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LETTERS

Scanning Tunneling Microscopy and Spectroscopy of Dialkyl Disulfide Fullerenes Inserted into Alkanethiolate SAMs

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Utilizing scanning tunneling microscopy, we have explored the self-assembling and electronic properties of unsymmetrical disulfides $CH_3(CH_2)_nSS(CH_2)_{n+1}NC_{60}$ (where $n = 5$ or 10, and C_{60} = buckminster-fullerene) adsorbed onto Au(111). We analyzed self-assembled monolayers (SAMs) derived from the fullerene disulfides as well as SAMs formed by the insertion of the disulfides into self-assembled alkanethiol monolayers. By studying various combinations of fullerene disulfides and alkanethiols, we found that the degree of insertion is governed primarily by the chain length of the C_{60} tether relative to the surrounding alkanethiol matrix. In addition, we used the insertion technique to probe the electronic properties of the tethered fullerenes as a function of alkyl chain length.

Self-assembled monolayers (SAMs) have become a key technology in fabricating devices on the micrometer and nanometer scales. The initial development of SAMs focused on their usefulness in patterning surfaces, such as forming masks for beams of metastable atoms[1] and microcontact printing.[2] However, SAMs have evolved to become an essential component in the devices themselves. The insulating characteristics of some of these molecules have proven beneficial in generating well-defined tunnel junctions in quantum dot arrays[3] and field-effect transistors.[4] By attaching a C_{60} molecule onto a dialkyl disulfide, we have combined the favorable characteristics of SAMs with the unique electronic and structural properties of fullerenes. In this letter, we explore the physical and electronic properties of the fullerene disulfides incorporated into an alkanethiolate SAM using the scanning tunneling microscope (STM). In conjunction with these studies, we also probe the electronic effects on the C_{60} molecular levels as a function of their proximity to the gold surface.

The details of the synthesis of $CH_3(CH_2)_nSS(CH_2)_{n+1}NC_{60}$ are described elsewhere.[5,6] In the present study, two molecules in which the C_{60} moieties are attached to the disulfide via an aziridine linkage were utilized: one tethered with a-short alkyl chain ($n = 5$) and the other with a long alkyl chain ($n = 10$). Due to the asymmetry of the adsorbates, pure solutions of the disulfides generate SAMs having a mixture of CH_3 and C_{60} termini that appear to be inhomogeneously distributed.[5] In the work reported in this letter, we have found that a uniform and dilute monolayer can be obtained by first adsorbing alkanethiols onto the gold surface and then inserting the fullerene disulfides. In previously reported insertion experiments performed by others, conjugated organic molecules were inserted into boundaries between structural domains and at substrate step edges of preassembled alkanethiolate monolayers.[7,8] These researchers

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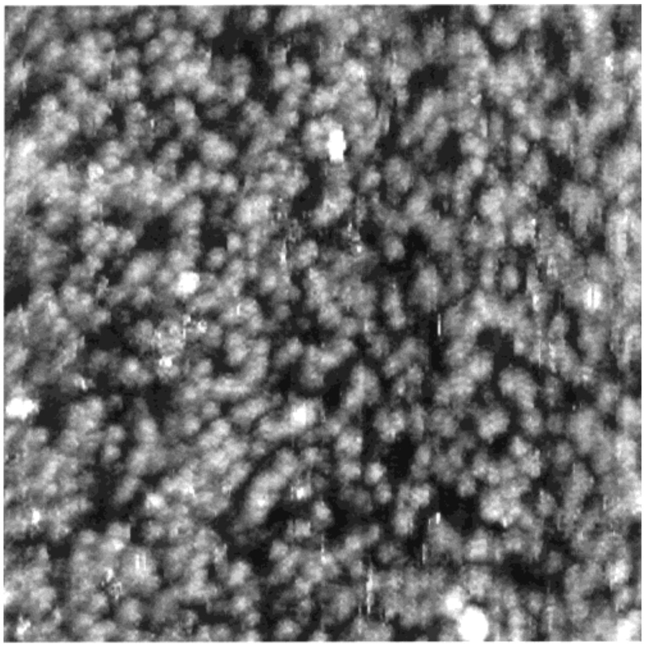

Figure 1. A large area STM image (75 × 75 nm) of the SAM generated from the short-chain C_{60} disulfide on Au(111). It was acquired at +1.0 V sample bias and 50 pA tunneling current. It has been median filtered along the slow scan direction to remove intermittent noise.

