) of Benzo-Zn $\delta$ (ppm) = 8.95 (d, 8H, $H_{\text{pyr}}$, $J = 5$ Hz), 8.88 (d, 8H, $H'_{\alpha}$, $J = 5$ Hz), 8.81 (d, 8H, $H_{\beta}$, $J = 5$ Hz), 8.56 (d, 8H, $H_{\alpha}$, $J = 5$ Hz), 8.18 (d, 8H, $H'_{\text{pyr}}$, $J = 5$ Hz), 7.41 (d, 8H, $H'_{\beta}$, $J = 5$ Hz), 6.26 (d, 8H, $H_{\text{ar}}$, $J = 5$ Hz), 6.22 (s, 8H, $H_{q}$), 6.06 (dd, 16H, $H_{\text{ar}}$, $J = 7.5$ Hz, 12.5 Hz), 5.92 (d, 8H, $H_{\text{ar}}$, $J = 5$ Hz), 3.07 (m, 8H, $H_{c}$), 2.37 (s, 24H, $H_{b}$), (1.52, d, 24H, $H_{a}$, $J = 7.5$ Hz) (1.42, d, 24H, $H_{a}$, $J = 7.5$ Hz)
DOSY NMR of Benzo-Zn and TBAPF$_6$

**Figure 2.10.** DOSY NMR of Benzo-Zn and TBAPF$_6$ in CD$_3$CN. Diffusion coefficient was found to be $4.11 \pm 0.0512 \times 10^{-6}$ cm$^2$/s.

Benzo-Zn and TBAPF$_6$ solutions in CD$_3$CN were analyzed by $^1$H NMR at 298 K on a Varian Inova-500 (broadband) instrument. The z-gradient coil constant was calibrated at $1.00 \times 10^{-3}$ G/cm/DAC. The BPPSTE pulse sequence was used. Sixteen transients were collected for each of 15 increments, where the z-gradient amplitude varied from 1.3 to 32.5 G/cm. The duration of each gradient in the pulse pair was 2.0 ms. A 1 s relaxation delay was used, and the diffusion delay time was 50 ms. Due to the overlap of TBAPF$_6$ peaks with the aliphatic peaks of the Zn...
Prism, only the aromatic peaks were used to determine the diffusion coefficient (Table S1). The error reported with the diffusion coefficient was calculated as standard deviation of the mean.

**Table S2.1.** Aromatic peaks used in the \(^1\)H DOSY to calculate the diffusion coefficient of Benzo-Zn.

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**FT-ICR-ESI-MS of Benzo-Co**
Figure 2.11. Full ESI-MS spectrum of **Benzo-Co** with peaks corresponding to **[Benzo-Co – 4 OTf]^{4+} (left)** and **[Benzo-Co – 3 OTf]^{3+} (right)**.
Figure 2.12. FT-IR-HATR spectrum of Benzo-Co.

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<td>1255 (s, CF₃)</td>
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Figure 2.13. UV-Vis spectrum of Benzo-Zn. UV-VIS (PhCN): Soret band: $\lambda_{\text{max}} = 438$ nm, $\varepsilon = 501,000$ M$^{-1}$cm$^{-1}$ Q band 1: $\lambda_{\text{max}} = 518$ nm, $\varepsilon = 49,000$ M$^{-1}$cm$^{-1}$ Q band 2: $\lambda_{\text{max}} = 565$ nm, $\varepsilon = 53,000$ M$^{-1}$cm$^{-1}$
Figure 2.14. UV-Vis spectrum of H₂TPyP. UV-Vis (PhCN, TFA): Soret band: \( \lambda_{\text{max}} = 429 \text{ nm}, \, \varepsilon = 184,000 \, \text{M}^{-1}\text{cm}^{-1} \) Q band 1: \( \lambda_{\text{max}} = 519 \text{ nm}, \, \varepsilon = 13,000 \, \text{M}^{-1}\text{cm}^{-1} \) Q band 2: \( \lambda_{\text{max}} = 555 \text{ nm}, \, \varepsilon = 4,300 \, \text{M}^{-1}\text{cm}^{-1} \) Q band 3: \( \lambda_{\text{max}} = 593 \text{ nm}, \, \varepsilon = 3,700 \, \text{M}^{-1}\text{cm}^{-1} \) Q band 4: \( \lambda_{\text{max}} = 650 \text{ nm}, \, \varepsilon = 1,500 \, \text{M}^{-1}\text{cm}^{-1} \)
Figure 2.15. UV-Vis spectrum of CoTPyP. UV-Vis (PhCN, TFA): Soret band: $\lambda_{\text{max}} = 437$ nm, $\varepsilon = 156,000 \text{ M}^{-1}\text{cm}^{-1}$ Q band 1: $\lambda_{\text{max}} = 522$ nm, $\varepsilon = 5,200 \text{ M}^{-1}\text{cm}^{-1}$ Q band 2: $\lambda_{\text{max}} = 552$ nm, $\varepsilon = 9,600 \text{ M}^{-1}\text{cm}^{-1}$
Figure 2.16. UV-Vis spectrum of Benzo-Co. UV-VIS (PhCN): Soret band: $\lambda_{\text{max}} = 436$ nm, $\varepsilon = 216,000$ M$^{-1}$cm$^{-1}$ Q band 1: $\lambda_{\text{max}} = 518$ nm, $\varepsilon = 25,000$ M$^{-1}$cm$^{-1}$ Q band 2: $\lambda_{\text{max}} = 550$ nm, $\varepsilon = 25,400$ M$^{-1}$cm$^{-1}$
Figure 2.17. Chemical reduction study blank. Absorbance of ferrocenium ($\varepsilon = 330$ M$^{-1}$ cm$^{-1}$) was monitored at 620 nm in PhCN in the presence of (saturated) O$_2$ and 0.1 M CF$_3$CO$_2$H.
Figure 2.18. Chemical reduction study of $\text{H}_2\text{TPyP}$ (0.04 mM). Absorbance of ferrocenium ($\varepsilon = 330$ M$^{-1}$ cm$^{-1}$) was monitored at 620 nm in PhCN in the presence of O$_2$ and CF$_3$CO$_2$H.
Figure 2.19. Chemical reduction study of ZnTPyP (0.04 mM), and Benzo-Zn (0.02 mM). Absorbance of ferrocenium ($\varepsilon = 330 \text{ M}^{-1} \text{ cm}^{-1}$) was monitored at 620 nm in PhCN in the presence of $O_2$ and $C_3F_7CO_2H$. 

[Graph showing concentration of ferrocenium over time for ZnTPyP and Benzo-Zn.]
Figure 2.20. Chemical reduction control of $[\text{Ru}_2(\eta^6-$iPrC$_6$H$_4$Me)$_2$(benzo)(OTf)$_2$] (0.1 M). Absorbance of ferrocenium ($\varepsilon = 330 \text{ M}^{-1} \text{ cm}^{-1}$) was monitored at 620 nm in PhCN in the presence of (saturated) O$_2$ and 0.1 M TFA
Figure 2.21. Iodometric titrations with NaI for the quantification of \( \text{H}_2\text{O}_2 \). Aliquots (50 µL of CoTPyP and 30 µL Benzo-Co) were added to a solution of PhCN and excess NaI. \( \text{I}_3^- \) absorbs at 365 nm (\( \varepsilon = 28,000 \text{ M}^{-1}\text{cm}^{-1} \)).

**UV-Vis Stability Controls**

Figure 2.22. UV-Vis spectra of **Benzo-Zn** before (red, circles) and after (black, squares) the addition of TFA, in acetonitrile.
Figure 2.23. UV-Vis spectra of chemical reduction stability of Benzo-Zn (0.1 M TFA in O₂ saturated acetonitrile). Benzo-Zn does not catalyze O₂ reduction and the data from this study suggests that the prism remains intact in acidic environments.
Figure 2.24. UV-Vis spectra of Benzo-Co before (red, circles) and after (black, squares) the addition of TFA, in acetonitrile.
Figure 2.25. UV-Vis spectra of 100 µL aliquots of 0.02 mM Benzo-Co (0.1 M TFA in O₂ saturated acetonitrile) during chemical reduction studies. (A) At t = 0 mins, 2 mg of Fc was added to the solution. The soret band shows at blue shift during catalysis and a red shift when the Fc is completely consumed. At t = 5 mins, 2 mg was added to the solution. (B) The soret band was monitored during the second loading of Fc. The same shift pattern from the first loading was observed. At t = 10 mins, additional 2 mg of Fc was added. (C) The same shift pattern of the soret band was observed during the third loading of Fc. At t = 15 mins, 2 mg of Fc was added to the
solution. (D) The soret band was monitored during the fourth Fc loading. The same previous shift pattern was observed. At $t = 20$ mins, 2 mg of Fc was added to the reaction solution. (E) During the fifth Fc loading, the same blue shift and red shift patterns were shown. At $t = 25$ mins, an addition 2 mg of Fc was added to the solution. (F) During the sixth and last Fc loading, the same shift patterns were observed.

**Electrode Behavior in the Absence of Catalyst**

![Cyclic voltammogram with legend](image)

**Figure 2.26.** Cyclic voltammogram blanks with a three electrode cell set-up: glassy carbon working electrode, Pt wire counter electrode, and Ag/AgNO₃ reference electrode, and under N₂ (blue), O₂ (red) N₂/TFA (purple), and O₂/TFA (green). Glassy carbon electrodes catalyze oxygen reduction in the presence of TFA and O₂ at high overpotentials. The onset of catalysis in the O₂/TFA solution occurs at ~0.6 V.
Cyclic Voltammetry of CoTPyP and Co Prism

Figure 2.27. Cyclic voltammogram of 0.2 mM CoTPyP, 100 mM TBAPF₆, and 100 mM TFA in acetonitrile under N₂. CV under N₂ only could not be obtained due to solubility of the porphyrin. An irreversible peak is observed at 0.67 V and a quasi-reversible couple is observed at $E_{\text{red}} = 1.18$ V. Scan rate: 100 mV/s

Figure 2.28. Cyclic voltammogram of 0.1 mM Benzo-Co, 100 mM TBAPF₆ in acetonitrile, under N₂ (red) and O₂ (blue). A quasi-reversible couple is observed at $E_{\text{red}} = -0.55$ V. Scan rate: 100 mV/s. The blank trace is also shown (black, 100 mM TBAPF₆ in acetonitrile under N₂).
Figure 2.29. Cyclic voltammogram of 0.1 mM Benzo-Co, 100 mM TBAPF$_6$, and 100 mM TFA, in acetonitrile under N$_2$. Scan rate: 100 mV/s

Electrochemical Behavior of CoTPyP and Benzo-Co utilizing Cyclic Voltammetry Techniques

Figure 2.30. Cyclic voltammograms of 0.2 mM CoTPyP, 100 mM TBAPF$_6$, 100 mM TFA, and oxygen saturated acetonitrile with initial scanning in reducing (blue) and oxidizing (red) directions. Scan rate: 100 mV/s
Figure 2.31. Cyclic voltammograms of 0.1 mM Benzo-Co, 100 mM TBAPF$_6$ (TBA = tetrabutylammonium), 100 mM TFA, and oxygen saturated acetonitrile with initial scanning in reducing (blue) and oxidizing (red) directions and the blank trace (black, O$_2$, 100 mM TBAPF$_6$, and 100 mM TFA in acetonitrile). Scan rate: 100 mV/s

Figure 2.32. Cyclic voltammograms of 0.1 mM Benzo-Co, 100 mM TBAPF$_6$ (TBA = tetrabutylammonium), 100 mM TFA, and oxygen saturated acetonitrile with initial scanning in reducing (blue) and oxidizing (red) directions and under just N$_2$ (green). Scan rate: 100 mV/s
Figure 2.33. Cyclic voltammograms of electrode from previous experiments with 0.1 mM Benzo-Co, placed in fresh solution of 100 mM TBAPF₆, 100 mM TFA, and oxygen saturated acetonitrile (solid red) and the blank trace (dotted blue, O₂, 100 mM TBAPF₆, and 100 mM TFA in acetonitrile). Scan rate: 100 mV/s

**Electrochemical Reduction Control Study with Benzo-Zn**

Figure 2.34. Cyclic voltammograms of 0.1 mM Benzo-Zn, 100 mM TBAPF₆, 100 mM TFA, and oxygen saturated acetonitrile (solid red) and the blank trace (dotted blue, O₂, 100 mM TBAPF₆, and 100 mM TFA in acetonitrile). Scan rate: 100 mV/s
Figure 2.35. Cyclic voltammograms of electrode from previous experiments with 0.1 mM Benzo-Co, placed in fresh solution of 100 mM TBAPF₆, 100 mM TFA, and oxygen saturated acetonitrile (solid red) and the blank trace (dotted blue, O₂, 100 mM TBAPF₆, and 100 mM TFA in acetonitrile). Scan rate: 100 mV/s

Electrochemical Reduction Control Study with Ru Clip

Figure 2.36. Cyclic voltammograms of 0.4 mM Ru-Benzo Clip, 100 mM TBAPF₆, 100 mM TFA, and oxygen saturated acetonitrile (dashed green) and the blank trace (dotted blue, O₂, 100 mM TBAPF₆, and 100 mM TFA in acetonitrile). Scan rate: 100 mV/s
Figure 2.37. Cyclic voltammograms of electrode from previous experiments with 0.4 mM Ru-Benzo Clip, placed in fresh solution of 100 mM TBAPF₆, 100 mM TFA, and oxygen saturated acetonitrile (solid red) and the blank trace (dotted blue, O₂, 100 mM TBAPF₆, and 100 mM TFA in acetonitrile). Scan rate: 100 mV/s
Rotating Ring-Disk Electrochemical Reduction Studies

Figure 2.38. RRDE blank voltammograms in 100 mM TBAPF6, 100 mM TFA, and oxygen saturated acetonitrile. The GC disk was scanned from EOC to 1.5 V vs. Ag/AgNO3 at a scan rate of 50 mV/s. The Pt ring was held at 1.5 V vs. Ag/AgNO3. Rotation rate: 1600 rpm (black), 2500 rpm (red).
Corrected RRDE disk current of 0.2 mM CoTPyP, 100 mM TBAPF$_6$, 100 mM TFA, and oxygen saturated acetonitrile. Rotation rate: 1600 rpm (red), 2500 rpm (black).

