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Controlling Oxygen Reduction Selectivity through Steric Effects: Electrocatalytic Two-Electron and Four-Electron Oxygen Reduction with Cobalt Porphyrin Atropisomers

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Abstract: Achieving a selective 2e⁻ or 4e⁻ oxygen reduction reaction (ORR) is critical but challenging. Herein, we report controlling ORR selectivity of Co porphyrins by tuning only steric effects. We designed Co porphyrin 1 with meso-phenyls each bearing a bulky ortho-amido group. Due to the resulted steric hinderance, 1 has four atropisomers with similar electronic structures but dissimilar steric effects. Isomers $\alpha\beta\alpha\beta$ and $\alpha\alpha\alpha\alpha$ catalyze ORR with n=2.10 and 3.75 (n is the electron number transferred per O_2), respectively, but $\alpha\alpha\beta\beta$ and $\alpha \alpha \alpha \beta$ show poor selectivity with n = 2.89 - 3.10. Isomer $\alpha\beta\alpha\beta$ catalyzes $2e^-$ ORR by preventing a bimolecular O_2 activation path, while aaaa improves $4e^-$ ORR selectivity by improving O_2 binding at its pocket, a feature confirmed by spectroscopy methods, including O K-edge near-edge X-ray absorption fine structure. This work represents an unparalleled example to improve $2e^{-}$ and $4e^{-}$ ORR by tuning only steric effects without changing molecular and electronic structures.

 O_2 can be reduced by two electrons (2e⁻) to H₂O₂ or by four electrons (4e⁻) to H₂O.^[1-3] The 4e⁻ ORR is required in many energy conversion techniques,^[4-7] while the 2e⁻ ORR makes H₂O₂, which is a widely used industrial oxidant and also

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a promising fuel.^[8-10] Recently, many molecular ORR catalysts have been reported.^[1-5,11-28] Although achievements have been made in improving the 4e⁻ ORR by providing rapid electron and proton transfers,^[17,29,30] introducing hydrogenbonding^[31,32] and electrostatic interactions,^[33] and using dinuclear cooperation,^[34-38] realizing these functionalities is challenging from both design and synthesis points of view. Unlike 4e⁻ ORR, few studies have been dedicated to improving the 2e⁻ ORR.^[27,39,40] Thus, achieving 2e⁻ and 4e⁻ ORR in a controllable manner is very rare, especially using one catalyst system.

In principle, O_2 tends to be reduced by $2e^-$ at single Co sites (Scheme 1 a), because one Co ion is not efficient to mediate O–O bond cleavage to form Co-oxo species, which is high in energy.^[41] However, Co complexes can also catalyze $4e^-$ ORR through a bimolecular path (Scheme 1 a).^[42,43] Due to the presence of both paths, Co complexes usually show poor or moderate selectivity for either $2e^-$ or $4e^-$ ORR. For examples, Co porphyrins have been largely studied as ORR catalysts by displaying high activity but poor selectivity.^[36] To improve selectivity, extensive efforts have been made to synthesize Co porphyrin cages with isolated Co sites^[40] for $2e^-$ ORR and dinuclear Co porphyrins^[34–38] for $4e^-$ ORR, in which peroxo-bridged Co porphyrins are proposed as intermediates (Scheme 1 b).



Scheme 1. a) Earlier proposed $2e^-$ and $4e^-$ ORR paths with Co catalysts. b) Proposed peroxo-bridged bimolecular Co porphyrin species.

Herein, we report achieving $2e^-$ and $4e^-$ ORR in a controllable manner by tuning only steric features of a catalyst system. Co porphyrin **1** was used (Figure 1). Due to the steric hinderance of the bulky *ortho*-amido group at each *meso*-phenyl substituent, **1** has four atropisomers with similar electronic structures but dissimilar steric effects (Figure 1b).^[44] Isomers $\alpha\beta\alpha\beta$ and $\alpha\alpha\alpha\alpha$ display significantly improved $2e^-$ and $4e^-$ ORR, respectively, but $\alpha\alpha\beta\beta$ and $\alpha\alpha\alpha\beta$ have poor ORR selectivity. Note that $\alpha\alpha\alpha\alpha$ has been

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Figure 1. a) Co porphyrins 1 and 2, showing their different substitution positions at *meso*-phenyls. b) Molecular structures of the four atropisomers of 1, namely $\alpha\beta\alpha\beta$, $\alpha\alpha\alpha\beta$, $\alpha\alpha\alpha\beta$ and $\alpha\alpha\alpha\alpha$.

studied previously for O_2 binding,^[45-47] but its electrocatalytic ORR has been rarely studied. In addition, we made Co porphyrin **2** as a substituent position isomer of **1**, which also displayed poor ORR selectivity. Our results underline the critical role of steric effects in controlling ORR selectivity. Therefore, without changing molecular and electronic structures, this work represents an unparalleled example to improve $2e^-$ and $4e^-$ ORR by tuning only steric effects of a catalyst system.

