Heat-induced formation of one-dimensional coordination polymers on Au(111): an STM study†

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The formation of one-dimensional coordination polymers of cyano-substituted porphyrin derivatives on Au(111) induced by thermal annealing is demonstrated by means of scanning tunnelling microscopy. The polymer is stabilised by an unusual threefold coordination motif mediated between an Au atom and the cyano groups of the porphyrin derivatives.

The recent increase of interest in the field of molecular self-assembly on surfaces has opened new avenues towards the development of various types of low-dimensional molecular architectures.† Among them, metal-coordinated one- and two-dimensional (1D and 2D) structures adsorbed on metal surfaces have attracted special attention. This is due to the possibility to control both the size and geometry of these architectures by properly selecting the organic ligands with respect to length, shape and functional endgroups together with the chemical nature of the metal centres and substrates.2 Moreover, an advantage of metal–organic coordination bonds, in comparison to other types of non-covalent and covalent bonds, is that they show an adequate balance between stability and lability due to their relative strength and reversibility.3 This offers the possibility to build-up robust 1D/2D structures with a high level of structural perfection,4 which is of utmost importance for the usage of such networks in future molecular electronic devices. To date, most of the reported metal–organic units stabilizing surface-supported molecular coordination networks are based on the combination of organic linkers bearing pyridyl, cyano, hydroxyl or carboxyl endgroups and transition-metal atoms such as Cu, Fe, Co, Ni.5 Up to now, reports on the formation of 1D/2D molecular coordination networks on an Au surface without the addition of transition-metal atoms are very rare.6

Herein, we report a low-temperature scanning tunnelling microscopy (STM) investigation on the formation of 1D coordination polymers on Au(111) induced by thermal annealing under ultrahigh vacuum (UHV) conditions. For this work, we synthesized porphyrin 1 (see ESI†) with two 3,5-di(tert-butyl)phenyl and two 4'-cyanobiphenyl groups attached to cis-meso-positions (Fig. 1a).