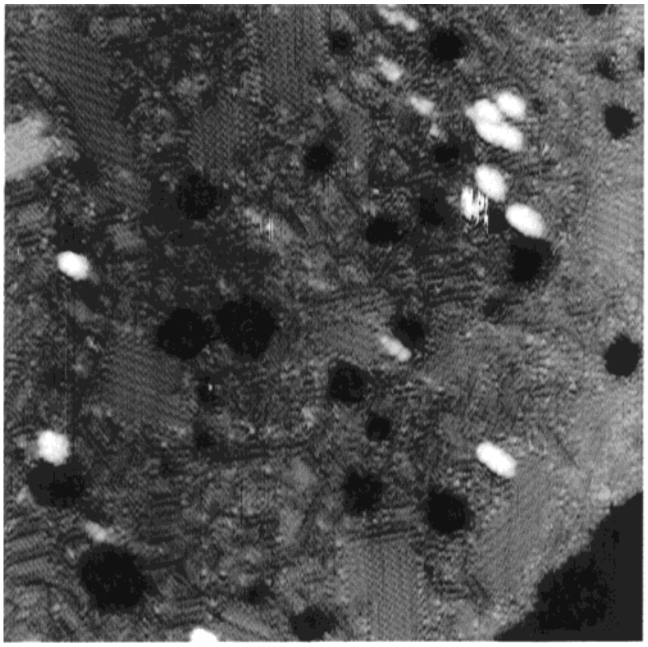

Figure 2. A 75 × 75 nm image of the short-chain C_{60} disulfide inserted into a hexanethiolate SAM. The bright areas are the fullerene moieties protruding above the alkyl chains, while the dark regions are etch pits in the gold surface arising from the self-assembly process. The tunneling parameters were $V_{\mathrm{bias}} = +1.0$ V and $I_t = 50$ pA.

found that, in contrast to codeposition strategies, the insertion technique preserves the crystalline lattice of the alkanethiol SAM.

The dynamics of self-assembly have been traditionally investigated using nonlocal techniques such as ellipsometry, contact angle measurements, infrared spectroscopy, and X-ray photoelectron spectroscopy. Scanning tunneling microscopy, on the other hand, offers molecular-scale resolution of the surface structure as well as the ability to perform electrical characterization on individual molecules. All the STM measurements reported here were performed under ambient conditions with a home-built STM operated by RHK electronics and software. Mechanically cut Pt/Rh (87/13) tips were used; however, the exact chemical identity of the tip apex during tunneling is not necessarily known. For substrates, Au(111) on mica was used as purchased from Molecular Imaging Corporation. SAMs derived from the fullerene disulfides or the alkanethiols were prepared by immersing the gold substrates for 24 hours in either 0.01 mM benzene solutions for the fullerene disulfides or 1 mM ethanol solutions for the *n*-alkanethiols. The alkanethiol samples used for molecular insertion were then removed and rinsed repeatedly with ethanol before a second, one-hour immersion in 0.01 mM fullerene disulfides dissolved in benzene. After removal, all the samples went through multiple benzene followed by ethanol rinses, and were then dried with nitrogen before scanning in the STM.

Figure 1 shows a large area image of a SAM derived from the short-chain C_{60} disulfide on Au(111). This image demonstrates a high coverage of surface-confined moieties, but no evidence of ordering or any discernible overlayer structure. The fullerene moieties can be readily distinguished with a nearest-neighbor distance of ~11 Å in the most densely packed regions. This corresponds well to the measured van der Waals diameter of underivatized C_{60} adsorbates found in previous STM measurements.[9,10] Through cross-sectional analysis of these images, it appears that most of the fullerene moieties are extended above the gold substrate by the alkyl chains. This proposed geometry is supported by the fact that stable images of the C_{60} moieties can be obtained only at very low tunneling currents, which is consistent with the imaging of an alkanethiol SAM but inconsistent with the imaging of C_{60} moieties directly adsorbed on metal surfaces.[10,11] However, the disordered nature of the film prevents an exact determination of their molecular orientation. In fact, it is quite likely that the molecules are adsorbed in a variety of configurations due both to the strong interaction of C_{60} with gold and with itself, and to the highly asymmetric nature of the molecule. Pure films formed from the long-chain fullerene disulfides exhibited a similar structure.

