4 Coverage-Controlled Mono- to Polymorphic Transition of H-bonded Networks on Au(111)

We report on the self-assembly of a conformational flexible organic compound on Au(111) using scanning tunneling microscopy and low-energy electron diffraction measurements. We observed different conformers of the compound upon adsorption on the reconstructed Au(111) surface. Increasing the lateral pressure, i.e., parallel to the surface, by means of increasing the molecular coverage revealed a coverage-controlled transition from a monomorphic system with only one molecular arrangement into a polymorphic system with two coexisting arrangements. Our results give insight into the role of substrate-induced conformational changes on the formation of polymorphic supramolecular networks.

4.1 Introduction

Two-dimensional self-assembly of molecules on surfaces has been widely employed to fabricate functional, supramolecular networks in a bottom-up fashion.1–3 Steering the self-assembly towards the envisioned supramolecular structure is often done through careful selection of the functional end groups of the molecular building blocks. However, surface-confined molecular assemblies can exhibit an energetic equivalence of different self-assembled structures leading to the emergence of polymorphism, i.e., the simultaneous presence of several self-assembled arrangements for the same compound. Transitions between those arrangements can be promoted, inter alia, by altering the number of
substituents for the molecular compound,\textsuperscript{4} adsorbing the same compound on a different substrate,\textsuperscript{5,6} providing energy by means of annealing of the sample,\textsuperscript{7,8} varying the molecular coverage,\textsuperscript{9–12} or a combination of these factors.\textsuperscript{13–15}

In this study, we report on the coverage controlled self-assembly of a linear molecule on Au(111). For the formation of well- and long-range ordered structures, we deployed molecular recognition based on H-bonding between substituted functional groups. H-bonding is commonly used due to its directionality, selectivity, and scalability.\textsuperscript{16,17} The linear molecule 1 used in our study bears two terminal 2,6-di(acetylamino)pyridyl recognition sites linked via a central a 1,4-diethynyl benzene (Scheme 4.1a). Scheme 4.1b shows conformation A of the recognition site that has been found to be energetically preferred in gas phase.\textsuperscript{18} This so-called donor-acceptor-donor (DAD) conformation for H-bonding can be involved in triple H-
bonding with a complementary ligand in ADA conformation. However, DADA, ADAD, and ADADA conformers (not shown) are also possible, potentially enabling intermolecular quadruple H-bonding.\textsuperscript{19,20} Scheme 4.1c displays another possible conformation B. This conformation is achieved by rotation of one acetylamino moiety around the C···NHR bond followed by a second rotation around the CO···NHR bond (indicated by red arrows in Scheme 4.1c), resulting in a cis conformation of the amidic group. The enhanced flexibility of the 2,6-di(acetylamino)pyridyl recognition site has previously promoted the successful assembly of various self-assembled structures on the surface.\textsuperscript{21,22} Moreover, compound 1 has been used to create mono and trimolecular structures on Ag(111) under ultra-high vacuum (UHV) conditions.\textsuperscript{23,24} At the solid-liquid interface, 1 enabled the successful engineering of dicomponent nanopolygons and porous networks.\textsuperscript{25,26}

Herein, we observed conformational changes upon adsorption on the Au(111) surface as a result of the conformational flexibility. Moreover, the presence of different conformers facilitated the formation of two energetically similar arrangements. Intriguingly, no complete conversion from one arrangement into the other could be achieved. Instead by exclusively controlling the molecular coverage, we were able to turn the monomorphemic system with only one molecular arrangement into a polymorphic system with two coexisting molecular arrangements. The observed behavior and arrangements on Au(111) were considerably different from earlier reported findings on the self-assembly of the same
compound on Ag(111) where different conformational changes were only observed after annealing the substrate and polymorphism was absent.\textsuperscript{23}

4.2 Methods

Sample Preparation

We prepared Au(111) by repeated cycles of sputtering with \( \text{Ar}^+ \) ions and subsequent annealing at 800 K under UHV conditions. Molecules were sublimed at 490 K onto the sample using a Knudsen cell evaporator (home-built). During deposition the sample was kept at room temperature (RT). Some samples were annealed after molecule deposition, which will be explicitly indicated throughout the text. We define one monolayer (ML) as the coverage where the substrate is fully covered by molecules in the densest possible arrangement.

