Supplementary information

Temperature-induced Polymorphism of a Benzothiophene Derivative: Reversibility and Impact on the Thin Film Morphology

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Cell parameters calculation

In a monoclinic system, such as the ones observed for C_8O-BTBT-OC_8 thin-film, *c* parameter can be directly determined from the out-of-plane spacing and the angle between *c* and *a*-axis (β), as described by equation S1:

$$c = d_{001}/sin\beta \qquad \text{(S1)}$$

In general, for crystal structures with the *(001)* plane parallel to the substrate surface, in-plane and out-of-plane components of the reciprocal vector q can be written as equations S2 and S3, respectively:

$$q_{xy}^2 = q_x^2 + q_y^2 = h^2 z_a^2 + k^2 z_b^2 - 2hk\, z_a\, z_b \cos\gamma \qquad \text{(S2)}$$

$$q_z = h a^* \cos\beta^* + k b^* \cos\alpha^* + l c^* \qquad \text{(S3)}$$

where $z_a = 2\pi / (a \sin\gamma)$ and $z_b = 2\pi / (b \sin\gamma)$, and a^*, b^*, c^*, α^*, β^* refer to reciprocal lattice parameters. Thus, from in-plane q-values (q_{xy}) the unit cell parameters *a*, *b*, and γ can be determined, while out-of-plane q-values (q_z) lead to parameters *c*, α, and β.[1]

According to equation S2, the lattice parameter *b* can be extracted from the in-plane position of the *(020)* peak. If γ is assumed to be 90°, *b* parameter is given by equation S4:

$$b = \frac{4\pi}{q_{xy(020)}} \qquad \text{(S4)}$$

Once the *b* parameter is calculated, the lattice parameter *a* can be extracted from the in-plane position of the *(-1-20)* peak, following the equation S5:

$$a = \frac{2\pi}{\sqrt{q_{xy(-1-20)}^2 - 4\,(\frac{2\pi}{b})^2}} \qquad \text{(S5)}$$

Additionally, since we observe a third diffraction rod, we can verify the calculated unit cell parameters by comparing the expected position for *(-1-10)* with the observed position. The expected position for *(-1-10)* is given by equation S6:

$$q_{xy(-1-10)} = \sqrt{4\pi^2(\frac{1}{a^2 sin^2\beta} + \frac{1}{b^2})} \qquad \text{(S6)}$$

For each lattice parameter we have considered the uncertainty given by the error propagation in the equation, considering the uncertainty of the peak position, i.e., the standard deviation given by the Gaussian fit for each peak.

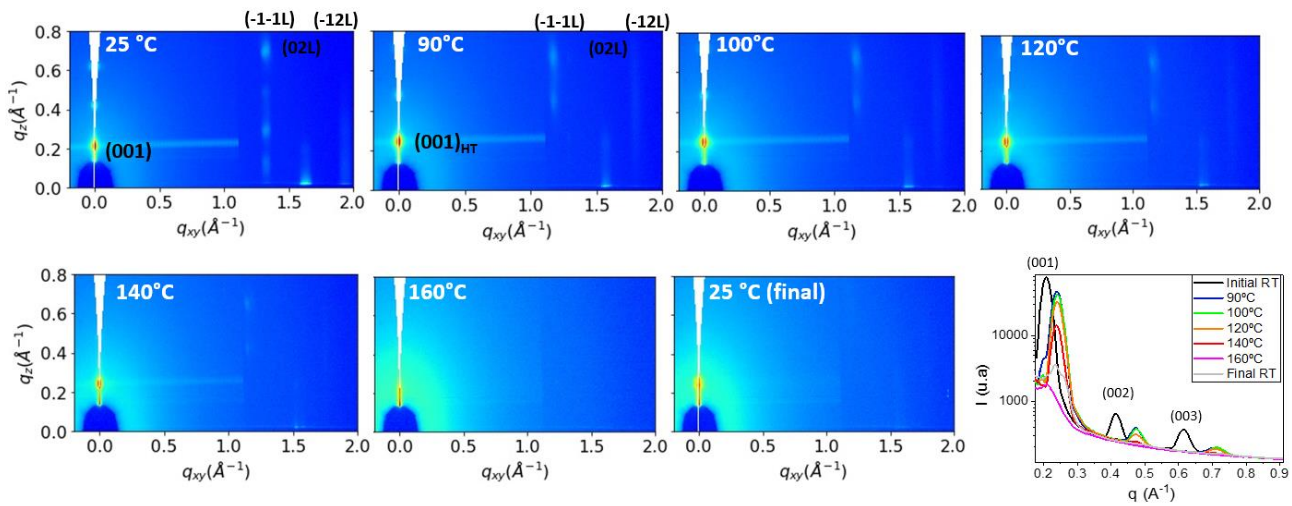
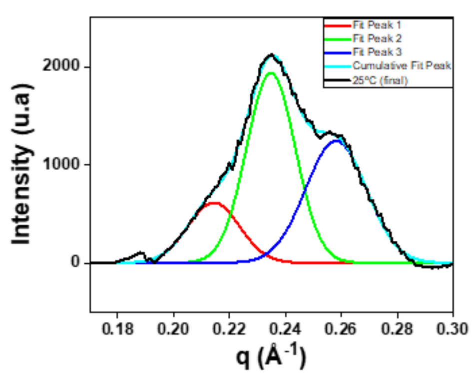


