



A₂B type copper(III)corroles containing zero-to-five fluorine atoms: Synthesis, electronic structure and facile modulation of electrocatalyzed hydrogen evolution



Minzhi Li ^{a,1}, Yingjie Niu ^{a,1}, Weihua Zhu ^{a,**}, John Mack ^{b,***}, Gertrude Fomo ^b,
Tebello Nyokong ^b, Xu Liang ^{a,*}

^a School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, PR China

^b Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

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ABSTRACT

Four low symmetric A₂B *meso*-substituted Cu(III)corroles with electron withdrawing *meso*-aryl rings have been synthesized and characterized. A detailed analysis of the optical and redox properties has been carried out by comparing their optical spectroscopy, electrochemistry and spectroelectrochemistry to a series of DFT and TD-DFT calculations. A series of experiments demonstrate that these Cu(III)corroles can be used as highly effective catalysts for hydrogen evolution reactions (HERs). Moreover, when the number of fluorine atoms at *meso*-position is increased, there is a marked enhancement in the catalytic ability of the corrole complexes, which demonstrates that modification to the structures of low symmetry corroles is a useful strategy for developing new HER catalysts.

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1. Introduction

In recent years, increased energy demands and serious environmental concerns, have made research on clean energy sources one of the most important tasks for modern society [1]. Hydrogen has many advantages in this regard and is widely considered to be the next generation energy source that will replace the use of fossil fuels [2]. In addition, there has been increasing interest in hydrogen evolution reactions (HERs) that involve the electrochemical reduction of protons, due to the convenient procedures that are involved and the availability of catalytic materials to convert electrical energy to chemical energy through the generation of H₂ [3]. Although platinum enables highly efficient electrocatalysis, less-expensive and more abundant transition metal

complexes would be preferable for use as catalysts in HERs. Additionally, recent research interest has identified complexes containing transition metal-centers such as iron [4], cobalt [5], nickel [6], and molybdenum [7] that are redox active for HER catalysis, but their low catalytic efficiencies and insufficient stability in the concentrated acid environments that are used in this context has limited the further development of this field of research [8].

The development of new and stable molecular catalysts with high-valent metal centers that can provide highly efficient and robust HER catalysts remains a significant challenge in the energy research community. Corroles are porphyrin analogues with a direct pyrrole-pyrrole bond and an extra NH proton on the inner ligand perimeter [9]. In recent decades, there has been a strong research focus on the use of corroles as functional ligands, largely due to their ability to stabilize higher oxidation states of the coordinated central metal [10]. Metallo-corroles with central ions in unusual valence states can be rationally prepared through structural modifications to the corrole rings [11]. These complexes have been used in various kinds of catalytic reactions including organic synthesis [12], the removal of environmental harmful pollutants [13] and HERs [14].

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: sayman@ujs.edu.cn (W. Zhu), j.mack@ru.ac.za (J. Mack), liangxu@ujs.edu.cn (X. Liang).

¹ These authors are contributed equally.