SPECIAL SECTION

Ordered Assembly of α-Quinquethiophene on a Copper Oxide Nanotemplate

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The organic semiconductor α-quinquethiophene (T5) is used as the active layer in organic field-effect transistors. We have investigated the adsorption of T5 on the (110) surface of copper and on the CuO nanotemplate formed by the high-temperature exposure of Cu(110) to molecular oxygen. The results were obtained with high-resolution scanning tunneling microscopy (STM) under ultra-high-vacuum (UHV) conditions. The adsorption of T5 on copper is an important model system because it mimics the active-layer–electrode interface in organic devices. The molecules were observed to adsorb onto both the pristine Cu(110) surface and the CuO nanotemplate, showing a greater affinity for the pristine copper surface. Surprisingly, however, the T5 molecules assembled with a much higher degree of long-range order on the oxygen-passivated portion of the surface.

1. Introduction

Thin films of organic π-conjugated molecules are of great interest as active layers in devices such as field-effect transistors,[1,2] light-emitting diodes,[3] and solar photovoltaic cells.[4] These films allow for the investigation of fundamental physical phenomena, such as charge transport, charge injection, and interface phenomena in organic layers, that critically depend on structure and morphology.[5] To this end, a thorough understanding of the growth process is needed.
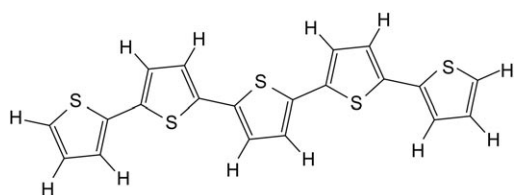
Particularly relevant in establishing film properties are the early stages of growth, which reveal information on the interactions between individual molecules and a substrate of choice. Although the adsorption of large organic molecules (average molecular weight $M_w \approx 1000$ amu) on metallic surfaces is beginning to be understood,[6,7] the number of investigations into the fundamental growth and adsorption of smaller molecules (typically used for organic devices) is still limited.[8–14] More common is the growth of organic thin-film semiconductors carried out on substrates of technological interest (e.g., SiO_2) and characterized by atomic force microscopy (AFM), often combined with X-ray diffraction (XRD) or reflectivity.[15,16]

Oligothiophenes are a versatile class of compounds widely used as active layers in electronic and optoelectronic devices.[17–21] Within this family a molecule of particular interest is α-quinquethiophene (T5), which consists of five α–α-linked thiophene aromatic rings (Scheme 1). T5 is more soluble in organic solvents than its longer homologue sexithiophene (one of the most studied organic semiconductors), which makes it attractive for solution processing. Its highest measured field-effect hole mobility is about

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Scheme 1. Molecular structure of α-quinquethiophene, T5.

$0.07\ cm^2\,V^{-1}\,s^{-1}$.[22] AFM and XRD have shown that T5 gives rise to continuous polycrystalline films when grown on SiO_2.[23,24] AFM and scanning electron microscopy (SEM) observations have shown that T5 forms ordered films on TiO_2.[25] Here, we compare the adsorption properties of T5 on Cu(110) and oxygenated-Cu (O–Cu) templates by means of scanning tunneling microscopy (STM) under ultra-high-vacuum (UHV) conditions.

The Cu(110) surface is particularly attractive in the study of the adsorption of organic molecules because of both its high anisotropy and its strong affinity with aromatic rings, which encourage molecules to lie flat. Moreover, a controlled oxidation of the Cu(110) surface can induce a surface reconstruction[26] that under particular experimental conditions leads to a striped, periodic supergrating consisting of alternating rows of Cu(110) and (2×1)O–Cu.[27,28] This nanoscale template has already been successfully used to pattern nanostructures of organic molecules.[29,30] A few STM studies of the growth of organic semiconductors on pristine Cu(110), namely, perylene,[9,11] tetracene, and pentacene,[10] have already been reported.

The study of the adsorption of organic molecules on metal surfaces is an important paradigm for exploring the self-assembly of organic semiconductors from a fundamental point of view.[31–36] At the same time, it yields precious information on organic–inorganic interfaces and in particular on the adsorption properties of such molecules with materials used as electrodes in organic devices.

In this investigation we find that, despite the higher affinity with pristine Cu(110), the T5 molecules adsorb on both the clean and the oxygenated Cu(110) surfaces. On the copper oxide nanotemplate, the higher sticking probability of T5 on Cu drives the ordered assembly of T5 on bare copper stripes less than 10 nm wide. On the oxygenated regions of the CuO template, T5 self-assembles with a much higher degree of long-range order than on the pristine Cu-(110) surface.