A plateau current ($i_p$) is obtained at $-0.6$ V and can be used to estimate $k_{obs}$. Figure2.39 shows the overlaid corrected disk current of CoTPyP at rotation rates of 1600 rpm and 2500 rpm. The wave shape and plateau current of the two traces occur independently of the rotation rate which indicates that the reaction is not limited by substrate diffusion and acts under purely kinetic conditions.
Figure 2.40. Corrected RRDE disk current of 0.1 mM Benzo-Co, 100 mM TBAPF$_6$, 100 mM TFA, and oxygen saturated acetonitrile. Rotation rate: 1600 rpm (red), 2500 rpm (black).

A plateau current is obtained at $-0.7$ V. **Figure 2.40** shows that the current responses at rotation rates of 1600 rpm and 2500 rpm have the same basic shape and plateau which means that the reaction is not limited by diffusion of substrate to the electrode and is acting under a kinetic conditions.
# 2.8 References


3 Tuning the Activity of Heterogeneous Cofacial Cobalt Porphyrins for Oxygen Reduction Electro catalysis through Self-Assembly

3.1 Introduction

Small molecule activation remains a key challenge in molecular solutions to carbon neutral energy conversion. Polynuclear catalysts are advantageous over mononuclear counterparts due to the possibility of pre-organized transition states and the ability to spread coordination and redox demands across multiple metals, which are useful for the multi-proton, multi-electron transformations associated with the activation of energy-relevant substrates such as N₂, O₂, H₂O, CO₂, etc.

Oxygen reduction has been of particular interest over the past few decades due to its application in fuel cell technologies. Cofacial porphyrin catalysts are known to be very efficient for the oxygen reduction reaction and other small molecule transformations due to the close orientation of the catalytically active sites that may act in concert on a substrate. Although

![Figure 3.1](image)

Figure 3.1. Tetrapyridyl porphyrin (top) assembles with molecular clips (bottom) to yield D₂A₄ prism architectures used in this study.
pioneering examples established that cofacial porphyrins were excellent catalysts for favoring four-electron four-proton reduction and were amenable as scaffolds for mechanistic studies, the complex, multi-step covalent syntheses and time consuming purification steps limit the practicality of such designs.\textsuperscript{16-19} The use of one-pot, coordination-driven self-assembly techniques, wherein metal-ligand bond formation drives formation, can greatly simplify the synthesis of these promising architectures.\textsuperscript{20}

Coordination-driven self-assembly offers a novel route to construct cofacial and related multi-centered catalysts.\textsuperscript{21} This approach has the potential to greatly ease the synthesis of new complexes with multiple, proximal active sites since each component can be prepared independently and then unified via self-assembly reactions which typically furnish thermodynamic products in quantitative yields and without the need for column chromatography or other purification techniques.\textsuperscript{22} Pyridyl-functionalized metalloporphyrins can be assembled into a cofacial conformation using a variety of metal-accepting clips.\textsuperscript{23-28} The syntheses of cofacial free base, Ni(II), and Zn(II) tetra pyridyl porphyrin prisms has been well established by Therrien and coworkers,\textsuperscript{29-30} and related self-assembled prisms are known.\textsuperscript{23, 28, 31-32} Applications of discrete metal-organic architectures has largely been dominated by host/guest chemistry owing to the well-defined internal cavities typically found in such structures.\textsuperscript{20, 33-36} The intersection of coordination-driven self-assembly and catalysis is most developed in the context of so-called “molecular flasks” wherein catalysis occurs within a metallacage that provides an environment to enhance reactivity or stabilize reactive intermediates.\textsuperscript{37-38}

Our previous work described \( \text{O}_2 \) reduction catalyzed by a cofacial porphyrin prism that was self-assembled in an overall 53\% yield in contrast to the <6\% yields for related covalent variants, and showed that under homogenous conditions there was approximately 39\% \( \text{H}_2\text{O}_2 \) produced using rotating-ring disk methods.\textsuperscript{39} It has been hypothesized that the cofacial separation is a critical determinant of the selectivity for the oxygen reduction reaction for \( \text{H}_2\text{O} \) versus \( \text{H}_2\text{O}_2 \).\textsuperscript{12}
Since our designs feature so-called “molecular clips” to enforce a cofacial arrangement of two planar building blocks, the bridging ligand between the two Ru centers may be tuned ultimately to vary porphyrin separation. Furthermore, we are interested in the effect a given clip may have on electronic structure. Towards this end, we have expanded our catalyst library to include the oxalato and oxamido-bridge variants shown in Figure 3.1. These designs are unique in that secondary metals may be incorporated to serve a functional, rather than just structural, role.

3.2 Synthesis and Characterization

The arene-ruthenium clips used for self-assembly were readily synthesized from the \( \{\text{Ru(}\eta^6-\text{PrC}_6\text{H}_4\text{Me})(\text{Cl})_2\}\) dimer and potassium oxalate monohydrate, N,N'-dimethyloxamide, or 2,5-dihydroxy-1,4-benzoquinone.\(^{23, 25}\) The chlorides of the clips were removed prior to self-assembly by a pre-treatment with AgOTf, after which the appropriate tetra pyridyl porphyrin\(^{40}\) was

![Figure 3.2. ESI-FT-ICR-MS (red) and simulated (black) peaks corresponding to [Oxa-Zn – 3 OTf]\(^{3+}\).](image-url)
Figure 3.3. ESI-FT-ICR-MS (red) and simulated (black) peaks corresponding to [Ox-Co – 3 OTf]$^{3+}$ (top) and [Oxa-Co – 3 OTf]$^{3+}$ (bottom).
added to the reaction vessel, as previously described. Since the building blocks of these cofacial prisms are independently synthesized, the specific donor and acceptor components may be freely swapped without necessitating a total redesign of the self-assembly process. Due to the solubility of the triflate variants of Benzo-Zn, and Benzo-Co in water, a salt metathesis was completed with NH₄PF₆ to obtain the PF₆ variants of Benzo-Zn and Benzo-Co. The PF₆ salts of the Benzo-M prisms were used in all electrochemical studies.

Evidence for the [2+4] stoichiometry of the self-assemblies was obtained from electrospray ionization mass spectrometry (ESI-FT-ICR-MS). Unlike many discrete metallacycles and cages whose mass spectrograms are dominated by peaks corresponding to fragments and undefinable species, the mass spectrograms of these prims are largely dominated by intact cores that are charged due to the loss of counterions. In fact, in all cases, the most intense peaks are the intact 3+ charge states. The mass ion peak 1483.16902 \([\text{Oxa-Zn} – 3 \text{OTf}]^{3+}\) is shown in Figure 3.2 which corresponds to the intact Oxa-Zn. Figure 3.3 shows the mass ion peaks for \textbf{Ox-Co}, \(m/z = 1442.11874 \ [\text{Ox-Co} – 3 \text{OTf}]^{3+}\), and \textbf{Oxa-Co}, \(m/z = 1478.82756 \ [\text{Oxa-Co} – 3 \text{OTf}]^{3+}\), that corresponds to the intact prisms. The full mass spectrum and other mass ion peaks of \textbf{Ox-Co}, \textbf{Oxa-Zn}, and \textbf{Oxa-Co} are shown in Figure3.20, Figure3.23, and Figure3.29. The isotopic spacing of the experimental data matches the simulated for all prisms and peaks. This provides strong evidence for the structural assignments of \textbf{Ox-Co}, \textbf{Oxa-Zn}, and \textbf{Oxa-Co}.

3.3 **X-ray Crystallography**

A crystal suitable for single crystal X-ray diffraction was grown by vapor diffusion of diethyl ether into a MeOH/CH₂Cl₂ solution of \textbf{Oxa-Zn}. As shown in Figure 3.4, two Zn(II)TPyP and four Ru(II) \textit{para}-cymene oxamido clips comprise the self-assembled prism. Each Zn(II) shows an axially coordinated water molecule. The Zn(II) atoms of each porphyrin sit upon a crystallographic four-fold rotational axis. The triflate counterions were disordered over multiple sites; however, all were located in the general vicinity of the Ru(II) clips. Of the two formula units found in the unit
cell, one exhibits positional disorder in the cofacial porphyrins which was effectively modeled. This disorder suggests that the two porphyrins are capable of contracting towards, or expanding away from one another. In the contracted form the Zn—Zn separation is 3.8 Å and in the expanded form 6.0 Å. The disorder free prism shows a Zn—Zn separation of 4.6 Å, the average separation of the expanded and contracted prism is 4.9 Å. A crucial detail in the modeled positional disorder is that the Zn(II) centers remain in a cofacial orientation in both forms. The oxamido molecule coordinated to the Ru(II) metal center was also disordered; however, it was successfully modeled. Despite the use of synchrotron radiation, diffraction beyond 1.1 Å was not achieved. This poor diffraction is not unexpected for self-assembled constructs containing heavy atoms. Several level

![Diagram](image)

**Figure 3.4.** a) Oak Ridge Thermal Ellipsoid Plot (ORTEP) of **Oxa-Zn** (CCDC number: 1585392) at the 30% probability level as viewed down the crystallographic c-axis. Primed atom labels refer to atoms on the lower face of the prism. Complete prisms are symmetry generated by two fragments; only one Ru and one Zn are required to generate the entire formula. Hydrogen atoms, counterions, and axially coordinated water removed for clarity. b) view of the Ru-oxamido clip fragment. c) Side on view of **Oxa-Zn** illustrating the 4.6 Å M—M separation.
A and B alerts arose during the final refinement and IUCr CheckCIF protocol; however, the alerts that were found can be explained primarily by the lack of diffraction beyond 1.1 Å. The aforementioned alerts do not detract from the conclusions made about the structure: that these prisms enforce a cofacial arrangement between porphyrin building blocks with ~4.6 Å separation.

Due to the poor diffraction beyond 1.1 Å, modeling the hydrogen atoms of the axial water ligands was challenging. Examination of the difference map (Figure 3.52) has ruled out the possibility of methanol, acetonitrile, or any other solvent used in the synthesis and crystallization. Moreover, analysis of the CCDC using ConQuest (version 1.19) revealed 42 reported structures of zinc-porphyrin complexes with axial aquo ligands, with an average Zn—OH$_2$ bond length of 2.17(9) Å. This is in good agreement with the experimentally determined Zn—O bonds found within Oxal-Zn, where (on average) 2.11(2) Å. To determine if the Zn—OH$_2$ bond’s found in Oxal-Zn were statistically different from the 42 examples found in the CCDC 1-way analysis of variance (ANOVA) was used, at the 95% confidence level it was determined that there was no statistical difference between the determined Zn—OH$_2$ bond and those found in literature. The empirical and statistical findings further lend to the conclusion that the identity of the axial ligands water molecules.

3.4 Cyclic Voltammetry of Co2 and Zn2 Catalysts

To immobilize our prisms as heterogeneous catalysts a Nafion ink was used as a matrix material. This ethanoic ink comprises 5% w/w Nafion and carbon black to facilitate conductivity.
The potential window of the modified electrodes with blank Nafion ink in 0.5 M H₂SO₄ in water with O₂ present was shown to be −0.3 V to 1.0 V vs. Ag/AgCl (Figure 3.42). Electrode films were made from 2 μL Nafion ink containing either 3 mM CoTPyP, or 1.5 mM Benzo-M, Ox-M, and Oxa-M. Control experiments were carried out using Zn(II) prisms to rule out catalysis due to the molecular clip portions of the prism. Figure 3.5 shows the cyclic voltammograms of the Co(II) prisms and their Zn(II) analogues in oxygen-saturated 0.5 M H₂SO₄. The CVs of Oxa-Co, Ox-Co, and Benzo-Co (red) show activity towards ORR, which have onset potentials of 0.25 V, 0.45 V, and 0.2 V, respectively. The CVs of Zn(II) analogues, Ox-Zn, Oxa-Zn, and Benzo-Zn did not show any activity towards ORR, which provides evidence for the inertness of the molecular clips. Figure 3.5 also shows the CV of CoTPyP with an onset potential of 0.2 V.

