Direct Observation of a Widely Spaced Periodic Row Structure at the Pentacene/Au(111) Interface Using Scanning Tunneling Microscopy

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ABSTRACT

The transition from surface to bulk pentacene at the Au(111) interface will have important implications for the mechanism of carrier transport across the interface. STM observations of pentacene molecules on the Au(111) surface, at more than a monolayer coverage, revealed periodic rows of molecules spaced 61 ± 5 Å apart. These widely spaced periodic rows consist of flat and edge-on molecules aligned with the initial layer of pentacene. Commensuration with the surface and characteristic bulk pentacene–pentacene interactions drive the formation of this unique structure.

The ability to assemble organic molecules on surfaces into nanometer size structures, such as one-dimensional wire-like arrangements, has technological implications. One-dimensional structures of atoms and molecules have been produced by substrate-mediated assembly at steps[1] and other surface defects.[2] Molecules interacting with each other[3] and/or the substrate through functional groups[4,5] have also been used to form ordered structures on a surface terrace. Substrate-mediated ordering has also been demonstrated using the reconstruction of the Au(111) surface.[3,6,7] These molecular systems can form large two-dimensional domains or one-dimensional rows. These self-assembled structures typically have repeating dimensions on the order of a length of one or two molecules. There have been very few reports of an assembly of atoms or molecules into repeating patterns separated by more than one or two molecular lengths.[8]

Highly purified pentacene single crystals have been shown to have one of the highest carrier mobilities measured for an organic semiconductor.[9,10] These high mobilities make pentacene a promising material for use in thin film transistors[11,12] and organic photovoltaic devices.[13−15] Gold is commonly used as an electrical contact to the organic semiconductor in these devices. Our previous studies of this interface revealed the existence of a large interface dipole barrier and a rich variety of ordered pentacene structures.[16] During the studies of the pentacene/Au(111) interface we observed widely spaced periodic (WSP) rows of pentacene molecules, with 61 Å separation. These widely spaced periodic structures will be described herein.

Experiments were performed in a commercial Omicron Multi-probe ultrahigh vacuum system described previously.[16,17] The Au(111) sample was produced by depositing a ~1 μm thick gold film onto a mica substrate at 300 °C. The Au(111) surface was cleaned with repeated sputter and anneal cycles until X-ray photoelectron spectroscopy verified chemical purity and scanning tunneling microscopy (STM) revealed the characteristic herringbone 23 × √3 reconstruction.[18] Pentacene was deposited onto the Au(111) surface in an attached deposition chamber from a resistively heated boron nitride crucible and monitored with a Leybold quartz crystal microbalance. The pentacene film thickness for these investigations was between 5.5 and 7 Å. The Au substrate was held at room temperature during the deposition. The STM images were obtained in a constant current mode with sample biases ranging from −2.0 to +2.0 V and tunneling currents between 0.1 and 0.5 nA. A background plane fit or slope correction was the only post collection processing applied to the images.

Previous STM experiments with pentacene on the Au(111) surface have shown that at approximately one monolayer coverage, rows of molecules are formed.[16] These structures are formed when pentacene molecules line up in a side-by-side orientation. The row structure with a 2 × √31 unit cell, labeled type C in ref 16, was found to be one of the predominate structures formed by pentacene at monolayer coverage. Single molecule wide rows, of or similar to the monolayer structure described above, will be referred to as single molecular width (SMW) rows throughout this report.