Figure 2 is an STM image of a hexanethiol SAM after immersion in a solution of the short-chain C_{60} disulfide. The white protrusions in this image are the tethered fullerenes, while the black holes are etch pits that form during the self-assembly process and correspond to a depth of one gold monolayer.[12,13] The atomic lattice of the underlying hexanethiol monolayer is clearly observed, demonstrating that the lattice of the SAM is preserved after the insertion process. As well as insertion near step edges, the fullerene molecules can also be found incorporated into the hexanethiol matrix itself. Presumably, these molecules are inserted at grain boundaries in the hexanethiol lattice. In some cases, however, the size of the C_{60} prevents a clear identification of the surrounding structure. In addition, we observe that the molecules can be inserted in small clusters as well as individually. It should be noted that the asymmetric shape of the white protrusions probably arises from an STM tip artifact.[9,14] We see a similar density (same order of magnitude) of long-chain C_{60} disulfides inserted into undecanethiol SAMs. This result is somewhat surprising given the larger size of the undecanethiols, which affords an increase in steric interactions that might plausibly inhibit the insertion process. This issue will be discussed below in greater detail. It does appear, however, that SAMs consisting of the long-chain C_{60} disulfides have a decreased tendency toward clusters of inserted molecules when compared to the short-chain case.

We also explored the insertion of the fullerene disulfides into alkanethiol SAMs that possess chain lengths in which the

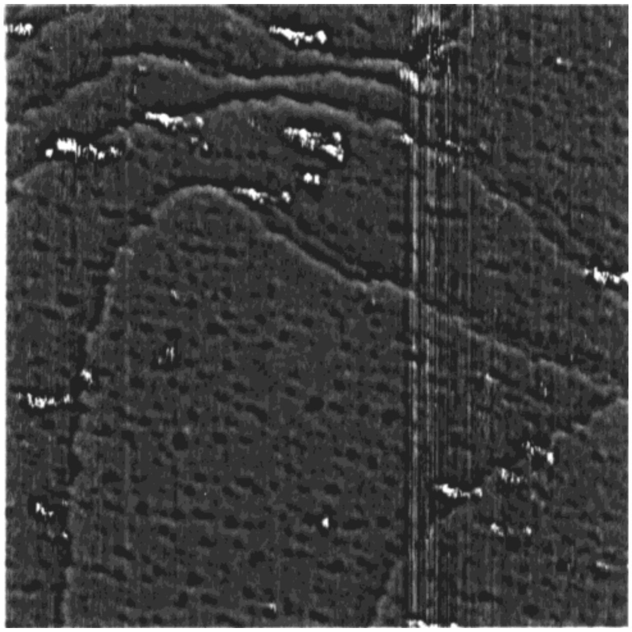

Figure 3. An image of the long-chain C_{60} disulfide inserted into a dodecanethiolate SAM. This image has been processed by unsharp masking to enhance the visibility of the inserted molecules. The scan size is 250 × 250 nm, and it was acquired at $V_{\text{bias}} = +1.0$ V and $I_t = 50$ pA.

number of methylene spacers differ from those of the disulfides. The insertion of the long-chain C_{60} disulfides into a dodecanethiol SAM is shown in Figure 3. This image was processed by an unsharp mask to enhance the images of the inserted molecules on the many terraces. As in Figure 2, the distorted appearance of the inserted molecules in this image probably arises from an STM tip artifact. Here we observe an order of magnitude decrease in the number of inserted molecules when compared to the insertion into the undecanethiol SAM. In addition, we observe that the insertion occurs almost exclusively at the terrace steps or at the edges of the etch pits. At least two hypotheses might plausibly explain the differences: (1) the odd/even orientation of the terminal methyl groups of the alkanethiol SAM might influence the adsorption process,[15] and/or (2) the twelve-carbon chain length of the dodecanethiol SAM might sterically block the attachment of the fullerene disulfide, which possesses only an eleven-carbon chain length. In the latter case, the predominant steric interaction would be that between the terminal methyl group of the dodecanethiol SAM and the inserting fullerene tail group; this interaction might prevent the disulfide head group from approaching the surface.

