A Well-Defined Surface-Confinable Fullerene: Monolayer Self-Assembly on Au(111)

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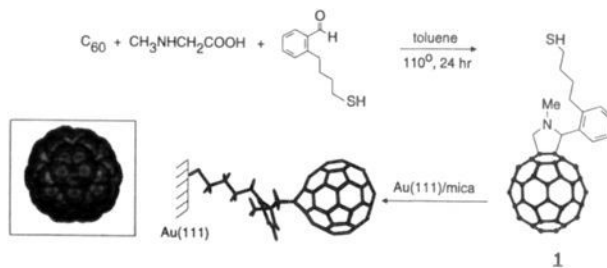*Department of Chemistry, Northwestern University Evanston, Illinois 60208*

We report the synthesis and characterization of a *well-defined* surface-confinable fullerene, **1**, for adsorption onto Au(111)/ mica substrates, Scheme 1. We also show that compound **1** spontaneously adsorbs onto such substrates to form densely packed, highly ordered monolayer films. This work complements the growing body of work relating to surface-adsorbed fullerene monolayer films,[1] but it is a distinct departure from past work in that, for the first time, it utilizes both a well-defined fullerene adsorbate molecule, **1**, and a well-defined Au(111) surface. The system described herein was designed with the following in mind: (1) The adsorption of alkanethiols on Au is known to involve immobilization of the adsorbate molecules through strong Au−S interactions[2] (i.e., the chemical identity of the fullerene portion of **1** is expected to remain intact upon its surface immobilization). (2) Au(111)/mica substrates may be used as electrodes, allowing for electrochemical characterization of the fullerene monolayers formed thereon. (3) Our Au-(111)/mica substrates are SERS-active with $\sim 10^3 - 10^4$ enhancement factors (with 752 nm laser excitation, λ_{ex})[3a] making Raman characterization of adsorbate species at monolayer or submonolayer coverages straightforward. (4) **1** is designed such that the C_{60} cage dominates its structure. Therefore, adsorbate packing and intermolecular interactions, which are important for the self-assembly process, will be dominated by the fullerene portion of **1**; see top view of a space-filling model of **1**, Scheme 1 (inset). (5) The cohesive energy ($E_{cohesive}$) for C_{60}, 1.7 eV/ molecule,[4] is substantially larger than that estimated for octadecanethiol ($E_{cohesive} = 0.6-1.0$ eV/molecule),[5] which is known to form densely packed, highly ordered SAMs on Au(111)/mica substrates. (6) Because of its large size and spherical shape (diameter = 7 Å), C_{60} serves as an excellent AFM probe molecule[1d,6] that allows for SAM structural characterization.

The Au(111)/mica substrates (average Au(111) domain size of $\sim$1000 Å; surface roughness factor = 1.35) were prepared by thermal evaporation of Au onto mica and characterized by atomic force microscopy (AFM) as previously reported.[3] Compound **1** was synthesized by the condensation of sarcosine ($CH_3NHCH_2CO_2H$), 2-(4-mercaptobutyl)benzaldehyde,[7] and C_{60}, Scheme 1. Using other aldehydes, Prato and co-workers

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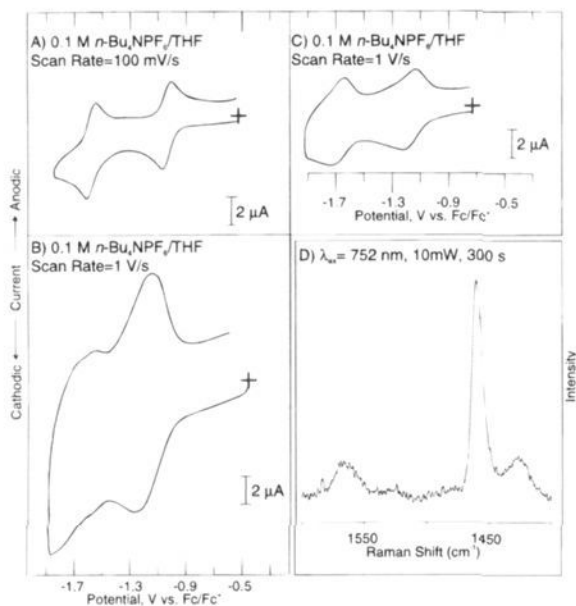(2) (a) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437. (b) Bain, C. D.; Whitesides, G. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 506.
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Scheme 1

