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Hydrogen bonded one-dimensional chains of quinacridone on Ag(100) and Cu(111): the role of chirality and surface bonding

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Abstract

The adsorption and ordering of the prochiral molecule quinacridone (QA) on the Ag(100) and Cu(111) surfaces were studied by low energy electron diffraction and scanning tunneling microscopy. Upon adsorption, the molecules form parallel homochiral chains of flat lying molecules linked together via hydrogen bonds on both surfaces, but these chains show surface dependent significant differences concerning their lateral order. On both substrates, the chains are not thermodynamically stable, but stabilized by kinetic barriers. On the Ag(100) surface, annealing induces a phase transition to a highly ordered and heterochiral structure with a reduced density of hydrogen bonds. This loss of bonding energy is overcompensated by a stronger bonding to the substrate yielding a commensurate structure. For QA on Ag(100), we propose that during the initial chain formation and the phase transition upon annealing, the molecules can change their handedness by rotating around their long axes. In contrast, the initial chain formation and the phase transitions of QA on the Cu(111) surface appear to be subject to stronger kinetic limitations. These are explained by stronger substrate molecule interactions on Cu(111), which reduce the diffusion and the possibility for a change of handedness in comparison to QA on Ag(100). We discuss how the intermolecular hydrogen bonds, the 2D chirality, and the different chemical reactivities of the two surfaces (Ag(100), Cu(111)) influence the structural formation of QA aggregates. We compare our results to results for QA on Ag(111) reported previously by Wagner et al. [JPCC 2014, 118, 10911-10920].

1. Introduction

Interfaces between organic semiconductors and metal surfaces play an important role in organic electronic devices, e.g. organic field-effect transistors (OFET),^{1,2} organic light emitting diodes (OLED),^{3,4} or organic photovoltaics (OPV).⁵ Most investigations so far have focused on organic molecules with large π -conjugated systems because these usually have high electron and hole mobilities. From this point of view, the molecule 5,12-dihydroquino[2,3-b]acridine-7,14-dione (quinacridone, QA) would be a poor candidate because its intramolecular conjugation is broken (cf. Fig. 1(a), below). However, Głowacki et al. found that QA exhibits promising properties for applications in electronic and optoelectronic devices.^{6,7} These findings have motivated investigations on the potential applications of QA, its derivatives, and QA-based polymers in OFET,⁸⁻¹¹ OLED,^{12,13} and OPV.¹⁴⁻¹⁶ An overview is given in the review by Wang et al.¹⁷ In particular, Głowacki et al. have reported a hole mobility of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and photocurrents of roughly 1 mA cm^2 for QA, which they attributed to strong intermolecular interactions via hydrogen bonds. Therefore, one goal of our experiments, which we report here, was to find out how the intermolecular hydrogen bonds determine the structure formation and nucleation of aggregates of QA on surfaces.

QA ($\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_2$) exhibits a total of four isomers (two angular and two linear forms).¹⁸ In this work, we investigated the linear *trans*-isomer, which is illustrated in Figure 1 (a). This isomer is a widely used organic pigment (Violet 19) and is industrially produced at low cost. Important applications of Violet 19 are for example given by its use as colorant in varnishes or printer toners.¹⁹⁻²¹ Its molecular skeleton consists of five annulated carbon rings and is thus similar to that of pentacene. However, in contrast to pentacene, QA contains four functional groups that are responsible for the broken intramolecular conjugation on the one hand, but enable the molecule to form intermolecular hydrogen bonds on the other hand. These hydrogen bonds also play an important role for its crystal structures.²²⁻²⁴ QA exhibits a variety of polymorphic crystal structures. These can be divided into two groups: The α - and β -phases consist of chains of parallel molecules with each molecule being bonded

Figure 1: a) Structural formula of quinacridone (QA) and a hard sphere model, which shows the dimensions of the molecule. The dimensions of the molecule result from the bond lengths and van der Waals radii that were used for this model (cf. section 2). The color code of the atoms is as follows: carbon = black, hydrogen = grey, nitrogen = blue and oxygen = red. b) Schematic illustration of the 2D-chirality of the adsorbed QA molecule on Ag(100) and the relationship between the two enantiomers. The two adsorption configurations are energetically equivalent. The angle $\gamma = 32^\circ$ was chosen such that the orientations of the molecules with respect to the Ag(100) surface corresponds to their azimuthal orientation in the α -phase (cf. Fig. 2). The adsorption site is chosen arbitrarily.

to both of its neighbors via two hydrogen bonds, whereas the γ -phase shows a crisscross pattern where every molecule is bonded to each of its four neighbors via a single hydrogen bond.²³

Besides the ability to form intermolecular hydrogen bonds, the concept of 2D-chirality is also an important structural aspect that is relevant for the adsorption of QA on surfaces.^{25,26} Among the many possibilities through which chirality on surfaces may arise, the one relevant for QA is the adsorption of a prochiral molecule on a surface. The planar QA molecule is of C_{2h} -symmetry which implies that it does not exhibit a mirror plane that is perpendicular to the molecular plane, and therefore it loses its mirror symmetry upon adsorption. This means that the handedness of the molecule on the surface depends on which of its two sides adsorbs. Statistically, the adsorption leads to equal probabilities of the two enantiomers

on the surface. The two enantiomers (denoted by R and L in the following) are expected to adopt energetically equivalent and mirror symmetric adsorption configurations. These are illustrated in Figure 1 (b) for QA on the Ag(100) surface, which will be subject of this work. Each enantiomer is rotated by either $+\gamma$ or $-\gamma$ with respect to the [10]-direction of the substrate, depending on its handedness. For one given enantiomer, the $+\gamma$ and $-\gamma$ orientations are not equivalent and yield different adsorption energies. In principal, QA can change its handedness on the surface by rotating around its long axis. This process involves the loosening of the bonds between the adsorbate and the surface and can therefore expected to be inhibited by a kinetic barrier. This is especially the case for a π -conjugated planar molecule as QA, for which a planar adsorption geometry is energetically favored.

A general question concerning the chirality of aggregates on surfaces concerns the preference towards hetero- or homochiral packing. A common hypothesis is that, on surfaces, homochiral packing is preferred over heterochiral packing.²⁷ This is in contrast to the 3D situation where heterochiral packing is more common because racemats tend to have a higher density than the corresponding conglomerates.²⁸ However, in a recent review, Dutta and Gellman reported the absence of a significant statistical preference towards one of the two possibilities.²⁷ It is believed that often only a subtle balance between the various forces is responsible for hetero- or homochiral packing. In many cases, a small change in certain parameters (e.g. temperature or coverage) can cause a phase transition between phases of hetero- and homochiral packing.^{26,27} However, these processes are not fully understood yet and whether there is a preference towards homo- or heterochiral packing is still an openly debated question, to which the present work contributes.

