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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

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Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

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Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

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- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Studying adsorption geometry of a perylene derivative by XSW before and after annealing	**Experiment number**: SI-1365
Beamline: ID32	**Date of experiment**: from: 05 July 2006 to: 10 July 2006	**Date of report**: 28. Feb. 2007
Shifts: 17	**Local contact(s)**: Dr. Jörg ZEGENHAGEN, Dr. Tien-Lin LEE	*Received at ESRF:*

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Report:

The investigation of molecular adsorbates, assemblies and thin films on both conducting and insulating surfaces has become a well established research field in recent years. This large research area has gained further importance by the emerging capability to build supramolecular structures at surfaces from specially synthesized building blocks. In most cases the assembly of these building blocks is based on noncovalent interactions shaping extended supramolecular entities with different dimensionality.

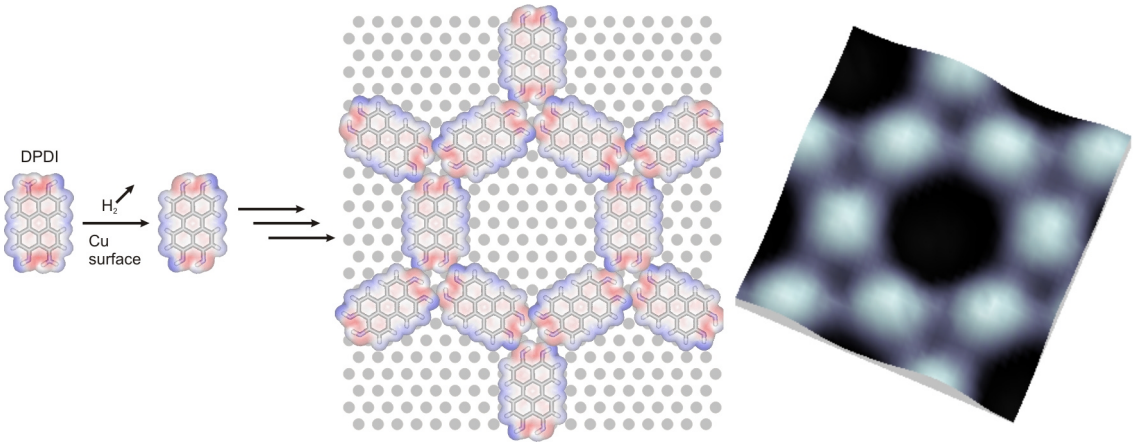

Figure 1: A thermally activated surface assisted dehydrogenation reaction turns the DPDI molecules into autocomplementary H-bond donor/acceptor molecules and thus, the honeycomb network which is commensurate to the Cu(111) substrate can be formed. The STM image on the right (3.8nm x 3.8nm) shows the honeycomb network in real space.

