

interactions and molecule-surface interactions influences the electronic structure of a molecule with scanning tunneling microscopy (STM) and spectroscopy (STS) and core-level spectroscopies (CLS).

Chapter 2. Experimental Techniques

All STM and STS data were obtained at 4.7 K with a low-temperature ultra-high vacuum (UHV) STM. CLS experiments were carried out at SPring-8, BL17SU, Japan. The characteristics of the beamline and undulator have been reported elsewhere [6]. Surfaces of Au(111) and Cu(110) were cleaned by repeating cycles of Ar⁺ sputtering and annealing. The molecules were evaporated onto the clean Au(111) and Cu(110) surfaces at 300 K for sub-monolayers (20 K for multilayer) by resistively heating the molecules powder inside a crucible under UHV.

Chapter 3. Self-Assembly of Functionalized Aromatic Molecules on Metal Surfaces

3.1. Benzoic Acid on Au(111) [7]

On Au(111), benzoic acid molecules physisorb and form dimers via hydrogen-bonding between carboxyl groups. These dimers have three orientations reflecting the Au(111) substrate three-fold symmetry and are adsorbed in the hcp and fcc regions of the Au(111) reconstruction, but seldom at the corrugation lines (boundary region between hcp and fcc stacking regions). They assemble into dimer rows with a total of six equivalent orientations.

3.2. Benzoate on Cu(110) [8]

In contrast to the case of Au(111), benzoic acid (C₆H₅COOH) molecules dissociatively chemisorb in the form of benzoate (C₆H₅COO⁻) on Cu(110) at 300 K and their self-assembly on Cu(110) has been reported before [1, 9]. However, some contradictions appear in the proposed models of previous reports as Cu-complexes with several molecules adsorbed on the same adatoms can hardly stand-up at high coverage and thus hardly explain the STM images of the coverage dependence. In this study, I discuss these contradictions and propose new molecular models of the self-assembly.

3.3. Meta-Aminobenzoate on Cu(110) [10, 11]

I characterized the molecular structures of *m*-AB on Cu(110), consisting of molecular chains, $\begin{pmatrix} 12 & 0 \\ 0 & 6 \end{pmatrix}$ and $\begin{pmatrix} 6 & \pm 5 \\ \mp 3 & 6 \end{pmatrix}$ superstructures with STM (Figure 1a), and proposed models of the molecular arrangements with precise lattice matching (Figure 1b). Coverage dependence measured with STM (Figure 1a) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy (Figure 1c) revealed that the molecules adsorb in a flat-lying orientation at low coverage, while some molecules adsorb in an upright orientation at high coverage due to local crowding. These upright molecules appear brighter in the STM images (Figure 1a D) and their proportion is directly related to

surface coverage. Additionally, thermal diffusion of the molecules induced a step-edge reconstruction, and a slow phase transition between the $\begin{pmatrix} 12 & 0 \\ 0 & 6 \end{pmatrix}$ and $\begin{pmatrix} 6 & \pm 5 \\ \mp 3 & 6 \end{pmatrix}$ structures.

