

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:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

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.

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.



	Experiment title: In-situ study of the growth and structure of ordered organic heterostructures of DIP and F16CuPc	Experiment number: SI-1021
Beamline:	Date of experiment: from: 7/04/04 to: 15/04/04	Date of report: 17.06.05
Shifts:	Local contact(s): B. Struth	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): E. Barrena*¹, D. García de Oteyza*¹, O. Ossó*², S. Sellner*¹ ¹ Max-Planck-Institut für Metallforschung, 70569 Stuttgart, Germany ² Institut de Ciència de Materials de Barcelona, CSIC, 08190 Bellaterra, Spain		

Report:

The experiment SI-1021 was proposed to investigate the kinetic aspects of the growth and structure of organic heterostructures of two organic semiconductors, DIP and F16CuPc. The objectives of this experiment have been successfully accomplished revealing important and unexpected aspects of the growth of organic on organic.

We have performed in-situ and simultaneously X-ray Specular reflectometry and GIXD during the growth of DIP on top of F16CuPc. Additionally Real-time measurement of the intensity at the 3/2 and 1/2 Bragg point Vs coverage have been performed.

First the DIP growth has been studied, for three different substrates temperatures, -10°C, 25°C and 120°C and for three different thicknesses of the underlying F₁₆CuPc films. The F₁₆CuPc films have been grown at 120°C in all the cases to obtain a well ordered film as template. The most striking results are summarized in the figure 1 corresponding to the growth of DIP on top of 1.7 ML of F₁₆CuPc (molecules standing upright).

First we draw our attention to the X-ray specular data. At -10°C, the growth of DIP takes place in a standing up configuration as evidenced by the position of the first and second order Bragg reflections ($d=16.6 \text{ \AA}$). This is the same structure observed for the growth on SiO₂. The formation of interference fringes (Kiessig oscillations) reveals the formation of smooth films. Additionally Real-time measurement of the intensity at the 3/2 and 1/2 Bragg point confirms that the growth occurs nearly layer by layer.

At 120°C a different growth mode is obtained. The first 17 Å of DIP (1 ML) form a flat layer, that is, DIP wets the F₁₆CuPc film. Further deposition of DIP leads to the development of high islands as evidenced by appearance of narrow Bragg reflections. This shows that DIP exhibits a Stranski-Krastanov growth mode at

120°C. In spite of the morphological changes, the DIP structure perpendicular to the surface is the same for low and high temperature (a layer spacing of ~ 16.6 Å). The profiles of the mean electronic density projected along the perpendicular to the surface have been obtained from a preliminary analysis of the X-ray reflectivity by Parratt formalism taking a model of boxes.

Especially interesting is the evolution of the in-plane structure. GIXD scans were measured simultaneously with the X-ray specular data (lower part of figure 1). The black curve shows the data for $F_{16}CuPc$ before DIP deposition. Two in-plane Bragg reflections are observed indicative of the structure of the standing phase. Thus, the GIXD and X-ray reflectivity data suggest the formation of a standing up phase with the molecules oriented in a cofacial stacking with a distance of 14.6 Å between molecular rows. This structure differs from that obtained for thicker films where a spacing of 10 Å is obtained [1]. We have determined that this structure forms only in the first monolayer. More work about the determination of the structure in $F_{16}CuPc$ films is in progress. Notice that when 1 ML of DIP is deposited on top of $F_{16}CuPc$ at 120°C, a shift in both peaks is observed, from $d=14.6$ Å to 11.91 Å and from $d=3.22$ Å to 3.34 Å. From the X-ray specular data we know that DIP is deposited on top of $F_{16}CuPc$ so we can discard the formation of an organic alloy by the intermixing of both molecules. This has been corroborated by AFM experiments performed recently in our lab. This evidenced that DIP induces a structural rearrangement of the $F_{16}CuPc$ molecules underneath. Further DIP deposition does not cause additional changes. In contrast, at -10°C, no changes in the $F_{16}CuPc$ in-plane structure are produced.

Surprisingly, the in-plane DIP structure does not change and is identical to that observed for the DIP growth on SiO_2 . Thus, we are in a completely inverse scenario to that observed for inorganic semiconductors where the lattice of the material deposited on top is often modified within the first layers due to the interaction in the interface.

The same structural changes are observed when DIP is grown on top of thicker $F_{16}CuPc$ films. But in these cases the changes occur partially. The analysis of the integrated intensity of the in-plane reflections allow us to estimate that about 2 ML of $F_{16}CuPc$ close to the organic-organic interface are modified.

The growth of $F_{16}CuPc$ on top of DIP has only been studied for 120°C. The specular data evidences the formation of a flat and smooth film of standing $F_{16}CuPc$ molecules. Thus, no islands are formed. Surprisingly, the in-plane data shows the formation of the observed modified-structure (with a 12 Å spacing) for the first layer of $F_{16}CuPc$ and for the subsequent layers (figure 2). Thus, we can conclude that the DIP- $F_{16}CuPc$ interaction lead to the formation of a new $F_{16}CuPc$ structure at 120°C.

To conclude, well ordered bilayers of DIP/ $F_{16}CuPc$ and $F_{16}CuPc$ /DIP can be formed at room or lower temperatures (-10°C). In contrast, at 120°C, DIP on $F_{16}CuPc$ leads to Stranski-Krastanov growth; we have determined that DIP deposition causes a structural change in the last 2 ML $F_{16}CuPc$ layers underneath. The formation of a new structural phase in the interface might be responsible for the Stranski-Krastanov growth. This study reveals completely new aspects of the growth of organic heterostructures whose mechanisms seem to differ from those of inorganic heterostructures. Further structural investigations are required at different temperatures to understand the kinetic and energetics of the structural changes. The investigation with a different organic molecule, combined either with DIP or with $F_{16}CuPc$, is mandatory in order to elucidate the specificity of the molecular interactions and to obtain a more general picture of the growth of organic heterostructures.

