Fullerenes in Calixarenes

Configurations of a Calix[8]arene and a C_{60}/Calix[8]arene Complex on a Au(111) Surface**

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Calixarenes and fullerenes have novel properties that make them ideal materials for nanoscale electronic devices.[1–4] If fullerenes can be placed within a calixarene to form an ordered array, it could be possible to operate them and fabricate nanoscale circuits. As an essential prerequisite, the configurations of calixarenes and fullerenes included within calixarene units at a solid surface must be understood to construct the nanoscalar architecture. Calixarenes have a highly flexible molecular conformation, which is important in various chemical reactions and host–guest chemistry.[5,6] To understand the variety of molecular conformations that exist, resolution at the atomic or submolecular level is important, and is a challenging research activity in calixarene studies.

Herein, we report the results of the construction and investigation of a calix[8]arene derivative, OBOCMC8 ($C_{104}H_{128}O_{24}$),[7] and the inclusion of C_{60} in OBOCMC8 (C_{60}/OBOCMC8). Scheme 1a illustrates the chemical insertion of the buckyball into the calix structure,[8,9] and the structures of the calixarene and the inclusion complex are shown in Scheme 1b and c, respectively. Well-ordered arrays of OBOCMC8 and C_{60}/OBOCMC8 can be constructed on a Au(111) surface, and are clearly observed by scanning tunneling microscopy (STM). The results directly demonstrate a stable conformation of OBOCMC8 and the possibility of C_{60} inclusion.

The electrochemical behavior of the Au(111) surface in a solution containing OBOCMC8 and C_{60}/OBOCMC8 was investigated by cyclic voltammetry. Cyclic voltammograms (CVs) were recorded in 0.1 M $HClO_4$ using the so-called hanging meniscus method. After recording the standard CV of a bare Au(111) surface, a small amount of OBOCMC8 solution was added into the electrochemical cell. As a result, the oxidation peak, which is found at +1.3 V for Au(111)

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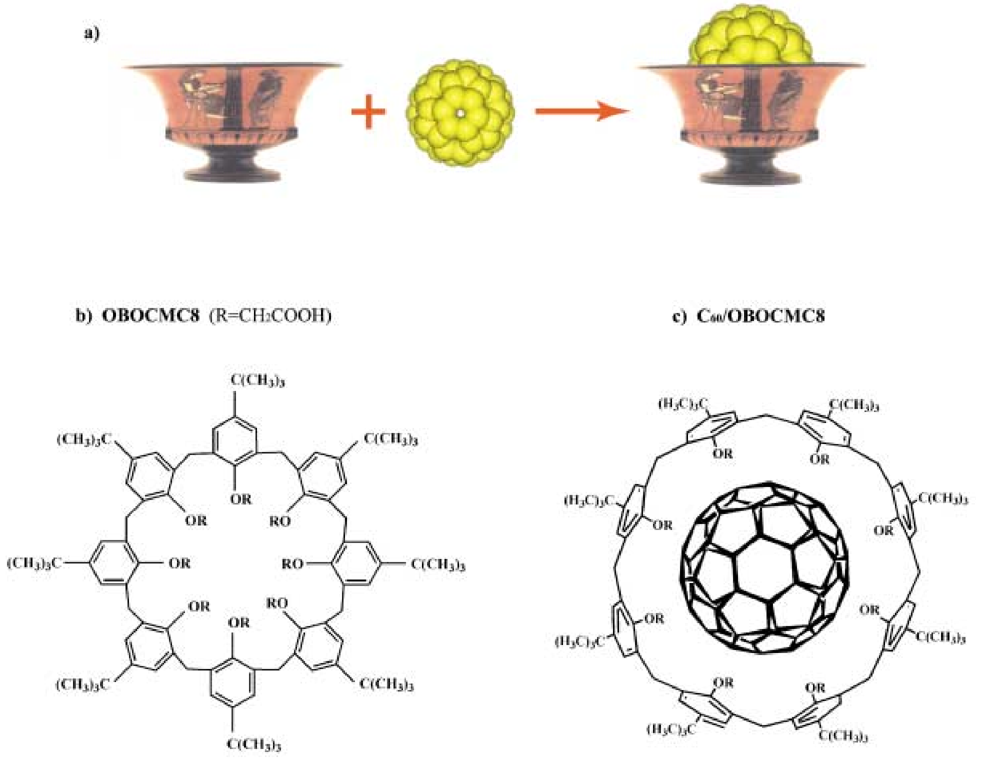

Scheme 1. a) Schematic representation of the formation of the C_{60}/OBOCMC8 complex; b,c) molecular structures of OBOCMC8 and C_{60}/OBOCMC8, respectively.

