Potential-Induced Phase Transitions in 2,2′-Bipyridine and 4,4′-Bipyridine Monolayers on Au(111) Studied by In Situ Scanning Tunneling Microscopy and Atomic Force Microscopy

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The formation and structure of 2,2′-bipyridine (22BPY) and 4,4′-bipyridine (44BPY) monolayers on Au(111) substrate have been studied as a function of the substrate potential. At high potentials, both molecules adsorb onto the substrate and stand vertically with their nitrogen atoms facing the Au(111). The vertically standing molecules stack, like rolls of coins, into polymer-like chains which pack closely in parallel to form ordered monolayers. Decreasing the potential to a critical value, the 22BPY chains become randomly oriented via a reversible order–disorder phase transition. The phase transition, as revealed by scanning tunneling microscopy, is driven by a potential-dependent attractive force between the chains. This attractive force is believed to be a substrate-mediated effective force which arises as an adsorbed electrolyte perturbs the substrate potential and thus the nearby molecules. This hypothesis is supported by a quantitative investigation of the local surface potential using a self-consistent density functional method. In contrast to 22BPY, the 44BPY chains dissolve instead of becoming randomly oriented at low potentials. This behavior may be due to that 44BPY is not as strongly adsorbed on the surface as 22BPY because it has only one nitrogen facing the surface.

Introduction

Organic thin films are attractive because of their broad applications ranging from electronic and optical materials to biological and chemical sensors.1 When prepared at an electrode–electrolyte interface, the growth and structure of the films may be flexibly controlled by varying the electrode potential.2–4 Various potential-induced phenomena in organic films at electrode–electrolyte interfaces have been studied by in situ thermodynamic and spectroscopic methods2 and by ex situ ultra high vacuum techniques.5 Recently STM (scanning tunneling microscopy) and AFM (atomic force microscopy) have been applied to directly probe molecular packing structure of monolayer organic films at electrode–electrolyte interfaces.6–9 Using STM, we have observed a novel potential induced order–disorder phase transition in 2,2′-bipyridine (22BPY) monolayers on Au(111) substrate.10 The phase transition resembles the well-known nematic–isotropic phase transitions in liquid crystal materials in three dimensions.11 In order to understand the origin of the phase transition, we have studied the effects of adsorbate coverage and substrate reconstruction in the

phase transition, investigated a substrate-mediated interaction between the adsorbates using a self-consistent density functional method, and extended the study to a structural similar molecule, 4,4′-bipyridine (44BPY).

Experiments

Au(111) substrates were grown epitaxially on mica under ultra high vacuum (UHV) conditions,12 which were briefly flame-annealed before each experiment. The 23 × 3 reconstruction was reproducibly observed at negative electrode charges.13 The STM and AFM experiments were carried out on a Pico-SPM (Molecular Imaging Co.) and on a Nanoscope III instrument (Digital Instrument Inc.). A home-made Teflon cell was used for the STM measurement, which was cleaned in 70% H2SO4 + 30% H2O2. The STM tips were electrochemically etched Pt0.85Ir0.15 wires which were coated with apiezon wax. These tips give a typical leakage current of less than a few picoampers. The STM images were obtained with a typical tunneling current of 150 pA and a bias voltage between 100 and 250 mV. Commercial glass (Nanoscope III) or Teflon (Pico-AFM) cells were used for the AFM experiments. The AFM images were acquired with a typical tunneling current of 150 pA and a bias voltage between 100 and 250 mV. Commercial glass (Nanoscope III) or Teflon (Pico-AFM) cells were used for the AFM experiments. The AFM images were acquired with a typical tunneling current of 150 pA and a bias voltage between 100 and 250 mV.

