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In Situ Scanning Tunneling Microscopy of Highly Ordered Adlayers of Aromatic Molecules on Well-Defined Pt(111) Electrodes in Solution: Benzoic Acid, Terephthalic Acid, and Pyrazine

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In situ scanning tunneling microscopy (STM) was employed to study adlayer structures of benzoic acid, terephthalic acid, and pyrazine at a well-defined Pt(111) electrode in an aqueous HClO₄ solution. Although benzoic acid formed disordered structures on Pt(111), high-resolution STM imaging was able to distinguish between the aromatic ring and two oxygen atoms of each flat lying benzoic acid molecule. Terephthalic acid formed a highly ordered adlayer with $c(2\sqrt{3} \times 4)$ rect symmetry. Two carboxylic acid functional groups at the para-position were clearly discerned. Intermolecular interactions, presumably through hydrogen bonding, played an important role in the formation of the ordered adlayer. Pyrazine molecules formed an ordered adlayer at a relatively negative potential of 0.2 V vs a reversible hydrogen electrode. It was assumed that the molecules adsorbed horizontally at 3-fold hollow sites, forming a long range ordered adlattice of $(\sqrt{7} \times \sqrt{7})R19.1^\circ$. Disordered structures were found when the electrode potential was stepped from 0.2 to 0.5 V, which suggests that the molecular plane of adsorbed pyrazine is tilted with respect to the surface of Pt(111).

Introduction

Understanding the coordination and structure of organic adsorbates at metal surfaces in solution constitutes a main subject of modern interfacial electrochemistry.¹ Although spectroscopic and capacitance techniques have been widely used,¹ scanning tunneling microscopy (STM) has made it possible to directly determine orientations, packing arrangements, and even internal structures of organic molecules adsorbed on electrodes in solution.^{2,3} Although a number of successful in situ experiments using STM and atomic force microscopy (AFM) have been reported, only a few materials, such as highly ordered pyrolytic graphite and Au electrodes, have almost exclusively been used as substrates in these studies.^{2–13}

On the other hand, it was demonstrated in our previous papers that highly ordered molecular arrays of porphyrin,

crystal violet, and linear aromatic compounds are formed more easily on iodine-modified Au(111), Ag(111), and Pt(100) than on their bare surfaces.^{14–17} High-resolution STM images allowed us to determine the packing arrangement and the shape of each molecule at the atomic scale. We have also intensively investigated the adsorption of simple aromatic molecules such as benzene, naphthalene, and anthracene on well-defined Rh(111), Pt(111), and Cu(111) to elucidate the role of interaction between molecules and substrates in ordering processes on the well-defined bare electrodes.^{18–20} For example, the structure of benzene on Rh(111), Pt(111), and Cu(111) unveiled the important role of substrates in organizing molecular adlayers. In general, highly ordered structures were formed on Rh(111) and Cu(111), whereas only local ordering was found for benzene and naphthalene adsorbed on Pt(111). It is also noteworthy that the adlayer structures of benzene and naphthalene on Rh(111) in solution are similar to those found at solid–gas interfaces,^{21–26} indicating that adsorbate–substrate interaction plays a critical role in the formation of ordered

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structures. Water molecules and ionic species are relatively unimportant in the structuring of these organic adsorbates on Rh(111). However, it has also been clearly demonstrated that intermolecular interaction plays a crucial role in the formation of ordered adlayers of several organic molecules, such as guanine and adenine, in solution.^{4–10}

To elucidate the effect of molecular structures on the packing arrangement, adlayer structures of benzoic acid (BA), terephthalic acid (TA) and pyrazine (PZ) on a well-defined Pt(111) electrode were investigated in this study. It will be shown that TA and PZ molecules formed long range ordered adlattices, whereas BA produced a disordered structure. High-resolution STM images revealed the packing arrangements and internal structures of each molecule.

Experimental Method

All experimental details were described in our previous reports of benzene and naphthalene on Rh(111) and Pt(111).^{18,19} The single-crystal Pt electrodes were annealed in a hydrogen–oxygen flame and quenched in ultrapure water saturated with hydrogen. A solution containing the organic compound was injected into the STM cell after achieving atomic resolution of Pt(111)–(1 × 1). All solutions were prepared with HClO₄ (Kanto Chemicals, Tokyo) and ultrapure water (Millipore-Q). Although the solubility of pyrazine is quite high, benzoic acid and terephthalic acid have relatively low solubilities of 0.21 and 0.001 g in 100 g pure water, respectively.²⁷ A saturated solution of terephthalic acid was made by sonicating for 10 min. All electrode potentials reported in this paper were referred to a reversible hydrogen electrode (RHE) in 0.1 M HClO₄ in the absence of organic molecules.

