



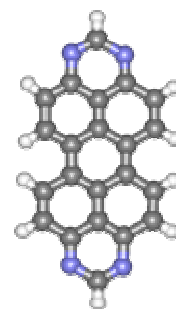
	Experiment title: Structural investigation of thermally activated assemblies of a perylene derivative on noble metal surfaces	Experiment number: SI 1821
Beamline: ID32	Date of experiment: from: 14th November 2008 to: 26th November 2008	Date of report: 28.08.2009
Shifts: 18	Local contact(s): Yanyu Mi, Blanka Detlefs, Jörg Zegenhagen	<i>Received at ESRF:</i>
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Report:

Introduction

The recent interest in organic nanostructures on surfaces [1] has been due to their possible applications in nanoscale electronic or optoelectronic devices [2] in which the spatially addressable functional units are assembled at the molecular level. By combining established methods of molecular and supramolecular synthesis with the remarkable capabilities of surface analytics, along with recently developed theoretical modeling tools, several strategies towards that goal have emerged. By vapor deposition of organic molecules of variable dimensions and level of functionality on well-defined crystal surfaces of the coinage metals in particular, well-defined surface assemblies have been obtained. It is the balance between intermolecular and molecule surface interactions, the reversibility or irreversibility of intermolecular bond formation and the resulting availability or non-availability of structural repair mechanisms, which governs the detailed structures and long range order of molecular surface assemblies. The molecule we investigated (a perylene derivative called tetraazaperopyrene = TAPP) is an ideal object for studying the aforementioned mechanisms since its molecular properties in combination with its contingent reactivity allow for probing the concepts of surface confined supramolecular chemistry as well as for obtaining new insight into the way in which a metal substrate with its mobile surface adatoms (at elevated temperatures) may chemically activate organic molecules for potential covalent coupling.

Recently, we reported on the investigation of the adsorption of TAPP on the Cu(111) surface in dependence of the annealing temperature of the sample [3]. For annealing at temperatures \leq room temperature, the molecules arrange in a herringbone structure and interact via van-der-Waals forces while annealing at 150°C results in the formation of a Cu-coordinated porous network. Further annealing at 250°C leads to the generation of covalently coupled 1D chains (see Figure 1). By performing XSW measurements, additional insight into the adsorption geometry as well as into the bonding mechanism of TAPP to the Cu surface was intended to be gained. The molecule substrate system at hand is an ideal candidate for such studies since the intermolecular interactions can be adjusted through the sample annealing temperature and by this, the effect of changed intermolecular interactions on the molecule substrate interactions can directly be studied.



Chemical structure of TAPP

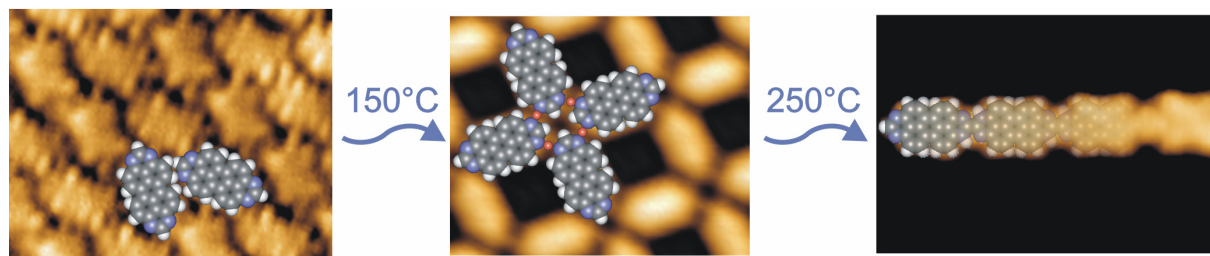


Figure 1: STM images (taken at 77K) for TAPP adsorbed on Cu(111). The left image (4.7nm x 3.6nm) shows the herringbone arrangement. The central image (4.5nm x 3.5nm) depicts the Cu-coordinated porous network which forms after annealing at 150°C and the right image (5nm x 3.5nm) shows a 1D chain in which the TAPP monomers are covalently coupled.

