

Effects of Hindered Internal Rotation on Packing and Conductance of Self-Assembled Monolayers

Arrelaine A. Dameron,[†] Jacob W. Ciszek,[‡] James M. Tour,^{*,‡} and Paul S. Weiss^{*,†}

Departments of Chemistry and Physics, The Pennsylvania State University, 104 Davey Laboratory, University Park, Pennsylvania 16802-6300, and Department of Chemistry and Center for Nanoscale Science and Technology, Rice University, Houston, Texas 77005-1892

Received: February 6, 2004; In Final Form: June 21, 2004

Self-assembled monolayers of 4-thiobiphenyl and 2-thiophenanthrene molecules on Au{111} were probed using scanning tunneling microscopy (STM) to investigate their assembled order, to measure the conductance through them, and to determine what molecular features are necessary for molecules to exhibit conductance switching. The 4-thiobiphenyl molecules assemble into two distinct packing structures, whereas no order is observed for 2-thiophenanthrene. Both molecules show rectifying behavior, but although 4-thiobiphenyl is more conductive at positive sample biases, 2-thiophenanthrene is more conductive at negative sample bias. Individual molecules of each type were also inserted into alkanethiol SAMs and tracked over several hours to investigate the conductance states of each molecule. Both molecules exhibit two conductance states, indicating that internal ring rotation is not required for conductance switching.

Introduction

The current objective of the field of molecular electronics is to derive ways to fabricate and to control individual molecular components so that one may couple them into nanoscale devices. Although control of local placement and molecular stability are essential for the fabrication of molecular devices, understanding conductance through nanoscale molecular assemblies aids in our ability to manipulate and to interface the assemblies with one another as well as with existing devices.¹ Our groups use synthetic chemistry and self-assembly to place conductive molecules in well-defined environments for study with scanning tunneling microscopy (STM).

Many groups^{2–8} have engineered molecules for molecular electronics (such as those containing a high degree of conjugation from the electron delocalization through π -bonds, leading to enhanced electron transfer⁹) and have experimented with functional group placement. By measuring the electronic properties of these molecules it should be possible to find general trends in conductivity with changes in structure. We have used the completely rigid, planar structure of 2-thiophenanthrene to take advantage of the conductivity of the π -band overlap, increased girth and rotational inflexibility afforded by such a configuration. It is expected that these considerations will have effects on both the molecule's configuration in self-assembled monolayers (SAMs) and its conductance.

Self-assembly uses the inherent chemical and physical properties of molecules to form controlled local geometries on a variety of substrates.¹⁰ Since their inception, much progress has been made in the fabrication of SAMs, and they are now accepted as a major component in many types of molecular assemblies because of their ease of preparation, stability and

high structural order.^{11–15} They have been used as insulating layers and a matrix in which a molecule of interest can be studied.^{16–19} SAMs are much more dynamic than thin films prepared from molecular beam epitaxy^{20,21} or chemical vapor deposition,^{11,22,23} and can be formed from a variety of molecules ranging in size and functionality.^{12,24–29} In addition to self-assembling the molecules themselves, we have also used alkanethiolate SAMs as a reproducible means to insert individual guest molecules for our conductance studies.

There are many quantitative ensemble measurements of conductance such as optical spectroscopy^{11,24,30} and electrochemistry,^{31–33} but measurements of one molecule (or a very few) are more difficult and rely on techniques such as lithographically fabricated pores or contacts,^{34–36} break junctions,^{35,37} and mercury drop^{38–40} experiments. However, determining whether the measured electronic properties of an assembly are a result of one molecule or a few molecules is often difficult. Scanning probe techniques such as STM and atomic force microscopy (AFM) have the advantage of localized imaging on the molecular scale.^{1,19,24,30} Furthermore, few techniques allow for the simultaneous electronic and topographic characterization on the nanoscale that is possible with the STM. Here we use ambient STM to characterize the topography of two molecules, 4-thiobiphenyl and 2-thiophenanthrene (Figure 1), self-assembled on a Au{111} substrate. Using STM, a circuit is created with the molecule chemically attached to one electrode (the Au{111} substrate) and the STM tip as the second electrode (although detached because of the tunneling gap). With this circuit, the electrical properties, in addition to the topographic features of each molecule are measured individually. These molecules switch conductance states when inserted into alkanethiolate matrices (Figure 1), as has been shown previously for similar molecules.⁴¹ The structures and conductivities of both 4-thiobiphenyl and 2-thiophenanthrene SAMs as well as their behavior after insertion into alkanethiolate SAMs are discussed.

* To whom correspondence should be addressed. E-mail: stm@psu.edu (PSW); tour@rice.edu (JMT).

[†] The Pennsylvania State University.

[‡] Rice University.

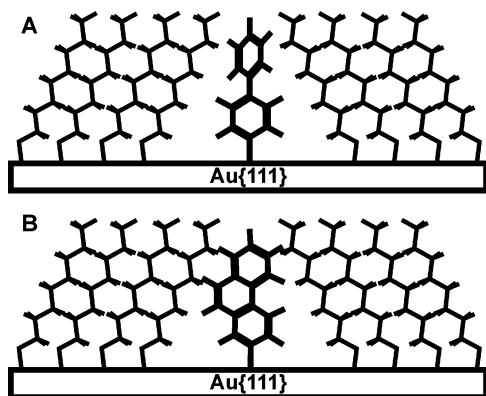


Figure 1. Schematics depicting insertion into an example of a defect in alkanethiol SAMs. (A) 4-thiobiphenyl inserted into an octanethiol SAM; (B) 2-thiophenanthrene inserted into an octanethiol SAM.