The STM was a Nanoscope III (Digital Instruments, Santa Barbara, CA), which was used with a Teflon electrochemical cell equipped with the RHE and a Pt counter electrode.

Results and Discussion

Voltammograms. Figure 1 shows cyclic voltammograms (CVs) of a well-defined Pt(111) electrode in 0.1 M HClO₄ with or without the organic molecules. The CV in Figure 1a shows a typical example for a well-defined Pt(111) electrode, which is consistent with the CV reported previously.^{2,28} The adsorption of organic adsorbates from solutions caused marked changes to the CV profile. The CVs in Figure 1b–d, were obtained with the Pt(111) electrode in 0.1 M HClO₄ solutions containing 0.1 mM benzoic acid (BA), saturated terephthalic acid (TA), and 1 mM pyrazine (PZ), respectively. The adsorption of BA, TA, and PZ on Pt(111) resulted in featureless double-layer regions, eliminating the butterfly peak in Figure 1a observed on clean Pt(111), in the absence of the organic substances. Asymmetric sharp peaks were observed at ca. 0.1 V for BA and TA. These peaks should be due to the adsorption and desorption of the organic molecules on Pt(111) and are associated with those of hydrogen. Similar sharp peaks have been found for benzene¹⁸ and aniline²⁹ on Pt(111). Note that a sluggish increase in anodic currents was seen at potentials more positive than 0.7 V for BA and TA, which was considered to be due to the electro-

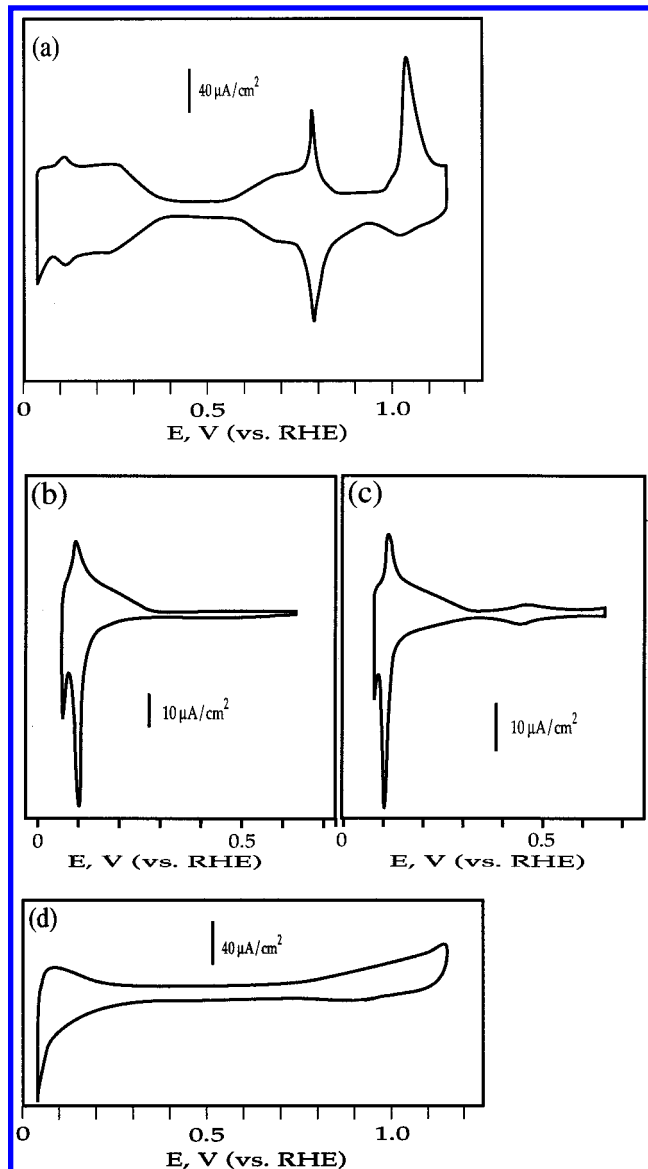


Figure 1. Cyclic voltammograms of Pt(111) in pure 0.1 M HClO₄ (a); in 0.1 M HClO₄ solutions containing 0.1 mM benzoic acid (b); in saturated amounts of terephthalic acid (c); and in 1 mM pyrazine (d). Scan rate was 50 mV/s.

oxidation of the adsorbed molecule. The oxidation behavior of BA has previously been reported by Hubbard's group.³⁰ Pt(111) electrodes appeared to catalyze the decomposition of BA and TA. The Pt(111) electrode was immersed in 0.1 M HClO₄ containing BA and TA for several min at the open circuit potential; it was then transferred in pure 0.1 M HClO₄. These BA- and TA-dosed Pt(111) electrodes also showed similar CVs in the pure HClO₄ solution during the first few cycles, whereas a CV identical to that shown in Figure 1a reappeared after ca. 15 cycles between 0.1 and 1.15 V, indicating that the adsorbed molecules were desorbed and that this potential window did not disturb the long-range ordered structure of Pt(111).

