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Spectroscopic Contrast of Diarylethene Molecules on Octanethiol Monolayer

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Spectroscopic Contrast of Diarylethene Molecules on Octanethiol Monolayer

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Abstract

We present a systematic scanning tunneling microscopy (STM) study of bias-dependent imaging of disulfur diarylethene (2S-DE) molecules on octanethiol (C8) monolayer at room temperature. In a rigid confinement of the C8 matrix, we did not observe any significant variation in the appearance of the 2S-DE. On the contrary, a reversal in the apparent height of the 2S-DE was present when the molecule was situated on a gold vacancy island. We attributed this finding to the presence of a new electronic state that became accessible for a tunneling event. In addition, the C8 surface structure underwent a reversible phase transformation from $\sqrt{3} \times \sqrt{3}$ R30° hexagonal to $c(4 \times 2)$ square superlattice when the bias voltage was reduced from -825 mV to -425 mV or *vice versa*. Under a finite bias voltage, an appreciable topographic variation of the 2S-DE signature was demonstrated for the first time. This finding can be ascribed to a finite overlap of the associated wave functions that occurred between the tip state and the 2S-DE molecular energy level. We believe that physical insight on the bias-dependent imaging of organic molecules on solid surface is important towards the advancement of molecular electronics-based devices.

Abstrak

Kontras Spektroskopi Molekul Diarylethene pada Monolayer Octanethiol. Makalah ini berisi hasil kajian sistematis yang telah dilakukan dengan menggunakan mikroskop penerowongan payaran (*scanning tunneling microscopy* (STM)) untuk mengamati perubahan perilaku molekul *disulfur diarylethene* (2S-DE) pada molekul monolayer *octanethiol* (C8) di suhu ruangan, tergantung pada parameter tertentu. Pengamatan atas molekul 2S-DE yang terletak di daerah kekosongan substrat emas tidak menunjukkan adanya perubahan signifikan atas bentuk molekul 2S-DE, yang kemungkinan disebabkan oleh keberadaan fasa elektronik yang memungkinkan terjadinya fenomena *tunneling*. Struktur topografi dari matriks molekul penyusun (C8) juga mengalami perubahan transformasi fasa dari bentuk heksagonal $\sqrt{3} \times \sqrt{3}$ R30° menjadi *square superlattice* $c(4 \times 2)$ jika parameter pengukuran voltase untuk STM diubah dari -825 mV menjadi -425 mV ataupun sebaliknya. Perubahan yang terlihat pada bentuk fasa molekul 2S-DE terjadi pada rentang parameter yang terbatas. Hasil pengamatan ini dapat dijelaskan sebagai hasil dari tumpangtuh yang terjadi antara fungsi gelombang *tip state* dan tingkat energi molekular dari 2S-DE. Hasil penelitian ini bermanfaat untuk memahami ketergantungan perilaku molekul organik di atas permukaan padat dalam rangka pengembangan perangkat berbasis elektronik molekular.

Keywords: Bias-dependent, tunneling, octanethiols, STM, diarylethenes

1. Introduction

Small organic molecules equipped with photochromic switching behaviors have attracted a considerable attention due to their peculiar properties [1-5]. One of them, known as diarylethene, exhibits physical properties such as ease of addressability, thermal stability, and fatigue resistance [1,3]. Dulic *et al.* [6] have determined that diarylethene molecules are electrically connected via Au-S covalent

bond on both gold electrodes using a mechanically controllable break junction technique. In addition, the reversible light-controlled conductance switching of diarylethene has been demonstrated at single molecule level [4,5,7].

The variation and reversal of contrast imaging in STM typically depend on the sign and magnitude of the tunnel bias or the chemical nature of the tip apex. One of the

fascinating features that can be used in the STM is to adjust the tip-sample distance with its high precision accuracy (the distance is in the range of 1-10 Å). Typical dimension of a molecule under study in STM is almost scalable within the separation of tip and sample surface. Therefore, it is important to investigate the contrasting variation of the adsorbed organic molecule on solid surface. Recent studies of the contrast mechanism have been explored extensively [8-11].

