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# Fast *vs.* Slow: Electrolyte and Potential Dependent Adlayer Switching of an Oligopyridine on Au(111)

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ABSTRACT

The structure of an oligopyridine (3,3′-bis(terpyridine) (3,3′-BTP)) monolayer at the Au(111)|electrolyte interface shows a strong dependence on type of electrolyte and pH. Neutral phosphate buffer, sulfuric acid, sodium sulfate and perchloric acid were employed as electrolytes. Structure transitions are fast and fully reversible under acidic conditions, while an extremely slow process in the range of hours could be observed in phosphate buffer. These findings are attributed to the relative weakness of (weak) hydrogen bonds in comparison to Coulomb interactions in buffer. The slow process allows time-dependent investigations of structure formation. The systems were investigated by cyclic voltammetry (CV) and electrochemical scanning tunneling microscopy (EC-STM).

## 1. Introduction

One of the key subjects in interfacial research is the study of the adsorption of organic molecules on metal electrode surfaces in solution, because it is closely related to many applications in molecular electronics like wires (columns), switches, or diodes. [1–6] The elucidation of the mechanism underlying the assembly of organic molecules on the electrode surface as well as their interactions with the metal surface is part of the development of molecular devices like scanning probe microscopy based single–molecule analyses, nanogap electrodes, or molecular machines. [7–10] Besides many investigations on the adsorption of organic sulfur-containing compounds in an electrochemical environment, [11–14] studies on non-sulfur-containing organic molecules, such as uracil, [15,16] cytosine, [17] hydroquinone derivatives, [18] or pyridine-ring containing compounds, [19,20] were also reported. A special type of the latter class of compounds, the so-called bis(terpyridine)-like oligopyridines (BTPs), were extensively investigated at the solid|organic solvent and solid|gas interfaces, respectively, showing a broad variety of monolayer structures all based on (weak) intermolecular hydrogen bonds $C-H\cdots N$ (ca. 10 kJ mol$^{-1}$ per bond, derived from model system). [21–29] If the organic solvent is exchanged for an acidic electrolyte (e.g. sulfuric acid) the nitrogen atoms of the pyridine rings are easily protonated, [30] which disrupts the $C-H\cdots N$ hydrogen bonds and, thus, prevents the formation of long-range order of the adlayers on Au(111) at electrode potentials $E > +0.4$ V as shown for the isomer 2,4′-BTP. [20] For $E < +0.4$ V, individual molecules were not detectable in STM images presumably due to a higher molecular mobility. Indeed, cyclic voltammetry (CV) signals the presence of an adsorbate-free gold surface. Out of the different BTP isomers 3,3′-BTP (Fig. 1) is especially intriguing as its monolayers can act as template for the formation of host – guest networks. [31]

Here, we report on the adsorption of 3,3′-BTP on an Au(111) electrode, which was investigated by CV and electrochemical scanning tunneling microscopy (EC-STM) in five different electrolytes. We focus on the influence of substrate potential, pH and electrolyte on the monolayer structure.

## 2. Experimental

### 2.1. Gold Substrates

The Au(111) electrodes were single-crystal discs (MaTeck, Juelich, Germany), 4 mm in diameter and height for electrochemical experiments and 12 mm in diameter and 2 mm thick for use in the scanning tunneling microscope (STM). Before each experiment, the electrodes were flame-annealed in a hydrogen

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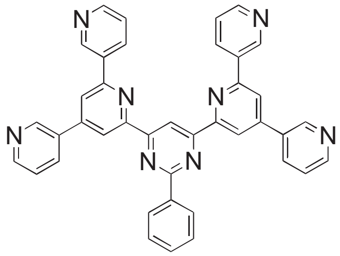

**Fig. 1.** Structure of bis(terpyridine)-like 3,3′-BTP.

flame for 3 to 5 min and cooled to room temperature in a stream of nitrogen.

### 2.2. *Preparation of 3,3′-BTP monolayers*

3,3′-BTP monolayers were prepared by immersing the previously annealed gold crystal into a 20 mM 3,3′-BTP solution in 1,2,4-trichlorobenzene (TCB) (Merck, >99%) for 30 min. After modification, the sample was removed from the solution, rinsed with TCB, acetone, and Milli-Q water (Millipore Corp. USA; 18.2 MΩcm), then blown dry with nitrogen. 3,3′-BTP was prepared according to the literature. [24]

### 2.3. *Electrolyte Solutions*

Different solutions were used for the study of the BTP monolayers. The electrolytes were prepared from Merck super pure chemicals and Milli-Q water.

### 2.4. *CV and EC-STM Measurements*

Cyclic voltammetry was performed in a three-compartment glass cell with standard electrochemical equipment. A saturated calomel electrode (SCE) served as reference electrode, the counter electrode was a platinum wire. A Topometrix TMX 2010 Discoverer STM was used. Experiments were performed with tungsten tips, etched from a 0.25 mm diameter wire in aqueous NaOH. The tips were then coated with an electrophoretic paint to reduce the faradaic current at the tip-electrolyte interface. All STM images were recorded in the constant-current mode. Two platinum wires served as counter and reference electrodes, but all potentials refer to SCE.

