

Fullerene-Terminated Alkanethiolate SAMs on Gold Generated from Unsymmetrical Disulfides

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We report the generation of new multicomponent self-assembled monolayers (SAMs) from the adsorption of unsymmetrical disulfides $R(\text{CH}_2)_4\text{SS}(\text{CH}_2)_6\text{NC}_{60}$ (where $R = \text{CH}_3\text{CH}_2-$ or $\text{CH}_3\text{O}-$ and $\text{C}_{60} = \text{Buckminsterfullerene}$) onto the surface of gold. These new SAMs expose a high coverage of fullerene moieties as judged by ellipsometric thickness, contact angle measurements, and imaging with a scanning tunneling microscope (STM). The contact angle measurements suggest a more robust coverage than fullerene-terminated SAMs generated from other approaches. Furthermore, the STM measurements represent, to our knowledge, the first direct molecular-scale images of fullerene moieties attached to the surface of a SAM.

Introduction

Due to their unique electronic, spectroscopic, and structural properties, fullerenes have been widely studied since their discovery in 1985.¹ Thin films of fullerenes have been prepared using a number of strategies including gas-phase deposition,² Langmuir–Blodgett,³ and self-assembly⁴ techniques. These films exhibit a wide range of properties such as charge transport,^{5,6} photochemical activity,⁷ superconductivity upon doping with alkali metals,^{8,9} biological activity,^{10,11} and photophysical behavior strongly influenced by intermolecular interactions.¹² Recently, Halas and co-workers have modified STM tips *via* the adsorption of a C_{60} molecule onto the tip apex,^{13–16} demonstrating improved atomic resolution on

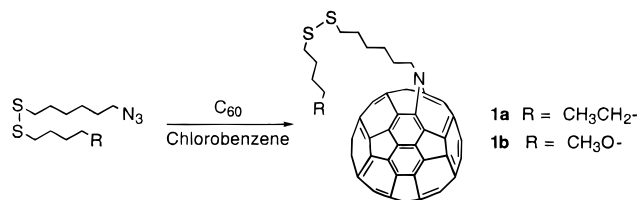


Figure 1. Synthesis of fullerene-terminated unsymmetrical disulfides **1a** and **1b**.

graphite¹³ as well as the first detection of 3-fold electron scattering from point defects on graphite.¹⁴

To further explore the development of fullerene thin films and fullerene-coated STM tips, we have targeted the covalent attachment of C_{60} to well-defined substrates. Our strategy involves functionalizing metal surfaces with organosulfur compounds that expose C_{60} moieties at the ω -terminus.^{17–19} This self-assembled monolayer (SAM) strategy permits the preparation of well-defined fullerene-terminated coatings without the need for ultrahigh vacuum deposition techniques. Furthermore, using methodologies well established in the characterization of SAMs,^{20–22} one can comprehensively evaluate the structure and properties of fullerene-terminated films prepared in this manner.

Figure 1 illustrates the synthesis of the fullerene-terminated unsymmetrical disulfides **1a** and **1b** that we have designed for these purposes. To our knowledge, this synthesis provides the first example of aziridine formation on C_{60} in the presence of a disulfide moiety. We chose to connect the fullerenes to the organosulfur moiety *via* an aziridine linkage for two reasons: (1) the aziridine group is small and highly symmetrical and would thus circumvent any unwanted effects due to steric crowding near the

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fullerene moiety, and (2) the chemistry of functionalizing C₆₀ with an aziridine group is well established.²³ To anchor the films to metal surfaces, we chose an unsymmetrical disulfide rather than a thiol for three reasons. First, in thiol-derived C₆₀ SAMs on gold, the large van der Waals diameter of C₆₀ (~10 Å)²⁴ would undoubtedly lead to films having an unusually low density of alkyl chains attached to the surface given that the proposed binding sites for the sulfur atoms (and the average distance between neighboring carbon atoms of the alkyl chains) lie ~5 Å apart in well-packed and highly ordered alkanethiolate-based SAMs on gold.²⁵ Moreover, since the diameter of C₆₀ is approximately twice the average distance between neighboring carbon atoms in normal SAMs on gold, we believed that the use of unsymmetrical disulfides **1a** and **1b** would afford, at least in principle, an ideal strategy for generating well-packed fullerene-terminated SAMs on gold. In this design, the steric bulk of the shorter R-terminated chains should give rise to underlying alkyl chain packing densities that are identical to those in normal SAMs on gold, thereby affording well-packed and highly ordered fullerene-terminated SAMs. Second, we wished to have the ability to adjust the nature of the R group and thereby "tune" the interfacial properties of the films. Third, aziridines and thiols are mutually incompatible.²⁶

