

An Easily Prepared Monomeric Cobalt(II) Tetrapyrrole Complex that Efficiently Promotes the $4e^-/4H^+$ Peractivation of O_2 to Water

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ABSTRACT: The selective $4e^-/4H^+$ reduction of dioxygen to water is an important reaction that takes place at the cathode of fuel cells. Monomeric aromatic tetrapyrroles (such as porphyrins, phthalocyanines, and corroles) coordinated to Co(II) have been considered as oxygen reduction catalysts due to their low cost and relative ease of synthesis. However, these systems have been repeatedly shown to be selective for O_2 reduction by the less desired $2e^-/2H^+$ pathway to yield hydrogen peroxide. Herein, we report the initial synthesis and study of a Co(II) tetrapyrrole complex based upon a *non-aromatic* isocorrole scaffold that is competent for $4e^-/4H^+$ ORR. This Co(II) 10,10-dimethyl isocorrole (**Co[10-DMIC]**) is obtained in a just four simple steps and excellent yield from a known dipyrromethane synthon. Evaluation of the steady state spectroscopic and redox properties of **Co[10-DMIC]** against those of Co(II) porphyrin (**[Co(TPFPP)]**) and corrole (**[Co(TPFPC)(PPh₃)]**) homologs demonstrated that the light harvesting and electrochemical properties of the isocorrole are distinct from those displayed by more traditional aromatic tetrapyrroles. Further, investigation of the ORR activity of **Co[10-DMIC]** using a combination of electrochemical and chemical reduction studies revealed that this simple, unadorned monomeric Co(II) tetrapyrrole is ~85% selective for the $4e^-/4H^+$ reduction of O_2 to H_2O over the more kinetically facile $2e^-/2H^+$ process that delivers H_2O_2 . By contrast, the same ORR evaluations conducted for the Co(II) porphyrin and corrole homologs demonstrated that these traditional aromatic systems catalyze the $2e^-/2H^+$ conversion of O_2 to H_2O_2 with near complete selectivity. Despite being a simple, easily prepared, monomeric tetrapyrrole platform, **Co[10-DMIC]** supports an ORR catalysis that has historically only been achieved using elaborate porphyrinoid-based architectures that incorporate pendant proton-transfer groups, ditopic molecular clefts, or which impose cofacially oriented O_2 binding sites. Accordingly, **Co[10-DMIC]** represents the first simple, unadorned, monomeric metalloisocorrole complex that can be easily prepared and which shows a privileged performance for the $4e^-/4H^+$ peractivation of O_2 to water as compared to other simple Co(II) tetrapyrroles.

The combustion of fossil fuels to power humankind's activities has brought about an exponential rise in atmospheric carbon dioxide concentrations, which is linked to climate change. Fossil fuels remain the major source of energy that powers our society¹⁻⁴ and there is an urgent need to increase our planet's capacity to better harness, store, and utilize renewable energy inputs. Small molecule activation chemistry provides an opportunity to develop improved carbon-neutral energy schemes. For example, the wide-spread transition from conventional fuels to H_2 generated via the renewable splitting of H_2O may be facilitated through improvements in fuel cell design,^{5,6} which is predicated, in part, on the development of efficient catalysts for the oxygen reduction reaction (ORR) that are not based on expensive and scarce metals such as platinum.⁷⁻⁹

Inspired by the active site of cytochrome *c* oxidase (CcO), which is a heme protein that proficiently drives the $4e^-/4H^+$ reduction of O_2 to H_2O (Figure 1, red reaction),¹⁰ the inorganic and small molecule activation communities have devoted significant energy toward the

development and study of cobalt(II) tetrapyrrolic macrocycles as ORR catalysts. However, simple monomeric metalloporphyrinoids (Figure 1) such as Co(II) phthalocyanines¹¹, Co(II) porphyrins¹²⁻¹⁴ and Co(II) corroles¹⁵⁻¹⁷ do not mimic the ORR activity of CcO and instead promote the less exothermic ($E^\circ = 0.69$ V), but kinetically more facile $2e^-/2H^+$ O_2 activation pathway to deliver H_2O_2 (Figure 1, blue reaction).^{18,19} To realize $4e^-/4H^+$ ORR activity ($E^\circ = 1.23$ V), more sophisticated tetrapyrrole constructs that include ditopic molecular clefts have generally been required.²⁰ Several such systems are highlighted in red in Figure 1, which include "face-to-face" cofacial porphyrins²¹⁻²⁴ and closely related pillared^{20,25-29} and "pacman" assemblies.^{30,31} Subsequent work showed that porphyrins and corroles adorned with pendant protonic functionalities over the face of the macrocycle (also highlighted in red in Figure 1) can support improved selectivity for reduction of O_2 to H_2O over H_2O_2 .³²⁻³⁸

