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Lateral-Standing of the Pentacene Derivative 5,6,7-trithiapentacene-13-one (TTPO) on Au(111): A Combined STM, DFT, and NC-AFM Study

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Abstract

High resolution STM investigation of the pentacene derivative, 5,6,7-trithiapentacene-13-one (TTPO), on close-packed gold surfaces reveal nanoscale structures ranging from molecular chains at low coverage to highly ordered self-assembled molecular monolayers. Robust, thermally stable and highly inert to photo-oxidation, TTPO is a promising organic semiconductor with potential applications in high-temperature photovoltaic devices. When adsorbed on a gold electrode, experiment and first-principle computation reveal a novel 3-D angular assembly of the TTPO molecules, with the long axis of the molecule parallel to the gold surface, distinctive from previously observed pentacene and pentacene derivative assemblies. Structures assembled are angularly dependent on TTPO molecular interactions while commensurate with the underlying gold substrate, allowing for potential tailoring of π-molecular orbital overlap through tilt-angle control. Rigourous non-contact AFM analysis was used to experimentally determine the molecular tilt of the molecule, consistent with calculated and observed structures at room temperature.

Introduction

The self-assembly of organic molecules, such as pentacenes, has technological potential for organic photovoltaic (OPV) applications.[1] Focusing on the self-assembly of organic molecules on metallic surfaces, understanding the organic-metal interface is a means of addressing efficiency problems at the nanoscale for OPV devices. Many scanning tunneling microscopy (STM) studies of pentacene on gold surfaces have been reported,[2–5] but with new pentacene derivatives emerging as promising candidates for organic electronics detailed atomic scale investigation is necessary. The robust and stable pentacene derivative, 5,6,7-trithiapentacene-13-one (TTPO), provides a new and interesting species for molecular self-assembly experiments in ultrahigh vacuum.[6]

When examining the TTPO molecule itself, the pentacene-backbone stands out. Pen-

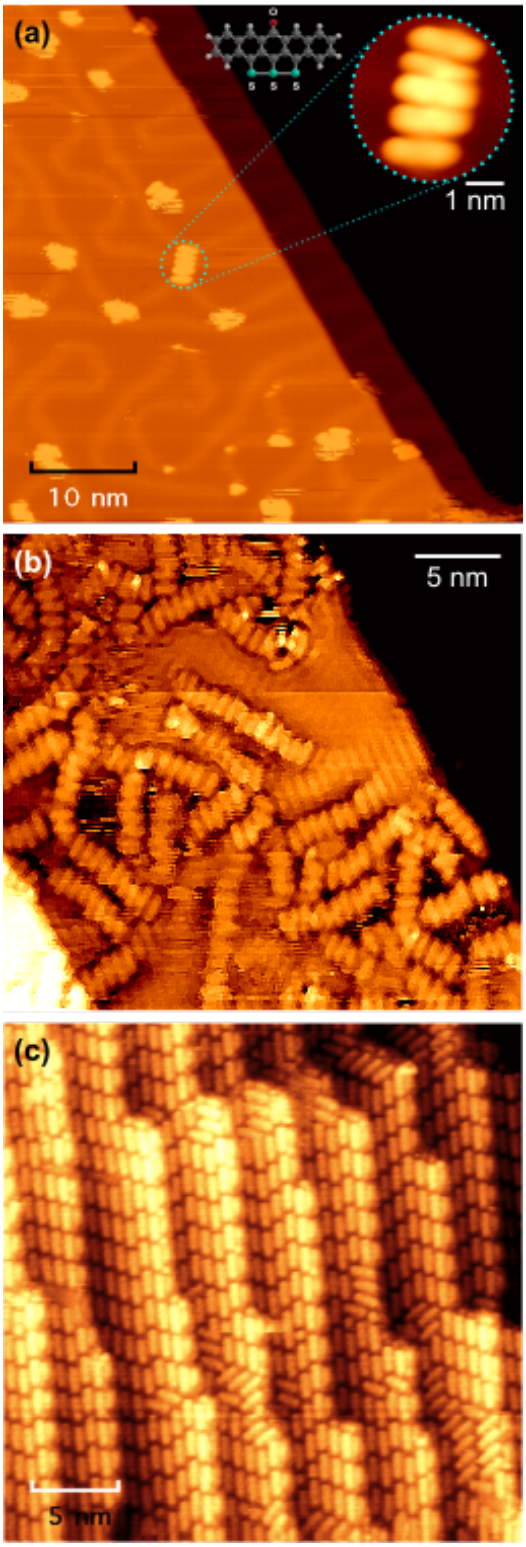

Figure 1: STM images of TTPO molecules on Au(788). (a) Low coverage of TTPO adsorbed at 'elbow' sites of herringbone reconstruction on wide (111) terrace. (0.1 nA, + 0.9 V sample bias) The molecular structure of a single molecule is overlaid next to a close-up image of five TTPO molecules. (b) Long molecular chains of TTPO on wide terrace at sub-monolayer coverage. (0.1 nA, + 1.1 V) (c) TTPO SAM on pristine (788) terraces. (0.06 nA, + 1.2 V)

tacene derivatives have gained interest because they can be tailored to overcome challenges such as low-solubility, photo-oxidative resistance, and adjustable bandgaps. Between the highest occupied and lowest unoccupied molecular orbitals, HOMO and LUMO, respectively, TTPO has an optical gap of 1.90 eV,[6] compare to 2.29 eV for pure pentacene. In particular, TTPO is a tailored pentacene derivative with a very high thermal stability; the crystalline phase melts at 386°C without molecular decomposition. Attached to the pentacene backbone are asymmetrical substituents; an oxygen ketone and a trithia-bridge of three sulfur atoms, seen in Figure 1 (a). These substituents make the molecule polar and facilitate technologically relevant adsorption properties on metal electrodes.

