

**Experiment title:**

Structural dynamics of excimer formation and phase transition in thin films of pyrene derivatives for organic photovoltaics

Experiment**number:**

HS-3347

Beamline: ID09B	Date of experiment: from: 08/02/2008 to: 13/02/2008	Date of report: Thursday, April 17, 2008
Shifts:	Local contact(s): Marco Cammarata	<i>Received at ESRF:</i>

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Report:

The beamtime was obtained for the purpose of investigating excitation dynamics of a newly developed material TDPEPy, which shows great promise a functional material for use in organic electronics. Spectroscopic experiments indicate that TDPEPy forms an excimer state with a high quantum efficiency. This state is generally expected to change the geometrical conformation between two monomers. We successfully characterized thin films of TDPEPy by X-rays at our home laboratory and at the diffractometer of BW2 (HASYLAB) without major experimental problems. However, during this beamtime we found that the focused X-ray intensity at ID09 ESRF damaged the sample severely at room temperature even though it was kept in a N₂ atmosphere. Since the comparably low degree of crystallinity demands highest possible statistics in order to obtain a sufficient timeresolved transient signal the sample was cooled to 150K using a cryostream. Even with this extreme cooling, the sample was still gradually destroyed in about one hour. The experimental data did not show any transient effects of high enough statistics to allow any conclusions about the structural changes in the excimer state. It has to be noted that the excimer state in TDPEPy was not investigated optically at this low temperatures and it can be argued to be less efficient and show less geometrical change as shown for similar systems. We reached the conclusion that the material is not suitable for time-resolved studies at ID09. From this experience it seems to be very challenging to find a liquid crystalline system robust enough to handle the X-ray intensity used in the optical pump X-ray probe setup at ID09.

The remaining beamtime was used for experiments on polycrystalline thin films of smaller molecules which show only very little beam damage. This includes follow up experiments to previous beamtimes (HS-3270), as well as feasibility tests for new beamtime applications (19774).

In earlier experiments on thin films of Perylene (HS-3270) we observed an oscillatory behaviour of the unit cell parameters. Since then we have been developing a model explaining these oscillations by standing modes of coherent vibrations of the lattice planes in direction of the crystal structure's a-axis. These standing waves

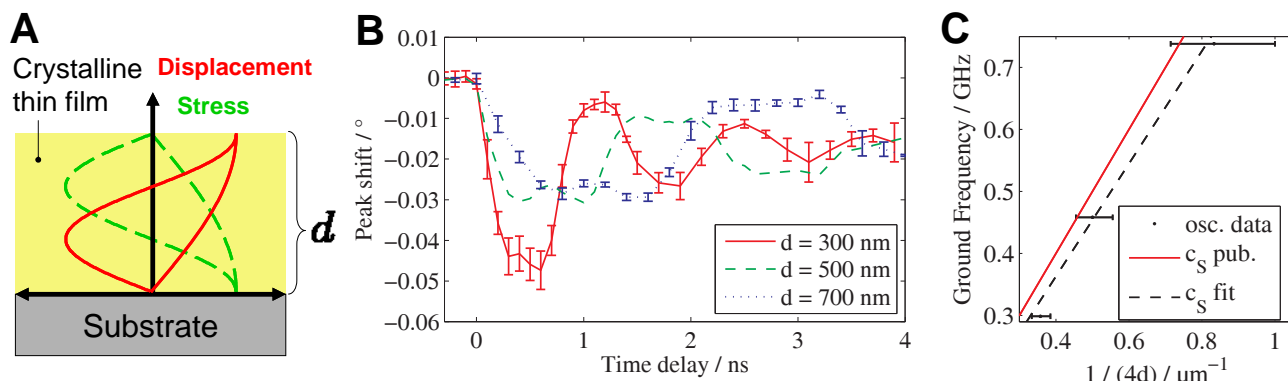


Fig. 2 (A) Mechanical model of standing vibration waves in a thin film. While the strain has a node at the fixed substrate interface, Stress has a node at the free surface. **(B)** Azimuthal transient shift of the -221 diffraction peak at different film thicknesses. **(C)** Observed frequency – thickness relation ($v_s = 900$ m/s) in comparison to the previously published speed of sound ($v_s = 1000$ m/s; Schleiffer et al. *Phys. Stat. Sol. B* 154, 153 (1989)).