The stability of the catalytically active prisms was established with cyclic voltammetry. An initial voltammogram of the Oxa-Co was acquired under O₂-saturated 0.5 M H₂SO₄ revealing a catalytic response with an onset potential of 0.45 V vs Ag/AgCl (Figure 3.6). The solution was then sparged with N₂ for 10 minutes to remove all O₂ and then cycled twenty-five times between 0 and 1 V; Lastly, O₂ was reintroduced via a 10 minute purge and another voltammogram was acquired. The current response of the Oxa-Co was unchanged after substrate-free cycling, which suggests that the immobilized catalyst was stable under the 0.5 M H₂SO₄ acidic conditions. CV
stability for Ox-Co and Benzo-Co were also carried out and similarly showed full stability after cycling (Figure 3.43 and Figure 3.44).

3.5 Hydrodynamic Voltammetry and Product Distribution

Due to possibility of forming H$_2$O$_2$ in addition to H$_2$O during ORR, rotating-ring disk studies were carried out to obtain selectivity information. The Co prisms were immobilized as heterogeneous catalysts on glassy carbon disk platinum ring electrode with the same Nafion ink method and compared to commercially available 10% platinum-on-carbon (Pt/C). The disk data from RRDE experiments is shown in Figure 3.7, wherein the top plot shows the normalized disk current and the bottom plot shows the selectivity of the catalysts. The raw disk and ring current responses are shown in the supporting information for all catalysts used (Figure 3.46-Figure 3.51).

A marked cofacial enhancement is observed relative to the CoTPyP with normalized current densities exceeding both the monomeric catalyst and 10% Pt/C wherein the normalized current densities reflect the total Co or Pt loading in the film. The onset currents for the heterogeneous catalysts occur at 0.2 V vs. Ag/AgCl for both Ox-Co and CoTPyP, 0.25 V vs. Ag/AgCl for Benzo-Co, 0.45 V vs. Ag/AgCl for Oxa-Co, and 0.55 V vs. Ag/AgCl for 10% Pt/C at 2000 rpm.

We can obtain product distributions (H$_2$O$_2$ vs. H$_2$O) using the equation for faradaic yield (equation 3.1)$^{41-42}$

$$\%H_2O_2 = \frac{2i_{\text{ring}}}{i_{\text{disk}} + i_{\text{ring}}} \times 100$$

(3.1)

in which $i_{\text{ring}}$ is the current response from the Pt ring, $i_{\text{disk}}$ is the current response from the glassy carbon disk, and $N$ is collection efficiency of the RRDE. The collection efficiency was experimentally determined to be 0.36 (Figure 3.45).$^{41}$
Figure 3.7. Normalized disc current response (top) and $\text{H}_2\text{O}_2$ selectivity (bottom) of prisms, CoTPyP, and 10% Pt/C catalyst in $\text{O}_2$-saturated 0.5 M $\text{H}_2\text{SO}_4$ at 2000 rpm
The average H$_2$O$_2$ selectivity of the heterogeneous CoTPyP catalyst was ~50%. There was an observed cofacial enhancement to selectivity for all cofacial prisms. Whereas we previously determined a H$_2$O$_2$ selectivity of ~39% for the Benzo-Co under homogeneous condition, under the current heterogeneous conditions, the selectivity is improved to an average of ~25%. The prisms enforcing a shorter metal-metal distance showed a further selectivity enhancement. Average faradaic efficiencies of hydrogen peroxide for Ox-Co and Oxa-Co was 13% and 3%, respectively. The drastic attenuation of the two-electron two-proton pathway for the oxalato-spaced and oxamido-spaced prisms supports our initial hypothesis that a shortening of the Co—Co distance would favor four-electron four-proton reactivity. The 10% Pt/C catalyst exhibited an average H$_2$O$_2$ selectivity of ~5%.

3.6 Tafel and Koutecký-Levich Analysis

The catalysts inks were deposited on a glassy carbon rotating disk electrode (RDE). The electrode was rotated at $\omega = 500, 800, 1200, 1600, 2000, 2500, 3000, \text{ and } 3500 \text{ rpm}$ and the disk current exhibited Levich behavior when the rotation rate was increased (Figure 3.8). Levich behavior indicates that the reaction is diffusion controlled, but this does not always mean that the diffusion of oxygen to the electrode surface is the rate determining step. Tafel and Koutecký-Levich analyses were used to determine the rate-determining step and rate constants for the catalysts.

The rotating disk data was plotted using the Tafel equation (equation 3.2).

\[ \eta = a + b \log(j) \]  

(3.2)

in which, $\eta$ is defined as overpotential (the difference between electrode and standard potentials, $\eta = E - E^\circ$), $j$ is the current density, $b$ is the Tafel slope, and $a$ is the exchange current density. Tafel plots of Ox-Co, Oxa-Co, and Benzo-Co are shown in Figure 3.9 and plots for CoTPyP and
10% Pt/C are located in the SI (Figure S40 and S41). Tafel slopes of approximately −120 mV/dec suggest that the first electron transfer is the rate determining step.\textsuperscript{43}

The rotating disk data for each catalyst was plotted at various overpotentials using the KL equation

\[
\frac{1}{i_{lim}} = \frac{1}{B} \omega^{-1/2} + \frac{1}{i_K} \tag{3.3}
\]

in which, \(i_{lim}\) is the limiting current (A), B is the Levich constant, \(\omega\) is the rotation rate (rad/s), and \(i_K\) is the kinetically limited current. Figure 3.10 shows the Koutecký-Levich (KL) plots of all catalysts. The observed linearity indicates a mixed kinetic-diffusion controlled reaction.\textsuperscript{44} The diffusion controlled region of the RDE voltammogram occurs when the plateau current is observed. The curved nature of the KL plots at low overpotentials indicates an electrode reaction with slow kinetics.\textsuperscript{41} It is also noted that the KL plots do not intersect the origin, which is also associated with slow electron transfer kinetics.\textsuperscript{41, 45-46}

The heterogeneous electron transfer rate constant, \(k_{het}\), was obtained using the y-intercept, \(\frac{1}{i_K}\), from the KL plot and calculated using equation 3.4\textsuperscript{47}

\[
i_K = nF \mathcal{A} k [O_2] \Gamma_{cat} \tag{3.4}
\]

in which \(n\) is the number of electrons, \(F\) is Faraday’s constant (96485 C mol\(^{-1}\)), \(\mathcal{A}\) is the surface area of the electrode (0.95 cm\(^2\)), \([O_2]\) is the bulk concentration of \(O_2\) and \(\Gamma_{cat}\) is the electrochemically active surface area. The concentration of \(O_2\) in 0.5 M H\(_2\)SO\(_4\) (1.1 × 10\(^{-6}\) M) was obtained from literature.\textsuperscript{48} The number of electrochemically active sites per surface area, \(\Gamma_{cat}\), was estimated from the concentration of catalyst in the inks and the volume pipetted on the electrode surface. We note that this approximation treats all metal sites as active, which means that the rate constants calculated are a lower limit. The number of electrons, \(n\), can be calculated from equation 3.5.\textsuperscript{49}
As shown in the Koutecký-Levich plots (Figure 3.10), $k_{het}$ changes as overpotential changes. We can plot $k_{het}$ and overpotential using equation 3.6.\(^{47}\)

$$k_{het} = k_0 e^{-\alpha \eta}$$

(3.6)

in which $k_{het}$ is the heterogeneous electron transfer rate constant, $k_0$ is the standard rate constant, $\eta$ is the overpotential associated with $k_{het}$, $R$ is the gas constant, $T$ is temperature, and $\alpha$ is the transfer coefficient. This plot is shown in each KL as an inset (Figure 3.10). We can use the y-intercept to find $k_0$.

A summary of the number of electrons transferred, total active sites per area, and standard rate constants for each catalyst can be found in Table 3.1. Catalysts Ox-Co and CoTPyP have rate constants that are approximately an order of magnitude larger than 10% Pt/C. Benzo-Co and Ox-Co have smaller rate constants of $3.80 \times 10^4 \text{ cm s}^{-1}$ and $4.57 \times 10^2 \text{ cm s}^{-1}$, respectively.

### Table 3.1. Summary of electrons transferred, ideal active site density, and rate constants of the catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$n$</th>
<th>$I_{cat}$ (mol/cm$^2$)</th>
<th>$k_0$ (cm s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ox-Co</td>
<td>3.52</td>
<td>$3.0 \times 10^{-9}$</td>
<td>$4.57 \times 10^2$</td>
</tr>
<tr>
<td>Oxa-Co</td>
<td>3.96</td>
<td>$3.0 \times 10^{-9}$</td>
<td>$3.24 \times 10^5$</td>
</tr>
<tr>
<td>Benzo-Co</td>
<td>3.15</td>
<td>$3.0 \times 10^{-9}$</td>
<td>$3.80 \times 10^4$</td>
</tr>
<tr>
<td>CoTPyP</td>
<td>2.91</td>
<td>$6.3 \times 10^{-9}$</td>
<td>$7.08 \times 10^5$</td>
</tr>
<tr>
<td>10% Pt/C</td>
<td>3.90</td>
<td>$4.0 \times 10^{-8}$</td>
<td>$6.67 \times 10^4$</td>
</tr>
</tbody>
</table>

$$n = 4 - 2 \left( \frac{\%H_2O_2}{100} \right)$$

(3.5)
Figure 3.8. Rotating disk current of all catalysts at \( \omega = 500, \ 800, \ 1200, \ 1600, \ 2000, \ 2500, \ 3000, \ \text{and} \ 3500 \text{ rpm.} \)
Figure 3.9. Tafel Slope analysis of all catalysts at $\omega = 500$, 800, 1200, 1600, 2000, 2500, 3000, and 3500 rpm.
Figure 3.10. Koutecký-Levich plots of all catalysts to obtain $k_{\text{het}}$. Inset shows plot for standard rate constant, $k_0$. 
Catalytic activity is also reported as mass activity (MA), which is the current response (mA) normalized by the amount of catalyst used (mg) at a certain potential. In Table 3.2, we have compared our best catalyst, Oxa-Co, to 10% Pt/C (used in this study), and several other heterogeneous catalysts.\textsuperscript{14, 50-52} It should be noted that ORR catalysts Fe-N-rGO, ZIF-TAA-p, and Fe\textsuperscript{II}-DPPD were prepared by pyrolysis, whereas the catalysts used in this study and the Fe rotaxane complex were not. The Oxa-Co system is competitive to other heterogeneous ORR catalysts based on a comparison of mass activities. At a potential of 0.46 V vs. Ag/AgCl, the prism has an activity of 1.5 mA/mg. Pt/C and first-row transition metals pyrolyzed in carbon matrices show activities between 1.5 – 2 mA/mg (see Table 3.2). The MA of 10% Pt/C was 1.9 mA/mg at 0.58 V vs. Ag/AgCl. Oxa-Co does obtain MA within range of the other catalysts but, operates at a slightly higher overpotential. We have demonstrated in this paper that the bridging ligand of the prisms has an effect on overpotential (Ox-Co vs. Oxa-Co). Self-assembly techniques allow us to envision a library of new clips that can be used to shift the onset of catalysis to more positive potential and make our prisms even more competitive with current heterogeneous catalysts.

**Table 3.2.** Summary of mass activity of heterogeneous catalysts in acidic conditions.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Mass Activity (mA/mg)</th>
<th>Potential (V) vs. Ag/AgCl\textsuperscript{[a]}</th>
<th>Acid used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxa-Co</td>
<td>1.5</td>
<td>0.46</td>
<td>0.5 M H\textsubscript{2}SO\textsubscript{4}</td>
</tr>
<tr>
<td>10% Pt/C</td>
<td>1.9</td>
<td>0.58</td>
<td>0.5 M H\textsubscript{2}SO\textsubscript{4}</td>
</tr>
<tr>
<td>Fe-N-rGO\textsuperscript{5, 50}</td>
<td>1.5</td>
<td>0.53</td>
<td>0.5 M H\textsubscript{2}SO\textsubscript{4}</td>
</tr>
<tr>
<td>ZIF-TAA-p\textsuperscript{52-53}</td>
<td>2</td>
<td>0.52</td>
<td>0.1 M HClO\textsubscript{4}</td>
</tr>
<tr>
<td>Fe\textsuperscript{II}-DPPD\textsuperscript{51, 54}</td>
<td>1.5</td>
<td>0.21\textsuperscript{[b]}</td>
<td>0.1 M HClO\textsubscript{4}</td>
</tr>
<tr>
<td>Fe rotaxane complex\textsuperscript{14}</td>
<td>1.5</td>
<td>0.50\textsuperscript{[b]}</td>
<td>0.5 M H\textsubscript{2}SO\textsubscript{4}</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} All potentials converted to Ag/AgCl from values given in refs \textsuperscript{[b]} Estimated from RRDE voltammogram
3.7 **Proposed Mechanism**

The proposed mechanism of the oxygen reduction reaction is shown in Scheme 3.1. Consistent with previously reported cofacial catalysts, the cofacial cobalt catalysts are pre-oxidized before entering the catalytic cycle, wherein one Co(II) porphyrin is oxidized to Co(III).

