Structural phase transition in self-assembled 1,10'-phenanthroline monolayer on Au(111)

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Abstract

The self-assembly of 1,10'-phenanthroline (phen) on Au(111) from aqueous solutions has been studied as a function of the substrate potential with in situ scanning tunneling microscopy (STM). The phen molecules adsorb spontaneously onto the substrate with a preference to decorate the reconstruction stripes of Au(111). The adsorbed molecules stand vertically with their nitrogen atoms facing the Au(111) and stack, like rolls of coins, into polymer-like chains. At high potentials, the chains pack closely in parallel and form an ordered monolayer. Decreasing the potential to a critical value, the chains become randomly oriented via a reversible order–disorder phase transition that resembles the nematic–isotropic transition in liquid crystal materials. High resolution images reveal each phen molecule as two blobs located at the two nitrogen atoms, indicating that the coupling between the nitrogen atoms and Au(111) is responsible for the tunneling current probed by STM. The phen monolayer contains pits with a depth of about one Au layer, which may be attributed to surface stress induced by the strong adsorption of the phen molecules on the surface. © 1997 Elsevier Science B.V.

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1. Introduction

Self-assembled monolayers are important both because of their potential applications as novel materials and because they provide nice model systems for understanding fundamental physical, chemical and biological processes [1]. On gold and silver surfaces, the most well-studied systems are probably alkanethiols [2]. A number of heterocyclic molecules, such as pyridine, have also been found to adsorb onto gold, silver and copper surfaces both from vacuum [3–6] and from aqueous solutions [7–10], and condense into monolayers. The adsorption energy of the molecules is several tens of kilojoules per mole [10], which is close to the binding energy [11] of alkanethiols to gold. The large adsorption energy is due to a strong interaction between the nitrogen lone-pair electrons of the heterocyclic molecules and the metal surfaces. This strong interaction allows the heterocyclic molecules to adsorb onto the metal substrates and self-assemble into monolayers when exposing the substrates to a solution containing the molecules in a fashion similar to that of alkanethiols.

A number of heterocyclic molecules on Au(111) have recently been studied by scanning tunneling microscopy (STM) [12–16] in the electrochemical environment. These studies found that several heterocyclic molecules (e.g. adenine [12], guanine [12], 2,2' bipyridine [15] and 4,4' bipyridine [16])
stand vertically on the surface and self-assemble into polymer-like chains in which the individual molecules stack like rolls of coins. The driving force in the stacking is believed to be a combination of the π-electron attraction, hydrophobicity and the London dispersion forces [17]. One great advantage in the electrochemical environment is that the substrate potential can be continuously varied over a wide range. By changing the potential, a structural phase transition corresponding to the transformation of the orientational order of the polymer-like chains between disordered and ordered phases has been observed [15,16]. In the disordered phase, the chains are randomly oriented on the surface. As the potential is raised to a critical value, the chains organize into ordered domains in which the individual chains pack closely in parallel. The disorder–order transition resembles the well-known nematic–isotropic phase transitions in liquid crystal materials in three dimensions [18]. A combined experimental and theoretical study indicates that the substrate potential-induced disorder–order phase transition is due to a substrate mediated attractive force between the chains [16]. In this work, we report an STM study of 1,10' phenanthroline (phen) on Au(111) as a function of the electrode potential in aqueous solutions. We find that, similar to the previously studied 2,2' bipyridine, phen self-assemble into polymer-like chains which can either organize into disordered or ordered phases depending on the substrate potential and the molecule concentration in the bulk solution. Our high resolution image reveals each phen molecule as two blobs located at the two nitrogen atoms. We also present a detailed in situ study of the adsorption process, kinks in the self-assembled polymer-like chains and defects in the monolayers.