XPS and XSW results

For the preparation of any of the three TAPP phases on Cu(111), always a coverage below a full monolayer was chosen. For the determination of the coverage, a quartz crystal microbalance and LEED measurements were used (the LEED pattern for the porous network has been well characterized before the measurements at ID32 were performed).

In Figure 2 the XPS N1s spectra for the three different TAPP phases are shown. For the porous network as well as for the chains only one N1s peak is found. This indicates that all the N atoms of the TAPP molecules have the same chemical environment in the porous network and for the chains, respectively. For both assemblies, the N atoms coordinate to Cu adatoms. The small chemical shift of 0.2 eV can be explained by the fact that within the chains the N atoms have a slightly different chemical environment compared to the porous network what is due to the covalent bonding of the TAPP monomers to each other. This chemical shift was confirmed by DFT calculations [4]. The spectrum for the herringbone phase prepared at -60°C is more difficult to explain. It consists of at least two or even three components – depending on which chemical environment of the N atoms is assumed. Up to now it is not clear to us why the spectrum consists not only of one component since the chemical environment for all the N atoms of TAPP should be the same in the herringbone phase. Overall, this means that additional experiments are needed to fully understand why such a spectrum occurs.

XSW measurements were performed for the herringbone arrangement and for the porous network. The XSW scans are shown in Figure 3 and Table 1 summarizes the values which are obtained after fitting the experimental data. For the herringbone phase the vertical height of the C atoms (which are essentially the perylene core) above the Cu substrate amounts to 2.68 Å what is quite similar to the value measured for another perylene derivative (PTCDA) on Cu(111) [5]. From this we conclude that TAPP (like PTCDA on Cu(111)) is chemisorbed. Since the N atoms are about 0.1 Å closer to the Cu surface than the C atoms it can be deduced that the N atoms participate in the bonding to the Cu substrate, in addition to the perylene core. For the porous network, the TAPP molecule moves away from the surface. The distance for the C atoms increases by 0.23 Å and for the N atoms by 0.31 Å when compared to the values for the herringbone arrangement. From this we conclude that the molecule substrate interaction is weakened while through the coordination of the N atoms to Cu adatoms the stabilization energy of the porous network increases with

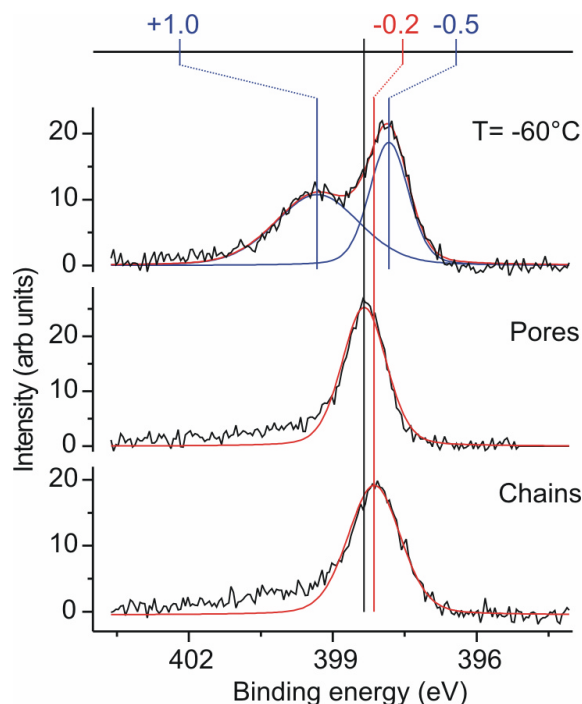


Figure 2: XPS N1s spectra for the herringbone structure (indicated by -60°C), the porous network and the 1D chains. Chemical shifts are determined from the fits of the XPS N1s spectra. All chemical shifts are referenced to the N1s peak of the porous TAPP network.

respect to the herringbone assembly. Furthermore, now the C atoms are closer to the Cu substrate than the N atoms by about 0.08 Å. Preliminary DFT calculations indicate that this effect is caused by the Cu adatoms.

