ABSTRACT

KIM, YUN-HO. Investigation of Terminal Alkynes Monolayers on Gold. (Under the direction of Professor Christopher B. Gorman.)

The primary goal of this investigation is to find the applicable geometry between terminal alkynes and a gold substrate as well as to explore its application. To identify the final geometry of the terminal alkyne binding on gold, various possible geometries were considered. However, based on some tentative results obtained by other researchers, we proposed that the interaction involves a 1,2-hydride shift to form a carbene which then could datively bond to gold. First, the carbene was generated from a carbonyl functional group by extrusion of nitrogen in a 1-diazoalkenes, which was then exposed to gold slide in situ. These samples showed evidence for the formation of a vinylidene carbene when bounded to gold. In other experiments, we explored the possibilities that the interaction between these molecules and a gold substrate occurs through physisorption, although the results indicate that this interaction is not through physisorption. Also, we explored the possibility that the interaction occurs via an acetylide anion, but this was also eliminated as a possible binding interaction through because generation of an acetylide anion by n-butyllithium showed no evidence for formation of a SAM. Third, we did experiments using Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), bulk (KBr) transmission infrared spectroscopy, and $^1$H NMR to investigate the presence of different functional groups on the surface when terminal alkynes are exposed to gold. These results suggested that the vinylidene interaction exist between terminal alkynes and gold slide, but that in the presence of bases a mixture of a vinylidene and acetylide interaction occurs on the surface of gold nanoparticles (AuNPs). In this research, additionally, it is shown that SAMs composed of
α,ω-diynes on gold have different structures depending on the concentration of molecules used to make the SAM. Evidence for both hairpinned and standing-up molecules is provided. This behavior is in contrast to SAMs of α,ω-dithiols on gold, which generally form SAMs with only the straight conformation. The looped SAMs composed of α,ω-diynes offer a less densely packed and thus somewhat accessible surface that may be useful when the underlying surface is used as an electrode. Furthermore, biasing the structure of the molecules in the SAM between looped and standing-up may be useful in the design of dynamic surface.
Investigation of Terminal Alkynes Monolayers on Gold

by
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DEDICATION

This work is dedicated to my grandmother (Boonye Jin), parents (Sungsuk and Hyunsoon Kim), parents in law (Sungho Kim and Byungjin Shon), and the rest of my family. Especially, to loving my wife (Jaeyeon) and son, Calivin (Youngwoong), you always believed in me and you never know how much I love you.
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CHAPTER 1. GENERAL INTRODUCTION

1.1 Self Assembled Monolayers on Gold: Alkanethiol Self Assembled Monolayers on Gold.

Organic thin films that are composed of single monolayers of molecules have been widely studied on various surfaces. Monolayers formed by the transfer of molecules from the air-water interface to a solid surface are called Langmuir Blodgett (LB) films.\(^1\) Langmuir films are usually composed of amphiphilic molecules with a hydrophilic head and a hydrophobic tail. Despite the potential of the LB technique which can lead to well ordered structures, it has severe limitations with respect to substrate size, film quality, and stability. An alternative technique for creating ultra thin monolayers that has been extensively studied on solid surfaces is self assembled monolayers (SAMs).\(^2,3\) SAMs are single monolayer films that spontaneously assemble on a surface.\(^4,5\) In general, the formation of these SAMs is driven by two separate forces. One is the attractive interaction between the binding group at the end of the organic chain and the substrate. The other is the collective intermolecular Van der Waals (VDW) interactions between the alkyl chains.

As early as 1946, Bigelow \textit{et al.} reported studies on the formation of organic monolayers of surfactants onto metal surfaces.\(^5\) The potential applications and usefulness of monolayers was not established at that time. Therefore, very little interest in monolayers was generated from these initial reports. In addition, surface characterization techniques were also limited at that time, thus their properties and structure were not well understood. As surface characterization methods have been improved, the potential of SAMs was recognized.
Since then, SAMs of a variety of different binding groups and substrate supports have been explored.

SAMs on various surfaces have many advantages over other types of thin films. For instance, in comparison with LB films, SAMs have a simpler structure with the binding group typically being localized at one end of the surfactant and a single alkyl chain extending from this group. With these structures, the interacting site with the substrate is predominantly the binding group. Therefore, the thickness of these thin films is fixed at one molecular layer. In contrast, LB films can deposit as multilayers onto a substrate if the deposition conditions are not well controlled or if the molecules do not organize well at the air-water interface. Thus, more stable and better organized SAMs can be formed compared to LB films because of the relatively strong interaction that occurs between the organic head group and substrate. In addition, SAMs are more appropriate and practical for studies in nanoscience and technology. First, SAMs can be prepared more easily than other thin films because they do not require ultrahigh vacuum or other specialized equipment (e.g., a trough and dipper used in the LB technique) to facilitate their formation. Second, there is little limitation on the area of these films which allows them to be critical components for stabilizing nanometer scale materials such as nanowires, colloids, and other nanostructures. Third, the surface properties of these films can be tuned by incorporating different functionalities within the tail group. The range of different functionalities that can be added allows for the electronic (current vs. voltage response, electrochemistry), and optical (local refractive index, surface plasmon frequency) properties of metallic structure to tailor the surfaces. Finally, their organization and structure at the nanoscale level determines
macroscale interfacial phenomena, such as wetting, adhesion, and friction. For the properties mentioned above, it seems reasonable to conclude that SAMs on substrates have a lot of advantages over other types of thin films.

When it comes to studying monolayer films, in particular SAMs, monolayers with sulfur containing binding groups are the most widely explored. There are numerous reported surface active organosulfur compounds that form monolayers on gold and the number of organosulfur compounds that are used in SAMs has increased throughout the years (Figure 1.1). These include, among others, di-alkyl sulfide, di-alkyl disulfides, thiophenols, mercaptopyridines, mercaptoanilines, thiophenes, cysteines, xanthates, thiocarbaminates, thiocarbamates, and mercaptoimidazoles. However, alkanethiolates SAMs on gold have various advantages over other SAMs, which have led to them being the most widely studied and understood thin films.
To show these advantages, various researchers have compared the feasibility of making SAMs using various metal substrates and different binding groups. The results of these studies have shown that SAMs made of alkanethiolates on the gold tend to be of the highest quality. For instance, Fenter et al. found, through X-ray diffraction (XRD) and scanning tunneling microscopy (STM), that alkanethiolates SAMs on gold form densely packed structures. Delamarche et al. showed the thermal stability of alkanethiolates SAMs on gold by X-ray photoelectron spectroscopy (XPS), water contact angle measurements, and STM. In addition to these examples, other researchers, through the use of similar techniques, have
observed that alkanethiolate SAMs on gold monolayers form densely packed, well ordered structures (Table 1.1).

Table 1.1.  Methods for the characterization of self assembled monolayers of alkanethiolates on gold.

<table>
<thead>
<tr>
<th>Method</th>
<th>Information</th>
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<tbody>
<tr>
<td>Wettability</td>
<td>Interfacial free energy of surface</td>
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<tr>
<td>Ellipsometry</td>
<td>Thickness of adsorbed layer(s)</td>
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<tr>
<td>X-ray Photoelectron Spectroscopy (XPS)</td>
<td>Chemical composition</td>
</tr>
<tr>
<td>Surface Raman Scattering</td>
<td>Structure of monolayer</td>
</tr>
<tr>
<td>Transmission (high energy) Electron Diffraction</td>
<td>Structure of monolayer</td>
</tr>
<tr>
<td>Low Energy Helium Diffraction</td>
<td>Structure of monolayer</td>
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<td>Infrared Spectroscopy</td>
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<tr>
<td>Electrochemical Methods</td>
<td>Degree of perfection of monolayer, electrical</td>
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<tr>
<td></td>
<td>properties of monolayer</td>
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<tr>
<td>Scanning Tunneling Microscopy (STM)</td>
<td>Structure and composition of monolayer</td>
</tr>
</tbody>
</table>

In order to understand the bonding between the thiolate and the gold, one needs to consider the mechanism of SAM formation. This mechanism has been shown to proceed
through two steps. Bain et al. showed that two individual adsorption steps can be observed when relatively dilute solutions (10^{-3} M) of the alkanethiol adsorbent were exposed to the gold surface during alkanethiol SAM formation. The first adsorption step occurs very fast requiring only a few minutes. During this step the contact angles become close to the final values and the thickness as measured by ellipsometry approaches 80–90% of the maximum values. The second step, a slow step, occurs over several hours. In this step, the thickness and contact angles reach their final values. The authors claimed that the initial step, a fast step, was found to highly dependent on thiol concentration and could be described as a diffusion-controlled Langmuir adsorption. On the other hand, the second step, a slow step, can be described as a surface crystallization process. More specifically, the alkyl chains transition from a more disordered state to a more ordered state, which can be described as two dimensional crystal that can be defined by a c(4 × 2) superlattice of a simple √3 × √3 R30° unit cells representing a hexagonal close-packed (hcc) ordering. These unit cells will be illustrated and explained below. The kinetics of the first step are governed by the attractive interaction between the surface and head group of the molecule. On the contrary, the kinetics of the second step, a slow step, is dependent on several effects. One factor influencing the kinetics of this step is the interactions between the alkyl chains, which is driven by the collective VDW forces between these chains. The other main factor is the surface mobility of the chains. To explain the relative effects of these two forces on the kinetics of the second step, the authors showed that the kinetics for longer alkyl chains is faster than those for the shorter alkyl chains by using advance contact angle, ellipsometry, and XPS techniques. They attributed this increase in rate to the increased VDW interactions
between the longer chains, which provide an additional stabilizing effect within the alkanethiol monolayer. Moreover, it was observed that an unbranched \( n \)-alkanethiol monolayer had faster rates of SAM formation compared to a sterically hindered \( tert \)-butanethiol monolayer. This observation further supports the idea that the second step is partly driven by collective VDW forces.

Although alkanethiol adsorbents are most widely used, disulfides have been found to form very similar monolayers with alkanethiols, but via a different mechanism. To explain why alkanethiols and di-alkyl disulfides form nearly identical SAMs, Biebuyck et al. suggested possible mechanisms of chemisorption of these two species onto gold.\(^{27}\) These researchers proposed that both alkyl disulfide and alkanethiols adsorption form a \( Au(I) \)-thiolate (RS-) species. They suggested that monolayers formed from di-alkyl disulfides occurred via an oxidative addition mechanism of the disulfide (S-S) bond to the gold (eq 1). In contrast, it was suggested that the monolayers formed from alkanethiol onto gold followed a slightly different mechanism (eq 2).

\[
\begin{align*}
RS-SR + Au_n^0 & \rightarrow RS-Au^+\cdot Au_n & \text{eq 1} \\
R-S-H + Au_n^0 & \rightarrow R-S\cdot Au^+\cdot Au_n^0 + 1/2H_2 & \text{eq 2}
\end{align*}
\]

More specifically, the reaction proceeds via an oxidative addition of the S-H bond to the gold surface, which is followed by a reductive elimination of dihydrogen. In the complete absence of oxygen, the hydrogen is expelled from the system in the form of \( H_2 \) gas.\(^9,28\) It should be noted that the rate of \( H_2 \) generation by the combination of hydrogen
atoms at the gold surface is likely to be a significantly exothermic step, allowing chemisorption to be more energetically favorable. That is one of the reasons why the alkanethiol adsorbents are favored. Furthermore, Biebuyck *et al.* compared the rate at which free disulfide molecules in solution replaced a di-alkyl disulfide SAM and the rate at which free alkanethiol molecules in solution replaced an alkanethiol SAM.\(^{27}\) In this study, the rate that free alkanethiol molecules replaced an alkanethiol SAM was ~50 times faster than the rate at which free disulfide molecules replaced a disulfide SAM. Through these studies, they suggested that the key factor of this difference in replacement rate is a contribution from steric hindrance because the dihedral angle of di-alkyl disulfides is about 90°. The process of alkanethiol adsorption onto gold has been studied by XPS,\(^{9,10,27,29}\) Fourier Transform Infrared (FTIR) Spectroscopy,\(^{17,30,31}\) Fourier Transform Mass Spectrometry,\(^{32,33}\) Electrochemistry,\(^{34}\) and Raman Spectroscopy,\(^{13,35}\) which have all helped confirm the thermodynamic favorability of this reaction.

As mentioned above, the final structure of alkanethiol monolayers on gold has been found to be densely packed and of high quality, although further details regarding the structure have been probed using several characterization techniques. For instance, electron diffraction studies of monolayers of alkanethiolates on Au(111) surfaces have shown that sulfur atoms arrange in a hexagonal structure with S to S spacing of 4.97 Å, and calculated area per molecule of 21.4 Å\(^2\).\(^{36,37}\) In addition, helium diffraction and atomic force microscopy (AFM) studies showed that the structure formed by docosanethiol on Au(111) is arranged in a simple \(\sqrt{3} \times \sqrt{3}R30^\circ\) overlayer with respect to the underlying gold lattice (Figure 1.2).\(^{38,39}\) As characterization techniques have continued to improve, more details
about the SAMs structure have been discovered. For example, ultrahigh vacuum STM has provided a lot of additional important information on the mechanism of formation and final structure of SAMs. In one case, this technique was able to reveal that the coexistence of a two-dimensional (2D) liquid phase at room temperature of the relatively short chain length butanethiolate and hexanethiolate, monolayers on Au(111). However, there was no 2D liquid observation for octanethiolate and decanethiolate monolayers.\textsuperscript{40}

![Scheme of hexagonal coverage for alkanethiolates on Au(111). The open circles are gold atoms and the shaded circles are sulfur atoms.\protect{\textcopyright}]

Figure 1.2. Scheme of hexagonal coverage for alkanethiolates on Au(111). The open circles are gold atoms and the shaded circles are sulfur atoms.\textsuperscript{9}

The shorter chain homologues exhibited slow desorption of surface thiolate that led to the nucleation and growth of ordered domains having a unit cell of $p \times \sqrt{3}$ where $8 \leq p \leq 10$. On the other hand, longer chain length molecules form densely packed SAMs with c(4 $\times$ 2) superlattice of a $\sqrt{3} \times \sqrt{3}$R30° lattice (Figure 1.3).\textsuperscript{40,41} From these results, they concluded that the nucleation and growth of ordered domains are dependent on their chain length and longer chain length thiolates pack more densely.
Figure 1.3. Diagram showing a proposed c(4 × 2) superlattice structure of an alkanethiol SAM on gold where wedges indicate the tilt direction of the chains and dark circles indicate the sulfur atoms. The smaller dashes show the c(4 × 2) structure and the large dashes show the equivalent $2\sqrt{3}a \times 3a$ unit cell where $a$ equals gold lattice constant.\textsuperscript{9}

As mentioned earlier in this chapter, both thiol and disulfide are able to form nearly identical SAMs on gold surface, but it has not always been clear what differences there are between the final structure of SAMs made from these two absorbents. To explore the difference in the final structures of thiol and disulfide monolayers on gold, Andreoni \textit{et al.} made calculations based on density functional theory to uncover more information about the adsorption configurations of methanethiol and dimethyl disulfide on Au(111) at low coverage (Figure 1.4).\textsuperscript{42} Through these calculations, a comparison was made of the
structures, binding energies, and the type of bonding between the two SAMs. Figure 1.4 shows three dimensional structures of various possible binding configuration for methanethiol and dimethyl disulfide on Au(111) surface. The stabilization energies of these possible binding configurations were compared to determine the most likely SAM structure for each adsorbent. They determined from this calculation that the binding energy with the gold surface for methanethiol is higher than that from the dimethyl disulfide, which is in agreement with experimental evidence at low coverage.\textsuperscript{30} Thus, while the final structures of these SAMs may be similar, intermediate structures are not.

![Equilibrium structures for the X-Au(111) systems considered here: (a) X=H\textsubscript{3}CS + H, (b) X=H\textsubscript{3}CSSCH\textsubscript{3}.\textsuperscript{42}](image)

In general, it has been difficult to explore the relative kinetics and thermodynamics of different binding configuration of alkanethiols on gold because few characterization techniques provide this type of information. In contrast, there are more opportunities to study these processes in solution. To this end, some researchers have been able to obtain more structural information for thiols on gold nanoparticles. Despite being a different type
of surface, one could expect similar structures to be present on a particle facet and metal substrate. However, structural information of SAMs on gold nanoparticles was initially limited, due in part to the problem of preparing homogeneous samples. However, recently, Jadzinsky et al. published details on the structure of a thiol monolayer protected gold nanoparticle at 1.1 Å resolution by powder X-ray diffraction.\textsuperscript{43} They reported the crystallization and X-ray structure determination of a \textit{p}-mercaptobenzoic acid (\textit{p}-MBA)-protected gold nanoparticle, which comprises 102 gold atoms and 44 \textit{p}-MBAs. From these results the researchers found that the \textit{p}-MBAs interact not only with the gold but also with one another, forming a rigid surface layer. The gold atoms in the center are a filled in Marks decahedron, surrounded by additional layers of gold atoms in unanticipated geometries.

\textbf{1.2 Other Interactions between an Organic Head Group and a Metal Surface.}

The first section describes the utility of organosulfur thin films, especially alkanethiol SAMs on gold substrate, but other binding groups on metal surfaces also have promise for forming high quality SAMs. Such systems are still relatively unstudied and novel. However, examples and available structural details of such SAMs are reviewed here.

In attempt to explore other binding groups on metal surfaces, various researchers have studied SAM formation from isocyanide molecules on various metals and their selectivity towards different metals. For example, Hickman et al. showed evidence for the selective formation of isocyanide SAMs on platinum over gold.\textsuperscript{44} More specifically, these researchers showed that there is a selective binding of 12-ferrocenyldodecyl isocyanide with platinum
and bis[10-(ferrocenylcarbonyl)-decyl] disulfide with gold by XPS and monitoring the cyclic voltammetry (CV) of these redox active molecules. By exposing a mixture of the two types of molecules to both surfaces simultaneously, the selectivity for binding 12-ferrocenyldecyl isocyanide versus bis[10-(ferrocenylcarbonyl)-decyl] disulfide on gold surface was ~8:1 in favor of the disulfide. However, the selectivity of the isocyanide SAMs on platinum depended on the surface pretreatment. For example, when platinum was oxidized by oxygen plasma, it showed a 200:1 selectivity for isocyanide over disulfide. This result is significantly greater than the 20:1 preference for the isocyanide observed on a hydrogen plasma treated platinum surface. In another report of SAM formation from isocyanide molecules on a metal, researchers explored the adsorption of aryl and alkyl isocyananides on powdered gold. In this study, the researchers suggested that the isocyananides bond end-on to a single gold atom through the terminal carbon atom of the isocyanide group, and distinguished them by examining υ(NC) frequency of 1,4-phenylene diisocyanide on gold by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT).

As shown previously in Table 1, there are many the characterization techniques for SAMs. In particular, infrared spectroscopic characterization has been most useful for isocyanide SAMs because the NC triple bonding vibration mode (υ(NC) (cm⁻¹)) has a very distinctly different peak from most other vibrational modes and has a different vibrational frequency compared to the bulk molecule. For instance, Henderson et al. explored the adsorption of rigid aryl or phenyl-ethynyl backbone diisocyanides on gold by reflection absorption infrared spectroscopy.
Figure 1.5 shows the presence of an additional peak when diisocyanide is bound to gold as opposed to when this molecule is in the bulk form. This additional peak, as shown in Figure 1.5b, appears at 2193 cm\(^{-1}\) (higher wavenumber) because it can be attributed to the bound isocyanide functional group that is involved in bonding to the surface with the bound isocyanide that is not involved in bonding giving rise to a peak at 2122 cm\(^{-1}\). Moreover, the figure shows a sharp decrease in peak intensity for both of these diisocyanide SAM peaks compared to the much greater intensity shown for infrared absorption of the this diisocyanide in the bulk state.

![Figure 1.5. Isocyanide absorption for 4,4-\(p\)-terphenyldiisocyanide in the region 2000-2300 cm\(^{-1}\): (a) on KBr pellet; (b) on a gold surface.\(^{46}\)](image)

Chen et al. formed isocyanide SAMs on metals and measured the electronic transport behavior through nanoscale metal-molecule-metal junctions with self assembled
1,4-phenylene diisocyanide layers. From these studies, they suggested two kinds of contact methods and determined the dominant conduction mechanism between metal (gold and palladium) and molecule (1,4-phenylene diisocyanide). They described chemisorbed and evaporated contact as two preparation methods and hopping and thermal emission as dominant conduction mechanisms. They concluded that the dominant electron transport mechanism in chemisorbed contacts was thermal emission for both metals (gold and palladium)-isocyanide junctions. On the other hand, in the evaporated contacts, both hopping and thermal emission could play a significant role for both metal-isocyanide junctions. Overall, they determined that the contact barriers in palladium-diisocyanides-palladium were smaller than that in a gold-diisocyanide-gold junction by measuring I(V, T) characteristics. This result can be a useful reference for molecular electronics as “alligator clips”.

A couple sources in the literature discuss possible bonding configurations of isocyanides on various metals, although it remains unclear exactly what type of bonding occurs. One of the early attempts to explore the bonding orientation of isocyanides on metals was made by Seminario et al. who suggested some possible energetically favorable bonding orientations of isocyanides on gold. These researchers reported ionization potentials, electron affinities, and binding energies for isocyanide on a gold surface to suggest a more favorable binding geometry. Also, Henderson et al. made suggestions about possible bonding configuration of isocyanides on various metal surfaces based on results from reflection absorption infrared spectroscopy (RAIRS) and DRIFT (Figure 1.6). Through results from RAIRS and DRIFT experiments, they suggested that isocyanides on a gold
surface has an orientation of type I($\eta^1$) with the molecule bound terminally to the gold surface (Figure 1.6). However, the authors suggested that the coordination geometries could vary depending on the metal that is employed. For instance, based on other experimental results they found that the bonding configuration of isocyanide on palladium was found to be of a bridging type IV($\mu_3-\eta^1$) geometry (Figure 1.6).

