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# Self-assembly of metal free porphyrin layers at copper-electrolyte interfaces: Dependence on substrate symmetry

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ABSTRACT

Combined Cyclic Voltammetry (CV) and in-situ Electrochemical Scanning Tunneling Microscopy (EC-STM) studies were employed to compare the self-assembly of redox-active 5,10,15,20-Tetrakis (4-trimethyl ammonium phenyl) porphyrin tetra (p-toluenesulfonate), abbreviated as $[H_2TTMAPP]^{+4}$ on Cu(100) and Cu(111) electrode surfaces in 10 mM HCl solution. Under these conditions, both surfaces are chloride pre-covered with a $c(2\times2)$ Cl- and $c\left(p\times\sqrt{3}\right)$ Cl-layer on Cu(100) and Cu(111), respectively. On both surfaces highly ordered $[H_2TTMAPP]^{+4}$ layers are spontaneously formed. The short range molecular arrangement is quadratic in nature on both surfaces which can be described by a $\left(\sqrt{58}\times\sqrt{58}\right)$ R23° unit cell on the $c(2\times2)$ Cl-Cu(100), and a $(3\times4)$ unit cell on the $c\left(p\times\sqrt{3}\right)$ Cl-Cu(111) substrate. Large scale domains are formed on both surfaces the orientation of which reflects the symmetry of the substrate, namely on Cu(100) [Cu(111)] equivalent domains are rotated by 90° [120°], respectively. Thus, the different symmetry of the respective substrate surface has an influence on the otherwise self-assembled organic molecules.

## 1. Introduction

The self-assembly of organic molecules is an attractive approach for the formation of supramolecular systems expected to be used in many future applications. In particular, self-assembled layers of porphyrin based molecules on metal surfaces, with the capability of sensing and discriminating chiral molecules, are known as a potential material for a wide range of applications such as optoelectronic devices [1] and molecular logic devices [2]. Some porphyrin derivates are already used as sensors, due to their sensitivity to metal ions [3–6], for detecting heavy metal ions in domestic water [7]. In addition, porphyrins are well-known as a very important component in heme for the transfer and storage of oxygen in blood or in chlorophyll for the photosynthesis of green plants [8], two functions which in the future may possibly also be done by artificial arrays of such molecules. Furthermore, they are, nowadays, also used for the photodynamic therapy of cancers [9].

In fact, adlayer structures of porphyrins on bare as well as anion modified metal surfaces have already been investigated in the past in UHV [10–13], or in electrochemical media [14–20]. Gimzewski et al. [10] investigated the adsorption of copper-tetra(3,5-di-tert-butylphenyl) porphyrin (CuTBPP) on Cu(100), Au(110), and Ag(110), respectively, in UHV. It was pointed out that the packing arrangement of the CuTBPP adlayer depends on the metal substrate used. In addition, Barth and his coworkers investigated the interaction of tetrapyridyl-porphyrin (TPyP) molecules with a Cu(111) surface [12]. Miyake et al. [14] studied molecular arrays of a series of meso-tetra-substituted porphyrins on an HOPG surface in electrochemical environment by using electrochemical scanning tunneling microscopy (EC-STM). As a result, slightly undulating rows were obtained with 5,10,15-tris-(4-octadecyloxyphenyl)-20-(4-pyridyl)porphyrin molecules, while rows with more kinks resulted from 5-(4-carboxyphenyl)-10,15,20-tris(4-octadecyloxyphenyl)porphyrin. Itaya and his coworkers reported on the self-assembly of water soluble 5,10,15,20-tetrakis (N-methyl-4-pyridinium)-21H,23H-porphine ($[H_2TMPyP]^{4+}$) on anion modified metal surfaces such as I/Au(111) [15], S/Au(111) [16], I/Ag(111) [17], and I/Pt(100) [18]. Recently, Hai et al. found that highly ordered adlayers of the $[H_2TMPyP]^{4+}$ molecules were formed on iodide [19], and sulfate [20] modified copper electrodes.

