Supporting information to

Induction of ´banana phases´ in binary systems composed of bent-core and calamitic mesogens

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Additional Figures:

System A/C

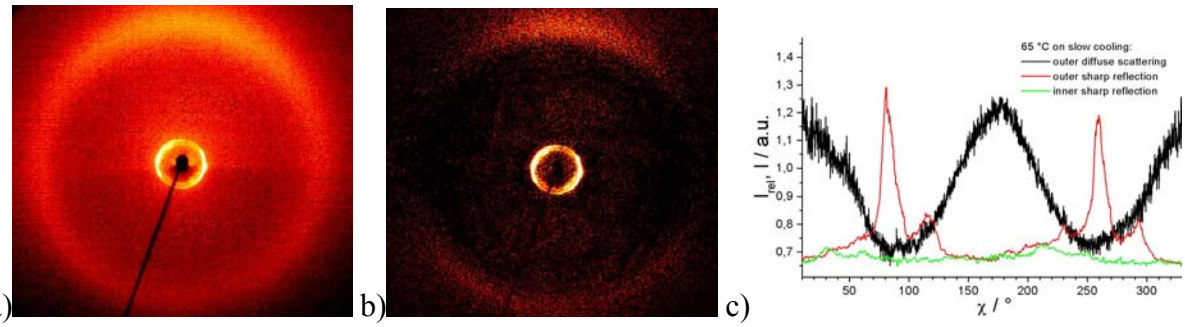


Figure S1: X-ray diffraction pattern for the B_X phase of a partially surface-aligned sample for a mixture of 74 % **C** and 26 % **A** at 65 °C on cooling a) original pattern, b) intensity of the isotropic liquid subtracted from the pattern in a) to enhance the maxima of the outer diffuse scattering, c) χ scan for the outer diffuse scattering ($I_{rel} = I_{65\ °C} / I_{95\ °C,\ isotropic\ liquid}$), red and green line: χ scans for the inner reflections for comparison.