For many sulfur-based small molecules, like thiols, the strong bond between the gold surface and the sulfur atoms in the molecule is expected to dominate the possible self-assembly.[7–10] Often this can be detrimental to long-range ordered assembly, since the sulfur can potentially affix the molecule where it adsorbs, inhibiting diffusion. Adequate balancing of molecule-molecule and molecule-substrate interactions is necessary for successful molecular self-assembly. TTPO is observed to be highly mobile on gold, allowing sufficient diffusion on the surface for self-assembly to occur.

TTPO molecules were deposited onto a single crystal Au(788) substrate and examined with STM at room temperature. Au(788) is a monatomic stepped surface of narrow, 3.9 nm wide, stable terraces. These close-packed terraces feature the herringbone reconstruction of the Au(111) surface, i.e. transition lines or Shockley partial dislocations, separating regions of hexagonal close packed (HCP) and face-centered cubic (FCC) surface layer stacking. Characteristic chevron-like 'V' patterns are formed across the surface with the 'elbow' located at the vertex of the 'V',[11] where a five-fold coordinated gold atom forms the point where two dislocation lines meet, i.e. the core of a threading dislocation. Wide terraces (defects of the ideal (788) surface) are structurally analogous to the Au(111) surface and the narrow stepped terraces Au(788) are known to facilitate long-ranged self-assembly of small molecules.[12] This surface offers insight into mobility across wide terraces, effects of surface reconstructions and

steps, and an ordered substrate 'template' for self-assembly.

Experimental and Computational Methods

Our approach towards molecular self-assembly in ultrahigh vacuum is as follows: The organic molecules are deposited in situ from a powder onto pristine surfaces via physical vapor deposition (PVD). The molecules then diffuse and arrange themselves on substrates in a way that an energy balance between molecule-molecule interaction and molecule-substrate interaction is reached. Data acquisition is completed via STM (SPECS-Aarhus) at room temperature. For this TTPO study, the single crystal gold (788) substrate was atomically clean after repeated cycles of ion sputtering and annealing, and the TTPO molecules were developed and synthesized by our collaborators.[13] The TTPO PVD source was home-built and the molecules were deposited from a green-black powder form. Au(788) is a stable high-index surface, a Au(111) vicinal with a miscut angle of 3.5° towards the $[\bar{2}11]$ direction (composed of close-packed {111}-like steps).[14,15] Pristine Au(788) steps of 3.9 nm terraces can be found as well as wider defect terraces, which all exhibit the Au(111) herringbone surface reconstruction, offering opportunities for self-assembled monolayer formations. TTPO was deposited at coverage less than a monolayer and annealed at room temperature for more than 20 minutes before beginning STM imaging.

The geometry of the TTPO molecules on the surface instigated additional investigation through theoretical modeling. Calculations were run using the Quantum ESPRESSO package[16] with a periodic supercell using local density approximation and Vanderbilt ultrasoft pseudopotentials on a 8-node cluster and a Cray XE6m-200 supercomputer. Calculations had a convergence threshold of at least 1×10^{-6} between self-consistent steps. In ionic relaxations, convergence was achieved when the total energy change between two consecutive steps was less than 0.0001 Ry and all components of all forces were smaller than 0.001 Ry/bohr. In the DFT calculations, the surface was approximated as one fixed, closed-packed

atomic layer of gold for calculations determining molecular structures, and more layers for accuracy were used in determining parameters like adsorption energy. Within the TTPO molecules, all atoms are allowed to relax and move to find their lowest energy configuration. Fermi-Dirac smearing was applied for electronic states near the Fermi-level when the gold slab was present. For determining structure and angles presented, supercells consisted of a single layer of close-packed gold held fixed below a vacuum region of 17 Å. Additional corrections increasing angle of assembly include: convergence threshold of 1×10^{-8}, four layer gold slab (bottom most layer held fixed), and vacuum distance increased to ≈ 30 Å. Calculations of adsorption energy on the gold surface used a grid of 4×8 k-points for cells of 148 and 184 atoms. Marzari-Vanderbilt smearing and a dipole correction ($E = 0$) were used with an increased convergence threshold (1×10^{-8}). Only the bottom most layer of the four layer gold slab was held fixed; the vacuum distance was ≈ 30 Å. To compare the three monolayer offset structures, large periodic supercells of 648 atoms were created. Fermi-Dirac smearing was utilized with a convergence threshold of 1×10^{-8}. The common supercell and consistent parameters allows for increased accuracy in relative energies of the monolayer structures.