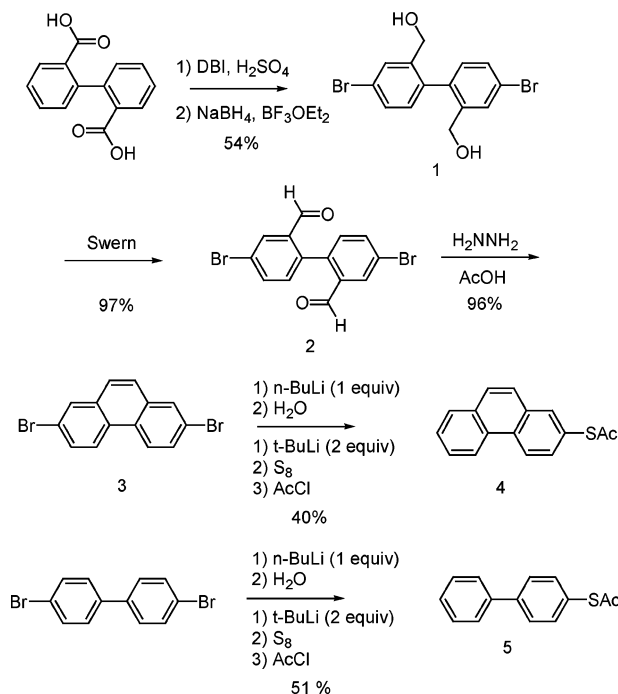


Figure 2. Synthetic scheme for 2-thioacetophenanthrene and 4-thioacetobiphenyl.

Experimental Methods

The detailed protocols of the syntheses have been described separately.⁴² In brief, the path to 2,7-dibromophenanthrene (**3**) (Figure 2) begins with diphenic acid, which is brominated with dibromoisocyanuric acid (DBI) to afford a mixture of brominated isomers that are subsequently reduced to the diols and separated to yield **1**. Swern oxidation of **1** gave the dialdehyde **2** followed by cyclization⁴³ to **3**. Hence **3** can now be synthesized in large quantities with an overall yield of 50% over three steps. The best previous methodology produced this simple material in only 16% overall using the more expensive dihydrophenanthrene and the now difficult to obtain solvent CCl₄.^{44–46} With **3** and the commercially available 4,4'-dibromobiphenyl halogenated precursors in hand, they could both be converted to a form conducive to ordered assembly in the STM testbed. The acetyl-protected form of the thiol is used since it is far easier to handle (it is not prone to oxidative dimerization as the thiol is) and can be deprotected in situ.⁴⁷ As shown in Figure 2, **4** and **5** were synthesized by monolithiation of the dihalide using *n*-butyllithium followed by quenching with water to give a mixture primarily containing the monohalogenated

compounds. This mixture was then treated with *tert*-butyllithium, followed by sulfur and acetyl chloride to give the monothioacetates after column chromatography.⁴⁸ Formation of the thioacetates in this manner proved to be simpler than selective monohalogenation of the aromatic core.

Sample Preparation

SAMs are assembled on Au{111} via solution deposition. Commercially available Au{111} on mica substrates (Molecular Imaging, Phoenix, AZ) are annealed just prior to deposition using a hydrogen flame. Alkanethiolate SAMs are prepared by immersing the annealed substrates in a 1 mM in ethanol solution for 24 h. The 4-thiobiphenyl and 2-thiophenanthrene SAMs are made using 1 mM in THF with 0.4 mM ammonium hydroxide to remove the acetyl protecting groups. 4-thiobiphenyl SAMs are made using protected or unprotected thiols and there is no observable difference in SAM quality. Postdeposition, each sample is rinsed in neat ethanol and blown dry twice with nitrogen. Insertion is performed in an oxygen free environment by exposing the assembled alkanethiol SAMs to nanomolar concentrations of the guest molecules in THF (and ammonium hydroxide, if deprotection is necessary) for a short period ranging from seconds to minutes. These samples are then rinsed with neat THF and dried with nitrogen before being exposed to air, rinsed with neat ethanol, and dried again with nitrogen before scanning with the STM. All samples are stored in a desiccator at room temperature. Although the SAMs remain stable for weeks, all experiments are performed within 48 h of fabrication of the samples. All STM and scanning tunneling spectroscopy (STS) measurements are performed under ambient conditions using custom-built STM, electronics, and software.^{49,50}

Results and Discussion

From theory, in solution the lowest energy conformation of a biphenyl molecule (it is presumed that the 4-thiobiphenyl will behave similarly) is with a $\sim 40^\circ$ offset between the two phenyl rings.^{51–53} This is due to competition between the energetically favorable π -bond overlap and the energetically unfavorable hydrogen steric repulsion that occurs in a planar formation. The maximum of the barrier to rotation from the lowest energy conformation to either a planar or an orthogonal conformation is calculated to be ~ 87 meV.^{51,52} In addition, there is a slight deformation of the middle carbon–carbon bond (less than 0.2 Å) between the two conformations.⁵¹ The 4-thiobiphenyl molecule is therefore estimated as 4.3 Å across and 12.4 Å long.⁴⁷

The planar 2-thiophenanthrene has a dissociation energy for the aromatic carbon–carbon bond, estimated from studies of benzene on copper substrates, as ~ 3 eV.^{54,55} From calculations performed on ethylene complexes,^{56,57} the rotational barrier around the central bond is assumed to be greater than 1.7 eV. Together, these estimations demonstrate that the movement of any of the phenyl rings of 2-thiophenanthrene out of a planar conformation is unlikely at room temperature ($kT \approx 26$ meV). All of the carbon–carbon bonds are assumed aromatic, and therefore, the 2-thiophenanthrene molecule is estimated to be 5.6 Å across and 12.3 Å long.

