Self-Assembly of TBrPP-Co Molecules on an Ag/Si(111) Surface Studied by Scanning Tunneling Microscopy [*]

LI Qing(李青)[1,2**], Shiro Yamazaki[2], Toyoaki Eguchi[2], MA Xu-Cun(马旭村)[1], JIA Jin-Feng(贾金锋)[1,3], XUE Qi-Kun(薛其坤)[1,3], Yukio Hasegawa[2]

[1]Institute of Physics, Chinese Academy of Science, Beijing 100190
[2]The Institute for Solid State Physics, The University of Tokyo, 5-1-5, Kashiwa-no-ha, Kashiwa 277-8581, Japan
[3]Department of Physics, Tsinghua University, Beijing 100084

Self-assembly of TBrPP-Co molecules on a Si(111)-$\sqrt{3}\times\sqrt{3}$ Ag substrate is studied by low-temperature scanning tunneling microscopy. With the same adsorbed amount (0.07 ML), the molecules deposited by low-temperature evaporation show three kinds of ordered structures whereas those deposited by high-temperature evaporation have size-dependent ordered structures. The distinct differences in the self-assembly structures and in the electron density of states inside the molecule near the Fermi energy demonstrate that the Br atoms of the molecule desorb at the higher evaporation temperature.

The formation of two-dimensional nano arrays by self-assembly of functional molecules is a central way to design nano devices on surfaces.[1] These self-assembled structures can modify the physical and chemical properties of the molecules dramatically, making the designed surfaces suitable for application in fields such as chemical detection,[2] catalysis[3] and molecular electronics.[4] This has led to a large number of recent studies focusing on functional molecular self-assembly.[5−8]

We choose a Si(111)-$\sqrt{3}\times\sqrt{3}$ Ag surface as a substrate in the present work for the following two advantages: firstly, the sample is based on the Si(111) substrate, making it much easier to be conducted in applications on molecular devices with the large scale integration (LSI) technique. The second reason is related to its electronic properties. The band structure of its surface states shows a parabolic shape,[9,10] indicating the existence of quasi free electrons on the surface. Besides that, the metallic or semiconducting nature of the surface state can be controlled by adjusting the amount of Ag adsorbates.[11]

In this Letter, we report self-assembly of 5, 10, 15, 20-Tetrakis-(4-bromophenyl)-porphyrin-Co (TBrPP-Co) molecules on the Si(111)-$\sqrt{3}\times\sqrt{3}$ Ag surface studied by low-temperature scanning tunneling microscopy (LT-STM). The molecule is composed of a porphyrin unit with a cobalt atom at its center and four bromophenyl groups surrounding the central unit. Recently, this molecule has acquired great interest because of its two types of conformations (Fig. 1(a)): planar and saddle shapes, as well as its controllability with a probe tip,[12] and the observation of the Kondo resonance on the central magnetic atom.[12,13]

Our experiments were performed with an ultrahigh vacuum (UHV) LT-STM (USM-1300, Unisoku, and SPM-100, RHK), in which both of the tip and sample can be cooled by liquid He (LHe). All the STM images shown here were taken at 5 K in UHV ($\sim 7\times10^{-9}$ Pa). The Si(111)-$\sqrt{3}\times\sqrt{3}$ Ag substrate was prepared by Ag deposition (> 1 ML) and subsequent annealing, the details of which are found elsewhere.[13] TBrPP-Co molecules were evaporated onto the substrate using a home-made alumina cell wrapped by a tungsten wire whose diameter is 0.2 mm. Because of the absence of a thermal couple on the cell, the precise temperature of the evaporator is unknown. Instead, we give the amount of electrical current passing through the tungsten wire during evaporation. To make the assembled structures, we cooled the substrate down to ~ 15 K by LHe during molecular deposition and then annealed at room temperature for several hours. As a probe, an electrochemically etched tungsten tip was treated *in situ* using both e-beam heating and field ion spectroscopy.

The deposited molecules formed self-assembled structures after room-temperature annealing for around 3 h. When the evaporation current was 1.72 A, a small amount of TBrPP-Co molecules (0.07 ML) aggregated into single-layer island structures, as illustrated in Fig. 1(b). No single isolated molecules are found at all, indicating high mobility of TBrPP-Co molecules on the Si(111)-$\sqrt{3}\times\sqrt{3}$ Ag substrate at room temperature.