(against a reversible hydrogen electrode (RHE)), is shifted to a more positive value. It is suggested that OBOCMC8 is adsorbed onto the Au(111) surface, which suppresses surface oxidation. No additional peaks are observed in the double-layer region, which suggests that no phase transition occurs. A similar result is obtained in the solution containing C_{60}/OBOCMC8. The CVs of Au(111) in different solutions are shown in the Supporting Information.

After achieving the atomic resolution of the Au(111) substrate, a small amount of saturated OBOCMC8 solution (in 0.1 M $HClO_4$) was added in an STM cell; the electrode potential of Au(111) was held at 0.6 V. Figure 1 a shows a typical large-scale STM image (20 nm × 20 nm) acquired for an OBOCMC8 adlayer with a bias voltage of −100–−250 mV and a set-point current of 500–1000 pA. A highly ordered OBOCMC8 array extends over the flat terrace of the Au(111) surface. The important features in the image are the well-ordered dark depressions. The structural details are revealed by a higher resolution STM image (Figure 1 b), which shows that the array consists of regular "calices". Each "calix", with an associated dark depression, can be clearly observed in the image. The chemical structure of OBOCMC8 suggests that it may be adsorbed on Au(111) through either the *tert*-butyl, carboxyl, or the phenyl groups. The carboxyl–gold interaction might be stronger than those of the phenyl and *tert*-butyl groups, as has been described elsewhere.[10,11] The distance between the centers of the dark depressions is 1.2 ± 0.1 nm along the **A** direction (equivalent to the ⟨121⟩ direction; Figure 1 b), and 1.7 ± 0.1 nm along the **B** direction. The molecular rows in the **A** and **B** directions cross each other at an angle of $95 \pm 2°$. These distances compare favorably to the size of the OBOCMC8 molecule and, therefore, each calix appearing in the STM image can be assigned as an individual OBOCMC8 molecule. The surrounding protrusion and dark depression can be attributed to the phenyl units and the molecular cavity, respectively. This feature can be more clearly seen in the height-shaded surface plot shown in Figure 1 c. Based on the above analysis, a schematic model can be constructed for the ordered array of OBOCMC8 (Figure 1 d). A rhombic unit cell is outlined in the model. The molecules are arranged in an upright orientation and form a depression in the center, which has a calix-like shape. The schematic model is consistent with the observed molecular array.

After recording the STM image at 0.6 V, the electrode potential was scanned in increments of 10 mV in both negative and positive directions. Almost identical images of the OBOCMC8 array as those shown in Figure 1 are observed in the potential region of 0 to 1.0 V, which indicates that no structural transformation occurs in this range; the molecular array with ordered calices is always seen. The molecules retain the same configuration and structural symmetry, which suggests that the molecule–substrate and intermolecular interactions play important roles in immobilizing molecular conformations.

The experimental procedure described above was also applied to investigate the array of C_{60}/OBOCMC8 on Au(111) in 0.1 M $HClO_4$. After the atomic image of the Au(111) surface was obtained, a small amount of saturated C_{60}/OBOCMC8 solution was injected directly into the STM

