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Wang, S
Goronzy, DP
Young, TD
et al.

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Formation of Highly Ordered Terminal Alkyne Self-Assembled Monolayers on the Au{111} Surface through Substitution of 1-Decaboranethiolate

Shenkai Wang,^{†,‡,§} Dominic P. Goronzy,^{†,‡,§} Thomas D. Young,^{†,‡,§} Natcha Wattanatorn,^{†,‡} Logan Stewart,^{†,‡} Tomáš Baše,^{*,||,§} and Paul S. Weiss^{*,†,‡,§}

[†]Department of Chemistry and Biochemistry, [‡]California NanoSystems Institute, and [§]Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California 90095, United States

^{||}Institute of Inorganic Chemistry, The Czech Academy of Sciences, Husinec-Řež 250 68, Czech Republic

ABSTRACT: The reaction aimed at completing and closing the open cages of 1-decaboranethiol self-assembled monolayers (SAMs) on Au{111} with 4-phenyl-1-butyne results in highly ordered monolayers of 4-phenyl-1-butyne. The initially disordered 1-decaboranethiolate changed into ordered ($\sqrt{3} \times \sqrt{3}$)R 30° lattices on Au{111} typical of alkyne SAMs, indicating the complete substitution of 1-decaboranethiolate moieties, as determined by nanoscale imaging with scanning tunneling microscopy and X-ray photoelectron spectroscopy. Vibrational spectroscopy results indicate that the process happens gradually and that alkynyl groups are not totally oxidized in the ordered 4-phenyl-1-butyne monolayer.

INTRODUCTION

Self-assembled monolayers (SAMs) have been intensively studied because of their well-defined and modular structures and chemical properties that provide functionalized surfaces for scientific studies and technological exploration and application.^{1–7} With a rational design of molecules in SAMs, we control the physical and chemical properties of the surface and use bottom-up approaches to fabricate nanostructures and devices.^{8–12} The most extensively studied class of SAMs is derived from the adsorption of alkanethiols on metal surfaces. The high affinity of thiols for the surfaces of noble and coinage metals makes it possible to generate well-defined organic surfaces with useful and highly alterable chemical functionalities displayed at the exposed interface.^{11–13} Other anchor groups have also been studied but are less commonly used because they typically result in weaker bonds and disordered SAMs.^{14–18} Terminal alkyne SAMs have received increasing attention^{19–24} because they offer a way to form covalent Au–C σ bonds that are an alternative to Au–thiolate and other conventional anchoring groups.^{21,25–29} However, reports of highly ordered terminal alkyne SAMs on gold surfaces have been rare because alkynyl groups tend to be oxidized during the formation of the SAMs, resulting in disordered structures.²⁴ Highly ordered terminal alkyne SAMs have been obtained when assembly was performed in an oxygen-free environment.²² This oxygen-free constraint for getting high-quality terminal alkyne SAMs restricts such surfaces for further detailed studies and applications.

In this study, we report a method to fabricate highly ordered SAMs of 4-phenyl-1-butyne (4p1b, Figure 1a) in air through

Figure 1. Molecular structure of (a) 4-phenyl-1-butyne (4p1b) and (b) 1-decaboranethiol.

the substitution of 1-decaboranethiol (Figure 1b) SAMs on Au{111}. 4p1b can react with the bridging hydrogen atoms on the open cage of 1-decaboranethiol under the catalysis of acetonitrile and form *o*-carboranethiol derivatives.³⁰ The heat released by the reaction caused the desorption of the original 1-decaboranethiol SAM, and 4p1b molecules fill in the remaining vacancies and form ordered structures. Exothermic reaction-induced disorder in SAMs has been observed previously for Fischer esterification reactions and was used to make regions of the monolayer labile to displacement.³¹ This

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disorder is important in *enabling* displacement. Defects in SAMs, such as domain boundaries, are necessary as they serve as nucleation sites for displacement (and insertion), as shown both for SAMs of molecules with both linear and rigid-cage backbones.^{10,31–36} The substitution process was characterized here by scanning tunneling microscopy (STM). 1-Decaboranethiol SAMs are disordered, but the SAMs formed by 4p1b after the substitution are consistent with the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ lattice on Au{111}. Grazing incidence Fourier transform infrared (FTIR) spectroscopy results indicate that the process happens gradually and X-ray photoelectron spectroscopy (XPS) confirms the ultimate complete substitution of 1-decaboranethiolate moieties.

EXPERIMENTAL METHODS

Materials. 4p1b (Sigma-Aldrich, St. Louis, MO), dichloromethane, and acetonitrile were used as received. 1-Decaboranethiol was synthesized and purified as previously described.³⁷ 1-Decaboranethiol SAMs were prepared by immersing freshly flame-annealed Au{111} on mica and Au{111} on silicon substrates into gravimetrically prepared 1 mM CH₂Cl₂ solutions of 1-decaboranethiol for 24 h at room temperature. Substrates were then rinsed thoroughly with CH₂Cl₂ and were blown dry using nitrogen.

