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Upright Structuring of Functional Carboxylate Anchored on Benzoate/Cu(110) Molecular Template Studied by Scanning Tunneling Microscopy

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Geometric control of *p*-aminobenzoate adsorbed on Cu(110) substrate has been demonstrated using the benzoate molecular template. Scanning tunneling microscopy was used to elucidate the local structures and electronic states of adsorbates on the molecular template.

Fabrication of two-dimensional (2D) molecular nanonetworks has been studied extensively because of the use in a variety of applicable systems.[1] Above all, self-assembled monolayers (SAMs) have been paid particular attention due to their potential applications such as nanopatterning[2] and nanobiosensors,[3] owing to their highly organized supramolecular arrays via intermolecular interaction. Chemical and physical properties of SAMs can be controlled by modifying the SAMs with functional substituents.

A challenging issue has been recognized as the three-dimensional (3D) extension of the molecular architecture, i.e., the vertical positioning of functionality, since the topmost molecular layer serves as an interface for the above applications. Donhauser and co-workers have succeeded in the upright structuring of phenylene–ethynylene oligomers imbedded in matrices of alkanethiolate SAMs and demonstrated the electrical conductance change of a single molecule.[4] However, standing molecules prefer to attach to the defect sites, indicating uncontrollability in the spatial domain.[5] An alternative approach has been also employed using tripod-shaped rigid molecules, owing to a substantial upstanding contact.[6,7] This approach, however, requires sophisticated organic synthesis. Host–guest molecular architectures, i.e., trapping guest molecule into a host open molecular network, have been recently reported especially for placing C_{60}.[8–10] Although this method has a great potential for the fabrication of spatially organized functional arrays, upright geometric control of the functional molecule has not been reported yet.

In this letter, we report the upright structuring of *p*-aminobenzoate (PAB) using a molecular template formed on Cu(110) investigated by scanning tunneling microscopy (STM). Although the structural isomer *m*-aminobenzoate (MAB) stands at high coverage,[11] the upright structure has been hardly accomplished for PAB by means of the sole deposition of PAB except the adsorption at the defect site, such as the domain boundary.[12] This is because of the strong intermolecular interaction via hydrogen bonding between amino and carboxyl substituents.[12,13] Here, we show that flat-lying benzoate (BA) template forms well-ordered voids, which offer a selective insert of carboxyl substituent, leading to vertical positioning of the amino group. In addition, electronic states of upright species are evaluated using scanning tunneling spectroscopy (STS).

All experiments were performed in the ultrahigh vacuum (UHV) chamber with the base pressure of 4×10^{-11} Torr. The Cu(110) surface was cleaned by repeating the Ar ion sputtering and annealing at 800 K. *p*-Aminobenzoic acid ($NH_2C_6H_4COOH$) and benzoic acid (C_6H_5COOH) were deposited onto Cu(110) under vacuum at room temperature (298 K). STM and STS experiments were carried out at 4.7 K using a low-temperature STM system.

The STM image of PAB on Cu(110) surface is shown in Figure 1a, which displays a well-ordered layer with a (4 × 3) periodicity.[12] Previous high-resolution electron energy loss spectroscopy (HREELS) and STM studies demonstrated that PAB is adsorbed at a short-bridged site with a flat-lying configuration due to hydrogen bonding between amino and carboxyl substituents.[12,13] Such a strong intermolecular interaction works even at high coverage, which prevents PAB from any geometric transformations. In contrast, the adsorption of BA on Cu(110) shows a quite different behavior in comparison with that of PAB. At lower coverages, BA forms flat-lying overlayer

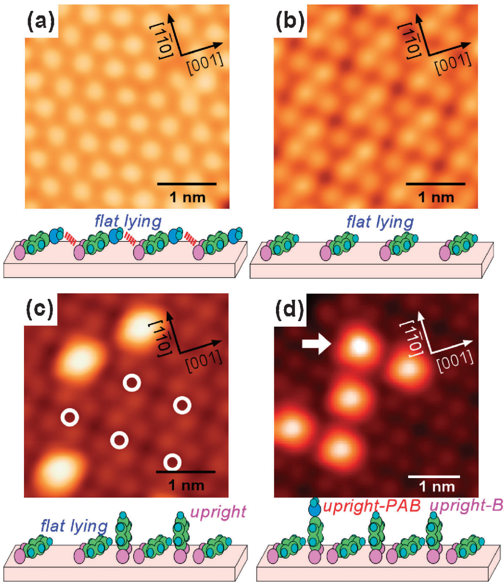

Figure 1. (a) STM image of PAB adsorbed on Cu(110), $V_s = 0.1$ V, $I_t = 1.0$ nA. (b) and (c) STM images of the coverage-dependent evolution of BA assembled on Cu(110), (b) $V_s = 0.1$ V, $I_t = 0.3$ nA, (c) $V_s = 0.1$ V, $I_t = 0.5$ nA. The white open circles marked in (c) indicate the voids which offer the preferential adsorption of upright BA. (d) STM image of PAB and BA coadsorbed on Cu(110), $V_s = 0.1$ V, $I_t = 0.5$ nA. The upright PAB is indicated by an arrow. The schematic adsorption models of each surface are shown at the bottom of STM images.

