

Porphyrin Self-Assembly at Electrochemical Interfaces: Role of Potential Modulated Surface Mobility

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Received March 6, 2002

Abstract: The self-assembly of 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphine (TPyP) on Au(111) electrodes was investigated. The adlayer structure was found to depend on the electrode potential. At positive potentials ($>0.5V_{SCE}$), a disordered layer of TPyP is formed on the Au(111) electrode. STM images showed that the disordered molecules are immobile. At negative potentials ($-0.2V_{SCE}$), however, the molecules are highly mobile and can no longer be imaged by STM, though they remain on the surface. At intermediate potentials (-0.2 to $+0.2V_{SCE}$), the TPyP formed a highly ordered adlayer. Once the ordered adlayer is formed, it persists even after the potential is stepped to higher values ($0.5-0.8V_{SCE}$). These results can be explained by the role of potential modulated adsorbate-substrate interaction and surface mobility. This suggests the intriguing prospect of using electrode potential to tune surface interactions and to drive surface processes, e.g., molecular self-assembly, in electrochemical systems.

Introduction

Controlled assembly of individual molecules on surfaces has the potential to supplement lithographic techniques in manufacturing, as nanoscale molecular engineering becomes an integral part of miniaturization in electronic and photonic devices.¹ However, precise control of supramolecular structures on surfaces requires that a number of fundamental questions be resolved regarding the nature of the controlled assembly process, including the roles of adsorbate-adsorbate and adsorbate-substrate interactions as well as related phenomena such as surface diffusion and adsorption. Noncovalent intermolecular interactions including hydrogen bonding,² weak electron donor-acceptor,^{3,4} and dipole-dipole interactions⁵ have been employed to control two-dimensional molecular self-assembly. However, the molecular self-assembly process is a result of an intricate balance between adsorbate-adsorbate and adsorbate-substrate interactions. Adsorbate-substrate interactions, and resulting surface mobility, play pivotal roles in forming ordered structures. Strong adsorbate-substrate interactions result in low surface mobility, hindering the assembly of the ordered structures that are favored by adsorbate-adsorbate interaction.

Common strategies to tune surface mobility at vacuum-solid and gas-solid interfaces include annealing at elevated temperature^{6,7} and weakening the adsorbate-substrate interaction through surface modification using a passivating layer.^{6,8}

Recently, Hipps et al. formed ordered adlayers of coadsorbed CoPc and F16CoPc. F16CoPc, which has 16 electron-withdrawing fluorine substituents, alone cannot form ordered adlayers due to strong electrostatic interaction with the surface.⁹ The coexistence of electron-withdrawing F16CoPc and electron-donating CoPc may adjust surface partial charges, therefore achieving optimum adsorbate-substrate interaction required by self-assembly processes.⁹ Under electrochemical conditions, it is known that the adsorbate-substrate interaction can be modulated by the surface charge density.¹⁰ Therefore electrochemical environments offer additional possibilities to control surface dynamics via the surface charge. Indeed, Cunha and Tao have demonstrated that the electrode potential can drive the order-disorder phase transition of 2,2'-bipyridine (2,2'-BP) on Au(111).¹¹ The ordering of 2,2'-BP at high potential was attributed to a charge induced increase in adsorbate coverage.¹¹ This raises the question as to whether one can tune the surface mobility to achieve optimum self-assembly via potential control under electrochemical conditions.

We chose to investigate the self-assembly of porphyrins for two reasons.

1. Porphyrins are polarizable due to the large π systems. Therefore, it may be possible to substantially modulate the adsorbate-substrate interaction via the surface charge density. In turn the surface mobility, mainly determined by the adsorbate-substrate interaction, may be controlled by the surface charge

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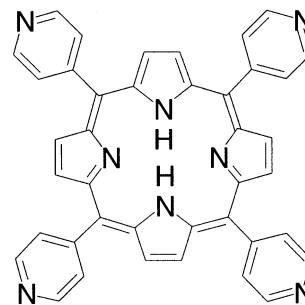
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density. Moreover, the large planar π systems are expected to assume a flat orientation due to their tendency to maximize the π bonding to the surface. Due to the absence of dipoles normal to the surface for porphyrins, we do not expect significant deviation from the flat orientation when surface charge density is altered. By contrast, polar molecules may undergo significant orientational transitions. A second harmonic generation study, for example, reveals that 2,2'-BP assumes a flat orientation, with the two N pointing to the surface in a dipolar configuration, on negatively charged electrode and vertical orientation at positively charged surface.¹² The change in orientation may fundamentally alter the nature of the adsorbate–adsorbate interaction, as illustrated by the vertical orientation induced π stacking interaction between the 2,2'-BP, which is impossible under a flat orientation.¹¹ The flat orientation of the large planar π systems may allow one to tune the binding energy, without altering the nature of intermolecular interactions at electrochemical interfaces. Therefore, using surface charge density, one may understand self-assembly on surface in a more simplified way and control it in a more predictable fashion.

