

# Adsorption and Electrochemical Activity: An In Situ Electrochemical Scanning Tunneling Microscopy Study of Electrode Reactions and Potential-Induced Adsorption of Porphyrins

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The effect of adsorption on molecular properties and reactivity is a central topic in interfacial physical chemistry. At electrochemical interfaces, adsorbed molecules may lose their electrochemical activity. The absence of in situ probes has hindered our understanding of this phenomenon and electrode reactions in general. In this work, classical electrochemistry and electrochemical scanning tunneling microscopy (EC-STM) were combined to provide molecular level insight into electrochemical reactions and the molecular adsorption state at the electrolyte–electrode interface. The metal-free porphyrin 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine (TPyP) adsorbed on Au(111) in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution was chosen as a model system. TPyP is found to irreversibly adsorb on Au(111) over a wide range of potentials, from  $-0.25$  to  $0.6$  V<sub>SCE</sub>. The adsorption state of TPyP has a dramatic effect on its electrochemistry. Preadsorbed, oxidized TPyP displays no well-defined cathodic peaks in cyclic voltammograms in sharp contrast to solution-phase TPyP. Our present work provides direct, molecular level evidence of the electrochemically “invisible” species. Electrochemical activity of adsorbed species is recovered by allowing the oxidized molecule sufficient time (tens of minutes) to reduce. The redox state of adsorbed TPyP also affects the nature of the adsorption. Oxidized species can apparently only form monolayers. However, multilayers, stable enough to be imaged by STM, can form when the adsorbed TPyP is in the reduced state. This suggests that by controlling the electrochemistry one can either promote or suppress the formation of multilayers.

## Introduction

The flexibility of the structural, electronic, and chemical properties of porphyrins has been recognized and utilized in applications ranging from organic electronics, solar cells, and electrocatalysis to nanoelectronics.<sup>1–3</sup> Many of these applications rely on the formation of thin films of ordered structures of porphyrins and related compounds.<sup>4–7</sup> Intermolecular interactions such as dipole–dipole,<sup>8</sup> hydrogen bonding,<sup>8</sup> and coordination<sup>9</sup> in porphyrin building blocks are being used to create self-assembled structures on surfaces with increasing sophistication. Itaya et al. demonstrated that the ordering of porphyrin molecules on metal surfaces can be promoted by a passivating layer of iodine, which reduces the adsorbate–substrate interaction and facilitates surface diffusion.<sup>10–12</sup> The effect of surface charge was demonstrated by Hipps et al. with the coadsorption of F16CoPc (Pc = phthalocyanines) and NiTPP in an ultra high vacuum environment.<sup>4</sup> The electron-withdrawing F16CoPc alone cannot form ordered adlayers due to strong electrostatic interaction with the surface.<sup>4</sup> It was proposed that ordered adlayers are achieved by coadsorption with the electron-donating NiTPP to achieve the optimum surface charge density required for self-assembly.<sup>4</sup>

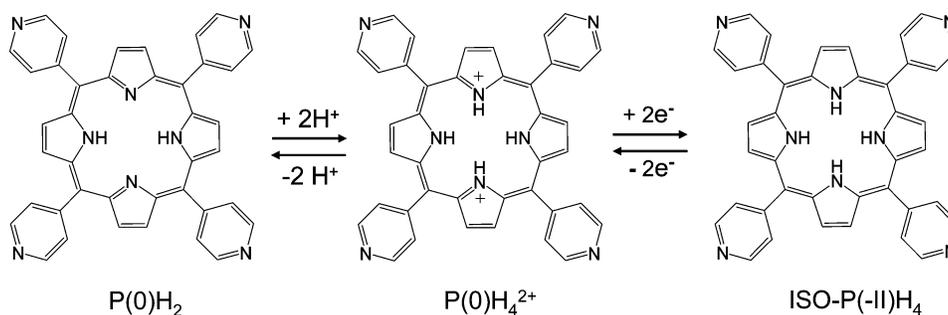
In a previous report, we demonstrated that in an electrochemical environment the interaction between adsorbed 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine (TPyP, Scheme 1) and the substrate Au(111) is tunable.<sup>13</sup> The adsorbate–substrate interaction was modified by adjusting the surface charge via external control of the electrode potential. It was shown that the formation of an ordered TPyP adlayer can be controlled by

surface charge.<sup>13</sup> Adsorption on positively charged surfaces results in disordered adlayers, due to excessive molecule–substrate interactions.<sup>13</sup> Ordered porphyrin monolayers can be prepared by adsorption at potentials between  $0.2$  and  $-0.2$  V<sub>SCE</sub>, where the surface is expected to be negatively charged (the potential of zero charge of reconstructed Au(111) in 0.1 M H<sub>2</sub>SO<sub>4</sub> is about  $0.27$  V<sup>14</sup>) and the molecule–substrate interaction is strong enough to confine TPyP in ordered surface lattices but weak enough to allow facile lateral reorganization, a key requirement for self-assembly on surfaces.<sup>15</sup>

In addition to controlling the structure of porphyrins adsorbed on surfaces, surface charge can control the reactivity of porphyrins. This is especially important for applications related to electrocatalysis.<sup>2</sup> It has been recognized that adsorption can affect the electrochemistry of the metal centers in porphyrins dramatically.<sup>16,17</sup> The general explanation is that adsorption changes the energetics of redox states and therefore alters the voltammetric responses of the molecules of interest.<sup>16,17</sup> However, the details of how the surface interactions with the adsorbates change the electrochemical dynamics and redox potentials remain poorly understood.

