Lateral Electrical Conduction in Organic Monolayer

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Electric conductivity of organic molecules was estimated with molecular resolution using self-assembled
techniques and scanning tunneling microscopy (STM). Conjugated molecules of [1,1′:4′,1″-terphenyl]-4-
methanethiol (TP) were embedded in self-assembled monolayers of insulative *n*-alkanethiols, and when observed
by STM, TP molecules appeared as protruding domains. The apparent height of the TP domains increases as
the lateral size of the domains grows from 1 to 10 nm, reflecting the increase in the vertical conductance of
the domains due to the lateral, intermolecular interaction. We assumed that the molecules are connected to
each other with resistors for estimating the effect of intermolecular interaction on the conductance and calculated
the height of conducting disks with various radii, which should roughly reproduce the size-dependent height
of the TP domains observed by STM. The estimated resistance of the single TP molecule was less than 40
GΩ, and the effective lateral conductivity corresponding to the large TP domains was larger than 0.01 S/cm.

1. Introduction

Since organic molecules are a good candidate for the
components of nanoscale devices, functions of organic mol-
ecules have been investigated in search of their potential
applications. The research in this field has been active since
the development of scanning probe techniques made it possible
to address individual molecules. The electrical conductance of
molecules is one of the most fundamental and important
properties, and there are many studies concerning the electron
transfer along the molecular axis theoretically and experi-
mentally.[1−3] There are some trials to form conductive self-
assembled monolayer (SAM) films on Au surfaces using
conjugated molecules.[3−8] Especially, Bumm et al. estimated
the conductance of single molecules embedded in the insulative
SAM film using scanning tunneling microscopy (STM).[3]
However, the evaluation of the intermolecular conduction in
the monolayer films was not successful so far.[9,10] The electron
transfer through organic conductors like xylene dithiols has been
studied extensively,[11,12] but little is known about the intermo-
lecular electronic conduction on a molecular scale. Therefore,
molecular scale experiments are necessary for the microscopic
understanding of the electrical properties of organic bulk
materials as well as nanoscale molecular assemblies. As for the
application, when the conductive monolayer films can be formed
on insulative substrates such as silicon oxides, we may utilize
the low dimensionality and quantum effects of the patterned
2-dimensional electron gas for various electronic devices and
sensors.

To measure the lateral conductance of organic molecules in
the nanometer scale, we also adopted the SAM technique.[13]
Formerly, we tried to measure the lateral conduction of the
alkylsilane SAMs on the mica directly using a conductive atomic
force microscope tip. Insulative substrates such as a mica or
thick silicon oxide were used for this lateral conduction
measurement to minimize the current through the substrate under
the controlled humidity. The estimated lateral conductivity of
octadecylsilanes was less than 10^{-11} S/cm,[10] which is much
smaller than the values reported for the conductive polymers
(10^{-10}−10^5 S/cm),[14] and thus, the lateral conductance of the
alkyl chain in the SAM can be neglected.

At the same time, we have been studying the pattern
formation of the binary SAM on Au through the phase
separation.[15,16] Meanwhile, Weiss and co-workers succeeded in
implanting a conductive molecule in alkanethiol SAMs using a
well-controlled fill-in technique,[3,7] and they discussed vertical
conduction of the single molecule. We synthesized a conjugated
molecule that can form a well-ordered SAM film by itself and
form nanoscale domains in the alkanethiol SAM. During the
study of the domain structures, we obtained results showing
the *lateral* conduction of the conjugated molecules in the SAM
film for the first time.

2. Experimental Section

The synthesized molecule ([1,1′:4′,1″-terphenyl]-4 -meth-
anethiol, TP) has three phenyl rings, as shown in Figure 1a. TP
was synthesized from *p*-terphenylmethyl bromide[17] via the
corresponding thioacetate followed by its hydrolysis.[18] SAM
films were formed on Au(111) substrates epitaxially grown on
a cleaved mica. STM images in this study were obtained in
ultrahigh vacuum to eliminate the effect of the humidity at a
tunneling current of 10−20 pA and a tip bias of 0.8−1.3 V
(the tunneling resistance was maintained more than 60 GΩ).