2. The second motivation arises from the technological importance of self-assembled thin films of porphyrins. The unique electronic properties and reactivities of porphyrins have been recognized and utilized in applications ranging from organic electronics to solar cells and electrocatalysis.^{13,14} The four peripheral groups and metal centers can be tailored to precisely control the lateral and vertical spacing and connections between porphyrin molecules.^{3–5} The combined electronic properties, chemical reactivity, and structural versatility render porphyrins promising building blocks for the rational design of self-assembled supramolecular structures in nanoelectronics applications.¹⁵ Ordered structures of porphyrin thin films have been extensively investigated in ultrahigh vacuum.^{9,16–18} However, successful preparation of highly ordered porphyrin adlayers directly on metal surfaces from the solution phase, more convenient and compatible with further wet chemistry such as attachment of ligands, has not been reported to our knowledge. Itaya et al. found that 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)-21*H*,23*H*-porphine (TMPyP) can only form a disordered monolayer on Au(111), presumably due to the slow surface diffusion resulting from strong adsorbate–substrate interactions.¹⁹ However, ordered TMPyP monolayers can be formed on iodine modified metal surfaces that provide weakened adsorbate to substrate binding energies.^{19–21}

We demonstrate that robust ordered porphyrin monolayers can be prepared by adsorption at potentials between +0.2 and –0.2 V_{SCE}. In this potential range, enhanced surface diffusion allows the adsorbate to assemble in ordered arrays, reminiscent of annealing under vacuum at elevated temperatures to prepare 2D crystalline structures.⁷ Our results reveal the control over

Chart 1. 5,10,15,20-Tetra(4-pyridyl)-21*H*,23*H*-porphine (TPyP)



2D self-assembly one may exert via the modulation of surface charge density.

Experimental Section

An Au(111) single crystal (Monocrystals Co.) and an Au(111) facet of a single crystalline bead were used as substrates. Prior to the experiments the substrate was cleaned by immersion in hot piranha solution [1:3 H₂O₂ (J. T. Baker, CMOS) and H₂SO₄ (J. T. Baker)] for 1 h, and immersion in hot HNO₃ (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 ultrasonication in ultrapure water (>18 M Ω ·cm) produced by a Barnstead, Nanopure Infinity system. After 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 H₂SO₄ solution (Fisher Scientific Co., trace metal grade).

5,10,15,20-Tetra(4-pyridyl)-21*H*,23*H*-porphine (TPyP, Chart 1) was purchased from Aldrich Chemical Co. and used without further purification. The 0.2 mM porphine solutions were prepared in 0.1 M H₂SO₄ solution. After the bare gold surface was imaged under neat 0.1 M H₂SO₄ solution, a drop of 0.2 mM TPyP solution was added to the STM cell, to produce a final concentration of about 10^{–5} M TPyP. In some cases, as indicated in the text, preadsorbed porphyrin was studied in a porphyrin-free solution. Preadsorption was achieved by holding the Au(111) crystal in 0.1 M H₂SO₄ solution with 2 \times 10^{–4} M TPyP at a potential of –0.25 V for 5 min. The electrode was then withdrawn from the cell, rinsed with ultrapure water, and immersed in a 0.1 M H₂SO₄ blank solution under potential control (–0.25 V).

The electrochemical cell was made of Teflon. All potentials were quoted against SCE, though a silver wire was actually 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). A bipotentiostat (Molecular Imaging) was used to control the sample and tip potential independently, as well as to perform cyclic voltammetry. Tungsten STM tips were fabricated by etching 0.25 mm W wire in a Pt–Ir loop (7 mm diameter) containing lamella of 3 M KOH at 8–10 V AC. The tips were subsequently insulated by dipping in melted paraffin wax (mp 58–62 °C, Aldrich). The Faradaic current of the insulated tips under imaging conditions is less than 10 pA. All 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.

