ESRF	**Experiment title:** Investigating in-situ structural effect of chemical doping	Experiment number: **25-02-904** Beamline:
~~Beamline:~~	**Date of experiment**: from: 20/08/17 to: 25/08/17	**Date of report**:
Shifts:15	**Local contact(s)**: Maria Vila Santos	*Received at ESRF:*
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We proposed the experiment (**25-02-904**) to access the role of side chain substitution, molecular structure of derivatives of didodecyl[1]benzothieno[3,2-*b*] [1]benzothiophene(BTBT) upon doping with two molecular dopants; and the stability with temperature. Only experiements with one molecular dopant, C60F48 were carried due to restricted tiem.

We have performed in-situ X-ray Specular reflectometry and GIXD with the mini detector and the 2D detector. Annealing experiments were also carried out in-situ under high vacuum.

Effect of Side chain Substitution and doping on BTBTs.

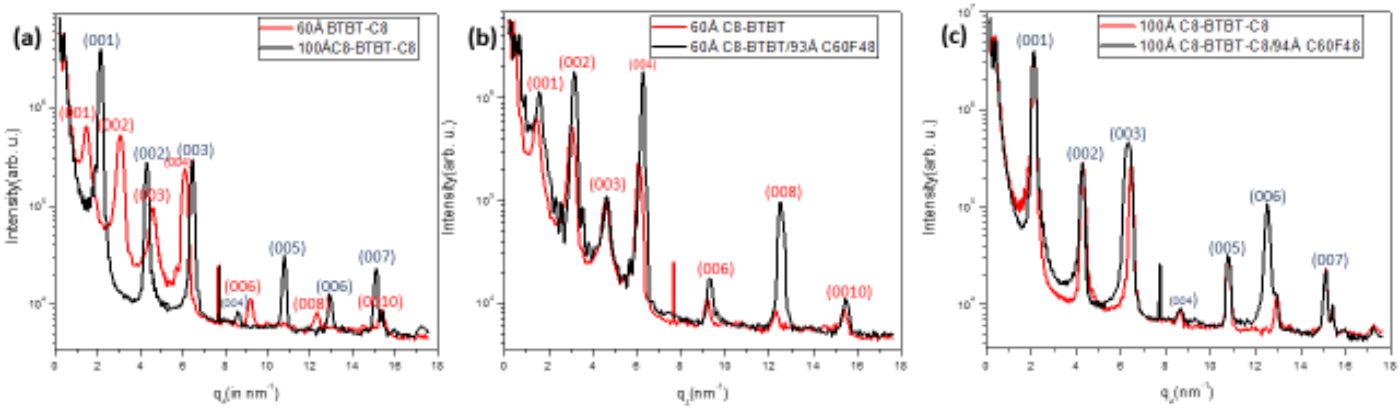

Fig. 1. Specular X ray diffraction for BTBT-C8, C8-BTBT-C8(a) and BTBT-C8/C60F48(b), C8-BTBT-C8/C60F48(c)

The figure 1a shows a comparison between Specular X-ray measurements for C8-BTBT and C8-BTBT-C8 films at room temperature. Figure 1b and 1c shows the specular X-ray measurements both films upon deposition of C60F48 (evaporated on top of them at room temperature). Both molecules form films with high degree of order as evidenced by the observation of Bragg reflections up to the 10th order for C8-BTBT and 7th for C8-BTBT-C8. The Bragg peaks corresponds to a layered structure with an out-of-plane lattice constant of 4.12nm for C8-BTBT and 2.91nm for C8-BTBT-C8. The analysis of the Kiessig fringes and Laure oscillations around the (001) and (002) Bragg reflections indicate a coherently ordered film across the entire thickness of the fims.

When C60F48 deposited on top of BTBT films, the bottom layer is not altered: the Bragg reflections appear with the same width and position **(**Fig. 1b and 1c). Contrary to other dopant molecules, C**60F48 does not diffuse within the underlying film** disrupting the molecular packing**.** However, a change in Bragg peak

intensity isobserved for some of the Bragg peaks of BTBT-C8 upon C60F48 deposition, which might indicate molecular reorientation within unit cell (fig. 1b). Without a modelling of the specular intensity, non-conclusion can be drawn. The increase intensity of the peaks at q≈ 6.5 5 nm-1 and 12.5 nm-1 can be atribured to the crystalline structure of C60F48, which overlap with Bragg peaks of BTBT-C8 and C8-BTBT-C8

C60F48 deposited on top

In order to make more visible the Bragg reflections of the structure of the C60F48 film, we evaporated C60F48 on top of a very thin-layer or PTCDI-CN (Figure 2a).