The reactivity of the porphine rings of water-soluble free-base porphyrins in bulk solutions has been investigated extensively, and surface effects have been noted.<sup>18,19</sup> It was found that the reduction potentials of the porphyrins were more negative on Au electrodes than on mercury electrodes, which was attributed to the effect of adsorption.<sup>19</sup> Devynck et al. reported that in an acidic medium TMPyP [5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)-21H,23H-porphine tetrakis(*p*-toluenesulfonate)] irreversibly adsorbed on Au and displayed no redox peaks between  $-0.4$  V and  $0.7$  V<sub>SCE</sub> in cyclic voltam-

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**SCHEME 1: Possible Electrochemical Reaction Mechanism of TPyP under Acidic Medium<sup>18,19 a</sup>**

<sup>a</sup> The pyridyl groups are most likely protonated in acidic solution.

mograms.<sup>20</sup> This is in stark contrast with its electrochemical behavior in the bulk solution.<sup>21</sup>

In this paper we report a systematic scanning tunneling microscopy (STM) and electrochemical study designed to understand the interplay between the redox properties, adsorption, and self-assembly processes of TPyP on Au surfaces. We found that the irreversible adsorption of TPyP had a dramatic effect on its electrochemistry. The reduction of adsorbed TPyP is orders of magnitude slower than that of solution-phase TPyP. The suppressed reduction of adsorbed TPyP is rationalized by the strong  $\pi$ -bonding interaction between TPyP molecules and the Au substrate. Our investigation also shows how redox reactions can influence the formation of multilayers. This suggests that, by controlling the electrochemistry, one can either promote or suppress the formation of multilayers.

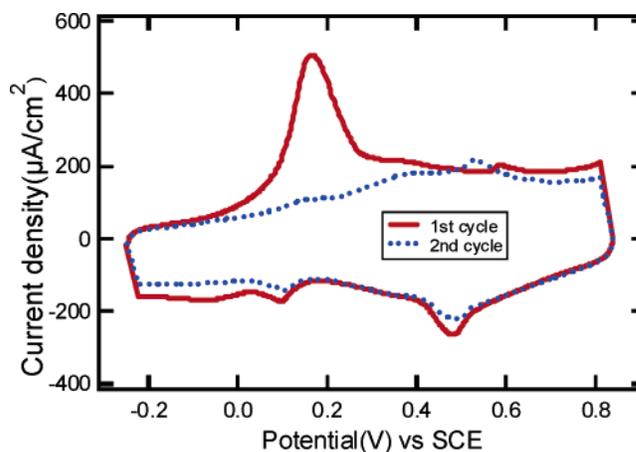
### Experimental Section

An Au(111) single crystal (Monocrystals Co., Medina, OH) and a single-crystal gold bead were used as substrates. Prior to the experiments the substrate was cleaned by immersion in hot piranha solution (1:3  $\text{H}_2\text{O}_2$  (J. T. Baker, CMOS) and  $\text{H}_2\text{SO}_4$  (J. T. Baker, CMOS)) for 1 h and immersion in hot  $\text{HNO}_3$  (EM SCIENCE GR) for 30 min. (Caution! The piranha solution is a very strong oxidizing agent and extremely dangerous. Eye protection and gloves should be used during handling.) After each step the sample was rinsed by sonication in ultrapure water ( $>18 \text{ M}\Omega \text{ cm}$ ) produced by a Barnstead, Nanopure Infinity system, equipped with a UV lamp to further remove organic impurities. After the chemical cleaning, the crystal was hydrogen flame annealed and allowed to cool in air. The crystal was transferred to the STM electrochemical cell and immersed under potential control (0.1 V) in 0.1 M  $\text{H}_2\text{SO}_4$  solution (Fisher Scientific Co., trace metal grade).

5,10,15,20-Tetra(4-pyridyl)-21H,23H-porphine (TPyP) was purchased from Aldrich and used without further purification. The 0.02 mM TPyP solution was prepared in 0.1 M  $\text{H}_2\text{SO}_4$  solution. After the bare gold surface was imaged under neat 0.1 M  $\text{H}_2\text{SO}_4$  solution, a drop of the TPyP solution was added to the STM cell, to produce a final concentration of about  $10^{-6}$  M TPyP. In some cases, as indicated in the text, preadsorbed TPyP was studied in a porphyrin-free solution.

The electrochemical cell was made of Teflon. All potentials were quoted against SCE, though a silver wire or a platinum wire was typically used as the quasi-reference electrode. A platinum wire was used as the counter electrode. All cell components were chemically cleaned in the same way as the crystal.