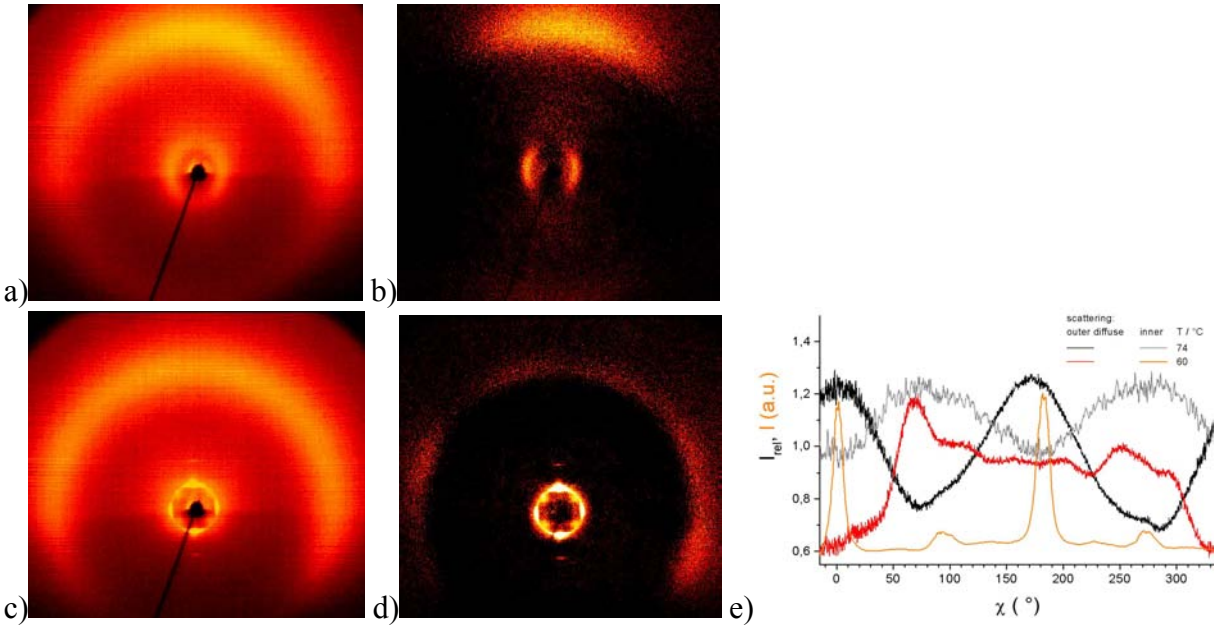


Figure S2: X-ray diffraction patterns of a partially surface-aligned sample for a mixture of 82 % **C** and 18 % **A** at two temperatures on cooling: a, c) original patterns, b, d) intensity of the isotropic liquid subtracted from these patterns to enhance the maxima of the outer diffuse scattering, a, b) nematic phase at 74 °C, c, d) B_X phase at 60 °C e) χ scans for the outer diffuse scattering ($I_{rel} = I_T / I_{95\ °C,\ isotropic\ liquid}$), light gray and orange line: χ scans for the inner reflections for comparison.

System A/D

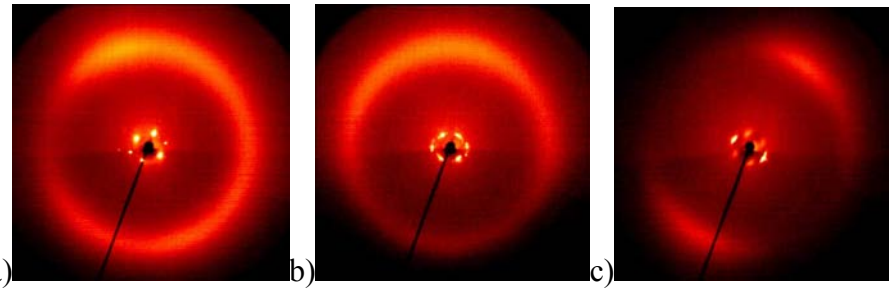
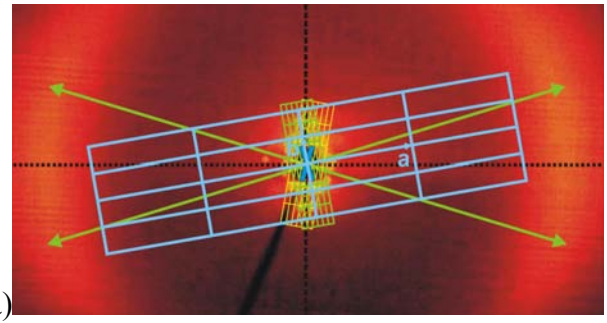


Figure S3: X-ray diffraction patterns of surface-aligned samples on cooling for system **A/D**, a) mixture of 50 % **A** and 50 % **D,** b) mixture of 40 % **A** and 60 % **D,** both at 90 °C in the Col_{rec} phase, c) mixture of 25 % **A** and 75 % **D** at 80 °C in the B_X phase

System B/F

a) 

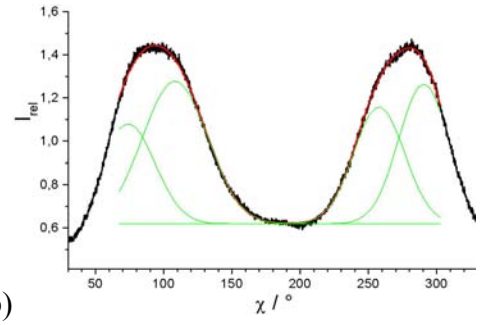
b) 

Figure S4: a) X-ray diffraction pattern of a surface-aligned sample for a mixture of 60 % **F** and 40 % **B** at 90 °C on cooling: Green, yellow … reciprocal 2D lattices, green arrows indicating the direction of the maximum diffuse scattering; dashed black … equator and meridian of the pattern, respectively; blue … corresponding real 2D lattice, blue rods indicating the two possible orientations of the long molecular axes. The approximate tilt of the ***b*** axis with respect to the meridian of the pattern is 10°, hence the molecules are tilted with respect to ***b*** by 17° -10° = 7° or by 17° + 10° = 27°, b) χ scan for the outer diffuse scattering (I_{rel} = $I_{90\ °C}/I_{110\ °C,\ isotropic\ liquid}$), Gaussian fit (red line) for 4 maxima (green lines) to the experimental one (black line)

