Structural Effects on Electrical Conduction of Conjugated Molecules Studied by Scanning Tunneling Microscopy

Takao Ishida,^{*,†,‡} Wataru Mizutani,^{†,⊥} Nami Choi,[§] Uichi Akiba,^{||} Masamichi Fujihira,^{||} and Hiroshi Tokumoto[†]

Joint Research Center for Atom Technology (JRCAT), National Institute for Advanced Interdisciplinary Research (NAIR), 1-1-4 Higashi, Tsukuba, Ibaraki, 305-8562, Japan, PRESTO-Japan Science and Technology Corporation (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan, JRCAT-Angstrom Technology Partnership (ATP), 1-1-4 Higashi, Tsukuba, Ibaraki, 305-0046, Japan, and Department of Biomolecular Engineering, Faculty of Bioengineering and Biotechnology, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8501, Japan

Received: May 18, 2000; In Final Form: August 25, 2000

We have studied electrical conduction of conjugated molecules with phenyl rings embedded into alkanethiol self-assembled monolayers (SAMs), to investigate the molecular structural effect on the electrical conduction. Scanning tunneling microscope (STM) images of this surface revealed that the conjugated molecules with phenyl rings adsorbed mainly on defects and domain boundaries of the pre-assembled alkanethiol (nonanethiol C9) SAM and formed conjugated domains. In the case of conjugated molecules with one or three methylene groups between the sulfur and phenyl rings, the measured height of the conjugated molecular domains depended on their lateral sizes, while a strong dependence was not observed in the case of conjugated molecules without a methylene group. By analyzing size dependence on the height of the conjugated molecular domain, we could evaluate the electronic conductivity of the molecular domains. As a result of the analysis, to increase the vertical conduction of the molecular domains, one methylene group was found to be necessary between the sulfur and aromatic phenyl rings. Local barrier heights on the conjugated molecular domains in all the cases were larger than on the C9 SAM surface, suggesting that the increase in the vertical conductivitity is not likely to be due to the lowering of the local barrier height, but can be attributed to the conjugated molecular adsorption. X-ray photoelectron spectra (XPS) and ultraviolet light photoelectron spectra (UPS) revealed that the carrier density among conjugated molecular SAMs does not depend on the number of methylene groups between the sulfur and phenyl rings, suggesting that the higher vertical conduction of conjugated molecules with one methylene group can probably be attributed to higher transfer probability of carriers during the STM measurements.

1. Introduction

As the trend toward smaller devices continues, the use of individual molecules to fabricate device components becomes more and more attractive. Organic molecules are inherently nanoscale in size and highly uniform in nature.¹ Furthermore, organic molecules can be synthesized with unique properties that could be used to promote their self-assembly with one another and to specific surfaces, and to perform functions that can provide memory and logic operations. For these reasons, the field of molecular electronics has generated considerable interest in recent years.

For the realization of molecular devices, new conductive organic materials, e.g., carbon nanotubes² or conjugated molecular wires³ have been discovered. Since these materials are very attractive, many interesting studies have appeared concerning the electron transfer along the molecular axis theoretically and experimentally using scanning probe microscope (SPM)

techniques⁴⁻⁹ or the mechanical break junction technique.¹⁰ For example, Bumm et al. estimated the conductance of single conjugated molecules embedded in an insulative SAM film using scanning tunneling microscopy (STM).⁴ They measured the height of the molecules adsorbed on a metal surface with the molecular axis almost vertical to the surface. Interestingly, the measured conductivities for conjugated molecules using SPM⁴⁻⁹ are larger than those of undoped conductive organic materials;¹¹ the measured conductivities are order of 10^{-3} S/cm, which are of the order larger than those of undoped conductive polymers $(10^{-7}-10^{-10} \text{ S/cm}^{-11})$. This is one of the unexplained areas concerning molecular conduction as measured with SPM techniques. Moreover, detailed experimental data regarding the effect of molecular structure on the electrical conduction are not yet available for measurements made with SPM techniques, even though there exist many kinds of effective conjugated groups, like phenylene or thiophene. For example, while the effect of molecular length (the number of phenyl rings) on the conductivity is important in understanding the electrical properties of conductive molecules, there has been no systematic experimental study suing STM, to evaluate the effect of the number of phenyl rings. The effect of the contact between the molecule and the metal electrode on the electrical conduction is another important problem which must be solved before the realization of molecular devices. Since the insertion of an insulating methylene group between the metal and aromatic

^{*} Corresponding Author. Present address: Mechanical Engineering Laboratory, 1-2 Namiki, Tsukuba, Ibaraki 305-8564, Japan. E-mail: tishida@mel.go.jp.

[†] JRCAT-NAIR.

[‡] PRESTO- JST.

[§] JRCAT-ATP.

^{||} Tokyo Institute of Technology.

