

Fabricating and Controlling Molecular Self-Organization at Solid Surfaces: Studies by Scanning Tunneling Microscopy

LI-JUN WAN*

Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100080, China

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ABSTRACT

This account presents a summary of recent work describing the control and fabrication of self-organized molecular adlayers on solid substrates. These results demonstrate that molecules, under appropriate conditions, will self-organize into well-ordered monolayers on various solid surfaces. Using scanning tunneling microscopy (STM) to probe the structure of these molecular architectures, it is possible to determine the surface quality to single molecule resolution. The surface structures can be controlled by external stimuli such as electrode potential and UV-light. The ability to control how these adlayers form is important for constructing surface molecular architectures with useful properties.

Introduction

Organic molecules such as porphyrin, calixarene, C_{60} , and polymers, which exhibit unique electrochemical, photochemical, or electronic properties have been extensively used to make self-organized or self-assembled monolayers (SAMs) on solid surfaces.^{1–6} It is generally believed that these studies will introduce new possibilities for fabricating novel molecular devices that cannot be constructed via standard microfabrication techniques. These “bottom-up” strategies of preparing devices is very powerful, and many studies have been undertaken using these principles.^{6–26} The results from these studies have shown that the formation of molecular structures at solid surfaces is not only dependent on the adsorbate molecules themselves, but also on the substrate material and the crystalline symmetry. In other words, the type of adlayer a molecule forms may not be the same on all materials. The self-organization of molecules on surfaces is governed by both molecule-molecule and molecule–substrate interactions. Furthermore, recent progress demonstrates that the structure of a self-organized adlayer can be controlled and transformed by applying external stimuli such as electrode potential, heat, and/or UV light.^{8–13,17,18,20,23} These results suggest that it may be possible to obtain nanometer-size molecular electronic devices such as molecular wires, switches, and molecular template by controlling the self-

organization of individual molecules on surfaces. Therefore, learning how to control the self-organization and self-assembly of adsorbates on surfaces is of wide interest in chemistry, physics, and material science.

The direct observation and investigation of molecular nanostructures at solid surfaces is a constant challenge in molecular science. It has been shown that scanning probe microscopy (SPM), particularly, scanning tunneling microscopy (STM), is a powerful tool for analyzing the structure of self-organizations.^{6–26} With recent developments in this field, it is possible to obtain submolecular or even atomic resolution of the self-organization, identify device-like characteristics in preexisting structures, and create new structures.

This Account summarizes our recent endeavor in the study and modification of molecular self-organization on solid supports.^{18,27–30} The examples provided illustrate different means to template surfaces: (1) crystallization with molecular hosts, (2) cocrystallization with charged polymers, and (3) controllable surface structure by UV-light and electrode potential. In this Account, we emphasize the formation, characterization, and transition of self-organized molecular adlayers on solid surfaces. The results demonstrate the possibility that a molecular self-organization could be prepared in mild conditions such as in air and electrolyte solution without the use of ultrahigh vacuum (UHV). All STM experiments were also carried out in air and solution. The substrates for the molecular adlayers were prepared by the methods such as electropolishing,¹⁸ flame-annealing,²⁴ or simple cleavage of HOPG.²⁹

Molecular Self-Organization of Calixarene and Its Complex with C_{60}

Calixarenes and fullerenes have novel properties that make them ideal materials for many fields.^{31–42} Calixarenes are important starting materials for the synthesis of host molecules and for the construction of large molecular systems with well-defined structures and functions.^{31–35} Fullerene and its derivatives are outstanding electron acceptors, which make them good candidates for the fabrication of devices such as solar cells and chemical sensors.^{36–42} If fullerenes are attached to calixarenes and an ordered adlayer forms on metal surfaces, it may be possible to obtain more interesting properties and employ them toward fabricating devices. As an essential prerequisite, the conformation of calixarenes and fullerenes included within calixarenes units at a solid surface must be fully examined and understood in order to achieve nanometer-scale architectures.

The STM observation of just C_{60} and its derivatives,^{43–48} as well as just calixarene adlayers^{49,50} was reported previously. The C_{60} molecular adlayer on Au(111) appears to be highly mobile and the C_{60} molecules quickly diffuse on the surface.^{47,48} To expand on these studies, we looked at the self-organizations of calix[4]arene, calix[6]arene and calix[8]arene on Au(111) by STM,^{27,51–53} and here we

* Telephone and Fax: (+86)-10-62558934. E-mail: wanlijun@iccas.ac.cn.

Li-Jun Wan received his B.S. and M.S. degrees in material science from Dalian University of Technology of China in 1982 and 1987, respectively, and earned a Ph.D. in materials chemistry in 1996 from Tohoku University of Japan. He joined the Institute of Chemistry of the Chinese Academy of Sciences (CAS) as a professor in 1999 and is currently director of the institute. His research has centered on physical chemistry, with an emphasis on molecular self-assembly, functional nanomaterials, electrochemistry, and scanning probe microscopy.

