Tailoring molecular nano-architectures on metallic surfaces
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Chapter 4

Pyridyl-functionalized molecule 2 on Au(111): Insight into Au-coordination

In this chapter, the de novo synthetized pyridyl-terminated molecule 2 adsorbed on Au(111) was investigated by scanning tunnelling microscopy and spectroscopy. After submonolayer deposition onto the surface kept at room temperature, two different Au-coordinated structures emerged on the surface with short- and long-range order, respectively. The one with short-range order was stabilized by a combination of hydrogen bonding and two-fold metal-coordination, while the one with long-range order was held together by three-fold metal-coordination only. Annealing at 120 °C promoted a structural transformation of the short-range ordered structure into a second long-range ordered one, stabilized by two-fold coordination, while the three-fold Au-coordinated structure still remained present. The structures with two- and three-fold coordination were observed to be the thermodynamically favoured phases.
4.1 Introduction

Molecular self-assembly on metallic surfaces has been extensively studied over the last two decades in order to gain fundamental insight into the mechanisms governing molecular self-assembly [1–5]. It has been shown, that the formation of molecular self-assembled structures relies on the delicate balance between intermolecular and molecule-substrate interactions [6–9]. The former can be tuned by choosing molecules with different sizes, shapes and functional groups to create a large variety of the self-assembled molecular structures stabilized by different non-covalent interactions such as van der Waals forces [10], dipolar coupling [11], π–π stacking [12], hydrogen bonding [13,14], and metal–ligand interaction [15,16]. Among all non-covalently bonded structures, those stabilized by metal-ligand interactions, namely metal-coordinated ones, gained increasing attention due to their enhanced mechanical and thermal stability [2]. The construction of metal-coordinated structures on metallic surfaces implies that the metal atoms can originate either from the underlying surface or can be provided in a separate deposition step. On coinage substrates such as Cu, Au and Ag, these metal coordination centres can also be generated by detachment from the atomic step edges or even from the terraces at elevated temperatures [17–23]. In this chapter, as in the previous one, we focus our attention on the coordination by Au atoms originating from the underlying substrate. The Au-coordinated structures on Au substrates reported so far exhibited two- [18–20,24–27], three- [25,26] and four-fold coordination symmetry [28]. In the previous chapter, pyridyl-functionalized triarylamine molecules 1 formed two Au-coordinated structures with two- and three-fold coordination symmetry on Au(111). We determined that the two-fold coordinated structure is the thermodynamically favourable one. In this chapter, we further explore Au-coordination by employing another pyridyl-functionalized triarylamine molecule 2 with simpler structure compared to triarylamine molecule 1. In particular, we further investigate what predetermines the formation of Au-coordinated structures with a particular number of coordinated ligands. Additionally, we question whether several metal-coordinated structures can survive the heat treatment.

Herein, the self-assembly of pyridyl-functionalized triarylamine molecule 2 is studied on Au(111). We show that the molecules can form long-range ordered Au-coordinated phases with two- and three-fold metal-ligand interactions. The aforementioned metal-coordinated structures are identified as the favourable ones after annealing. After making a comparison of the self-assembly of molecule 2 with the one of molecule 1, we discuss the interplay between the self-assembly behaviour and structures of the molecules. In addition, the electronic properties of the Au-coordinated structure with two-fold coordination were investigated with scanning tunnelling spectroscopy.
4.2 STM characterization of the molecular networks

The pyridyl-functionalized triarylamine (tris(4-pyridin-4-ylphenyl)amine) molecule denoted as 2 (Figure 4.1) has a triangular shape. It consists of three identical molecular arms connected to a central nitrogen atom. Each arm has a terminal pyridyl group and an aryl group which serves as a spacer between the pyridyl functional group and the central nitrogen atom. The aryl and pyridyl groups can rotate around the single C-C bonds connecting them.

![Chemical structure of molecule 2.](image)

Figure 4.1: Chemical structure of molecule 2.

To investigate the self-assembly of molecule 2 on Au(111), the molecules were deposited under ultra-high vacuum (UHV) conditions onto the substrate held at room temperature (RT) and investigated with scanning tunnelling microscopy (STM) measurements. Figure 4.2a shows an STM image of an individual molecule 2 on Au(111). The molecule exhibits four protrusions: the central protrusion with higher contrast corresponds to the nitrogen atom in the centre, while the three outer protrusions with lower contrast are assigned to the peripheral pyridyl groups. For comparability, the structural model of molecule 2 is overlaid on the STM image in Figure 4.2b.

