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Interfacial Hydrogen Bonding. Self-Assembly of a Monolayer of a Fullerene−Crown Ether Derivative on Gold Surfaces Derivatized with an Ammonium-Terminated Alkanethiolate

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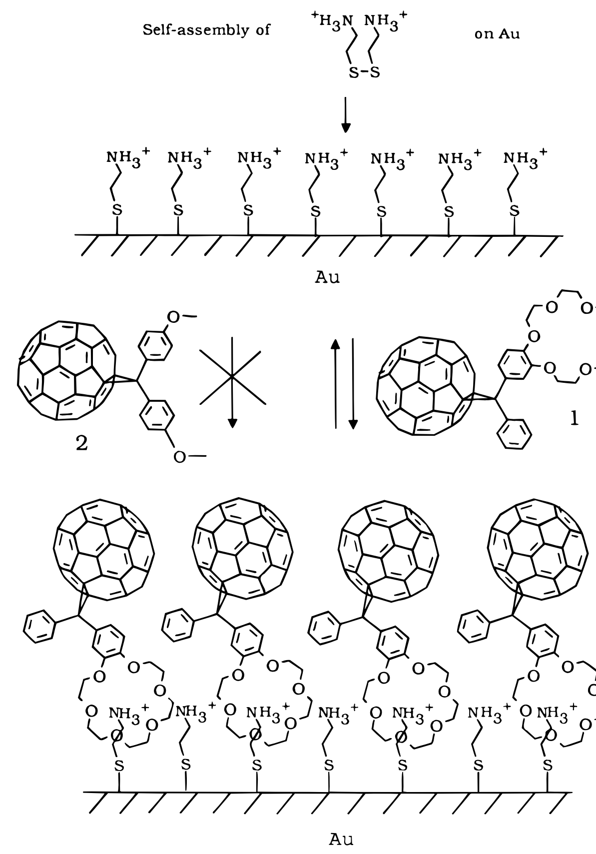
The successful formation of a fullerene monolayer was first reported by Bard et al. using a Langmuir trough.[1] Other groups have also used this technique to prepare Langmuir as well as Langmuir−Blodgett (LB) films of fullerenes[2] or fullerene amphiphile derivatives.[3] Self-assembled monolayers (SAM's) provide an alternative methodology to prepare thin film assemblies of "buckyball" structures. To our knowledge, no reports have appeared in which molecular recognition principles have been used in conjunction with preformed SAM's to induce the formation of monolayer films of C_{60} structures. Furthermore, the use of the well-known ammonium−crown ether interaction[5] as the driving force for the formation of SAM's via specific interactions at the electrode−solution interface has never been reported for any system. Herein we report the first example of a monolayer film of a crown ether fullerene derivative, compound **1** in Scheme 1,[6] exploiting these interactions. The principle, as illustrated in the scheme, involves initially the formation of a thiolated SAM terminated in ammonium groups, followed by a secondary self-assembly of the crown−fullerene monolayer driven by the interaction between the crown ethers and the ammonium groups.[5]

Scheme 1



In a typical experiment a freshly-prepared gold-bead electrode[7] was immersed overnight in a 10 mM ethanol solution of Cl^- $NH_3^+(CH_2)_2SS(CH_2)_2NH_3^+$ Cl^- (see top of Scheme 1).[8] The electrode was then washed with pure ethanol before being immersed in a 0.13 mM solution of **1** in CH_2Cl_2 also containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$). A platinum wire was used as the counter electrode and Ag/AgCl was used as the reference electrode. A BAS-100-W system was used to record all of the voltammetric responses.

Initial attempts to record the cyclic voltammetric (CV) responses of the cystamine-modified gold electrodes in these fullerene solutions resulted in poorly resolved voltammograms with large capacitive currents. In fact, the presence of the cystamine monolayer increased the capacitive currents (see supporting information) to the point where they masked the faradaic currents and thus made the analyses essentially impossible. While CV has been the technique of choice to characterize similar monolayer systems under comparable conditions, we decided to use Osteryoung Square Wave Voltammetry (OSWV) due to its inherently greater sensitivity.

A typical OSWV for compound **1** on a cystamine-modified Au electrode is shown in Figure 1a. The scan toward negative potentials was adjusted to encompass only the first reduction process (at −0.64 V vs Ag/AgCl) of this fullerene in order to avoid desorption of the thiolated monolayer (which occurs at −0.93 V vs sodium saturated calomel electrode in 0.5 M aqueous KOH). After recording the OSWV several times in order to obtain an accurate value of the peak current, the electrode was removed from the solution and immersed in aqueous 0.5 M KOH, and the potential was scanned to −1.1 V to reductively desorb the cystamine monolayer. Integration of the irreversible reduction wave yields a cystamine surface coverage of 2.8×10^{-10} mol/cm^2, a value which represents ~35% of the maximum coverage expected for a perfectly