 $^{^\}perp$ Permanent Address: Electrotechnical Laboratory, Tsukuba, Ibaraki 305-8568, Japan.

phenyl ring is expected to be useful for understanding the metal-molecule contact, changing the number of methylene **CHART 1: Molecular Structures of Conjugated Molecules Used in This Study**

Mo groups is effective for the investigation of the contact effect. In this case, we can easily imagine that the molecular conduction with many methylene spacers should be lower than the conjugated molecule without methylene groups. Meanwhile, phase-separation for mixed SAMs has been

investigated by SPM from the viewpoint of nanoscale patterning.¹²⁻²¹ Recently, we used conjugated molecules, e.g., phenylene oligomers to form a phase-separated surface,¹⁸⁻²¹ and found that various sizes of domains of these conjugated molecules implanted into the insulate alkanethiol SAMs. We further evaluated both the vertical and lateral conductivities of conjugated molecular domains using a conducting disk model, where the intermolecular interaction may increase the electrical conduction.^{18,19} The investigation of nanometer molecular scale domains is important when the conjugated molecule is to be used as one of the interconnection units of molecular device. From this point of view, we believe that our data concerning the size and height can provide a useful information for future molecular device fabrication. In addition to the above significant experimental studies, some interesting theoretical calculations were performed concerning the conduction of conjugated molecules present between two metal electrorodes.^{22,23}

In the present study, we extended the above experiment to several kinds of phenylene oligomers with thiol groups in order to understand molecular structural effects on the electrical conduction. We used several kinds of conjugated molecules with two or three aromatic rings to evaluate the effect of the number of aromatic rings. Since it was expected that the presence of a methylene group affects both the molecular arrangements²⁴ and electrical conduction, we used conjugated molecules having one or three methylene groups between the sulfur and the aromatic rings, or no methylene group to investigate the metal-molecular contact effect. We evaluated the electrical conduction of conjugated molecules by analyzing the dependence of the measured height of the conjugated molecular domains on their lateral sizes. We present our data of local barrier height images taken simultaneously with STM images, to discuss the reason for the increase in the vertical conductivity of conjugated domains. Finally, we display the photoelectron spectra to discuss the relationship between the carrier density among the monolayer and electrical conduction data.

2. Experimental Section

Chemicals. We used the following molecules: nonanethiol (C9, Aldrich), [1,1':4',1''-terphenyl]-4-thiol (TP0), [1,1':4',1''-terphenyl]-4-methanethiol (TP1), [1,1':4',1''-terphenyl]-4-propanethiol (TP3), 4-biphenylthiol (BP0), and 4-biphenylmethanethiol (BP1). The molecular structures are shown in Chart 1. Synthesis methods of TP0, TP1, BP0, and BP1 molecules have been described elsewhere.^{24–26} TP3 molecules were synthesized as shown in Scheme 1.²⁷

Au Deposition and SAM Formation. An atomically flat Au (111) surface was epitaxially grown on mica by vacuum deposition under a base pressure of about 4×10^{-8} Torr. The mica was preheated at 440 °C for 4 h before deposition. The deposition rate of Au was kept at 0.2 nm/s. After the deposition, the substrate was annealed at 480 °C for 30–60 min to obtain large terraces on the Au surface. The flatness of the terraces of the Au surface was checked by STM to be atomically flat over 200 nm. For the C9 SAMs, the Au substrates were immersed into 1 mM ethanol solution for 24 h or more. In the case of conjugated molecules, we used chloroform (TP1) and methylene



chloride as solvents (TP3, TP0, BP0, and BP1). After being taken out of the solution, the Au substrates were rinsed with pure solvent to remove physisorbed multilayers. To insert the conjugated molecules, the Au substrate with pre-assembled SAMs, were immersed into 0.1 mM solution for 1-12 h.

STM Measurements. STM images were obtained using a Seiko Instruments SPA340 unit in air, or a homebuilt UHV-STM system with a typical tunneling current of 20 pA and a tip biases of 0.85-1.2 V, corresponding to a tunneling resistance of 40-60 G Ω . The local barrier height (LBH) image was taken simultaneously with the STM topography.^{13,19} The LBH images were measured by applying a small sinusoidal voltage to the *z*-axis piezoactuator to give the gap *s* a small modulation *ds* and then measuring the corresponding variation of the tunneling current with a lock-in amplifier. The LBH can be calculated from the following equation:²⁸

$$\phi_{\rm A}({\rm eV}) = 0.952[d(\ln I)/ds({\rm \AA})]^2$$
 (1)

where *I* is the tunneling current and *s* is the tip-sample separation. To obtain a LBH image simultaneously with a STM image, we measured the $d(\ln I)$ at each point, in addition to measuring the tip height. In our experiment the modulation frequency was set at 4.0 kHz, which was higher than the cutoff frequency of the feedback loop (less than 1.0 kHz), but lower than the response cut off the current amplifier of the STM. The amplitude of the modulation was such that the corresponding ds was 0.03 nm, whose value is smaller than the gap distance of about 0.2 nm.

XPS and UPS Measurements. High-resolution XPS spectra were recorded using a VG Scientific Inc. ESCALAB 220iXL system with a monochromatic Al k α X-ray source (1486.6 eV). The binding energy was calibrated using the Au (4f_{7/2}) peak energy (84.0 eV) as an energy standard. The X-ray power, the pass energy of the analyzer, and take-off angle of the photoelectrons were set at 180 W, 20 eV, and 90°, respectively. XPS peaks were fitted using the spectra processing program in the XPS system.²¹ In the case of UPS measurements, He I line (21.2 eV) was used as a light source. The UV light power and take-off angle were 150 W and 20°, respectively.