Figure SI1. 2D GIWAXS patterns of a C_8O-BTBT-OC_8 thin film (incidence angle of 0.13°) acquired at each temperature. The horizontal line appearing $q_z \simeq 0.24$ Å^{-1} is a blooming effect from the CCD camera employed. Line cuts along the out-of-plane direction are plotted.



Model	Gauss		
Equation	y=y0 + (A/(w*sqrt(pi/2)))*exp(-2*((x-xc)/w)^2)		
y0	3.60497 ± 5.09011	3.60497 ± 5.09011	3.60497 ± 5.09011
xc	**0.21431 ± 0.00142**	**0.23476** ± 3.13516E-4	0.25808 ± 6.0576E-4
w	0.01849 ± 0.00159	0.01749 ± 8.51026E-4	0.02175 ± 7.8747E-4
A	14.19056 ± 2.22215	42.35017 ± 3.45375	33.84385 ± 1.80722
Reduced Chi-Sqr	1659.64057		
R-Square (COD)	0.99658		

Figure SI2. Multiple peak Gaussian fit of the (001) peak from C_8O-BTBT-OC_8 films at 25°C after post-annealing at 160 °C (grey spectrum in Figure 1b after background subtraction). The table corresponds to the results of the fits with Gaussian functions. The three peaks are centered at 0.214 Å^{-1}, 0.235 Å^{-1}and 0.258 Å^{-1}.

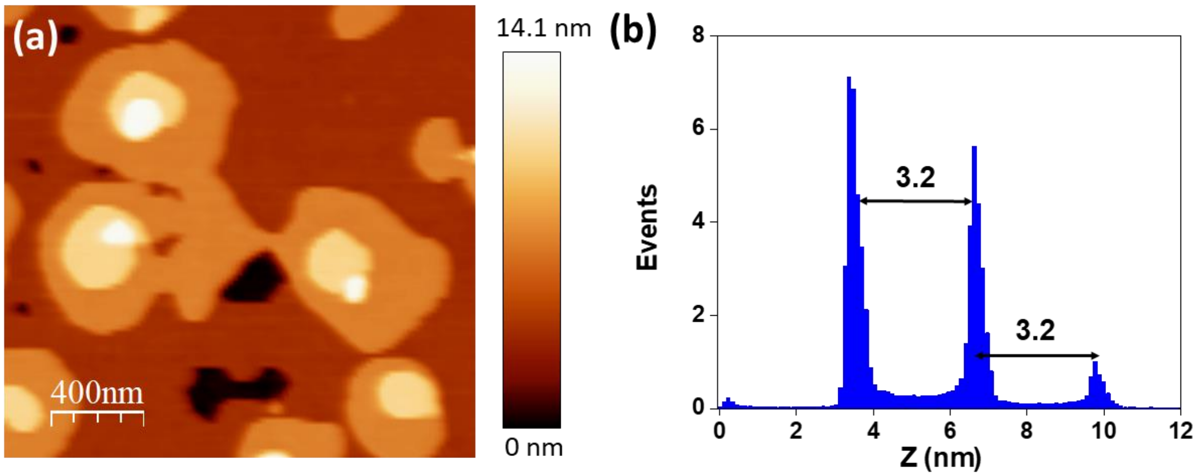


Figure SI3. Topographic AFM image of the C_8O-BTBT-OC_8 film (nominal thickness of 14 nm) grown at RT (a). (b) Height distribution of the image in (a).

