Supporting Information

Light controls polymorphism in thin films of sexithiophene

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1. Needle shaped LT phase crystallites with flat lying molecular orientation

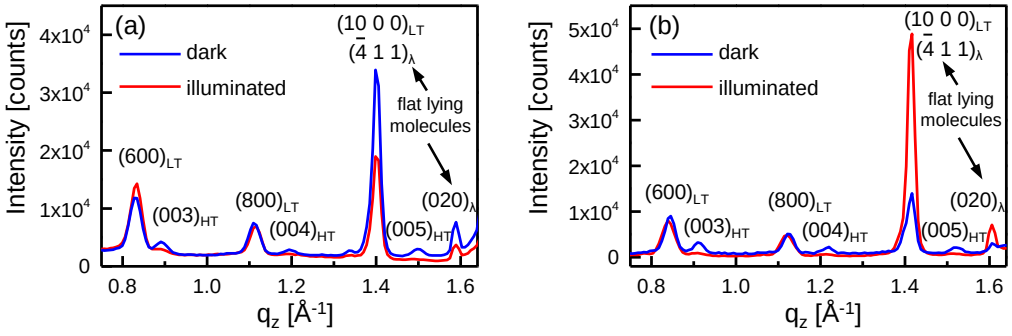

Figure S1: $\theta/2\theta$- scan of 6T thin films grown at 60°C with and without illumination on four different substrates. Independent of substrate for standing upright molecules we find a reduction of the HT phase with respect to the LT phase in the experiments in a) and b). For the flat lying molecules no systematic effect of the laser is found with a reduction of flat lying molecules upon illumination in a) and an increase in b).

For crystallites of flat lying molecules the microscopic structure of the KCl substrate surface and not the laser illumination seems to play a dominant role with respect to the amount of molecules crystalizing in this orientation. All measurements presented in Figure S1 were conducted on samples grown under similar conditions on four different, cleaved KCl crystals. In the first batch of substrates (in Fig. S1 a)) more flat lying molecules (which only occur in the LT phase) are found on the sample grown in the dark, whereas in the second batch (in Fig. S1 b)) more lying molecules are found in the illuminated case, so that no clear trend due to illumination is obvious. However, the reflections originating from upright

standing molecules behave similarly in both sets of measurements, that is there exists a robust light induced effect on the coexistence ratio for standing upright molecules as discussed in the main paper.

2. Quantitative phase analysis as used in Rietveld method

In terms of the Rietveld method the integrated intensity of a reflection is given by

$$I_{hkl} = S\, m_{hkl}\, (LP)_{hkl}\, F_{hkl}^2$$

where S is the scale factor, m_{hkl} the multiplicity, $(LP)_{hkl}$ the Lorentz-polarization factor and F_{hkl} the structure factor. [1] In samples consisting of phase mixtures the scale factor S can be expressed in terms of m_p the mass of phase p present in the sample. This involves Z_p the number of formula units per unit cell, M_p the mass of one formula unit and V_p the unit cell volume. S is given by

$$S = \frac{m_p}{Z_p\, M_p\, V_p} C$$

with $C = \frac{\Phi_0\, \lambda^3 h\, w\, t}{8\, \pi\, r^2}$ bundling the experimental quantities Φ_0 flux, λ wavelength, r specimen-to-counter distance and h, w, t the aperture height, width and counting time.[2]

The intensity ratio between two peaks of two phases A and B can the written as

$$\frac{I_{(hkl)_A}}{I_{(hkl)_B}} = \frac{m_{(hkl)_A}\, (LP)_{(hkl)_A}\, F^2_{(hkl)_A}}{m_{(hkl)_B}\, (LP)_{(hkl)_B}\, F^2_{(hkl)_B}} \frac{m_A}{m_B} \frac{Z_B\, M_B\, V_B}{Z_A\, M_A\, V_A} \quad .$$

Assuming the two crystal phases A and B are crystal polymorphs involving the same formula unit we can write $M_A = M_B$ and restricting ourselves to reflections with the same multiplicity there is $m_{(hkl)_A} = m_{(hkl)_B}$. Further restriction to reflections that appear in close proximity leads to the approximation $(LP)_{(hkl)_A} = (LP)_{(hkl)_B}$.

From this we can deduce for the mass ratio $\frac{m_A}{m_B}$ of the two phases

$$\frac{m_A}{m_B} = \frac{F^2_{(hkl)_A}}{F^2_{(hkl)_B}} \frac{Z_B\, V_B}{Z_A\, V_A} \frac{I_{(hkl)_A}}{I_{(hkl)_B}}$$

In the case of the $(003)_{HT}$ resp. $(600)_{LT}$ reflection of the Sexithiophene LT and HT structure we find $F^2_{(003)_{HT}} = 607$, $F^2_{(600)_{LT}} = 2683$, $Z_{HT} = 2$, $Z_{LT} = 4$, $V_{HT} = 1064.3$ Å^3 and , $V_{LT} = 2116.5$ Å^3 so that

$$\frac{m_{HT}}{m_{LT}} = 0.9\, \frac{I_{(003)_{HT}}}{I_{(600)_{LT}}}$$

Due to the identical rocking width of the $(00l)_{HT}$ resp. $(k00)_{LT}$ reflection it is appropriate to use the intensity of a θ-2θ scan as measure for the integrated intensity. In Figure S2 we exemplarily show the rocking curve of the $(800)_{LT}$ and $(004)_{HT}$ reflection for a 6T film grown under illumination at 60°C under illumination. We observed no influence of the illumination on the rocking width.

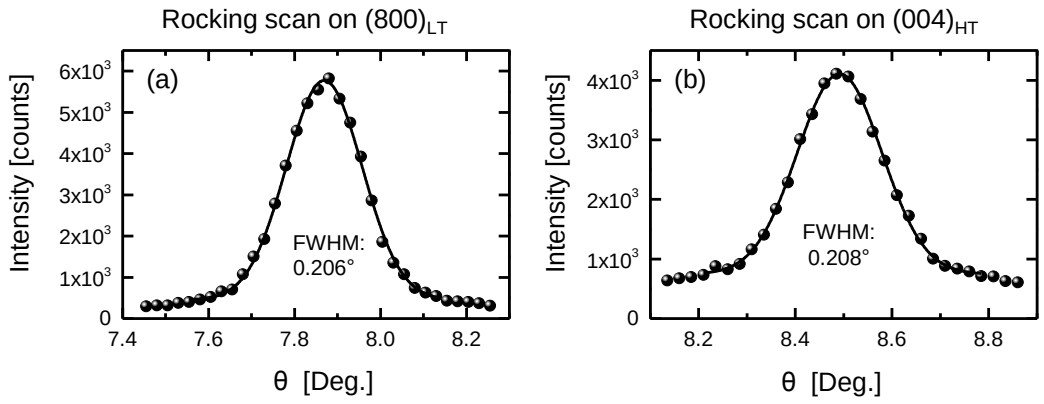

Figure S2: Rocking scans of the $(800)_{LT}$ reflection in (a) and the $(004)_{HT}$ reflection in (b) on a sample grown under illumination at 60°C.

(1) Langford, J. I.; Louër, D. *Reports Prog. Phys.* **1996**, *59*, 131–234.

(2) Hill, R. J.; Howard, C. J. *J. Appl. Crystallogr.* **1987**, *20*, 467–474.