Supporting Information for

High-Potential Electrocatalytic O\textsubscript{2} Reduction with NitroxyI/NO\textsubscript{x} Mediators: Implications for Fuel Cells and Aerobic Oxidation Catalysis

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1. Experimental procedures.

**UV-visible studies of nitroxy species.** Reactions conditions employed for the UV-visible spectroscopic studies of nitroxy speciation under acidic conditions and their reactions with NO\textsubscript{x} species are provide in the figure captions associated with each experiment. UV-visible spectra were measured using a 1 cm path length Schlenk cuvette with a sidearm bulb. Solutions for spectroscopic measurements under nitrogen were deoxygenated by freeze-pump-thaw degassing. For reactions with NO\textsubscript{x} species, sodium nitrite was added as an aqueous solution to the sidearm bulb of the Schlenk cuvette, which was then evaporated under vacuum to leave a solid deposit of the desired amount of NaNO\textsubscript{2}. The reaction was initiated by tipping the solution from the cuvette into the bulb, shaking vigorously, and then tipping the solution back into the cuvette. The solution and gas in the cuvette headspace were mixed further between the acquisitions of each spectrum.

**Cyclic voltammetry studies.** Cyclic voltammetry (CV) measurements were performed at a glassy carbon electrode that was polished with alumina before each experiment. An Ag/Ag\textsuperscript{+} reference electrode and Pt wire counter-electrode were also used. At the end of each experiment, ferrocene (Fc) was added to the solution and a CV scan was taken to determine the Fc/Fc\textsuperscript{+} potential relative to the reference electrode. All measured potentials are reported relative to Fc\textsuperscript{+}. Electrolysis experiments were performed in a glass cell with a frit dividing the working and counter electrode compartments (Figure S1). The solution volume in the working electrode compartment during electrolysis experiments was 40 ml. The working electrode consisted of a block of reticulated vitreous carbon (RVC), carbon rods were used as the counter electrode, and an Ag/Ag\textsuperscript{+} reference electrode was placed near the working electrode. The immersed area of the RVC electrode (28 cm\textsuperscript{2}) was determined by capacitance comparison between it and a glassy carbon disc of known area. After each experiment, Fc was added to the solution and a CV scan was taken to determine the Fc/Fc\textsuperscript{+} potential relative to the reference electrode. Prior to electrolysis, the solution was purged with either nitrogen or oxygen and electrolysis was performed with the cell sealed under a static atmosphere of the desired gas. CV experiments utilizing NO\textsubscript{x} were performed by adding NaNO\textsubscript{2} to the electrolysis cell after gas purging and allowing the mixture to stir until dissolution of the solid was complete. For electrolysis experiments utilizing NO\textsubscript{x}, the electrolysis was begun while the NaNO\textsubscript{2} was still dissolving to prevent its decomposition before the start of the experiment.

![Figure S1. Divided cell for bulk electrolysis under N\textsubscript{2} or O\textsubscript{2}](image)
2. Synthesis of [TEMPOH₂]BF₄ and [CoTPP]BF₄.

[TEMPOH₂]BF₄: To 2 ml of CH₃CN in an ice-cooled flask were added 0.25 g of TEMPO. Once dissolved, 48 % aqueous HBF₄ was added dropwise until the solution was a distinct yellow color. An excess (~ 0.5 ml) of benzyl alcohol was added and the solution was allowed to warm to room temperature and stir overnight. After stirring with activated charcoal and filtering, the solvent was removed under vacuum. Countercurrent extraction between ethyl acetate and water was performed to remove benzaldehyde and excess benzyl alcohol. The aqueous phase was concentrated under vacuum and azeotropically dried with toluene to give the hydroxylammonium salt as an odorless white solid. Material for UV-visible spectroscopy was purified by recrystallization from an ethyl acetate solution layered under heptane to give clear, colorless prismatic crystals that were bench stable and not hygroscopic (ambient dewpoint of ca. -15 °C). The ¹H-NMR spectrum (500 MHz, CD₃CN) showed peaks at δ 9.854 (s, 1H), 9.285 (s, 1H), 1.92 - 1.72 (overlapping multiplets, 5H), 1.61 (br m, 1H), 1.392 (s, 6H), 1.371 (s, 6H). The ¹³C{¹H} NMR spectrum (126 MHz, CD₃CN) showed peaks at δ 69.195, 36.287, 27.117, 18.690, 15.095 ppm. A ¹H-¹⁵N HMBC spectrum (500 MHz, CD₃CN) gave the following correlations δ 1.91:132, 1.88:132, 1.85:132 ppm.