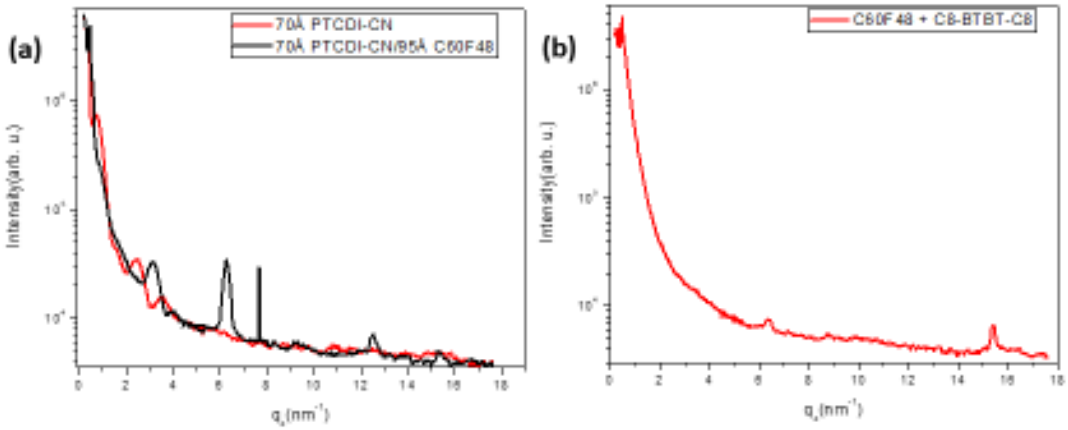

Fig. 2. Specular X ray diffraction for PTCDI-CN/C60F48 (a), Co-evaporation of C8-BTBT-C8 and C60F48 (b) and C60F48 on different materials (c)

Only the first Bragg peak of PTCDI-CN was observed for this thin film (see fig. 2a). Upon evaporation of C60F48 on top of this film, we could identify C60F48 characteristic peaks at q= 6.28 nm-1 and 12.53 nm-1 in the specular x-ray diffraction Thus we can conclude, that the underlying organic layer has a templatting effect. For co-evaporated films, no crystalline order is observed(Fig. 2b). C60F48 films does not order on SiO_2.

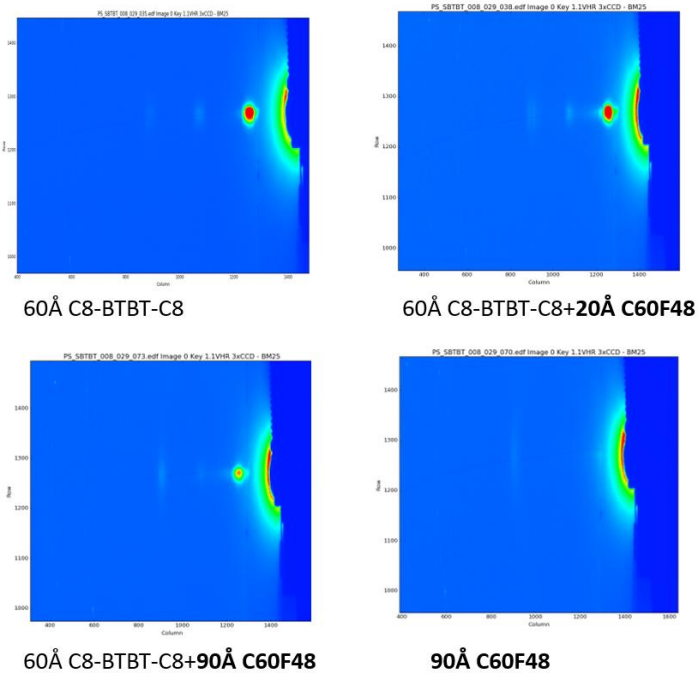

Fig. 3. GIXD image for different annealing temperatures for C8-BTBT/C60F48 using 2D detector.

GIXD studies with 2D detector confirmed previous conclusions (Figure 3).

The obtained lattice parameters from the specular X-ray diffraction measurements for BTBT structures matches well with the previously reported data. The analysis of the data is in progress.