For deposition of submonolayer coverage of molecule 2 onto Au(111) held at RT two different phases labelled α and β were observed to co-exist (Figure 4.2c). Phase α can be recognized as a disordered phase exhibiting only short-range order, while phase β appears as a phase with long-range order. For both phases, the herringbone reconstruction of Au(111) remains intact. This suggests that the interaction between 2 and the Au(111) surface is relatively weak and that the intermolecular interactions dominate over the molecule-substrate ones [29]. The co-existence of two different phases evidences polymorphism of the self-assembled structures formed by molecules 2 on Au(111). Polymorphism was also observed for the related molecule 1 on Au(111) (Chapter 3) as well as for other pyridyl-functionalized molecules on Au(111) [26,30,31], Cu(111) [30,32], and Ag(111) [26,33,34].
Figure 4.2: a) High-resolution STM image of molecule 2 adsorbed on Au(111) (1.9 × 1.7 nm², U = -2 V, I = 60 pA). b) The structure of molecule 2 superimposed onto a). Carbon atoms are grey, nitrogen atoms blue and hydrogen atoms white. c) Overview STM image for submonolayer coverage of molecule 2 on Au(111) (80 × 80 nm², U = -1.8 V, I = 20 pA). Two different molecular phases α and β are present and labelled by blue symbols.

In the following, each phase of molecule 2 on Au(111) will be individually discussed. Figure 4.3a shows phase α in detail and allows precise determination the molecular arrangement. Based on our STM observations, a tentative structural model of phase α was constructed (Figure 4.3b). Phase α is a disordered porous phase which is simultaneously stabilized by two types of bonding motifs: metal-ligand interactions between the pyridyl nitrogen atoms and native Au atoms (blue oval) and hydrogen bonding between the pyridyl nitrogen atoms and H atoms of adjacent molecules (red oval). These two types of bonding motifs simultaneously stabilizing the

Figure 4.3: a) Detailed STM image of phase α (7 × 7 nm², U = -1 V, I = 60 pA). b) Tentative structure model of phase α. The blue and red ovals indicate the stabilizing bonding motifs: metal-ligand interactions between the pyridyl nitrogen atoms and native Au atoms, and H-bonding between the pyridyl nitrogen atoms and H atoms of adjacent molecules, respectively.
structures were earlier reported in literature for other pyridyl-functionalized molecules [33,27].

The STM image of the arrangement of molecules 2 within phase β is shown in Figure 4.4a. In Figure 4.4b, the tentative structural model of phase β is given. In phase β, the molecules arrange in a hexagonal pattern. The related unit cell (marked with the blue rhombus in Figures 4.4a and b) has the dimensions of $a = b = 1.94 \text{ nm}$, $\theta = 60^\circ$ and contains one molecule resulting in a density of 0.31 molecules/nm$^2$. Each molecule within phase β is surrounded by six adjacent molecules. Three nitrogen atoms of the pyridyl groups from the three nearest molecules are oriented towards one common central point. At this point a native Au atom is located to which the nitrogen atoms coordinate. Phase β is stabilized by three-fold metal-ligand interactions between the pyridyl nitrogen atoms and native Au atoms. Such a three-fold metal-coordination motif was also observed for molecule 1 (Figure 3.4 in Chapter 3). The average distance between the pyridyl nitrogen atoms and the coordinated Au atoms is 2.7 Å. This distance coincides with the Au-N distances reported for phase β formed by molecules 1 and for the three-fold metal-coordinated phase of pyridyl-functionalized benzene molecules on Au(111) [26]. The STM measurements showed that the molecular islands of phase β exhibited domain orientations of ±20° with respect to the principal Au directions.

After annealing submonolayer coverage of molecule 2 adsorbed on Au(111) at 120 °C, phase β was still present on the surface and additionally, a new phase denoted as phase γ appeared (Figure 4.5a). Figure 4.5b shows phase γ in detail. Based on our STM measurements, the tentative structural model of phase γ was constructed.

