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Self-Assembled Monolayers of Terminal Alkynes on Gold

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Since the demonstration that organothiols can bind to gold to form self-assembled monolayers (SAMs),[1−3] use of these thin films has become ubiquitous in biochemical, materials science, and other applications. The search for other anchoring groups to metals has revealed few other options. Among these are isonitriles,[4−9] aryl diazoniums,[10] aryl iodoniums,[11] and thiocyanates (as a thiolate precursor).[12,13] Particularly, in molecular electronics applications where the electronic state mixing between the binding group and the metal is a principal concern,[14,15] new binding motifs may be useful and important.

Here, we show that terminal acetylenes form relatively organized and stable SAMs on gold which can also be used to stabilize gold nanoparticles. Adsorption of small alkynes (e.g., butyne and pentyne) on silver and gold was previously examined by surface-enhanced Raman spectroscopy, but no information on the organization of the monolayer was obtained.[16,17] Gold substrates were incubated with 10 mM ethanolic solutions of the molecules shown in Figure 1. Ellipsometry and contact angle measurements were taken, and these are presented in Table 1. For comparison, several other 12-carbon molecules were also evaluated.

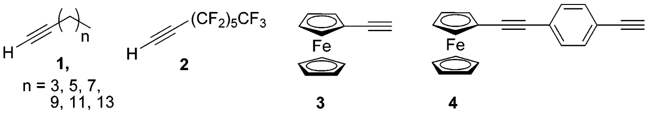

Figure 1. Structures of the molecules studied.

Table 1. Ellipsometric Film Thicknesses and Contact Angles of Water for SAMs of Compounds **1**−**4** on Au

molecule	film thickness (Å)	molecular length (Å)[a]	advancing H_2O contact angle (°)[b]
1, $n = 3$	5.6	8.0	79
1, $n = 5$	8.9	10.4	86
1, $n = 7$	10.3	12.8	90
1, $n = 9$	14.0	15.3	96
1, $n = 11$	15.1	17.8	98
1, $n = 13$	17.0	20.2	91
2	11.3	10.2	59
$CH_3(CH_2)_{11}SH$	12.5	16.9	103
$CH_3(CH_2)_{11}CH_3$	*c*	15.5	63
$CH_3(CH_2)_{11}NH_2$	*c*	15.9	76
$CH_3(CH_2)_{11}OH$	*c*	16.5	73

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

The ellipsometric thickness and advancing contact angle for the 1-alkyne-based SAMs were slightly less than that found in a densely packed, quasi-crystalline SAM, such as that found from *n*-alkanethiols on gold. However, the advancing contact angle of SAMs from dodecyne was clearly higher than those found when the 12-carbon alkane, amine, and alcohol were exposed to gold. These values were also similar to those found for SAMs derived from dodecyl isothiocyanates.[13] The fluorinated alkyne (**2**)-based adlayer showed a reasonable ellipsometric thickness and XPS spectrum (Figure S1) but a very low advancing contact angle—lower than that expected even for generically physisorbed material. The 1-alkyne-derived SAMs showed C(1s) XPS signals that fit well to the expected ratio of sp- and sp^3-hybridized carbons (Figure S2, Table S1).

To probe the integrity and stability of these acetylene-based SAMs further, their ability to block the redox response of ferricyanide ions at gold was probed.[1,2] Figure 2 shows that this response is attenuated significantly by the presence of the SAM. In contrast, when gold was exposed to dodecane, 1-dodecyl amine, and 1-dodecanol, little or no diminution of the redox response was observed (Figure S3). These results indicate that these SAMs are blocking, although again not to the extent of *n*-alkanethiol SAMs. The blocking ability was stable over multiple voltage sweeps, indicating the SAMs are stable in an aqueous environment.

These results indicate that relatively stable SAMs can be formed from terminal alkynes. However, they beg the question as to what type of interaction exists between the acetylene and gold. We initially reckoned that a gold−acetylide interaction was possible. Acetylide anion is isoelectronic with isocyanide, which is thought to bind to gold via a dative interaction.[5] SAMs were prepared from tetrahydrofuran/alkyne solutions into which *n*-butyllithium was added to effect deprotonation of the alkyne. However, these SAMs did not show any appreciable thickness by ellipsometry and did not show a water contact angle suggestive of monolayer formation.