In this coverage, the molecular islands show three kinds of ordered structures, phase A, B and C, whose unit cells are $3\sqrt{3}\times3\sqrt{3}$, 9×9 and $\begin{pmatrix} 4 & 5 \\ 1 & -4 \end{pmatrix}$ of

the Si(111) unit cell, respectively (Fig. 1(c)). It is well known that TBrPP-Co molecules usually adsorb on surfaces via two kinds of conformations: planar and saddle, as shown in Fig. 1(a), whose sizes are 1.5 nm × 1.5 nm and 1.8 nm × 1.1 nm, respectively.[12] Highly resolved STM images reveal that molecules in the single phases do not in fact have identical shapes. Figure 1(d) presents an empty-state STM image taken on phase C, where detailed structures of the molecules can be clearly seen. Some of the molecules have apparent rod-like protrusions along the molecular symmetry axis, proving that they are saddle-conformation molecules. Other molecules have a dark line across the center, having planar conformation. Detailed analysis of these structures can be found elsewhere.[15]
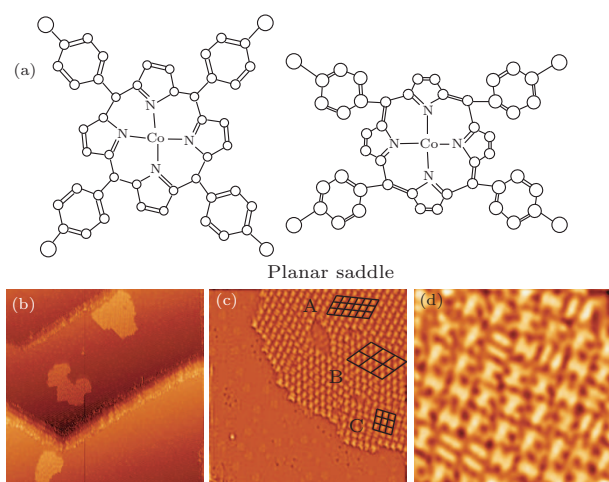

Fig. 1. (a) Model of two conformations of the TBrPP-Co molecules. (b) Large-sized STM image taken on the sample made by low-temperature evaporation. (c) Three kinds of ordered structures formed by TBrPP-Co molecules. The unit cell of each phase is shown by black lines. (d) Highly resolved STM images taken inside phase C with its molecular model attached. The molecular coverage is 0.07 ML. The image size is 200 nm × 200 nm for (b), 50 nm × 50 nm for (c) and 12 nm × 12 nm for (d). The sample bias voltage and tunneling current were all set at +2.0 V and 20 pA, respectively.

However, when the evaporation current was raised up to 1.82 A, the situation changed dramatically. Figure 2 is a large size (500 nm × 500 nm) STM image of the Si(111)-$\sqrt{3} \times \sqrt{3}$ Ag surface covered with the same amount of TBrPP-Co molecules (0.07 ML). It is clear that the molecules accumulate and form island structures both near step edges and on terraces at this coverage.

Further studies revealed that the molecular arrangement in these islands is related to the size of the islands. Figure 3 gives STM images showing the molecular arrangement typical for small sizes of islands. In the image of relatively large area (34 nm × 16.3 nm) in Fig. 3(a), it is clear that the molecules form flat networks and show regularly arranged holes. From highly resolved STM images, we

find that those holes are formed by the gathering of the surrounding six TBrPP-Co molecules. We describe this assembled structure by a nearly rectangular unit cell with four molecular "dimers" at each corner and a central molecular "dimer" in a different azimuthal orientation. The unit cell parameters are as follows: $a = b = 3.17 \pm 0.3$ nm, $\theta = 37 \pm 1°$. As none of the element of the matrix is integer, we conclude that the TBrPP-Co overlayer is not commensurate with the underlying Ag/Si(111) substrate.
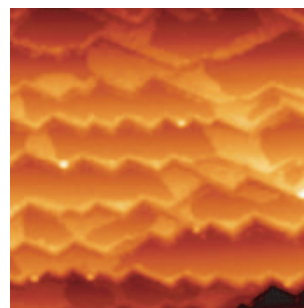

Fig. 2. Large-sized STM image of the sample made by the higher evaporation temperature. The molecular coverage is 0.07 ML. The image size is 500 nm × 500 nm. The bias voltage and tunneling current were set at +2.0 V and 20 pA, respectively.
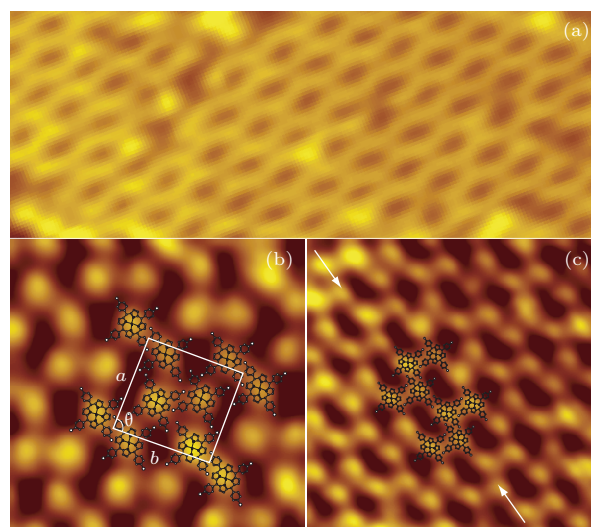