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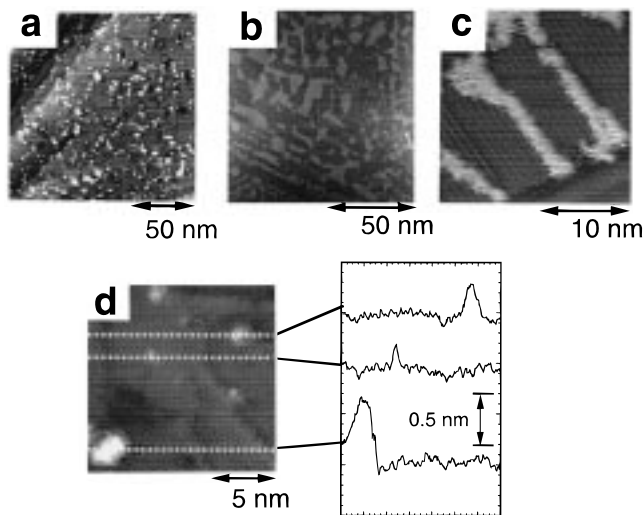ba, Ibaraki 305-8568 Japan.
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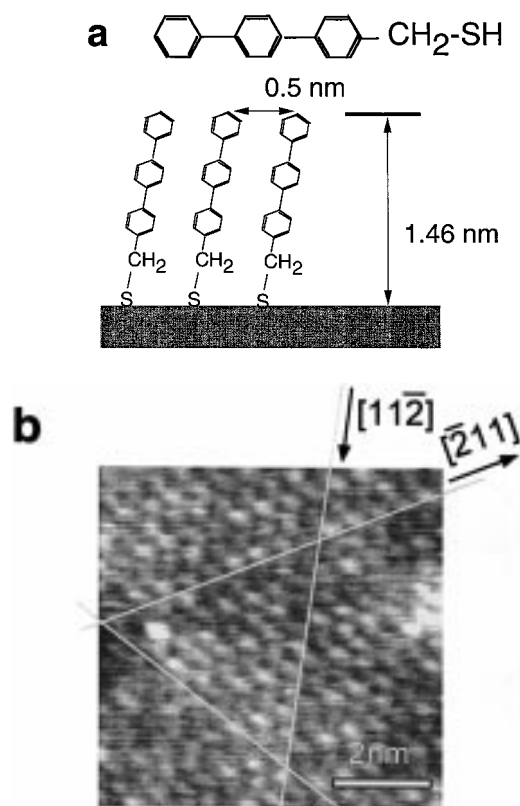
Figure 1. (a) Structure of the TP molecule and the monocomponent TP-SAM. The thickness of monocomponent TP-SAM was estimated to be 1.46 nm by XPS signal intensities.[21] (b) STM image of monocomponent TP-SAM prepared by immersing a gold substrate into the 1 mM TP chloroform solution for 24 h. The TP molecules adsorbed on the $\sqrt{3} \times \sqrt{3}$ sites on Au(111) surfaces with a molecular distance of 0.5 nm. Crystallographic orientation of the Au(111) surface was deduced from the straight steps in large scale images (not shown).

Figure 2. Constant-current STM images of the C9 + TP SAM. The TP molecules were introduced by immersing preassembled C9 SAMs into 0.1 mM TP chloroform solution for 1 h. The surface was imaged by STM at a bias voltage of 0.9 V and a current of 15 pA (60 GΩ). (a) TP molecules are observed as white dots mostly at the domain boundaries of the underlying C9 SAM. Images (b) and (c) are phase-separated patterns of C9 + TP SAM observed after annealing at 85 °C for 3 h in a vacuum. The preassembled C9 SAM seems to be well crystallized. TP molecules form patterns consisting of straight lines, like nanowires. (d) Magnified image of (a), and the cross-sections of the TP domains. The measured height of the TP domains increases with the domain size. The molecular lattice of the underlying C9 molecules is visible in the magnified images of (c) and (d).

A single-component SAM of TP molecules (TP-SAM) was prepared by exposing the substrate to a 1 mM TP chloroform solution for 24 h. The STM image in Figure 1b shows the TP molecules arranged at the $(\sqrt{3} \times \sqrt{3})R30°$ sites on Au(111) as the *n*-alkanethiols,[19,20] benzyl mercaptans, and 4-biphenyl-methanethiol.[4] The thickness of the monocomponent TP-SAM was estimated to be 1.46 nm by X-ray photoelectron spectroscopy (XPS) signal intensities using the method described in ref 21. We needed to adjust some parameters to reproduce the ellipsometric thicknesses of the octanethiol (C8) and dodecanethiol (C12) SAMs.[22] The estimated thickness of the TP-SAM is larger than the ellipsometric thickness (1.1 nm) of the *p*-terphenyl mercaptan SAM,[23] probably due to the additional CH₂ and higher ordering of TP molecules. In the following experiments, we introduced the TP molecules in preassembled alkanethiol SAMs and observed the domain structure using STM.

