Adlayer Structures of Binaphthyl Derivatives on Cu(111)

Mei-Juan Han,[†,††] Qing-Dao Zeng,[†] Li-Jun Wan,*[†] and Chun-Li Bai*[†]
[†]*Institute of Chemistry, the Chinese Academy of Sciences, Beijing 100080, P. R. China*
[††]*Graduate School of Chinese Academy of Sciences, Beijing, P. R. China*

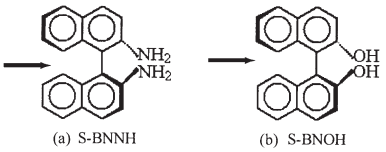
(Received March 31, 2003; CL-030268)

Adsorption of two binaphthyl derivatives on Cu(111) electrode were investigated by STM and cyclic voltammetry. Both molecules adsorbed on the Cu(111) electrode surface in 0.1 M $HClO_4$ solution and formed well-defined adlayers with a (4×4) symmetry in the double layer potential region. With the high resolution STM images, the configurations of individual molecules were determined. According to the experimental results, structural models are proposed for the adlayers.

The adlayer structure and conformation of molecules at interfaces is of particular importance in surface chemistry and catalysis. The well-established in situ scanning tunneling microscopy (STM) has been well recognized as a direct method for performing structural characterization with an atomic or molecular resolution.[1] The bonding and coordination of organic molecules with electrode surfaces have been successfully determined by STM.

1,1′-binaphthyl derivatives represent an important class of chiral auxiliaries.[2] The nonplanar arrangement of two naphthalene moieties in the molecules ensure a dissymmetric environment suitable for obtaining high degree of stereoselectivity.[3] In addition, 1,1′-binaphthyl has been used as an important building block for the preparation of more sophisticated system in application such as asymmetric catalysis, molecular recognition, nonlinear optics, and photoluminescence.[4] Chirality is a very important phenomenon in nature. So far, many chirality systems have been already successfully explored.[5] Although studies have been succeeded in the observation of molecules with central chirality, axial chirality is reported rarely. A pioneering work by Ohtani and co-workers reported the self-assembling and covalent binding of 1,1′-binaphthalene-2,2′-dithiol (BNSH) molecules and found that it fabricated a well-ordered two-dimensional arrangement on a Au(111) surface.[6] The structural details of *R*- and *S*-BNSH molecular adlayers in STM images are different each other due to the molecular chirality. To further explore the adsorption of molecules with axial chirality on solid surface, we have studied 1,1′-binaphthyl derivatives with different functional groups. Scheme 1 shows the chemical structures of two binaphthyl derivatives of *S*-BNNH (*S*-1,1′-binaphthalene-2,2′-diamino) and *S*-BNOH (*S*-1,1′-binaphthalene-2,2′-dihydroxy) molecules. The effort is made to know how the different functional groups affect the adlayer structures and to understand the STM image features of the two molecules on Cu(111) surface. This preliminary study is the first step for investigating enantiomer of binaphthyl derivatives.

The adlayers were constructed on Cu(111) electrode surface in 0.1 M $HClO_4$. The in situ STM apparatus used was a Nanoscope E (Digital Instruments Inc.). The STM images shown here were acquired in the constant-current mode. Solutions of *S*-BNNH and *S*-BNOH (ACROS) were prepared with Millipore water. All electrode potentials are reported with respect to the RHE.



Scheme 1. Chemical Structures of (a) *S*-BNNH ($C_{20}H_{16}N_2$) (b) *S*-BNOH ($C_{20}H_{14}O_2$).

Cyclic voltamograms (CVs) of Cu(111) as shown in Figure 1 were measured in (1) 0.1 M $HClO_4$, (2) 0.1 M $HClO_4$ + 0.1 mM *S*-BNNH, (3) 0.1 M $HClO_4$ + 0.1 mM *S*-BNOH. With the addition of the various molecules, the overall shapes of the CVs were almost the same as that of Cu(111) in pure 0.1 M $HClO_4$.[7] However, the electric charge involved in the double-layer potential region became smaller due to the molecular adsorption.

In situ STM imaging was first carried out on the *S*-BNNH adlayer at −0.25 V. Figure 2a shows a typical STM image of *S*-BNNH on Cu(111) in 0.1 M $HClO_4$ solution. It can be seen that the molecules form a highly-ordered adlayer. On the basis of the orientation of molecular rows and the intermolecular distance, we conclude that the observed structure of the *S*-BNNH adlayer possesses a (4×4) structure as the superimposed unit cell in Figure 2a. More details of the molecular adlayer are revealed by higher resolution STM images. The high resolution STM image can reveal the internal structure of each *S*-BNNH molecule. It is clear that every four bright spots in Figure 2b

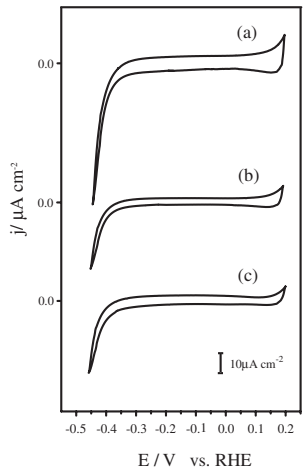


Figure 1. Cyclic Voltammograms of Cu(111) electrode in (a) 0.1 M $HClO_4$, (b) 0.1 M $HClO_4$ + 0.1 mM *S*-BNNH, (c) 0.1 M $HClO_4$ + 0.1 mM *S*-BNOH. The potential scan rate was 50 mV s^{-1}.

