ESRF	**Experiment title:** In-situ GIXRD on organic thin films, blends and OSCs stacks on flexible or stretchable substrates under uniaxial tensile stretching	**Experiment number**:
Beamline: BM02	**Date of experiment**: from: 18/01/23 to: 22/01/23	**Date of report**: 15/03/23
Shifts: 15	**Local contact(s)**: Gilbert CHAHINE, Nils BLANC	*Received at ESRF:*

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Samples:

In this experiment, two sets of samples were analysed. The first set are thin layers of donor polymers (PM6, PTQ10), acceptor (Y12) and donor-acceptor blends (PM6:Y12, PTQ10:Y12), using doctor-blading technique, on glass substrates and on glass precoated with a layer of PEDOT:PSS polymer complex. The second set are the same materials coated on stretchable Thermoplastic Polyurethane (TPU) and PEDOT:PSS-precoated TPU. Thin layers were deposited by doctor-blading with 3mm/s speed. TPU substrates, PEDOT:PSS layers and polymer/acceptor/blend films were respectively about 200µm, 100nm and 200nm thick. The preparation of TPU new substrates and the deposition of PEDOT:PSS had to be optimized before this experiment.

Experimental setup :

We analyzed all the samples using Grazing Incidence X-ray Diffraction (GIXD), to restrict information to thin layers, at an energy of 15keV and incidence angles ranging from 0.05° to 0.12°. To collect diffraction data, we used a D5 2-dimensionnal detector in vertical position. Calibration was performed using LaB_6 and AgBh. We worked in two different configurations :

- Vertical samples, with samples directly attached to goniometer support, for rigid samples. We performed laser alignment for this configuration.
- Horizontal samples, with stretchable samples placed on a tensile stage (designed at the University of Siegen), for in-situ measurements under tensile load (fig. 1 and 2).

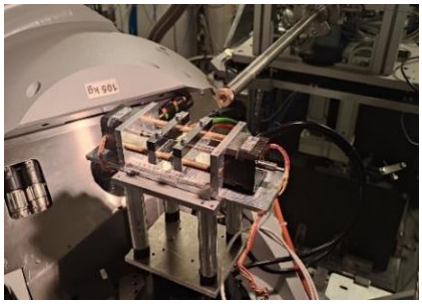

Figure 1. Experimental setup (horizontal configuration) with tensile stage installed on goniometer

Data analysis :

The collected data are used to determine the dominant polymer chain orientation and crystallographic parameters: lamellar and π- π stacking distances, in real and reciprocal space (respectifvely noted d_l, $d_{\pi-\pi}$, q_l and $q_{\pi-\pi}$,), calculated using Bragg's law. Coherent domain length was calculated using Sherrer's equation. We then measure the evolution of these parameters under tensile load, to correlate the mechanical and structrural properties. The D5 detector allows data collection simultaneously for in-plane and out-of-plane directions. An azimuthal integration of raw data, with an angle chosen according to the selected direction (see fig. 3,4), provides

the corresponding plots of signal intensity as a function of 2θ or q (fig. 5 below). Fitting the relevant peaks using a Gaussian model allows the extraction of characteristic parameters.

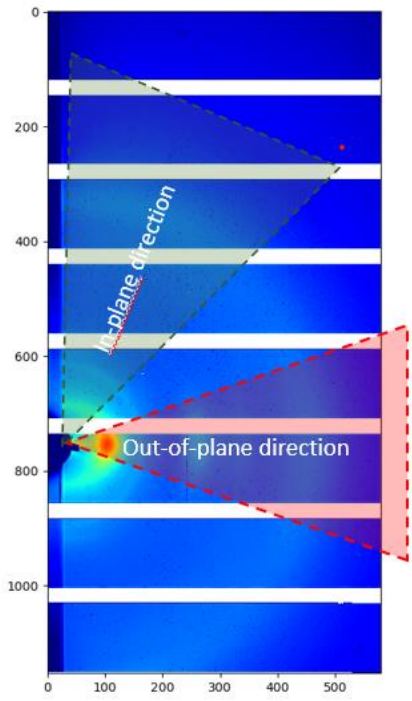

Figure 3. Azimuthal integration angle following In-plane and Out-of-plane directions, for the vertical configuration, on raw data for PM6 neat film on PEDOT:PSS-precoated glass.