Reaction between 1-Decaboranethiolate and 4p1b. Substrates with 1-decaboranethiol SAMs were immersed in acetonitrile. The solutions were maintained at 82 °C for 2 h before 4p1b was added to prepare a 0.02 M solution. The reaction was then allowed to continue at 82 °C for another 24 or 48 h, and the substrates were then rinsed thoroughly by acetonitrile and blown dry using nitrogen.

Scanning Tunneling Microscopy. All STM measurements were conducted using custom beetle-style STM under ambient conditions.³⁸ Piezoelectric scanner gains were calibrated using the lattice spacing of a known adsorbate, 1-dodecanethiolate on Au{111}. The measured spacings of the alkanethiolate SAMs were measured in a variety of scanning directions. The vertical scale was calibrated using the monatomic step heights of the Au{111} substrate in subsequent images.

Grazing Incidence FTIR. Infrared spectra were collected using a Nicolet 6700 FTIR spectrometer (Thermo Electron Corp., Waltham, MA) equipped with a liquid nitrogen-cooled mercury–cadmium–telluride detector and a Seagull variable-angle reflection accessory (Harrick Scientific, Inc., Ossining, NY). An FTIR purge gas generator (Parker Balston, Cleveland, OH) removed water and CO₂ from the gas stream used to purge the spectrometer and its accessory. The data were collected at grazing incidence (82° relative to the surface normal) in reflection mode with *p*-polarized light and a mirror speed of 1.27 cm/s, with a resolution of 8 cm^{−1}. All spectra were averaged over 1024 scans. Scans were normalized with spectra of perdeuterated *n*-dodecanethiolate monolayers on Au{111}.

RESULTS AND DISCUSSION

Self-Assembly of 1-Decaboranethiol. 1-Decaboranethiol was synthesized and purified according to literature reports,³⁷ and SAMs were prepared by immersing flame-annealed Au{111} on mica substrates into gravimetrically prepared 1 mM CH₂Cl₂ solutions of 1-decaboranethiol for 24 h at room temperature. The substrates were then characterized

by custom beetle-style STM under ambient conditions.³⁹ The STM images in Figure 2 show that 1-decaboranethiolate

Figure 2. STM images of 1-decaboranethiol SAMs at the scales of (a) 100 nm × 100 nm and (b) 30 nm × 30 nm on Au{111}. All images were collected at a sample bias of 1.00 V and a tunneling current of 12.0 pA.

molecules in the SAM tend to form small clusters rather than long-range ordered nanostructures, which results in evenly distributed vacancies within the SAMs (displayed as dark regions).

The random cluster pattern on the surface, which is characterized by many disordered and varied protrusions (Figure 2b), can be explained by the lower symmetry of the molecules compared to upright, symmetric carboranethiols⁴⁰ and their different orientations with regard to the surface. The difference in the interactions between neighboring molecules results in different tilt angles and thus different intermolecular distances (Figure 3b). The lack of long-range order and the molecular tilt makes it difficult to extract useful information about the assembly structure under ambient conditions at room temperature.

Figure 3. (a) Molecular structure of 1-decaboranethiol viewed from different angles. (b) Diagram explaining the formation of vacancies in SAMs of 1-decaboranethiol.

Reaction of 1-Decaboranethiol with the Alkynyl Group. The four acidic bridging hydrogen atoms in decaborane enable it to react with alkynyl groups catalyzed by acetonitrile through the steps shown in Scheme 1.³⁰

Scheme 1. Reaction of Decaborane with the Alkynyl Group Catalyzed by Acetonitrile

4p1b was used to study the reactivity of 1-decaboranethiol assembled on the Au surface. A 1-decaboranethiol SAM was prepared on flame-annealed Au{111} on a mica substrate, and then, the substrate was immersed in acetonitrile to prepare the bis(acetonitrile)decaborane adduct, which is necessary for the formation of *ortho*-carborane by the insertion of an alkyne moiety in the open decaborane cage. The solution was maintained at 82 °C for 2 h before 4p1b was added. The reaction was held at 82 °C for another 48 h, and the substrate was then washed with acetonitrile. STM images of the surface after the reaction (Figure 4a,b) show that the molecules

Figure 4. STM images of 1-decaboranethiol SAM after reaction with 4p1b in acetonitrile at the scale of (a) 30 nm $\times$ 30 nm and (b) 15 nm $\times$ 15 nm. The inset shows the Fourier transform of (b) from which the nearest neighbor spacing was calculated. All images were collected at a sample bias of 1.00 V and a tunneling current of 12.0 pA. (c) Scheme of the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ lattice.