2. Experiments

The experiments were carried out on a Nanoscope III instrument (Digital Instruments Inc.) and on a Pico-SPM (Molecular Imaging Co.) controlled by a Nanoscope III controller. In the experiments we used home-made Teflon cells which were cleaned in 70% H2SO4+30% H2O2 before each experiment. We used Apiezon wax coated tips made of two materials, 0.25 mm W and Pt0.8Ir0.2 wires, electrochemically etched in 1 and 10 M KOH respectively. The W tips were used for measurements at very negative substrate potentials, and the Pt0.8Ir0.2 were used for positive potentials. The STM images were typically obtained with a bias voltage of 0.1 V and a tunneling current of 150 pA for the Nanoscope III and 25 pA for the Pico-STM. A platinum wire was used as a counter electrode and a silver wire was used as a quasi-reference electrode which was calibrated against an Ag/AgCl (in 3 M KCl) reference electrode. The potentials in this paper will be quoted versus the Ag/AgCl electrode.

Au(111) substrates were grown epitaxially on mica under ultrahigh vacuum using a procedure described in Ref. [19]. The substrates were stored in a chamber filled with argon gas. Before each experiment, each substrate was briefly annealed in a H2 flame and immediately mounted on the STM sample cell to minimize contamination. 1,10' Phenanthroline monohydrate (99% pure) purchased from Fluka was used without further purification. As supporting electrolytes we used either 0.1 M NaClO4 (Johnson and Mathey) or 0.05 M KClO4 (Fluka) using recrystallized KClO4. The solutions were prepared using Nanopure water from a Bioresearch Grade purification system (Barnstread Co.) fed with campus distilled water.

3. Results

3.1. Molecular packing structure

A monolayer film of phen can easily be obtained by exposing a clean Au(111) substrate to an aqueous solution of phen (e.g. 1 mM phen + 0.1 M
NaClO$_4$) for a few minutes. Similar to previously studied adenine, guanine and 22BPY, phen self-assembles into polymer-like chains on Au(111). The chains can exist in either a disordered (Fig. 1(A)) or an ordered (Fig. 1(B)) phase, depending on the substrate potential (we will return to this later). In the ordered phase, the chains organize into domains within which the chains pack closely in parallel along one of the three equivalent Au(111) directions. The separation between two adjacent parallel chains in the ordered phase is measured as $1.07 \pm 0.02$ nm, which is slightly greater than $0.90 \pm 0.02$ nm, the separation between the 22BPY chains [15,16]. In the disordered phase, the chains are not closely packed and their orientations do not strictly follow the Au(111) directions. Along each chain, high resolution STM (Fig. 2(A)) reveals each individual molecule as an elongated blob, positioned $0.38 \pm 0.01$ nm apart along the chain, the same as for 22BPY within experimental uncertainty. From the STM data, we propose that each phen molecule stands vertically on the Au(111) substrate with the two nitrogens facing the substrate surface, and the vertically standing molecules self-assemble into chains in which the individual molecules stack like rolls of coins (Fig. 2(B)). The tendency of phen to stack into polymeric aggregates has been studied by NMR [20], but only aggregates consisting of a few phen molecules are stable in bulk solution at room temperature. The STM images show that, with the help of the surface, long polymeric chains can be stable at room temperature. The image also shows that each molecule is tilted from the chain direction by $60 \pm 5^\circ$, which is also similar to that for 22BPY. By taking into account this $\sim 60^\circ$ tilt, the perpendicular distance between two adjacent molecules is calculated as $0.33$ nm, which corresponds well with the distance between two stacked planar molecules as found in many other systems [17]. The $60^\circ$ tilt may be attributed to the fact that each phen molecule avoids stacking perfectly over the top of its neighbor by shifting aside a distance of $\sim 0.19$ nm (see Fig. 2(B)). This behavior of avoiding perfect alignment between two adjacent stacking molecules has been observed in nucleic acid bases and many aromatic molecules [17].

