adsorbate leads to formation of $C_5D_5NH^+$ ions which can be nearly as intense as the scattered $C_5H_5NH^+$ ions. Furthermore, primary ion fluxes $>10^{13}$ cm^{-2} lead to observable changes in the scattered ion signal; this ion flux is similar to that which defines the boundary between the static and dynamic regimes of secondary ion mass spectrometry.[25]

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Fullerene Self-Assembly onto $(MeO)_3Si(CH_2)_3NH_2$-Modified Oxide Surfaces

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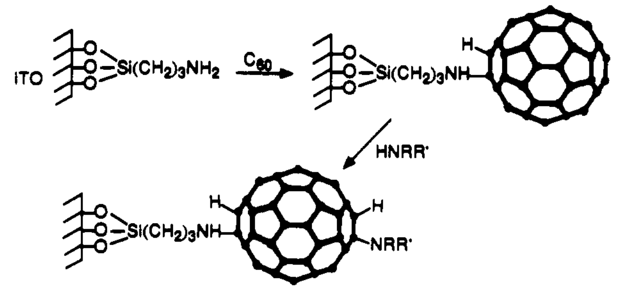
Physisorbed, multilayer fullerene films formed via Langmuir-Blodgett (LB) techniques,[1] solution evaporation,[2] and thermal evaporation of solid-phase fullerenes[3] have exhibited interesting mechanical, electrical, electrochemical, and optical properties. Developing synthetic methodology for the self-assembly of fullerenes into organized, *covalently bound* two-dimensional structures is the first step toward developing robust, rationally designed mono- and multilayered structures from fullerenes. Herein, we report the first self-assembled monolayer (SAM) of C_{60}, its spectroscopic and electrochemical characterization, and initial chemistry with respect to its further modification, Scheme I.[4] The latter demonstration is significant since it illustrates the potential for growing covalently bound three-dimensional structures from fullerenes in a stepwise fashion via the self-assembly process.[5]

Scheme I. Synthetic Scheme for the Modification of Oxide Surfaces with C_{60}[a]



[a] SAMs of C_{60} may be further modified with amine reagents, Table I.

Table I. Contact Angles for H_2O

surface	contact angle, deg
base-treated ITO	20
ITO treated with $(MeO)_3Si(CH_2)_3NH_2$	46
SAMs of C_{60}	72
$HN(CH_3)CH_2CH_3$	63
$H_2N(CH_2)_2CH_3$	60
$HN(CH_3)CH_2CH_2OH$	42
p-ferrocenylaniline	67

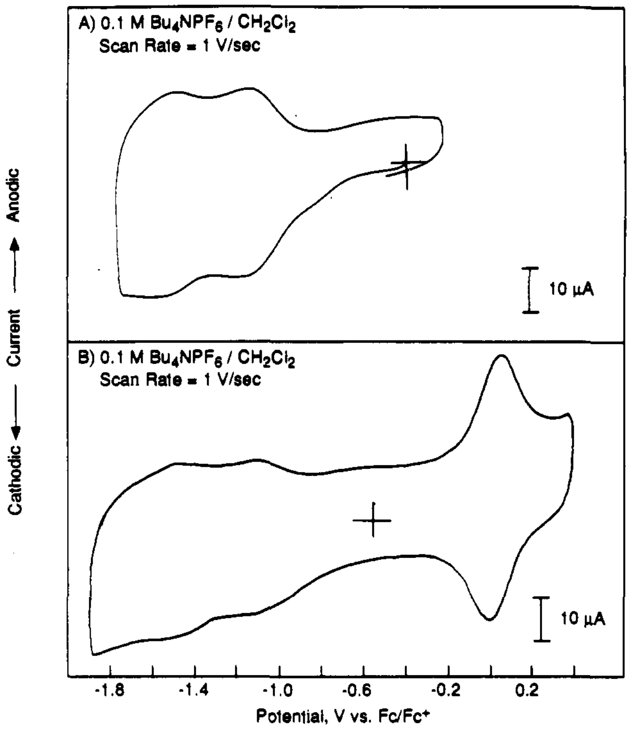


Figure 1. (A) Cyclic voltammetry of a SAM of C_{60} on $(MeO)_3Si(CH_2)_3NH_2$-treated ITO (0.5 cm^2) in CH_2Cl_2/0.1 M Bu_4NPF_6. (B) Cyclic voltammetry of a SAM of C_{60} on $(MeO)_3Si(CH_2)_3NH_2$-treated ITO (0.8 cm^2) after refluxing in a 5 mM benzene solution of *p*-ferrocenylaniline for 2 days.

Two approaches may be taken towards fullerene self-assembly onto surfaces. Either a fullerene can be modified in solution with functionalities that allow for self-assembly, or a surface may be chemically modified with a reagent that undergoes a bond-forming reaction with a fullerene in solution. Herein, we report success via the latter approach. Others have shown that primary and secondary amines undergo N-H addition reactions across the C=C bonds in C_{60} which fuse two six-membered rings.[6] Accordingly, the immobilization of $(MeO)_3Si(CH_2)_3NH_2$ onto oxide substrates[7] results in surfaces that undergo spontaneous reactions

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with C_{60} to form monolayer films of the fullerene, Scheme I.

In a typical experiment, a base-treated indium-tin-oxide (ITO) electrode is soaked in a 0.25 M benzene solution of $(MeO)_3Si(CH_2)_3NH_2$ under reflux conditions for 8–12 h. The electrode is then rinsed with benzene, dichloromethane, and acetonitrile; and the decreased hydrophilicity of the resulting surface is verified with contact angle measurements $(\Theta = 46^\circ)$, Table I.[8] The $(MeO)_3Si(CH_2)_3NH_2$-treated electrode is then soaked in a 1 mM benzene solution of C_{60} for 1–2 days under reflux conditions. The electrode is rinsed and sonicated in benzene for 2 min to remove residual physisorbed C_{60}. The relative hydrophobicity of the resulting C_{60}-modified surface is confirmed via contact angle measurements $(\Theta = 72^\circ)$, Table I. Quartz and glass may be modified with C_{60} in a similar manner.