Experimental Section

Materials and Methods. Gold shot (99.99%) was obtained from Americana Precious Metals., and polished single-crystal silicon(100) wafers were obtained from Silicon Sense, Inc. The liquids used for the contact angle measurements were of the highest purity available from Aldrich Chemical Co. and were used without further purification. Buckminsterfullerene (C₆₀) was purchased from Bucky USA and used as received. Chlorobenzene was purchased from Aldrich Chemical Co. and distilled before use. Dimethyl sulfide was purchased from EM Sciences. Hexanethiol and 4-chlorobutanol were purchased from Aldrich Chemical Co. 4-Methoxybutanethiol was synthesized using established methods. Column chromatography was carried out using silica gel (60–200 mesh) purchased from EM Sciences. Thin-layer chromatography (TLC) was carried out using 250 mm thick Whatman silica gel plates. Nuclear magnetic resonance (NMR) spectra were recorded on a General Electric QE-300 spectrometer operating at 300 MHz for ¹H nuclei. The data were collected in C₆D₆ and referenced to δ 7.15 for ¹H spectra. MALDI-MS were obtained at the University of Texas Medical Center in Houston, TX.

Synthesis of Fullerene-Terminated Unsymmetrical Disulfides. The details of the synthesis of the azide precursors R(CH₂)₄SS(CH₂)₆N₃ are included as Supporting Information. The strategy used to synthesize the fullerene-terminated unsymmetrical disulfides is shown in Figure 1. A general procedure is provided below; analytical data are provided for both products.

Synthesis of 1a. A mixture of C₆₀ (246 mg; 0.342 mmol) and CH₃(CH₂)₅SS(CH₂)₆N₃ (94.0 mg; 0.342 mmol) was dissolved in 450 mL of chlorobenzene and refluxed for 24 h under nitrogen. The solvent was removed by vacuum distillation. The brown residue was purified by column chromatography on silica gel using CS₂ as eluant. The second purple band was collected, and subsequent vacuum evaporation of the solvent yielded **1a** in 19% yield. ¹H NMR (C₆D₆): δ 3.36 (t, *J* = 7.7 Hz, 2 H, NCH₂CH₂), 2.60 (t, *J* = 8.0 Hz, 2 H, SCH₂CH₂), 2.56 (t, *J* = 8.0 Hz, 2 H, SCH₂CH₂), 1.99–1.90 (m, 2 H), 1.76–1.56 (m, 6 H), 1.45–1.36 (m, 2 H),

Table 1. Ellipsometric Thicknesses (Å) of SAMs on Au(111) Derived from Various Substrates^a

	1a	1b	CH ₃ (CH ₂) ₅ SH	CH ₃ O(CH ₂) ₄ SH
thickness	16.5	15.3	5.5	9.3

^a Average values of at least six independent measurements are reported. Measured values were reproducible within ±3 Å of the reported values.

1.30–1.13 (m, 6 H), 0.86 (t, *J* = 7.7 Hz, 3 H, CH₂CH₃). MALDI-MS (FAB+): calcd, 968.129; measd, 968.510.

Synthesis of 1b. This molecule was prepared from CH₃O(CH₂)₄-SS(CH₂)₆N₃ using the procedure described for the preparation of **1a**. Compound **1b** was purified by column chromatography on silica gel (CS₂/ethyl acetate = 10/0 → 9/1). Recrystallization from a mixture of CH₂Cl₂/hexane gave **1b** in 16% yield. ¹H NMR (C₆D₆/CS₂ = 1/1): δ 3.60 (t, *J* = 8.3 Hz, 2 H, NCH₂CH₂), 3.17 (t, *J* = 6.7 Hz, 2 H, OCH₂CH₂), 3.11 (s, 3 H, OCH₃), 2.59 (t, *J* = 8.0 Hz, 2 H, SCH₂CH₂), 2.54 (t, *J* = 8.0 Hz, 2 H, SCH₂CH₂), 1.91–1.83 (m, 2 H), 1.77–1.62 (m, 8 H), 1.56–1.44 (m, 4 H). MALDI-MS (FAB+): no molecular ion was observed.