Upon deposition of submonolayer coverage of 1 on Au(111) held at room temperature (RT), nanoribbon-like structures were observed by STM (Fig. S3, ESI†). Besides, isolated clusters...
were also found at the elbow sites of the Au(111) herringbone reconstruction which are well-known as preferential nucleation sites. Close to monolayer (ML) coverage, a well-ordered close-packed 2D pattern was observed (Fig. 1b and Fig. S4, ESI†). Notably, this 2D pattern is based on the nanoribbon-like structures observed at submonolayer coverage. The high-resolution STM image in Fig. 1b reveals that the nanoribbon-like structures are attached back to back resulting in the close-packed 2D pattern. Interestingly, the co-existence of two different conformational isomers of 1 in the 2D pattern can be clearly discerned (Fig. 1b). The conformational isomers can be identified by the dark bridge, which either separates the 4′-cyanobiphenyl from the 3,5-di-(tert-butyl)phenyl substituents (A isomer) or acts as a mirror plane for the molecule (B isomer) (blue and green coloured lines in Fig. 1b and c), respectively. This is similar to our earlier study of 1 adsorbed on Cu(111). More information on the conformational isomers can be found in the ESI† (Fig. S5). As determined from STM analysis, the molecules are arranged in a rhombic unit cell with dimensions of \( a = (43 \pm 1.2) \, \text{Å}, \quad b = (70 \pm 1.6) \, \text{Å} \quad \text{and} \quad \gamma = (60 \pm 3) ^\circ \). The axes of the molecular unit cell are parallel to principal Au directions. The co-existence of three rotational domains having an angle of 120° to each other was observed, reflecting the threefold symmetry of the underlying substrate (Fig. S4b, ESI†). Moreover, the characteristic dark bridges of 1 are aligned along one of the three principal Au directions. These findings point out the significant influence of the underlying substrate on the adsorption behaviour as well as the conformational states of 1 deposited on Au(111). Fig. 1c shows the tentative molecular model for the observed 2D pattern (see also Fig. S6, ESI†). In this model, the molecules are organized in alternating single and twin rows (marked by 1 and 2, respectively), which are parallel to each other. Remarkably, only the A isomer appears in the single rows, whereas both A and B isomers co-exist in the twin rows. The single rows are characterized by the alignment of neighbouring molecules into an antiparallel fashion with an interdigitation of the 4′-cyanobiphenyl legs, resulting in the formation of a metal coordination bond is based on supplying additional energy to the system by thermal annealing which enables the lateral distortion of the 4′-cyanobiphenyl legs. This finding is in good agreement with the dependence of the structural transformation on the annealing temperature observed in the present work. Herein, the thermal energy at RT is insufficient for the bending of the 4′-cyanobiphenyl legs, resulting in the formation of mostly nanoribbon-like structures. In contrast, at elevated temperatures, the energy gain is high enough to vary the opening angle of the 4′-cyanobiphenyl legs to coordinate to Au atoms enabling the formation of flexible 1D coordination polymers. We conclude that the 1D polymer chains are stabilised by a threefold coordination motif mediated by the nitrogen lone-pair electrons of the three 4′-cyanobiphenyl legs and one Au atom positioned at the centre. It should be noted that there are two possibilities for
the formation of the \( \text{CN} \cdots \text{Au} \) coordination motif depending on whether the Au centres are Au adatoms or Au surface atoms. Our density functional theory (DFT) calculations indicate that Au adatoms are involved in the threefold coordination motif (see Fig. S14, ESI†). It was recently reported that the creation of Au adatoms on Au(111) leads to the reordering of the herringbone reconstruction.9 However, in our case, the herringbone reconstruction is completely unaffected upon submonolayer coverage of 1 on Au(111) at 160 °C. Now, four CN-groups of four \( \text{CN} \cdots \text{Au} \) coordination motifs, which is considered as a basic unit of the 1D molecular chains aligned along the step edges (see also Fig. S10, ESI†). As expected, three N atoms of the 4’-cyanobiphenyl groups point toward one Co atom to form the threefold coordination motif, which is responsible for the 1D polymer formation. Within the 1D polymers both conformational isomers can be clearly discerned (marked by blue and green bars in Fig. 2d). They are randomly distributed within the 1D coordination polymer with equal amounts of each as determined from a statistical analysis. Importantly, the lateral distortion of the 4’-cyanobiphenyl legs, imposed by the coordination to the Co centres, was again observed (Fig. 3b and c). In addition to the 1D polymers, rosette structures are formed upon addition of Co, which were not observed in the annealing case. Rosettes of two different sizes are present (Fig. 3d and Fig. S11, ESI†) and they are stabilised by the same coordination motif as in the 1D coordination polymers (Fig. 3e). Notably, the dark bridges due to the saddle shape conformation of 1 do not align along the principal Au directions. That is in contrast to what we observed for the 2D close-packed structure. From this observation we conclude that the molecule–substrate interaction is mainly mediated by the Co atoms, and the porphyrin core–Au surface interaction is only of weak physisorptive nature.11 Putting it differently, a dominant \( \text{CN} \cdots \text{Au} \) coordination interaction is thought to allow for different rotational alignments of 1 with respect to the principal Au directions, thus enabling the formation of rosette structures. Other types of rosette structures have been found recently for the coordination of Fe atoms to pyridyl-substituted porphyrins on Au(111).12 Based on the results obtained from the control experiment, we conclude that the 1D polymers formed upon annealing submonolayer coverage of 1 on Au(111) are indeed stabilised by a threefold \( \text{CN} \cdots \text{Au} \) coordination motif. The molecular model for the heat-induced 1D coordination polymers is shown in Fig. 2e.

Another difference between the Au- and Co-coordinated structures can be observed upon studying the molecular arrangement at the Au(111) step edges. Fig. 4a and c show overview STM images of samples prepared by annealing and Co deposition, respectively, exhibiting several step edges. In both cases, the step edges are almost completely covered by molecules. The close-up STM images (Fig. 4b and d) reveal a significant difference in the molecular arrangement at the step edges for the two cases. Upon annealing at 210 °C, the molecules have a preferred orientation with their tert-butyl groups aligned along the step edges. Now, four CN-groups of four neighbouring molecules point toward each other. They meet in a fourfold node, resulting in the formation of a square-like tetramer which is considered as a basic unit of the 1D molecular chains aligned along the step edges (see also Fig. S12, ESI†). In this configuration, the formation of such fourfold nodes is very unlikely for uncoordinated CN-groups due to the electrostatic repulsion of the nitrogen lone-pair electrons. Thus, we suggest that a fourfold Au–CN coordination motif stabilises the 1D chains aligned along the step edges. This observation is in line with recent reports on other CN-substituted molecules adsorbed on Au(111).12,13 Notably, a lateral distortion of the CN-legs with an opening angle larger than 90° due to the coordination bonding was observed (see molecular model in Fig. 4b). In contrast, no such fourfold coordination motifs were observed at the step edges upon Co deposition (Fig. 4d). Importantly,
an influence on the observed types of intermolecular interactions. Close-up STM images (20 × 20 nm²) of the areas marked by white dashed squares in (a) and (c), respectively. In (b) four molecular models are shown to illustrate the fourfold coordination motif. The STM images were taken at 77 K with U = −1.8 V, I = 20 pA.

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Notes and references