In addition to the systems highlighted above, several other platforms have been developed as selective $4e^-/4H^+$

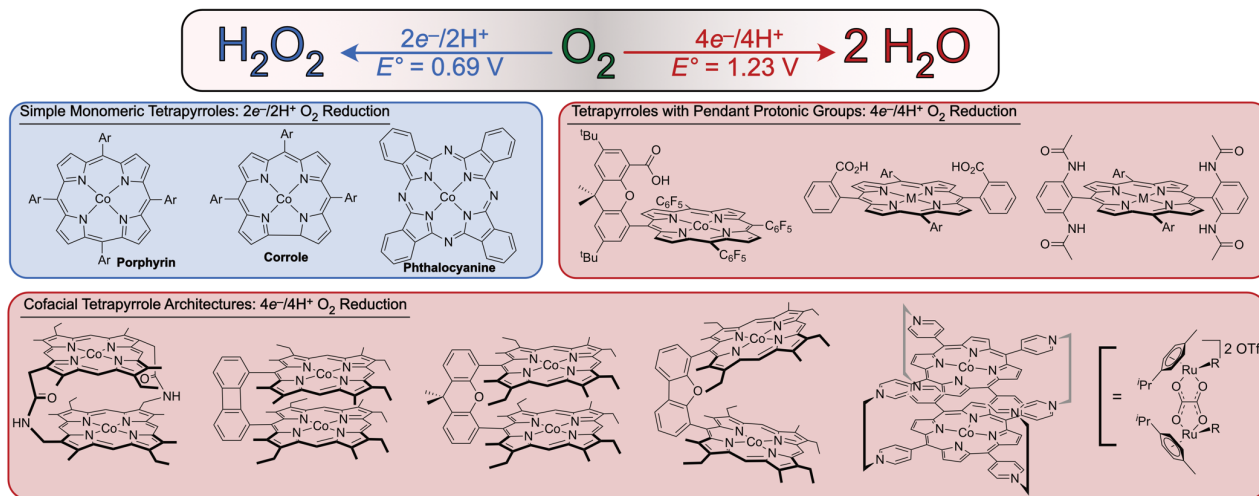


Figure 1. Balanced reactions for $2\text{e}^-/2\text{H}^+$ (blue) versus $4\text{e}^-/4\text{H}^+$ (red) O_2 activation pathways to generate H_2O_2 and H_2O , respectively. Presented below the O_2 activation pathways is an overview of unadorned monomeric aromatic tetrapyrroles that promote $2\text{e}^-/2\text{H}^+$ oxygen reduction (highlighted in blue) and more elaborate tetrapyrrole platforms that can catalyze $4\text{e}^-/4\text{H}^+$ ORR (highlighted in red).

ORR catalysts, including Schiff base calixpyrrole macrocycles^{39–41} and mixed cofacial corrole–porphyrin complexes.^{25,42,43} However, all of these elaborate architectures, many of which are illustrated in Figure 1, have engineered ditopic molecular clefts, which are considered to be critical to the enhanced $4\text{e}^-/4\text{H}^+$ ORR activity that these systems support as compared to that for simple unfunctionalized monomeric porphyrinoids (Figure 1).¹⁸

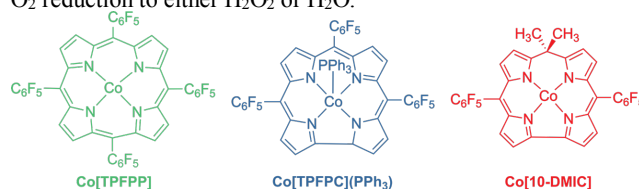
Although cofacial porphyrinoid complexes and tetrapyrroles with properly positioned acid/base groups can mimic CcO, preparation of these systems generally requires lengthy multistep syntheses and arduous chromatography,^{31,32,44} which complicates widespread study and/or adoption of such platforms for ORR applications. Cook and coworkers have utilized a thoughtful self-assembly strategy to construct cofacial prisms built from monomeric Co(II) porphyrins and “molecular clips”.⁴⁵ The coordination-driven approach to prepare the cofacial prism of Figure 1 obviates the complicated syntheses needed to generate other cofacial porphyrinoids and delivers highly selective platforms for ORR catalysis.^{46,47} The self-assembly approach requires the “molecular clips” to be based on kinetically inert ions such that eight Ru(II) centers are used for the construction of each catalytically active prism, which increases the cost associated with their fabrication/use.