Non-contact - Atomic Force Microscopy (NC-AFM) was utilized to experimentally determine the tilt of the TTPO molecules. The NC-AFM[17,18] capability at Brookhaven National Laboratory's Center for Functional Nanomaterials[19] using a upgraded Createc-based low temperature (LT) STM system[20,21] was used for sample preparation and imaging. We directly deposited small amounts of TTPO on a Au(111) sample at 5 K base temperature, rising temporary but staying below 15 K, while briefly opening the cryostat door for deposition. TTPO was evaporated thermally from a small transferable source consisting of a dusting of TTPO on a SiO surface heated by direct current. Low coverages of TTPO were annealed to 100 °C for 5 minutes while inside the cryostat shield. The sputtered PtIr tip was prepared by picking up a CO molecule as deposited on the Au(111) surface via close proximity scanning. The DFT calculated TTPO structures were used as model input for a NC-AFM simulation assuming a CO functionalized tip. The mechanical-probe-particle

model was used for simulation[22,23] and implemented in GXSM.[20,21] STM overview images were taken to identify TTPO assemblies. Of selected TTPO assemblies, constant height NC-AFM force maps at 10 pm vertical spacing intervals were recorded to assemble a volume force map over the molecules. Volume force maps were transformed into iso-force surfaces to reveal actual Z-topography to determine the characteristic molecule tilt. A scan mode developed and implemented real time with GXSM for taking constant height tunneling current images simultaneously with frequency force shift measurements utilized a modified fuzzy current height regulation with a current compliance setting which effectively retracts the tip to safety when moving over areas of disruptive imaging.[20,21] This scanning mode was crucial to imaging due to the close proximity required for discerning between the three dimensional aspects of this molecule assembly.

Results

Self-assembled Stuctures

At low coverages, the TTPO molecules are highly mobile on the wide surface terraces until they interact with a herringbone reconstruction elbow site, energetically favorable locations for molecular adsorption. Nucleating at the reactive elbow sites, the TTPO molecules start to self-assemble with molecule-molecule interactions overcoming molecule-substrate interactions. It is not until a stable molecular configuration is reached that the TTPO molecules can be imaged at room temperature. This is evident in Figure 1 (a), where bright agglomerations of TTPO molecules are blurred except for the one stable molecular configuration of a chain of five TTPO molecules, see circled region in Figure 1 (a). The blurred agglomerations are groups of molecules that are still moving around before reaching the stable energetic minima observed for the molecule chain. Chains form of molecules slightly offset from one another, with intermolecular forces between molecules stabilizing these structures. Transitioning from diffuse individual molecules to molecular chains, the onset of self-assembly can be imaged

with the effects of all competing forces at work.

On wide terraces, increased adsorption of TTPO molecules results in the formation of longer molecular chains of varying lengths, Figure 1 (b). The seemingly flat area is not the underlying gold surface but in fact disordered molecular TTPO. It is likely the size of the terrace mitigates the maximum length of the chains, and with large terraces longer chains may form. The disordered direction of chain growth will also affect the chain lengths, but possibly annealing or deposition at an elevated substrate temperature could overcome this and lengthen the chains.

Lastly, a highly ordered self-assembled monolayer (SAM) of TTPO molecules forms on Au(788) at room temperature, Figure 1 (c). The molecules orient along the length of the step edges, creating order across the steps, differing from the molecular chains observed on the wide terraces. On the narrow (788) terraces, rows of molecules assemble in very similar offset structures, Figure 2, with observed shifts in direction between adjacent rows or terraces.[24]

The monolayer structures observed on the Au(788) surface are commensurate with the underlying gold substrate. Experiments also suggested a three-dimensional component to the self-assembled structures which can not be adequately examined with STM alone. Density Functional Theory (DFT) methods were utilized to computationally determine energetically favorable TTPO adsorption geometries on close-packed gold surfaces. The calculated structures accurately represent the experimentally observed molecular chain structures and monolayer.[24]

The TTPO molecule is calculated to assemble tethered along three close-packed Au atoms, Figure 3 (a). For common configurations of TTPO molecules on close-packed terraces, consecutive molecular rows are structurally correlated by one of two commensurate offsets, Figure 3 (b). The bottom blue and top yellow S atom, plus the two S atoms in the row above or below, mark Offset 1 and Offset 2 in Figure 3 (d) and (e), respectively. Both correspond to positions for which the sulfur atoms in the molecule are binding above surface Au atoms, with the center S atom on-top and the other two slightly tilted inward; see Figure 3 (a) and

