***In-situ* STM observation of the phase transition of two-dimensional 2,5-distyrylpyrazine nanostructure adsorbed on Au(111) in an electrochemical environment**

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The phase transition of 2,5-distyrylpyrazine (DSP) adsorbed on Au(111) substrate was studied as a function of the substrate potential in 0.1 M HClO₄, using an *in situ* scanning tunneling microscope (STM). Depending on the applied electric field, DSP formed three distinctly different, two-dimensionally (2D) ordered, supramolecular nanostructures on the Au(111) surface. In the potential range of 0.55 V < *E* < 0.75 V, the DSP molecules formed a close-packed stripe pattern with the adlayer structure $\begin{pmatrix} -1 & 3 \\ 8 & 6 \end{pmatrix}$. When the potential was reduced to 0.45 V < *E* < 0.55 V, a ridge-like pattern built from dimer subunits was observed, with the adlayer structure $\begin{pmatrix} 4 & 5 \\ -12 & 4 \end{pmatrix}$. Further decreasing in the electrode potential to 0.2 V < *E* < 0.45 V caused the appearance of a herringbone-like pattern consisting of dimer subunits, with the adlayer structure $\begin{pmatrix} 9 & 0 \\ 3 & 9 \end{pmatrix}$. The potential-induced phase transitions revealed the structure-determining role of substrate-adsorbate coordination and intermolecular interaction in forming the distinct 2D adlayer motifs.

2,5-distyrylpyrazine, Au(111), scanning tunneling microscopy, phase transition

1 Introduction

Owing to their unique properties, nanostructures have attracted much attention in modern science and technology for applications such as optoelectronic devices, chemical sensors, surface wettability, lubrication, and lithography [1–4]. Great efforts have been made to fabricate nanostructures using various techniques, including the Langmuir-Blodgett method, sol-gel synthesis, electrochemical deposition, chemical vapor deposition, and self-assembly [5, 6]. In particular, the self-assembly technique has been widely used

to prepare artificial nanostructures, and has become one of the major “bottom-up” approaches to construct molecular architectures [7]. Molecules in self-assembled monolayers (SAMs) take on special orientations, and can form well-defined arrays, depending on the interactions between the molecules and the substrate and the neighboring molecules. However, for the development of future nanodevices, it is desirable for the individual molecules in SAMs to have the ability to take the form of various nanoblocks. There is also great interest in molecular electronics for developing the capability to better control nanopatterns. There is therefore a need to fabricate nanoblocks by operating individual molecules using non-traditional processing methods. Although the ability of an STM tip to manipulate molecules

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has been well demonstrated, the limitation is its low efficiency [8]. If the molecules in SAMs could be induced using special stimuli such as magnetism, electricity, or thermal annealing, this would provide a breakthrough in the fabrication of nanoblocks.

On surfaces and at interfaces, 2D phase behavior is mainly governed by a complex interplay between the intermolecular and molecule-substrate interactions [9]. In an electrochemical environment, the charge density at the metal electrodes can be tuned via changes in the external electric field; this can change the configuration and strength of adsorption, and can even result in the formation of different patterns [10–15]. Wan *et al.* found that the orientational transition of 2,2'-bipyridine from flat to vertical was completely potential dependent and reversible on Cu(111) [11]. Trimesic acid can reversibly form different patterns under different charge densities at Au(111)/0.1 M HClO₄ or Au(111)/0.05 M H₂SO₄ interfaces [14, 15]. It is therefore a very appealing concept to fabricate functional nanostructures by tuning the substrate potential.

In this paper, for the first time, we report *in situ* electrochemical scanning tunneling microscopy (ECSTM) results for the two-dimensional (2D) self-assembly of a 2,5-distyrylpyrazine (DSP) film deposited on Au(111), and its electrode potential-dependent phase transition in an electrochemical environment. As shown in Scheme 1, DSP consists of two aromatic rings, one pyrazine ring, and two olefinic double bonds. The molecule as a whole is not planar, with a dihedral angle 12.09° between the planes of the pyrazine ring and the benzene rings [16]. The results of this study showed that three types of 2D supramolecular nanostructures formed by DSP were resolved at differently charged interfaces. It is noteworthy that the different self-assembled nanopatterns on the solid surfaces could be tuned by changing the applied electrode potential.