So far, QA has been subject to only few investigations on surfaces, e.g. on the Ag(111) surface by Wagner et al.²⁹ and on graphene and MoS₂ by Trixler et al.^{30,31} Beyond that, several studies of derivatives of QA on metal surfaces have been reported.^{32–36} Typically, QA and its derivatives are found to adsorb intact in a planar orientation and to form ordered layers. Here, we report on the structures of ordered QA layers on the Ag(100) and Cu(111)

surfaces. In comparison to QA on Ag(111),²⁹ it is of interest to investigate QA on Ag(100) because this surface exhibits a lower symmetry and is more open than the Ag(111) surface. For the Cu(111) surface, a higher reactivity compared to the Ag(111) surface and hence a stronger bonding and corrugation of the bonding potential of QA can be envisaged. This is also expected to hinder the change of the chirality of the QA ($L \leftrightarrow R$) on the surface more effectively, which should manifest in a higher kinetic barrier for the ordering. We will report structure models for QA/Ag(100) and QA/Cu(111), compare them to results obtained for QA on Ag(111),²⁹ and discuss how the surface symmetry and corrugation influence the ordering in competition with the formation of intermolecular hydrogen bonds.

2. Experimental

The experiments were carried out under ultrahigh vacuum (UHV) conditions with a base pressure of 3×10^{-10} mbar. Investigations were conducted using a beetle type scanning tunneling microscope (STM, type UHV 300) from RHK technology, a spot profile analysis low energy electron diffraction (SPA-LEED) instrument manufactured by Omicron, a microchannel plate LEED (MCP-LEED) from OCI Vacuum Microengineering Inc., and a quadrupole mass spectrometer (QMS) of the type PRISMA from Pfeiffer Vacuum. The Ag(100) and Cu(111) crystals were cleaned by cycles of sputtering with Ar^+ ions (800–1000 eV, 7 μA) for 30 minutes and subsequent annealing at 850 K (Ag) or 1000 K (Cu) for 1 hour. The structural quality of the substrate crystals was checked by LEED. The quinacridone was purchased from HOECHST and purified by gradient sublimation.¹¹ It was evaporated from homebuilt evaporators at crucible temperatures of 650–670 K while the substrates were held at room temperature (RT). During the evaporation process, the QMS signal of a QA fragment ($m/z = 128$, $m(\text{QA}) = 312$) was recorded and integrated over time. Optionally, the samples were annealed after deposition at 400 K (Ag) or 500 K (Cu) for 15 minutes. The coverages θ were determined from the analysis of STM images. We define the coverage of one monolayer (1 ML) as the coverage of a closed layer of flat-lying molecules in the β -phase on Ag(100) (see below).

All SPA-LEED measurements were carried out at a sample temperature of 110 K in order to minimize the thermal diffuse background. In order to avoid beam damage, which was reported by Wagner et al. for QA on Ag(111),²⁹ the beam current was always kept as small as possible (< 5 nA). Thus, no problems with degrading LEED patterns were encountered. The coverages were determined from the deposition integrals. A 2D image with sharp spots (Figure 2 (d), below) was assigned to a coverage of $\theta = (1 \pm 0.05)$ ML. With this all the other coverages were determined with help of the corresponding deposition integral. The distortions of the 2D SPA-LEED images were corrected by using a self-written plug-in for the free software Fiji.³⁷ This plug-in can correct radial and tangential distortion

according to the Brown-Conrady’s distortion equation.³⁸ For this purpose the images were superimposed with a simulated diffraction pattern of the substrate. Then the images were dewarped by hand until the experimental substrate spots were in good agreement with those of the simulation. The analysis of the LEED patterns was carried out via a trial and error procedure. For this purpose the program Spot-Plotter³⁹ was used to simulate a diffraction pattern that is in good agreement with the LEED pattern.

Prior to starting the STM measurements, the prepared layers were checked using an MCP-LEED in order to ensure the presence of a well ordered layer and comparability to the SPA-LEED images of the same system. All STM images were recorded in the constant current mode at RT. As tip a self-cut Pt/Ir (90:10) wire was used. The bias voltage refers to the sample, while the tip was on ground potential. The images were processed using the programs Gwyddion⁴⁰ and SPIP.⁴¹ The coverages were determined by pixel counting. Pixel above a certain intensity threshold were attributed to molecules and the rest to the bare substrate. We estimate the margins of error for the coverages to be ± 0.05 . If not stated otherwise, the processing consisted only of filtering out horizontal, vertical or non-directional noise, and adjusting the contrast of the images. The structure models of the investigated systems were created with the free program Graphics Layout Engine.⁴² The hardsphere model of QA was drawn using bond lengths⁴³ and van der Waals radii⁴⁴ from the literature.

3. Results and discussion

We start with the presentation of the results for QA on Ag(100) in section 3.1 and then move to the more disordered structures of QA on Cu(111) in section 3.2. An overview on all considered structures is given by Table 1.

3.1. QA/Ag(100)

In the sections 3.1.1 and 3.1.2 we report on the phase that forms directly after deposition of a full or submonolayer on Ag(100) at RT. We will call this phase α -phase from now on. After annealing, it transforms into a second two-dimensional ordered and commensurate phase. This phase is named β -phase and will be discussed in section 3.1.3.

3.1.1. QA/Ag(100) – α -phase (complete monolayer)

Figure 2 (a) shows an STM image of a complete monolayer of the α -phase. The ordered layer consists of domains which can grow up to 100 nm in width, but which do not grow across step edges. Each domain consists of parallel chains of lengths between 5 and 100 nm. The chains exhibit distinct azimuthal orientations rotated by $\pm(31.2 \pm 0.5)^\circ$ with respect to the [10] direction of the Ag(100) substrate (cf. Fig. 1 (b)). Hence, the combination of two mirror domains and the fourfold rotational symmetry of the Ag(100) surface yields a total of four symmetry equivalent azimuthal orientations of the QA domains. These orientations are illustrated by the white lines A–D in Figure 2 (a). The existence of four symmetry equivalent domains and their azimuthal orientations with respect to the substrate is in agreement with SPA-LEED results which will be discussed later.

An STM image with molecular resolution is displayed in Figure 2 (b). It shows that the QA chains consist of parallel flat lying molecules with their long sides next to each other. This arrangement can be attributed to two strong intermolecular $\text{O} \cdots \text{H}-\text{N}$ hydrogen bonds which can form between neighboring molecules within a chain. This is illustrated by the hard

Figure 2: Complete monolayer of QA on the Ag(100) surface in the α -phase. a) Overview STM image ($U_{\text{Bias}} = -1.5$ V, $I = 0.25$ nA). The structure consists of domains of parallel chains with four distinct orientations A–D which are marked by the white lines. Image size: $65 \times 65 \text{ nm}^2$. b) Zoom in of a) that shows the molecular arrangement. Image size: $12 \times 12 \text{ nm}^2$. The arrows in the top right corner indicate the $[10]$ and $[01]$ directions of the substrate. The inset shows two molecules with a characteristic S-shape. The upper right one is superimposed with the calculated HOMO of the isolated molecule.⁴⁵ c) Structure model of the α -phase of QA on the Ag(100) surface for a coverage of one monolayer. The unit cell corresponds to the red unit cell in (d). d) SPA-LEED pattern ($E = 81.4$ eV). On the right hand side, the pattern is superimposed with the corresponding simulated LEED pattern. The unit cells of two mirror domains which resemble different enantiomers are depicted in blue and red. The circles and triangles mark spots belonging to two rotational domains of one enantiomer. Spots that are not reproduced by the simulation can be explained by multiple scattering.

sphere model given in Figure 2 (c). However, the formation of these two hydrogen bonds is only possible if two neighboring molecules have the same handedness since otherwise we would not have opposing NH- and CO-groups. Therefore, we deduce that the chains are enantiopure. We further propose that not only the individual chains, but the entire domains are enantiopure. This means that all chains in one domain are composed of molecules with the same handedness. This is a consequence of the fact that for a change in the handedness we expect a change in the molecular orientation ($+\gamma \rightarrow -\gamma$) and hence the orientation of the chains. This conclusion is also in agreement with our STM results. The molecules in Figure 2 (b) show a characteristic S-shape that was already reported for QA on graphene,³⁰ and which can be used to distinguish between enantiomers. The STM image confirms that the individual chains as well as the whole domains are, except for the occasional defects, enantiopure. As shown in the inset of Figure 2 (b), the observed S-shape can be understood by the shape of the highest occupied molecular orbital (HOMO) of an isolated QA molecule in the gas phase, which was calculated by DFT.⁴⁵ Thus, the handedness of the molecules on the surface can be determined and the two different enantiomers can be distinguished.

