

Effect of underlying coronene and perylene adlayers for [60]fullerene molecular assembly

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Supramolecularly assembled layers of C₆₀ on coronene- and perylene-modified Au(111) surfaces were investigated and the structure of the C₆₀ adlayer was found to be strongly influenced by the underlying organic layers, suggesting that the latter underlying organic adlayers play an important role in the process of formation of the C₆₀ molecular adlayer.

Recently, supramolecular assemblies on metal surfaces are being explored to control surface properties.¹ To fabricate high quality thin films with superlattices, the two- or three-dimensional construction of such films by epitaxial growth is important in pattern formation at the nano-scale.² Especially, fullerenes are considered to be suitable building blocks for three-dimensional molecular architectures because of their strong π -electron accepting ability.³ We succeeded in forming a 1:1 supramolecular assembly consisting of C₆₀ or open-cage C₆₀ derivatives and zinc octaethylporphyrin (ZnOEP) on the Au(111) surface.^{4,5} Such a supramolecular assembly produced through donor–accepter interaction would be useful for the design and organization of functional organic molecules. As described in our previous papers, coronene, which is an electron donating molecule, forms a highly ordered array with (4 × 4) symmetry on Au(111), which was characterized by scanning tunneling microscopy (STM)⁶ and low energy electron diffraction (LEED).^{6b} The adlayer structure of C₆₀ on such a coronene-modified Au surface is expected to be controlled by donor–accepter interaction in supramolecular assembly systems.

In this report, we propose a simple method for the preparation of epitaxial thin films of fullerene C₆₀ adlayers on coronene- and perylene-modified Au(111) surfaces for the application to nano-patterning. The C₆₀ arrays formed on coronene- and perylene-adlayers on Au(111) revealed several interesting molecular assemblies.

Coronene, perylene and C₆₀ were purchased from Aldrich and used without further purification. Benzene was obtained from Kanto Chemical Co. (Spectroscopy Grade). Au(111) single-crystal electrodes were prepared by the Clavilier method,⁷ and they were annealed in hydrogen flame and quenched into ultrapure water (Milli-Q SP-TOC; ≥ 18.2 M Ω cm) saturated with hydrogen before use.⁶ The C₆₀ adlayers were formed by immersing the Au(111) electrode in to a benzene solution containing either 10 μ M coronene or 100 μ M perylene for 10–60 s, followed by immersing it into a benzene solution containing *ca.* 10 μ M C₆₀ for 10–60 s. The C₆₀/coronene- or C₆₀/perylene-adsorbed Au(111) thus obtained was then rinsed with ultrapure water and transferred into an

electrochemical STM cell filled with 0.1 M HClO₄ (Cica–Merck, ultrapure grade). Electrochemical STM measurements were performed in 0.1 M HClO₄ by using Nanoscope E (Digital Instruments, Santa Barbara, CA) with a tungsten tip etched in 1 M KOH. To minimize residual faradaic currents, the tips were coated with nail polish. All potential values are referred to the reversible hydrogen electrode (RHE).

Fig. 1 shows typical high-resolution STM images of a coronene and perylene adlayers on Au(111) acquired in 0.1 M HClO₄. As shown in Fig. 1(a), each coronene molecule is clearly seen as a hexagon consisting of small spots. The intermolecular spacing along the <110> direction was measured to be 1.17 ± 0.03 nm, which corresponds to four times the Au lattice constant (4×0.289 nm). The molecular rows consist of bright spots and cross each other at an angle of either 60° or 120° within an experimental error of $\pm 3^\circ$. A precise comparison between this image and that of the underlying Au(111)–(1 × 1) lattice revealed that the molecular rows are in parallel with the atomic directions of Au(111). As described in our previous papers, the (4 × 4) symmetry was also confirmed by *ex situ* LEED measurement in ultrahigh vacuum (UHV).^{6b} Perylene, which consists of five benzene rings, was also investigated on the Au(111)–(1 × 1) surface in 0.1 M HClO₄ by means of *in situ* STM. Fig. 1(b) shows a typical high-resolution STM image of a perylene adlayer adsorbed on the Au(111)–(1 × 1) surface acquired at 0.8 V vs. RHE in 0.1 M HClO₄. Individual perylene molecules are clearly seen to be butterfly-shaped on the Au(111)–(1 × 1) surface. From a cross-sectional profile, the lengths of long and short axes of one bright spot were found to

