

Electrochemical Charging of a Fullerene-Functionalized Self-Assembled Monolayer on Au(111)

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Received January 8, 2004

A fullerene derivative **10** with a terminal thiol group dissolves easily in common organic solvents and forms a densely packed self-assembled monolayer on gold surfaces. The functionalization of C₆₀ is based on the 1,3-dipolar cycloaddition of the azomethine ylide generated in situ from the corresponding aldehyde and *N*-methylglycine. The monolayers were characterized by grazing angle reflectance FTIR spectroscopy, scan tunneling microscopy, and cyclic voltammetry. The cyclic voltammogram of a SAM of **10** showed two well-resolved reversible cathodic waves corresponding to the first two one-electron reductions of the fullerene fragment.

Introduction

Scientific interest in nanotechnology^{1a-e} and in the optical, magnetic, and electronic properties of nanoarrays^{1f,g} derives from a desire for a full understanding of how complex organic aggregates and organic-inorganic composite assemblies can be constructed from simple molecular precursors. It is also important to establish how the physical properties of the resulting material vary with the size of the component array.¹ Current theories fail to provide a convincing predictive model of how the aggregated properties of integrated chemical systems differ from those in which the individual molecular components are randomly dispersed.^{1h-p} Advances in this field thus require architecturally defined arrays in which a clear correlation between structure and photochemical reactivity can be explored.

Our research group has focused on preparing self-assembled ω -functionalized alkanethiol monolayers on freshly deposited metal surfaces.^{2a-e} The unique three-dimensional structure of C₆₀ has prompted many researchers to employ it in various material science applications, and we have chosen to examine its disposition when bound through a rigid and a flexible linker to a

solid surface. C₆₀ moieties serve as excellent electron acceptors in molecularly designed donor acceptor diad and triad systems.^{2f-i} There have been some reports of SAMs of C₆₀ and its derivatives, including preparation, electrochemistry, and surface structural characterization.^{2j-r}

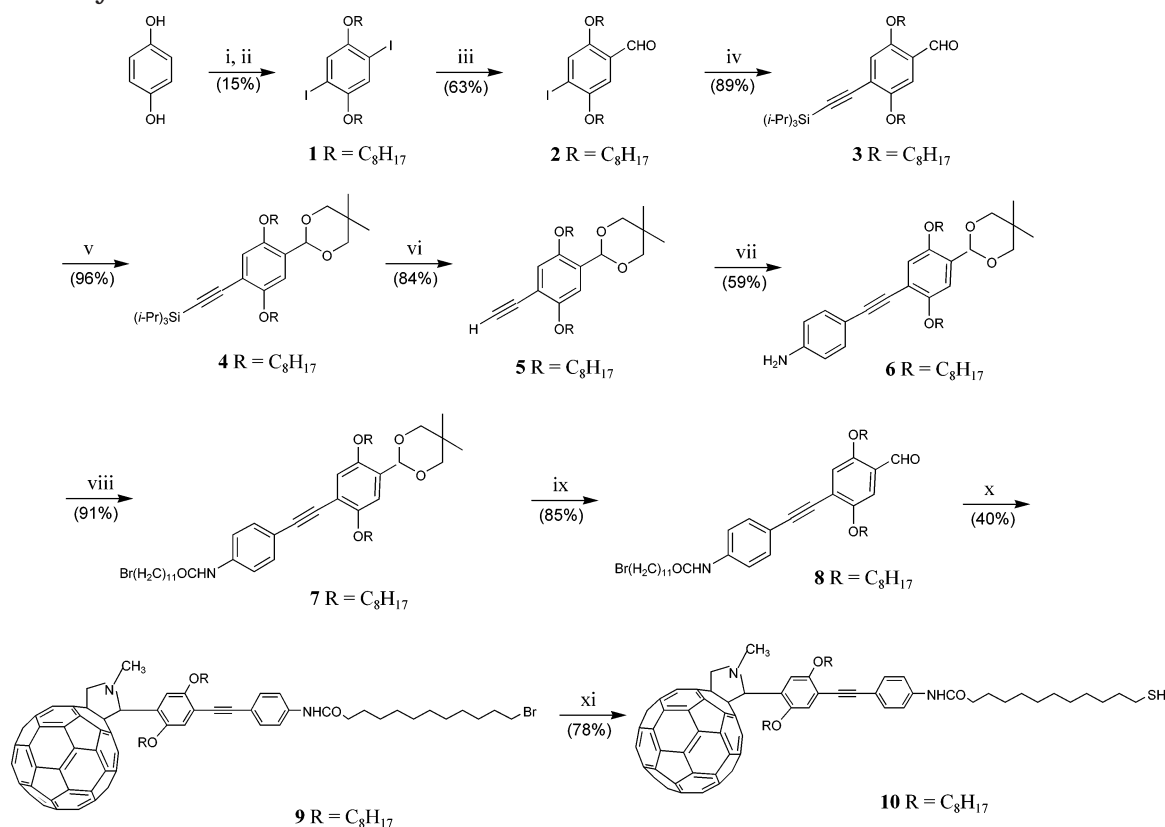
It is well established that alkanethiols with a polymethylene chain (number of the methylenes ≥ 10) form densely packed monolayers on gold surfaces.³ In addition, the presence of an amido group in a chain enhances the stability of monolayers as a result of the intermolecular hydrogen bonding.⁴ Accordingly, a fullerene connected through a rigid diphenylacetylene amide linker to a terminal thiol was designed. The long linker and the incorporation of the lateral alkoxy chains give this derivative **10** appreciable solubility. The physical properties of the C₆₀-alkanethiol in bulk solution and as a two-