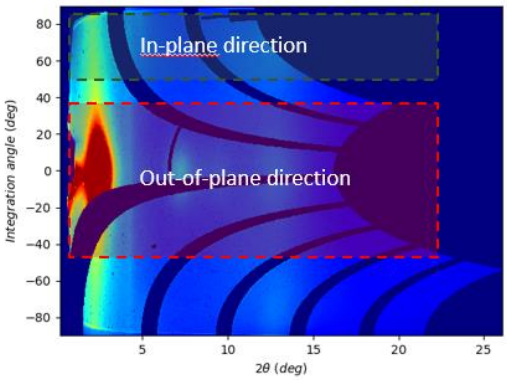

Figure 4. 2D integration result for PM6 neat film on PEDOT:PSS-precoated glass with chosen angle ranges for in-plane and out-of-plane integration

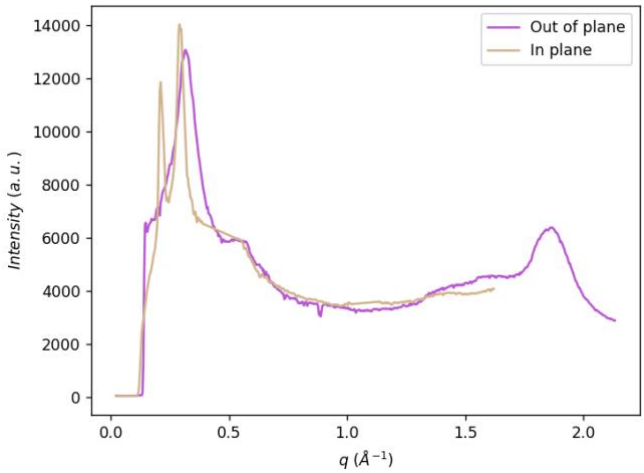

Figure 5. Extraction of I=f(q) for in-plane and out-of-plane directions, for PM6 :Y12 layer on PEDOT:PSS-precoated glass. The intense 100 peak in the In-Plane direction indicates a predominant Face-on orientation.

Results :

A- Rigid samples :

PM6 neat polymer shows a predominantly edge-on orientation, less cristallinity was observed when the material was coated on a PEDOT:PSS film, as the 200 peak is less prominent. The PM6:Y12 blend has a tendancy towards an isotropic orientation.

PTQ10 polymer, on the other hand, adopts an orientation more isotropic. PTQ10:Y12 blend showed a face-on predominant orientation. Including Y12 small molecule acceptor in the two blends seems to contribute by adding a face-on chain-oriented tendancy to the initial neat polymer structure.

Table 1 gathers all peak parameters for rigid samples.

B- Stretchable samples :

We show the results for 2 stretchable samples, showing some trends. For the 1st sample, consisting of a PM6 layer coated on TPU with a PEDOT:PSS buffer layer, we studied the evolution of the laminar distance under uniaxial tensile strain. For the 2nd one, a PM6:Y12 layer coated on TPU with a buffer layer, the same study was conducted on the π- π distance. Figure 6 describes out-of-plane strain evolution, as stretching represents relative elongation. The figure shows a similar behaviour in both samples, where the layers undergo a compressive strain up until 8% stretching, at which point they start relaxing to go back to initial distance before stretching,