Here, we are interested to investigate the bias-dependent behavior of a photochromic molecule called S,S'-((4,4'-(cyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))bis(4,1-phenylene)) diethanethioate (abbreviated as 2S-DE) on a gold surface. To illustrate, the chemical structure is shown in Figure 1. A dedicated immobilization agent of octanethiol (C8) molecules is used to confine the 2S-DE molecules. In this work, a variation of the 2S-DE features in different geometric conditions is explored at room temperature. It turned out that the signature of the 2S-DE differed slightly, especially in a freely isolated geometry of the C8 matrix. In addition, the dynamic behavior of the C8 under a variation of bias voltages is also investigated extensively.

2. Experiment

Materials. A mixed monolayer of 2S-DE and octanethiol was self-assembled on a thin film of Au (111). The octanethiol was used as received (Aldrich). 150 nm-thick Au (111) films on mica and self-assembled monolayers (SAMs) were prepared according to procedures similar to those previously reported [12].

A freshly prepared Au (111) sample with 150 nm thickness was immediately inserted into dodecanethiol solution for 24 hours. The samples were subsequently rinsed three times with ethanol (uvasol, Merck). The gold substrate containing C8 matrix was subsequently heated at 40 °C for 5 hours, rinsed with ethanol, and dried under a flow of nitrogen. The second step consisted of immersing the samples in a 0.5 mM solution of 2S-DE in ethanol overnight. The next day, a repetitive cleaning procedure described in the previous step was again repeated to remove the unattached molecules on the gold surface.

Ambient STM. STM measurements were carried out using a PicoLE STM (Agilent) equipped with a low tunneling current STM scanner head (type: N9501-A) and

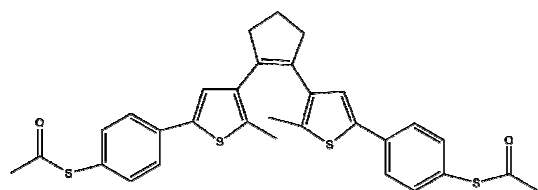


Figure 1. The Chemical Structure of Disulfur Diarylethene Molecule

a digital instrument from Agilent Technologies model N960A. Tips were obtained by mechanically cutting 0.25 mm Pt_{0.8}Ir_{0.2} wire (Goodfellow). The STM images were acquired in a constant current operating mode, at room temperature. Typical scanning parameters for obtaining STM images of As-DE and DT matrix surface structures are in the range of 10 to 15 pA with the tip bias voltage ranging from -0.8 to -1.2 V.

3. Results and Discussion

We determined the presence of 2S-DE molecules in octanethiol mixed monolayers by the presence of bright spots as previously demonstrated [4,13-14]. Due to a different conductivity of the molecules, the closed form of 2S-DE is associated with the presence of a bright spot on the surface of gold. On the contrary, the open form is indicated by the disappearance of such feature in the STM image. In Figure 2, we observe that the appearance of the 2S-DE molecules was confined to a geometrical preference at the defective sites of the C8 monolayers. Most of the bright spots were located at the substrate step edges or the domain boundaries and at the edges of the Au vacancy islands.

We assigned a protrusion with a typical apparent height ranging from 5 to 6.5 Å, an indication of the closed form of 2S-DE molecules. In order to further confirm the