We used *n*-alkanethiols (C*n*) like nonanethiol (C9) and C12 for the preassembled SAMs. These preassembled SAMs were prepared by immersing Au substrates in a 1 mM alkanethiol ethanol solution for more than 24 h. After the SAM formation, the Au substrates were taken out of the solution, rinsed with pure ethanol to remove the physisorbed multilayer, and dried. Then, the substrates with the preassembled SAMs were immersed in a 0.1 mM TP chloroform solution for 1 h. The TP molecules in the solution are considered to adsorb gradually on the Au surface, mainly on the uncovered areas such as defects and domain boundary of the preassembled SAM. After the

adsorption process, small TP domains formed selectively in the domain boundary of alkanethiol SAMs, as shown in Figure 2a.

3. Results and Discussion

The interaction energy between thiol molecules can be roughly expressed in terms of the number of carbon atoms. Since the TP molecule has 19 carbon atoms, the difference of the interaction energy from C12 should correspond to 7 carbon atoms, which is about the estimated threshold energy (7−8 carbon atoms) for the phase separation at room temperature.[16] In the case of C9 and TP, the difference of the interaction energy is larger than is the case of C12 and TP. We found that C9 and TP are phase-separated and formed nanowire structures after annealing at 85 °C for 3 h in a vacuum (Figures 2b,c). We believe that the TP molecules forming the protruded domains mostly bind chemically to the Au substrate and do not physisorb on the preassembled SAM surface, because we only detected bound sulfur peaks by XPS.[24]

We found that the apparent height difference of the TP domains in the STM image is not uniform but changes as shown in Figure 2d. There is a tendency that the larger TP domains appear higher than the smaller domains. Figure 3 shows the relationship between the TP lateral domain size and the observed height of the TP domains measured from the preassembled SAM surface, supporting the tendency seen in Figure 2d. The smallest protrusion, presumably the single TP molecule, appears lowest. Up to the domain size of 5−10 nm, the domain height increases and finally saturates at about 0.7 nm.

The ellipsometric thicknesses of the C9 and C12 SAMs are estimated to be 1.01 and 1.46 nm, respectively.[22] Although the parameters used to estimate the thickness of the TP-SAM (1.46 nm) were adjusted to reproduce the ellipsometric thickness, the value must be compared with care. However, unless the absolute TP-SAM thickness should play a critical role in the discussion,
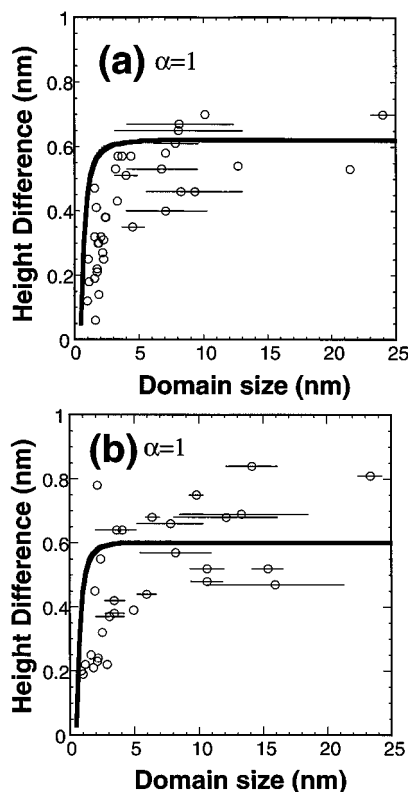
Figure 3. Relationship between TP domain size and observed height difference in the preassembled SAMs C9 (a) and C12 (b). Because the large domains in the C9 SAM are formed as a result of the phase separation, the saturated height is well-defined. On the other hand, C12 + TP does not show clear phase separation, which might cause the large fluctuation in the data. Error bars indicate the shortest and longest dimension of noncircular domains. Solid curves show the height of the domain with a lateral size $2a$ calculated using a model described in the text. The same curves were plotted for both data with a slight adjustment of the vertical offset to compensate the apparent thickness difference between C9 and C12.

we can discuss relative height differences of C9 + TP and C12 + TP with the estimated value. The expected height differences should be 0.45 nm between C9 + TP and C12 + TP, while the observed height difference of large TP domains is about 0.6 nm for both samples. The discrepancy of the expected and measured height difference of C12 + TP is larger than that of C9 + TP, and can be explained by electronic effects involved in the STM height measurement process. When conductive molecules such as TP are present in the highly insulative molecules such as the C12 SAM, the observed height difference between the conductive and insulative domains should be larger than the expected height difference.