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SCHEME 1. Synthesis of Fullerene–Alkanethiol **10**^a

^a Reagents and conditions: (i) 1-bromooctane, K_2CO_3 , DMF, $80\text{ }^\circ\text{C}$, 24 h; (ii) I_2 , KIO_3 , H_2SO_4 , CH_3COOH , $80\text{ }^\circ\text{C}$, 12 h; (iii) *n*-BuLi (1 equiv), Et_2O , $0\text{ }^\circ\text{C}$, 15 min, and then DMF, $0\text{ }^\circ\text{C}$ to room temperature (rt), 2 h; (iv) (triisopropylsilyl)acetylene, $PdCl_2(PPh_3)_2$, CuI, Et_3N , rt, 24 h; (v) 2,2-dimethylpropane-1,3-diol, *p*-TsOH, C_6H_6 , heating, 24 h; (vi) TBAF, THF, $0\text{ }^\circ\text{C}$, 1 h; (vii) iodoaniline, $PdCl_2(PPh_3)_2$, CuI, Et_3N , rt, 24 h; (viii) $Br(CH_2)_{11}COOH$, CDMT, THF, $0\text{ }^\circ\text{C}$; (ix) CF_3CO_2H , CH_2Cl_2 , H_2O , rt, 5 h; (x) C_{60} , *N*-methylglycine, toluene, reflux, 16 h; (xi) hexamethyldisilathiane, TBAF, $-10\text{ to }0\text{ }^\circ\text{C}$, 30 min.

dimensional self-assembled monolayer (SAM) on gold were therefore explored.

Results and Discussion

Synthesis. The synthesis of the fullerene derivative studied here is depicted in Scheme 1. Reaction of hydroquinone with 1-bromooctane in DMF at $80\text{ }^\circ\text{C}$ in the presence of K_2CO_3 , followed by iodination of the resulting 1,4-dioctylbenzene, yielded **1**. Compound **2** was obtained in 63% yield by treatment of **1** with *n*-BuLi (1 equiv) in Et_2O at $0\text{ }^\circ\text{C}$ followed by quenching with DMF. Compound **2** was then subjected to a Pd-catalyzed cross-coupling reaction⁵ with (triisopropylsilyl)acetylene to give alkynylated **3** in 89% yield. Reaction of **3** with 2,2-dimethylpropane-1,3-diol in refluxing benzene in the presence of a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) gave the protected aldehyde **4** in 96% yield. Terminal alkyne **5** was obtained in 84% yield by deprotection of **4** with tetrabutylammonium fluoride (TBAF). **6** was obtained in 59% yield by Pd-catalyzed cross coupling between **5** and iodoaniline. Condensation of compound **6** with 12-bromododecanoic acid in the presence of 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) af-

forded **7** in 91% yield. Deprotection of **7** with CF_3CO_2H in CH_2Cl_2/H_2O afforded aldehyde **8** in 85% yield.

The functionalization of C_{60} is based on the 1,3-dipolar cycloaddition of the azomethine ylide generated in situ from the corresponding aldehyde and *N*-methylglycine.⁶ In a typical procedure, a solution of the aldehyde **8** (200 mg), C_{60} (234 mg), and *N*-methylglycine (145 mg) in toluene (250 mL) was heated to reflux under Ar for 16 h. After cooling, the resulting solution was evaporated to dryness and column chromatography yielded fullerene–alkyl bromide **9** (160 mg, 40%).

The thiol was introduced by a convenient (trimethylsilyl)thioxy–dehalogenation reaction.⁷ Tetrabutylammonium trimethylsilylanethiolate ($Me_3SiS^-Bu_4N^+$), generated in situ by adding a solution of TBAF to hexamethyldisilathiane in THF, reacted rapidly with **9** at ambient temperature. Fullerene–alkanethiol **10**, obtained in good yield (78%), dissolved easily in common organic solvents such as chloroform, methylene chloride, toluene, etc. But the solubility decreased markedly after the compound was dried, probably because of autoxidation of the terminal thiol to the corresponding disulfide. Self-assembled monolayers may be formed either by the direct self-assembly of the thiol or of the corresponding disulfide produced during the workup. The absorption spectrum

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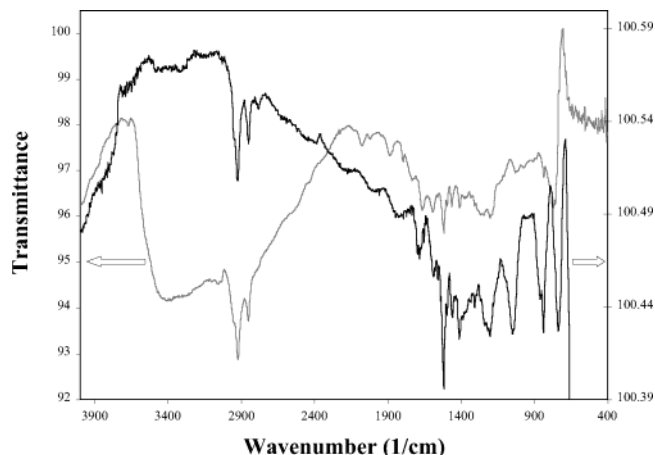


FIGURE 1. GAR-FTIR of SAMs of fullerene–alkanethiol **10** on Au(111) (full line) and the FTIR of fullerene–alkanethiol **10** in KBr (dotted line).