[CoTPP]BF₄: In a modification of the procedure by Sakurai, et al., 30 mg of cobalt (II) tetraphenylporphyrin were suspended in 30 ml of methanol. With stirring, 0.25 ml of 48 % aqueous HBF₄ was added and allowed to stir overnight. The claret-colored solution was filtered through celite and concentrated under vacuum. After addition of water, the solid was filtered and dissolved in CH₃CN. Concentration under vacuum afforded flakes of a vivid purple, iridescent solid. The ¹H-NMR spectrum (500 MHz, CD₃CN) showed peaks at δ 9.201 (s, 2H), 8.216 (m, 2H), 7.849 (m, 3H) ppm in accord with literature data. The ¹³C{¹H} NMR spectrum (126 MHz, CD₃CN) showed peaks at δ 143.141, 135.282, 134.024, 128.336, 127.251 ppm.

3. Electrolysis of TEMPO and NOₓ species under N₂.

Electrolysis experiments performed under N₂ result in stoichiometric reduction of the electroactive species present. In a representative experiment, 0.83 mmol of NaNO₂ were added after a pre-electrolysis period during which the TEMPO was reduced until no current continued to flow (Figure S2, blue trace). During the electrolysis, TEMPO catalyzed the reduction of nitrite (which is in the NO⁻ oxidation state), and 91.9 Coulombs were passed (Figure S2, red trace). This amount of charge corresponds to 0.95 mmol of electrons, or 1.1 e⁻ per nitrite, suggesting that nitrite is reduced to NO. In contrast, under oxygen, current flows for a longer time even with a lower catalyst loading (cf. the red traces in Figures S2 and S3). In the presence of O₂, the charge passed is equal to 149 e⁻ per nitrite, or the reduction of 37 equivalents of oxygen.
Figure S2. Controlled-potential electrolyses of 10 mM NaNO₂, 10 mM TEMPO, or 20 mM NaNO₂ + 10 mM TEMPO at 0.20 V vs. Fc/Fc⁺ in 9:1 CH₃CN:CF₃CO₂H with 0.5 M KPF₆ under N₂.

4. Control experiments probing the origin of catalyst deactivation.

Several control experiments were performed to probe the origin of the loss of catalytic activity during the course of the reaction. If loss of NOₓ is responsible for the decrease in activity, then addition of nitrite during the electrolysis should return the catalytic system to full (or improved) activity. This hypothesis was tested by adding the original amount of nitrite in two portions, such that the initial TEMPO/NOₓ stoichiometry is 2:1 (Figure S3). The electrolysis was performed under otherwise identical conditions, and the observed current fell to a lower value during steady-state catalysis, but the rate of decrease in activity appeared similar. Addition of the second half of the nitrite revived the catalyst to its initial level of activity. Curiously, the system showed the same break in slope and loss of activity as when the nitrite is added in one portion.

A subsequent experiment with ABNO as the catalyst and an initial ABNO:NaNO₂ ratio of 1:1 showed that addition of a second full equivalent of NaNO₂ regenerated the initial level of activity with the rapid loss of current taking place immediately (Figure S4)
Figure S3. Controlled-potential electrolyses of 1.25 mM TEMPO + 1.25 mM NaNO₂, 1.25 mM TEMPO + 0.63 mM NaNO₂ with the addition of another 0.63 mM NaNO₂ at the indicated time, at 0.20 V vs. Fc/Fc⁺ in 9:1 CH₃CN:CF₃CO₂H with 0.5 M KPF₆ all under O₂.

Figure S4. Controlled-potential electrolyses of 1.25 mM ABNO + 1.25 mM NaNO₂, or 1.25 mM ABNO + 1.25 mM NaNO₂ with the addition of another 1.25 mM NaNO₂ at the indicated time at 0.19 V (ABNO) vs. Fc/Fc⁺ in 9:1 CH₃CN:CF₃CO₂H with 0.5 M KPF₆ all under O₂.

When water is added to the TEMPO/NOₓ catalyst system, the break in slope appears at an earlier time, suggesting that water plays a role in limiting the catalyst lifetime (Figure S5). The changes and spikes in current immediately after addition of water are due to slight shifts in the position of the stirbar in the cell. Addition of trifluoroacetic anhydride, a water scavenger, to the system has no immediate effect. The subsequent addition of NaNO₂ restores activity, with a subsequent period of steady-state catalysis.
Figure S5. Controlled-potential electrolyses of 1.25 mM TEMPO + 1.25 mM NaNO₂, with the addition of 10 or 20 mM H₂O, 40 mM trifluoroacetic anhydride, and 1.25 mM NaNO₂ at the indicated time, or no added catalyst or mediator, at 0.20 V vs. Fc/Fc⁺ in 9:1 CH₃CN:CF₃CO₂H with 0.5 M KPF₆ all under O₂.