3. Results and Discussion

3.1. STM Images of Mono-component SAMs. First, we describe STM data of the mono-component SAMs of series of C9 and conjugated molecules because the molecular arrangement of these conjugated molecules on the Au surface is important to discuss the electrical conduction of the nanometer



Figure 1. STM images of the SAMs (1); (a) C9 SAM as deposited; (b) magnified image of (a); (c) TP0 SAM after dipping into 0.1 mM TP0 solution for 48 h; (d) TP1 SAM after dipping into 0.1 mM TP1 solution for 48 h; (e) magnified image of (d); (f) TP3 SAM after dipping into 0.1 mM TP3 solution for 48 h; (g) magnified image of (f). In (b), (e), (g), we observed structures with a molecular distance of about 0.5 nm, while this arrangement was not obtained in the TP0 SAM. STM images of C9 and TP3 SAMs were measured with a typical tunneling current of 20 pA and a tip bias of 0.85 V. On the other hand, the STM images of TP0 and TP1 SAMs were obtained with a typical tunneling current of 100 pA and a tip bias of 0.5 V.





molecular domains. Figure 1 shows the STM images of the mono-component SAMs. For the C9 SAM, after the immersion of C9 solution for 24 h, we could see ($\sqrt{3} \times \sqrt{3}$) R30°

structures with a molecular distance of 0.5 nm, with domain boundaries and depressions (Figure 1a,b).^{29,30} On the other hand, in the case of TP0, the TP0 molecules are likely to adsorb on

the Au surface while retaining the herringbone structure which is observed for the clean Au (111) surface (Figure 1c).³¹ Although it has been reported that TP0 molecules arranged with the same ($\sqrt{3} \times \sqrt{3}$) R30° structure on a Au surface,²⁵ we could not observe a clear molecular arrangement with STM in the magnified image. Similar STM images were taken in the case of BP0 (data not shown). However, we obtained molecular images in the cases of TP1 (Figure 1d,e), TP3 (Figure 1f,g) and BP1 (data not shown). For the conjugated molecular SAMs, the height difference of the depression is about 0.2 nm, whose value is almost the same as that of C9 SAM. However, the density of depressions is higher than that of C9 SAM.

Tao et al. evaluated the structure of these aromatic derivatized thiols with SPM and made electrochemical measurements and concluded that the structure and molecular densities of these SAMs were dependent on the number of the aromatic rings and substituted groups.²⁴ They proposed that there exist two types of molecular orientations, when one methylene group is not present between the sulfur and aromatic rings such as BP0, TP0, i.e., sp and sp³ configurations, causing molecular disordering (see inset in Figure 1). The presence of these molecular orientations was predicted from theoretical calculations.³² On the other hand, if the molecule has one methylene group between the sulfur and aromatic rings, these conjugated molecules form a well-ordered structure, i.e., commensurate ($\sqrt{3} \times \sqrt{3}$) R30° structures.

Poirier reported that Au surface atoms are forced out of the surface layer by relaxation of the compressed herringbone structure, and then the depressions as shown in Figure 1 are formed during the n-alkanethiol adsorption.33 Poirier described in the same paper, however, that such a feature did not appear in the case of aromatic thiols with shorter chains.³³ In addition, Hara et al. reported that the adsorption of 4-mercaptopyridine with an aromatic ring induced the periodic herringbone structure without making depressions.³⁴ Thus, the remaining of the herringbone structure for TPO adsorption is likely to be a characteristic feature in the case of conjugated molecules without a methylene group and should be related to the two molecular orientations in these kinds of molecular species. One possible explanation of the difference is as follows. Conjugated molecules such as TPO without a methylene group, adsorbed along the corrugations on the Au reconstructed surface at the initial stage of SAM growth, with two kinds of molecular orientation. However, since the bond between the sulfur and conjugated aromatic ring is expected to be rigid and needs a large energy to change the molecular direction, these molecules could not form commensurate ($\sqrt{3} \times \sqrt{3}$) R30° structures. On the other hand, in the case of conjugated molecules with some methylene groups, $(\sqrt{3} \times \sqrt{3})$ R30° structures appear after immersion, because the methylene groups may provide some flexibility to arrange the molecular directions.

Also, the increase in the depressions of the TP1 and TP3 SAMs compared with C9 SAM could be attributed to the surface layer relaxation. Perhaps the conjugated molecules with one or more methylene groups, like TP1 or TP3, generate stronger stress during adsorption than C9, while TP0 cannot give such a stress to Au surface.

3.2. STM Images and Observed Height Dependence on Domain Sizes of Conjugated Molecules (1): TP1, TP3, and BP1. Here, we describe the STM images of conjugated molecules implanted into C9 SAMs and the apparent height dependence on the conjugated molecular domain size.^{18–20} Figure 2 shows a series of STM images and cross-sectional profiles of C9 + conjugated molecular SAMs. After dipping

into 0.1 mM TP1 solution for 1 h (Figure 2a), a phase-separated STM image was observed. For the C9 SAMs, the C9 molecules form 10-20 nm diameter domains, and these domain boundaries are clearly seen in the STM image (cf. Figure 1a). After insertion, protrusions which could be assigned to conjugated molecular domains surround the C9 domains and have a diameter of 10-20 nm whose size is almost identical to that of C9 domains (cf. Figure 2a,c,d). Therefore, we can conclude that the conjugated molecules in the solution are considered to adsorb gradually on the Au surface, mainly on the uncovered areas such as defects and domain boundaries of the pre-assembled C9 SAM.²⁰