**Scheme 3.1.** Proposed oxygen reduction mechanism using self-assembled cofacial prism catalysts.
Figure 3.11. ESI-FT-ICR-MS experimental (red) and calculated (black) that correspond to the intact Ox-Co prism as a mixed valent Co(III,II) species with and without O₂ bound.
As a note, the cofacial catalysts were synthesized without rigorous air-free techniques and stored in air. Even though we did not see a pre-oxidation event of the catalysts in electrochemical experiments, oxygen could have acted as a sacrificial oxidizing agent and oxidize the Co(II) to a Co(III). Oxygen then binds to the mixed-valent Co metal centers and is reduced to superoxide, the second Co(II) is oxidized to a Co(III). We were able to isolate peaks in the ESI-FT-ICR-MS that correspond to the intact Ox-Co prism as a mixed valent Co(III,II) species with and without O$_2$ bound (Figure 3.11), which supports the initial steps of the mechanism. The experimental and calculated m/z is shown in Table 3.3 for each species.

Spectroelectrochemistry data of Ox-Co and Oxa-Co were collected to probe the initial species of the catalytic cycle. A quartz spec-echem cell was used, along with a small platinum mesh as the working electrode, platinum wire as the counter electrode, and Ag/AgNO$_3$ as the reference electrode. A potential of 0.8 V vs. Ag/AgNO$_3$ was applied to the cell to bulk oxidize the solutions while under oxygen. UV-Vis spectra were collected at various times during the bulk oxidation and the soret band of the porphyrin prisms was monitored. The soret band of Ox-Co exhibited a red shift from 415 nm to 422 nm and Oxa-Co displayed a soret band red shift from 416 nm to 427 nm (Figure 3.12). This indicates a one electron oxidation of the Co prisms and

<table>
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<th>Experimental m/z</th>
<th>Calculated m/z</th>
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<tr>
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<tr>
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<td>1089.26919</td>
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<tr>
<td>[Ox-Co(III,II) – 4 OTf]$^{5+}$</td>
<td>837.64503</td>
<td>837.62763</td>
</tr>
</tbody>
</table>
possible binding of oxygen to the metal centers.\textsuperscript{56-57} The porphyrin prisms exhibit pure Co(III) character in the UV-Vis spectra, as there was no growth of a peak that corresponds to $\pi$-radical character in the 700 nm to 900 nm region. The full spectra are shown in Figure 3.41. The spectroelectrochemical experiment and the mass spectrum supports the first and second intermediates shown in Scheme 3.1. When oxidized, the Co prism is a multi-valent Co(III,II) complex that can bind oxygen and enter the catalytic cycle.

The distance-dependent selectivities highlight the importance of the critical O–O bond cleavage step that requires both metal centers to interact with the O$_2$ in order to drive the formation of H$_2$O over H$_2$O$_2$. It was suggested in literature that the bound oxygen needs to be reduced by three electrons and protonated to weaken the O–O bond to favor H$_2$O formation.\textsuperscript{55} In this self-assembled prism library, the shorter Co–Co (Oxa-Co vs. Benzo-Co) drastically reduced the amount of H$_2$O$_2$ produced and favored the reduction of O$_2$ to H$_2$O (97% H$_2$O vs. 75% H$_2$O).

3.8 Conclusion

A library of self-assembled cofacial catalysts were synthesized with high yields (50-79%) and without the need for any column chromatography. A suite of different ruthenium clips were
used to assembled porphyrins with different metal—metal separations, a relatively simple modification that manifests in significant changes to catalytic activity. The nature of the molecular clips also contributed to the redox properties of the catalysts. Each species was immobilized as a heterogeneous catalyst material using a Nafion ink. Electrochemical rotating ring-disk electrode studies of the catalyst inks provided information about selectivity, wherein a drastic decrease of the two-electron two-proton pathway was observed for the cofacial systems. The most selective of the cofacial catalysts, Ox-Co had an average faradaic efficiency for $\text{H}_2\text{O}_2$ of 3%, where the faradaic efficiency towards $\text{H}_2\text{O}_2$ of Ox-Co, Benzo-Co, and CoTPyP was 13% 25% 50%, respectively. Koutecký-Levich and Tafel analyses provided rate constants for catalysis. The Ox-Co ($k_0 = 3.24 \times 10^5 \text{cm s}^{-1}$) system with smaller Ru—Ru distance showed improved kinetics over Benzo-Co ($k_0 = 3.80 \times 10^4 \text{cm s}^{-1}$). Catalysts Ox-Co and CoTPyP have rate constants that are approximately an order of magnitude larger than 10% Pt/C. Benzo-Co and Ox-Co have smaller rate constants of $3.80 \times 10^4 \text{cm s}^{-1}$ and $4.57 \times 10^2 \text{cm s}^{-1}$, respectively. This work demonstrates that self-assembly is an enabling synthetic method for constructing cofacial porphyrins in a practical and efficient manner. Furthermore, we have shown that the resulting catalysts remain operative under heterogeneous conditions that further enhance the remarkable gains in selectivity and current densities that have long been associated with cofacial systems.

3.9 Experimental section

Materials. All chemicals were used as purchased unless otherwise noted. Zinc meso-tetra(4-pyridyl)porphine (ZnTPyP) was purchased from Frontier Scientific. Dichloro($\rho$-cymene)ruthenium(II) dimer was purchased from Alfa Asar. All solvents used were reagent grade or better. Acetonitrile used in electrochemical experiments was purified from a Pure Process Technology free standing solvent purification system. Nanopure water (>18MΩcm) used in electrochemical experiments was obtained from 50k light Sliex deionizer by AmeriWater. UV−Vis absorption spectra were acquired with a Cary 8454 UV-Vis Diode Array System. All NMR
experiments were carried out on Varian Mercury-300 (broadband) and Varian Inova-500 (broadband) instruments. Evans Method was used to obtain effective magnetic moment. Mass spectra were acquired with Bruker Daltonics SolariX 12T Fourier Transform Ion Cyclotron Resonance Mass Spectrometer and calibrated with >90% Angiotensin I purchased from Sigma Aldrich. Infrared spectra were acquired with Perkin Elmer 1760 FTIR spectrometer with horizontal attenuated total reflectance (HATR). All experiments were carried out at room temperature, unless otherwise noted.

**Crystallographic Details.** Singles crystals of **Oxa-Zn** were grown by vapor diffusion of diethyl ether into a solution of dichloromethane and methanol (approximate ratio of 3:1). The datum crystal was deep red parallelepiped (0.40 x 0.15 x 0.10 mm³). An initial structure was obtained on a lab source diffractometer (Bruker D8 Venture equipped with a PHOTON-100 CMOS detector and a Mo X-ray source), however crystals were weakly diffracting and resolution beyond 1.5 Å, even with extended exposure times, was not achievable. Furthermore, *para*-cymene and triflate moieties were unresolvable in the home source data sets. The greater intensity of synchrotron radiation (\(\lambda = 0.7749\) Å) was used to push diffraction to 1.1 Å resolution allowing for the elucidation of the *para*-cymene and triflate counterions. Data was collected at the Advanced Light Source housed at Lawrence Berkeley National Labs on beamline 11.3.1. Diffractometer was a Bruker D8 diffractometer equipped with a PHOTON-II CPAD detector. A series of \(\varphi\) and \(\omega\) scans were used to cover reciprocal space. Following integration and scaling (multi-scan), the structure was solved in Olex2\textsuperscript{59} using SHELXT via intrinsic phasing.\textsuperscript{60} The structure was then refined using full-matrix least squares refinement using SHELXL.\textsuperscript{61} **Oxa-Zn** crystallizes into the \(P422\) space group, the asymmetric unit contains 1/4\textsuperscript{th} of a formula unit (\(Z' = 0.25\), \(Z = 2\)).

During the refinement process, several different constraints and restraints were used. All methyl groups were constrained to a staggered conformation using at AFIX 33 command. The exact orientation of the methyl groups can be difficult to ascertain in lower resolution data sets,
especially given the number of heavy atoms the local environment. The SIMU and rigid bond restraint DELU were used to restrain atomic displacement parameters (ADPs). ISOR commands were used on the trflate counterions to refine the anisotropic atoms isotropically. SADI restraints were used in the disorder modeling to ensure the equivalent bonds remained of similar lengths. RIGU restraints were applied to the trflate counterions as well. DFIX restraints were employed to better model the isopropyl and methyl groups of the \textit{para}-cymene ligands to yield a chemically sensible model. A solvent mask was applied using Olex2 to account for disordered solvent molecule.

**Catalyst Ink Method.** The procedure to make catalysts inks was adapted from the literature. In a scintillation vial, 5.4 mg of carbon black, 1 µmol catalyst (or 2 µmol porphyrin), 100 µL of ethanol, and 500 µL CH$_2$Cl$_2$ were sonicated for 1 hour. The solvent was evaporated completely, followed by the addition of 70 µL of Nafion (5% w/w) and 600 µL of ethanol and sonicated for 1 hour. For comparison studies, 25 mg of 10% Pt on carbon was used to make catalyst ink. Blank ink was also prepared with the same procedure without catalyst for electrochemical window studies. 2 µL of the ink was pipetted onto a glassy carbon disk electrode to completely cover the surface and allowed to air dry before immediate use in electrochemical studies.

**Electrochemical Measurements.** All electrochemical experiments (cyclic voltammetry and rotating ring-disk experiments) were acquired with a Bio-Logic SP-300 bipotentiostat/galvanostat. All voltammograms are reported versus a Ag/AgCl reference electrode (CH Instruments, Austin, TX). Glassy carbon was used for the working electrode and platinum wire was used for the counter electrode (CH Instruments, Austin, TX). The working electrodes were carefully polished with 0.05 µM alumina powder/water slurry, rinsed with distilled water, sonicated in distilled water for 30 seconds, rinsed with acetone, and allowed to air dry. Tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte in homogenous CV studies and was recrystallized from
ethanol three times and dried under vacuum prior to use. Sulfuric acid in nanopure water was used as the supporting electrolyte and proton source in all electrochemical catalytic studies.

**Rotating Ring Disk Voltammetry (RRDE).** A Pine MSR rotator (PINE Research, Durham, NC) was used for all rotating ring-disk electrode (RRDE) voltammetry. A glassy carbon fixed-disk/platinum ring PEEK shroud working electrode (PINE Research, Durham, NC) and a platinum mesh counter electrode were used for RRDE experiments. The electrodes were prepared in the same way as the electrodes used for cyclic voltammetry; 2 µL of the ink was pipetted onto the glassy carbon disk electrode to completely cover the surface and allowed to air dry before immediately using it for the electrode studies. The glassy carbon (GC) disk was scanned from the \(E_{OC}\) (open circuit potential) to 0 V vs. Ag/AgCl at a scan rate of 20 mV/s. The Pt ring was held at 1.0 V vs. Ag/AgCl to oxidize \(H_2O_2\) formed during the course of the experiment. The working electrode was rotated at rates of 500, 800, 1200, 1600, 2000, 2500, 3000, and 3500 rpm. The collection efficiency was experimentally determined to be 0.36 using the \(K_4Fe(CN)_6\) \(Fe^{3+/2+}\) couple.

### 3.10 Supporting Information

**Experimental Section**

**Synthetic Procedure.** Literature procedures were used to prepare the following: CoTPyP\(^{52}\), [Ru\(_2(\eta^6-iPrC_6H_4Me)_2(Benzo)Cl_2)\]\(^{23}\), [Ru\(_2(\eta^8-iPrC_6H_4Me)_2(Ox)Cl_2)\]\(^{30}\), [Ru\(_2(\eta^8-iPrC_6H_4Me)_2(Oxa)Cl_2)\], Ox-Zn\(^{30}\), Benzo-Zn\(^{30}\), and Benzo-Co\(^{39}\).