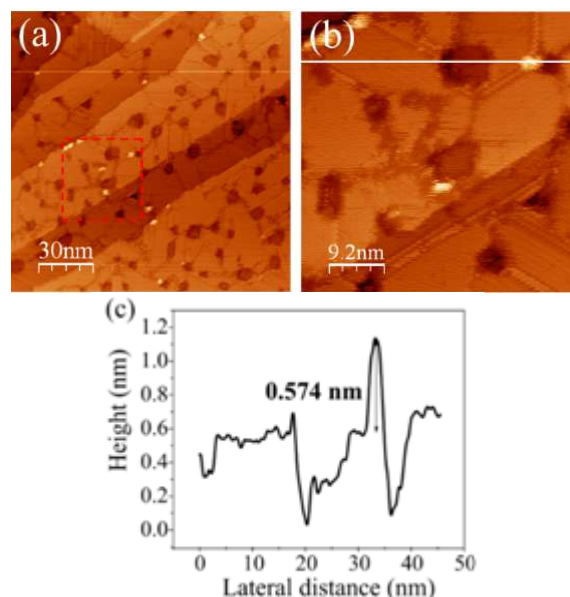


Figure 2. The Presence of 2S-DE Molecules on the Mixed Octanethiols Monolayers on Gold Surface. (a) 150 nm x 150 nm STM Image shows the Presence of 2S-DE Molecules Immobilized in the Octanethiol Matrix. (b) High Resolution of STM Image Exhibiting 2S-DE Molecules that are Located at the Step Edges ($I_t = 15$ pA; $V_{\text{sample}} = 0.7$ V; Height Scale = 2.45 nm). (c) Line Profile which Indicated the Protrusion with an Apparent Height Value of 5.74 Å

the originating physical appearance of the 2S-DE, we present a lateral profile showing the cross-section of the distinctive protrusion of bright spots with respect to the surrounded C8 molecules. Due to high local conductivity of the 2S-DE, we expected a large difference in terms of apparent height of the STM image between the closed form of the 2S-DE and the C8 molecules. Another parameter to confirm the presence of a single molecule is the diameter of the bright spot. It turned out that the average diameter of the bright spots was 3.53 nm. This result was comparable to the previous observation in which the diameter of an inserted molecule within the matrix should be larger than 2 nm [13,14].

The phase transition of the C8 matrix and the apparent height variation of the bright spots of the 2S-DE molecules can be monitored by tuning the bias voltages as depicted in the sequential STM images in Figure 3. Beforehand, to exclude any tip effect that might affect the acquisition of STM topographic image, the same area was probed for 30 minutes. Thus, we focused on the experimental results that do not suffer from significant lateral drift during the STM imaging.

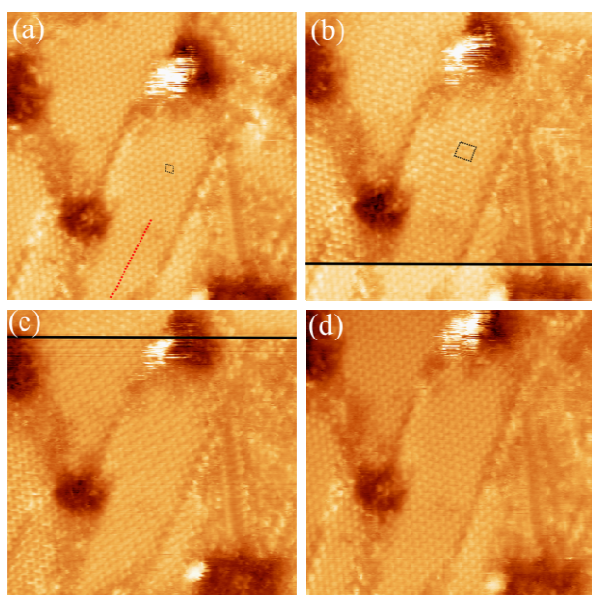


Figure 3. Four Consecutive Constant-current STM Images Represent the Reversible Structural Phase Transformation of C8 Molecules in High Spatial Resolution. (a) Topographic STM Image Displays the Hexagonal Structure of C8 and the Bright Spot of 2S-DE Probed Under a Bias Voltage of -825 mV. (b) A Conversion of C8 Structure to the Square Superlattice is Visible and the Black Horizontal Line Marked the Transition Bias Voltage from -825 mV to -425 mV. (c) The Structural Resolution is Slightly Reduced when the Bias Voltage is Adjusted to -325 mV. (d) The Bias Voltage is Adjusted to -825 mV and as a Result the Initial C8 Structure is Preserved. All the STM Images were Acquired Under the Same Tunneling Condition; $I_t = 6$ pA and Scan Size is 19.6 nm x 19.6 nm