Results and Discussions

Adsorption of TPyP at high electrode potential (>0.5 V) typically results in a disordered structure, Figure 1A. Each molecule is imaged individually as a square with four bright lobes. The four bright lobes are due to the pyridine rings, nearly perpendicular to the substrate, as reported for NiTPP on

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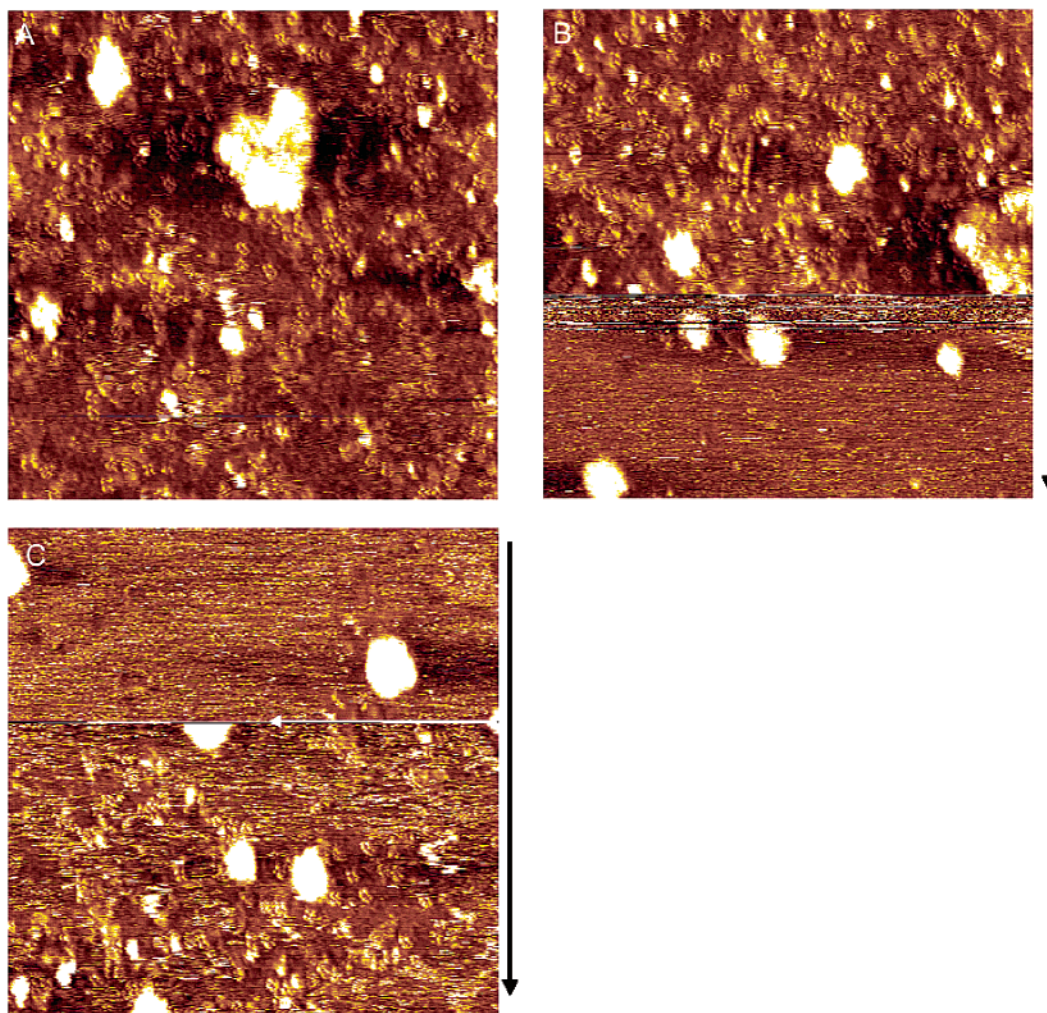


Figure 1. In-situ STM images ($50 \times 50 \text{ nm}^2$) of TPyP on Au(111) in $0.1 \text{ M H}_2\text{SO}_4 + 10^{-5} \text{ M TPyP}$ solution. Scan directions are indicated by black arrows. (A) Electrode potential $+0.5 \text{ V}$; (B) electrode potential $+0.5 \text{ V}$ (upper part) and -0.3 V (lower part); (C) -0.3 V (upper part) and $+0.5 \text{ V}$ (lower part).