SAM Structures

STM images of the 4-thiobiphenyl and 2-thiophenanthrene SAMs are shown in Figure 3. As has been observed for similar self-assembled thiolate systems,^{27,29} both molecules greatly

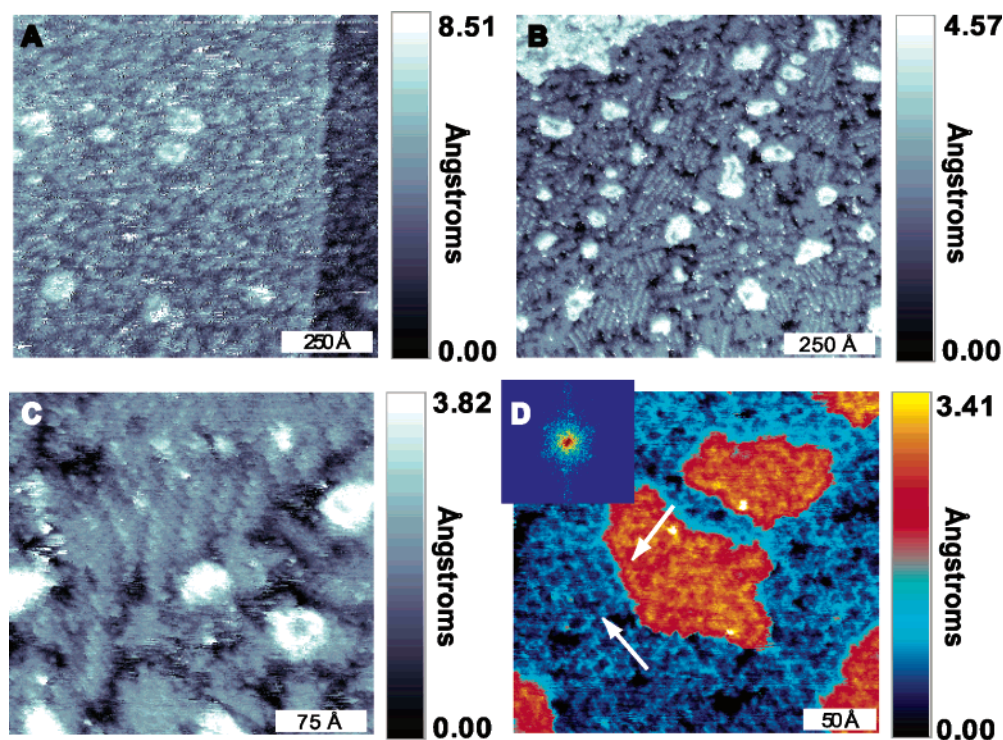


Figure 3. STM images of a 4-thiobiphenyl and 2-thiophenanthrene SAMs. Both molecules greatly reorganize the Au{111} substrate upon deposition, but while 4-thiobiphenyl shows two packing structures, 2-thiophenanthrene shows no perceivable order. (A) A 2-thiophenanthrene SAM deposited from solution for 24 h. 1000 Å × 1000 Å, sample bias: 1 V, current: 1 pA. (B) A 4-thiobiphenyl SAM deposited from solution for 30 min showing domains of striped phase and smaller but greater numbers of Au substrate islands. 1000 Å × 1000 Å, sample bias: 750 mV, current: 2 pA. (C) A 4-thiobiphenyl SAM deposited from solution for 30 min. 300 Å × 300 Å, sample bias: 750 mV, current: 2 pA. (D) A 4-thiobiphenyl SAM deposited from solution for 36 h with larger and fewer Au substrate islands as well as resolution of the well-ordered SAM and the respective FFT showing the hexagonal lattice. 200 Å × 200 Å, sample bias: 750 mV, current: 2 pA.

affect the gold substrate, creating jaggedness at the step edges as well as islands and vacancies comparable in height to one atomic layer of gold.

Shown in Figure 3B–D are two observed structures for the 4-thiobiphenyl SAM. A primarily striped phase is observed for insertion times up to 12 h, a hexagonal close-packed formation is observed for insertion times longer than 30 h and a mix of both phases is seen for insertion times between 12 and 30 h. In the striped phase, the molecules assemble in rows in three orientations that are rotated 60° from one another. In this conformation, the molecules lie along the surface with a measured apparent height difference from head to tail of 1.8 ± 0.3 Å. This apparent height difference is a convolution of geometric and electronic structure and is not easily interpreted in terms of a molecular tilt; the difference is most likely due to the relative position of the aromatic units rotated around the molecular axis, which is nearly parallel to the surface.^{10,26} The measured distance between rows is ~ 21 Å and the distance along the rows of ~ 11 Å, corresponding to a square packing structure similar to that seen for methyl-4'-mercaptobiphenyl.^{10,11,26}

In the hexagonal close-packed formation, the molecules demonstrate a zigzag orientation with respect to each other with a nearest neighbor distance of 4.7 ± 0.5 Å (measured from the two-dimensional Fourier transform of the STM images shown in Figure 3D), which corresponds to the preferred sulfur orientation on Au{111} of $(\sqrt{3} \times \sqrt{3}) R30^\circ$.^{11,25,29} The formation of this zigzag structure can be seen in Figure 3D as the mottled slight protrusions and depressions (shown as lighter and darker blue) throughout the image. In addition, there is alignment of the molecules perpendicular to the step edges that is most visible on the Au islands (Figure 3D, middle island).