The self-assembled polymeric chains are often disrupted by kinks. We have observed two kinds of kinks which can be naturally explained based on the stacking model described above. One is a sudden translation of a section of a chain in the

Fig. 1. STM images of disordered (A) and ordered (B) phases of phen monolayer on Au(111) in 0.1 M NaClO$_4$. The disordered phase (A) was obtained at $-0.2$ V in 20 $\mu$M phen + 0.1 M NaClO$_4$ and the ordered phase (B) was obtained at the rest potential in 1 mM phen + 0.1 M NaClO$_4$. The images and subsequent images are raw data or otherwise, as will be specified.
relative to its neighbor. If the shift is always in the same direction, a perfect chain is formed and each molecule in the chain is tilted by ~60° from the chain axis. However, when one molecule shifts in a wrong direction, all the subsequent molecules can either shift in the original direction or continue in the wrong direction (Fig. 2(B)). The former case leads to a kink of the first kind, while the latter case results in a kink of the second kind. We have also observed an interesting situation in which a kink of the first kind occurs every three molecules, which results in a superperiodic order along the chain direction (Fig. 3).

Higher resolution STM resolves the elongated blob of each molecule as two blobs separated by 0.3 nm (Figs. 3 and 4(A)). This distance corresponds to the separation between the two nitrogen atoms in the molecule, so electron tunneling that flows through the nitrogen atoms between the substrate and the tip dominates the STM image. To illustrate the point, a simulated STM image based on the assumption that only the nitrogen atoms contribute to the STM current is shown in Fig. 2(A). A high resolution STM image reveals each phen molecule as an elongated blob (obtained at the rest potential in 1 mM phen + 0.1 M NaClO₄). “1” and “2” in the image label two kinds of kinks along the stacked phen chains. High frequency noise has been removed from the image. (B) Proposed molecular packing of the phen monolayer. Each molecule stands vertically with the two nitrogen atoms (filled circles) facing the surface. The individual molecules stack into polymeric chains which align in parallel to form a two-dimensional lattice. The phen dimensions from X-ray crystallography are used in this model.

perpendicular direction of the chain by ~0.2 nm (marked by 1 in Fig. 2(A)), which does not change the orientation of the chain in relation to the underlying Au(111) lattice direction. The other is a sudden bending of a chain by 120° (marked by 2 in Fig. 2(A)), which ensures the chain follows an equivalent direction of the Au(111) lattice. We have discussed the fact that each phen molecule is shifted aside in the molecular plane by 0.2 nm relative to its neighbor. If the shift is always in the same direction, a perfect chain is formed and each molecule in the chain is tilted by ~60° from the chain axis. However, when one molecule shifts in a wrong direction, all the subsequent molecules can either shift in the original direction or continue in the wrong direction (Fig. 2(B)). The former case leads to a kink of the first kind, while the latter case results in a kink of the second kind. We have also observed an interesting situation in which a kink of the first kind occurs every three molecules, which results in a superperiodic order along the chain direction (Fig. 3).

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Fig. 2. (A) A high resolution STM image reveals each phen molecule as an elongated blob (obtained at the rest potential in 1 mM phen + 0.1 M NaClO₄). “1” and “2” in the image label two kinds of kinks along the stacked phen chains. High frequency noise has been removed from the image. (B) Proposed molecular packing of the phen monolayer. Each molecule stands vertically with the two nitrogen atoms (filled circles) facing the surface. The individual molecules stack into polymeric chains which align in parallel to form a two-dimensional lattice. The phen dimensions from X-ray crystallography are used in this model.

Fig. 3. A kink of the first kind can occur every three molecules, which results in a superperiodic ordering along the phen chains. The STM image was obtained at the rest potential in 1 mM phen + 0.1 M NaClO₄. High frequency noise has been removed from this image.
Fig. 4. (A) A higher resolution STM image resolves each elongated blob (a phen molecule) as two blobs. The image was obtained at the rest potential in 1 mM phen+0.1 M NaClO₄. (B) A simulated image illustrates that the two blobs are due to the two nitrogen atoms. The image was obtained by assuming a Gaussian distribution of width 0.2 nm for the local density of states at each of the two nitrogen atoms.

This observation is reasonable since the nitrogen atoms interact directly with the substrate which provides electronic coupling between the molecular and the substrate states near the Fermi level. In a recent study of Cu-TBP-porphyrin, only the part of the molecule that is in contact with the substrate is observed in the STM image [21].