2 Experimental section

DSP was synthesized as described in an earlier paper [17]. The electrolyte solution was prepared using ultrapure HClO₄ (Kanto Chemical Co., Japan) and Millipore (Milli-Q, 18 MΩ, TOC ≤ 4 ppb) water. The self-assembled DSP monolayer was obtained by immersing the gold single crystal into the saturated DSP-ethanol solution for 60 s. It was

Scheme 1 (a) Structural formula of DSP; (b) space-filling models for the DSP molecule.

then rinsed successively with ethanol and water, so that excess molecules were gently removed.

Cyclic voltammetry experiments were performed using the so-called hanging meniscus method, using an EG&G PAR Basic Electrochemical System (Princeton Applied Research). A reversible hydrogen electrode (RHE) and a platinum wire were used as the reference and counter electrodes, respectively. The solutions were deaerated with high purity nitrogen before experiments were carried out. All of the potentials were reported with respect to a reversible hydrogen electrode (RHE) in 0.1 M HClO₄.

In situ STM measurements were carried out using a Nanoscope E microscope (Digital Instrument Inc., Santa Barbara, CA) in 0.1 M HClO₄. The electrodes (Au(111)) were prepared using the bead method, by melting a Au wire (99.999% in purity, 0.8 mm in diameter) [18]. The tunneling tip was prepared from a W wire (0.25 mm in diameter) electrochemically being etched in 0.6 M KOH. The side-walls of the tips were sealed with transparent nail polish, to minimize the faradaic current. All of the images were collected in the constant-current mode to evaluate the height of the corrugations present in the adsorbed molecules.

3 Results and discussion

3.1 Cyclic voltammetry

Figure 1 shows typical current versus potential curves for bare Au(111) (dashed line) and the self-assembled DSP film on Au(111) (solid line) in 0.1 M HClO₄, recorded at a scan rate of 50 mV s⁻¹. It can be seen that the adsorption of DSP resulted in a decrease in the electric charge in the double-layer region. New oxidation and reduction peaks were observed at 0.92 V and 0.87 V, respectively. According to the literature [19], this pair of peaks might be related to the pyrazine rings in DSP. A detailed understanding of these results requires a qualitative and quantitative product analysis based on spectroscopic experiments, which is beyond the scope of the present work. We focused on investigating the adlayer structures of the DSP film in the double-layer po-

Figure 1 Cyclic voltammograms for bare Au(111) (dashed line), and DSP-modified Au(111) (solid line), measured in 0.1 M HClO₄ at a scan rate of 50 mV/s.

tential region from 0.2 V to 0.75 V.

3.2 Stripe pattern (0.55 V→0.75 V)

A freshly prepared DSP film on Au(111) was transferred directly into the electrochemical STM cell, where it was in contact with an 0.1 M HClO₄ electrolyte solution at approximate 0.63 V. As shown in Figure 2(a), an adlayer with long-range order was observed on the large terrace of the Au(111) surface, with a parallel stripe pattern. Figure 2(b) shows an STM image obtained at a higher resolution, using a bias voltage of −193 mV and a setpoint current of 527.9 pA. This image revealed the details of the internal molecular structure, orientation, and packing arrangement in the ordered adlayer. Each individual DSP molecule could be resolved as a linear configuration with a rodlike shape, which was attributed to the conjugated backbone. The rod length was measured to be approximately 1.8 nm, in agreement with the theoretical length of the DSP molecule. The series of bright protrusions in a linear configuration are a contrast feature typical of STM images for a planar-oriented conjugated aromatic molecule physisorbed on a substrate surface [20, 21]. A similar STM contrast and stripe pattern was also reported for a DSP derivative adsorbed in a flat configuration on highly orientated pyrolytic graphite [22]. Similar molecular stripe patterns have been found in the crystallographic structure of DSP [23].

