Long-Range Self-Assembly of a Polyunsaturated Linear Organosilane at the n-Tetradecane/Au(111) Interface Studied by STM

Alexandr Marchenko,[†] Nathalie Katsonis,[†] Denis Fichou,*,[†] Corinne Aubert,[‡] and Max Malacria[‡]

*CEA-Saclay, Service de Physique et Chimie des Surfaces et Interfaces, DRECAM/DSM,
91191 Gif-sur-Yvette, France, and Laboratoire de Chimie Organique, UMR CNRS 7611, Université P&M Curie,
75252 Paris, France*

Introduction. Surface modification by self-assembled monolayers (SAMs) currently attracts considerable attention because of the potential applications in chemical sensing, corrosion inhibition, wetting control, and nanopatterning.[1] SAMs can also be used in electronic applications to derivatize electrode surfaces[2] or serve as the gate insulator[3] or the semiconductor[4] in nanoscale organic field-effect transistors. SAMs are important in surface science since they form a variety of 2D-lattices, depending on deposition conditions and substrate surface.[5] The most widely investigated SAMs compounds possess a sulfur-based anchoring group (n-alkanethiols for example) and are deposited on an atomically flat Au(111) surface.

However, the need for alternative SAM systems with improved order and stability is crucial for the development of new material technologies. A number of SAMs of silicon-based molecules have recently been studied, such as alkylsilanes on SiO_2.[6] Nevertheless, we found no report on direct visualization of organosilane SAMs on Au(111) in the literature. However, Owens et al.[7] have recently reported that a series of reactive alkylsilanes $R-SiH_3$ form monolayers on freshly evaporated gold in UHV.

We report here on the formation of SAMs of 13-(trimethylsilyl)-1-tridecene-6,12-diyne (**1**) at the n-tetradecane/Au(111) interface and their characterization using scanning tunneling microscopy (STM). **1** is a polyunsaturated organosilane with a linear chain of 13 carbon atoms containing two triple bonds and one double bond and terminated by a trimethylsilyl group.[8] In its fully linear conformation the length of **1** is ∼19.5 Å, given that the triple bond directly linked to the silicon atom rigidifies the $-C\equiv C-Si(CH_3)_3$ segment into a linear rod. Note that the terminal double bond ($-CH=CH_2$) could be used to introduce a variety of functional substituants. Compound **2**, where the Si atom is substituted by a carbon one, has also been studied for comparison.

Experimental Section. Compounds **1** and **2** are colorless oils synthesized following a procedure described elsewhere.[8a] For deposition on gold substrates, a small quantity of **1** or **2** (∼0.05 mg/ml) is mixed in n-tetradecane (99+% purity, Aldrich). A droplet of the solution is then deposited on the Au(111) substrate. Reconstructed Au(111) surfaces are prepared from gold films (thickness ≈ 150 nm) deposited in ultrahigh vacuum onto a freshly cleaved mica surface. STM imaging is carried out in a thin layer of the tetradecane solution using a Pico-SPM (Molecular Imaging). Multiple STM images are recorded in the constant-current mode on various samples to ensure reproducibility. All monolayer preparations and imaging are carried out at room temperature (∼20 °C). All STM images have been flattened by software routines.

1   **2**
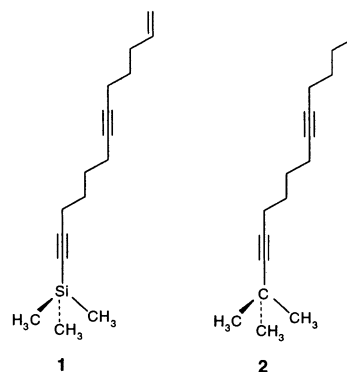
Results and Discussion. Figure 1a−c shows three STM images of silane **1** on Au(111) recorded at different scales. In Figure 1a, beneath the organic monolayer, the image shows the typical terraces of the Au(111) surface delimited by linear monatomic steps extending over several hundreds of nanometers.[9,10] The $23 \times \sqrt{3}$ herringbone reconstruction was visible before adsorption of silanes but is no longer visible after coverage by silane **1**. Figure 1a−b show that after deposition the gold surface does not remain atomically flat but consists of a network of domains separated by randomly distributed "pits" (dark spots in Figure 1b). These depressions are also often observed in alkanethiol monolayers on Au(111)[5b,11] and have the same depth (∼2.4 Å), consistent with a gold single-atom step height.[12] The density of these defects is approximately 9 ± 1%. The pits are covered with highly organized molecules of **1** and do not induce molecular vacancies in the monolayer. These similarities between thiol and silane SAMs on Au(111) account for the possible presence of a strong Si−Au interaction.

Under our experimental conditions, the monolayer appears to be stable during several hours. After 4 h of scan, the solvent has evaporated leaving a dry film of silane on gold. In these conditions, there is no visible change in the surface morphology, and the recorded images are highly reproducible. The stability of the layer should thus be a consequence of a static anchoring of the molecules.