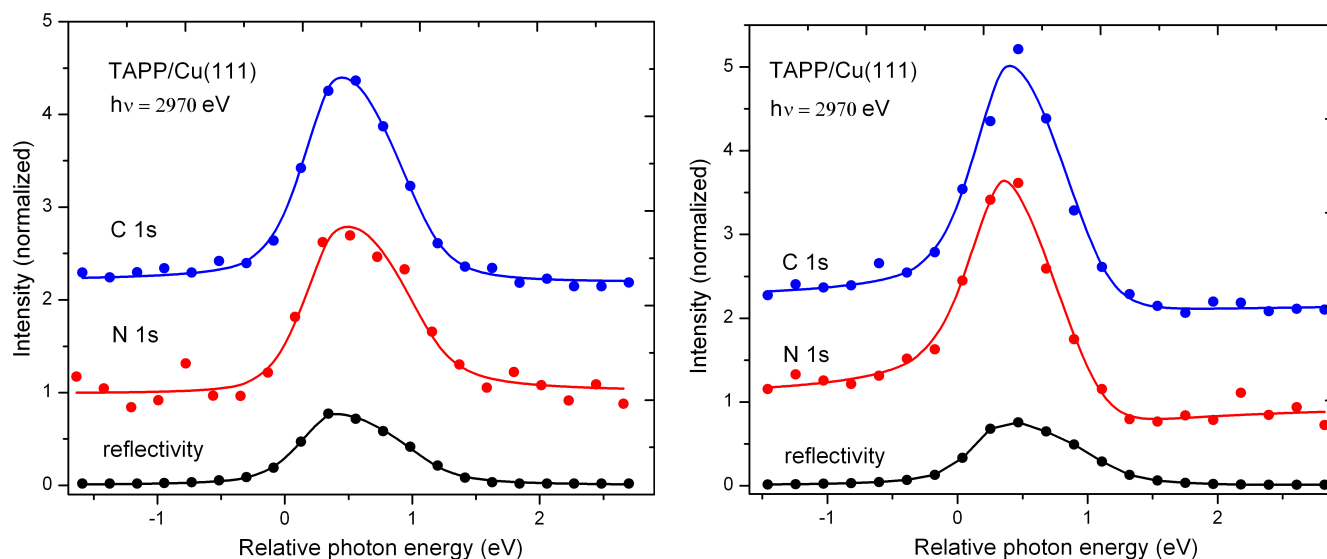


Figure 3: Reflectivity and photoelectron yield curves (dots represent measured values and the solid lines represent the fit) for the herringbone structure prepared at -60°C (left) and the porous network prepared by annealing the sample at 150°C (right).

	C1s (herringbone)	N1s (herringbone)	C1s (pores)	N1s (pores)
Coh. fraction	0.422	0.318	0.529	0.466
Coh. position	0.285	0.24	0.349	0.387
Distance d_H	2.68 Å	2.58 Å	2.81 Å	2.89 Å

Table 1: Summary of the XSW results for TAPP adsorbed on Cu(111). Both the herringbone arrangement and the porous network were studied in detail.

Summary

Currently, we are preparing a manuscript which includes the XPS data for the porous network and the chains [4] and we are working towards a further publication which will deal with the XSW results and which will also include DFT calculations. In addition, we are trying to understand the XPS spectrum for the herringbone arrangement of TAPP and for this, we are designing further experiments in order to elucidate the underlying nature of this feature.

We like to thank our local contact and the ID32 staff for the excellent support during our beamtime.

References

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