Figure 2 (d) shows a SPA-LEED pattern of the α -phase. In addition to the specular spot, the first and second order spots of the substrate are seen. The analysis of the pattern yields the following superstructure matrix:

$$\mathbf{M}_{\alpha} = \begin{pmatrix} 2 & 1.25 \\ -3 & 4.80 \end{pmatrix}.$$

The margin of error on the non-integer matrix elements is estimated to be ± 0.03 . Spots that are not reproduced by the simulation can be explained by multiple scattering at the first or second order spots of the substrate. The matrix corresponds to a rectangular unit cell ($\alpha = 90 \pm 1^\circ$) with $b_1 = (6.8 \pm 0.1) \text{ \AA}$ and $b_2 = (16.4 \pm 0.1) \text{ \AA}$. The unit cell contains one molecule. The superstructure exhibits two mirror domains with two rotational domains each. For the definitions of $\mathbf{b}_1$ and $\mathbf{b}_2$, we refer to the structure model for the α -phase of QA on Ag(100) in Figure 2 (c). The length b_1 corresponds to the intermolecular distance

between neighboring molecules within one chain. The distance between two chains is given by b_2 and corresponds to the length of the molecule (i.e. 16.26 Å). The vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ of the unit cell are rotated symmetrically by $\pm(32.0 \pm 0.5)^\circ$ with respect to the [10] or [01] direction of the Ag(100) surface. Both, the size and shape of the unit cell, and its azimuthal orientation with respect to the substrate are in agreement with the STM results.

Because the values in the first column of the matrix are integers the structure is of the point-on-line type.⁴⁶ This means that all lattice points of the superstructure fall on the same set of lattice lines of the substrate (here, those in the [01] direction). This indicates that besides the intermolecular interactions, the substrate-adsorbate interactions also play a significant role in the structure formation. A comparison of the observed structure to that of the net planes of QA bulk crystals shows that it is very similar to the $(1\bar{1}2)$ plane of the α^I -QA bulk structure.²³ Like the α -phase, the $(1\bar{1}2)$ plane consists of parallel molecular chains. In particular, the distance b_1 is identical to the distance between the molecules in the chains of the $(1\bar{1}2)$ plane within the margin of error. The distance b_2 deviates by only 3.6% from the distance between the chains in the $(1\bar{1}2)$ crystal plane. Thus, we assume that the molecular arrangement within the α -phase is related to very similar intermolecular interactions as those in the α^I -QA bulk structure.

The SPA-LEED pattern (Fig. 2 (d)) consists mainly of two prominent sets of spots. For a constant scattering vector, both sets consist of 4 pairs of spots. The two spots of a pair enclose an angle of $(23.5 \pm 0.5)^\circ$ and are located symmetrically around the [11] direction of the substrate. The spots of the first set are sharp and are partly very close to the specular spot at a distance of b_2^* . The second set is further away at a distance of b_1^* . The spots of the second set show a strong broadening into streaks in the direction of $\mathbf{b}_2^*$, but they are sharp in the direction of $\mathbf{b}_1^*$. This broadening is not due to azimuthal disorder because the streaks are straight and not circular with respect to the specular spot. The broadening is caused by defects in the structure that are quite frequent, namely neighboring chains are not correlated in the direction of $\mathbf{b}_1$, i.e. the chains are shifted relative to each other in the

chain direction. This absence of correlation leads to the strong broadening of the spots at $(\pm 1, 0) = \pm \mathbf{b}_1^*$ in the direction of $\mathbf{b}_2^*$, i.e. the direction perpendicular to the chains. These defects can also be seen in the STM image in Figure 2 (b). However, for the considered full layer, the distance between the chains (in the direction of $\mathbf{b}_2$) is well defined. Therefore, the spots at $(0, \pm k) = \pm k \cdot \mathbf{b}_2^*$ (with $k = 1, 2$, and 3) are sharp in the direction of $\mathbf{b}_2^*$.

3.1.2 QA/Ag(100) – submonolayer coverage

So far, we have considered the α -phase at a coverage of a complete monolayer. Figures 3 (a) and (b) show STM images of the α -phase of QA on Ag(100) for $\theta = 0.50$ ML. The layer is similar to the full monolayer, except that the average distance between neighboring chains b_2 is roughly twice as large as that in the full monolayer. Furthermore, this distance is not constant within one domain but varies between 2.8 and 3.9 nm. On average it is $b_2 = (3.3 \pm 0.3)$ nm. (The error margin denotes the standard deviation.) The intermolecular distance between molecules along the chains b_1 remains unchanged. This is in agreement with our above conclusion that the distance b_1 is given by the intermolecular hydrogen bonds and is therefore independent of the coverage.

The dependency of the length b_2 on the coverage was investigated for six coverages between 0.4 and 1 ML by SPA-LEED. An exemplary SPA-LEED pattern at $\theta = 0.45$ ML is displayed in Figure 3 (c). The lowering of the coverage has two significant effects on the diffraction pattern. The first is that the length of the vector $\mathbf{b}_2^*$ decreases, which corresponds to the increased average distance between neighboring chains. The second more obvious effect is that the sharp spots related to $\mathbf{b}_2^*$, which were observed for the full monolayer, are smeared out into streaks. The reason is that the distance between neighboring chains is not constant. This leads to a radial broadening of the spots related to $\mathbf{b}_2^*$ and the corresponding higher order spots. Of course, the broadening related to the lack of a correlation between the chains in the $\mathbf{b}_1$ direction, which we described for the α -phase, is also present. The analysis of this SPA-LEED pattern (Fig. 3 (c)) yields an averaged unit cell that is similar to that of the full

Figure 3: Submonolayer of QA on the Ag(100) surface. a) Overview STM image ($U_{\text{Bias}} = -1.5$ V, $I = 0.25$ nA). With decreasing coverage of QA the distance between the chains increases. Image size: $55 \times 55 \text{ nm}^2$. b) Zoom in of a). Image size: $12 \times 12 \text{ nm}^2$. c) SPA-LEED pattern ($E = 81.4$ eV). The inset shows a blow-up of the region around the specular spot. The unit cells of one domain is depicted in red. The spots are smeared out into streaks (cf. text) due to a lack of inter-chain correlations. d) The distance between the chains b_2 in dependency of the coverage. The length was determined by SPA-LEED. The data point for $\theta = 0.45$ ML in (c) is not included because no line profile was recorded for this preparation. The point at $\theta = 0.20$ ML was extracted from STM data. How the coverages were determined is explained in the Experimental section.