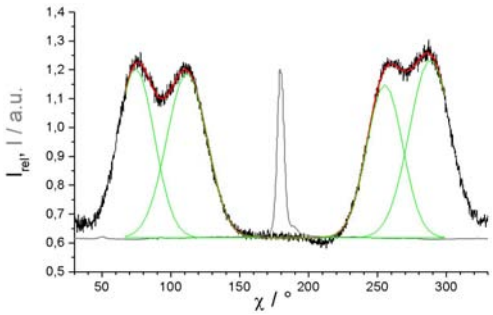


Figure S5: a) χ scan for the outer diffuse scattering (I_{rel} = $I_{92\ °C}/I_{110\ °C,\ isotropic\ liquid}$) in the X-ray diffraction pattern of a surface-aligned sample for a mixture of 70 % **F** and 30 % **B**, Gaussian fit (red line) for 4 maxima (green lines) to the experimental one (black line, gray line: layer reflection for comparison) revealing a 18° tilt of the molecules with respect to the normal to the b axis (i.e. to the normal of the "broken" layers)

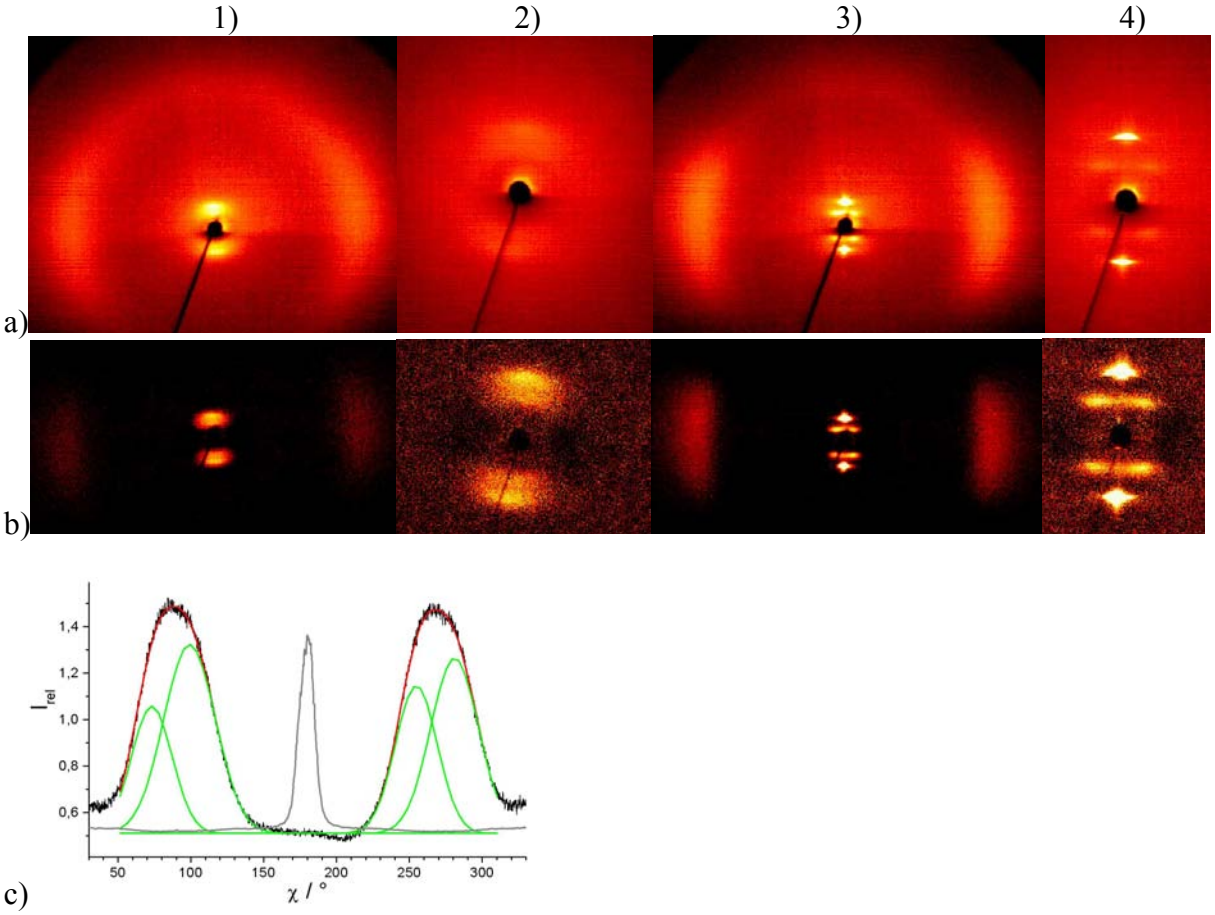


Figure S6: X-ray diffraction patterns of a surface-aligned sample for a mixture of 84 % **F** and 16 % **B** on cooling**,** row a) original XRD patterns, row b) intensity of the isotropic liquid at 125 °C subtracted from these patterns for clarity, columns 1, 2) nematic phase at 108 °C, columns 2, 3) B_X phase at 90 °C, columns 1, 3) WAXD, columns 2, 4) SAXD, c) determination of the maxima for the outer diffuse scattering at 90 °C by fitting 4 Gaussian