Preparation of SAMs. Gold substrates were prepared by thermally evaporating ca. 100 Å of chromium onto the polished surfaces of the silicon wafers, followed by evaporating ca. 2000 Å of gold. The gold-coated wafers were cut into slides (ca. 1 × 3 cm) using a diamond stylus. Solutions of the thiols (ca. 1 mM in benzene) and disulfides (**1a** and **1b**; ca. 0.01 mM in benzene) were prepared in weighing bottles that were cleaned by soaking for 1 h in "piranha" solution (ca. 7:3, H₂SO₄/H₂O₂). *Caution!* "Piranha" solution reacts violently with organic materials and should be handled carefully. The bottles were thoroughly rinsed with deionized water and absolute ethanol and were dried before use. After being washed with absolute ethanol and dried under a flow of ultrapure nitrogen, the slides were immersed in solutions of the adsorbates. All adsorptions were allowed to equilibrate for a period of 24 h. The resultant SAMs were exhaustively rinsed with toluene and ethanol, and dried under a flow of ultrapure nitrogen before characterization.

Characterization of SAMs. The thicknesses of the SAM films were measured using a Rudolf Research Auto EL III ellipsometer equipped with a He–Ne laser operating at a wavelength of 632.8 nm at an angle of incidence of 70°. The optical constants for the bare gold were measured immediately after evaporation. A refractive index of 1.45 was assumed for all measurements. The data were collected and averaged over three separate slides using three spots per slide for each type of SAM.

Advancing contact angles of liquids were measured using a ramé-hart model 100 contact angle goniometer at 293 K and ambient relative humidity with the pipet tip in contact with the drop. Using a Matrix Technologies micro-Electrapette 25, the contacting liquids were dispensed and withdrawn at the slowest possible speed (ca. 1 μL/s). The data were collected and averaged over three separate slides by depositing three drops on each slide and measuring angles from the opposite edges of each drop.

Scanning tunneling microscopy measurements were carried out under ambient conditions with a home-built STM operated by RHK electronics and software. Although mechanically cut Pt/Rh (87/13) tips were used, the exact chemical identity of the tip apex during tunneling is not necessarily known. For these experiments, Au(111) on mica was used as purchased from Molecular Imaging Corp.

Results and Discussion

We compared the thicknesses of the SAMs generated from **1a** and **1b** to those generated from simple thiols that constitute the R-terminated portion of the unsymmetrical disulfide. Table 1 shows that the thicknesses of the SAMs derived from **1a** and **1b** are comparable but markedly greater than those derived from the thiols. Assuming that **1a** and **1b** generate true monolayer films, these data strongly suggest that the SAMs generated from the unsymmetrical disulfide are substantially (if not predominantly) composed of fullerene moieties. Due, however, to uncertainties involved in ellipsometric measurements

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Table 2. Advancing Contact Angles of Various Liquids on the Relevant SAMs and Graphite^a

surfaces	H ₂ O	GL	FA	DI	NB	BN	HD
1a	89	66	62	13	<10	<10	<10
1b	80	64	59	<10	<10	<10	<10
CH ₃ (CH ₂) ₅ SH	108	92	89	64	61	59	37
CH ₃ O(CH ₂) ₄ SH	63	54	51	<10	<10	<10	<10
graphite	86	71	69	47	28	21	<10

^a H₂O = water; GL = glycerol; FA = formamide; DI = diiodomethane; NB = nitrobenzene; BN = benzonitrile; HD = hexadecane. Measured values were reproducible within $\pm 2^\circ$ of the reported values.

(e.g., the use of the correct refractive indices or the cleanliness of the bare gold), this interpretation should be regarded with some degree of reservation.

Measurements of contact angle provide a sensitive probe of the structure and order of organic thin films.²⁷ Table 2 shows the advancing contact angles of several liquids on the surfaces relevant to our study. The high contact angles of H₂O on the SAMs generated from **1a** and **1b** (89 and 80°, respectively) suggest the presence of hydrophobic surfaces, which is consistent with exposure of fullerene moieties at the interface. Significantly, the contact angles of H₂O on SAMs derived from **1a** and **1b** are higher than those previously reported for fullerene-terminated SAMs (65–76°).^{10,17,28,29} While one might infer that the higher contact angles observed here result from the presence of the coadsorbed CH₃(CH₂)₅S⁻ and CH₃O(CH₂)₄S⁻ moieties, the magnitude of the difference between the contact angles of water on the SAMs generated independently from these two species is $\Delta\theta(108-63^\circ) = 45^\circ$; the corresponding difference on the SAMs generated from **1a** and **1b** is significantly smaller, $\Delta\theta(89-80^\circ) = 9^\circ$. These results, therefore, strongly suggest that the wettability by water of the SAMs generated from **1a** and **1b** is predominantly influenced by the presence of the terminal fullerenes rather than the terminal R groups. This interpretation is further supported by the similar contact angle observed for H₂O on **1a**, **1b**, and graphite (Table 2). From these observations, we conclude that the relatively high contact angles of H₂O measured on the present films, when compared to those measured on previously reported fullerene-terminated SAMs,^{10,17,28,29} indicate that our approach provides an improved method for generating fullerene-terminated SAMs.