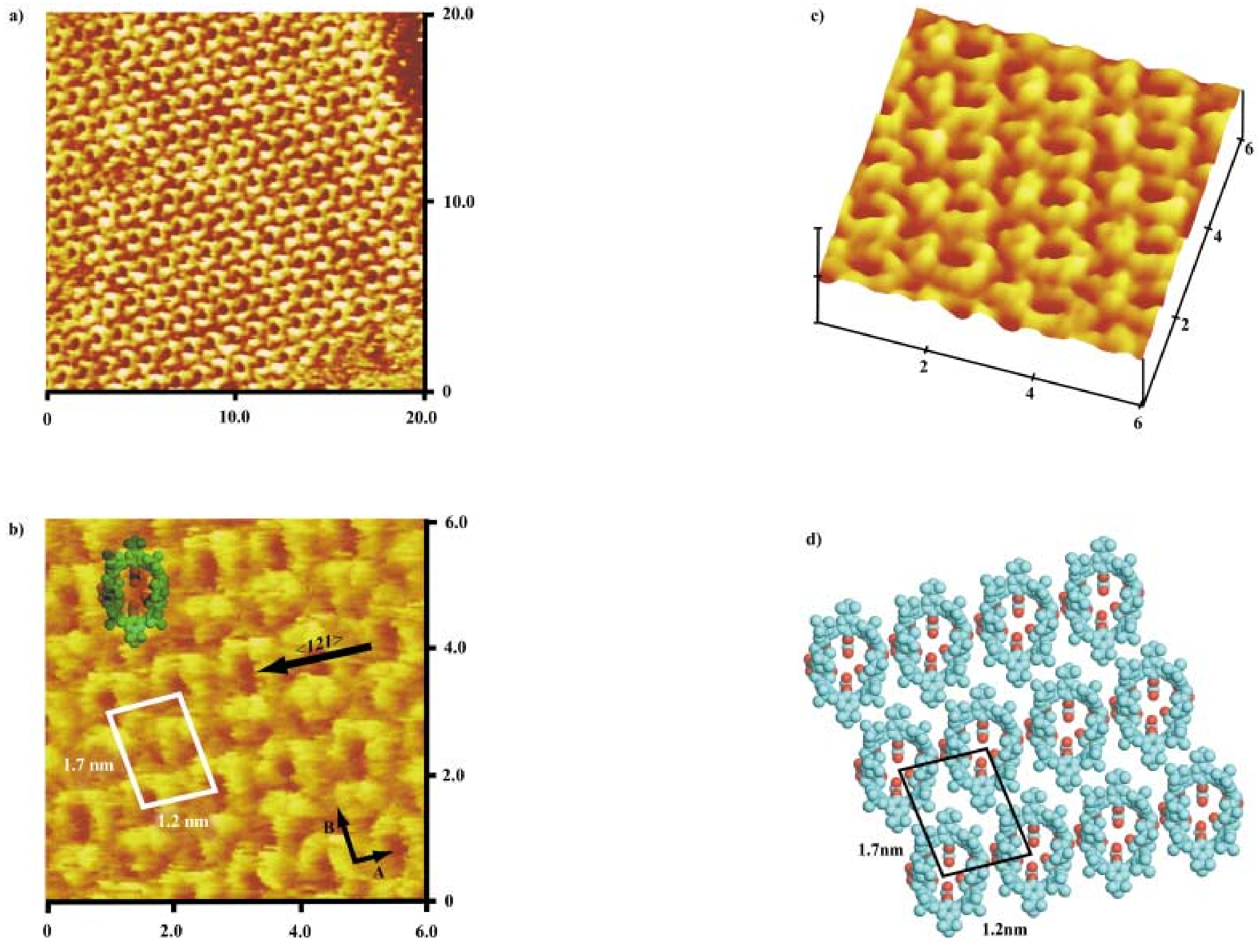

Figure 1. A typical large-scale STM image (a) of an OBOCMC8 array on a Au(111) surface, and a top view (b) and height-shaded surface plot (c) of the same OBOCMC8 array, recorded using high-resolution STM; d) a proposed structural model for the ordered array of OBOCMC8. The bias voltage and tunneling current were −213 mV and 670 pA, respectively. The scales are given in nm.

cell; again, the electrode potential of the Au(111) substrate was held at 0.6 V. After approximately 30 min, a completely different pattern is observed. Figure 2a shows an STM image, taken with a bias voltage of −100–−200 mV and a set-point current of 500–1300 pA. It is evident that the flat Au(111) surface is now covered by a highly-ordered C_{60}/OBOCMC8 array, which is free of molecular defects over the whole 25 nm × 25 nm area observed. This array extends over wide, flat terraces of more than 50 nm × 50 nm in area. An interesting feature of the C_{60}/OBOCMC8 array is the well-ordered bright spots, which can be clearly seen in the image. The feature is different from the dark depressions appearing in pure OBOCMC8 array (Figure 1), which suggests the existence of C_{60} associated with the OBOCMC8 molecule.

