Formation of molecular wires on nanostructured KBr

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Abstract. The formation of molecular wires on a nanostructured KBr(001) substrate is observed by non-contact atomic force microscopy. Locally polarized cyano porphyrin molecules evaporated on this sample assemble in a linear fashion along straight pit edges forming one dimensional structures.

1. Introduction

Molecular electronics has become a field of great interest during the last few years. One of the major reasons for the growing success is the large stock of organic molecules with a variety of tunable properties which affect the intermolecular interaction and the intramolecular charge distribution. Scanning tunneling microscopy (STM) has successfully revealed the atomic scale spatial resolution as well as the complex mechanism[1] of the interplay between ordered molecular layers and the substrate. However, STM in its application is limited to conducting substrates, which makes an electrical decoupling of the molecules more difficult and is often done by using ultrathin insulating films[2] or spacer groups. Non-contact atomic force microscopy (nc-AFM) offers complementary information about local forces and the unique possibility of studying organic molecules on insulating substrates[3, 4, 5, 6, 7].

We previously presented a nc-AFM study of confined molecules in nanometer sized pits on KBr[5]. The dipole of the molecule interacted with the electrostatic corrugation of the surface in order to keep the molecules pinned on the substrate. The molecule substrate interaction on insulating surfaces is of the same order of magnitude as on conducting substrates while the diffusion barrier is significantly lower. Therefore, many of the molecules investigated on metals are unsuitable on insulators. In the present work porphyrin based molecules were used. The chemical composition of the cyano-porphyrin is shown in figure 1. The core of the molecule is apolar while the strong negative polarization of the nitrogen atom induces a dipolar momentum which should provide a strong enough interaction with the sample in order to prevent the diffusion of the molecule. Porphyrin based molecules tend to π-π stack closely with each other and in order to lower the intermolecular interaction large apolar side groups (Ar= 3,5-di(tert-butyl)phenyl) were attached to the body keeping the distance between the molecules fixed.
Figure 1. Chemical sketch of a cyano-substituted porphyrin. Estimated dipole moment = 4.37 D [8]

Figure 2. Topographical image of the irradiated KBr surface. Frame edge = 200 nm, $\Delta f = -5$ Hz, $\Delta z = 2$ nm

2. Experimental

The dynamic atomic force microscope is a home built instrument placed in a chamber with a base pressure below $1 \times 10^{-10}$ mbar operated at room temperature. We used a standard silicon cantilever (resonance frequency $f_0 = 157$ kHz, quality factor $Q = 28'600$, nominal spring constant $k = 48$ N/m), fabricated by Nanosensors.

To obtain the pit structure, the KBr sample was mechanically cleaved in air and introduced into ultrahigh vacuum (UHV) immediately afterwards. After heating the sample at 393 K for 60 minutes in order to remove the water layer it was irradiated for a few seconds with a 1 keV electron beam of a LEED electron source as described in [9] to produce rectangular pits with a size of 5 - 20 nm showed in figure 2.

During the evaporation of the cyano-porphyrin molecules the sample was held at 353 K while the sublimation temperature of the molecule crucible was 463 K. The deposition rate was $\approx 1$ Å/min calibrated by a quartz microbalance. An equivalent of around 0.3 ML was deposited on the sample with an estimated error of $\pm 20\%$.

3. Results

Figure 3 shows a nc-AFM image of the KBr(001) surface at a constant frequency shift of -20 Hz, after the evaporation of the cyano-porphyrin molecules. The structure of the irradiated pattern is still apparent and decorated steps are clearly visible. Atomic resolution was obtained on flat terraces and inside the pits but not close to any molecular structure. The picture shows also that only the straight step edges are decorated with the porphyrins. As soon as the steps are rounded the molecular wire becomes interrupted or the molecules do not aggregate there at all. However, the wire remains intact across small dislocations as marked in figure 3.

Figure 4 reveals more details about the molecular wire itself. In the lower part of figure 4 an instability is observed where part of the molecular wire is removed, revealing the KBr step underneath it.

The cross section in figure 5 shows the dimensions of the wire more precisely. The height of
the structure (≈ 1 nm) corresponds roughly to the length of the porphyrin, while the width of the wire indicates an asymmetric shape of the tip. The small peak of ≈ 0.5 Å height corresponds to the faint vertical dotted line visible in figure 4. These dots have a distance between each other of ≈ 0.6 nm which corresponds to the distance between porphyrins as shown in figure 6. This distance also coincides to the length of two KBr unit cells. So far, this substructure could only be observed once. Therefore, it cannot be ruled out that the substructure is observed due to an imaging artifact rather than due to the real molecule structure. Further studies and measurements are needed to clarify this question.
If we consider possible arrangements of the molecules along the pit edges it is most likely a similar mechanism as shown in [5] where the strong electrostatic potential at the vertices of the pits trapped the polar chlorine atom of the molecule. In our case the sinusoidal potential along the pit edge may provide an interaction with the nitrogen atom of the molecule strong enough to prevent the porphyrins from diffusing away. Therefore, it is likely that the molecules stand on the substrate with the cyano-group pointing downwards and the plane of the porphyrin body perpendicular to the pit edge direction forming the $\pi - \pi$ structure as described in [10, 11] and shown in figure 6. Since the porphyrins do not stack centered, they are most probably tilted towards the substrate plane.

The potential across flat terraces is not strong enough to prevent the molecules from diffusing away. Therefore no porphyrins were observed on these flat areas. Even more than in [5] the potential enhancement at the step edges seems to be the crucial factor for immobilizing the molecules on place.

As already mentioned, the molecules only aggregate at the straight step edges. This can be explained by considering the relatively weak interaction of the stacking. A round edge bends the wire structure and enlarges the intermolecular distance reducing the interaction even more which might lead to a breaking of the wire.

4. Summary
In conclusion we investigated the formation of molecular wires on a nanostructured KBr(100) surface. While the exact mechanism of the arrangement still remains unclear the asymmetric charge distribution of the cyano-porphyrin has a tremendous potential in the field of molecular electronics. The next challenge will now be to verify the proposed alignment and to find ways to reveal the electrical properties of the molecular wire.

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6. References
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