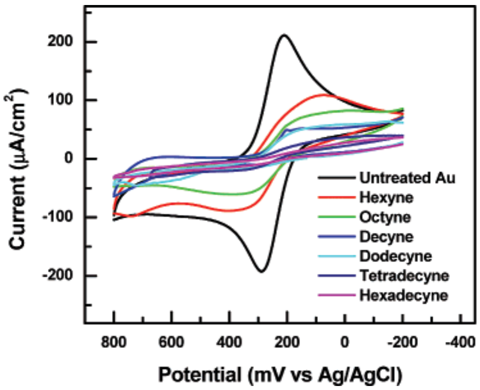

Figure 2. Cyclic voltammograms at 100 mV/s of $Fe(CN)_6^{3-/4-}$ at bare gold bead and SAM-modified gold bead electrodes with compounds **1**.

Another possibility is the interaction of the acetylene with the gold on a side on (π-type) interaction. If this were the case, we hypothesized that molecules **3** and **4**, if lying flat, would show similar electron transfer kinetics between the ferrocene and the gold. However, this was not the case. SAMs of molecule **3** showed an average electron transfer rate (k_0) of 20.6 ± 3.0 s^{-1} and a surface coverage of 3.78×10^{-10} mol/cm^2. In contrast, SAMs of molecule **4** showed an average electron transfer rate (k_0) of 3.7 ± 0.5 s^{-1} and a surface coverage of 2.93×10^{-10} mol/cm^2 (Figures S4−S7 and Tables S2 and S3). The surface coverage of these SAMs was

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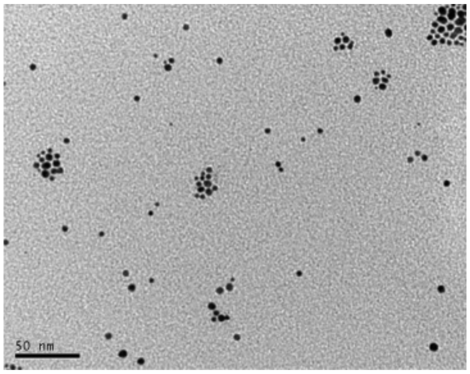

Figure 3. TEM image of dodecyne-functionalized gold nanoparticles.

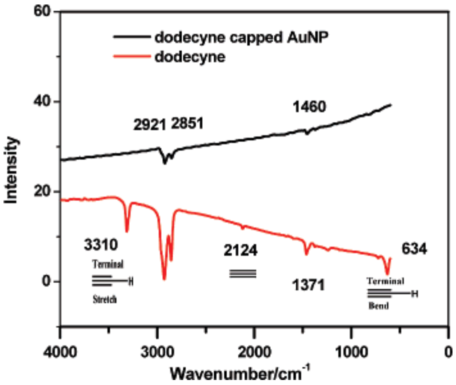

Figure 4. Transmission infrared spectra of dodecyne and dodecyne-capped gold nanoparticles.

similar to that found in ferrocenyl-terminated thiol SAMs, indicating high coverage.[18,19] This order of magnitude difference in rate for similar coverage is more consistent with through bond electron transfer through upright SAMs than electron transfer directly from the gold to the ferrocenyl group which would be expected if the molecules were lying parallel to the substrate.

Gold nanoparticles were made in the presence of dodecyne by reducing chloroauric acid in toluene/water containing 6 mM dodecyne. The expected plasmon resonance at 524 nm was observed in the resulting solution, typical for gold nanoparticles (Figure S8). Transmission electron micrographs (an example of which is shown in Figure 3) showed nanoparticles with a two size ranges (4.5 ± 0.3 and 2.6 ± 0.3 nm, Figure S9). These were stable against aggregation for up to 8 weeks as evidenced by a lack of change of their UV/visible absorption spectrum over this period of time. Transmission infrared spectra (Figure 4) showed a loss of the terminal CH stretch and bending modes in the dodecyne-capped nanoparticles (also see Supporting Information).

From these data, we conclude that terminal acetylenes form SAMs on gold substrates and nanoparticles that are relatively densely packed and stable. The data available thus far suggest an upright orientation of the molecules via some type of end-on interaction between the alkyne and substrate. A recent theoretical analysis of the interaction of phenyl acetylene with gold suggested a vinylidene/Au interaction as the most stable.[20] This interaction would involve a 1,2-hydride shift to form a carbene which then could datively bond to gold. There are several viable ways to make these species independently so SAMs derived from them could be compared to those reported here. This work is in progress.

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Supporting Information Available: Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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