Figure 1d displays a CV of Pt(111) in 0.1 M HClO₄ containing 1 mM pyrazine (PZ). The CV is essentially featureless, and there are no defined current peaks at 0.1 V, such as those observed with BA and TA. The slow increase of cathodic current between 0.05 and 0.25 V for

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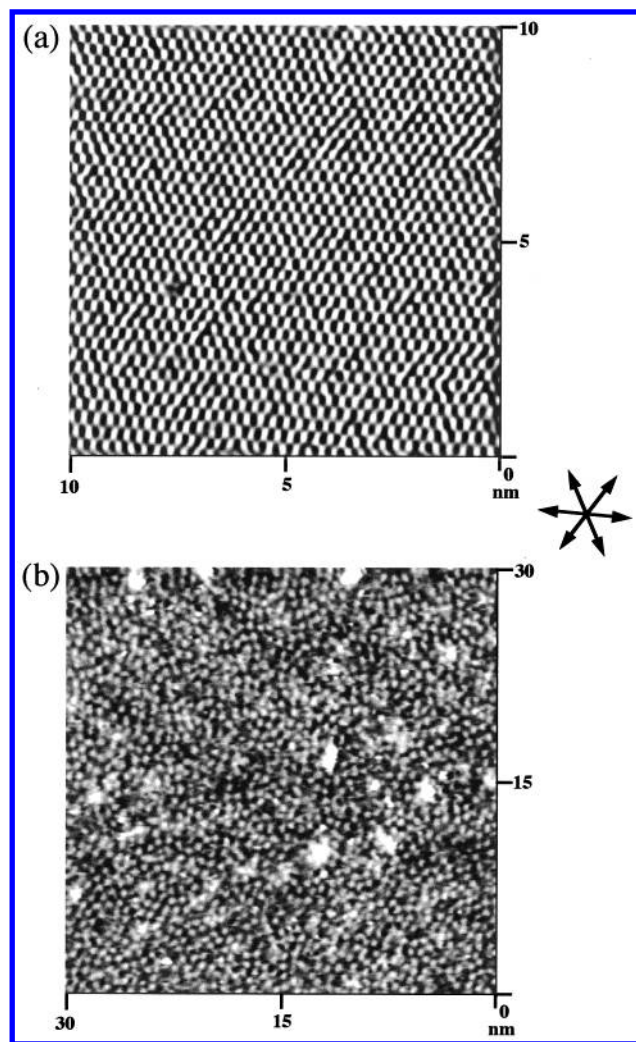


Figure 2. In situ STM images of the Pt(111) substrate (a) and adsorbed benzoic acid (b). Image (a), 2D Fourier transform filtered, was obtained at 0.3 V in pure 0.1M HClO₄, whereas (b), unfiltered, was obtained at 0.3 V in 0.1 M HClO₄ containing 1 mM of benzoic acid. The potential of the tip electrode was 0.35 V; tunneling current was 10 nA. The arrows show the close-packed directions of the Pt(111) substrate.

PZ implies a stronger interaction with the Pt(111) electrode than BA or TA. The featureless double-layer potential range extended up to 0.8 V, but the anodic current increased slowly at potentials more positive than 0.8 V, as shown in Figure 1d. This anodic current might be due to the oxidation of adsorbed PZ molecules.³¹

In Situ STM. Benzoic Acid (BA). The lattice directions of the Pt(111) electrode used in this study were first determined by high-resolution STM imaging at 0.3 V in 0.1 M HClO₄ in the absence of the organic molecule. Figure 2a shows a typical STM atomic image of the hexagonal Pt(111)-(1 × 1) structure with an interatomic distance of 0.28 nm. As previously described,¹⁸ the resolution of STM imaging was affected by the operating conditions, and this image was obtained with a low bias voltage of 50 mV and a high set-point current of 10 nA.