STM and LEED Measurements

We performed our experiments in a UHV system with two chambers. The first chamber hosted a low-temperature scanning tunneling microscopy (STM) setup (Scienta Omicron GmbH) and had a base pressure of \(<5 \times 10^{-11} \text{ mbar}\). The second chamber had a base pressure of \(<1 \times 10^{-10} \text{ mbar}\) and was equipped with a multi-channel plate low-energy electron diffraction (MCP-LEED) system (Scienta Omicron GmbH) as well as the Knudsen cell evaporator. The samples were at RT for LEED measurements, while STM measurements were performed at 77 K. We used tips made from mechanically cut Pt/Ir wire to obtain STM images in constant current mode. All voltages are given with respect to a grounded tip. We processed the STM images using the software WSxM.\textsuperscript{27}
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4.3 Results and Discussion

Molecular Arrangements of 1 on Au(111)

Fig. 4.1a depicts an STM image of the self-assembly of 1 on Au(111) for a coverage below 0.5 ML. The sample was measured directly after molecule deposition, i.e., without any annealing. We observed no long-range order. Molecules arranged into small patches that seemed to nucleate at the elbow sites of the Au(111) reconstruction. A high-resolution STM image of the same sample (Fig. 4.1b) reveals that molecules in these patches assembled only in one kind of arrangement, labeled I. Annealing the same sample to 370 K yielded an increased long-range order, i.e., larger islands of molecules were present (Fig. 4.1c). Notably, we still observed arrangement I exclusively.

Fig. 4.1d shows an STM image of a sample with coverage close to 1 ML before annealing. As expected, more molecules were found on the sample. We again observed no long-range order. In contrast to the sample with low coverage (Fig. 4.1a), we found different arrangements. In addition to arrangement I, a high-resolution STM image shows a second arrangement, labeled II (Fig. 4.1e). Annealing to 370 K again induced long-range order (Fig. 4.1f). Both arrangement I and II coexisted on the surface and showed increased island sizes when compared to the unannealed sample (Fig. 4.1d). Independently of coverage or temperature, the unmodified herringbone pattern of the reconstructed 22 × \sqrt{3} - Au(111) surface\textsuperscript{28} can be seen through the arrangement.
4.3 Results and Discussion

Fig. 4.1: Self-assembly of 1 on Au(111) in dependence of molecular coverage and annealing temperature. (a) STM image for a coverage below 0.5 ML (80 x 80 nm$^2$, -1.5 V, 30 pA). The sample was prepared without annealing after deposition at RT. (b) High-resolution STM image (20 x 20 nm$^2$, -0.6 V, 80 pA) of the same sample shown in (a). For coverages below 0.5 ML, the molecular arrangement I was exclusively present. (c) STM image of the sample shown in (a,b) after annealing at 370 K (80 x 80 nm$^2$, 1.2 V, 20 pA). Compared to (a) the island size is significantly increased (80 x 80 nm$^2$, 1.2 V, 20 pA). We still only observed arrangement I. (d) STM image for close to 1 ML coverage prepared without annealing (100 x 100 nm$^2$, 0.4 V, 80 pA). (e) High-resolution STM image (40 x 40 nm$^2$, -1.2 V, 20 pA) of the same sample shown in (d). For coverages above 0.5 ML, the molecular arrangements I and II were observed. (f) STM image of a sample similar to (d,e) after annealing at 370 K (100 x 100 nm$^2$, 1.0 V, 20 pA). For both arrangements, the island size increased.
Fig. 4.2: Comparison of the molecular arrangements I and II. (a) High-resolution STM image of molecular arrangement I (8 x 8 nm², 0.1 V, 170 pA). The black lines indicate the principal directions of the Au(111) substrate. The unit cell is shown in green. A molecular model of 1 is overlaid to guide the eye. (b) Tentative structural model of arrangement I. The long unit cell vector aligns with the [1-10] direction of the Au(111) substrate. (c) Cartoon of arrangement I. A combination of single and double H-bonds (marked yellow and orange, respectively) between adjacent molecules stabilizes the molecular overlayer. (d) High-resolution STM image of molecular arrangement II (7 x 7 nm², 0.1 V, 170 pA). The unit cell is shown in cyan. (e) Tentative structural model of arrangement II. The unit cell is rotated by γ = ±8° with respect to the [1-10] Au direction. (f) Cartoon of arrangement II. Besides single and double H-bonds (marked yellow and orange, respectively), cyclic trimeric H-bonds involving three molecules (marked pink) stabilize the molecular overlayer.