have demonstrated the utility of this condensation reaction for the formation of pyrrolidine−fullerene adducts where the pyrrolidine functionality forms at a 6:6 ring juncture of C_{60}.[8] In a typical experiment, C_{60} (72.0 mg, 0.1 mmol), sarcosine (8.9 mg, 0.1 mmol), and 2-(4-mercaptobutyl)benzaldehyde (19.4 mg, 0.1 mmol) were dissolved in 300 mL of toluene and refluxed for 24 h under an N_2 atmosphere. The solvent then was removed, and the residue was chromatographed on silica gel with 1:1 benzene/hexane as an eluent. The first brown band was collected, and subsequent vacuum evaporation of the solvent yielded **1** as a microcrystalline amber solid in 55% yield. Compound **1** has been characterized by high-resolution FAB mass spectrometry (M^+ calcd, 942.132; measured, 942.115), ^{1}H NMR spectroscopy,[9] UV−vis spectroscopy,[9] and cyclic voltammetry. The cyclic voltammetry of **1** in THF/0.1 M n-Bu₄-NPF₆ in the potential window between −0.50 and −1.90 V exhibits two electrochemically reversible, one electron reduction waves with $E_{1/2} = -1.03$ and −1.56 V (vs Fc/Fc⁺), respectively, Figure 1A.[10] These electron transfer processes are presumably fullerene centered. The first and second reduction potentials for **1** are shifted −130 and −120 mV (± 10 mV), respectively, from the first and second reduction potentials of C_{60}. Such shifts are diagnostic of chemical modification of the fullerene and are a consequence of the disruption of the extended fullerene π network upon its chemical modification.

Compound **1** spontaneously self-assembles into monolayer films on Au(111)/mica substrates. In a typical experiment, an Au(111)/mica substrate is soaked in a 1 mM benzene solution of **1** for 36 h under an N_2 atmosphere with subsequent rinsing with copious amounts of benzene. Cyclic voltammetry of an Au(111)/mica substrate modified with **1** exhibits an adsorbate molecule coverage-dependent response, Figure 1B,C. The cyclic voltammetry for a film prepared in the aforementioned manner exhibits a nonideal response and shows one wave at $E_{1/2} = -1.21$ V and a second smaller wave at $E_{1/2} = -1.58$ V, respectively, Figure 1B. These are assigned to the first and second one electron reduction/oxidation processes for the Au−fullerene thiolate species formed from **1**. The integrated current associated with the first reduction/oxidation of the monolayer is $\sim$20 times larger than that for the second reduction/oxidation; for solution **1**, the current associated with these two processes are comparable; compare panels A and B of Figure 1.

(7) 2-(4-Mercaptobutyl)benzaldehyde was synthesized from the thioesterification of 2-[2-(4-iodobutyl)phenyl]-1,3-dioxane with subsequent deprotection of the dioxane and thioester groups; see the supplementary material.
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(9) Compound **1**: ^{1}H NMR (C_6D_6) 1.04 (t, $J = 7.7$ Hz, 1H, SH), 1.34 (m, $J_{HH} = 13.3$ Hz, 4H, $CH_2CH_2CH_2S$), 2.16 (m, $J_{HH} = 5.7$ Hz, 2H, CH_2S), 2.41, 3.14 (m, m, 1H, 1H, PhCH_2, diastereotopic), 2.52 (s, 3H, NCH_3), 3.86 and 4.46 (2d, $J = 7.2$ Hz, 2H, NCH_2C_{60}, diastereotopic), 5.22 (s, 1H, PhCHN), 6.98−7.25 and 8.25 (m, 4H, Ph); UV−vis (hexanes) $\lambda_{max} = 256$, 328, 404, 430, 482, 534, 598, 622, 702 nm. Compare with UV−vis for C_{60} (hexanes): $\lambda_{max} = 254$, 330, 404, 518, 588, 596, 608, 620, 698 nm.
(10) A third reversible electrochemical reduction/oxidation is accessible for **1** in THF/0.1 M Bu₄NPF₆ ($E_{1/2} = -2.13$, vs Fc/Fc⁺).
(11) Surface coverage was determined by integrating the current associated with reduction of surface-confined **1**. One electron reduction processes and complete electrochemical accessibility for **1** are assumed.

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Figure 1. The cyclic voltammetry for (A) **1** at a glassy carbon disk electrode (7 mm²), first scan; (B) a SAM of **1** on Au(111)/mica (0.20 cm²), first scan; and (C) **1** adsorbed on Au(111)/mica in submonolayer coverages ($\Gamma = 1.2 \times 10^{-11}$ mol/cm² assuming complete electrochemical accessibility, surface coverage = 0.1 monolayers), first scan. (D) A SERS spectrum of a SAM of **1** on Au(111)/mica in air.