STM images were obtained with a PicoScan STM system (Molecular Imaging). STM tips were electrochemically etched tungsten STM tips insulated with paraffin wax. The Faradaic



**Figure 1.** Cyclic voltammograms of Au(111) with preadsorbed TPyP in a blank 0.1 M  $\text{H}_2\text{SO}_4$  solution. Preadsorption was at  $-0.25$  V. Initial potential  $-0.25$  V, scan rate 2 V/s (first cycle —, second cycle ···)

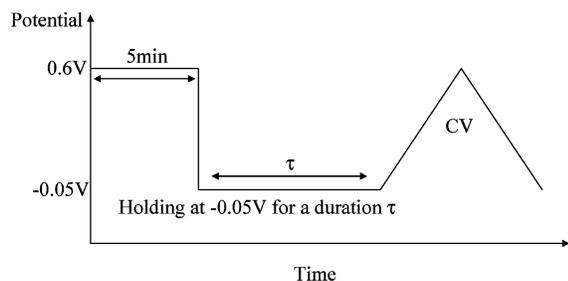
current of the insulated tips under imaging conditions was typically less than 10 pA. All of the STM images were obtained under constant current mode, 0.2–0.3 nA. The tip potential was maintained at 0.0 V to minimize the Faradaic current. A bi-potentiostat (Molecular Imaging) was used to control the sample and tip potential independently. Cyclic voltammetry was performed using the same bi-potentiostat under argon purging.

### Results and Discussion

**3.1. Cyclic Voltammetry Results.** The electrochemical reaction mechanisms of free-base porphyrins in the solution phase have been extensively investigated (Scheme 1).<sup>18,19</sup> The unreduced form, P(0), exists as the free base,  $\text{P}(0)\text{H}_2$ , or the diacid,  $\text{P}(0)\text{H}_4^{2+}$ , depending on the pH of the solution. In a low pH solution, the main reduced form P(0) exists as the diacid,  $\text{P}(0)\text{H}_4^{2+}$ . At about  $-0.2$  V, P(0) can undergo a two-electron reduction process to form phlorin,  $\text{P}(-\text{II})\text{H}_4$ . At potentials lower than  $-0.4$  V, further reduction occurs, from P(-II) to P(-IV) (not shown).<sup>18,19</sup>

**3.1.1. Cyclic Voltammograms of TPyP Preadsorbed at  $-0.25$  V.** To study the redox chemistry of TPyP adsorbed on Au(111) electrodes without the interference of TPyP from the bulk solution, a cyclic voltammetry experiment involving Au(111) with preadsorbed TPyP at  $-0.25$  V was employed. To prepare the preadsorbed TPyP, the Au(111) electrode was emersed from the TPyP solution at  $-0.25$  V, then the Au electrode was rinsed with 0.1 M  $\text{H}_2\text{SO}_4$ . The Au electrode was then transferred into an electrochemical cell containing 0.1 M  $\text{H}_2\text{SO}_4$  for electrochemical measurements.

The first scan of the cyclic voltammogram (CV, Figure 1) of the preadsorbed TPyP shows a peak, at 0.15 V, which we assign



**Figure 2.** Waveform for the cyclic voltammetric experiment of TPyP preadsorbed at a positive electrode potential.

to the oxidation of adsorbed P(−II) species as suggested by previous studies of related species.<sup>18,19</sup> In the cathodic scan of the first cycle, surprisingly a much smaller peak than that observed in the anodic scan appears at 0.08 V. Moreover, in the second cycle, the anodic peak became much smaller than it had been in the first anodic scan. The pair of redox peaks at 0.46 and 0.53 V, which appear in the second cycle, may reveal the adsorption/desorption of  $\text{SO}_4^{2-}$  at Au(111).<sup>22</sup> Through the use of the second scan as the background, the lower limit of the amount of charge per unit area consumed for the surface oxidation reaction is calculated to be about  $30 \mu\text{C}/\text{cm}^2$ . Dividing the total number of electrons by 2 (number of electrons involved in the oxidation) yields a TPyP coverage of about  $9.4 \times 10^{13}$  molecules/ $\text{cm}^2$ . This corresponds to about 2.2 monolayers, assuming that each molecule occupies an area of  $1.55 \times 1.55 \text{ nm}^2$ , as determined by STM.<sup>13</sup> The magnitude of the oxidation peak clearly shows that multilayers of TPyP can be adsorbed on Au(111) and survive the rinsing and transfer to another electrochemical cell.

The small cathodic peak and the dramatic difference between the first and the second scans suggest irreversibility of the redox reaction. The possible explanations are:

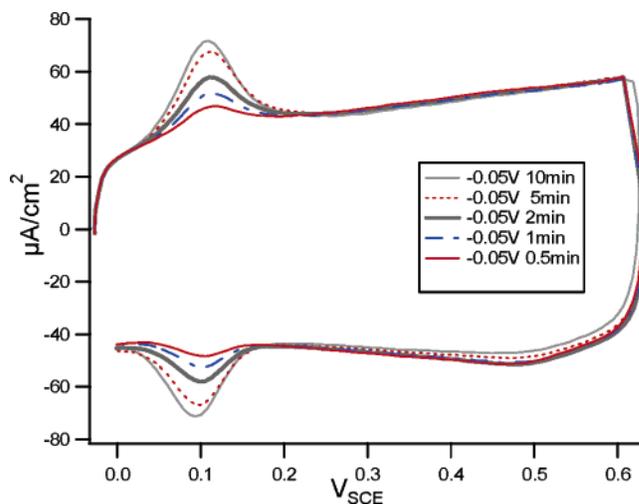
(1) The anodic peak at 0.15 V is accompanied by significant desorption. Once the TPyP molecules are desorbed from the electrode and diffuse into the bulk solution (0.1 M  $\text{H}_2\text{SO}_4$ ), they can no longer contribute to the electron-transfer processes at the electrode surface. This explanation seems in contradiction with our previous STM result that the interaction between TPyP molecules and the Au(111) surface is strong at a high electrode potential but weak at a low electrode potential.<sup>13</sup> However, the strong molecule–substrate interaction, deduced from STM, involves only the first layer and not the multilayer.

(2) After oxidation, the oxidized P(0) species at the surface is difficult to reduce. Adsorbed first layer species with low reactivity have been noted previously.<sup>23,24</sup> This has been an important phenomenon in electrochemistry. Our present work provides direct, molecular level evidence of the electrochemically “invisible” species by combining classical electrochemistry with in situ STM.

(3) A third possible explanation involves a combination of 1 and 2. After oxidation, the outer layer TPyP is desorbed from the surface, while most of the first layer of TPyP remains on the surface. The remaining adsorbed oxidized TPyP molecules are difficult to reduce, showing very low electrochemical activity so that only very small redox peaks can be seen.

The plausibility of these explanations is discussed in detail in section 3.3 after presentation of the STM results.

**3.1.2. Cyclic Voltammograms of TPyP Preadsorbed at 0.6 V.** To understand in more detail the electrochemical reactivity of irreversibly adsorbed TPyP, another series of voltammetric experiments (Figure 2) was carried out. TPyP molecules were preadsorbed at 0.6 V before the Au electrode was rinsed,



**Figure 3.** Cyclic voltammograms of preadsorbed TPyP on Au(111)/0.1 M  $\text{H}_2\text{SO}_4$ . The electrode surface was equilibrated at  $-0.05 \text{ V}$  for different durations. Scan rate  $1 \text{ V/s}$ .

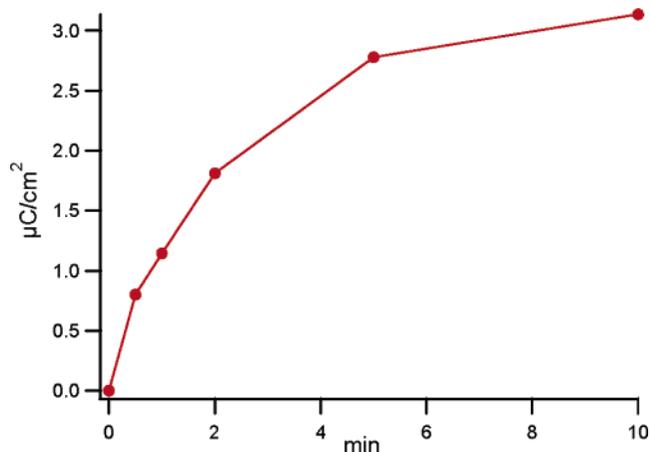
transferred to an electrochemical cell containing 0.1 M  $\text{H}_2\text{SO}_4$ , and held at 0.6 V for 5 min to ensure complete oxidation of the adsorbed species. Then the electrode was stepped to a negative, reductive potential,  $-0.05 \text{ V}$ , for a duration  $\tau$ , after which a CV scan was initiated (Figure 2). Interestingly, a pair of symmetric anodic and cathodic peaks, characteristic of a reversible redox reaction of adsorbed species, was observed. The peaks grew with increasing time spent at  $-0.05 \text{ V}$  (Figure 3). Though the growth appeared to slow for times longer than 5 min, there was no clear sign of reaching a plateau (Figure 3). Since the experiment was carried out in a porphyrin-free electrolyte, the generation of an oxidative wave could not be attributed to the adsorption of redox-active porphyrin molecules from the solution phase. Rather it provides evidence that at least some porphyrin adsorbates remain on the surface at 0.6 V, though at times they may be electrochemically “invisible” to the voltammetric experiments. The electrochemical signal can be restored by equilibrating the electrode at negative potential for a sufficient duration (Figure 3).

The reduction of P(0) adsorbed on the surface appears slow. Even after 10 min at  $-0.05 \text{ V}$ , only about 0.2 ML of TPyP is reduced, based on the integrated charge density. This suggests that the adsorption can alter the redox kinetics dramatically.

Considering the voltammetric results (Figure 3) discussed above, we may infer that the small cathodic peak in the second cycle of Figure 1 is evidence that not all of the TPyP molecules have desorbed from the surface after oxidation in the first cycle. In fact, subsequent STM results will show that a monolayer of TPyP remains on the surface over a wide range of electrode potentials. The probable interpretation of the difference between the two scans in Figure 1 is that oxidation results in desorption of multilayers of TPyP in the first cycle and that only the first layer of TPyP is left on the Au(111) surface. The reduction of the remaining first layer of adsorbed P(0) is not rapid enough to produce a significant cathodic peak in the second cycle of Figure 1.