No instance of a well-ordered 2-thiophenanthrene SAM has been observed (Figure 3A) for either long or short deposition times. At longer deposition times (greater than 24 h), the surface becomes increasingly difficult to image with the STM. The width of the 2-thiophenanthrene molecule prevents it from packing in either of the two biphenyl orientations. It has been shown that the phenyl rings of the biphenyl molecule are oriented askew in the striped phase and it is presumed that internal rotation helps to achieve a minimum packing energy,²⁶ something that is not possible for the fused rings of the 2-thiophenanthrene molecule.

Molecular Conductance

The conductances of both kinds of SAMs were measured using STS. For these measurements, at chosen points during imaging, the probe tip stops at those points, the feedback loop controlling the STM the tip–sample separation is blanked and the voltage is ramped while recording the current. The voltage is ramped in forward and reverse directions for several sweeps (usually three). Between each sweep, the feedback loop is reset to compensate for any drift in the tip–sample separation during the previous sweep and the imaging tunneling conditions are reestablished. After recording the spectra at one point, imaging resumes until the next selected point.

From Figure 4, parts A and B, it can be seen that reproducible current versus voltage curves are generated regardless of the area of the SAM that is chosen for spectroscopy, further indicating that the observed islands are due to substrate mesas and are not multilayers of the SAM.

Figure 4, parts C and D, shows the current versus voltage and conductance spectra over the two types of SAMs taken at

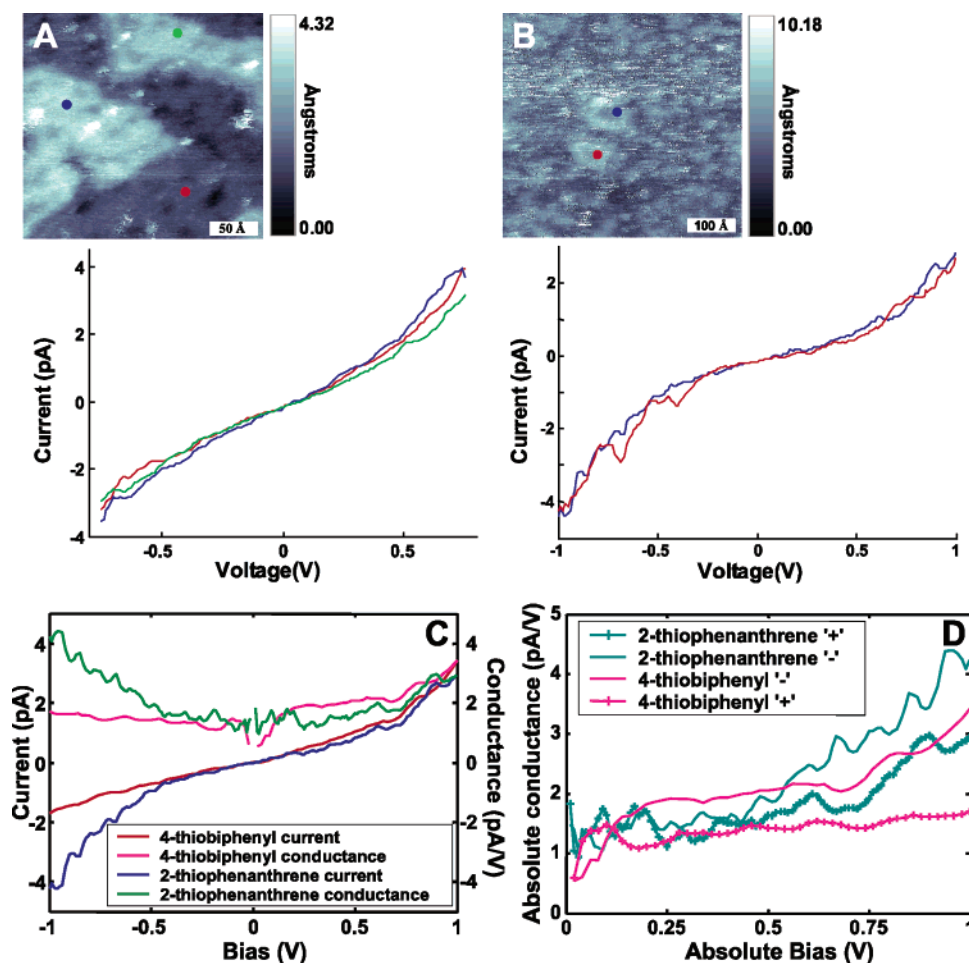


Figure 4. Current versus voltage spectra of the 4-thiobiphenyl and 2-thiophenanthrene SAMs. (A) Three representative points of a 4-thiobiphenyl matrix and their spectra. Image size: $250 \text{ \AA} \times 250 \text{ \AA}$, sample bias: 750 mV, current: 3 pA. (B) Two representative points over a 2-thiophenanthrene SAM and their spectra. Image size: $500 \text{ \AA} \times 500 \text{ \AA}$, sample bias: 1 V, current: 3 pA. (C) A comparison of representative current versus voltage and conductance versus voltage plots for both 4-thiobiphenyl and 2-thiophenanthrene SAMs taken with the same setpoint of sample bias: 1 V and current: 2 pA. Note: At each point the feedback was blanked and three sweeps were made in the forward and reverse direction. The spectra shown are each averages of the three sweeps. (D) The same conductance curves from C plotted as absolute conductance versus absolute bias.

the same setpoint. In the positive sample bias regime, the 4-thiobiphenyl SAM increases steadily up to 0.5 V, when the conductance suddenly increases. Between -0.4 and $+0.4$ V, the SAM shows a nearly linear conductance of ~ 1.5 pA/V. This trend continues for negative sample biases with only a very small increase in conductance for sample biases below -0.4 V. This results in an asymmetric curve with a 1.5 pA/V difference in conductance between -1 and $+1$ V.