Thermal stability studies

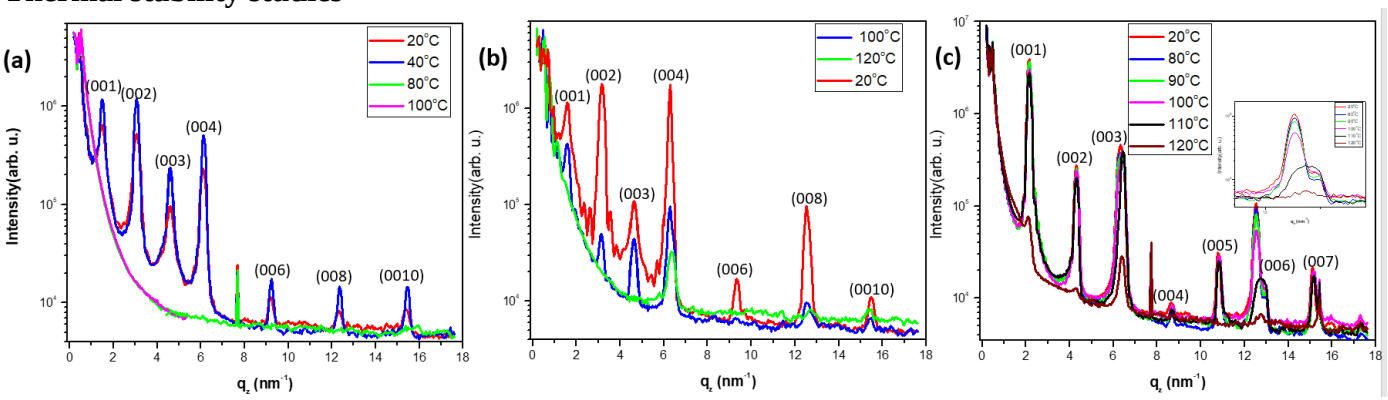

Fig. 4. Specular X ray diffraction for different annealing temperatures for C8-BTBT(a), C8-BTBT/C60F48 (b) and C8-BTBT-C8/C60F48 (c) inset graph is zoom of (006).

The effect of post-annealing has a beneficial effect on the molecular ordering, as observed by the increased intensity of C8-BTBT Bragg reflections when the temperature increased from 20 ^{o}C to 40 ^{o}C $_{z}$ (see fig. 3a). Without C60F48 on top, C8-BTBT could not withstand 80^{o}C since the molecular fims desorb from the surface (Fig. 3a). However, when C60F48 has been despoited on top, C8-BTBT Bragg peaks are visible even at 100 ^{o}C (Fig. 3b). The similar effect observed in C8-BTBT-C8 up to 110 ^{o}C (Fig. 3c). This shows that C60F48 acts as a caping layer increasing the thermal stability of the films.

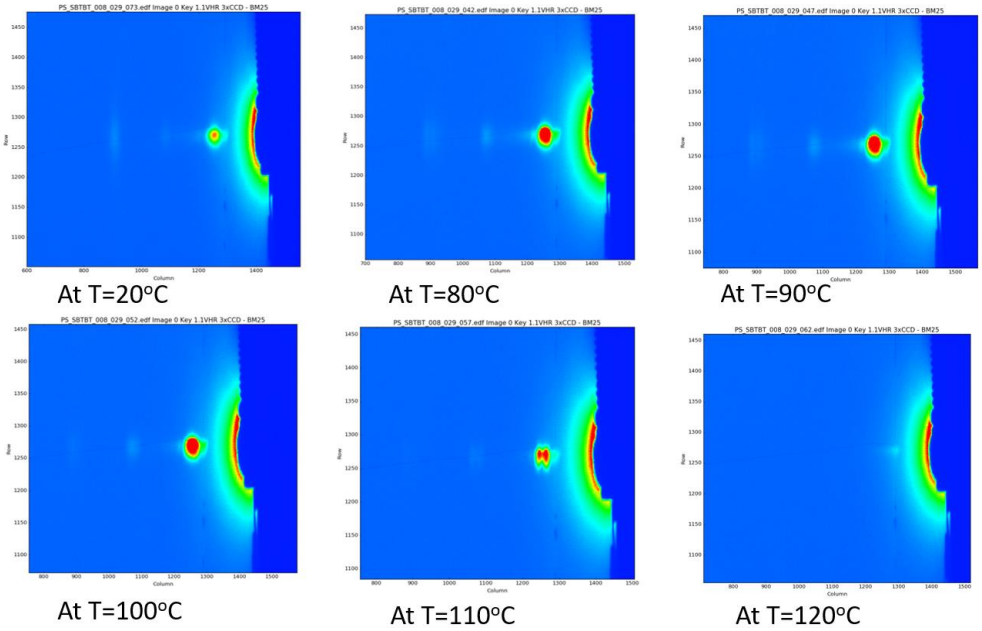

Fig. 5. GIXD image for different annealing temperatures for C8-BTBT/C60F48 from 2D detector.

The GIXD scans also measured to investigate the effect of post annealing for the particular case of C8-BTBT/C60F48. The Bragg peaks of BTBT show significant difference with an increase in temperature.

Summary

In Summary, we could infer that the C60F48, a strong p-type dopant, does not alter the crystalline properties of the layer beneath. Moreover, C60F48 gives more thermal stability to the layer beneath. The underlying organic layer has a templatting effect on the crystalline order of C60F48.