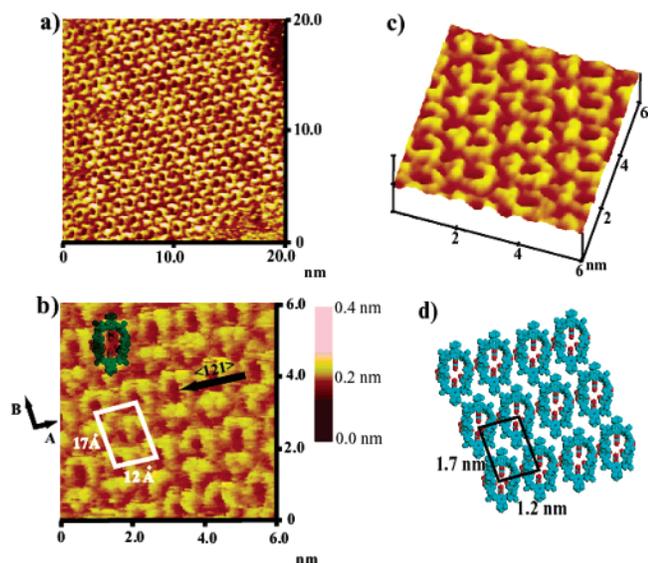


FIGURE 1. (a) Large scale STM image of OBOCMC8 adlayer on Au(111). Top view (b) and height-shaded surface plot (c) of a high-resolution STM image of the adlayer. (d) Proposed structural model. The biased voltage and tunneling current were -213 mV and 670 pA, respectively.

describe the adlayer of a calix[8]arene derivative ($C_{104}H_{128}O_{24}$, OBOCMC8) in detail. The calixarene molecules formed ordered self-organizations on the Au(111) surface, whose orientations are dependent on the chemical structure such as the low rims of the calixarenes. Then, C_{60} was synthesized into a OBOCMC8 resulting in a C_{60} /OBOCMC8 complex (Schemes 1a and 1b).^{27,42} A stable and ordered OBOCMC8 adlayer and C_{60} /OBOCMC8 adlayer were then prepared on Au(111). The self-organized molecular adlayers of OBOCMC8 and C_{60} /OBOCMC8 on Au(111) were investigated by STM.

Figure 1a is a typical STM image of the OBOCMC8 adlayer on Au(111) surface in 0.1 M $HClO_4$. A highly ordered adlayer of OBOCMC8 extends over the atomically flat terrace of the Au(111) surface. The structural details are resolved in the high-resolution STM image (Figure 1b), and the molecular adlayer consists of regular rows of round shaped molecules with dark depressions in the center. On the basis of its chemical structure, the OBOCMC8 molecules must adsorb on the Au(111) surface

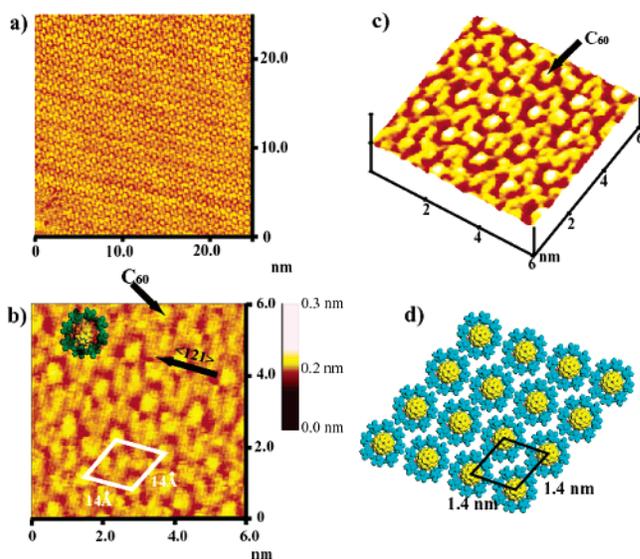
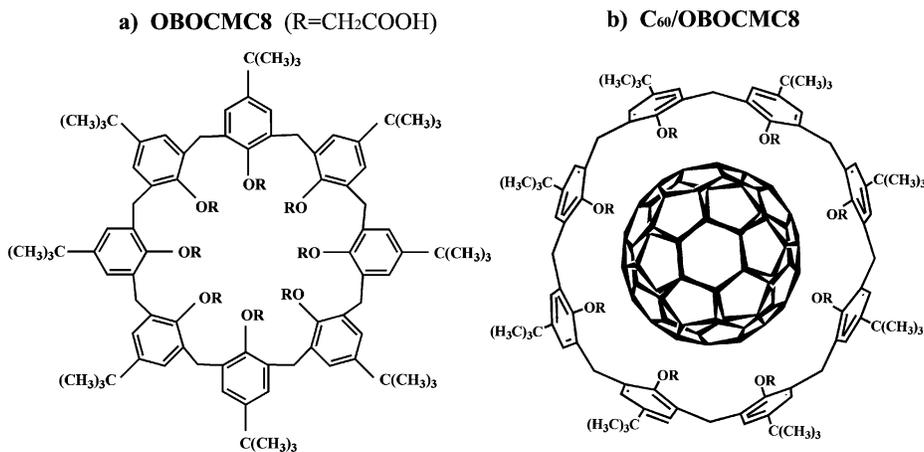


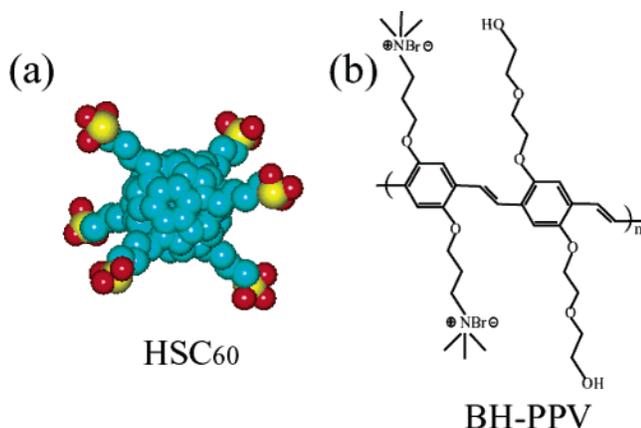
FIGURE 2. (a) Typical large scale STM image of C_{60} /OBOCMC8 adlayer on Au(111). (b) Top view and (c) height-shaded surface plot of a high-resolution STM image of the adlayer. (d) Proposed structural model. The biased voltage and tunneling current were -140 mV and 1.0 nA, respectively.