5. UV-Visible spectroscopic studies on ACT, 3-CARP, and ABNO disproportionation.

UV-visible studies similar to those performed with TEMPO (see Figure 1 of the main text) were carried out with the other three nitroxyls considered in this study: ACT, 3-CARP and ABNO. As presented below (Figures S6-S9), ACT and 3-CARP disproportionate at a slower rate and to a smaller degree relative to TEMPO.

Figure S6. UV-visible spectra of 10 mM ACT (λₘₐₓ = 460 nm, εₘₐₓ = 10.5 M⁻¹·cm⁻¹), ACT⁺ (λₗₜₜₜₜ = 472 nm, εₗₜₜₜₜ = 26.0 M⁻¹·cm⁻¹, ε₄₆₀ = 27.2 M⁻¹·cm⁻¹), and fully equilibrated acidified ACT in acetonitrile. ACT BF₄⁻ synthesized via Bobbitt's protocol.⁵
**Figure S7.** UV-visible spectra of 10 mM 3-CARP ($\lambda_{\text{max}} = 424$ nm, $\varepsilon_{\text{max}} = 6.0$ M$^{-1}$·cm$^{-1}$), 3-CARP$^+$ ($\lambda_{\text{max}} = 379$ nm, $\varepsilon_{\text{max}} = 380$ M$^{-1}$·cm$^{-1}$, $\varepsilon_{424} = 138$ M$^{-1}$·cm$^{-1}$), and fully equilibrated acidified 3-CARP in acetonitrile. 3-CARP$^+$ synthesized in situ by aerobic oxidation with acid and NaNO$_2$.

**Figure S8.** UV-visible spectra obtained following addition of trifluoroacetic acid to a 10 mM solution of ACT in acetonitrile, corresponding to the disproportionation of ACT into ACT$^+$ and ACTH. The linear fit to [ACT]$^{-1}$ (inset, $k_{\text{disp}} = 0.23$ M$^{-1}$·s$^{-1}$, [ACT$^+$]/[ACT] = 0.82 at equilibrium) incorporates data from two independent experiments. Conditions: 10 mM nitroxyl in CH$_3$CN, 130 mM TFA added at $t = 0$. 
Figure S9. UV-visible spectra obtained following addition of trifluoroacetic acid to a 10 mM solution of 3-CARP in acetonitrile, corresponding to the disproportionation of 3-CARP into 3-CARP\textsuperscript{+} and 3-CARPH. The linear fit to [3-CARP]\textsuperscript{-1} (inset, $k_{\text{disp}} = 0.1 \text{ M}^{-1}\text{s}^{-1}$, [3-CARP\textsuperscript{-}]/[3-CARP] = 0.28 at equilibrium) shows second-order kinetics. Conditions: 10 mM nitroxyl in CH\textsubscript{3}CN, 130 mM TFA added at $t = 0$.

The bicyclic nitroxyl 9-azabicyclo[3.3.1]nonane-N-oxyl (ABNO) also undergoes disproportionation in CH\textsubscript{3}CN on the addition of acid, but the reaction is much faster than with TEMPO and is complete by the time of the first spectrum (Figure S10). Similar to TEMPOH, ABNOH undergoes NO\textsubscript{x}-catalyzed aerobic oxidation (Figure S11). As with disproportionation, the NO\textsubscript{x}-catalyzed aerobic oxidation of ABNOH is faster than TEMPOH. From this result, it is possible to establish that the TEMPOH oxidation described in the main text is not limited by O\textsubscript{2} mass-transport. Although the presence of peaks at 350 - 400 nm associated with HNO\textsubscript{2} during the aerobic oxidation of ABNOH (Figure S11) suggest that the solution is not oxygen-starved, more detailed studies of the kinetics of the disproportionation and NO\textsubscript{x}-catalyzed aerobic oxidation of structurally diverse hydroxylamines and nitrooxyls are both necessary and beyond the scope of the present work.

Figure S10. UV-Vis spectra of 10 mM ABNO in acetonitrile ($\lambda_{\text{max}} = 461$ nm, $\varepsilon_{\text{max}} = 10.7 \text{ M}^{-1}\cdot\text{cm}^{-1}$). On addition of trifluoroacetic acid, disproportionation takes place. ABNO reacts quickly,
and all traces subsequent to the addition of acid overlap. Conditions: 10 mM nitroxyl in CH$_3$CN, 130 mM TFA added at time = 0, air atmosphere.

**Figure S11.** Aerobic oxidation of disproportionated ABNO catalyzed by nitrite. The initial spectrum of ABNO$^+$ with colorless ABNOH shifts to higher absorbance as more ABNO$^+$ is formed (blue - red, 1 minute scan interval). The gray points represent the expected spectrum for full conversion to ABNO$^+$ (ABNO$^+$ $\lambda_{\text{max}}$ = 437 nm, $\varepsilon_{\text{max}}$ = 28.1 M$^{-1}$·cm$^{-1}$, $\varepsilon_{461}$ = 25.4 M$^{-1}$·cm$^{-1}$). Conditions: 10 mM ABNO in CH$_3$CN with 130 mM TFA, 0.9 mM NaNO$_2$ added at time = 0, O$_2$ atmosphere, cuvette shaken between time points.