![Figure 1.6. The possible coordination structures for isocyanide on a metal surface.](image)

One other novel type of SAM that has been investigated is ones formed by aryl radical attack on various surfaces. Aryl radicals were generated via aryldiazonium salts. Stewart et al. described a one step, room temperature route to form a covalently bonded $\pi$-conjugated aryldiazonium salt SAM on three different surfaces: Si, GaAs, and Pd (Figure 1.7). They proposed that the diazonium salts were activated at the surface in the absence of an externally applied potential, quickly forming a reactive intermediate, followed by surface attachment. This was carried out by spontaneous electron transfer at the open circuit potential (OCP) of the substrate material in solution. Because silicon hydride-passivated surfaces are well known to activate metal salts and dioxygen in solution, undergoing OCP reduction at the
Si(111):H electrode surface. Figure 1.7 shows an electron transfer from the surface at the OCP generates a diazenyl radical and then an aryl radical upon loss of N$_2$. The oxidative process is followed by removal of a proton from the surface by BF$_4^-$ followed by radical diffusion within the solution, and ultimately the irreversible formation of a covalent bond with the surface. In order to confirm the formation of these SAMs on the different surfaces, evidence was gathered from ellipsometry, DRIFT, XPS, CV, and AFM. Overall these SAMs were found to be air stable and very easy to form. Therefore, this spontaneous diazonium activation reaction offers an attractive route for forming high quality, robust monolayers, and multilayers on many surfaces that allow for strong bonds between carbon and surface atoms. Such bonding tends to generate molecular species that are near perpendicular to the surface.
Another example of a head group that is useful for SAM formation is a thiocyanate. It has been shown that this group can also be a precursor binding group that then cleaves to allow for adsorption of a thiolate binding group. For instance, Ciszek et al. demonstrated thiocyanates can temporarily adsorb onto gold, silver, or platinum. When this group is cleaved from the molecule, a thiolates binding group can then bind to the surface. In all cases, it was suggested that a similar mechanism is followed to yield the final thiolate binding event (Figure 1.8). First, the thiocyanate reacts with gold to form an intermediate thiocyanate SAM, which upon reduction, cleaves to form a thiolate bound monolayer. However, sometimes, a fraction of the intermediate species (Au-CN$_{ads}$) remained on the
surface following the reduction step (as seen by the N 1s signal in XPS), but these species could be removed by an etching process. As mentioned above, this process for thiolate SAM formation via a thiocyanate intermediate was employed on platinum and silver surfaces, which yielded similar results.

![Figure 1.8. The mechanism for thiocyanate assembly on gold.](image)

Another example of a head group used in SAM formation is the iodonium group which forms SAMs on silicon and platinum surfaces. Dirk et al. developed a novel technique for the electrografting of iodonium salts onto hydride terminated silicon and platinum surfaces. Figure 1.9 shows a cartoon of the apparatus employed. The iodonium salt was dissolved in a solution of 0.1 M Bu$_4$NBF$_4$ in CH$_3$CN and a negative bias was applied to the substrate for 10 minute. The resulting iodonium SAMs were characterized by XPS and AFM. The results of this experiment showed a new method to pattern organic molecules onto silicon and metal surfaces via a unique binding group.
As discussed above, various binding group SAMs have been explored as possible alternatives to thiol binding group SAMs for certain applications in molecular electronics, biochemical, molecular electronics, materials science, medical science, and other fields where thiol binding groups have frequently not been good enough to be applied.

1.3 Self Assembled Monolayers of Terminal Alkynes on Gold Surface.

Several years ago, acetylene terminated molecules were identified as being capable of forming SAMs on gold by Gorman et al. These acetylene binding group SAMs have much potential for application in molecular electronics where the binding state between the organic head group and metal surface is of primary interest. This acetylene terminated binding group offers one possibility to extend conjugation between the molecule and the metal surface. This stronger coupling/conjugation is critical for the transfer of charge through the molecule/metal surface. This point is of great general interest for applications in molecular
electronics where it is necessary to bridge the molecular scale with the macroscale without sacrificing the electronic properties.

In studies of relatively organized and stable terminal alkyne SAMs on gold, they employed various acetylene terminated molecules to make SAMs on gold (Figure 1.10). First, ellipsometry, water contact angle, and X-ray photoelectron spectroscopy were used to characterize them. The film thicknesses and advancing water contact angles for acetylene terminated SAMs were similar to the alkanethiol counterparts on gold, which is known to form high quality, densely packed SAMs (Table 1.2). In contrast, the advancing water contact angle for SAMs of dodecyne on gold were significantly higher than dodecane, dodecylamine, and dodecanal, adsorbents exposed to gold, which are not known to form high quality, densely packed SAMs. Moreover, X-ray photoelectron spectroscopy showed a carbon (1s) signal, which was assigned to carbons in the alkyl chains of the terminal alkyne bound to gold. These signals corresponded well to the expected assigned ratio of C(sp) and C(sp$^3$) hybridized carbons.

![Structure of the molecules studied](image)

**Figure 1.10. Structure of the molecules studied.**

[^54]
Table 1.2. Ellipsometric film thicknesses and contact angles of water for SAMs of compounds 1-4 on gold.\textsuperscript{54}

<table>
<thead>
<tr>
<th>molecule</th>
<th>film thickness (Å)</th>
<th>molecular length (Å)\textsuperscript{a}</th>
<th>advancing H\textsubscript{2}O contact angle (°)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, n = 3</td>
<td>5.6</td>
<td>8.0</td>
<td>79</td>
</tr>
<tr>
<td>1, n = 5</td>
<td>8.9</td>
<td>10.4</td>
<td>86</td>
</tr>
<tr>
<td>1, n = 7</td>
<td>10.3</td>
<td>12.8</td>
<td>90</td>
</tr>
<tr>
<td>1, n = 9</td>
<td>14.0</td>
<td>15.3</td>
<td>96</td>
</tr>
<tr>
<td>1, n = 11</td>
<td>15.1</td>
<td>17.8</td>
<td>98</td>
</tr>
<tr>
<td>1, n = 13</td>
<td>17.0</td>
<td>20.2</td>
<td>91</td>
</tr>
<tr>
<td>2</td>
<td>11.3</td>
<td>10.2</td>
<td>59</td>
</tr>
<tr>
<td>CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{11}SH</td>
<td>12.5</td>
<td>16.9</td>
<td>103</td>
</tr>
<tr>
<td>CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{11}CH\textsubscript{3}</td>
<td>c</td>
<td>15.5</td>
<td>63</td>
</tr>
<tr>
<td>CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{11}NH\textsubscript{2}</td>
<td>c</td>
<td>15.9</td>
<td>76</td>
</tr>
<tr>
<td>CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{11}OH</td>
<td>c</td>
<td>16.5</td>
<td>73</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Theoretical thicknesses were calculated for the molecule in a fully extended conformation using molecular mechanics (MM2). \textsuperscript{b} Contact angles are an average of a minimum of three measurements and have a standard error of ±3°. \textsuperscript{c} Not measured.

To support these results and to provide further evidence for terminal acetylene monolayer formation, cyclic voltammetry (CV) was employed for SAMs on gold surface. In order to confirm the integrity and stability of these alkyne terminated SAMs on gold, the ability of the SAM to electrochemically block a redox probe, ferricyanide ions, was explored by CV. As shown in Figure 1.11, the current response of ferricyanide and thus the electrochemical blocking of that its reduction and redoxidation varies with chain length of the terminal acetylene SAM. Longer chain lengths exhibit almost complete electrochemical blocking. However, gold slides that were incubated in ethanol solutions of dodecyalcohol, dodecane, and dodecylamine showed little ability to electrochemically block redox response
Moreover, the alkyne terminated SAMs were stable towards multiple successive voltage sweeps.

Figure 1.11. Cyclic voltammograms at 100 mV/s of Fe(CN)$_{6}^{3-/4-}$ at bare gold bead and SAM-modified gold bead electrodes with compounds 1.$^{54}$

Figure 1.12. Cyclic voltammograms at 100 mV/s of Fe(CN)$_{6}^{3-/4-}$ at gold slides immersed into ethanol of dodecyl alcohol (black line), dodecane (red line), dodecyl amine (green line), and dodecyne (blue line ).$^{54}$
However, it remains unclear as to what type of interaction occurs between the acetylene and the gold surface. A couple of observations by Gorman et al. helped eliminate some of the possible binding motifs. When the terminal acetylene SAM were formed from a tetrahydrofuran solution containing $n$-butyllithium, which create optimum condition to generate the acetylide, unreasonable values were obtained for water contact angle and thickness by ellipsometry. This observation provides evidence to suggest the bonding interaction is not of a dative acetylide-metal bond. Another possible bonding interaction between the acetylene and gold is a $\pi$-type interaction, which would give the bonding molecules an orientation that is parallel to the surface plane. However, if this were the case, the molecules 3 and 4 in Figure 1.10 should show similar electron transfer kinetics at the interface between the ferrocene and the gold electrode. However, the average electron transfer rate ($k_\text{on}$) was $20.6 \pm 3.0 \text{ s}^{-1}$ for compound 3 and $3.7 \pm 0.5 \text{ s}^{-1}$ for compound 4 (and surface coverages were $3.78 \times 10^{-10}$ and $2.93 \times 10^{-10}$ mol/cm$^2$ respectively from integration of the voltammogram). This difference in electron transfer rates suggests that electron transfer occurred along the chain of each molecule and the orientation of these species must be closer to perpendicular to the surface plane.

The above results do not support an unambiguous assignment of the molecule/metal binding interaction. A tentative assignment has been made, however, that is largely based on a theoretical report of the bonding energies associated with several different types of bonding interactions of terminal alkyne on gold. More specifically, this report explored the bonding energies of three possible bonding interactions of phenyl acetylene on gold. These were a dative bonding interaction, a vinylidene intermediate interaction, and a flat $\pi$-bonding
interaction (Figure 1.13). These authors suggested that a 1,2-hydride shift can occur to form a vinylidene carbene, which then could datively bond to gold (Figure 1.14). They found that the vinylidene intermediate should theoretically be the most exothermic interaction. Moreover, this bonding interaction between vinylidene carbene and a metal surface has also been confirmed experimentally. Tulevski et al. showed the carbene intermediate could form a monolayer with a ruthenium surface. Therefore, a vinylidene carbene derived from a 1,2-shift of alkyne terminated molecules has the possibility to form SAMs on gold surfaces. If the vinylidene intermediate can be formed directly by organic synthesis and is found to form the same SAM as an acetylene molecule, this could be important evidences that the vinyl carbene is indeed the species binding to the metal.

![Figure 1.13](image1.png)

**Figure 1.13.** Configuration of surface-bound molecule: (a) final state, (b) vinylidene intermediate, and (c) flat intermediate.

![Figure 1.14](image2.png)

**Figure 1.14.** Scheme of the 1,2-hydride shift and the resulting vinylidene carbene.
1.4 References.


CHAPTER 2. SYNTHESIS OF A CARBENE PRECURSOR: THE GENERATION OF PRIMARY AND SECONDARY VINYL CARBENE AND DIRECT CARBENE GENERATION FROM CARBONYL FUNCTIONAL GROUP

2.1 Introduction.

Generally, a carbene is described as a neutral molecule having a carbon atom with two unshared electrons and formula of RR'C: (Figure 2.1). The first postulated carbene was generated by Eduard Buchner in 1903 when exploring cyclopropanation of ethyl diazoacetate with toluene. Also, Hermann Staudinger in 1912 generated cyclopropanes from alkenes and diazomethane using carbene as an intermediate. In 1954, Doering et al. identified the existence of dichlorocarbene, Cl₂C: which ever since, has been a well studied carbene.

Figure 2.1. Structure of methylene (carbene).

Specifically, unsaturated carbenes, also termed alkylidene carbenes, have been widely studied as a reactive intermediate in many reactions. Understanding the electronic energy states of unsaturated carbenes may assist us in understanding their reactivity. A carbene may be in one of three of the following low energy states: 1) singlet state (S₀) where one carbon p orbital is empty and the second contains two unshared spin-paired electrons, 2) singlet state (S₁) in which both orbitals are singly occupied with spins anti-parallel, and 3) triplet state (T₁) in which two electrons with parallel spins singly occupy two carbon orbitals. Theoretical
calculations using different procedures all predict a singlet ground state for vinylidene carbenes with a singlet-triplet splitting of 20 ~ 46 kcal/mol.\textsuperscript{5-7}

\[
\begin{array}{c}
\text{(S}_0\text{)} \\
\text{(S}_1\text{)} \\
\text{(T}_1\text{)}
\end{array}
\]

Taber and co-workers reported some detailed theoretical work on vinylidene carbenes.\textsuperscript{8} In this study, \textit{ab} initio calculations employing a 6-31G basis set for vinylidene carbene indicated that the lowest energy state is a singlet carbene, which is essentially \textit{sp} hybridized (\textit{S}_0). In this case, the highest occupied molecular orbital (HOMO) extends linearly as with an alkyne and the \textit{p} orbital becomes empty which has the potential to be the lowest unoccupied molecular orbital (LUMO).\textsuperscript{8} Moreover, experimental evidence for carbenes preferentially obtaining a singlet state was found work done by Gilbert and Ohira.\textsuperscript{9-12} They confirmed that C-H insertion into a sterochemically defined methine proceeded with retention of absolute configuration.

Here, we determine whether a vinyl carbene can be prepared directly and exposed to gold in order to explore whether this molecule can form SAMs on gold via vinylidene intermediate. As mentioned in Chapter 1, one energetically favorable mechanism for the formation of terminal alkyne SAMs on gold is through generation of a vinyl carbene by 1,2-shift of the triple bond, which then leads to the carbene datively bonding to gold. If carbene-terminated organic molecules can be synthesized directly and are found to form the
same SAM as an terminal alkyne molecule, this could be significant evidence that the vinyl carbene is indeed the species binding to the metal.

Synthesis of vinylidene carbenes can be performed via several methods through the use of various precursors. As was mentioned above, carbenes can be produced by retro-1,2-shift of alkynes, which is thought to be the mechanism for formation alkyne SAMs. Since 1,2-shifts are reversible at high temperatures, the vinylidene carbenes shown in Scheme 2.1, can be generated in equilibrium with the precursor alkyne at elevated temperatures.

\[
\text{Scheme 2.1. Carbene generation by 1,2-shift: } R=\text{H, CH}_3, \text{Si(CH}_3)_3.\]

Carbenes can also be generated by \(\alpha\)-elimination methods. For instance, Eisler et al. showed that a carbene can be generated by lithium-halogen exchange of a 1,1-dibromoalkenes to yield an alkyl lithium intermediate, which can then undergo \(\alpha\)-elimination to form the product (Scheme 2.2).\(^{13,14}\) In this case, alkyne migrations in a Fritsch-Buttenberg-Wiechell rearrangement via lithium-halogen exchange in 1,1-dibromo-2,2-diethynylethenes using \(\alpha\)-elimination was shown and this rearrangement can be effected on a variety of substrates, and it tolerates silyl, aryl, acetylenic, and alkyl substitution on the precursor dibromo-olefines. Additionally, a carbenes can be produced by extrusion of nitrogen from 1-diazoalkenes, which will be discussed later in this Chapter.\(^{15,16}\)
Another method for vinylidene carbene generation by α-elimination which will be employed here is the mild generation of vinylidene carbenes from silylvinyl triflates reported by Stang et al. (Scheme 2.3). They showed a route for the formation of silylvinyl triflate 5, which was precursor before generating the carbene 6. In this route 2-isopropyl-1,3-dithiane 1 was converted from isobutyraldehyde and 1,3-propanedithiol in an isolated yield of 72%. The conversion of the dithiane 1 into 2-lithiodithiane 2 is most conveniently achieved by adding an equimolar amount of n-butyllithium to dithiane in a tetrahydrofuran (THF) at -20 °C. The reaction time varied with the steric and electronic character of the group R-group at the α-carbon. For example, if the R group was C₆H₅, metalation occurred within a few minutes but if the R-group was tert-butyl, complete metalation required about 5 hours. Next, the 2-lithiodithiane 2 has been found to react with chlorotrimethylsilane to afford the expected displacement product, 2-isopropyl-2-trimethylsilyl-1,3-dithiane 3, in high yield (88%). Acylsilane 4 was prepared in 54% overall yield by reaction of 3 with mercuric chloride and cadmium carbonate in 10% aqueous dimethyl sulfoxide (DMSO). For the conversion of acylsilane 4 to silylvinyl triflate 5, several different amine bases could be used. Use of pyridine gave 5 in 34% yield after 3 days of reaction, while use of N,N-diisobutyl-2,4-dimethyl-3-penylamine as the amine base resulted in a 51% yield of 5 after 7 hours of reaction. When 2,6-di-tert-butyl-4-methylpyridine was employed as an
amine base, the best yield for the formation of the triflate (5) was achieved (78%, 10 hours of reaction). However, the most appropriate amine base was \(N,N\)-diisobutyl-2,4-dimethyl-3-penylamine when considering purity, yield, and cost. For the conversion of 5 to the vinyl carbene (6), Stang et al. reported relatively high yields (92%) of the carbene adduct when 5 was treated with fluoride anion in a large excess of cyclohexene.\(^{19}\)

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO} + \text{HSCH}_2\text{CH}_2\text{SH} & \xrightarrow{\text{BF}_3\cdot\text{Et}_2\text{O}} \text{S}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SH} \\
n\text{-BuLi} & \xrightarrow{\text{TMSCl}} \text{S}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SiCH}_2\text{Li} \\
\text{HgCl}_2, \text{CdCO}_3 & \xrightarrow{10\% \text{ H}_2\text{O in DMSO}} \text{O}_\text{S}_\text{Si} \\
\text{CH}_2\text{Cl}_2, \text{Tf}_2\text{O} & \xrightarrow{\text{Base}} \text{O}_\text{S}_\text{Si} \xrightarrow{\text{KF} \text{ 18-crown-6}} \text{O}_\text{S}_\text{Si} \\
\end{align*}
\]

Scheme 2.3. Reported synthetic routes to carbenes.\(^{17}\)

As mentioned above, there are several different ways to generate carbenes, but an appropriate method must be chosen in order to explore whether a carbene is actually the binding species when making terminal alkyne SAMs. In order to probe whether terminal alkynes yield carbene species via a 1,2-hydride shift upon reaction to from SAMs, it is necessary to make a carbene that is analogous to what would be generated by this mechanism.
for SAM formation from terminal alkynes. Thus, it is not only important to focus on an adequate method for generation of a carbene, but it is important to verify that the method of interest yields a carbene with the appropriate alkyl chain. The reaction to synthesize carbenes has been shown to be highly affected by the steric and electronic character of the group R-group in the α-carbon position. Therefore, throughout this chapter, dodecyl aldehyde was employed as a starting material and various conditions different from literature procedures were employed to account for differences in the R-group in order to successfully synthesize the silylvinyl triflate as a carbene precursor. Initially, the procedure developed by Stang et al. was followed to convert dodecyl aldehyde to the corresponding vinylidene carbene, then other procedures were explored for forming a appropriate carbene.

2.2 Results and Discussion.

2.2.1 Synthesis of a Primary Vinyl Carbene.

2.2.1.1 Synthesis of 2-undecyl-1,3-dithiane (8).

As mentioned above, the procedure developed by Stang et al. for generating an vinylidene carbene was followed except dodecyl aldehyde 7 was employed as a starting molecule instead of isobutyraldehyde because dodecyl aldehyde should provide a carbene that has an appropriate chain length to potentially allow for a well-organized SAM and is more comparable to the alkyne based SAMs made by Gorman et al.\textsuperscript{19,21}

First, through modified reaction conditions from the procedure developed by Stang et al., the protection reaction of dodecyl aldehyde 7 to form the dithiane product 8 was
done successfully. The protection reaction of dodecyl aldehyde 7 was performed under various reaction conditions, different from what was employed by Stang et al. in order to determine optimal conditions for forming the dithiane product 8 because the alkyl chain, R, is different from alkyl chain used from the reference literature procedure.\textsuperscript{18,20} Specifically, the dodecyl aldehyde in chloroform was combined with an equimolar amount of propane-1,3-dithiol at room temperature for 1 hour. Then, this reaction mixture was lowered to -20 °C and boron trifluoride was added dropwise via a syringe with the solution being stirred under nitrogen (N\textsubscript{2}). When the reaction temperature during addition of the boron trifluoride to the stirred solution was kept below -25 °C, the solution became frozen within the reaction flask. Presumably, freezing of the reaction solution occurred because the molecular weight of the aldehyde 7 was higher than the shorter chain length molecule used in the reference. Alternately, when the reaction was allowed to proceed at any temperature above -15 °C, the yield was poor because the formation of side products became more prevalent. However, at a reaction temperature of about -20 °C under N\textsubscript{2}, the reaction gave good yield of the product (8). On the other hand, the reaction time had little effect on the outcome of the reaction. After adding the boron trifluoride at -20 °C, the reaction was allowed to proceed for 1 to 24 hours at room temperature. However, after 1 hour, it was found that this protection reaction was fully converted to compound 8 with ~97% yield. Identification of the dithiane was made through \textsuperscript{1}H nuclear magnetic resonance (NMR) spectroscopy.
2.2.1.2 Synthesis of 2-undecyl-2-trimethylsilyl-1,3-dithiane (10).

In the procedure by Stang et al., several different reaction conditions were employed in the deprotonation step to form the 2-lithiodithiane followed by displacement of lithium ion to make trimethylsilyl-1,3-dithiane because this reaction is thought to be highly sensitive to steric hindrance of the R-group in the α-position.\textsuperscript{19,22} For example, in this displacement step, when R was simply \(-\text{H}\) or \(-\text{CH}_3\), reaction times of only 30 minutes to 2 hours at -25 °C were needed for conversion to the product with overall 73% yield. On the contrary, when R-group provided more steric hindrance, as tert-butyl, the reaction time was 3 days at -15 °C to -20 °C.

The synthesis of 2-undecyl-2-trimethylsilyl-1,3-dithiane 10 was prepared based on the procedure by Stang et al.\textsuperscript{19,22} Since, it has been clearly shown that the R-group has a substantial effect on the conversion to the dithiane during this step, it was anticipated that molecule 8 might require different conditions for this reaction to proceed efficiently to the desired product, 2-undecyl-2-trimethylsilyl-1,3-dithiane 10. In order to determine the correct conditions for the conversion of dithiane 8 to TMS-dithiane 10, experiments were done where this reaction was allowed to proceed for various reaction times and at under different temperatures. To avoid side reactions, the reaction was first cooled to -78 °C during the
deprotonation step. However, there was poor conversion of the reactant to the product with a significant amount of starting material recovered. In contrast, when the reaction was performed at higher temperatures, above -15 °C during the deprotonation step, there were a lot of impurities observed by thin layer chromatography (TLC) of the reaction mixture. When the deprotonation step proceeded at -35 °C for 2 hours and the displacement step was performed at -25 °C for 3 hours, a high yield (98%) of the desired product was observed.

Scheme 2.5. Synthesis of \textit{n}-alkyl-2-trimethylsilyl-1,3-dithiane.