Irreversible adsorption of BA occurred immediately after the injection of its dosing solution into the STM cell at 0.3 V. The constant-current STM scan (Figure 2b) over a relatively large area of 30 × 30 nm revealed a typical real-space arrangement of benzoic acid. No long-range

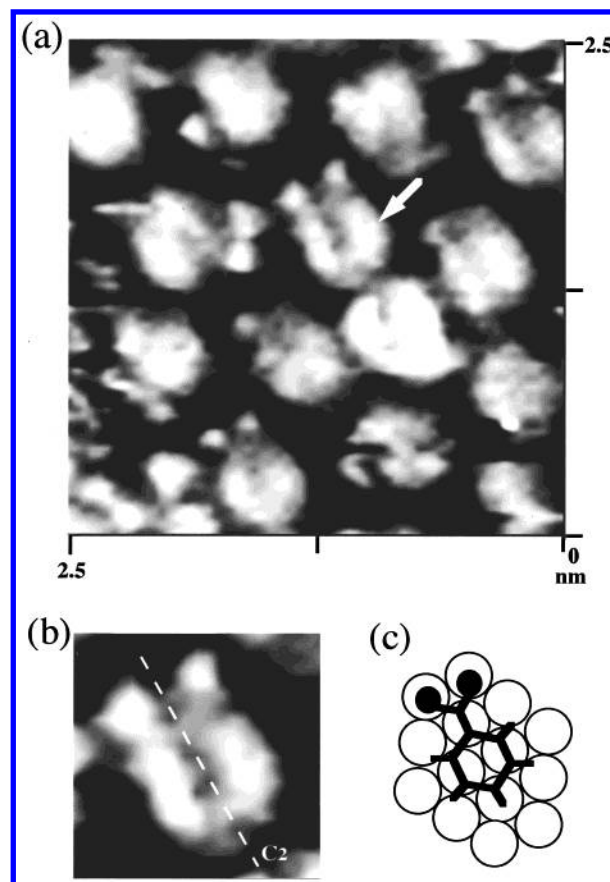


Figure 3. High-resolution unfiltered STM image of adsorbed benzoic acid on Pt(111) acquired in an area of 2.5 × 2.5 nm (a). The expanded image shown in (b) is for the single benzoic acid molecule marked by an arrow in (a). A real space model is shown in (c).

ordered pattern was observed; only protrusions of similar intensities were observed, evenly distributed on the surface. Adjacent spots are separated by ca. 0.7 nm, comparable to the van der Waals' diameter of a BA molecule.

The high-resolution STM image acquired in an area of 2.5 × 2.5 nm and shown in Figure 3a discloses the packing arrangement and even the internal structure of a single BA molecule. Figure 3b shows an enlarged image of the single BA molecule marked by the arrow in Figure 3a. The pair of elongated features and two bright spots on the sides are thought to correspond to the aromatic ring and the carboxylate group of the BA molecule. These STM images strongly suggest that BA molecules are adsorbed with their molecular plane parallel to the Pt(111) surface. It can also be seen that the in-plane rotational relationship of BA molecules with respect to the Pt(111) substrate is indicated by their C₂ axes, aligned along the $\sqrt{3}$ directions. The C₂ axis of a BA molecule runs along two apical carbons and bisects the two oxygen atoms of the -COOH group, as indicated by the dashed line in Figure 3b. In addition, the elongated appearance of the aromatic ring, with a dumbbell shape, indicates that the BA molecules are adsorbed at 2-fold bridge sites on Pt(111). The tentative molecular model in Figure 3c assigns the aromatic ring to a 2-fold bridge site with the carboxylic acid group aligned along the $\sqrt{3}$ direction. Two oxygen atoms of the -COOH group play an important role in determining the packing arrangement. Note that a previous study by Hubbard's group using high-resolution electron energy-loss spectroscopy (EELS) reported that BA molecule, like hydroquinone, is dehydrogenated at the -COOH group upon

