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Communication

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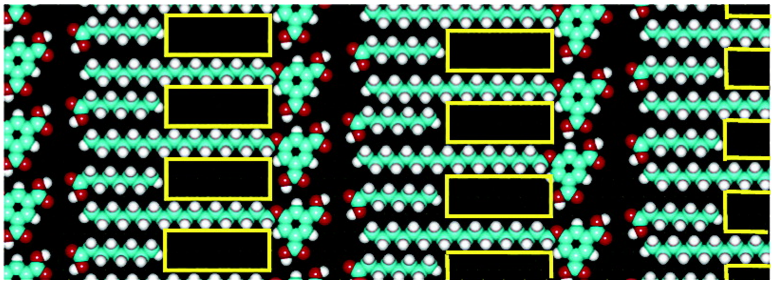

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Two-Dimensional Self-Assembly of a Two-Component Molecular System: Formation of an Ordered and Homogeneous Molecular Mesh

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Surface modification by self-assembled monolayers currently attracts research attention due to promising applications in patterning at the nanometer scale, the development of molecular electronic devices, chemical sensors, and corrosion inhibition layers. With the aid of STM, the self-assembled monolayers of hydrocarbons on HOPG have been widely studied.[1−3] In a typical lamella, adjacent molecules are aligned through chain−chain van der Waals interactions and the match of the all-*trans* alkyl chain with the underlying HOPG lattice. The ordered lamellae are packed into domains by various noncovalent interactions, such as van der Waals interactions, hydrogen bonding, electrostatic interactions, and dipolar interactions. However, very few results have been reported on the 2-D self-assembly of two-component systems, although 3-D multicomponent self-assembly has been well studied.[4] This is possibly (1) because the insertion of lamella of the second component requires breaking the original lamella−lamella interaction, and (2) because of the competition between self-assembly of the individual molecules independently. A successful example[5−8] of two-component self-assembly is the lamellae of carboxylic acid (*A*) and bipyridine (*B*) to form domains via O−H···N hydrogen bonding, which are comprised of interdigitating *A* and *B* lamellae. The carboxylic acid group of component *A* acts as hydrogen-bonding acceptor, and the N atom of component *B* behaves as donor, inducing a lamella-by-lamella coadsorption. In this communication, a novel example of the self-assembly of a two-component system on a solid surface at the molecular, rather than the lamellar, level is demonstrated. This leads to the formation of an array of ordered and homogeneous nanometer-sized openings, which might be used as a template for formation of an ordered array of quantum dots or guest molecules.[9] There are some examples of randomly mixed lamellae[10] or ordered co-crystals[11] in two-component self-assemblies, but none exhibiting the formation of ordered and homogeneous nanostructured openings described here.

Figure 1 shows a STM image of a self-assembled monolayer formed from 5-octadecyloxyisophthalic acid (5OIA) dissolved in phenyloctane. The image demonstrates an ordered assembly of 5OIA molecules on HOPG at atomic resolution. The bright isophthalic headgroups and dim alkyl chains of 5OIA molecules can be clearly recognized. The bright feature of the headgroup originates from the higher tunneling current of the phenyl ring, as observed in STM images of molecules containing an aromatic moiety.[12−14] The direction of the headgroups can be readily identified. A lamella defined as the section between two adjacent blue lines includes the dim area of alkyl chains and two bright rows of triangle-like headgroups. The headgroups of two neighboring 5OIA molecules in a lamella assemble at the two edges of the lamella. Because all headgroups point in the same direction, two adjacent molecules in a lamella must use different faces (lower part of Figure 1) to match with the graphite lattice. This alternate packing of opposite faces in a lamella maximizes the chain−chain van der Waals interaction and the surface occupancy of molecules, forming a stable monolayer. A line-profile analysis of the section marked with a turquoise dashed line in Figure 1 shows that the chain−chain distance in the lamella is ∼4.2 Å, as expected for close packed alkane chains in a lamella. It should be noted that this structural model is different from that postulated previously.[15] In that model, the angle between dim alkyl chain and the bright row of headgroups deviates from the corresponding image[15] and the image in Figure 1.

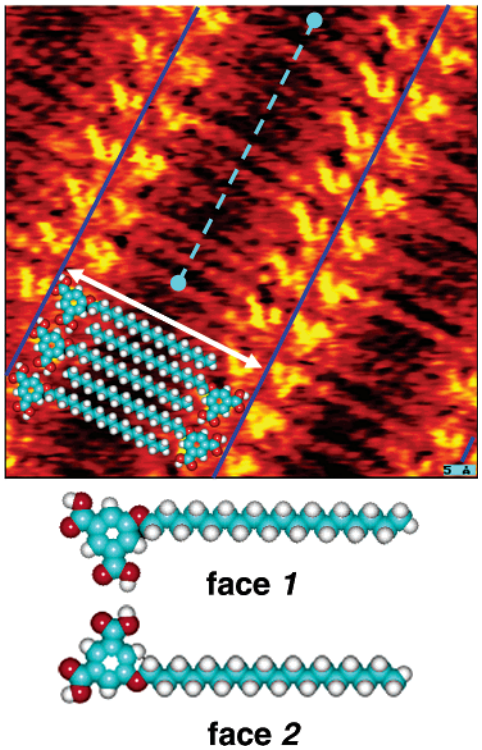

Figure 1. High-resolution image of 5OIA self-assembled monolayer on HOPG. Scan area is 80 Å × 80 Å. The superimposed overlapping sphere molecular models show the molecular arrangement of 5OIA on HOPG. The turquoise dashed line indicates the line-profile analysis. The white double-headed arrow shows the width of one lamella. The lower part presents two opposite faces of 5OIA.