6. **Comparison of nitrite vs. nitrate as NO$_x$ sources.**

Formation of reactive NO$_x$ species NO and NO$_2$ by protonation of nitrite is straightforward. In contrast, nitrate is typically less reactive. However, under acidic, dehydrating conditions, nitrite will also react with nitrate to form NO$_2$ (Scheme 4 in the main text). The presence of TEMPO will make this activation of nitrate autocatalytic, as is seen from a longer induction period when NaNO$_3$ is used as the NO$_x$ precursor (Figure S12).

**Figure S12.** Early time period of controlled-potential electrolys of 1.25 mM TEMPO + 1.25 mM NaNO$_2$ (red trace), or 1.25 mM TEMPO + 1.25 mM NaNO$_3$ (black trace) at 0.20 V vs. Fc/Fc$^+$ in 9:1 CH$_3$CN:CF$_3$CO$_2$H with 0.5 M KPF$_6$ under O$_2$, showing the induction period observed with nitrate as the NO$_x$ source.
7. Literature rate constants of nitrooxyl and NOx reactions, and their ramifications.

Table S1. Measured rate constants associated with nitrooxyl and NOx reactions.\textsuperscript{6}

| Eq | Reaction | Rate Constant(s) | Comments | Refs. |
|----|----------|------------------|----------|-------|
| S6 | \[ \begin{array}{c} \text{N} \text{O} \text{N} \text{O} \\ + \text{CF}_3\text{CO}_2\text{H} \end{array} \xrightleftharpoons[\text{CF}_3\text{CO}_2^-]{k_6} \begin{array}{c} \text{O} \text{N} \text{O} \text{N} \\ \text{O} \text{H} \end{array} \] | $k_6 = 2.5 \text{ M}^{-1}\text{s}^{-1}$ | acetonitrile solution, excess acid | this work |
| S9 | \[ \begin{array}{c} \text{N} \text{O} \\ \text{O} \text{H} \end{array} \xrightleftharpoons{\text{NO} \text{N} \text{O}}{k_9} \begin{array}{c} \text{O} \text{N} \text{O} \\ \text{O} \text{H} \end{array} \] | $k_9 = 4.4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ | acetonitrile solution | 10 |
| S10 | \[ \begin{array}{c} \text{N} \text{O} \\ \text{O} \text{H} \end{array} + \text{NO}_2 \xrightleftharpoons{\text{NO} \text{N} \text{O}}{k_{10}} \begin{array}{c} \text{O} \text{N} \text{O} \\ \text{O} \text{H} \end{array} + \text{NO}_2^- \] | $k_{10} = 7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ | aqueous phosphate buffer | 14 |
| S11 | \[ \begin{array}{c} \text{N} \text{O} \\ \text{O} \text{H} \end{array} + \text{NO}_2 \xrightleftharpoons{\text{NO} \text{N} \text{O}}{k_{11}} \begin{array}{c} \text{O} \text{N} \text{O} \\ \text{O} \text{H} \end{array} + \text{HNO}_2 \] | $k_{11} < 1 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ | aqueous phosphate buffer, NO\textsubscript{2} decomposition interferes | 16 |
| S12 | \[ \text{NO}_2 + \text{NO}_2 \xrightleftharpoons{\text{NO} \text{N} \text{O}}{k_{12}} \text{NO}_2^+ + \text{NO}_2 \] | $k_{12} = 9.6 \text{ M}^{-1}\text{s}^{-1}$ | best estimate | 7,13 |
| S13 | \[ \text{2HNO}_2 \xrightleftharpoons{\text{H}_2\text{O} + \text{NO}_2 + \text{NO}}{k_{13}} \text{H}_2\text{O} + \text{NO}_2 + \text{NO} \] | $k_{13} = 10 \text{ M}^{-1}\text{s}^{-1}$ | acidic anaerobic aqueous solution | 18,19 |
| S14 | \[ \text{2NO} + \text{O}_2 \xrightleftharpoons{\text{2NO}_2}{k_{14}} \text{2NO}_2 \] | $k_{14} = (2.2 \times 10^8 \text{ M}^{-2}\text{s}^{-1}$ | relatively medium-independent rate | 8 |
| S15 | \[ \text{NO}_2 + \text{NO}_2 \xrightleftharpoons{\text{N}_2\text{O}_4}{k_{15}} \text{N}_2\text{O}_4 \] | $k_{15} = 4.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ | aqueous solution, $K_{15} = 3.3 \times 10^4$ in CH\textsubscript{3}CN | 9,18,19 |
| S16 | \[ \text{H}_2\text{O} + \text{N}_2\text{O}_4 \xrightleftharpoons{\text{HNO}_2 + \text{NO}_3^- + \text{H}^+}{k_{16}} \text{HNO}_2 + \text{NO}_3^- + \text{H}^+ \] | $k_{16} = 10^3 \text{ M}^{-2}\text{s}^{-1}$ | acidic aqueous solution | 18,19,20 |