Multiple decades of impressive synthetic efforts to deliver sophisticated porphyrinoid complexes capable of $4\text{e}^-/4\text{H}^+$ ORR and the thoughtful strategies to leverage self-assembly to streamline generation of active O_2 reduction catalysts have been undertaken. A major driver for these efforts has been *the general consensus that simple monomeric aromatic tetrapyrrole complexes (i.e., the porphyrin, corrole and phthalocyanine frameworks of Figure 1) do not competently catalyze $4\text{e}^-/4\text{H}^+$ ORR.*^{18–20,24,48}

Recent work has been aimed at development of *non-aromatic* tetrapyrrole scaffolds (e.g. phlorins,^{49–56} biladienes,^{57–60} and isocorroles^{61–67}) that include an sp^3 -hybridized *meso*-carbon and which support unique photo-physical and multielectron redox properties. These non-traditional tetrapyrroles provide alternate platforms to consider for ORR and other small molecule activation processes and may offer distinct reactivity profiles and catalytic activities.

In recent years, our lab has elaborated the synthesis, coordination chemistry, photophysics and redox chemistry of the 10,10-dimethyl-5,15-dipentafluorophenylbiladiene (**DMBill**).⁶⁸ Herein we report that metalation of **DMBill** with Co(II) followed by oxidation of the resulting **Co[DMBill]** complex yields the corresponding Co(II) 10,10-dimethyl isocorrole (**Co[10-DMIC]**) shown in Chart 1 in outstanding yield. Evaluation of **Co[10-DMIC]** as a catalyst for ORR using a combination of hydrodynamic voltammetry and chemical reduction studies reveal that this simple, unadorned, monomeric Co(II) tetrapyrrole readily promotes the $4\text{e}^-/4\text{H}^+$ reduction O_2 to H_2O with efficacy that is comparable or better to that observed for most of the ditopic systems of Chart 1. Comparison of the ORR performance of **Co[10-DMIC]** against the O_2 reduction ability of the homologous aromatic Co(II) porphyrin (cobalt 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin [**Co(TPFPP)**]) and corrole (cobalt 5,10,15-tris(pentafluorophenyl)corrole triphenylphosphine [**Co(TPFPC)(PPh₃)**]),⁶⁹ (Chart 1),

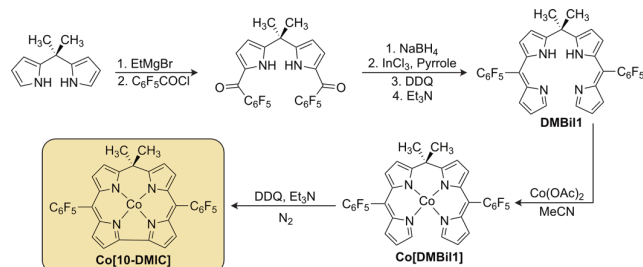
Chart 1. Monomeric Co(II) tetrapyrroles assessed as catalysts for O_2 reduction to either H_2O_2 or H_2O .



highlight the privileged catalytic properties of the non-aromatic isocorrole based platform for O₂ activation.

Results and Discussion

The Co(II) dimethylisocorrole complex (**Co[10-DMIC]**) was prepared in high yield as outlined in Scheme 1 and as described in the Supporting Information. Briefly, the 10,10-dimethylisocorrole scaffold was generated upon metalation and oxidation of the oligo-tetrapyrrole 10,10-dimethyl-5,15-dipentafluorophenyl-biladiene (**DMBil1**).⁶⁸ The biladiene synthon was readily synthesized in just two steps from 5,5'-dimethyldipyrrolemethane.⁷⁰ Metalation of **DMBil1** with Co(OAc)₂ to deliver **Co[DMBil1]** followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) delivered **Co[10-DMIC]** in 85% yield from the **DMBil1** ligand.



Scheme 1. Synthetic routes employed for the synthesis of **Co[10-DMIC]**.

X-ray quality single crystals of **Co[10-DMIC]** were obtained by slow evaporation of a concentrated CH₃CN/Et₂O (1:5) solution. The solid-state structure of this isocorrole complex is shown in Figure 2. Two **Co[10-DMIC]** molecules are contained within the crystalline asymmetric unit; one of the two **Co[10-DMIC]** complexes bears an axial CH₃CN ligand and the other exists as the parent square-planar Co(II) tetrapyrrole. Both these structures are shown in Figure S1, and crystallographic parameters and structural metrics are provided in Table S1. The structure of the isocorrole complex lacking the axial CH₃CN is shown in Figure 1, which illustrates how the Co(II) center lies within the plane of the 10-DMIC

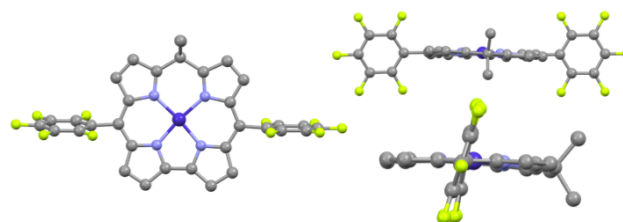


Figure 2. Solid-state structure of **Co[10-DMIC]** shown from the top down (left) and in profile (right). All hydrogen atoms and disordered solvent molecules have been omitted for clarity. More crystallographic data are presented in the Supporting Information.