via the *tert*-butyl, carboxyl and/or phenyl groups. Since carboxyl–gold interactions are most likely stronger than the other two groups of *tert*-butyl and phenyl with gold in this system,⁴⁹ each round shape in the STM image was assigned to a single OBOCMC8 molecule. The surrounding protrusions and the dark depressions were attributed to the phenyl groups and the molecular cavity, respectively. These features are easier to recognize in the height-shaded surface plot shown in Figure 1c. The distance between the centers of the dark depressions along direction **A** is 1.2 ± 0.1 nm, and along direction **B** it is 1.7 ± 0.1 nm. These rows cross, forming a $95 \pm 2^\circ$ angle. A unit cell for the OBOCMC8 adlayer is defined in Figure 1b, and a structural model is proposed in Figure 1d.

A self-organized array of the C_{60} /OBOCMC8 complex on a Au(111) surface was also investigated by STM, and a typical image is shown in Figure 2a. An interesting feature of the C_{60} /OBOCMC8 adlayer is the well-ordered bright spots, which appear to fill the dark depressions that were observed in the OBOCMC8, presumably due to the C_{60}

Scheme 1. Chemical Structures of (a) OBOCMC8 and (b) C_{60} /OBOCMC8



Scheme 2. Chemical Structures of (a) HSC₆₀ and (b) BH-PPV

molecules included in the OBOCMC8 adlayer. From the high-resolution STM image (Figure 2b) of the C₆₀/OBOCMC8 adlayer, the molecular rows are parallel to the $\langle 121 \rangle$ direction of Au(111) substrate. The rows cross each other forming alternating 60° and 120° angles with an experimental error of $\pm 2^\circ$, resulting in a two-dimensional hexagonal lattice. Careful examination showed that the individual bright spots, indicated by the arrow in Figure 2b, are surrounded by circular protrusions. The bright spots are separated by 1.4 ± 0.1 nm, which is approximately the size of the C₆₀/OBOCMC8 complex. The data suggest that C₆₀/OBOCMC8 tends to be upright on the Au(111) surface bonded through the carboxyl groups. Therefore, the bright spot and circular protrusion can be assigned as C₆₀ and phenyl units, respectively, with each OBOCMC8 cavity filled with a C₆₀ molecule. These structural details can be more clearly seen in the height-shaded surface plot (Figure 2c), and a structural model for the C₆₀/OBOCMC8 adlayer is proposed in Figure 2d. The unit cell for the adlayer is outlined in Figure 2b and 2d. The adlayer symmetries for the OBOCMC8 and C₆₀/OBOCMC8 complexes are different, even though both bind to the Au(111) surface through the COOH groups. It was concluded that the differences in the molecular conformation of the two adlayers are due to the existence of C₆₀ molecules.

On the basis of the STM observations, it is clear that both the OBOCMC8 and C₆₀/OBOCMC8 complexes adsorb on Au(111) surfaces and self-organize into well-ordered adlayers. The cavity of the OBOCMC8 molecule appears as dark depressions, which are filled with C₆₀ molecules in the C₆₀/OBOCMC8 complex. The structural details of the adlayers have been resolved by STM, and unit cells and structural models have been proposed for both. The architecture should be interested in fabricating nanodevice with fullerene molecules due to the important property with them.

Binary Component Adlayers with Fullerene and PPV Derivative and Its Conductance

The formation of self-organized adlayers of a single component has been intensively investigated, and recently there has been growing interest in the fabrication of multicomponent nanostructures.^{6,12,28,54} The coadsorption of organic molecules on solid surfaces may be a powerful

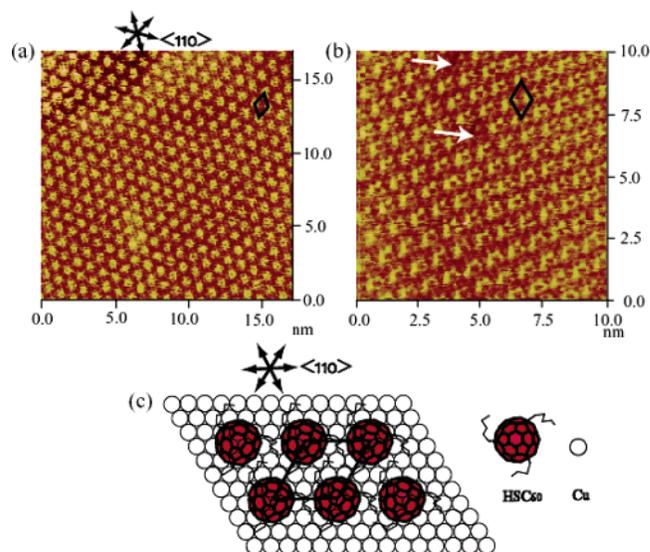


FIGURE 3. (a) Large-scale STM image of a Cu(111)-(4 × 4)-HSC₆₀ adlayer acquired at -0.2 V in 0.1 M HClO₄. Tunneling current was 2 nA. (b) High-resolution STM image of (a). (c) Proposed model for the HSC₆₀ adlayer on Cu(111) surface, respectively.

tool for constructing materials with multiple components, whose properties are expected to possess enhanced performance and function over the single component devices. Many physical methods, such as Langmuir–Blodgett (LB)⁵⁵ and Molecular Beam Epitaxy (MBE),⁵⁶ have been used to prepare thin film devices, using a layer-by-layer approach; however, electrochemical techniques such as STM may prove to be a quicker and more convenient way of constructing two- and three-dimensional structures with multiple components.