Materials	100 peak (laminar distance)									010 peak (π- π distance)		
	In plane						Out of plane			Out of plane		
	1st peak			2nd peak								
	q(Å^{-1})	d(Å)	L_{CD}(Å)	q(Å^{-1})	d(Å)	L_{CD}(Å)	q(Å^{-1})	d(Å)	L_{CD}(Å)	q(Å^{-1})	d(Å)	L_{CD}(Å)
PM6	/	/	/	0,28	22,67	50,6	0,33	19,07	60,1	/	/	/
PM6 on PEDOT :PSS	/	/	/	0,28	22,5	57,7	0,33	19,02	60	/	/	/
PTQ10	/	/	/	0,27	23	60,4	0,28	22,79	73,5	1,75	3,59	28,1
PTQ10 on PEDOT :PSS	/	/	/	0,27	23,24	65,2	0,3	20,88	63,3	1,76	3,55	23,4
Y12	0,21	29,28	324,2	0,31	20,32	225,7	0,32	19,71	277,7	1,89	3,33	27,4
PM6 :Y12	0,21	30,12	322,2	0,29	21,62	177,3	0,31	20,14	62,6	1,81	3,47	29,9
PM6 :Y12 on PEDOT :PSS	0,21	29,88	295,7	0,29	21,38	161,5	0,32	19,81	64,7	1,86	3,38	55,8
PTQ10 :Y12	0,21	29,53	420,2	0,3	21,16	230,3	0,3	21,01	69,4	1,83	3,43	21,1
PTQ10 :Y12 on PEDOT :PSS	0,21	29,37	310,9	0,29	21,34	151,1	0,31	20,51	54,4	1,86	3,38	26

Table 1: Measured parameters for rigid samples

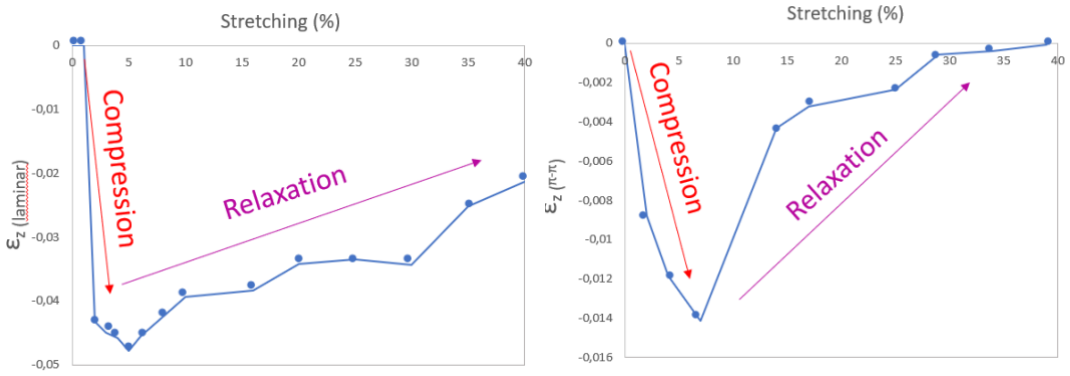

Figure 6: Evolution of chain deformation under uniaxial tensile strain for stretchable samples. On the left : PM6 on PEDOT:PSS, laminar distance deformation. On the right : PM6:Y12 on PEDOT:PS distance deformation

This behavior can be explained by Poisson's effect leading to a compressive deformation up until crack onset point, cracks then start to propagate significantly and active layer degradation shows through chain relaxation. Practically, in-situ optical miscroscopy under strain is necessary to observe the point at which crack formation and propagation begins. Aditionnaly, developing a method to make sure the measured area is being stretched will help make the results more accurate. Next samples will consist on more complex stacks with different intermediate layers, in order to study the whole solar cell behavior.

Technical issues :

We have encountered several technical issues during the experiment, resulting in the loss of about 3 shifts in total. Some of these include : loss of beam (18/01 at 22:40), issues with the newly introduced command software BLISS, inadequate beamstop surface (we had to replace it with a homemade one), hardware problems requiring the intervention of beamline expert to replace parts (22/01) and unproper scale selection which made direct beam go undetected. This has induced some pixel burn on the detector and a loss of beamtime at the end of the experiment.