The Co-free forms of the four atropisomers of **1** were first synthesized (Scheme S1) and characterized (Figures S1–S3). Next, their corresponding Co complexes were each isolated and purified. Isomer $\alpha\beta\alpha\beta$ showed an ion at a mass-to-charge

ratio of 1067.4363 in high-resolution mass spectrometry (HRMS, Figure S4) and displayed characteristic Soret (419 nm) and Q (535 nm) bands in its UV-vis spectrum in tetrahydrofuran (THF, Figure S10a).^[48] These results confirmed its identity and purity.

Significantly, the $\alpha\beta\alpha\beta$ configuration was confirmed (Figure 2 a). X-ray studies showed that $\alpha\beta\alpha\beta$ crystallized in the tetragonal space group $I4_1/a$. Each Co is incorporated by a porphyrin ring through four N atoms. An aqueous molecule axially binds to Co with a long Co···O distance of 2.331(15) Å. The four Co–N bond distances are identical 1.959(3) Å. The Co^{II} state was suggested based on bond valence sum and charge balance calculations. The $\alpha\beta\alpha\beta$ configuration with alternating up and down orientations of the four bulky amido groups creates large steric encumbrance on both sides of the porphyrin ring.

For isomers $\alpha\alpha\beta\beta$, $\alpha\alpha\alpha\beta$, and $\alpha\alpha\alpha\alpha$, their identity and purity were confirmed by HRMS (Figures S5–S7) and UV-vis spectra (Figures S10b–S10d). Identical UV-vis spectra of these atropisomers suggest their very similar electronic structures. We structurally characterized the Co-free forms of $\alpha\alpha\beta\beta$ (Figure 2b) and $\alpha\alpha\alpha\alpha$ (Figure 2c). In the structure of Co-free $\alpha\alpha\beta\beta$, two close amido groups orientate upward, while the other two orientate downward. In the structure of Co-free $\alpha\alpha\alpha\alpha$, all four amido groups orientate upward, creating a pocket. In addition, we made Co porphyrin 2 (Scheme S2, Figures S9 and S10e). As the position isomer of 1, the four amido groups of 2 are located at the *para*-position of its *meso*-phenyls, leading to tiny steric hinderance on both porphyrin sides.

The redox features of these Co porphyrins were first studied in dimethylformamide (DMF, 0.1 M Bu₄NPF₆) under N₂. As shown in Figure 3 a and Table 1, all five Co porphyrins displayed two well-defined reversible redox waves, which were attributed to formal Co^{II/1} and Co^{II/0} redox couples, respectively.^[48,49] Importantly, their redox potentials for Co^{II/1} (-1.06 to -1.08 V versus ferrocene) and Co^{II/0} (-2.16 to -2.18 V versus ferrocene) are very close to each other, confirming their very similar electronic structures.

Next, we loaded Co porphyrins on carbon black (CB) for ORR studies. The resulted hybrids were analyzed by scanning electron microscopy and transmission electron microscope (Figure S11), showing no aggregated particles of Co porphyrins. The cyclic voltammogram (CV) of $\alpha\beta\alpha\beta$ @CB on a glassy



Figure 2. Thermal ellipsoid plots (50% probability) of the X-ray structures of $\alpha\beta\alpha\beta$ (a), Co-free $\alpha\alpha\beta\beta$ (b), and Co-free $\alpha\alpha\alpha\alpha$ (c).

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structures.

which is consistent with their similar electronic

carbon (GC) electrode displayed a catalytic wave in 0.1 M KOH solution under

 O_2 (Figure 3 b). Similar electrocatalytic behaviors were observed with the other three atropisomers of **1** and with **2** (Figures S13–S16). Note that catalytic ORR waves of all these Co porphyrins have identical onset potentials,

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Figure 3. a) CVs of 0.5 mM αβαβ, αααβ, αααβ, αααα, and 2 in DMF with a scan rate of 50 mVs⁻¹. b) CVs of GC electrode loaded with αβαβ@CB under O₂ and N₂ in 0.1 M KOH solution at a scan rate of 50 mVs⁻¹. c) LSVs of RRDE disk electrode loaded with αβαβ@CB, αααβ@CB, αααβ@CB, αααα@CB, and 2@CB under O₂ in 0.1 M KOH with a scan rate of 5 mVs⁻¹.