The porphyrin chosen in this work is the water soluble porphyrin named 5,10,15,20-Tetrakis(4-trimethyl ammonium phenyl) porphyrin tetra(p-toluenesulfonate), in the following abbreviated as $[H_2TTMAPP]^{4+}$ (Fig. 1). In this molecule the substituents are longer than in the previously reported ones and, therefore, are expected to lead to the formation of different structures due to additional intermolecular side-group and substrate/side-group interactions.

We have studied both the electrochemical behavior as well as the self-assembly of the $[H_2TTMAPP]^{4+}$ molecules on chloride modified Cu(100) and Cu(111) electrodes, respectively, for the first time, using our home-built high resolution in-situ electrochemical scanning tunneling microscopy (EC-STM).

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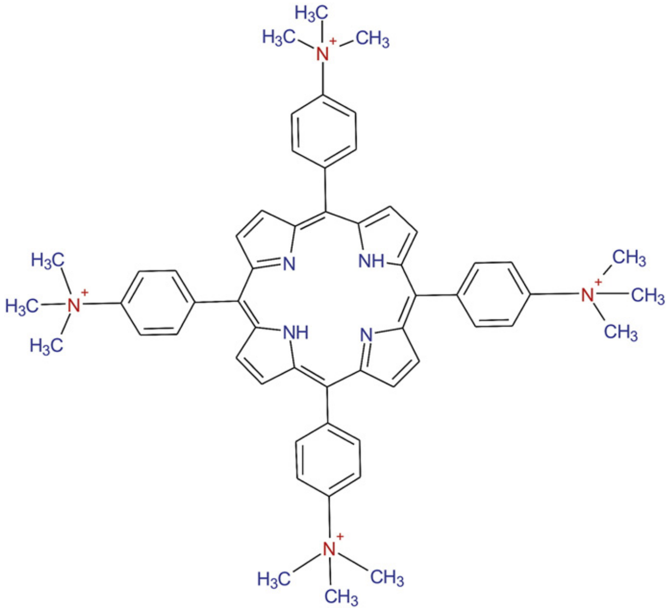

**Fig. 1.** The molecular structure of $[H_2TTMAPP]^{4+}$ cations.

This study particularly aims at an understanding of the influence of the crystallographic surface orientation on the self-assembled porphyrin structures on the chloride modified copper electrodes. Our STM results provide clear evidence for a dependence of the adsorbed structures on the symmetry of the substrate surface. Although the short range structure within the assembled layers is quadratic on both the Cu(100) and the Cu(111) substrate, on the large scale, however, domains reflect the symmetry of the Cu(100) and the Cu(111) substrate, i.e. they are rotated by 90° and 120°, respectively.

## 2. Experimental setup

All the STM experiments performed in this work were carried out using a home-built electrochemical scanning tunneling microscope (EC-STM) described in detail by Wilms et al. [21,22].

The tunneling tips used in our experiments were electrochemically etched from a 0.25 mM tungsten wire in 2 M KOH solution and subsequently coated by passing the tip through a hot-melt glue film.

For all solutions, high purity water (Milli-Q purification system, conductivity > 18 MΩ.cm, TOC < 4ppb), halide-free redox-active 5,10,15,20-Tetrakis (4-trimethyl-ammonium-phenyl) porphyrin tetra (p-toluenesulfonate) purchased from Aldrich-Sigma (Germany), and other reagent grade chemicals were used. All electrolyte solutions were purged with suprapure argon gas for several hours before use. The potentials of the copper electrode given in this paper refer to a reversible hydrogen electrode (RHE) even though in practice, a Pt wire was employed as counter-electrode. In order to guarantee a reproducibly smooth surface even after several electro-polishing cycles, a surface orientation of less than 0.5° off the (100) and (111) planes was required (MaTech company, Julich, Germany). The copper samples were electropolished before each STM experiment in order to remove the native oxide film, formed in air, and other contaminations from the surface by immersing the electrode surface into 50% orthophosphoric acid. Subsequently, an anodic potential of 2 V was applied between the copper electrode and a platinum foil for about 20 to 40 s.