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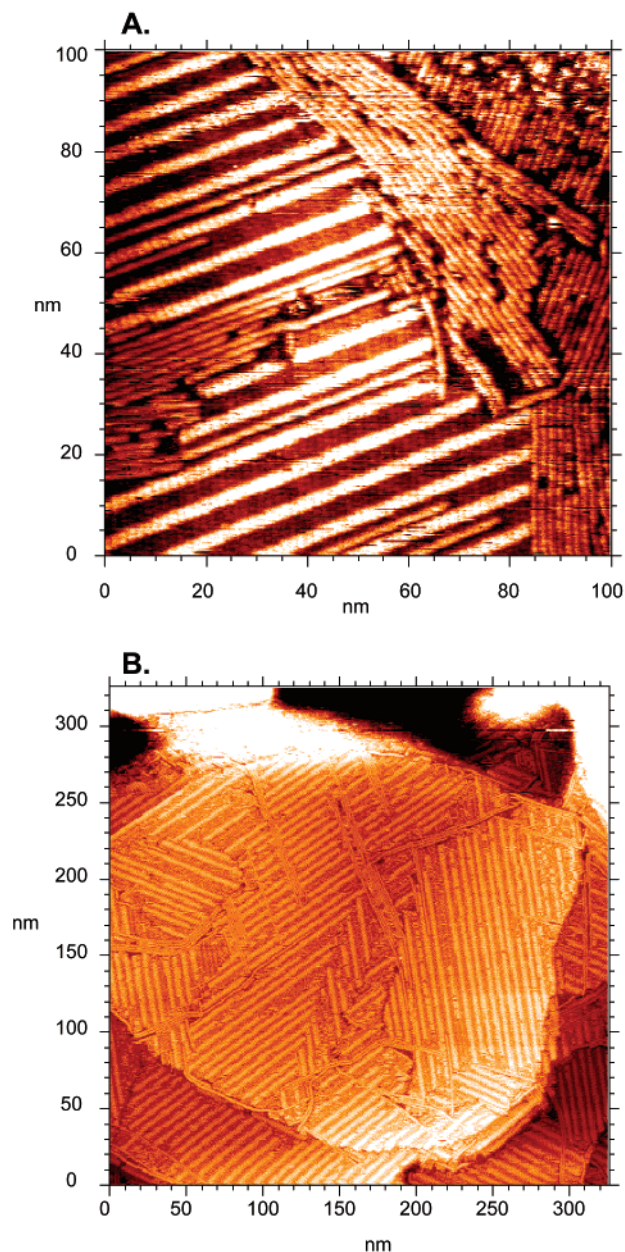
Figure 1. STM images of the widely spaced periodic (WSP) rows of pentacene molecules on the Au(111) surface. 5.5 Å of pentacene was deposited in (A) and the WSP rows are seen on the left side of the image. The $23 \times \sqrt{3}$ Au(111) reconstruction can be seen going nearly perpendicular to the WSP rows. (B) Increased numbers of the WSP rows are observed with a 7 Å pentacene film. Max z-height for image (A) and (B) are 0.198 nm and 0.808 nm respectively.

Upon deposition of slightly more than a monolayer of pentacene[19] (film thickness of 5.5 Å), STM revealed a new surface structure. Figure 1A shows this new structure across the left side of the image. The right side of the image is composed of SMW rows. The separation between the middle of the large WSP rows is 61 ± 5 Å, with the rows at the bottom of the image being spaced further apart than the rows at the top. Between the WSP rows, first layer SMW rows can be seen. These SMW rows run approximately 60° to the WSP rows and are parallel to the SMW rows on the right side of the image. The $23 \times \sqrt{3}$ reconstruction of the

Au substrate can be seen through the overlayer and is oriented nearly perpendicular to the WSP row direction (Figure 1A). Pentacene adsorption does not lift the Au(111) reconstruction as is frequently observed with more strongly bound adsorbate molecules.[4] SMW row structures can also be seen running parallel and between the WSP rows within a second layer.

Deposition of an additional 1.5 Å (total film thickness of 7 Å) of pentacene results in the entire surface being covered with the WSP row structures. The 61 Å center-to-center distance between the structures remains nearly constant at this higher coverage. Domains of these structures completely cover large Au(111) terraces as shown in the 325×325 nm STM image of Figure 1B. The angles between the WSP rows in the different domains are 60 and 120°. Some second layer SMW rows can be seen on the center of the large Au terrace (Figure 1B). These rows tend to run parallel to the WSP rows or between the domains.