Working from the repeating molecular arrays, the rhombus unit cell is outlined in Figure 2(b), with $a = 0.73 \pm 0.10$

nm, $b = 1.98 \pm 0.14$ nm, and $\alpha = 58 \pm 5^\circ$. The area per molecule was estimated to be $A_{\text{exp}} = \sim 1.23 \text{ nm}^2$, corresponding to a coverage of $\Gamma_{\text{exp}} = \sim 1.35 \times 10^{-10} \text{ mol cm}^{-2}$. Within the error range, the length of vector $a = 0.73 \pm 0.10$ nm from the repeating motif was equal to $\sqrt{7}$ times the distance of the primitive gold lattice ($\sqrt{7} \times a_{\text{Au}} = \sqrt{7} a_{\text{Au}}$), while the length of vector $b = 1.98 \pm 0.14$ nm was close to $2\sqrt{13} a_{\text{Au}}$. The detailed characteristic dimensions are listed in Table 1.

Based on the experimental data, it was difficult to resolve the exact positional alignment between the molecular adlayer and the Au(111) substrate. Referring to data shown in the literatures [24, 25], the aromatic phenyl rings in the DSP molecules were assumed to be preferentially bound to or to be near high-symmetry three-fold hollow sites on the Au(111) surface, via d- π^* coordination between the molecule and substrate. With this assumption and the experimental data described above, the structural models shown in Figure 2(c) were tentatively proposed. The structure was represented by a rhombus unit cell with dimensions $a' = \sqrt{7} a_{\text{Au}}$, $b' = 2\sqrt{13} a_{\text{Au}}$, and $\alpha' = 55^\circ$. A $(\sqrt{7} \times 2\sqrt{13})$ structure containing one molecule was defined, giving rise to a theoretical coverage of $\Gamma' = 1.29 \times 10^{-10} \text{ mol cm}^{-2}$. The lateral positions of the neighboring molecules in each molecular row were controlled mainly by the intermolecular and molecule-substrate interaction. With the primitive vectors of the gold lattice a_{Au} and b_{Au} ($|a_{\text{Au}}| = |b_{\text{Au}}| = 0.288 \text{ nm}$) as indicated in Figure 2(c), the unit cell was determined in matrix notation as

$$\begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} -1 & 3 \\ 8 & 6 \end{pmatrix} \begin{pmatrix} a_{\text{Au}} \\ b_{\text{Au}} \end{pmatrix}$$

The parallel stripe pattern was stable in the range of 0.55 V < E < 0.75 V. Decreasing the potential below this range caused the dissolution of the parallel stripe pattern. However, when the electrode potentials was higher than 0.75 V, no ordered adlayer was detected via *in situ* STM, which is probably hindered kinetically.

3.3 Ridge-like pattern (0.45 V→0.55 V)

Decreasing the electrode potential to give 0.45 V < E < 0.55 V (i.e., a slightly more negatively charged electrode) resulted in the appearance of a ridge-like pattern on the electrode surface, accompanied by the dissolution of the close-packed stripe phases. Panels (a) and (b) in Figure 3 show large-scale and high-resolution STM images of the DSP adlayer at 0.5 V, respectively. This adlayer consisted of alternating rows I and II. The high-resolution STM image in Figure 3 revealed that both rows were built from dimer-type subunits with two linear configurations. Each linear configuration was assigned as an individual DSP molecule. However, careful inspection of Figure 3(b) showed that the mutual molecular alignment in the dimers in molecular row I

Figure 2 (a) Typical large-scale STM image, (b) high-resolution STM image of parallel stripe pattern on Au(111) in 0.1 M HClO₄ at 0.63 V; (c) tentatively suggested structural models for the parallel stripe pattern on Au(111).

Table 1 Characteristic dimensions of the unit cell for the various ordered DSP adlayers at the Au(111)/0.1 M HClO₄ interface

Sample	a/a' (nm)	b/b' (nm)	α/α' (°)	Area A/A' per molecule (nm ²)	Coverage Γ/Γ' 10^{-10} mol cm ⁻²
Stripe pattern	0.73 ± 0.10	1.98 ± 0.14	58 ± 5	~ 1.23	~ 1.35
	0.76	2.07	55	1.28	1.29
Ridge-like pattern	1.20 ± 0.25	4.34 ± 0.21	80 ± 5	~ 1.28	~ 1.29
	1.32	4.15	84	1.36	1.22
Herringbone-like pattern	2.71 ± 0.26	2.01 ± 0.27	76 ± 4	~ 1.32	~ 1.26
	2.59	2.29	79	1.45	1.14

The first row for each pattern gives the experimentally determined values. The second row (italics) for each pattern gives the parameter determined using the theoretically suggested model, considering the relationship between the substrate surface and the adlayer, and the intermolecular interaction.