curves (green lines) to the experimental χ-scan (black line, relative intensity $I_{rel}=I_{100°C}/I_{125°C}$) revealing a 13° tilt of the molecules with respect to the layer normal

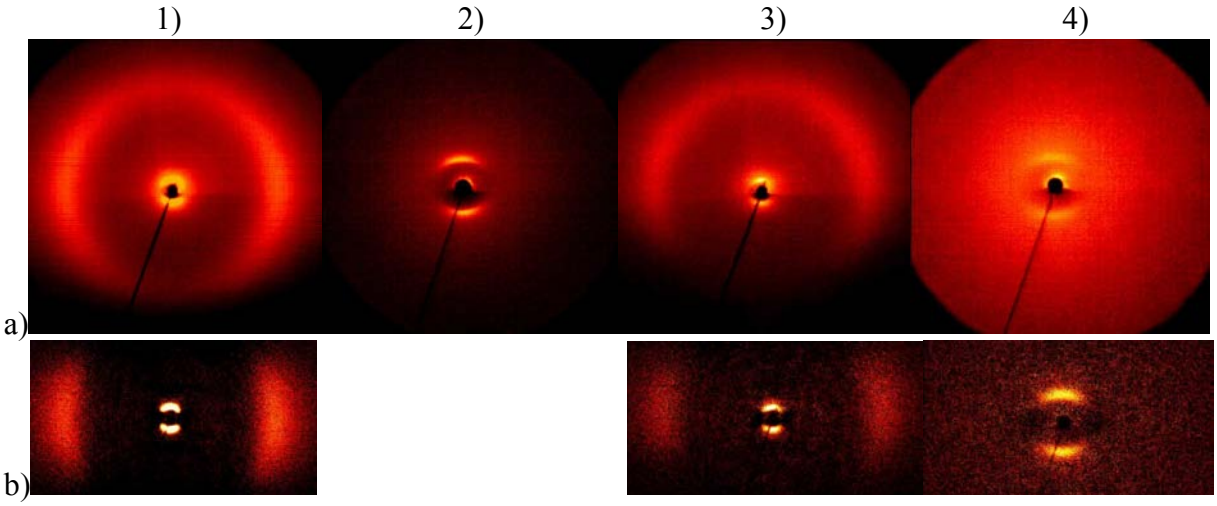


Figure S7: X-ray diffraction patterns for the nematic phases of surface-aligned samples for mixtures of 60 % **F** / 40 % **B** [columns 1) WAXD and 2) SAXD, 100 °C] and 70 % **F** / 30 % **B** [columns 3) WAXD and 4) SAXD, 102 °C] on cooling**,** row a) original XRD patterns, row b) intensity of the isotropic liquid at 110 °C subtracted from these patterns for clarity.

Molecular Models

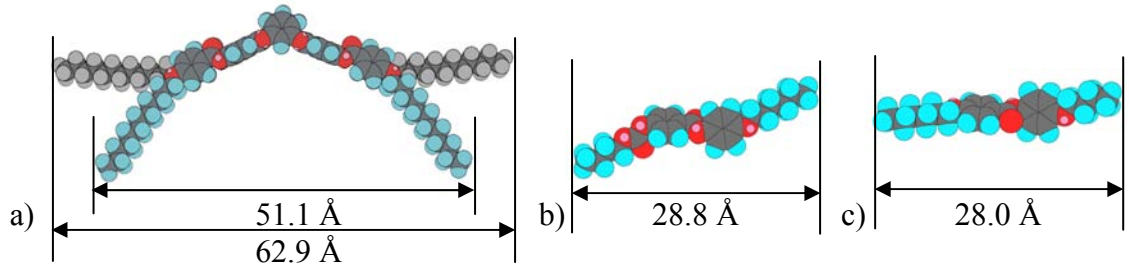


Figure S8: Molecular lengths estimated from modelling in Chem3D, measured for a) the bent-core molecule **A** with two extreme orientations of the all-trans chains with respect to the core (colour and gray scale, respectively; bending angle of the core = 120° [1], ***L*** = 54.5 Å [2])**,** and for the most extended conformation of b) **C** and c) **D.**

