

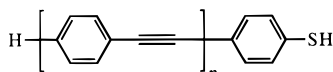
Self-Assembly of Conjugated Molecular Rods: A High-Resolution STM Study

Al-Amin Dhirani,[†] Robert W. Zehner,[‡] Richard P. Hsung,[‡] Philippe Guyot-Sionnest,^{*†} and Lawrence R. Sita^{*‡}

James Franck Institute, The University of Chicago
5640 South Ellis Avenue, Chicago, Illinois 60637, and
Searle Chemistry Laboratory, Department of Chemistry
The University of Chicago, 5735 South Ellis Avenue
Chicago, Illinois 60637

Received November 10, 1995

The formation, properties, and potential applications of self-assembled monolayers (SAMs) on metal and metal oxide surfaces have recently been demonstrated¹ and reviewed,² and it is clear that the investigation of these structures represents a target of opportunity for the discovery of new physical phenomena and technologies. In this regard, the determination of the nature and degree of order in a SAM can be a prerequisite for its eventual utilization, yet to date, only SAMs based on *n*-alkane systems [i.e., CH₃(CH₂)_{*n*}CH₂SH chemisorbed on the Au(111) surface³] have been characterized with molecular resolution.⁴ For this reason, the *n*-alkanethiol/Au(111) SAM model has become the most popular platform for experiments requiring a well-ordered structure. However, for the further investigation and utilization of monolayer assemblies, the need is great to develop and characterize new SAM systems that can rival those derived from *n*-alkanethiols with respect to order. Along these lines, we have undertaken investigations of the structures and properties of monolayers derived from conjugated arylthiol derivatives, and specifically, those related to the series of oligo(phenylethyne)benzenethiols represented by **1** (*n* ≥ 1).



1a: *n* = 0
1b: *n* = 1
1c: *n* = 2

Herein, we report a molecular resolution STM study of SAMs

[†] James Franck Institute.

[‡] Searle Chemistry Laboratory.

(1) For instance: (a) Chidsey, C. E. D. *Science* **1991**, *251*, 919. (b) Prime, K. L.; Whitesides, G. M. *Science* **1991**, *252*, 1164. (c) Chan, K. C.; Kim, T.; Schoer, J. K.; Crooks, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 5875. (d) Jackman, R. J.; Wilbur, J. L.; Whitesides, G. M. *Science* **1995**, *269*, 664.

(2) (a) Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* **1987**, *3*, 932. (b) Ulman, A. *An Introduction to Ultrathin Organic Films: From Langmuir-Blodgett to Self-Assembly*; Academic Press: San Diego, CA, 1991. (c) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.

(3) It is now widely accepted that *n*-alkanethiols form a close-packed commensurate $\sqrt{3} \times \sqrt{3} R 30^\circ$ overlayer structure with a $c(4 \times 2)$ superlattice, see: (a) Camillone, N., III; Chidsey, C. E. D.; Liu, G.-Y.; Scoles, G. *J. Chem. Phys.* **1993**, *98*, 3503. (b) Poirier, G. E.; Tarlov, M. *J. Langmuir* **1994**, *10*, 2853.

(4) For structural studies of other *n*-alkanethiol-based systems, see: (a) Liu, G.-Y.; Fenter, P.; Chidsey, C. E. D.; Ogletree, D. F.; Eisenberger, P.; Salmeron, M. *J. Chem. Phys.* **1994**, *101*, 4301 and references cited therein. (b) Wolf, H.; Ringsdorf, H.; Delamarche, E.; Takami, T.; Kang, H.; Michel, B.; Gerber, C.; Jaschke, M.; Butt, H.-J.; Bamberg, E. *J. Phys. Chem.* **1995**, *99*, 7102. (c) Caldwell, W. B.; Campbell, D. J.; Chen, K.; Herr, B. R.; Mirkin, C. A.; Malik, A.; Durbin, M. K.; Dutta, P.; Huang, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 6071.

(5) For the synthesis of **1a–c**, see: (a) Hsung, R. P.; Babcock, J. R.; Chidsey, C. E. D.; Sita, L. R. *Tetrahedron Lett.* **1995**, *36*, 4525. (b) Hsung, R. P.; Chidsey, C. E. D.; Sita, L. R. *Organometallics* **1995**, *14*, 4808.