Figure SI3a is the topography of a thin film of C_8O-BTBT-OC_8 with a nominal thickness of 14 nm, grown at 25 ℃ (room temperature). The film consists of 4 complete layers (each with single layer height) plus one nearly complete layer (large brown layer in the image) and islands with two or three layers. The height estimated from the histogram (Figure SI3b) indicates that the molecules within the film are nearly perpendicular with respect to the silicon substrate, as corresponds to the SIP structure.

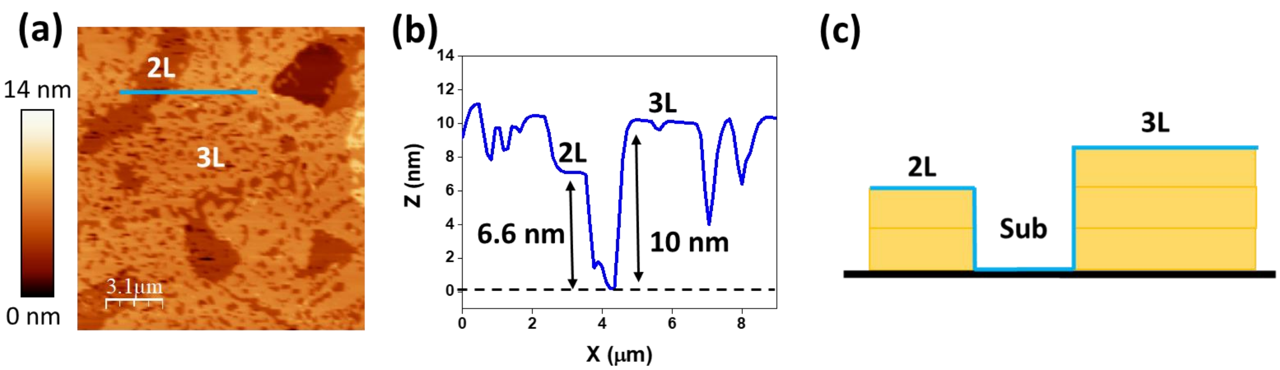


Figure SI4. (a) Topographic AFM image of a C_8O-BTBT-OC_8 film (nominal thickness of 14 nm) grown at RT and cooled down to RT after post-annealing at 130 ℃, (b) height profile corresponding to the blue segment in (a). The sketch in (c) illustrates schematically the height profile correspondence between height and number of layers indicated in (b).

As it can be seen from the topographic profile (blue line) in Figure SI4b, reaching the substrate, the film consists of regions 2 and 3 layers thick.