monolayer. The length of the vector $\mathbf{b}_1$ and its azimuthal orientation are unchanged. The only difference resides in the length of the vector $\mathbf{b}_2$, which depends on the coverage θ . The dependency of b_2 on θ is illustrated in Figure 3 (d). Most data points were obtained from SPA-LEED line profiles through the specular spot in the direction of $\mathbf{b}_2^*$. Only the data point at $\theta = 0.20$ ML was inferred from STM images. We found that the average chain distance grows with decreasing coverage. In the simplest model, one expects a $b_2 \sim \theta^{-1}$ correlation. This is illustrated by the red curve in Figure 3 (d), which is roughly compatible with the data. However, we cannot exclude that b_2 drops to the value of ~ 17 Å, which is close to b_2 of the α -phase (16.4 Å), around a coverage of $\theta = 0.60$ ML. This may indicate a phase transition to islands of the α -phase coexisting with a gas like phase.

STM images (Fig. 3 (a) and (b)) reveal that neighboring chains are always aligned parallel to each other as in the full monolayer, although their distance is increased. Even for a coverage of only 0.2 ML, where neighboring chains have distances of up to 6 nm between them, this is still the case. A similar behavior was already found by Lukas et al. for chains of pentacene on Cu(110).⁴⁷ The authors attributed this behavior to long-range substrate mediated repulsive interactions between the chains that are induced by charge density waves in the 2D electron gas of a surface state.^{48,49} Such a mechanism may play a role here, too. Other examples for this kind of long distance interaction of molecular chains on a metal surface are the self-assemblies of L-methionine on Cu(111)⁵⁰ and Ag(111).⁵¹

3.1.3 QA/Ag(100) - β -phase

After annealing at 500 K for 15 min, the α -phase changes irreversibly into a different, but also highly ordered phase, which we call β -phase. Upon annealing, the superstructure LEED pattern of the α -phase completely vanished at roughly $T = 470$ K. Faint spots of the β -phase started to appear at roughly 430 K and steadily increased in intensity upon further cooling to RT. This means that the α -phase does not directly transform into the β -phase, but via a disordered phase at higher temperatures that transforms into the β -phase upon cooling. The

transformation is irreversible because the transition between the β -phase and the disordered phase can be induced again by heating, but it is impossible to go back to the α -phase.

Two STM images of the β -phase are displayed in Figures 4 (a) and (b). The image in (a) shows two mirror domains separated by the edge of a double step of the substrate. Due to symmetry reasons, for both of these domains a symmetry equivalent rotational domain exists, which yields again a total of four symmetry equivalent domains. The domains can reach sizes of at least 100 nm in both lateral dimensions and are limited in size only by Ag steps. Accordingly, we were not able to find domain boundaries between symmetry equivalent domains, except for the noted ones at step edges of the substrate. The molecular arrangement within these domains is shown in Figure 4 (b).

Figure 4 (c) shows a SPA-LEED pattern of the β -phase. As expected from the STM images, the diffraction pattern is highly symmetric and consists of sharp spots. In contrast to the α -phase, no broadening of the spots can be detected. The analysis was carried out as described above and yielded a simulated diffraction pattern that accounts for all of the observed spots and fits the experimental pattern. The corresponding superstructure matrix is:

$$\mathbf{M}_{\beta} = \begin{pmatrix} 4 & 3 \\ -5 & 3 \end{pmatrix}.$$

This corresponds to a unit cell with $b_1 = 14.445 \text{ \AA}$, $b_2 = 16.848 \text{ \AA}$ and $\alpha = 112.2^\circ$ with α being the angle between $\mathbf{b}_1$ and $\mathbf{b}_2$. Like the α -phase, this superstructure also exhibits two mirror domains, both have two rotational domains, which is in agreement with the STM results. The unit cell contains two molecules and the vector $\mathbf{b}_2$, which corresponds to the direction of the long axes of the molecules, is rotated by 31° with respect to the $[10]$ direction of the substrate (32° for the α -phase for comparison). All the elements of the matrix are integer numbers, which reveals that the structure is commensurate.

A structure model of the β -phase is displayed in Figure 4 (d). The molecular arrangement was derived from STM images. The molecules arrange in dimers that form periodically

Figure 4: A full monolayer of QA on the Ag(100) surface in the β -phase after annealing the α -phase at 500 K for 15 minutes. a) Overview STM image ($U_{\text{Bias}} = -1.5$ V, $I = 0.25$ nA) with a double step edge. Every bright ellipsoid corresponds to a single QA molecule. The image shows two different mirror domains. Image size: $35 \times 35 \text{ nm}^2$. b) Zoom in of a) for better visibility of the molecular arrangement. Image size: $5 \times 5 \text{ nm}^2$. c) SPA-LEED pattern ($E = 81.3$ eV). On the right hand side, the pattern is superimposed with the corresponding calculated LEED pattern. The unit cells of two mirror domains are depicted in blue and red. The inset shows the area around the specular spot of the β -phase at an electron energy of $E = 51.3$ eV. d) Structure model of a full monolayer QA on the Ag(100) surface in the β -phase. The unit cell corresponds to the red unit cell in (c) and depicts a different domain than the one that is shown in (b). It can be translated into the domain depicted in (b) by mirroring at the plane along $\mathbf{a}_1$ and rotating it by 90° . (Structure models of all four domains can be found in the supplementary information.) STM and SPA-LEED measurements yield the small unit cell given by the vectors $\mathbf{b}_1$ and $\mathbf{b}_2$. The large unit cell takes into account the chirality (indicated by the colors yellow and green) of the molecules and is therefore twice as large as the small one. For detailed explanations see text. The adsorption sites were chosen arbitrarily. All molecules on the corners of the unit cell are on identical adsorption sites.

indented and parallel chains. Evidently, the two molecules of a dimer have to be of the same handedness (RR or LL) in order to form two hydrogen bonds between them. However, due to the periodic offsets within the chains it is impossible to form two hydrogen bonds between neighboring dimers. In order to form at least one hydrogen bond, it is necessary to switch the handedness periodically from dimer to dimer (RRL or LLR). However, this leads to a structure with two different enantiomers on the corners of the unit cell as derived from LEED and STM (cf. Fig. 4 (d)). Thus, the size of the unit cell in the direction of $\mathbf{b}_1$ has to be doubled if the chirality is accounted for. The fact that neither the STM nor the SPA-LEED images indicate this larger unit cell can be explained as follows. The differences in the geometric structures between the two enantiomers are very small with respect to identical parts and the expected additional spots are thus very weak. Apparently, the LEED images do not resolve these and hence cannot distinguish between the two enantiomers and yield the smaller unit cell. As noted in section 3.1.1, for the α -phase we could distinguish between the two enantiomers in STM images. However, for the β -phase, we were not able to achieve this.

It is interesting to note that the orientation of the vector $\mathbf{b}_2$, which corresponds to the direction of the long axis of the molecule, differ by only 1° (3.3%) for the two phases (α/β). This shows that the orientation of the molecules with respect to the substrate is identical before and after the phase transition. Furthermore, a comparison of the unit cells reveals that this is also true for the molecular density. In the β -phase, it is reduced by only 1.08% with respect to the α -phase. However, the number of hydrogen bonds per molecule is reduced by a factor of 0.75 compared to the α -phase.