First, let us discuss the changes in the appearance of the C8 surface structure as a function of the bias voltage. A highly covered hexagonal structure of the C8 on the surface of the gold is shown in Figure 3a. We addressed the occurrence of bright spots situated close to the step edge as a signature of the 2S-DE molecule. Further, the value of the apparent height and the diameter of the bright spots can be attributed to the features of the 2S-DE apart from the heavy debate whether it is the methyl tail group [15,16] or the S head group [17-19] that is observed as bright spots in the STM image. Our analysis does not depend on solving this puzzle by assuming that the alkane chains tilt uniformly covering the surface of the gold. Under a high bias voltage, we observed a reversible structural transformation of the C8 at a high voltage (assigned at -825 mV). As the tip-sample distance was lowered by decreasing the bias voltage to -425 mV, we immediately observed significant changes on the C8 structure. We observed that a transition from the $\sqrt{3} \times \sqrt{3} R30^\circ$ hexagonal structure into the $c(4 \times 2)$ square super lattice was successfully resolved and presented in Figure 3b. These structures became smeared out as we further decreased the bias voltage to 100 mV (Figure 3c). Surprisingly, we were able to recover the hexagonal structure of the C8 within the same region as we increased the bias voltage to -825 mV (Figure 3d).

The most interesting part of this study was that we were able to monitor the reversible process of the phase transformation of the C8 molecular structures at room temperature. That is to say, the transition from the hexagonal to the square lattices or *vice versa* was observed in many successive frames. One way to assign each successful attempt is by interpreting the lateral spatial periodicity across the C8 molecule at the given bias voltages. For the sake of clarity, we presented the example of lattice spacing variation upon the respective applied bias voltages in Figure 4. Indeed, we clearly observed a conversion reversal of typical lattice distance of C8 from the hexagonal (0.5 nm) to the less packed structure (0.99 nm) or *vice versa*, as illustrated in Figures 4(a-b). At a glance, we qualitatively recognized that the regular fashion of the hexagonal structure can be presented by the lattice difference of 0.5 nm between the C8 molecules (Figure 4a).

As the bias voltage was reduced to -425 mV, consequently, the lateral distance of the C8 simultaneously transformed into two features: a regular pattern of hexagonal lattice at the left corner (0.447 nm) and the $c(4 \times 2)$ square superlattice (0.99 nm). As the voltage was further reduced to a lower value, the square superlattice of the C8 dominantly covered the entire surface of the structure (Figure 4c). Thus, we recovered the hexagonal structure of the C8 by increasing the bias voltage to -825 mV. These findings served as solid indications that the coexistence of both C8 structures can be controlled upon variation of an applied bias.

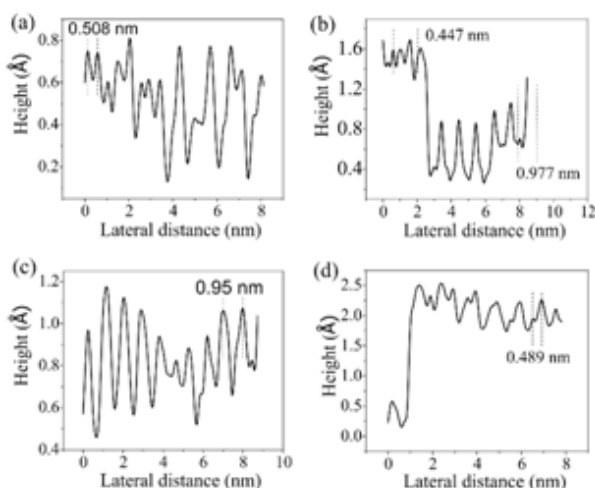


Figure 4. Lateral Cross-sections that Correspond to the same Corrugation with the Respective Red Line Drawn in Figures 3(a-d). (a) A Lattice Periodicity of C8 Showing the Extracted Value of 0.508 nm. (b) A Lateral Cross-section Taken from Figure (b) Exhibit Peak to Peak Distance of 0.447 nm. (c) Large Peak to Peak Distance was Observed in this Case Due to the Presence of Less Ordered Phase. (d) Regular Lattice Spacing Close to 0.5 nm was Recovered

