

Supplementary Information

## Reversibility of temperature driven discrete layer-by-layer formation of dioctyl-benzothieno-benzothiophene films

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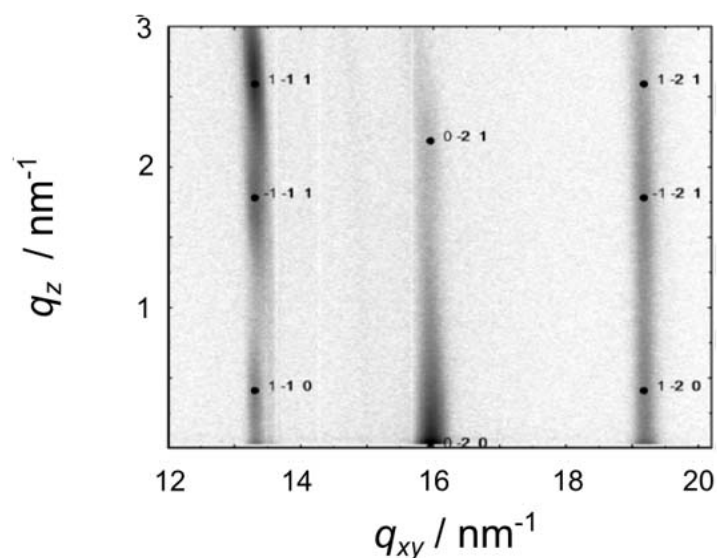


Fig. S1: Reciprocal space map of a spin coated C8-BTBT film obtained via grazing incidence X-ray diffraction on the multilayer film at 298 K; points indicate calculated peak positions of the crystal structure on the basis of its bulk phase.

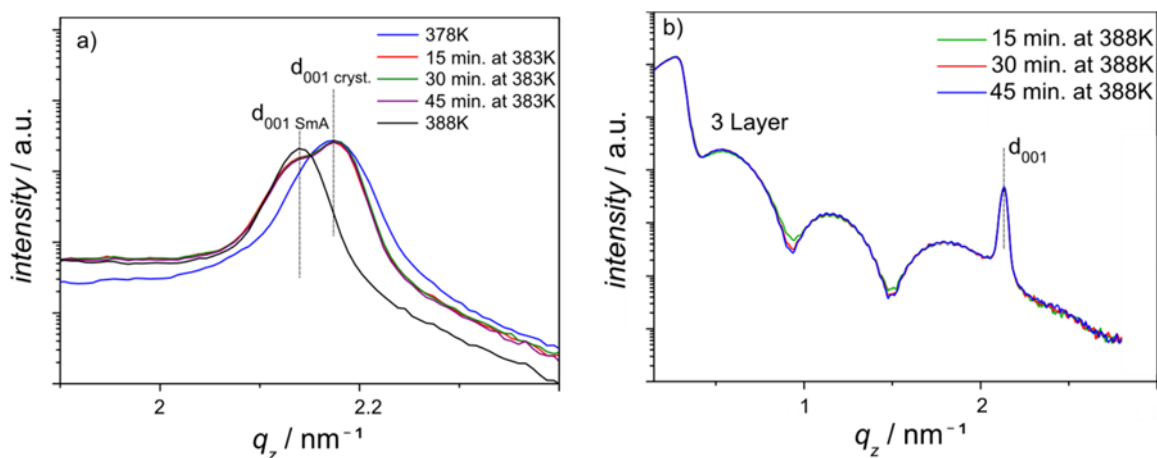


Fig. S2: Specular X-ray scattering curves of a spin coated C8-BTBT film at different temperatures and at different dwell times of 15, 30 and 45 minutes. (a) Diffraction pattern at temperatures of 378 K, 383K and 388 K around the 001 Bragg peak of the crystalline phase ( $d_{001 \text{ cryst}}$ ) and of the smectic A phase ( $d_{001 \text{ SmA}}$ ). (b) X-ray reflectivity curve at a temperature of 388K.

T [K]	a [nm]	b [nm]	c [nm]	$\alpha$ [deg]	$\beta$ [deg]	$\gamma$ [nm]	V [nm <sup>3</sup> ]
298 <sup>+</sup>	0.592	0.789	2.90	90.00	92.17	89.97	1.3494
323	0.593	0.791	2.90	90.00	92.29	90.21	1.3567
343	0.591	0.804	2.89	90.00	90.59	90.12	1.3738
358	0.591	0.811	2.89	90.00	89.77	90.07	1.3879
373	0.591	0.820	2.89	90.00	89.42	90.13	1.3996
303 <sup>#</sup>	0.591	0.798	2.89	90.00	91.67	90.04	1.3636
293 <sup>*</sup>	0.5927(7)	0.788(1)	2.918(4)	90	92.433(4)	90	1.361606

<sup>+</sup> as prepared film before heating,

<sup>#</sup> annealed film after heating,

<sup>\*</sup>single crystal data from T. Izawa E.Miyazaki and K. Takimiya, *Adv. Mater.* 2008, **20**, 3388.

Tab. S1: Crystallographic unit cell of C8-BTBT as a function of temperature, for comparison values after the heat treatment and of the single crystal investigations are given.