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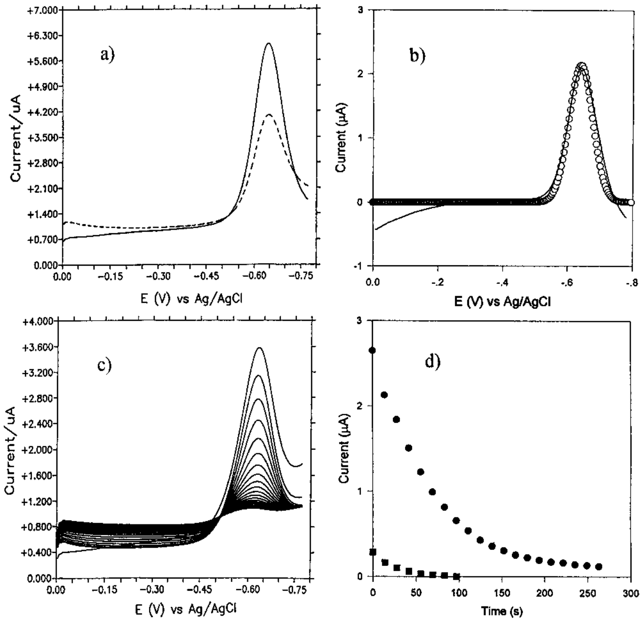

Figure 1. (a) OSWV for a 0.13 mM solution of compound **1** in CH_2Cl_2 in the presence of a $-S(CH_2)_2NH_3^+$ monolayer on the gold surface (continuous line) and after removal of the monolayer (discontinuous line). Note the decrease in current upon monolayer removal, which was reproduced several times using different electrodes and solutions. (b) Difference OSWV obtained by subtraction of the two OSWV's in Figure 1a. The circles were calculated by digital simulation. (c) Successive OSWV responses obtained with a cystamine-modified electrode in CH_2Cl_2/0.1 M $TBAPF_6$. The electrode had been previously immersed in a 0.13 mM solution of **1** in CH_2Cl_2/0.1 M $TBAPF_6$. (d) Time dependence of the observed peak current in the experiment of Figure 1c (circles). Time dependence observed when the same experiment was performed with C_{60} (squares) under identical conditions.

packed monolayer. The electrode was then rinsed with ethanol and immersed again in the same fullerene solution and the OSWV re-recorded. The OSWV response on the bare gold electrode always exhibited lower currents, see Figure 1a, but the peak potential is the same as that observed before removal of the thiolated monolayer. The current reduction indicates that there is a surface preconcentration effect at the cystamine-modified electrode. This experiment was performed at least four times, and the reported values are averages of these separate runs.

Several control experiments were recorded using pure C_{60} (99.5% from Southern Chemical Group). The first reduction process appears at −0.55 V vs Ag/AgCl under identical conditions as those described above for **1**. In each case recorded with C_{60}, removal of the cystamine monolayer in aqueous base did not result in any change in the observed current, indicating that there is no surface concentration effect with C_{60}. Identical results were observed in two other control experiments, one with compound **2** (see Scheme 1) on a cystamine-modified gold electrode and another one with **1** on a gold electrode modified with $HS(CH_2)_3OH$. Clearly, these data confirm that the observed effect between **1** and the cystamine monolayer is the result of specific binding interactions between the NH_3^+ and the crown ether.

In order to obtain a quantitative assessment of the surface coverage of **1** at the cystamine-modified electrodes, we subtracted the OSWV response on the bare electrode from that obtained on the derivatized electrode. The faradaic currents measured on the electrode derivatized with cystamine result from the reduction of molecules of **1** confined at the electrode surface by the crown$-NH_3^+$ binding forces and from the reduction of the freely diffusing molecules. By contrast, the faradaic currents on the bare electrode result exclusively from the reduction of diffusing molecules of **1**. Therefore, the "difference" OSWV reflects only the reduction of surface-confined fullerene−crown derivatives. The OSWV response of surface-confined species can be easily simulated following the method reported by Bowden and co-workers.[9] Since the electrode surface can be independently determined,[10] fitting of the difference OSWV response to simulations (see Figure 1b) affords a convenient method to determine the surface coverage of **1**. Our measurements yielded a value of 1.4×10^{-10} mol/cm^2 (after correction for surface roughness) which is close to the experimentally determined values for compact monolayers of C_{60} or with calculated values assuming fcc packing and an area of 100 Å^2/molecule ($\sim 1.9 \times 10^{-10}$ mol/cm^2).[11]

Another experiment was designed to verify that the adsorption of **1** on the ammonium-terminated SAM's was fully reversible. For this purpose, a cystamine-modified gold electrode was first immersed for 30 s in a 0.13 mM solution of **1** in CH_2Cl_2 (also containing 0.1 M $TBAPF_6$) and then transferred to a fullerene-free CH_2Cl_2/0.1 M $TBAPF_6$ solution. The current associated with the first reduction wave of **1** decreased continuously as a function of time (see Figure 1c), effectively monitoring the gradual desorption of **1** from the electrode surface. Identical control experiments with C_{60} and with **2** on a cystamine monolayer yielded a much smaller initial wave after the transfer and a much faster loss of the fullerene voltammetric response (see Figure 1d). That was also the case for **1** on a $HS(CH_2)_3$-OH monolayer. These desorption experiments clearly showed that, under the conditions of our experiments, no covalent attachment of any of the fullerenes to the SAM-covered electrode takes place. However, **1** is much more strongly retained at the cystamine-covered electrode surface than C_{60} or **2**, thus verifying the presence of specific ammonium−crown interactions at the electrode−solution interface.

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Supporting Information Available: CV data for **1** (4 pages). See any current masthead page for ordering and Internet access instructions.

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