![Figure 4.4: a) Detailed STM image of phase β (7 × 7 nm$^2$, $U = -1.8 \text{ V}, I = 20 \text{ pA}$). b) Tentative model of phase β which is stabilized by three-fold metal-ligand interactions. The purple spheres represent Au atoms. The blue rhombus marks the unit cell of phase β in both a) and b). At each node, three pyridyl groups of three adjacent molecules point towards one central common point where a coordinated Au atom is located. The set of three lines at the bottom right corners of a) and b) indicate the principal Au directions.](image)
Figure 4.5: a) Overview STM image of submonolayer coverage of molecule 2 annealed at 120 °C (200 × 200 nm², U = -1.8 V, I = 20 pA). Both phases β and γ are present. The molecular islands with the network-lattice orientations of 30° and +12° with respect to the principal Au directions are marked by the blue and green star, respectively. b) Detailed STM image of phase γ (6.5 × 6.5 nm², U = -2 V, I = 60 pA). The unit cell is marked by the blue rhombus. c) Tentative structural model of phase γ. The unit cell is indicated by the blue lines. The purple spheres represent the coordinated Au atoms. The pyridyl groups of two adjacent molecules point towards each other and are involved in metal-ligand interactions with two-fold coordination symmetry. The set of three lines at the bottom right corner indicates the principal Au directions.

(Figure 4.5c). Molecules 2 within phase γ arrange in a hexagonal porous structure on the Au(111) surface. For phase γ, the unit cell (blue rhombus in Figure 4.5b) with the dimensions of a = b = 3.45 nm, Θ = 60° contains two molecules, which results in a molecular density of 0.19 molecules/nm². Each molecule in phase γ has three nearest
neighbours. Two adjacent molecules in phase $\gamma$ are linked via a linear pyridyl-Au-pyridyl coordination considering that the two pyridyl nitrogen atoms point towards each other. Such a bonding motif was also observed for molecules 1 in phase $\gamma$ described in Chapter 3 (Figure 3.5) and reported for pyridyl-functionalized porphyrin molecules [19] and pyridyl-functionalized benzene molecules on Au(111) [26,27]. The average distance between the pyridyl nitrogen atoms and the coordinated Au atom is 1.5 Å. This distance coincides with the ones observed for molecules 1 in phase $\gamma$ and agrees well with the N-Au distance values of 1.5 Å - 2.7 Å reported for two-fold Au-pyridyl coordination of porphyrin [19] and benzene derivatives on Au(111) [26,27]. Based on our STM data, phase $\gamma$ has three different network-lattice orientations: 30° (blue star in Figure 4.5a) and ±12° (+12° network-lattice orientation is marked by a green star in Figure 4.5a), relative to the principal Au directions. Further annealing did not lead to the exclusive formation of one phase, either $\beta$ or $\gamma$ phase. Both phases remained on the surface until decomposition of the molecules at temperatures higher than 200 °C set in. For this reason, we conclude that phases $\beta$ and $\gamma$ have a similar stability on Au(111).

The structural differences between pyridyl-functionalized molecules 1 and 2 were found to result in different self-organized structures. Molecules 1 and 2 can both form molecular structures with two- and three-fold coordination symmetry (denoted as phases $\gamma$ and $\beta$ in Chapters 3 and 4) on Au(111). For both molecules phase $\beta$ appeared after molecular deposition on Au(111) kept at room temperature. On the other hand, phase $\gamma$ appeared for molecule 1 at room temperature, while for molecule 2 annealing at 120 °C was required. Moreover, for molecule 1, the post-deposition annealing at 180 °C resulted in exclusive formation of phase $\gamma$, while for molecule 2, the annealing treatment did not lead to the exclusive formation of any phase. Instead, phases $\gamma$ and $\beta$ co-existed on Au(111) up to annealing temperatures at which the decomposition of molecules 2 was observed. By assuming that during annealing, molecules 1 and 2 had similar access to the Au metal centres, the difference between the assembling behaviours of molecules 1 and 2 is thus associated with the structural differences between these molecules. It is suggested that upon adsorption of molecules 1 on Au(111), the pyridyl functional groups of the molecules point towards the surface establishing attractive molecule-substrate interactions and thereby, helping to anchor the molecules to the surface. The out-of-plane methyl groups serve as a spacer and slightly lift the core of the molecules away from the surface. The molecular core-surface interaction is assumed to contribute only little to the molecule substrate interactions. A very similar adsorption conformation of a related molecule which is functionalized by cyano instead of pyridyl groups was reported [24,35]. It was shown that the cyano-functionalized molecule undergoes arching with cyano groups pointing towards the surface and methyl groups rotating away from the surface. As a result, the central nitrogen atom of the adsorbed molecule appeared
above the cyan nitrogen atoms. In molecules 2, the carbon bridges constraining the rotation of the aryl rings as well as the out-of-plane methyl groups, which can increase the adsorption height of the molecules, are absent. Thereby, a different adsorption geometry of molecules 2 with a closer distance of both the central nitrogen atoms and the aryl rings to the Au(111) surface compared to molecules 1 is expected implying stronger molecule-substrate interactions for molecules 2 than for 1. This may alter the ratio of molecule-substrate to intermolecular interactions leading to the observed differences, namely that the formation of phase γ from molecules 2 requires larger substrate temperatures compared to phase γ from molecules 1.