To distinguish between these two hypotheses, we examined the insertion of the long-chain C_{60} disufides into a decanethiol SAM. For this SAM, the orientation of the terminal methyl group is the same as that for a dodecanethiol SAM.[15] The length of the underlying tether, however, is one carbon shorter than that of the fullerene disulfide and two carbons shorter than that underlying a dodecanethiol SAM. Figure 4 shows that the insertion behavior into the decanethiol SAM is similar to that for the undecanethiol SAM, and thus distinguishably different from that for the dodecanethiol SAM. This result supports the hypothesis that steric interactions arising from sufficiently long underlying tethers can strongly inhibit the insertion of fullerene disulfides into alkanethiol SAMs. We believe that this type of inhibition will likely occur in other systems in which the inserting molecules possess bulky head groups (e.g., fullerenes or similarly large functional groups).

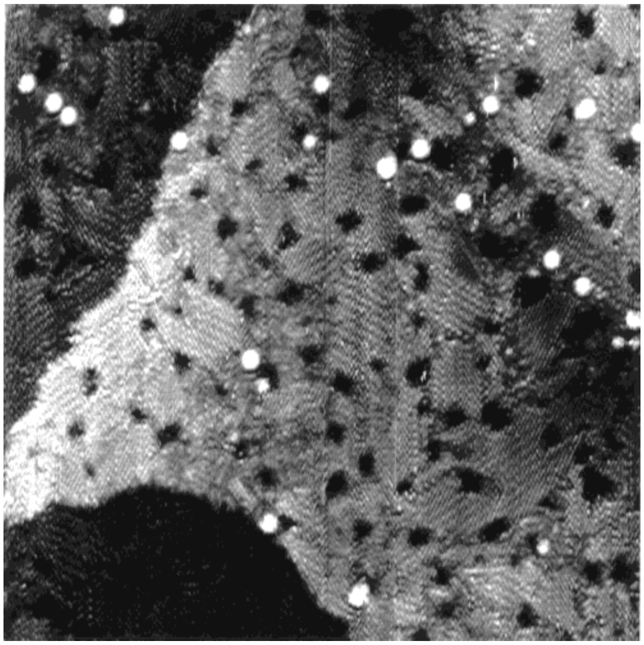

Figure 4. A 75 × 75 nm image of the long-chain C_{60} disulfide inserted into a decanethiolate SAM. The tunneling parameters were $V_{\text{bias}} = +1.0$ V and $I_t = 20$ pA.

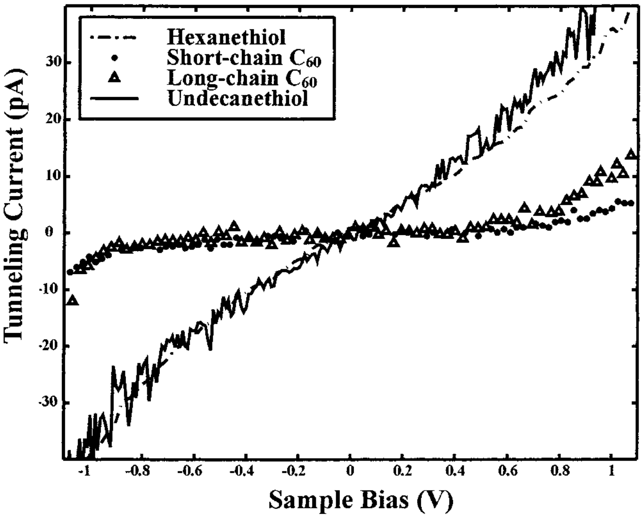

Figure 5. Scanning tunneling spectroscopy obtained both on and away from the short-chain and long-chain disulfides inserted into hexanethiol and undecanethiol matrixes, respectively. The tunneling gap was fixed at +1 V and 50 pA for all measurements.