Au(111)⁹ in UHV and TPyP on I modified Au(111) under electrolyte.¹⁹ The equivalent appearance of the lobes suggest that the molecule is lying flat on the Au(111) surface. No significant displacement of the molecules was observed for up to an hour. This result is consistent with the observation that immobilized TPyP molecules adsorb on bare Au(111) at high potential with a disordered structure.¹⁹ The large bright structures are Au islands that result from the lifting of the Au(111) reconstruction, a process that occurs at high electrode potential ($>0.45 \text{ V}_{\text{SCE}}$ in $0.1 \text{ M H}_2\text{SO}_4$).^{22,23}

To probe the effect of the electrode potential on the binding of TPyP to the Au surface, and the resulting structures, the electrode potential was stepped from $+0.5$ to -0.3 V in the middle of the image (Figure 1B). While isolated species, resolved as disordered TPyP molecules, were observed at $+0.5 \text{ V}$, the TPyP molecules can no longer be observed on the surface at -0.3 V . These STM images suggest two possibilities: (1) the TPyP molecules cannot be imaged because they desorb from the surface at negative potentials; (2) the TPyP molecules remain on the surface, but the adsorbate–substrate interaction is too weak for the molecules to remain sufficiently immobilized to be imaged by STM. To test whether TPyP is adsorbed on

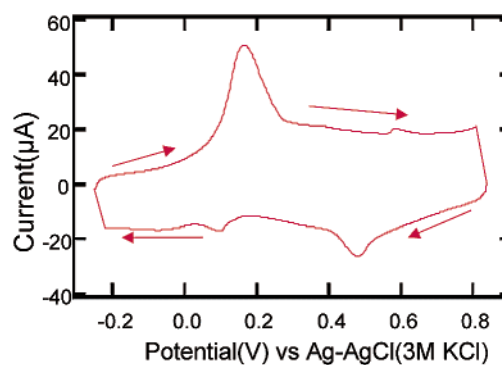


Figure 2. First scan cyclic voltammogram of Au(111) with preadsorbed TPyP in a neat $0.1 \text{ M H}_2\text{SO}_4$ solution, initially held at -0.25 V (scan rate, 2 V/s).

Au(111) at negative potential, Au(111) was immersed in the TPyP solution at -0.25 V for a few minutes. Then the electrode was emmersed and rinsed with water before immersion in TPyP free $0.1 \text{ M H}_2\text{SO}_4$ at -0.25 V . The first scan of the cyclic voltammogram (CV; Figure 2) shows a peak associated with the oxidation of TPyP from Au(111) at a potential of 0.17 V . This provides evidence that the TPyP is adsorbed on the surface at -0.25 V . The inability to image the molecules at low potential ($<-0.2 \text{ V}$) suggests that they are highly mobile.

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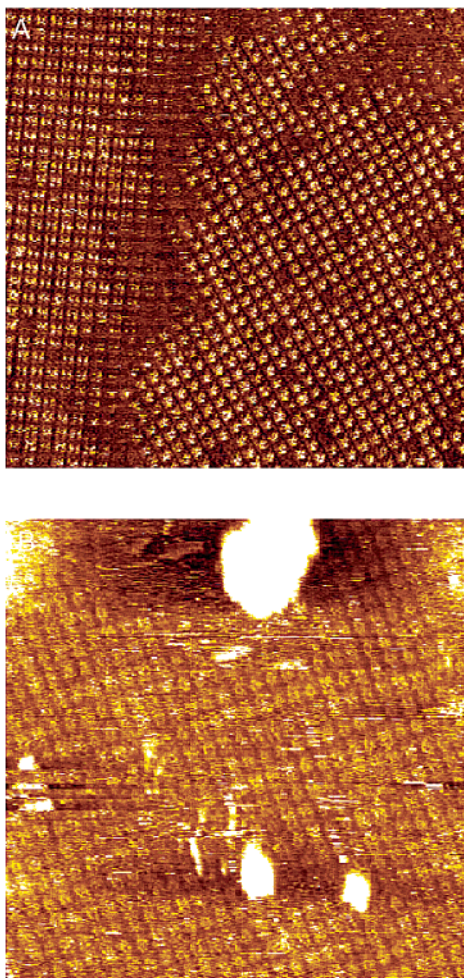


Figure 3. STM images of TPyP adlayers on reconstructed Au(111) in 0.1 M H₂SO₄ solution. (40 × 40 nm²): (A) electrode potential, −0.05 V. (B) The electrode potential was stepped progressively to +0.5 V after the ordered monolayer was formed at 0 V.

