EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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 via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can 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.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

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.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 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:** X-ray investigations of the molecular switch TBA on gold and real-time x-ray studies of DIP growth on gold	**Experiment number**: SC-3173
Beamline: ID10B	**Date of experiment**: from: 30.03.2011 to: 05.04.2011	**Date of report**: 07.02.2012
Shifts: 18	**Local contact(s)**: Alexei Vorobiev	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

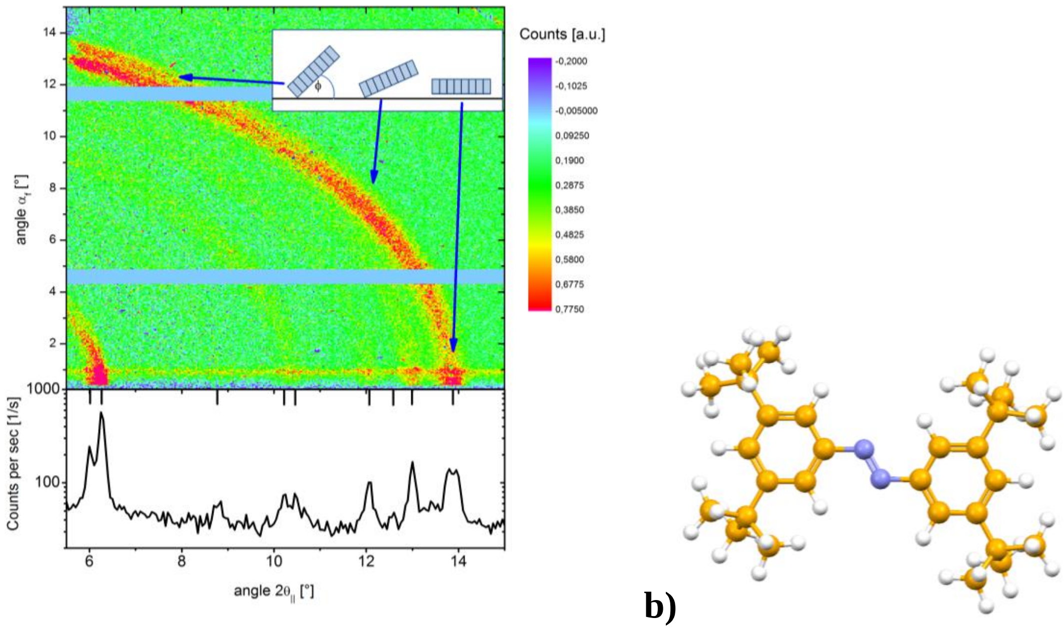
*Stefan Kowarik[1], *Peter Schäfer[1], *Sebastian Bommel[1], *Christopher Weber[1]

[1]Institut für Physik, Humboldt Universität zu Berlin,
Newtonstraße 15, 12489, Germany

Report:

We performed real-time and *in situ* investigations during growth and optical switching of molecular switches and organic semiconductors on gold surfaces. The first studied system was the molecular switch tetra-tert-butyl-azobenzene (TBA, see Figure 1b). The thin film structure has been analyzed with GIXD and XRR using a *Dectris* PILATUS 300K in combination with a scintillation counter.

Figure 1a shows a GIXD reciprocal space map of a TBA thin film on polycrystalline gold. As is evident from the diffraction rings TBA crystallizes in a 3d powder-like structure with weak texturing. Regions with higher intensity correspond to preferred molecular orientations of TBA on gold. While weak texturing is visible and



a) b)

Figure 1: a) Reciprocal-space map of TBA on polycrystalline gold b) atomic structure of the molecular switch TBA (shown is the planar trans-conformation)

some of the molecules are lying flat as expected from the known monolayer strutcure, growth does not result in an ordered structure but in orientational disorder for thicker films.
Measurements performed at ID10B showed that beam-damage is an issue that has to be looked at carefully for investigations of molecular switches with synchrotron radiation. The adsorption of molecules was hindered by long x-ray exposure during real-time growth studies. Also experiments using a laser for switching could not be followed in real time due to the sensitivity of molecules to beam exposure. Future experiments have to make use of a motorised stage to continuously move the sample through the beam so as to always measure on fresh sample spots.

