Electronic Supporting Information:

Additional Figures and Tables

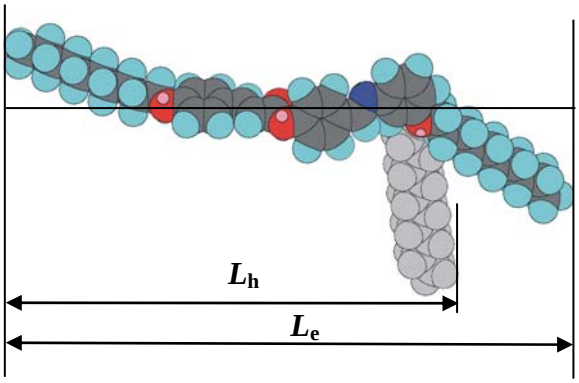


Figure S1: Molecular model of compound **10/10** with the length ***L*** of the molecule measured along a line roughly connecting the centres of the aromatic rings for two extreme orientations of the terminal chain in meta-position (both chains all-trans) for the most extended conformation, $\boldsymbol{L_e}$ = 42.5 Å, and for the "hockey stick"-like orientation (light gray), $\boldsymbol{L_h}$ = 34.3 Å (Chem3D models, energy minimized with MM2). Presumably, conformations of the "hockey-stick" type have only minor influence on the average molecular shape in the liquid crystalline phases.

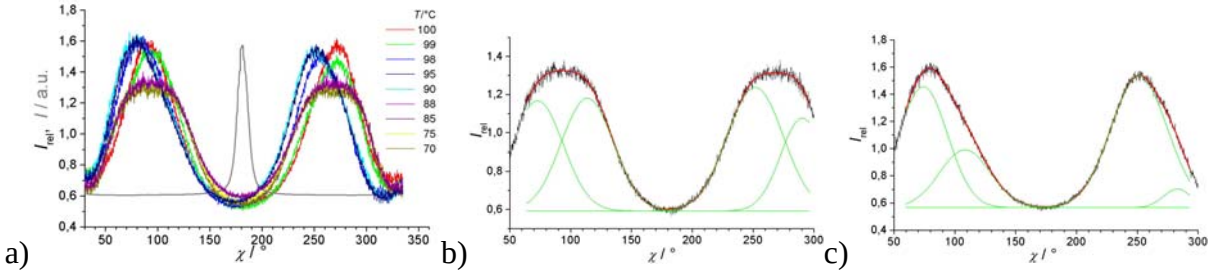
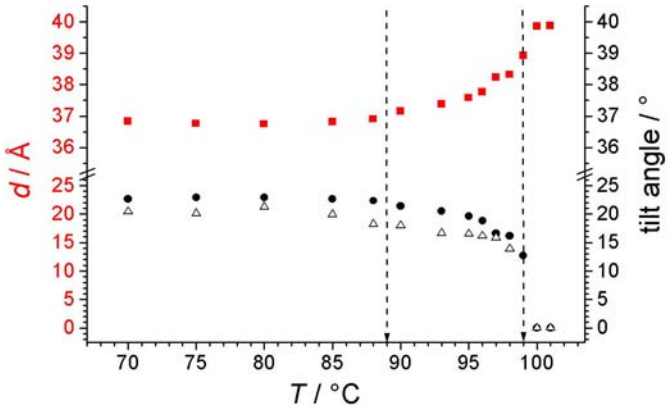


Figure S2: Chi-distribution of the outer diffuse scattering in the 2D X-ray patterns of compound **10/10** on cooling [I_{rel} = I(T) / I(105 °C, isotropic liquid)]: a) for selected temperatures (gray line: position of the layer reflections for 98 °C at χ = 180° for comparison), b) for 85 °C showing the Gaussian fits with four maxima of almost equal intensity in the SmC_A phase (deviations are due to the experimental setup), and c) for 95 °C showing the Gaussian fits with 2 pairs of maxima with strongly differing intensities as only observable for synclinic tilted molecules in the SmC phase.

Table S1 and Figure S2: Temperature dependence of layer spacing d of compound **10/10** determined from the 2D X-ray measurements (solid squares) and tilt angle τ_{obs} observed from the 2D patterns (open triangles) and τ_{calc} = arccos(d/d_{SmA}) calculated from d_{SmA} = 39.9 Å (solid circles) for comparison (all on cooling). The difference between τ_{obs} and τ_{calc} may result from measuring errors in τ_{obs} in the SmC phases (± 2°) and d_{obs} in the SmA phase with its comparatively small temperature range, and/or from conformational changes of the molecules at the SmA – SmC transition. The arrows in the diagram point to the approximate phase transition temperatures.

T/°C	$d_{obs,2D}$/Å	τ_{obs}/°	τ_{calc}/°	τ_{obs}-τ_{calc}/°
70	36.8	20	23	-2
75	36.8	20	23	-3
80	36.7	21	23	-2
85	36.8	20	23	-3
88	36.9	18	22	-4
90	37.2	18	21	-3
93	37.4	17	20	-4
95	37.6	17	20	-3
96	37.8	16	19	-3
97	38.2	16	17	-1
98	38.3	14	16	-2
99	38.9	-*	13	
100	39.9	0	0	
101	39.9	0	0	



* Due to the temperature gradient within the sample, the 2D pattern at about 99 °C shows the scattering of both, the SmA and the SmC phase near the transition temperature and the portions of the outer diffuse scattering resulting from both phases could not be sufficiently well resolved to determine the tilt angle in the SmC phase experimentally.