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Immobilization of tetra-amine substituted metallophthalocyanines at gold surfaces modified with mercaptopropionic acid or DTSP-SAMs

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Abstract

This paper shows that amine substituted cobalt phthalocyanine (CoTAPc) can be deposited on gold surfaces by using an interconnecting layer of a self-assembled monolayer (SAM) of mercaptopropionic acid or Lomant's reagent (dithiobis(*N*-succinimidyl propionate) (DTSP)). In both cases the new bond formed is obtained by the creation of an amide. The layers were characterized by electrochemistry and showed high coverage fractions (near 100%). Reductive and oxidative desorption of the SAMs limit the useful potential window from −0.6 to +0.5 V versus Ag|AgCl. The SAM-CoTAPc layers show electrocatalytic activities towards oxygen reduction through the Co(I) central metal ion. The amount of CoTAPc molecules deposited (obtained from the Co central metal ion activity in nitrogen purged solutions) revealed that the CoTAPc molecules are bonded in a perpendicular manner at the surface. Taking into account a surface of 200 Å^2 for a flatly bonded MPc, this should result in a four times less amount of deposited CoTAPc compared to the experimental value obtained. Both methods showed good results and promising long-term stability and will be interesting tools for further research in surface modification and sensor development.

Keywords: CoTAPc; Gold; Electrocatalysis; Deposition; SAM

1. Introduction

Phthalocyanines (Pcs) are well-known blue-green pigments because of their ever-increasing diverse applications in various technologically important redox reactions [1]. Important applications can be found in photovoltaic cells [2], molecular electronics [3], sensors [4], catalysis [5,6] and gas sensors [7,8]. A number of devices, which may result from this research, will ultimately depend upon the fabrication of the phthalocyanine compounds as thin films. Thus, there has been a growing interest in thiol-derivatized metallophthalocyanines (MPcs) in recent years for the fabrication of self-assembled monolayers (SAMs) and Langmuir–Blodgett (L.B.) films [9–12]. SAMs are an incredibly versatile means of extending the functions of an electrode and have been known to offer greater advantages over other film formation techniques [9,13]. The modification of electrodes, especially a gold electrode, with SAMs of alkanethiols or their derivatives has been well studied [13–17]. However, the response of electrodes on which thiol-derivatized Pc molecules have been assembled is not well known. MPc complexes substituted with sulfur donors are rather few [18–23]; hence not much is known about their SAMs or electrochemistry.

Previously, various thiol-derivatized MPcs were synthesized and characterized, such as octabutylthiometallophthalocyanine (MOBTPc) complexes of cobalt(II), CoOBTPc [24,25] and iron(II), FeOBTPc [26] and complexes of octa-(hydroxyethylthio)-phthalocyanine of cobalt(II), CoOHETPc [27] and iron(II), FeOHETPc [27]. These molecules resulted in stable and electroactive SAMs on gold. As part of our program in the search for novel deposition methods of metallophthalocyanines we attempt to immobilize commercially available MPcs by anchorage at a previously deposited SAM. In this way one avoids complex synthesis to develop thiol-derivatized MPcs, which is not simple and demands a well-established laboratory with the necessary in house expertise. Voltammetric techniques are the most convenient and sensitive methods for

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