The adsorbate–substrate interaction is clearly potential dependent. At 0.5 V the interaction between the molecules and the substrate is so strong that it hinders surface diffusion, preventing the formation of an ordered adlayer structure. However, at low potential, −0.3 V, the adsorbate–substrate interaction is too weak and the molecules are too mobile to be imaged by STM. The process is quite reversible. When the potential was stepped down to −0.3 V, molecules could no longer be imaged. However, when the potential was stepped to +0.5 V in the middle of Figure 1C, disordered molecules appeared rapidly, providing additional evidence that desorption did not occur. At −0.3 V, TPyP molecules are disordered because the binding energy is not sufficient to confine molecules in 2D ordered structures. Upon applying a potential step to +0.5 V, the increased binding energy “freezes” the TPyP molecules rapidly in a disordered state. Due to the low surface mobility, the ordering process is kinetically hindered.

The preceding results, namely, low mobility at high potential and high mobility at low electrode potential, suggest that by tuning the electrode potential one can control the mobility of the adsorbates and ultimately the self-assembly process. Indeed, ordered structures of TPyP molecules were observed by STM on Au(111) at −0.05 V. These typically consisted of several domains, rotated by 120° with respect to each other (Figure

3A). Concurrent with the formation of ordered adlayers, continuous motion of adsorbates at the domain boundaries was observed in STM images, suggesting that the molecules can move at this potential.

To further prove that surface mobility is a critical factor in forming ordered structures, and that the disordered adlayer at high potential (Figure 1A) is a result of the strong adsorbate–substrate interaction that hinders surface diffusion, molecules were adsorbed on the surface at +0.1 V, by adding TPyP to the neat electrolyte, and observed to form ordered adlayers. Then the electrode potential was increased by increments of +0.1 V at intervals of several minutes. Even at +0.5 V ordered structures are still observed (Figure 3B). In fact we observed that the ordered structures were stable up to +0.8 V. The ordered structure seen in Figure 3B is in contrast to Figure 1A, in which molecules are adsorbed at the same potential (+0.5 V), but where a disordered structure was observed. This is also in remarkable contrast with Figure 1C, where disordered structure was observed after potential step from −0.3 to +0.5 V. The fact that the adlayer structure depends on the sample history provides strong evidence that the ordering process can be kinetically limited by the low surface mobility at positive potential (>+0.5 V). If the potential is gradually increased to +0.5 V, the molecules have the opportunity to self-assemble into ordered structure at intermediate potentials (from −0.2 to +0.2 V). Once they are locked into ordered arrays, the molecules remain ordered at potentials as high as +0.8 V. However, if the potential is stepped quickly to +0.5 V, the suddenly increased binding energy “freezes” the TPyP molecules rapidly in a disordered state. This suggests the crucial role of potential dependent surface mobility in determining the formation of an ordered adlayer.

Dynamics of the Preadsorbed TPyP Adlayer. One may expect to study the growth of ordered adlayer after addition of TPyP to the electrochemical cell. However, this study is rather complicated and not instructive for the following reasons. Upon injection of TPyP solution into the electrochemical cell, one has to allow some time (ca. 10 min) for the drift of the STM to settle before one can monitor the dynamics in situ. However, typically 10 min after injection, we found that the adlayer had already reached equilibrium. Therefore no dynamics information can be achieved in this experiment. Reducing the TPyP concentration is no more helpful because the adsorption is more likely to be the rate-limiting factor, obscuring the role of surface mobility in the growth process. To further understand the role of potential dependent adsorbate–substrate interactions and surface mobility in the dynamics of self-assembly processes, we instead chose to study the preadsorbed TPyP adlayer in blank electrolyte. We applied potential perturbations to the system, expecting to extract dynamics information concerning the ordering process.