The underlying physical mechanism governing the reversible surface transitions of the C8 is proposed. First, we shall discuss the role of the physical structure of the SAMs. It has been proposed that the STM contrast of alkanethiols marked the alteration of either the positions of the S atom [20] or the top methyl group [16,21]. In the latter case, the $c(4 \times 2)$ brightness modulation can be caused by height differences among molecules. Indeed, recent non-contact AFM experiments [22] have shown that height variations within the unit cells of both $c(4 \times 2)$ structures were observed. The second aspect was that we cannot omit the influence of local density of states (LDOS) [23,24]. By taking into account the effects of LDOS, these simulations predicted that the $c(4 \times 2)$ contrast dependence can originate from bias voltage, adsorption site, S hybridization, chain length, or tip-SAMs separation. During the forward and backward transitions, more than one $c(4 \times 2)$ regions are usually observed. Transformations from one type of $c(4 \times 2)$ to another has also been found [25] since the various $c(4 \times 2)$ structures are frequently found to exist simultaneously on the surface, and they were also found to coexist within the regular $\sqrt{3} \times \sqrt{3} R30^\circ$ phase.

The interpretation of these structure reversal transformations could also be related to the role of tip-molecule interactions that depended on the tunneling parameters. In this approach, we regularly alter the bias voltage while maintaining other tunneling current at fixed value. The fact that we used a relatively low tunneling current (in our experiment it was within the range of 6-10 pA) has

led to the avoidance of any strong physical interactions between metallic tips and molecules that might occur during imaging. However, changes in the molecular structure reveal that we cannot completely rule out the role of overlapping wave functions among the molecules and the tip states. As the bias voltage was modulated from high to low values, we basically changed the proportion of the tip-molecule wave functions from the lowest to the highest possible free energy that accommodated the presence of structural transitions.

To support our findings, Zeng *et al.* [23] have described in their paper that the presence of the new electronic state upon chemisorption of heptanethiol (C7) and decanethiol (C10) on Au (111) is mainly governed by the mixture of gold and sulphur orbitals and small amount of orbitals at the alkyl part. Another comparable finding has been previously discussed by Ripsan *et al.*, where the SAMs of close-packed undecanethiol on Au (111) under UHV condition showed two distinctive $c(4 \times 2)$ structures with four non-equivalent molecules per cell unit (25). They found that for both structures, the reversible contrast variations were visible upon systematic alterations of the bias voltage, the current, and the termini distance of the tip. Li *et al.* [24] have described that the internal patterns in the simulated STM images of alkanethiols were heavily dependent on the bias voltage. Moreover, the changes in appearance of the SAMs were the results of the topographic variations modulated by the electronic effect. In an earlier study, Bucher *et al.* [26] observed variations in the STM patterns between $c(4 \times 2)$ and $\sqrt{3} \times \sqrt{3} R30^\circ$ upon changing the tunneling conditions. Pflaum *et al.* [27] reported a reversible transition in the SAMs of decanethiol upon changing the bias voltage, which was believed to be due to the electronic effect.

Now, we shall continue with the second discussion that is focused on the topographic variation of the 2S-DE as a function of bias voltage. Unlike previous cases with octanethiols, the appearance of the 2S-DE did not exhibit any dramatic bias-dependent variations throughout the sequential STM images. Instead, the bright spot signatures remained largely unaffected. Here we introduced two parameters to monitor the effect of applied bias voltages to the local conductance properties of the 2S-DE, namely, the apparent height and root mean square (RMS) roughness. First, let us discuss the variation in the apparent height as a function of bias voltage. Interestingly, an appreciable decrease in the apparent height was observed at the bias voltage of -325 mV compared to the rest of the acquired data. Intuitively, these observations demonstrated that a finite LDOS of the 2S-DE was quite sensitive under the corresponding tip-sample separation.

We measured the small decrease in the apparent height from the initial value of 0.47 nm to 0.39 nm. This might be due to the fact that we gradually decreased the resonant tunneling event from the occupied state of the 2S-DE to

the empty state of the tip. Thus, the local conductivity of the 2S-DE was marginally affected to some degree, and the brightness of the 2S-DE decreased slightly. These systematic differences in apparent height can be associated to the fact that the tip and sample distance became larger as the bias voltage gradually decreased and consequently, the electronic effect contribution to the tunneling event also decreased gradually.