2. Results and Discussion

2.1. Adsorption on Pristine Cu(110)

STM images of T5 molecules adsorbed on Cu(110) with an increasing degree of coverage are shown in Figure 1a and b. The chemistry of the surface encourages the molecules to lie flat so as to optimize the interaction between the aromatic rings and the underlying copper surface. This is in agreement with data reported in the literature and is
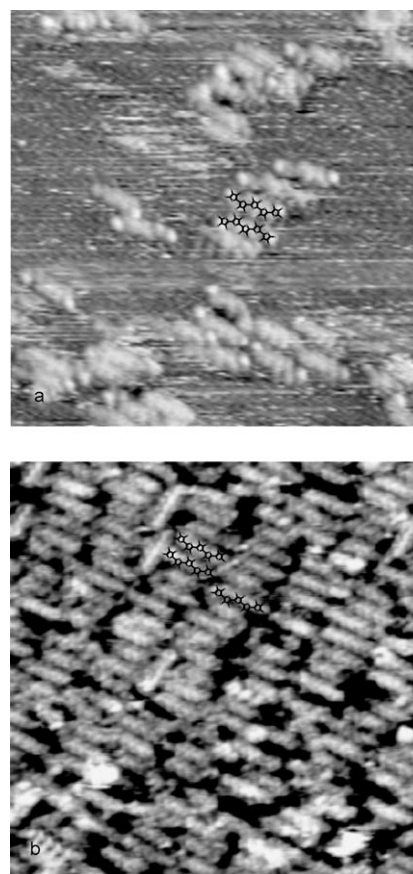

Figure 1. STM image of the adsorption of T5 on Cu(110) with an increasing degree of coverage. Imaged area $A = 20 \times 20\ nm^2$. Tunneling parameters: a) Bias voltage $V_t = 619$ mV, tunneling current $I_t = 1.10$ nA, coverage: 0.35 monolayers (ML). b) $V_t = -758$ mV, $I_t = 0.905$ nA, coverage: 1 ML.

consistent with a situation where the growth morphology is determined by substrate–molecule interactions rather than molecule–molecule interactions. Due to the anisotropy of this substrate, T5 molecules tend to align along the close-packed [1$\bar{1}$0] direction of the surface. The molecules appear as elongated structures with bright protrusions, which correspond to a single thiophene ring. This is clarified by the overlay of a molecular model on individual molecules in the STM images (see also the line profiles given in Figure 2a and b).

Figure 1b demonstrates that T5 did not form a perfectly ordered monolayer on Cu(110); in fact, 90–95% of the molecules aligned along the [1$\bar{1}$0] direction and the remainder aligned along the [001] direction. The molecules along the [001] direction only appeared when the monolayer was almost complete. The close-packed direction is, thus, the most energetically favorable for adsorption. T5 molecules lying along the [001] direction fit into the monolayer only where there was empty space in order to optimize the overall packing. A similar behavior has been observed for tetracene and pentacene adsorbed on Cu(110).[11]

Figure 2 shows the overlay of a molecular model on a magnified region of Figure 1b together with length and width line profiles. The length line profile clearly shows five
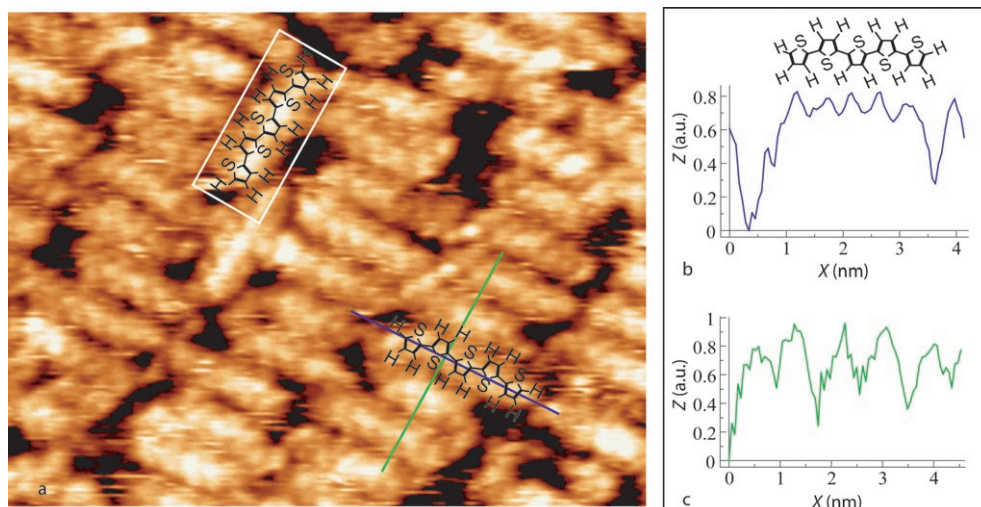
Figure 2. Left panel: a) STM image of T5 at full monolayer coverage. At saturation, T5 is found to adsorb with two geometries: parallel (crosshairs) and perpendicular (rectangle) to the close-packed [001] direction of the lattice. Right panel: length (b) and width (c) line profiles and molecular model for full monolayer coverage. Length (blue) and width (green) line profiles are determined to be ≈2.3 and ≈0.7 nm, respectively. Imaging parameters: $V_t = -758$ mV, $I_t = 0.905$ nA, $A = 11.9 \times 9.2$ nm^2.