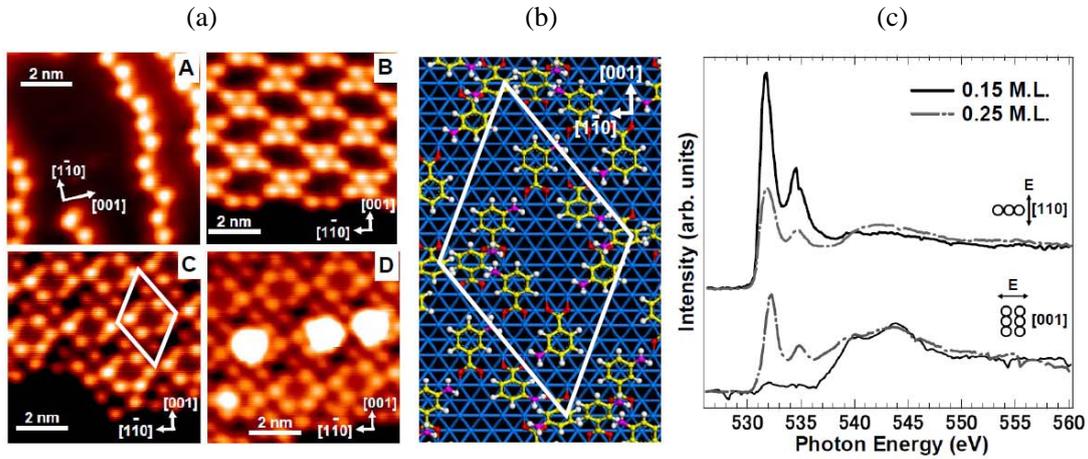


Figure 1: (a) STM images of the chain (A), $\begin{pmatrix} 12 & 0 \\ 0 & 6 \end{pmatrix}$ (B) and $\begin{pmatrix} 6 & 5 \\ -3 & 6 \end{pmatrix}$ structure (C) and brighter molecules adsorbed inside $\begin{pmatrix} 6 & 5 \\ -3 & 6 \end{pmatrix}$ (D). (b) Model of molecular arrangement for the $\begin{pmatrix} 6 & 5 \\ -3 & 6 \end{pmatrix}$ structure. (c) O1s NEXAFS spectra of *m*-AB with coverage dependence.

Chapter 4. Electronic Structure of Functionalized Aromatic Molecules on Metal Surfaces [12]

Investigation with coverage dependence of benzoate, *m*-AB and *p*-AB on Cu(110) with STM-STs and CLS reveals that the molecules orientation affect their own electronic structure by inducing a shift of their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (Figure 2). Measured X-ray photoelectron spectroscopy (XPS) data at O1s, C1s and N1s reveals that coverage-dependent charge transfers occur between the molecule and the Cu(110) and are most probably at the origin of the energy shifts in HOMO and LUMO levels and core-levels.

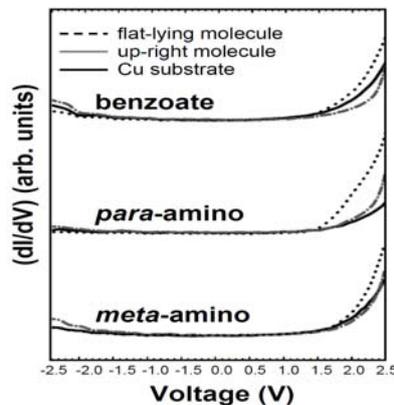


Figure 2: STS spectra of benzoate, *para*-aminobenzoate and *meta*-aminobenzoate on Cu(110).

Chapter 5. Tunneling Electron Induced Chemical Reactions of 4-Aminobenzenethiolate on Cu(110) [13]

This study reveals that both 4-aminobenzenethiol ($4\text{-H}_2\text{NC}_6\text{H}_4\text{SH}$; 4-ABT) and 4,4'-Diamino-Diphenyl Disulfide ($4,4'\text{-H}_2\text{NC}_6\text{H}_4\text{SSC}_6\text{H}_4\text{NH}_2$; 4,4'DDD) adsorbs on Cu(110) at 298 K in the form of 4-aminobenzenethiolate ($4\text{-H}_2\text{NC}_6\text{H}_4\text{S}^-$; 4-ABTA) via S-H and S-S bonds dissociation, respectively. Independently of the precursor (4-ABT or 4, 4' DDD) two kinds of protrusions with different apparent heights appear on the surface, corresponding to two different molecular orientations. I found that it is possible to selectively induce change of orientation (1.7 eV), amine group dissociation (2.1 eV) or S group dissociation (2.5 eV) of the chemisorbed 4-ABTA molecule by controlling the energy of tunnel electrons injected into the molecules, as given in the parentheses.

Chapter 6. Summary and Future Directions

The influence of the substrate, coverage and temperature on molecular self-assembly has been investigated. Interestingly, *m*-AB molecules form a large variety of angles with the surface. This is quite different from the long belief that this kind of molecules has only two orientations (namely, fully up-right and fully flat-lying). Moreover, the molecule-surface interactions are coverage-dependent and are responsible for charge transfers resulting in energy shifts of core-levels, HOMO and LUMO levels. I also shown that it is possible to *selectively* induced changes in orientation and chemical groups dissociation of 4-ABTA.

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