



# Halogen substituted A<sub>2</sub>B type Co(III)triarylcorroles: Synthesis, electronic structure and two step modulation of electrocatalyzed hydrogen evolution reactions



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## ARTICLE INFO

### Article history:

Received 27 December 2016  
Received in revised form  
18 February 2017  
Accepted 20 February 2017  
Available online 2 April 2017

### Keywords:

A<sub>2</sub>B corrole  
Electronic structure  
TD-DFT calculation  
HER reaction

## ABSTRACT

Seven low symmetry A<sub>2</sub>B type Co(III)triarylcorroles with electron withdrawing *meso*-aryl substituents 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 trends predicted in a series of DFT and TD-DFT calculations. The results demonstrate that Co(III)corroles are highly effective catalysts for hydrogen evolution reactions (HERs). Moreover, there is a marked enhancement in their homogeneous catalytic ability when halogen atoms are introduced at the B position, which demonstrates that facile modifying the *meso*-aryl rings is an effective strategy for developing new HER catalysts. The electrochemical results demonstrate that an unusual two step modulation of HER reactions can be achieved by using singly and doubly electrochemically reduced cobalt triarylcorrole anions.

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## 1. Introduction

Metallo-corroles are ring-contracted porphyrin analogues with the presence of a direct pyrrole-pyrrole bond, that have attracted significant interest in recent decades, due to the stabilization of high-valence metal ions by various *meso*- and/or  $\beta$ -substituted ligands [1]. The interest in corrole coordination chemistry is driven by the unusual structures and topologies of these molecules [2] but also by their interesting properties, such as their electronic structures [3] and magnetism [4], and potential applications such as bioimaging [5], biosensors [6], organocatalysis [7] and electrocatalysis [8]. On the other hand, clean renewable energy sources that do not increase atmospheric carbon dioxide levels are required to meet the ever increasing global demand for energy. The use of

hydrogen for energy storage so that supply from renewable energy sources can be balanced with demand through the use of fuel cells 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 in many contexts [9]. 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 H<sub>2</sub> gas [10]. Although platinum enables highly efficient electrocatalysis, the use of less-expensive and more abundant transition metals would be preferable.

Recent research interest has shown that complexes containing high-valent metal-centers such as iron [11], cobalt [12], nickel [13] and molybdenum [14] 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 further development of this field of research [15]. Although modulation of electrocatalyzed HER reactions has recently been reported for singly or doubly reduced nickel porphyrin anions [13b], similar behavior has yet to be reported for metallo-corroles. The

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