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Accessibility
Formation of Highly Ordered Self-Assembled Monolayers of Alkynes on Au(111) Substrate

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Supporting Information Placeholder

ABSTRACT: Self-assembled monolayers (SAMs), prepared by reaction of terminal n-alkynes (HC≡C(CH₂)ₙCH₃, n = 5, 7, 9, and 11) with Au(111) at 60ºC were characterized using scanning tunneling microscopy (STM), infra-red reflection absorption spectroscopy (IRRAS), X-ray photoelectron spectroscopy (XPS), and contact angles of water. In contrast to previous spectroscopic studies of this type of SAMs, these combined microscopic and spectroscopic experiments confirm formation of highly-ordered SAMs having packing densities and molecular chain orientations very similar to those of alkanethiols on Au(111). Physical properties—hydrophobicity, high surface order, and packing density—also suggest that SAMs of alkynes are similar to SAMs of alkanethiols. The formation of high-quality SAMs from alkynes requires careful preparation and manipulation of reactants in an oxygen-free environment: trace quantities of oxygen lead to oxidized contaminants and disordered surface films. The oxidation process occurs during formation of the SAM; via oxidation of the –C≡C– group (most likely catalyzed by the gold substrate in the presence of O₂).

Thin organic films based on self-assembled monolayers (SAMs) are ubiquitous in surface science. The reaction of organic thiols (RSH) with group Ib metals (Au and Ag) to generate SAMs with composition Au/AgSR is the reaction most commonly used to prepare SAMs, although reactions that generate organosilanes on silicon (SiR) and organic carboxylates on silver (Ag₂O₂CR) have attractive properties, and a number of other precursors have been surveyed. There have also been scattered descriptions of SAMs formed on gold from solutions of alkynes (HC≡C(CH₂)ₙCH₃, n = 3, 5, 7, 9, 11, and 13), ethynylbenzene (HC≡C(CH₃)₂), or n-alkylmercury(II) tosylates (CH₃(CH₂)ₙHgOTs, n = 4 and 18) on Au(111). Although the potential interest of SAMs having Metal≡C≡CR bonds is high, since they offer a new type of metal-organic bond, most of these studies have used preparations analogous to those employed with n-alkanethiols, and have generated SAMs that have not seemed to be highly ordered, and are thus, perhaps, unsuitable for detailed studies of the physical chemistry of the surface. In particular, there are no procedures that describe the formation of SAMs that are highly ordered in two dimensions—a key requirement for high-quality surface science. The most recent analyses of n-alkyl-based SAMs on Au(111) indicate a “liquid-like” structure of the monolayer, and XPS analyses of SAMs formed from alkynes suggest that these SAMs are sensitive to oxidation at an undefined point in their formation; that is, oxidation occurs either during or after SAM formation (for example, by reaction of the Au≡CR bond with O₂). Contact angle analyses of increasing lengths of alkynes (HC≡C(CH₂)ₙCH₃, n = 5, 7, 9 and 11) also suggest that the quality of these SAMs is lower than those based on n-alkanethiols.

Although SAMs have enabled studies of wetting, adhesion, and charge transport (inter alia), most of this work has focused on the terminal part of the SAM that is exposed to air, and there is relatively little work devoted to understanding the contribution of the anchoring groups of the SAM (as opposed to the terminal group, the thickness, or the electronic structure). In the current work, we characterize the SAMs formed by reactions of n-alkynes (HC≡C(CH₂)ₙCH₃, n = 5, 7, 9 and 11) with Au(111). We believe that the Au≡CR group is particularly interesting as the basis for SAMs on Au for two reasons: i) the acetylene group connects with gold atoms on the surface by a strong σ-bond; ii) the orbital structure of the acetylene group, and the existence of a variety of stable organometallic compounds containing the Au≡CR group, suggests that the interface between the metal, Au, and the saturated organic component of the SAM (R = (CH₂)ₙCH₃), might be especially informative in studies in which the interface connecting the SAM to the metallic substrate might contribute to its properties.

The objective of this work was to address the question of the order of n-alkyne-derived SAMs on gold through a combination of microscopic, spectroscopic and contact angle measurements. Our results show that the disorder and mixed organic functionality implied by previous work are artefacts reflecting oxidation of the terminal acetylene by oxygen in solution during formation of the SAM (perhaps in a reaction catalyzed by gold) and that using appropriate experimental conditions (e.g., rigorous exclusion of oxygen; a slightly elevated temperature of 60ºC during formation of the SAM) results in well-organized SAMs of alkynes that have qualities similar to that of alkanethiols on Au(111). These studies thus establish that SAMs of the surface composition Au≡CR provide a new type of SAM for use in physical- and physical-organic studies having an interface to gold (Au≡CR), and are complementary to the well-understood SAMs of alkanethiols (AuSR).

SAMs of alkynes were prepared on gold by submerging freshly evaporated Au(111) substrates in a 1mM ethanolic solution of n-alkyne (HC≡C(CH₂)ₙCH₃, n = 5, 7, 9, and 11) for 15 hours at 60ºC. Importantly, the preparation of the SAMs was performed in...
an oxygen-free environment to avoid oxidation of the acetylene group. The supporting information (SI) provides a more detailed description of the experimental procedure, as well as additional details of measurements.

Figure 1 summarizes the results obtained by scanning tunneling microscopy (STM) for decyne (n = 7) chemisorbed on Au(111). Analysis on a larger scale (Figure 1a) shows formation of depressions on the substrate with depths compatible with substrate lattice steps due to a single atomic layer of gold (as indicated by the respective cross-section, marked by A). Such depressions are also characteristic of formation of both thiol\(^1\) and selenol\(^16\) based SAMs on Au(111), and probably result mainly from lifting the Au(111) herringbone reconstruction upon chemisorption of these molecules.\(^1\) The detection of similar features for alkynes suggests the formation of densely packed chemisorbed structures on Au(111).