The 2-thiophenanthrene SAM behaves nearly identically in the positive regimes. It also shows linear trends between ± 0.4 V, almost overlapping the 4-thiobiphenyl spectrum. At voltages below -0.4 V, however, the SAM greatly increases conductance down to -1 V, when it exceeds the conductance at $+1$ V by 1 pA/V.

Seen most clearly in Figure 4D, both SAMs display asymmetric conductance curves, although the 2-thiophenanthrene spectrum is more symmetric. The 2-thiobiphenyl SAM is more conductive at positive sample bias, whereas the 4-thiophenanthrene SAM is more conductive at the opposite polarity.

We attribute the asymmetry observed for both molecules to the sulfur–gold contacts in the circuit.⁵⁸ At the metal–molecule interface, there is a thiolate bond to the gold through which electrons can flow, but on the tip side of the molecule, there is only a terminal aromatic ring and small gap through which the electrons must tunnel. This difference in bonding may cause a

Schottky barrier responsible for the observed rectification.⁵⁸ We discount that the anomaly is a result of drift of the tip–sample separation during data acquisition, because this trend remains at many points within the SAM and occurs for many tunneling conditions.

The difference in conductance between the 4-thiobiphenyl and the 2-thiophenanthrene we attribute to increased π -orbital overlap in the 2-thiophenanthrene molecule because of the fused aromatic rings that constrain the molecule to being coplanar, thus maximizing the π -orbital overlap. However, it is expected that the enhanced conductance because of π -orbital overlap would be observed at both positive and negative biases. It may be that for the small bias range measured the observed asymmetry of the contacts has a larger influence on the overall conductance than the comparative conductances of the molecules. We do not believe that *this* conductance difference arises from molecular motion due to forces applied by the electric field due to the tip via the molecular dipole.^{10,59} The molecules here have similar dipoles and would be expected to behave similarly to a tip-induced electric field.

Insertion into Alkanethiolate SAMs

To understand what effect the geometry of molecules has on their conductance states, both the 2-thiophenanthrene and the 4-thiobiphenyl molecules were inserted into octanethiolate