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peaks, each corresponding to a thiophene unit and gives a length of 2.3 ± 0.2 nm for each T5 molecule. The width line profile gives a value of 0.7 ± 0.1 nm. Both values agree well with the expected model estimates of ≈2.0 and ≈0.8 nm, respectively.[24]

2.2. Adsorption on the CuO Nanopattern

Figure 3a shows an STM image of the Cu/O–Cu periodic nanopattern obtained after the controlled oxidation of the Cu(110) surface at 623 K. The pattern consists of alternating rows of Cu(110) and (2×1)O–Cu. Rows of oxygen molecules grow along the [001] direction, forming a (2×1) structure. The oxygen stripes are 6–7 nm wide, separated by Cu(110) regions of a similar width. The width of the stripes
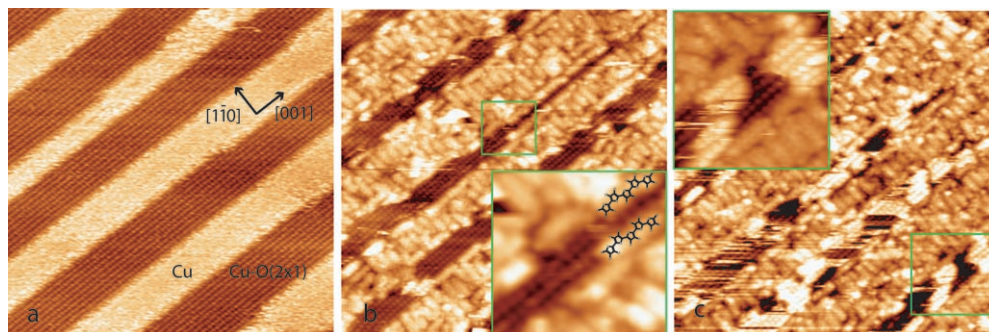
can be adjusted, and to some extent controlled, by varying the oxygen pressure and the substrate temperature.[28–30]

Figure 3b and c displays STM images of T5 growth on the Cu/O–Cu template with increasing dosage. The molecules adsorb preferentially on the Cu(110) stripes, in agreement with results previously reported for large organic molecules.[29]

In the middle of the Cu-(110) stripes the molecules align along the close-packed direction of the surface (as seen for the majority of the molecules in Figure 1). At the Cu/O–Cu interface the molecules tend to align parallel to the direction of the stripes (see insets of Figure 3). This observation indicates that the molecules also adsorb on the O–Cu regions. To investigate this further, the nanopattern was exposed to a higher dose of T5. This resulted in the adsorption of T5 molecules even towards the center of the oxygenated stripes (Figure 3c). Here, the molecules aligned along the close-packed direction of the O–Cu regions (i.e., perpendicular to the majority of the molecules adsorbed on Cu(110)) and lay flat on the substrate as they had done on the Cu(110) substrate.

The growth of T5 on the Cu/O–Cu nanopattern reflects the higher sticking probability of T5 on the pristine Cu(110) surface. At low T5 doses (0.2 monolayers (ML), as determined by STM) the molecules adsorb preferentially on pristine Cu(110); at higher doses (0.4 ML) they also adsorb on O–Cu. Adsorption of T5 molecules on O–Cu occurred after the saturation of the pristine Cu rows and started on the border with the Cu(110) rows. This occurs because the molecules impinging on the O–Cu surface diffuse until they find an energetically favorable nucleation site that is provided by the molecules adsorbed on pristine Cu(110).