2.2.1.3 Synthesis of 1-(trimethylsilyl)-dodecane-1-one (11).

To obtain a purified undecyl trimethylsilyl ketone, various reactions were employed. When following the reported procedure in above, hydrolysis to convert compound 3 to isobutyl trimethylsilyl ketone 4 was observed in 54% overall yield by using mercuric chloride and cadmium chloride as a Lewis acid in aqueous 90% DMSO.\textsuperscript{17,22} However, when using the above reaction conditions and reagents for the conversion of TMS-dithiane 10 to undecyl trimethylsilyl ketone 11, there was not only decomposition of the starting material but also practical issues with filtering the products for purification. The \textsuperscript{1}H NMR of the crude product showed a lot of side products and unreacted materials, which could be seen in the TLC as well. Purification to remove the mercury and cadmium salts by filtration after the
reaction was performed proved difficult because of the size of the mercury and cadmium salt particles, which were too small to filter by filter paper. In the reference procedure, the same problem was encountered, so they purified the reaction mixture by distillation. However, upon forming 11, the higher molecular weight and boiling point of this product compared to reported compound 4 made distillation not feasible. Specifically, when distillation was performed under higher temperatures, over 185 °C, most of the product was decomposed. Table 2.1 shows a summary of several of these reactions where conditions were varied to determine optimal conditions for yielding the product, but all were unsuccessful in forming the product. However, when a different route using mercuric chloride and mercuric oxide as a Lewis acid in aqueous 80% acetonitrile was employed, the reaction gave the compound 11 in high yield (98% Scheme 2.6). In this reaction, a fritted glass filter was employed to remove the all of the mercury and cadmium salt particles.
Table 2.1. Various attempts for the synthesis of undecyl trimethylsilyl ketone.

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Solvent</th>
<th>Temperature</th>
<th>Reaction time</th>
<th>result</th>
</tr>
</thead>
<tbody>
<tr>
<td>HgCl₂, CdCO₃</td>
<td>10% H₂O in DMSO</td>
<td>25°C</td>
<td>6 hours</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12 hours</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>24 hours</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>48 hours</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>120 hours</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>168 hours</td>
<td></td>
</tr>
<tr>
<td>140~180°C</td>
<td></td>
<td></td>
<td>0.5 hours</td>
<td>X</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4 hours</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5 hours</td>
<td></td>
</tr>
<tr>
<td>N-Bromosuccinimide (NBS)</td>
<td>20% H₂O in CH₃CN</td>
<td>-5°C</td>
<td>5 minute</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>15 minute</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30 minute</td>
<td></td>
</tr>
</tbody>
</table>

Scheme 2.6. Synthesis of undecyl trimethylsilyl ketone.

2.2.1.4 Synthesis of 1-trimethylsilyl-1-dodecenyl-triflate (12).

To convert compound 11 to compound 12, various conditions were explored, which resulted in successful formation of this product in relatively high yield, although 12 was not able to successfully be purified. This was done by using a base to deprotonate the proton at
the α-position of compound 11 to generate an anion of this compound 11a, which could be reacted with trifluoromethanesulfonic anhydride (Tf₂O) to yield silylvinyl triflate 12. For this conversion, various bases, solvent, reaction time, and electrophiles at their appropriate temperature were employed to identify suitable reaction condition (Table 2.2.). However, all reaction conditions failed to yield the desired product. When 2,6-di-tert-butyl-4-methyl pyridine was used as the base at room temperature for 0.5 to 2 hours with Tf₂O in dichloromethane (DCM) at -5 °C for 6 hours, a 43% overall yield was obtained, which was estimated by integration percent of vinyl proton in ¹H NMR. However, though 43% overall yield was obtained, the purification of this silylvinyl triflate (12) was too difficult presumably because the molecular weight of silylvinyl triflate (12) was higher than the molecular weight of reported product 5, thus this product could not be isolated.

Scheme 2.7. Synthesis of silylvinyl triflate.
Table 2.2. Various attempts for the synthesis of silylvinyl triflate.

<table>
<thead>
<tr>
<th>Base</th>
<th>Solvent</th>
<th>Reaction Time</th>
<th>TEMP. (°C)</th>
<th>Electrophile</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Time for Anion</td>
<td>Time for Nu with Tf₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,6-di-tert-butyl-4-methyl pyridine</td>
<td>DCM</td>
<td>0.5, 1, 2 hours</td>
<td>4, 6 hours</td>
<td>-5</td>
<td>Tf₂O 43</td>
</tr>
<tr>
<td>2,6-di-tert-butyl-4-methyl pyridine</td>
<td>DCM</td>
<td>0.5, 1, 2 hours</td>
<td>24, 48 hours</td>
<td>-5</td>
<td>Tf₂O 0</td>
</tr>
<tr>
<td>2,6-di-tert-butyl-4-methyl pyridine</td>
<td>DCM</td>
<td>0.5, 1, 2 hours</td>
<td>4, 6 hours</td>
<td>-5</td>
<td>Tf₂NPh trace</td>
</tr>
<tr>
<td>2,6-di-tert-butyl-4-methyl pyridine</td>
<td>DCM</td>
<td>0.5, 1, 2 hours</td>
<td>24, 48 hours</td>
<td>-5</td>
<td>Tf₂NPh 0</td>
</tr>
<tr>
<td>2,6-di-tert-butyl-4-methyl pyridine</td>
<td>THF</td>
<td>0.5, 1, 2 hours</td>
<td>1,2,3 days</td>
<td>-5</td>
<td>Tf₂O 0</td>
</tr>
<tr>
<td>2,6-di-tert-butyl-4-methyl pyridine</td>
<td>THF</td>
<td>0.5, 1, 2 hours</td>
<td>1,2,3 days</td>
<td>-5</td>
<td>Tf₂NPh 0</td>
</tr>
<tr>
<td>Pyridine</td>
<td>DCM</td>
<td>0.5, 1, 2 hours</td>
<td>1,2,3 days</td>
<td>0</td>
<td>Tf₂O trace</td>
</tr>
<tr>
<td>Pyridine</td>
<td>DCM</td>
<td>0.5, 1, 2 hours</td>
<td>1,2,3 days</td>
<td>0</td>
<td>Tf₂NPh 0</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>DCM</td>
<td>1 hour</td>
<td>1, 4 hours</td>
<td>0</td>
<td>Tf₂O 0</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>DCM</td>
<td>1 hour</td>
<td>1, 4 hours</td>
<td>0</td>
<td>Tf₂NPh 0</td>
</tr>
<tr>
<td>Dimethylamino-pyridine</td>
<td>DCM</td>
<td>1 hour</td>
<td>1, 4 hours</td>
<td>0</td>
<td>Tf₂O 0</td>
</tr>
<tr>
<td>LDA</td>
<td>THF</td>
<td>1 hour</td>
<td>2 hours</td>
<td>-78</td>
<td>Tf₂O 0</td>
</tr>
<tr>
<td>LDA</td>
<td>THF</td>
<td>1 hour</td>
<td>2 hours</td>
<td>-78</td>
<td>Tf₂NPh 0</td>
</tr>
<tr>
<td>LDA</td>
<td>DME</td>
<td>1 hour</td>
<td>2 hours</td>
<td>-78</td>
<td>Tf₂O 0</td>
</tr>
<tr>
<td>LDA</td>
<td>DME</td>
<td>1 hour</td>
<td>2 hours</td>
<td>-78</td>
<td>Tf₂NPh 0</td>
</tr>
</tbody>
</table>

* Tf₂O : Trifluoromethanesulfonic anhydride
* Tf₂NPh : N-Phenyl-bis(trifluoromethanesulfonimide)
* LDA : Lithium diisopropylamide
Although it was anticipated that the primary vinyl carbene (13) could be formed by using fluoride as a base in cyclohexane with 18-crown-6, further perusal of the literature suggested that carbene (13) would convert rapidly to the more stable terminal alkyne (14) by a 1,2-shift (Scheme 2.8). In fact, the relative migratory aptitudes of various groups associated with alkyl carbenes have been studied but the relative migratory aptitudes of groups associated with vinylidene carbenes have not been reported.

![Scheme 2.8. Rearrangement from primary carbene to terminal alkyne.](image)

In reporting, the synthesis of vinylidene carbenes from primary and secondary vinyl triflates compared the tendency of these carbenes to subsequently be trapped by a trapping agent, which gives insight into the lifetime of these species. In these reports, when a primary vinyl triflate was converted to the vinyl carbene in the presence of trapped an unsymmetrical olefin trap to form a cyclic olefinic adduct, only a terminal alkyne was observed. Presumably, the vinylidene carbene rearranged to the terminal alkyne by 1,2-migration before it could react with the olefin. However, when the secondary vinyl triflate was used, the desired, cyclic olefinic adduct was obtained in overall 85% yield. This result suggests that the lifetime of the secondary vinylidene carbene is higher than that of the
primary vinylidene carbene. In the work here, it was realized that, since primary vinylidene carbenes have been shown to undergo rapid rearrangement, this fact would not allow for a successful demonstration. Specifically, it would not be possible to tell whether the primary vinylidene carbene that was generated reacted with the surface or rearranged to the terminal alkyne which then reacted with the surface.

For this reason, it was decided that it would be better to synthesize a more stable secondary vinyl carbene analogue and explore whether this molecule could form SAMs. Specifically, a methyl 1,2-shift for the secondary vinyl carbene should be much slower than a hydrogen 1,2-shift for the primary vinyl carbene because it is anticipated that the methyl shift has more steric hindrance than the hydrogen shift. The relative strengths of the carbon-carbon bond compared to the carbon-hydrogen bond also may be a factor. The secondary vinyl carbene has an additional methyl group, which could generate unfavorable steric interactions that disrupt the ability to densely pack the molecules during the formation of SAMs. However, we still hypothesized that if the alkyne based SAMs form via a primary carbene, a secondary carbene should still show a tendency to form monolayers on gold even though they may be less densely packed. Therefore, it was decided that one could still synthesize the secondary vinyl carbene of compound 13 and use this molecule to explore the study of the interaction between terminal alkyne and gold surface.
2.2.2 Synthesis of a Secondary Vinyl Carbene.

2.2.2.1 Synthesis of 2-(2-methyldecyl)-1,3-dithiane (16).

To synthesize the secondary vinyl carbene of compound 13, 2-methylundecane aldehyde 15 was employed as a starting molecule and was reacted with boron trifluoride to form 16 (Scheme 2.9). In this protection reaction, when the boron trifluoride was added to a mixture of 15 and 1,3-propanedithiol at -20 ºC and the solution was allowed to warm to room temperature slowly overnight, the product was obtained in 98% overall yield. The identity of the dithiane (16) was confirmed by $^1$H NMR spectroscopy.

\[
\begin{align*}
\text{15} & \quad \text{BF}_3 \cdot \text{Et}_2\text{O} \\
\text{HS} & \quad \text{SH} \\
\text{16} & 
\end{align*}
\]

Scheme 2.9. Synthesis of 2-(2-methyldecyl)-1,3-dithiane.

2.2.2.2 Synthesis of 1-methyldecyl-2-trimethylsilyl-1,3-dithiane (18).

The synthesis of 1-methyldecyl-2-trimethylsilyl-1,3-dithiane 18 was successfully done according to Scheme 2.10. Similar conditions to those for the synthesis of 2-undecyl-2-trimethylsilyl-1,3-dithiane 10 were employed (Scheme 2.5). Specifically, the reaction was performed at -35 ºC for 2 hours during the deprotonation step to produce 17 in situ, and -25 ºC for 3 hours during the displacement step to yield 18 in an overall yield of
89%. For this reaction, $^1$H NMR was used to confirm that 1-methyldecyl-2-trimethylsilyl-1,3-dithiane 18 was formed.

Scheme 2.10. Synthesis of 1-methyldecyl-2-trimethylsilyl-1,3-dithiane.

2.2.2.3 Synthesis of 2-methyl-1-(trimethylsilyl)undecan-1-one (19).

The synthesis of 2-methyl-1-(trimethylsilyl)undecan-1-one 19 used the same reaction conditions employed for the formation of undecyl trimethylsilyl ketone (11). As shown in Scheme 2.11, the reaction was performed at 80 °C (reflux) for 6 hours in aqueous 80% acetonitrile. The compound 19 was purified by column chromatography and had a 79% overall yield.

Scheme 2.11. Synthesis of 1-methyl-1-decyl trimethylsilyl ketone.
2.2.2.4 Synthesis of 1-trimethylsilyl-2-methyl-1-undecenyl triflate (20).

The synthesis of the secondary silylvinyl triflate, 20 was attempted under the same reaction conditions employed for the synthesis of the primary silylvinyl triflate, 12, as shown in Scheme 2.7. Similar to the results given in Table 2.2., when 2,6-di-tert-butyl-4-methyl pyridine was used as the base (with Tf₂O in DCM) to react with compound 19 at -5 °C, this resulted in 38% overall yield (Scheme 2.12). In the formation of 20 from 19, the crude product showed the presence of 20 as a dominant product as shown by ¹H, ¹³C NMR, and IR spectroscopy. However, some difficulties were encountered in the purification of 20. When column chromatography was used for purification, ¹H NMR characterization showed peaks consistent with the disappearance of the trimethylsilyl group. Furthermore, normal distillation was unsuccessful for purification of this crude product 20 presumably because of the high boiling point, which is estimated to be 170 °C. Thus, to separate 20 from the crude product, a high vacuum distillation was performed. Through this purification, the pure product, 20 was obtained at 85 °C and 1.5 × 10⁻³ mm Hg. The existence of the pure product 20 was verified using ¹H, ¹³C NMR, and IR spectroscopy.

However, the reproducibility of the synthesis of 20 was relatively poor because the purification of desired product (20) was difficult even though it was possible using high vacuum distillation. Therefore, it was decided that it might be better to investigate methods for generating a carbene from extrusion of nitrogen from a 1-diazoalkenes, which has been shown to be a successful method for generating a carbene because our final goal is not on the synthesis of carbene precursor molecules but carbene intermediate self assembled monolayers on gold. It was anticipated that a modification to the olefination reaction done by Peterson26 would be and easier method for forming an appropriate carbene that could potentially form a self assembled monolayer on gold.

2.2.3 Generation of Carbene from Carbonyl Functional Group and Formation of Vinylidene Carbene SAMs on Gold: Extrusion of Nitrogen from 1-diazoalkenes.

To use the carbene intermediate as vinylidene on monolayer formation directly, a new preparation of methylenecyclopropanes utilizing trimethylsilyldiazomethane, which was introduced by Saki and his co-worker in 1999 was employed.16 Previously, they had revealed that the reaction of lithium trimethylsilyldiazomethane with carbonyl compounds proceeds smoothly to generate vinylidene carbenes.27 As shown in Scheme 2.13, the vinylidene carbene was generated by reaction of a molecule containing a carbonyl group with lithium trimethylsilyldiazomethane. This intermediate then underwent a cyclization reaction in the presence of an alkene, which yielded a methylenecyclopropane relatively high yield (69%).
Scheme 2.13. Literature synthetic routes by modified Peterson Olefination.\textsuperscript{16}

Following this new method, the formation of vinylidene carbene SAMs on gold was attempted. In Scheme 2.14, deprotonation of trimethylsilyldiazomethane (21) occurred using a strong base, \( n \)-butyllithium at \(-78 \, ^{\circ}\text{C}\) under nitrogen. Then, the reaction solution temperature was changed to \(-50 \, ^{\circ}\text{C}\) for 30 min. Dodecyl aldehyde and 2-methyl-1-((trimethylsilyl)undecan-1-one were added to form the 1-diazoalkene (23). As shown in Scheme 2.14, the oxygen in the carbonyl group was anticipated to be substituted with diazomethane via a \( S_N 2 \) substitution. Then, the intermediate, 1-diazoalkene (23) was then expected to spontaneously extrude to generate the vinylidene carbene (24), which would be exposed to a cleaned gold slide. Various surface characterization techniques could then be used to determine whether a SAM was formed.
Scheme 2.14. Generation process of vinylidene carbene from carbonyl with lithium trimethylsilyldiazomethane.

At the same time, various control experiments were employed to verify that all the components in Scheme 2.14 were necessary to form the SAM. These control experiments are shown in Scheme 2.15. Dodecyl aldehyde was submerged in tetrahydrofuran with a cleaned gold slide to determine whether dodecyl aldehyde SAMs on gold could be formed without any of the other reagents in Scheme 2.14 (Scheme 2.15a). In another control experiment, \( n \)-butyllithium was exposed to a gold slide to determine whether SAMs of \( n \)-butyllithium could be formed on gold (Scheme 2.15b). Moreover, a control was done where a gold slide was submerged in a solution of trimethylsilyldiazomethane in tetrahydrofuran with \( n \)-butyllithium to determine whether trimethylsilyldiazomethane SAMs on gold could be formed. The resulting samples were then analyzed by various surface characterizations to determine whether a SAM was formed.
Scheme 2.15. Various control experiments to rule out SAM formation on gold without the presence of aldehyde, base or trimethylsilyldiazomethane. \( R_1 = C_{11} \) and \( R_2 = H \).

Table 2.3. Advancing water contact angles and ellipsometric film thickness for vinylidene carbene intermediate SAMs on gold.

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Contact Angle (°)</th>
<th>Film thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheme 2.14</td>
<td>84</td>
<td>13.0</td>
</tr>
<tr>
<td>Scheme 2.15a</td>
<td>70</td>
<td>0.0</td>
</tr>
<tr>
<td>Scheme 2.15b</td>
<td>68</td>
<td>0.0</td>
</tr>
<tr>
<td>Scheme 2.15c</td>
<td>69</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 2.3 shows the results from water contact angle and ellipsometric thickness measurements of the SAMs made following Scheme 2.14 and Scheme 2.15 (control experiments). The samples made following Scheme 2.14 showed an ellipsometric thickness and advancing contact angle less than that found in a densely packed such as that found from terminal alkyne SAMs on gold.\(^{21}\) In reported results, a calculated length of 1-dodecyne in a
full extended conformation using molecular mechanics (MM2) was 15.3 Å, its ellipsometric thickness was 14.0 Å, and advancing contact angle from the 1-dodecyne SAMs on gold was 96°.\textsuperscript{21} In contrast, the thickness of the SAMs made following Scheme 2.14 was 13.0 Å and an advancing water contact angle of 84° was obtained by advancing water contact angle. These lower values than expected could be explained by the presence of physisorbed salt residues, which could be potentially result in the SAM being less densely packed due to these contaminates impeding complete formation of the SAM. However, clearly, the control experiment did not show any appreciable thickness by ellipsometry and did not show a water contact angle suggestive of monolayer formation (Table 2.3). These results indicated that the SAMs following Scheme 2.14 were formed by the vinylidene carbene generated from the carbonyl.

Additionally, to further confirm the formation of SAMs on gold made following Scheme 2.14, electrochemical characterization was employed. Various electrochemical techniques have been employed to confirm the formation of SAMs, although in this work we explored the blocking ability of the non-redox active SAMs towards the oxidation/reduction of a redox active molecules in solution (Figure 2.2). Redox blocking of ferricyanide has been used as a model system for electrochemical characterization techniques,\textsuperscript{28-30} for study of electrode kinetics,\textsuperscript{31,32} and for determination of diffusion coefficients.\textsuperscript{33}
Figure 2.2. Scheme showing the surface of a gold electrode where methyl terminated alkanethiolates SAMs are present with Fe(CN)$_6^{3-/4-}$ in solution and no SAM is present.

Gold surfaces exposed to the conditions shown in Schemes 2.14 and 2.15 were characterized by cyclic voltammetry. Figure 2.3 shows the redox response of Fe(CN)$_6^{3-/4-}$ at a gold electrode treated following the procedure outlined in Scheme 2.14 and 2.15 (control experiments) compared to the redox response at a bare gold electrode. With the gold covered by a vinylidene carbene monolayer, the strong redox response that was present at the bare gold electrode was almost absent. However, all of control experimental yielded samples that could not block the redox response of Fe(CN)$_6^{3-/4-}$. These results were consistent with the ellipsometric thickness and advancing water contact angle results presented above, which suggest that a pre-generated carbene could be used to form SAMs on gold.
Figure 2.3. Cyclic voltammograms at 100 mV/s of Fe(CN)$_6^{3/-4-}$ at bare gold and SAM modified gold electrodes with vinylidene carbene intermediate and controls. (a) Bare gold, (b) SAMs prepared from Scheme 2.1, (c) 2.14, (d) 2.15, and (e) 2.15c.

2.3 Conclusion.

To confirm the type of interaction that exists between a terminal alkyne and gold surface, attempts were made to synthesize various carbenes and exposed them to gold. It was thought that, if such molecules could be synthesized and formed SAMs on gold that are similar to that which is obtained from primary alkyne, this should be good evidence that primary alkyne SAMs are formed through vinyl carbene. In the synthesis of the primary carbene, the alkyl TMS ketone, which was a starting molecule to make the precursor of the vinylidene carbene was successfully synthesized by given steps. The synthesis of the
precursor of the vinylidene carbene, silylvinyl triflate was attempted using various reaction conditions. The best results were obtained using 2,6-di-tert-butyl-4-methyl pyridine as a base with Tf₂O in DCM. However, under these conditions, ¹H NMR data indicated only ca. 40% yield from integration of the vinyl proton versus the trimethylsilyl protons. A number of side products were also observed. We later became concerned that this primary vinyl carbene target would convert to the more stable terminal alkyne form by a 1,2-shift, frustrating our demonstration. Therefore, the synthetic target was changed to a secondary vinyl carbene which was anticipated to be much less susceptible to rearrangement. Following the reaction conditions used in the synthesis of the primary vinyl carbene, the synthesis of a secondary vinyl carbene was pursued. Although the precursor of the secondary vinylidene carbene was synthesized, the purification of the desired products has not yet been achieved because of its decomposition during column chromatography and high boiling point making distillation inefficient. High vacuum distillation obtained the desired product but the yield was poor.

Therefore, we changed our procedure for generating these carbenes from α-elimination of enol triflates with bases to extrusion of nitrogen from 1-diazoalkenes. A slightly modified version of the Peterson Olefination reaction was employed and the vinylidene carbene was successfully generated from dodecyl aldehyde by lithium trimethylsilyldiazomethane. Measurements by contact angle, ellipsometry, and cyclic voltammetry support the fact that SAMs were successfully formed on gold from this alkylidene carbene. These experiments, however, do not rule out the rapid rearrangement of the alkylidene carbene to the 1-alkyne and subsequent monolayer formation from that species. Future work could involve
formation of a 1,1-disubstituted carbene which would have to undergo a less likely alkyl shift to re-form the alkyne.

2.4 Experimental Section.

2-undecyl-1,3-dithiane (8). A reported procedure\textsuperscript{18,20} was followed with slight modification. A solution (0.6 M) of dodecyl aldehyde 7 (27.7 g, 150 mmol) in chloroform was mixed with an equimolar amount of 1,3-propanedithiol (16.2 g, 150 mmol) at room temperature. The solution was stirred at room temperature for 1 hour prior to cooling to -20 °C. Then boron triflate etherate (BF$_3$·Et$_2$O, 10.64 g, 75 mmol) was slowly added as dropwise via a syringe. The solution was allowed to warm to room temperature for approximately 3 hours. The reaction mixture was worked up by successively washing with water, 10% aqueous potassium hydroxide (KOH), and water and drying the organic layer over sodium sulfate (Na$_2$SO$_4$). Evaporation of the solvent furnished a crude product (yellowish oil) which was purified by column chromatography (gradient elution using up to 2% ethyl acetate in hexanes) in 97% yield; $^1$H NMR (CDCl$_3$) δ (ppm) 4.08 (s, 1H), 2.81 (m 4H), 1.78 (m 2H), 1.51 (br m 2H), 1.22 (m 18H), 0.81 (t 3H).

