Self-Assembled Fullerene-Derivative Monolayers on a Gold Substrate Using Phenanthroline-Au Interactions

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Bromination of commercially available 5,6-dimethyl-1,10-phenanthroline with N-bromosuccinimide led to the formation of 5,6-bis(bromomethyl)-1,10-phenanthroline, a new compound, in 33% isolated yield. Conversion of the brominated compound to its corresponding o-quinodimethane intermediate was accomplished by reaction with tetrahexylammonium iodide. Reaction of this intermediate with C60 in refluxing toluene resulted in the formation of the final product, phenanthroyl[60]fullerene, compound 1, in a 43% isolated yield. Spontaneous self-assembly of 1,10-phenanthroline on a Au(111) surface resulted in the formation of well-ordered monolayers. Addition of 1 to these monolayers resulted in the intercalation of the phenanthroyl group directly into the stacks. Self-assembly from a solution of 1 containing small amounts of 1,10-phenanthroline resulted in the formation of a secondary layer of fullerene moieties. Since the fullerene diameter is approximately 1.0 nm and the phenanthroline-phenanthroline distances are about 0.33 nm (almost exactly 1/3), the fullerene packing is approximately commensurate with that of the phenanthrolines.

Fullerene as well as fullerene derivative monolayers have been prepared and characterized by a variety of techniques, and these were reviewed recently.1 After the large scale preparation method for fullerene films first appeared in 1990,2 reports of the formation of fullerene films via thermal evaporation and solution casting soon followed.3 The techniques of scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have been fundamental in the characterization of these films.3 Besides evaporation and casting methods, Langmuir trough techniques have also been employed to prepare monolayer films of fullerenes and of their amphiphilic derivatives.4,5 Moreover, well-ordered fullerene films have been obtained using self-assembly techniques, in which the molecules spontaneously adsorb on a variety of surfaces selected on the basis of their chemical complementarity.5 For example, thiol derivatives of C60 spontaneously adsorb on Au surfaces to yield well-ordered monolayers.3,6,7

A much less explored area in the field of self-assembly is the use of bipyridine (bpy) and pyridyl-like compounds to form monolayers on Au surfaces.6 In these reports it has been found that pyridyl nitrogens adsorb strongly on Au surfaces, in much the same way as thiol sulfurs do. For example, recent solution STM studies have shown that very well-ordered stacks of bpy monolayers can be formed on a Au(111) surface.7 Presumably, both the interaction between the pyridyl nitrogens and the gold surface as well as the lateral π–π interactions between the bpy’s contribute to the significant stability of these monolayers. Most importantly, once these well-ordered monolayers are formed, they are very robust and remain intact even after rinsing with a water–electrolyte solution.7b They are thus comparable to the thiol-based self-assembled monolayers (SAMs) which are currently being exploited in many applications.8 Particularly noteworthy in the field of pyridyl-based monolayers is the work of Abruna and co-workers.9,10 They have used pyridyl
nitrogen tethers to adsorb transition-metal complexes directly onto Au(111) and Pt(111) surfaces. Here we report the first solution STM evidence for the formation of a well-ordered 1,10-phenanthroline (phen) monolayer on a Au(111) substrate. We also report the first evidence of the incorporation of a novel phenanthrolyl[60]fullerene derivative (1) into these monolayers and suggest that the stability of the resulting layers derives from the phen−Au interactions, the phen−phen π−π interactions, and from the fullerene−fullerene interactions. The methods presented here may represent a useful alternative for the preparation of stable and well-ordered fullerene layers on gold.

The preparation of compound 1 was recently reported in a preliminary communication. Briefly, it was synthesized by reacting 5,6-bis(bromomethyl)-1,10-phenanthroline with C_{60} in refluxing toluene, in the presence of tetrahexylammonium iodide, Scheme 1.10 The reaction, which proceeds via an o-quinodimethane intermediate, resulted in a 42.8% isolated yield of 1. The precursor 5,6-bis(bromomethyl)-1,10-phenanthroline, an unreported compound, was prepared in 33% yield from 5,6-dimethyl-1,10-phenanthroline and N-bromosuccinimide (NBS) in CHCl_3 as described in more detail in ref 9.

Au(111) substrates were grown epitaxially on mica under ultrahigh vacuum (UHV) conditions and then were briefly flame-annealed before each experiment. The 23 perfect aromatic molecules stand vertically with the nitrogen atoms facing the substrate and self-assemble into polymer-like chains in which individual molecules (elongated blobs) stack with a repeat distance of 0.38 ± 0.01 nm along a chain (see Figure 1b). The image also shows that each molecule is tilted from the chain axis by 65°, leading to an intermolecular distance of 0.33 ± 0.01 nm (Figure 1b), which corresponds well to the distance between two perfectly π-stacked aromatic molecules.14 The separation between two adjacent chains (see Figure 1b) is about 1.07 ± 0.02 nm, remarkably close to the value reported for the nearest neighbor distance in crystalline C_{60}.15