TABLE 1. Mode Assignments and Frequencies (cm^{-1}) for a Transmission FTIR Spectrum of Compound **10** in KBr and GAR-FTIR Spectrum of SAM of Compound **10**

assgn ^a	10 in KBr	SAM of 10
arom CH str	3056	
aliph CH ₂ asym str	2922	2934
aliph CH ₂ sym str	2851	2852
C=O str	1664	1690
arom C–C ring str	1593	1593
arom C–C ring str	1516	1521
N–H deformation	1495	1500
CH ₃ asym deformation or CH ₂ scissor	1463	1460
CH ₂ –C=O deformation	1410	1419
CH ₂ wag and twist or C–O–C asym str	1201	1209
CH ₂ out of plane bend or C–O–C sym str	1030	1055

^a The following abbreviations are used: arom for aromatic; aliph for aliphatic; str for stretch; sym for symmetric; asym for asymmetric.

of **10** in CH₂Cl₂ exhibited the characteristic peaks expected for a C₆₀–pyrrolidine at 432 and 706 nm⁶ and for aromatic rings at 306 and 334 nm.

Grazing Angle Reflectance Infrared Spectrum of SAMs of 10. Infrared spectroscopy is a powerful tool for the investigation of SAMs of thiols on gold. At the simplest level, reflectance spectroscopy can confirm the presence of molecules adsorbed on a surface. A comparison of the reflectance spectrum of the SAM with a transmission spectrum of the compound as KBr pellet confirms the identity of the molecules in the SAM, i.e., that the deposition process did not induce unexpected cross-reaction.

The peaks of the GAR-FTIR spectrum of the SAMs of the fullerene–thiol compound correspond well with the peaks in transmission FTIR of the bulk fullerene–thiol in KBr (Figure 1 and Table 1). For example, the 1521 and 1593 cm^{-1} peaks assigned as aromatic C–C ring stretches, 1660–1700 cm^{-1} carbonyl peak, and the 1030 cm^{-1} ether peak group appear in both spectra. A band from the thiol S–H stretch is not present in the bulk spectrum, but these bands are characteristically weak so their absence is understandable.⁸ Alkyl C–H asym-

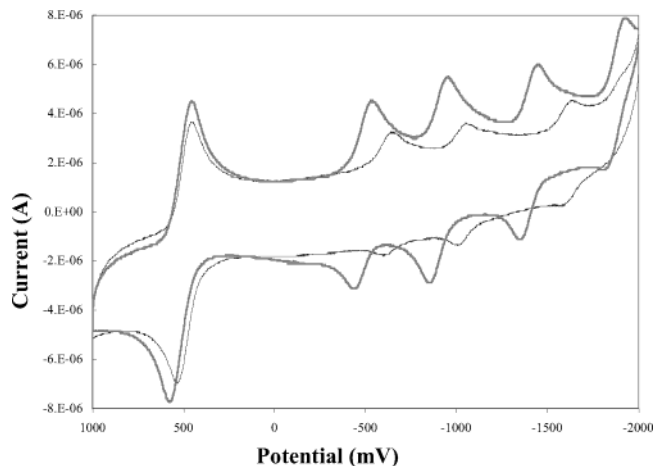


FIGURE 2. Cyclic voltammograms of C₆₀ (dotted line) and C₆₀-derivative **10** (full line) in acetonitrile/toluene (1:4 v/v) on a glassy carbon electrode with 0.1 M *n*-Bu₄NPF₆ as supporting electrolyte at 100 mV/s scan rate at room temperature.

metric stretching 2920 cm^{-1} and alkyl C–H symmetric stretching 2850 cm^{-1} are moderately stronger than aromatic stretching in the bulk spectrum, whereas they have similar intensities in the GAR-FTIR of the SAM.

That is, the aromatic stretching bands became relatively stronger compared to the alkyl stretching bands in the SAM and compared to the bulk. Selection rules⁹ for reflectance infrared spectroscopy of anisotropic films on a conducting surface allow only those transition moments that have a component perpendicular to the plane of the substrate surface to exhibit appreciable absorbance. However, because the aromatic absorptions result from overtones and are therefore complex in origin, it is not possible to use the infrared data conclusively to establish the orientation of the rigid diphenylacetylenes relative to the gold surface.