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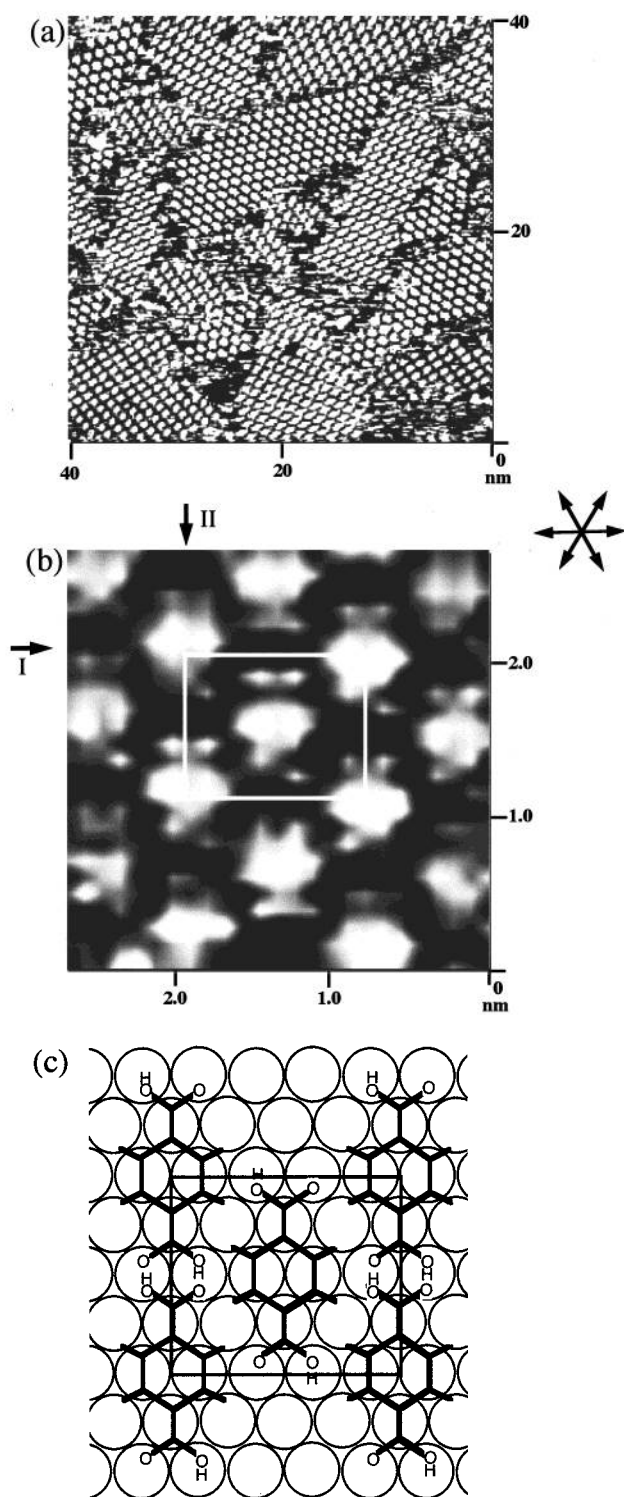


Figure 4. High-resolution STM images of an ordered terephthalic acid adlayer on Pt(111). The high-resolution scan in (b) reveals the internal features. These images were obtained at 0.4 V with a bias voltage and feedback current of 100 mV and 10 nA, respectively. A corresponding ball model is depicted in (c). Arrows show the close-packed directions of the Pt(111) substrate. (a) Unfiltered; (b) 2D Fourier-transform filtered.

adsorption on Pt(111).³⁰ In addition to the π -bond of the aromatic ring, the oxygen atoms of the $-\text{COOH}$ group can form s-bonds with the Pt substrate.

Terephthalic Acid (TA). Surprisingly, it was found in this study that TA formed highly ordered adlayers on Pt(111). The typical arrangement of a monolayer of TA at Pt(111) is revealed by the STM image in Figure 4a, which

was obtained at 0.4 V, with a bias voltage of 100 mV and a feedback current of 10 nA. Well-ordered arrays consisting of oriented TA molecules can immediately be identified, which contrasts markedly to the disordered arrangement of BA. The patchy appearance of these ordered structures is actually attributed to rotational domains of an ordered structure. The presence of a long-range ordered pattern allowed STM imaging with molecular resolution.

Figure 4b displays a high-resolution STM image, from which the internal structure of TA molecules can be discerned. With the aid of the Pt(111) image in Figure 2a, one identifies two orthogonally intersected molecular rows of **I** and **II** in parallel with the close-packed and $\sqrt{3}$ directions of the Pt(111) substrate, respectively. The intermolecular distances of ca. 1.1 and 0.96 nm along these two directions can be interpreted as the unit vectors of 4 and $2\sqrt{3}$, respectively. This structure is thus characterized as $c(2\sqrt{3} \times 4)\text{rect}$, $\theta = 0.125$, and the rectangular unit cell is outlined in Figure 4b.