Table 1: Co porphyrin redox couple $E_{1/2}$ potentials (versus ferrocene) under N₂.

Complex	αβαβ	ααββ	αααβ	aaaa	2
E _{1/2} of Co ^{II/I}	-1.08	-1.07	-1.08	-1.07	-1.06
$E_{1/2}$ of Co ^{1/0}	-2.18	-2.16	-2.17	-2.18	-2.17

The number (*n*) of electrons transferred per O₂ molecue was determined by rotating-ring disk electrode (RRDE) measurements. As shown in Figure 3 c, the linear sweep voltammogram (LSV) of $\alpha\beta\alpha\beta$ @CB displayed large catalytic ORR currents with the half-wave potential $E_{1/2} = 0.73$ V versus reversible hydrogen electrode (RHE, all potentials reported in aqueous solutions are referenced to RHE). For the other three atropisomers and **2**, their ORR waves had similar $E_{1/2}$ values of 0.72–0.73 V. However, $\alpha\alpha\alpha\alpha$ @CB and $\alpha\beta\alpha\beta$ @CB displayed the largest and the smallest ORR current, respectively, while the currents with $\alpha\alpha\beta\beta$ @CB, $\alpha\alpha\alpha\beta$ @CB and **2**@CB are moderate and are close to each other. This result indicates that these Co porphyrins have different ORR selectivity.

The *n* values were then determined (Figures 4 a to d), giving n = 2.10 for $\alpha\beta\alpha\beta$ @CB, n = 3.75 for $\alpha\alpha\alpha\alpha$ @CB, n = 2.89-3.10 for $\alpha\alpha\beta\beta$ @CB, $\alpha\alpha\alpha\beta$ @CB, and 2@CB (Figures 4 e). By using carbon nanotubes (CNTs) as supports, the same *n* values were obtained (Figure 4 f), indicating that the ORR selectivity of these Co porphyrins does not change when loaded on different carbon materials. In addition, Koutecky-Levich (K-L) analysis gave similar *n* values as RRDE obtained for all Co porphyrins loaded on CB and CNTs (Figures S18 to S27).

Our results show that all five Co porphyrins have similar ORR activities, but they display different selectivities. For



Figure 4. ORR RRDE data with αβαβ@CB (a), ααββ@CB (b), αααβ@CB (c), and αααα@CB (d). The ORR *n* value of the five Co porphyrins loaded on CB (e) and on CNT (f) as determined from RRDE. Conditions: GC disk electrode (area 0.125 cm²), Pt ring electrode (area 0.188 cm²), scan rate: 10 mV s⁻¹, 20 °C.

ααββ, **αααβ**, and **2**, they displayed poor selectivity for either $2e^-$ or $4e^-$ ORR with n = 2.89-3.10, which is commonly observed for Co porphyrins without tethered functional groups to assist electron and proton transfers and to stabilize O₂-adduct through hydrogen-bonding and electrostatic interactions. As discussed above, due to the presence of both $2e^-$ and $4e^-$ paths (Scheme 1 a), Co porphyrins usually display poor or moderate ORR selectivity.

For $\alpha\beta\alpha\beta$, due to large steric encumbrance on both porphyrin sides, the bimolecular path is blocked. As a result, $\alpha\beta\alpha\beta$ displays high $2e^-$ ORR selectivity. For $\alpha\alpha\alpha\alpha$, its improved $4e^-$ ORR is likely due to improved O_2 binding at the Co site. In principle, O_2 can bind in and out of the pocket of $\alpha\alpha\alpha\alpha$. Previous studies showed that $\alpha\alpha\alpha\alpha$ could bind an O_2 molecule in the pocket, when the out-of-the-pocket site was occupied by an imidazole group.^[45-47] This axial imidazole can improve O_2 binding and activation through a so-called "push effect".