In summary, the voltammetric results show that preadsorbed TPyP displays distinct electrochemical reactivity from TPyP in solution. The electrochemical reactivity of adsorbed TPyP is strongly related to the molecular adsorption state. Reduced species are electrochemically active while the activity of oxidized species is suppressed.

**3.2. STM Results.** Electrochemical experiments suggest that at reductive potentials multilayer adsorption is possible. Oxida-



**Figure 4.** Integrated charge, resulting from oxidation of preadsorbed TPyP, as a function of duration at  $-0.05$  V extracted from the CVs in Figure 3.

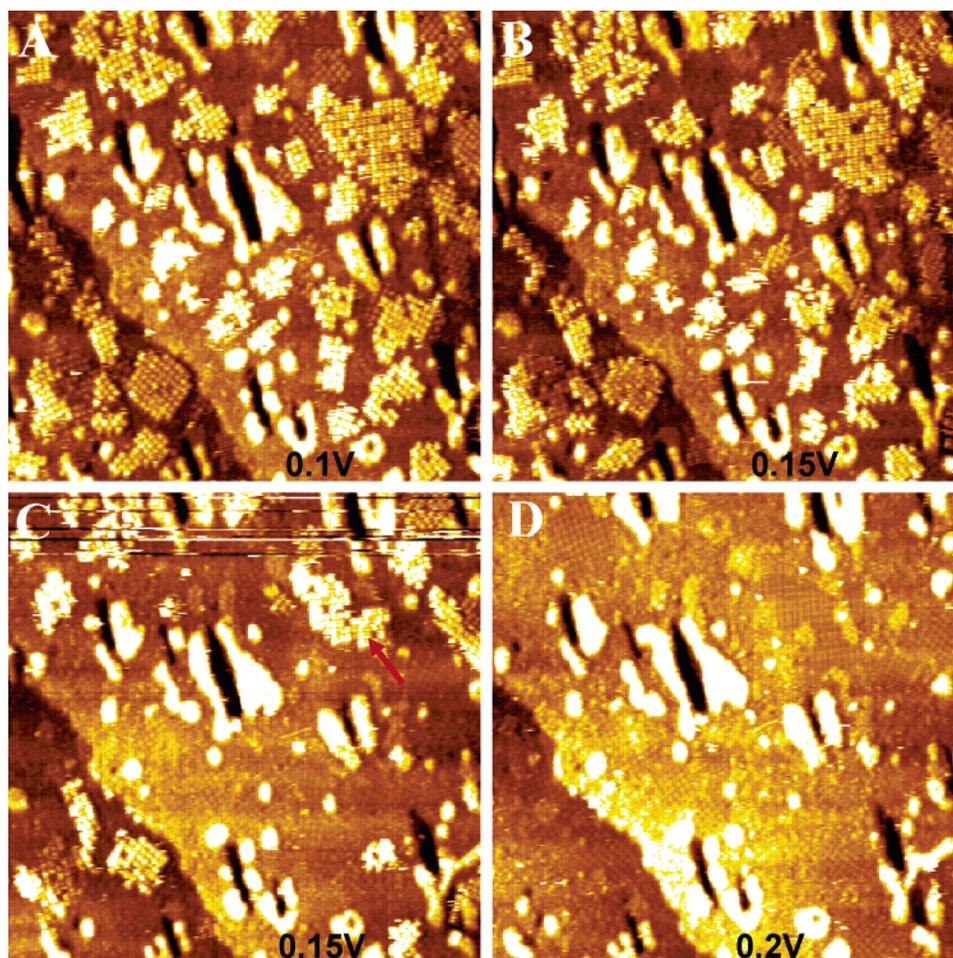
tion ( $>0.15$  V) of a preadsorbed multilayer of TPyP results in significant desorption. The remaining adsorbed oxidized TPyP species show very low electrochemical reactivity. No significant cathodic peak appeared in the CV (Figure 1). However, on their own, the electrochemical experiments do not provide a molecular level understanding of the electrode reaction mechanisms and the potential-dependent adsorption of TPyP.

**3.2.1. Potential-Dependent Adsorption–Desorption Processes of TPyP at Au(111).** To obtain a molecular level understanding

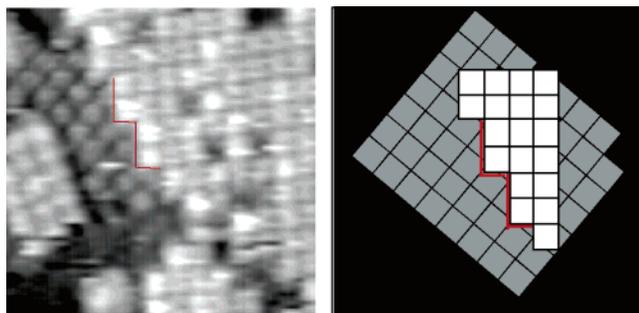
of the oxidation of adsorbed TPyP and to answer the question of how the electrode potential affects TPyP adsorption and electrode reactions at the Au(111)/0.1M  $\text{H}_2\text{SO}_4$  interface, the potential dependence of the adlayer structure was studied by STM.