A higher resolution STM image (Figure 2b) shows that the molecular rows of the array are parallel to the ⟨121⟩ direction of the underlying Au(111) substrate, and cross each other at an angle of either 60° or 120°, within an experimental error of ±2°, to form a two-dimensional hexagonal lattice with associated bright spots. The structural symmetry of the C_{60}/OBOCMC8 array is significantly different from that of OBOCMC8. From careful observation, it can be seen that each individual bright spot (as indicated by the arrow; Figure 2b) is surrounded by a circular protrusion. The nearest distance between the centers of the bright spots is approximately 1.4 ± 0.1 nm, which is comparable to the size of the C_{60}/OBOCMC8 complex, as estimated from a molecular model. The C_{60}/OBOCMC8 complex tends toward having an upright orientation on the Au(111) surface; the molecular structure suggests that the carboxyl groups are responsible for this arrangement. Therefore, the bright spot and circular protrusion can be assigned as C_{60}, *tert*-butyl, and phenyl units, respectively. In other words, the cavity of the OBOCMC8 molecule is now filled with a C_{60} unit, observed as the additional bright spot in the STM image.[8,9] The STM images prove that the calix in C_{60}/OBOCMC8 complex retains an upright configuration despite containing a buckyball, which has been synthetically included within the calix structure.[8,9] This structural feature can be more clearly seen in the height-shaded surface plot shown in Figure 2c. C_{60} molecules appear within protrusions throughout the array. On the basis of the STM results, a tentative model for the C_{60}/OBOCMC8 array can be proposed (Figure 2d), in which a unit cell with a parameter of 1.4 nm is outlined.

After recording the STM images at 0.6 V, the electrode potential was scanned incrementally in 10 mV stages between