(Figure 1b). The STM image is modulated due to the coexistence of the two different geometries of the flat-lying BA.[14] Increasing BA exposures, however, provides the appearance of higher protrusions on the STM image in addition to the flat-lying monolayer (Figure 1c). The highly protruded molecule was assigned to BA with the upright configuration. The upright BA is selectively anchored in the site as indicated by white circles in Figure 1c. Further increase in BA exposure results in the formation of c(8 × 2) layer, which was discussed in previous reports.[14,15]

Structural change of BA/Cu(110) depending on the coverage increase stems from the fact that flat-lying BA assembled with a weak intermolecular interaction. As indicated by white circles in Figure 1c, small voids between flat-lying BAs offer a selective attachment of carboxyl groups, which results in the formation of upright configuration. Figure 1d shows an STM image of PAB coadsorbed with BA on Cu(110). The surface was prepared by exposing Cu(110) to BA followed by the deposition of PAB at 298 K. In addition to upright BA molecules, a highly protruded molecule indicated by an arrow was observed in the same STM image. The adsorption structure of flat-lying BA in the domain was not changed by the exposure of PAB although the edge of flat-lying BA domain was slightly modified with the flat-lying PAB. The 3D STM image of Figure 1d is shown in Figure 2a, which makes it easy to distinguish the species. On the basis of the topographic image analysis, the newly appeared molecule is resolved 0.14 Å higher than upright BA (Figure 2b). As would be expected, the highly protruded molecule is assigned to PAB with an upright configuration. In our previous paper, we have clarified that the STM image of isolated flat-lying PAB consists of bright protrusion and dark depression.[16] Dark depression correlates with the position of the amino substituent, indicating the amino group has less density of states than other parts at a given sample bias. The actual height of upright PAB is roughly estimated to be 0.8 Å higher than that of BA. Therefore, observed difference in apparent height can be explained by the fact that the STM contrast generally results from the convolution of the geometric and electronic factors. In addition, it turned out that the preformed BA layer on Cu(110) prevented forming a hydrogen bonding between adjacent PAB molecules.

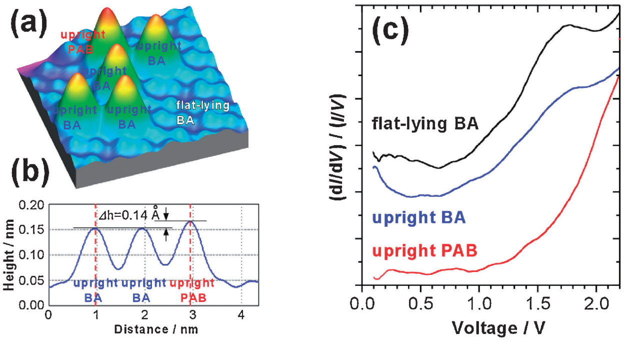

Figure 2. (a) 3D STM image of PAB on BA/Cu(110) template, $V_s = 0.1$ V, $I_t = 0.5$ nA and the scanning area of 4 nm × 4 nm. (b) Height profile of upright PAB and upright BA on Cu(110). (c) STS spectra of flat-lying BA, upright BA, and upright PAB on Cu(110). All the spectra were obtained with the set voltage of 1.0 V and set tunneling current of 0.5 nA followed by turning off the feedback loop.

More detailed analysis was made using STS measurement in order to probe the electronic structure of individual molecules standing on the BA template. Figure 2c shows STS spectra obtained from the flat-lying BA, upright BA, and upright PAB adsorbed on Cu(110). The STS spectra of BA show a peak at 1.8 V. This peak is characterized to the electronic state of the lowest unoccupied molecular orbital (LUMO) of BA, which is localized at the phenyl ring in parts of benzoate.[16] In comparison with the STS spectrum of flat-lying BA,[16] peak position of LUMO for upright BA remains constant whereas its intensity appears to be reduced. In contrast, the STS measurement for upright PAB reveals a different result. The spectrum shows the absence of a peak at 1.8 V, indicating that it has a different electronic state. We previously performed STS measurement on the isolated PAB with the flat-lying configuration, showing the resonance tunneling at 2.0 eV, arisen from the LUMO.[16] Therefore, we consider the STS spectrum of PAB in Figure 2c to be part of the LUMO state of PAB. The peak position of PAB is apparently shifted to higher energy, which might be caused by the structural transformation, i.e., flat-lying to upright configuration. This is explained by the following reason. For the flat-lying PAB, the LUMO of PAB, which is localized at the phenyl ring,[16] would rather interact with the Cu substrate in comparison with the case of the BA adsorption.

In summary, we demonstrated the preparation of upright PAB using BA/Cu(110) template. SAMs of BA form well-ordered voids. The molecular BA network provides specific adsorption site for the carboxylate substituent, leading to the vertical positioning of PAB. STS measurements clarified the electronic states of PAB and BA distinctly from each other. The present method would be applicable to other molecular systems having a carboxylate substituent.

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