To quantify these phenomena more carefully, we also extracted another parameter called a root-mean-squared (RMS) surface roughness (using Gwyddion version 2.90). Surprisingly, a rapid change in terms of RMS values was found immediately as we modified the bias voltage from -825 mV to -425 mV. Based on these results, we concluded that the surface roughness was dramatically affected by a large variation in an applied bias voltage compared to the apparent heights. These findings strongly emphasized that the size and shape fluctuations of the 2S-DE were not purely affected by the tip-sample separation as demonstrated earlier in the C8 case. Other considerations such as the rigidity of geometrical confinement of the 2S-DE might also contribute to some extent.

In the case of molecular adsorption at the gold vacancy islands, two entangled bright spots were found at the center of the dark regions in Figure 5a. We used the information from the previous section, in which the C8 surface structures were significantly affected by tuning the bias voltages from -825 mV to -425 mV and *vice versa*. It turned out that one of the spots nearly disappeared at the given -425 mV bias voltage, as shown in Figure 5b. If we re-biased the sample at -825 mV, then the same features as those observed in the initial STM image were recovered, as shown in Figure 5c. From this preliminary result, we continued our attempt by repeatedly adjusting the tunneling parameters between those bias voltages to evaluate the reproducibility of such a phenomenon. As a result, we summarized these attempts in Figure 5d, which demonstrate the repetition of the reversal feature of the bright spots. The apparent height of the corresponding bright spot was modulated in the range of 6-8 Å to 0.15-0.45 Å. Thus, we proposed that this observation originated from the large difference in the local variations of LDOS of the 2S-DE upon the application of two bias voltages.

In constant-current mode of STM imaging, the tunneling current was fixed and remained constant throughout the scanning process. Assuming that the initial tunneling distance was 10 Å between the tip and the substrate, then a corresponding potential barrier of 4.8 eV can be realized based on the work function difference between the gold and Pt/Ir tips. A huge potential barrier was expected to produce the highest corrugations (8 Å) on the bright spots. This seemed physically unrealistic since the working tunneling parameters by far surpassed this energetically unfavorable condition. Secondly is a modi-

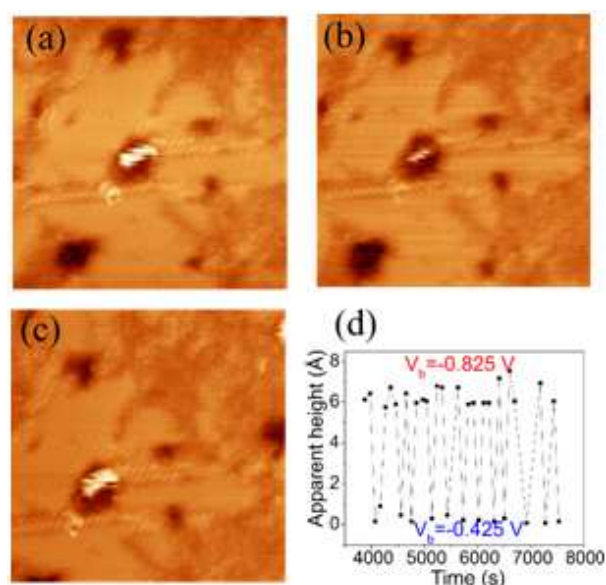


Figure 5. The Periodical Appearance of Bright Spots as a Function of Bias Voltage. (a) Two Closely Located Bright Spots were Found at the Dark Region. (b) Reduction of Voltage to -0.425 V Resulted in the Disappearance of One of the Bright Spots. (c) As we Increased the Bias Voltage, we were able to Retain the Bright Spot Signature. (d) A Complete Demonstration of the Tunable Apparent Height as a Function of Observation time. The Upper Data Points were Acquired when we Applied a Bias Voltage of -825 mV, whereas the Lower Data Points were Obtained with -425 mV

fication in the local density of electronic states of the molecules.