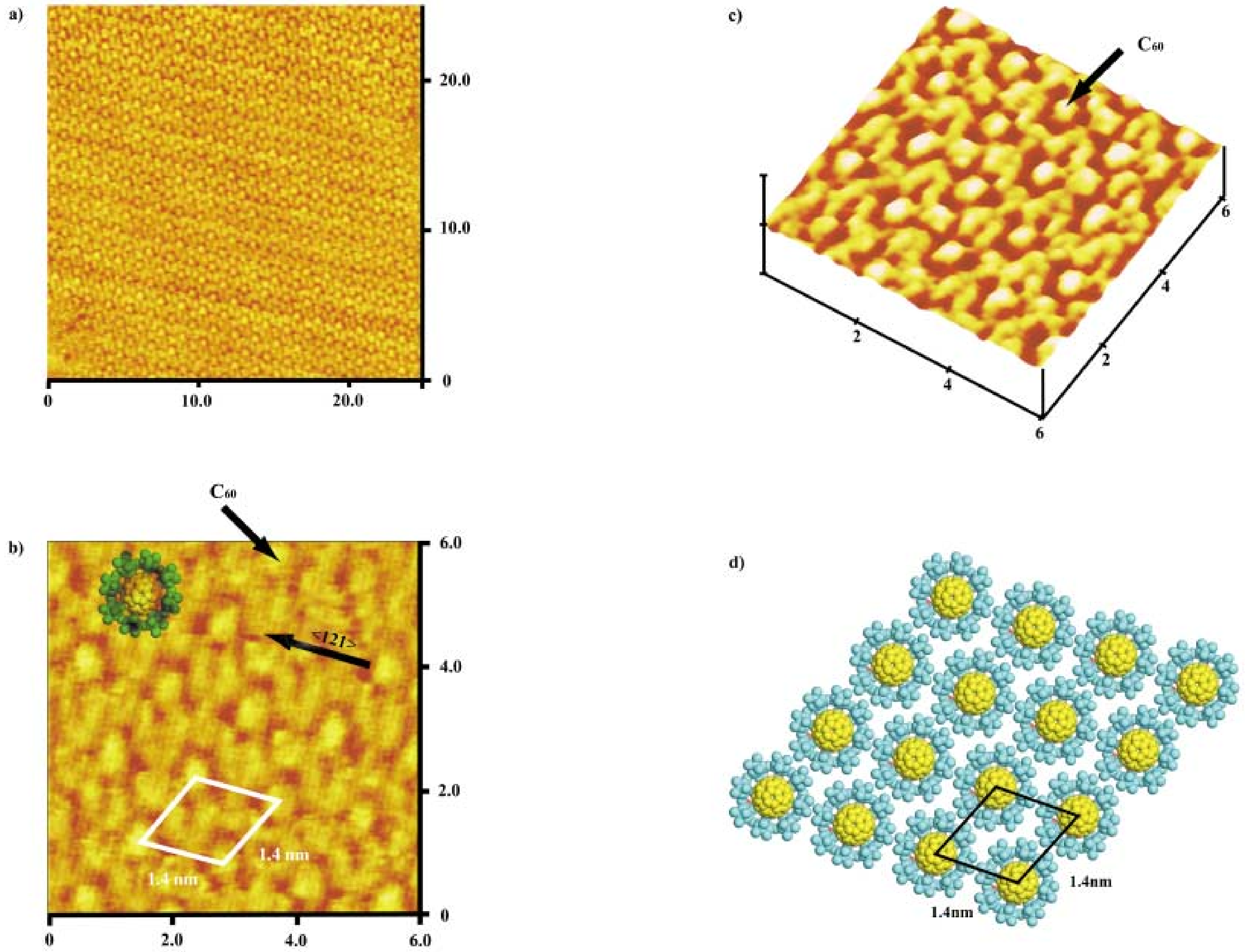

Figure 2. A typical large-scale STM image (a) of an C_{60}/OBOCMC8 array on a Au(111) surface, and a top view (b) and height-shaded surface plot (c) of the same C_{60}/OBOCMC8 array, recorded using high-resolution STM; d) a proposed structural model for the ordered array of C_{60}/OBOCMC8. The bias voltage and tunneling current were −140 mV and 1.0 nA, respectively. The scales are given in nm.

0 and 1.0 V; an identical structure for the C_{60}/OBOCMC8 array is always observed. There was no evidence for structural transformations or the release of C_{60} from the OBOCMC8 calix, even in the negative potential region, where molecular desorption from the Au(111) surface takes place. It is important to point out that different STM contrasts have been observed for both OBOCMC8 and C_{60}/OBOCMC8 arrays in the present experiment when the bias voltage between tip and substrate is varied; this phenomenon has been described in a previous study under vacuum and ambient conditions.[12] The images shown in the communication give clear structural details under the indicated imaging conditions. However, the different image contrasts could not produce different structures, even under conditions that resulted in unclear images. It is obvious that more straightforward experimental techniques, such as IR spectroscopy, and theoretical calculations must be applied to obtain further structural information to support the models suggested in this preliminary study. A more detailed investigation is now in progress.

In summary, the molecules of OBOCMC8 and C_{60}/OBOCMC8 can adsorb onto a Au(111) surface and self-organize into ordered adlayers. The configurations of the two molecules are clearly revealed by high-resolution STM images. OBOCMC8 molecules adsorb onto the substrate with an upright orientation. The intrinsic cavity of the molecule appears as a dark depression. The structure of the C_{60}/OBOCMC8 array is completely different, in that bright spots corresponding to C_{60} molecules can be clearly resolved in individual C_{60}/OBOCMC8 units. The contents of the calix could be changed to other fullerenes, clusters, and organic molecules by utilizing various methods. The stable configuration and well-defined array should be useful for nanostructure construction and for nanodevices.

Experimental Section

OBOCMC8 was synthesized by the method described in the literature.[13] C_{60} was inserted into the intrinsic cavity of OBOCMC8 by the method reported by Atwood and Shinkai.[8,9] OBOCMC8 and C_{60} (1:1 stoichiometry) were dissolved in dry toluene and heated under reflux for 4 h. After this procedure, a green-yellow solid, the C_{60}/OBOCMC8 complex, was formed.

Single-crystal beads of Au were prepared by the crystallization of a molten ball formed at the end of a pure Au wire in a hydrogen–oxygen flame.[14] Au(111) facets on the beads were used for STM observation. For voltammetric measurements, the bead was cut and mechanically polished with successively finer grades of Al_2O_3. Before each measurement, the electrode was further annealed and quenched in deionized (Millipore) water, saturated with hydrogen.

A solution of 0.1M $HClO_4$ was prepared from ultrapure $HClO_4$ solution (Kanto Chemical Co., Japan) and deionized water. Saturated aqueous solutions of OBOCMC8 and C_{60}/OBOCMC8 were prepared for STM and electrochemical analysis. The solutions were deaerated with high-purity nitrogen before experiments were carried out. Cyclic voltammetry experiments were performed by the hanging meniscus method with an EG&G PAR (Princeton Applied Research) Basic Electrochemical System. A reversible hydrogen electrode and a platinum wire were used as the reference and counter electrodes, respectively. All potentials are reported versus a reversible hydrogen electrode (RHE) in 0.1M $HClO_4$.

In situ STM measurements were carried out with a Nanoscope E microscope (Digital Instrument Inc., Santa Barbara, CA). The tunneling tips were prepared from an electrochemically etched tungsten wire (0.25 mm in diameter) in 0.6M KOH. The sidewalls of the tips were sealed with transparent nail polish to minimize the faradaic current.

The molecular models of OBOCMC8 and C_{60}/OBOCMC8 were built and optimized by the AM1 method included in the HyperChem 6.0 package (Hypercube, Inc.). The interatomic separations and molecular sizes quoted in this study were estimated from these molecular models.

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