

Promotion of Catalytic Oxygen Reduction Reactions: The Utility of Proton Management Substituents on Cobalt Porphyrins

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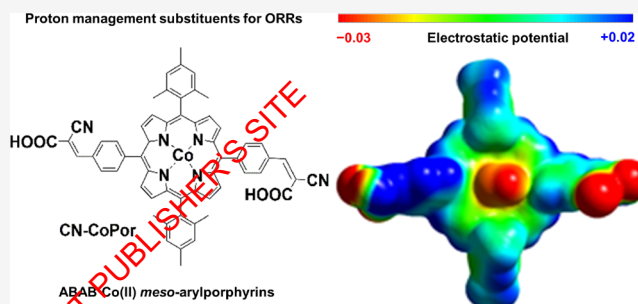


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ABSTRACT: Three ABAB-type cobalt *meso*-tetraarylporphyrins with fluorine (F-CoPor), acetic acid (AC-CoPor), and cyanoacetic acid (CN-CoPor) groups at the *para*-positions of phenyl rings at the 10,20-positions are synthesized and evaluated as catalysts for oxygen reduction reactions (ORRs). In density functional theory calculations, the frontier molecular orbitals of these complexes were found to be stabilized relative to model complexes with electron-withdrawing atoms or moieties on the *meso*-aryl rings. Electrochemical measurements suggest that electrodes with CN-CoPor (CN-CoPor/C) exhibit the most positive ORR potential values and the highest limiting current density in both acidic and alkali electrolytes, while the F-CoPor/C electrocatalyst exhibits extremely low ORR performance. The electron transfer numbers for the electrocatalysts are more than 3.0, indicating that a mixture of 2- and 4-electron transfer pathways occurs. The results demonstrate that coupling the hydrogen bonding properties and electron-withdrawing abilities through rational design of the substituent at the *meso*-position is an efficient way to modify the ORR performance.



1. INTRODUCTION

Oxygen reduction reactions (ORRs) are one of the core research directions in electrochemical hydrogen peroxide production, fuel cells, and zinc–air battery research, which have been the focus of intense investigation over the past several decades.^{1,2} Metal macrocyclic complexes, typically those with M–N₄ structures, are considered to be promising electrocatalysts for enabling efficient ORRs.^{3–5} Metalloporphyrins are a class of macrocyclic complexes, whose central ion species, the axial coordination, the substituents, porphyrin post-treatment, and the catalyst substrate can all affect the catalytic activity during oxygen reduction.^{6–8}

Attaching auxiliary groups with proton release properties near the active site of a metal-containing catalyst has been reported to be an effective way to improve the selectivity and kinetics of ORRs.^{9,10} For example, attaching NMe₃⁺ as a cationic ancillary group to an asymmetric cobalt porphyrin resulted in excellent selectivity of oxygen reduction to water over the acidic to neutral pH range.¹¹ In contrast, the ORR selectivities of a range of other substituted porphyrins were found to vary with the pH of the electrolyte. The effect of the proton release property may also be affected by the coordination state of the central metal. A density functional theory (DFT) study on several iron porphyrins provided evidence that the hydrogen bonding interaction between the carboxylic acid as the secondary coordination sphere and the central metal-bound species as the axial ligands may affect the

Fe–O bonding in a manner that further increases the reduction potential.¹²

In principle, a proton management group, i.e., a proton relay substituent, can activate the O–O bond by increasing the concentration of protons around the catalyst, promoting the formation of the intermediate product H–O–M and facilitating the cleavage of the O–O bond.¹³ Typically, they need to have appropriate dissociation constants. Weak rather than strong acid groups are often used, such as hydrogen bonds, Brønsted acids/bases like carboxylic acids, or pyridinium, to enhance the proton concentration near the active site.^{14,15} Hangman and Pacman porphyrins provide the functionality for a feasible proton-coupled electron transfer, which may enhance the overall ORR efficiency.¹⁵ A hangman cobalt corrole with a carboxylic acid at the substituent exhibited a selective reduction of oxygen to water since the proton-donating group can promote the O–O bond activation.¹⁶ The position of the acid groups may also strongly influence the ORR selectivity and activity. Two iron tetraarylporphyrins bearing carboxylic acid groups at the 2-

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