The electrode reaction for oxidation of TEMPO is fast ($k_3$ in Scheme 4 in the main text), consistent with the rapid electron self-exchange reaction of TEMPO$^\text{7-}$TEMPO observed previously by EPR line broadening.\textsuperscript{10,12} This feature may be contrasted with the poor electrode reduction of NO\textsubscript{2}, which is explained by slow NO\textsubscript{2}/nitrite electron self-exchange (eq S12).\textsuperscript{13} Nevertheless, the oxidation of TEMPO by NO\textsubscript{2} to produce an oxoammonium nitrite (eq S10) is a facile thermodynamically favorable reaction.\textsuperscript{14} The much faster reduction of NO\textsubscript{2} by TEMPO compared to reduction at the electrode may be explained by the involvement of an inner-sphere mechanism for the TEMPO/NO\textsubscript{2} process.\textsuperscript{15} Oxidation of TEMPOH by NO\textsubscript{2} is also rapid (eq S11), although previous studies suggest that it is at least 3 orders of magnitude slower than the oxidation of TEMPO.\textsuperscript{16,17}

Protonolysis of nitrite to form water, NO, and NO\textsubscript{2} is understood to proceed as shown in Scheme 4 in the main text, but the best available literature data we are aware of give only a composite rate for this process (eq S13; $k_c$ and $k_d$ in Scheme 4 in the main text).\textsuperscript{18,19} This reaction sequence is disfavored in aqueous solution, but the present experiments feature low water and NO concentrations that will favor the forward reaction. The rapid and irreversible reaction of NO with O\textsubscript{2} (eq S14) also will drive the process forward. This reaction has been studied in great depth and is relatively medium-independent.\textsuperscript{8} As the reaction proceeds, trifluoracetate and water will build up in the reaction medium. Dimerization of NO\textsubscript{2} to N\textsubscript{2}O\textsubscript{4} and hydrolysis of N\textsubscript{2}O\textsubscript{4} (eqs S15, S16) is the process that we believe ultimately limits the catalyst lifetime in this system.\textsuperscript{18-21}
8. Justification of NO as the lowest NO\textsubscript{x} oxidation state in the catalytic reaction.

Some NO\textsubscript{x}-mediated alcohol oxidations are proposed to involve a 2-electron reduction from the nitrite oxidation state to HNO\textsuperscript{22}.\textsuperscript{23} In these oxidations, a nitrite ester is formed that eliminates HNO to give the carbonyl product. In contrast, the oxidation of TEMPO or TEMPOH by NO\textsubscript{x} can be expected to have NO as the lowest NO\textsubscript{x} oxidation state. The O-H bond strength of TEMPOH is \(\sim23\) kcal/mol higher than the N-H bond strength of HNO, implying that NO cannot abstract H-atoms from TEMPOH.\textsuperscript{24,25,26} Direct electrochemical reduction of NO\textsubscript{x} to HNO is also not relevant at the potentials used for this electrocatalytic reduction.\textsuperscript{27} This is fortunate, since HNO must be trapped by an oxidant before it undergoes a very facile dimerization and dehydration to N\textsubscript{2}O, which is kinetically inert under ambient conditions.\textsuperscript{26} This difference in nitrogen oxidation states accessed by different catalytic O\textsubscript{2} reduction mechanisms, as well as the reductive trapping of NO\textsubscript{2} noted above, may explain the enhanced stability of combined nitroxy/NO\textsubscript{x} aerobic oxidation reactions\textsuperscript{28} as well as the electrocatalytic results of the present study.