Poly-phenylene-vinylene (PPV) and its derivatives are some of the most extensively investigated conjugated polymers. These materials have been used in solar cells, sensors, and long-living electroluminescent devices, due in part to the ease of fabrication and low cost of the material.^{57,58} A composite adlayer, prepared with PPV and C₆₀, may result in enhanced electronic and electroluminescent properties, which cannot be obtained from the individual materials. To begin, single component adlayers composed of HSC₆₀ (Hexa(sulfobutyl)C₆₀: C₈₄H₄₈O₁₈S₆Na₆) and BH-PPV (poly{2,5-bis(3-bromotrimethylammonio)propoxy)-phenylene-1,4-divinylene)-*alt*-1,4-(2,5-bis(2-(2-hydroxyethoxy)ethoxy)phenylenevinylene)}: C₃₆H₅₆O₈N₂Br₂) (Scheme 2) on a Cu(111) surface were investigated.

(1) HSC₆₀ Adlayer. An STM image of Cu(111)-(1 × 1) on atomically flat Cu(111) terraces in 0.1 M HClO₄ was recorded. Then a solution of HSC₆₀ was injected into the electrochemical cell, and a HSC₆₀ adlayer formed. The HSC₆₀ molecules form ordered adlayers on Cu(111) surfaces at ambient temperature, and the STM image is shown in Figure 3a. By comparison with the Cu(111)-(1 × 1) atomic image, it was determined that the molecular rows of HSC₆₀ molecules are parallel to the $\langle 110 \rangle$ direction of the underlying Cu(111) lattice. The intermolecular distances in the $\langle 110 \rangle$ direction were measured to be 0.98 ± 0.02 nm, corresponding to four times the Cu(111) lattice. From these data it was concluded that the HSC₆₀ complex forms a (4

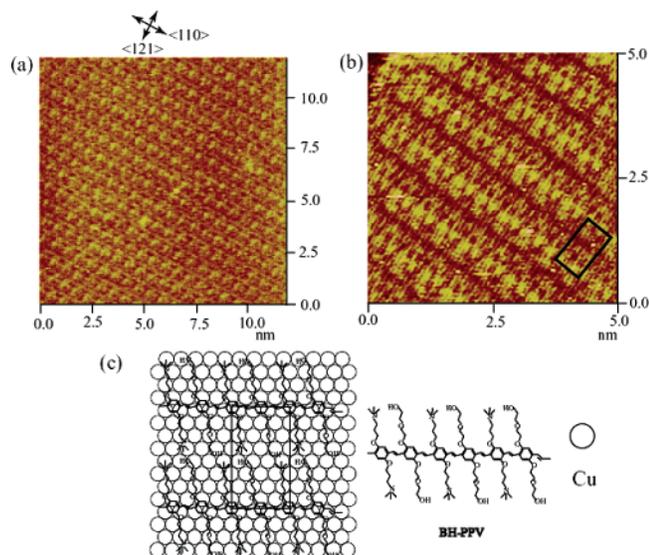


FIGURE 4. (a) STM image of BH-PPV molecules on Cu(111) at -0.2 V in 0.1 M HClO_4 . Tunneling current was 2 nA. (b) High-resolution STM image. (c) Schematic representation for the $(4 \times 4\sqrt{3})$ structure.

$\times 4$) structure, which is consistent with the type of adlayers C_{60} molecules form on Cu(111) in UHV.⁴³

A high-resolution STM image of the HSC_{60} adlayer with two single molecular defects, indicated by the white arrows, is shown in Figure 3b. Each bright spot in the low resolution image, which corresponded to a single HSC_{60} molecule, is split into a set of three bright spots in this high resolution image. This conformation is consistent with that determined both experimentally and theoretically for molecular adlayers of C_{60} on Cu(111) and Si(111) in UHV.^{43–44,59} It is clear from these images that the HSC_{60} cages form ordered and stable molecular adlayers on Cu(111) surfaces. A tentative structural model is proposed in Figure 3c, with the molecular center placed on the 3-fold hollow site of the underlying substrate, similar to the models reported in the literature for C_{60} .⁴³

(2) BH-PPV Adlayer. Figure 4a is a typical STM image of the BH-PPV adlayer formed on a Cu(111) surface. A higher resolution STM image in Figure 4b shows the details of the packing arrangement and the internal structure of the BH-PPV adlayer. Two bright spots, attributed to two benzene rings of a BH-PPV unit, along with the side chains form a rectangular unit. These molecules form an ordered two-dimensional adlayer, which from the molecular arrangement and orientation to the Cu(111) lattice, was determined to have a $(4 \times 4\sqrt{3})$ structure. A unit cell (Figure 4b) and a structural model (Figure 4c) is proposed for the molecular adlayer.

(3) HSC_{60} and BH-PPV Composite Adlayer. Alternating the adsorption of oppositely charged adsorbates results in the formation of a HSC_{60} /BH-PPV binary composite adlayer. The two-component adlayer on Cu(111) was prepared by first generating a well-defined adlayer of BH-PPV and then adding a layer of HSC_{60} on top of it. Experiments in a reversed order of adsorption were found to result in analogous structures. Figure 5a is an STM image of the composite adlayer showing a two-dimensional net-

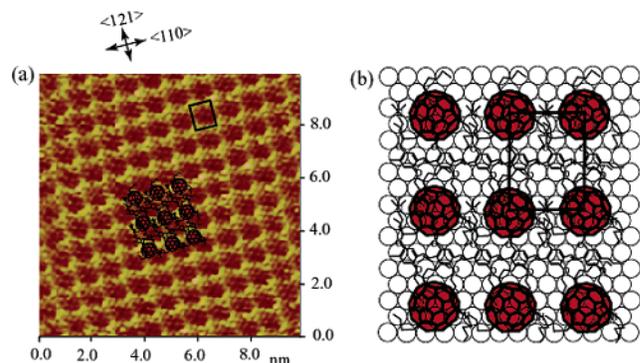


FIGURE 5. (a) High-resolution STM image of the composite adlayer of HSC_{60} and BH-PPV on Cu(111) in 0.1 M HClO_4 . Tunneling current was 2 nA. (b) Structural model for the composite adlayer.