Figure 4 shows an STM image of T5 adsorbed on the Cu/O–Cu nanopattern. During scanning, the contrast in the image suddenly inverted due to a change in the tip state. This was presumably
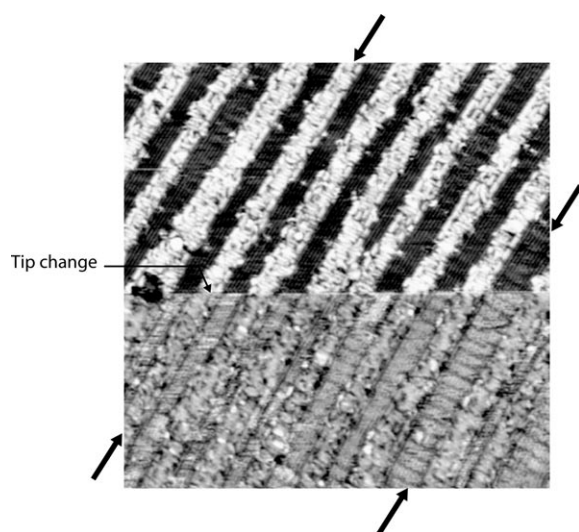

Figure 3. a) STM image of the Cu/O–Cu nanopattern (partial (2×1) reconstruction) obtained by exposing the Cu(110) surface to 0.5 langmuir (L) (1 L = 10^{-5} Torr s^{-1}) of oxygen at 623 K. Imaging parameters: $V_t = -645$ mV, $I_t = 1.06$ nA, $A = 34 \times 34$ nm^2. b) 0.4 ML T5 coverage of the nanopattern. $A = 34 \times 34$ nm^2. The inset ($A = 5.9 \times 5.4$ nm^2) shows a high-resolution image of T5 adsorbed on the border between the Cu(110) and the O–Cu regions. Imaging parameters: $V_t = -2866$ mV, $I_t = 1.06$ nA. c) As the T5 coverage increased to 0.8 ML, the molecules began to adsorb in the middle of the O–Cu regions. A highly resolved image of the islands is shown in the inset ($A = 8.1 \times 8.1$ nm^2). Imaging parameters: $V_t = 526$ mV, $I_t = 1.06$ nA, $A = 34 \times 34$ nm^2.

Figure 4. Saturation coverage of T5 on both the Cu(110) and O–Cu stripes of the nanopattern. During scanning the tip underwent a change of state, as inferred by the change in contrast. In the lower half of the image, the adsorption of T5 on the O–Cu regions is better resolved (indicated by the arrows to the left of the image). In the upper part, the molecules on Cu(110) are more clearly resolved (indicated by the arrows to the right of the image). Imaging parameters: $V_t = -475$ mV, $I_t = 1.06$ nA, $A = 80 \times 80$ nm^2.

caused by a T5 molecule, inadvertently picked up by the tip itself (alternatively, the tip released a T5 molecule that had previously adsorbed at its apex).[37] In the lower part of the image, the T5 molecules on the O–Cu regions appear to adsorb onto the surface with a higher degree of order compared to the pristine Cu(110) surface (indicated by arrows to the right of the image). This observation led to an investigation of T5 adsorption on a template that consisted of very wide O–Cu regions (≈ 40 nm) and very thin Cu stripes (≈ 3–5 nm). This enabled us to study T5 adsorption of a nearly saturated oxygen-passivated Cu(110) surface. However, note that Figure 4 shows that a single monolayer of T5 extends over the entire nanotemplate. A unique nanopattern is obtained because T5 adsorbs on both types of template surface and the two surfaces drive T5 to adsorb with geometries perpendicular with respect to one another.