The enhancement of the local conductivity of the 2S-DE as a function of the bias voltages at the freely-isolated C8 region was due to the presence of the new electronic state of the adsorbed molecules on the gold surface. Owing to the high conductance property of 2S-DE compared to C8, the 2S-DE molecules were expected to govern the local conductivity properties due to their small HOMO-LUMO gaps. Therefore, we suggest that the reversal in apparent height in a freely-isolated matrix was due to the event of the metallic tip probing the new electronic state once the gold-2S-DE-tip junction was formed. In other words, the resonance tunneling event occurred from the conducting tip to the new electronic state of the molecule that was realized by two different energy biases. Ultimately, we correlate that the disappearance and appearance of the bright spots were due to a selective controllable tunneling process that can be controlled by two distinctive bias voltages.

We investigate further the local variations of the electronic structure of the 2S-DE under small bias voltage variations in Figure 6. It has been realized that at a low bias voltage the transport behavior of a molecular junction

is determined by the perturbed molecular orbitals (MOs) located near the Fermi level [28,29]. As soon as the 2S-DE molecules became covalently attached to the gold, the MOs were modified as such that their positions relative to the Fermi level were shifted. In this discussion, we focus on investigating the importance of the STM as a surface characterization tool to probe the LDOS of a molecule at a relatively low bias voltage range.

In Figures 6(a-e), the only difference was that we adjusted the tip-sample separation by a small distance by gradually applying low bias voltages (in the range of -0.115 V to -0.20 V). In the following discussion, we turn our attention to one particular bright spot, which is highlighted by the red circle in Figure 6a. Initially, we extracted a normal apparent height (7 Å) at -0.20 V. Then, a gradual decrease in the apparent heights was observed as soon as the

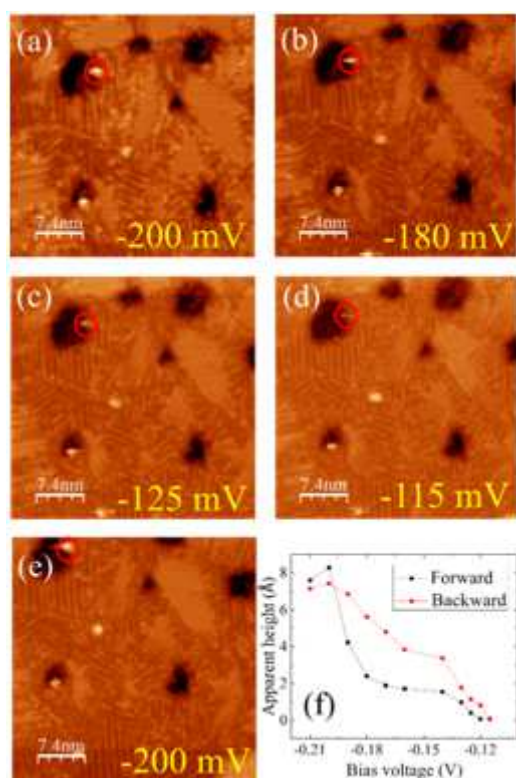


Figure 6. Voltage Dependence of the 2S-DE under Finite Applied Bias Voltages. (a) A Representative STM Image of the 2S-DE is Indicated by the Red Circle where the Apparent Heights Vary as a Function of the Bias Voltage. (b) A Smeared Signature was Clearly Observed as the Bias Voltage was Reduced to 20 mV. (c and d) Spot Signatures were Almost Invisible as we Moderately Decreased the Bias Voltage. (e) The Bright Spot was Recovered as the Bias Voltage was Increased. (f) A Plotted Hysteresis-like Curve where the x-axis is the Apparent Height and y-axis is the Bias Voltage. Forward Curve Means that we Initially Probed from Higher (-0.2 V) to Lower (-0.115 V) Voltage and Backward Curve was Acquired in a Reverse Manner

metallic tip-molecule distance was decreased. For example, we probed the sample with -115 mV and we were no longer able to preserve the same brightness as shown in the initial scan (Figure 6d). The 2S-DE molecule can be recovered when the bias voltage was switched back to -0.20 V. We systematically summarized these topographic observations in a hysteresis-like plot as shown in Figure 6f. As expected, we observed a similar phase transformation in the accompanying C8 molecules throughout the STM measurements. The formation of the c(4x2) phase marked the structural conversion from the regular hexagonal structure of the C8 by reducing the bias voltage to -0.125 V (Figure 6c).