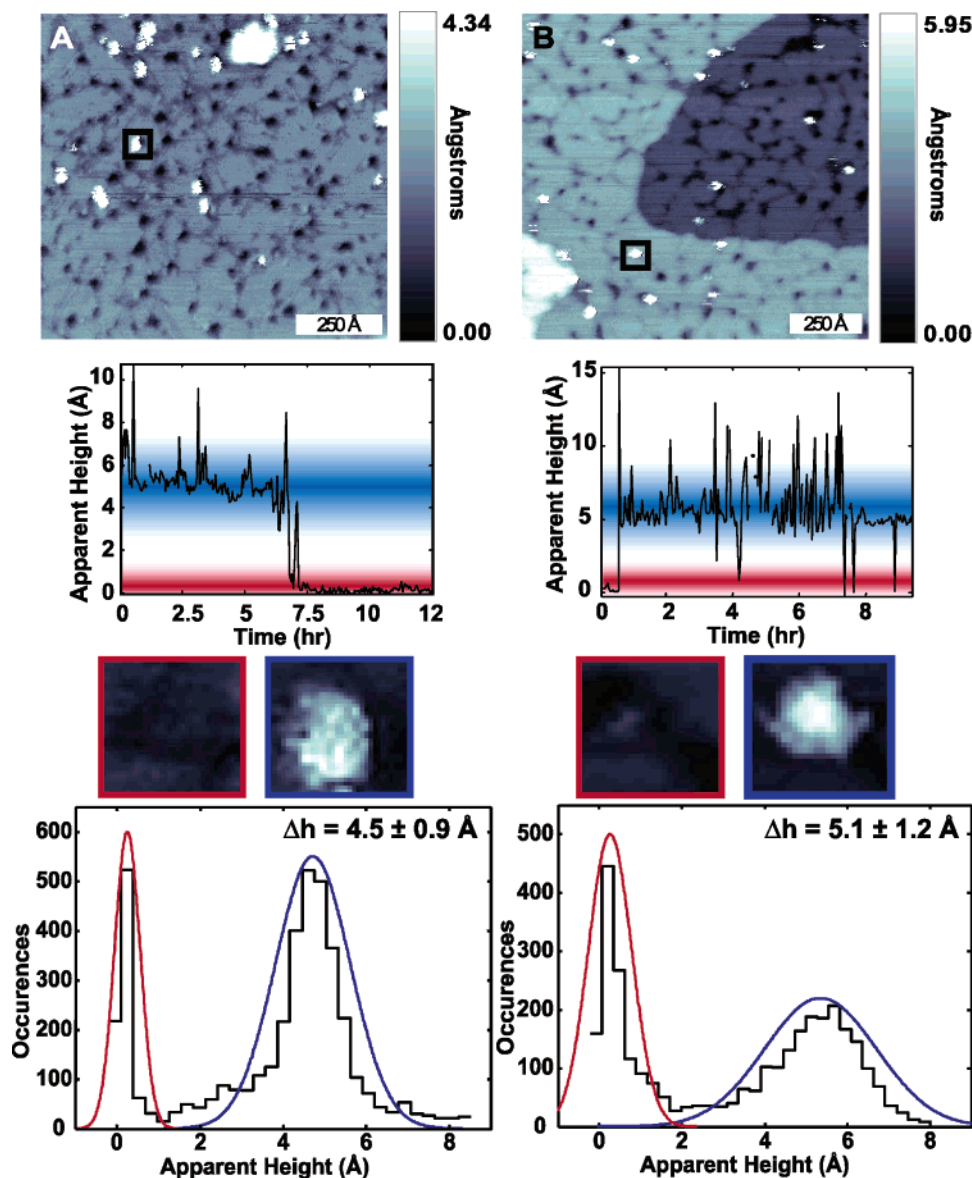


Figure 5. Height distributions for 4-thiobiphenyl (A) and 2-thiophenanthrene (B). For each distribution the ON (blue) and OFF (red) heights are shown with typical correlating images and a height versus time plot for one representative molecule (black circle). The distribution data are digitally extracted from sequential images taken over ≥ 10 h. Tunneling conditions: $1200 \text{ \AA} \times 1200 \text{ \AA}$, sample bias: 1 V, current: 3 pA. (A) Octanethiol SAM with 4-thiobiphenyl inserted $h_{\text{on}} = 4.7 \pm 0.9 \text{ \AA}$, $h_{\text{off}} = 0.3 \pm 0.2 \text{ \AA}$ (b) Octanethiol 24 h SAM with 2-thiophenanthrene inserted $h_{\text{on}} = 5.4 \pm 1.1$, $h_{\text{off}} = 0.4 \pm 0.2 \text{ \AA}$.

SAMs and were studied on individual bases. Insertion of the molecules into SAMs reproducibly isolates each molecule (or small bundle of molecules) from one another and restricts them to the SAM defects and gold step edges, thus controlling the placement of the molecule within the SAM.^{16–18} At these sites, the guest molecules insert nearly normal to the surface with the headgroups adhering to the exposed gold and the conjugated region of the molecule sticking up out of the SAM.^{16–18} Similar to the methods reported previously,⁴¹ large areas ($1200\text{--}1700 \text{ \AA}$ on a side) are imaged repeatedly for 10 or more hours. The data for each molecule are extracted from those images and the statistics for many individual molecules are extracted simultaneously. Using tracking software,^{60,61} the data extracted from each image are correlated to the next image to piece together the conductance history (as observed by changes in apparent height) over the duration of the movie (a collection of sequential images). An example apparent height versus time plot for the duration of the movies is given for each type of molecule in Figure 5. As discussed elsewhere, the apparent height changes

of the molecules throughout the duration of the movie are not correlated to any changes in tip geometry, changes of the gold substrate, or movement across substrate step edges.^{41,61,62} It is also possible to distinguish single molecules from bundles of molecules and to interpret separately each molecule's conductance state.⁶¹ It should be noted that this sampling method favors molecules that start in or switch to a high conductance state, as molecules in a high conductance state are more easily discernible from the surrounding matrix and are therefore more likely to be included.

As shown by the histogram (extracted from a 250 frame movie taken over a ~ 12 h period) in Figure 5A, the 4-thiobiphenyl demonstrates two conductance states: a high conductance state, termed ON (blue), and a low conductance state, termed OFF (red). From Gaussian fits to the distributions, the difference in apparent height of the ON and OFF states is $4.5 \pm 0.9 \text{ \AA}$. The apparent height of the molecule is measured from the height of the SAM and changes with the height of the SAM. Although an OFF state is usually still visible protruding from

the SAM, any molecule that falls below the level of the SAM will have an apparent height of zero resulting in narrower distributions for the OFF states.

The 2-thiophenanthrene also exhibits two conductance states, with an apparent height difference between them of 5.1 ± 1.2 Å. The topographic height of these two molecules normal to the surface is comparable, so the deviations in apparent height are associated with differences in conductance. It is expected that the 2-thiophenanthrene molecule is more conductive because of the increased conjugation of the middle ring extending the overlap of the π orbitals.^{62–64} The existence of switching in the 2-thiophenanthrene molecule eliminates internal ring rotation as the sole mechanism responsible for the change in conductance states. In addition, internal rotation of biphenyl at room temperature would give states that are too short-lived to be observed by these methods.^{8,63,64}

Qualitatively, the 2-thiophenanthrene molecules switch states less frequently and favor the off state. This is quantitatively verified by the calculated ON/OFF ratios (calculated from the areas under the Gaussian fits) of 2.45 for the 2-thiophenanthrene and 4.61 for the 4-thiobiphenyl molecules. Considering that both molecules are in similar environments, this difference can be explained by the degrees of freedom available to each molecule. In both cases, the alkanethiol SAM is surrounding the molecule (see Figure 1). Due to size and rotation constraints, the 2-thiophenanthrene molecule needs larger defect sites to be able to insert and to have the same degrees of freedom afforded to the 4-thiobiphenyl. For the same defect site, one would expect that the biphenyl is more likely to switch, but we do not know if the distributions of sites at which the two molecules insert are equivalent. Theory predicts that a tilted thiolate bond is the energetically favorable and a more conductive (ON) molecular conformation, although it is not possible to measure experimentally only the thiolate-substrate bond angle with the STM.^{9,65,66} It is expected that a molecule that is increasingly constrained by the host SAM is less likely to undergo motion that will result in a dramatic change of conductivity.

