

A Monolayer of C₆₀ Tethered to the Surface of an Inorganic Substrate: Assembly and Structure

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Buckminsterfullerene (C₆₀) and its three-dimensional crystalline phases are of considerable interest in both condensed matter chemistry/physics and materials research due to its unusual structure and extended π -electron system.¹ To exploit the novel electronic properties of C₆₀ to modify the macroscopic electronic/optical response of solid surfaces, we have developed a novel method to covalently tether the C₆₀ cage to a silicon oxide surface, based on our recently disclosed protocol to tether protein molecules to the surface of self-assembled monolayers (SAMs)² and the structure of the (pyridyl)₂-OsO₄-C₆₀ coordination complex, obtained by reaction of C₆₀ with OsO₄ in the presence of pyridine.³

The method entails the self-assembly of pyridyl-terminated alkylsiloxane monolayers on the surface of both quartz and molecular beam epitaxy (MBE) fabricated Ge/Si multilayer substrates (Scheme I).⁴ To this end, bromine-terminated self-assembled monolayers of the alkylsiloxane type, formed via chemisorption of (11-bromoundecanyl)trichlorosilane on the surface of quartz or Ge/Si multilayer substrates, were reacted in THF at -40 °C with the anion derived from 4-methylpyridine and lithium diisopropylamide. The resultant pyridyl-terminated SAMs were in turn reacted at room temperature with OsO₄ in toluene, washed with toluene, treated with C₆₀ in toluene at room temperature to tether the C₆₀ to the pyridyl endgroups via OsO₄, and washed with toluene. The presence of the pyridyl endgroups and subsequent formation of the (pyridyl)_n-OsO₄-C₆₀ coordination compound on the surface of the pyridyl-terminated SAM were qualitatively monitored by UV/vis absorption spectroscopy employing the quartz substrates. Comparison at each stage of the fabrication with the corresponding spectra of relevant model compounds (i.e., 4-methylpyridine, its 2:1 complex with OsO₄, and its 2:1 complex with OsO₄-C₆₀)⁵ provided support for each transformation.

(1) Fischer, J. E.; Heiney, P. A.; Smith, A. B., III. *Acc. Chem. Res.* **1992**, *25*, 112–118. Hebard, A. F. *Physics Today* **1992**, *45*, 26–32.

(2) Amador, S. M.; Pachence, J. M.; Fischetti, R.; McCauley, J. P., Jr.; Smith, A. B., III; Dutton, P. L.; Blasie, J. K. *Mater. Res. Soc. Symp. Proc.* **1989**, *177*, 393–398. Amador, S. M.; Pachence, J. M.; Fischetti, R.; McCauley, J. P., Jr.; Smith, A. B., III; Dutton, P. L.; Blasie, J. K. *Langmuir* **1993**, *9*, 812–817. **Note Added in Proof:** After submission of our manuscript a related study was reported by Mirkin et al. (Chen, K.; Caldwell, W. B.; Mirkin, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 1193–1194).

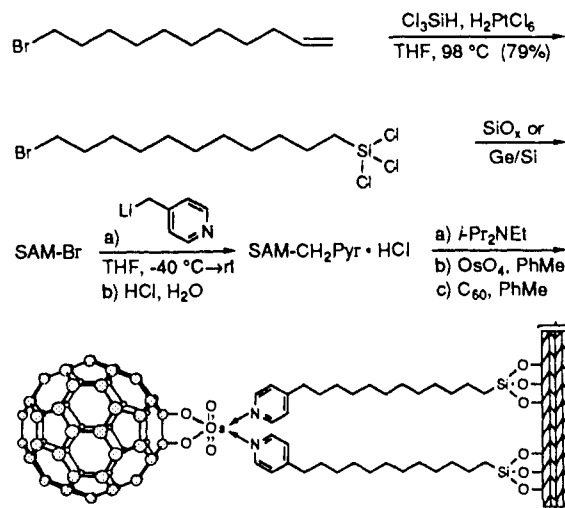
(3) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S.; Hollander, F. J. *Science* **1991**, *252*, 312–313.