DIP on top of 1.7 ML of F16CuPc

T=120°C

T=-10°C

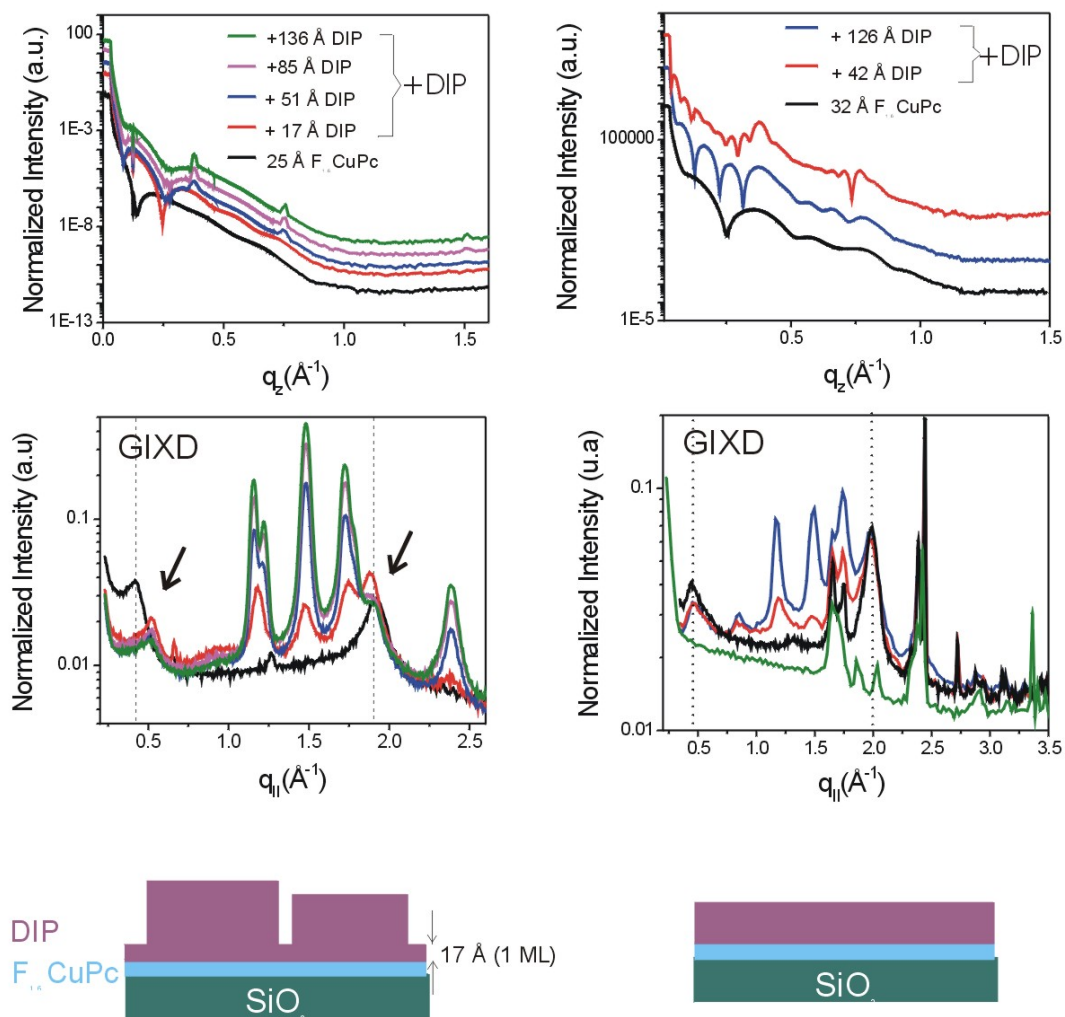


Fig. 1 Specular scans (top) and GIXD radial scans (down) of the growth of DIP on top of 1.7 ML of F₁₆CuPc for 120°C (left) and -10°C (right).

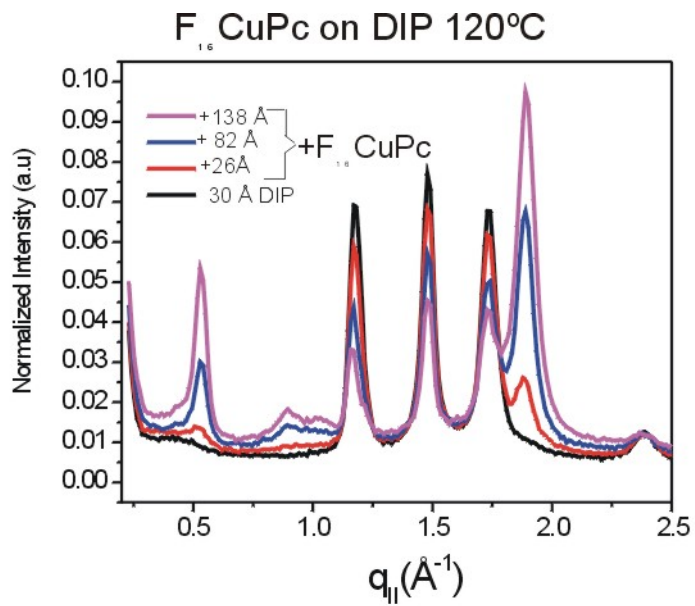


Fig. 2 GIXD radial scans of the growth of F₁₆CuPc on top of 2 ML of DIP for 120°C

[1] E. Barrena, J. O. Ossó, F. Schreiber, M. Garriga, M. I. Alonso, H. Dosch, *J. Mater. Res.* **2004**, *19*, 2061