Conclusions

In order for the mechanism of molecular switching to be more fully understood, 2-thiophenanthrene has been used to maximize the conductance and to minimize the mechanical freedom present in 4-thiobiphenyl. The mechanical hindrances are apparent in the structural order of the SAMs made from each molecule. The 2-thiophenanthrene SAMs exhibit no observable ordered structures, regardless of insertion time. 4-thiobiphenyl SAMs display two packing structures with a primarily striped phase for insertion times less than 12 h and a hexagonal phase for insertion times greater than 30 h. Conductively, the 2-thiophenanthrene SAMs are slightly more symmetric around zero sample bias than the 4-thiobiphenyl SAMs, although further investigation of the system is needed. Upon insertion into alkanethiolate SAMs, both molecules exhibit similar bistable conductance switching. While internal rotation is therefore not the sole mechanism responsible for conductance switching, it does allow the molecules to relax conformationally within the matrix, making switching more likely.

Acknowledgment. The authors acknowledge Brent Mantooth and Penelope Lewis for their experimental and analytical assistance and Kevin Kelly and Charlie Sykes for their helpful discussions. The Army Research Office, Defense Advanced Research Projects Agency, National Science Foundation, and Office of Naval Research are gratefully acknowledged for their support.

Supporting Information Available: A detailed description of the synthesis of 2-thioacetyl-biphenyl. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- Bumm, L. A.; Arnold, J. J.; Dunbar, T. D.; Allara, D. L.; Weiss, P. S. *J. Phys. Chem. B* **1999**, *103*, 8122.
- Dirk, S. M.; Tour, J. M. *Tetrahedron* **2003**, *59*, 287.
- Flatt, A. K.; Tour, J. M. *Tetrahedron Lett.* **2003**, *44*, 6699.
- Hwang, J. J.; Tour, J. M. *Tetrahedron* **2002**, *58*, 10387.
- Price, D. W.; Tour, J. M. *Tetrahedron* **2003**, *59*, 3131.
- Price, D. W.; Dirk, S. M.; Maya, F.; Tour, J. M. *Tetrahedron* **2003**, *59*, 2497.
- Tour, J. M.; Rawlett, A. M.; Kozaki, M.; Yao, Y. X.; Jagessar, R. C.; Dirk, S. M.; Price, D. W.; Reed, M. A.; Zhou, C. W.; Chen, J.; Wang, W. Y.; Campbell, I. *Chem. Eur. J.* **2001**, *7*, 5118.
- Reed, M. A.; Chen, J.; Rawlett, A. M.; Price, D. W.; Tour, J. M. *Appl. Phys. Lett.* **2001**, *78*, 3735.
- Sellers, H.; Ulman, A.; Shnidman, Y.; Eilers, J. E. *J. Am. Chem. Soc.* **1993**, *115*, 9389.
- Ulman, A. *Acc. Chem. Res.* **2001**, *34*, 855.
- Kang, J. F.; Ulman, A.; Liao, S.; Jordan, R.; Yang, G. H.; Liu, G. Y. *Langmuir* **2001**, *17*, 95.
- Azzam, W.; Cyganik, P.; Witte, G.; Buck, M.; Woll, C. *Langmuir* **2003**, *19*, 8262.
- Kelly, K. F.; Shon, Y. S.; Lee, T. R.; Halas, N. J. *J. Phys. Chem. B* **1999**, *103*, 8639.
- Allara, D. L.; Dunbar, T. D.; Weiss, P. S.; Bumm, L. A.; Cygan, M. T.; Tour, J. M.; Reinherth, W. A.; Yao, Y.; Kozaki, M.; Jones, L. In *Molecular Electronics: Science and Technology*; New York Academy of Sciences: New York, 1998; Vol. 852, p 349.
- Smith, R. K.; Lewis, P. A.; Weiss, P. S. *Prog. Surf. Sci.* **2004**, *75*, 1.
- Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.
- Dunbar, T. D.; Cygan, M. T.; Bumm, L. A.; McCarty, G. S.; Burgin, T. P.; Reinherth, W. A.; Jones, L.; Jackiw, J. J.; Tour, J. M.; Weiss, P. S.; Allara, D. L. *J. Phys. Chem. B* **2000**, *104*, 4880.
- Cygan, M. T.; Dunbar, T. D.; Arnold, J. J.; Bumm, L. A.; Shedlock, N. F.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *J. Am. Chem. Soc.* **1998**, *120*, 2721.
- Lewis, P. A.; Donhauser, Z. J.; Mantooth, B. A.; Smith, R. K.; Bumm, L. A.; Kelly, K. F.; Weiss, P. S. *Nanotechnology* **2001**, *12*, 231.
- Forrest, S. R. *Chem. Rev.* **1997**, *97*, 1793.
- Koma, A. *Prog. Cryst. Growth Ch.* **1995**, *30*, 129.
- Takeishi, S.; Kudo, H.; Shinohara, R.; Hoshino, M.; Fukuyama, S.; Yamaguchi, J.; Yamada, M. *J. Electrochem. Soc.* **1997**, *144*, 1797.
- Li, H. B.; Sharma, R. K.; Zhang, Y.; Tay, A. A. O.; Kang, E. T.; Neoh, K. G. *Langmuir* **2003**, *19*, 6845.
- Stapleton, J. J.; Harder, P.; Daniel, T. A.; Reinard, M. D.; Yao, Y. X.; Price, D. W.; Tour, J. M.; Allara, D. L. *Langmuir* **2003**, *19*, 8245.
- Sabatani, E.; Cohenboulakia, J.; Bruening, M.; Rubinstein, I. *Langmuir* **1993**, *9*, 2974.
- Leung, T. Y. B.; Schwartz, P.; Scoles, G.; Schreiber, F.; Ulman, A. *Surf. Sci.* **2000**, *458*, 34.
- Ishida, T.; Mizutani, W.; Azebara, H.; Miyake, K.; Aya, Y.; Sasaki, S.; Tokumoto, H. *Surf. Sci.* **2002**, *514*, 187.
- Frey, S.; Shaporenko, A.; Zharnikov, M.; Harder, P.; Allara, D. L. *J. Phys. Chem. B* **2003**, *107*, 7716.
- Dhirani, A. A.; Zehner, R. W.; Hsung, R. P.; Guyot-Sionnest, P.; Sita, L. R. *J. Am. Chem. Soc.* **1996**, *118*, 3319.
- Zhang, W. W.; Ren, X. M.; Li, H. F.; Lu, C. S.; Hu, C. J.; Zhu, H. Z.; Meng, Q. J. *J. Colloid Interface Sci.* **2002**, *255*, 150.
- Protsailo, L. V.; Fawcett, W. R.; Russell, D.; Meyer, R. L. *Langmuir* **2002**, *18*, 9342.
- Schweiss, R.; Werner, C.; Knoll, W. *J. Electroanal. Chem.* **2003**, *540*, 145.
- Reese, S.; Fox, M. A. *J. Phys. Chem. B* **1998**, *102*, 9820.
- Zhou, C.; Deshpande, M. R.; Reed, M. A.; Jones, L.; Tour, J. M. *Appl. Phys. Lett.* **1997**, *71*, 611.
- Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. *Science* **1997**, *278*, 252.
- Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, *286*, 1550.
- Reed, M. A.; Zhou, C.; Deshpande, M. R.; Muller, C. J.; Burgin, T. P.; Jones, L.; Tour, J. M. In *Molecular Electronics: Science and Technology*; New York Academy of Science: New York, 1998; Vol. 852, p 133.