(4) All new compounds gave satisfactory IR, 500-MHz ¹H NMR, and 62.5-MHz ¹³C NMR spectra as well as appropriate parent ion identification by high-resolution mass spectrometry.

(5) Conversion of the bromide-terminated self-assembled monolayer on the surface of the quartz substrates to a pyridyl-terminated self-assembled monolayer was evidenced by the appearance of a strong UV absorption maximum at ~255 nm similar to that of other pyridine and 4-substituted pyridine model compounds. The magnitude of the absorption indicated virtually 100% conversion of the bromide to pyridyl endgroups. Subsequent formation of the (pyridyl)_n-OsO₄-C₆₀ complex on the pyridyl-terminated self-assembled monolayer on the quartz substrates was evidenced by the appearance of a strong UV absorption maximum at ~319 nm similar to that of the (4-decylpyridine)₂-OsO₄-C₆₀ model compound.

(6) Blasie, J. K.; Xu, S.; Murphy, M.; Chupa, J.; McCauley, J. P., Jr.; Smith, A. B., III; Bean, J. C.; Peticolas, L. J. *Mater. Res. Soc. Symp. Proc.* **1992**, *237*, 399–409.

Scheme I



Definitive structural evidence for the presence of the pyridyl-terminated self-assembled monolayer on the SiO_x surface of the Ge/Si multilayer substrates and for the subsequent formation of a single monolayer of the (pyridyl)_n-OsO₄-C₆₀ complex at the surface of the pyridyl-terminated self-assembled monolayer was established via analysis of their meridional X-ray diffraction data $I(Q_z, Q_{xy}=0 \text{ \AA}^{-1})$, employing X-ray interferometry/holography,⁶ the resolution of the so-derived profile structures was $\approx 7 \text{ \AA}$. The profile structure of the (pyridyl)_n-OsO₄-C₆₀ complex (Figure 1b), identified via comparison with the profile structure of the pyridyl endgroup itself in the pyridyl-terminated self-assembled monolayer (Figure 1a), possesses internal structure at this resolution consisting of a distinct (pyridyl)_n-OsO₄ feature, namely,

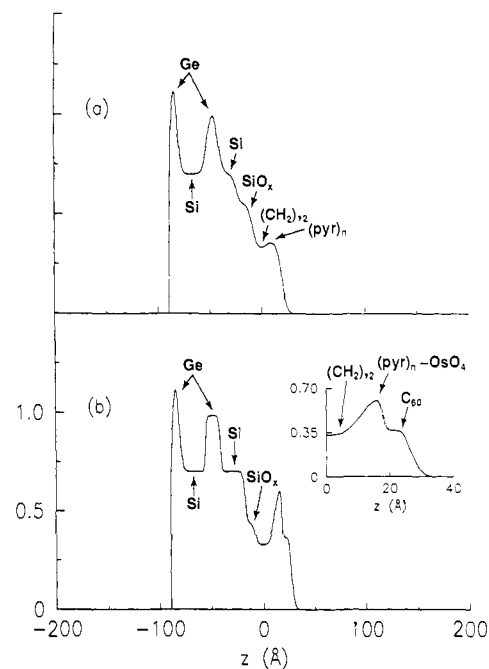


Figure 1. (a) The refined, absolute electron density model profile for the pyridyl-terminated self-assembled monolayer on a Ge/Si multilayer substrate. (b) The refined, absolute electron density model profile for the (pyridyl)_n-OsO₄-C₆₀ complex tethered to the surface of a Ge/Si multilayer substrate. These two profiles were derived via X-ray interferometry and proven unique by X-ray holography. The relevant features in the two profile structures are noted and described in the text. The inset in b is an expansion of the region containing the (pyridyl)_n-OsO₄-C₆₀ complex.