2-undecyl-1,2-trimethylsilyl-1,3-dithiane (10). A solution (0.24 M) of the dithiane 8 (7.68 g, 28 mmol) in distilled tetrahydrofuran (THF) at -35 °C under nitrogen was stirred and treated with one equivalent of 1.6 M n-butyl lithium (21 mL, 35 mmol) in hexane at the rate of 1-2 mL/min for 2 hours to generate the anion. Then, an equimolar amount of distilled chlorotrimethylsilane (3.04 g, 28 mmol) was added dropwise to a stirred solution of the lithium dithiane 9 under nitrogen at -25 °C for 3 hours. At the end of reaction, 10 vol.% of
water was added, and most of the THF was removed under reduced pressure. Water (120 mL) and DCM (120 mL) were added, the layers were separated, and the aqueous phase was extracted several times with the 40 mL of DCM. The organic layers were washed successively with water, 10% KOH, and water, dried over Na₂SO₄, and a column purification (in 100% hexane) gave compound 10 (colorless oil) in 98% yield; ¹H NMR (CDCl₃) δ (ppm) 2.91 (t, 2H), 2.38 (t 2H), 2.01 (t 1H), 1.81 (t 1H) 1.41 (br m 2H), 1.20 (m 18H), 0.81 (t 3H), 0.19 (s 9H).

1-(trimethylsilyl)dodecan-1-one (11). A solution (0.1 M) of the n-alkyl TMS dithiane 10 (9 g, 26 mmol) in aqueous 80% acetonitrile (270 mL) was added at room temperature to an efficiently stirring solution of mercuric chloride (15.48 g, 57.2 mmol) in the aqueous 80% acetonitrile followed by mercuric oxide (6.21 g, 28.6 mmol). The dithiane-mercuric chloride complex usually separated as a white precipitate. The mixture was stirred and heated at reflux under nitrogen for 6 hours, cooled and filtered through Celite, and the precipitate was washed thoroughly with 1:1 hexane-dichloromethane. The organic phase of the filtrate was washed successfully with 5 M aqueous ammonium acetate, water, and brine, dried over Na₂SO₄. Evaporation of the solvent furnished a crude product (yellowish oil) which was purified by column chromatography (gradient elution using up to 2% ethyl acetate in hexanes) in 98% yield; ¹H NMR (CDCl₃) δ (ppm) 1.58 (br m 2H), 1.18 (m 18H), 0.81 (t 3H), 0.18 (s 9H).

1-Trimethylsilyl-1-dodecenyl Triflate (12). To a flask equipped with a stopper under nitrogen were placed 0.06 g of triflic anhydride in 0.6 mL of distilled DCM. The reaction
flask was cooled to -5 ºC with an ice bath, and 2,6-di-tert-butyl-4-methyl pyridine (0.024 g, 0.2 mmol) followed by undecyl trimethylsilyl ketone 11 (0.05 g, 0.2 mmol) were each added dropwise via a syringe to the stirring solution. After stirring the reaction mixture for 3 hours at -5 ºC and 4 hours at room temperature, the solvent was removed under reduced pressure and pentane was added to the yellow semisolid mixture. A white solid precipitated and was removed by suction filtration. The organic solution was extracted successively with three portions of ice-cold 1N HCl and then with three portions of water. The organic mixture was dried with Na$_2$SO$_4$: NMR (CDCl$_3$) δ (ppm) 5.61 (s 1H), 1.50 (br m 2H), 1.18 (m 18H), 0.81 (t 3H), 0.18 (s 9H).

2-(2-methyldecyl)-1,3-dithiane (16). A solution (0.54 M) of dodecyl aldehyde 15 (2.5 g, 13.56 mmol) in chloroform was mixed with an equimolar amount of 1,3-propanedithiol (1.47 g, 13.56 mmol) at room temperature. The solution was stirred at room temperature for 1 hour prior to cooling to -20 ºC. Then BF$_3$·Et$_2$O (1 g, 6.78 mmol) was slowly added as dropwise via a syringe. The solution was allowed to warm to room temperature for approximately 3 hours. The reaction mixture was worked up by successively washing with water, 10% aqueous KOH, and water and drying the organic layer over Na$_2$SO$_4$. Evaporation of the solvent furnished a crude product (yellowish oil) which was purified by column chromatography (gradient elution using up to 1% ethyl acetate in hexane) in 98% yield; $^1$H NMR (CDCl$_3$) δ (ppm) 4.08 (s, 1H), 2.81 (m 4H), 2.09 (m 1H), 1.78 (m 2H), 1.51 (br m 1H), 1.22 (m 16H), 1.02 (d 3H), 0.81 (t 3H).
**1-methyldecyl-2-trimethylsilyl-1,3-dithiane (18).** A solution (0.18 M) of the dithiane 16 (1.51 g, 5.5 mmol) in distilled THF at -35 °C under nitrogen was stirred and treated with the one equivalent of 1.6 M n-butyl lithium (4.3 mL, 6.88 mmol) in hexane at the rate 1-2 mL/min for 2 hours to generate the anion. Then, an equimolar amount of distilled chlorotrimeylsilane (0.6 g, 5.5 mmol) was added dropwise to a stirred solution of the lithium dithiane 17 under nitrogen at -25 °C for 3 hours. At the end of reaction, 10 vol.% of water was added, and most of the THF was removed under reduced pressure. Water (30 mL) and DCM (30 mL), and the layers were separated. The aqueous layer was extracted several times with the 10 ml of DCM. The organic layers were washed successively with water, KOH (10%), and water, dried over Na₂SO₄. Column purification (in 100% hexane) gave compound 18 in 89% yield; ¹H NMR (CDCl₃) δ (ppm) 2.91 (t, 2H), 2.38 (t 2H), 2.01 (t 1H), 1.81 (t 1H) 1.41 (br m 1H), 1.20 (m 16H), 1.17 (d 3H), 0.81 (t 3H), 0.19 (s 9H).

**2-methyl-1-(trimethylsilyl)undecan-1-one (19).** A solution (0.1 M) of 1-methyldecyl-2-trimethylsilyl-1,3-dithiane 18 (0.65 g, 1.88 mmol) in aqueous 80% acetonitrile (20 mL) was added at room temperature to an efficiently stirring solution of mercuric chloride (1.12 g, 4.14 mmol) and mercuric oxide (0.45 g, 2.06 mmol) in the aqueous 80% acetonitrile. The dithiane-mercuric chloride complex usually separated as a white precipitate. The mixture was stirred and heated at reflux under nitrogen for 6 hours, cooled down to room temperature. The white precipitate, which is dithiane-mercuric chloride complex, was filtered through Celite, and washed thoroughly with 1:1 hexane-dichloromethane. The organic phase of the filtrate was washed successively with 5 M aqueous ammonium acetate, water, and brine, dried over Na₂SO₄. After under reduced
pressure, the crude products (yellowish oil) were purified by column chromatography (gradient elution using up to 2% ethyl acetate in hexanes) in 79% yield; IR 1640 (C=O), 1460, 1374, 1249, 981, 842, 755 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ (ppm) 2.79 (m 1H), 1.19 (m 16H), 0.90 (d 3H), 0.81 (d 3H), 0.18 (s 9H).

1-trimethylsilyl-2-methyl-1-undecenyl triflate (20). A solution (0.25 M) of the 2-methyl-1-(trimethylsilyl)undecan-1-one 19 (0.2 g, 0.8 mmol) in distilled DCM (3.2 mL) was added at room temperature to the triflic anhydride (0.25 g, 0.8 mmol). Then, the reaction flask was cooled to -5 $^\circ$C with an ice bath, and 2,6-di-tert-butyl-4-methyl pyridine (0.19 g, 0.8 mmol) were added as dropwise to the stirring solution. After 3 hours at -5 $^\circ$C and 4 hours at room temperature, the solvent was removed under reduced pressure and pentane was added to the light yellow precipitate. A white solid was removed by suction filtration and organic phases were extracted with three portions of ice-cold 1N HCl and then with three portions of water. The organic mixture was dried with Na$_2$SO$_4$, and purified by high vacuum distillation at 85 $^\circ$C and 1.5 $\times$ 10$^{-3}$ mm Hg for 2 hours: IR 1627 (C=C), 1461, 1394, 1249, 1143, 943, 845, 763 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ (ppm) 1.75 (s 3H), 1.38 (br m 2H), 1.18 (m 14H), 0.81 (t 3H), 0.42 (s 9H).

Monolayer preparation. The gold coated glass substrates were acquired by previous group members. Trials were performed to find an optimal method for cleaning the gold surface. The optimal method was defined as that resulting in a surface that was most similar to that previously reported by Gorman et al.$^{21}$ The optimal method for cleaning the gold slides is described as follows. First, the gold slides were cleaned in a “piranha” solution (3:7
H₂O₂/H₂SO₄) for 15 min, then washed thoroughly with deionized (DI, nanopure 18Ω·cm²) water by sonication for 10 min and rinsed with ethanol. *Caution! “piranha” solution should be handled carefully because of its violent reactivity with organic molecules.* Next, the substrate was cleaned by sonication in ethanol for 10 minutes, and then rinsed with ethanol again. This cleaning cycle was performed one more time except the samples were not cleaned in the piranha solution. To make the vinylidene carbene intermediate monolayers, n-butyllithium (1.87 mL, 3 mmol) was added dropwise to 0.3 M of trimethylsilyldiazomethane in THF at -50 °C under nitrogen and then stirred for 30 min. 2.49 mmol of dodecyl aldehyde and cleaned gold slide was added slowly. The mixture was stirred at -50 °C for 1 hour and then warm up to room temperature for 2 days.

**Electrochemical Measurements.** Electrochemical redox blocking experiments were performed with a BAS CV-50W voltammetric analyzer and a 100 mM potassium chloride (KCl) solution containing 1 mM potassium ferricyanide [K₃Fe(CN)₆]. The solutions were prepared with deionized water and purged with nitrogen for over 3 min. A single-compartment, standard three-electrode glass cell was used with silver/silver chloride (Ag/AgCl, saturated KCl) as reference electrode, a platinum (Pt) coiled wire as counterelectrode, and a monolayer-modified gold substrate as working electrode.

**Ellipsometric Film Thickness Measurements.** The thicknesses of SAMs were measured by variable-angle spectroscopic ellipsometer (J. A. Woollam, Inc., Lincoln, NE) and single-wavelength ellipsometer, with incident angle of 70° (AutoEL, Rudolph Research, Flanders). The average refractive index value of the clean gold substrate was used in the determination
of thickness by use of a three-layer model (ambient/organic film/gold). A refractive index of $n = 1.5$ was used in the thickness calculations.\textsuperscript{34}

**Contact Angle Measurements.** The water contact angle measurements were performed by the sessile drop technique in an optical contact angle device with electronic syringe (8 $\mu$L). The water droplets on the SAM modified gold surface were viewed with a charge-coupled device (CCD) video camera, and a minimum of three measurements on each surface were performed.
2.5 References.


CHAPTER 3. SYNTHESIS OF ALKYNE MONOLAYER STABILIZED GOLD NANOPARTICLES

3.1 Introduction.

Among various metal nanoparticles (NPs), gold nanoparticles (AuNPs) are the most studied. There is an immense difference between the properties of these nano size materials and their bulk counterparts. For example, AuNP can display a plasmon resonance. Generally, these properties allow for AuNPs to potentially be applied to many important application such as catalysis, nanoelectronics, cell biology, biological microscopy, medicine, and sensors, etc. AuNPs hold much promise as a vital building block in the bottom-up approach of nanotechnology.

In the synthesis of AuNPs, the most widely studied and well known method for forming these NPs is through reduction of hydrogen tetrachloroaurate(III) (HAuCl₄) in water by citrate. Initially, ca. 20 nm sized, citrate-stabilized AuNPs were formed by Turkevitch in 1951 using this method, and then Frens and his co-workers reported 16 and 147 nm sized, citrate-stabilized AuNPs. In this study, the size of AuNPs depended on the ratio between reducing/stabilizing agent (trisodium citrate) and gold(III). The citrate stabilized AuNPs has been used very widely employed because the citrate ligands provide a good precursor for preparing various AuNPs-based materials.

The synthesis of AuNPs using other types of stabilizing agents has been explored as well. For instance, thiols were first reported as a stabilizing agent in 1993 by Mulvaney and
They showed that AuNPs can be stabilized by various chain length of alkanethiols. The most popular method of the synthesis of thiol stabilized AuNPs was introduced in 1994 by Brust-Schiffrin,\textsuperscript{31} which is a two-phase synthesis, which results in the AuNPs being stabilized by an alkanethiol. This method has provided a facile synthesis of thermally stable AuNPs in which the size of the AuNPs can be very easily controlled. Other methods for synthesizing alkanethiol stabilized AuNPs have been explored by other researchers involving better control of the size of AuNPs,\textsuperscript{32-36} synthesis in a single-phase system,\textsuperscript{31-33,37} “place exchange” of a controlled proportion of thiol ligands by various functional thiols,\textsuperscript{38} etc. Moreover, other types of sulfur containing molecules besides thiols as a stabilizer have been explored for the synthesis of AuNPs such as di-sulfides, which is not as stable of protector towards aggregation of AuNPs.\textsuperscript{39-42} In addition, trithiols,\textsuperscript{43} xanthates,\textsuperscript{44} and tetradeutate thioethers\textsuperscript{45} have been studied as other stabilizers for the synthesis of AuNPs.

Exploring other binding group molecules as stabilizing agents on AuNPs may be useful because there is the potential to improved or fine tune the properties of the AuNPs.\textsuperscript{3} For instance, Weare and co-workers used triphenylphosphine (PPh\textsubscript{3}) as a stabilizer in order to improve the synthesis of AuNPs.\textsuperscript{46} Specifically, they employed the biphasic AuNP synthetic method reported by Brust using hydrogen tetrachloroaurate trihydrate and tetraoctylammonium bromide (TOAB) as a phase transfer agent in a water-toluene mixture. PPh\textsubscript{3} was used as a stabilizer and then a reducing agent (sodium borohydride, NaBH\textsubscript{4}) was added in the solution for the formation of phosphine-stabilized AuNPs. Using PPh\textsubscript{3} as a stabilizer, they easily made 1.5 nm size of AuNPs with relatively homogeneous size.
Various studies of molecules containing amine,\textsuperscript{47-50} isocyanide,\textsuperscript{51-53} acetone,\textsuperscript{54} and iodine\textsuperscript{55} binding groups as stabilizer for the synthesis of AuNPs were also reported.

As shown previously Chapter 1, Gorman \textit{et al.} reported the synthesis of terminal alkyne-stabilized AuNPs following the Brust-Schiffrin method involving a two-phase synthesis.\textsuperscript{56} They employed sodium tetrachloroaurate (NaAuCl\textsubscript{4}) in water/toluene with TOAB to transfer the gold salt into organic layer. Then, the gold(III) was reduced by NaBH\textsubscript{4} with 1-dodecyne in the presence of a terminal alkyne molecule as a stabilizer. These AuNPs showed a plasmon resonance at 524 nm, which is typical for gold nanoparticles. They also performed a transmission infrared spectroscopy, which showed a loss of the terminal $\equiv$C-H stretch. Furthermore, transmission electron microscopy (TEM) images supported the formation of 1-dodecyne-stabilized AuNPs (4.5 ± 0.3 nm and 2.6 ± 0.3 nm). Transmission infrared spectrum of 1-dodecyne-stabilized AuNPs also showed a loss of the terminal $\equiv$C-H. However, if other molecules in solution such as TOAB instead of the terminal alkyne-stabilized the AuNPs, the transmission infrared spectrum would show a loss of the terminal $\equiv$C-H stretch also. A control experiment where the same methodology was employed without 1-dodecyne was performed to confirm that the 1-dodecyne was stabilizing the AuNPs. Interestingly, the reduced gold could be also stabilized by TOAB. The UV-Vis spectra for TOA-AuNPs indicated the typical plasmon resonance at 530 nm. More convincingly, nuclear magnetic resonance spectroscopy (NMR) showed peaks consistent with the formation of TOA-AuNPs.
Because TOA is a potentially competing ligand during nanoparticle synthesis, we explored a new method for forming homogeneous terminal alkyne-stabilized AuNPs without TOA present. Here we provide evidences for their formation. This novel synthesis of a homogeneous terminal alkyne AuNPs may be useful and important for applications, especially in catalysis because less densely packed AuNPs could potentially provide more active sites for such catalytic reactions.

3.2 Results and Discussion.

3.2.1 Synthesis of Terminal Alkyne-Stabilized Gold Nanoparticles by Ligand Replacement.

3.2.1.1 Synthesis of Citrate-Stabilized Gold Nanoparticles.

To use a citrate-stabilized AuNPs for making a terminal alkyne-stabilized AuNPs by citrate replacement by terminal alkyne, the citrate-stabilized AuNPs were prepared by the conventional synthetic procedure which was introduced by Turkevich (Scheme 3.1).25 Usually, H\textsubscript{2}AuCl\textsubscript{4} is used using when following this method, but many researchers have employed NaAuCl\textsubscript{4}\textsuperscript{57-60} and KAuCl\textsubscript{4}\textsuperscript{27,61-63} in aqueous and organic solvent. In this Chapter, both H\textsubscript{2}AuCl\textsubscript{4} and NaAuCl\textsubscript{4} were employed to form the AuNPs and both yielded similar results except for slight differences in solubility.

\[
\text{NaAuCl}_4 \xrightarrow{\text{H}_2\text{O, boiling,}} \text{Citrate-AuNPs}
\]

\text{Trisodium Citrate (Na}_3\text{C}_6\text{H}_5\text{O}_7 \text{1 w\% in DI H}_2\text{O})

Scheme 3.1. Preparation procedure of citrate-stabilized AuNPs in DI water.
Various combinations of stabilizer/gold salt ratio were employed to obtain a smaller citrate AuNPs and well dispersed citrate-stabilized AuNPs were synthesized. Table 3.1 in trial 2 shows the optimized combination as 0.4 mM of NaAuCl₄ and 2 mL of 2% trisodium citrate and they were characterized by TEM and UV-Vis spectroscopy. Figure 3.2a shows a representative TEM image of relatively homogeneous citrate-stabilized AuNPs made above in trial 2 and the corresponding histogram of the diameter of the particles (10.98 ± 1.1 nm) is shown in Figure 3.1d. Moreover, the citrate-stabilized AuNPs had a plasmon resonance in the UV-Vis spectra around 518 nm, which is a typical plasmon resonance for AuNPs of this size (Figure 3.1c).
Table 3.1. Various combinations of stabilizer/gold salt ratio.

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* Reference²⁷
Figure 3.1. (a) A TEM image of the citrate-stabilized AuNPs, (b) photograph of citrate-stabilized AuNPs, (c) UV-Vis absorption spectrum for sample #2, and (d) a size histogram of 10.98 ± 1.1 nm citrate-stabilized AuNPs.

The color of the solution gives a rough indication of the gold clusters that are formed. Generally, a formation of large aggregates causes a change in color of the AuNPs solution from red to violet due to coupling of the surface plasmons in aggregated colloids. When the size of AuNPs becomes smaller, the color of solution changes: violet (~100 nm) → red (~20 nm) → orange (8 nm) → deep brown (~1 nm). As shown in Figure 3.2b, the color of this solution was red, which is the representative of AuNPs of around 10 nm in size.
3.2.1.2 Synthesis of Terminal Alkyne-Stabilized Gold Nanoparticles by Replacement of the Citrate Ligand by a Terminal Alkyne.

Replacement of SAMs on various substrate has been studied previously and has been utilized in the synthesis of monolayer protected AuNPs, usually with the AuNPs initially being protected by citrate. Figure 3.2a shows a schematic of the synthesis of terminal alkyne (1-dodecyne) stabilized AuNPs from citrate-stabilized AuNPs in water. In Figure 3.3a, initially the hydrophilic citrate-stabilized AuNPs are well dissolved in an aqueous solvent such as water. However, 1-dodecyne has a low solubility in water, so replacement of the citrate with this molecule in water is not feasible. Therefore, as shown in Figure 3.2a, toluene was added to the red aqueous solution containing the citrate-stabilized AuNPs, which created two separated liquid phases (Figure 3.2a 2). As mentioned above, 1-dodecyne dissolves well in toluene. Then, a 1:1 volume ratio of toluene and 10 mM of 1-dodecyne in ethanol was added (Figure 3.2a 3). In this case, if the citrate is replaced by 1-dodecyne on the AuNPs, then the aqueous layer will become clear and the organic layer will become red in color (Figure 3.2a 4). Figure 3.3b shows photographs of an experiment where this was done, which is consistent with the schematic indicating that the citrate on the AuNPs (hydrophilic) was replaced by the terminal alkyne (hydrophobic).
Figure 3.2. (a) Schematic indicating the expected results of stabilizer replacement of terminal alkyne (hydrophobic) onto citrate-stabilized gold nanoparticles (hydrophilic) and (b) Photographs of experimental results of stabilizer replacement.

To further confirm the synthesis of 1-dodecyne-stabilized AuNPs following this method, measurements were taken with transmission FTIR, \(^1\)H NMR, and UV-Vis. Figure 3.3 shows the results of these measurements for 1-dodecyne-stabilized AuNPs which indicated that there were no evidence for citrate compared with reported results for citrate-stabilized AuNPs.\(^{70}\) More detailed discussion of these results of transmission FTIR, \(^1\)H NMR, and UV-Vis for 1-dodecyne-stabilized AuNPs will be shown in Chapter 4.
3.2.2 Synthesis of Terminal Alkyne-Stabilized Gold Nanoparticles by Method of Direct Synthesis.

3.2.2.1 Synthesis of Thiol-Stabilized Gold Nanoparticles by Brust-Schiffrin Method: Two-Phase Synthesis and Stabilization by Thiols and Terminal Alkyne.