This inference of a dense monolayer is confirmed by high-resolution STM, accompanied by Fourier analysis (using Fast Fourier Transform, FFT), which shows a hexagonal lattice. The data obtained after FFT filtering (Figure 1c) suggest a hexagonal structure with a period of ca. 5 Å, as indicated by the line scans along the axes. The structure inferred from this analysis (shown schematically in Figure 1d) is consistent with the \((\sqrt{3} \times \sqrt{3})R30^\circ\) structure with arbitrary taken adsorption seats.

Figure 2. Overview of IRRAS data for n = 5, 7, 9 and 11 alkynes on Au(111) together with the corresponding DDT/Au(111) in the characteristic C-H stretching range.
surface selection rules, IRRAS intensities are sensitive to the orientation of the molecules within the SAM (with respect to the metal substrate); the data in Figure 2 suggest slightly different twisting and/or tilting of the \((\text{CH}_3)_2\text{CH}_2\) chain for the n-alkynyl and alkanethiolate on Au(111). These differences are not surprising considering the different bonding geometries for each SAM. We also note that the observed differences in the IRRAS spectra for n-alkynyl and alkanethiol on Au(111) are much smaller than those reported previously\(^{19}\) for alkanethiolates on Au(111) and Ag(111), which have similar surfaces structures.

Figure 3 shows a more detailed analysis of the IRRAS spectra for tetradeceyne, including a fitting for the C–H stretching modes. The inset in Figure 3 shows that an increase in the length of the aliphatic chain (from \(n = 5\) up to \(n = 11\)) correlates linearly with the intensity of the CH\(_2\)-related symmetric (2920 cm\(^{-1}\)) mode. This observation indicates that the conformation of n-alkynes on Au(111) is preserved across the entire series of alkenes that we investigated; Nuzzo et al. reported a similar observation in earlier spectroscopic studies of alkanethiols on Au.\(^{19}\) In contrast to our observations, recent PM-IRRAS experiments by Scholz et al.\(^6\) (based on analysis of the C–H stretching range) performed for alkyl-based SAMs—\(n\)-butylmercury tosylate \((\text{C}_4\text{H}_9\text{HgOTs})\) and \(n\)-octadeclmercury tosylate \((\text{C}_{18}\text{H}_{17}\text{HgOTs})\) on gold—demonstrated fundamental differences in the relative intensities and broadening between these SAMs and analogous alkanethiols: that is, the \(n\)-alkyls had a liquid-like structure (in contrast to the crystalline structure observed for \(n\)-alkanethiols).

In contrast, the IRRAS data presented in Figures 2 and 3 demonstrates that it is possible to form alkenes that have order similar to that of alkanethiols on Au(111).

Figure 4 shows X-ray photoelectron spectroscopy (XPS) analysis of the alkyne-based SAMs. In contrast to previously reported XPS data for increasing lengths of alkenes \((\text{HC}=\left(\text{CH}_2\right)_n\text{CH}_3, n = 5, 7, 9, and 11)^{6}\), the C\(_1\)s signal in Figure 4 shows a single symmetric peak at 285 eV, with no additional higher energy components (e.g., peaks at 287 eV, 289 eV). The C\(_1\)s peaks are also consistent with the corresponding data obtained for DDT (Figure 4), as well as other literature data\(^{20}\) for un-oxidized alkanethiols on Au(111). We calculated the film thickness using the C\(_1\)s/Au4f intensity ratios (assuming an exponential attenuation of the photoelectron signal\(^{21}\) and using attenuation lengths reported earlier).\(^{22}\) The calculated values (summarized in Figure 5) show a linear increase in thickness as a result of an increase in the length of the chain (from \(n = 5\) to \(n = 11\)). Importantly, the XPS data are consistent with the IRRAS data shown in Figure 3; they indicate a linear increase in the IR signal with an increasing number of methylene units (CH\(_2\)). Moreover, using the linear relation obtained from our XPS measurements data, we can extrapolate the thickness of the film for \(n = 0\) to a value of 5.9 Å; this value corresponds to the length expected for a –C=CH\(_3\) fragment. This extrapolation is also consistent with the ca. 5.6 Å dimensions of an upright configuration of the –C=CH\(_3\) molecule on Au(111), on the basis of the bonds lengths provided by previous DFT\(^{23}\) calculations. Thus, the estimation of thickness using XPS is consistent with SAMs of \(\text{HC}=\left(\text{CH}_2\right)_n\text{CH}_3\) on Au(111) having the –C=– group perpendicular to the surface.\(^{14}\)

Previously reported XPS data for SAMs derived from ethynylbenzene \((\text{HC}=\text{C}\equiv\text{C}_2\text{H}_3)\) on gold\(^3\) suggested that the SAM contained oxidized components, as is inferred from both a significant O\(_1\)s signal and higher-energy contributors to the C\(_1\)s peak (e.g., peaks at 287 eV, 289 eV). In contrast, data shown in Figure 4 show virtually no O\(_1\)s signal for all SAMs analyzed, which were prepared carefully in an oxygen-free environment (the SI details the procedure). The oxidation of alkenes is indeed clearly visible for samples that were exposed to oxygen (ambient condi-
The authors declare no competing financial interests.

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REFERENCES


ASSOCIATED CONTENT

Supporting Information

Experimental details are available free of charge via the Internet at http://pubs.acs.org

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