Electrochemical Properties of the 10-Functionalized Gold SAM. Fullerene–alkanethiol **10** in solution (CH₃CN/toluene) exhibited voltammetric behavior (Figure 2) very similar to that of C₆₀ itself.^{2j} Three reversible reduction peaks were observed when the potential was scanned to –1.9 V ($E_{1/2} = -1.116, -1.526, \text{ and } -2.105$ V vs Fc/Fc⁺). These electron-transfer processes are presumably fullerene centered but shifted –110, –110, and –180 mV, respectively, from those observed for C₆₀. Such shifts are diagnostic of chemical modification of the fullerene and are a consequence of the disruption of the extended fullerene π network affected by chemical modification.⁶

Fullerene–alkanethiol SAM was prepared by soaking a polished gold electrode for 24 h in a 1 mM toluene solution of **10**. The electrode was then thoroughly rinsed with toluene and absolute ethanol and water and dried under Ar before being immersed in acetonitrile–toluene with 0.1 M *n*-Bu₄NPF₆. The cyclic voltammogram of a SAM of **10** showed two well-resolved reversible cathodic waves with $E^{\circ}_1 = -0.65$ V and $E^{\circ}_2 = -1.04$ V vs Ag/AgCl corresponding to the first two one-electron reductions of the fullerene fragment (Figure 3).

Within the range of scan rates investigated, peak currents increased linearly with the scan rate while the

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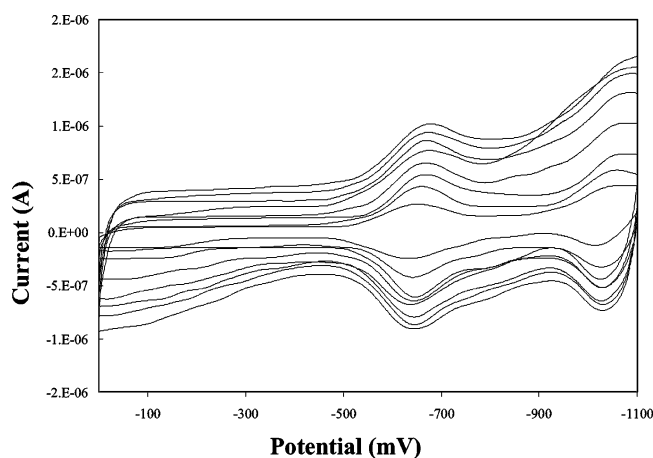


FIGURE 3. Cyclic voltammograms of a SAM of fullerene–alkanethiol **10** on a gold electrode in acetonitrile/toluene (1:4 v/v) with 0.1 M *n*-Bu₄NPF₆ as supporting electrolyte at room temperature, with scan rates between 100 (smallest current) and 800 (largest current) mV/s.

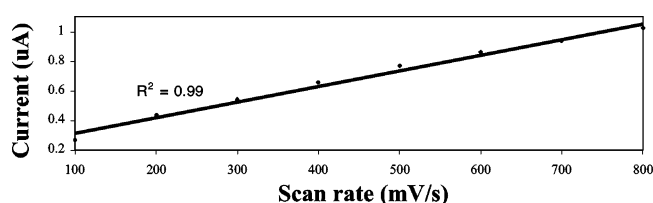


FIGURE 4. Anodic peak current at -0.65 V as a function of sweep rate.

peak potentials and peak-to-peak separations (ΔE_p) (17 and 29 mV for the first and the second reductions, respectively) were independent of scan rates (Figure 4). These characteristics together with the Gaussian shape of the CV waves are typical for surface-confined electroactive species.^{2k–m}

Integration of the area under the curve of SAM **10** on Au observed for the first reduction led to a surface coverage of Γ of $(0.833\text{--}1.149) \times 10^{-10}$ mol cm⁻² (140–200 Å² molecule⁻¹, calculated from 100 and 200 mV/s scan rate, respectively). The occupied area/molecule is somewhat larger than that of the hexagonal (78 Å² molecule⁻¹) or the simple square (98–100 Å² molecule⁻¹) packing in similar C₆₀ LB films.^{2n–q} This is likely related to the steric blockage by the alkoxy chains on the aromatic ring.

In solution, when C₆₀ itself is reduced, it may surround itself with charge-compensating cations. When the SAM of fullerene–thiol derivative undergoes sequential reduction processes, only those portions of the monolayer that can incorporate charge-compensating ions will be electrochemically active. Mirkin et al.^{2r} reported that the coverage-dependent electrochemical responses of fullerene–thiol are attributed to the relative amounts of free volume available in the different types of films. In our case, however, there is sufficient free volume in the full monolayer to incorporate charge-compensation ions to satisfy the requirements of the dianion formed upon electrochemical reduction of the film because the lateral soft alkoxy chains incorporated into the C₆₀–thiol compound do not pack into a solid-phase matrix.

The SAMs of **10** were stable under repetitive cycling in the reduction region up to -1.1 V vs Ag/AgCl.