3.2 QA/Cu(111)

We turn to the results for QA on the Cu(111) surface. Section 3.2.1 deals with the structure of the full monolayer directly after the deposition at RT. We will call it the α' -phase. In Section 3.2.2, we continue with the structure of a full monolayer of QA on Cu(111) after

annealing, named β' -phase. The structural order of the β' -phase is significantly limited by kinetic limitations. Section 3.2.3 describes our results for submonolayer coverages prior to and after annealing. Due to the lower coverages, the results after annealing differ from those of the full monolayer.

3.2.1 QA/Cu(111) - α' -phase (complete monolayer)

Figure 5 (a) displays an STM image of a layer with a coverage of roughly 0.95 ML, which was obtained directly after deposition at RT. Similar to QA on Ag(100), the molecules form homochiral parallel chains on Cu(111) due to intermolecular hydrogen bonds. Due to the higher symmetry (sixfold instead of fourfold) of the Cu(111) surface every chain exhibits one of six distinct orientations instead of four (as on Ag(100)). However, the structure appears to be significantly more disordered than its counterpart on Ag(100). On Cu(111), the chains do not form large ordered domains, and there are even single chains that have no parallel neighboring chains at all. The high amount of only small stripe-like domains leads to a high density of uncovered surface areas between the domains. We believe that this growth behavior is due to the stronger substrate adsorbate interactions compared to those on Ag(100). Such stronger interactions support the nucleation of new chains, but inhibit the ordering of the chains into larger domains and hence, in total, lead to more disorder. When molecules are deposited onto a full monolayer of QA at RT, a second layer begins to form on top. This is illustrated in Figure 5 (b). The STM image shows that the molecules form the same kind of chains in the second layer. The difference from the first layer, however, is that the chains are not straight and adopt fully arbitrary azimuthal orientations, which is likely due to smaller interactions between the molecules in the second layer and the first layer below.

A representative LEED pattern of the monolayer structure is given in Figure 5 (c). It consists of six pairs of sharp spots around the specular and first order spots of the substrate that correspond to the distance b_2 between neighboring chains. The rest of the pattern is

Figure 5: Complete monolayer of QA on the Cu(111) surface in the α' -phase. a) Overview image at a coverage of $\theta = 0.95$ ML ($U_{\text{Bias}} = -1.5$ V, $I = 0.25$ nA). Image size: 100×100 nm². The inset shows a zoom-in of the structure. Image size: 25×25 nm². b) Overview image at a coverage of $\theta = 1.40$ ML. It shows the growth of QA chains in the second layer on top of the monolayer of the α' -phase. Image size: 100×100 nm². c) SPA-LEED image at a coverage of $\theta = 0.50$ ML ($E = 55$ eV). The superstructure is almost identical to the one observed for the complete monolayer except that the vector $\mathbf{b}_2^*$ is ca. 50% shorter (cf. Fig. 7 (b) and text). d) Structure model of QA on Cu(111) in the α' -phase. The model encompasses three symmetry equivalent chain directions.

made up of streaks, which indicates the lack of correlation between neighboring chains. The displayed pattern was actually recorded at submonolayer coverage ($\theta = 0.50$ ML) using the SPA-LEED instrument. However, it can be considered as representative for the full monolayer, too, because the patterns are almost identical. We will discuss this LEED pattern in more detail later. A corresponding structure model is shown in Figure 5 (d). For the superstructure matrix and the corresponding structure parameters we refer to Table 1. Except for the much smaller size of domains, the α' -phase on Cu(111) is very similar to the α -phase of QA on Ag(100). Like on Ag(100), the straight segments of the chains need to be enantiopure in order to form two intermolecular hydrogen bonds between neighboring molecules. However, on Cu(111), the chains contain much more defects due to a higher amount of molecules of the 'wrong handedness'. The unit cell that describes this structure is given in Table 1.

3.2.2 β' -phase (complete monolayer)

Like the α -phase on Ag(100), the α' -phase on Cu(111) is metastable and transforms upon annealing at $T \geq 400$ K. However, for QA on Cu(111), we did not succeed in preparing an ordered complete monolayer of the same quality as on Ag(100). We believe that this is due to larger kinetic barriers at high coverages, which in turn are due to the large QA/Cu(111) interaction. These prevent the molecules from rearranging properly in a long range ordered structure. The best results were achieved after annealing at 500 K for 15 minutes and subsequent cooling to RT. These will be presented in the following.

An STM image of the β' -phase at a coverage of $\theta = 0.95$ ML is displayed in Figure 6 (a). It shows an area with a gradual transition from an ordered structure (left side), which, however, contains a large amount of small holes and larger defects, to a disordered structure composed of chain-like aggregates (right side). The molecular arrangement within the ordered structure can be seen in Figure 6 (b), and a corresponding structure model is given in Figure 6 (d). The structure consists of parallel molecular chains, which are held together by hydrogen bonds. But here (in contrast to the α' -phase), the chains consist of two regularly alternating

Figure 6: Complete monolayer of QA on the Cu(111) surface in the β' -phase. a) Overview image at a coverage of $\theta = 0.95$ ML ($U_{\text{Bias}} = -1.5$ V, $I = 0.25$ nA). Image size: 21×21 nm². The blue circles mark a common type of defect that can also be seen in (d) on the right hand side. b) Close-up of the structure ($U_{\text{Bias}} = -1.5$ V, $I = 0.25$ nA). Image size: 5×5 nm². It shows a symmetry equivalent domain to the one shown in (a). The unit cell determined from the STM image is depicted in white. c) LEED image at a coverage of $\theta = 0.95$ ML ($T = 300$ K, $E = 20$ eV). The right hand side is superimposed with a simulation of the diffraction pattern. The corresponding unit cell is depicted in red and corresponds to the matrix given in the text. The long black lines point towards first order spots of the substrate. d) Structure model of QA on Cu(111) in the β' -phase. The blue circle marks a certain kind of defect, which can be seen in (a). The image in (a) depicts a different mirror domain, which leads to the mirrored shape of the defects. The white lines mark the unit cell. Note that the unit cell in (c) corresponds to a domain that is symmetry equivalent to the one shown here. The handedness of the molecules was determined by the position of the molecules relative to their next neighbors in the chain. If there is an offset in the direction of $\mathbf{b}_1$ between two molecules, they do not have the same handedness. The displayed unit cell does not take into account the handedness of the molecules.

segments. One segment is a dimer that consists of two molecules of the same handedness which are connected via two hydrogen bonds (LL or RR). The second segment is given by two molecules with different handedness (LR or RL). Both molecules of this segment form only one hydrogen bond with their outer next neighbors because they have a different handedness than these. This means that the handedness switches three times between two dimers of the LL and RR type (LLRLRR or RRLRLL). One defect that occurs quite regularly is that only a single molecule instead of two is located between two dimers (RRLRR or LLRLL). This leads to a gap in the direction of the long QA axis between two adjacent chains that causes uncovered Cu patches apparent as the 'holes' with a characteristic S shape. These are indicated by the blue circles in Figures 6 (a) and (d).