In the case of small TP domains, the TP molecules might be tilted more and exhibit a lower apparent height. However, the estimated thicknesses of the TP and C12 SAMs are almost identical, while the observed height differences are more than 0.2 nm. Therefore, we consider that the height of domains measured by STM should be mainly due to the increased conductance of the domain. As shown in Figure 2d, we can observe the molecular lattice of the underlying SAMs in the area around the small TP domains, suggesting that the TP molecules are inserted nicely without disturbing the adjacent alkanethiols and, thus, should not have large tilt angles. In addition, since the height difference of the TP domains in C9 and C12 SAMs seems to obey the same rule, we assume that the tilting angle of the TP molecules in the alkanethiol SAM should be constant regardless of the domain size.

In comparison, dynamic mode atomic force microscopy (AFM) measurements in air showed the TP domains of about 0.27 nm high in the C12 SAM. In the case of AFM, the deformation of the alkyl chain due to the applied force may slightly enhance the apparent TP domain height, since the phenyl rings in the TP molecules should be stiffer than the single bond alkyl chain. In addition, under the ambient conditions, we have to consider the surface water layer with the thickness depending on the humidity and surface energy. We also observed C8 + C12 SAMs using STM. The observed height difference of 0.1−0.2 nm was independent of the domain size and much smaller than the alkyl chain length difference (about 0.6 nm). In the case of STM, the measured height difference between the alkanethiols is smaller than the value expected from the alkyl chain length difference, because the resistance of alkanethiol molecules is not proportional to the molecular length, as demonstrated by Salmeron et al.[25]

For correlating the height difference with the resistance, we measured the tunneling resistance R_t vs z-displacement value (dR_t/dz) on TP domains. The (dR_t/dz) value depends on distance z from the surface. In the case of STM on adsorbed molecules, however, the dependence is not strong, because the apparent work function (or barrier height) becomes considerably low. For example, Shönenberger et al. reported the work function lowering of a thiol-covered Au surface due to the dipole moment generated at the Au−S interface.[26] The (dR_t/dz) value contributing to the observed height change should be measured close to the top of the film, so we selected a low gap resistance. For changing the tunneling resistance from 40 to 20 GΩ, the z-displacement of about 0.1 nm was needed, which gives 200-GΩ /nm. However, this cannot cover the observed height difference of about 0.6 nm. We thus changed the gap resistance from 40 to 4 GΩ, and the induced z-displacement was 0.4 ± 0.04 nm, yielding 90 GΩ/nm. We consider that this value is *averaged* over the range in question and can be applied to the estimation of the observed height difference.

For the rough approximation, we consider the measured tunneling resistance as a sum of the resistance of the film and the vacuum gap. In reality, the electron conduction in the molecules is complicated; e.g., energy levels of the molecular orbitals must be considered when we discuss the conduction as a function of applied voltages. Since we measured the conduction under the almost fixed condition in this study, such a simplified model may be applied. Under the constant current condition, the vacuum gap increases when the film resistance is small. Since the estimated thickness of the TP-SAM is almost the same as that of C12, the observed height difference, about 0.6 nm, can be assigned to the increased tunneling gap on the large TP domains, corresponding to 54 GΩ; namely, the resistance of C12 is about 54 GΩ larger than that of the TP-SAM.