Electrodes with submonolayer coverages of **1** exhibit more ideal electrochemical responses than SAMs of **1**. For example, a film prepared by soaking an Au(111)/mica electrode in a 1 mM solution of **1** for 10 min exhibited two distinct waves at −1.20 and −1.69 V, respectively, with comparable currents associated with both oxidation/reduction processes, Figure 1C. These waves are persistent and are typical of a surface-confined redox-active species ($i_p \propto$ scan rate; surface coverage = 1.2×10^{-11} mol/cm²). The coverage-dependent electrochemical responses of **1** can be attributed to the relative amounts of free volume available in the two types of films. When a monolayer film based on a molecule such as **1** undergoes sequential reduction processes, only the portions of the monolayer that can incorporate charge-compensating ions will be electrochemically active; indeed, we have shown that redox processes in SAMs may be regulated by controlling the structure of a monolayer and the free volume therein.[12] In solution, when C_{60} is reduced, it may surround itself with charge-compensating cations. Reduction of a fullerene monolayer will be limited by the free volume within the film and, that for a layer of finite, but unknown, thickness, directly above the film. For a SAM of **1**, the current associated with the first reduction is substantially larger than that observed for the second reduction because the available free volume is significantly reduced upon the first reduction process; only a fraction of the sites have enough room to incorporate additional charge-compensating ions into the monolayer. Consequently, the second reduction will be accessible for only a fraction of the absorbate species. When surface coverage of **1** is reduced to ~0.1 monolayer, there is sufficient free volume in the film to incorporate charge-compensating ions to satisfy the requirements of the dianion formed upon electrochemical reduction of the film. Consequently, a more ideal response is observed for an incomplete monolayer film of **1** than for a full monolayer of **1**. Therefore, although the electrochemical response for Au(111)/mica modified with a full monolayer of **1** is not ideal, it is indicative of a densely packed, chemically homogenous monolayer. It is worth noting that for this reason the surface coverage for a SAM of **1** may not be extracted accurately from electrochemical data. Finally, although monolayers of **1** are indefinitely stable in THF solution,

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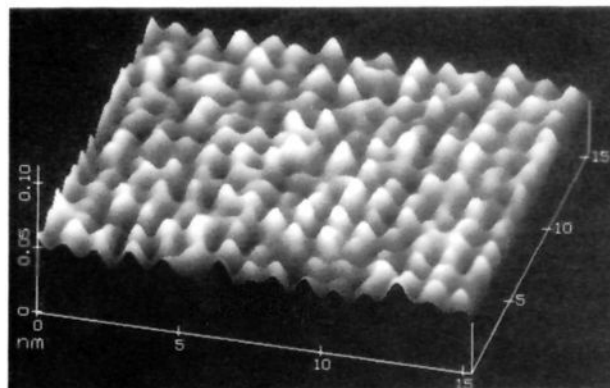
Figure 2. 15 nm × 15 nm AFM image of a SAM of **1** on Au(111)/mica with light $x-y$ spectrum filtering. The image is given in a surface view presentation with the lighter areas denoting higher regions and the darker areas representing lower regions. The height axis is in nN.

upon repeated cycling to negative potentials (−1.90 V at 1 V/s for 1 h), the electrochemical signal for **1** is lost. The chemical nature of the resulting surface is unknown.

The SERRS spectrum of an Au(111)/mica substrate modified with a SAM of **1**, Figure 1D, also is consistent with the formation of a chemically homogeneous fullerene monolayer film and exhibits characteristic fullerene bands at 1569, 1460, and 1424 cm⁻¹, Figure 1D. The most intense band at 1460 cm⁻¹ is assigned to the "pentagonal pinch" A_g vibration for surface-confined **1** and compares well with the A_g "pentagonal pinch" vibrations for other C_{60} compounds modified at the 6:6 ring juncture.[13]

Although it is not immediately apparent, the structure of **1** is suited well for self-assembly. Space-filling models of **1** generated from the computer program SYBYL (Tripos Associates, Inc., St. Louis, MO) show that the fullerene cage dominates its structure and that the aryl−alkanethiol appendage may be tucked beneath the sphere defined by its 60 fullerene carbon atoms, Scheme 1 (inset). Indeed, AFM images of Au(111)/mica modified with **1**, acquired in air in contact force mode with a Digital Instruments Nanoscope II microscope, reproducibly reveal an image with spherical features regularly spaced in a distorted hexagonal arrangement, Figure 2. Each spherical feature is assigned to a C_{60} core of **1**, and the fullerene−fullerene nearest neighbor distance of 1.09 nm ± 0.08 nm is in excellent agreement with the nearest neighbor distance for the (111) face of crystalline C_{60} (1.07 ± 0.13 nm) as determined by AFM.[6] Although the lattice is not defect free, it exhibits a distinct degree of order and extends for hundreds of square nanometers.

This study is significant for the following reasons: (1) it shows that adsorbate molecules that are dominated by the C_{60} core, either by virtue of spherical shape and/or strong intermolecular interactions, will self-assemble onto Au(111) surfaces to form ordered overlayers, the extent of which may be measured by AFM; and (2) it represents the next major step toward *rationally* organizing fullerenes into well-characterized materials via monolayer self-assembly methodology.

Supplementary Material Available: Experimental details for the preparation of 2-(4-mercaptobutyl)benzaldehyde and atomic force microscopy (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see current masthead page for ordering information.

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