



Self-assembled monolayers formed by 5,10,15,20-tetra(4-pyridyl)porphyrin and cobalt 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine on iodine-passivated Au(111) as observed using electrochemical scanning tunneling microscopy and cyclic voltammetry

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ABSTRACT

Self-assembled monolayers (SAMs) of 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) and cobalt 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine (CoTPyP) were formed by in situ equilibrium adsorption onto Au(111) electrodes passivated by an interposed adlayer of iodine. Adsorption of the porphyrins onto Au(111) was confirmed by cyclic voltammetry, and each of the SAMs was imaged using electrochemical scanning tunneling microscopy (EC-STM). The TPyP and CoTPyP SAMs were found to contain highly ordered domains on I-Au(111) at positive potentials where a disordered SAM would be expected for bare Au(111). Cyclic voltammetry was also used to observe in situ the assembly of binary SAMs containing TPyP and CoTPyP as they formed.

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1. Introduction

The formation of self-assembled monolayers (SAMs) under electrochemical conditions is of interest to fields such as chemical sensing, molecular electronics, and electrocatalysis, where SAM-modified electrodes offer surfaces with chemically tailored properties [1–4]. For many applications, preference is given to SAMs that exhibit high long-range 2-D order and, thereby, extremely well defined surface characteristics. Therefore, there is great value in a thorough understanding of SAM-ordering processes and self-assembly techniques that promote the formation of ordered SAMs.

Porphyryns derivatives such as 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP, Fig. 1) are particularly attractive for the formation of SAMs since they form planar metal complexes that permit the formation of SAMs exposing different metal centers towards the solution [5,6]. Moreover, the solubility of porphyryns derivatives can be tuned by the choice of the substituents in meso position and on the pyrrole rings. Indeed, both hydrophilic and hydrophobic porphyryns are commercially available. Porphyryns SAMs have been investigated extensively using scanning tunneling microscopy (STM) in vacuum and inert liquids [7,8], and the formation of

porphyryns SAMs on metal surfaces in electrolyte solutions has also received attention from multiple groups. In particular, Borguet et al. have extensively investigated porphyryns SAMs on bare Au(111) electrodes [9–12]. Importantly, they found that the electrode potential can be used to control ordering in TPyP monolayers on bare Au(111). They showed that in 0.1 M HClO₄ and at potentials above 0.54 V vs. Ag/AgCl, TPyP SAMs form in a disordered arrangement due to strong interaction between the conjugated π -system of TPyP and the positively charged electrode surface [9]. In contrast, with the electrode potential set between –0.16 and +0.24 V vs. Ag/AgCl, optimal self-assembly of TPyP into highly ordered domains proceeds.

Modification of the electrode surface with a layer of specifically adsorbed anions offers a complimentary route to controlling SAM ordering [13–18]. In pioneering work by Kunitake et al., ordered SAMs of 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)-21H,23H-porphine were formed on Au(111) electrodes modified with a passivating layer of iodine [13,14]. The iodine adlayer weakens the interaction between the porphyryns and the electrode, allowing them greater lateral mobility on the surface. This results in the formation of highly ordered SAMs in wider and more positive potential windows than what is possible with potential control alone. Besides Au(111), similar results using iodine modification have been reported for Ag(111) [15] and Cu(111) [18] electrodes. We

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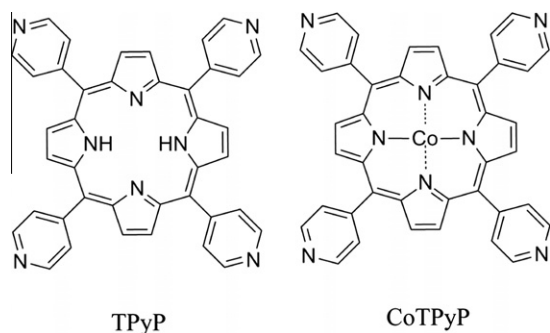


Fig. 1. Structures of 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) and cobalt 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine (CoTPyP).

have found surface modification with bromine to be a useful alternative to iodine due to the higher potentials of surface bromine oxidation as well as solution-phase bromide oxidation [19,20]. We have been able to observe highly ordered TPyP SAMs at potentials between 0.0 and +1.3 V vs. Ag/AgCl on Au(111) electrodes in 0.1 M HClO₄ solutions containing 150 μM KBr [21].

Here, we apply the iodine passivation technique to 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) and cobalt 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine (CoTPyP) SAMs on Au(111). CoTPyP differs from TPyP only by the presence of the cobalt (II) ion in the porphyrin center (Fig. 1), and we sought to investigate what effect, if any, metallation of the porphyrin would have on SAM formation on iodine-passivated Au(111) surfaces (referred to in the following as I–Au(111) surfaces).