9. Self-exchange rate and electrode exchange current conversion - worked examples.

The electrode reaction for oxidation of TEMPO is observed to be reversible by CV (cf. Figure 2 in the main text). The electron exchange reaction of TEMPO and substituted nitroxyls (eq S1) has been measured by EPR line broadening,\textsuperscript{10} and is also observed to be relatively fast. In contrast, the direct reduction of NO\textsubscript{2} at the electrode is observed to be slow, which is correlated with the slowness of the NO\textsubscript{2} - nitrite electron exchange reaction (eq S2).\textsuperscript{13}

\[
\text{NO}^+ + \text{NO}^+ \rightarrow \text{NO} + \text{NO}^+ \\
k = 4.4 \times 10^7 \text{M}^{-1}\text{s}^{-1} - 2.6 \times 10^8 \text{M}^{-1}\text{s}^{-1} \\
\text{(S1)}
\]

\[
\text{NO}_2 + \text{NO}_2^{-} \rightarrow \text{NO}_2^{-} + \text{NO}_2 \\
k = 10^{-2} - 600 \text{M}^{-1}\text{s}^{-1} \\
\text{(S2)}^7
\]

Given an experimentally determined self-exchange rate for a reaction, such as S1, it is possible to estimate what the exchange current of that species at an electrode would be. The exchange current corresponds to the current of one half-reaction of an electrochemical equilibrium, and is an important kinetic parameter, e.g., in the Tafel equation (eq S3). A higher exchange current indicates that the redox reaction has a lower barrier and will have a more dynamic equilibrium.

\[
j = j_{ex} e^{-\alpha F(E - E^*)/RT} \\
\text{(S3)}
\]

The conversion from self-exchange to electrochemical rates takes advantage of the fact that the electrode can act as an imperturbable sink or source of electrons while the reorganization of the solution species in response to redox changes is the same.\textsuperscript{11} Thus, the barrier height is halved at the electrode because only one solute molecule is in the reaction. Converting rates is then possible via eq S4, where \(k_{\text{electrode}}\) is the rate at which molecules react when striking a unit area of electrode and \(k_{\text{se}}\) is the second-order self-exchange rate constant.
The $Z$ terms are the collision frequencies of the reacting molecules with either a unit area of the electrode or each other, and have the same units as their respective rate constants. For self-exchange reactions, $Z_{se}$ is the ca. $10^{11}$ M$^{-1}$s$^{-1}$ from Eyring theory, while Randles has two estimates for the electrode collision frequency $Z_{electrode}$ that are ca. $10^{4}$ cm$^{-1}$s$^{-1}$. The most conceptually straightforward electrode collision factor estimate is obtained by multiplying the frequency factor, $kT/h$, by the fraction of a unit volume that is in the inner Helmholz layer adjacent to a unit area of the electrode surface, since only those molecules colliding with the electrode can react. The units for the electrochemical rate constant are typically in cm$^{-1}$s$^{-1}$. As a result, exchange current densities in units of A·cm$^{-2}$ can be readily calculated from Eq. S5 if the concentration $C$ is expressed in mol·cm$^{-3}$. The current density will be in mA·cm$^{-2}$ if the concentration is in mol·l$^{-1}$.

$$j_{ex} = F/k_{electrode}C$$  \hspace{1cm} (S5)

Returning now to reaction S1, whose rate constant $k_{se}$ can be approximated as $10^{8}$ M$^{-1}$s$^{-1}$, one can estimate its $k_{electrode}$ as ~300 cm$^{-1}$s$^{-1}$. Assuming a 10 mM solution, an exchange current density of ~300 A·cm$^{-2}$ is calculated. In contrast, using the best value of 10 M$^{-1}$s$^{-1}$ for the NO$_2$/NO$_2^-$ reaction in eq S2, a $k_{electrode}$ of ~0.1 cm$^{-1}$s$^{-1}$ is estimated, with an exchange current density of ~0.1 A·cm$^{-2}$. While the quantitative values derived here are rather crude estimates and are influenced by mass transport from the stirred bulk solution to the electrode, the difference of $k_{electrode}$ between the two species is significant and is believed to account for the importance of TEMPO as an electron transport mediator.

10. Electrocatalytic O$_2$ reduction with CoTPP.$^{29}$

A solution of 0.5 M KPF$_6$ in 9:1 CH$_3$CN:CF$_3$CO$_2$H was purged with nitrogen until CV showed no sign of the irreversible single-electron reduction of O$_2$. To this solution was added 1 mM of CoTPP$^+\text{BF}_4^-$, which was allowed to dissolve with stirring. Subsequent CV scans showed a quasi-reversible feature at ~ -100 mV vs Fe/Fe$^+$. On purging the system with air, this feature became a slowly-rising catalytic wave with an onset at the same potential (Figure S13).

![Figure S13. CV scans at 100 mV/s of 1 mM CoTPP$^+$ in 9:1 CH$_3$CN:CF$_3$CO$_2$H with 0.5 M KPF$_6$ under N$_2$ (black trace) and O$_2$ (red trace).](attachment:image.png)
11. H⁺/H₂ potential measurement and overpotential estimation.