Experimental Results

(a) 22BPY. A previous thermodynamic study of 22BPY adsorption on Au(111) indicates that the 22BPY molecule

would adsorb onto the substrate and stand vertically with their nitrogen atoms facing the Au(111). The vertically standing molecules stack, like rolls of coins, into polymer-like chains which pack closely in parallel to form ordered monolayers. Decreasing the potential to a critical value, the 22BPY chains become randomly oriented via a reversible order–disorder phase transition. The phase transition, as revealed by scanning tunneling microscopy, is driven by a potential-dependent attractive force between the chains. This attractive force is believed to be a substrate-mediated effective force which arises as an adsorbed electrolyte perturbs the substrate potential and thus the nearby molecules. This hypothesis is supported by a quantitative investigation of the local surface potential using a self-consistent density functional method. In contrast to 22BPY, the 44BPY chains dissolve instead of becoming randomly oriented at low potentials. This behavior may be due to that 44BPY is not as strongly adsorbed on the surface as 22BPY because it has only one nitrogen facing the surface.

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A molecule is tilted from the chain axis by 60°. The individual chains are randomly found in the stacking of nucleic acid bases and many aromatic molecules. This tendency of avoiding perfect alignment is similar to the stacking between two adjacent layers in graphite and has been removed from these images. 

We have also studied the disorder → order transition in a 22BPY monolayer in a bare 0.1 M NaClO₄. In this case, the number of chains does not increase as the potential increases since no 22BPY molecules are present in the bulk solution. The monolayer was formed by exposing a Au(111) substrate to 10 mM 22BPY + 0.1 M NaClO₄ for a few minutes then rinsing it thoroughly with 0.1 M NaClO₄. At low potentials, the electrode is covered uniformly by a 22BPY monolayer in which the chains are essentially randomly oriented. 

Increasing the potential to 0.25 V, the chains begin to align in parallel and pits are also forming during the process. As more chains align in parallel at higher potentials, the size and number of the pits increase. These pits are bare gold surface freed as the chains diffuse together and line up in parallel to pack closely. As more chains align in parallel at higher potentials, the size and number of the pits increase.
chains are organized into domains within which the chains are in parallel (Figure 3D). The chains in each domain align along one of the three equivalent Au(111) lattice directions as we have previously observed. Similar to the result in 5 µM 22BPY described as above, the transition kinetics is also significantly more sluggish than that in concentrated 22BPY solutions. Lowering the potential, the disordered phase begins to return (Figure 3E). It starts as the chains near the edges of the pits diffuse into the pits and become randomly reoriented because of the extra space in the pits (Figure 3F,G). The space freed by the diffusion of the chains into the pits allows nearby chains to become randomly oriented. In this fashion, the disordered phase eventually spreads out over the entire surface (Figure 3F). We note that the coverage of the chains changes little during the phase transition, which means no appreciable amount of desorption during the experiment. The involvement of the diffusion during the phase transition is the cause of the sluggish kinetics in electrolytes that contain a small amount or no 22BPY. When a large amount of 22BPY is present in the bulk electrolyte, the adsorption of 22BPY allows new chains to form during the disordered—order transition, which makes the transition in 1 mM 22BPY more swift.

Au(111) is well-known to exhibit the $p \times \sqrt{3}$ ($p \sim 23$) reconstruction in which the surface Au atoms vary in registry with the subsurface layer between hollow sites of face-centered-cubic (fcc) and hexagonal-close-packed (hcp) stacking order. This variation results in a periodic modulation in the height of the surface atoms which is revealed as parallel stripes with a separation of $\sim 65 \text{ Å}$ by STM. In electrolytes that contain only weak adsorption species, the reconstruction is stable at low potentials and transforms into the $1 \times 1$ ideal phase at high potentials. Recently X-ray and second harmonic generation studies have shown that the adsorption of 22BPY on reconstructed Au(111) tends to stabilize the reconstruction. In this work, we have studied the role of the reconstruction in the molecular ordering in 22BPY monolayers. We started the experiment by imaging a reconstructed Au(111) in a bare 0.1 M NaClO$_4$ at rest potential. While scanning, we then introduced a drop of 1 mM 22BPY + 0.1 M NaClO$_4$ into the solution cell and monitored the adsorption of 22BPY onto the surface in real time. Figure 4A is an STM image that shows a reconstructed Au(111) in 0.1 M NaClO$_4$. A few minutes after introducing 22BPY into the solution cell, 22BPY molecules begin to adsorb on the surface as pointed by an arrow in Figure 4B. Waiting for longer time, more 22BPY molecules adsorb onto the surface and it becomes clearer that the molecules preferentially adsorb along the stripes of the reconstruction (Figure 4C, D). Figure 5A is an image obtained after a monolayer 22BPY has completely covered the surface and it shows clearly the decoration of the reconstruction stripes by 22BPY molecules. A higher resolution image (Figure 5B) shows that 22BPY molecules in the hcp stacking regions are more ordered than those in the fcc regions. The orientations of the chains are 30° from the direction of the reconstruction stripes which means that the chains align along the [110] direction of Au(111).