4.3 STS study: Electron confinement observation inside the molecular network pores

Scanning tunnelling spectroscopy (STS) was employed to investigate the electronic properties of the Au(111) surface patterned by molecular phase γ. The STS spectra were recorded above the molecular centre and above the expected coordinated Au atom (blue and red squares, respectively, in Figures 4.6a and b). The lowest unoccupied molecular orbital (LUMO) of molecules 2 on Au(111) was detected at +1.77 V (green vertical line), while their highest occupied molecular orbital (HOMO) was detected at -1.64 V. Interestingly, for the bias voltages more negative than -1.64 V, the molecules had the appearance with higher contrast around their centres (Figure 4.6b), while for the bias voltages more positive than -1.64 V, the molecules appeared with relatively equal contrast for all substituents (Figure 4.6c). Such contrast dependence was observed for all molecules 2 in all molecular phases on Au(111).

In order to compare the electronic properties of the bare Au(111) surface and the surface modified by molecules 2, STS spectra were acquired on the bare Au(111) surface and on the area with phase γ (Figure 4.7). The STS spectrum acquired on the bare Au(111) surface (black curve) serves as a reference for the spectra acquired on the surface area with phase γ. Typically, the STS spectra obtained on the bare Au(111) surface exhibit a step function with an onset around -0.5 V. This step function represents the surface state of Au(111) [36–39]. In our STS spectrum taken on the bare Au(111) surface, we observe a pronounced peak at -0.48 V (blue vertical line) instead of the step function due to tip imperfections. In addition, we observed three less pronounced peaks (indicated by three black arrows) which were attributed to the tip local density of states and their presence has to be taken into account when the spectra acquired of phase γ are considered. In Figure 4.7, the STS spectrum marked in blue was acquired at the centre of the pore within phase γ, while the STS spectrum marked in red was taken at the halfway between the centre and the rim of a pore. The corresponding acquisition positions are indicated by the squares with the colour code
Figure 4.6: a) STS spectra taken at the centre of molecule 2 (blue curve) and the expected coordinated Au atom (red curve). The acquisition positions are marked by the squares with the same colours as the corresponding curves in the spectra (blue and red ones) in the inset and also in b). The green (+1.77 V) and blue (-1.64 V) vertical lines indicate the LUMO and HOMO of molecule 2 on Au(111), respectively. b) (7 × 7 nm², U = -2 V, I = 20 pA) and c) (7 × 7 nm², U = -1V, I = 20 pA) Constant current STM images of molecules 2 taken at bias voltages of -2 V and -1 V, respectively, to depict the difference in the molecule’s appearances. The structure of molecule 2 is superimposed onto the STM images in b) and c) in the top left corners.

of the STS curves (blue and red) in the inset, respectively. These two STS spectra were acquired with the same tip which was used for the acquisition of the STS spectra on the bare Au(111) surface. The spectrum taken at the centre exhibits a clear difference compared to the one taken on bare Au: a broad peak at +0.14 V can be observed (green vertical line). Similar features have been earlier observed for porous molecular overlayers on metallic surfaces [40–44]. They were attributed to the confinement of the surface state electrons inside the molecular network pores.