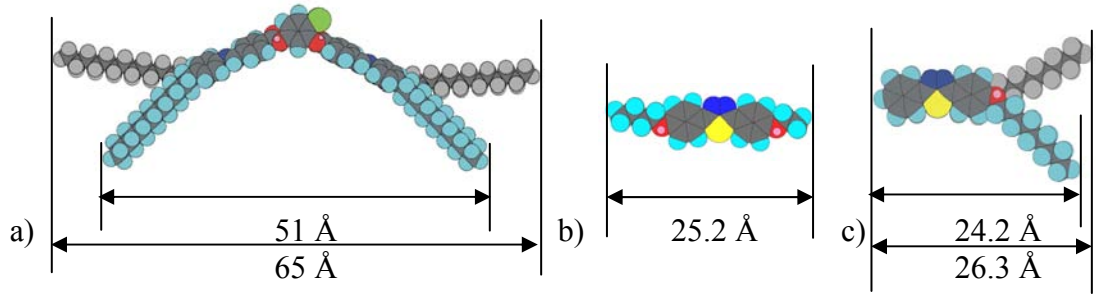


Figure S9: Molecular lengths estimated from modelling in Chem3D, measured for a) the bent-core molecule **B** with two extreme orientations of the all-trans chains with respect to the core (colour and gray scale, respectively; bending angle of the core = 130° [2])**,** b) the most extended conformation of **E,** and c) **F** with two extreme chain orientations**.**

Additional Tables:

Table S1: Data derived from the 2D X-ray patterns for systems **A/C**, **A/D**, **B/E**, and **B/F**; ***T*** … temperature (°C), 2θ ... diffraction angle (°), d_{exp} ... experimental d value(Å), ***n*** … order of the reflection, ***h, k*** … Miller indices, ***a, b,*** γ … lattice parameters (Å and °, respectively), d_{calc} … d value calculated from the layer distance or the lattice parameters, respectively (Å), phases: N … nematic, SmCP … polar smectic layer structure, SmCP' … not clearly specified polar smectic layer structure, presumably undulated, USmCP .. undulated smectic layer structure, Col_{rec} … modulated layer structure with a rectangular 2D lattice, Col_{ob} … modulated layer structure with an oblique 2D lattice, B_X … modulated layer structure with a lower degree of order (short-range ordered modulation)

Compound/ Mixture	**Phase**	***T***	2θ	d_{exp}	***n/ hk***	***a***	***b***	γ	d_{calc}	d_{exp}- d_{calc}
System A/C										
A90/C10	SmCP	90	2.450	36.1	1				36.2	-0.1
			4.870	18.1	2				18.1	0.0
			7.339	12.0	3				12.0	0.0
A60/C40	Col_{rec}	92	2.829	31.2	11	40.1	49.6			
			3.562	24.8	02					
		80	2.868	30.8*	11	39.0	50.2			
			3.526	25.1	02					
A30/C70	Col_{rec}	81	2.942	30.0	11	37.3	50.4			
			3.504	25.2	02					
	Col_{rec}	75	3.010	29.4*	11	36.2	50.4			
			3.501	25.2	02					
	B_X	65	2.998	29.5*	11	36.2	50.8			
			3.477	25.4	02					
A26/C74	B_X	65	3.014	29.3*	11	36.3	50.7			
			3.479	25.4	02					
A18/C82	N	74	3.892	22.7*						
	B_X	60	3.261	27.1*	11	32.0	50.8			
			3.471	25.4	02					
System A/D										
A50/D50	Col_{rec}	90	2.970	29.7	11	37.5	49.0			
			3.609	24.4	02					
A40/D60	$Col_{rec.}$	90	2.909	30.3	11	38.7	49.0			
			3.604	24.5	02					
A25/D75	B_X	80	3.002	29.4	11	36.7	49.1			
			3.595	24.5	02					
A20/D80	B_X	70	3.588	24.6	02					
System B/E										
B50/E50	N	122	1.953	45.2*						
	SmCP	115	1.785	49.5	1				50.0	-0.5
			3.461	25.5	2				25.0	0.5
B70/E30	N	125	2.104	42.0*						
	SmCP'		1.806	48.9	1				49.3	-0.4
			3.558	24.8	2				24.7	0.1

Table S1: (cont.)