tetrapyrrole. Although the Co(II) center lies within the plane of the N4 core of the isocorrole, the coordination environment is not strictly square planar, as the bond lengths between Co(II) and the two pyrrole nitrogen atoms bridged by the *sp*³-hybridized *meso*-carbon (N1 and N4) are 1.902 Å and 1.906 Å, which are longer than the distances between Co(II) and the nitrogens (N2 and N3) of the pyrroles that are directly fused (1.879 Å and 1.873 Å). We note that a similar deviation from rigorous square planar coordination has also been observed for highly brominated isocorrole complexes of Co(II)⁶⁷ and Pd(II).⁷¹ The two ancillary pentafluorophenyl groups of **Co[10-DMIC]** are canted by 82.66° and 76.07° relative to the tetrapyrrole framework.

The photophysical and electrochemical properties of **Co[10-DMIC]** were evaluated against those of the homologous Co(II) porphyrin (**Co[TPFPFPP]**) and corrole (**Co[TPFPFPP](PPh₃)**) complexes. UV-vis absorption spectra recorded for **Co[10-DMIC]**, **Co[TPFPFPP]**, and **Co[TPFPFPP](PPh₃)** are shown in Figure 3a. Compared with the homologous porphyrin (**Co[TPFPFPP]**) and corrole (**Co[TPFPFPP](PPh₃)**) complexes, **Co[10-DMIC]** displays more intense Soret and Q-band absorbances at λ_{abs} = 429 nm (50,365 M⁻¹cm⁻¹) and 719 nm (10,416 M⁻¹cm⁻¹), respectively. Both the Soret and Q-band absorbances are red shifted relative to those observed for **Co[TPFPFPP]** and **Co[TPFPFPP](PPh₃)**. The absorbance features resolved for **Co[10-DMIC]** are reminiscent of

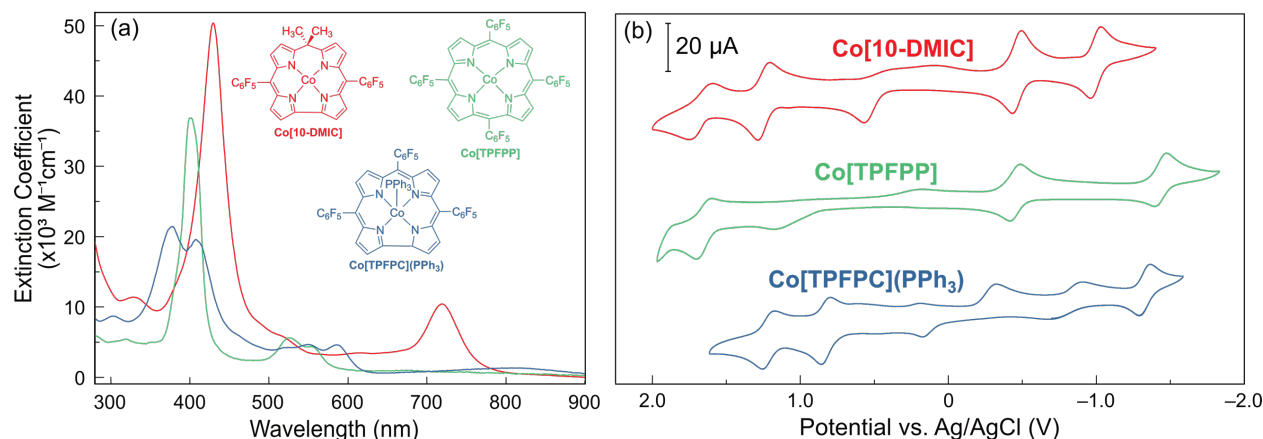


Figure 3. (a) UV-vis absorption spectra collected for **Co[10-DMIC]** (red), **Co[TPFPFPP]** (blue) and **Co[TPFPFPP](PPh₃)** (green) in THF at 298 K under N₂. (b) Cyclic voltammograms recorded for **Co[10-DMIC]** (red), **Co[TPFPFPP]** (blue) and **Co[TPFPFPP](PPh₃)** (green) at a scan rate of 100 mV/s in anhydrous acetonitrile containing 0.1 M TBAPF₆ under N₂.

those previously described for other metalloisocorrole complexes of copper, nickel, and palladium.^{61,66,67}

Cyclic voltammetry (CV) and differential pulsed voltammetry (DPV) experiments were conducted in anhydrous acetonitrile containing 0.1 M TBAPF₆ as supporting electrolyte under N₂ atmosphere, for each of the above tetrapyrroles. The resulting CVs are shown in Figure 3b with DPVs being reproduced in Figure S2. The apparent redox potentials for each of these compounds as judged by their DPV data are listed in Table S2.

