Control of Alkanethiolate Monolayer Structure Using Vapor-Phase Annealing

Zachary J. Donhauser,[†] David W. Price II,[‡] James M. Tour,[‡] and Paul S. Weiss*,[†]

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, and Department of Chemistry and Center for Nanoscale Science and Technology, Rice University, Houston, Texas 77005

Control of the local composition of surfaces and local environment of functional molecules is critical to assembly and operation of molecular electronic devices.[1] We focus on the rational design of self-assembling surface structures to control and to study molecular electronic systems. We typically use self-assembled monolayers (SAMs) of alkanethiolates on gold[2] as host matrixes in which we insert candidate molecule electronic components.[3] Our work has focused on one family of conjugated phenylene-ethynylene oligomers. Recent work has demonstrated the functionality of these molecules as molecular wires,[3b,c] switches,[3a,4] and diodes[5] in bundles of thousands and individually. The present work utilizes scanning tunneling microscopy (STM) to study vapor annealing as a technique to modify the local environment of 4,4′-di(ethynylphenyl)-2′-nitro-1-benzenethiolate (**P2**) and other functional molecules isolated in SAM matrixes.

We have previously found that the local environment and the degree of order in the SAM play a crucial role in mediating the switching of single molecules.[3a] Here, we demonstrate that a simple self-assembly strategy can be used to tailor SAM structures and modify the nature of film defects as a means to control the environment around inserted guest molecules. Adsorption and desorption in SAMs is most favorable at monolayer and substrate defects, allowing the introduction of new molecules from the vapor phase to modify the local environments of inserted molecules.

Samples were made using a three-step procedure (Scheme 1). In the first step, SAM matrixes were prepared on commercial Au-{111} on mica substrates,[6] which were annealed immediately prior to film preparation using a hydrogen flame. The gold substrates were submersed in a 1 mM ethanolic solution of decanethiol (**A10**) for ~24 h. They were then rinsed with ethanol and blown dry with nitrogen. In the second step, the SAM matrixes were placed in a solution containing 0.1 mM **P1** and 0.3 mM NH$_4$OH in dry THF for 2 h. The aqueous ammonia hydrolyzes the thioacetyl protecting group, generating the thiolate (**P2**) in situ. In the third step, each film was held above the liquid in a sealed 1 mL v-vial[7] containing 10−20 μL of neat dodecanethiol (**A12**). The vial was held at 80 °C for 2 h, exposing the monolayer to vapor-phase **A12**. STM imaging was performed under ambient conditions as previously described.[8]

During the insertion step used to isolate **P2**, these molecules may have access to the underlying gold at monolayer defect sites and substrate step edges.[3b,c] Because of the limited space available in such sites, molecules that insert into the film are forced to stand upright on the gold surface, with the sulfur terminus bound to the gold surface.[3] It has previously been shown that solution-phase annealing can result in substantial structural changes in alkanethiolate monolayers.[9] This would be undesirable in these experiments because we seek to preserve film integrity to maintain inserted

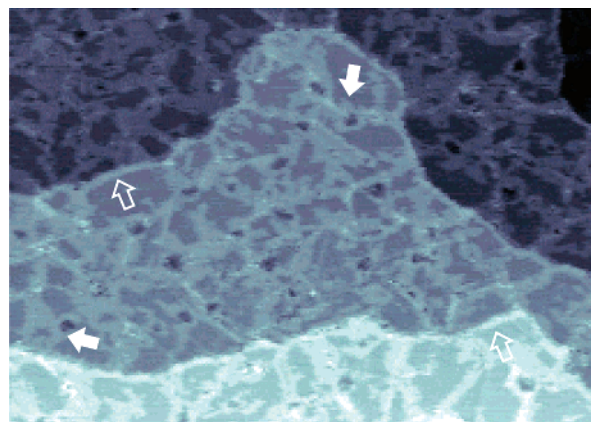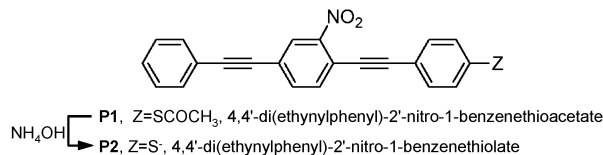† The Pennsylvania State University.
‡ Rice University.