A LEED pattern of this structure is displayed in Figure 6 (c). It consists of six pairs of spots that are very close to the specular spot and show a strong radial broadening. These smeared out spots are likely due to the disordered areas that were observed in the STM images (cf. Fig. 6 (a)). Further away from the specular spot two groups of relatively sharp spots are seen that can be attributed to the ordered domains. All spots are only visible at low electron energies (≤ 30 eV). Because the first order spots of the substrate are not visible at these low energies, we used a combination of STM and LEED images to analyze the structure. We extracted an initial unit cell from the STM images and used it as starting point for the analysis of the LEED pattern. We adjusted the obtained unit cell slightly in order to make it fit better with the observed spots in the diffraction pattern. The corresponding superstructure matrix is:

$$\mathbf{M}_{\beta'} = \begin{pmatrix} 6.0 & -1.1 \\ 8.2 & 13.1 \end{pmatrix}.$$

We estimate that the error margin for all elements of the matrix is ± 0.2 . The matrix corresponds to a unit cell with $b_1 = (16.9 \pm 0.5)$ Å, $b_2 = (29.3 \pm 0.5)$ Å and $\alpha = (90 \pm 2)^\circ$ with α being the angle between $\mathbf{b}_1$ and $\mathbf{b}_2$. The length b_1 matches the length of the molecule and the length b_2 corresponds to four times the width of the molecule. Notably, all elements of the

first row of the matrix are close to integer values, which might indicate a commensurability in the direction of $\mathbf{b}_1$.

Overall, there are two aspects in which the β' -phase differs from the α' -phase: the disordered assembly of mostly straight and homochiral chains has transformed into ordered domains. In contrast to the α' -phase, these are made up by heterochiral (not homochiral) chains with periodic offsets. However, the orientation of individual molecules with respect to the substrate remains unchanged, namely the long axis of the molecule is at an angle of 18° and 42° with respect to the close packed Cu rows ($\mathbf{a}_1$ and $\mathbf{a}_2$).

3.2.3 QA/Cu(111) - submonolayer coverage

We turn to our results for submonolayer coverages of QA on Cu(111) directly after deposition at RT and after subsequent annealing at 600 K. After annealing at 400 or 500 K and subsequent cooling to RT, various chain-like structures were observed. For annealing at 600 K, a single structure prevailed, which did not change upon further annealing, and we will focus on this structure below.

We start with the phase, which was present on the surface directly after deposition. An STM image at a coverage of $\theta = 0.40$ ML is displayed in Figure 7 (a). As on Ag(100), the submonolayer structure differs from that of the full monolayer mainly by a larger average distance between neighboring chains. Here, the distance between neighboring chains varies strongly. It was measured for 50 pairs of neighboring chains and ranges from 24 Å to 53 Å with the average distance being (37 ± 7) Å. (The error margin denotes the standard deviation.) This is presumably caused by similar long-range repulsive interactions that were deduced before for QA on Ag(100). The intermolecular distance within a chain was obtained from averaging over ~ 100 distances and is (6.4 ± 0.1) Å. This value is within the margin of error identical with the corresponding value for QA on Ag(100). This reveals that the main driving force for the formation of QA chains on Cu(111) directly after deposition at RT are the intermolecular hydrogen bonds between neighboring molecules.

Figure 7: Submonolayer structures of QA on the Cu(111) surface after deposition at RT ((a) and (b)) and after annealing at 600 K ((c) and (d)). a) STM image ($U_{\text{Bias}} = -1.5$ V, $I = 0.35$ nA) at a coverage of $\theta = 0.50$ ML. b) Structure model corresponding to (a). The average unit cell was determined from a SPA-LEED image and is indicated in white. The length b_2 varies with coverage. c) STM images ($U_{\text{Bias}} = -1.5$ V, $I = 0.25$ nA) at a coverage of $\theta = 0.50$ ML after annealing at 600 K for 15 minutes. The two smaller images show chains in the same direction, which consist of different enantiomers. d) Structure model corresponding to (c). Each chain adopts one out of three directions that correspond to the main directions of the substrate ($[10]$, $[01]$, $[11]$). The individual chains are homochiral but all chains in all three directions can be made up of both enantiomers. The arrow in the bottom right corner indicates the $[12]$ -direction of the substrate.

Like the α' -phase, the submonolayer of QA on Cu(111) looks significantly more disordered than its counterpart on Ag(100) because the chains on Cu(111) contain significantly more defects than those on Ag(100). The most typical defect is an offset of a molecule with respect to its neighboring molecule in the direction of $\mathbf{b}_2$ (cf. structure model in Fig. 7 (b)). These defects appear quite often; we were not able to find a single chain without such defects. The longest defect free distance within a chain, which we could find, was 280 Å, which corresponds to a segment of 40 QA molecules. For QA on Ag(100), these defects were also observed, but they were comparatively very rare. A defect of this type occurs whenever the handedness of the molecules along the chain changes. This leads to an offset perpendicular to the chain, which preserves at least one hydrogen bond between the two neighbors of the opposite handedness. The higher amount of defects on Cu(111) compared to Ag(100) is likely due to the stronger substrate adsorbate interactions, since they make the flipping of the molecules and diffusion less likely and therefore prevent the healing of defects.

A SPA-LEED pattern of QA on the Cu(111) surface at a coverage of roughly $\theta = 0.50$ ML is displayed in Figure 5 (c). As noted above, the LEED pattern is very similar to that of the full monolayer of the α' phase. These two patterns only differ in the length of the vector $\mathbf{b}_2^*$. The pattern mainly contains two prevalent features. One is a set of 12 spots around the specular spot and the first order spots of the substrate that are given by the vector $\mathbf{b}_2^*$. Compared to the rest of the diffraction pattern, the $\mathbf{b}_2^*$ spots are relatively sharp. However, they clearly show a radial broadening and the corresponding higher order spots are not visible. The other prevalent feature is given by the streaks that make up the rest of the diffraction pattern. The lack of sharp spots of higher order is an indicator for a high amount of lateral disorder, which is in agreement with the STM results. The analysis of the pattern turned out to be rather difficult, and it was not possible to derive the averaged unit cell from the LEED pattern alone but additional information from STM was required. It was possible to determine the lengths of the two vectors of the unit cell from SPA-LEED. The orientation of the vector $\mathbf{b}_2$ with respect to the substrate was determined from the few sharp spots in

the diffraction pattern. The angle α between the two vectors was obtained from the STM images. This led to a unit cell with $b_1 = (7.0 \pm 0.3) \text{ \AA}$, $b_2 = (23.2 \pm 1.0) \text{ \AA}$, and $\alpha = (90 \pm 1)^\circ$. The corresponding superstructure matrix is:

$$\mathbf{M}_{\text{Cu}}^{\text{sub}} = \begin{pmatrix} 2.1 & -1.0 \\ 7.9 & 9.9 \end{pmatrix}.$$

We estimate the errors to be ± 0.1 for the elements of the first row and ± 0.3 for those of the second row. A structure model is given in Figure 7 (b). It shows the straight chains and the noted defects. The structure differs from that of the full monolayer of the α' -phase only by the value of b_2 , which is elongated by a factor of 1.4. Consequently, the same symmetry aspects apply. Notably, the vector $\mathbf{b}_2$ of the unit cell (cf. Fig. 7 (b)) corresponds to an average distance vector between neighboring chains, since these local distances vary.