As mentioned above, AuNPs stabilized with thiol as well as terminal alkynes have been made following the Brust-Schiffrin method, which involves a two-phase synthesis. Scheme 3.2 shows a general procedure for the synthesis of these AuNPs. In this case, the
AuCl₄⁻ dissolves in water. Then, toluene is added to this water layer, to make two individual liquid phases. AuCl₄⁻ is transferred to toluene layer when TOAB is added as a phase transfer reagent. These gold ions will be reduced by NaBH₄ and stabilized by either a thiol or terminal alkyne:

\[
\text{AuCl}_4^- (\text{aq}) + N(C_8H_{17})_4^+(C_6H_5\text{Me}) \rightarrow N(C_8H_{17})_4^+\text{AuCl}_4^-(C_6H_5\text{Me})
\]

\[
m\text{AuCl}_4^-(C_6H_5\text{Me}) + n\text{RSH or } n\text{RC\equivCH(C}_6\text{H}_5\text{Me}) + 3m^- \rightarrow
\]

\[
4m\text{Cl}^- (\text{aq}) + \left[Au_m(\text{RSH})_n \text{ or } Au_m(\text{RC\equivCH})_n \right](C_6H_5\text{Me})
\]

**Scheme 3.2. Preparation procedure for the synthesis of the thiol or terminal alkyne-stabilized AuNPs.**

Following this conventional procedure, the synthesis of phenylethanethiol and 1-dodecyne stabilized AuNPs was explored. By following the change in color of the solution, the progress of the synthesis was monitored. AuCl₄⁻ in water was yellow and the color changed to orange in the toluene layer when TOAB was added. Gradually, the toluene layer became clear in color when a phenylethanethiol or 1-dodecyne was added into this solution.
as a stabilizer. This time interval called the “aging time” is one of the key factors in this procedure. For instance, when a reducing agent was added before the solution became clear, the reduced gold aggregated. In contrast, if the reducing agent was added well past the aging time, the clear solution changed to a dark gray color, and then the reduced gold aggregated. The ideal aging time was approximately 10 minutes when thiol was employed as the stabilizing agent and 40 minutes when terminal alkyne was employed as the stabilizing agent. Under these conditions, the clear solution immediately changed to dark brown color when phenylethanethiol was employed and dark red color when 1-dodecyn e was employed (Figures 3.4a and c). Then, the solutions were washed by methanol and acetonitrile to remove all of unbound molecules. Figures 3.4b and d show UV-Vis spectra of AuNPs stabilized with phenylethanethiol and 1-dodecyn e where the plasmon resonance peaks can clearly be seen. These results are consistent with reported results.56,71
Figure 3.4. (a) Photograph of the phenylethanethiol-stabilized AuNPs; (b) UV-Vis absorption spectrum of phenylethanethiol-stabilized AuNPs; (c) photograph of the 1-dodecyne-stabilized AuNPs; and (d) UV-Vis absorption spectrum of 1-dodecyne-stabilized AuNPs.

NMR has been used to characterize the configuration of stabilizers on AuNPs.\textsuperscript{2,36,72-75} NMR was used to characterize the phenylethanethiol-stabilized AuNPs synthesized above. However, the \textsuperscript{1}H NMR of these thiol-stabilized AuNPs showed a strong peaks corresponding to tetraoctylammonium (TOA) even though the NPs were washed thoroughly by various solvents such as alcohol and acetonitrile to remove unreacted materials.\textsuperscript{76,77} Figure 3.5 shows a representative \textsuperscript{1}H NMR of a solution of phenylethanethiol-stabilized AuNPs in CDCl\textsubscript{3}. Here, one can observe peaks that can be attributed to the phenylethanethiol (phenyl
protons at 7 ppm and ethyl protons at 2.9 ppm), but one can also see peaks corresponding to TOA, which appear at 3.3, 1.2, and 0.8 ppm.

![NMR spectrum](image)

**Figure 3.5.** $^1$H NMR spectra of purified phenylethanethiol-stabilized AuNPs (solvent: CDCl$_3$), red arrow indicates three peaks of tetraoctylammonium onto AuNPs.

In order to confirm the role of TOAB in this two-phase synthesis, a control experiment following the Brust-Schiffrin Method was employed where stabilizer was excluded. Figure 3.6a shows a schematic representing what was done during this control experiment. It was hypothesized that without the stabilizing agent, the AuNPs would aggregate. As shown in the insert in Figure 3.6, the AuNPs synthesized during this control experiment yielded a dark, red-colored solution, which is a typical color of AuNPs that are well dispersed. After removing most of the residue, an absorbance of the plasmon resonance was obtained, which was a typical absorbance of AuNPs. All of these results indicate that the TOAB participated
in the reaction as a protecting ligand as well as a phase transfer. Therefore, to obtain a homogeneous terminal alkyne SAMs on AuNPs, a different synthetic route was required because it was anticipated that both protecting ligands (e.g. TOA and alkyne) can exist on reduced gold surface, and thus the AuNPs cannot strictly be regarded as thiol or terminal alkyne-stabilized AuNPs.

Figure 3.6. (a) Preparation procedure of tetraoctylammonium-stabilized AuNPs, without thiol stabilizer and (b) the corresponding UV-vis absorption spectrum. Inset is image of TOA-stabilized AuNPs in toluene.
3.2.2.2 Novel Method of Synthesis of Terminal Alkyne-Stabilized Gold Nanoparticles: Absence of Phase Transfer Reagent, One Phase Synthesis.

To synthesize a homogeneous terminal alkyne-stabilized AuNPs, a new synthetic method omitting TOAB was followed (Scheme 3.3). In this sort of method involving only one phase, one requirement is that a solvent, an alcohol, can dissolve not only NaAuCl₄ but also the terminal alkyne.

\[
\text{NaAuCl}_4 + \text{Alcohol} \xrightarrow{1) \text{Toluene}} 2) \text{Terminal alkyne} \xrightarrow{3) \text{NaBH}_4} \text{Terminal Alkyne-AuNPs}
\]

Scheme 3.3. Modified preparation procedure of terminal alkyne-stabilized AuNPs.

In order to find the optimum ratio of alcohol to toluene, various trials were conducted where this ratio was changed (Table 3.2). Only a minimum amount of alcohol was required because a solubility of terminal alkyne as well as the terminal alkyne-stabilized AuNPs after forming the AuNPs was higher in toluene mixed with alcohol. The optimum mixture was 0.5 vol.% of alcohol in toluene. When less than 0.5 vol.% of alcohol was employed, NaAuCl₄ was not fully dissolved and the solution formed a yellow precipitate. In this case, when the NaAuCl₄ was reduced to gold(0), the gold particles aggregated. The amount of added terminal alkynes (C₆⁻C₁₄) was also important and the optimized amount was 1.4 ~ 3 mM of terminal alkynes. Too small of an amount of terminal alkyne (less than 1.4 mM) led to aggregation. In contrast, when greater than 3 mM of terminal alkyne was used, formation of stable AuNPs seemed to occur. However, despite obtaining the AuNPs, it
was still difficult to remove all of the unbound terminal alkynes. In this case, it was impossible to dry the unbound terminal alkynes in high vacuum.

The other important factor regarding the reaction conditions is the amount of reducing agent added. It was found that the ideal amount was 0.27 mM. When the volume of the reducing agent added was less than 0.3 mL or greater than 0.4 mL of 0.27 mM of NaBH₄, the gold(0) aggregated. As mentioned above, aging time was important, and the optimized aging time was 30 ~ 40 minutes before injecting the reducing agent.

Table 3.2. Various attempts for optimum condition of the formation of terminal alkyne-stabilized AuNPs.

<table>
<thead>
<tr>
<th>NaAuCl₄ (μmol)</th>
<th>Alcohol (0.5%)</th>
<th>Toluene (ml)</th>
<th>Alkyne (C₁₂, mM)</th>
<th>Aging time (min)</th>
<th>NaBH₄ (0.27 mM, ml)</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ~ 30</td>
<td>X</td>
<td>X</td>
<td>✓</td>
<td>4.5</td>
<td>1.4 ~ 3</td>
<td>30 ~ 40</td>
</tr>
<tr>
<td>&lt; 10 or &gt; 30</td>
<td>X</td>
<td>X</td>
<td>✓</td>
<td>4.5</td>
<td>1.4 ~ 3</td>
<td>30 ~ 40</td>
</tr>
<tr>
<td>10 ~ 30</td>
<td>X</td>
<td>X</td>
<td>✓</td>
<td>4.5</td>
<td>&lt; 1.4</td>
<td>30 ~ 40</td>
</tr>
<tr>
<td>10 ~ 30</td>
<td>X</td>
<td>X</td>
<td>✓</td>
<td>4.5</td>
<td>&gt; 3</td>
<td>30 ~ 40</td>
</tr>
<tr>
<td>10 ~ 30</td>
<td>X</td>
<td>X</td>
<td>✓</td>
<td>4.5</td>
<td>1.4 ~ 3</td>
<td>&lt; 30 or &gt; 40</td>
</tr>
<tr>
<td>10 ~ 30</td>
<td>X</td>
<td>X</td>
<td>✓</td>
<td>4.5</td>
<td>1.4 ~ 3</td>
<td>30 ~ 40</td>
</tr>
</tbody>
</table>

X: aggregation, ✓: no aggregation, *a: not reproducible

To confirm the formation of 1-dodecyne-stabilized AuNPs, the plasmon resonance was measured by UV-Vis spectroscopy and TEM images were obtained to determine the size distribution of the AuNPs. Figure 3.7a, b, and d show a TEM image, a photograph of relatively uniform, 1-dodecyne-stabilized AuNPs, and the corresponding histogram of the diameter of the particles (2.51 ± 1.44 nm). Additionally, the plasmon resonance from the
UV-Vis spectra (Figure 3.7c) was present at 532 nm, which is a reasonable absorbance of AuNPs of around 2 ~ 3 nm in diameter as mentioned previously. Moreover, various other chain length terminal alkynes were employed as the stabilizing agent and all formed stable AuNPs (not shown here). To further confirm the synthesis of 1-dodecyne-stabilized AuNPs following this method, measurements were taken with $^1$H NMR and transmission FTIR, which indicated that there were no evidences for the existence of the TOA-AuNPs, and there was homogeneous terminal alkyne-stabilized AuNPs. We will show the results of $^1$H NMR and transmission FTIR to further confirm the terminal alkyne-stabilized AuNPs in Chapter 4.

Figure 3.7. TEM image of the (a) 1-dodecyne-stabilized AuNPs, (b) photograph of 1-dodecyne-stabilized AuNPs, (c) UV-Vis absorption spectra, and (d) size histograms of 2.51 ± 1.44 nm.
3.3 Conclusion.

Terminal alkyne-stabilized AuNPs were successfully formed by replacement of citrate-stabilized AuNPs. Citrate-stabilized AuNPs were synthesized by a commonly used procedure and used as a precursor to form the terminal alkyne-stabilized AuNPs. When the citrate was replaced by 1-dodecyne on the AuNPs, the aqueous layer became clear as the AuNPs transferred to the organic layer, which became red. To confirm the synthesis of 1-dodecyne-stabilized AuNPs following this replacement, data taken from TEM, UV-Vis absorption spectra, FTIR spectra, and $^1$H NMR supported the formation of the terminal alkyne-stabilized AuNPs.

Using a two-phase synthesis method, AuNPs stabilized by organic ligands were synthesized. In these cases, phase transfer reagent is typically used. However, it was difficult to remove the phase transfer reagent from the AuNPs. The $^1$H NMR spectra of these solutions showed peaks consistent with the presence of a phase transfer reagent, even after repeated washing. Thus, to obtain a homogeneous terminal alkyne-stabilized AuNPs without a significant amount of impurities or unreacted material, a novel synthetic route was developed where AuNPs were synthesized in the absence of a phase transfer. Various attempts to make AuNPs under various conditions without the presence of a phase transfer reagent eventually led to appropriate conditions to successfully form homogeneous terminal alkyne-stabilized AuNPs using a modified version of the Brust-Schiffrin method. To confirm the synthesis of terminal alkyne-stabilized AuNPs following this method, TEM,
UV-Vis absorption spectra, FTIR spectra, and $^1$H NMR were used and indicated that the homogeneous terminal alkyne-stabilized AuNPs were successfully formed.

3.4 Experimental Section.

**Materials and Chemicals.** 1-hexyne (Aldrich 97%), 1-heptyne (Aldrich 98%), 1-nonyne (Aldrich 99%), 1-decyne (Aldrich, 98%), 1-dodecylene (Acros, 97%), 1-hexadecyne (Aldrich), 2-phenylethanethiol (Aldrich, 98%), Tetraoctylammonium bromide (Aldrich, 98%), Sodium tetrachloroaurate(III) dihydrate (NaAuCl$_4$$\cdot$2H$_2$O, Alfa aesar, 99.99%), Hydrogen tetrachloroaurate(II) trihydrate (HAuCl$_4$$\cdot$3H$_2$O, Alfa aesar, 99.9%) and Sodium citrate (Na$_3$C$_6$H$_5$O$_7$, Fisher) were used as purchased.

**Synthesis of AuNPs.** The citrate-stabilized AuNPs are prepared following a method introduced by Turkevich.$^{25}$ Sodium tetrachloroaurate(III) dihydrate (NaAuCl$_4$$\cdot$2H$_2$O, 0.4 g, 1 mmol) was dissolved in deionized water (250 mL), and the solution was brought to a vigorous boil with stirring in a Erlenmeyer flask. A aqueous solution of sodium citrate (Na$_3$C$_6$H$_5$O$_7$, 1 w%) was added to the NaAuCl$_4$$\cdot$2H$_2$O solution slowly. The solution was allowed to boil for an additional 20 min. At this moment, the color of gold solution changed from pale yellow to dark red. Then, the AuNP solution was cooled to room temperature and stored at -4 °C, which was stable for several weeks. The terminal alkyne-stabilized AuNPs are following a modified method introduced by Brust-Schiffrin Method$^{31}$ but one phase synthesis. Sodium tetrachloroaurate(III) dihydrate (NaAuCl$_4$$\cdot$2H$_2$O, 83 μg, 10 mmol) was dissolved in 0.5 vol.% of butanol (0.2 mL). 4.5 mL of toluene was injected in the solution and then 1.4 mM of terminal alkyne was added with stirring in vial. After stirring for
30 ~ 40 min as an aging time, increase the speed of stirring to maximum and 0.4 mL of 0.27 mM of NaBH₄ in DI water was added dropwise. The color of solution was changed to dark red in a few seconds. After further stirring for 12 hours, the organic layer was washed with DI water to remove polar residue and then the solution was exposed in high vacuum to evaporate the toluene. The black solid was washed by acetonitrile many times until the spot of residue disappeared in TLC indicating the removal of the unbound terminal alkyne. The sample was then dried under vacuum.

**Transmission Electron Microscopy.** The size of citrate-capped gold nanoparticles and distribution of particle sizes monitored by TEM were determined with Philips CM12 TEM operated at 100 kV. Images were captured by use of a Gatan 780 camera and Digital Micrograph software. The samples were prepared by dropping three drops of the gold nanoparticles in water onto a 200-mesh carbon-coated copper grid. To determine the size of NPs, ImageJ 1.42q, Java 1.6.0_10 (32-bit) was used and a range of the circularity was between 0.5 and 1.0.
3.5 References.


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CHAPTER 4. INVESTIGATION OF TERMINAL ALKYNES MONOLAYERS ON GOLD: STUDIES OF BINDING GEOMETRY

4.1 Introduction.

Metal–alkyne complexes have been widely studied.\textsuperscript{1,2} Particularly, vinylidenes, which are unsaturated carbenes, have been explored as a catalyst in terminal alkynes metathesis.\textsuperscript{3,4} As mentioned in Chapter 2, the reactivity of unsaturated carbenes, which are tautomeric with alkynes has been summarized by Stang.\textsuperscript{5,6} Interestingly, the ligand undergoes spontaneous isomerization between the vinylidene and alkyne, but tends to favor the formation of the alkyne.\textsuperscript{2,3,7-13}

 Unsaturated carbenes generated from terminal alkynes can datively bond to various kinds of metals.\textsuperscript{2} For example, Kadyrov \textit{et al.} reported the synthesis of Ru–vinylidene complexes: (PCy\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}Ru=C=CHR (R = Ph and n-Bu) and (PCy\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}Ru=CHR (R = Ph and n-Bu), which are both precursors for metathesis catalyst.\textsuperscript{14} In various studies of Ru complexes, the Ru=C=CHR group has been shown to be an effective catalysis in coupling reaction of allylic alcohols with terminal alkynes.\textsuperscript{15-17} It is noteworthy that catalytic reactions involving metal vinylidene intermediates are promoted by Ru(II).\textsuperscript{18} Bianchini \textit{et al.} showed that CC formation between a vinylidene and an alkynyl ligands occurs at Ru complexes.\textsuperscript{19} In this study, they introduced a method to convert the vinylidene ligand to the alkynyl ligand via deprotonation. Using Ru–vinylidene complexes as catalyst precursor, highly selective ring opening metathesis polymerization of norbornene was shown by Koten.\textsuperscript{20} In general, with these reactions involving Ru–vinylidene complexes, 1,2-migration of internal alkynes played
an important role in preparing the Ru—vinylidene complexes. Also, Au—vinylidene complexes have been reported as proposed intermediates. These intermediates are proposed to result from the 1,2-migration of a hydrogen on a terminal alkyne.²¹ For example, Xia et al. suggested that the Au—vinylidene complexes, Au=C=CR₁R₂, acted as an intermediate in the cycloisomerization of propargylpyridines.²²,²³ Moreover, various other metal—vinylidene complexes containing tungsten (W), molybdenum (Mo), rhodium (Rh), iridium (Ir), cobalt (Co), manganese (Mn), osmium (Os), and rhenium (Re) have been explored and show similar bonding geometries with various vinylidenes.³,⁴,⁸,¹³,²⁴-²⁷

In studies of metal—alkyne complexes, an alkynyl binding configuration has been reported as the final geometry between the alkyne and the metal.² For example, Ipaktschi et al. demonstrated that the electrophilic addition to acetylide anion, which was bound to metal complexes gave rise to a variety of products such as η²-carbamoyl-(Z)-vinyl complexes.²⁸,²⁹ They also reported a synthesis of bimetallic tungsten gold complexes by addition of ClAuPPh₃ to the acetylide Li[(η⁵-C₅H₅)(CO)(NO)W(C≡C-R)].²⁵ In addition, using this alkynyl—gold(I) complexes, Puddephatt et al. showed various metal complexes such as angular arenediethynyl complexes of gold(I),³⁰ organometallic polymers with gold(I) centers bridged by diphosphines and diacetyldienes,³¹ luminescent gold(I) acetyldienes,³² rigid rod polymer of platinum(II) or gold(I) including diacetyldienes, diisocyanides, and diphosphines.³³

In case of gold(I) coordinated alkynes, the gold(I)—alkyne complexes were formed as a side-on geometry. For example, Kroll et al. showed an unstrained alkyne, which was synthesized using AuCl and 3-hexyne and characterized by X-ray crystallography. In this
studies, they suggested gold(I)—alkyne complexes as a side-on geometry and provided the X-ray crystal structure of Au(EtC≡CEt)Cl.\textsuperscript{34} Additionally, in studies of bimetallic tungsten gold complexes as mentioned above, the gold(I) was coordinated to alkyne as a side-on geometry.\textsuperscript{25}

A vinylidene bonding to single metal atoms has been shown in the formation of organometallic complexes, but it has also shown that these vinylidene molecules can bind to metal surfaces.\textsuperscript{35} Heck \textit{et al.} suggested that 1,1-dichloroethene binds to the surface of Pd/Au nanoshells in a vinylidene conformation.\textsuperscript{35} In this study, the vinylidene adsorbed to the surface following removal of chlorine atoms from 1,1-dichloroethene to form the vinylidene.

Carbene molecules do not always bind to metal surfaces through a vinylidene. They can also bind via a saturated carbene ligand (M=CR\textsubscript{1}R\textsubscript{2}), especially when the surface is gold and ruthenium nanoparticles (AuNPs and RuNPs). Zhou \textit{et al.} showed a catalytic reaction involving carbene intermediates binding to bulk gold, which were generated from diazoalkanes (R\textsubscript{2}C=N=N).\textsuperscript{36} Another example of a carbene binding to a metal surface was reported by Tulevski \textit{et al.} They found that diazomethane could form carbene monolayers on Ru surface where a double bond was formed between carbon and Ru.\textsuperscript{37} Chen \textit{et al.} reported a carbene functionalized RuNPs via carbenes generated from diazoalkanes.\textsuperscript{38-40} In addition, they showed an alkyne stabilized RuNPs using acetylide.\textsuperscript{41,42} However, there is still a lot of uncertainty as to what the final geometry of many these carbene intermediates on these metal surfaces are because of a lack of sufficient evidence to support any proposed structure.
In studies involving the formation of terminal alkyne SAMs on gold, a vinylidene binding configuration has been proposed as the final geometry between the alkyne and the substrate, which would involve a 1,2-hydride shift to form a carbene that can then datively bond to gold.\textsuperscript{43,44} As discussed in Chapter 1, a couple of observations by Gorman \textit{et al.} helped eliminate some of the possible binding motifs to find the applicable final geometry between the terminal alkyne molecules and the gold surface even though it still remains unclear as to what type of interaction occurs.\textsuperscript{44} The proposed binding motifs were based on a theoretical report of the bonding energies associated with several different types of bonding interactions of terminal alkynes on gold.\textsuperscript{43} This report suggested three possible bonding interactions of phenyl acetylene on gold, a dative bonding interaction, a vinylidene intermediate interaction, and a flat $\pi$-bonding interaction. It was suggested that the vinylidene geometry had the most exothermic interaction.

Here, we perform experiments to explore all the possibly binding geometries suggested by Gorman \textit{et al} along with some additional possible bonding geometries, which are a physical adsorption interaction, a standing-up geometry via an acetylide anion interaction, a flat geometry (side-on) via a $\pi$ interaction, and a vinylidene geometry (end-on) via a carbene interaction between the alkyne and substrate (Figure 4.1).
4.2 Results and Discussion.

4.2.1 Possibilities of Terminal Alkyne Binding Between Head Group and Gold.

First experiments were done to reproduce the results obtained by Gorman et al. In the same manner that Gorman et al. did, 1-dodecyne, 1-dodecyl alcohol, 1-dodecyl amine, and dodecane were exposed to gold and the blocking ability of these surfaces towards the redox response of ferricyanide ions in solution was explored. As shown in Figure 4.2, there are no diminishations of the redox responses for all of samples except 1-dodecyne SAMs on the gold electrode. These results indicate that the interaction between the terminal alkyne and gold was not from physical adsorption.
Figure 4.2. Cyclic voltammograms at 100 mV/s of Fe(CN)$_6^{3-}/4^-$ at gold electrode immersed into ethanolic solutions of 1-dodecyne, 1-dodecyl alcohol, 1-dodecyl amine, and dodecane.