Figure 3 (a) Large-scale and (b) high-resolution STM image of the ridge-like pattern of DSP molecules on Au(111) in 0.1 M HClO₄ at 0.5 V; (c) tentatively suggested structural models for the ridge-like pattern on Au(111).

was different from that in molecular row II. Working from the repeating molecular arrays, the rhombus-shaped unit cell was outlined with $a = 1.20 \pm 0.25$ nm ($\sim \sqrt{21} a_{\text{Au}}$) and $b = 4.34 \pm 0.21$ nm ($\sim 4\sqrt{13}$), enclosing $\alpha = 80 \pm 5^\circ$, as illustrated in Figure 3(b). This unit cell contained four individual, flat-lying DSP molecules. The area per molecule was estimated to be $A_{\text{exp}} = \sim 1.28$ nm², which was larger than the value for the stripe pattern, and corresponded to a coverage of $\Gamma_{\text{exp}} = \sim 1.29 \times 10^{-10}$ mol cm⁻².

The registry between the adlayer and the substrate could not be determined unambiguously in the present experiments. Referring to the molecular arrangement as well as literature data [24, 25], structural models were proposed, as shown in Figure 3(c). The aromatic phenyl rings were pref-

erentially bound to or near high-symmetry three-fold hollow sites on the Au(111) surfaces, via d- π^* coordination between the molecule and substrate [24, 25]. At the electrochemical interface, 2D phase behavior is mainly governed by a complex interplay between the intermolecular and molecule-substrate interactions. It is thus assumed that the formation of the ridge-like dimer pattern resulted from the intermolecular and molecule-substrate interactions varied by the electrode potential. Referring to the experimentally observed repeat motif, we proposed a $(\sqrt{21} \times 4\sqrt{13})$ adlayer structure, giving rise to a theoretical coverage of $\Gamma' = 1.22 \times 10^{-10}$ mol cm⁻². Using the vectors of the primitive gold lattice with $|a_{\text{Au}}| = |b_{\text{Au}}| = 0.288$ nm as a basis, one obtains in matrix notation:

$$\begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} 4 & 5 \\ -12 & 4 \end{pmatrix} \begin{pmatrix} a_{\text{Au}} \\ b_{\text{Au}} \end{pmatrix}$$

3.4 Herringbone-like pattern (0.2 V $\rightarrow$ 0.45 V)

When the electrode potential was scanned in the region $0.2 \text{ V} < E < 0.45 \text{ V}$ (i.e., with a more negatively charged electrode), a different STM contrast pattern appeared on the electrode surface in place of the ridge-like pattern. Figure 4(a) shows a large-scale STM image of the DSP adlayer at 0.4 V, which revealed a herringbone-like pattern. The alternating molecular rows I and II were identified. However, the high resolution STM image shown in Figure 4(b) revealed that both rows were constructed from two types of dimer subunits with two linear configurations. Each linear configuration identified was assigned as an individual DSP molecule. Adjacent dimers in the neighboring molecular rows appeared to be aligned with the upper right and the lower left, respectively. The angle β between the molecular alignment directions in the two types of dimers in the neighboring molecular rows was $50^\circ \pm 3^\circ$. Working from the repeating molecular arrays, a rhombus-shaped unit cell containing four molecules was outlined, with $a = 2.71 \pm 0.26$ nm ($\sim 9a_{\text{Au}}$), $b = 2.01 \pm 0.27$ nm ($\sim 3\sqrt{7}a_{\text{Au}}$), and $\alpha = 76 \pm 4^\circ$, as illustrated in Figure 4(b). The area per molecule was estimated to be $A_{\text{exp}} = \sim 1.32$ nm², corresponding to a coverage of $\Gamma_{\text{exp}} = \sim 1.26 \times 10^{-10}$ mol cm⁻². On the basis of the STM observations, it was concluded that the

Figure 4 (a) Large-scale and (b) high-resolution STM image of the herringbone-like pattern of DSP molecules on Au(111) in 0.1 M HClO₄ at 0.4 V; (c) tentatively suggested structural models for the herringbone-like pattern on Au(111).