**Metalation of CoTPyP**

A mixture of H\(_2TPyP\) (220 mg, 0.36 mmol) and Co(OAc)\(_2\)· 4 H\(_2O\) (360 mg, 1.4 mmol) in DMF was refluxed for 5 hours. The reaction mixture was poured into water to precipitate a dark crystalline product, which was filtered, and washed with (3 × 10 mL) water, (3 × 10 mL) ethanol, and (2 × 25 mL) chloroform. Yield 98% (240 mg), UV-Vis (PhCN, TFA): Soret band: \(\lambda_{max} = 437\) nm, \(\epsilon = 156,000\) M\(^{-1}\)cm\(^{-1}\) Q band: \(\lambda_{max} = 552\) nm, \(\epsilon = 9,600\) M\(^{-1}\)cm\(^{-1}\)
**Synthesis of \([\text{Ru}_2(\eta^6-\text{iPrC}_6\text{H}_4\text{Me})_2(\text{benzo})\text{Cl}_2]\) (Ru benzo clip)**

A mixture of dichloro(p-cymene) ruthenium (II) dimer (300. mg, 0.489 mmol) and 2,5-dihydroxy-1,4-benzoquinone (70. mg, 0.49 mmol) was stirred at room temperature in methanol (50 mL) for 2 hours and a red precipitate formed. The reaction mixture was filtered and washed with (3 × 10 mL) diethyl ether to afford the product as a red solid. Yield 70% (240 mg) ¹H NMR (300 MHz, CDCl₃) δ (ppm) = 5.80 (s, 2H), 5.62 (d, 4H J = 10 Hz), 5.38 (d, 4H J = 10 Hz), 2.92 (m, 2H), 2.29 (s, 6H), 1.34 (d, 12 H J = 10 Hz), UV-Vis (PhCN): λₘₐₓ = 300 nm, ε = 23,000 M⁻¹cm⁻¹ λₘₐₓ = 508 nm, ε = 28,000 M⁻¹cm⁻¹

**Synthesis of \([\text{Ru}_2(\eta^6-\text{iPrC}_6\text{H}_4\text{Me})_2(\text{ox})\text{Cl}_2]\) (Ru ox clip)**

A mixture of dichloro(p-cymene) ruthenium(II) dimer (150 mg, 0.25 mmol) and potassium oxalate monohydrate (45 mg, 0.25 mmol) in chloroform/methanol (1:1; 30 mL) was refluxed for 18 h. The solvent was evaporated and dichloromethane was added to precipitate salts. The precipitate was removed by vacuum filtration and the filtrate was evaporated until an orange solid was obtained. Yield 96% (147 mg)

**Synthesis of \([\text{Ru}_2(\eta^6-\text{iPrC}_6\text{H}_4\text{Me})_2(\text{oxa})\text{Cl}_2]\) (Ru oxa clip)**

To a solution of N,N′dimethyloxamide (oxa-H₂) (27.9 mg, 0.240 mmol) in THF (60 mL)at −78°C, n-BuLi (0.30 mL, 0.48 mmol) was added, warmed to rt, and stirred for 2 hrs. The mixture was added to a solution of \([\text{Ru}(\eta^6-\text{p-cym})\text{Cl}_2]\)₂ (147 mg, 0.240 mmol) in THF (20 mL), and stirred overnight. The solvent was evaporated and the residue was dissolved in CH₂Cl₂. The resulting mixture was filtered and dried. Yield 91% (140 mg) ¹H NMR (300 MHz, CDCl₃) of Ru-oxa clip δ (ppm) = 5.36 (d, 2H, J = 5.7 Hz), 5.33 (d, 2H, J = 5.9 Hz), 5.26 (d, 2H, J = 5.7 Hz), 5.04 (d, 2H, J = 5.6 Hz), 3.32 (s, 6H), 2.74 (m, 2H), 1.21 (t, 12H, J = 5.5 Hz)
$^1$H NMR of Ru oxa clip

**Figure 3.13.** $^1$H NMR (300 MHz, CDCl$_3$) of Ru-oxa clip $\delta$ (ppm) = 5.36 (d, 2H, J = 5.7 Hz), 5.33 (d, 2H, J = 5.9 Hz), 5.26 (d, 2H, J = 5.7 Hz), 5.04 (d, 2H, J = 5.6 Hz), 3.32 (s, 6H), 2.74 (m, 2H), 1.21 (t, 12H, J = 5.5 Hz)
Synthesis of [Ru₈(η⁶-iPrC₆H₄Me)₆(ox)(ZnTPyP)₂][OTf]₈ (Ox-Zn)

A mixture of AgOTf (20.34 mg, 0.07938 mmol) and [Ru₂(η⁶-p-cymene)₂(oxalato)Cl]₂ (25 mg, 0.040 mmol) in methanol (8 mL) was stirred at rt for 3 hrs, then filtered. To the red filtrate, ZnTPyP (13.53 mg, 0.01984 mmol) was added and refluxed for 24 hrs. The solution was filtered through a glass fiber disc and the solvent was evaporated under vacuum. The solid was dissolved in 20 mL CH₂Cl₂, filtered through a glass fiber disc, and concentrated to approx. 2 mL. Diethyl ether was added and the green solid was isolated. Yield 76% (36 mg, 0.0074 mmol) ¹H NMR (300 MHz, CD₃CN) of Ox-Zn δ (ppm) = 9.21 (d, 8H, Hpyr, J = 5 Hz), 8.92 (d, 8H, H′a, J = 5 Hz), 8.65 (d, 8H, Hβ, J = 5 Hz), 8.14 (d, 8H, Hα, J = 5 Hz), 8.06 (d, 8H, H′pyr, J = 5 Hz), 7.96 (d, 8H, H′β, J = 5 Hz), 6.15 (m, 24H, Har, J = 5 Hz), 5.96 (d, 8H, Har, J = 7.5 Hz), 3.14 (m, 8H, Ha, J = 5 Hz), 2.50 (s, 24H, Hc), 1.60 (d, 48H, Hb, 5 Hz) UV-VIS (MeCN): Soret band: λmax = 422 nm, ε = 540,000 M⁻¹cm⁻¹ Q band 1: λmax = 568 nm, ε = 22,000 M⁻¹cm⁻¹ Q band 2: λmax = 607 nm, ε = 11,000 M⁻¹cm⁻¹ IR (cm⁻¹): 3090 (w, CHaryl), 1626 (s, C=O), 1254 (s,CF₃) ESI-FT-ICR-MS experimental (calc.) m/z: 2247.23624 (2247.01198) [Ox-Zn – 2 OTf]²⁺, 1445.44787(1445.36042) [Ox-Zn – 3 OTf]³⁺, 1048.57650 (1048.53175) [Ox-Zn – 4 OTf]⁴⁺, 808.86262 (808.83494) [Ox-Zn – 5 OTf]⁵⁺ IR (cm⁻¹): 2878 (w, CHaryl), 1625 (s, C=O), 1254 (s,CF₃)
Figure 3.14. $^1$H NMR (300 MHz, CD$_3$CN) of Ox-Zn δ (ppm) = 9.21 (d, 8H, Hpyr, J = 5 Hz), 8.92 (d, 8H, H'α, J = 5 Hz), 8.65 (d, 8H, Hβ, J = 5 Hz), 8.14 (d, 8H, Hα, J = 5 Hz), 8.06 (d, 8H, H'pyr, J = 5 Hz), 7.96 (d, 8H, H'β, J = 5 Hz), 6.15 (m, 24H, Har, J = 5 Hz), 5.96 (d, 8H, Har, J = 7.5 Hz), 3.14 (m, 8H, Ha, J = 5 Hz), 2.50 (s, 24H, Hc), 1.60 (d, 48H, Hb, 5 Hz)
**FT-IR-HATR of Ox-Zn**

**Figure 3.15.** Normalized FT-ATR-IR of Ox-Zn (*left, green*) and Ox-Zn as ink (*right, gray*).

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UV-Vis of Ox-Zn

Figure 3.16. UV-Vis spectrum of Ox-Zn. UV-VIS (MeCN): Soret band: $\lambda_{\text{max}} = 422$ nm, $\varepsilon = 540,000$ M$^{-1}$cm$^{-1}$ Q band 1: $\lambda_{\text{max}} = 568$ nm, $\varepsilon = 22,000$ M$^{-1}$cm$^{-1}$ Q band 2: $\lambda_{\text{max}} = 607$ nm, $\varepsilon = 11,000$ M$^{-1}$cm$^{-1}$
Figure 3.17. ESI-FT-ICR-MS experimental (calc.) m/z: 2247.23624 (2247.01198) [Ox-Zn – 2 OTf]^{2+}, 1445.44787 (1445.36042) [Ox-Zn – 3 OTf]^{3+}, 1048.57650 (1048.53175) [Ox-Zn – 4 OTf]^{4+}, 808.86262 (808.83494) [Ox-Zn – 5 OTf]^{5+}
Synthesis of \([\text{Ru}_8(\eta^6-/Pr\text{C}_6\text{H}_4\text{Me})_8(\text{ox})_4(\text{CoTPyP})_2][\text{OTf}]_8\) (Ox-Co)

A mixture of AgOTf (20.36 mg, 0.07938 mmol) and \([\text{Ru}_2(\eta^6-p\text{-cymene})_2(\text{oxalato})\text{Cl}_2]\) (25 mg, 0.040 mmol) in methanol (8 mL) was stirred at rt for 3 h, then filtered. To the red filtrate, CoTPyP (13.53 mg, 0.02004 mmol) was added and refluxed for 24 hrs. The solution was filtered through a glass fiber disc and the solvent was evaporated under vacuum. The solid was dissolved in 20 mL CH$_2$Cl$_2$, filtered through a glass fiber disc, and concentrated to approx. 2 mL. Diethyl ether was added and the red solid was isolated by filtration. Yield 62% (60 mg, 0.01 mmol) UV-VIS (MeCN):

Soret band: $\lambda_{\text{max}} = 415$ nm, $\varepsilon = 274,000$ M$^{-1}$cm$^{-1}$

Q band 1: $\lambda_{\text{max}} = 547$ nm, $\varepsilon = 21,000$ M$^{-1}$cm$^{-1}$

ESI-FT-ICR-MS experimental (calc.) m/z: 2242.23306 (2242.02164) \([\text{Ox-Co} – 2 \text{OTf}]^{2+}\), 1442.11874 (1442.03050) \([\text{Ox-Co} – 3 \text{OTf}]^{3+}\), 1045.32929 (1045.28462) \([\text{Ox-Co} – 4 \text{OTf}]^{4+}\), 806.46546 (806.43720) \([\text{Ox-Co} – 5 \text{OTf}]^{5+}\)

IR (cm$^{-1}$): 3049 (w, CH$_{aryl}$), 1624 (s, C=O), 1252 (s, CF$_3$)
Figure 3.18. Normalized FT-ATR-IR of Ox-Co (left, pink) and Ox-Co as ink (right, gray)

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UV-Vis of Ox-Co

Figure 3.19. UV-Vis spectrum of Ox-Co. UV-VIS (MeCN): Soret band: $\lambda_{\text{max}} = 415\, \text{nm}$, $\varepsilon = 274,000\, \text{M}^{-1}\text{cm}^{-1}$ Q band 1: $\lambda_{\text{max}} = 547\, \text{nm}$, $\varepsilon = 21,000\, \text{M}^{-1}\text{cm}^{-1}$
FT-ICR-ESI-MS of Ox-Co

**Figure 3.20.** ESI-FT-ICR-MS experimental (calc.) m/z: 2242.23306 (2242.02164) [Ox-Co – 2 OTf]^{2+}, 1442.11874 (1442.03050) [Ox-Co – 3 OTf]^{3+}, 1045.32929 (1045.28462) [Ox-Co – 4 OTf]^{4+}, 806.46546 (806.43720) [Ox-Co – 5 OTf]^{5+}
Synthesis of [Ru$_8$(η$^6$-iPrC$_6$H$_4$)$_8$(oxa)$_4$(ZnTPyP)$_2$][OTf]$_8$ (Oxa-Zn)

A mixture of AgOTf (19.55 mg, 0.07622 mmol) and [Ru$_2$(η$^6$-p-cymene)$_2$(Oxa)Cl]$_2$ (25 mg, 0.038 mmol) in methanol (8 mL) was stirred at rt for 3 h, then filtered. To the red filtrate, ZnTPyP (13 mg, 0.019 mmol) was added and refluxed for 24 hrs. The solution was filtered through a glass fiber disc and the solvent was evaporated under vacuum. The solid was dissolved in 20 mL CH$_2$Cl$_2$, filtered through a glass fiber disc, and concentrated to approx. 2 mL. Diethyl ether was added and the green solid was isolated by filtration. Yield 73% (35 mg, 0.0071 mmol)

UV-Vis spectrum of Oxa-Zn. UV-Vis (MeCN): Soret band: $\lambda_{max} = 430$ nm, $\epsilon = 300,000$ M$^{-1}$cm$^{-1}$ Q band 1: $\lambda_{max} = 549$ nm, $\epsilon = 25,000$ M$^{-1}$cm$^{-1}$ 1H NMR (300 MHz, CD$_3$CN) of Oxa-Zn $\delta$ (ppm) = 9.19 (4H), 9.06 (4H), 8.93 (4H), 8.83 (4H), 8.74 (4H), 8.69 (8H), 8.26-8.19 (20H), 7.83(4H) 6.16-5.58 (32H), 3.93 (12H), 3.83 (12H), 2.99 (8H), 2.09 (24H), 1.47-1.41 (48H) ESI-FT-ICR-MS experimental (calc.) m/z: 2299.28191 (2299.14228) [Oxa-Zn $-$ 2 OTf]$^{2+}$, 1483.16902 (1483.11079) [Oxa-Zn $-$ 3 OTf]$^{3+}$, 1075.38282 (1075.34494) [Oxa-Zn $-$ 4 OTf]$^{4+}$, 830.10719 (830.08552) [Oxa-Zn $-$ 5 OTf]$^{5+}$ IR (cm$^{-1}$): 3072 (w, CH$_{aryl}$), 1611 (s, C=O), 1256 (s,CF$_3$)
FT-IR-HTIR of Oxa-Zn

Figure 3.21. Normalized FT-ATR-IR of Oxa-Zn (left, yellow) and Oxa-Zn as ink (right, gray).