In order to understand the appearance and disappearance of the 2S-DE signatures in the case of low bias regime, we should consider the role of geometric contribution towards a gradual decrease in the tip-surface distance. The existing qualitative observation by Clarke *et al.* [30] confirms that there is a reduction in atomic corrugations as the tip-sample separation is decreased. Possible argument to this attenuation has been brought up in the existing literature [31]. This event might occur due to the fact that the tip atom is in a close proximity with the surface atoms and thereby the motion of the apex atom comes into the picture. The other possibility is that a quenching of the surface exists due to the creation of high electric fields [32].

A substantially low tunneling current (varied from 6-10 pA) was applied in our experiments. Then, we expect this tunneling parameter to lead to a condition where the tip atom was brought close to the sample surface without touching the molecule of interest. To exclude this proposal, we have evaluated the tip effect by probing the same area under the same tunneling parameter for prolonged imaging. Thus, the molecularly resolved 2S-DE and C8 did not demonstrate any significant variations in the topographic STM image. As a result, we concluded that the atomic apex tip did not change significantly. In this regard, we ruled out that this aspect might contribute to the contrast reversal of the bright spots under bias voltages. Instead, we propose that this finding originated from the accumulation of high electric field at low bias. Thus, a narrowing electronic state in the isolated 2S-DE might exist [33,34]. For comparison, we illustrate this point by using the work of Calleja *et al.* (10) as an example for the contrast reversal of oxygen atoms on Ru(0001) surface.

A quantitative comparison between STM experiment and first principle calculation revealed that the shape of the atomic adsorbates in the STM images depended heavily on the tunneling resistance and it can reversibly change its shape from circular (high resistance) to triangular (low resistance). A similar approach has also been used by Ramoino *et al.* [35] to distinguish the changes in appearance of self-assembled Copper-octaethylporphyrin

rin on NaCl islands by repeatedly altering the bias voltage within the range of -1.6 V to -1.9 V. Voltage-dependent STM studies revealed the differences in the electronic structures for molecules adsorbed on metals and NaCl/metal areas.

In this regard, we correlate that the brightness reversal of the bright spots was due to a large variation in the electric field that was experienced by the adsorbed molecule at the isolated C8 matrix and thereby acted as a "trigger", mimicking its switchability in appearance. At a finite bias, the absence of the bright spots can be attributed to the lack of resonant MOs within the addressed bias range. The normal tip-sample distance in the STM experiments is about 4-7 Å. Within this range, we can deduce three crucial forces that might occur between two contributing electrodes: van der Waals force, resonance force, and repulsive force. In the tunneling regime under a small bias, it was believed that resonance force is the dominant factor governing the tunneling event. Thus, if we assign an energy resonance equal to the tunneling matrix and element based on the Heisenberg and Pauling term, this event would lead to a split in energy level of the samples and tip states [36]. As a result, a different phase of overlapping wave functions at a finite bias regime can be observed. Therefore, we suggest that within the addressed bias range of 110-120 mV, the sample and tip wave functions overlap could take place. Consequently, the bright spots of the 2S-DE were slightly disrupted within the aforementioned bias range.

4. Conclusion

In summary, we have been able to successfully use an advantage of the STM technique to study the bias voltage-dependent imaging of 2S-DE in C8 matrix. The reversible contrast enhancement of the C8 structure was successfully demonstrated. We addressed that these observations can be associated with the contribution of molecular wave functions at different energy levels. However, the 2S-DE molecules did not show any structural variations in the immobilized mixed mono-layers matrix. Interestingly, a significant change in the apparent height was observed when the 2S-DE was located at the gold vacancy island. We propose that the apparent height reversal of the 2S-DE in a freely-isolated matrix was due to the direct probing of the metallic tip on the molecular level of the new electronic state.

The behavior of the small variations of the 2S-DE signature at a finite bias regime can be rationalized due to an accumulation of high electric fields that impinged the 2S-DE molecules. Consequently, a narrow electronic state became accessible for the tunneling event at a certain bias voltage regime. In other words, the smeared out signal can be attributed to the lack of corresponding resonant molecular orbital levels within the addressed bias range.

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