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- 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: Switching kinetics and cooperative behavior of molecular switches in self-assembled monolayers	Experiment number: SC- 3775
Beamline: ID 03	Date of experiment: from: 12. Feb. 2014 to: 18. Feb. 2014	Date of report:
Shifts: 18	Local contact(s): Francesco Carlà	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Christopher Weber ¹ , *Anton Zykov ¹ , *Linus Pithan ¹ , *Stefan Kowarik ¹ ¹ Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, 12489 Berlin, Germany		

1. Abstract

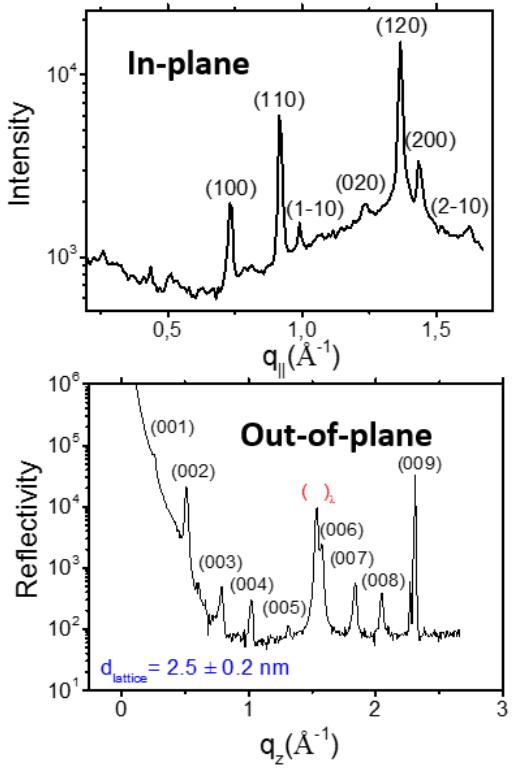
We determined the thin film crystal structure of optically switchable azobenzene trimers with XRR and GIXD. Real-time and *in situ* measurements during UV-irradiation show that the crystal structure of the molecular switches can be switched off and on with light. Using real-time X-ray diffraction we studied the light-induced structural changes in the photoactive thin films.

Then we studied the effect of introducing local dipole moments into the molecule para-hexyphenyl (6P) through chemical modification on the thin film crystal structure. We found a strong impact of dipole moments on the growth-mode, crystal-phase purity and molecular orientations. Chemical tuning may thus become a new parameter to control organic thin-film growth beyond the established parameters like substrate temperature and growth rate. We recently published the results of this second part *Phys. Chem. Chem. . Phys.*, **16**, 26084 (2014). We also plan to submit a paper about the kinetics of the light-induced structural transition in thin films of azobenzene trimers.

2. Experimental Results

Switching the crystallinity with light in thin films of azobenzene trimers.

Using XRR and GIXD we determined the thin film structure of the multiazobenzene compounds (see Figure 1). Interestingly the molecular switches we studied remain photoaddressable even in highly crystalline thin films.



Unit Cell:
a = 8.7 Å
b = 10.2 Å
c = 24.3 Å
α = 90°
β = 90°
γ = 85°

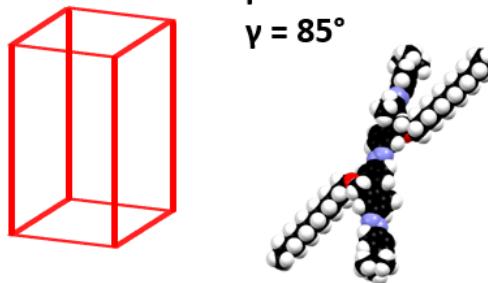


Figure 1: Real-time GIXD during switching of azobenzene-trimer thin films. After about 30 minutes, the UV-LED was switched on and the in-plane Bragg peak disappeared. After the UV-LED was switched off, the Bragg peak intensity increased again.

For the first time we were able to follow the switching of azobenzene-trimers in a crystalline thin film in situ and in real time. Figure 2 shows the evolution of an in-plane Bragg reflection over time. The z-axis shows the GIXD intensity, the x-axis shows the time in minutes and the y-axis shows the in-plane detector angle 2θ . Irradiation of the sample with UV-light leads to a rapid decrease of the Bragg peak intensity. After the UV-light is switched off, the Bragg peak slowly reappears at a slightly shifted center position, corresponding to a slightly different lattice spacing. Simultaneously recorded optical reflectance spectra allow us to compare the kinetics of the light-induced structural transition with the kinetics of the azobenzene isomerization. Our preliminary analysis suggests that the time constant of the structural transition from crystalline to amorphous might be shorter than the corresponding time constant of the E-Z isomerization.