With these high-resolution STM images, determination of the packing arrangement of adsorbed molecules is straightforward. It can be concluded that the TA molecules are adsorbed horizontally, similar to BA. The elongated dumbbell-shaped image and the two pairs of adjacent spots are attributed to the aromatic ring and two $-\text{COOH}$ functional groups at the para-positions of each benzene ring. The space of ca. 0.22 nm observed between two oxygen spots, corresponding to a $-\text{COOH}$ functional group, agrees with the value derived from the molecular structure. It is worthwhile noting that all the molecules are arranged in the same orientation, with their longer C_2 axes aligned along the $\sqrt{3}$ direction and the two acidic groups of the two neighboring molecules facing each other. The nearest oxygen spots belonging to the two neighboring TA molecules are separated by 0.25 nm.

The STM image of Figure 4b leads to a structural model of TA on Pt(111), as shown in Figure 4c. As in the model for benzoic acid shown in Figure 3c, TA molecules are assigned to 2-fold bridge sites, with all oxygen atoms in the $-\text{COOH}$ groups residing near the bridge sites. The two $-\text{COOH}$ groups at the para-positions of the TA molecule have exactly the same coordination environment with the Pt substrate. In fact, a bulk crystal of TA has a layered structure, and the molecular arrangement within each layer is very similar to that presented in Figure 4c.³² As intermolecular hydrogen bonding is crucial to the layer-type packing, it is anticipated that similar intermolecular interaction exists in the overlayer of TA. If this view is valid, adsorbed TA molecules should not be deprotonated, unlike hydroquinone or benzoic acid molecules adsorbed on Pt(111). The 0.24 nm spacing between two oxygen atoms of two neighboring $-\text{COOH}$ groups appears to be optimal for the formation of $\text{OH}\cdots\text{O}$ hydrogen bonding. The $-\text{COOH}$ groups are stabilized by intermolecular H-bonding. Note that the $(2\sqrt{3} \times 4)\text{rect}$ structure did not change at potentials more positive than 0.55 V, which suggests that the small peaks at 0.45 V in Figure 1c are not associated with structural changes in the adlayer of TA. Close examination of the STM image in Figure 4a reveals that the shape of each ordered domain is roughly rectangular and frequently more extended in the diagonal direction of the unit cell of $c(2\sqrt{3} \times 4)\text{rect}$, which suggests that the lateral growth rate of TA should be anisotropic as a result of the intermolecular interaction among the adsorbed TA molecules.

Finally, a further attempt was made to confirm the importance of intermolecular interactions in forming

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ordered adlattices by examining the adsorption of phthalic acid under similar conditions. However, irrespective of electrode potentials and concentrations, phthalic acid always formed a disordered array. These results indicate that molecular symmetry is an essential factor for the formation of ordered arrays of TA.

Pyrazine (PZ). The coordination chemistry of heterocyclic compounds such as pyridine and pyrazine at metal surfaces has been extensively examined in ultrahigh vacuum (UHV)^{31,33–39} and in electrochemical environments.^{1,40–44} More recently, in situ STM was used for investigating the adsorption of pyridine on Au(111) in acidic⁴⁵ and neutral solutions.⁴⁶ Osawa's group reported that flat-lying, tilted, and vertically standing pyridine molecules were observed by in situ STM under controlled potential conditions.⁴⁶ Their direct observation is in accord with previous results obtained by chronocoulometry, radiochemistry and spectroscopic methods.^{1,41–43}

We conducted in situ STM imaging experiments for the adsorption of pyridine on Pt(111) at various concentrations of pyridine and pH. Disordered structures were found consistently in acidic solutions, whereas an ordered phase was seen when the concentration was lower than 0.1 mM in a 0.1 M NaClO₄ solution. Our images were very similar to the image obtained by Osawa's group (see Figure 6d in ref 46), although the size of ordered domains were rather small on Pt(111).⁴⁷

Instead of pyridine, we focused our attention on adlayer structures of PZ on Pt(111) in an acidic solution. Eventually, we succeeded in obtaining a highly ordered adlayer of PZ on Pt(111) in a negative potential range. Figure 5a reveals a typical arrangement of a pyrazine overlayer at 0.2 V, which is near the onset of cathodic current as seen in Figure 1d. The pyrazine adlayer is clearly ordered, and the internal molecular structure can be discerned in the high-resolution image shown in Figure 5b. A precise comparison between this image and that of Pt(111)–(1 × 1) revealed that the two molecular rows of **I** and **II** are rotated by ca. 19° ($\sqrt{7}$ directions) from the lattice directions of Pt(111). This molecular array is hexagonal with a nearest-neighbor spacing of 0.74 nm in the **I** and **II** directions, indicating a $(\sqrt{7} \times \sqrt{7})R19.1^\circ$, $\theta = 0.14$ structure. These results unambiguously indicate the horizontal configuration of PZ at the cathodic potential. In the high-resolution STM image of Figure 5b, each PZ molecule was imaged as an equilateral triangle, as previously found for 3-fold coordinated benzene molecules lying horizontally on Rh(111).^{18,24} The averaged corruga-