Again, this structure changes upon annealing. In Figure 7 (c), an STM image at a coverage of $\theta = 0.45 \text{ ML}$ after annealing at 600 K for 15 minutes is displayed. At first glance, the structure looks rather disordered. The image shows that this structure consists of molecular chains, too. However, many of these chains are neither straight over long distances, nor parallel to neighboring chains. Remarkably, the chains and molecules no longer exhibit six, but only three distinct azimuthal orientations with respect to the substrate, and the chains contain regular kinks with angles of 120° . From this observation and a corresponding LEED pattern (not displayed) we conclude that the chains are oriented along the $[10]$ - and the long axes of the molecules along the $[12]$ -direction of the substrate.

A structure model is displayed in Figure 7 (d). The internal structure of the chains is the same as that of the chains prior to the annealing. However, they are rotated by 18° with respect to their orientation prior to annealing and are now aligned with the $[10]$ -direction of the substrate. A further difference concerns the long range order of the structure. Prior to annealing, the chains formed domains that consisted of many parallel chains. After annealing, the amount of parallel chains has significantly decreased, and the structure looks more like an assembly of individual chains. Another important difference, which contributes

to an increased disorder, is given by the high number of 120° kinks of the chains. An example showing such a 120° , is given in the top right corner of the structure model in Figure 7 (d). The STM image on the upper right hand side in Figure 7 (c) shows the typical S-shape of the molecules that was discussed above and reveals that the chains are homochiral here as in the α' -structure. However, the image on the lower right hand side in Figure 7 (c) shows a chain of the same azimuthal orientation where the handedness is flipped. This means that homochiral chains in all three directions can consist of both enantiomers. We believe that this is due to the fact that the chains are oriented along the high symmetry $[10]$ -direction of the Cu(111) substrate. Consequentially, upon mirroring of the chains at a plane in the $[10]$ -direction, the molecules will change their handedness, but they maintain their adsorption configurations. Hence, chains of both types of enantiomers are energetically equivalent.

Table 1: Overview on the structure parameters of QA on Ag(100) and Cu(111), which were obtained in this work, those of QA on Ag(111), which were obtained by Wagner et al.,²⁹ and those of the (1 $\bar{1}2$) plane of the α^I -QA polymorph.²³ All structures belong to the space group *P2*. The angle between the vectors b_1 and b_2 is called α , Z denotes the number of molecules per unit cell, and the area of the unit cells is named *A*. Errors for the matrix entries are given in the text. For the calculation of the vector lengths of the unit cells, the lattice constants at 300 K for Cu (3.597 Å) and Ag (4.079 Å) were used.⁵²

	Ag(100)		Cu(111)		Ag(111)		$\alpha^I - \text{QA}$ (1 $\bar{1}2$)-plane
M	α -phase	β -phase	α' -phase	β' -phase	α -phase	β -phase	not applicable
b_1 / Å	$\begin{pmatrix} 2 & 1.25 \\ -3 & 4.80 \end{pmatrix}$	$\begin{pmatrix} 4 & 3 \\ -5 & 3 \end{pmatrix}$	$\begin{pmatrix} 2.1 & -1.0 \\ 5.6 & 7.1 \end{pmatrix}$	$\begin{pmatrix} 6.0 & -1.1 \\ 8.2 & 13.1 \end{pmatrix}$	$\begin{pmatrix} 3 & 2 \\ -1.5 & 6 \end{pmatrix}$	$\begin{pmatrix} 5 & 5 \\ -1 & 5 \end{pmatrix}$	not applicable
b_2 / Å	6.6 ± 0.1	14.445	7.0 ± 0.3	16.9 ± 0.5	7.0 ± 0.5	14.445	6.9
α / °	16.4 ± 0.1	16.848	16.6 ± 1.0	29.3 ± 0.5	20.0 ± 0.2	16.088	16.9
Z	90 ± 1	112.2	90 ± 1	90 ± 2	90	111.1	110.3
A / Å ²	1	2	1	4	1	2	1
	111.5 ± 0.2	225.4	116 ± 10	496 ± 30	142.1	216.8	109.2

4. Final Discussion

The structures of QA investigated in this work, as well as those of QA on Ag(111) reported by Wagner et al.,²⁹ result from a subtle interplay between intermolecular interactions and substrate adsorbate interactions. An overview on the structure parameters of QA on Ag(100), Cu(111), Ag(111), and in the α^I -QA polymorph of the bulk phase was given in Table 1.

The formation of homochiral chains, which is very typical for QA, occurs directly upon the deposition at RT and is induced by the intermolecular interactions, where each molecule forms two hydrogen bonds to its next neighbors. We believe that the substrate has little to no influence on the internal structure of these chains because it is identical within the margins of error on all three metal substrates and in the α^I -QA polymorph. The azimuthal orientation of the chains, however, is influenced by the substrate because on all investigated substrates the chains do not arrange randomly, but along distinct orientations. This is also supported by the fact that the chains in the second layer, where the interactions to the QA layer below are weaker (as reported here for Cu(111)) adopt arbitrary orientations. Furthermore, the azimuthal orientation of the QA molecules and of the chains is a criterion to distinguish between the enantiomers. Chains that consist of different enantiomers (R or L) exhibit different orientations ($+\gamma$ and $-\gamma$) with respect to the $[10]$ directions of the surfaces, which leads to large enantiopure domains of these chains on both the Ag(100) and the Ag(111) surface. This result is remarkable because during and directly after deposition, a homogeneous and statistical mixture of both enantiomers is expected. In order to separate and to form large enantiopure domains, the molecules need a high mobility due to diffusion. However, it seems unlikely that diffusion alone is responsible for such a separation process because especially at high coverages (~ 1 ML) there is not much space between the molecules and the lateral motion is hindered. Hence, we would expect plenty of molecules of the 'wrong handedness' that are trapped in the large enantiopure domains during the separation process. As we did not observe many of such defects in the α -phase on Ag(100), we propose that on Ag(100) the molecules can change their handedness by a rotation around their long axes at

RT ($L \leftrightarrow R$). The "flipping" of a surface-adsorbed molecule to change its handedness is no uncommon process and was observed for molecules of similar size before.^{53,54} This mechanism allows the formation of enantiopure domains even at high coverages.

On Cu(111) however, kinetic barriers play an even more pronounced role. Directly after deposition at RT, the monolayer on Cu(111) consists mostly of individual chains (or only very small domains), rather than large homochiral domains. The chains on Cu(111) also contain a higher amount of defects (offsets due to changes in handedness of the molecules) than their counterparts on Ag(100). These phenomena indicate a lower likelihood of chiral segregation of the molecules after deposition in comparison to the Ag surfaces. This indicates that the diffusion and/or the ability of QA to rotate around the long axis are reduced on Cu(111) compared to the Ag(100) and Ag(111) surfaces.