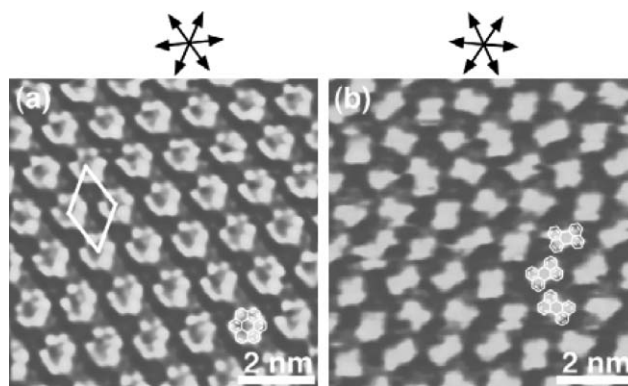


Fig. 1 Typical high-resolution STM images (8×8 nm²) of (a) coronene-adlayer and (b) perylene-adlayer on Au(111)–(1 × 1) in 0.1 M HClO₄ acquired at (a) 0.75 V and (b) 0.8 V vs. RHE. Tip potentials and tunneling current were 0.35 V and (a) 28.6 nA and (b) 23.6 nA, respectively. The sets of three arrows indicate atomic directions of Au.

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measure *ca.* 0.95 and 0.6 nm, respectively, which are expectable values for perylene molecule. It was found that the molecular rows are aligned along the close-packed directions of Au substrate. The intermolecular distances along the $\langle 110 \rangle$ direction was 1.18 ± 0.03 nm, which corresponds to four times the Au lattice constant. Without taking into account the micro-orientation of each perylene molecule, the adlayer structure of perylene roughly fits a (4×4) symmetry. The perylene adlayer on the Au(111) surface is consistent with that formed in UHV.⁸ The (4×4) symmetry was dominant for the perylene adlayer on the Au(111) surface, although another adlayer structure with the molecular row aligned in the $\sqrt{3}$ direction was also observed on atomically-flat terraces.

After confirming the adlayer structures of coronene and perylene formed on Au(111), we immersed either coronene- or perylene-modified Au(111) substrates in to a C₆₀ benzene solution for 10–60 s. Fig. 2 shows typical STM images of a C₆₀ adlayer formed on the well-defined (4×4) coronene adlayer on an Au(111) surface in 0.1 M HClO₄. It is well-known that the epitaxial film of C₆₀ on Au(111) forms hexagonally close-packed ($2\sqrt{3} \times 2\sqrt{3}$)R30° and (38×38) structures, both in UHV⁹ and in solution.^{10,11} The STM image shown in Fig. 2(a) is totally different from that of C₆₀ directly attached to the Au(111) surface. The honeycomb-like structure was found in the entire scanned area. The result suggests that C₆₀ adlayer was not attached directly on Au(111), and that the coronene adlayer was not replaced by C₆₀. When the coverage was low, both coronene and C₆₀ layers were observed. A high-resolution STM image of the C₆₀ honeycomb array is shown in Fig. 2(b). The honeycomb array is assumed to be composed of multiple sets of two C₆₀ spots. The intermolecular distance between nearest neighbor C₆₀ molecules was measured to be 1.1 nm, which is slightly greater than that of a C₆₀ adlayer directly

attached to the surface of Au(111),^{9–11} whereas the distance between nearest neighbor cavities (dark areas) consisting of C₆₀ molecules was *ca.* 1.75 nm.