It is possible to determine the H⁺/H₂ potential of a solution through open-circuit potential measurements at a Pt electrode. Using a recently reported protocol, we measured the H⁺/H₂ potential of an acetonitrile solution containing 1 M each of TFAH, NaTFA, and water under 1 atm H₂ (local atmospheric pressure of 752 mm Hg, correction to 1 atm < 1 mV). These conditions were chosen to give a medium that has stable, well-defined thermodynamics for both the H⁺/H₂ and O₂/H₂O equilibria. A stable open-circuit potential was observed, and this potential was corrected to be versus Fc/Fc⁺ by adding ferrocene and performing CV at a second, glassy carbon working electrode (Figure S14). The observed H⁺/H₂ potential of -0.61 V vs. Fc/Fc⁺ corresponds to an O₂ reduction potential of +0.62 V, assuming that the O₂ reduction potential is 1.23 V above the H⁺/H₂ potential in this medium.

**Figure S14.** OCP vs. Fc/Fc⁺ of 1 M each of TFAH, NaTFA, and H₂O in CH₃CN under 1 atm H₂. The black line shows the average OCP of -0.609 mV vs. Fc/Fc⁺, inset shows the experimental set-up.

**Figure S15.** CV of 1 mM ACT (black trace) at 10 mV/s in CH₃CN with 1 M each of TFAH, NaTFA, and H₂O under N₂. Addition of 5 mM NaNO₂ led to formation of ACT⁺ and the development of a catalytic wave (red trace). A blank scan in this electrolyte (orange trace), and 5 mM NaNO₂ (blue trace), each under oxygen show no current. The potential of an electrolysis experiment is shown in blue, arrows indicate the start point of each CV scan.
CV measurements were also performed on ACT in the absence and presence of NaNO₂ in this medium (Figure S15). An \( E_{1/2} \) of 0.322 V vs. Fc/Fc⁺ was observed, along with little evidence of disproportionation. A catalytic wave appeared at a similar potential on the addition of NaNO₂. Under O₂, but otherwise similar conditions, a steady-state ORR electrolysis experiment was then performed with the ACT/NO₂-mediator system under these conditions at an applied potential of + 0.321 V vs. Fc/Fc⁺. The current was somewhat lower than that observed under the unbuffered conditions described above; however, >26 turnovers with respect to ACT were observed over a 4 hour period.

12. Potentials of Porphyrin and Corrole Molecular ORR Catalysts.

Selected porphyrin, corrole, and enzyme active site mimic complexes discussed in the main text are reproduced below in Table S2 along with their ORR \( E_{1/2} \) potentials and redox potential references as originally reported. The reader who just can't get enough is referred to several review articles on these complexes and references therein.\(^{31}\)

### Table S2. Selected Molecular ORR Catalysts Exhibiting Various Selectivities for Reduction of O₂ to Water (reported potentials converted to Fc⁺/Fc reference to facilitate comparison).\(^{32}\)