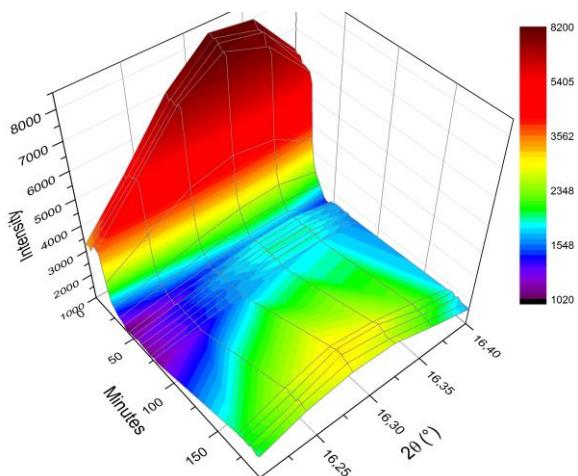


Figure 2: Real-time GIXD during switching of azobenzene-trimer thin films. After about 30 minutes, the UV-LED was switched on and the in-plane Bragg peak disappeared. After the UV-LED was switched off, the Bragg peak intensity increased again.

Controlling the growth and crystal structure of 6P through introduction of local dipole moments.

For the investigation of the impact of chemical tuning of 6P on the growth and crystal structure we performed real time and *in-situ* X-ray reflectivity (XRR) measurements during the growth of 6P and 6P-F4 using a MAXIPIX detector. The chosen wavelength was kept fixed at $\lambda=1.305\text{\AA}$ throughout the experiments. We monitored the XRR intensity of the growing film over a wide q_z range of 0.05 to 0.35\AA^{-1} including the region of the 001 Bragg reflection. The chosen deposition time of ~ 26 min per ML was slow compared to each XRR scan (duration 1.5-2 min) enabling a good temporal resolution of the evolution of the X-ray reflectivity of the growing film. Complementary post-growth measurements of the in- and out-of-plane crystal structure of thick films were performed.

The molecules were deposited on the substrate by OMDB (organic molecular beam deposition) inside our UHV chamber at a base pressure of $<1.0 \times 10^{-9}$ mbar. The substrate temperature was kept constant at room temperature.

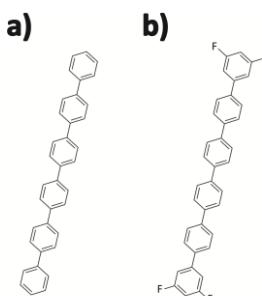


Figure 3: a) and b) chemical structure of 6P and 6P-F4.

Concerning the influence of chemical tuning on organic thin-film growth we found the following three main effects.

Achieving smooth layer-by-layer growth through fluorination

In Fig. 2 the temporal evolution of the XRR intensity of an exemplary growth run of 6P and 6P-F4 on ZnO (1010) is depicted.

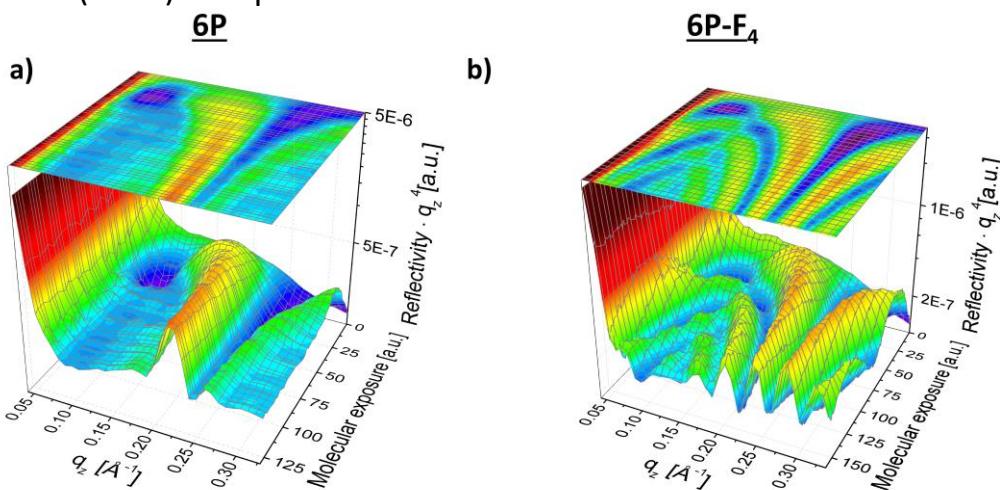


Figure 4: Evolution of the XRR intensity during the growth of 6P and 6P-F4 films on ZnO (1010).