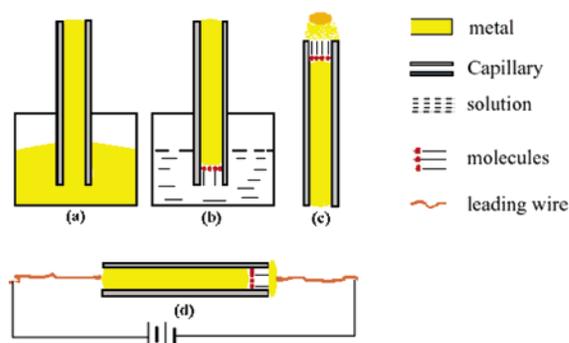


FIGURE 6. Illustration for preparing a capillary tunneling junction.

work with a 4-fold symmetry. UV-visible spectroscopy was used to probe the existence of the composite structure and suggested that BH-PPV and HSC_{60} were both present on the surface.²⁸ From the intermolecular distance and the orientation of the molecular rows, the composite adlayer is a $(4 \times 3\sqrt{3})$ structure, and the proposed unit cell is outlined in Figure 5a. The bright spots in the STM image presumably originate from the C_{60} cages, and the BH-PPV molecules are observed as much weaker spots. A tentative model for the composite adlayer on Cu(111) is proposed in Figure 5b.

Understanding the property of a single molecule or monolayer is an important issue in molecular science.^{6,60–63} Using a capillary tunneling junction we developed a method to measure the current–voltage (I – V) curve of a molecular monolayer (Figure 6).³⁰ An electrode surface, prepared at one end of a glass capillary with metals (Figure 6a), was modified with organic molecules (Figure 6b), while the opposite end of the capillary was covered by metals as an electrode (Figure 6c). The sandwich-configuration circuit was then used to measure the conductance of the molecules (Figure 6d). The results from this method is in agreement with those obtained using other methods such as SPM, mercury drop, and break-junction.^{45,60–62} Figures 7 shows typical I – V curves of the three different adlayers measured using the capillary tunnel junction method.²⁸ Repeated measurements of independently prepared junctions produced reliable and reproducible results. Nonlinear characteristics have been observed in the junctions of all three types of molecular adlayers. The

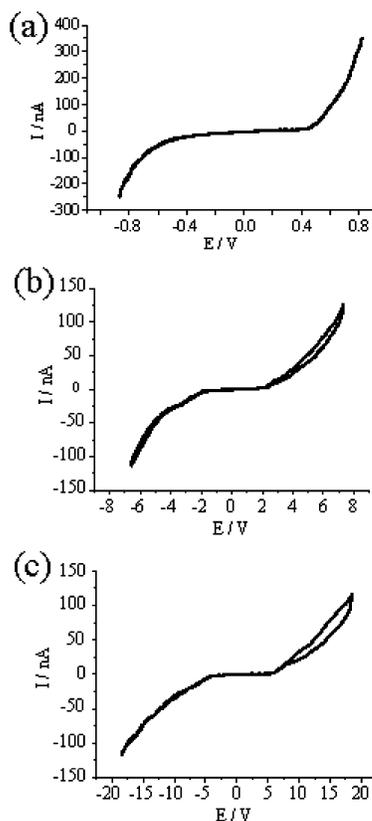


FIGURE 7. Current-voltage curves of the adlayers of (a) HSC₆₀, (b) BH-PPV, and (c) HSC₆₀ and BH-PPV.

rectified region of the HSC₆₀ adlayer in Figure 7a is from -0.5 to 0.5 V consistent with the result of C₆₀,^{44,45} BH-PPV from -2 to 2 V in Figure 7b. The rectified region of the composite monolayer in Figure 7c is extended considerably broader than those in its component adlayer. This result is likely due to the interactions between the HSC₆₀ and the BH-PPV molecules. The interactions enhance the potential barrier of the composite adlayer and broaden the energy gap, showing that the composite functional

molecules are promising candidates for the application of electronic nanodevices.

Controlling Surface Molecular Structures by Electrode Potential and Photochemical Reaction

(1) Photoinduced Organic Nanowires from a Self-Assembled Monolayer. A continuing challenge in molecular nanotechnology is to control how individual molecules self-organize on solid supports. The ability to control how these self-organized adlayers form is the first step to producing useful devices from this technology. One possibility is to modify the surface, either chemically or physically, after the individual molecules self-organize on the surface and the molecular adlayers form. The ability, technique, and knowledge necessary to control the fabrication of nanodevices and nanomaterials have drastically improved in recent years.^{12,17–18,20,23,29,64} The molecular orientation and symmetry of a self-organized adlayer can be tuned and individual molecules can be polymerized into molecular dimers and nanowires by STM-tip-induction, electrode potentials, photochemical reactions, and annealing.^{6,12,18,20}