In order to further investigate the confinement of the surface state electrons within the pores formed by molecules 2, a set of dI/dV maps was acquired (Figure 4.9, a full set of the dI/dV maps is given in Appendix B, Figure B.1). Figure 4.9a shows
Figure 4.7: Comparison between the STS spectra taken at the bare Au(111) surface and inside the molecular pore. The STS spectrum taken on the bare Au(111) substrate (black curve) is used as a reference spectrum. The blue vertical line at -0.48 V marks the peak related to the Au(111) surface state. The black arrows indicate the peaks which originate from the tip contaminations. These peaks create artefact features in the STS spectra taken inside the pore. The STS spectra taken at the centre and halfway between the centre and the rim of the pore are indicated in blue and red, respectively. The respective positions are marked by the blue and red squares in the inset. The green vertical line (+0.14 V) marks the peak position of the confined state.

A dI/dV map taken at a bias voltage of -0.45 V close to the onset of the surface state of Au(111). This dI/dV map does not display a pronounced change of the dI/dV contrast associated with the confinement of surface state electrons. Figure 4.9a, shows the corresponding STM image simultaneously acquired with the dI/dV map in Figure 4.9a. Figure 4.9b shows a dI/dV map taken at a bias voltage of +0.05 V close to the position of the dI/dV peak associated with the confined state. Figure 4.9b, shows the corresponding STM image. In the dI/dV map in Figure 4.9b, seven bright protrusions were assigned to one molecular pore. The largest protrusion in a shape of a circle is located at the centre of each pore, while the six other bright protrusions with a relatively equal size are observed at the rim of the network pore. Moreover, the dI/dV contrast of the described pattern starts to appear at a bias voltage of -0.15 V, at +0.05 V the contrast is the most pronounced, and at +0.2 V the contrast vanishes, covering the bias voltage range of 0.35 V (Appendix B, Figure B.1).

An STS study was also performed for the pores within phase β (see Scanning tunnelling spectroscopy study of phase β in Appendix B). In order to draw reliable conclusions on the electron confinement within the pores of phase β more investigations are needed.
Figure 4.9: a) \((9 \times 9 \text{ nm}^2, U = -0.45 \text{ V}, I = 150 \text{ pA})\) and b) \((9 \times 9 \text{ nm}^2, U = 0.05 \text{ V}, I = 150 \text{ pA})\) Experimentally acquired \(\frac{dI}{dV}\) maps taken on phase \(\gamma\) at different bias voltages of \(-0.45 \text{ V}\) and \(+0.05 \text{ V}\), respectively. \(a_1, b_1\) STM images simultaneously acquired with the \(\frac{dI}{dV}\) maps shown in a) and b), respectively. Blue hexagons outline pores of phase \(\gamma\).
4.4 Conclusions

In conclusion, for pyridyl-functionalized molecule 2 adsorbed on Au(111), we observed that two long-range ordered Au-coordinated phases are the most favourable structures, with two- and three-fold coordination, respectively. We compared our results to the ones obtained for the pyridyl-functionalized molecule 1. Our findings suggest that the differences between the chemical structures of the molecules lead to different molecule-substrate interactions, which facilitate the formation of the phase for molecule 1 with two-fold coordination at a lower substrate temperature, in comparison to molecule 2. In addition, we found that the porous Au-coordinated phase with two-fold coordination can confine the Au surface state electrons inside its pores.

4.4 Experimental details

The experiments were performed in an ultra-high vacuum (UHV) system with a base pressure of $2 \times 10^{-10}$ mbar. The Au(111) single crystal was prepared by several cycles of Ar$^+$ sputtering and subsequent annealing at temperatures between 700 K and 800 K. Molecules 2 were deposited from a quartz crucible inside a commercial molecule evaporator (OmniVac) onto the Au(111) substrate held at room temperature (RT). In this study, one monolayer (1 ML) coverage of molecule 2 describes a complete monolayer of the molecules arranged in the most densely-packed structure, namely phase β. Before molecule deposition the molecules were thoroughly degassed. The STM and STS measurements were performed with a commercial low-temperature STM (Scienta Omicron GmbH) at 77 K and 4.5 K, respectively. The STM images were acquired in the constant current mode using a wire-cut Pt-Ir tip. All bias voltages are given with respect to a grounded tip. The software WSxM was used to process the STM data [45]. In order to acquire the STS data, a lock-in modulation amplitude of 10 mV and frequency of 678 Hz were used.
References