formed ordered structures on the surface, which are *not* observed for 1-decaboranethiol SAMs. We note that the heat of the reaction on the surface can have a substantial effect on ordering (or disordering) reactions of monolayers or inserted molecules, as we have previously observed in a number of systems.^{31,39,41}

Fourier transforms of the images in Figure 4a,b yield nearest neighbor spacings of 5.04 ± 0.09 Å. The structure is consistent with the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ lattice, which characterizes the structure formed by alkanethiols and ordered terminal

alkynes²² on Au{111} but is substantially more dense than typical carboranethiolate SAMs.⁴⁰ Such results indicate that the ordered SAMs we observed are formed purely by 4p1b and 1-decaboranethiolate molecules were driven away after reaction with 4p1b. The complete removal of 1-decaborane molecules was further confirmed by XPS analysis. The XPS data in Figure 5a show that there is no boron left on the surface indicating that 1-decaboranethiolates were completely substituted by 4p1b after the reaction.

Detailed analysis of the O 1s spectrum (Figure 5b) shows two peaks with binding energies of 533.2 and 531.2 eV, indicating that oxidized species (carboxyl group) exist on the surface. Deconvolution of the C 1s spectrum (Figure 5c) gives two peaks with binding energies of 285.5 and 284.3 eV, which we assign to carbon atoms of the aromatic ring. The signal representing carbon atoms in oxidized species at 288 eV is negligible, suggesting that the defects observed in the STM images in Figure 4 might be formed by these oxidized species.

In order to test and understand the substitution process, we immersed a 1-decaboranethiol SAM prepared on Au{111} in pure acetonitrile for 24 h at 82 °C; the STM images characterizing the surface are shown as Figure 6a,b. Also shown in Figure 6 are the images for the surfaces where the substitution of 1-decaboranethiolate with 4p1b was carried out for 24 h (Figure 6c,d) and 48 h (Figure 6e,f), respectively. The roughness of the SAM increased after 1-decaboranethiolate reacted with acetonitrile (Figure 6a,b) but the SAM remained disordered (cf. Figure 2). We assign the evenly distributed protrusions to the acetonitrile decaborane adducts formed by the reaction between basic acetonitrile and the acidic bridging H atoms of the open decaborane cage.

Figure 6c,d shows the surface after 1-decaboranethiol SAM was reacted with 4p1b for 24 h. There are regions of the surface with different apparent heights in STM images, and the shapes of the regions are irregular. Such patterns are *not* observed on the surface after the reaction with 4p1b took place for 48 h (Figure 6e,f), where the regions with greater apparent height appear to be relatively intact. The differences in the surface patterns indicate that the substitution of 1-decaboranethiolate by 4p1b starts randomly on the surface and proceeds until all 1-decaboranethiolate molecules have been replaced.^{35,36}

In order to test if the ordered structures of 4p1b were formed because of the reaction followed by the substitution of 1-decaboranethiolates, we performed a control experiment where the 1-decaboranethiol SAM was immersed in 0.02 M ethanol solution of 4p1b for 24 h at 78 °C. STM images characterizing the surface are shown in Figure 7a,b. No

Figure 5. X-ray photoelectron spectra of 1-decaboranethiol SAM after reaction with 4p1b for 48 h in acetonitrile for (a) B 1s, (b) O 1s, and (c) C 1s.

Figure 6. (a,b) 1-Decaboranethiol SAM reacted with acetonitrile at 82 °C for 24 h. (c,d) 1-Decaboranethiol SAM reacted with 4p1b at 82 °C for 24 h. (e,f) 1-Decaboranethiol SAM reacted with 4p1b at 82 °C for 48 h. All images were collected at a sample bias of 1.00 V and a tunneling current of 12.0 pA.

Figure 7. (a,b) STM images of 1-decaboranethiol SAMs immersed in ethanol solution of 4p1b at the scale of 100 nm × 100 nm and 30 nm × 30 nm. (c,d) STM images of 4p1b SAMs directly deposited on Au{111} at the scale of 30 nm × 30 nm and 10 nm × 10 nm. All images were collected at a sample bias of 1.00 V and a tunneling current of 12.0 pA.

ordered structure was observed in the STM images, which means that 4p1b molecules can only form ordered SAMs after reacting with 1-decaboranethiol SAMs. We assign the protrusions scattered on the surface in Figure 7a,b to 4p1b molecules inserted into the evenly distributed pinhole defects in 1-decaboranethiol SAMs.

