



Structural modification of Rh^{III}triarylcorroles for enhanced electrocatalyzed hydrogen evolution reactions

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ABSTRACT

A series of A₃ type Rh^{III}triarylcorroles **2a-c** with different meso-substituents with differing electron-donating and withdrawing properties and two A₂B type Rh^{III}triarylcorroles **4a-b** with meso-methylthiophenyls at the B position have been prepared and characterized. An analysis of structure-property relationships of **2a-c** and **4a-b** has been carried out by comparing the optical spectroscopy and electrochemistry of the dyes to trends predicted in DFT and TD-DFT calculations. Rational structural modification strategies that enhance the suitability of **2a-c** for use as highly efficient catalysts for hydrogen evolution reactions on glassy carbon electrodes coated with **2a-c**/reduced graphene oxide composites and of **4a-b** in surface-modified Au electrodes are explored.

1. Introduction

Energy-related small molecules activation reactions have been the focus of a considerable amount of research for over 30 years, and interest in the field is still growing [1–4]. Energy conversion can be achieved through photocatalysis, and chemical and electrochemical catalysis [5–8]. Metalloporphyrins provide bio-inspired catalysts since metalloporphyrins originally come from the human body and natural plants [9–11]. In 1996, the first example of a Rh^{III}porphyrin electrocatalyzed hydrogen evolution reaction (HER) was reported [12]. Several subsequent studies focused on the modulation of metalloporphyrin HER electrocatalysis by changing the metal-center, the meso- and/or β-substituents, and via through-space interactions [13–18]. However, the design and synthesis of highly efficient and stable molecular catalytic systems remain a challenge. Metalloporroles, one of the most important set of metalloporphyrin analogues, have also been studied extensively for use in both homogenous and heterogeneous catalysis [19–23]. Although the first synthesis and characterization of a corrole was reported over 50 years ago, the use of rational structural modification strategies to enhance the catalytic efficiency of metalloporroles is still not fully understood. The following strategies have been used to modulate the electronic structure and catalytic properties of

metalloporroles: (1) meso- and/or β-substituents; (2) the coordinated metal-center; (3) the axial ligands; (4) enhanced surface and interface interactions; (5) direct surface chemical bonding interactions; (6) electron conductive polymers [24–29]. Rh^{III}triarylcorrole complexes with low spin d⁶ electronic structure have been reported to have higher chemical activities than the analogous Co^{III}corroles due to Rh^{III} cation contains electrons on the 4d orbitals [30–32]. To the best of our knowledge, due to the difficulties of Rh^{III}corrole preparation, only a limited amount of systematic research has been carried out on the relationship between the rational molecular design of Rh^{III}triarylcorroles and the surface interactions and electrocatalytic properties. In this study, two series of A₃ and A₂B type meso-substituted Rh^{III}triarylcorroles have been prepared with axial triphenylphosphine ligands, Scheme 1, and the relationship between trends in their optical and redox properties and hydrogen evolution reaction (HER) electrocatalysis properties have been analyzed. The A₃ type complexes (**2a-c**) have electron-donating and withdrawing groups introduced at the para-positions of meso-phenyl rings to investigate how changes to electron density around the metal center modulates the HER catalysis properties of glassy carbon electrodes (GCEs) coated with reduced graphene oxide (rGO) supported **2a-c**/rGO composites. The HER catalytic results obtained in this context are also compared to those obtained with

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