The CV results obtained for both **Co[TPFPF]** and **Co[TPFPC](PPh₃)** are in agreement with those disclosed in previous studies.^{48,69,72} All potentials cited herein are referenced relative to Ag/AgCl. The Co^{III/II} couple for **Co[10-DMIC]** ($E = 1.028$ V) is observed at similar potentials as compared to that for **Co[TPFPF]** ($E = 1.029$ V), but is more positive than that of **Co[TPFPC](PPh₃)** ($E = -0.253$ V). **Co[10-DMIC]** also displays two reduction waves ($E_{red(1)} = -0.620$ V and $E_{red(2)} = -0.972$ V) that can be ascribed to reduction of the tetrapyrrole core with some metal-ligand mixing.^{66,73} While the first reduction potential is similar to those observed for the corresponding waves for the homologous porphyrin complex, the second tetrapyrrole reduction wave is observed at a significantly more positive potential for the Co(II) isocorrole as compared to that for **Co[TPFPF]** ($E_{red(2)} = -1.435$ V) and **Co[TPFPC](PPh₃)** ($E_{red(2)} = -1.297$ V) vs Ag/AgCl). In addition, **Co[10-DMIC]** showed two quasi-reversible oxidations ($E_{ox(1)} = 1.844$ V; $E_{ox(2)} = 1.464$ V vs Ag/AgCl). These oxidation potentials are not as positive as the corresponding processes for **Co[TPFPF]** ($E_{ox(1)} = 1.845$ V; $E_{ox(2)} = 1.569$ V vs Ag/AgCl), but are more positive than those observed for **Co[TPFPC](PPh₃)** ($E_{ox(1)} = 1.215$ V; $E_{ox(2)} = 0.821$ V).

Having characterized the basic physical properties of **Co[10-DMIC]**, the ORR activity supported by this monomeric tetrapyrrole was evaluated against that of the homologous Co(II) porphyrin and corrole. Each of the Co(II) tetrapyrroles of Chart 1 were immobilized within a catalyst ink on a rotating ring disc electrode (RRDE) and evaluated as ORR catalysts using voltammetric methods. The tetrapyrrole catalyst inks consisted of suspended multi-wall carbon nanotubes (MWCNT) and 5% Nafion in THF, which were cast on the glassy carbon electrode rotating electrode assemblies.³² LSVs were recorded in an O₂-saturated 0.5 M H₂SO₄ electrolyte solution at rotation rates of $\omega = 0, 100, 400, 900$, and 1600 rpm. Representative RRDE LSV traces for all three Co(II) tetrapyrroles recorded at $\omega = 1600$ rpm are reproduced in

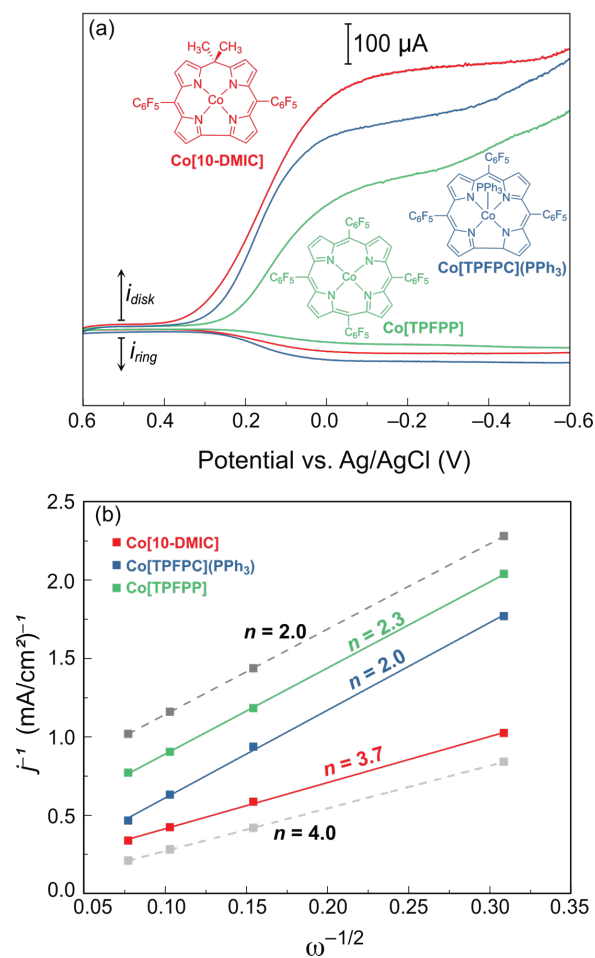


Figure 4. (a) RRDE LSVs recorded for **Co[10-DMIC]**, **Co[TPFPF]**, and **Co[TPFPC](PPh₃)** immobilized on a carbon disk suspended in O₂-saturated 0.5 M H₂SO₄ electrolyte ($\nu = 20$ mV/s; $\omega = 1600$ rpm). (b) Koutecky-Levich plots for **Co[10-DMIC]**, **Co[TPFPF]** and **Co[TPFPC](PPh₃)** compared to the simulated slopes for the two-electron vs four-electron ORR.