Fig. 4.2a shows a high-resolution STM image of arrangement I. The rectangular unit cell is drawn in green and a model of one molecule is
overlaid to guide the eye. The principal directions of the Au surface are indicated by black lines in Fig. 4.2a. The length of the unit cell vectors are $a = 5.0$ nm, $b = 3.0$ nm, and the angle is $\Theta = 90^\circ$. The unit cell contains six molecules, which results in a molecular density of 0.40 molecules/nm. The long axis of the unit cell is furthermore parallel to the [1-10] direction of the Au(111) surface as shown in the tentative structural model (Fig. 4.2b). Fig. 4.2c is a cartoon of the structural model visualizing key properties of the molecules in arrangement I. Individual molecules of 1 are displayed as black stick figures. A long line represents the diethynyl benzene backbone. Two short lines are attached to each side of it and represent the di(acetylamino)pyridyl recognition sites. The opening angle between these short lines varies, depending on the conformation of the recognition site. We observed the conformations A as well as B. Specifically, one molecule in the unit cell exhibited both recognition sites in the B conformation, three molecules showed a combination of A and B, and the
other two molecules had both recognition sites in the A conformation. Fig. 4.3a-c shows a set of high-resolution STM images of the different conformations of 1 found in arrangement I. Additionally, we observed the molecular backbone bent for three molecules in the unit cell. Similar bending has been reported for flexible substituents of porphyrins and is facilitated by a slight distortion along the acetylene linkers of 1, i.e., the C···C bond angle deviates from the common 180°.²⁹ Arrangement I is stabilized by a combination of intermolecular single and double H-bonds (marked yellow and orange, respectively). Neighboring molecules, whose backbone points in the same direction, are connected via the double H-bonds, while single H-bonds are found between molecules aligned in different directions.

Fig. 4.2d shows a high-resolution STM image of arrangement II. The rhombic unit cell is displayed in cyan and a pair of molecules is overlaid to guide the eye. We measured \( a = b = 4.0 \) nm for the length of the unit cell vectors and an angle of \( \Theta = 120° \). The unit cell again contains six molecules, leading to a molecular density of 0.44 molecules/nm. The unit cell is slightly rotated by \( \gamma = \pm 8° \) with respect to the [1-10] direction of the Au(111) surface (Fig. 4.2e). Fig. 4.2f shows the cartoon of the structural model of arrangement II. All six molecules in the unit cell exhibit a combination of A and B conformation of their H-bonding recognition sites. A high-resolution STM image of this combination of conformations is shown in Fig. 4.3d. We did not observe any bending of the molecular backbone. Arrangement II is stabilized with a combination of different H-
bonding motifs. For each molecule, the recognition site in conformation A binds to three neighboring molecules in the following fashion: two times via double H-bonding (marked orange) and one time via a single H-bond (marked yellow). The recognition site in conformation B for each molecule also engages in H-bonding with three other molecules. However, it does so via one single H-bond (marked yellow) and one cyclic motif (marked pink). In the latter motif, three molecules are involved in single H-bonding in a cyclic trimeric fashion. A summary of the properties of arrangement I and II is shown in Table 3.1.
We gained complementary insight into the arrangements of I on Au(111) using LEED. Fig. 4.4a shows a LEED pattern for a sample with close to 1 ML coverage after annealing it at 370 K for 30 min. We observed clear diffraction spots for several orders of diffraction. Fig. 4.4b and Fig. 4.4c show the simulated LEED pattern of arrangement I (b) and II (c). (d) Both simulated patterns combined and overlaid onto (a).

Fig. 4.4: LEED pattern for molecular arrangements I and II. (a) LEED pattern for a coverage close to 1 ML (11.5 eV). The black lines indicate the principal directions of the Au(111) substrate. Simulated LEED pattern of arrangements I (b) and II (c). (d) Both simulated patterns combined and overlaid onto (a).

We observed clear diffraction spots for several orders of diffraction. Fig. 4.4b and Fig. 4.4c show the simulated LEED pattern of arrangement I and II, respectively. Combining and overlaying these onto the measured LEED pattern (Fig. 4.4d) results in a good agreement. The LEED data corroborate the observations made in STM: (i) arrangement II exhibits indeed a rotation of $\gamma = \pm 8^\circ$ with respect to the [1-10] Au direction and (ii) the good long-range order of the molecular structure after annealing.

Up to this point, we observed arrangement I exclusively at coverages below 0.5 ML, while at higher coverages arrangements I and II coexisted. We saw that annealing the sample at 370 K had no influence on this polymorphism and only led to increased long-range order. Naturally, this raises the question of the influence of further annealing. Annealing samples above 400 K lead to a decrease of island size coinciding with an
increasing amount of disordered structures that follow the herringbone reconstruction as well as defective molecules (Fig. 4.5a,b). After annealing at 470 K, we observed one-dimensional chains and decorated step edges (Fig. 4.5c). We suggest that 1 decomposed at temperatures above 400 K.

Additional to coverage and annealing, we also studied the influence of other sample preparation parameters. We therefore prepared samples with molecular deposition rates between 0.1 ML/min and 1 ML/min. Furthermore, we varied the cool-down rate of the sample after annealing. This was achieved by either cooling the sample down to 77 K immediately after annealing or leaving it cooling down to RT first, followed by cooling down to 77 K. We found no influence on the individual arrangements or
Table 4.2: Varied parameters and their influence on the molecular arrangements.