Figure 1. 2000 Å × 1400 Å STM image of an **A10** monolayer on Au{111} that has been vapor-annealed in **A12**. The image was acquired with a tip bias of −1.0 V and a tunneling current of 5.0 pA. Unfilled arrows: **A12** at step edges. Solid arrows: **A12** at defect sites.

Scheme 1

NH$_4$OH ⌐ **P1**, Z=SCOCH$_3$, 4,4'-di(ethynylphenyl)-2'-nitro-1-benzenethioacetate
         └→ **P2**, Z=S$^-$, 4,4'-di(ethynylphenyl)-2'-nitro-1-benzenethiolate

molecules in their restricted, upright geometry. Thus, in the annealing step, we use vapor deposition to add matrix molecules while avoiding exchange processes inevitable with solution-phase annealing.[10,11] Vapor-phase molecules have an opportunity to fill unoccupied adsorption sites around inserted molecules of **P2**, further reducing the space within the host defect site. The use of **A12** in the vapor annealing step (as compared to the **A10** of the native SAM) is important here in that it allows us to distinguish between the primary SAM and the secondary (added) matrix molecules. As observed previously with the STM, the difference in apparent height of the two molecules is about 1 Å.[12]

Figure 1 is an image of an **A10** monolayer that has been vapor-annealed in **A12** vapor. Several gold substrate terraces are visible in this image, with the step height of ~2.4 Å corresponding to that of a monatomic gold step.[13] Within each terrace are raised domains of **A12**, which appear approximately 1.1 Å higher than the **A10** domains. The **A12** domains have a high degree of connectivity, forming a network that surrounds the more islandlike domains of **A10**. This observation is evidence of vapor-phase adsorption at domain boundaries. Vapor-phase adsorption also occurs at substrate vacancy islands that are characteristic of alkanethiolate monolayers; the **A12** molecules occupy most of the areas around the edges of the vacancy islands, and at substrate step edges. The relatively high surface coverage (50−60%)[14] of the **A12** molecules suggests that desorption of the native **A10** SAM must also occur during vapor

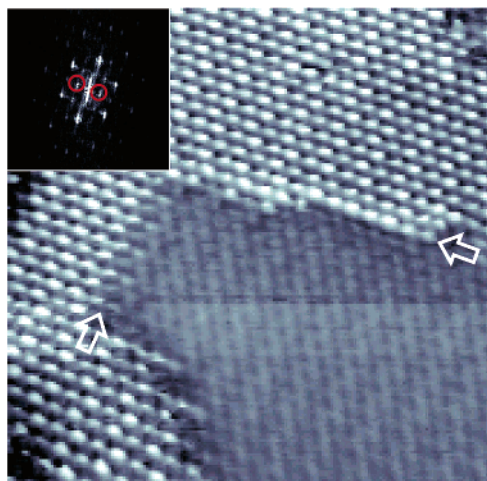**Figure 2.** 130 Å × 130 Å STM image of a phase boundary (indicated with arrows) between **A10** and **A12** domains. The image was acquired with a tip bias of +1.0 V and a tunneling current of 3.0 pA. Inset: Fourier transform of the image. The brightest peaks are indicative of hexagonal packing; $c(4 \times 2)$ superlattice peaks are circled.

annealing. This can occur through direct exchange of the **A10** SAM molecules with vapor **A12** molecules or through desorption of **A10** followed by opportunistic adsorption of vapor-phase **A12** molecules at the vacant substrate sites.[10] The majority of the exchange of **A10** and **A12** occurs at monolayer and substrate defects for two reasons: (1) desorption of **A10** is most favorable where lattice order is low, and (2) incoming molecules can access the substrate for adsorption.