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<th>Peak</th>
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UV-Vis of Oxa-Zn

Figure 3.22. UV-Vis spectrum of Oxa-Zn. UV-VIS (MeCN): Soret band: $\lambda_{\text{max}} = 430 \text{ nm}$, $\varepsilon = 300,000 \text{ M}^{-1}\text{cm}^{-1}$ Q band 1: $\lambda_{\text{max}} = 549 \text{ nm}$, $\varepsilon = 25,000 \text{ M}^{-1}\text{cm}^{-1}$
FT-ICR-ESI-MS of Oxa-Zn
Figure 3.23. ESI-FT-ICR-MS experimental (calc.) m/z: 2299.28191 (2299.14228) [Oxa-Zn – 2 OTf]^{2+}, 1483.16902 (1483.11079) [Oxa-Zn – 3 OTf]^{3+}, 1075.38282 (1075.34494) [Oxa-Zn – 4 OTf]^{4+}, 830.10719 (830.08552) [Oxa-Zn – 5 OTf]^{5+}

'H NMR of Oxa-Zn

Figure 3.24. 'H NMR (300 MHz, CD_{3}CN) of Oxa-Zn δ (ppm) = 9.19 (4H), 9.06 (4H), 8.93 (4H), 8.83 (4H), 8.74 (4H), 8.69 (8H), 8.26-8.19 (20H), 7.83(4H) 6.16-5.58 (32H), 3.93 (12H), 3.83 (12H), 2.99 (8H), 2.09 (24H), 1.47-1.41 (48H)
DOSY NMR of Oxa-Zn

**Figure 3.25.** DOSY NMR of Oxa-Zn in CD$_3$CN

Oxa-Zn in CD$_3$CN was analyzed by $^1$H NMR at 298 K on a Varian Inova-500 (broadband) instrument. The z-gradient coil constant was calibrated at $1.00 \times 10^{-3}$ G/cm/DAC. The BPPSTE pulse sequence was used. Sixteen transients were collected for each of 15 increments, where the z-gradient amplitude varied from 1.3 to 32.5 G/cm. The duration of each gradient in the pulse pair was 2.0 ms. A 1 s relaxation delay was used, and the diffusion delay time was 50 ms.
COSY NMR of Oxa-Zn

Figure 3.26. COSY of Oxa-Zn
Synthesis of [Ru₈(η⁶-iPrC₆H₄)₈(oxa)₄(CoTPyP)₂][OTf]₈ (Oxa-Co)

A mixture of AgOTf (19.55 mg, 0.07622 mmol) and [Ru₂(η⁶-p-cymene)₂(oxamido)Cl]₂ (25 mg, 0.038 mmol) in methanol (8 mL) was stirred at rt for 3 h, then filtered. To the red filtrate, CoTPyP (12.83 mg, 0.01901 mmol) was added and refluxed for 24 hrs. The solution was filtered through a glass fiber disc and the solvent was evaporated under vacuum. The solid was dissolved in 20 mL CH₂Cl₂, filtered through a glass fiber disc, and concentrated to approx. 2 mL. Diethyl ether was added and the red solid was isolated by filtration. Yield 87% (41 mg, 0.0084 mmol) UV-Vis spectrum of Oxa-Co Prism. UV-VIS (MeCN): Soret band: λ_max = 416 nm, ε = 398,000 M⁻¹cm⁻¹ Q band 1: λ_max = 549 nm, ε = 25,000 M⁻¹cm⁻¹ ESI-FT-ICR-MS experimental (calc.) m/z: 2293.26190 (2293.14825) [Oxa-Co – 2 OTf]²⁺, 1478.82756 (1478.78135) [Oxa-Co – 3 OTf]³⁺, 1071.37322 (1071.34792) [Oxa-Co – 4 OTf]⁴⁺, 827.50615 (827.48783) [Oxa-Co – 5 OTf]⁵⁺ IR (cm⁻¹): 3070 (w, CHaryl), 1609 (s, C=O), 1255 (s,CF₃)
FT-IR-HATR of Oxa-Co

Figure 3.27. Normalized FT-ATR-IR of Oxa-Co (left, red) and Oxa-Co as ink (right, gray).

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<th>Peak</th>
<th>Wavenumber (cm⁻¹)</th>
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<td>1609 (s, C=O)</td>
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Figure 3.28. UV-Vis spectrum of Oxa-Co. UV-VIS (MeCN): Soret band: $\lambda_{\text{max}} = 416$ nm, $\varepsilon = 398,000$ M$^{-1}$cm$^{-1}$ Q band 1: $\lambda_{\text{max}} = 549$ nm, $\varepsilon = 25,000$ M$^{-1}$cm$^{-1}$
Figure 3.29. ESI-FT-ICR-MS experimental (calc.) m/z: 2293.26190 (2293.14825) [Oxa-Co – 2 OTf]$^{2+}$, 1478.82756 (1478.78135) [Oxa-Co – 3 OTf]$^{3+}$, 1071.37322 (1071.34792) [Oxa-Co – 4 OTf]$^{4+}$, 827.50615 (827.48783) [Oxa-Co – 5 OTf]$^{5+}$
Synthesis of \([\text{Ru}_8(\eta^6-\text{PrC}_6\text{H}_4\text{Me})_6(\text{Benzo})_4(\text{ZnTPyP})_2][\text{OTf}]_8\) (Benzo-Zn)

A mixture of AgOTf (38 mg, 0.15 mmol) and \([\text{Ru}_2(\eta^6-\text{PrC}_6\text{H}_4\text{Me})_2(\text{Benzo})\text{Cl}_2]\) (50 mg, 0.07 mol) in methanol (10 mL) was stirred at room temperature for 3 hr. A white precipitate was formed and was filtered out with a glass fiber disc. The red filtrate was added to ZnTPyP (25 mg, 0.037 mmol) and refluxed for 24 hours. The solvent was removed under vacuum, remaining solid was dissolved in dichloromethane and filtered with a glass fiber disc. Ether was added to precipitate the product as a dark red solid. Yield 47% (40 mg, 0.009 mmol) \(^1\)H NMR (500 MHz, CD\(_3\)CN) of Benzo-Zn δ (ppm) = 8.95 (d, 8H, H\(_{\text{pyr}}\) J = 5 Hz), 8.88 (d, 8H, H\(^{'}\text{a}\), J = 5 Hz), 8.81 (d, 8H, H\(^{'\text{b}}\) J = 5 Hz), 8.56 (d, 8H, H\(_{\text{a}}\) J = 5 Hz), 8.18 (d, 8H, H\(_{\text{pyr}}\) J = 5 Hz), 7.41 (d, 8H, H\(^{'\text{b}}\) J = 5 Hz), 6.26 (d, 8H, H\(_{\text{ar}}\) J = 5 Hz), 6.22 (s, 8H, H\(_{\text{a}}\)), 6.06 (dd, 16H, J = 7.5 Hz, 12.5 Hz), 5.92 (d, 8H, H\(_{\text{ar}}\) J = 5 Hz), 3.07 (m, 8H, H\(_{\text{c}}\)), 2.37 (s, 24H, H\(_{\text{b}}\)), 1.42, (d, 24 H, J = 7.5 Hz), 1.52 (d, 24 H, H\(_{\text{a}}\) J = 7.5 Hz), UV-Vis (PhCN): Soret band: \(\lambda_{\text{max}} = 438\) nm, \(\varepsilon = 501,000\) M\(^{-1}\)cm\(^{-1}\) Q band 1: \(\lambda_{\text{max}} = 518\) nm, \(\varepsilon = 49,000\) M\(^{-1}\)cm\(^{-1}\) Q band 2: \(\lambda_{\text{max}} = 565\) nm, \(\varepsilon = 53,000\) M\(^{-1}\)cm\(^{-1}\)
Figure 3.30. ESI-FT-ICR-MS experimental (calc.) m/z: 2347.17788 (2347.04742) [Benzo-Zn – 2 OTf]$^{2+}$, 1514.09520 (1514.04763) [Benzo-Zn – 3 OTf]$^{3+}$, 1098.32648 (1098.29760) [Benzo-Zn – 4 OTf]$^{4+}$, 848.86649 (848.84758) [Benzo-Zn – 5 OTf]$^{5+}$
Salt Metathesis of $[\text{Ru}_8(\eta^6-\text{iPrC}_6\text{H}_4\text{Me})_8(\text{dhbq})_4(\text{ZnTPyP})_2][\text{PF}_6]_8$ (Benzo-Zn)

$[\text{Ru}_8(\eta^6-\text{iPrC}_6\text{H}_4\text{Me})_8(\text{dhbq})_4(\text{ZnTPyP})_2][\text{OTf}]_8$ (10 mg, 0.002 mmol) was added to 1 mL of acetone in a 2 dram vial. A saturated solution of $\text{NH}_4\text{PF}_6$ in water was added dropwise until a red precipitate formed. The vial was placed into the centrifuge for 15 mins and the solution was decanted. The pellet was washed with water and dried under vacuum. Yield 92% (9.2 mg) IR (cm$^{-1}$): 3091 (w, CH$_{aryl}$), 1513 (s, C=O), 831 (s, PF$_6$) ESI-FT-ICR-MS experimental (calc.) m/z: 1102.57444 (1102.56968) $[\text{Benzo-Zn– 4 PF}_6]^{4+}$, 853.06245 (853.06581) $[\text{Benzo-Zn – 5 PF}_6]^{5+}$

**FT-IR-HATR of Benzo-Zn**

![Normalized FT-ATR-IR of Benzo-Zn Prism (left, red) and Benzo-Zn Prism as ink (right, gray).](image)

**Table 3.31.** Normalized FT-ATR-IR of Benzo-Zn Prism *(left, red)* and Benzo-Zn Prism as ink *(right, gray)*.

<table>
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<tr>
<th>Peak</th>
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<tr>
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<td>1513 (s, C=O)</td>
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<td>3</td>
<td>831 (s, PF$_6$)</td>
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</table>
FT-ICR-ESI-MS of Benzo-Zn

**Figure 3.32.** ESI-FT-ICR-MS experimental (calc.) m/z: 1102.57444 (1102.56968) [Benzo-Zn– 4 PF₆]⁴⁺, 853.06245 (853.06581) [Benzo-Zn – 5 PF₆]⁵⁺,

**Synthesis of [Ru₈(η⁶-iPrC₆H₄Me)₂(Benzo)₄(CoTPyP)₂][OTf]₈ (Benzo-Co)**

A mixture of AgOTf (38 mg, 0.15 mmol) and [Ru₂(η⁶-iPrC₆H₄Me)₂(Benzo)Cl₂] (50. mg, 0.074 mol) in methanol (10 mL) was stirred at room temperature for 3 hr. A white precipitate was formed and filtered out with a glass fiber disc. The red filtrate was added to CoTPyP (25 mg, 0.037 mmol) and refluxed for 48 hours. The solvent was removed under vacuum, remaining solid was dissolved in dichloromethane and filtered with a glass fiber disc. Ether was added to precipitate the product as a dark red solid. Yield 75% (86 mg, 0.014 mmol), ESI-FT-ICR-MS experimental (calc.) m/z: 1510.79035 (1510.71698) [Benzo Co – 3 OTf]³⁺, 1095.58687 (1095.55200) [Benzo Co – 4 OTf]⁴⁺,

UV-Vis (PhCN): Soret band: λₛₐₜₐₜ = 436 nm, ε = 216,000 M⁻¹cm⁻¹ Q band: λₛₐₜₐₜ = 550 nm, ε = 25,400 M⁻¹cm⁻¹, IR (cm⁻¹): 3070 (w, CH aryl), 1515 (s, C=O), 1255 (s,CF₃). Magnetic moment (300 MHz): μₑffective = 2.59, Elemental Analysis for C₁₉₂H₁₆₈Co₂F₂₄N₁₆O₄₀Ru₈S₈ with two CH₂Cl₂ calc: C, 45.26; H, 3.37; N, 4.35; found: C, 44.71; H, 3.44; N, 4.63
Salt Metathesis of $[\text{Ru}_6(\eta^6-\text{PrC}_6\text{H}_4\text{Me})_6(\text{Benzo})_4(\text{CoTPyP})_2][\text{PF}_6]_8$ (Benzo-Co)