The reconstruction affects not only the adsorption of 22BPY but also the disordered—order phase transition. Figure 6A is an image at 0.11 V which shows a disordered phase, where the white lines mark the direction of the reconstruction stripes. An increasing of the potential to 0.24 V, the disordered phase begins to transform into the ordered phase, starting preferentially from the chains that follow the reconstruction stripes (i.e., in the hcp regions) as pointed by two arrows (Figure 6B). At 0.38 V, the disordered phase has nearly completely transformed into the ordered phase (Figure 6C). Although the chains that originally follow the reconstruction stripes have changed their orientation, the tendency of following the reconstruction stripes is still visible after the phase transition. So the reconstruction stripes may provide nucleation sites for the first-order disorder—order transition, but they also tend to hinder the formation of large domains of the ordered phase.

(b) 44BPY. 44BPY is structurally similar to 22BPY except that the two nitrogen atoms are located at the ends of the two hexagonal rings. The adsorption of 44BPY onto gold electrodes have been studied because the adsorbed 44BPY layers allow cytochrome c to be immobilized on the electrodes in a conformation close to its native one. It has been proposed that 44BPY molecules stand vertically on gold electrodes with one nitrogen atom anchoring on the electrodes and the other one pointing into the solution to bind cytochrome c. In this work, we determine the molecular packing structure of 44BPY monolayer on the Au(111) electrode, study its dependence on the electrode potential, and compare the results to those of 22BPY.

Figure 7A is an STM image of 44BPY monolayer on the Au(111) obtained in 10 mM 44BPY + 0.1 M NaClO₄. The image and a higher magnification image (Figure 7B) show a periodic structure with $a = 12.8 \pm 0.2$ Å, $b = 13.2 \pm 0.2$ Å, and $\gamma = 72 \pm 1^\circ$. The lattice constants are independent of the tip–electrode bias voltage and tunneling current, but the feature within each unit cell (outlined in Figure 7B) is sensitive to the tunneling parameters which makes it difficult to determine the molecular packing structure of the 44BPY monolayer based on the STM images alone. We have thus imaged the monolayer with the AFM under the same condition. The AFM reveals a similar periodic structure with nearly identical lattice constants (Figure 7C), indicating that the periodic structure in the STM images is not solely due to an electronic modulation in the adsorbate lattice by the underlying substrate lattice, as observed in other organic adsorbates. Higher magnification images (Figure 7D) reveal blob-like features within each unit cell.