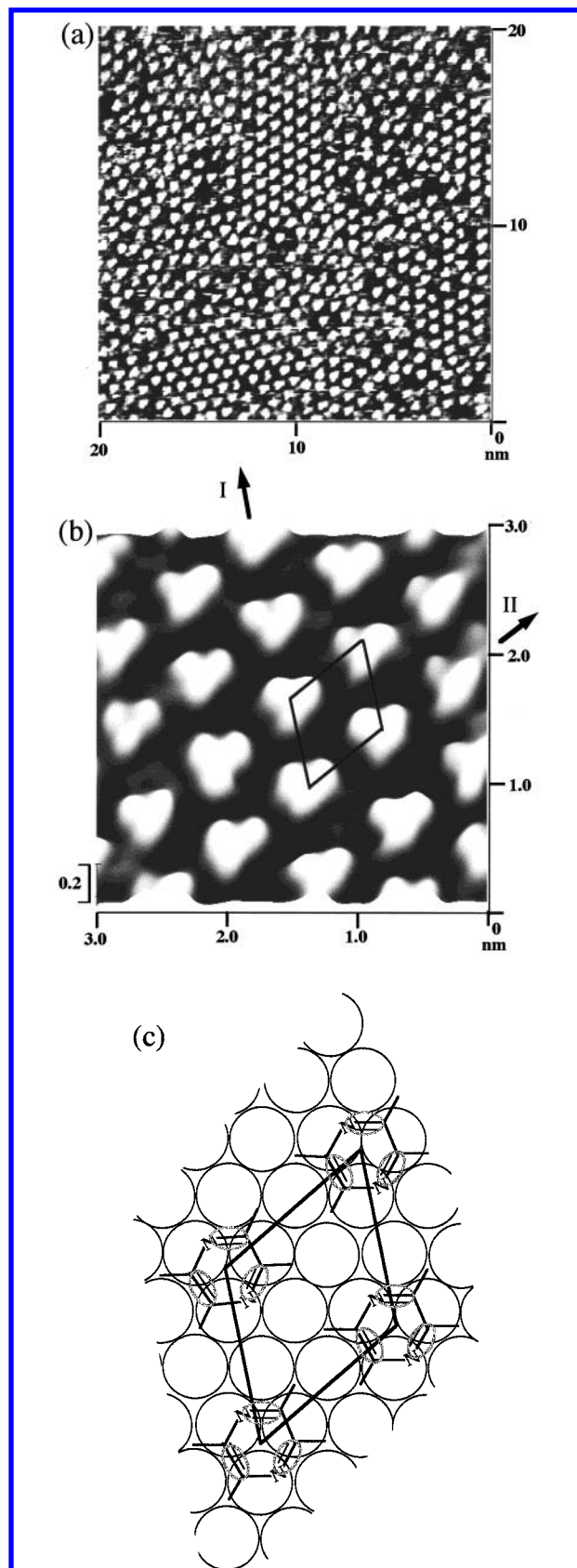


Figure 5. High-resolution STM images of an ordered pyrazine adlayer on Pt(111) obtained at 0.2 V in 0.1 M HClO₄. The higher resolution scan in (b) reveals the triangular features, which can be explained by the model structure, with a $(\sqrt{7} \times \sqrt{7})$ - $R19.1^\circ$ symmetry, in (c). The images were obtained with a bias voltage and feedback current of 200 mV and 5 nA, respectively. (a) Unfiltered; (b) 2D Fourier transform filtered.

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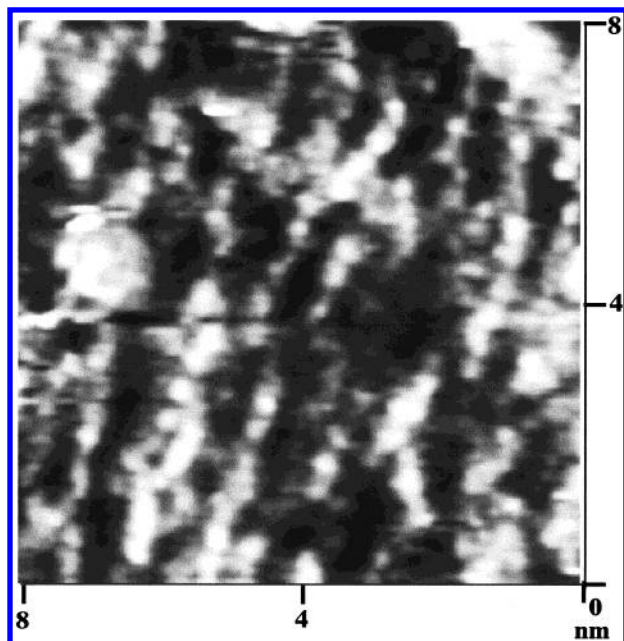