Fig. 3. Assembled structures on the small islands. (a) Large size STM image of the small islands zoomed from Fig. 2. (b) Highly resolved STM image of the ordered structures of the small islands with the molecular model attached. White lines indicate the unit cell of the assembled structure. (c) Typical phase boundary of the ordered structures highlighted by white arrows. The image size is 34 nm × 16.3 nm for (a), 10 nm × 10 nm for (b) and 15 nm × 15 nm for (c). The bias voltage and tunneling current were all set at +2.0 V and 20 pA, respectively.

Although small islands have well ordered structures, there are still some defects. Fig. 3(c) gives a typical phase boundary inside the molecular islands, as highlighted by the arrows. We can see that this phase boundary is formed by the accumulation of molecular

"dimers" with the same orientation along a given line. So far, this is the only kind of phase boundary found in the small islands.

As explained above, this unique self-assembly has a regular hole array. Such an array is very useful in modern material science. In particular, it has potential applications in the field of information storage by the adsorption of functional molecules such as C_{60}.[16−18]

The ordered structures in large islands are quite different from those of the smaller islands. Figure 4(a) shows a large-sized (40 nm × 40 nm) STM image acquired inside a large island. The molecules make a wide single-layer assembled structure with some line-like vacancy, which is highlighted by an arrow in Fig. 4(a). Figure 4(b) gives a zoomed image of Fig. 4(a) with a molecular model attached. After careful measurements, we acquired the parameters of the unit cell: $a = b = 1.54 \pm 0.4$ nm, $\theta = 87 \pm 1°$.
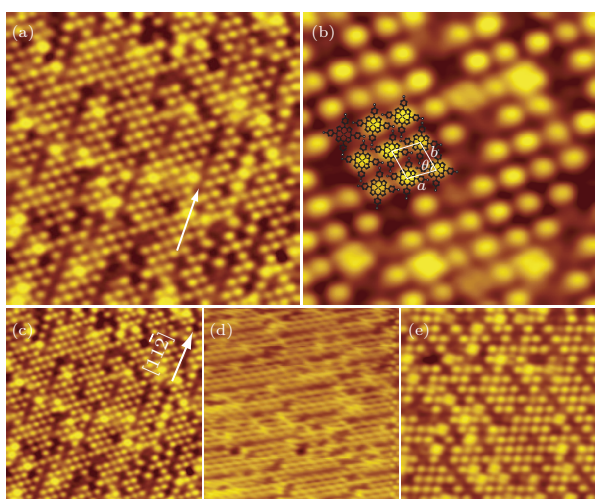

Fig. 4. Assembled structures on the large islands. (a) Large size STM image of the large islands zoomed from Fig. 2. The white arrow indicates the orientation of the vacancy lines. (b) Highly resolved STM image of the ordered structures of (a) with the molecular models attached. White lines indicate the unit cell of the assembled structures. (c), (d) and (e) Three kinds of directions of the vacancy lines. The image size is 40 nm × 40 nm for (a), 15 nm × 15 nm for (b), 40 nm × 40 nm for (c), 50 nm × 50 nm for (d) and 30 nm × 30 nm for (e). The bias voltage and tunneling current were all set at +2.0 V and 20 pA, respectively.

Checking the azimuthal orientation of the characteristic linear vacancy relative to the substrate, we find that the linear vacancy is rotated by an angle $\alpha = 4 \pm 1°$ away from the $[11\bar{2}]$ direction of the substrate. As the Si(111)-$\sqrt{3} \times \sqrt{3}$ Ag substrate has three fold symmetry, altogether the linear vacancy has three kinds of orientations, which means $\alpha = 4°$, 124° or 244°, as illustrated in Figs. 4(c)–4(d). The fixed orientation of the linear vacancy indicates that the assembly structure in the large islands is mediated by the interaction with the substrate.