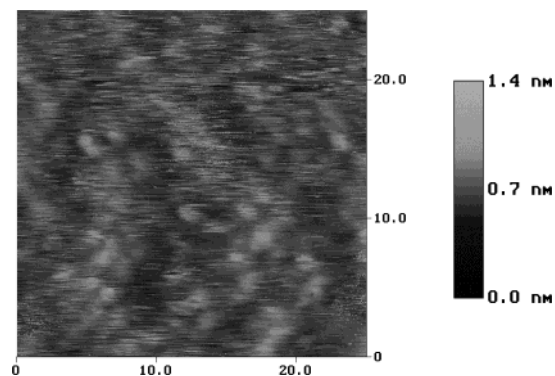


FIGURE 5. High-resolution STM image (25×25 nm) of SAMs generated from fullerene derivative **10** on Au(111). The tunneling conditions were 700 mV bias and 70 pA tunneling current.

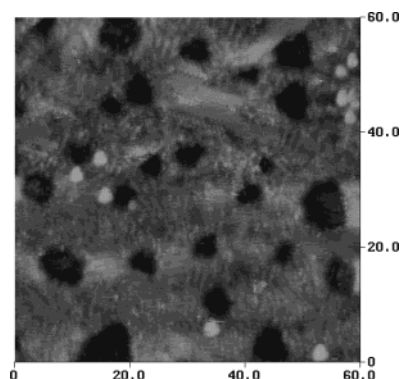


FIGURE 6. STM image of a 60×60 nm area of a decanethiolate monolayer containing inserted fullerene derivative molecules **10** on Au(111). The tunneling conditions were 1.0 V bias and 10 pA tunneling current.

Scanning Tunneling Microscopy. Figure 5 shows an STM image of a SAM derived from the C₆₀ derivative on Au (111). This image demonstrates a high coverage of surface-confined moieties but no evidence of ordering or any discernible overlayer structure.

The fullerene moieties can be readily distinguished with a nearest-neighbor distance of 13 Å in the most densely packed regions. This corresponds well with the electrochemistry measurements. This distance is higher than the measured van der Waals diameter of underivatized C₆₀ adsorbates found in previous STM measurements,¹⁰ which is understandable because of the existence of the lateral chains of the C₆₀ derivative.

We also studied SAMs formed by the insertion of the fullerene–thiol or/and –disulfide into self-assembled decanethiolate monolayers. Figure 6 shows an STM image of a decanethiolate SAM after immersion in a C₆₀ derivative solution for 1 h. The white protrusions in this image are assigned as fullerenes, while the black holes are etch pits that form during the self-assembly process and correspond to a depth of one gold monolayer.¹¹ These protrusions are absent in pure decanethiolate SAMs.^{12a}

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The atomic lattice of the underlying decanethiolate monolayer is clearly observed, demonstrating that the lattice of the SAM is preserved after the insertion process.¹² The fullerene molecules were found to be bound near the step edges. Presumably, these molecules are physisorbed at grain boundaries in the decanethiolate lattice. Thus, the C₆₀ derivative molecules prefer to insert into a preformed decanethiol monolayer as small clusters rather than individually.

The incorporation of lateral chains in **10** improved solubility necessary to form uniform SAMs. Also, the ideal first and second one-electron reduction for the gold electrode with a full monolayer of fullerene derivative was obtained because of the sufficient free volume present at the modified surface. At the same time, the surface coverage decreased because of steric hindrance by the lateral alkoxy chains on the aromatic ring.

Conclusions

A fullerene–thiol **10** dissolved easily in common organic solvents because of the presence of a lateral soft alkoxy chain. Electrochemical measurements showed that the surface-confined self-assembled monolayer of **10** exhibits ideal behavior (for the first and second one-electron reductions) because the softly packed alkoxy chains permit easy penetration of counterions into the preformed monolayer. STM demonstrates a high coverage of surface-confined fullerene–alkanethiol **10**.

Experimental Section

Grazing angle reflectance FTIR spectra were acquired using p-polarized light at an incidence angle of 80°, equipped with a liquid-nitrogen-cooled MCT/A detector. Typically, 512 scans at a resolution of a 4 cm⁻¹ were collected.

Cyclic voltammetry was performed using a conventional three-electrode configuration, with a 3-mm-diameter glassy carbon electrode or 1.6-mm-diameter modified Au electrode as the working electrode and a platinum counter electrode and Ag/AgCl as a pseudoreference. A glassy carbon electrode was polished with alumina before being used. The gold electrode was polished on the nylon disk with 1 μm diamond polish slurry first and then with a microcloth disk with alumina polish. STM measurements were performed with mechanically cut Pt–Ir tips. Compounds **1–3** were prepared according to previously reported procedures.¹³

Compound 4. A solution of aldehyde **3** (18 g, 33 mmol), 2,2-dimethylpropane-1,3-diol (6.9 g, 66 mmol), and *p*-TsOH (200 mg) in benzene (300 mL) was heated to reflux for 24 h using a Dean–Stark trap. After cooling, the solution was washed with water, dried over MgSO₄, and evaporated to dryness to afford **4** (21 g, 96%) as a yellow liquid.