TPyP molecules were preadsorbed on Au(111) as described in the Experimental Section. Subsequently, the TPyP covered Au(111) was imaged under TPyP free H₂SO₄ solution. The surface packing of TPyP in the presence of neat electrolyte is similar to that in the presence of TPyP containing solution, Figure 4A. This proved that ordered adlayer endured emersion from the cell and cycles of rinsing with water or H₂SO₄ solution. This observation highlights the robustness of the supramolecular surface structure formed in this potential controlled manner. At

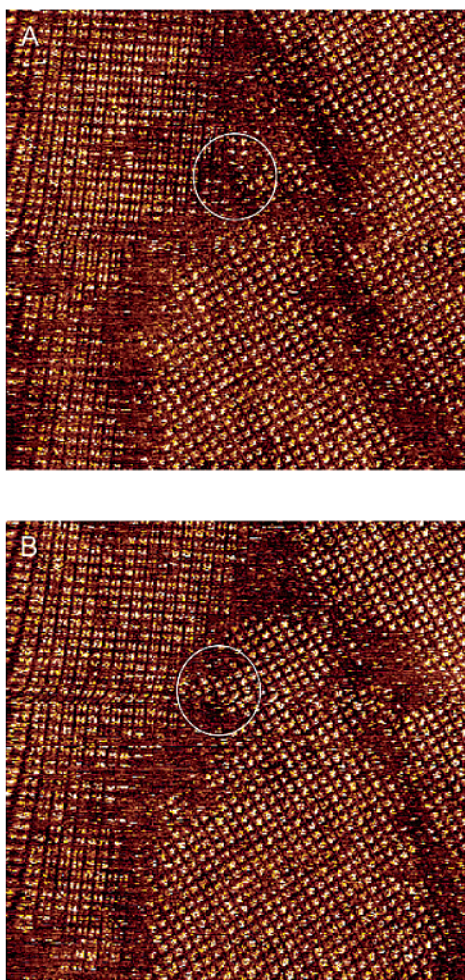


Figure 4. Sequential STM images ($62 \times 62 \text{ nm}^2$) of TPyP on reconstructed Au(111) in neat 0.1 M H_2SO_4 solution at -0.05 V . A circle highlights a domain that recrystallized between images.

a potential of -0.05 V , ordered domains of TPyP molecules, separated by domain boundaries (Figure 4A), are clearly resolved. The presence of multiple domains may result from different nucleation sites from which the molecules adsorbed to the surface crystallize into two-dimensional structures. A sequential image, Figure 4B, suggests that the domain edges were moving significantly at this potential. Part of the molecular domain indicated by a circle is converted to a domain rotated by 60° . Also there is significant noise in the domain edges, suggesting higher mobility of molecules in those areas. This intermediate potential significantly enhanced the mobility of molecules compared to $+0.5 \text{ V}$, where no motion of molecules was observed over extended periods of time, Figure 1A.

To probe the stability of the ordered structure at negative potentials, the potential was stepped from -0.05 to -0.25 V . The ordered TPyP molecules disappeared rapidly. The image (Figure 5B) showed clearly the double row reconstruction features of Au(111), which were 0.2 \AA high and separated from the next pair by 6.3 nm . We postulate that the TPyP molecules remain adsorbed on the Au(111) surface at the potential of -0.25 V , as verified in the CV experiment discussed above, but that the adsorbate–substrate interaction is too weak to form an ordered phase.

As a probe of the dynamics of self-assembly, the potential was stepped from -0.25 V back to -0.05 V , and ordered

molecular domains grew almost immediately (Figure 5C). The time scale of the ordering process is estimated to be within seconds. It should be noted that the new molecular domain, imaged in the same area, was rotated with respect to the domain observed in Figure 5A. This result suggests that the TPyP molecules form a new ordered phase, distinct from the structure seen in Figure 5A, after the potential returned to -0.05 V . Once the potential was stepped to -0.05 V , the TPyP molecules self-assembled into an ordered phase from the reservoir of molecules in the disordered phase (liquidlike) that had been produced at -0.25 V . Furthermore, the rapid appearance of molecular domains at -0.05 V under clean electrolyte requires the availability of a high concentration TPyP molecules near the surface. Since this experiment was performed under TPyP free electrolyte, this provides further direct evidence that the molecules remain adsorbed on the surface at -0.25 V even in TPyP free electrolyte, supporting the CV results in Figure 2. Had the molecules been desorbed by stepping the potential from -0.05 to -0.25 V , the molecules would have diffused away into solution, slowing down or, more likely, preventing the appearance of the ordered structures observed in Figure 5C. However, the high concentration of adsorbates is not the only prerequisite for such rapid formation of ordered phases. The enhanced surface mobility at -0.05 V (demonstrated in Figure 4) ensures facile lateral reorganization of disordered molecules, promoting the ordering process.