The size dependence of the TP domain height indicates that the electron tunneling probability becomes larger than that of a single molecule, when larger numbers of molecules are interacting. The degree of the interaction and how far and how strongly the molecules interact, may be estimated by quantum chemical calculations. However, the physical description of the phenomena is not so apparent, and many interpretations are possible, e.g., delocalization, band formation, polaron. Although it may not be appropriate to equate the tunneling probability with the conductance of the sample, the measuring system senses only the total current and does not distinguish the origins of the change in current. We measured the barrier height distribution and found that the barrier height on TP domains is larger than

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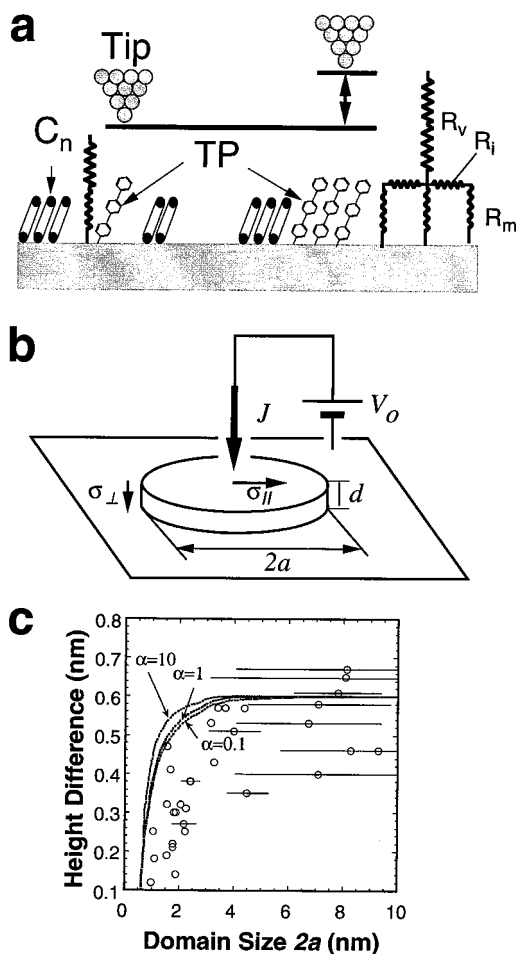
Figure 4. Schematic of lateral conduction effect on STM measurements. (a) In the case of conductive molecules (TP), the tunneling resistance is given by a sum of the molecular resistance R_m and the vacuum R_v. The total resistance of the TP domain is expressed by the network of the resistors laterally connected by R_i due to the lateral conduction. On the larger domains, the number of the connected conductive molecules becomes larger, and due to the parallel connection, the resistance of the domain itself would decrease. Then the STM tip position goes up to keep the total current constant by increasing R_v. (b) Calculation of the conductance of TP domains with a radius a and a thickness d, assuming the SAM as a continuous disk with a radial conductivity $\sigma_\parallel$ and a vertical conductivity $\sigma_\perp$ (see text). (c) Calculated domain height as a function of the domain size $2a$ using $\alpha = 0.1$, 1, and 10 nm^{-2}. The vertical scale was normalized to show the difference of the three curves. (Plotted data are those of C9 + TP.)

that on surrounding C9 SAM (data are not shown). But we did not detect the change in barrier height depending on the domain size. At the moment, the observed phenomena may be explained phenomenologically by assuming the change in conductance of the domains.

The size dependence of the conductance can be understood classically by assuming a *resistor* network (Figure 4a). In the case of a single conductive molecules, R_t is given by a sum of the molecular resistance R_m and the vacuum R_v. A similar model was used by Heike et al. to estimate the conductivity of a silicon surface.[27] On the larger domains, the number of the connected conductive molecules becomes larger, and due to the parallel connection through the lateral resistance R_i, the vertical conduction of the domain would increase. For convenience, we calculated the conductance of a circular disk with a radius a and a height d (Figure 4b). When the disk with a radial conductivity $\sigma_\parallel$ and a vertical conductivity $\sigma_\perp$ is placed on a perfect conductor, the conduction from the center of the disk

surface to the back electrode should increase with a. The measured height difference Δh of two disks with different radii a and a' is expressed as[28]

$$\Delta h \sim \left(\frac{dR_t}{dz}\right)^{-1} (R_a - R_a')$$

where R_a is the resistance of the disks, and we assume that the measured change in the tunneling resistance is mainly due to the vacuum gap, i.e., $(dR_t/dz) \sim (dR_v/dz)$.