Statistical analysis of 607 measurements, obtained from multiple images, determined the average separation of the repeating center-to-center distances between the WSP rows was 61 ± 5 Å. Figure 2A shows a histogram of the center-to-center separation; the distances vary over ±10 Å but peak at 61 Å. One hundred sixty-one measurements of the width of the WSP rows at full width half-maximum (fwhm) averaged 30 ± 5 Å. Figure 2B is a histogram from 76 measurements showing that the angle between the WSP rows and the first layer SMW rows under the WSP rows is 66 ± 7°.

The similar distance between the unit cell of the Au reconstruction (64 Å)[20] and the WSP rows suggested that this row structure could possibly be templated by the substrate. STM images of the WSP rows, with the reconstruction visible under the pentacene overlayer, showed that the WSP rows were not aligning with the reconstruction (Figure 1A). Furthermore, the fact that the angle between the lower layer SMW rows and the WSP rows was slightly larger than 60° indicates that the WSP rows were templated from the structure of the first layer. Epicalc[21] was used to investigate any commensuration between the Au(111) substrate and the pentacene overlayer. The $2 \times \sqrt{31}$ monolayer structure was not found to be coincident with the reconstructed substrate (unit cell I in Figure 3A). We believe a commensurate interaction is achieved through the formation of defects or offsets in the monolayer structure. When the first pentacene molecules of the second layer are deposited, they preferentially adhere to these defect sites. A proposed model of this new pentacene layer is shown in Figure 3A. The formation of a $\sqrt{31} \times \sqrt{(381)}/2$ (16×28.1 Å) (unit cell II in Figure 3A) overlayer structure was found to be coincident with the reconstructed substrate. The angle between the substrate a1 lattice vector (23 Au atoms, see unit cell III in Figure 3A) and the b1 overlayer vector ($\sqrt{31}$ Au atoms, see unit cell II in Figure 3A) was calculated to be 9°, whereas the angle is predicted to be 8.95° by the model.

Cross sections of high-resolution images have shown that the WSP rows are composed of a pair of rows (see Figure 3B) and since the fwhm of the WSP rows is almost two
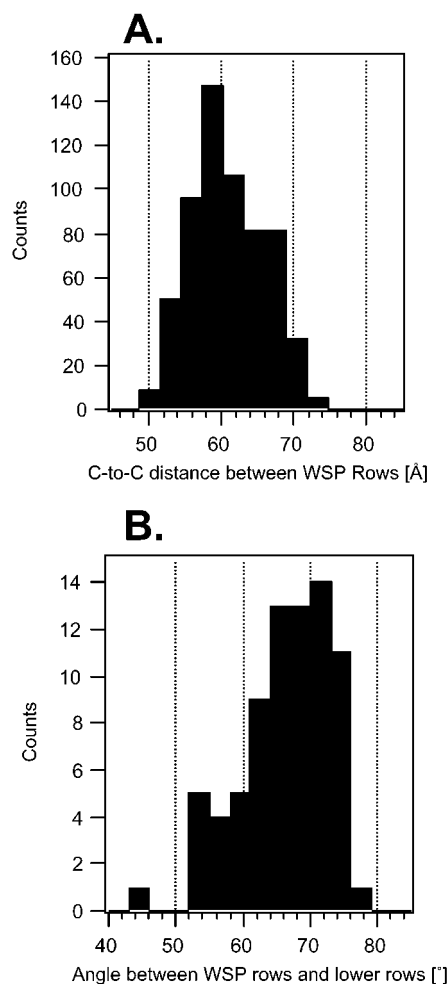
Figure 2. (A) Histogram of 607 measurements of the repeating center-to-center distance between the WSP rows; the average was found to be 61 ± 5 Å. (B) Histogram showing the measured angle between the WSP rows and the first layer SMW rows under them. The average angle was found to be 66 ± 7° from 76 measurements.