The cross-sectional profiles across the TP1 domains embedded in the C9 SAM (Figure 2b) indicate that the apparent height difference of the TP1 domains in the STM image is not uniform and depends on the TP1 domain size. In cases of TP3 and BP1, the phase-separated STM images were obtained in a similar way to those of TP1 (Figure 2c,d). We investigated the relationship between the domain sizes of conjugated molecules and the observed height differences of phase-separated SAMs. Figure 3 shows the relationship between the domain sizes of the conjugated molecules and observed height differences. It should be noted that the apparent height difference of the TP1 domains in the STM image is not uniform, but changes as shown in Figure 2b. The smallest protrusion which can be probably attributed to a single TP1 molecule shows lowest (Figure 3a). Additional bars indicate the shortest and longest dimensions of the noncircular domains. Up to a domain size of 3-6 nm, the TP1 domain height increases and saturates at around 0.6-0.7 nm. In the case of TP3 implanted into C9 SAM, the domain height saturates at around 0.5-0.6 nm (Figure 3b). For the BP1 embedded into C9 SAM, the saturated height value decreased to be at about 0.3 nm (Figure 3c).

The size dependence of the conductive molecular domain height indicates that the vertical conductance of the domains increases as the number of molecules in the domain increases.¹⁸⁻²⁰ To discuss the electrical conduction, here we show a schematic drawing of conjugated molecules embedded into C9 SAMs (Figure 4). The lengths of TP and BP units are expected to be about 1.4 and 1.0 nm, respectively.²⁵ When one methylene group is located between sulfur and TP or BP unit, the molecular length of 0.12 nm is increased.³⁵ Thus, the molecular lengths of TP1, TP3, and BP1 are expected to be 1.55, 1.85, and 1.15 nm, respectively. Since the tilt angle of these molecules is considered to be about 20° and these molecules are expected to adsorb onto an Au surface at sp3 configuration from our previous XPS data about TP1,18 the thickness of TP1, TP3, and BP1 SAMs are estimated to be 1.46, 1.73, and 1.08 nm, respectively. From the XPS data the thickness of C9 SAM is 1.01 nm. Thus, the expected height differences of TP1 + C9, TP3 + C9, and BP1 + C9 systems are 0.45, 0.72, and 0.07 nm, respectively. We made measurements with a tapping mode atomic force microscope (AFM) and obtained height differences between the C9 and these conjugated molecules. These values of TP1 + C9 and TP3 + C9 are 0.40 nm and 0.80 nm, respectively. On the other hand, we could not observe specific topography higher region on the AFM image in the case of BP1 + C9 SAM. The AFM data agrees with the estimated height difference from the XPS data. In the case of TP1 + C9 SAM, if we determine the tunneling gap between C9 and tip to G_0 (nm), the tunneling gaps at the single molecule and larger molecular domains are estimated to be $G_0 - 0.24$ nm and G_0 + 0.18 nm. In the same manner, for the TP3 + C9 and BP1 +



Figure 2. STM images of the SAMs (2); (a) TP1 in C9 SAM after dipping into 0.1 mM TP chloroform for 1 h; (b) the cross-sectional profiles across of the TP1 domains embedded in C9 SAM (c) TP3 in C9 SAM after dipping into 0.1 mM TP3 methylene chloride solution for 10 h; (d) BP1 in C9 SAM after dipping into 0.1 mM BP1 methylene chloride solution for 10 h. In these binary SAMs, all the STM images were taken with a typical tunneling current of 20 pA and a tip bias of between 0.85 and 1.3 V with UHV-STM.



Figure 3. (a) Relationship between the domain sizes of TP1 in C9 SAM and observed height differences: (b) same plot of TP3 in C9 SAM; (c) same plot of BP1 in C9 SAM.

C9 SAMs, these values are assumed to be $G_0 - 0.52$ nm, $G_0 - 0.22$ nm (TP3), $G_0 + 0.05$, and $G_0 + 0.30$ nm (BP1).

In some cases, e.g., TP1 + C9 SAM, where the structural height difference is expected to be more than 0.4 nm, the observed height difference seems to be explained by the domainsize-dependent ordering of the molecules. In our previous paper, we investigated TP1 + C12 SAMs where the structural height difference is negligibly small as well, to check this effect.¹⁸ In this case, the estimated thicknesses of the TP1 and C12 SAMs are almost identical, while the observed height differences in the STM image are more than 0.2 nm. In the present study, in the case of BP1 + C9 SAM, a similar tendency was observed. We consider these data to be the strong evidence that size dependence is mainly due to electronic condition. These data suggested that the ordering effect on the size dependence is smaller than that of the conduction as expected, when the conjugated molecules can form ordered structure.