## 3. Results and Discussion

### 3.1. *Investigations in phosphate buffer*

*Cyclic voltammetry.* In order to minimize protonation of the oligopyridine we have chosen a neutral and pH-stable electrolyte, i.e. phosphate buffer (0.05 M $K_2HPO_4$/0.05 M $KH_2PO_4$). Fig. 2 shows the CVs for bare and 3,3′-BTP-modified Au(111) in the buffer.

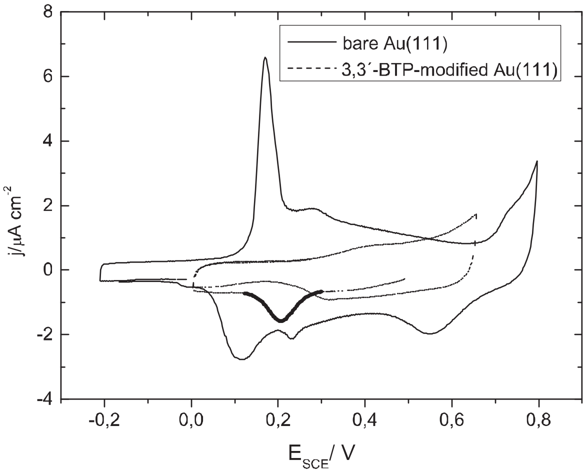

**Fig. 2.** CVs of bare Au(111) (solid line) and 3,3′-BTP-modified Au(111) (dashed line) in phosphate buffer with new peak in bold. The potential sweep rate was 10 mV $s^{-1}$.

The CV of bare Au(111) resembles those reported in literature, [32,33] exhibiting three distinctive peak pairs. Despite several attempts no structural information on the phosphate adlayer could be obtained by STM, which is in accordance with literature reports where no adlayer structure could be imaged, too. [32] Thus, the assignment of the peaks is based on another paper in which an ordered adlayer could be observed but only temporarily in small patches. [33] This finding is attributed to the high mobility of the oxoanions. The broader peaks at +0.10 V and +0.28 V correspond to the anion-induced lifting of the Au surface reconstruction and phosphate adsorption, respectively. It also shows a second small peak pair at a potential of about +0.73 V, which can be attributed to the transition of the partially ordered phosphate adlayer phase. [33] In contrast, when the CV measurement is performed for the 3,3′-BTP covered electrode (starting at +0.5 V), the characteristic peaks of bare Au(111) are not observed, indicating a dense coating of the gold surface by BTP molecules, which prevents the adsorption of $HPO_4^{2-}$/$H_2PO_4^{-}$ ions. Decreasing the electrode potential below +0.3 V leads to a gradual broadening of the curve, however, no evident peaks appear. If the potential is kept at +0.5 V for 15 h and then lowered, surprisingly, a new peak at +0.2 V shows up (marked in Fig. 2) indicating the dissolution of a structure, which was formed on the electrode during the waiting time of 15 h. Performing the next cycle with the standard sweep rate (10 mV $s^{-1}$) does not show anymore a peak at +0.2 V, as expected. Thus, we speculate that the structure develops very slowly but dissolves quickly but such structural processes can only be proven by time-dependent direct imaging.

*Scanning tunneling microscopy.* Hence, in-situ EC-STM was employed to verify the assumptions from CV and to elucidate the structural processes. Fig. 3 shows several time-dependent STM images of SAM-modified Au(111) at +0.50 V in phosphate buffer.

Remarkably, the herringbone structure can be observed at +0.50 V (see Fig. 3a), although at such high electrode potentials usually the reconstruction is lifted on bare Au(111) [32] as well as on SAM-modified Au(111). [20] Depending on the height and duration of the potential, the herringbone structure is maintained for 45 min with an adlayer growing simultaneously (Fig. 3b). In about 60 min, the adlayer covers the entire surface of Au(111) (Fig. 3c). As any excess molecules were removed by rinsing the Au substrate extensively after modification, we speculate that at low potential the molecules are adsorbed somewhere on the substrate as agglomerates eventually in upright position. At high potential, the molecules spread over and coat the entire surface of the electrode. A high-resolution STM image ($30 \times 30$ $nm^2$) demonstrates the molecular arrangement after 80 min (Fig. 3d) with each bright spot representing a single 3,3′-BTP molecule. More ordered adsorption is only observed after 5.5 h (Fig. 3e) showing submolecular resolution with the typical shape of single molecules (inset in Fig. 3e). Furthermore, a short-range hexagonal order can be observed. When the electrode potential is stepped down from +0.5 V to 0 V, the structure disappears immediately (cf. CV, Fig. 2). Presumably the molecules become too mobile to be observed by STM (Fig. 3f).

### 3.2. *Investigations in sulfuric acid*

*Cyclic voltammetry.* The much slower kinetics of structure formation in the presence of the buffer compared to our previous