| Compound   | Conditions          | reported \( E_{1/2} \) vs. ref. | \( \eta \) (V) | \( E_{1/2} \) vs. \( \text{Fc/Fc}^+ \) | \( \text{H}_2\text{O}_2/\text{H}_2\text{O} \) selectivity | Refs. |
|------------|---------------------|-------------------------------|--------------|--------------------------|---------------------------------|-------|
| FeTPP      | on graphite, 0.1 M aq. HClO₄ | -0.04 V vs. SSCE             | 0.96         | -424 mV                  | 15 % \( \text{H}_2\text{O}_2 \) | \(^{33}\) |
| CoTPP      | in CH₂CN w/ 0.02 M HClO₄, in 9:1 CH₂CN:CF₃CO₂H | 0.35 V vs. SCE, -0.1 V vs. \( \text{Fe/Fc}^+ \), 0.27 V vs. SCE | 0.71, 0.71 | -30 mV, -100 mV, -110 mV | mostly \( \text{H}_2\text{O}_2 \), N/D, > 60 % \( \text{H}_2\text{O}_2 \) | \(^{34c}\) this work, \(^{34b}\) |
| FeTPFPFP⁺ | on graphite, 0.5 M aq. H₂SO₄ | ~ 0.35 V vs. NHE             | 0.88         | ~280 mV                  | < 2 % \( \text{H}_2\text{O}_2 \) | \(^{35}\) |
| CoTMPyP⁺   | 0.3 mM in 0.1 M aq. H₂SO₄ | ~ 0.2 V vs. Ag/AgCl          | 0.77         | ~230 mV                  | 100 % \( \text{H}_2\text{O}_2 \) | \(^{36}\) |
| FeToCPP⁺   | 0.2 mM in CH₂CN w/ 0.02 M HDMF⁺ | ~400 mV vs. \( \text{Fe/Fc}^+ \) | ~400 mV      | < 2 % \( \text{H}_2\text{O}_2 \) | | \(^{37}\) |
| Co₂(FTF₄) | on graphite, 1 M aq. TFAH   | 0.47 V vs. SCE              | 0.52         | 90 mV                    | < 1 % \( \text{H}_2\text{O}_2 \) | \(^{34a}\) |
| CoFe(FTF₄) | on graphite, 1 M aq. TFAH   | 0.25 V vs. SCE              | 0.74         | -130 mV                  | mostly \( \text{H}_2\text{O}_2 \) | \(^{34a}\) |
| Compound                     | Surface                  | pH       | Potential vs. Reference | Current vs. Reference | Percentage H₂O₂ | Notes                      |
|------------------------------|--------------------------|----------|-------------------------|-----------------------|-----------------|----------------------------|
| CoAl(FTF4)                   | on graphite, 1 M aq. TFAH |          | 0.22 V vs. SCE          | -160 mV              | mostly H₂O₂     | 34a                        |
| CuFe(TBTrP)                 | on graphite, 0.025 M aq. |          | ~250 mV vs. NHE         | ~380 mV               | 20 % H₂O₂      | 38a                        |
| related heme-Cu analogues    | on graphite, 0.5 M aq.   |          | 0.43 V vs. SCE          | 50 mV                | < 8 % H₂O₂      | 34b                        |
| related heme-Cu analogues    | on graphite, 0.5 M aq.   |          | 0.46 V vs. SCE          | 80 mV                | < 8 % H₂O₂      | 34b                        |
| related heme-Cu analogues    | on graphite, 0.5 M aq.   |          | 0.37 V vs. Ag/AgCl      | -60 mV               | 20 % H₂O₂      | 34d                        |
| related heme-Cu analogues    | on graphite, 0.5 M aq.   |          | 0.38 V vs. Ag/AgCl      | -50 mV               | 28 % H₂O₂      | 34d                        |
| CoCuDPA                      | on graphite, 0.1 M aq. TFAH |          | ~0.25 V vs. SCE         | ~130 mV              | ~100 % H₂O₂     | 39                         |
| FeFeDPA                      | on graphite, 0.1 M aq. TFAH |          | ~0.1 V vs. SCE          | ~280 mV              | ~0 % H₂O₂      | 39                         |
| CoFeDPA                      | on graphite, 0.1 M aq. TFAH |          | ~0.175 V vs. SCE        | ~205 mV              | ~0 % H₂O₂      | 39                         |
| CoHCX1-CO₂H                  | on graphite, 0.5 M aq. H₂SO₄ |          | 0.54 V vs. RHE          | 69 mV                | 45 % H₂O₂      | 40                         |
| CoHCX1-CO₂Me                 | on graphite, 0.5 M aq. H₂SO₄ |          | 0.58 V vs. RHE          | -                    | 70 % H₂O₂      | 40                         |
| (Me₂P₂Cor)Co                | on graphite, 1 M aq. HClO₄ |          | 0.38 V vs. SCE          | 0 mV                 | 55 % H₂O₂      | 41                         |
| (PCA)Co₂                    | on graphite, 1 M aq. HClO₄ |          | 0.47 V vs. SCE          | 90 mV                | 5 % H₂O₂       | 41                         |
| (BCA)Co₂                    | on graphite, 1 M aq. HClO₄ |          | 0.39 V vs. SCE          | 10 mV                | 30 % H₂O₂      | 41                         |
| related porphyrin/corrole dyads | on graphite, 1 M aq. HClO₄ |          | 0.35 - 0.47 V vs. SCE   | -30 - 90 mV          | 5 - 80 % H₂O₂  | 41                         |
| Cu₂Phen₇e                    | "clicked" on graphite, 0.1 M acetate buffer, pH 4.8 |          | ~50 mV vs. NHE          | ~580 mV              | 20 % H₂O₂      | 42                         |
| CuDPicA₂, Cu₂DPicA₄f         | on carbon, Britton-Robinson buffer, pH 1 - 13 |          | 0.25 - 0.65 V vs. RHE   | ~0.58                | 2.5 - 10 % H₂O₂ | 43                         |
| [(TPA)M²⁺]n⁺               | on carbon, 0.1 M aq. HClO₄ |          | ~0.3 V vs. RHE          | ~0.93                | 0 - 28 % H₂O₂  | 44                         |

a Potential from Fig. 6 in the original report. b Potential from Fig. 5 in the original report. c Potential from Fig. 2 in the original report. d Potential from Fig. 1 in the original report. e Potential from Fig. 4 in the original report, Phen = 1,10-phenanthroline. f Potential from Fig. 5 in the original report, DPicA = 2,2'-dipicolylamine, DPicA₂ = bis-(2,2'-dipicolylamine) with various linkers. g Potential from Fig. 7 in the original report, TPA = tris(2-pyridylmethyl)amine.
13. References.

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