2.3. Adsorption on the (2×1)O–Cu Surface

STM images of T5 molecules adsorbed on a (2×1)O–Cu surface are shown in Figure 5. The images confirm that T5 also grows on the completely oxygenated surface, which is similar to its shorter homologue, bithiophene.[38] T5 has a lower chemical affinity for O–Cu compared to Cu(110). For this reason, a dose 2.5 times higher than that on pristine Cu(110) is required to achieve full monolayer coverage. Figure 5a displays an island of T5 molecules formed on one of the terraces of the O–Cu surface. The molecules are still fairly diffusive, as seen in Figure 5b. The appearance and disappearance of the islands was observed during scanning (not shown) at suitably high tunneling resistances, thus ex-
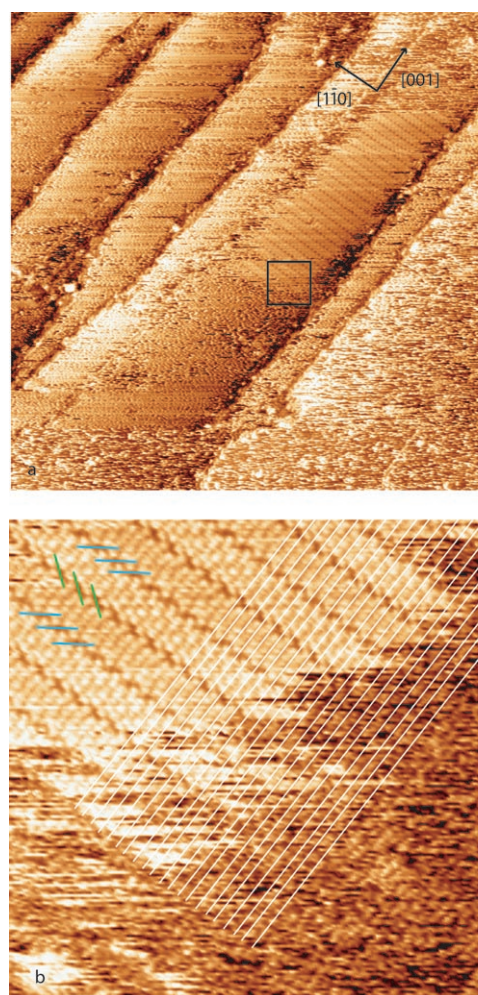

Figure 5. a) T5 island on the (2×1)O–Cu reconstructed surface. Imaging parameters: $V_t = -758$ mV, $I_t = 0.772$ nA, $A = 132.4 \times 132.4$ nm^2. b) High-resolution image at the edge of the island, showing both T5 molecules and oxygen rows. The white grid corresponds to the oxygen atoms running along the [001] direction of the copper lattice. The blue and green lines indicate the direction of tilt of the holes in the assembled structure. Imaging parameters: $V_t = -758$ mV, $I_t = 0.996$ nA, $A = 28.9 \times 27.7$ nm^2.

cluding molecular manipulation by the STM tip. We conclude that the islands are less stable than on pristine Cu(110), probably due to the weaker molecule–surface interaction caused by the oxygen coverage.

As seen for the previous case of T5 adsorbed onto a Cu/O–Cu nanopattern, the molecules are aligned with their axis along the close-packed direction of the (2×1)O–Cu reconstructed surface. The molecules are stacked together in columns that run perpendicular to the close-packed direction of the (2×1)O–Cu surface. A high-resolution image taken at the border of one of these islands (Figure 5b) shows both the submolecular resolution of the molecules and the atomic resolution of the oxygen rows (bottom right corner). Superimposing a grid on the oxygen rows, the adsorption geometry of the molecules was determined. Every other column of T5 molecules resides between two adjacent oxygen rows. The neighboring columns are slightly offset

from the oxygen troughs, in order to reduce steric hindrance between molecules both within and between columns.

Upon increasing the T5-molecule coverage to saturation, the molecules assemble with a high degree of order over several hundred square nanometers (not shown); the driving force for assembly is weak Van der Waals attractive interactions. Such interactions are favored by the presence of the oxygen layer, which reduces the interaction between the metallic d orbitals and the molecular π orbitals. A high-resolution image of complete monolayer coverage is shown in Figure 6a. Molecular models are superimposed on the
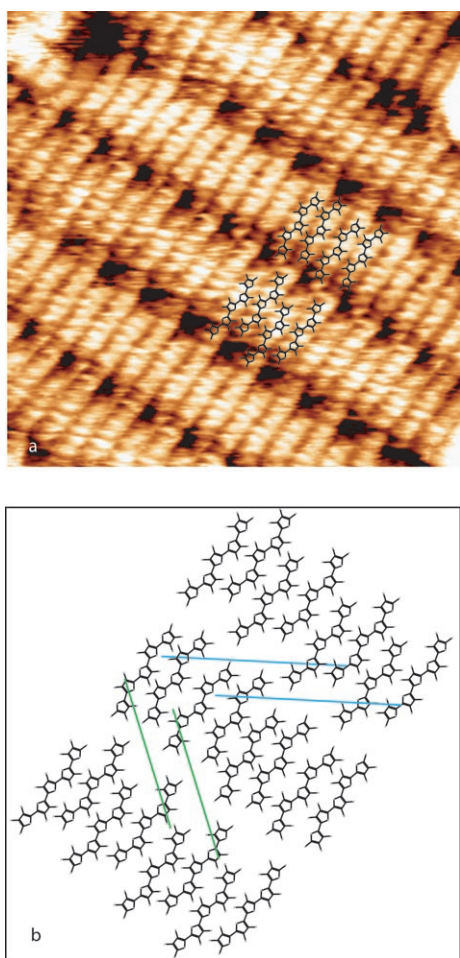
such that the sulfur atoms of the thiophenes at each end of the molecule point in the same direction. In this scenario, steric interactions are reduced as the T5 molecules within a column are shifted by approximately a single thiophene ring (≈ 0.7 nm) with respect to one another. In neighboring columns the molecules adsorb such that the sulfur atoms of the end thiophene rings point in opposite directions. As a result of the different orientation of the molecules in adjacent columns, the molecules often appear to be bent, as seen in Figure 5b. The holes are mirror images of each other, reflected across single columns. The tilt of the holes is highlighted with blue and green lines shown on the STM image (Figure 5b) and in the model (Figure 6b). The dimensions of the holes (approximately 1 nm in diameter) in the STM image are in agreement with those of the model.