We also immersed the clean Au{111}/mica substrate in 0.02 M acetonitrile solution of 4p1b for 48 h at 82 °C to see if 4p1b itself can form ordered SAMs in air. As seen in the STM images of the surface in Figure 7c,d, we observe striplike structures formed along different directions, which are *not* found in the STM images of the ordered 4p1b SAMs in Figures 4 and 6e,f. Such strip structures can be explained by previous reports that the AuC≡CR bond can be oxidized by O₂ during the SAM formation and the molecules then lie flat on the surface.^{22,24} The absence of strip structures in the ordered 4p1b SAMs in Figures 4 and 6e,f indicates that the gradual reaction and substitution of 1-decaboranethiol SAMs facilitates the formation of highly ordered 4p1b SAMs.

The substitution process was also characterized by grazing incidence FTIR. 1-Decaboranethiol SAMs were prepared on Au{111} on Si substrates, and the substitution was carried out by immersing the samples in 0.02 M acetonitrile solution of 4p1b for 24 and 48 h separately at 82 °C. Examples of the FTIR spectra for both substrates and for pure 1-decaboranethiol SAM are shown in Figure 8a. A spectrum for the surface prepared by immersing clean Au{111}/mica in the same solution at 82 °C for 48 h is also shown in Figure 8a for comparison. The method we use is more sensitive to the fingerprint region;²⁴ so, in the 1-decaboranethiol SAM spectrum, the intensity of the peak at 2550 cm⁻¹, which represents that the B–H stretching vibration is small compared to the bridging hydrogen peak (B–H–B) at 1450 cm⁻¹.⁴² From the spectra characterizing the surfaces after 24 and 48 h substitution, we observe a new peak at 1650 cm⁻¹, and the intensity of the broad peak at 1450 cm⁻¹ decreased after 24 h substitution and disappeared after 48 h substitution. Through the 4p1b direct deposition spectrum, we assign the peak at 1650 cm⁻¹ to the aromatic ring stretch of 4p1b. The results suggest that the substitution occurs gradually, which corresponds to the STM images characterizing the process in Figure 6. 1-Dodecane-*d*₂₅-thiol SAM was used as the background to obtain the IR spectra, and the negative peaks at ~2200 cm⁻¹ are because of the stretches of C–D bonds. However, there is a signal in the 48 h substitution spectrum at ~2200 cm⁻¹ that overlapped with the background C–D stretching. In order to extract the information, we used 1-decaboranethiol SAM as the background to obtain the same spectrum again, shown in Figure 8b. We assign the two peaks at 2206 and 2163 cm⁻¹ as the stretch of the alkynyl group, suggesting that most of the alkynyl groups are *not* oxidized during the substitution of 1-decaboranethiolate, which results in the highly ordered SAMs observed by STM.

CONCLUSIONS AND PROSPECTS

In this study, we characterized the reaction between 1-decaboranethiol SAM and 4p1b on the Au{111} surface by STM, XPS, and FTIR. We observed a ($\sqrt{3} \times \sqrt{3}$)R 30° lattice on Au{111} after exposure of 1-decaboranethiol SAMs to 4p1b. XPS results suggest that 1-decaboranethiolate molecules were completely substituted by 4p1b molecules after the reaction; control experiments indicate that the complete substitution of 1-decaboranethiolate only happens in acetonitrile solution, so the reaction between 1-decaboranethiolate and alkynyl group is necessary for the displacement process. STM results and IR spectra also show that the substitution of 1-decaboranethiolate moieties by 4p1b starts at random sites on the surface and proceeds until all the 1-decaboranethiolate molecules are completely removed. This process provides a

Figure 8. (a) FTIR spectra of 1-decaboranethiol SAMs on a gold surface (green line), 1-decaboranethiol SAMs substituted by 4p1b for 24 h (blue line) and 48 h (red line), and 4p1b SAMs prepared by direct deposition on the clean gold surface in air (black line). (b) FTIR spectrum of 1-decaboranethiol SAMs substituted by 4p1b for 48 h obtained using 1-decaboranethiol SAMs as the background.

facile way to fabricate highly ordered terminal alkyne SAMs in air that cannot be achieved through direct deposition of alkynes. The 4p1b solution after the substitution is also worth testing further because our results indicate that *o*-carboranethiolate molecules were desorbed from the surface after the reaction and should be in solution. Furthermore, the evenly distributed defects in the 1-decaboranethiol SAM provides the possibility of inserting other molecules and fabricating blended SAMs on the surface.^{10,32,34,43,44}

AUTHOR INFORMATION

Corresponding Authors

*E-mail: tbase@iic.cas.cz (T.B.).

*E-mail: psw@cnsi.ucla.edu (P.S.W.).

ORCID

Shenkai Wang: 0000-0002-2151-8664

Dominic P. Goronzy: 0000-0003-2856-4732

Thomas D. Young: 0000-0002-3234-7418

Tomáš Baše: 0000-0003-2533-8705

Paul S. Weiss: 0000-0001-5527-6248

Notes

The authors declare no competing financial interest.

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