We also explored the electronic properties of the inserted molecules through scanning tunneling spectroscopy (STS). The insertion method has been previously shown to be ideal for studying the electronic properties of isolated molecules.[7] The spectroscopic measurements were performed in the following manner. First, the region of interest was scanned in topographic mode after which points for STS were selected. On the subsquent scan, the I−V curves were acquired simultaneously with the topographic image, assuring the location of the STS over the molecules. The curves obtained for the alkylthiol and the derivatized C_{60} were taken with the same tip in the case of each film, but in some cases different tips were used for different films. We found almost no variation in the STS results between different tips. Displayed in Figure 5 are the current-versus-voltage (I−V) curves taken both on and away from the short-chain and long-chain disulfides inserted into hexanethiol and undecanethiol matrixes, respectively. The near-linearity of the alkanethiol spectra are in good agreement with previously published I−V data acquired under the same conditions.[16,17] The similar curves obtained from the different alkanethiols can be rationalized by the fact that tunneling through these molecules occurs nonresonantly with a decay constant similar to that of free space, and that all I−V curves were acquired under similar gap impedances.[18] However, it should not be inferred from this data that the conductivity of the two alkanethiolates are necessarily equivalent. Due to the configuration of the STM junction, a more detailed analysis including I−Z measurements would be necessary to obtain the actual conductivity of the alkyl chains.[18,19]

The ∼2 eV bandgap measured for the inserted fullerene disulfides is similar to the spectra measured for a second monolayer of C_{60} molecules on a gold surface but drastically different from those measured for a single C_{60} monolayer on gold.[11] In the latter studies, the electronic difference between the first and second fullerene monolayers arose from a charge-transfer interaction with the gold surface. Similar charge-transfer effects of C_{60} on gold and other metal surfaces have also been observed by ultraviolet photoemission spectroscopy and high-resolution electron energy loss spectroscopy.[20−24] Our results, in contrast, suggest that there is very little coupling between the molecular levels of the fullerene disulfides and the underlying gold surface. Consequently, unlike previous fullerene monolayers formed on metal surfaces, the fullerene disulfides appear to retain the semiconducting properties of bulk C_{60}. The symmetric character of the functionalized C_{60} spectra can be rationalized in terms of the chemical potential and applied bias voltage, and is similar to that observed on certain other SAM systems.[25] The symmetry of the states is a reflection of how effectively the molecular energy levels are affected by the metal reservoir of electrons. Thus, our data indicate that both alkyl chains can serve as a highly effective insulating layer inhibiting charge-transfer between the C_{60} molecule and the gold surface. This effect has been seen with a similar hydrocarbon SAM on Si, where the leakage current was found to be independent of monolayer thickness.[26] The shortest alkyl chain investigated in that study, however, consisted of twelve carbon atoms. Our results demonstrate that similar insulating characteristics apply for alkyl chains of half that length.

In conclusion, we have investigated the adsorption of C_{60}-functionalized dialkyl disulfides onto Au(111) with the STM. We have demonstrated that the fullerene disulfides can be inserted into alkanethiol matrixes of varying chain length. From these experiments, we observe differences in the adsorption dynamics that depend on the relative chain lengths of the fullerene disulfide and the underlying alkanethiol matrix. The insertion technique also permitted the electrical characterization of isolated tethered fullerenes. The tunneling spectroscopy of these molecules indicate that the C_{60} moieties maintain their semiconducting nature even when the length of the alkyl chain separating it from the metal surface is as short as six methylene units. By using a molecular semiconductor instead of a bulk one, this work represents an important step in the creation of an all-organic electronic device. Although we are confident that techniques such as annealing may lead to ordered films, we have not yet observed this characteristic for the molecules used in this study. This technique should also prove useful for probing the electronic effects of other chemical modifications made to fullerene molecules.

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