<table>
<thead>
<tr>
<th></th>
<th>arrangement I</th>
<th>arrangement II</th>
</tr>
</thead>
<tbody>
<tr>
<td>coverage dependency</td>
<td>no; visible for all coverages</td>
<td>yes; only observed above 0.5 ML coverage</td>
</tr>
<tr>
<td>temperature dependency</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>deposition rate dependency</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>cool-down rate dependency</td>
<td>no</td>
<td>no</td>
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</table>

We conclude that the polymorphism of 1 is neither kinetically driven nor a result of quenching.

Discussion

We will discuss our findings in light of a previous study of 1 on Ag(111). In this study, 1 formed a porous network stabilized by double H-bonding upon deposition on the Ag(111) surface. In this network, all recognition sites of the molecule were in the energetically preferred A conformation. Upon annealing, one amidic group rotated around the CO···NHR bond into a cis conformation (Scheme 4.2c), enabling quadruple H-bonding per bounding site. This resulted in a second, densely packed arrangement. Both arrangements were exclusively present and only dependent on the temperature. The results of this study contrasts with the behavior of 1 on Au(111) in three aspects: (i) conformation of 1, (ii)
4.3 Results and Discussion

We will consider each point in more detail. In contrast to 1 on Ag(111), we found conformational changes of 1 already upon adsorption on Au(111). Therefore, the reconstructed Au(111) surface seems to be instrumental in facilitating the conformational changes of 1. We suggest that any energy penalty associated with the conformational change to B is overcome by increased molecule-substrate or intermolecular interactions. A similar conformational dependency on the underlying substrate has previously been observed for flexible substituents of a porphyrin derivative.\(^{30}\)

Temperature can commonly be used to induce conformational changes of molecules resulting in a transformation of the molecular arrangement.\(^{7,8,31}\) For 1 on Ag(111), the conformational changes caused by annealing resulted in a transition from one arrangement to the other.\(^{23}\) This observation stands in contrast to the observations for 1 on Au(111). Annealing our samples only led to increased long-range order followed by decomposition of the compound at very elevated temperatures. We did not observe any influence of the temperature on either the conformation of 1.

Scheme 4.2: Different conformation of the recognition site of 1. (a) In gas phase optimal conformation A. (b) Conformation B found on Au(111) upon adsorption. (c) Conformation C found on Ag(111) after annealing the sample.
or the formation of arrangements I or II. Attempts to drive one arrangement into the other or possibly a different, third arrangement by means of temperature were also unsuccessful. We can infer from these observations that: (i) The energy barrier between arrangements I and II is higher than the energy needed for decomposition. (ii) No third arrangement exists that is thermodynamically favored and accessible.

Coverage has often been reported to promote transitions between different structures of a polymorphic system.\textsuperscript{15,32–34} In cases of flexible molecules, this coverage induced transition can go along with a conformational change of the molecules.\textsuperscript{35–37} While no coverage dependence has been reported for 1 on Ag(111), increasing the lateral pressure by means of molecular coverage was the sole driving factor for the polymorphism of 1 on Au(111). Arrangement II emerged for coverages above 0.5 ML. In contrast to arrangement I, molecules in arrangement II notably did not exhibit any bending. However, all molecules in arrangement II featured a conformational change, i.e., exhibited the A+B conformations of their recognition sites. While this is certainly associated with an energy penalty, arrangement II exhibited an increased density, thus minimizing the surface free energy more efficiently than the less dense arrangement I. We furthermore were unable to achieve a completely transition from arrangement I into arrangement II. Instead, both arrangements coexisted above the threshold coverage of 0.5 ML and furthermore grew in a uniform fashion until 1 ML was reached, i.e., at all time, arrangement I was dominant.
4.4 Conclusion

In conclusion, we studied the self-assembly of a linear molecule with conformational flexible H-bonding recognition sites on Au(111). We observed conformational changes upon adsorption on the reconstructed Au(111) surface. By controlling the coverage, we were able to transition from a monomorphic system with only one molecular arrangement into a polymorphic system with two coexisting molecular arrangements. The polymorphism itself was unaffected by variation of other preparation parameters including temperature, making the molecular coverage the sole driving force of the mono- to polymorphic transition. These results stand in contrast to previous findings for the same molecule on Ag(111). Our findings not only illustrate the role of conformational changes in polymorphic supramolecular networks, but also showcase how molecules with high conformational flexibility can be utilized to achieve different self-assembly behavior on structurally similar surfaces.
4.5 References

4.5 References

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