DSP molecules formed herringbone-like dimer patterns at $0.2 \text{ V} < E < 0.45 \text{ V}$. The herringbone pattern had a lower surface density than the ridge-like dimer pattern, which itself had a lower surface density than the parallel stripe pattern.

Experimentally, it is rather difficult to determine the exact positions of the aromatic rings with respect to the substrate geometry. Working from the information obtained from the STM experiments, a structural model for the herringbone-like dimer pattern was tentatively proposed, as shown in Figure 4(c). This model was in agreement with the properties of the experimentally observed unit cell (Table 1 gives a comparison of the parameters), and maximized the number of the flat-oriented DSP molecules located in “close-to” high-coordination three-fold hollow sites on the Au(111) surface. The formation of herringbone-like dimer pattern resulted from the intermolecular and molecule-substrate interactions varied by the electrode potential. Referring to the experimentally observed repeat motif, we proposed a $(9 \times 3\sqrt{7})$ adlayer structure, giving rise to a theoretical coverage of $\Gamma' = 1.14 \times 10^{-10} \text{ mol cm}^{-2}$. With the primitive vectors of the gold lattice a_{Au} and b_{Au} , one obtains, in matrix notation:

$$\begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} 9 & 0 \\ 3 & 9 \end{pmatrix} \begin{pmatrix} a_{\text{Au}} \\ b_{\text{Au}} \end{pmatrix}$$

3.5 Structural transitions and dynamic processes

The steady-state STM experiments in an electrochemical environment demonstrated that, depending on the substrate charge density, three types of ordered patterns could be observed on the Au(111) surface in 0.1 M HClO₄. These nanostructures could be dissolved or formed by tuning the electrode potential. According to the suggested models, the theoretical surface coverage was $1.29 \times 10^{-10} \text{ mol cm}^{-2}$ for the parallel stripe pattern, $1.22 \times 10^{-10} \text{ mol cm}^{-2}$ for the ridge-like dimer pattern, and $1.14 \times 10^{-10} \text{ mol cm}^{-2}$ for the herringbone-like dimer pattern. The coverage decreased upon negative polarization of the electrode surface, and this was accompanied by changes in the spatial arrangement.

As an illustration, the transformation process from parallel stripe pattern to ridge-like dimer pattern was investigated. If newly prepared DSP films were transferred into the electrochemical cell within the thermodynamically stable range of the parallel dimer pattern, the deposited parallel stripe patterns were observed initially. However, the parallel dimer patterns were not thermodynamically stable in this potential region. Over time, these structures began to dissolve, while the new ridge-like dimer pattern evolved via the rearrangement of the DSP molecules. The long-range order of the new pattern increased with increasing observation time. A snapshot of this process is presented in Figure 5, where the evolution of the structural changes is monitored as a function of time. The rate of the transformation process was rapid once it started, and it was easily promoted by tip scanning, reduced tunneling resistance, or even a small potential step. The transition phases appeared to be fluid-like. This suggested that individual DSP molecules were highly mobile, and that a rather weak adsorbate-substrate corrugation potential existed in this region for the stripe pattern. The whole process revealed that an appropriate negative polarization of the electrode surface could result in the formation of the ridge-like dimer patterns.

The formation of the pattern on a surface was the result of a delicate interplay between the adsorbate-adsorbate and adsorbate-substrate interactions. A change in either one, or both, will produce a structural transition. In an electrochemical environment, the charge density at the metal electrodes can be tuned via changes in the external electric field. The different electronic properties of substrates by the variation of the externally applied electric field are thought to

Figure 5 Time-dependent phase transition from the parallel stripe pattern to the ridge-like pattern at 0.5 V. (a) $t = 0$; (b) $t = 30 \text{ s}$; (c) $t = 60 \text{ s}$.

play an important role in the adlayer structure and coverage of DSP on surface [26]. The effect of the electrode surface polarization on the adsorption structures and coverage has been reported for 2,2'-bipyridine at Cu(111)/HClO₄ [11], 4,4'-bipyridine at Cu(111)/HClO₄ [27], trimesic acid at Au(111)/HClO₄ or Au(111)/H₂SO₄ [14, 15], isophthalic acid at Au(111)/HClO₄ [28], and picric acid at Au(111)/HClO₄ [29].