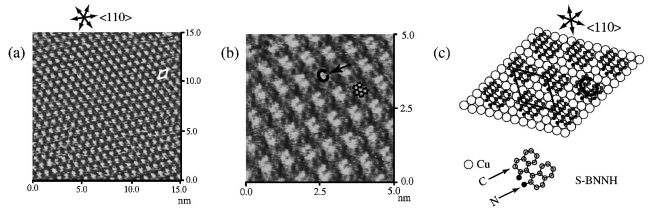


Figure 2. (a) STM top view of *S*-BNNH adlayer on Cu(111) in 0.1 M $HClO_4$ + 0.1 mM *S*-BNNH at −0.1 V. Tunneling current was 10 nA. Scanning rate was 17.44 Hz. (b) High-resolution STM image of a Cu(111)-(4 × 4)-*S*-BNNH adlattice acquired at −0.1 V. Tunneling current was 15.00 nA. Scanning rate was 24.41 Hz. (c) A schematic representation for the (4 × 4) structure.

represent an *S*-BNNH molecule. From the Scheme 1 we can see that a geometrical gap exists in the molecule due to its stereoscopic structure as shown by arrows. This feature outlined by using a letter 'C' is clearly observed in the STM image of Figure 2b indicating by an arrow. According to the previous results investigated by using STM, the most universal feature of the adsorption geometries proposed for the superstructures of the naphthalene in the STM image is two bright spots align their C_2 axes along the close-packing direction of the substrate.[8] On the basis of the above consideration and the obtained STM images, a tentatively proposed model for the adlayer of *S*-BNNH on Cu(111) is depicted in Figure 2c. The two naphalene rings is arrayed along the close-packing direction of the substrate.

The observation of *S*-BNOH adlayer was carried out in a solution of 0.1 M $HClO_4$ + 0.1 mM *S*-BNOH. A well-defined adlayer similar to that of *S*-BNNH shown in Figure 3a is observed. The same (4 × 4) adlayer structure is obtained by analyzing the intermolecular distance and orientation of the molecular rows on Cu(111). A unit cell with the (4 × 4) symmetry is superimposed in Figure 3a. Much effort has been made to obtain the details of the molecular structures, and the higher resolution STM image as shown in Figure 3b is acquired. It is found that each molecule is also composed of four bright spots and the molecular feature is also outlined by using a letter 'C'. The features of molecule adlayers are almost the same as those in *S*-BNNH adlayers. The results implicate that the molecules take the same

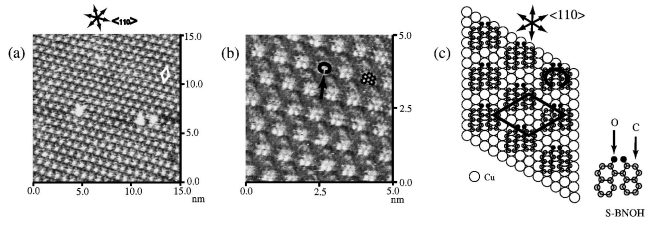


Figure 3. (a) STM top view of *S*-BNOH adlayer on Cu(111) in 0.1 M $HClO_4$ + 0.1 mM *S*-BNOH at −0.1 V. Tunneling current was 10.00 nA. Scanning rate was 17.44 Hz. (b) High-resolution STM image of a Cu(111)-(4 × 4)-*S*-BNOH adlattice acquired at −0.1 V. Tunneling current was 15.00 nA. Scanning rate was 24.41 Hz. (c) Molecular model of *S*-BNOH monolayer on the Cu(111)-1 × 1.

coordination with the Cu(111) lattice as *S*-BNNH molecules. The gap of the molecule also can be seen. That is to say the structural similarity results in the similar STM images, although the functional groups are different. The results indicate that the intermolecular interactions are less important than those between molecule and substrate. Based on the above mentioned results, it is natural to propose the model for the adlayer as shown in Figure 3c.

It is known that the molecular appearance in STM images is depended on chemical structure of the molecule and crystallography of the underlying substrate. The two molecules observed here have the same molecular structures in spite of the difference in functional atoms of nitrogen and oxygen. The structural similarity of these molecules implicates the similarity in their electronic states that could result in the similar STM features. The results are coincident with previous papers.[9] On the other hand; the features in STM images of an enantiomer either BNNH or BNOH must be different in arrangement such as that one side of "C" should be higher than another owing to the effect of chirality of adsorbed molecules. The details are in progress.

In summary, (s)-isomers BNNH and BNOH form ordered adlayers on Cu(111) in 0.1 M $HClO_4$ with (4 × 4) symmetry. The STM image feature for each molecule is a set of bright spots. Structural models are proposed for the adlayers. The adlayer structure and coordination are attributed to the molecular structure and interactions between molecules as well as molecule-substrate.

The work is supported by National Natural Science Foundation of China (Nos. 20025308, 20177025 and 20103008), National Key Project on Basic Research (Grant G2000077501, 2002 CCA03100).

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Published on the web (Advance View) July 14, 2003; DOI 10.1246/cl.2003.702