Our data indicated that the single molecular resistances of these molecules are decreased in the order of TP3 > TP1 > $C9 \ge BP1$. However, the domain resistances of these molecules



Figure 4. Schematic drawing of conjugated molecules embedded into C9 SAMs. (a) TP1 in C9; (b) TP3 in C9; (c) BP1 in C9.

are expected to be in the order TP3 > C9 > TP1 > BP1. Both the single molecular and domain resistance were decreased by increasing the number of phenyl rings, suggesting that there may exist a sum law in the conduction of conjugated molecule. For example, Samanta et al. calculated that the resistance is expected to increase with the number of phenyl rings.²²

Both the single and domain resistances of TP3 are expected to be higher than those of TP1, suggesting that the increase in the number of methylene groups between the sulfur and phenyl rings increases the molecular resistance. Possible reasons for the higher resistance of TP3 than those of TP1 are as follows: (a) the decrease in the carrier transport probability between the metal surface and molecules by the increase in the number of methylene groups; (b) there may exist a specific doping effect where large amounts of carrier at the metal surface penetrate into the conjugated molecules, when the number of methylene groups is 0 or $1.^{36}$ We will discuss the reason on the basis of the XPS and UPS data later.

In our previous studies, we estimated the single molecular resistances or molecular conduction by assuming that this junction behaves ohmically and the gap between the STM tip and molecule linearly change.^{18–20} However, the junction STM tip/molecules/Au was considered to be a tunneling junction.²² In the case of tunneling junction, the quantitative estimation became very complicated and the numbers of the parameters (e.g., work function) increased. Moreover, more discussions are still needed to decide the transfer mechanism through the junction STM tip/molecules/Au. Therefore, we do not estimate molecular resistance values in this study. In our previous paper, we also calculated the lateral conduction of TP1 molecules by assuming a resistor network model from the size dependence of height difference.^{18,19} The lateral conduction of nanometer molecular domains reflect the increase in the vertical conduction, i.e., the maximum vertical conduction becomes a higher value when the lateral conduction is large. Since the physical description of the size dependence of height difference is not clear and many interpretations are possible, we do not estimate the lateral conduction values either in this paper. We will discuss the physical description of the increase in the vertical conduction of the molecular domain later based on the LBH data.

3.3. STM Images and Observed Height Dependence on Domain Sizes of Conjugated Molecules (2): TP0 and BP0. In cases of binary SAMs of TP0 + C9 and BP0 + C9, the size dependence of the height difference plots are different from those as shown previously. Figure 5 shows the relationships between the domain sizes of conjugated molecules and observed height differences of TP0 + C9 (Figure 5a) and BP0 + C9 SAMs (Figure 5b). In these SAMs, the apparent heights at around single molecule (less than 1 nm) were in the range 0.2-0.5 nm. In the case of TP0 + C9, with the increase in the domain size, the apparent height difference decreased and saturated at around 0.3 nm (cf. Figure 5a). A similar tendency was observed in the case of BP0 + C9 SAM (Figure 5b). As described before, these conjugated SAMs without a methylene group between the sulfur and the aromatic rings, tend to have two molecular directions due to the existence of the two sulfur-Au bond orientation.²⁴ We consider that our data on the apparent height might reflect the above structural change. Even in the conjugated molecular domain at an exact size larger than 5 nm, it is expected that these two kinds of molecular orientation can cause molecular disordering. Figure 5c,d shows schematic drawings of TP0 + C9 (Figure 5c) and BP0 + C9 (Figure 5d) SAMs. By assuming sp conformation, BP0 and TP0 molecules are expected to have thicknesses of more than 1.0 and 1.4 nm, respectively. Tapping mode AFM images showed 0.3 nm height difference in the case of TP0 + C9, while no clear difference was observed in the BP0 + C9 SAM, supporting the above structural assumption.

These data may suggest that the domain resistance of conjugated molecules without any methylene group between the aromatic rings and the sulfur, did not increase at larger size, if we assumed the domain height difference was nearly constant. In Section 3.1, ordered structures were not observed in these kinds of molecular SAMs without a methylene group. The height differec data is likely to be due to the fact that the molecular disordering prevents the lateral connection of molecules.

3.4. LBH Measurements of Conjugated Molecules. The origin of conductivity change can be considered as follows:(i) increase in the density of states with the domain size. This phenomena is reported by Zeppenfeld et al., in the case of



Figure 5. Relationship between the domain sizes and observed height differences of (a) TP0 in C9; (b) BP0 in C9. Schematic drawing of TP0 (c) and BP0 (d) embedded into C9 SAMs.

TABLE 1: Relative LBH Values of Conjugated MoleculesEmbedded in the C9 SAMs. All the LBH Values WereTaken with a Typical Tunneling Current of 20 PA and a TipBias of between 0.85 and 1.3 V with UHV-STM

conjugated molecules	TP0	TP1	TP3	BP0	BP1
relative LBH values (eV)	0.61	0.24	0.11	0.84	0.24

submonolayer metal deposition;³⁷ (ii) lowering of the local barrier height due to conjugated molecule adsorption. In this case, the local barrier height on the conjugated molecules would be lower than that on the C9 surface. Direct observation of the local barrier height with the STM technique is possible,^{12,19} while it is difficult to observe the increase in the density of states by STM. To obtain information on the density of states at valence band directly, photoelectron spectroscopy is suitable. However, in the case of phase-separated SAMs, photoelectron spectroscopy is not available because the spatial resolution of photoelectron spectroscopy is not so high (about μ m order). Therefore, we measured LBH of these conjugated molecules embedded into C9 SAMs to understand the origin of the conductivity change of conjugated molecule on the domain size.