pentacene molecular lengths, (30 ± 5 Å) it is expected that the width of each WSP row be composed of a pair of molecules. The paired row structure in combination with the angles between the WSP and SMW rows, discussed above, indicates that the molecules in the WSP rows are aligned with the pentacene molecules of the first layer. At present, the reason for the formation of a paired row is unclear; however, the formation of a coincident overlayer appears to take place by pentacene molecules adhering to defects in the first layer and forming the WSP rows. Tilting of the WSP row molecules to form a herringbone structure is suspected because of the limited amount of space available for the defects. As we continue to investigate this structure, two possible orientations of the molecules in the WSP rows are conceivable. Providing the defects or offsets in the first layer are large enough, tilted pentacene molecules could be inserting through the first layer with an edge on interaction with the Au(111) surface. The molecules in the WSP rows could also be a second layer structure where the pentacene molecules are tilted over the defect sites of the first layer to maximize edge/face interactions. These interactions are similar to those in the herringbone structure that is prevalent
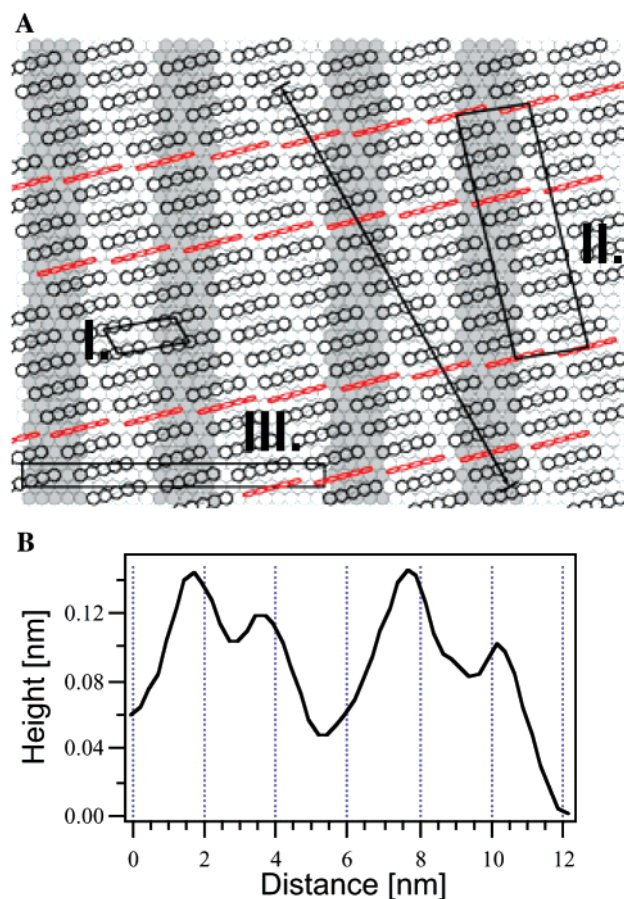
Figure 3. (A) A proposed model for the WSP row structure. The three unit cells are (I) the $2 \times \sqrt{31}$ pentacene monolayer SMW structure, (II) the $\sqrt{31} \times \sqrt{(381)/2}$ WSP row structure, and (III) the $23 \times \sqrt{3}$ reconstructed Au surface (the dark Au atoms represent the location of the reconstruction solitons). A line is also drawn on the model that represents the placement of the STM line profile in 3B. (B) A line profile taken from an STM image that shows the double peaks characteristic of the WSP rows.

in the bulk crystal structure.[22-24] The possibility of pentacene molecules neighboring the WSP rows tilting cannot be ruled out, indicating these periodic rows could be a transition to a bulk pentacene structure.

A widely spaced periodic row structure formed by pentacene molecules on the Au(111) surface has been observed. This unique structure consists of rows of paired molecules spaced approximately 61 Å apart. From careful analysis of the STM images, and calculations of possible commensurate structures using Epicalc, we believe the formation of these WSP rows takes place because of the total free energy gain from commensurate growth on the substrate and bulk pentacene−pentacene interactions. The many structures formed by pentacene on the Au(111) surface at different coverages point to the complexity of this important interface.[16] A detailed study of many lower coverage structures will be presented elsewhere.[25]

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