Figure 1c is a typical STM image of a monolayer of **1** showing that it consists of a close-packed hexagonal arrangement. The lateral repeat distance between molecules is quantified in the cross-sectional profile and equal to 5.0 ± 0.2 Å. This distance corresponds precisely to the diameter of the trimethylsilyl group (5.0 Å), suggesting that each molecule has an overall linear conformation and stands upright on the surface plane. This is corroborated by the shape of each molecular spot of the STM image, showing that molecule **1** is not lying flat on gold.

* To whom correspondence should be addressed. E-mail: fichou@drecam.cea.fr.
† CEA-Saclay, Service de Physique et Chimie des Surfaces et Interfaces.
‡ Laboratoire de Chimie Organique.
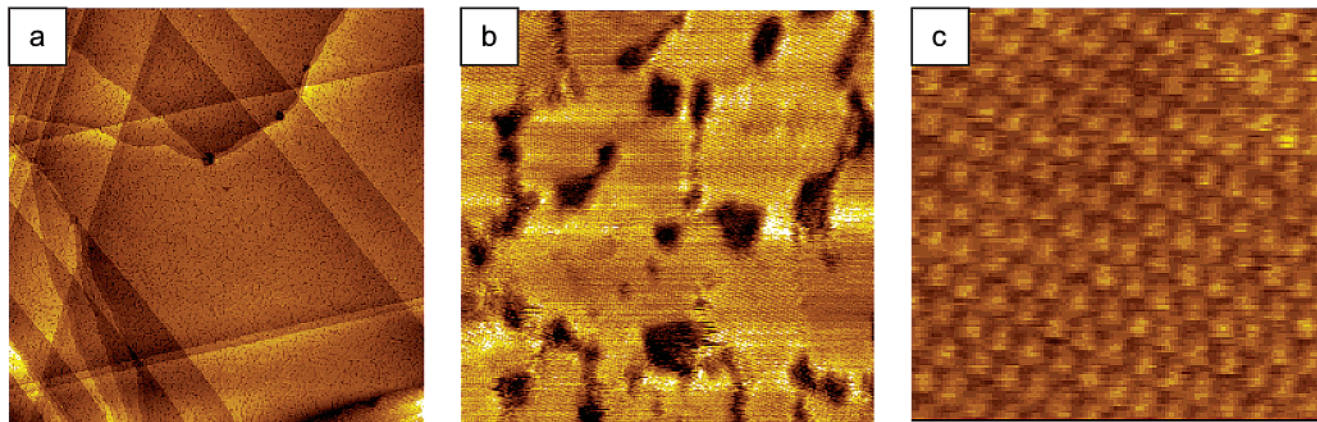
Figure 1. STM images (setpoint: $I_t = 150$ pA; $U_t = 250$ mV) of a self-assembled monolayer of silane **1** recorded at the n-tetradecane/Au(111) interface at various scales: (a) 1050×1050 nm², (b) 62×62 nm², and (c) 55×55 Å². The high-resolution image in (c) shows a periodic array of bright spots corresponding to individual molecules in a hexagonal close-packed arrangement.

In this geometry, it is very likely that the $-C \equiv C-Si(CH_3)_3$ terminal group is in contact with the gold surface, the other end of the molecule (the $-CH \equiv CH_2$ unsaturation) being at the n-tetradecane interface. Another argument in favor of such an arrangement is that molecule **2** (which bears a carbon atom instead of a silicon one) does not self-assemble on gold, pointing out the importance of the Si atom in self-assembly and grafting of **1** on Au(111).

It comes out from the STM images in Figure 1c that neighboring molecules are separated by a distance equal to $\sqrt{3}T \approx 5$ Å, T being the interatomic distance on the Au(111) surface ($T = 2.88$ Å). In other words, the separation between molecules ($\sim$5 Å) is similar to the distance between second-neighboring $\langle 110 \rangle$ Au rows. It means that molecules are bound either in equivalent three-fold hollow sites or on top sites of Au(111) for which the same lattice vectors are expected. Consequently, the monolayer appears to be commensurate with the gold adlattice along the $\langle 112 \rangle$ direction. Then, monolayers of **1** on Au(111) substrates form a so-called $(\sqrt{3} \times \sqrt{3})R30°$ structure with lattice vectors $a = b = 5.0 \pm 0.2$ Å. Importantly, commensurability probably contributes to the stability and long-range ordering of **1** on gold. Note that the *tert*-butyl group of compound **2** is substantially smaller (diameter = 4.3 Å) than the trimethylsilyl group and thus could not have induced commensurability on Au(111).