Figure 6. An unfiltered, typical STM image of pyrazine obtained at 0.5 V in 1 mM pyrazine and 0.1 M HClO_4 .

tion height for each molecule is ca. 0.1 nm. The characteristic triangular shape of PZ also implies 3-fold coordination, as depicted by the ball model in Figure 5c. Because this triangular appearance of benzene molecules is associated with the Kekule-like structure,^{26,48,49} similar molecular distortion is also expected for PZ. It is reasonably expected that the three ovals within each molecule, as shown in Figure 5c, correspond to the locations of protrusions. It is intriguing to find that both benzene and pyrazine form ordered structures at the same coverage of 0.14, and yet their real-space arrangements are totally different. Whereas pyrazine molecules are 3-fold coordinated and form a $(\sqrt{7} \times \sqrt{7})R19.1^\circ$ structure, benzene molecules adsorb at 2-fold bridging sites and pack into a $(\sqrt{21} \times \sqrt{21})R10.9^\circ$ structure, as shown in our previous paper.¹⁸

The effect of potential on molecular configurations was briefly examined by stepping the potential from 0.2 to 0.5 V. Figure 6 is a typical STM image acquired at 0.5 V. It is clear that the ordered overlayer becomes disordered, despite the fact that some local chains can be seen in the image. This image also shows that the separation between two protrusions is uniformly 0.4 nm, which strongly suggests that adsorbed pyrazine molecules adapt a tilt orientation, similar to that of pyridine. Previous in situ measurements using Auger spectroscopy and electron energy loss spectroscopy EELS indicated that PZ adsorbs on Pt(111) through one of the N-atoms with its molecular plane tilting from the substrate by 79° .³¹ Our result shown

in Figure 6 might be consistent with the reported data,³¹ but the flat-lying configuration of PZ observed at 0.2 V, as described above, was not previously reported on Pt(111).

Being a planar molecule with no permanent dipole moment, PZ is expected to adsorb horizontally on surfaces, as observed on Ag(111) in gas-phase studies.^{34,37} On the other hand, it was reported using in situ X-ray photoelectron spectroscopy that structure transition from flat to vertical was observed for PZ on Au(111).^{38,39} Note that the adsorption of PZ on Au(111) was investigated using chronocoulometry, with a reorientational phase transition observed at the potential of zero charge (pzc).⁴⁴ PZ molecules were found to adsorb horizontally at potentials more negative than pzc but turned upright at potentials more positive than pzc.⁴⁴ Intermolecular hydrogen bonding was thought to stabilize the PZ adlayer.^{1,40} The behavior of pyrazine on Pt(111), as revealed by the present STM results, bears a strong resemblance to that on Au(111). Although hydrogen-bonded water molecules were not shown in Figure 5c, we strongly believe that PZ molecules on Pt(111) can be partly associated with the formation of water-mediated hydrogen bonding, like that discussed previously for the adsorption of PZ on mercury electrodes.⁴⁰

Conclusions

It was demonstrated that molecular structure is critical in forming ordered adlayers at a well-defined Pt(111) electrode. Molecules of higher symmetry, such as TA and PZ, formed the characteristic ordered structures of $c(2\sqrt{3} \times 4)rect$ and $(\sqrt{7} \times \sqrt{7})R19.1^\circ$, respectively, whereas adlayers of BA and pyridine were mostly disordered. The high-resolution STM images reported in the present paper allowed us to determine packing arrangements and even internal structures. It was proposed that BA and TA molecules were adsorbed at 2-fold bridging sites, with their molecular planes parallel to the Pt(111) substrate. The adlayer of TA formed a $c(2\sqrt{3} \times 4)rect$ structure, which was thought to be stabilized by hydrogen bonding between adjacent $-\text{COOH}$ groups, formed molecular chains along the $\sqrt{3}$ direction. The internal molecular structures of pyrazine were revealed by high-resolution STM imaging. The triangular appearances indicate that they adsorb at 3-fold hollow sites. It was assumed that hydrogen-bonded water molecules exist in the highly ordered PZ adlayer observed at a negative potential.

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