3. Conclusions

The adsorption of T5 on Cu(110), on Cu/O–Cu supergratings, and on a (2×1)O–Cu reconstructed surface has been compared. T5 adsorbs on both clean and oxygenated Cu(110) surfaces with a higher affinity for pristine surfaces. The molecules lay flat on the substrate along the close-packed direction of the Cu(110) and the (2×1)O–Cu surfaces. On the Cu/O–Cu nanopattern molecules were simultaneously observed aligned along both directions.

The studies of T5 on the Cu(110) surface provide an insight into the adsorption geometry, which is important for improving the quality of organic–inorganic interfaces between films and electrodes. The ordered assembly of molecular overlayers on the copper oxide surface is particularly interesting for applications in organic electronics because oxide layers are often an essential component in such devices. In perspective, the selective affinity of T5 for Cu(110) and O–Cu paves the way for the fabrication of novel nanostructures of organic semiconductors.

4. Experimental Section

STM images were obtained in situ under UHV conditions (base pressure $\approx 5 \times 10^{-11}$ mbar, measured with a Bayard–Alpert gauge) with an Omicron VT-STM/AFM equipped with a Knudsen cell for the evaporation of organic molecules. A chemically etched tungsten tip was used.

The substrate used was a Cu(110) single crystal. Clean Cu-(110) surfaces were obtained by repeated cycles of argon-ion sputtering at 600 eV, followed by annealing to 873 K. O–Cu supergratings were obtained by dosing ≈ 0.5–1.0 Langmuir (L) (1 L $= 10^{-5}$ Torr s^{-1}) of oxygen via a precision leak valve onto the Cu(110) surface held at 623 K. Higher doses (5 L) at the same temperature resulted in a template with very wide O–Cu regions.

T5, synthesized and purified via a procedure described in the literature,[39] was thoroughly degassed in UHV prior to deposition. Film growth was achieved by evaporating T5 onto the Cu surfaces, kept at room temperature. T5 doses are expressed in

Figure 6. a) Saturation coverage of T5 on the (2×1)O–Cu reconstructed surface. Imaging parameters: $V_t = -0.526$ V, $I_t = 0.659$ nA, $A = 12 \times 12$ nm^2. b) Proposed adsorption geometry of T5. The blue and green lines show the direction of tilt of the holes and correspond to the lines shown in Figure 5b.

image for clarity. A higher degree of order is achieved compared to that of the Cu(110) surface as all the T5 molecules lie along the close-packed direction. This observation suggests that the registry of the molecules with respect to the surface is improved on the (2×1)O–Cu reconstructed surface compared with the pristine Cu(110) surface. The T5 molecules are clearly interdigitated. A model for their orientation within the layer is proposed in Figure 6b. The molecules within a column are aligned in the same direction

ML normalized to full coverage on a pristine Cu(110) surface, as determined by STM.

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[37] This tip change was fortuitous. The imaging mode for the upper portion of the image is more amenable for observing the adsorption of T5 onto the bare copper regions, while the lower portion is optimized for studying the adsorption of T5 on CuO. In the lower half of the image a multilayer seems to have formed on the Cu(110) stripes but this is clearly not the case, as seen in the upper part (indicated by the arrows to the left of the image). Here, the majority of the molecules were found to align along the close-packed direction as observed on the pristine surface.

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