Summary

From our present results, it is clear that TPyP forms ordered or disordered structures at the Au(111)/0.1 M H_2SO_4 solution interface, depending on the potential at which the molecules self-assemble. We attributed this to the potential dependent binding energy and surface mobility. An alternative explanation for the disordered structure for Figure 1A is unfavorable adsorbate–adsorbate interactions. A high electrode potential results in induced dipoles normal to the surface in the polarizable TPyP molecules. These parallel induced dipoles may significantly increase repulsion between adsorbates. One may suggest that the disordered structure at high electrode potential is a result of repulsion between parallel dipoles. However, if there were significant modulation of adsorbate–adsorbate interactions, e.g. repulsion between induced dipoles, leading to disordering at high potential, the ordered TPyP monolayer, prepared by “annealing” at lower potential, would have appeared disordered at high potential ($+0.5$ to $+0.8 \text{ V}$). Instead, an ordered adlayer was observed in Figure 3B. Therefore, the disordered TPyP at high potential ($+0.5 \text{ V}$), Figure 1A, is kinetically limited by slow surface diffusion/strong adsorbate–substrate interactions rather than an equilibrium structure caused by unfavorable adsorbate–adsorbate interactions.

A plausible explanation for the modulation of the TPyP–substrate interaction is electron donation from the π orbitals of TPyP. The strong electric field across the double layer (10^7 to 10^8 V/m) may significantly modulate the electron donating effect to the substrate. The electron donating effect may be enhanced at high electrode potential (positive surface charge density) and reduced at low electrode potential (negative surface charge density). We note that while the electrode potential modulates electrostatic interactions between molecules and the substrate, the potential induced change of the redox state of porphyrins may also change the adsorbate–substrate interaction. A thorough

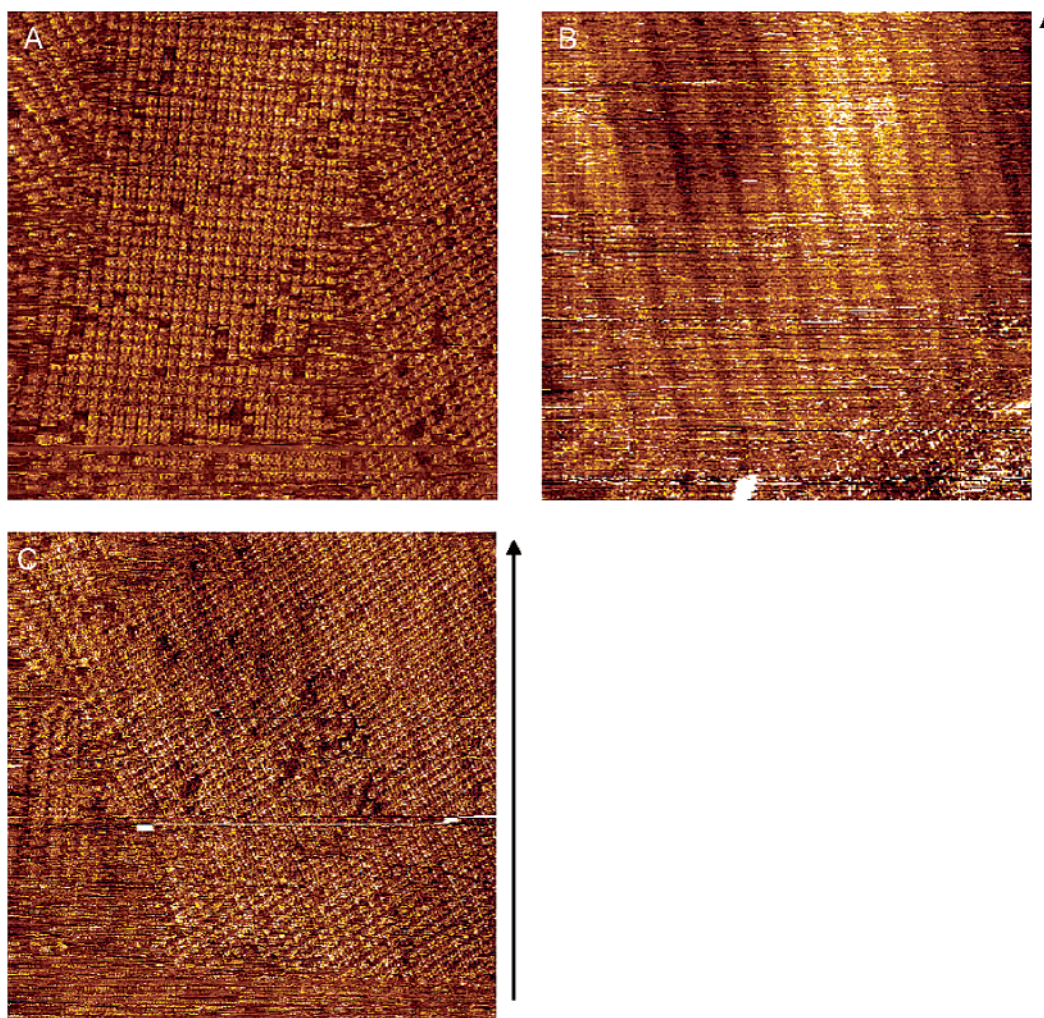
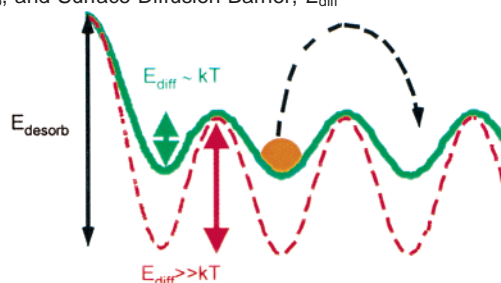