4 Conclusions

The formation of 2D DSP nanostructures at an electrified Au(111) electrode in contact with 0.1 M HClO₄ was studied using *in situ* scanning tunneling microscopy, to develop a molecular-level understanding of the potential-controlled self-assembly of DSP. In the potential range of 0.55 V < E < 0.75 V, DSP molecules formed a close-packed parallel stripe pattern, in which the lateral positions of neighboring molecules were mainly controlled by the intermolecular and the molecule-substrate interaction. By decreasing the potential to 0.45 V < E < 0.55 V, a ridge-like pattern built from dimer subunits was produced. The formation of dimers resulted from the intermolecular and molecule-substrate interactions varied by the electrode potential. Further decreasing the electrode potential to the range of 0.2 V < E < 0.45 V caused the appearance of a herringbone-like pattern built from dimer subunits. The formation of three distinctly different types of molecular adlayers indicated that controlling over the electrochemical environment conferred the ability to steer the molecular self-assembly, and to establish equilibrium structures via the subtle variation of the externally applied electric field.

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- Berger R, Delamarche E, Lang HP, Gerber C, Gimzewski JK, Meyer E, Güntherodt HJ. Surface stress in the self-assembly of alkanethiols on gold. *Science*, 1997, 276(5321): 2021–2024
- Yan L, Huck WST, Zhao XM, Whitesides GM. Patterning thin films of poly(ethylene imine) on a reactive SAM using microcontact printing. *Langmuir*, 1999, 15(4): 1208–1214
- Li M, Zhu JE, Zhang L, Chen X, Zhang H, Zhang F, Xu S, Evans DG. Facile synthesis of NiAl-layered double hydroxide/graphene hybrid with enhanced electrochemical properties for detection of dopamine. *Nanoscale*, 2011, 3(10): 4240–4246
- Wang Z, Xing R, Yu X, Han Y. Adhesive lithography for fabricating organic electronic and optoelectronics devices. *Nanoscale*, 2011, 3(7): 2663–2678
- Xu L, Liu Y, Zhang X. Interfacial self-assembly of amino acids and peptides: Scanning tunneling microscopy investigation. *Nanoscale*, 2011, 3(12): 4901–4915
- Pan GB, Li HJ, Yuan QH, Chen YJ, Wan LJ, Bai CL. Ordered arrays of semi-crown ligands on an Au(111) electrode surface: *in situ* STM study. *Sci China Ser B: Chem*, 2004, 47(4): 320–325
- Su GJ, Jia MK, Gan LH, Shi RF. ECSTM study of adsorption of C₆₀, C₇₀, C₈₆ and Y@C₈₂ on Au(111). *Sci China Chem*, 2010, 53(8): 1705–1710
- Crommie MF, Lutz CP, Eigler DM. Confinement of electrons to quantum corrals on a metal surface. *Science*, 1993, 262 (5131): 218–220
- Yan HJ, Li SS, Yan CJ, Chen Q, Wan LJ. Adsorption of TTF, TCNQ and TTF-TCNQ on Au(111): An *in situ* ECSTM study. *Sci China Ser B: Chem*, 2009, 52(5): 559–565
- Zhang JD, Kuznetsov AM, Medvedev IG, Chi QJ, Albrecht T, Jensen PS, Ulstrup J. Single-molecule electron transfer in electrochemical environments. *Chem Rev*, 2008, 108(8): 2737–2791
- Wan LJ, Noda H, Wang C, Bai CL, Osawa M. Controlled orientation of individual molecules by electrode potentials. *ChemPhysChem*, 2001, 2(10): 617–619
- Ciesielski A, Samorì P. Supramolecular assembly/reassembly processes: molecular motors and dynamers operating at surfaces. *Nanoscale*, 2011, 3(4): 1397–1410