Much of this work has been focused on conjugated organic polymers because of their unique electronic and optical properties. In particular, one-dimensional π -conjugated polymers, such as polydiacetylene (PDA), appear to be promising candidates due to the extended π -electron delocalization along their skeletons.^{57,65} The 10,12-pentacosadiynoic acid (DA) adlayer was prepared on a HOPG surface, and a high-resolution STM image of the DA adlayer is shown in Figure 8a. The individual DA molecules form a close-packed structure and organize into well-ordered lamellar structures. The diacetylene units appear as large bright spots in contrast to the alkyl chains. In Figure 8a, the dark area, indicated by the red arrow, corresponds to hydrogen bonded carboxylic groups which

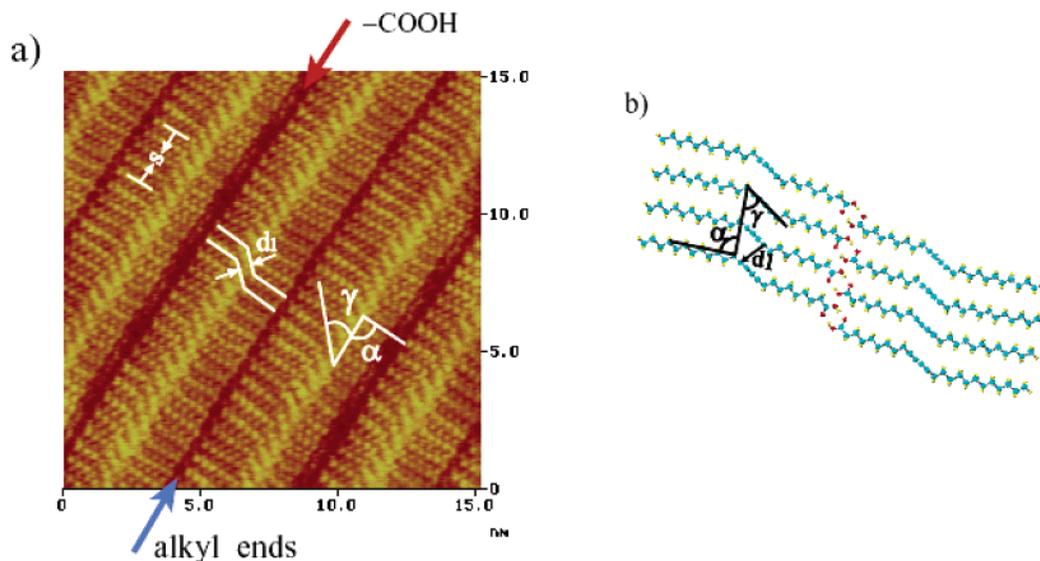


FIGURE 8. (a) STM image of the self-organized adlayer of DA on HOPG surface. The imaging conditions are 776 pA and -328 mV. (b) Molecular model of the DA monolayer.

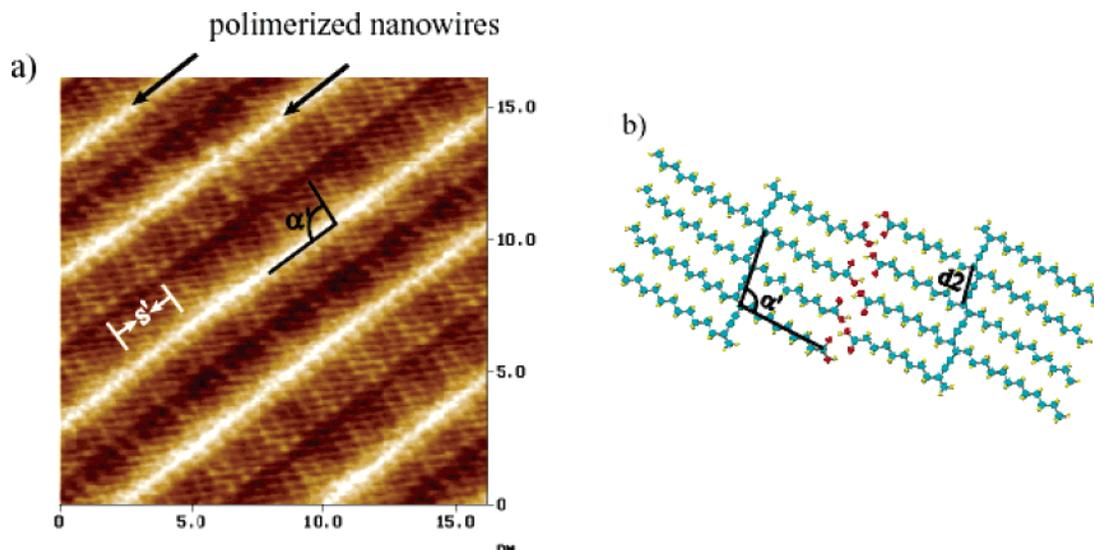


FIGURE 9. (a) STM image of the self-organized adlayer of polymerized DAs. The imaging conditions are 366 pA and -440 mV. (b) A schematic model of the polymerized DA adlayer.