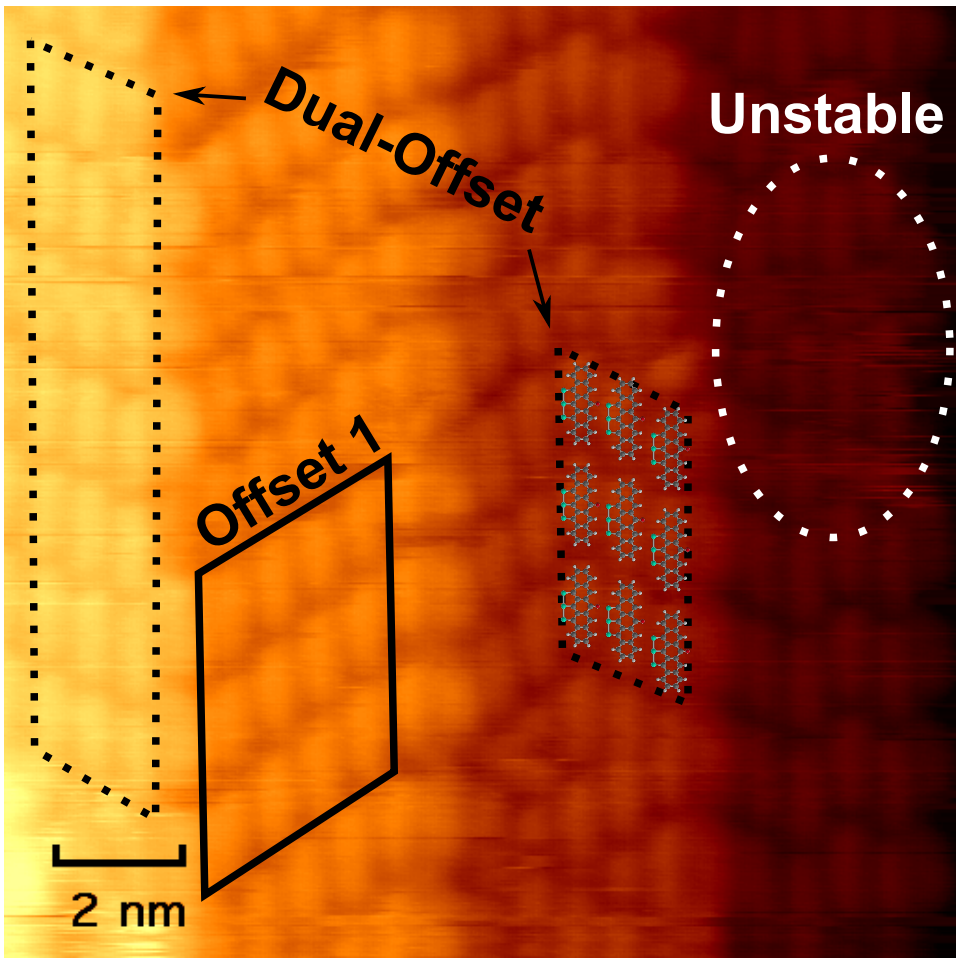

Figure 2: STM image of four terraces of Au(788) surface. Domains of Dual-Offset and Offset 1 structures are highlighted, emphasizing changing offset directions in monolayer. (0.06 nA, + 1.05 V sample bias)