- Dai PX, Chen T, Wang D, Wan LJ. Potential dependent adsorption geometry of 2,5-dihydroxybenzoic acid on a Au(111) surface: An *in situ* electrochemical scanning tunneling microscopy study. *J Phys Chem C*, 2012, 116(10): 6208–6214
- Su GJ, Zhang HM, Wan LJ, Bai CL, Wandlowski Th. Potential-induced phase transition of trimesic acid adlayer on Au(111). *J Phys Chem B*, 2004, 108(6): 1931–1937
- Li Z, Han B, Wan LJ, Wandlowski Th. Supramolecular nanostructures of 1,3,5-benzene-tricarboxylic acid at electrified Au(111)/0.05 M H₂SO₄ Interfaces: An *in situ* scanning tunneling microscopy study. *Langmuir*, 2005, 21(15): 6915–6928
- Sasada Y, Shimanouchi H, Nakanishi H, Hasegawa M. The crystal and molecular structure of 2,5-distyrylpyrazine. *Bull Chem Soc Jpn*, 1971, 44(5): 1262–1270
- Hasegawa M, Suzuki Y. Four-center type photopolymerization in the solid state: Poly-2,5-distyrylpyrazine. *J Polym Sci Part B: Polym Let*, 1967, 5(9): 813–815
- Wan LJ, Shundo S, Inukai J, Itaya K. Ordered adlayers of organic molecules on sulfur-modified Au(111): *in situ* scanning tunneling microscopy study. *Langmuir*, 2000, 16(5): 2164–2168
- Hamm UW, Lazarescu V, Kolb DM. Adsorption of pyrazine on Au(111) and Ag(111) electrodes an *ex situ* XPS study. *J Chem Soc, Faraday Trans*, 1996, 92(20): 3785–3790
- Su GJ, Li ZH, Aguilar-Sanchez R. Phase transition of two-dimensional chiral supramolecular nanostructure tuned by electrochemical potential. *Anal Chem*, 2009, 81(21): 8741–8748
- Xu LP, Wan LJ. STM investigation of the photoisomerization of an azobis-(benzo-15-crown-5) molecule and its self-assembly on Au(111). *J Phys Chem B*, 2006, 110(7): 3185–3188
- An SY, Xu SD, Zeng QD, Tan ZY, Wang C., Wan LJ, Bai CL. The self-assembly structure of pyrazine derivative on highly oriented pyrolytic graphite. *Acta Phys Chim Sin*, 2005, 21(8): 925–928
- Peachey NM, Eckhardt CJ. Energetics of organic solid-state reactions: the topochemical principle and the mechanism of the oligomerization of the 2,5-distyrylpyrazine molecular crystal. *J Am Chem Soc*, 1993, 115(9): 3519–3526
- Chiang S. Scanning tunneling microscopy imaging of small adsorbed molecules on metal surfaces in an ultrahigh vacuum environment. *Chem Rev*, 1997, 97(4): 1083–1096
- Sautet P. Images of adsorbates with the scanning tunneling microscope: theoretical approaches to the contrast mechanism. *Chem Rev*, 1997, 97(4): 1097–1116
- Wang D, Wan LJ, Bai CL. Formation and structural transition of molecular self-assembly on solid surface investigated by scanning tunneling microscopy. *Mater Sci Eng R*, 2010, 70(3–6): 169–187
- Diao YX, Han MJ, Wan LJ, Itaya K, Uchida T, Miyake H, Yamakata A, Osawa M. Adsorbed structures of 4,4'-bipyridine on Cu(111) in acid studied by STM and IR. *Langmuir*, 2006, 22(8): 3640–3646
- Li ZH, Wandlowski Th. Structure formation and annealing of isophthalic acid at the electrochemical Au(111)-electrolyte interface. *J Phys Chem C*, 2009, 113(18): 7821–7825
- Wen R, Pan GB, Wan LJ. Oriented organic Islands and one-dimensional chains on a Au(111) surface fabricated by electrodeposition: an STM study. *J Am Chem Soc*, 2008, 130(36): 12123–12127