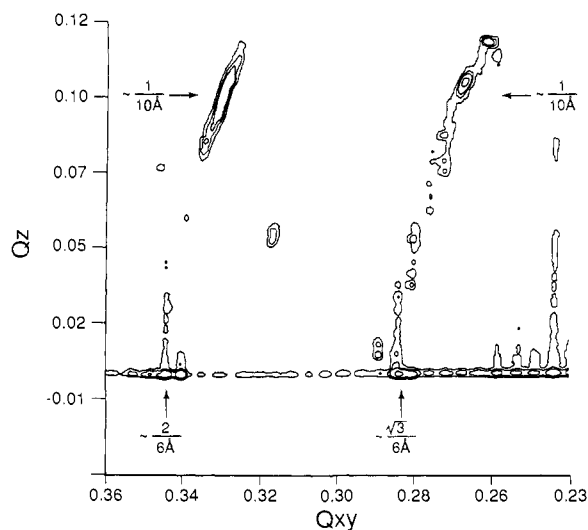


Figure 2. The in-plane/out-of-plane X-ray diffraction $I(Q_{xy}, Q_z)$ from the tethered (pyridyl) $_n$ -OsO $_4$ -C $_{60}$ complex on the surface of the Ge/Si multilayer substrate. Four of the six reflections at $Q_{xy} \approx 1/(6 \text{ \AA})$, $3^{1/2}/(6 \text{ \AA})$, and $2/(6 \text{ \AA})$ at $Q_z = 0 \text{ \AA}^{-1}$ and at $Q_z = 1/(10 \text{ \AA})$ are shown here with a small mosaic spread comparable to that of the pyridyl-terminated self-assembled monolayer. That the three "layer-line" reflections at $Q_z \approx 1/(10 \text{ \AA})$ are not centered directly above their counterparts at $Q_z \approx 0 \text{ \AA}^{-1}$ can be explained by the mosaic spread of the underlying pyridyl-terminated self-assembled monolayer coupled with a correlation length for the epitaxial C $_{60}$ overlayer of $<50 \text{ \AA}$.

an asymmetric peak of high local electron density at the surface of the pyridyl-terminated self-assembled monolayer, with a distinct plateau feature of lower local electron density on the surface corresponding to the profile structure of a single overlayer of C $_{60}$. The pronounced asymmetry in the profile structure of the (pyridyl) $_n$ -OsO $_4$ feature is most likely due to the pyridyl endgroups on the substrate side of the OsO $_4$ peak feature, based on the local electron densities of the pyridyl endgroups vs OsO $_4$ for a 2:1 complex and their positions in the profile structure (as compared to the pyridyl endgroups alone in the profile structure of the pyridyl-terminated self-assembled monolayer). While we have not specified the stoichiometry number "n" for the (pyridyl) $_n$ -OsO $_4$ -C $_{60}$ tethered monolayer complex, it is probably $n = 2$ based on coordination chemistry and the "epitaxial" nature of the C $_{60}$ overlayer relative to the pyridyl endgroup underlayer (*vide infra*).

The in-plane structures of the pyridyl-terminated self-assembled monolayers on the surface of these substrates and of the (pyridyl) $_n$ -OsO $_4$ -C $_{60}$ single monolayer complex were investigated via their "in-plane/out-of-plane" X-ray diffraction $I(Q_{xy}, Q_z)$, employing doubly-focused synchrotron radiation and a two-dimensional position-sensitive detector (Figure 2). These preliminary data suggest that the tethered C $_{60}$ monolayer occurs as a primitive, planar hexagonal lattice ($a_{C_{60}} \approx 12 \text{ \AA}$, correlation length $<50 \text{ \AA}$), epitaxial 2×2 on the underlying planar hexagonal lattice of the pyridyl-terminated self-assembled monolayer ($a_{pyr} \approx 6 \text{ \AA}$, correlation length $\approx 400 \text{ \AA}$) and centered $9 \pm 1 \text{ \AA}$ above the pyridyl endgroups (Figure 3).