Compound/ Mixture	**Phase**	***T***	**2θ**	**d_{exp}**	***n/ hk***	***a***	***b***	**γ**	**d_{calc}**	**d_{exp}-d_{calc}**
System B/F										
F	SmA	100	3.382	26.1					25.5[#]	0.6
			6.789	13.0					12.8[#]	0.2
B75.5/F24.5	SmCP	100	1.871	47.2					46.5[#]	0.7
B40/F60	N	100	1.943	45.5*						
	USmCP	90	1.748	50.5	11	204	52.2		50.5	0.0
			1.902	46.4	12				46.4	0.0
			3.355	26.3	20				26.1	0.2
			3.440	25.7	21				25.9	-0.2
			3.495	25.3	22				25.3	0.0
B30/F70	N	102	2.137	41.4*						
	Col_{ob}		1.985	44.5	11	122	53.5	102.5	44.6	-0.1
			3.370	26.2	02				26.2	0.0
			3.970	22.3	22				22.3	0.0
B16/F84	N	108	2.345	37.7*						
			3.311	26.7*						
	B_X	90	2.183	40.5*	11	63.5	52.6			
			3.356	26.3	02					

* maximum of the diffuse reflection, [#] layer spacing derived from Guinier patterns

Table S2: A rough estimate of the numbers of molecules in the cross section of the 2D unit cell for selected mixtures of systems **A/C** and **A/D**

Mixture	$V_{Mol,C,D}$	$V_{Mol,A}$	$x_{C,D}$	x_A	V_{cell}	n_{cell}	$n_{C,D,cell}$	$n_{A,cell}$
A60/C40, crystal	559.6	1289.0	0.4	0.6	10342.6 at 92 °C	10.4	4.1	6.2
liquid	712.2	1640.5				8.1	3.3	4.9
Average in l.c.						9.3	3.7	5.6
A30/C70, crystal	559.6	1289.0	0.7	0.3	9562.6 at 65 °C	12.3	8.6	3.7
liquid	712.2	1640.5				9.7	6.8	2.9
Average in l.c.						11.0	7.7	3.3
A40/D60, crystal	522.7	1289.0	0.6	0.4	9860.8 at 90 °C	11.9	7.1	4.8
liquid	655.3	1640.5				9.4	5.6	3.8
Average in l.c.						10.7	6.4	4.3
A25/D75, crystal	522.7	1289.0	0.75	0.25	9370.2 at 80 °C	13.1	9.8	3.3
liquid	655.3	1640.5				10.4	7.8	2.6
Average in l.c.						11.8	8.9	2.9

$V_{mol,crystal}$ ... molecular volume in the crystal calculated using crystal volume increments: Immirzi and Perini [3], average packing coefficient in the crystal k = 0.7 according to Kitaigorodski [4], $V_{mol,liquid}$ ... molecular volume in the isotropic liquid, average packing coefficient k = 0.55, V_{cell} ... unit cell volume obtained from the lattice parameters and assuming a height of h = 0.52 nm (assuming a stacking in bend direction of the bent-core molecules with a bend angle of 120°), x_A, $x_{C,D}$ … molar fraction of compound **A** and **C**,**D**, respectively, n_{cell} ... number of molecules in a unit cell with crystal-like density (crystal) according to $n_{cell} = V_{cell}/(x_A \cdot V_{molA} + x_{C,D} \cdot V_{molC,D})$, with liquid-like density according to $n_{cell} = n_{cell,crystal} \cdot 0.55/0.7$, and in the liquid crystalline phase (Average in l.c.) estimated as the intermediate between that in the crystalline and the liquid phase, numbers of molecules of compound **A** and **C**,**D**, respectively, in a cell: $n_{A,cell} = n_{cell} \cdot x_A$ and $n_{C,D,cell} = n_{cell} \cdot x_{C,D}$.

References:

[1] G. Pelzl, S. Diele, W. Weissflog, Adv. Mater. 1999, **11**, 707-724

[2] M. W. Schröder, S. Diele, G. Pelzl and W. Weissflog, ChemPhysChem, 2004, **4**, 99.

[3] A. Immirzi, B. Perini, *Acta Cryst. Sect. A* 1977, *33*, 216-218

[4] A. I. Kitaigorodski, "Molekülkristalle", Akademieverlag Berlin, 1979