3.2. Phase transition

We have shown above that the self-assembled phen chains can exist in either the disordered (Fig. 1(A)) or the ordered phases (Fig. 1(B)). We demonstrate here that the transition between the disordered and ordered phases can be controlled by the substrate potential. Fig. 5 shows a series of images of a phen monolayer in 20 μM phen + 0.1 M NaClO₄ recorded at various substrate potentials. Fig. 5(A) is an image of the ordered phase obtained at 0.11 V which shows ordered domains in which the phen chains pack closely in parallel. A single atomic step of Au across the lower portion of the image serves as a reference for us to identify potential induced changes at a particular area. Lowering the surface potential to −0.04 V, chains near the domain boundaries at the center and lower left portions of the image become disordered (pointed out by arrows in Fig. 5(B)). Lowering the potential to −0.14 V (Fig. 5(C)), while the disordered area expands, chains near the domain boundary at the upper right also begin to become disordered. Further lowering the potential, the two disordered areas grow and coalesce into a larger disordered area (Fig. 5(D)). At −0.17 V, almost the entire scanned area has transformed into the disordered phase (Fig. 5(E)). This in situ study clearly shows that the order–disorder transition is a nucleation and growth process in which the defects at domain boundaries may serve as nucleation sites for the disordered phase. Since the chains in the disordered phase are less compactly packed than those in the ordered phase, desorption of phen molecules back to the bulk solution must take place as the ordered phase transforms into the disordered phase. We note that disordered chains can be clearly resolved only for small tunneling current (<150 pA). Setting the current at higher values results in streaky images, which is presumably due to the lateral force applied to the chains by the scanning tip.

The phase transition is completely reversible. Raising the potential to 0.08 V, a few small
Fig. 5. Potential induced reversible disorder–order phase transition in a phen monolayer on Au(111) in 20 μM phen + 0.1 M NaClO₄. The images (A–F) were obtained at potentials of 0.11 V (A), −0.04 V (B), −0.14 V (C), −0.16 V (D), −0.17 V (E), 0.08 V (F), 0.13 V (G) and 0.23 V (H). Each image was obtained ~1 min after stepping the potential to a new value.
domains of ordered chains appear immediately (Fig. 5(F)). These ordered domains are not very stable at the potential, they can either suddenly disappear or change their orientations during the scanning. Further increasing the potential to 0.13 V, the ordered domains increase both in number and size and become more stable (Fig. 5(G)). At 0.23 V, nearly the entire area has returned to the ordered phase (Fig. 5(H)). Comparing the ordered phase in Fig. 5(H) with the original ordered phase shown in Fig. 5(A), we can see that the chain orientations in the newly formed ordered domains do not necessarily remember the original orientations.

We observed the order–disorder phase transition only in the dilute solutions of phen. At higher concentrations (>0.1 mM) we failed to observe the phase transition at the potential. Lowering the potential further, the STM image contrast decreases quickly and eventually the polymer chains become invisible, which prevents us from studying the concentration effect on the phase transition potential. This observation indicates that transition potential shifts to more negative values at higher concentrations, which can be understood based on the Onsager theory [18]. According to the theory, higher concentrations result in more polymer-like chains which are forced to align in parallel (ordered phase) in order to accommodate themselves on the surface with a fixed area.

3.3. Adsorption

We have studied the adsorption of phen from 0.1 M NaClO$_4$ onto Au(111) with STM in real time. We started the experiment by imaging Au(111) in bare 0.1 M NaClO$_4$ at the rest potential. While scanning, we then introduced a droplet of saturated phen dissolved in 0.1 M NaClO$_4$ into the solution cell and monitored the adsorption of phen onto the surface as a function of time. Fig. 6(A) is an image recorded before the introduction of phen. The arrow in the image marks the direction of the stripes of the $p \times \sqrt{3}$ ($p < 23$) reconstruction [22–24]. Although the stripes are not well-resolved in the particular image, the subsequent images (Fig. 6(B)–Fig. 6(C)) show more clearly the existence of the stripes. A few seconds after the introduction of phen into the solution, phen molecules begin to adsorb onto the surface preferentially along the reconstruction stripes marked by an arrow (Fig. 6(B)). As time goes by, more reconstruction stripes become decorated with the adsorbed molecules (Fig. 6(C)). This observation also shows that the adsorption of phen does not lift the $p \times \sqrt{3}$ reconstruction. Recently, X-ray [25], second harmonic generation [9] and STM studies [15] have shown that the adsorption of 22BPy on reconstructed Au(111) tends to stabilize the reconstruction.