The size-dependent conductance of the disk changes with the conductivity anisotropy $\alpha = d^{-2}(\sigma_\perp/\sigma_\parallel)$ where $d = 1.46$ nm. Figure 4c shows calculated STM heights of the disk as a function of the size using $\alpha = 0.1$, 1, and 10 nm^{-2}. Since the measured height seems to be saturated at 5−10 nm, as shown in Figure 3, we estimated that $\alpha < 1$ nm^{-2}. (We used the C9 + TP data for the determination.) More precise determination would require improvement of the experimental techniques. The calculated results of Δh using $\alpha = 1$ nm^{-2} are plotted in Figure 3. There are some deviations of the measured data from the idealized model. The observed domain size should be larger than the actual size at the region where the finite probe size is not negligible. The deviations come from the approximations made in our analysis as well. For example, we assumed ohmic resistance for the conductive domains instead of nonlinear current−voltage characteristics. As the vacuum gap increases, the voltage applied to the domain decreases, which may cause the deviation.

In Figure 3, some domains exhibit a lower height than the calculated value, probably because of the poor lateral interaction in those domains. In such domains, the electronic conduction might be disturbed by defects, and the total conductance becomes smaller than the value expected from the apparent size. In the magnified STM image of C9 + TP or C12 + TP, we could not obtain a molecular lattice image on the TP domains, e.g., Figure 2c, suggesting that TP molecules might not be close-packed in the domains. Our calculation is valid while the molecular domains are locally connected at least 10 nm in the lateral dimension, because the height becomes almost constant for the domains larger than the size. The domains smaller than 10 nm can be locally disconnected, for example, due to incomplete phase separation; namely, the other molecules are mixed in TP domains. Because the interaction energy difference between TP and C12 molecules is smaller, they can mix more easily than TP and C9, and the TP domain boundary is less defined, which may cause the observed large deviation in the case of C12 + TP. On some of the TP domains, occasional spike noises due to the unstable molecules might be superimposed,[29] which made the apparent domain height larger and caused the deviation in the plot.

The saturated resistance of the disk is calculated at smaller than 3 GΩ for $\alpha < 1$ nm^{-2}. A disk with a radius corresponding to a single TP molecule (an effective molecular radius of 0.26 nm derived from the density of SAM was used) has a resistance smaller than 40 GΩ. We also calculated the conductivities for the disk with $\alpha < 1$ nm^{-2} at $\sigma_\perp > 0.02$ (S/cm) and $\sigma_\parallel > 0.01$ (S/cm). Since the vertical resistance of the TP domains is small, the resistance of C12 SAM is estimated from the height difference and the (dR_t/dz) to be 54−57 GΩ, which is close to 50 GΩ given by Salmeron et al.[25,30] The single molecular resistance estimated for molecules similar to TP, for example, benzene-1,4-dithiol is 22 MΩ.[31] The conductivity of bulk polyphenylene ranges from 10^{-10} (undoped) to 10^2 (S/cm) (doped).[14]

As we stated before, we were unable to separate the current conducting through the molecules from other current components; for example, current directly tunnels from the substrate. More sophisticated analysis may be needed to correlate the conductance of the molecule and the molecular assembly with the observed size dependence. In addition, we cannot conclude that the TP domains have the *real* conductivity estimated for the disk. The lateral conductivity assumed for the disk represents the strength of the intermolecular interaction, but the interaction between the TP molecules does not necessarily contribute to the electron transport, and we should confirm the lateral conduction of the SAM using more direct methods.[10]

4. Conclusion

The STM image of a single component TP-SAM shows the TP molecules arranged at the $(\sqrt{3} \times \sqrt{3})R30°$ sites on Au(111) as the *n*-alkanethiols. We embedded TP molecules in alkanethiol SAMs, and phase-separated TP domains and nanowire structures were obtained after annealing. We observed the size dependence of the TP domain height using STM. Assuming that the intermolecular interaction increases the conduction and using a conducting disk model, we evaluated the conductivity that could reproduce the observed size dependence.

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(28) Precisely, the equation should be expressed in an integral form, $S(dR/dz)^{-1} dR$, since (dR_t/dz) depends on z (or R). We assumed that the dependence is not strong in the range of small height differences (∼0.6 nm) and used (dR_t/dz) value measured in the proximity of the film using ΔR_t obtained for $\Delta z \sim 0.4$ nm.

(29) Large spikes were also observed in the STM images of ref 7, which made the quantitative analysis difficult. Our molecules seemed to be stabilized better, but still made occasional noises, and some of them were difficult to distinguish from the height signal, which is consistent with our model. As shown in Figure 2d, the domain is highest around the center. We plotted this highest value as the height of the domains without averaging the height over each domain, which may cause the scattering of the data.

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