Figure 6 shows the STM and LBH images taken simultaneously. For all the cases, the LBH on the conjugated molecular domains are larger than that on the C9 surface. The estimated LBH value of the C9 surface is 1.7 ± 0.9 eV. The estimated LBH values of conjugated molecules are higher than that of the C9 region, as listed in Table 1. There is a tendency that the LBH value decreased with the number or presence of methylene groups between the sulfur and phenyl rings, and our estimated electrical conduction of conjugated molecules depended on the number of methylene groups as shown before. Thus, this tendency should be related to the molecular electrical conduction. It has been considered that the adsorbed organic molecules on a metal surface formed a dipole layer at the metal/molecule

interface, and then caused the work function change.^{38–40} Perhaps the strength of the dipole moment can be slightly controlled by the insertion of a methylene group between sulfur and conjugated phenyl rings.³⁹ Therefore, the change of LBH values are likely to be reflected to both the conduction and dipole moment.

It should be noted that the LBH values were not dependent on the domain size, while the height difference changed with the domain size in the case of conjugated molecules such as TP1.¹⁸ These data suggest that the increase in the vertical conductivity of molecular domains is not due to the lowering of barrier height, but likely to be due to the increase in the density of states.

3.5. XPS and UPS Data on the Mono-component TP1 and TP3 SAMs. Our data on the vertical conductivity,^{18–20} as well as other groups^{5–10} measured with SPM, exhibited higher conductivity than an undoped conductive polymer $(10^{-7}-10^{-10}$ S/cm¹¹), even at zero bias, as described in the Introduction. One possible origin is likely to be the doping effect from the Au surface to the conjugated molecules. If such a doping occurred, the carrier density (e.g., electron, hole, etc.) among the monolayer should depend on the conductivity.

To observe the change of carrier density, XPS or UPS techniques are considered to be appropriate. For conjugated molecules such as benzene, C60, it is well-known that the C(1s) $\pi - \pi^*$ shake-up satellite peaks appear at a higher binding energy region of major peak at around 284–285 eV.^{41–43} Since the appearance of these satellite peaks is related to the carrier density at the valence band, we can expect that the XPS data would depend on the molecular conduction. For example, Onoe et al.⁴³ reported that the C(1s) satellite peak intensity decreased with the dimerization of C60 molecules due to the decrease in the carrier density.



Figure 6. Schematic drawing of the reason for the increase in the vertical conduction (a) increase in the density of states; (b) decrease in the barrier height. STM topograpical image (c) and local barrier height image (d) of TP in C9 SAM. All the STM images were taken with a typical tunneling current of 20 pA and a tip bias of 0.85–1.3 V with UHV-STM.



Figure 7. C(1s) XPS and UPS spectra of (a) TP3 C(1s) region; (b) TP1 C(1s) region; (c) TP3 valence band; (d) TP1 valence band region.

We measured mono-component TP1 and TP3 SAMs to observe information on carrier densities. At the C(1s) region between 280 and 300 eV (Figure 7a,b), weak and broad structures were detected in the cases of TP3 (Figure 7a) and TP1 (Figure 7b). We magnified satellite peaks, the shape of satellite peaks of TP1 and TP3 are almost identical. The ratios of the C(1s) satellite/Au(4f) of the TP1 and TP3 SAMs are also the same values and about 0.08. The peak intensities in both the SAMs are weaker than those as reported previously.^{41–43} Our data suggest that the amount of carrier among the monolayer is very small.

It is also possible to observe valence band structure with XPS. However, the effect of Au surface on the spectra cannot be ignored in the case of XPS measurements of organic monolayer less than 2 nm, because the escape depth of photoelectron from the Au substrate is longer than 2 nm.⁴⁴ Thus, we measured UPS spectra of the valence band region instead of XPS. The UPS spectra between -5 and 20 eV in TP3 (Figure 7c) and TP1 (Figure 7d) are also identical. The Fermi level at both the UPS spectra shifted about 1.7 eV, due to the dipole layer formation by the adsorption of organic molecules.⁴⁰

If the increased vertical conduction, with the decrease in the number of methylene group was due to the doping effect from the Au substrate, the shape and intensity of both the satellite peak and valence band should be different.⁴³ However, since the intensity of satellite peaks and valence bands on the TP1 and TP3 SAMs are identical, the carrier density among the monolayer is expected to be almost the same in both the SAMs. Therefore, we could not confirm the doping effect on the molecular conductivity in these SAMs and the decrease in the vertical conduction of TP3 might simply be attributed to the decrease in the transfer probability of carriers, by inserting the methylene groups between the sulfur and phenyl rings. Moreover, the bulk conductivities of conductive polymers includes inter-intra hopping and tunneling effects, which decrease with the conductivity. However, our XPS and UPS data necessarily mean denying the doping effect, because the experimental conditions of photoelectron spectroscopy are different from STM measurements. To confirm the doping effect, further detailed study is essential.

New and interesting physical phenomena of organic molecules may be found to control and determine molecular conduction. For example, recently, large negative differential resistance was observed in the SAM of conjugated molecules containing nitroamine redox center.^{45,46} Such new physical phenomena should be helpful in developing molecular devices in the future.