The XRR data presented in Fig. 2 contains rich information about the growth mode and the roughness evolution of the growing 6P and 6P-F4 films. At fixed q_z one observes an oscillation of the XRR intensity (Fig. 3). These growth oscillations are a measure for the roughening of the film. A fast damping of the oscillations as in the case of 6P (Fig. 3 a) indicates a rough film growth. In contrast the damping of the oscillations is much lower for 6P-F4 which stands for smooth, layer-by-layer growth mode.

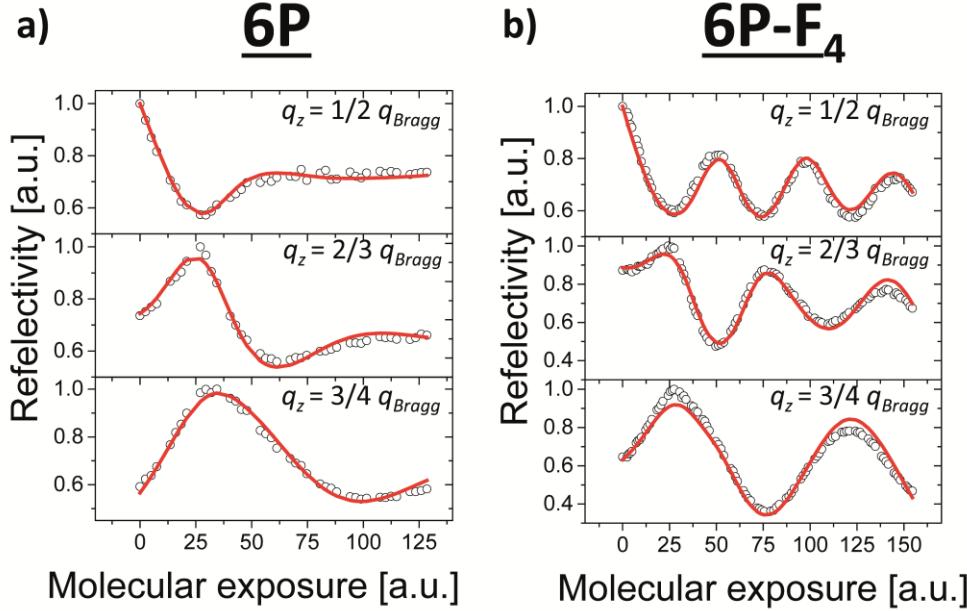


Figure 5: Growth oscillations at different q -values for 6P and 6P-F4 showing the smoother growth of the chemically modified molecule 6P-F4.

By applying an analytical growth model proposed by Trofimov *et al.* [3-5] we were able to fit these oscillations (red curves in Fig. 3) and to quantify the roughness evolution as well as the coverage of the substrate by each ML as a function of time. Our analysis has shown that for thick films (~ 6 ML) the roughness of the 6P is almost twice as large as of the 6P-F4 film (see ref [A] for details). However, smooth films are often preferred in applications since they can for example show enhanced charge carrier mobility [1].

Crystal-phase purification through fluorination

One of the reasons for the rough film growth of 6P molecules may be their polymorphism. As our post-growth XRR measurements of thick films revealed, in the case of 6P growth on ZnO (1010) two crystal phases grow in parallel. The unit cells of these two crystal phases differ slightly [6-7], which may cause grain boundaries and surface roughening. However, after fluorination at both termini crystal-phase purification with only one growing crystal phase was achieved as shown in Fig. 4. The post-growth XRR measurements underline the overall good crystal quality of both films, since Bragg reflections up to the 6 order were acquired.