Figure 4a. Of the three tetrapyrrole complexes surveyed, **Co[10-DMIC]** displayed the most positive onset potential for ORR current at $E \sim 400$ mV, followed by **Co[TPFPC](PPh₃)** ($E \sim 350$ mV), and **Co[TPFPF]** at $E \sim 250$ mV (see Table 1). The full sets of RRDE data collected for each of the Co(II) tetrapyrroles as a function of rotation rate are shown in Figure S3.

Comparison of disk (i_{disk}) versus ring (i_{ring}) current normalized with respect to the collection efficiency ($N = 0.45$) of the RRDE assembly provided an initial assessment for the selectivity with which each of the three Co(II) tetrapyrroles promotes O₂ activation via $2e^-/2H^+$ versus $4e^-/4H^+$ pathways. This analysis revealed that both **Co[TPFPF]** and **Co[TPFPC](PPh₃)** are essentially incapable of catalyzing the peractivation of O₂ and mainly

Table 1. ORR performance of Co(II) tetrapyrroles as determined from RRDE paired with KL analysis.

Catalyst	E_{onset} (mV)	n_{app}	j_k (mA/cm ²)	% H ₂ O	% H ₂ O ₂
Co[10-DMIC]	400	3.7 ± 0.2	8.7 ± 2.5	85 ± 10	15 ± 10
Co[TPFPF]	250	2.3 ± 0.3	2.4 ± 0.5	15 ± 15	85 ± 15
Co[TPFPC](PPh₃)	350	2.0 ± 0.0	5.5 ± 1	0 ± 2	100 ± 2

drive the $2e^-/2H^+$ process to deliver H_2O_2 with selectivity of 85-90%. This result was expected based on prior work documenting the ORR activity of simple Co(II) porphyrins and corroles.^{32,33,74} *By contrast, however, Co[10-DMIC] was found to support a disparate reactivity with O_2 and displayed excellent activity for $4e^-/4H^+$ ORR catalysis, producing water with ~85% selectivity.*

Koutecky-Levich (KL) analysis of reciprocal measured current density (j^{-1}) vs reciprocal square root of rotation rate ($\omega^{-1/2}$) provides a more detailed means to analyze a catalyst's ORR performance. Such analysis was carried out for the RRDE data presented in Figure S3 for each of the monomeric Co(II) tetrapyrroles. The corresponding KL-plots are shown in Figure 4b. From the KL plots, the number of electrons for oxygen reduction and the kinetic current density (summarized in Table 1) was determined using Equation 1,

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_l} = j_k^{-1} + \frac{1}{0.62nFD_0^{2/3}\nu^{-1/6}C_0} \cdot \omega^{-1/2} \quad (\text{Eq 1})$$

where j_k is kinetic current density, j_l is limiting current density, n is the number of electrons transferred, F is Faraday's constant (96,485 C/mol), A is the electrode area (0.2475 cm²), D_0 is the diffusion coefficient of O_2 (1.15 x 10⁻⁵ mol/cm²), ν is the kinematic viscosity of the electrolyte (1.0 x 10⁻² V s⁻¹), C_0 is concentration of O_2 (1.4 x 10⁻⁶ M), and ω is the angular rotation rate of the electrode ($2\pi f$, where f is revolutions per second).

KL analysis of the RRDE data confirms the $4e^-/4H^+$ ORR selectivity for **Co[10-DMIC]** which is markedly enhanced with respect to that observed for the homologous Co(II) porphyrin and corrole. That the Co(II) 10,10-dimethylisocorrole shows the apparent ability to consume $n_{app} = 3.7 \pm 0.2$ electrons per equivalent of O_2 (Table 1) with impressive kinetics of $j_k = 8.7 \pm 2.5$ mA/cm² reflects a vastly improved ORR activity relative to other simple, unadorned Co(II) tetrapyrroles. Indeed, the ability of **Co[10-DMIC]** to effect heterogeneous electrocatalytic reduction of O_2 to H_2O (over H_2O_2) is especially impressive relative to that of the homologous Co(II) porphyrin (**Co[TPFPFP]**) and corrole (**Co[TPFPC](PPh₃)**) complexes that we have evaluated and which show (as expected) near complete selectivity for the $2e^-/2H^+$ ORR pathway to generate H_2O_2 (see Table 1). Accordingly, **Co[10-DMIC]** supports a privileged ORR catalysis that is not observed for other simple aromatic tetrapyrroles of Co(II) and which has historically only been observed for more elaborate architectures bearing ditopic molecular clefts, such as those highlighted in Figure 1.