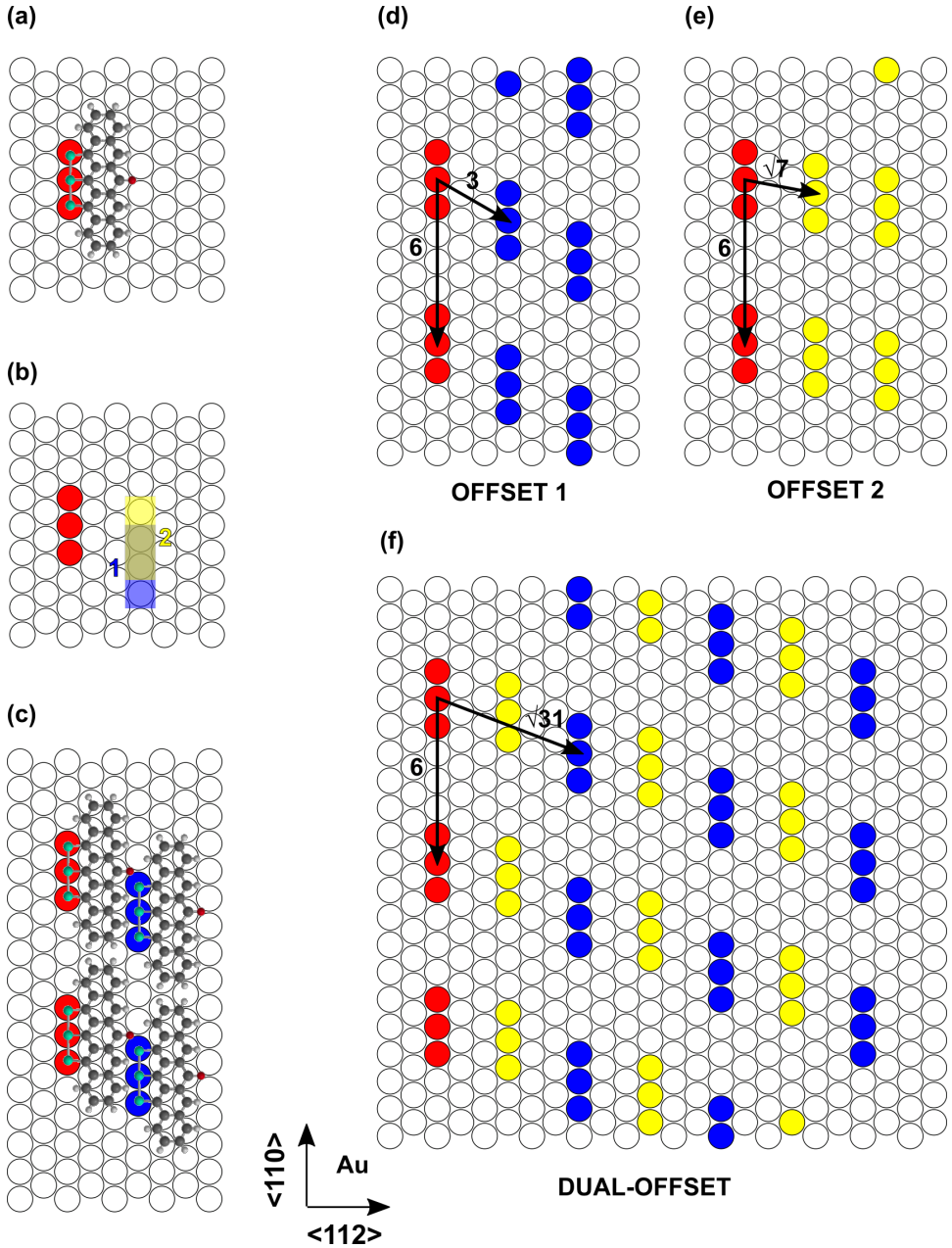

Figure 3: Schematic of the close-packed Au(111) surface. TTPO structures commensurate with the surface are highlighted based on where the sulfur-substituent is tethered to the Au surface. (a) S atoms of TTPO molecule (overlaid) span three closed-packed Au atoms (red). (b) TTPO molecule in next consecutive row ($3\sqrt{3}/2$ Au atoms) spans one of two offset positions (yellow or blue). (c) TTPO molecular overlap of consecutive rows. (d) Offset 1 (blue), 6×3 structure. (e) Offset 2 (yellow), $6 \times \sqrt{7}$ structure. (f) Dual-offset structure, alternating positions of Offset 1 (blue) and Offset 2 (yellow), $6 \times \sqrt{31}$ structure.

(c); their difference is related to the close-packed distance between gold atoms. The Dual-offset structure, shown in Figure 3 (f) is composed of both offsets, i.e. alternating Offset 1 and Offset 2. The Dual-offset and Offset 1 are noticeable as domains in STM images of TTPO monolayer structures; see Figure 2. DFT calculations of the offset structures were undertaken to unravel the driving forces and the possible variation of molecular row assemblies. The calculated SAM structures found for stepped and unstepped gold surfaces are consistent for molecules away from the immediate step edge.

Comparison between the total energy of the three offset structures is given in Table 1.

Table 1: Energy differences between DFT calculated monolayer structures on flat close-packed Au

Compared Structures	Δ E (eV)
Offset 1 - Dual-offset	0.1016
Offset 2 - Dual-offset	0.0988
Offset 1 - Offset 2	0.0028
$k_B T$ at $T = 20°C$	0.0250

Calculations revealed that the Dual-offset structure is more energetically favorable than the two pure offset structures. The two composing structures have an energy difference an order of magnitude less than the thermal energy of molecules at room temperature, which may explain molecular switching between structures seen in STM images at room temperature. In terms of probability, *Dual-offset* > *Offset 2* $\gtrapprox$ *Offset 1* for the formation of SAMs.

Molecular Tilt

All offset and molecular chain structures, as seen in experiment and verified with computation, require that the TTPO molecules be tilted laterally on the surface. Now, angled-molecule assemblies on surfaces are not uncommon, i.e. alkanethiols on gold[7–10] and picene on Ag,[25] but to the best of our knowledge, no examples exist for the lateral assembly of a rigid sulfur-based pentacene derivative. Usually pentacene and its derivatives lie-down flat

on metals[3,12,26–28] or stand-up (long axis of the molecule perpendicular to the substrate, possibly with a very small cant angle) on semi-metals and insulators;[27,29–31] see Figure 4. The TTPO molecule assembles with the sulfur bridge substituent angled down towards the gold surface, with a small angle between the molecular plane of TTPO and the gold surface; the pentacene backbone remains parallel to the surface. This lateral standing of the molecule is unique to TTPO assembly on gold. Considering the known width of Au(788) terraces and the physical size of the molecule, for assemblies where TTPO molecules lie-down completely flat on gold, only five molecules could be expected to fit across the width of the terraces. However, in experimental STM images, six molecules can be seen across an Au(788) terrace, suggesting that this increased packing is due to the 3-D aspect of the assembly. This position is similar to packing in bulk pentacene crystals, but is unusual on a metal surface. Variations in the structure of the TTPO derivative may allow for fine-tuning of the TTPO cant angle and ultimately improved charge carrier transport due to increased $\pi - \pi$ overlap.

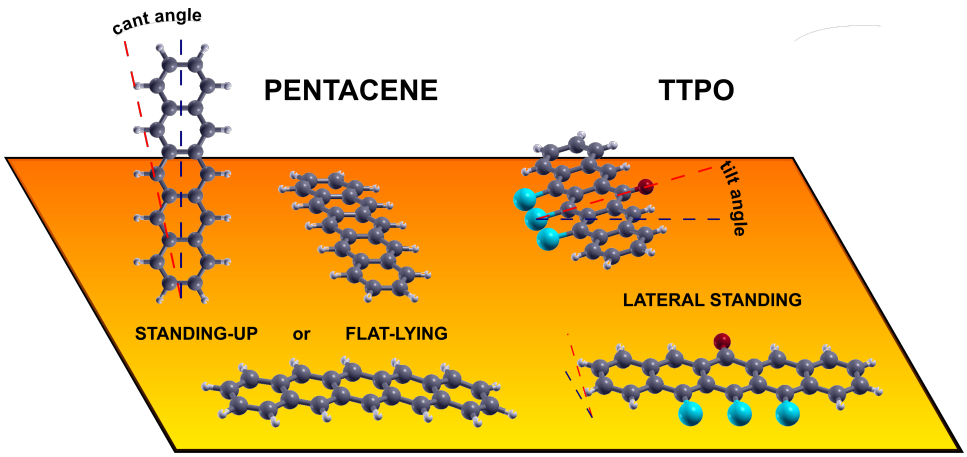

Figure 4: TTPO is the first pentacene-based molecule that adsorbs neither standing-up nor flat with its benzene rings oriented parallel to the surface. Relaxation of pentacene on gold results in the molecular bending seen here, whereas TTPO is calculated to have a more rigid structure with minimal bending.

