Metal-Organic Frameworks on Surfaces

Heat-Induced Formation of 1D Molecular Coordination Networks

The formation of one-dimensional molecular coordination networks from cyano-substituted porphyrin derivatives on Au(111) could be achieved upon thermal annealing. The coordination network is stabilized by an unusual threefold coordination motif mediated between a native Au atom and the cyano groups of the porphyrin derivatives.

Introduction

Over the past few years, considerable efforts have been devoted to develop efficient approaches for the construction of sophisticated molecular networks on metal surfaces, which are expected to open up new avenues towards the fabrication of innovative future molecular devices [1]. In this context, metal-coordinated low-dimensional molecular networks adsorbed on metal surfaces have attracted great interest due to the possibility to steer both the size and geometry of these structures via the choice of the organic ligands, the transition metal centers as well as the underlying substrates [2]. Besides, compared to other types of non-covalent bonds, coordination bonds exhibit an adequate balance between stability and lability due to their relative strength and reversibility, which is of paramount importance for the creation of robust molecular networks with a high degree of structural order [3]. Among the reported metal-organic units stabilizing surface-supported coordination networks, the combination of organic ligands bearing functional cyano endgroups and transition-metal atoms has been frequently exploited in recent years [4-6]. However, the construction of such molecular coordination networks on a Au surface with native Au atoms, i.e. without addition of transition metal atoms is very rare and not well understood. In this regard, we could recently demonstrate that a Au cyano coordination bond can be spontaneously formed upon adsorption of cyano-substituted triarylamine derivatives on Au(111) held at room temperature [7].

Herein, we report a low-temperature scanning tunneling microscopy study on the formation of 1D coordination polymers of cyano-substituted porphyrin derivatives 1 (fig. 1a) on Au(111) induced by thermal annealing.
The newly formed polymer is stabilized by a threefold coordination motif formed between a native Au atom and the nitrogen atoms of three cyano groups of the porphyrin derivatives. Interestingly, we found that the angle between the cyanobiphenyl units changes upon thermal annealing which is important for the formation of the coordination networks.

**Results and Discussion**

Upon deposition of submonolayer coverage of 1 on Au(111) held at room temperature (RT), nanoribbon-like structures were observed (fig. 1b), while for close to monolayer (ML) coverage, a well-ordered close-packed 2D pattern was found (fig. 1c). Notably, this 2D pattern is based on the nanoribbon-like structures observed at submonolayer coverage. The high-resolution STM image (fig. 1c) reveals that the nanoribbon-like structures are attached back to back resulting in the close-packed 2D pattern with unit cell dimensions of $a = (43 \pm 1.2)$ Å, $b = (70 \pm 1.6)$ Å and $\alpha = (60 \pm 3)^\circ$. 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 classified depending on the dark bridge, which either separates the 4′-cyanobiphenyl from the 3,5-di(tert-butyl)phenyl substituents (A isomer) or acts like a mirror plane for the molecule (B isomer), as illustrated by blue and green colored lines in figure 1d and e, respectively. Figure 1f shows the tentative molecular model for the observed 2D pattern in which the molecules are organized in alternating single and twin rows (marked by 1 and 22, respectively). This model illustrates that the molecular network is stabilized by a combination of H-bonds and vdW interactions.

Upon annealing submonolayer coverage of 1 adsorbed on Au(111) at 160 °C, 1D flexible molecular chains are formed (fig. 2a). The close-up STM image (fig. 2b) clearly reveals that the 4′-cyanobiphenyl units of two molecules face each other in an antiparallel way and another 4′-cyanobiphenyl unit of a third molecule is coming
from the side to form a threefold node. Each molecule connects to two threefold nodes which results in the formation of trimers as basic units of the 1D chains. Importantly, the 4′-cyanobiphenyl units of 1 in each trimeric unit exhibit some flexibility. This can be associated with a variation of the opening angle of the two cyanobiphenyl units which differs from the intrinsic opening angle of 90° (fig. 2b and f). It was previously reported that 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 [5]. Herein, we suggest that the thermal energy at RT is insufficient to bend 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 native Au atoms enabling the formation of the flexible 1D coordination network. Thus, we conclude that the 1D polymer chains are stabilized by a threefold coordination motif mediated by the nitrogen lone-pair electrons of three 4′-cyanobiphenyl legs and one Au atom positioned at the center. The molecular model for the heat-induced 1D coordination polymers is shown in figure 2e.

To get additional evidence for the formation of the 1D molecular coordination network from 1 on Au(111), we performed a control experiment where cobalt atoms were deposited onto submonolayer coverage of 1 on Au(111) held at RT. As expected, flexible 1D polymers were observed again, similar to the case for annealing of 1 on Au(111) at 160°C (fig. 2c). Figure 2d shows that the binding motif stabilizing the 1D chains is the same as observed for 1 on Au(111) upon annealing. Importantly, the lateral distortion of the 4′-cyanobiphenyl legs, imposed by the coordination to the Co centers, was again observed (fig. 2d and f). In addition to the 1D polymers, rosette structures are found upon addition of Co, which were not observed for the annealing case (fig. 3a). Rosettes of two different sizes are present (fig. 3b and c). They are stabilized by the same coordination motif as in the 1D coordination polymers (fig. 3d). Based on the results obtained from the control experiment, we conclude that the 1D molecular networks formed upon annealing submonolayer coverage of 1 on Au(111) are indeed stabilized by a threefold cyano-Au coordination motif.

**Conclusion**

We investigated the formation of flexible 1D coordination polymers from porphyrin derivatives 1 on Au(111) induced by thermal annealing. The polymer is stabilized by an unusual threefold coordination motif which is based on the interaction of one Au
surface atom with the N atoms of three terminal cyano groups. The control experiment, in which the formation of similar 1D coordination polymers with the same binding motif was observed upon Co deposition, strongly supports our finding. Our study demonstrates the possibility of Au to undergo coordination bonding and exemplifies that Au is not as inert as often assumed.

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