Tetradecane and silane **1** have a comparable length, which raises the question of a possible coadsorption. This possibility is excluded because of the three following arguments. First, in the case of coadsorption one could expect the presence of grain boundaries in the monolayer, like those for n-alkanethiols.[5] However, we never observed this kind of defects. Second, independent experiments on adsorption of alkanes on Au(111) show that alkanes lie flat on Au-(111), with their main axis parallel to the surface.[13] Finally, deposition of silane **1** from pure ethanol shows that the dry layer has exactly the same morphology as when deposited from tetradecane.

These results raise the essential question of the nature of the interaction between organosilane **1** and gold. They suggest that, besides commensurability, a chemical reaction between Si and Au atoms may have occurred. In particular, it has been reported that Si directly linked to an electron-withdrawing and sterically compact group (such as in the $-C \equiv C-Si(CH_3)_3$ motif of **1**) can become pentacoordinated and adopt a bipyramidal geometry when in contact

with an electron-donating atom (such as Au).[14] In our system, this "supervalent" Si would then be covalently bonded to Au to form a local surface complex. Such a chemical interaction would contribute to the long-range ordering, stability, and creation of pits described above. We are presently investigating this assumption and more generally the nature of the molecule−substrate interaction by using surface analysis techniques such as X-ray photoelectron spectroscopy and vibrational spectroscopies. Further developments in the design of new SAMs based on trimethylsilyl end-capped compounds could represent an alternative for applications based on alkanethiols self-assembled monolayers.

Supporting Information Available: Complementary STM images, cross-sectional line scan of Figure 1b−c (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Ulman, A. *Introduction to Ultrathin Organic Films from Langmuir−Blodgett to Self-Assembly*; Academic Press: San Diego, CA, 1991. (b) Kumar, A.; Whitesides, G. M. *Science* **1994**, *263*, 60. (c) Schoer J. K.; Crooks, R. M. *Langmuir* **1997**, *13*, 2323. (d) Zhao, J. W.; Uosaki, K. *Nano Lett.* **2002**, *2*, 137.
(2) (a) Jones, L.; Pearson, D. L.; Lamba, J. J. S.; Tour, J. M.; Whitesides, G. M.; Muller, C. J.; Reed, M. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*, 564. (b) Kondo, T.; Yanagida, M.; Zhang, X. Q.; Uosaki, K. *Chem. Lett.* **2000**, *8*, 964.
(3) Collet, J.; Tharaud, O.; Chapoton, A.; Vuillaume, D. *Appl. Phys. Lett.* **2000**, *76*, 1941.
(4) Schön, J. H.; Meng, H.; Bao, Z. *Science* **2001**, *294*, 2138.
(5) (a) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533. (b) Poirier, G. E. *Chem. Rev.* **1997**, *97*, 1117. (c) Dhirani, A.-A.; Zehner, R. W.; Hsung, R. P.; Guyot-Sionnest, P.; Sita, L. R. *J. Am. Chem. Soc.* **1996**, *118*, 3319. (d) Hooks, D. E.; Fritz, T.; Ward, M. D. *Adv. Mater.* **2001**, *13*, 227.
(6) Finnie, K. R.; Haatsch, R.; Nuzzo, R. G. *Langmuir* **2000**, *16*, 6968.
(7) Owens, T. M.; Nicholson, K. T.; Banaszak Holl, M. M.; Suzer, S. *J. Am. Chem. Soc* **2002**, *124*, 6800.
(8) For synthesis and chemical reactivity, see: (a) Sternberg, E. D.; Vollhardt, K. P. C. *J. Org. Chem.* **1984**, *49*, 1564. (b) Slowinski, F.; Aubert, C.; Malacria, M. *Tetrahedron Lett.* **1999**, *40*, 707.
(9) Yamada, R.; Uosaki, K. *Langmuir* **1998**, *14*, 855.
(10) Woll, C.; Chiang, S.; Wilson, R. J.; Lippel, P. H. *Phys. Rev. B* **1989**, *39*, 7988.
(11) (a) Chailapakul, O.; Sun, L.; Xu, C.; Crooks, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 12459. (b) Delemarche, E.; Michel, B.; Kang, H.; Gerber, C. *Langmuir* **1994**, *10*, 4103. (c) Durig, U.; Zuger, O.; Michel, B.; Haussling, L.; Ringsdorf, H. *Phys. Rev. B* **1993**, *48*, 1711.
(12) Edinger, K.; Goelzhaeuser, A.; Demota, K.; Woell, C.; Grunze, M. *Langmuir* **1993**, *9*, 4.
(13) (a) Marchenko, A.; Cousty, J. *Phys. Rev. Lett.* **2000**, *84*, 5363. (b) Yamada, R.; Uosaki, K. *J. Am. Chem. Soc.* **1999**, *121*, 4090.
(14) (a) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371. (b) Denmark, S. E.; Griedel, B. D.; Coe, D. M.; Schnute, M. E. *J. Am. Chem. Soc.* **1994**, *116*, 7026.

JA027002Z