The determination of the angle of assembly of TTPO molecules was possible with the help of DFT calculations. The Au-S attraction likely facilitates the rotation of the molecule, and the angle of assembly is dependent on the surrounding molecules. For a lone TTPO

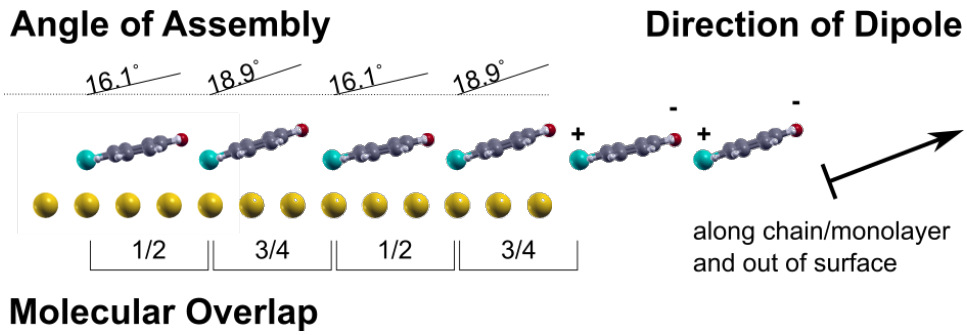

Figure 5: The angle of assembly in the Dual-offset structure alternates between the half molecule overlap associated with Offset 1 and the three-quarter overlap of Offset 2. The tilted dipole vector of a molecular chain or monolayer would point along the structural direction, away from the surface.

molecule adsorbed on Au(111), the angle was calculated to be about 11° on one layer, and with additional corrections; e.g. four layers Au, dipole correction, and increased conversion threshold, the tilt angle increases by about 3°. For the molecular chains and monolayers, depending on the overlap, the angle of assembly increases to either ∼16.1° or ∼18.9°; see Figure 5. For calculations on four Au layers, TTPO molecules adsorb with the sulfur bridge substituent 2.50 Å above gold surface atoms.

To conclusively demonstrate that TTPO molecules are angled on the gold surface, NC-AFM capabilities were employed in a separate experiment conducted at 5 K. Before deposition, the feasibility of TTPO as an experimental subject was verified through simulations,[20–23] verifying anticipated image contrast and a reasonable signature of the tilt across the pentacene core short axis, uninhibited by substituents. Very low coverages of TTPO are seen in Figure 6. In this overview STM image, pairs of TTPO molecules angled towards one another are the dominant structures at this coverage. These pairs can come together to form longer chains. Odd numbered chains may contain one or more pentacene quinone molecule, an impurity of the TTPO sample. Figure 7 is a close up constant height NC-AFM force map on two of the TTPO pairs; the underlying pentacene backbone is clearly visible as well as the oxygen and sulfur-bridge substituents. To reconstruct the molecule adsorption geometry, it is necessary to convert the frequency shift or force data acquired into a real space geometry. This is achieved by converting the force map, Figure 7 (c), for slices at constant height, into

an iso-force topography (classic constant frequency shift). This real space geometry can be used to measure height differences.[32] This is particularly true when examining geometrically equivalent molecular structures, such as a plain benzene ring; but caution must be taken when looking at structures involving substituents or additional atoms. Utilizing the outer most ring of the TTPO molecule, the angle relative to the surface is approximately 11°.