(6) For instance: (a) Jelley, E. E. *Nature* **1936**, *138*, 1009. (b) Wang, N.; Chernyak, V.; Mukamel, S. *J. Chem. Phys.* **1994**, *100*, 2465. (c) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277. (d) Waldeck, D. H.; Beratan, D. N. *Science* **1993**, *261*, 576. (e) Martin, A. S.; Sables, J. R.; Ashwell, G. *J. Phys. Rev. Lett.* **1993**, *70*, 218.

derived from **1a–c**⁵ which reveals that the degree of order in these systems increases with chain length and that, for **1c**, an ordered SAM is formed. Due to the conjugated, rigid rod framework of **1c**, this SAM represents an important new platform upon which a variety of optical/electronic studies related to nanostructured materials can be based.^{6,7}

SAMs prepared on Au substrates were characterized by ellipsometric, contact angle, and Fourier transform infrared (FTIR) measurements.⁸ FTIR data confirm the chemical identity of the monolayer, while ellipsometric film thickness values are consistent with a near vertical orientation of close-packed molecular subunits for **1b,c**. Finally, advancing contact angles for water increase with the chain length of the adsorbates, and the value obtained for **1c** ($80 \pm 3^\circ$) is close to that of a densely packed structure with the phenyl rings exposed in an “edge-on” fashion.^{7c,9}

Molecular order of the monolayers prepared on Au(111)/mica was investigated by scanning tunneling microscopy (STM) at high impedances ($10 \text{ G}\Omega$ – $1 \text{ T}\Omega$) which permits imaging of the poorly conducting SAMs.^{3b,4b,10} STM images were taken in air at room temperature.

As shown in Figure 1a, thiophenol (**1a**) significantly affects the gold surface, inducing the formation of islands, pits, and jagged step edges. However, no molecular periodicity is ever observed despite the use of a variety of imaging conditions, thus suggesting that **1a** does not form an ordered SAM.

In contrast, monolayers of **1b** exhibit a degree of order, although it is not always possible to image ordered regions from sample to sample, and a wide range of behavior occurs even within the same sample (Figure 1b). Frequently observed characteristics are as follows: (1) terraces show texture due to the presence of molecules with no apparent order; (2) terrace edges and small regions of terraces appear elevated compared with the surroundings by $\sim 2 \text{ \AA}$; (3) when ordered regions are resolved within surrounding disordered regions, they also appear $\sim 2 \text{ \AA}$ higher; and (4) when order is resolved at steps, rows appear to be oriented away from the edge. Although the elevations may be due to both electronic and topographic effects, the possibility that the molecules adopt a more vertical orientation upon ordering^{7c} would be consistent with the observation that ordered regions always appear elevated.

Remarkably, monolayers of **1c** always display a highly ordered pattern (Figure 1c). This SAM consists of domains that are typically about 100 \AA in size and have a row structure that adopts three orientations (labeled 1, 2, and 3 in Figure 1c). At higher resolution (see inset), the rows appear composed of oval-shaped subunits within which two lobes can sometimes be discerned. The measured lattice vectors are consistent with a $2\sqrt{3} \times \sqrt{3}$ structure (cf. $|a|$, $|b|$, and θ equal to $9.7 \pm 0.9 \text{ \AA}$, $5.2 \pm 0.4 \text{ \AA}$, and $55 \pm 5^\circ$ for the SAM of **1c** vs 9.98 \AA , 4.99 \AA , and 60° for the $2\sqrt{3} \times \sqrt{3}$ structure; see Figure 2). This structure may be the result of the gold–sulfur interaction, which favors the $\sqrt{3} \times \sqrt{3} R 30^\circ$ lattice, as well as additional interactions between the sulfur head groups¹¹ and/or between

(7) For previous studies of SAMs derived from conjugated arylthiols in which order has been proposed but not unequivocally established, see: (a) Chang, S. C.; Chao, I.; Tao, Y. T. *J. Am. Chem. Soc.* **1994**, *116*, 6792. (b) Tour, J. M.; Jones, L. II; 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. (c) Sabatini, E.; Cohen-Boulakia, J.; Bruening, M.; Rubinstein, I. *Langmuir* **1993**, *9*, 2974.

(8) Detailed information is provided in the supporting information.

(9) Fox, H. W.; Hare, E. F.; Zisman, W. A. *J. Colloid Sci.* **1953**, *8*, 194.

(10) (a) Schönenberger, C.; Sondag-Huethorst, J. A. M.; Jorritsma, J.; Fokkink, L. G. J. *Langmuir* **1994**, *10*, 611. (b) Dhirani, A.; Hines, M. A.; Fisher, A. J.; Ismail, O.; Guyot-Sionnest, P. *Langmuir* **1995**, *11*, 2609.

(11) Fenter, P.; Eberhardt, A.; Eisenberger, P. *Science* **1994**, *266*, 1216.

(12) (a) Desiraju, G. R.; Gavezzotti, A. *J. Chem. Soc., Chem. Commun.* **1989**, 621. (b) Rietveld, H. M.; Maslen, E. N.; Clews, C. J. B. *Acta Crystallogr., Sect. B* **1977**, *33*, 1586.