¹H NMR (300 MHz, CDCl₃): δ 7.12 (s, H), 6.91 (s, H), 5.70 (s, H), 3.99 (t, *J* = 6.5 Hz, 2H), 3.93 (t, *J* = 6.5 Hz, 2H), 3.75 (d, *J* = 11 Hz, 2H), 3.64 (d, *J* = 11 Hz, 2H), 1.77 (m, 4H), 1.47 (m, 4H), 1.31 (m, 20H), 1.14 (s, 21H), 1.10 (s, 3H), 0.90 (t, *J* = 6.5 Hz, 3H), 0.89 (t, *J* = 6.5 Hz, 3H), 0.79 (s, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 154.9, 149.5, 128.5, 117.6, 113.9, 110.9, 103.3, 96.9, 94.6, 77.8, 69.4, 69.1, 31.85, 31.78,

30.2, 29.52, 29.47, 29.3, 26.2, 26.0, 23.2, 22.7, 21.8, 18.7, 18.5, 14.1, 11.34, 11.26.

Anal. Calcd for C₃₉H₆₈O₄Si·0.5H₂O: C, 73.41; H, 10.89. Found: C, 73.17; H, 11.08.

Compound 5. To a stirring solution of **4** (12 g, 18 mmol) in 300 mL of THF at 0 °C was slowly added 20 mL of TBAF (1.0 M solution in THF). After 1 h, several drops of water were added and diluted with CH₂Cl₂. The organic phase was washed with H₂O (3×), dried over MgSO₄, and concentrated. The crude compound was purified by column chromatography (SiO₂, 1:1 hexane/CH₂Cl₂) to give **5** (7.7 g, 84%) as a yellow liquid.

¹H NMR (300 MHz, CDCl₃): δ 7.18 (s, H), 6.96 (s, H), 5.71 (s, H), 4.04 (t, *J* = 6.5 Hz, 2H), 3.92 (t, *J* = 6.5 Hz, 2H), 3.72 (d, *J* = 11 Hz, 2H), 3.65 (d, *J* = 11 Hz, 2H), 3.26 (s, H), 1.78 (m, 4H), 1.45–1.31 (m, 23H), 0.89 (m, 6H), 0.80 (s, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 154.7, 149.6, 128.7, 117.6, 112.5, 111.4, 96.7, 81.0, 80.2, 77.8, 69.5, 69.3, 31.8, 30.2, 29.5, 29.2, 26.0, 25.9, 23.1, 22.6, 21.8, 18.1, 17.6, 14.1, 13.3, 12.2.

Anal. Calcd for C₃₀H₄₈O₄·1.5H₂O: C, 72.1; H, 10.28. Found: C, 72.29; H, 11.0.

Compound 6. To a solution of **5** (7.7 g, 15 mmol) and iodoaniline (3.3 g, 15 mmol) in 250 mL of dry triethylamine under argon atmosphere were quickly added catalyst PdCl₂(PPh₃)₂ and CuI. The reaction mixture was stirred at room temperature for 24 h and filtered. The concentrated solution was purified by chromatography (SiO₂, 1:1 hexane/CH₂Cl₂) to afford **6** (5.4 g, 59%) as yellow crystals. Mp: 67–69 °C.

¹H NMR (300 MHz, CD₂Cl₂): δ 7.34 (d, *J* = 8 Hz, 2H), 7.17 (s, H), 6.97 (s, H), 6.63 (t, *J* = 8 Hz, 2H), 5.72 (s, H), 4.05 (t, *J* = 6.5 Hz, 2H), 3.95 (t, *J* = 6.5 Hz, 2H), 3.80 (s, 2H), 3.76 (d, *J* = 11 Hz, 2H), 3.66 (t, *J* = 11 Hz, 2H), 1.81 (m, 4H), 1.55–1.28 (m, 20H), 1.30 (s, 3H), 0.89 (m, 6H), 0.80 (s, 3H).

¹³C NMR (75 MHz, CD₂Cl₂): δ 153.9, 149.8, 146.5, 132.9, 127.5, 116.7, 114.6, 112.94, 111.6, 96.9, 94.3, 83.9, 77.8, 69.6, 69.3, 31.8, 31.5, 30.2, 29.42, 29.37, 29.27, 26.04, 26.01, 23.2, 22.6, 21.8, 14.1.

Anal. Calcd for C₃₆H₅₃NO₄·0.5H₂O: C, 75.48; H, 9.5; N, 2.44. Found: C, 75.59; H, 9.56; N, 2.49.

Compound 7. To a solution of 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) (0.96 g, 5.5 mmol) and 12-bromododecanoic acid (1.5 g, 5.5 mmol) in 150 mL of THF at 0 °C was added dropwise 4-methylmorpholine (NMM) (0.55 g, 5.5 mmol). After 0.5 h, the white precipitate appeared. **7** (2.7 g, 4.5 mmol) was added and stirring continued at room temperature for 3 h. The concentrated solution was purified by chromatography (SiO₂, 1:1 to 0:1 hexane/CH₂Cl₂) to afford **7** (3.59 g, 91%) as a yellow gel.