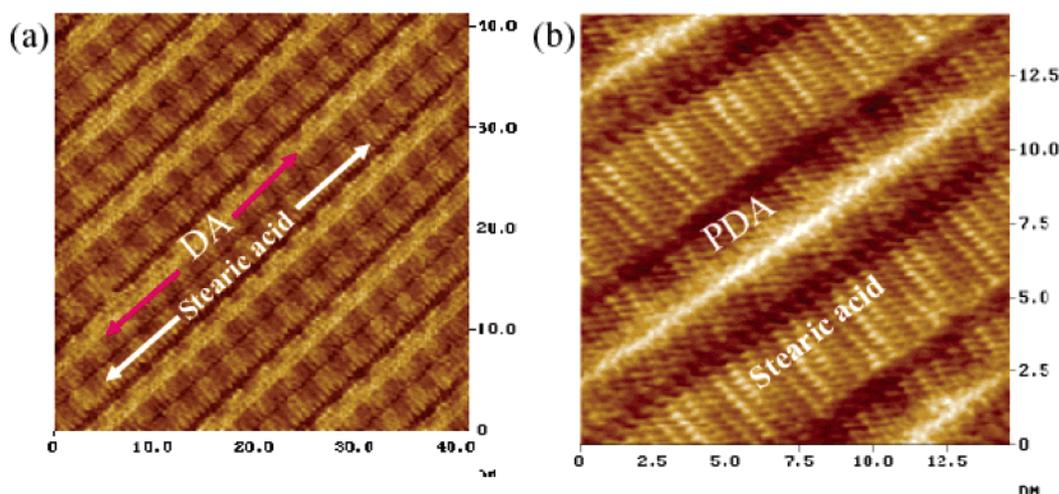


FIGURE 10. (a) STM image of an adlayer formed by coadsorption of DAs and stearic acid. The imaging conditions are 636 pA and -500 mV. (b) STM image of the adlayer after UV light irradiation.

form head-to-head structures, whereas the blue arrow points to the end of the alkyl chains. The alkyl chains form an angle (α) of $90 \pm 2^\circ$ with respect to the direction of the lamella axis, and the average distance (S) for every fifth alkyl chain is 2.02 ± 0.02 nm. An illustrative model for the molecular arrangement is proposed in Figure 8b. The stacking distance, d_1 , between two neighboring diacetylene units is 0.504 ± 0.02 nm and the angle (γ) between the diacetylene rod and the stacking axis is $45 \pm 2^\circ$.

Figure 9a shows a typical STM image of the adlayer after UV irradiation for 5 min. A new structure is observed, with bright lines corresponding to the diacetylene units suggesting the individual DA molecules polymerized along the lamella direction. These bright PDA nanowires are highlighted by arrows in Figure 9a. The average distance for every fifth alkyl chain increases from 2.02 ± 0.02 nm to 2.52 ± 0.02 nm after irradiation ($S \rightarrow S'$). Furthermore, another marked change is the angle ($\alpha \rightarrow \alpha'$) of the alkyl chains relative to the lamella direction which increased

from $90 \pm 2^\circ$ in the unpolymerized image to $100 \pm 2^\circ$ in the polymerized structures. A structural model for the polymerized adlayer is proposed in Figure 9b. The values measured from the images correlate quite well with that of the theoretical model. The repeating distance d_2 in the polymer backbone, indicated by the solid line in Figure 9b, is 0.490 ± 0.02 nm.

Figure 10a is an STM image recorded on the composite adlayer showing a uniform adlayer with alternative molecular rows formed by DA and stearic acid. After irradiation with UV light, the DA molecules polymerize into molecular wires and the stearic acid is not affected as observed in the high-resolution STM image (Figure 10b). These images show that it is possible to control the spacing between linear polymer nanowires using non-photoactive species as a spacer. The length of the alkyl chain can be changed by chemical synthesis, thereby shrinking or increasing the spacing between the PDA nanowires. However, it should be possible to control the

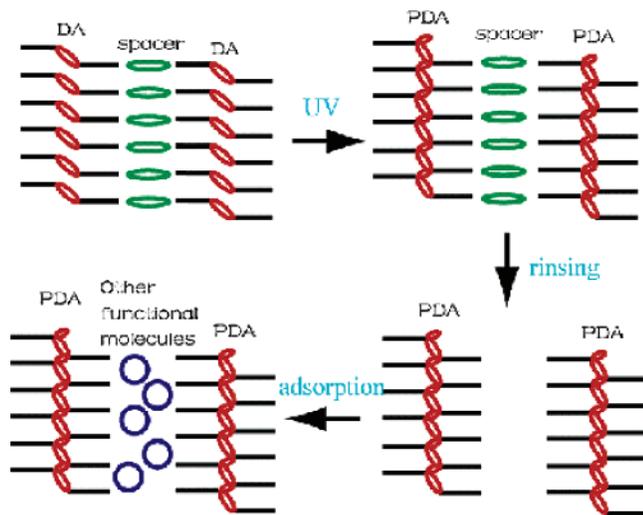


FIGURE 11. Proposed schematic illustration for a molecular template consisting of coadsorbed molecules.

spacings by coadsorption of different compounds with the DA molecular template as well.

In addition, photoinduced polymerization of self-organized molecular adlayers suggests that it may be possible to fabricate a controllable molecular template, as illustrated by Figure 11. A photochemically inert molecule such as stearic acid, is used as a spacer. In this composite adlayer, the spacer regulates the distance between the photochemically active molecules in the template. After polymerization, the spacer molecules can be removed by washing, and the DA molecules become the template. With this molecular template, other functional molecules such as nanoparticles or cluster materials could be inserted into the spaces. However, due to surface diffusion, the complexity in using such a template needs to be considered. To achieve a successful exchange during the rinsing process, it may be necessary to choose a washing compound which has a higher affinity for the surface than the spacer.