are defined by the elastic constants of the crystal material and the boundaries of the thin film which are the contact to the underlying substrate and the free film surface (Fig. 1, A). In this continuum mechanical model only odd harmonics of vibration frequencies are allowed which are related to the speed of sound by $v_s = (2n - 1) 4d f_n$, where n is an integer, d is the film thickness and f_n is the frequency of the n 'th mode. In order to prove this model we wished to determine the unit cell oscillation frequency as function of film thickness. During this beamtime we obtained good data for three different film thicknesses which prove the proposed dispersion relation in the thin film (Fig 1, B, C) and show the same speed of sound as previously published for bulk perylene crystals.

Upon optical excitation Perylene forms an excimer state, for which calculations predict a decreased intermolecular distance between two Perylene monomers. This corresponds to a change in the structure factor and would therefore alter peak intensities. In order to maximize this effect we excited the thin films at intensities near the damage threshold. During this intensity sensitive experiment we observed instabilities of several percent in the intensity of the total diffracted X-ray signal which were neither correlated with the pump-probe delay time nor with intensity fluctuations of the incoming X-ray beam. We interpret this behavior to originate from slight instabilities of the vertical X-ray beam position. In the grazing incidence geometry in which the experiment was performed, the vertical cross section of the sample material is smaller than the vertical beam size. Variations in the vertical beam position therefore leads to a shift of the part of the vertical beam profile which irradiates the sample. As the beam profile is very narrow this can cause a big change of X-ray intensity on the sample.

We are currently working on the extraction of the changes in peak intensities, which are smaller than the instabilities, applying careful background subtraction in combination with a reference peak from the crystal lattice. This task, however, is very challenging due to the experimental conditions, which are “pink” radiation in order to maximize intensity and the rotation around the sample normal during exposure which allows us to average over all crystallites in the excited volume. We hope to overcome the problems by changes in the setup during the next experiment.

Apart from these small fluctuations, the beamline was running extremely well. Therefore, by the end of the beamtime, we had the possibility to test an experiment on thin films of Dibromoanthracene (DBA). Optical characterization of Dibromoanthracene shows a broad and Stokes shifted fluorescence spectrum typical for excimer

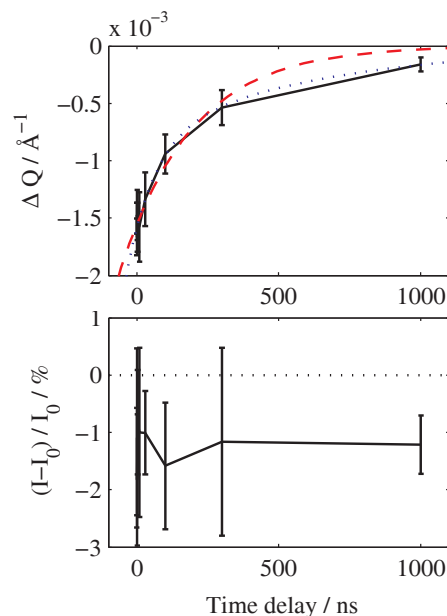


Figure 2: (A) Transient shift of the 010 reflection (solid). An initial shift of 1.5 \AA^{-1} decays exponentially (dashed: single exp. fit; dotted: double exp. fit). Error bars correspond to one standard deviation of 4 repeated measurements. **(B)** Transient relative intensity variation of the 100 reflection.

formation. Hence this molecule is a prime candidate for observing the structural change accompanying the formation of excimers, especially as the monomers are stacked parallelly in the DBA crystal structure. We performed a short delay time series on the thin film to investigate both, if there was a time dependent signal from the film and to test the X-ray integrity of the sample for future experiments. The films did not show considerable beam damage during the experiment. We observed a transient response of the unit cell (Fig 2A) as well as indication of a change in structure factor in the bragg reflection corresponding to the stacking distance between DBA monomers(Fig 2B). The first effect can be explained by a thermal expansion upon excitation by light. The latter effect would be in agreement with expected structural change in the excimer state. We hope therefore to investigate this effect further with higher statistics during a dedicated beamtime.

References

- A.Hayer et al; J. Phys. Chem. B, 110, 7653-59 (2006)
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J. Tanaka and M. Shibata; Bull. Chem. Soc. Jpn, 41, 34-41 (1968)