¹H NMR (400 MHz, CDCl₃): δ 7.51 (d, *J* = 9 Hz, 2H), 7.48 (d, *J* = 9 Hz, 2H), 7.19 (s, H), 7.15 (s, H), 6.98 (s, H), 5.72 (s, H), 4.06 (t, *J* = 6.5 Hz, 2H), 3.95 (t, *J* = 6.5 Hz, 2H), 3.76 (d, *J* = 11 Hz, 2H), 3.66 (d, *J* = 11 Hz, 2H), 3.41 (t, *J* = 6.5 Hz, 2H), 2.36 (t, *J* = 7 Hz, 2H), 1.83 (m, 4H), 1.75 (m, 4H), 1.55–1.29 (m, 34H), 1.33 (s, 3H), 0.89 (t, *J* = 6.5 Hz, 3H), 0.87 (t, *J* = 6.5 Hz, 3H), 0.80 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 171.4, 154.1, 149.8, 137.8, 132.3, 128.1, 119.5, 119.1, 116.8, 114.0, 111.5, 96.8, 93.2, 85.7, 77.8, 69.6, 69.3, 37.8, 34.1, 32.8, 31.8, 30.3, 29.4, 29.34, 29.31, 29.27, 29.25, 29.19, 28.7, 28.1, 26.02, 26.01, 25.5, 23.2, 22.65, 22.63, 21.8, 14.1.

Anal. Calcd for C₄₈H₇₄BrNO₅: C, 69.88; H, 9.04; N, 1.69. Found: C, 69.37; H, 8.82; N, 1.65. UV–vis (CH₂Cl₂): 306, 337, 400 (shoulder) nm.

Compound 8. A mixture of **7** (2.5 g, 3.0 mmol) and CF₃CO₂H (40 mL) in 2:1 CH₂Cl₂/H₂O (120 mL) was stirred at room temperature for 5 h. The organic layer was then washed with water (3×), dried over MgSO₄, and evaporated to dryness. Column chromatography (SiO₂, CH₂Cl₂) gave **8** (1.9 g, 85%) as a yellow solid. Mp: 66–67.5 °C.

¹H NMR (300 MHz, CDCl₃): δ 10.44 (s, H), 7.56 (d, *J* = 9 Hz, 2H), 7.51 (d, *J* = 9 Hz, 2H), 7.31 (s, H), 7.22 (s, H), 7.10 (s, H), 4.06 (t, *J* = 6.5 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 3.14 (t,

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$J = 6.5$ Hz, 2H), 2.37 (t, $J = 7$ Hz, 2H), 1.88–1.73 (m, 8H), 1.53–1.29 (m, 34H), 0.89 (t, $J = 6.5$ Hz, 3H), 0.87 (t, $J = 6.5$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 189.2, 171.5, 155.6, 153.5, 138.5, 132.6, 124.6, 120.7, 119.2, 118.3, 117.2, 109.8, 97.2, 85.1, 69.3, 69.2, 37.8, 34.0, 32.8, 31.7, 29.34, 29.29, 29.25, 29.14, 29.10, 28.7, 28.1, 26.0, 25.5, 22.6, 14.1.

Anal. Calcd for $\text{C}_{43}\text{H}_{64}\text{BrNO}_4 \cdot 0.5\text{H}_2\text{O}$: C, 69.05; H, 8.75; N, 1.87. Found: C, 69.02; H, 8.9; N, 1.87.

Fullerene-Alkyl Bromide 9. A mixture of **8** (200 mg, 0.271 mmol), C_{60} (234 mg, 0.325 mmol), and *N*-methylglycine (145 mg, 1.624 mmol) in toluene (250 mL) was heated to reflux under Ar for 16 h. After cooling, the resulting solution was filtered and concentrated. The crude compound was purified by column chromatographies (SiO_2 , 1:1 hexane/ CH_2Cl_2) and preparative TLC (SiO_2 , 1:1 hexane/ CH_2Cl_2) to give **9** (160 mg, 40%) as a brown-black solid. Mp: 154–155 °C.

^1H NMR (300 MHz, CDCl_3): δ 7.58 (s, 1H, Ar-H), 7.50 (d, $J = 8$ Hz, 2H, Ar-H), 7.45 (d, $J = 8$ Hz, 2H, Ar-H), 7.19 (s, 1H, Ar-H), 7.02 (s, 1H, Ar-H), 5.54 (s, 1H, $-\text{CH}<$), 4.97 (d, $J = 9$ Hz, 1H, $-\text{CH}_2-\text{N}$), 4.31 (d, $J = 9$ Hz, 1H, $-\text{CH}_2-\text{N}$), 4.17–3.98 (m, 3H, $-\text{OCH}_2$), 3.70 (m, 1H, $-\text{OCH}_2$), 3.40 (t, $J = 7$ Hz, 2H, BrCH_2), 2.82 (s, 3H, $-\text{N}-\text{CH}_3$), 2.35 (t, $J = 7.5$ Hz, 2H, COCH_2), 1.89–1.28 (m, 48H), 0.87 (m, 6H).