The obvious difference in the self-assembled structures between the molecules deposited in the different evaporation temperatures can be explained by the two following possible reasons: one is due to different evaporation flux, which may influence the initial cluster formation. The other is structural modification of the molecules by thermal heating. Since the sample was cooled down to around 15 K during the molecular deposition, the surface diffusion of the molecules was suppressed before room temperature annealing. Consequently, with the same coverage, the initial clustering should be the same, and thus the former explanation should be ruled out. Actually, in both planar and saddle conformations, there are four Br atoms at the corner of the TBrPP-Co molecules via a C-Br bond. It has been known that the bonding energy of the C-Br bond is much smaller than the bonding energy inside the central framework,[19] which makes it possible to break the C-Br bond by simple heating[20,21] or tip manipulation.[22] Furthermore, since the bonding energy of the C-H and C-C bonds is almost twice or three times that of C-Br bonds,[19,23] the TPP-Co central unit will remain when the Br atoms desorb. Actually, Grill *et al.*[20] pointed out that the desorption of Br atoms occurs when the temperature of TBrPP increases up to 590 K. Thus we believe that the desorption of the Br atoms is a possible reason for the molecules to form different ordered structures at a higher evaporation temperature. Besides that, unlike the case in Fig. 1(d), we notice that the molecules in Figs. 3 and 4 are recognized as bright protrusions only while they do not show their inner structures, indicating the distribution of the electron density of states inside the molecule near the Fermi energy changes by high temperature evaporation. This observation can also be explained by the desorption of Br atoms at high temperature.

In summary, we have studied the self-assembled structures of TBrPP-Co molecules on the Si(111)-$\sqrt{3} \times \sqrt{3}$ Ag substrate using LT-STM. When the evaporation temperature is low, the molecules form three kinds of ordered structures whereas at high-temperature evaporation, the molecules form size-dependent ordered structures. The clearly different self-assembled structures and the different distribution of the density of states inside the molecule near the Fermi energy demonstrate that the Br atoms desorbed at the high-temperature evaporation.

References

[1] Forrest S R 1997 *Chem. Rev.* **97** 1793
[2] Ke Y, Lindsay S, Chang Y, Liu Y and Yan H 2008 *Science* **319** 180
[3] Baddeley C J 2003 *Top. Catal.* **25** 17
[4] Lei S, Luis J P, Minoia A, Auweraer M V D, Rovira C, Lazzaroni R, Amabilino D B and Feyter S D 2008

Chem. Commun. **6** 703

[5] Rosei F, Schunack M, Jiang P, Gourdon A, Laegsgaard E, Stensgaard I, Joachim C and Besenbacher F 2002 *Science* **296** 328

[6] Yanagi H, Mukai H, Ikuta K, Shibutani T, Kamikado T, Yokoyama S and Mashiko S 2002 *Nano Lett.* **2** 601

[7] Barlow D E, Scudiero L and Hipps K W 2004 *Langmuir* **20** 4413

[8] Ge S P, LÜ C and Zhao R G 2006 *Chin. Phys. Lett* **23** 1558

[9] Aizawa H, Tsukada M, Sato N and Hasegawa S 1999 *Surf. Sci.* **429** L509

[10] Hasegawa S 2000 *J. Phys.: Condens. Matter* **12** R463

[11] Nakajima Y, Takura S, Nagao T and Hasegawa S 1997 *Phys. Rev.* B **56** 6782

[12] Iancu V, Deshpande A and Hla S W 2006 *Nano Lett.* **6** 820

[13] Li Q, Yamazaki S, Eguchi T, Kim H, Kahng S J, Jia J F, Xue Q K and Hasegawa Y 2009 *Phys. Rev.* B **80** 115431

[14] Ono M, Nishigata Y, Nishio T, Eguchi T and Hasegawa Y 2006 *Phys. Rev. Lett.* **96** 016801

[15] Li Q, Yamazaki S, Eguchi T, Hasegawa Y, Kim H, Kahng S J, Jia J F and Xue Q K 2008 *Nanotechnology* **19** 465707

[16] Stöhr M, Wahl M, Spillmann H, Gade L H and Jung T A 2007 *Small* **3** 1336

[17] Spillmann H, Kiebele A, Stöhr M, Jung T A, Bonifazi D, Cheng F Y and Diederich F 2006 *Adv. Mater.* **18** 275

[18] Macleod J M, Ivasenko O, Perepichka D F and Rosei F 2007 *Nanotechnology* **18** 424031

[19] Kerr J A and Dickenson A F T 1976 *Handbook of Chemistry and Physics* (Cleveland, OH: CRC) p 57

[20] Grill L, Dyer M, Lafferentz L, Persson M, Peters M V and Hecht S 2007 *Nat. Nanotechnol.* **2** 687

[21] Veld M I, Iavicoli P, Haq S, Amabilino D B and Raval R 2008 *Chem. Commun.* **13** 1536

[22] Hla S W, Bartels L, Meyer G and Rieder K H 2000 *Phys. Rev. Lett.* **85** 2777

[23] Lauhon L J and Ho W 2000 *J. Phys. Chem.* A **104** 2463