$[\text{Ru}_6(\eta^6-\text{PrC}_6\text{H}_4\text{Me})_6(\text{Benzo})_4(\text{CoTPyP})_2][\text{OTf}]_8$ (10 mg, 0.002 mmol) was added to 1 mL of acetone in a 2 dram vial. A saturated solution of $\text{NH}_4\text{PF}_6$ in water was added dropwise until a red precipitate formed. The vial was placed into the centrifuge for 15 mins and the solution was decanted. The pellet was washed with water and dried under vacuum. 77% (7.6 mg) IR (cm$^{-1}$): 3070 (w, $\text{CH}_\text{aryl}$), 1513 (s, $\text{C}═\text{O}$), 829 (s, $\text{PF}_6$) ESI-FT-ICR-MS experimental (calc.) m/z: 1508.44426 (1508.40121) [Benzo-Co – 3 PF$_6]^3+$, 1095.07422 (1905.05973) [Benzo-Co – 4 PF$_6]^4+$, 847.05484 (847.06184) [Benzo-Co – 5 PF$_6]^5+$
FT-IR-HATR of Benzo-Co

**Figure 3.33.** Normalized FT-ATR-IR of Benzo-Co (left, blue) and Benzo-Co as ink (right, gray).

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Figure 3.34. ESI-FT-ICR-MS experimental (calc.) m/z: 1508.44426 (1508.40121) [Benzo-Co – 3 PF₆]³⁺, 1095.07422 (1905.05973) [Benzo-Co – 4 PF₆]⁴⁺, 847.05484 (847.06184) [Benzo-Co – 5 PF₆]⁵⁺
Cyclic Voltammetry

Figure 3.35. Cyclic voltammogram of Ox-Zn in 100 mM TBAPF$_6$ (MeCN) under N$_2$ (red) and blank (black). Electrode set up: glassy carbon working electrode, Pt wire counter electrode, and Ag/AgNO$_3$ reference electrode. Scan rate: 100 mV/s

Figure 3.36. Cyclic voltammogram of Ox-Co in 100 mM TBAPF$_6$ (MeCN) under N$_2$ (green) and blank (black). Electrode set up: glassy carbon working electrode, Pt wire counter electrode, and Ag/AgNO$_3$ reference electrode. Scan rate: 100 mV/s
**Figure 3.37.** Cyclic voltammogram of Oxa-Zn in 100 mM TBAPF$_6$ (MeCN) under N$_2$ (yellow) and blank (black). Electrode set up: glassy carbon working electrode, Pt wire counter electrode, and Ag/AgNO$_3$ reference electrode. Scan rate: 100 mV/s

**Figure 3.38.** Cyclic voltammogram of Oxa-Co in 100 mM TBAPF$_6$ (MeCN) under N$_2$ (pink) and blank (black). Electrode set up: glassy carbon working electrode, Pt wire counter electrode, and Ag/AgNO$_3$ reference electrode. Scan rate: 100 mV/s
Figure 3.39. Cyclic voltammogram of **Benzo-Zn** in 100 mM TBAPF$_6$ (MeCN) under N$_2$ (*purple*) and blank (*black*). Electrode set up: glassy carbon working electrode, Pt wire counter electrode, and Ag/AgNO$_3$ reference electrode. Scan rate: 100 mV/s

Figure 3.40. Cyclic voltammogram of **Benzo-Co** in 100 mM TBAPF$_6$ (MeCN) under N$_2$ (*green*) and blank (*black*). Electrode set up: glassy carbon working electrode, Pt wire counter electrode, and Ag/AgNO$_3$ reference electrode. Scan rate: 100 mV/s
Spectroelectrochemistry of Ox-Co and Oxa-Co

Figure 3.41. Full UV-Vis spectral changes of **Ox-Co (left)** and **Oxa-Co (right)** observed during bulk oxidation at 0.8 V vs. Ag/AgNO₃ in MeCN and 100 mM TBAPF₆ under O₂.
Oxygen reduction studies of electrode modified with blank ink

**Figure 3.42.** Cyclic voltammograms of modified (blank ink) electrode with a three electrode cell set-up: glassy carbon working electrode, Pt wire counter electrode, and Ag/AgCl reference electrode, and under N_2/0.5 M H_2SO_4 (*blue*), O_2/0.5 M H_2SO_4 (*red*). The onset of catalysis in the O_2/H_2SO_4 solution occurs at −0.3 V vs. Ag/AgCl.
Cyclic Voltammetry Stability Studies with Catalyst Inks

Figure 3.43. Catalyst stability cyclic voltammetry study of a single Ox-Co film. The film was first cycled under O$_2$/0.5 M H$_2$SO$_4$ (left). Next, all O$_2$ was removed from solution by sparging with N$_2$ (center) and cycled twenty-five times between 0 and 1 V vs. Ag/AgCl. Finally, the solution was resaturated with O$_2$ with no significant change to the catalytic wave (right). Electrode set up: glassy carbon working electrode, Pt wire counter electrode, and Ag/AgCl reference electrode. Scan rate for ORR: 100 mV/s Scan rate for cycling: 20 mV/s

Figure 3.44. Catalyst stability cyclic voltammetry study of a single Benzo-Co film. The film was first cycled under O$_2$/0.5 M H$_2$SO$_4$ (left). Next, all O$_2$ was removed from solution by sparging with N$_2$ (center) and cycled twenty-five times between 0 and 1 V vs. Ag/AgCl. Finally, the solution was resaturated with O$_2$ with no significant change to the catalytic wave (right). Electrode set up: glassy carbon working electrode, Pt wire counter electrode, and Ag/AgCl reference electrode. Scan rate for ORR: 100 mV/s Scan rate for cycling: 20 mV/s
Collection Efficiency of Rotating-Ring Disk Electrode

*Figure 3.45.* Collection Efficiency of RRDE using 10 mM $K_4Fe(CN)_6$ and 1 M KCl in water under different rotation rates ($\omega = 500, 800, 1200, 1600, 2000, 2500, 3000, \text{and} 3500$ rpm).

Due to the reversible redox chemistry of $K_4Fe(CN)_6$ ($Fe^{3+/2+}$), it was used in the determination of RRDE collection efficiency (*Figure 3.45*) in water. The glassy carbon disk electrode under different rotation rates ($\omega = 500, 800, 1200, 1600, 2000, 2500, 3000, \text{and} 3500$ rpm) was scanned from $E_{oc}$ to 0.6 V vs. Ag/AgCl at a scan rate of 20 mV/s. The Pt ring electrode was held at 0.2 V vs. Ag/AgCl. Equation S1 was used for determining collection efficiency:

$$N = \frac{i_{\text{ring}}}{i_{\text{disk}}}$$  \hspace{1cm} (S1)

in which $N$ is collection efficiency, $i_{\text{disk}}$ is disk current, and $i_{\text{ring}}$ is ring current. The collection efficiency was experimentally determined to be 0.36, using published methods.$^{42, 63}$
Rotating Ring-Disk Voltammetry

Figure 3.46. Rotating Ring-Disk Voltammograms of Ox-Co, Oxa-Co, Benzo-Co, CoTPyP, and 10% Pt/C in oxygen-saturated 0.5 M H₂SO₄ at 2000 rpm.
Figure 3.47. RRDE (right) of **Ox-Co** catalyst ink in 0.5 M H$_2$SO$_4$ and bubbling O$_2$ under different rotation rates (ω = 1600, 2000, and 2500 rpm) and H$_2$O$_2$ produced during the course of the experiment.

Figure 3.48. RRDE (right) of **Oxa-Co** catalyst ink in 0.5 M H$_2$SO$_4$ and bubbling O$_2$ under different rotation rates (ω = 1600, 2000, and 2500 rpm) and H$_2$O$_2$ produced during the course of the experiment (left).
Figure 3.49. RRDE (right) of Benzo-Co catalyst ink in 0.5 M H$_2$SO$_4$ and bubbling O$_2$ under different rotation rates ($\omega = 1600$, 2000, and 2500 rpm) and H$_2$O$_2$ produced during the course of the experiment (left).

Figure 3.50. RRDE (right) of CoTPyP catalyst ink in 0.5 M H$_2$SO$_4$ and bubbling O$_2$ under different rotation rates ($\omega = 1600$, 2000, and 2500 rpm) and H$_2$O$_2$ produced during the course of the experiment (left).
Figure 3.51. RRDE (right) of 10% Pt/C catalyst ink in 0.5 M H₂SO₄ and bubbling O₂ under different rotation rates (ω = 1600, 2000, and 2500 rpm) and H₂O₂ produced during the course of the experiment (left).
## Crystallographic Details

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The unweighted R-factor is \( R₁ = \sum (|F_o| - |F_c|)/\sum |F_o|; I > 2 \sigma(I) \) and the weighted R-factor is \( wR₂ = \sqrt{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2} \).
Figure 3.52. Difference map of Oxa-Zn.
3.11 References


56. Ke, X.; Kumar, R.; Sankar, M.; Kadish, K. M., Electrochemistry and Spectroelectrochemistry of Cobalt Porphyrins with π-Extending and/or Highly Electron-


Towards Cofacial Salens and Porphyrinoids as Self-Assembled Oxygen Reduction Catalysts

4.1 General Conclusions

This work establishes self-assembly as an enabling synthetic method for constructing cofacial catalysts. The main goal was to populate a library of catalysts with an application towards the oxygen reduction reaction. A collection of self-assembled cofacial catalysts with varied metal-metal separations and bridging ligands were synthesized with high yields (50-79%) and without the need for any column chromatography. We have demonstrated that this is a substantial improvement over traditional step-wise routes that are associated with overall yields of ~3% or lower, while the catalysts still maintained oxygen reduction activity. We have also established that our catalyst, Oxa-Co is competitive with commercial platinum-on-carbon (10% Pt/C) and other heterogeneous species.

The major conclusions drawn from this work are the following:

1. In the homogeneous studies, Benzo-Co (66 hr\(^{-1}\)) showed an enhanced turnover frequency over CoTPyP (6 hr\(^{-1}\)) and catalyzed oxygen reduction to hydrogen peroxide almost exclusively (90%) in the chemical reduction experiments. We attributed H\(_2\)O\(_2\) selectivity to the ~7.9 Å separation between the Benzo-Co metal centers.

2. Electrochemical studies provided rate constants for ORR using both the cofacial and monomeric catalysts. The selectivities of CoTPyP and Benzo-Co were similar in the electrochemical studies, with an average faradaic efficiency of hydrogen peroxide of 44% and 39%, respectively. The rate constant for Benzo-Co \(k_{\text{obs}} \approx 1.1 \text{ hr}^{-1}\) exceeded that of CoTPyP \(k_{\text{obs}} \approx 0.05 \text{ hr}^{-1}\) by over an order of magnitude, attributed to a strong cofacial enhancement.

3. We hypothesized that a shorter metal-metal distance would favor the four-electron four-proton pathway and we were able to exploit the modular nature of self-assembly using alternative
bridging ligands in the “Ru clips” that optimized metal-metal separation and redox properties of the final prisms, Ox-Co and Oxa-Co. This demonstrated that it is possible to tune different metrics of polynuclear catalysis using simple synthetic methods. The Ox-Co and Oxa-Co prisms attenuated the metal-metal separation to ~4.6 Å based on isostructural Zn(II) analogues, approaching the 4.1 Å distance expected to favor H₂O formation.³

4. Each species was immobilized as a heterogeneous catalyst material using a Nafion ink. Electrochemical rotating ring-disk electrode studies of the catalyst inks provided information about selectivity, wherein a drastic decrease of the two-electron two-proton pathway was observed for the cofacial systems. The most selective of the cofacial catalysts, Oxa-Co had an average faradaic efficiency for H₂O of 3%, where the faradaic efficiencies towards H₂O₂ of Ox-Co, Benzo-Co, and CoTPyP were 13%, 25%, and 50%, respectively.

5. The Oxa-Co \((k_0 = 3.24 \times 10^5 \text{ cm s}^{-1})\) system with smaller Ru—Ru distance showed improved kinetics over Benzo-Co \((k_0 = 3.80 \times 10^4 \text{ cm s}^{-1})\). Catalysts Oxa-Co and CoTPyP have rate constants that are approximately an order of magnitude larger than 10% Pt/C. Benzo-Co and Ox-Co have smaller rate constants of \(3.80 \times 10^4 \text{ cm s}^{-1}\) and \(4.57 \times 10^2 \text{ cm s}^{-1}\), respectively. We have shown that the resulting catalysts remain operative under heterogeneous conditions that further enhance the remarkable selectivities and current densities associated with cofacial systems.

6. Ox-Co and Oxa-Co prisms are isostructural, but the selectivities and kinetics are drastically different. This suggests that the bridging ligand plays a role in the overall electronic structure, contributing to the difference in H₂O vs H₂O₂ formation and \(k_0\).

7. Our best cofacial catalyst, Oxa-Co prism, generates only ~3% hydrogen peroxide, making it competitive with platinum (~5% H₂O₂). The current density of the Oxa-Co also plateaus at five times that of Pt/C when normalized per Co/Pt. Most importantly, the greatly enhanced current densities and selectivity of the Oxa-Co prism do not come at the cost of overpotential; the
onset of current for the **Oxa-Co** is competitive with the 10% Pt/C catalyst. The **Oxa-Co** prism is the most effective cofacial porphyrin catalyst known to date.