We recently reported the formation of a hexagonal molecular network generated by thermal dehydrogenation of 4,9-diaminoperylene-quinone-3,10-diimine (DPDI) on a Cu(111) surface [1]. By thermal activation, these molecules form autocomplementary hydrogen-bond donors/acceptors which preposition themselves in the formation of the surface network (Fig.1). The highly regular honeycomb structure is commensurate with the Cu substrate [in the form of a p(10×10) superlattice with a lattice constant of 2.55 nm] and thermally highly stable (up to > 300°C) as a consequence of a combination of strong π-bonding between the organic molecules and the surface metal atoms and resonance-assisted H-bonding (RAHB) between the molecules.
In recently performed NIXSW (Normal Incidence X-ray Standing Wavefield) experiments [2], [3], [4] which are ideally suited to probe the adsorption geometry of large organic molecules, the influence of the molecule's endgroups on the adsorption mechanism were investigated in detail. The NIXSW technique uses the fact that a standing X-ray wavefield is created in and above a crystalline substrate if the Bragg conditions for periodic lattice planes are met. Adsorbates located at the positions of the antinode planes of this standing X-ray wavefield exhibit a maximum in the photoemission (PE) yield. Therefore, XPS (X-ray Photoelectron Spectroscopy) spectra taken at slightly different energies of the X-ray beam can be used as a ruler to determine the adsorbates positions relative to the lattice plane distances. This method is thus ideally suited to get both further insight into the binding geometry of DPDI on Cu(111) and to answer the question why the network exhibits such an exceptionally high stability. From our lab based XPS measurements it is known that prior to annealing two N 1s peaks are found at 399.8 eV and 397.9 eV due to the different chemical shifts of the N-atoms belonging either to the imine or the amine endgroup of DPDI. After annealing at 300°C only one peak at 399.8 eV with approximately double the intensity remains. This observation is attributed to the "symmetrization" of all DPDI N-atoms upon the release of two H-atoms per molecule during the thermally activated dehydrogenation.
The aim of the project was to determine the vertical – and if possible the horizontal - positions of the N-atoms of DPDI before and after annealing the sample. For this purpose, several samples have been prepared and investigated under UHV conditions during our beam time at ID32. Special care was taken to avoid effects of beam damage. Therefore, a single NIXSW experiment was divided into several XPS scans with a small number of repeats taken at different sample positions. In order to gain not only information on the position of the N-atoms perpendicular to the Cu(111) surface but also on the lateral adsorption site measurements in the (-111) Bragg condition have been carried out.
Fig. 2 *left* shows N 1s spectra of the DPDI covered sample before and after annealing at 300°C. Besides a shake-up satellite at 402.5 eV, the N 1s peak of the imine and the amine endgroups are found at 399.8 eV (before and after annealing) and at 397.9 eV before annealing. After annealing the amine peak is vanished and only the imine peak at 399.8 eV remains with increased intensity. In Fig. 2 *right* the corresponding NIXSW scans (peak intensity vs. photon energy) for the different N-species are shown (Bragg condition at 2969 eV). The peak intensities have been obtained by fitting two/three Gauss-Lorentz peaks for the two N-species and the shake-up satellite together with a linear background to the experimental data. Clearly a different behaviour of the PE yield profiles can be concluded for the two N species.
Further data analysis is in progress in order to determine the coherent position and fraction of the different N species. These values and ab initio calculations currently under way will most probably lead to a more sound argumentation of the binding mechanisms involved in this system.

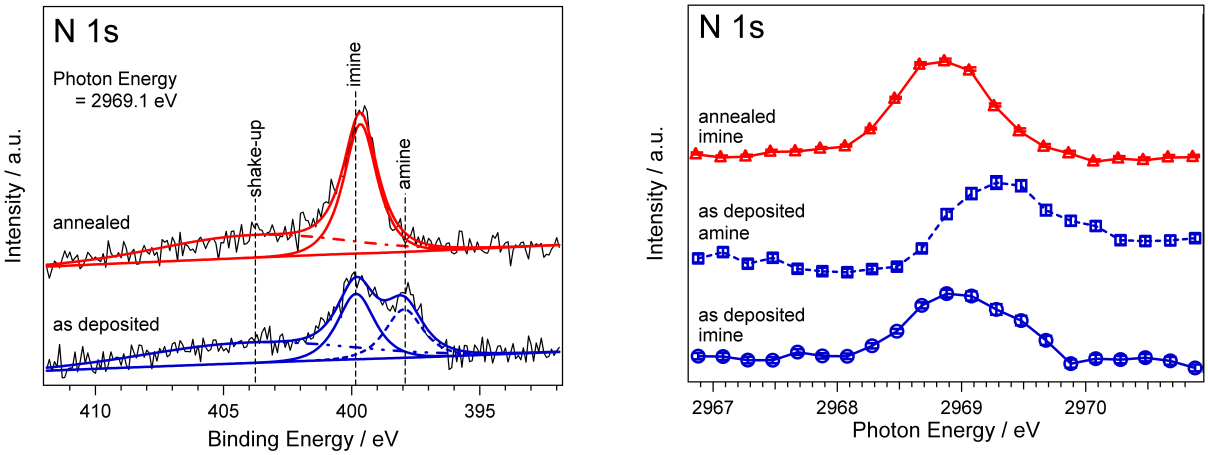

Figure 2: *left* N 1s XPS spectra of DPDI as deposited on the sample and after annealing the sample at 300°C. The spectra have been obtained at a photon energy of 2969.1 eV, which is close to the Cu(111) Bragg condition at normal incidence. Three (two for the annealed sample) peaks were fitted to the data, corresponding to the imine (399.8 eV) and the amine group (398.9 eV) and to a shake-up satellite (403.7 eV). *right* NIXSW signals of the different N 1s peaks of DPDI on Cu(111) before and after annealing. The distinct shape clearly indicates different positions of the N-atoms relative to the lattice planes and therefore a different distance above the Cu surface.

References:

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[2] A. Hauschild, K. Karki, B.C.C. Cowie, M. Rohlfing, F.S. Tautz, M. Sokolowski, Phys. Rev. Lett. 94 (2005) 036106

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