(2) Potential Dependent Molecular Orientation. If a reversible molecular event such as orientation or two-dimensional motion could be triggered and subsequently regulated by applying an electric perturbation, it would represent a definitive milestone toward the development of a functional molecular element.^{1,2} A self-organized molecular adlayer of 2,2'-bipyridine (bpy) was prepared on a Cu(111) surface in HClO₄ solution.¹⁸ Figure 12a shows a typical STM image of a bpy adlayer at -0.25 V (vs Reversible Hydrogen Electrode: RHE), which consists of paired rows. Two spots in a paired row form an ellipse, and each ellipse indicated in the figure represents an individual bpy molecule. A high-resolution STM image (Figure 12b) is employed to ascertain the structural details. Each bpy molecule appears in a dumbbell shape with two blobs. The distance between the centers of two adjacent blobs is ca. 0.4 nm, as expected from the chemical structure of a bpy molecule. Thus the two blobs are attributed to the two pyridine rings of a single bpy molecule. A careful observation indicates that a height difference exists in a bpy molecule between two pyridine

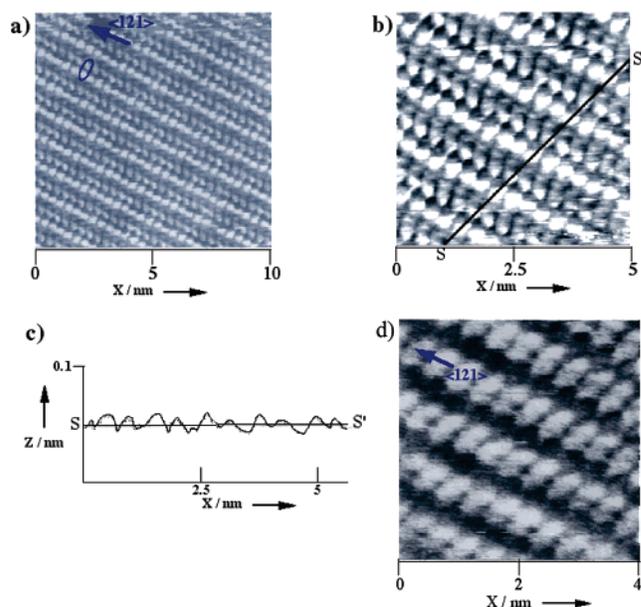


FIGURE 12. (a) Large scale and (b) high-resolution STM images of bpy molecules on Cu(111). (c) Cross-sectional profile of bpy adlayer along S–S' in (b). (d) A higher resolution STM image of the bpy adlayer.

blobs. The corrugation height difference is measured to be ca. 0.02 nm along S–S' as shown in Figure 12c that can be attributed to a molecular torsion from trans to cis transition. The molecular distance in the same rows along $\langle 111 \rangle$ is ca. 0.42 ± 0.2 nm. The theoretical width of a bpy molecule from the N atom to the opposite H atom is ca. 0.4 nm. From the STM image and the chemical structure, it was determined that the bpy molecule assumes a flat-lying orientation on the Cu(111) surface.

It was clearly seen that the molecular orientation varied when a more positive electrode potential was applied. Figure 12d is a high-resolution STM image recorded at 0 V, which shows different molecular features than the images recorded at -0.25 V vs RHE. The “thickness” of each molecule is measured at ca. 0.35 nm, which is near the thickness of π electrons.⁶⁶ From this it is reasonable to consider that at 0 V vs RHE, the bpy molecules reside vertically on the Cu(111) surface (Figure 12d).

The orientation transition from flat-lying to vertical is completely potential dependent and reversible. Surface-enhanced infrared adsorption spectroscopy (SEIRAS) confirms the orientation of the bpy molecule on the surface (Figure 13). The two bands at 1597 and 1486 cm^{-1} are assigned to the adsorbed bpy molecules. When the molecule assumes a flat-lying orientation on the electrode surface, no signal was detected for the in-plane vibration as observed at -0.25 V. As the electrode potential is scanned to positive values, peaks emerge with increasing intensities at 1597 and 1486 cm^{-1} . At 0.1 V the intensity reaches the maximal value and remains consistent until 0.3 V, indicating that the molecule rearranges and assumes a vertical orientation, confirming that the orientation of the bpy molecules on Cu(111) surface can be tuned by adjusting the electrode potential.

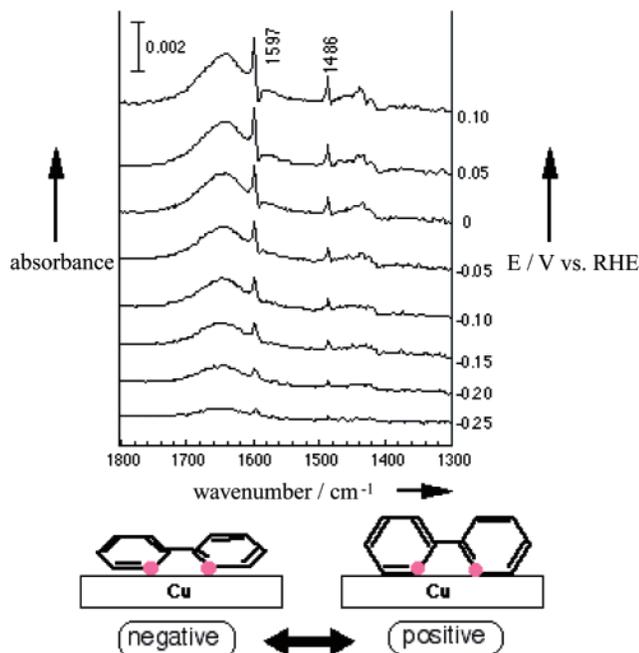


FIGURE 13. SEIRAS spectra of bpy molecules on Cu(111) with electrode potentials from -0.25 to 0.1 V at a scan rate of 5 mV s^{-1} .

Conclusion and Outlook

Fabricating and controlling molecular architectures with desired structures and properties remains a constant challenge in chemistry and material science. The results presented in this Account show that self-organization on a solid support is governed by molecule-substrate coupling, adjacent molecular interactions, and intramolecular interactions. The data suggest that by using these properties, one may be able to successfully modify and control the surface adlayer formed via self-organization, which is a prerequisite if these techniques are to become promising candidates for the development of functional nanomaterials and nanodevices.

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