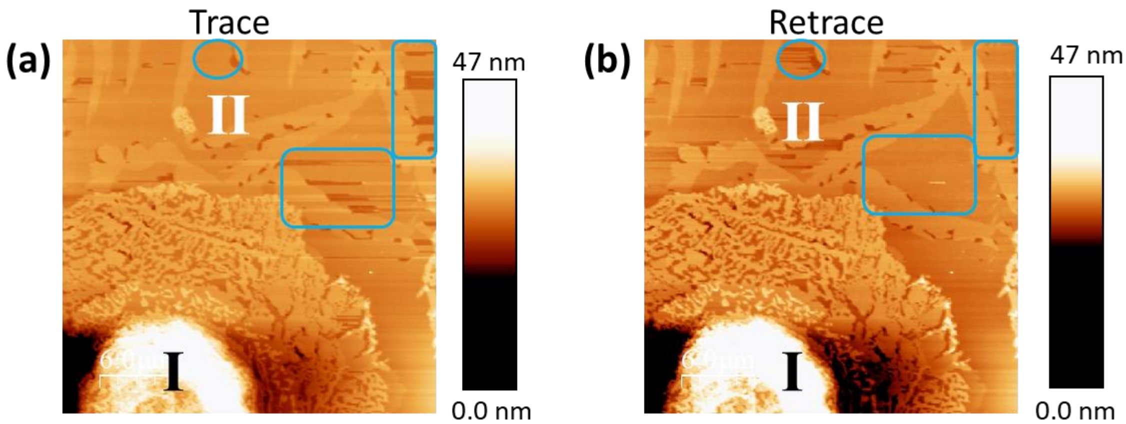


Figure SI5. Trace (a) and retrace (b) topographic AFM images for a C_8O-BTBT-OC_8 film (nominal thickness of 14 nm) grown at RT and cooled down to RT after post-annealing at 150 °C. As it can be seen at the areas marked in blue, the lower layer is easily penetrated by the tip during scanning. The lateral size of the image is 30 µm x 30 µm.

In Figure SI5 we show the trace and retrace images of the sample post-annealed at 150 °C. In region I (see detailed explanation in the main manuscript), the flat film of 2.5 nm thickness is easily damaged by tip scanning. In addition, some holes appear between the HTP and SIP structures arising from the different molecular density of these phases.

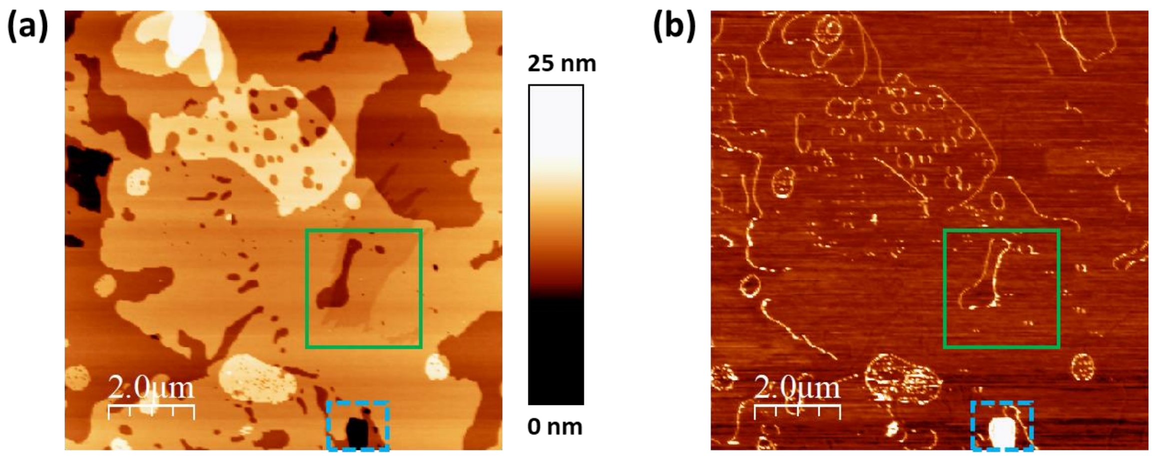


Figure SI6. Topographic AFM image (a) and simultaneously obtained later force image (b) for a C_8O-BTBT-OC_8 film (nominal thickness of 14 nm) grown at 130 ºC. The area marked by green and dashed blue squares correspond to Fig.6c and a hole reaching down the substrate, respectively**.**

Figure SI6 is a larger image of the region imaged in Figure 6c of the main manuscript. It is clearly seen that the low 0.6 nm steps do not show any contrast in the lateral force (LF) image. Some other regions with similar steps can be identified, this fact demonstrates that, upon cooling at RT after the post-annealing treatment, some regions remain in the HTP structure while other regions convert to the most stable SIP at RT.

[1] J. Simbrunner, C. Simbrunner, B. Schrode, C. Röthel, N. Bedoya-Martinez, I. Salzmann and R. Resel, Indexing of grazing-incidence X-ray diffraction patterns: The case of fibre-textured thin films, *Acta Crystallogr. Sect. A Found. Adv.*, 2018, **74**, 373–387.