^{13}C NMR (75 MHz, CDCl_3): δ 171.3, 156.5, 154.9, 154.0, 153.7, 151.4, 147.2, 146.7, 146.6, 146.15, 146.13, 146.08, 146.02, 146.01, 145.99, 145.96, 145.85, 145.6, 145.5, 145.4, 145.2, 145.1, 144.5, 144.4, 144.3, 143.0, 142.6, 142.5, 142.3, 142.2, 142.0, 141.7, 141.6, 140.2, 140.1, 139.7, 139.4, 137.9, 136.4, 136.3, 136.1, 134.6, 132.3, 127.1, 119.3, 119.0, 116.0, 114.7, 113.2, 93.5, 85.6, 75.6, 70.0, 69.8, 69.2, 68.7, 68.0, 40.1, 39.2, 37.9, 31.9, 31.8, 29.7, 29.5, 29.4, 29.31, 29.28, 29.24, 29.16, 28.4, 26.1, 25.6, 25.5, 22.73, 22.66, 14.2, 14.1.

HRMS: calcd for $\text{C}_{105}\text{H}_{69}\text{BrN}_2\text{O}_3$, 1485.4570; found, 1485.4427. FTIR (KBr, cm^{-1}): 2920, 2850, 1633, 1592, 1515, 1493, 1463, 1429, 1411, 1383, 1331, 1306, 1271, 1177, 1029. UV-vis (CH_2Cl_2): 306, 331, 430, 704 nm.

Fullerene-Alkanethiol 10. A stirred solution of **9** (40 mg, 0.027 mmol) in 10 mL of freshly distilled THF was cooled to -10 °C, and hexamethyldisilathiane (6.8 μL , 0.032 mmol) and TBAF (29 μL , 0.029 mmol) were added. The resulting reaction mixture was allowed to warm to room temperature while being stirred for 30 min. The mixture was then diluted with CH_2Cl_2 and washed with aqueous NH_4Cl (saturated). The organic phase was dried over MgSO_4 and concentrated to afford **10** (30 mg, 78%) as a brown-black solid.

^1H NMR (300 MHz, CDCl_3): δ 7.58 (s, 1H, Ar-H), 7.50 (d, $J = 8$ Hz, 2H, Ar-H), 7.45 (d, $J = 8$ Hz, 2H, Ar-H), 7.29 (s, 1H,

N-H), 7.02 (s, 1H, Ar-H), 5.54 (s, 1H, $-\text{CH}<$), 4.97 (d, $J = 9$ Hz, 1H, $-\text{CH}_2-\text{N}$), 4.31 (d, $J = 9$ Hz, 1H, $-\text{CH}_2-\text{N}$), 4.16–3.98 (m, 3H, $-\text{OCH}_2$), 3.70 (m, 1H, $-\text{OCH}_2$), 2.82 (s, 3H, $-\text{N}-\text{CH}_3$), 2.67 (t, $J = 7$ Hz, 2H, SHCH_2), 2.35 (t, $J = 7.5$ Hz, 2H, COCH_2), 1.89–1.27 (m, 48H), 0.87 (m, 6H).

^{13}C NMR (75 MHz, CDCl_3): δ 171.4, 156.6, 155.0, 154.1, 153.8, 151.5, 147.3, 146.7, 146.6, 146.24, 146.20, 146.1, 145.9, 145.7, 145.5, 145.4, 145.3, 145.2, 145.1, 144.6, 144.5, 144.4, 144.3, 143.0, 142.6, 142.5, 142.3, 142.2, 142.0, 141.7, 141.6, 140.2, 140.1, 139.7, 139.4, 137.9, 136.4, 136.3, 136.1, 134.6, 132.3, 127.1, 119.3, 119.0, 116.0, 114.7, 113.2, 93.5, 85.6, 75.6, 70.0, 69.8, 69.2, 68.7, 68.0, 40.1, 39.2, 37.9, 31.9, 31.8, 29.7, 29.5, 29.4, 29.31, 29.28, 29.24, 29.16, 28.4, 26.1, 25.6, 25.5, 22.73, 22.66, 14.2, 14.1.

FTIR (KBr, cm^{-1}): 2922, 2851, 1664, 1593, 1516, 1495, 1463, 1410, 1242, 1201. UV-vis (CH_2Cl_2): 306, 334, 432, 706 nm.

Preparation of SAM. The gold surface to which the monolayer was attached was prepared on a Si wafer by evaporation of Cr (ca. 80 Å), followed by Au (ca. 2000 Å). The metal evaporation of gold was conducted at the Biomedical Microsensor Laboratory at North Carolina State University. The freshly prepared gold surfaces were washed sequentially with 7:3 H_2SO_4 /40% aqueous H_2O_2 , copious amounts of Millipore-filtered water, and absolute ethanol, before being dried under a stream of Ar. Monolayers of fullerene derivatives were prepared by allowing a freshly cleaned gold wafer to soak for 24 h at room temperature in the dark in 5 mL of dilute solution of fullerene derivative in toluene that had been degassed by bubbling with Ar for 15 min. The SAMs were rinsed sequentially with toluene, absolute ethanol, water, and then again with ethanol, before being dried under Ar just before the experiment.

Acknowledgment. This work was supported by the United States Department of Energy. The authors gratefully acknowledge Matthew Lewis and Dr. Christopher B. Gorman for assistance with the STM experiments. Mass spectra were obtained at the Mass Spectrometry Laboratory for Biotechnology. Partial funding for the facility was obtained from the North Carolina Biotechnology Center and the National Science Foundation.

Supporting Information Available: ^1H NMR and ^{13}C NMR spectra for all the new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO049939J