The chain-like structures, formed directly after deposition on Ag(100), Ag(111) and Cu(111), are thermodynamically not stable because they transform irreversibly upon annealing. They are stabilized by kinetic barriers that are partly given by the intermolecular hydrogen bonds, which are activated and opened during the annealing. However, this is likely not the only reason for the barriers as we will explain further below. Generally, the α - and α' -phases of QA on these three surfaces that form prior to the annealing are mainly determined by the intermolecular interactions (i.e. intermolecular hydrogen bonds), while the β -phases, formed after annealing, are more strongly determined by the substrate-adsorbate interactions. This is deduced from the fact that on Ag(100) and on Ag(111), the β -phases are both commensurate. Upon the phase transitions, the overall number of hydrogen bonds is reduced, but in the commensurate structures all molecules occupy one of two distinct adsorption sites. This is supposed to lead to an energetically more favorable situation overall. However, the fact that the two β -phases on Ag(100) and on Ag(111) are structurally almost identical (cf. Table 1) shows that the intermolecular interactions still play an important role. (We note that the agreement of the b_1 values to the third decimal place is likely coincidental.)

The phases of QA on Cu(111) differ significantly from the ones on the two Ag surfaces, but the phase transition ($\alpha' \rightarrow \beta'$) occurs for likely similar reasons. At low coverages, the chains reorient along the high symmetry directions of the Cu(111) surface upon annealing at 600 K. The full monolayer transforms into a heterochiral, two-dimensional, and long range ordered structure (the β' -phase), which may be commensurate and exhibits only 5/8 as many hydrogen bonds as the α' -phase. The phase transitions of the submonolayer and the full monolayer of QA on Cu(111) are both driven by an increase of the substrate adsorbate interactions.

A further interesting aspect regarding the phase transitions of QA on Ag(100), Ag(111), and Cu(111) concerns the azimuthal orientation of the molecules on the surfaces before and after the phase transitions. On Ag(100), the orientations of the molecules in the α - and β -phase are identical within the margins of error, revealing that the molecules already adopt their preferred azimuthal orientations upon deposition. The same behavior can be observed for the phase transitions of full monolayers of QA on the Ag(111)²⁹ surface ($\alpha \rightarrow \beta$) and on the Cu(111) surface ($\alpha' \rightarrow \beta'$). On Ag(100) and Ag(111), due to the high mobility of the molecules at RT, it is plausible that the molecules adopt their preferred azimuthal orientation upon deposition. In comparison, the mobility on Cu(111) is reduced. Hence, the above result reveals that the molecules may still rotate in the plane of the Cu(111) surface to adopt the most favorable azimuthal orientation upon deposition. Interestingly, the six preferred symmetry equivalent azimuthal orientations of QA chains on Ag(111) are the same as those of QA on Cu(111). This indicates that the local six-fold geometry is the main determining factor for the azimuthal orientation of QA, despite the different lattice constants and chemical reactivities of the two substrates.

We come to the central question regarding the phase transitions ($\alpha' \rightarrow \beta'$) that we have not fully discussed, yet. Considering the high mobility of the molecules on Ag(100) and Ag(111) and the fact that they can change their handedness at RT, we question why the annealed phases do not form directly upon deposition. Since the β -phases are both com-

mensurate and hence thermodynamically more stable than the α -phases, there must exist further kinetic barriers that prevent their formation directly upon the deposition at RT. We suggest that this may possibly be explained by a small reconstruction of the top Ag layer of the substrate surface due to the adsorbate layer. At RT, the β -phases cannot form on the unreconstructed surfaces because the geometric fit between to QA molecules and the surfaces is not sufficient to allow an instantaneous formation of a commensurate structure. However, upon annealing, the atoms of the top layers of the substrate can rearrange slightly in a concerted manner in lateral and vertical directions to better fit to the adsorbed molecules, making the formation of commensurate structures possible. This reconstruction is hindered at RT, and it hence constitutes a kinetic barrier that must be overcome in order to form the β -phases on Ag(100) and Ag(111). A similar process may be present on Cu(111). Such reconstructions of the first layer of the substrate by adsorption of a flat lying organic molecule were observed before. Examples of this phenomenon were reported by Held and coworkers.⁵⁵⁻⁵⁷ Another example for an adsorbate induced reconstruction is the adsorption of C₆₀ on the Ag(111) surface.⁵⁸

The structures of QA and their temperature dependent behavior on Ag(100) and Ag(111) are very similar, but they differ significantly from those of QA on Cu(111). We have already mentioned the reduced mobility of QA on the Cu(111) surface, which we explain by a stronger corrugation of the QA/Cu(111) bonding potential related to stronger QA/Cu(111) interactions. Besides that, there are further differences between the behavior of QA on the surfaces. On Ag(100), annealing a submonolayer of QA results in island formation of the closely-packed commensurate phase. On Cu(111) however, a layer of QA with a similar coverage behaves differently. Upon annealing, the molecular chains alter their orientation with respect to the substrate, but mostly remain separated from other chains. Moreover, the annealed full monolayer of QA on Cu(111) exhibits a significant amount of disorder. In addition, many of our experimental attempts to prepare it resulted in disordered structures. This demonstrates that the rearrangement of QA molecules on the Cu(111) surface is significantly

inhibited by kinetic barriers even at high temperatures. Furthermore, upon annealing QA on the Ag(100) surface the diffraction pattern vanishes at about 470 K and it reappears at about 430 K upon cooling. Differently, the diffraction pattern of QA on the Cu(111) surface does not vanish completely during annealing at comparable temperatures. Upon heating it loses intensity and changes gradually with time. All these differences between QA on the Cu(111) surface and QA on the Ag(100) and Ag(111) surfaces can be consistently explained by a stronger bonding of the QA on the Cu(111) compared to the Ag surfaces.

Like many other prochiral molecules on surfaces,²⁷ QA on Ag(100) and Cu(111) as well as QA on Ag(111)²⁹ form structures that are given by the subtle balances of different forces and that undergo phase transitions upon annealing. The observed phase transitions transform homochiral into heterochiral structures, which is an aspect that is not uncommon for structures of prochiral molecules on surfaces.²⁷ In case of QA on Ag(100), Ag(111), and Cu(111), the initial formation of the homochiral structures is mainly driven by intermolecular hydrogen bonds. The heterochiral structures are thermodynamically more stable due to stronger substrate adsorbate interactions and form upon annealing the as grown and kinetically trapped chain like structures.

5. Conclusion

In summary, we have investigated the adsorption and ordering of quinacridone (QA) on Ag(100) and Cu(111) directly after deposition at room temperature and after annealing. On both surfaces, we found homochiral domains of metastable chain-like structures after deposition. These are mainly a consequence of intermolecular hydrogen bonds and are stabilized by kinetic barriers. The heterochiral structures that form after annealing have a reduced density of hydrogen bonds and are more strongly dominated by the substrate adsorbate interactions. We suggest that the phase transition on Ag(100) is associated with a reconstruction of the first layer of the substrate, which constitutes the kinetic barrier. A similar situation might presumably be present on Cu(111). On the Ag(100) and Ag(111) surfaces, the homochiral chain formation upon deposition reveals a high mobility and the activation of the rotation around the long molecular axis of QA allowing a change of the handedness. In contrast, these degrees of freedom are reduced on the Cu(111) surface. We attribute these differences to the stronger bonding between the QA and the Cu(111) surface compared to that on the Ag surfaces.

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Supporting Information Available

The following files are available free of charge.

- Supporting Information.pdf: This file contains an illustration of all four symmetry equivalent domains of the β -phase of QA on Ag(100).

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