2. Experimental

2.1. EC-STM and CV measurements

A Au(111) single crystal electrode was purchased from icryst (Jülich, Germany) and used for all experiments described. The electrode consisted of a Au bead formed on the end of a pure Au wire and subsequently cut perpendicular to the (111) face, as described by Clavilier et al. [22], to yield a Au(111) disk of 2 mm diameter. Before each experiment, the electrode was cleaned by heating to red heat for 5 min in a pure hydrogen flame, followed by cooling in air for 10 s and lastly immersion in pure water. A droplet of water was left on the electrode surface during transfer to the electrochemical cell to limit surface contamination from the air.

Cyclic voltammetry was performed using a CH Instruments Electrochemical Analyzer (CH Instruments, Austin, TX, USA). The cyclic voltammetry cell was used with a Ag/AgCl reference (Bioanalytical Systems, West Lafayette, IN, USA; 3 M KCl filling solution, glass frit separation to the sample) and a Pt wire auxiliary electrode. Contact between the Au(111) working electrode and the sample solution was made using the hanging meniscus method to isolate the (111) face [21,23,24]. The Supporting Information contains a drawing that illustrates the hanging meniscus contact. Unavoidable wetting of the bead sides during the hanging meniscus CV may explain small irregularities in the observed peak shapes for all of the CVs shown in this work. However, the overall peak positions were highly reproducible over several experiment preparations. Sample solutions were degassed by bubbling high purity Ar through the stirred solutions for 15 min prior to each experiment.

The electrochemical STM consisted of a PicoSPM scan head with a PicoStat auxiliary potentiostat from Molecular Imaging (now Agilent Technologies, Santa Clara, CA) and an RHK SPM-100 controller (RHK Technology, Troy, MI, USA). The EC-STM cell, constructed in

house, [17] consisted of a quartz glass cup (1 mL volume) fitted with a Teflon bushing designed to hold the Au working electrode and was sealed with a Viton O-ring (Dupont, Newark, DE, USA). The O-ring was stored in pure water for several days before experiments to permit leaching of any water-soluble contaminants. The quartz glass and Teflon pieces of the cell were flushed with piranha solution (1:3 mixture of 30% hydrogen peroxide and concentrated sulfuric acid) and rinsed with copious amounts of pure water prior to each experiment. *Caution: piranha solution is highly oxidizing and should never be stored in closed containers.* For EC-STM experiments, a Ag wire quasi-reference electrode and Pt wire auxiliary electrode were used. The potential of the Ag wire was verified against the Ag/AgCl reference in solutions identical to those used for EC-STM, and all potentials listed in this work are quoted with respect to the Ag/AgCl electrode.

W tips were prepared by mechanically cutting W wire (0.25 mm diameter, 99.95% purity, Alfa Aesar, Ward Hill, MA, USA). To minimize the electrochemical contribution to the tip current during EC-STM imaging, tips were coated with an electrophoretic paint (Clearclad HSR, Clearclad, Harvey, IL, USA) using a procedure described previously [25]. STM images were recorded in constant-current mode using tunneling setpoints between 0.5 and 2.0 nA, and are shown without any filtering. The potential of the tip was kept between 0.00 and +0.20 V for all experiments in order to prevent the formation of tungsten oxide.

2.2. Reagents

All solutions were prepared using water deionized and charcoal treated in a Milli-Q Plus reagent grade purification system (Millipore, Bedford, MA, USA). The 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) was purchased from Sigma–Aldrich (St. Louis, MO, USA) and used without further purification. Analytical reagent grade KBr, KI, and CoCl₂ were purchased from Mallinckrodt (St. Louis, MO, USA), and HClO₄ and H₂SO₄ from Fisher Scientific (Pittsburg, PA, USA).

Cobalt 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine (CoTPyP) was prepared by metallating TPyP using a procedure from the literature [26]. Briefly, tetrapyrrolylporphyrin was refluxed for 3 h with an excess of cobalt chloride in a 1:1 acetic acid and dimethyl formamide solution. The acetic acid was dried for 12 h over molecular sieves before use. The resulting solids were filtered and washed with pure water and diethyl ether. Mass spectra of the compound showed fragments with an m/z number and isotope distribution appropriate for CoTPyP. ¹H NMR spectra recorded in chloroform-*d* with 5% dimethylsulfoxide-*d*₆ and 5% trifluoroacetic acid showed three signals with chemical shifts different from those of the free base TPyP, and no other signals but those of the solvent were observed. No change in the ¹H NMR spectrum was detected for the CoTPyP sample after several weeks of storage, indicating that CoTPyP is stable in the acidic medium.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammetry was used to verify adsorption of TPyP and CoTPyP to Au(111). Fig. 2a shows hanging meniscus cyclic voltammograms (CVs) taken using the flame annealed Au(111) electrode in 0.1 M HClO₄ solution containing 150 μM KI, before and after the addition of 30 μM TPyP to the electrochemical cell. In aqueous solution and at potentials above the potential of zero charge (PZC), iodide adsorbs onto Au(111) electrodes to form a monolayer of iodine, referred to in the following as the iodine adlayer [27–29]. Before the introduction of TPyP, the CV features observed below –0.1 V correspond to changing iodine surface coverage as well as

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