



Effect of the substituent on metal–molecule hybridization

Masafumi Hori^{a,b}, Satoshi Katano^a, Yousoo Kim^a, Maki Kawai^{a,b,*}

^a Surface Chemistry Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

^b Department of Advanced Materials Science, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan

ARTICLE INFO

Available online 11 July 2008

Keywords:

Density functional calculations
Scanning tunneling microscopy
Scanning tunneling spectroscopies
Surface electrical transport (surface conductivity, surface recombination, etc.)
Surface electronic phenomena (work function, surface potential, surface states, etc.)
Surface structure, morphology, roughness and topography
Aromatics
Low index single crystal surfaces

ABSTRACT

Local electronic structures of benzoate ($C_6H_5COO^-$) and aminobenzoate ($NH_2C_6H_4COO^-$) isomers (*meta* and *para*) adsorbed on Cu(110) have been investigated with scanning tunneling microscopy (STM) and spectroscopy (STS) at 4.7 K. STS and molecular orbital calculation study indicate that the energy level of the lowest unoccupied molecular orbital (LUMO) of free *meta*-aminobenzoate molecule is largely shifted to a lower energy level by adsorption on Cu(110), whereas an energy shift is relatively small for benzoate and *para*-aminobenzoate molecules. The large energy shift of LUMO level for *meta*-aminobenzoate is ascribed to the strong metal–molecule hybridization. It turns out that the electron donation from amino substituent to the phenyl ring plays a key role in this hybridization, which is also influenced by the substituted position.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Aromatic molecules adsorbed on metal surfaces have been extensively investigated for the application to bottom-up approach to fabrication of molecular devices, which would provide a novel way of overcoming the technical limitation of traditional silicon-based devices [1,2]. Precise measurement of molecular conductance at a metal–molecule junction is one of the important issues in regard to designing and constructing molecular devices [3]. In order to evaluate electric property of individual molecules, it would be necessary to (i) recognize each molecule and even its components, i.e. molecular frame, substituents and metal–molecule contact, and (ii) make a relation between molecular components and electronic conductance. Previous density functional theory (DFT) calculation studies reported that the local density of states (DOS) of metal–molecule junction is closely related to the conducting property, and is also strongly affected by the molecular components [4–6]. One can expect that both the assembled pattern [7,8] and the electronic property of aromatic

molecule are intensively affected by the position (*ortho*, *meta* and *para*) and electronic property (electron-donating and attracting) of substituents. The detailed experimental study of effect of each component on the electronic structures at the metal–molecule junctions would enable us to have insights into the nature of electron transport through a single molecule and a novel way to design functional molecular devices in a controlled manner.

Scanning tunneling microscopy (STM) and spectroscopy (STS) have been widely used as strong techniques for identifying individual components of isolated molecule adsorbed on metal or semiconductor surface [9–11] and probing local electronic structures under the STM tip [9,10,12]. In this study, we investigated the benzoate ($C_6H_5COO^-$) and two geometrical isomers, *meta*- and *para*-, of aminobenzoate ($NH_2C_6H_4COO^-$) adsorbed on Cu(110) using low-temperature STM under ultrahigh vacuum (UHV) condition. Benzoate derivatives simply consist of three components, phenyl ring, substituents bonded to the phenyl ring, and carboxylate ($-COO^-$) group making metal–molecule contact. As a carboxylic acid derivatives is adsorbed onto the Cu(110) at room temperature, deprotonation of $-COOH$ group occurs leading to formation of carboxylate on the Cu(110) surface [13–16]. Here, we report the effect of the introduction of amino substituent (NH_2), which is known as a resonant electron-donative substituent, on local electronic and geometric structures of adsorbed molecule.

* Corresponding author. Address: Surface Chemistry Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan. Tel.: +81 48 467 9405; fax: +81 48 462 4663.

E-mail address: maki@riken.jp (M. Kawai).

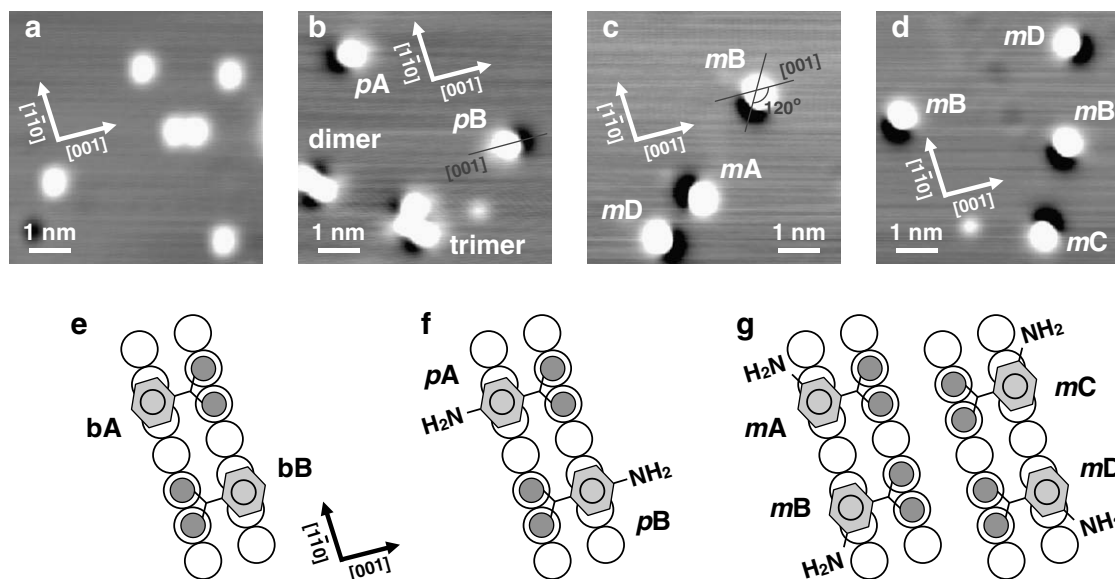


Fig. 1. STM images of (a) benzoate, (b) *para*-aminobenzoate and (c, d) *meta*-aminobenzoate adsorbed on Cu(110) ($V_s = 0.1$ V, $I_t = 1.0$ nA). Schematic model of adsorption orientations of (e) benzoate, (f) *para*-aminobenzoate and (g) *meta*-aminobenzoate on Cu(110). White circles represent top layer Cu atoms and dark grey circles represent O atoms.