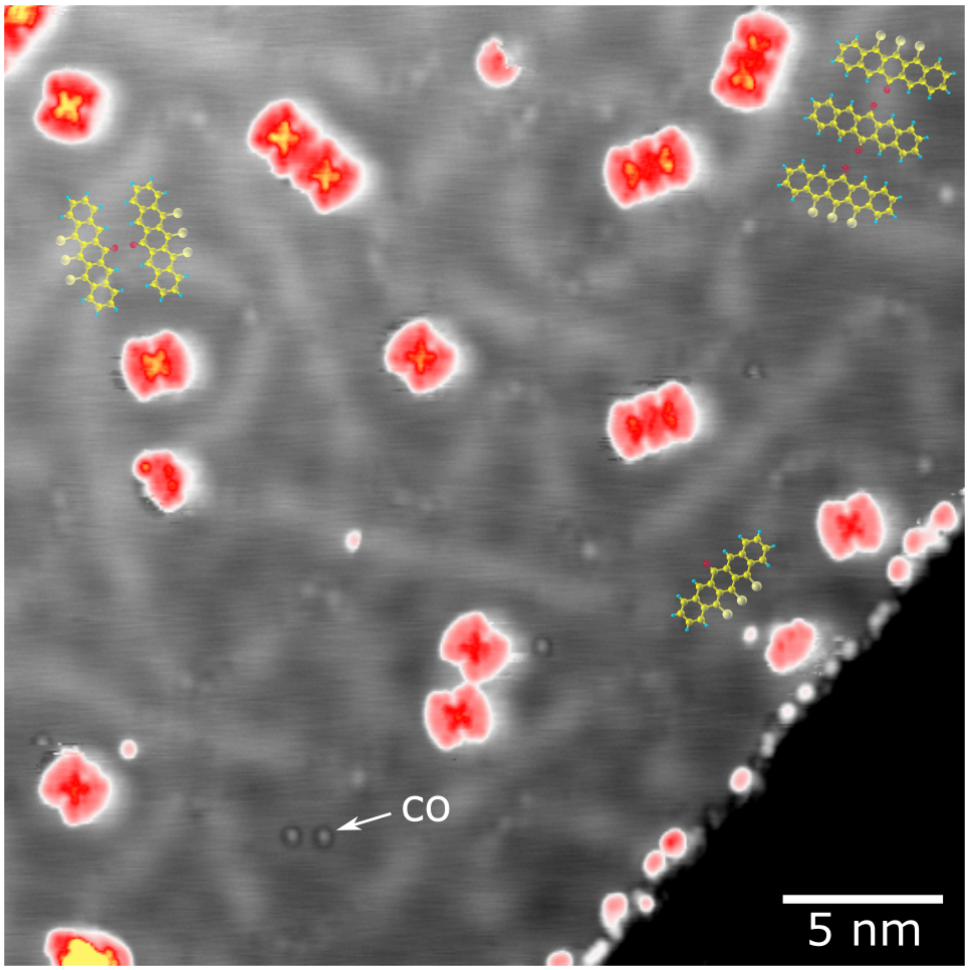

Figure 6: Low-temperature STM image showing prevalence of TTPO molecules to form 2-member units. Three member units incorporate pentacene-quinone. Single TTPO molecules are seen near defects and step edges, inferior locations for AFM measurements. CO used to selectively terminate the tip for NC-AFM can be seen on the bare Au surface. (0.01 nA, 0.10 V)

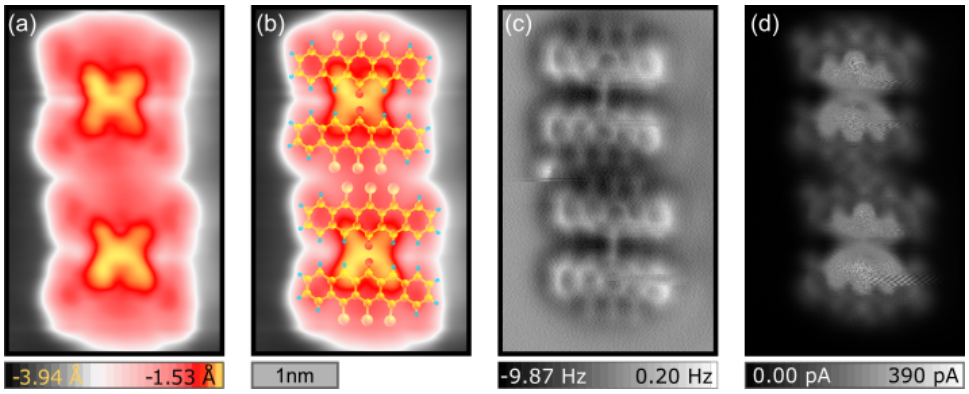

Figure 7: TTPO molecules form two member units at 5 K, where molecules orient head on forming an arch; units combine into longer even numbered chains. (a) 5 K STM image of a four TTPO chain, two arched units. (0.01 nA, 0.10 V) (b) Molecular schematic overlaid on image. (c) NC-AFM frequency shift image depicting inter-molecular resolution of TTPO molecules; constant sample bias 50 mV, 70 pm amplitude setpoint, and CO functionalized tip. (d) Constant height tunneling current image acquired simultaneously with (c) at -2.9 Å. The speckled pixels over the top-most area of the molecules seen in (d) are from utilizing a modified fuzzy constant height regulation with a current compliance setting to move the tip when conditions become disruptive.[20,21]

Discussion

The self-assembled monolayer which forms on the Au(788) surface is complex in structure. The Dual-offset, Offset 1 and Offset 2 are all viable monolayers that could form according to DFT calculations. The fact that Offsets 1 and 2 are so close in energy is a possible explanation for why the parallel rows on the steps have so many configurations; see Figure 1 (c). The effect of the varied configurations on the surface electronics is unknown, but no matter the offset, the molecules overlap which is conducive to charge transport. It is possible that with controlled annealing, all of the domains seen on the Au(788) steps could shift into the most energetically favorable Dual-offset structure.