By exposing the self-assembled phen monolayer to a saturated solution of 1 in THF for several minutes and then rinsing with 0.1 M NaClO_4, it was possible to intercalate 1 within the phen chains. Figure 2 shows a STM image of the phen monolayer with embedded 1(bright reconstruction was reproducibly observed at negative electrode charges.12 The STM experiments were carried out on a Pico-SPM (Molecular Imaging Co.) or on a Nanoscope III instrument (Digital Instrument Inc.). While all measurements reported herein were performed in a 0.1 M NaClO_4 solution to reduce contamination, images obtained in air were very similar. A homemade Teflon cell, which was cleaned in 70% H_2SO_4 + 30% H_2O_2, was used for the STM measurements. The STM tips were electrochemically etched Pt_{0.8}Ir_{0.2} wires which were coated with Apiezon wax. These tips give a typical leakage current of less than a few picoamperes. The STM images were obtained with a typical tunneling current of 150 pA and a bias voltage between 100 and 250 mV.

Figure 1a is an image of a phen monolayer self-assembled on Au(111) by dipping a Au(111) substrate either in a 1.0 mM phen + 0.1 M NaClO_4 solution or in a saturated phen solution in tetrahydrofuran (THF). Similar to the previously studied heterocyclic compounds adenine,13 guanine,13 2,2'-bpy, and 4,4'-bpy,7 phen molecules stand vertically with the nitrogen atoms facing the substrate and self-assemble into polymer-like chains in which individual molecules (elongated blobs) stack with a repeat distance of 0.38 ± 0.01 nm along a chain (see Figure 1b). The image also shows that each molecule is tilted from the chain axis by 65°, leading to an intermolecular distance of 0.33 ± 0.01 nm (Figure 1b), which corresponds well to the distance between two perfectly π-stacked aromatic molecules.14 The separation between two adjacent chains (see Figure 1b) is about 1.07 ± 0.02 nm, remarkably close to the value reported for the nearest neighbor distance in crystalline C_{60}.15

(10) Phenanthrolyl[60]fullerene (1): A solution of 5,6-bis(bromomethyl)-1,10-phenanthroline (8.7 mg, 0.024 mmol) and C_{60} (81.9 mg, 0.114 mmol) in 125 mL of toluene was prepared and purged with nitrogen for 15 min. Then tetrahexylammonium iodide (THAI in Scheme 1, 62.8 mg, 0.130 mmol) dissolved in 20 mL of toluene was added, and the mixture was heated to reflux and allowed to react for 16 h under a nitrogen atmosphere. The solution was then filtered and dried. The solid was washed with ethanol and redissolved in carbon disulfide to proceed with column chromatography (Silica Gel). Unreacted C_{60} was recovered via elution with toluene, whereas pure compound 1 was eluted with a 9:1 mixture of chloroform−methanol to afford a 42.8% isolated yield. ^1H NMR (400 MHz, CDCl_3) (S_2: (1,1), 295 K) δ 5.13 (s broad, 4H), 7.85 (dd, 2H), 8.86 (dd, 2H), and 9.31 (dd, 2H) ppm; measurement at 243 K: δ 4.89 (d, 2H) and 5.34 (d, 2H) ppm; UV−vis (THF) 259, 289, 304, 407, 434, 706 nm; MS (FAB) 926.78 (M^+) and 720.31(C_{60}).

dots). The apparent diameter and apparent height of an isolated fullerene derivative from the STM image are about 1.0 and 0.3 nm, respectively, which are similar to the results obtained for an isolated C₆₀.¹⁶ Noticeably important from Figure 2 is that no fullerene derivative molecule is located between the phen chains, which suggests that each one of them is intercalated into the chains (see Figure 3). This phenomenon is energetically favorable since it allows the phen groups of 1 to participate in the π-stacking interactions of the phen monolayer. We have varied the exposition time of the phen monolayer to the fullerene derivative solution from several minutes to 5 h and observed no large increase in the coverage of the C₆₀ derivative. This suggests that the few molecules of 1 that

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monolayer lattice until saturation is reached.
To increase the coverage of $1$, we have dipped the Au
substrate into a saturated solution of $1$ in THF ($\sim 10^{-2}$
mM) that also contained $2$ mM phen. Figure 4 is an STM
image of this sample, which shows a much higher coverage
of $1$ than that evident in Figure 2. The tendency of the
fullerene derivative molecules to stack is also visible as
outlined in the figure. Along a chain, the center-to-center
distance between two adjacent C$_{60}$ derivative molecules
is about $1.1$ nm, which corresponds roughly to the distance
of three stacked phen molecules (see Figure 3). Signifi-
cantly, in the absence of phen, pure compound $1$ forms a
disordered layer on Au(111) from a saturated THF
solution, and it is not stable enough to resist the scanning
tip. Continuously scanning over a small area of this layer
triggers a diminution in the coverage of $1$ as the fullerene
derivative molecules are swept away by the tip. Zooming
out to a larger area clearly shows a window created by the
scanning tip in the C$_{60}$ derivative monolayer. This
observation supports the suggestion that the $\pi-\pi$
interaction between phen and $1$ stabilizes the adsorption of
the latter onto the Au surface via $\pi$-stacking. Conditions
to improve the level of coverage of the Au surface with $1$
are currently under investigation.

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