However, no imidazole axially binds to Co of $\alpha\alpha\alpha\alpha$ in our case. We therefore determined the O₂-binding site. Upon reacting with O₂ in THF, $\alpha\beta\alpha\beta$ showed slight changes in UV-vis (Figure 5a). Unlike $\alpha\beta\alpha\beta$, the UV-vis spectrum of $\alpha\alpha\alpha\alpha$ changed significantly after reacting with O₂ (Figure 5b), showing the disappearance of the bands at 419 and 535 nm and the appearance of new bands at 428 and 544 nm. These results indicate the binding and activation of O₂ at Co^{III} sites to give Co^{III}-superoxo species.^[50–52] Electron paramagnetic res-

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Communications



Figure 5. UV-vis spectra of $\alpha\beta\alpha\beta$ (a) and $\alpha\alpha\alpha\alpha$ (b) under N₂ and O₂ in THF at room temperature. EPR spectra of $\alpha\beta\alpha\beta$ (c) and $\alpha\alpha\alpha\alpha$ (d) under N₂ and O₂ in THF at 100 K. Infrared (e) and NEXAFS (f) spectra of $\alpha\alpha\alpha\alpha$ under N₂ and O₂.

onance (EPR) spectra of $\alpha\beta\alpha\beta$ (Figure 5c) and $\alpha\alpha\alpha\alpha$ (Figure 5d) under N₂ are identical, further supporting the same coordination and electronic structures of their Co^{II} sites.^[27,53,54] However, $\alpha\beta\alpha\beta$ under O₂ showed both Co^{II} and Co^{III}-superoxo signals in EPR,^[53,55,56] while $\alpha\alpha\alpha\alpha$ under O₂ showed only Co^{III}-superoxo signals in EPR. These results suggest that $\alpha\alpha\alpha\alpha$ has a stronger O₂-binding affinity than $\alpha\beta\alpha\beta$. Moreover, the infrared spectrum of $\alpha\beta\alpha\beta$ under N₂ and O₂ showed tiny difference (Figure S28), but significant changes were observed for $\alpha\alpha\alpha\alpha$ under N₂ and O₂ at amide-related resonances (Figure 5e). The changes of amide N–H and C=O resonances indicated potential hydrogen-bonding interactions between O₂-adduct and the amide groups in the pocket of $\alpha\alpha\alpha\alpha$.

All these results suggest that even without an axial imidazole to block the out-of-the-pocket site of Co and to improve O_2 binding, $\alpha\alpha\alpha\alpha$ can strongly bind an O_2 molecule in the pocket. Note that the O_2 -adduct of $\alpha\alpha\alpha\alpha$ is not likely to undergo a bimolecular ORR path due to the steric encumbrance of the pocket. It is proposed that partially reduced O_2 species are stabilized at the pocket for further reduction, leading to improved $4e^-$ ORR at single Co sites. Proving this effect is the on-going work in our group.

To examine the Co^{III}-superoxo, we collected O K-edge near-edge X-ray absorption fine structure (NEXAFS) of $\alpha\alpha\alpha\alpha$ (Figure 5 f). Under N₂, the O signals can be assigned to

peptide (-CONH-), including the $1s \rightarrow 1\pi^*$ transition of the carbonyl O at 534.2 eV and the σ^* resonance at 538–542 eV. Importantly, the spectrum under O₂ showed two additional shoulder peaks at 531 and 545.4 eV for π^* and σ^* peak, respectivley. This result suggests the effective chemisorption of O₂ in *aaaa*.^[57] The small but significant shoulder peak next to the chemisorpted O₂ shifts to lower energy, indicating an enlarged O–O bond distance, which is consistent with electron transfer from Co^{II} to O₂ to form superoxo species.

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In conclusion, we report controlling ORR selectivity by tuning only steric effects. Five Co porphyrins show identical ORR activity but different selectivity. With large steric encumbrance to prevent bimolecular path, $\alpha\beta\alpha\beta$ catalyzes $2e^-$ ORR; with improved O₂ binding in the pocket, $\alpha\alpha\alpha\alpha$ catalyzes $4e^-$ ORR; without these steric effects, $\alpha\alpha\beta\beta$, $\alpha\alpha\alpha\beta$ and 2 showed poor selectivity for either $2e^-$ or $4e^-$ ORR. This work is significant to achieve $2e^-$ and $4e^-$ ORR by tuning only steric effects without changing molecular and electronic structures and is valuable for catalyst design with the aim to understand ORR mechanisms and to further improve catalyst performance.

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Conflict of interest

The authors declare no conflict of interest.

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H. T. Lei, F. Wang, X. T. Jin, Q. X. Zhang, W. Zhang, R. Long,* Y. J. Xiong, U.-P. Apfel, R. Cao* _____ ▮▮▮■-■↓↓↓

Controlling Oxygen Reduction Selectivity through Steric Effects: Electrocatalytic Two-Electron and Four-Electron Oxygen Reduction with Cobalt Porphyrin Atropisomers



Cobalt porphyrin atropisomers with similar electronic structures but dissimilar steric effects were synthesized. One isomer is selective for the $2e^-$ ORR, one is selective for the $4e^-$ ORR, while the other two show poor selectivity for either $2e^-$ or $4e^-$ ORR.

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