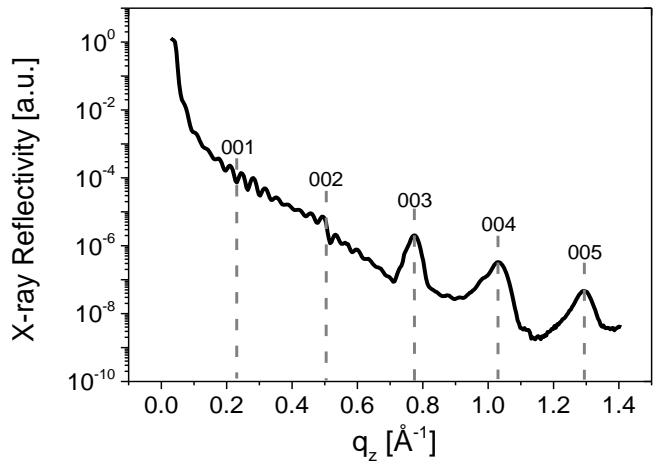
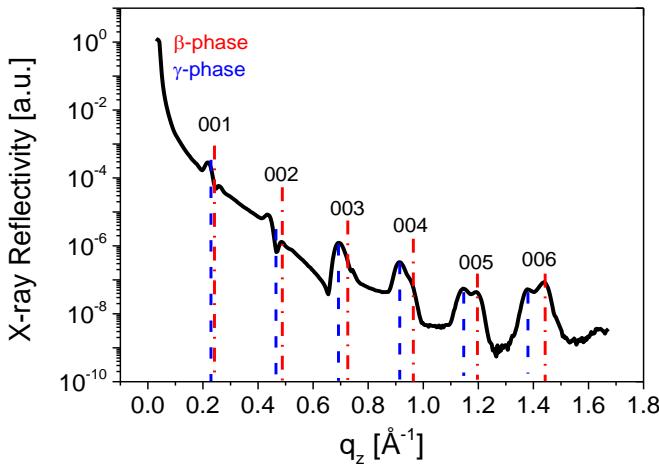


Figure 6: Post-growth measurements of the out-of-plane crystal structure of several ML thick 6P and 6P-F4 films.

Tuning the molecular orientation

By analyzing the q_z position of higher order Bragg peaks in 6P-F4 films of different thickness we were able to identify a surface induced phase. As shown in Fig. 5 exemplarily for the (004) the q_z value of the Bragg reflection shifted towards higher q_z values for increased film thicknesses. This accounts for a different crystal structure of 6P-F4 at the interface and in the bulk. In particular the peak shift goes ahead with a change in the ML thickness (right side of Fig. 5) and, thus, with a change of the molecular tilt. Since e.g. the optical properties of the molecules are dependent on the molecular tilt this finding of importance in application related interface design.

6P-F₄

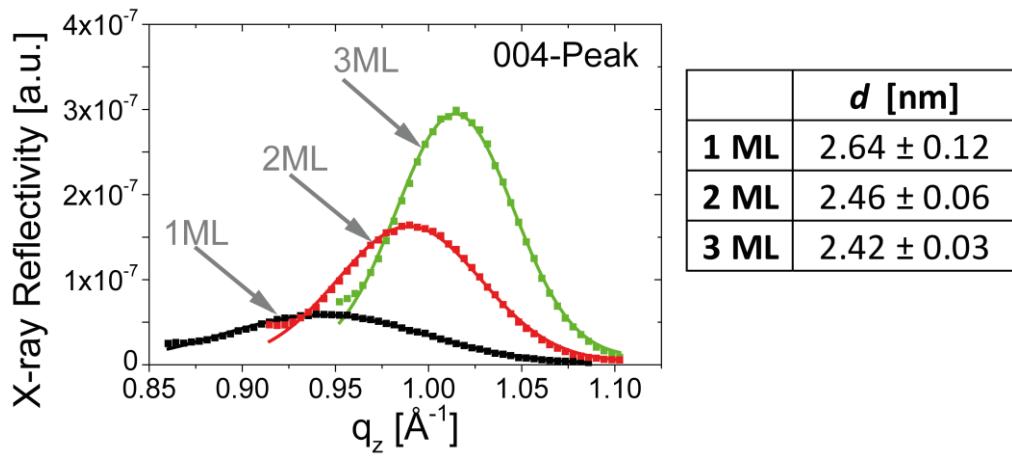


Figure 7: Shift of the (004) out-of-plane Bragg reflection towards higher q_z values with increasing film thickness.

3. Conclusion

We were able to determine the crystal structure of thin films of switchable azobenzene trimers. We showed that the azobenzenes remain photoswitchable even in highly crystalline domains and that the photoisomerization triggers a rapid structural transition in the thin film.

Concerning the study on the impact of chemical tuning on molecular growth kinetics we were able to show that fluorination of 6P at both termini has a crucial influence on the growth-mode, crystal-phase purity and molecular orientation in the thin-film. For the performance of future hybrid organic-inorganic applications, like OLEDs, a rational design of the interface morphology is of crucial importance. Here, chemical tuning presents a viable strategy to realize application-oriented hybrid structures.

4. Publications resulting from work

[A] M. Sparenberg*, A. Zykov*, P. Beyer, L. Pithan, C. Weber, Y. Garmshausen, **F. Carlà**, S. Hecht, S. Blumstengel, F. Henneberger, S. Kowarik, Phys. Chem. Chem. Phys., 2014, **16**, 26084–26093.

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5. References

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