3.4. Defects

We have observed two kinds of defects in the phen monolayers. One is defects at the boundaries of ordered domains which always disappear as the ordered phase transforms into the disordered phase. This kind of defect has also been observed in 22BPy and adenine monolayers [16]. The second kind of defect has an irregular shape, which has not been observed in the previously studied heterocyclic monolayers (Fig. 7(A)). The defects have an apparent depth of about 0.25 nm, corresponding roughly to the thickness of a gold atomic layer. A higher resolution image shows that self-assembled phen chains also exist inside the defects (Fig. 7(B)). This kind of defect is not due to defects on gold substrates. We have characterized the substrate surfaces before and after the formation of phen monolayers many times, and found that the defects always appear only on the phen-covered Au(111). We attribute these defects to pits of a single atomic depth on the Au substrate which are induced by surface stress as the phen molecules adsorb strongly on the surface. A similar mechanism has been proposed previously to explain defects in monolayer alkanethiol on gold [26,27]. This proposal is supported by the study of the dependence of the defects on surface potential. Fig. 8(A) is an image of a phen monolayer in 1 mM phen + 0.1 M NaClO$_4$ at 0.2 V which shows
the defects. Lowering the potential to $-0.2 \text{ V}$, the defects shrink in size (Fig. 8(B) and 8(C)) and islands of one atomic height are also observed to form (pointed out by arrows). The shrinking of the defects at low potentials is reasonable since the adsorption energy, and thus the surface stress, decreases as the substrate potential decreases.

It is interesting to note that the phen chains tend to align along the edges of the defects. This phenomenon may be understood based on the step-edge induced oscillations in the local electron density of states which are parallel to the step edge and decay over several nanometers from the step edge [28]. This oscillation results in an oscillation in the local surface potential [16]. Since the adsorption energy of phen depends on the surface potential, the oscillatory potential forces the phen chains to align parallel to the step edges.
Fig. 8. The defects in the phen monolayer shrink in size as the potential decreases. The images (A–C) were recorded at potentials of 0.2 V (A), −0.2 V (B) and −0.2 V (C) in 1 mM phen + 0.1 M NaClO₄.

4. Conclusions

Phen adsorbs spontaneously onto Au(111) from aqueous solutions with a strong tendency to follow the 23 × √3 reconstruction stripes. Similarly to the previously studied 22BPy, adenine and guanine, phen molecules stand vertically with the nitrogen atoms facing the Au(111) substrate. The coupling between the two nitrogen atoms and the substrate is responsible for the electron tunneling current probed by STM. The vertically standing molecules self-assemble into polymer-like chains in which the individual molecules stack with a separation of 0.33 ± 0.01 nm between two adjacent molecules. Each molecule is shifted from its neighbors by 0.19 nm along the molecular plane to avoid a perfect alignment with the neighboring molecules, which results in an approximately 30° rotation of the molecules from the chain axis. The shift is also responsible for the kinks along the self-assembled phen chains. At high substrate potentials, the self-assembled chains organize into ordered domains in which all the chains pack closely along one of the three equivalent directions of Au(111). Lowering the potential, the chains become randomly oriented, which starts preferentially from defects near domain boundaries. This order–disorder phase transition is similar to that in the 22BPy monolayer, which is driven by a potential dependent substrate mediated interaction between the chains. The phen monolayer contains defects that shrink in size as the substrate potential decreases. The defects have a depth of a single gold atomic layer, and are attributed to pits on the surface induced by surface stress resulting from the strong adsorption of the phen molecules on Au(111).

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