In summary, we have devised a novel approach to tether the fullerene C $_{60}$ to silicon surfaces via a (pyridyl) $_n$ -OsO $_4$ -C $_{60}$ coordination complex employing a pyridyl-terminated, self-assembled monolayer chemisorbed to the substrate. The structure of the (pyridyl) $_n$ -OsO $_4$ -C $_{60}$ monolayer complex tethered to the SiO $_2$ surface of the substrate, shown schematically in Figure 3, is fully consistent with both the profile and in-plane structures determined by high-resolution X-ray diffraction as well as the three-dimensional crystal structure of the bis(pyridyl)-OsO $_4$ -C $_{60}$ complex available from X-ray crystallography.³ While the profile structure has been derived by X-ray interferometry and proven to be unique by X-ray holography, the in-plane/out-of-plane structure is simply a model consistent with the six stronger

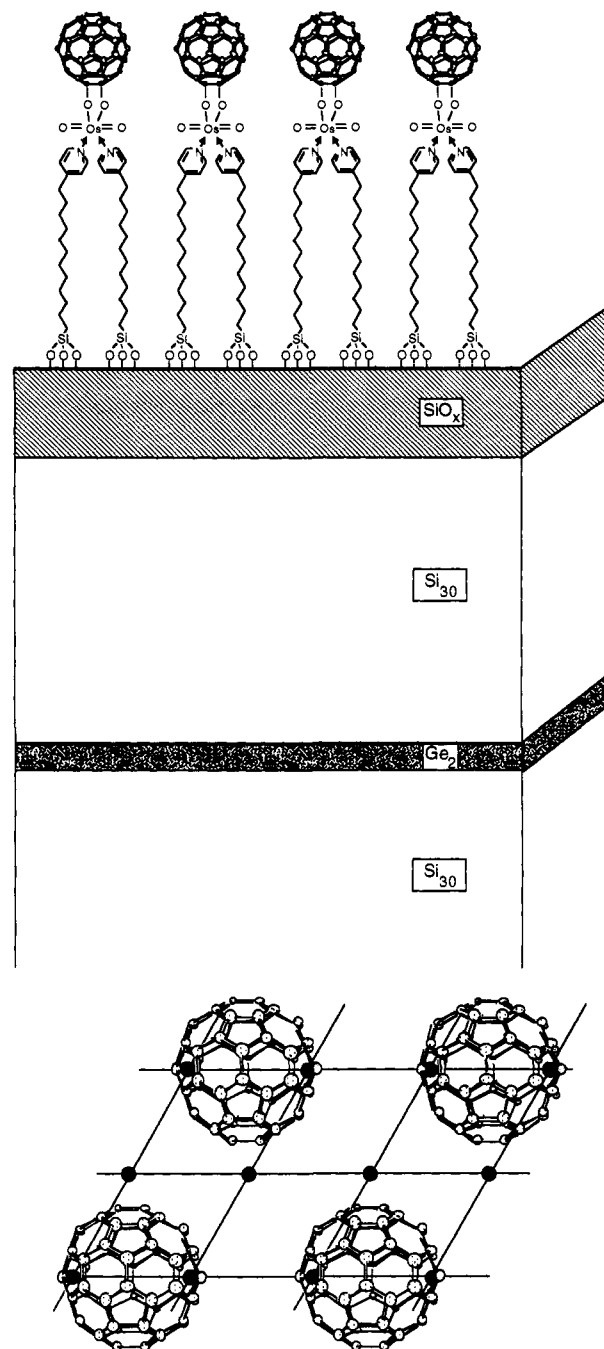


Figure 3. Schematic showing a side view and a top view of the three-dimensional structure of the tethered (pyridyl) $_n$ -OsO $_4$ -C $_{60}$ complex with the primitive, planar hexagonal C $_{60}$ monolayer ($a_{C_{60}} \approx 12 \text{ \AA}$, correlation length $<50 \text{ \AA}$), epitaxial 2×2 on the underlying pyridyl-terminated self-assembled monolayer ($a_{pyr} \approx 6 \text{ \AA}$, correlation length $\approx 400 \text{ \AA}$) and lying $\approx 10 \text{ \AA}$ above it. The solid circles in the top view represent the pyridyl endgroups. This 3-D structure is fully consistent with both the electron density profile structure and the in-plane/out-of-plane X-ray diffraction for the tethered complex.

reflections in the relevant $I(Q_{xy}, Q_z)$ diffraction data. A full report of this work will appear in due course.

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Supplementary Material Available: Comment on the analysis of the available X-ray diffraction data for the tethered (pyridyl) $_n$ -OsO $_4$ -C $_{60}$ monolayer on the surface of a Ge/Si multilayer substrate (3 pages). Ordering information is given on any current masthead page.