The ordered adlayer of TPyP on unreconstructed Au(111) was observed at potential 0.1 V (Figure 5A). In addition to the Au islands resulting from the lifting of Au(111) reconstruction,<sup>14</sup> clusters containing porphyrin adsorbates can be resolved, as 1.55 nm wide squares.

Interestingly, the distribution of molecular domain heights is binary. The majority of the molecular clusters are 2.5–3.1 Å higher than the island-free areas while some of the molecular clusters are only 1.2–1.5 Å high. Closer inspection of the boundaries between the layers with more apparent height and the layers with less apparent height provides evidence that the former are adsorbed on top of the latter. The STM image shows that, in the boundaries, the layer with more apparent height sometimes blocks the view of molecules in the layer with less apparent height (Figure 6). Only parts of molecules in the “lower” layers are resolved in the STM while, without exception, the entire molecules in the “higher” layers are resolved. This provides evidence that the molecules at the perimeter of a molecular cluster with greater apparent height partially overlap with the molecules at the underlying layer. Therefore the “higher” layer is assigned to a second adsorption layer adsorbed on top of a monolayer. This is not unreasonable as it is well-



**Figure 5.** In situ STM images of TPyP on unreconstructed Au(111) under  $1.0 \times 10^{-6}$  TPyP + 0.1 M  $\text{H}_2\text{SO}_4$  solution: (A) obtained at an electrode potential of 0.1 V, (B and C) obtained after potential step to 0.15 V, 0–109 and 109–218 s, respectively (the red arrow in C indicates a disappearing molecular cluster), (D) after potential step to 0.2 V, 0–109 s. All images are 62 nm  $\times$  62 nm. Setpoint:  $I = 0.1$  nA. Tip potential: 0.0 V. Scan direction: downward.



**Figure 6.** (A) STM image (20 nm  $\times$  20 nm) of a TPyP domain boundary under  $1.0 \times 10^{-6}$  TPyP + 0.1 M  $\text{H}_2\text{SO}_4$  solution. The molecular layer 2.5–3.1 Å high coexists with the molecular layer 1.2–1.5 Å high. The molecules in the layer that has a greater apparent height are fully resolved, while only partial molecules in the lower layer are resolved at the boundary highlighted by the red line. (B) Model for the proposed multilayer structure.

known that, in the solution phase, macrocycles tend to aggregate due to  $\pi$ -stacking interactions.<sup>25</sup> Multilayer adsorption of corone onto an electrode surface was observed by Kunitake et al.<sup>26</sup>

When the potential was stepped from 0.1 to 0.15 V, the coverage of the second layer diminished slowly (Figures 5B and 5C) as can be seen by comparison with Figure 5A, the initial state. The observation of the second layer in successive images indicates that the desorption of adsorbed TPyP at 0.15 V is not a fast process. Only a few percent of the TPyP molecules were observed to desorb from the second layer in over 100 seconds. However, once the potential reached 0.2 V, the second layer desorption accelerated dramatically (Figure 5D), and most of the bilayer clusters, such as the one indicated in Figure 5C, disappeared. Apparently a higher potential increased the oxidation/desorption of the second layer. Ordered domains, apparently no higher in STM images than the surrounding, appeared at the same locations as the clusters. The ordered domains are stable up to 0.8 V. The remaining ordered domains correspond to monolayer structures of oxidized TPyP. Therefore we conclude that after oxidation of P(–II) the top layer is desorbed, leaving behind an oxidized monolayer on the surface that has lower apparent contrast in the STM image.

This STM observation of TPyP during oxidation on the Au(111) surface (Figure 5) confirms the previous electrochemical results discussed in 3.1:

(1) Reduced TPyP, P(–II), tends to form multilayers at the Au(111) surface.

(2) Oxidation results in desorption of the multilayer, leaving a monolayer of oxidized TPyP on the surface.

There remains an important question concerning the irreversibility of the oxidation of adsorbed TPyP in the CV experiments (Figure 1), which is in contrast to the electrochemical behavior of porphyrins in the solution phase.<sup>18,19</sup> Apparently, we can rule out the explanation that the irreversibility is solely due to the desorption of all oxidized species, P(0). STM results provide definitive evidence that TPyP remains adsorbed in a monolayer state on Au(111) at oxidative potentials (Figure 5). A more plausible explanation is that the P(0) species remain adsorbed in a monolayer but that the rate of the redox reaction is significantly altered by adsorption. Then, the question is why P(0) shows very low electrochemical reactivity on Au(111); e.g., why is the reduction of preadsorbed oxidized TPyP monolayer such a slow process (Figure 3)?

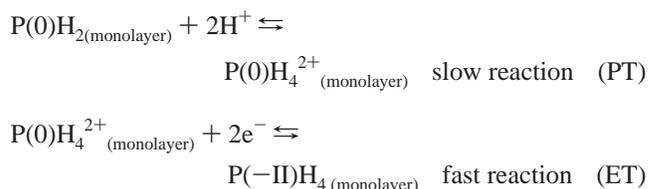
**3.2.2. Influence of the Redox State on the Molecule–Substrate Interaction.** To understand the effect of the redox state of

adsorbed species on the molecule–substrate interaction, we imaged a preadsorbed monolayer of TPyP on the reconstructed Au(111) surface in neat 0.1 M  $\text{H}_2\text{SO}_4$  solution, at different electrode potentials. In this process, we were especially interested in the change of the molecule–substrate interaction as the adsorbed monolayer of TPyP molecules was oxidized from its reduced state. At –0.05 V, where TPyP is in its reduced form (P(0) $\text{H}_4^{2+}$ ), a lattice of squares  $\sim 1.5$  nm in size is resolved (Figure 7A), indicating the presence of ordered TPyP adlayers.