Interpreting each blob as a 44BPY molecule, a model for the molecular packing of 44BPY in the monolayer is proposed as shown in Figure 8. In the model, the 44BPY molecules stand vertically on Au(111) with a nitrogen atom facing the electrode surface (Figure 8C). The vertically standing 44BPY molecules stack into polymeric chains with repeat distance of $3.7 \pm 0.2$ Å, similar to that of 22BPY on Au(111) (Figure 1A). In the case of 22BPY, the STM clearly shows that the molecules are tilted from the chain direction by $\sim 30^\circ$. Unfortunately, we could not determine if the 44BPY molecules are also tilted based on the STM and AFM images because each 44BPY is revealed as a round blob. However, to explain the observed $4.7 \pm 0.2$ Å separation between two adjacent 44BPY chains, we have to assume that the individual 44BPY molecules are
alsotiltedfromthechaindirectionby \sim 30^\circ, otherwisethe closestpackingdistancebetweentwochainswouldbe5.5 Å. This assumption also changes the perpendicular distance between two adjacent molecules to \sim 3.3 Å, a more reasonable distance between stacked planar molecules. The 44BPY chains are rotated from the substrate [110] direction by \sim 15^\circ as determined by comparing the 44BPY lattice and the underlying Au(111) lattice imaged after dissolving the 44BPY monolayer by lowering the electrode potential (We will return to this potential induced dissolution later). The periodic structure in the STM and AFM images may be explained, according to the model, Figure 4. STM images of a reconstructed Au(111) in 0.1 M NaClO₄ 5 min (A), 9 min (B), 17 min (C), and 23 min (D) after introducing a drop of 1 mM 22BPY + 0.1 M NaClO₄ into the cell. The line in (A) marks the direction of the reconstruction stripe and the arrow in (B) points the formation of 22BPY polymeric chains.

Figure 5. (A) STM image of a reconstructed Au(111) decorated with a 22BPY monolayer at rest potential. The spacing between two adjacent stripes is about 70 Å, consistent with that of bare Au(111). (B) A zoom-in image that shows the packing of individual 22BPY chains on the reconstructed surface.
as a result of periodic variation in the registry of the 44BPY molecules on the Au(111). Using van der Waals radii for the C and N atoms and lattice constant, 2.88 Å, for Au(111), the model indeed produces lattice constants, \( a = 12.55 \text{ Å}, \ b = 13.20 \text{ Å}, \) and \( \gamma = 72.5^\circ \), which are in good agreement with the experimental values. The height difference between the molecules sitting at the top and bridge sites of Au(111) estimated from the van der Waals radii is \( \sim 0.3 \text{ Å} \), which is comparable to \( \sim 0.5 \text{ Å} \) measured from a typical AFM image. However, an apparent height difference of as large as 1 Å was also observed sometimes in the AFM images which might be due to tip-induced deformations in the AFM. The failure to observe a similar height variation in the 22BPY monolayer is probably because the 22BPY has two nitrogen and two carbon atoms directly facing the Au(111) lattice. Figure 6. Potential-induced disorder—order transition in a 22BPY monolayer on reconstructed Au(111). Images A, B, and C, were obtained at 0.11, 0.24, and 0.38 V, respectively. Lines in A and B indicate the direction of the reconstruction stripes. Arrows in B point the formation of the ordered phase as the potential is raised to 0.24 V.

Figure 7. STM (A and B) and AFM (C and D) images of 44BPY monolayers in 1 mM 44BPY + 0.1 M NaClO₄ at rest potential. Both STM and AFM reveal a periodic structure (outlined in white). High-frequency noise has been removed from these images.

entire dissolution process of the 44BPY monolayer has been monitored by the AFM in real time. Figure 10A shows a 44BPY monolayer at 0.26 V. With the potential lowered to 0.16 V, pits (pointed by arrows in Figure 9B) begin to develop in the monolayer, which signals the beginning of the dissolution process. At about −0.14 V, the monolayer has completely dissolved (Figure 10D). Higher resolution images of the surface reveal the hexagonal Au(111) lattice. The potential induced dissolution is fully reversible. With the potential increased to −0.06 V, the 44BPY monolayer begins to grow back (Figure 10E). At 0.26 V, the monolayer has completely recovered. We did not observe the coexistence of the 44BPY and the 23 \times \sqrt{3} reconstruction within the studied potential range. Large scale images typically reveal blob-like features that might be due to gold islands released from higher density reconstructed phase.