4. Conclusions

We have measured electrical conduction and LBH of conjugated molecules embedded into C9 SAMs by STM to investigate the structure effect on the electrical conduction. We further measured XPS and UPS for some molecular SAMs, to understand the origin of higher electrical conduction of these conjugated molecules. Our experimental data leads to the following conclusions.

(i) The measured height of the conjugated molecular domains depended on their lateral sizes, in the case of conjugated molecules with a methylene group between the sulfur and the phenyl rings. By analyzing size dependence on the height of the conjugated molecular domain, we could estimate the electronic conductivity of the molecular domains. To increase the vertical conduction of molecular domains, a methylene group is necessary between the sulfur and aromatic rings. The obtained single molecular resistances are in the order TP3 > TP1 > C9 \geq BP1. In the cases of TP0 and BP0 without any methylene group, strong dependences were not observed, suggesting that the increase in the vertical conduction of the molecular domain is not so strong.

(ii) The LBH values on the conjugated molecular domains in all the cases were larger than that on the C9 surface. The LBH values were not dependent on the domain size, while the height difference changed with the domain size in the case of conjugated molecules such as TP1. These data suggest that the increase in the vertical conductivity is not due to the lowering of the local barrier height, but can likely be attributed to the conjugated molecular adsorption.

(iii) The XPS C(1s) satellite peaks and UPS spectra of TP1 and TP3 are almost identical, indicating that the carrier densities among these SAMs are almost the same. If the vertical conduction increase with the decrease in the number of methylene groups is attributed to the doping effect, then the shape and intensity of both the satellite peaks and valence bands should be different. Thus, the reason for the higher electrical conduction *might be* due to the higher carrier transfer probability through the conjugated molecules with one methylene group.

Acknowledgment. This work was supported by the New Energy and Industrial Development Organization (NEDO) of Japan. We thank Hodogaya Contact Lab. for synthesizing some useful conjugated molecules. We gratefully acknowledge Drs. I. Kojima and N. Fukumoto (National Institute of Materials and Chemical Research, Tsukuba, Japan) for their helpful suggestions and experimental assistance in the XPS measurements. We also thank Dr. S. P. Jarvis (JRCAT-NAIR) for her help in English correction.

References and Notes

(1) Carter, F. L. *Molecular Electric Devices*; Marcel Dekker: New York, 1982.

(2) Iijima, S. Nature 1991, 354, 56.

(3) Tour, J. M.; Jones, L., II.; Pearson, D. L.; Lamba, J. J.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parkh, A. N.; Atre, S. V. J. Am. Chem. Soc. **1995**, *117*, 9529.

(4) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Jones, L., II.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705. Cygan, M. T.; Dunbar, T. D.; Arnold, J. J.; Bumm, L. A.; Shedlock, N. F.; Burgin, T. P.; Jones, L., II.; Allara, D. L.; Tour J. M.; Weiss P. S. *J. Am. Chem. Soc.* **1998**, *120*, 2721.

(5) Leatherman, G.; Durantini, E. N.; Gust, D.; Moore, T. A.; Moore, A. L.; Stone, S.; Zhou, Z.; Lez, P.; Liu, Y. Z.; Lindsay, S. M. J. Phys. Chem. **1999**, *B103*, 4006.

- (6) Kelly, K. F.; Shom, T.-S.; Lee, T. R.; Halas, N. J. J. Phys. Chem. **1999**, *B103*, 8639.
- (7) Kergueris, C.; Bourgoin, J. P.; Palacin, S. Nanotechnology 1999, 10, 8.
- (8) Salmeron, M.; Neubauer, G.; Folch, A.; Tomitori, M.; Ogletree, D. F.; Sautet, P. *Langmuir* **1993**, 8, 3600.

(9) Bumm, L. A.; Arnold, J. J.; Dunbar, T. D.; Allara, D. L.; Weiss,P. S. J. Phys. Chem. 1999, B103, 8122.

(10) Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. Science **1997**, 278, 252.

(11) Epstein, A. J. MRS Bulletin 1997, 22, 16.

- (12) Stranick, S. J.; Parikh, A. N.; Allara, D. L.; Weiss, P. S. J. Phys. Chem. 1994, 98, 11136.
- (13) Bumm, L. A.; Arnold, J. J.; Charles, L. S.; Dunbar, T. D.; Allara,
 D. L.; Weiss, P. S. J. Am. Chem. Soc. 1999, 121, 8017.
- (14) Tamada, K.; Hara, M.; Sasabe H.; Knoll, W. Langmuir 1997, 13, 1558.

(15) Ishida, T.; Yamamoto, S.-I.; Mizutani, W.; Motomatsu, M.; Tokumoto, H.; Hokari, H.; Azehara, H.; Fujihira, M. *Langmuir* **1997**, *13*, 3261.

(16) Hobara, D.; Sasaki, T.; Imabayashi, S.; Kakiuchi, T. *Langmuir* **1999**, *15*, 5073.

- (17) Nishida, N.; Hara, M.; Sasabe, H.; Knoll, W. Jpn J. Appl. Phys. 1997, 36, 2379.
- (18) Ishida T.; Mizutani, W.; Akiba, U.; Umemura, K.; Inoue, A.; Choi, N.; Fujihira, M.; Tokumoto, H. J. Phys. Chem. **1999**, *B103*, 1686.