Figure 2 is a high-resolution image of a phase boundary between **A12** and **A10** domains after annealing. The topographically higher (brighter) portion of the image shows part of a molecularly resolved **A12** domain, while the topographically lower area of the image shows a region of **A10**. This image demonstrates that the SAM molecular lattice can be preserved across phase boundaries, despite the differing alkyl chain lengths. The inset in Figure 2 is the Fourier transform of the real space image, which shows the hexagonal lattice structure. Additionally, peaks that are indicative of a $c(4 \times 2)$ superlattice are visible between the more intense hexagonal peaks.[15]

Figure 3 is an image of an **A10** film with molecules of **P2** inserted, which has been subsequently vapor-annealed with **A12**. The networked domain structure of the **A12** is again visible, with several substrate vacancy islands surrounded by **A12**. One molecule of **P2** is found near a substrate vacancy island as an apparent 6 Å protrusion from the matrix of **A10** (see Figure 3, inset). **A12** molecules supplied from the vapor phase have adsorbed at lattice sites around the inserted molecule.[16] While the chemical nature of the surroundings remains the same, the conformational freedom of the inserted molecule may be restricted if **A12** occupies lattice sites previously unoccupied by the host matrix. The ability to modify the local environment of individual molecules is important in mediating their behavior,[3a] in molecular electronics and elsewhere.

We have illustrated a new strategy for the modification of local surface structure and demonstrated its utility when applied to self-assembling systems. Additionally, we have shown a method of forming unique patterns on the surface at the nanometer scale: discrete islandlike domains and 2D networks. It may also be possible to utilize vapor annealing to surround inserted molecules with specific chemical functionality to manipulate electronic or structural characteristics of each individual guest molecule.
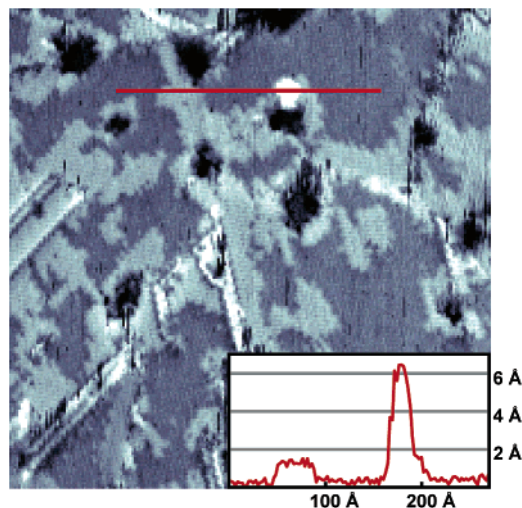

Figure 3. 500 Å × 500 Å STM image of an **A10** film with **P2** inserted, which has been vapor-annealed in **A12**. A molecule of **P2** is visible as a protrusion near a substrate vacancy island. Inset: Line-scan (from image) showing an apparent difference in height of ~1.0 Å between the **A10** and **A12**, and an apparent height difference of ~6.0 Å between the **A10** and **P2**. The bright linear features in the image are domain boundaries typical of alkanethiolate SAMs; the height difference likely originates from a difference in the twist or tilt of the alkane chains at these locations.

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(11) **A10** and **A12** are miscible when coadsorbed, and they form randomly intermixed monolayers. However, vapor annealing selectively places the vapor-phase **A12** molecules in the host **A10** film, forming discrete domains.
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(14) Surface coverages were determined using the area under Gaussian peaks that were fit to the distribution of heights for each terrace.
(15) Here, the hexagonal lattice is best resolved in the **A12** domain, and the $c(4 \times 2)$ superlattice is best resolved in the **A10** domain, visible as periodic rows.
(16) Features with high aspect ratios (such as inserted molecules) cannot be fully resolved with the STM tip and produce image features that are inverted images of the tip. Thus, the apparent width of inserted molecules is much larger than the actual width, obscuring the nearby matrix. Because of the general continuity of the vapor annealing domains, we infer that the domain of **A12** continues adjacent to and surrounds the inserted molecule.

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