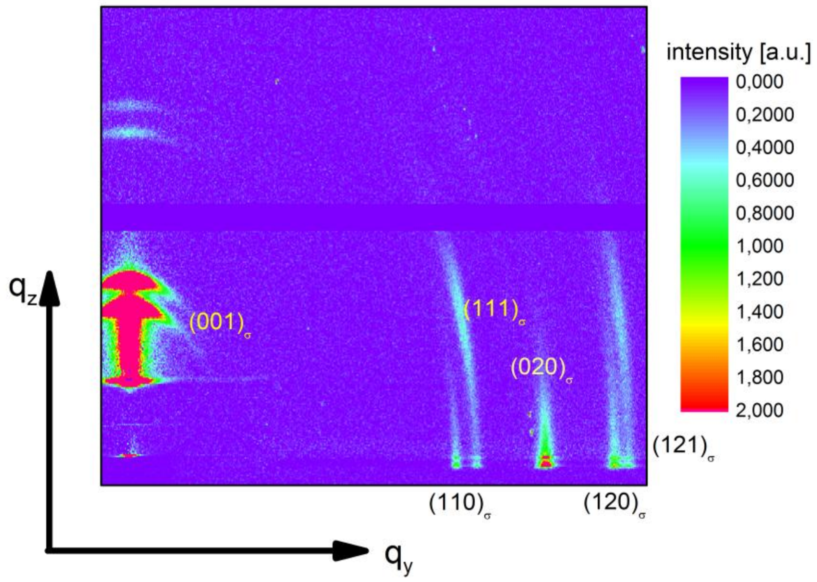


Figure 2: Reciprocal-space map of DIP on polycrystalline gold, showing coexistence of low- and high-temperature bulk phase.

Part of the beamtime was used to study the organic semiconductor diindenoperylene (DIP) on gold. Real-time and *in situ* measurements during growth showed that the unit cell parameters are changing during growth. The PILATUS 300K allowed us to monitor the positions of six Bragg reflections which made it possible to calculate the unit cell parameters at each point in time during growth (see Figure 2).

We have been able to make the first measurement of the complete unit cell as a function of growth time / film thickness for DIP molecules. While for film thicknesses below two monolayers the long axis of the molecules aligns nearly perpendicular to the substrate surface, the molecules tend to tilt a little bit as the film gets thicker (see Figure 3). Apart from the unit cell changes in the beginning of growth GIXD scans of the DIP film after growth revealed two coexisting molecular structures, that we could identify as high-temperature and the low-temperature bulk phase both coexisting at a single temperature as a result of the kinetics of growth. Certain structural changes have been observed during heating, indicating a negative thermal expansion coefficient for the c-parameter (long axis of the unit cell), perpendicular to the substrate surface an interesting result that has similarly been observed for pentacene molecules. Theoretical modelling using molecular dynamics to explain these measured changes is currently under way in preparation of a publication.

We wish to acknowledge the excellent collaboration with the local contact Alexei Vorobiev which made this challenging experiment a success.

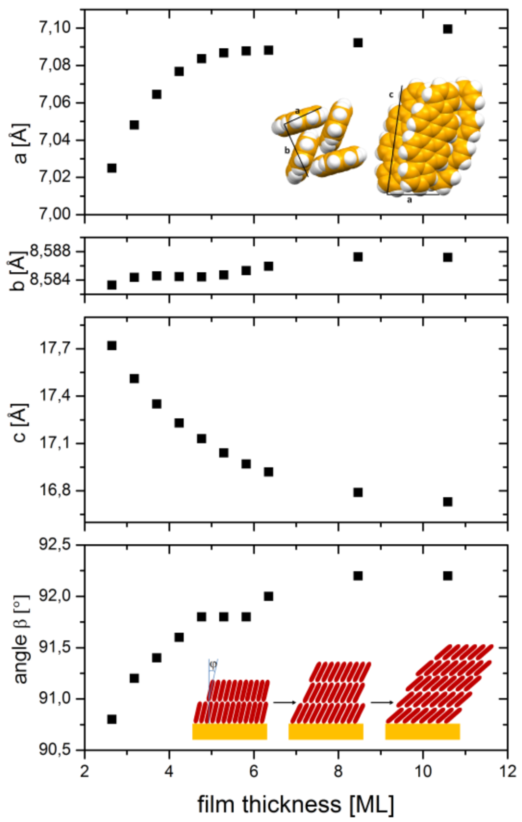


Figure 3: Time dependence / Thickness dependence of unit cell parameters of the organic semiconductor diindenoperylene (DIP) during growth on polycrystalline gold. Inlays: unit cell of DIP and illustration of the change of molecular tilt during growth.