

Copolymers of Bipyridinium and Metal (Zn and Ni) Porphyrin Derivatives

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Abstract

In the presence of 4,4'-bipyridine (4,4'-bpy) as a bridge nucleophile, this study describes the electropolymerization of new keto functionalized octaethyl metal porphyrins (Zn^{2+} and Ni^{2+}). Electrochemical, spectroscopic (UV-Vis, XPS, FT-IR, and Raman spectroscopy), and imaging (AFM and SEM) techniques were used to characterise the polymer films. The presence of porphyrin and 4,4'-bipyridine units in the film is confirmed by the absorption and electronic spectra. The surface morphology shows homogenous coating deposition with roughness values of about 8 nm on average. Theoretical investigations were conducted to learn more about how different metal centres (Zn^{2+} and Ni^{2+}) interact with the porphyrin unit's keto functionality in the creation of copolymer films. The electrochemical interaction of polymer films with CO_2 shows that CO_2 is trapped and released in a reversible manner with low energy barriers for both polymers

Keywords : Polyhydrin; Electropolymerization; Porphyrin

Introduction

Remarkable development has been seen over the past few decades for compounds containing transition metal complexes due to their versatile conjugated π electron molecular structures and variable catalytic and electronic properties. Catalysts based on Metal-Nitrogen-Carbon (M-N-C) extended structures have the distinct advantage of well-defined, efficient, and resilient molecular structures, which allow for atomic-level functionalization and customization to improve overall catalytic performance and ease of mechanistic study. Porphyrins, phthalocyanines, cyclam, and their equivalents, which combine the greatest properties of bioinspired and artificial transition metal complexes, open a new path toward efficient catalyst for a wide range of processes. Combining the best features of bioinspired and manmade transition metal complexes those including porphyrins, phthalocyanines, cyclam and their analogues pave a new route towards efficient catalyst for a broad range of reactions. When used as an electro catalyst, porphyrin an N_4 macrocycles are a great electronic mediator and are widely investigated because they exhibit fascinating activity in homogeneous media and are restricted to the electrode surface. The metal in the ring centre can also be changed to alter their qualities. When restricted to an electrode surface, metalloporphyrins have a variety of redox characteristics that tend to boost active site utilization and promote electron

transport processes. Aside from these benefits, the functionalized porphyrin has been shown to have dramatically different chemical, molecular, and physical characteristics. Due to their high surface area, which is an important attribute in gas storage and capture, functionalized porphyrins in the form of metal-organic frameworks and covalent polymers have gotten a lot of interest in material science. The functional groups are added to the macrocycles at either the periphery or the core, affecting the aromaticity and degeneracy of the electronic structure. Electropolymerization, for example, provides for the creation of polymer films with increased stability and surface area, as well as compact layers with precise thickness control. The nucleophilic interaction between the Lewis bases and the produced dication of the octaethylporphyrins was identified as the critical step. Changing the bridging nucleophile or functionalizing the porphyrins, while maintaining at least two accessible meso locations, can also change polymer properties like conductivity by extended conjugation. Immobilized metalloporphyrin electrodes have been extensively explored for their wide range of applications. In this paper, we show that keto functionalized metal porphyrins (NiOEPK and ZnOEPK) electropolymerize on the FTO surface in the presence of the bridging ligand 4,4'-bpy (4,4'-bipyridine). In quest of a system based on non-precious metals that is abundant on the planet. The investigations of the two porphyrin units, ZnOEPK and NiOEPK, are fascinating because Ni porphyrins ring oxidise with the central metal, but Zn porphyrins have two ring oxidation steps with an unreacted central metal. Bipyridine complexes are another molecular catalyst that has received a lot of attention. The role of 4,4'-bpy as a bridge nucleophile and a peripheral substituent is critical, since it has a broad impact on the system's electronic structure, which in turn determines its electrochemical activity. All chemical reagents and solvents used were analytical grades or higher. Zinc octaethyl porphyrin ketone (ZnOEPK) and nickel octaethyl porphyrin ketone (NiOEPK) were synthesized. In an argon-filled glove box, anhydrous acetonitrile (ACN) (Sigma Aldrich 99.9%), dichloromethane (DCM) (VWR chemicals 99.8%), and Di Chloro Ethane (DCE) (Alfa Aesar 99.9%) were stored over found molecular sieves. AGA-Finland provided nitrogen (N₂), carbon dioxide (CO₂), and argon (Ar). At a scan rate of 200 mV s⁻¹, the sequential voltammetric scans recorded during electropolymerization of metal octaethyl porphyrin ketones M=Zn²⁺ (ZnOEPK 0.6 to 1.6 V vs. Ag/AgCl) and Ni²⁺ (NiOEPK 0.55 to 1.55 V vs. Ag/AgCl) in the presence of 4,4'-bpyNiOEPK revealed one oxidation peak at 0.71 V and a rising current commencing at 1.2 V during the first cycle, and one reduction peak at 0.31 V during the reverse scan. Three oxidation peaks can be visible at 0.69, 1.05, and 1.38 V starting with the second cycle. The metal porphyrin's cation and dication production give rise to the first two peaks. The porphyrin dication suffers nucleophilic attack by 4,4'-bpy to generate isoporphyrin cation because it is a powerful electrophile. As the electrode coating progresses, all of these peaks change to a more positive potential, eventually merging into a single broad peak at 1.41 V. The last two are from isoporphyrin and bipyridinium reductions, and they're merging into a huge cathodic peak of 0.18 V. The reduction of the oxidized porphyrin in the solution is shown by the peak generated at 0.31 V. A regulated and repeatable electro synthesis of a new keto functionalized porphyrin and 4,4'-bpy copolymer has been demonstrated. Except for small shifts and broadening of bands in the polymer film, the spectroscopic results of the polymer films resemble those of the monomer unit, demonstrating that porphyrin molecules are maintained and remain intact in the film. The topographical properties of the polymer films are identical. The effect of the central metal atom and the keto functional group on the mechanism of polymerization is studied theoretically. In ZnOEPK, the nucleophilic addition of 4,4'-bpy happens at the 20th meso position, near to the keto group, whereas it occurs at the 10th meso position, opposite the keto group, in NiOEPK. However, when a second 4,4'-bpy unit is introduced, coupling occurs perpendicular to the plane of porphyrin, in the opposite direction of the first unit, resulting in polymers with linear orientation, according to theoretical research..