After etching the copper surface was rinsed with degassed 10 mM hydrochloric acid, and mounted into the electrochemical cell of the EC-STM system. Initial CV and STM measurements were performed in the same solution as supporting electrolyte. This initial treatment in chloride containing solution is particularly useful because the high density of surface defects deriving from the electropolishing treatment process is thereby significantly reduced, i.e. by the so-called “electrochemical annealing” mechanism [21,23,24]. For the adsorption of redox-active porphyrin molecules on the chloride modified copper electrode, the pure supporting electrolyte was routinely substituted by a solution of 10 mM HCl containing 0.1 mM $[H_2TTMAPP]^{4+}$ in the potential range of the double layer regime of the copper electrodes in hydrochloric acid, e.g. +50 mV.

An inert highly oriented pyrolytic graphite (HOPG) crystal was also employed as working electrode in order to investigate the mere electrochemical behavior of the porphyrin molecules. HOPG has the advantage that no anions adsorb specifically on this surface and that this electrode offers a much broader potential window, from −500 mV to +2000 mV vs RHE, which allows to study the redox behavior of the molecules also outside the potential window of copper electrodes [25] and, hence, to arrive at a reliable assignment of current peaks in the CV to individual redox transitions of the molecules. An absolutely clean HOPG surface is easily obtained by peeling off the topmost graphite layer by adhesive tape. The CVs with HOPG were registered in the same working electrolyte (10 mM HCl + 0.1 mM $[H_2TTMAPP]^{4+}$) as used with the copper electrodes.

## 3. Experimental results and discussion

### 3.1. Characterization of the porphyrin redox-activity

The electrochemical properties of porphyrin derivatives have been studied quite extensively in the past [26–31]. For instance, Hambrigh et al. found that the free base 5,10,15,20-Tetrakis-(N-methyl-4-pyridyl)-21H,23H-porphyrin tetratosylate ($[H_2TMPyP]^{4+}$) undergoes several acid–base and electron transfer reactions [26] leading to the formation of porphyrin diacid and porphdimethene and/or porphdimethene diacid, respectively. These findings were confirmed by Wilson et al. [27–30] and recently by Hai et al. [31].

In the porphyrin derivative used in this work the four hydrogen atoms at the four meso positions of the central porphyrin core are replaced by four trimethy-ammonium-phenyl groups. It is expected that the tetra cationic form of this $[H_2TTMAPP]^{4+}$-porphyrin undergoes the same acid–base reactions and electron transfer steps as $[H_2TMPyP]^{4+}$ but at different potentials.

The voltammetric curve of HOPG, at first in the pure electrolyte (10 mM HCl), is depicted in Fig. 2 (dashed gray curve) showing the broad potential window without the appearance of any cathodic and anodic peaks, demonstrating that the HOPG surface is not affected by the presence of the halide anions, namely the chloride anions in this case. The CV is considerably altered as soon as the supporting electrolyte is substituted by the working electrolyte containing the $[H_2TTMAPP]^{4+}$ molecules (solid black curve in Fig. 2) including several anodic and cathodic current peaks. The first observation is, that both the cathodic and anodic limits of the CV are shifted to more negative potentials, i.e. the hydrogen evolution reaction (HER) is retarded by the presence of the molecules, while the oxygen evolution reaction (OER) starts already at less positive potentials. Next we concentrate on the redox processes only which fall into the potential window of copper, i.e. the range between −500 mV and +300 mV as indicated in Fig. 2. The first porphyrin redox process represented by a (quasi) reversible pair of peaks with $P_1 = -210$ mV and $P'_1 = -30$ mV vs RHE (see inset in Fig. 2) is assigned to the diffusion controlled first two-electron transfer process, namely reduction ($P_1$) and reoxidation ($P_1'$). The further reduction process underlying peak $P_2$ has no obvious reoxidation counterpart indicating, in agreement with the literature [28–31], that this reduction process is irreversible.

It is well known that all redox processes detectable within the potential window of HOPG affect the inner ring system of the porphyrin molecules only, those affecting the outer ligands are outside this potential range [26]. This is even more true for the CVs with copper