- (38) Slowinski, K.; Fong, H. K. Y.; Majda, M. *J. Am. Chem. Soc.* **1999**, *121*, 7257.
- (39) Slowinski, K.; Majda, M. *J. Electroanal. Chem.* **2000**, *491*, 139.
- (40) Rampi, M. A.; Whitesides, G. M. *Chem. Phys.* **2002**, *281*, 373.
- (41) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **2001**, *292*, 2303.
- (42) Ciszek, J. W.; Tour, J. M. *Tetrahedron Lett.*, **2004**, *45*, 2801.
- (43) Bacon, R. G. R. L.; W. S. *J. Chem. Soc.* **1958**, *80*, 1375.
- (44) Miller, J. C.; Meek, J. S.; Strickler, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 8175.
- (45) Bochenkov, V. N. *J. Org. Chem. USSR (Engl. Transl.)* **1977**, *12*, 2355.
- (46) Brown, W. G. B., B. A. *J. Am. Chem. Soc.* **1943**, *65*, 1235.
- (47) Tour, J. M.; Jones, L.; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529.
- (48) Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376.
- (49) Bumm, L. A.; Arnold, J. J.; Charles, L. F.; Dunbar, T. D.; Allara, D. L.; Weiss, P. S. *J. Am. Chem. Soc.* **1999**, *121*, 8017.
- (50) Mantooth, B. A.; Weiss, P. S. *WinSTM Data Aquisition Software* <http://stm1.chem.psu.edu/~bam/WinSTM/index.html>
- (51) Cacelli, I.; Prampolini, G. *J. Phys. Chem. A* **2003**, *107*, 8665.
- (52) Sadlej-Sosnowska, N. *J. Phys. Chem. A* **2003**, *107*, 8671.
- (53) In a crystal packing conformation, biphenyl is planar because the packing forces offset the steric hindrances. As a SAM, the barrier to rotation may differ from that in solution.
- (54) Lauhon, L. J.; Ho, W. *J. Phys. Chem. A* **2000**, *104*, 2463.
- (55) Hla, S. W.; Meyer, G.; Rieder, K. H. *Chem. Phys. Lett.* **2003**, *370*, 431.
- (56) Benassi, R.; Taddei, F. *J. Mol. Struct.-Theochem* **2001**, *572*, 169.
- (57) Taddei, F. *J. Mol. Struct. (THEOCHEM)* **2001**, *544*, 141.
- (58) Kushmerick, J. G.; Holt, D. B.; Yang, J. C.; Naciri, J.; Moore, M. H.; Shashidhar, R. *Phys. Rev. Lett.* **2002**, *89*.
- (59) Lewis, P. A.; Inman, C. E.; Yao, Y.; Tour, J. M.; Hutchison, J. E.; Weiss, P. S. *J. Am. Chem. Soc.* **2004**, *126*, 12214.
- (60) Mantooth, B. A.; Donhauser, Z. J.; Kelly, K. F.; Weiss, P. S. *Rev. Sci. Instrum.* **2002**, *73*, 313.
- (61) Moore, A. M.; Mantooth, B. A.; Donhauser, Z. J.; Weiss, P. S. In preparation.
- (62) Mantooth, B. A.; Weiss, P. S. *Proc. IEEE* **2003**, *91*, 1785.
- (63) Seminario, J. M.; De la Cruz, C. E.; Derosa, P. A. *J. Am. Chem. Soc.* **2001**, *123*, 5616.
- (64) Seminario, J. M.; Zacarias, A. G.; Derosa, P. A. *J. Phys. Chem. A* **2001**, *105*, 791.
- (65) Kornilovitch, P. E.; Bratkovsky, A. M. *Phys. Rev. B* **2001**, *64*19.
- (66) Emberly, E. G.; Kirczenow, G. *Phys. Rev. Lett.* **2003**, *91*.