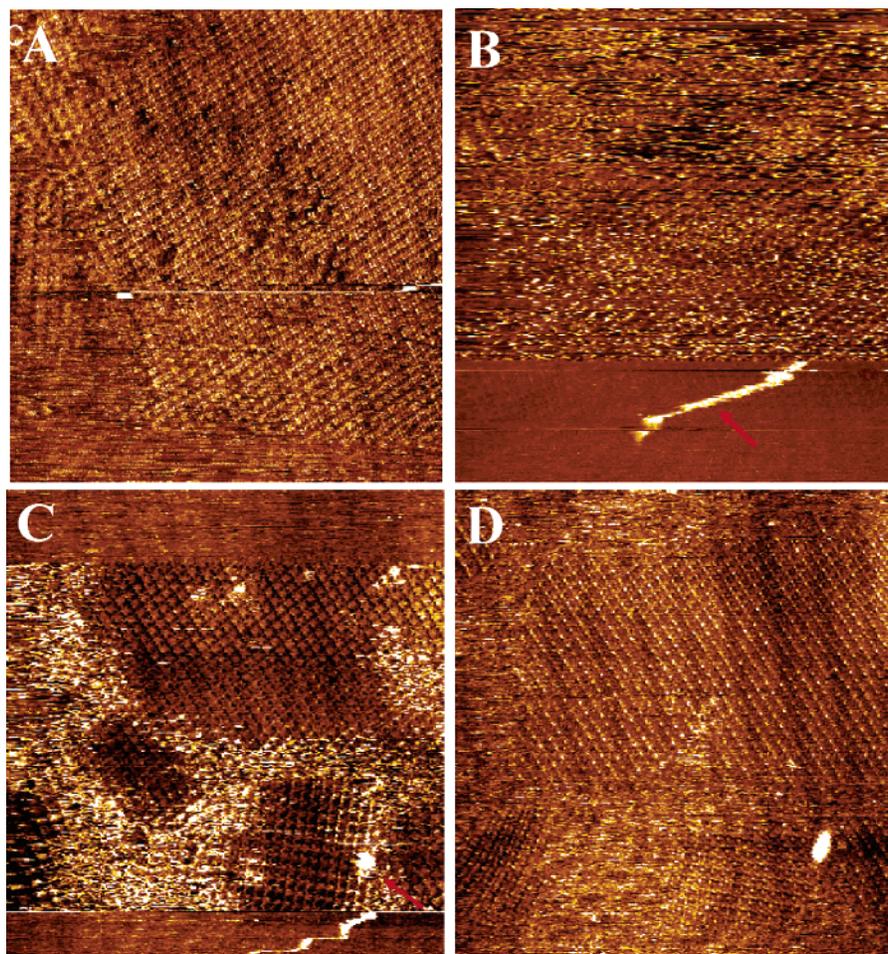
The electrode potential was stepped to 0.15 V, where the adsorbed TPyP molecules should be oxidized as suggested by the CV (Figure 3). The resulting image is very noisy. The noise is not due to a change in tip condition because both noisy domains and clear domains, with ordered molecular lattices, are resolved in the next image, Figure 7C, obtained under the same conditions. The most probable cause of the noise is molecular diffusion<sup>27–30</sup> or rearrangement induced by oxidation of TPyP. In an image taken 340 s later at the same potential, Figure 7D, the noisy areas have almost completely disappeared. Both the ordered molecular lattice and the reconstruction stripes under the adlayer are resolved clearly. In comparison with Figure 7A, the domains in the bottom right-hand corner in Figure 7D have assumed different orientations, suggesting that the molecules have rearranged. Furthermore an island, presumably resulting from the partial lifting of the Au(111) reconstruction, appeared at the bottom right-hand corner.

The STM observation of oxidation of the preadsorbed TPyP monolayer on reconstructed Au(111) provides evidence that oxidation of the TPyP monolayer can result in a molecular rearrangement and partial lifting of the Au(111) reconstruction. This suggests that oxidation of the adsorbed TPyP monolayer may cause a change in molecular conformation and the molecule–substrate interaction. For example, when the adsorbed P(0) $\text{H}_4^{2+}$  converts to a neutral P(0) $\text{H}_2$  on the Au(111) surface, the change in charge state of the molecule suggests that the molecule–substrate interaction is changed. In the acidic medium, the positively charged diacid form, P(0) $\text{H}_4^{2+}$ , is the main form in solution. However, P(0) $\text{H}_2$ , which, with a more planar porphyrin ring than the diacid form P(0) $\text{H}_4^{2+}$ ,<sup>31</sup> may be thermodynamically more favored on the Au(111) surface than P(0) $\text{H}_4^{2+}$  because of its stronger  $\pi$ -bonding interaction. Adsorption-induced changes in the molecular conformation have been reported before. Itoh's surface-enhanced resonance Raman scattering spectroscopy (SERRS) studies suggested that a water-soluble porphyrin, meso-tetrakis(2-*N*-methylpyridyl)porphine is converted to a mixture of a phlorin free base and a phlorin monocation from its diacid form as it adsorbed on an Ag electrode from 1 M HCl solution.<sup>21</sup>