In addition to assessing a catalyst's ORR performance while immobilized on an electrode support, O_2 reduction to deliver either H_2O or H_2O_2 (via $4e^-/4H^+$ or $2e^-/2H^+$ pathways, respectively) can be surveyed under homogeneous conditions. Such chemical reduction experiments often employ ferrocene (Fc) as a source of electrons and provide alternate means to evaluate ORR product distributions. In particular, homogeneous ORR studies

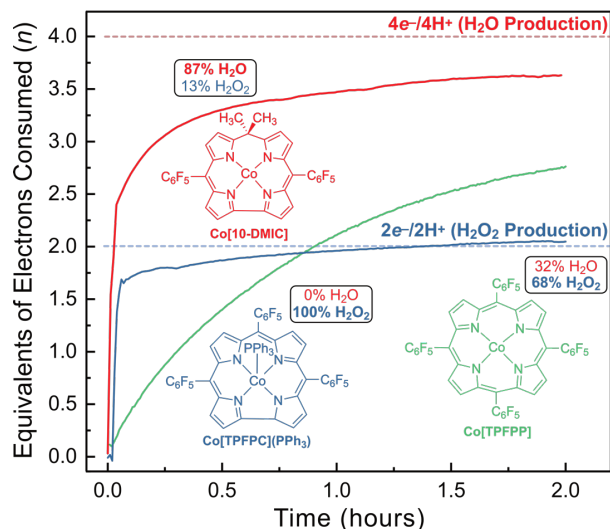


Figure 5. Traces showing the equivalents of electrons consumed by **Co[10-DMIC]**, **Co[TPFPFP]**, and **Co[TPFPC](PPh₃)** under homogeneous O_2 reduction conditions employing 100 mM Fc and 20 mM $HClO_4$ in air saturated PhCN (*i.e.*, O_2 limiting conditions). ORR catalysis was monitored by observing the concentration of Fc^+ produced ($\lambda = 620$ nm, $\epsilon = 330$ M⁻¹cm⁻¹) as a function of time. Inset selectivities for H_2O and H_2O_2 generation for each catalyst are based on iodometric titrations performed following complementary ORR experiments conducted under Fc limiting conditions.

employing ferrocene as a chemical reductant, as initially developed by Fukuzumi and Guillard,⁷⁵ provide a way to detangle the influence of binder or close proximity of catalyst sites upon immobilization on an electrode support.

Figure 5 shows the rise in ferrocenium (Fc^+) concentration as a function of time in air saturated PhCN solutions containing 100 mM of ferrocene (Fc), 20 mM $HClO_4$ and 25 μ M of each of the homologous Co(II) tetrapyrroles considered in this study. Under these O_2 limiting conditions, **Co[10-DMIC]** showed fast kinetics and high apparent selectivity for the homogeneous peractivation of O_2 ($n_{app} = 3.6 \pm 0.02$; H_2O selectivity = $81 \pm 1\%$). Consistent with prior work,^{45,76,77} much slower kinetics and low selectivity for H_2O generation were observed for the homologous monomeric Co(II) porphyrin (**Co[TPFPFP]**), which overwhelmingly generates H_2O_2 over the course of two hours (see Figure 5 and Table 2). Evaluation of the corrole complex (**Co[TPFPC](PPh₃)**) showed this platform supports fast O_2 activation but exclusively promotes the $2e^-/2H^+$ pathway to generate H_2O_2 (Figure 5 and Table 2), which is also consistent with prior work.^{16,78}

Table 2. ORR performance of Co(II) tetrapyrroles as determined from homogeneous chemical reduction experiments.

Catalyst	^a n_{app}	^a % H_2O	^a % H_2O_2	^b % H_2O_2
Co[10-DMIC]	3.6 ± 0.02	81 ± 1.0	19 ± 1.0	13.7 ± 0.9
Co[TPFPFP]	2.9 ± 0.2	48 ± 9	52 ± 9	67.9 ± 0.4
Co[TPFPC](PPh₃)	2.1 ± 0.2	5 ± 8	95 ± 8	100.2 ± 0.8

^aDetermined based on Fc^+ generated during the course of homogeneous ORR experiments under O_2 limiting conditions. ^bDetermined based on independent iodometric titration following catalysis under Fc limiting conditions.