Figure 2 presents the STM image obtained from the monolayer formed from 5OIA dissolved in octanoic acid on HOPG. Distinctly different from the image in Figure 1, each lamella (the part between two pink dashed lines) in the images of the 5OIA/octanoic acid mixture only has *one* row of headgroups. The width of the bright row of headgroups along the chain direction is 5−6 Å, consistent with the size of the isophthalic headgroup. By changing the contrast of each image in Figure 2, no second row of headgroups in any lamella was found. If the images in Figure 2 are only due to the self-assembly of 5OIA, each bright band should be made of two rows of headgroups, and the width of one lamella marked with a double-headed white arrow between the two pink lines (Figure 2a)

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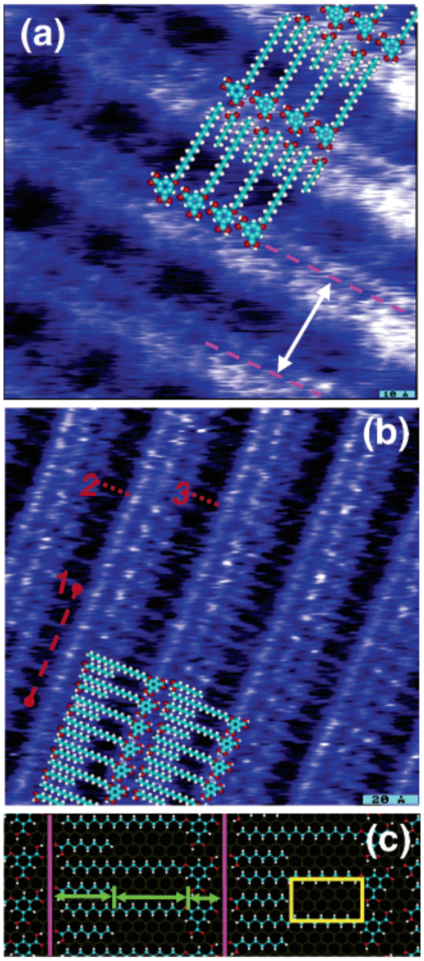

Figure 2. (a and b) Images of supramolecular coadsorbed monolayer of 5OIA and octanoic acid. The sections used for line-profile analyses are shown with red dashed lines in image b. (c) The molecular packing model for the self-assembled monolayer of 5OIA/octanoic acid. The headgroup, the region without octanoic acid, and the area with octanoic acid of one lamella are labeled with green double-headed arrows. The yellow box marks one formed hole.

should be 37−38 Å, equal to that in Figure 1. However, the lamella width in Figure 2a and b is 32−34 Å. These features in Figure 2a and b indicate that the 5OIA/octanoic acid system displays a packing pattern significantly different from that of 5OIA in phenyloctane, though the packing pattern of Figure 1 is observed in the monolayer of 5OIA/octanoic acid, as well (Supporting Information, Figure S2). Because of the single row of headgroups in each lamella, the coverage of 5OIA in the monolayer of 5OIA/octanoic acid is only half of that in 5OIA/phenyloctane. Half of the 5OIA molecules cannot self-assemble into a stable domain without the coadsorption of octanoic acid, due to the weaker chain−chain van der Waals interaction because of the much larger chain−chain separation of 8.5 Å in this structure. Therefore, the octanoic acid occupies the space between two adjacent 5OIA molecules in a lamella. Each molecule of octanoic acid forms two hydrogen bonds with one 5OIA molecule in its adjacent lamella, producing a new two-component self-assembled monolayer mixed at the molecular level. Because the octanoic acid is shorter than the alkyl chain of 5OIA, an unoccupied hole is formed between two adjacent 5OIA molecules in the lamella. Figure 2b clearly shows the formed holes.

On the basis of these image features of the self-assembled monolayer of 5OIA/octanoic acid, a packing model is proposed in Figure 2c. The 5OIA molecule interdigitates with the octanoic acid molecule in each lamella at the molecular level. There is only one row of headgroups in each lamella. Every lamella can be divided into three parts: the headgroup, the region without octanoic acid, and the region with octanoic acid. The ratio of their lengths along the direction of the alkyl chain is expected to be ∼1:3:2, based on this model, and the measured ratio of the three parts is seen to be ∼1:3:2. In addition, the measured chain−chain distance in the region without octanoic acid and the area with octanoic acid is 8−9 and 4−4.5 Å, respectively, further indicating that the octanoic acid molecule inserts into the space between two adjacent 5OIA molecules in a lamella. Figure 2a−c clearly demonstrates a two-component self-assembly at the molecular level in this structure. This self-assembly produces an ordered and homogeneous mesh of nanometer-sized holes, due to the difference in the alkyl chain length of the two molecular components. Each opening in the mesh has a dimension of ∼8.5 Å × 13.5 Å × 1.8 Å, indicated by line-profile analyses for the sections marked with red-dashed lines ***1***, ***2***, and ***3*** in Figure 2b (Supporting Information, Figure S3). In addition, the size of the opening should be controllable by changing the length of the alkyl chain of the *n*-carboxylic acid or that of the isophthalic acid without disrupting the 2-D lattice. We have observed similar structures for 5OIA coadsorbed with stearic acid and dodecanoic acid, altering the size of the opening. Images of these structures do not exhibit the high resolution seen for the 5OIA/octanoic acid structure shown here, suggesting somewhat less stability for these structures.

In summary, these studies have revealed a 2-D self-assembly of a two-component mixture at the molecular level. This finding demonstrates an approach to precisely grow 2-D stoichiometric composite materials at the molecular scale and to controllably fabricate ordered and homogeneous 2-D structures of nanometer dimension.

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Supporting Information Available: Experimental section, molecular packing model of Figure 1, and line-profile for Figures 1 and 2b. The material is available free of charge via the Internet at http://pubs.acs.org.

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