Additionally, experiments were performed to explore whether the type of interaction between terminal alkynes and gold is a π-type interaction merely due to physical adsorption. If the type of interaction is a π-type interaction, then ethynylferrocene and vinylferrocene should form similar SAMs. Here, both these molecules have the same structure except the terminal functional groups are an alkyne and alkene (Figure 4.3), which are both capable of forming a π-type interaction with a surface. Thus, experiments were done where gold was exposed to ethanolic solutions of ethynylferrocene and vinylferrocene, then the surface coverage of ferrocene was determined through cyclic voltammetry. The surface coverage of ethynylferrocene modified gold was $4.1 \times 10^{-10}$ mol/cm$^2$, which was determined from the
anodic current generated when doing cyclic voltammetry, and the electrochemical behavior was relatively reversible. The value for the surface coverage is comparable to the surface coverage of other ferrocene terminated SAMs on gold from the literature.\textsuperscript{45,46} This indicates that ethynylferrocene SAMs were successfully formed on gold. In contrast, the vinylferrocene modified gold electrode showed a relatively low surface coverage of $2.3 \times 10^{-11}$ mol/cm$^2$, which implies that a SAM was not formed. These results indicate that a $\pi$-type interaction is not the type of interaction that exists between a terminal alkyne and a gold surface.

![Figure 4.3](image)

**Figure 4.3.** Schematic indicating the coverage of ethynylferrocene and vinylferrocene adsorbed on gold.

Next, experiments were done to explore the possibility that the interaction between terminal alkynes and gold is through an acetylide anion. The acetylide anion is isoelectronic with isocyanide and, previously, it has been suggested that the acetylide could potentially binds to gold via a dative interaction.\textsuperscript{47-49} When employing ethanol as the solvent during solution deposition of a terminal alkyne onto gold, generation of the acetylide anion is hindered because the pKa of ethanol is 16 while the pKa of terminal alkynes is around 24,
ethanol will rapidly protonate any acetylide anion formed. Therefore, to explore whether an acetylide anion can bind to gold, a tetrahydrofuran/alkyne solution was exposed to a gold surface after adding n-butyllithium. Figure 4.4 shows a schematic of the procedure that was done. In this case, these samples did not show any evidence of SAM formation by ellipsometry, water contact angle, and cyclic voltammetry. Usually, ethanol has been used as the solvent during solution deposition to form terminal alkyne SAMs on gold, but tetrahydrofuran was used here. Thus, to eliminate the possibility that the use of THF was not what hindered the formation of a stable SAM, a control experiment was done where a tetrahydrofuran/1-dodecyne solution was used to make 1-dodecyne SAM on gold via solution deposition. When following this method for forming 1-dodecyne SAMs on gold, an ellipsometric thickness of 14 Å, a water contact angle was 98°, and diminution of the redox response of ferricyanide ion was found, which suggest that a high quality SAM was formed. These results indicate that terminal alkynes do not bind to gold via an acetylide.

![Diagram of SAM formation](attachment:image)

**Figure 4.4.** Generation process of the acetylide anion and its application making SAMs on gold.

Experiments were done to explore the possibility that terminal alkynes bind to gold in a mode that renders the CC bond more like a double bond. These modes could be a lying down configuration via a flat \( \pi \)-binding interaction (Figure 4.1c) or a standing-up
configuration via a dative bond (Figure 4.1d). When a carbene if formed from a 1,2-hydride shift of a terminal alkyne having a triple bond, a vinyl carbene is formed, which contains a double bond. To explore whether a double bond was present within the SAM formed from terminal alkynes attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was employed. Bulk (KBr) transmission infrared spectra of free 1-dodecyne (Figure 4.5a) showed a terminal ≡C─H stretch at 3314 cm$^{-1}$, a C≡C stretch at 2119 cm$^{-1}$, and a ≡C─H bend fundamental at 630 cm$^{-1}$. In contrast, the ATR-FTIR spectra of 1-dodecyne SAMs on gold showed a loss of terminal ≡C─H stretch, C≡C stretch, and ≡C─H bend fundamental signals and a gain of a new signal at 1670 cm$^{-1}$. A peak between 1500~1900 cm$^{-1}$ can be attributed to a molecule having alkene functional group, but also other functional groups. Therefore, these results suggest one of these binding modes but do not do so conclusively.
Figure 4.5. Transmission infrared spectra of (a) free 1-dodecyne and (b) ATR-FTIR spectra of a 1-dodecyne SAM on gold.

In the IR spectrum, a peak in the region of 1680 ~ 1820 cm\(^{-1}\) can also be assigned to a carbonyl functional group where the exact position is highly dependent on environment.\(^{50}\) To justify the possible formation of a carbonyl functional group from the terminal alkyne molecule, a proposed keto-enol tautomerization reaction can be proposed and is shown in Figure 4.6. No efforts were made to remove water from the absolute ethanol used throughout these experiments. Thus, water was present in this solvent, which could facilitate the formation of a molecule containing a carbonyl functional group from the terminal alkyne molecules.
Figure 4.6. Possibilities of the generation of carbonyl from terminal alkyne with water on gold.

In order to explore whether SAMs made from terminal alkynes contain a carbonyl group, Auger Electron Spectroscopy (AES) was used to analyze the elements on samples. This was done making four samples (1) one sample of gold treated with Ultra Violet Ozone (UVO), (2) a sample where no further treatment was performed, (3) a 1-decanethiol SAM on gold, and (4) a 1-dodecyne SAM on gold. Then, these samples were analyzed by AES. Figure 4.7 shows Auger spectra of 1-decanethiol on gold, 1-dodecyne on gold, gold exposed only to UVO, and gold that was untreated. In all cases, peaks attributed to gold (18, 42, 98, and 119 eV) and carbon (240 eV) were present, even with the sample not passivated with a monolayer, which suggest that the bare gold samples were probably contaminated with organic matter from the atmosphere.\textsuperscript{51-53} The Auger spectra of 1-dodecyne on gold did not show any peak that could be attributed to oxygen around 520 eV. This result indicates that the new peak at 1670 cm\textsuperscript{-1} was not from a carbonyl group and suggests that this peak is likely from the presence of a double bond, especially from a vinylidene group.
Figure 4.7. Auger spectrum of (a) decanethiol SAMs on gold, (b) 1-dodecyne SAMs on gold, (c) UVO treated gold, and (d) bare gold.

In order to obtain more convincing evidence for the existence of a double bond when terminal alkyne SAMs are formed on gold, 1-dodecyne stabilized gold nanoparticles (AuNPs) were analyzed by IR where it was hoped that a strong peak associated with this functional group would be observed. In these experiments the AuNP were prepared by a modified version of the Brust-Schiffrin method as shown in Chapter 3. Using those 1-dodecyne capped AuNPs, bulk (KBr) transmission infrared spectra were taken. Figure 4.8 shows IR spectra of free 1-dodecyne and 1-dodecyne stabilized AuNPs. Compared to the IR spectra of free 1-dodecyne, the IR spectra of 1-dodecyne stabilized AuNPs showed the absence of
typical signals associated with an alkyne (a terminal $\equiv$C–H stretch at 3314 cm$^{-1}$, a C=C stretch at 2119 cm$^{-1}$, and a $\equiv$C–H bend fundamental at 630 cm$^{-1}$) and a new peak at 1718 cm$^{-1}$ appeared, which is consistent with the ATR-FTIR results in Figure 4.5b (Figure 4.8b). Interestingly, the IR spectra of 1-dodecyne stabilized AuNPs showed another new peak at 2005 cm$^{-1}$, which we suggest is from an alkyne functional group. Therefore, it can be suggested that both an alkyny1 and vinylidene version of the terminal alkyne may bind to the AuNPs simultaneously.

Figure 4.8. Transmission infrared spectra of (a) free 1-dodecyne and (b) 1-dodecyne stabilized AuNPs.
In order to explore whether both conformations (vinylidene and alkynyl ligands) are formed on AuNPs simultaneously, experiments additional experiments were performed. As mentioned in Chapter 4.1, terminal alkynes can be present in vinylidene and alkynyl geometry simultaneously when bonded to Ru and Mo. The report showed that the exact positions of the peaks associated with this functional group in the IR spectra are dependent on the type of ligand and metal.\textsuperscript{3,19,27} Therefore, these two new signals at 1718 cm\textsuperscript{-1} and 2005 cm\textsuperscript{-1} could be from the presence of both a vinylidene and alkynyl species at the surface. It can be suggested that the presence of the alkynyl species is more favored in this case because sodium borohydride (NaBH\textsubscript{4}), which is involved in the synthesis of 1-dodecyne stabilized AuNPs, could facilitate the generation of an acetylide anion because the hydride from NaBH\textsubscript{4} behaves as not only reducing agent but also strong base with a pKa ~36.\textsuperscript{54} Experiments were performed where conditions were setup to favor the deprotonation of the terminal alkyne and more strongly favor the presence of the alkynyl species over the vinylidene species.\textsuperscript{19} Figure 4.9 shows a schematic of this experiment where \textit{n}-butyllithium is used to more strongly favor the formation of the alkynyl species. We hypothesized that this would be reflected in the IR spectra as a stronger peak at 2005 cm\textsuperscript{-1} and a weaker one at 1718 cm\textsuperscript{-1}.

\textbf{Figure 4.9.} Schematic indicating the deprotonation reaction from vinylidene ligand and the formation of alkynyl ligand on AuNPs.
The above experiments were performed and then transmission IR spectra were taken of the 1-dodecyne stabilized AuNPs. Figure 4.10c shows IR spectra where the peak at 1718 cm\(^{-1}\), which was previously assigned to be associated with a vinylidene group, is absent now. This result suggests that both the vinylidene and acetylide are present on the surface of the AuNP when a terminal alkyne is used as the stabilizer, especially under basic conditions, which tends to favor the presence of the acetylide. In contrast, experiments were performed where conditions were setup to favor the protonation of the alkynyl ligand and more strongly favor the presence of the vinylidene species over the alkynyl species. However, when weak acid such as acetic acid was used, no protonation of the alkynyl ligand was observed as monitored by IR spectroscopy. In addition, however, when various concentrations of strong acid such as hydrochloric acid were added in 1-dodecyne stabilized AuNPs solution, all NPs aggregated. To further interpret the IR spectroscopy data, it would be desirable to examine the transmission IR for deutero-dodecyne-stabilized AuNPs and SAMs composed from 2-alkynes.
Figure 4.10. Transmission infrared spectra of (a) free 1-dodecyne, (b) 1-dodecyne stabilized AuNPs, and (c) deprotonated 1-dodecyne stabilized AuNPs.

The migratory abilities of methyl and phenyl groups in alkynes terminated with these groups can be used to provide more details about the binding geometry of terminal alkynes on gold. Various kinds of carbene trapping experiments have been reported by Stang et al.\textsuperscript{5,6,55} Particularly, they reported that methyl terminated alkyne could generate the vinyl carbene by a 1,2-methyl shift. The resulting carbene reacted with cyclohexene in 70\% yield (Figure 4.11a). In contrast, there was no trapping with cyclohexene when a phenyl terminated alkyne was employed (Figure 4.11b).\textsuperscript{55} Therefore, it was hypothesized that if the final geometry of the terminal alkyne on gold is a vinylidene conformation (end-on), a
methyl terminal alkyne should be able to form a SAM on gold, but a phenyl terminated alkyne should not be able to form a SAM on gold. In contrast, if the final geometry between terminal alkynes and gold is a flat geometry (side-on), both methyl and phenyl terminal alkyne should be able to form SAMs on gold. This schematic of this hypothesis is described in Figure 4.12.

![Figure 4.11](image)

Figure 4.11. Schematic showing the trapping of carbenes using cyclohexene when carbene is generated from a (a) methyl terminal alkyne and (b) phenyl terminal alkyne.\textsuperscript{55}
Figure 4.12. Schematic indicating the expected results for the formation of alkyne SAMs on gold in an end-on and side-on configuration when starting with a methyl and phenyl terminated alkyne.

To confirm this hypothesis, methyl and phenyl terminated alkynes were synthesized, and then exposed to cleaned gold surfaces to make the SAMs, which were characterized to determine whether monolayer formation occurred. First, tridec-2-yn and 1-(dodec-1-ynyl)benzene were synthesized in 97% and 87% yield (Figure 4.13). Then, gold slides were exposed to these molecules in ethanol for 2 days. In order to verify the formation of methyl and phenyl terminal alkyne SAMs on gold, cyclic voltammetry was used to check their ability to block the redox response of a redox couple, ellipsometry was used to determine film thickness, and water contact angle measurements were taken. The data in Table 4.1 and Figure 4.14 show reasonable evidence for the formation of methyl terminated alkyne SAMs on gold. In contrast, the data suggest that phenyl terminal alkyne SAMs did not form. These results indicate that the generation of a carbene played an important role in
formation of SAMs from these molecules. In general, this provides more evidence supporting the vinylidene geometry when terminal alkynes SAMs on gold are formed.

![Reaction Scheme](image)

**Figure 4.13.** Synthesis of (a) tridec-2-yne and (b) 1-(dodec-1-ynyl)benzene.

**Table 4.1.** Water contact angles and film thickness for gold electrode modified with methyl and phenyl terminal alkynes.

<table>
<thead>
<tr>
<th></th>
<th>contact angle (°)</th>
<th>film thickness (Å)</th>
<th>Molecular length (Å)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tridec-2-yne</td>
<td>89</td>
<td>15.7</td>
<td>16.7</td>
</tr>
<tr>
<td>1-(dodec-1-ynyl)benzene</td>
<td>68</td>
<td>0.0</td>
<td>19.2</td>
</tr>
</tbody>
</table>

* Theoretical thickness was calculated for the molecule in a fully extended conformation using molecular mechanics (MM2).
Figure 4.14. Cyclic voltammograms of Fe(CN)$_6^{3-/4-}$ at 100 mV/s at bare gold and SAM-modified gold electrode with tridec-2-yne and 1-(dodec-1-ynyl)benzene.

To provide further evidence to support the vinylidene geometry of terminal alkynes on gold and determine more exactly what type of interaction exists between the alkyne and the gold, we employed $^1$H NMR to study terminal alkynes on AuNPs. Murray et al. has studied thiol stabilized AuNPs, especially phenylethanolthiol protected AuNPs.$^{56-64}$ In these reports, $^1$H NMR was usually used, which was very sensitive to the size of the AuNPs. When the size of AuNPs was greater than ~3 nm, the peaks were broad and, as a result, there was no observable peak splitting. In contrast, when the size of AuNPs was smaller than ~3 nm, they obtained relatively narrow peaks. Utilizing $^1$H NMR, we hypothesized that if the final geometry between the terminal alkynes and the AuNPs is end-on, then the peak associated with the olefin proton should be present as a triplet (Figure 4.15a) due to a measurable, 3-bond coupling to the nearest methylene group ($^3J_{HH}$). In contrast, if the final geometry is a
flat geometry via a side-on interaction, then the peak associated with the olefin proton will be present as a singlet due to a smaller and probably unnoticeable, 4-bond coupling to the nearest methylene group ($^4J_{HH}$) (Figure 4.15b).

![Diagram](image)

**Figure 4.15. Structure of the final geometry by (a) end-on and (b) side-on conformation indicating their splitting of olefin proton.**

Terminal alkyne stabilized AuNPs were studied using $^1$H NMR in CDCl$_3$. In almost every case, the $^1$H NMR spectra did not show any peaks that could be assigned to a vinyl proton near 5 ppm, which is the typical chemical shift of vinyl protons in a vinylidene ligand when bound to a metal (Figure 4.16).$^{18-20}$ This result may be explained by the size of AuNPs. They were measured to be 2.51 ± 1.44 nm by transmission electron microscopy. These particles may have been sufficiently large that fast nuclear relaxation might result in a lack of a measurable signal. Moreover, there could be not only vinylidene but also alkynyl ligand on AuNPs as mentioned in IR studies. Thus, if more of the terminal alkynes molecules are
bound to the AuNP in an alkynyl configuration, a peak near 5 ppm that is associated with an olefin proton might not be visible in the $^1$H NMR.

![Diagram of AuNP with alkynyl configuration](image)

**Figure 4.16.** $^1$H NMR spectra in CDCl$_3$ solutions of 1-dodecyne stabilized AuNPs.

Occasionally, a peak at 5.15 ppm was observed in the $^1$H NMR spectrum, which could be assigned to a vinyl proton (Figure 4.17), but, as mentioned above, more often, this peak was absent. Figure 4.17a is a $^1$H NMR spectrum of 1-dodecyne on AuNPs with a size range of 2.5 ± 1.4 nm. In this spectrum, peaks b and c are shifted compared to peaks b' and c' in Figure 4.17d, which is a $^1$H NMR spectrum showing the proton chemical shift of the free 1-dodecyne. These peaks can be assigned to analogous protons where peaks b and c are shifted in Figure 4.17a due to the presence of the AuNP attached to these molecules. The peak position attributed to the acetylenic proton in the free terminal alkyne (a') is completely
absent in the $^1$H NMR spectrum of 1-dodecyne stabilized AuNPs, and a new peak, which can be attributed to a alkylidene proton appeared, consistent with the above hypothesis. However, the expected a triplet splitting of this peak was difficult to observe due to the small, broad signal. To eliminate the possibility that this peak originated from impurities, these AuNPs were dissolved in hexane and washed again by water. Then, AuNPs were dried and washed by acetonitrile. The resulting $^1$H NMR spectra showed almost the same proton chemical shift (Figure 4.17b). One could argue that this new peak, which we attribute to a vinyl proton, was actually a peak from CHDCl$_2$. It has been suggested that the NMR solvent, CDCl$_3$, could potentially spontaneously exchange one of its deuterium atoms with a proton atom.$^{65}$ However, in our results we occasionally observed a separate peak at 5.3 ppm, which can be assigned to the proton in CHDCl$_2$ as shown in the NMR spectrum in Figure 4.17c, which is completely different with the new signal at 5.15 ppm. These $^1$H NMR results indicate that 1-dodecyne stabilize AuNPs contain vinylidene ligands (end-on) consistent with all other evidence mentioned above.
Figure 4.17. $^1$H NMR spectra in CDCl$_3$ solutions of (a) 1-dodecyne stabilized AuNPs, (b) washed 1-dodecyne stabilized AuNPs, (c) 1-dodecyne stabilized AuNPs in CD$_2$Cl$_2$ showing the proton chemical shift of CHDCl$_2$, and (d) free 1-dodecyne.

4.3 Conclusion.

Several possibilities for the binding interaction between a terminal alkyne and gold can be suggested. To find the appropriate geometry among these proposed possibilities, several different experiments were performed. Electrochemical blocking experiments using gold surfaces coated with a terminal alkyne, an alcohol, an amine, and an alkane were performed
to determine whether the type of interaction between the terminal alkyne and gold is physisorption or chemisorption. Experiments were performed to determine whether this interaction is a $\pi$-type interaction by determining the surface coverage of gold surfaces coated with ethynylferrocene and vinylferrocene SAMs using cyclic voltammetry. These results showed that the interaction was not a $\pi$-type interaction.

Next, conditions were employed to promote the formation of an acetylide anion and determine whether this favored formation of a SAM. The freshly prepared gold slide was exposed to a solution of a terminal alkyne under basic conditions, which should favor the formation of an acetylide. However, as evidenced by water contact angle measurements, ellipsometry measurements, and measurements of the ability of these films to electrochemically block a redox response from a solution species, no SAM formation occurred. This result indicated that terminal alkynes do not bind to gold via an acetylide anion.

Infrared spectra of terminal alkyne SAMs on a gold surface and AuNPs was useful methodology to determine more information about how these molecules bind to these surfaces. When forming an alkyne SAMs on a gold surface, ATR-FTIR showed a loss of a peak that can be attributed to a triple bond and a gain of a new peak consistent with a vinylidene. When forming alkyne-stabilized AuNPs, transmission IR spectra showed losses of typical signals associated with an acetyllic group. Interestingly, the IR spectra of these AuNPs showed a peak at $\sim1781$ cm$^{-1}$, which is consistent with the presence of a vinyl group, but also another new frequency at $\sim2005$ cm$^{-1}$. Under basic conditions, which should favor
the acetylide, the IR spectra of these AuNPs showed a loss of the signal at 1718 cm$^{-1}$ assigned to a vinyl group and an increase in the intensity of the peak at $\sim$2005 cm$^{-1}$. These results indicate that the terminal alkyne molecule can bind to the surface of the AuNP as an acetylide or vinyl carbene depending on the acidity of the solution.

In addition, experiments were done where methyl and phenyl terminal alkynes were synthesized and then used to make SAMs on gold to add further confirmation for the formation of carbene when terminal alkynes bind to gold. The ellipsometry, water contact angle, and electrochemical blocking measurements confirmed the formation of a monolayer when the methyl terminated alkyne was employed, but not when the phenyl terminated alkyne was used. These results indicate that terminal alkyne molecules bind to gold as a carbene. In particular, these molecules bond to a gold surface via a vinylidene (end-on).

Also, $^1$H NMR was used to explore the binding of terminal alkynes on AuNPs. Though occasionally, a signal at 5.15 ppm was obtained, which can be assigned to the vinyl proton. This signal could tentatively be assigned as a triplet but it might be different with typical singlet in $^1$H NMR. These $^1$H NMR results indicate that 1-dodecyne binds to AuNPs in the vinylidene geometry (end-on).

4.4 Experimental Section.

Materials and Chemicals. Gold-coated slides (1000 Å) with a titanium adhesion layer were purchased from Evaporated Metal Films Corp. 1-dodecyne (Acros, 97%), 1-dodecyl alcohol (Acros, 98%), 1-dodecyl amine (Aldrich, 97%), dodecane (Acros, 98%), ethynylferrocene
(Acros, 98%), vinylferrocene (Acros, 98%), methyl iodide (Acros, 97%), 1-iododecane (Aldrich, 99%), phenylethyne (Aldrich, 99%), and Sodium tetrachloroaurate(III) dihydrate (NaAuCl₄·2H₂O, Alfa aesar, 99.99%) were used as purchased.

**Monolayer Preparation.** The gold substrates were precleaned in hot H₂SO₄/H₂O₂ (30%), “piranha” solution for 10 m, and washed with deionized water (DI water, Milli-Q, 18 MΩ cm). The pre-cleaned gold substrates were immersed in ethanol, DI water, acetone, and ethanol for 10 min each with sonication and dried using flowing nitrogen gas. **Caution!** “piranha” solution should be handled carefully because of its violent reactivity with organic molecules.