Model Calculations. The experimental results described above have demonstrated that a potential-dependent long range attractive force between the 22BPY chains is responsible for the disorder–order phase transition. What is the origin of this attractive force? Although the van der Waals force between the chains is attractive, it is not expected to depend on the substrate potential strongly and therefore cannot explain the potential-induced phase transition. We propose that the attractive force is an effective force mediated by the gold substrate which arises as the adsorbed 22BPY induces a screening potential in the substrate. This occurs because the electrons of the substrate try to screen out the electrostatic potential of the adsorbed molecule. The local surface potential may differ significantly from the average surface potential. Since the adsorption energy depends sensitively on the surface potential,\(^\text{14}\) the local potential will modulate the local adsorption energy. As the substrate potential increases, it becomes more positively charged and attracts more strongly the negatively charged nitrogen on the 22BPY. The increase of adsorbate–substrate interaction leads to a stronger induced local potential and thus a stronger modulation of the local adsorption energy. When the local adsorption energy becomes larger than the thermal energy, an ordered phase will occur. This substrate-mediated interaction between adsorbates was proposed\(^\text{25}\) to explain benzene ordering on Cu(111) surface steps.\(^\text{26}\) For the current system, the ordering is much more stable and does not exhibit periodicity of the substrate Fermi wave vector.

To investigate quantitatively the phase transition mechanism discussed above, we have performed calculations for the induced local potential using the local density functional theory\(^\text{27}\) of interacting electronic system. The 22BPY has an electrostatic dipole of 3.8D which is caused by the lone pair on each of the two N atoms. In our calculation the 22BPY is modeled by two electrostatic dipoles of 1.9D each, separated by 1.6 Å. The dipoles are formed by uniform charge spheres of diameter 1.06 Å (inset of Figure 11), and the dipoles are placed at 2.4 Å above the substrate surface. The gold substrate is represented by a jellium slab 12.7 Å thick (about four layers of gold atoms). With such a model constructed for the system and the local density approximation,\(^\text{27}\) the electronic wave functions of the substrate are calculated self-consistently using plane wave expansion.\(^\text{28}\) About 1200 plane waves with kinetic energy up to 68 eV are used. The Fermi surface of the substrate is sampled with 64k points in the

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1C) while the 44BPY has only one nitrogen facing the surface (Figure 8C). Finally, we note that the 44BPY adlattice is not perfectly in registry with the Au(111) lattice as shown in the model. A small mismatch in the direction pointed by an arrow in Figure 9 results in a superperiodic change in the height of the molecules.

We have studied the molecular packing structure of the 44BPY monolayer as a function of substrate potential with the 44BPY concentration varied from 0.2 to 10 mM but observed no noticeable changes in the structure over the studied potential range. The upper bound of the potential is limited by an oxidation reaction that starts at about 0.9 V, while the lower bound is limited by the dissolution of the 44BPY lattice. As expected, the dissolution potential increases as the 44BPY concentration decreases. The

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Figure 8. Top (A) and side (B) views of proposed molecular packing of 44BPY molecules on Au(111). The 44BPY molecule (shaded) stands vertically with one of two nitrogen atoms facing the surface. Similar to 22BPY in the ordered phase, the individual 44BPY molecules stack into polymeric chains (in the direction of a black arrow) which closely pack in parallel to form a two-dimensional lattice. The molecular dimensions of 44BPY and Au(111) lattice constants from x-ray crystallography are used in this model. A unit cell is outlined by solid lines and the angle between the 44BPY chains and the Au(111) is 15°. Gold atoms are represented by open circles.