We note that negligible Fc^+ was formed in the absence of Co(II) catalyst and that ferrocene consumption is fully attributable to O_2 reduction catalyzed by the tetrapyrroles.^{76,79} Moreover, the amount of H_2O_2 generated by each Co(II) tetrapyrrole was independently quantified by iodometric titrations (See Table 2).⁴⁵ It is interesting that despite showing fast kinetics for O_2 activation, **Co[TPFPC](PPh₃)** was found to generate H_2O_2 exclusively (Table 2). **Co[TPFPP]** showed the slowest rate of ORR and moderate selectivity for H_2O production. As was also observed by RRDE voltammetry, **Co[10-DMIC]** operates under homogeneous conditions with considerably faster kinetics than **Co[TPFPP]** and shows the highest selectivity for H_2O production out of the monomeric tetrapyrroles surveyed, with just over ten percent of the reduced O_2 generating H_2O_2 as product (Figure 5 and Table 2).

Conclusions and Future Directions

Metal centers complexed within non-aromatic tetrapyrrole architectures such as phlorins, biladienes and isocorroles can support unique electronic and redox properties that are well suited for small molecule activation processes. Herein, we have described the synthesis, structural and physical characterization of a 10,10-dimethylisocorrole complex of Co(II) that can be easily prepared in excellent yield in four succinct synthetic steps. This **Co[10-DMIC]** architecture supports light harvesting and redox properties that are distinct from other aromatic tetrapyrroles such as the homologous porphyrin (**Co[TPFPP]**) and corrole (**Co[TPFPC](PPh₃)**) complexes. Moreover, **Co[10-DMIC]** supports the catalytic reduction of O_2 by $4e^-/4\text{H}^+$ to generate H_2O with kinetics and selectivity that are greatly distinguished with respect to other simple monomeric metallotetrapyrroles.

The efficacy with which **Co[10-DMIC]** promotes ORR was assessed using a combination of electrochemical and chemical reduction studies. RRDE experiments along with hydrodynamic voltammetry coupled to Koutecky-Levich analysis revealed that the Co(II) isocorrole is ~85% selective for the $4e^-/4\text{H}^+$ reduction of O_2 to H_2O over the more kinetically facile $2e^-/2\text{H}^+$ process that delivers H_2O_2 . The ability of **Co[10-DMIC]** to promote peractivation of O_2 to H_2O was also demonstrated under homogeneous conditions in experiments that employed ferrocene as a chemical reductant. By contrast, the same ORR evaluations conducted for the homologous Co(II) porphyrin and corrole based tetrapyrroles demonstrated that the traditional systems catalyze the $2e^-/2\text{H}^+$ conversion of O_2 to H_2O_2 with near complete selectivity.

The above results are consistent with the canonical view that simple unadorned monomeric aromatic tetrapyrrole complexes are not in and of themselves active $4e^-/4\text{H}^+$ ORR catalysts. That the Co(II) isocorrole (**Co[10-DMIC]**) supports an ORR catalysis that is privileged as compared to the homologous monomeric

porphyrin (**Co[TPFPP]**) and corrole (**Co[TPFPC](PPh₃)**) demonstrates that non-aromatic tetrapyrrole architectures can provide new platforms and opportunities to effectively activate small molecules. Despite being a simple, easily prepared, monomeric tetrapyrrole platform, **Co[10-DMIC]** supports an ORR catalysis that has historically only been achieved using architectures that incorporate pendant proton-transfer groups or construction of cofacial assemblies, such as those highlighted in Figure 1. These platforms that present elaborate ditopic molecular clefts as active sites for O_2 activation are generally afforded only through arduous low-yielding syntheses or through self-assembly approaches that require superstoichiometric amounts of semiprecious metals (e.g., Ru). Accordingly, to the best of our knowledge, **Co[10-DMIC]** represents the first simple, unadorned, monomeric metalloisocorrole complex that can be easily prepared and which shows excellent performance for the $4e^-/4\text{H}^+$ peractivation of O_2 to water.

When considered against the backdrop described above, the work detailed herein demonstrates that it is possible to realize the benefits of highly complex ORR catalyst platforms with a simple monomeric Co(II) tetrapyrrole. Since non-traditional biladiene and isocorrole frameworks can be easily prepared in high yields using modular synthetic strategies, generation of suites of metalloisocorroles with varying substituents and symmetries can be readily pursued in an effort to tailor the resultant complexes' coordination chemistry, redox properties, and stability. Efforts continue in our laboratory to both probe the pathway(s) by which Co(II) isocorroles support efficient and selective ORR, and to expand the library of isocorrole-based catalysts for activation of O_2 and other small-molecule substrates of consequence to energy conversion.

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ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

Synthetic procedures as well as crystallographic, and electrochemical data. Crystallographic data are also available from the Cambridge Crystallographic Data Centre (CCDC 2103129)

Notes

The authors declare no competing financial interests.

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