**3.3. Proposed Mechanism of Reactivity of Adsorbed Species.** From the slow recovery of the reversible redox properties, after holding the surface at a reducing potential in Figure 3, we propose the following surface electrode reaction mechanism shown in Scheme 2.

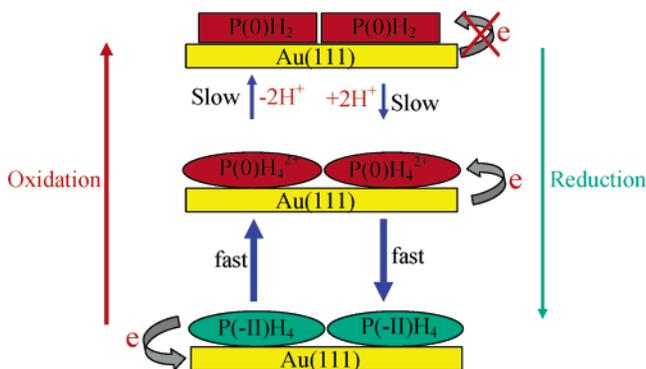


The electron-transfer (ET) processes in the adsorbed monolayer may be coupled with protonation and deprotonation reactions (PT). The protonation and deprotonation reactions may



**Figure 7.** In situ STM images of preadsorbed TPyP on reconstructed Au(111) in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution: (A) obtained after stepping potential from  $-0.25$  to  $-0.05$  V, (B) obtained after stepping potential from  $-0.05$  V to  $0.15$  V, (C) acquired 170 s after (B) at  $0.15$  V, (D) acquired 340 s after (B) at  $0.15$  V. All images are  $62\text{ nm} \times 62\text{ nm}$ . Setpoint:  $I = 0.2\text{ nA}$ . Tip potential:  $0.0\text{ V}$ . Scan direction: upward.

### SCHEME 2: Proposed Mechanism of Electrode Reaction and Adsorption of TPyP on Au(111)



involve slower conformational changes in the porphyrin ring. At a sufficiently positive potential, P(0)H<sub>2</sub>, which has suppressed reactivity, is favored on the surface compared to the positively charged P(0)H<sub>4</sub><sup>2+</sup>. However, holding the surface at a sufficiently negative potential results in the gradual growth of the anodic peak in Figure 3. This suggests that the adsorbed P(0)H<sub>2</sub> is undergoing a slow process, e.g., a protonation reaction to form P(0)H<sub>4</sub><sup>2+</sup> (PT), which then can be reduced to P(-II)H<sub>4</sub> (ET). Once P(-II)H<sub>4</sub> is oxidized to P(0)H<sub>4</sub><sup>2+</sup>, the deprotonation may again be slow. If the potential is scanned fast enough, and the final oxidative potential is set not too high, then P(0)H<sub>4</sub><sup>2+</sup> has the opportunity to be reduced on the cathodic scan, before it undergoes the slower process of conversion to the less active

P(0)H<sub>2</sub>. This may explain why symmetric cathodic and anodic peaks were observed in Figure 3.

### 4. Conclusions

Our combined CV and STM investigation reveals a complex interplay between redox reactions and the adsorbed state (e.g., monolayer and multilayer) of TPyP. The distinct redox chemistry of TPyP adsorbates is clearly influenced by their interaction with the substrate. In turn, changing the chemical nature of the adsorbed species changes the surface interactions and the resultant surface structures.

- Adsorbed TPyP forms monolayers and multilayers that can survive rinsing. The monolayer is present over a wide range of potentials ( $-0.25$  to  $0.8\text{ V}$ ), suggesting that TPyP is irreversibly adsorbed on Au(111). However, multilayers desorb after the oxidation of TPyP.

- Reduced TPyP can adsorb in monolayer and multilayer states.

- Oxidized TPyP only supports an adsorbed monolayer state.

- Monolayer or multilayers can be selectively prepared by adsorption at appropriate potentials, oxidative for monolayer or reductive for multilayer.

- TPyP adsorbates in the monolayer display distinct electrochemical reactivity from TPyP in solution. The oxidized TPyP monolayer at Au(111) does not display well-defined cathodic peaks in CVs, in sharp contrast to solution-phase TPyP. We attribute the sluggish reduction to interaction with the substrate.

•The conversion between an electrochemically inactive species and an active species can be induced by changing electrode potential: Oxidized TPyP on the Au(111) surface may lose electrochemical activity. Our present work provides direct, molecular level evidence of the electrochemically “invisible” species. However, the electrochemically “invisible” species can be made electrochemically “visible” again by equilibrating the electrode at a negative potential for a sufficient duration.

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