Figure 5. In-situ STM images ($62 \times 62 \text{ nm}^2$) sequence of TPyP on reconstructed Au(111) in neat 0.1 M H_2SO_4 solution. Scanning directions are indicated by the black arrows. (A) Electrode potential, -0.05 V ; (B) image obtained after electrode potential was stepped to -0.25 V ; (C) image obtained after electrode potential was stepped back to -0.05 V .

understanding of the nature of the potential dependent adsorbate–substrate interaction requires further spectroscopic and theoretical investigations. Notwithstanding of the exact origin of potential modulation, the role of potential dependent surface mobility is highlighted in the formation of ordered self-assemblies under electrochemical conditions.

Our results are in agreement with Itaya's investigation in that the surface diffusion play a critical role in the formation of a highly ordered structure of porphyrins.¹⁹ However, the major difference between our result and that of Itaya et al. is that TMPyP molecules, structurally similar to TPyP, do not form ordered structures on bare Au(111). Highly ordered adlayers of TMPyP could only be prepared on iodine modified Au.¹⁹ Our results suggest that it may be a consequence of the higher potential ($0.57 \text{ V}_{\text{SCE}}$), at which TMPyP on bare Au(111) was adsorbed. High electrode potentials result in a strong adsorbate–substrate interaction, hindering surface diffusion. The present investigation suggests a convenient approach to form ordered porphyrin structures directly on Au surfaces. One can control the adsorbate–substrate interactions by adjusting electrode potential. Scheme 1 illustrates a simplistic view of the relationship between surface diffusion and binding energy. The reduction of binding energy E_{desorb} is accompanied by a decrease in

Scheme 1. Influence of Potential on Adsorbate Binding Energy, E_{desorb} , and Surface Diffusion Barrier, E_{diff}



diffusion barrier E_{diff} . Once E_{diff} is reduced to be comparable to thermal energy kT , the surface mobility is significantly enhanced. This is reminiscent of the thermal annealing commonly employed at vacuum–solid and gas–solid interfaces to facilitate the surface diffusion required for molecular self-assembly. The difference is that enhanced surface mobility in thermal annealing is achieved via increasing the thermal energy (kT) relative to a constant diffusion barrier E_{diff} , while the increase in adsorbate diffusivity in the potential modulation approach is achieved via a lowering of the diffusion barrier E_{diff} relative to a constant thermal energy (kT). Future spectroscopic and theoretical investigations into the nature of the adsorbate–

substrate interaction and how it is modulated by the electrode potential will be of great interest. From a technological point of view, it will be interesting to utilize the electrode potential to tune surface processes, such as surface diffusion, to direct the growth of self-assembled structures of large planar aromatic molecules.

Acknowledgment. The authors acknowledge the generous support of the NSF and Research Corporation. E.B. acknowledges the NSF for a CAREER award (Grant No. CHE-9734273) and the Research Corporation for a Research Innovations Award.

JA026115F