### 4.2 Exploring the Electronic Effects of Molecular Clips used in Self-Assembled Cofacial Porphyrin Oxygen Reduction Catalysts

![Chemical Reaction](attachment:image.png)

**Figure 4.1.** Bridging ligands for substituted Oxa molecular clips of interest

The first generation **Oxa-Co** system established that metal-metal separation is not the only determinant of selectivity and kinetics for the ORR, otherwise its reactivity would have matched the isostructural **Ox-Co** prism. We want to study the role that bridging ligands of the molecular clips have on cofacial porphyrin ORR reactivity. The parent oxamido-bridge molecular clip is readily modified from our first-generation **Oxa-Co** species by altering the R-group off of each nitrogen site. A series of alkyl and aryl-based functional groups differ in their electron-donating and withdrawing ability based on commercially available primary amines (Figure 4.1). Treatment of oxalyl chloride to the amines in the presence of a base will deliver the functionalized oxamide species. The oxamide ligands will then be treated with n-BuLi and the para-cymene ruthenium dimer to furnish the molecular clip. Since the resulting molecular clips will remain
competent for self-assembly reactions, we can readily populate a library of seven core prisms comprising three types: free base porphyrin, Zn(II) porphyrin, and catalytically active Co(II) porphyrin.

We can further probe electronic structure effects using oxalimidamide bridging ligands, as shown in Figure 4.2. The parent oxamide ligand can be further modified by chlorination after addition to PCl₅ under refluxing conditions.⁵ The oxalimidoyl dichloride derivatives can be treated with any primary amines, differing in electron-donating and withdrawing ability, to furnish the final oxalimidamide ligand.⁴,⁶ These ligands will be treated with n-BuLi and the para-cymene ruthenium dimer to provide the new molecular clips. Using the oxalimidamide bridging ligand, the library of clips will be only limited by the number of primary amines used.

Electrochemical experiments with the free-base and Zn(II) porphyrin prisms will take place to probe the activity of the ruthenium clips. Past experiments have shown that catalytic oxygen reduction does not occur at the coordinatively-saturated Ru(II) and the clips serve only as a structural element.⁷ The hypothesis is that the clips with the more electronegative bridging ligands with push the onset potential of oxygen reduction towards the thermodynamic potential (1.23 V vs. SHE). The more electron withdrawing the substituent is, the easier the catalyst will be to reduce, which will lower the overpotential of the reaction.

4.2.1 Experimental Details

Materials. All chemicals were used as purchased unless otherwise noted. All solvents used were reagent grade or better. All NMR experiments were carried out on Varian Mercury-300
(broadband) instrument. All reactions were performed at room temperature unless otherwise noted. Synthetic procedures were modified from literature. Preliminary results of the syntheses are noted below.

Synthesis of N,N'-diphenyloxamide (phenoxa-H₂). THF (40 mL) and aniline (1.38 mL) were added to a 100 mL schlenk flask. The flask was cooled to −78°C with stirring and oxalyl chloride (0.700 mL) was added dropwise. The reaction mixture was slowly warmed to room temperature and stirred for 24 h. After, the solvent was reduced by half and the white solid was filtered. The white solid product was recrystallized from ethanol with no need for further purification. Yield 1.15 g (60%) ¹H NMR (300 MHz, CD₂Cl₂) δ 9.36 (s, 2H), 7.70 (d, J = 8.0 Hz, 4H), 7.41 (t, J = 7.7 Hz, 4H), 7.22 (t, J = 7.4 Hz, 2H).

Figure 4.3. ¹H NMR phenoxa-H₂ (300 MHz, CD₂Cl₂) δ 9.36 (s, 2H), 7.70 (d, J = 8.0 Hz, 4H), 7.41 (t, J = 7.7 Hz, 4H), 7.22 (t, J = 7.4 Hz, 2H).
Synthesis of N,N'-ditolyloxamide (tolyloxa-H₂). THF (100 mL), triethylamine (0.700 mL, 5 mmol) and p-toluidine (6.43 g, 60 mmol) were added to a 200 mL schlenk flask. The flask was cooled to −78°C with stirring and oxalyl chloride (2.14 mL, 25 mmol) was added dropwise. The reaction mixture was slowly warmed to room temperature and stirred for 24 h. After, the solvent was reduced by half and the white solid was filtered. The white solid product was recrystallized from ethanol with no need for further purification. Yield 4.79 g (72%) \(^1\)H NMR (300 MHz, DMSO-d₆) δ 10.73 (s, 2H), 7.74 (d, J = 8.3 Hz, 4H), 7.18 (d, J = 8.2 Hz, 4H), 2.28 (s, 6H).

Synthesis of N,N'-bis(4-trifluoromethyl)phenyloxamide (fluoroxa-H₂). THF (100 mL), triethylamine (0.046 mL, 0.33 mmol) and 4-trifluoromethylaniline (0.4 mL, 3 mmol) were added to a 200 mL schlenk flask. The flask was cooled to −78°C with stirring and oxalyl chloride (0.114
1.33 mmol) was added dropwise. The reaction mixture was slowly warmed to room temperature and stirred for 24 h. After, the solvent was reduced by half and the white solid was filtered. The white solid product was recrystallized from ethanol with no need for further purification. Yield 110 mg (22%) \(^1\text{H} \text{ NMR (300 MHz, DMSO-}d_6) \delta 11.23 \text{(s, 2H), 8.08 \text{(d, J = 8.4 Hz, 4H), 7.75 \text{(d, J = 8.5 Hz, 4H).}}

**Synthesis of \([\text{Ru}_2(\eta^6-\text{iPrC}_6\text{H}_4\text{Me})_2(\text{phenoxa})\text{Cl}_2] \) (Ru phenoxa clip).** To a solution of

![Figure 4.5. \(^1\text{H} \text{ NMR fluoroxa-H}_2 \text{ (300 MHz, DMSO-}d_6) \delta 11.23 \text{(s, 2H), 8.08 \text{(d, J = 8.4 Hz, 4H), 7.75 \text{(d, J = 8.5 Hz, 4H).}}

\text{N,N'}\text{diphenyloxamide (phenoxa-H}_2\text{) (39.21 mg, 0.16 mmol) in THF (12 mL) at −78°C, }\text{n-BuLi (0.204 mL, 0.327 mmol) was added. The solution was warmed to room temperature and stirred for 2 hrs. The mixture was then added to a solution of [Ru(\eta^6-p-cym)\text{Cl}_2]_2 (100 mg, 0.16 mmol) in THF (4 mL), and stirred overnight. The solvent was evaporated and the residue was dissolved in}
CH₂Cl₂. The resulting mixture was filtered and dried. Yield 90 mg (70%) ¹H NMR (300 MHz, CDCl₃) δ 7.47 (d, J = 7.3 Hz, 4H), 7.40 – 7.29 (m, 4H), 5.15 (m, 2H), 5.09 (d, J = 5.1 Hz 2H), 5.00 (d, J = 5.1 Hz, 2H), 4.63 (d, J = 5.5 Hz, 2H), 2.50 (d, J = 6.7 Hz, 2H), 1.95 (s, 6H), 1.08 (dd, J = 11.3, 6.9 Hz, 12H).

Figure 4.6. ¹H NMR (300 MHz, CDCl₃) δ 7.47 (d, J = 7.3 Hz, 4H), 7.40 – 7.29 (m, 4H), 5.15 (m, 2H), 5.09 (d, J = 5.1 Hz 2H), 5.00 (d, J = 5.1 Hz, 2H), 4.63 (d, J = 5.5 Hz, 2H), 2.50 (d, J = 6.7 Hz, 2H), 1.95 (s, 6H), 1.08 (dd, J = 11.3, 6.9 Hz, 12H).

Synthesis of [Ru₂(η⁶-iPrC₆H₄Me)₂(tolyloxa)Cl₂] (Ru tolyloxa clip). To a solution of N,N'ditolyloxamide (phenyltolyl-H₂) (21.89 mg, 0.08 mmol) in THF (6 mL) at −78°C, n-BuLi (0.102 mL, 0.160 mmol) was added. The solution was warmed to room temperature and stirred for 2 hrs. The mixture was then added to a solution of [Ru(η⁶-p-cym)Cl₂]₂ (50 mg, 0.08 mmol) in THF (2
mL), and stirred overnight. The solvent was evaporated and the residue was dissolved in CH$_2$Cl$_2$. The resulting mixture was filtered and dried. Yield 56 mg (85%) $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.39 (d, $J = 7.7$ Hz, 4H), 7.12 (d, $J = 7.3$ Hz, 4H), 5.13 (d, $J = 5.9$ Hz, 2H), 5.05 (d, $J = 5.6$ Hz, 2H), 4.99 (d, $J = 5.6$ Hz, 2H), 4.61 (d, $J = 5.4$ Hz, 2H), 2.67 – 2.46 (m, 2H), 2.36 (s, 6H), 1.98 (s, 6H), 1.17 – 1.01 (m, 12H).

Figure 4.7. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.39 (d, $J = 7.7$ Hz, 4H), 7.12 (d, $J = 7.3$ Hz, 4H), 5.13 (d, $J = 5.9$ Hz, 2H), 5.05 (d, $J = 5.6$ Hz, 2H), 4.99 (d, $J = 5.6$ Hz, 2H), 4.61 (d, $J = 5.4$ Hz,
4.3 Exploring A$_2$B$_2$ Porphyrinoid Prisms as Oxygen Reduction Catalysts

Despite the exploitation of cofacial porphyrin catalysts in literature, there have been minimal reports of other polypyrrole macrocycles held in cofacial architectures, especially given interesting electrochemistry.$^{1,3,9}$ Porphyrinoid macrocycles like corroles, diazaporphyrins, and phlorins can be adapted for use in self-assembly schemes similar to those used for cofacial porphyrin architectures with pyridyl substituents at the available meso positions.

Iron tetrapyridylporphyrins have been shown to have higher selectivities towards H$_2$O than H$_2$O$_2$ (~5-15% H$_2$O$_2$) but oftentimes are associated with large overpotentials and onset currents of approximately 300 mV vs NHE.$^{10-11}$ Tanaka and coworkers have described a Fe(III) porphyrin–Fe(III) phthalocyanine rotaxane complex that had a low overpotential (onset potential: 0.78 V vs RHE) and high selectivity for the four-proton, four-electron reduction of O$_2$ (12% H$_2$O$_2$), but had low overall synthetic yields of ~4%.$^{12}$ We hypothesis that the poor yields associated with such complexes can be mitigated by the use of coordination-driven self-assembly. Phthalocyanines do not offer easily accessible routes for pyridyl-functionalization to facilitate self-assembly, so instead

![Diagram of A$_2$B$_2$ porphyrin prisms using arene-ruthenium clips and cis-phosphine acceptors](image)

**Figure 4.8.** (top) A$_2$ porphyrin prisms using arene-ruthenium clips and cis-phosphine acceptors (bottom) Proposed polypyrrole macrocycles to tune electronic structure.
diazaporphyrins can be used due to the available meso positions. These cores provide a route to install trans pyridyl groups for self-assembly using D_2A_2 schemes. The synthesis of 5,15-Diaza-10,20-dipyridylporphyrins can be adapted from literature.\textsuperscript{13}

The 3-pyridyl versions will be self-assembled with simple 90° acceptors that will result in short metal-metal separations to favor four-electron chemistry (Figure 4.8). The 4-pyridyl variants will be combined with our library of arene-Ru clips. The D_2A_2 scaffold will be extended to phlorins and corroles that offer unique electrochemistry characterized by multiple redox events that can provide the basis for lower overpotentials.\textsuperscript{14-18}

4.4 Designing Salen Catalysts for the Oxygen Reduction Reaction

![Figure 4.9](image)

**Figure 4.9.** 3-pyridyl and 4-pyridyl salens will assemble with 90° acceptors (*blue*) or molecular clips (*red*) to furnish cofacial catalysts.

Although cofacial porphyrins are well-studied, other macrocyclic catalytically-active ligands, like salens, remain underdeveloped in the context of cofacial architectures. Mononuclear cobalt salen complexes have been used before as homogeneous oxygen reduction catalysts that operated at moderate overpotentials, but converted oxygen via the two electron pathway exclusively.\textsuperscript{19} Vanadium salen complexes have shown oxygen reduction activity at moderate overpotentials and it was suggested that a dimer forms in solution.\textsuperscript{20} Oxo-bridged salen dimers are also known to effect the transformation of O\textsubscript{2} to H\textsubscript{2}O.\textsuperscript{21} We hypothesize that cofacial salen
complexes will have the same benefits as cofacial porphyrin catalysts due to the multiple metal centers available to spread the coordination and redox demand.

A bis-functionalized salen with either 4-pyridyl or 3-pyridyl, as seen in Figure 4.9, can be assembled together with either 90° acceptors or molecular clips to obtain a cassette-like cofacial architecture. Pyridyl-functionalized salen ligands have been previously explored by Hupp.22-23 The salens pictured will be metallated with either cobalt(II) or iron(III) and the furnished assembly will be used as catalysts towards oxygen reduction.

4.5 References