Figure 9. AFM image of 44BPY monolayer obtained in 1 mM 44BPY \(+\) 0.1 M NaClO\(_4\) at 0.2 V that shows even a larger superperiodic structure marked by arrows.
two-dimensional Brillouin zone. The total energy of the system as well as surface local potentials are obtained once the electronic wave functions and electronic interaction energies are obtained self-consistently.29

The adsorption energy for an isolated molecule on a 13 × 13 Å² square jellium surface is found to be 14 kJ/mol by our calculation. This agrees reasonably well with ∼35 kJ/mol extracted from the Henry isotherm.14 In order to investigate the local potential near a polymeric chain, the model molecules are stacked up with a distance of 5.3 Å to form the chain. The local potential is obtained for interchain distance of 32 Å, well beyond the range of local potential (see Figure 11). The fully converged local potential at 2.1 Å above the jellium surface is plotted in Figure 11 as a function of distance from the polymeric chain. It can be seen that the induced potential is positive as one approaches the chain, indicating additional attractive force for the negative N side of the 22BPY. The sharp dip near the origin is due to the electrostatic potential of the double dipole. The induced potential decays to zero beyond ∼14 Å, and there are several oscillations, as predicted by Friedel oscillation. Since a higher potential results in a larger adsorption energy,14 the result demonstrates that there is an effective attractive interaction between the adsorbed molecules, and the attractive interaction increases as the substrate potential increases. According to the STM images, the distance between molecules in two adjacent chains is about 8.5 Å. At this distance the induced potential is about 70 mV, which corresponds to about 3.5 kJ/mol of energy, as estimated from the substrate potential versus adsorption energy curves in ref 14. This energy is comparable to the room temperature thermal energy (2.4 kJ/mol) and therefore is sufficient to drive the phase transition.

The substrate-mediated effective attractive force discussed above may also play a role in the stacking of the molecules into polymeric chains on Au(111). In bulk solution, although planar molecules such as bipyridines and DNA bases7 have a tendency to stack, they do not form stable polymeric chains at room temperature. On the electrode surface, the surface-mediated attractive force provides an additional force for the stacking.

Although the molecular packing structure of 44BPY in the ordered phase is similar to that of 22BPY, the ordered phase of 44BPY does not undergo the order–disordered phase transition. This difference may be attributed to the fact that 44BPY has nearly zero dipole moment with only one nitrogen atom facing the gold substrate and therefore a much weaker adsorption energy. As the substrate potential decreases, it is easier for 44BPY molecules to lie flat on the surface or to dissolve back into the bulk solution. The weaker adsorption of 44BPY on Au(111) also explains why the 44BPY ordered phase consists of large domains while the 22BPY ordered phase

Figure 10. Potential-induced dissolution in a 44BPY monolayer. (A), (B), (C), (D), (E), and (F) are AFM images obtained at 0.26, 0.16, 0.04, −0.14, −0.06, and 0.26 V.

Figure 11. Induced local potential as a function of distance from the center of a 22BPY molecule.

consists of small domains aligned along the three equivalent Au(111) directions.

Conclusions

22BPY and 44BPY adsorb onto Au(111) from aqueous solutions and stand vertically with the nitrogen atoms facing the positively charged substrate. The adsorbed molecules self-assemble into polymer-like chains in which the individual molecules stack with a repeat distance of \( \sim 3.3\,\text{Å} \). At high substrate potentials, the polymeric chains of both 22BPY and 44BPY align in parallel to form ordered phases. As the potential decreases, the 22BPY chains become randomly oriented via a first-order order—disorder phase transition. The real-space STM images show that the phase transition is driven by a potential dependent attractive force between the 22BPY chains. The attractive force may be attributed to a substrate mediated effective attraction between the adsorbed molecules. This substrate-mediated force, as demonstrated by a self-consistent density functional calculation, provides enough attraction between the chains to sustain room temperature thermal agitation. The formation and the phase transition of the 22BPY monolayer are also affected by the \( 23 \times \sqrt{3} \) reconstruction. 22BPY adsorbs preferentially at the hcp regions of the reconstructed surface, and the disorder to order transition tends to start from the chains at the hcp regions. In contrast to that of 22BPY chains, the 44BPY chains dissolve at low potentials instead of becoming randomly oriented. This behavior may be due to the 44BPY molecule having a lower adsorption energy than that of 22BPY because the former has only one nitrogen atom anchored on the Au(111) substrate while the latter has two nitrogen atoms.

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