(19) Mizutani, W.; Ishida, T.; Tokumoto, H.; Jpn. J. Appl. Phys. 1999, 38, 3892.

- (20) Ishida, T.; Mizutani, W.; Tokumoto, H.; Choi, N.; Akiba, U.; Fujihira, M. J. Vac. Sci. Technol. 2000, A18, 1437.
- (21) Ishida, T.; Choi, N.; Mizutani, W.; Tokumoto, H.; Kojima, I.; Azehara, H.; Akiba, U.; Hokari, H.; Fujihira, M. *Langmuir* **1999**, *15*, 6799.
- (22) Samanta, M. P.; Tian, W.; Datta, S.; Henderson, J. I.; Kubiak, C. P. *Phys. Rev.* **1996**, *B53*, R7626.
- (23) Magoga, M.; Joachim, C. Phys. Rev. 1999, B59, 16011.
- (24) Tao, Y.-T.; Wu, C.-C.; Eu, J.-Y.; Lin, W.-L.; Wu, K.-C.; Chen, C. Langmuir 1997, 13, 4018.
- (25) Sabatani, E.; Cohne-Boulakia, J.; Bruening, M.; Rubinstein, I. Langmuir 1993, 9, 2974.

(26) Himmel, H.-J.; Terfort, A.; Wöll, Ch. J. Am. Chem. Soc. 1998, 120, 12069.

(27) [1,1':4',1"-terphenyl]-4-propanethiol ¹H NMR (400 MHz, CDCl₃) δ 1.39 (t, 1H), 1.99 (m, 2H) 2.58 (q, 2H) 2.79 (t, 2H) 7.26–7.67 (m, 13H)

- ¹³C NMR δ 24.02 (CH₂) 33.59 (CH₂) 35.42 (CH₂) 127.01–127.46 (benzene
- ring) 128.79 (ring), 128.86 (ring), 138.27 (ring) 139.88-140.71 (ring).
- (28) Sasaki, M.; Komai, M.; Ozawa, R.; Yamamoto, S. Jpn. J. Appl. Phys. **1998**, *37*, 6186.
 - (29) Poirier, G. E.; Tarlov, M. J. Langmuir 1994, 10, 2853.
- (30) Delamarche, E.; Michel, B.; Gerber, C.; Anselmetti, D.; Guntherodt, H.-J.; Wolf, H.; Ringsdorf, H. *Langmuir* **1994**, *10*, 2869.
- (31) Wöll, Ch.; Chiang, S.; Wilson, R. J.; Lippel, P. H. Phys. Rev. 1989, B39, 7988.

(32) Sellers, H.; Ulman, A.; Shindman, Y.; Eilers, J. E. J. Am. Chem. Soc. 1993, 115, 9389.

- (33) Poirier, G. E. Langmuir 1997, 13, 2019.
- (34) Hara, M.; Sasabe, H.; Knoll, W. Thin Solid Films 1996, 273, 66.
- (35) Bain, C. D.; Troughton, E. B.; Tao Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo; J. Am. Chem. Soc. **1989**, 111, 321.
- (36) Nakanishi, S.; Tsukada, M. Jpn. J. Appl. Phys. 1998, 37, 3805.
 Nakanishi, S.; Tsukada, M. Jpn. J. Appl. Phys. 1998, 37, L1400. Nakanishi,

S.; Tsukada, M. Surf. Sci. 1999, 438, 305.

- (37) Zeppenfeld, P.; Lutz, C. P.; Eigler, D. M. Ultramicroscopy **1992**, 42–44, 128.
- (38) Campbell, I. H.; Rubin, S.; Zawodzinski, T. A.; Kress, J. D.; Martin, R. L.; Smith, D. L.; Barashkov, N. N.; Ferraris, J. P. *Phys. Rev.* **1996**, *B54*,
- R14321. Campbell, I. H.; Kress, J. D.; Martin, R. L.; Smith, D. L. Appl.
- Phys. Lett. 1997, 71, 3528.

(39) Zehner, R. W.; Parsons, B. F.; Hsung, R. P.; Sita, L. R. Langmuir **1999**, *15*, 1121.

(40) Narioka, S.; Ishii, H.; Yoshimura, D.; Sei, M.; Ouchi, Y.; Seki, K.; Hasegawa, S.; Miyazaki, T.; Harima, Y.; Yamashita, K. Appl. Phys. Lett. **1995**, 67, 1899.

(41) Benning, P. J.; Poirier, D. M.; Ohno, T. R.; Chen, Y.; Jost, M. B.; Stepniak, F.; Kroll, G. H.; Weaver, J. H.; Fure, J.; Smalley, R. E. *Phys. Rev.* **1992**, *B45*, 6899.

(42) Enkvist, Ch.; Lunell, S.; Söjgren, B.; Brühwiler, P. A.; Svensson,S. J. Chem. Phys. 1997, 103, 6333.

- (43) Onoe, J.; Nakao, A.; Takeuchi, K. Phys. Rev. 1997, B55, 10051.
- (44) Bain, C. D.; Whitesides, G. M. J. Phys. Chem. 1989, 93, 1670.
- (45) Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. Science 1999, 286, 1550.
- (46) Seminario, J. M.; Zacarias, A. G.; Tour, J. M. J. Am. Chem. Soc. 2000, 122, 3015.