Hexathiapentacene (HTP) and 6,13-bis (methylthio)pentacene (BMTP) are two sulfur-based pentacene derivatives that are substituted symmetrically about the pentacene backbone, HTP even has the same trithia-bridge as TTPO. They form wires where molecules stack face-to-face increasing π-stacking.[33–35] These wires, however, are essentially nanocrystals which are vapor or solution deposited for use in devices. The wire growth is not directly dependent on the surface they are ultimately deposited. TTPO can also form wire-like,

columnar structures in the bulk, but the molecular chains grown on gold are different. Growing tethered to the substrate, it is not a far stretch to assume it may be possible to engineer a template for which TTPO chains can be grown from one defect atom site to another. A truly one molecule wide nanowire could be formed using TTPO molecules on an appropriate surface. Because these molecules form chains where the molecules overlap, π-stacking across the chain will be beneficial for charge transport. The theoretical study by Yong Hu, et al. emphasizes the importance of face-to-face stacking of TTPO molecules (and derivatives) for beneficial charge transport properties.[36] Complimentary to the presented study, molecular dynamics simulations modeling TTPO chain formation on close-packed gold found an activation energy for diffusion of 0.142 eV,[37,38] an order of magnitude higher than pentacene[39] and thermal energy at room temperature. With TTPO observed to diffuse at room temperature, the mobility observed is not purely thermally-activated diffusion.

The angular assembly and subsequent overlap of TTPO molecules increases π-stacking between adjacent molecules in both the molecular chains and the SAM. Additionally, the possibility of an Au-S bond and the fact that the TTPO molecule is dipolar has implications for the band alignment between the molecule and the surface. The resulting tilted dipole vector also has a significant component parallel to the surface. The dipole nature of the molecule will affect the potential barrier across the interface and result in a modified work function, as in the case of thiols on Au.[10] More detailed studies are needed to determine the charge transfer at this novel metal-organic molecular interface.

It is non-trivial to determine three dimensional structures with scanning probe techniques.[40] The room temperature aspect of the STM study of TTPO on Au(788) greatly complicates this. Non-contact AFM at cryogenic temperatures offers inter-molecular resolution into the structure of TTPO molecules adsorbed. Direct observation of the height differences between identified structural components of the molecule allowed for confirmation that TTPO molecules do in fact tilt on gold surfaces as suggested by surface template constraints and calculated geometries. The small angles calculated between 11° and 18°

for TTPO in a number of assemblies correspond well with the 11° determined in the AFM experiment.

The error in the experimental tilt angle is difficult to determine. Due to the time intensive nature of acquiring data for force iso-surfaces, only a small sampling of tilt angles could be acquired. As to the instrumental error in this method, it should be considered minimal in that iso-force topography images from simulated data can be used for comparison. Apart from the NC-AFM examination, the majority of the data was collected at room temperature. At 5 K and very low coverages, clusters of two TTPO molecules orient with ketone substituents towards one another. This geometry we originally believed unfavorable due to the counter alignment of the molecular dipoles, but it is the predominant structure seen in the low-temperature AFM study of single molecular adsorption studies. Now for coverages less than a ML, it may be possible that chain structures seen at room temperature also contain these paired units; Figure 1 (a). However for the monolayer structures seen on Au(788) at room temperature, the paired units seen at 5 K are not present as in that case the apparent offset between adjacent rows would be missing; Figure 1 (c). Thus the arrangement of TTPO molecules observed in the AFM study of single molecular structures allows for the direct observation of the adsorption tilt angle while it is compatible with the proposed model for the room temperature monolayer structures.

We demonstrate NC-AFM as a viable method of determining 3-D geometries of small angled molecules. TTPO is uniquely suited to determining the molecular tilt angle for a number of reasons: (i) The molecule is rigid, with very little molecular bending along the pentacene backbone (as compared to pentacene itself on gold, see Figure 4); (ii) The molecular tilt for TTPO at low coverages is expected to be shallow such that the molecule would have a large 2-D footprint on the surface; (iii) The ketone and sulfur bridge substituents do not adversely interfere with the image quality or the CO terminated tip. Besides three dimensional analysis, NC-AFM allowed for molecular identification of pentacene-quinone within some TTPO structures not resolvable in STM images.

Conclusions

In summary, this experimental and computational study of TTPO molecules on gold surfaces offers insight into the self-assembly of single mobile molecules to the formation of molecular chains and an ordered monolayer. TTPO molecules adsorb on gold in a lateral position in an angular assembly. The sulfur-bridge substituent is angled down towards the gold and the oxygen substituent away. The angle of assembly is dependent on the overlap between surrounding TTPO molecules. The angular assembly and subsequent overlap of TTPO molecules increases π-stacking between adjacent molecules. This lateral tilting of the molecule is unique and the first observed for pentacene derivatives, offering potentially new self-assembled monolayer properties. NC-AFM proved a viable method of experimentally determining small angle tilt of this rigid molecule.

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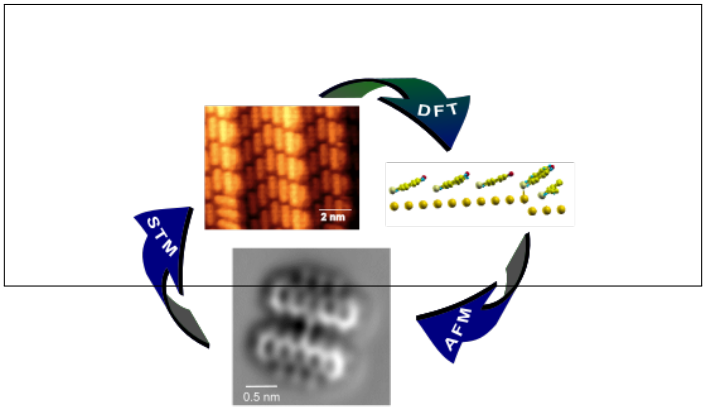
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