The transmission UV–vis spectrum of quartz first treated with $(MeO)_3Si(CH_2)_3NH_2$ and then with C_{60} is similar to the spectrum of C_{60} cast on quartz and shows three bands with λ_{max}'s at 226, 256, and 286 nm. The cyclic voltammetry of a $(MeO)_3Si(CH_2)_3NH_2$-treated ITO electrode modified with C_{60} yields the electrochemical response shown in Figure 1A.[9] The $E_{1/2}$ values for the reductive waves (−1.14 and −1.51 vs Fc/Fc^+) observed in Figure 1A are substantially more negative than the $E_{1/2}$ value for the first two reductions for unmodified C_{60} (−0.98 and −1.38 V).[10] These shifts of −0.16 and −0.13 V, respectively, are consistent with a bond-forming reaction between the self-assembled C_{60} molecules and the underneath amine layer. Similar shifts in potential, although substantially larger in magnitude (−0.50 and −0.54 V, respectively), have been reported for a hexasubstituted amine (morpholine) adduct in solution.[6] Although the number of surface amine units which react with each C_{60} molecule cannot be unequivocally determined, on the basis of comparison between the electrochemical data for SAMs of C_{60} and the hexaamine adduct,[6] we suspect that no more than two surface amine units react per C_{60} molecule. The resolution of the waves in Figure 1A reflects the homogeneity of the surface fullerene species and suggests that each of the fullerenes in the SAM has a similar chemical identity, mono- and/or disubstituted adducts. Assuming that each wave in Figure 1A corresponds to a one-electron transfer, integration of the current associated with these waves is consistent with monolayer coverage ($\sim 1.7 \times 10^{-10}$ mol/cm^2). Models based on crystallographic data for C_{60}[11] predict a surface coverage of $\sim 1.9 \times 10^{-10}$ mol/cm^2 for a closed packed monolayer of C_{60}.

Significantly, SAMs of C_{60} can be further modified with a series of amine reagents; the water contact angles of the resulting films were measured and are displayed in Table I. There is excellent correlation with the type of amine reacted with SAMs of C_{60} and the expected wettability of the surface obtained from such a reaction. For example, ethylmethylamine yields a surface with a contact angle of 63° while 2-(methylamino)ethanol yields a relatively hydrophilic surface $(\Theta = 42^\circ)$ because of its pendant alcohol functionality. *p*-Ferrocenylaniline yields a hydrophobic surface $(\Theta = 67^\circ)$ with redox activity associated with the pendant ferrocene, Figure 1B. The cyclic voltammetry of a SAM of C_{60} on amine-treated ITO after reaction with *p*-ferrocenylaniline shows reductive waves ($E_{1/2}$ = −1.16 and −1.56 V vs Fc/Fc^+) expected for materials containing C_{60} as well as an additional wave which we assign to ferrocene oxidation ($E_{1/2}$ = 0.04 V vs Fc/Fc^+). The surface coverage of the *p*-ferrocenylaniline layer is 1.2×10^{-10} mol/cm^2 as determined by integration of the current associated with the wave assigned to ferrocene oxidation, Figure 1B. The $E_{1/2}$ for the adsorbed *p*-ferrocenylaniline is 0.10 V more positive than the $E_{1/2}$ for *p*-ferrocenylaniline in solution (−0.06 V vs Fc/Fc^+). This indicates that the NH_2 of *p*-ferrocenylaniline has reacted with C_{60}, and the shift in $E_{1/2}$ to more positive values reflects the electron-withdrawing nature of C_{60}.[12] The broadness of the waves associated with reduction of C_{60} may be attributed to the variety of possible ferrocenylaniline–C_{60} adducts formed from such a reaction. The regiochemistry of the amine addition to the surface C_{60} molecules may not be determined experimentally. The *p*-ferrocenylaniline–C_{60} bilayer films are indefinitely stable to cycling through ferrocene oxidation, but electrodes modified with these bilayer films lose electrochemical activity when held at negative potentials (−1.8 V) for extended periods of time. XPS studies before and after electrochemical cycling confirm the removal of the ferrocenylaniline and C_{60} layers from the surface.[13]

The self-assembly of C_{60} onto oxide surfaces is the first example of covalent attachment of a fullerene to a surface and represents the first step toward rationally designed, supramolecular multilayered structures consisting of alternating layers of fullerenes and other chemical reagents. Indeed, the demonstration that such films may be modified with a variety of amine reagents illustrates the potential of the self-assembly process for growing layered three-dimensional fullerene structures. We are currently probing the chemical and physical properties of these novel films and exploring the possibilities of using other fullerene building blocks to grow layered structures with desirable properties.

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[11] The model assumes a molecular diameter of 7 Å and a mean distance between molecular centers of 3 Å. See: Liu, S.; Lu, Y.; Kappes, M. M.; Ibers, J. A. *Science* **1991**, *254*, 408.

[12] Fagan, P. J.; Calabrese, J. C.; Malone, B. *Acc. Chem. Res.* **1992**, *25*, 134 and references therein.

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Crown Ether Ionophores. Construction of Neutral Carrier Ion-Selective Electrodes

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We report the synthesis of novel crown ether ionophores which contain a 1,4-bridged cubyl system as a rigid lipophilic component.[1]

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