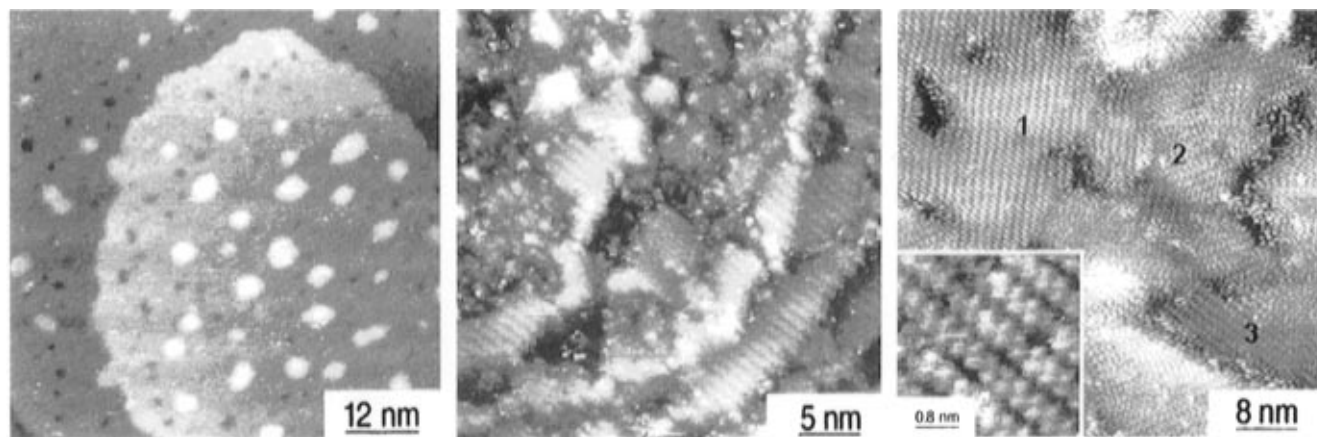


Figure 1. STM images taken in air of SAMs on Au (111)/mica derived from (a, left) **1a** ($I = 5$ pA, $V = 200$ mV, vertical scale ranges 6.4 \AA from dark to bright), (b, center) **1b** ($I = 5$ pA, $V = 200$ mV; vertical scale ranges 7.6 \AA from dark to bright), and (c, right) **1c** ($I = 5$ pA, $V = 200$ mV; vertical scale ranges 5.6 \AA from dark to bright). The three row orientations are labeled 1, 2, and 3, and the inset (vertical scale range 1.6 \AA) reveals the dimerization of the molecules.

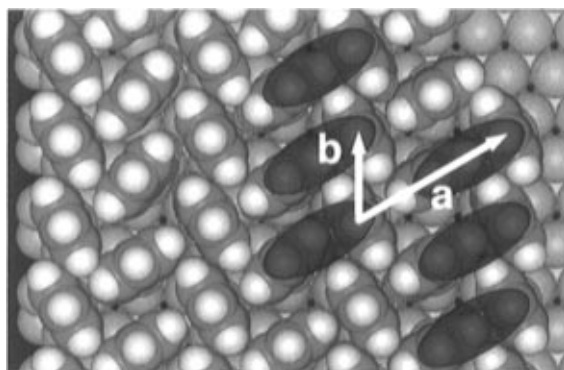


Figure 2. Top-down view of a $2\sqrt{3} \times \sqrt{3} R 30^\circ$ model for SAMs of **1c** on Au(111). The lattice vectors are a and b , and the angle between them is θ (see text). Ovals indicate a possible dimerization scheme.

the molecular backbones. Based on the STM images and the observation of herringbone packing in bulk aromatic hydrocarbons,¹² the sterically permitted model shown in Figure 2 is proposed.¹³

(13) van der Waals dimensions of the phenyl head groups are $6.4 \text{ \AA} \times 3.3 \text{ \AA}$.

In conclusion, we find that, while a *monolayer* is formed in all cases, the STM indicates an increase in order from **1a** to **1b** to **1c**, culminating in the formation of a highly *ordered* SAM for **1c**. This represents the first direct observation of order in a SAM that is not based on an *n*-alkanethiol derivative. The design of new SAMs that are patterned after the general structural motif of **1c** represents an opportunity to investigate new electrical/optical phenomena, at both the molecular and monolayer level, that might arise from the highly ordered, conjugated nature of this particular array. Studies along these lines are now in progress.

Acknowledgment. This work was supported by the MRSEC program of NSF under DMR-9400379. A.D. acknowledges support from the Hulda B. and Maurice L. Rothschild Fellowship. P.G.S. is a Fellow of the David and Lucille Packard Foundation. L.R.S. is a Beckman Young Investigator (1995–1997) and a Camille Dreyfus Teacher Scholar (1995–2000).

Supporting Information Available: Details of the preparation of the substrates and monolayers and macroscopic characterization of monolayers of **1a–c** (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA953782I