Cleaned gold substrates were immersed into 50 mM of ethanolic solutions of 1-dodecyne, 1-dodecyl alcohol, 1-dodecyl amine, dodecane, ethynylferrocene, vinylferrocene, tridec-2-yne, and 1-(dodec-1-ynel)benzene for 2 days. To generate the alkylidene anion SAMs on gold, n-butyllithium (1.87 mL, 3 mmol) was added dropwise to 50 mM of 1-dodecyne in ethanol at -78 °C under nitrogen and then stirred for 30 min. The mixture was stirred at -50 °C for 1 hour and then stopped stirring. All mixture and a cleaned gold slide put the nitrogen purged glove bag immediately and fresh nitrogen was flowed into the glove bag for 10 min and then isolated from air. In glove bag, a cleaned gold slide was added slowly into the solution and exposed to this solution at room temperature for 2 days. After the formation of SAMs on gold substrates, all of these gold slides were washed by sonication in ethanol for 3 minutes and dried using flowing nitrogen gas.
**Tridec-2-yne.**  *n*-butyllithium (5.27 mL, 8.5 mmol) was added dropwise to 7.7 mmol of 1-dodecyne in THF (25.7 mL) at -78 °C under nitrogen and then stirred for 60 min. Methyl iodide (8.47 mL, 0.53 mmol) was added dropwise to this solution at -78 °C under nitrogen. The mixture was stirred at -78 °C for 1 hour and then warm up to room temperature for 12 hours.

**1-(dodec-1-ynel)benzene.**  *n*-butyllithium (6.8 mL, 11 mmol) was added dropwise to 1.22 g of phenylethyne (12 mmol) in THF (50 mL) at -78 °C under nitrogen and then stirred for 30 min. 1-iododecane (2.14 mL, 10 mmol) was added dropwise to this solution at -78 °C under nitrogen. The mixture was stirred at -78 °C for 1 hour and then warm up to room temperature for 12 hours.

**Deprotonation of vinylidene.**  *n*-butyllithium (0.1 mL, 0.16 mmol) was added dropwise to 4 mL of 1-dodecyne stabilized AuNPs in DCM at -78 °C under nitrogen and this solution was stirred for 1 hour. The solution was exposed in high vacuum to evaporate the entire DCM and 4 mL of toluene was added to dissolve the black solid, which was washed by DI water and then the solution was dried again in high vacuum. The black solid washed by acetonitrile several times to remove residues and then dried.

**Synthesis of AuNPs.**  Sodium tetrachloroaurate(III) dihydrate (NaAuCl₄·2H₂O, 83 µg, 10 mmol) was dissolved in 0.5 vol.% of butanol (0.2 mL). 4.5 mL of toluene was injected in the solution and then 1.4 mM of terminal alkyne was added with stirring in vial. After stirring for 30 ~ 40 min as a aging time, increase the speed of stirring to maximum and 0.4 mL of 0.27 mM of NaBH₄ in DI water was added dropwise. The color of solution was
changed to dark red in second. After further stirring for 12 hours, the organic layer was washed by DI water to remove polar residue and then the solution was exposed in high vacuum to evaporate the entire toluene. The black solid washed by acetonitrile many times until the spot of residue was disappeared in TLC to remove unbound terminal alkyne and then dried.

**Ellipsometric Film Thickness Measurements.** The thicknesses of SAMs were measured by variable-angle spectroscopic ellipsometer (J. A. Woollam, Inc., Lincoln, NE) and single-wavelength ellipsometer, with incident angle of 70° (AutoEL, Rudolph Research, Flanders). The average refractive index value of the clean gold substrate was used in the determination of thickness by use of a three-layer model (ambient/organic film/gold). A refractive index of $n = 1.5$ was used in the thickness calculations.66

**Electrochemical Measurements.** Electrochemical redox blocking experiments were performed with a BAS CV-50W voltammetric analyzer and a 100 mM potassium chloride (KCl) solution containing 1 mM potassium ferricyanide $[K_3Fe(CN)_6]$. The solutions were prepared with deionized water and purged with nitrogen for over 3 min. A single-compartment, standard three-electrode glass cell was used with silver/silver chloride (Ag/AgCl, saturated KCl) as reference electrode, a platinum (Pt) coiled wire as counterelectrode, and a monolayer-modified gold substrate as working electrode.

**Contact Angle Measurements.** The water contact angle measurements were performed by the sessile drop technique in an optical contact angle device with electronic syringe (8 μL). The water droplets on the SAM modified gold surface were viewed with a charge-coupled
device (CCD) video camera, and a minimum of three measurements on each surface were performed.
4.5 References.


CHAPTER 5. STANDING UP VERSUS LOOPING OVER: CONTROLLING THE GEOMETRY OF SELF-ASSEMBLED MONOLAYERS OF $\alpha,\omega$-DIYNES ON GOLD

This chapter is the subject of a publication: “Standing Up versus Looping Over: Controlling the Geometry of Self-Assembled Monolayers of $\alpha,\omega$-Diynes on Gold” Kim, Y.-H.; Gorman, C. B. Langmuir, 2011, 27(10), 6069-6075.

5.1 Introduction.

Self assembled monolayers (SAMs) are a much-exploited class of structures to control the properties of a surface. The majority of these SAMs are composed of amphiphilic molecules containing a binding headgroup that chemisorbs to the surface and a tail that protrudes from the surface. Another class of SAMs comprises molecules containing two or more binding groups.

Here, the second binding group can also adhere to the surface or it can protrude from the surface. For example, $\alpha,\omega$-alkanedithiols typically form densely packed SAMs on gold in which one thiol adheres to the gold and the other thiol group exists at the terminus of the SAM. This type of organization has been exploited in several ways. Multilayers of these molecules can be grown by forming disulfides from the terminal thiol group on the SAM and a thiol group of an incoming dithiol from solution. The terminal thiol group can also be used to adhere nanoparticles to one another when the SAM is a capping layer on the particles and to SAM-covered surface. Only at extremely low surface coverage do both thiol in an
alkanedithiol adhere to the gold, and under these conditions, a striped pattern of molecules parallel to the surface is found. \textsuperscript{1-9,27} Looped structures composed of \(\alpha,\omega\)-alkanedithiols, where both thiols bind to the surface yet the molecule protrudes from the surface, are elusive.\textsuperscript{28} Chelating dithiol molecules have been reported that bind via both sulfurs to gold,\textsuperscript{29-31} and Lee and co-workers\textsuperscript{32-37} have explored chelating dithiol molecules at some length and have discussed the potential utility of loosely packed SAMs in controlling protein adsorption. In these cases, the molecules are specifically designed to enforce the bidentate binding.

SAMs composed of flexible, looped structures would be less densely packed, and this lower packing density may be useful in some instances. For example, in the design of amperometric sensors, a densely packed SAM may be useful for the binding event, but the dense packing impedes current flow and thus potential signal transduction. SAMs in which one of the binding groups is relatively loosely adsorbed can form the basis of dynamic, responsive surfaces. Langer and co-workers\textsuperscript{38} have employed reversible hydrolysis of bulky, terminal ester groups in a SAM to create a sparsely covered, monolayer surface composed of molecules that alternate between looped and standing-up conformations. Thus, binding groups that have moderate adhesion to a surface and can form loosely packed SAMs would be interesting in this regard.

Previously, we showed that SAMs composed of linear, terminal alkynes on gold and platinum are relatively densely packed yet not as densely packed as SAMs composed of linear, terminal thiols on gold.\textsuperscript{39} Hypothesizing that this is due to a somewhat weaker
interaction between the alkyne and metal surface compared to the thiol/metal gold could show the hallmarks of looped structures. Here, we show that this is indeed the case. By controlling the concentration of the diyne solution used to form the SAM, it is possible to smoothly access a range of SAM structures that transition from the fully extended structure to a looped structure. A range of experiments are presented here to document this behavior.

5.2 Results and Discussion.

5.2.1 Formation of Standing-Up and Looping Over Structure by Various Chain Length of α,ω-Diyne Self Assembled Monolayers on Gold.

To estimate the ellipsometric thickness of films that should result from hairpinned and upright SAMs, geometry optimizations of 1,9-decadiyne [HC≡C(CH₂)₅C≡CH] in a looped and standing-up conformation (Figure 5.1) were computed. From these, it was anticipated that an ellipsometric thickness of ca. 5.4 Å would be obtained for a SAM in the looped conformation and an ellipsometric thickness of ca. 13.0 Å would be obtained for a SAM in the standing-up conformation.
Figure 5.1. Cartoons depicting the proposed thickness of two types of diyne-based SAMs in the case of 1,9-decadiyne: (a) standing-up (formed at high diyne concentration) and (b) hairpinned (formed at low diyne concentration) conformations.

We then sought to determine the minimum number of carbons required to form a hairpinned SAM. We speculated that if the molecule was too short, it would lack the conformational flexibility to form a hairpinned SAM. SAMs of $\alpha,\omega$-diynes containing 7–10 carbons were formed on gold and the ellipsometric thicknesses of the resulting films were measured. Loop SAMs should form from relatively low concentrations of diyne. A concentration of 1 mM was used, which, in later experiments, was confirmed to be appropriate (\textit{vide infra}). The data in Table 5.1 show that both the 1,8-nonadiyne- and 1,9-decadiyne-modified surfaces showed and ellipsometric film thickness suggestive of a hairpinned structure. The ellipsometric film thickness of 1,6-heptadiyne and 1,7-octadiyne deposited on gold had values more suggestive of the standing-up conformation. This experiment does not rule out any hairpinned molecules from the shorter diynes. Indeed, cyclic voltammetry blocking experiments (\textit{vide infra}) paint a somewhat different picture.
The data, however, do indicate that a chain of nine carbons (five sp\(^3\)-hybridized carbons and four sp-hybridized carbons) is the minimum for facile formation of a hairpinned structure.

**Table 5.1. Film thicknesses and water contact angles for gold surfaces modified with 1 mM concentrations of various diynes.**

<table>
<thead>
<tr>
<th>diyne</th>
<th>contact angle (deg)(^a)</th>
<th>film thickness (Å)</th>
<th>molecular length (Å)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bare gold</td>
<td>71</td>
<td>NA(^c)</td>
<td>NA(^c)</td>
</tr>
<tr>
<td>1,6-heptadiyne</td>
<td>75</td>
<td>7.2 ± 0.5</td>
<td>8.7</td>
</tr>
<tr>
<td>1,7-octadiyne</td>
<td>72</td>
<td>9.1 ± 0.9</td>
<td>10.9</td>
</tr>
<tr>
<td>1,8-nonadiyne</td>
<td>69</td>
<td>4.2 ± 0.4</td>
<td>11.1</td>
</tr>
<tr>
<td>1,9-decadiyne</td>
<td>62</td>
<td>5.1 ± 0.9</td>
<td>13.1</td>
</tr>
</tbody>
</table>

\(^a\) Water contact angles are an average value of over three measurements and have a ±3° standard error. \(^b\) Theoretical thickness was calculated for the molecule in a fully extended conformation by molecular mechanics (MM2). \(^c\) Not applicable

Water contact angles of all of these films were low. Those assigned to the hairpinned structure were of relatively low hydrophobicity (<70°) which is lower than, for example, low-density polyethylene or low-density SAMs described previously (>90°).\(^{35}\) Those assigned to the standing-up structure were also low (ca. 70–75°) which is even more puzzling. The one report of contact angles of mixed alkyne, alkene-terminated SAMs [via coupling of non-1-yne-8-ene on hydrogen terminated Si(100)] were found to have a value of ca. 80°.\(^{40}\) These results suggest that both the hairpinned SAMs composed of the longer molecules and the standing-up SAMs composed of the shorter molecules have low packing
densities, allowing the water to “feel” the relatively higher surface energy of the underlying gold.\(^{41}\)

We then questioned what concentration of diyne would result in standing-up versus hairpinned SAMs. In separate trials, three molecules, 1-decyne \([\text{CH}_3(\text{CH}_2)_{7}\text{C}≡\text{CH}]\), 1,8-nonadiyne, and 1,9-decadiyne were exposed to cleaned gold surfaces at various concentrations. Table 5.2 shows the ellipsometrically-determined thicknesses and water contact angles of the resulting SAMs. In order to make a decyne SAM, a concentration of \(>10\) mM 1-decyne was required, and the ellipsometric film thickness was slightly less than the theoretical length of the molecule in a fully extended conformation, consistent with our earlier report.\(^{39}\) Furthermore, the advancing water contact angles reached values consistent with a hydrophobic surface that is not quite as densely packed as those obtained from an analogous 1-alkanethiol.

The ellipsometric thickness of the 1,8-nonadiyne and 1,9-decadiyne SAMs fell into four overlapping categories depending on the concentration of the diyne used (Table 5.2). A minimum concentration of 0.1—0.5 mM was required to observe any material on the surface by ellipsometry. At slightly higher concentrations, a thickness of ca. 5 Å was measured, consistent with a SAM composed of the molecules in a hair-pinned conformation. At concentrations of 50 and 100 mM, a thickness of ca. 13 Å was measured, consistent with a SAM composed of the molecules in a standing-up conformation. At intermediate concentrations, intermediate thicknesses were observed, suggesting a mixed geometry.
Table 5.2. Film thicknesses and water contact angles for gold surfaces modified with various concentrations of 1,8-nonadiyne, 1,9-decadiyne, and 1-decyne.

<table>
<thead>
<tr>
<th>concentration (mM)</th>
<th>1,8-nonadiyne</th>
<th>1,9-decadiyne</th>
<th>1-decyne</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>contact angle (°)</td>
<td>film thickness (Å)</td>
<td>molecular length (Å)</td>
</tr>
<tr>
<td>0</td>
<td>71</td>
<td>--</td>
<td>No SAM</td>
</tr>
<tr>
<td>0.1</td>
<td>72</td>
<td>c</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>70</td>
<td>3.9 ± 0.2</td>
<td>5.1 (Hairpinned)</td>
</tr>
<tr>
<td>1.0</td>
<td>69</td>
<td>4.2 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>74</td>
<td>4.9 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>72</td>
<td>8.1 ± 1.3</td>
<td>Mixed</td>
</tr>
<tr>
<td>50.0</td>
<td>73</td>
<td>12.9 ± 0.5</td>
<td>11.1 (Standing-Up)</td>
</tr>
<tr>
<td>100.0</td>
<td>72</td>
<td>11.8 ± 0.7</td>
<td>(Standing-Up)</td>
</tr>
</tbody>
</table>

* Water contact angles are an average value of three measurements with a ± 3° standard error.  

* Theoretical thickness was calculated for the molecule in a fully extended conformation using molecular mechanics (MM2).  

* Values <1 Å were obtained, which might indicate either no coverage or molecules oriented completely parallel to the surface.
In a standing-up geometry, one alkyne group should be present at the solid-air surface, and in a hairpinned geometry it should not. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to illustrate the standing-up and hairpinned geometries. Bulk (KBr) transmission infrared spectra of 1,9-decadiyne (Figure 5.2a) showed a terminal C≡CH stretch 3300 cm⁻¹. When the SAM was prepared from 100 mM 1,9-decadiyne, ATR-FTIR (Figure 5.2b) showed a terminal C≡CH stretch consistent with an unbound alkyne and a standing-up geometry. In comparison, the ATR-FTIR spectrum of a SAM prepared from 1 mM 1,9-decadiyne (Figure 5.2c) indicated a loss of that signal, consistent with a lack of terminal alkyne group at the surface and a hairpinned geometry.

![Figure 5.2](image)

**Figure 5.2.** (a) Transmission infrared spectra of free 1,9-decadiyne and (b,c) ATR-FTIR spectra of (b) standing-up (100 mM) and (c) hairpinned (1 mM) 1,9-decadiyne SAMs on gold.
As the low water contact angle suggest a low packing density for these SAMs, a complementary way of assessing packing density is desirable. The blocking of the redox response of ferricyanide ions by a SAM-covered working electrode is another useful technique to assess the relative coverage of that SAM on the surface. Figure 5.3 shows the results of the electrochemical blocking of the redox response of ferricyanide ion by these films. Several observations are made from these data.

![Graph](image-url)

**Figure 5.3.** Plots of the ratio of the maximum reduction current (i.e., that at $E_{pc}$) for Fe(CN)$_6^{3-/-}$ on bare gold and gold modified by exposure to various concentrations of 1-decyne and various diynes. Lines are provided only as guides to the eye.

The redox currents generated when 1-decyne was deposited on the gold electrode show well-attenuated responses when >10 mM concentrations of alkyne were used to make the
film. In comparison, the redox currents generated when 1,8-nonadiyne or 1,9-decadiyne was deposited on the gold electrode show nearly complete blocking down to concentrations of ca. 0.5 mM used to make the film. These results are consistent with the ellipsometry results presented above. Concentrations greater than 10 mM 1-decyne are required to form high surface coverage SAMs on gold, but concentrations as low as 0.5 mM for 1,9-decadiyne and 1,8-nonadiyne yield SAMs of high coverage and blocking ability. Moreover, although water may penetrate the SAM (cf. the contact angle data in Table 5.2), a solvated ion (ferricyanide) is blocked by the SAM even when it is hairpinned. It is also possible that a monoalkyne SAM undergoes some desorption, which might be prevented by bidentate binding in the case of a diyne SAM.

Why should diyynes form blocking SAMs at lower concentrations than monoalkynes? It is not clear how to answer this question experimentally. However, consider that these alkyne SAMs do not show any of the hallmarks of dense packing. In a densely packed SAM, the collective van der Waals interactions create an enthalpic incentive that, in conjunction with the metal–headgroup binding interaction, outweighs the loss of configurational entropy upon SAM formation. In a loosely packed SAM, that contribution to the enthalpy is lower. Having foregone that, the favorable enthalpy of binding for the second alkyne to the surface appears to outweigh the unfavorable entropy of hairpinning.

The blocking ability of 1,6-heptadiyne and 1,7-octadiyne SAMs in the ca. 1–10 mM concentration range is intermediate between that of 1-decyne and the two longer diyynes. We interpret these data to suggest that there is some hairpinning (and thus enhanced ferricyanide
blocking) in these films. Ellipsometry indicates that it is a modest enough amount to avoid a significant decrease in the measured thickness of these films. Hairpinned structures could form at defect and/or lower density sites in the film, and this behavior would account for the results shown here. In any event, these electrochemical blocking experiments provide information about the structure of the SAMs that is not available from ellipsometry.

5.2.2 \( \alpha,\omega \)-Alkanedithiol Self Assembled Monolayers on Gold.

For comparison, 1,8-octanethiol SAMs were prepared and studied. Even when a 0.1 mM concentration of this molecule was used to form the SAM, an ellipsometric thickness of 10 Å (with an expected molecular length of 12.8 Å in a standing-up conformation, Table 5.3) and essentially complete blocking of ferricyanide anion (Figure 5.4) were observed. These data are consistent with the relative unwillingness of \( \alpha,\omega \)-dithiols to form hairpinned structures on gold. All of the data presented here and previously\(^{39}\) indicate that 1-alkynes and \( \alpha,\omega \)-diynes form relatively loosely packed SAMs on gold compared to those of \( n \)-alkanethiols. Thus, these molecules never achieve the large, collective set of van der Waals interactions that can exist in a densely packed SAM (e.g., that of an \( n \)-alkanethiol or \( \alpha,\omega \)-dithiol). Those stabilizing interactions could be important in driving \( \alpha,\omega \)-diynes forming both looped and standing-up conformations. The relative strength of the headgroup—substrate interaction and concomitant reversibility of alkyne—gold binding could be lower than that of the thiol—gold binding. A more reversible binding could also play a role. Thiols displace alkynes on gold,\(^{42}\) suggesting that the thiol/gold interaction is stronger (and thus perhaps less reversible) than the alkyne/gold interaction.
Figure 5.4. Cyclic voltammograms of Fe(CN)$_6^{3-/4-}$ at 100 mV/s at bare gold and gold electrode modified with ethanolic solutions of 1,8-octanedithiol at various concentrations.

Table 5.3. Film thickness and water contact angle for 1-octanethiol modified surface.

<table>
<thead>
<tr>
<th>concentration (mM)</th>
<th>contact angle (°)$_a$</th>
<th>film thickness (Å)</th>
<th>molecular length (Å)$_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>bare gold</td>
<td>72</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>57</td>
<td>10.4 ± 2.4</td>
<td>12.8</td>
</tr>
<tr>
<td>1.0</td>
<td>70</td>
<td>12.1 ± 1.6</td>
<td></td>
</tr>
<tr>
<td>100.0</td>
<td>73</td>
<td>33.6 ± 7.9$_c$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Water contact angles are an average value of over three measurements and have a uncertainty of ± 3°.  $^b$Theoretical thickness was calculated for the molecule in a fully extended conformation using molecular mechanics (MM2).  $^c$This value suggests multilayer formation as has been reported previously.$^{43}$
5.2.3 Trapping of gold nanoparticles using a α,ω-Diyne Self Assembled Monolayers on Gold.

In a standing-up geometry, one alkyne group should be presented at the surface, and in a hairpinned geometry it should not. Since alkynes have been shown to bind to gold-nanoparticles (AuNP) as well as gold surfaces.\(^{39}\) It seems reasonable that AuNP can be used as tags for free alkyne groups on a surface. This experiment is illustrated schematically in Figure 5.5. A hairpinned SAM should not be able to trap AuNP, and a standing-up SAM should be able to trap AuNP.

![Figure 5.5](image)

**Figure 5.5.** Schematic indicating the expected results of a trapping experiment with citrate-capped gold nanoparticles on hairpinned and standing-up SAMs.

A solution of citrate-capped AuNP of 11 ± 1 nm (Figure 3.2 in Chapter 3) was exposed to SAMs prepared from various concentrations of 1,9-decadiyne. These substrates were then imaged via tapping-mode atomic force microscopy (TM-AFM), a relatively nonperturbative technique (Figure 5.6). The results agree with the hypothesis. When low concentrations of 1,9-decadiyne were used to make the SAMs, few or no free alkyne groups were available,
and few AuNP were found on the surface. As the concentration increased, more AuNP were found on the surface. The AuNP could be distinguished by height and size from back-ground gold grains and could be counted. Figure 5.7 shows the average number of AuNP counted on samples previously incubated with various concentrations of 1,9-decadiyne. With a greater number of AuNP on the surface, the surface roughness also increased (Figure 5.7). Thus, by visual inspection, particle counting, and roughness measurements, evidence for AuNP binding was obtained. These particles suggest the presence of free alkyne on the surface due to molecules in a standing-up conformation. The results are consistent with ellipsometry and electron blocking results presented above.
Figure 5.6. TM-AFM images of gold nanoparticles trapped on 1,9-decadiyne-modified gold surfaces. All images have a 1 μm × 1 μm scan size. Images are (a) bare gold with no 1,9-decadiyne or AuNP treatment; (b) bare gold with no 1,9-decadiyne treatment but incubated with AuNP; gold incubated with 1,9-decadiyne and subsequently AuNP at the following concentrations of 1,9-decadiyne: (c) 0.1, (d) 0.5, (e) 1, (f) 5, (g) 10, (h) 50, (i) 100 mM. Inset cartoons are the hypothesized conformation(s) of the diyne molecules.
Figure 5.7. Root-mean-square (rms) roughness of surfaces that were prepared from incubation of 1,9-decadiyne on gold followed by no further treatment (black circles) and incubation with AuNP (red squares). The number of AuNP counted on SAMs prepared from various concentrations of 1,9-decadiyne (blue diamonds) is also shown. Error bars represent the 90% confidence interval of values obtained. Lines are provided only as guides to the eye.