For all of the surfaces and contacting liquids examined here (Table 2), the wettabilities increase with decreasing surface tension of the liquids. While a comparison of these wettabilities to those obtained on other fullerene-terminated SAMs would undoubtedly shed further light on the nature and overall robustness of the present SAMs,²⁷ the wettability data for liquids other than water are not available for these other systems.

Scanning tunneling microscopy has been used to characterize fullerene thin films on a wide variety of substrates formed by evaporation of C₆₀ under ultrahigh vacuum (UHV) conditions.^{24,30–33} To our knowledge, however, there have been no reports of STM studies of

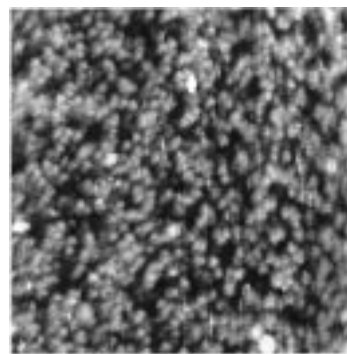


Figure 2. Large area STM image (76 × 76 nm) of SAMs generated from compound **1a** on Au(111). The image was acquired at +1.0 V sample bias and 50 pA tunneling current and was median-filtered along the slow scan direction to remove intermittent noise.

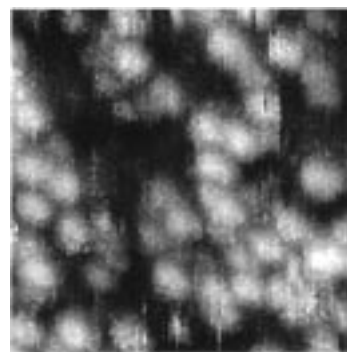


Figure 3. High-resolution STM image (18 × 18 nm) of SAMs generated from compound **1a** on Au(111). The scan parameters for this median-filtered image were +700 mV sample bias and 80 pA tunneling current.

fullerene-terminated SAMs on gold. Figure 2 shows a large area image (76 × 76 nm) of a SAM derived from **1a** on atomically flat Au(111). This image demonstrates a high coverage of surface-confined moieties but no evidence of ordering or any discernible overlayer structure. A more detailed image of the SAM (18 × 18 nm) is shown in Figure 3. The fullerene moieties can be readily distinguished with a nearest-neighbor distance of $\sim 11 \text{ \AA}$ in the most densely packed regions. This distance corresponds well to the measured van der Waals diameter of underivatized C₆₀ adsorbates obtained in previous STM measurements.^{15,24} Through cross-sectional analysis of these images, the fullerene moieties appear to extend above the gold substrate *via* the alkanethiolate tail. This interpretation is supported by the fact that stable images of these molecules can only be obtained at very low tunneling currents, which is consistent with the imaging of alkanethiol SAMs but inconsistent with the imaging of unfunctionalized C₆₀ molecules adsorbed on metal surfaces.

Conclusion

We have shown that C₆₀ can be functionalized via an aziridine linkage in the presence of a disulfide group. The resultant unsymmetrical disulfides **1a** and **1b** can be used to generate new multicomponent SAMs on gold. Measurements of ellipsometric thickness, contact angle wet-

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tability, and scanning tunneling microscopy support the formation of fullerene-terminated monolayers. Imaging of the films by STM shows a high coverage of discrete fullerene moieties.

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Supporting Information Available: Text describing procedures for the synthesis of the azide precursors $R(\text{CH}_2)_4\text{-SS}(\text{CH}_2)_6\text{N}_3$, where $R = \text{CH}_3\text{CH}_2\text{-}$ and $\text{CH}_3\text{O-}$ (4 pages). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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