



Push–pull type Co(III)corroles: Synthesis, electronic structure and electrochemical catalysis

Yingjie Niu^a, Weihua Zhu^a, John Mack^{* \diamond c}, Nadine Dubazana^c,
Tebello Nyokong ^{\diamond c}, Bo Fu^b, Haijun Xu^{*bd} and Xu Liang^{*a}

^aSchool of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, P. R. China

^bJiangsu Co-innovation Center of Efficient Processing and Utilization of Forest Resources, College of Chemical Engineering, Jiangsu Key Lab of Biomass-based Green Fuels and Chemicals, Nanjing Forestry University, Nanjing 210037, P.R. China

^cCentre for Nanotechnology Innovation, Department of Chemistry, Rhodes University, Makhanda 6140, South Africa

^dSchool of Chemistry and Chemical Engineering, Henan Normal University, Xixiang 453007, P. R. China

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ABSTRACT: The rational design and preparation of three A₂B type Co(III)triarylcorroles with push- and pull-substituents are reported. The structure-property relationships were identified by comparing their optically spectroscopic and electrochemical properties to trends predicted in DFT and TD-DFT calculations. The results demonstrate that the Co(III)triarylcorroles are highly efficient catalysts for electrocatalyzed hydrogen evolutions (HERs) and oxygen reductions (ORRs), and that their reactivity can be modulated by changing the *meso*-B-substituent of the Co(III)Corroles.

KEYWORDS: Co(III)corrole, electronic structure, TD-DFT calculations, electrochemical catalysis.

INTRODUCTION

In recent years, the rapidly growing global population, heavy environmental pollution and the intermittent nature of renewable energy, has led to more and more researchers studying the design of new energy conversion processes, including the development of efficient electrocatalysts [1]. Bio-inspired catalysis has become one of the most important branches in the field of molecular catalysis [2]. For this reason, porphyrinoid molecules are widely used in various catalytic processes, such as chemical catalysis, photocatalysis, biological catalysis and even electrochemical catalysis [3]. Although researchers have reported several interesting results for metalloporphyrin molecular catalysts, enhancing their

catalytic efficiency and stability remains challenging [4]. Synthetic chemistry makes it possible to introduce functional substituents to change the nature of the macrocycle and modulate the electronic structure of the porphyrinoid ligand [5]. Metalloporroles have been identified as suitable candidates for use as molecular catalysts since the contracted ring structures readily stabilize high-valence metal centers, such as Co(III)triarylcorroles with d^6 low spin state. As reported previously, many different research groups have demonstrated the key relationships between electronic structure and catalytic efficiency in this context, but there is still scope for further fine-tuning of the catalytic properties by modifying the *meso*-aryl substituents and using low symmetry A₂B type substitution patterns [6]. Within this aim, efforts to introduce both electron-donating (push) and electron-withdrawing (pull) substituents at *meso*-positions that cause destabilization and stabilization of the HOMO and LUMO, and the synergetic effect of the push–pull substituents generally results in a decrease in the HOMO–LUMO

^{\diamond} SPP full member in good standing.

*Correspondence to: Xu Liang, email: liangxu@ujs.edu.cn, Haijun Xu, email: xuhaijun@njfu.edu.cn, John Mack, email: j.mack@ru.ac.za; tel.: +27-46-603-7234.

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