2. Experiment

All experiments were performed using a low-temperature STM (LT-STM, Omicron GmbH) with an electrochemically etched tungsten tip in a UHV chamber (base pressure: 3×10^{-11} Torr). The Cu(110) surface was cleaned by repeated cycles of Ar^+ sputtering and annealing to 800 K, until clean surface was confirmed by STM imaging. Benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) and *meta*- and *para*-isomers of aminobenzoic acid ($\text{NH}_2\text{C}_6\text{H}_4\text{COOH}$) were evaporated onto the clean Cu(110) surface at 298 K by resistive heating under UHV conditions. The evaporation temperature was estimated to be 303–373 K as monitored by a K-type alumel–chromel thermocouple. All STM images were acquired at 4.7 K with the constant current mode.

3. Results and discussion

Fig. 1a shows a STM image of isolated benzoate molecules adsorbed on Cu(110). Each benzoate molecule appears as an elliptical protrusion in the STM image. Whereas, isolated *meta*- (Fig. 1b) and *para*- (Fig. 1c and d) isomers of aminobenzoate molecules adsorbed on Cu(110) are resolved as a pair of a protrusion and a depression. We observed two equivalent orientations of *para*-aminobenzoate (labeled as pA and pB in Fig. 1b) and four equivalent orientations of *meta*-aminobenzoate (labeled as mA, mB, mC and mD in Fig. 1c and d) in the STM images. A dumbbell shape and a dogleg shape shown in Fig. 1b are considered as a dimer and a trimer of aminobenzoate molecules.

High resolution electron energy loss spectroscopy (HREELS) study revealed that benzoate derivatives are adsorbed at short bridge sites on Cu(110), where two O atoms of carboxylate group are bonded to the nearest-neighbor Cu atoms along the close-packed direction [14–16]. The phenyl ring of benzoate derivatives is aligned nearly parallel to the surface at low surface coverage [16, 17]. A schematic model of the adsorption of isolated benzoate molecule on Cu(110) is proposed in Fig. 1e. Two possible adsorption orientations (labeled as bA and bB in Fig. 1e) of benzoate molecule on Cu(110) are not distinguishable in the STM image.

Two (*para*-) and four (*meta*-) equivalent adsorption orientations of isolated aminobenzoate isomers on Cu(110) are proposed in Fig.

1f (*para*) and g (*meta*). As depicted in the models, N–C bonding between phenyl ring and amino group within a molecule is parallel to [001] for *para*-isomers (Fig. 1f) or rotated by 120° with respect to [001] for *meta*-isomers (Fig. 1g). Indeed, the STM images clearly show that protrusion–depression pairs are aligned parallel to [001] for *para*-isomers (Fig. 1b), whereas the position of depression on protrusion is rotated by ca. 120° with respect to [001] for *meta*-isomers (Fig. 1c). Thus, the depression in the STM image is assigned to the position of amino group. Adsorption models shown in Fig. 1f and g are labeled as pA and pB for *para*-isomers and mA, mB, mC and mD for *meta*-isomers, corresponding to the isolated molecules in the STM images (Fig. 1b–d).

The adsorption of molecules on metal surfaces leads to generation of new electronic states near the Fermi level of the substrate due to the hybridization of orbitals between molecules and substrate surface. The dI/dV spectroscopy enables us to obtain information about the local electronic states of adsorbed molecule on the surface. Fig. 2 shows dI/dV spectra of (a) benzoate, (b) *para*-aminobenzoate and (c) *meta*-aminobenzoate molecules on Cu(110). These spectra were measured on the protrusions of each isolated molecule shown in Fig. 3a–c. The dI/dV spectrum measured on the benzoate (Fig. 2a) exhibits a peak at 1.8 V, whereas the spectrum measured on the Cu substrate exhibits no notable peak. In our measured bias region, both benzoate and substrate do not exhibit any peak in the occupied region of their spectra. Spatial distribution of an electronic state was measured by taking a two-dimensional dI/dV mapping image at a certain sample bias corresponding to the peak position [9]. A dI/dV mapping image (Fig. 3d) was simultaneously obtained with a topographic image (Fig. 3a) of a benzoate molecule at a sample bias of 1.8 V. From the comparison of the topographic and the dI/dV mapping image, it turns out that high-intensity dI/dV signals (colored by red¹ in dI/dV images) at 1.8 V are distributed at the upper right part of protrusion in the topographic image. However, we cannot affirm whether the strong dI/dV signals come from phenyl ring or carboxylate group from only the STM experiments.

¹ For interpretation of color in Fig. 3, the reader is referred to the web version of this article.

Download English Version:

<https://daneshyari.com/en/article/5424413>

Download Persian Version:

<https://daneshyari.com/article/5424413>

[Daneshyari.com](https://daneshyari.com)