The C₆₀ adlayer on the perylene-modified Au(111) surface was prepared in the same manner. Fig. 2(c) shows a typical large-scale STM image of C₆₀ arrays formed on the perylene-modified Au(111) surface. Clearly, the STM image of C₆₀ arrays is more complicated, *i.e.*, a *ladder-like* structure consisting alternately of bright and dark rows is seen in this STM image. The terraces were entirely covered with C₆₀ molecules. They also adsorbed near the step edges. A close-up view of the *ladder* part is shown in the high-resolution STM image in Fig. 2(d). Each *ladder* part was composed of either four or five C₆₀ molecules with an intermolecular distance of *ca.* 1.3 nm, which is greater than that in the C₆₀ honeycomb array formed on the coronene-modified Au(111) surface. As indicated by the white arrow shown in Fig. 2(d), the C₆₀ molecular rows aligned along this arrow are shifted to the left or to the right at every fifth or sixth molecule of C₆₀. No structural change in the C₆₀ adlayer was observed on either coronene- or perylene-modified Au(111) surfaces in the potential range between 0.95 and 0.1 V vs. RHE. However, the C₆₀ adlayer on the perylene-modified Au(111) surface was found to be disordered when scanning was performed at a tunneling current higher than 1 nA or at a low bias voltage, whereas the C₆₀ adlayer on the coronene-modified Au(111) surface was very stable at high tunneling currents. A similar phenomenon was observed with the 1:1 supramolecularly assembled layer consisting of C₆₀ or open-cage C₆₀ derivative and highly ordered ZnOEP arrays.^{4,5} This result indicates that the interaction between C₆₀ and perylene adlayers is weaker than that between C₆₀ and coronene adlayers. Thus, the C₆₀ molecular assemblies were clearly different from C₆₀ on coronene-modified Au(111) and that on perylene-modified Au(111) surfaces. The dependence of C₆₀ molecular assembly on the underlying organic layer might be attributable to the difference in molecular interaction between C₆₀ and underlying coronene on one hand and that between C₆₀ and perylene on the other. We found in our previous study on several organic molecules adsorbed on iodine-modified Au(111), that the iodine adlayer allowed the adsorbed molecules to diffuse on the surface, resulting in the formation of highly ordered arrays.¹² Although C₆₀ molecules do not form a highly ordered array on an iodine-covered Au(111) surface because of their high mobility,^{10a} the insertion of a coronene or perylene adlayer as a buffered layer is one of promising methods for controlling the interaction between fullerene and Au substrate, *i.e.*, the relatively weak interaction with the underlying organic layer is a key factor in controlling the molecular assembly of C₆₀. We investigated structural effects of fullerenes such as C₇₀, C₆₀–C₆₀ (C₁₂₀) dimer, and C₆₀–C₇₀ (C₁₃₀) cross-dimer, and details will be described in a separate paper.¹³

In conclusion, by immersing an Au(111) substrate successively into a benzene solution containing either coronene or perylene and one containing C₆₀, unique molecular assemblies of C₆₀ were obtained as a result of the formation of supramolecular assemblies of C₆₀ molecules on either coronene- or perylene-modified Au surfaces.

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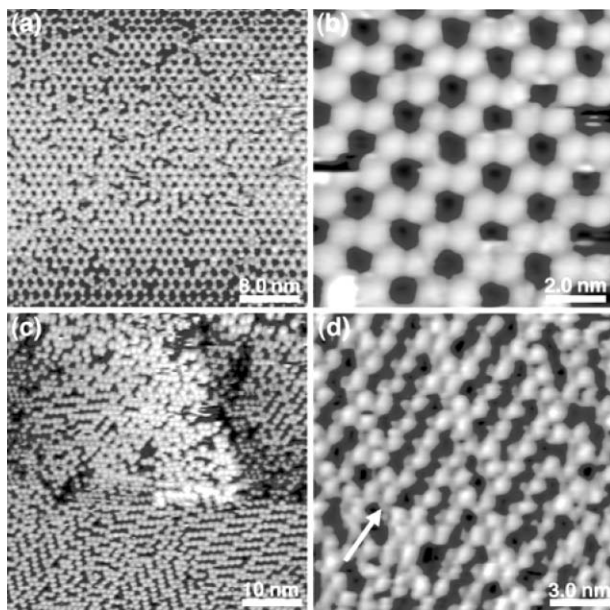


Fig. 2 Typical large-scale and high-resolution STM images of C₆₀ arrays on (a and b) coronene- and (c and d) perylene-modified on Au(111) in 0.1 M HClO₄ acquired at 0.8 V for (a and b) and 0.84 V for (c and d) vs. RHE. Tip potentials and tunneling currents were (a) 0.37 V and 1.2 nA, (b) 0.37 V and 0.35 nA, (c) 0.42 V and 0.73 nA, (d) 0.42 V and 0.6 nA, respectively.

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