5.3 Conclusion.

Diynes bind to gold in either a hairpinned (bidentate) or a standing-up (monodentate) conformation, depending on the chain length of the diyne and concentration of the molecule in the solution used to make the SAM. The hairpinned conformation is supported by ellipsometry and nanoparticle binding studies. This behavior is in contrast to that of SAMs
prepared from \(\alpha,\omega\)-alkanedithiols, which do not form hair-pinned structures at any reasonable concentration range (>0.1 mM). Examination of a series of \(\alpha,\omega\)-diynes showed that 1,6-heptadiyne and 1,7-octadiyne SAMs may have had some hairpinned structures in the ca. 1–10 mM concentration range, and 1,8-nonadiyne and 1,9-decadiyne certainly had some hairpinned structures in the ca. 0.1–1 mM concentration range. The hair-pinned and standing-up SAMs are all relatively loosely packed, as evidenced by water contact angle and ferricyanide blocking studies. All of these results document a new way to make an organic-modified gold substrate that results in a partially accessible, underlying surface.

5.4 Experimental Section.

Materials and Chemicals. Gold-coated slides (1000 Å) with a titanium adhesion layer were purchased from Evaporated Metal Films Corp. 1,6-heptadiyne (Aldrich, 97%), 1,7-octadiyne (Aldrich, 98%), 1,8-nonadiyne (Alfa Aesar, 97%), 1,9-decadiyne (Alfa Aesar, 97%), 1-decyne (Aldrich, 98%), 1,8-octanedithiol (Aldrich, 97%), sodium tetrachloroaurate(III) dihydrate (NaAuCl\(_4\)\(\cdot\)2H\(_2\)O, Alfa aesar, 99.99%), and sodium citrate (Na\(_3\)C\(_6\)H\(_5\)O\(_7\), Fisher) were used as purchased.

Monolayer Preparation. The gold substrates were precleaned in hot H\(_2\)SO\(_4\)/H\(_2\)O\(_2\) (30%) “piranha” solution for 10 min, and washed with deionized water (DI water, Milli-Q, 18 M\(\Omega\)·cm). The precleaned gold substrates were immersed in ethanol, DI water, acetone, and ethanol for 10 min each with sonication and dried under flowing nitrogen gas. Caution! “piranha” solution should be handled carefully because of its violent reactivity with organic molecules.
All cleaned gold substrates were immersed into various concentrations (0.1, 0.5, 1, 5, 10, 50, and 100 mM) of ethanolic solutions of 1-decyne or diyne for 2 days. After the formation of SAMs on gold substrates, the gold slides were washed by sonication in ethanol for 5 min and dried under flowing nitrogen gas.

**Computations.** Geometry optimizations were performed with MM2 in Chem3D. The estimated SAM thickness was taken as the distance between the terminal carbons for the standing-up conformation. For the looped conformation, a line was drawn connecting the terminal carbons. The thickness was taken as the largest distance perpendicular to that line and the methylene carbons. For the hairpinned conformation, the distance between the terminal carbons was fixed at various values and a geometry optimization was performed under that one constraint. The value that gave a minimum energy after optimization was selected. Slight variation of this value did not change the estimated SAM thickness significantly.

**Ellipsometric Film Thickness Measurements.** The thicknesses of SAMs were measured by variable-angle spectroscopic ellipsometer (J. A. Woollam, Inc., Lincoln, NE) and single-wavelength ellipsometer, with incident angle of 70° (AutoEL, Rudolph Research, Flanders). The average refractive index value of the clean gold substrate was used in the determination of thickness by use of a three-layer model (ambient/organic film/gold). A refractive index of $n = 1.5$ was used in the thickness calculations.\(^{44}\)

**Synthesis of Au Nanoparticles.** The citrate-stabilized gold nanoparticles are prepared following a method introduced by Turkevich.\(^{45}\) Sodium tetrachloroaurate(III) dihydrate
(NaAuCl₄·2H₂O, 0.4 g, 1 mmol) was dissolved in deionized water (250 mL), and the solution was brought to a vigorous boil with stirring in a Erlenmeyer flask. A aqueous solution of sodium citrate (Na₃C₆H₅O₇, 1 w%) was added to the NaAuCl₄·2H₂O solution slowly. The solution was allowed to boil for an additional 20 min. At this moment, the color of gold solution changed from pale yellow to dark red. Then the AuNP solution was cooled to room temperature and stored at −4 °C, which was stable for several weeks.

**Electrochemical Measurements.** Electrochemical redox blocking experiments were performed with a BAS CV-50W voltammetric analyzer and a 100 mM potassium chloride (KCl) solution containing 1 mM potassium ferricyanide [K₃Fe(CN)₆]. The solutions were prepared with deionized water and purged with nitrogen for over 3 min. A single-compartment, standard three-electrode glass cell was used with silver/silver chloride (Ag/AgCl, saturated KCl) as reference electrode, a platinum (Pt) coiled wire as counterelectrode, and a monolayer-modified gold substrate as working electrode.

**Transmission Electron Microscopy.** The size of citrate-capped gold nanoparticles and distribution of particle sizes monitored by TEM were determined with Philips CM12 TEM operated at 100 kV. Images were captured by use of a Gatan 780 camera and Digital Micrograph software. The samples were prepared by dropping three drops of the gold nanoparticles in water onto a 200-mesh carbon-coated copper grid.

**Contact Angle Measurements.** The water contact angle measurements were performed by the sessile drop technique in an optical contact angle device with electronic syringe (8 μL). The water droplets on the SAM modified gold surface were viewed with a charge-coupled
device (CCD) video camera, and a minimum of three measurements on each surface were performed.

**Atomic Force Microscopy Experiments.** All experiments of surface topography were carried out by tapping-mode AFM on a Digital Instruments Nanoscope IIIa microscope. Images were captured at a scan resolution of 512 points/line, scan rate of 1 Hz, scan area of $1 \, \mu m \times 1 \, \mu m$, and z-range of 50 nm. The drive frequency was set approximately to the resonant frequency of the cantilever being used. All cantilevers used had a resonant frequency of approximately 71 kHz.
5.5 References.


(41) Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. 


CHAPTER 6. DYNAMIC GRADIENT SURFACE: CONTROLLING THE GEOMETRY OF SELF ASSEMBLED MONOLAYERS OF α,ω-DIYNES ON GOLD

6.1 Introduction.

Molecular and macromolecular gradients constitute a gradual change of the density and/or the chemical nature of a surface-anchored species on a substrate. This leads to a position-dependent variation of the properties of the surface, which has a lot of potential to be applied in nanotechnology. Particularly, these surface-bound gradients can potentially be used in creating “smart materials” and “surface-bound engines”. The use of a “smart surface” has a promising potential and many of studies were explored. For example, Chaudhury and Whitesides reported the movement of water droplets on a surface concentration of \( n \)-decyltrichlorosilane on a silicon wafer. In this study, the movement of the water droplets was from the more hydrophobic region toward the more hydrophilic region. In addition, multiple studies of “surface-bound engines” have been published that reported on the response of living cells to the variation of surface properties such as chemotaxis and haptotaxis, light intensity (phototaxis), electrostatic potential (gavanotaxis), gravitational field (geotaxis), and mechanical properties (durotaxis).

Novel methods for forming a gradient of surface properties on a substrate have been the subject of great interest. Here, we will discuss a method for the formation of a surface-bound gradient composed solely of \( \alpha,\omega \)-diyne on gold. For example, Figure 6.1 shows a schematic illustrating a process developed by Tomlinson and Genzer for forming a gradient in molecular weight of a polymer on a silicon wafer. In this study, the initiator
was bound to the silicon substrate. This initiator-treated silicon substrate was then immersed into a solution containing monomer and catalyst to cause polymerization from the surface. The time of polymerization at a given location on the surface was controlled by a micro-pump which was employed to drain the system at a steady rate. The upper region of the silicon coated slide was exposed to the reaction solution for a shorter amount of time compared to the lower part of the slide. Since the molecular weight of grafted polymer was dependent on the time various regions of the silicon substrate were exposed to the reaction solution, the molecular weight of the polymer was controlled accordingly and a gradient of molecular weight of the polymer grafted to the surface was formed.

Figure 6.1. Schematic experimental equipment for the formation of polymer gradient via solution draining method.
To confirm the formation of a surface-bound gradient, various characterization techniques have been employed. One of useful method that has been employed, providing the surface species has an affinity for gold nanoparticles (AuNPs), is to expose the surface to AuNPs and allow them to become trapped on the surface. Genzer and co-worker formed a gradient molecules having amino groups and showed that the amount of AuNPs trapped on the surface was dependent on the density of amino group on the surface. Figure 6.2 shows a tapping-mode atomic force microscopy (TM-AFM) image of AuNPs adsorbed along a gradient substrate prepared by vapor diffusion of an n-aminopropyl triethoxysilane/paraffin oil mixture across the surface for 5 min followed by immersion in a 16 nm diameter AuNPs solution for 24 hours. One can see more particles on the region of the surface that was closer to the silane/oil reservoir during the vapor diffusion process. In this case, AuNPs were prepared by the citrate reduction. Citrate stabilized AuNPs have an inherent negative charge and weakly bound anions served as capping ligands for the particles. As a consequence, the negatively charged AuNPs are repelled from one another and discouraged from aggregating in solution. The authors suggested when the amino group modified gradient substrate was immersed into citrate stabilized AuNPs solution, the $\text{--NH}_2$ group were protonated, forming $\text{--NH}_3^+$ because a citrate stabilized AuNP solution was slightly acidic in nature (pH $\approx$ 6.5). It was proposed that the electrostatic interactions between negatively charged citrate stabilized AuNPs and positively charged gradient surface led to the binding between these entities.
Figure 6.2. AFM images of AuNPs adsorbed onto (3-aminopropyl) triethoxysilane gradient. x indicates the distance from left edge of the substrate (mm).

In Chapter 5, we showed that terminal alkyne and $\alpha,\omega$-diyne SAMs on gold are relatively densely packed in a standing-up orientation for the terminal alkyne SAMs while the $\alpha,\omega$-diyne SAMs on gold adopt a hairpinned or standing-up orientation depending on the concentration. Here, we successfully formed a dynamic surface gradient by controlling the geometry of SAMs of $\alpha,\omega$-diyne on gold and characterize these gradients using ellipsometry and cyclic voltammetry. In addition, we characterized the $\alpha,\omega$-diyne on gold by trapping AuNPs on the surface and imaging these AuNPs via TM-AFM. This alkyne functional gradient may be of great value for smart surface application such as bio-sensor fabricated by click chemistry, functionalization of carbon nanotubes, and others.

6.2 Results and Discussion.

6.2.1 Fabrication of Dynamic Gradient Surface via $\alpha,\omega$-Diynes Self Assembled Monolayers on Gold.

As described in Chapter 5, SAMs of $\alpha,\omega$-diynes on gold were made using various concentration of the adsorbent and geometry was dependent on the concentration employed.
A hairpinned geometry was observed at lower concentration (0.5 ~ 5.0 mM of α,ω-diyne in ethanol) and a standing-up conformation was observation at higher concentration (≥50 mM of α,ω-diyne in ethanol). It was proposed that by gradually changing the concentration of α,ω-diyne in ethanol exposed to the surface, one could create a gradient. Scheme 6.1 shows a cartoon of this idea. In this case, a gradient of the configuration of the molecule on the surface should provide variation of both physical and chemical properties.

Scheme 6.1. Schematic showing the possibility for the formation of a surface-bound chemical gradient of an α,ω-diyne SAMs on gold.

To form the surface-bound gradient of α,ω-diyne on gold, the method developed by Tomlinson and Genzer\textsuperscript{38} was modified. Figure 6.3 shows the experimental apparatus employed for the formation of the surface-bound chemical gradient of α,ω-diyne SAMs on gold. A gold slide was put into a vessel. Initially, at the bottom of vessel, 100 mM of 1,9-decadiyne in ethanol was injected, which was intended to lead to a standing-up conformation of 1,9-decadiyne on the lower region of the gold (Figure 6.3 right). In order to systematically control the concentration of the adsorbent in solution, pure ethanol was slowly added to the vessel in which a gold slide was immersed vertically. As pure ethanol was added, the concentration of the 1,9-decadiyne solution was diluted to a final concentration of 3 mM, which was intended to generate more of the hairpinned conformation of the molecule.
as the solution reached the top of the slide. Consequently, the bottom of the gold slide was thus exposed to the highest concentration of 1,9-decadiyne and, as the vessel filled, upper regions of the gold slide were exposed to the lower concentration of 1,9-decadiyne.

Figure 6.3. (left) Cartoon depicting the experimental apparatus for the formation of a surface-bound chemical gradient of an \( \alpha,\omega \)-diyne SAMs on gold. (right) Photograph of the apparatus.

To confirm the formation of the surface-bound gradient of 1,9-decadiyne on gold, different regions of the surface were analyzed by ellipsometry, electrochemical blocking, and TM-AFM. Figure 6.4 shows eight, approximately evenly spaced regions on the surface where these experiments were performed.
Figure 6.4. Illustration of the gold slide containing the surface-bound chemical gradient of the α,ω-diyne SAM. Arrows indicate the positions at which data in Figure 6.5 are collected.

To estimate the integrity and stability of the surface-bound gradient of α,ω-diyne SAMs on gold, the ability to block the redox response of ferricyanide ions was analyzed. Figure 6.5 shows that the redox responses at all positions along the sample was significantly hindered. In order to better show the contrast between the redox response along the sample and a bare gold sample, a ratio of the maximum reduction current of each sample versus the maximum reduction current for bare gold was plotted in Figure 6.5b. Position “0” along the x-axis is the value for this quantity using bare gold as the electrode. Bare gold should show the maximum reduction current with this electrode under these conditions. This we describe as “open”. In contrast, the reduction currents from all positions along the gradient are almost completely blocked relative to the bare electrode (Figure 6.5b). Moreover, the blocking ability was stable over several voltage sweeps, indicating that the SAMs were stable when

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exposed to these conditions. Based on these results, the 1,9-decadiyne SAMs formed here were stable and of high surface coverage across the whole gradient.

**Figure 6.5.** (a) Cyclic voltammograms of Fe(CN)$_6^{3/-4-}$ at 100 mV/s at bare gold and at different positions of a gradient modified gold electrode and (b) plot of the ratio of the maximum reduction current versus maximum reduction current when using bare gold (i.e. that at $E_{pc}$) for (a). Numbers in the legend for (a) and along the x-axis for (b) are the position on the surface as shown in Figure 6.4 and 0 = bare gold in x-axis for (b).

Although the electrochemical data above for the redox response of Fe(CN)$_6^{3/-4-}$ from each position along the gradient showed similar response, the physical and chemical properties at each of the positions could be different. To determine the thickness along various positions along the gradient, ellipsometry measurements were taken. Figure 6.6 shows the ellipsometrically determined thicknesses of the resulting gradient SAMs. As shown in Chapter 5, the ellipsometric film thicknesses of 1,9-decadiyne SAMs made from higher concentration of the adsorbent was ca. 13 Å, consistent with a SAM composed of these molecules in a standing-up conformation. Along the gradient at a position of $\leq$10 mm
from the left edge of the sample higher concentrations of the adsorbent were exposed to the surface and a thickness of ca. 13 Å was measured, which is consistent with the results from Chapter 5. The measured film thicknesses by ellipsometry decreased to a thickness of ca. 5 Å along the gradient along positions where decreased concentration of the adsorbent was exposed to the surface. These results are suggest the gradient is composed of mostly standing-up oriented 1,9-decadiyne molecules at a position of ≤10 mm from the left edge of the sample, which was exposed to higher concentrations of the adsorbent, and at a position of ≥30 mm the left edge of the sample where progressively lower concentrations of the adsorbent were exposed to the surface, the more of the molecules adopt a hairpinned orientation.

Figure 6.6. Ellipsometrically determined thickness at various points on a surface-bound chemical gradient of 1,9-decadiyne.
As shown in Chapter 5, an alkyne group should be presented at the surface in a standing-up region, and in a hairpinned region it should not. Since alkynes have been shown to bind to AuNPs as well as gold surfaces, it seemed reasonable that AuNP could be used as tags for free alkyne groups on a surface.\textsuperscript{45,50} We hypothesized that the alkyne groups will be presented in standing-up region, whereas they will not in a hairpinned region. This hypothesis is illustrated schematically in Fugue 6.7 top. Here, one can see, that on one end of the gradient, the region exposed to higher concentrations of the diyne, there are a greater density of AuNPs on the surface. In regions exposed to progressively lower concentrations of the diyne, one can see in the TM-AFM images that less AuNPs binding occurred (Figure 6.7 center and bottom). Therefore, the results are consistent with the hypothesis above.
Figure 6.7. (top) Cartoon showing the schematic indicating the expected results of a trapping experiment using citrate stabilized AuNPs on surface-bound gradient, (center) TM-AFM images of AuNPs trapped on surface-bound gradient of 1,9-decadiyne SAMs on gold. All images have a $1\mu m \times 1\mu m$ scan size, and (bottom) black and white threshold of the image above describing exactly what each part of the figure is showing. Insert number shows the positions on the surface at which the data were taken as shown in Figure 6.4.

The trapped AuNPs could be discriminated by height and size from background gold grains and could be counted. Figure 6.8 shows the average number of AuNPs counted from TM-AFM images. Across the surface, the number of AuNPs on the surface decreased. The result is strong evidence for the formation of surface-bound gradient of 1,9-decadiyne on gold. These results are also consistent with the ellipsometry and electron blocking results presented above.
Figure 6.8. Plots of the number of AuNPs at various points of a surface-bound chemical gradient of 1,9-decadiyne.

6.3 Conclusion.

As discussed in Chapter 5, the configuration of α,ω-diyn SAMs on gold can have a standing-up or hairpinned conformation, depending on the concentration of the α,ω-diyn in the solution used to make the SAM. Using this dependence of conformation on the surface on concentration of the adsorbent, a gradient of conformation of α,ω-diyn on gold was made using a solvent addition method. To confirm the presence of this gradient of α,ω-diyn conformation on gold, various techniques were employed. First, electrochemical measurements were taken to estimate the integrity of the surface-bound gradient of α,ω-diyn on gold. At all positions along the gradient, the redox responses of ferricyanide ions were significantly attenuated by the presence of the SAM. This result provided evidence of the
existence of $\alpha,\omega$-diyne on gold. Second, the film thickness was measured by ellipsometry to show the variation of thickness across the surface gradient. The results showed a gradual diminution of the film thickness across the surface, which is consistent with the conformation changing from standing-up to hairpinned. Third, a AuNPs trapping experiment was employed and showed a variation in the amount of trapped AuNPs, which provided further evidence that there was a gradient of conformation of $\alpha,\omega$-diyne across the surface. All of these results support a novel method for the formation of a surface-bound gradient of $\alpha,\omega$-diyne where the conformation of this species changes from standing-up to hairpinned, which may have a useful purpose in applications.

6.4 Experimental Section.

Materials and Chemicals. Gold coated slides (1,000 Å) with a titanium adhesion layer were purchased from Evaporated Metal Films Corporation. 1,9-decadiyne (Alfa Aesar, 97%), Sodium tetrachloroaurate(III) dihydrate (NaAuCl$_4$·2H$_2$O, Alfa Aesar, 99.99%), and Sodium citrate (Na$_3$C$_6$H$_5$O$_7$, Fisher) were used as purchased.

Gradient Preparation. The gold substrates were pre-cleaned in hot H$_2$SO$_4$/H$_2$O$_2$ (30%), “piranha” solution for 10 min, and washed with deionized water (DI water, Milli-Q, 18 MΩ·cm). The pre-cleaned gold substrates were immersed in ethanol, DI water, acetone, and ethanol for 10 min each with sonication and dried using flowing nitrogen gas. Caution! “piranha” solution should be handled carefully because of its violent reactivity with organic molecules.
A piece of rectangular shape (25 mm × 50 mm) of cleaned gold substrates was put into a vessel (2000 mL volume) under nitrogen held by an alligator clip. Then, 40 mL of 1,9-decadiyne in ethanol (100 mM) was injected by syringe. The immersed height was 10 mm. After incubating for 12 hours, the pure ethanol was slowly injected by syringe (10 mm/day for 3 days). After the formation of the gradient, the gold slides were washed by sonication in ethanol for 5 min and dried using flowing nitrogen gas.

**Synthesis of citrate stabilized AuNPs.** The citrate stabilized AuNPs were prepared following a method introduced by Turkevich. Sodium tetrachloroaurate(III) dihydrate (NaAuCl₄·2H₂O, 0.4 g, 1 mmol) was dissolved in deionized water (250 mL), and the solution was brought to a vigorous boil with stirring in a Erlenmeyer flask. A aqueous solution of sodium citrate (Na₃C₆H₅O₇, 1 w%) was added to the NaAuCl₄·2H₂O solution slowly. The solution was allowed to boil for an additional 20 min. At this moment, the color of gold solution changed from pale yellow to dark red. Then, the AuNP solution was cooled to room temperature and stored at -4 °C, which was stable for several weeks.

**Ellipsometric Film Thickness Measurements.** The thicknesses of SAMs were measured by variable-angle spectroscopic ellipsometer (J. A. Woollam, Inc., Lincoln, NE) and single-wavelength ellipsometer, with incident angle of 70° (AutoEL, Rudolph Research, Flanders). The average refractive index value of the clean gold substrate was used in the determination of thickness by use of a three-layer model (ambient/organic film/gold). A refractive index of \( n = 1.5 \) was used in the thickness calculations.
**Electrochemical Measurements.** Electrochemical redox blocking experiments were performed with a BAS CV-50W voltammetric analyzer and a 100 mM potassium chloride (KCl) solution containing 1 mM potassium ferricyanide [K₃Fe(CN)₆]. The solutions were prepared with deionized water and purged with nitrogen for over 3 min. A single-compartment, standard three-electrode glass cell was used with silver/silver chloride (Ag/AgCl, saturated KCl) as reference electrode, a platinum (Pt) coiled wire as counterelectrode, and a monolayer-modified gold substrate as working electrode.

**Atomic Force Microscopy Experiments.** All experiments of surface topography were carried out by tapping-mode AFM on a Digital Instruments Nanoscope IIIa microscope. Images were captured at a scan resolution of 512 points/line, scan rate of 1 Hz, scan area of 1 μm × 1 μm, and z-range of 50 nm. The drive frequency was set approximately to the resonant frequency of the cantilever being used. All cantilevers used had a resonant frequency of approximately 71 kHz.
6.5 References.


