Supplementary Material (ESI) for Chemical Communications

Supporting information:

Equipment

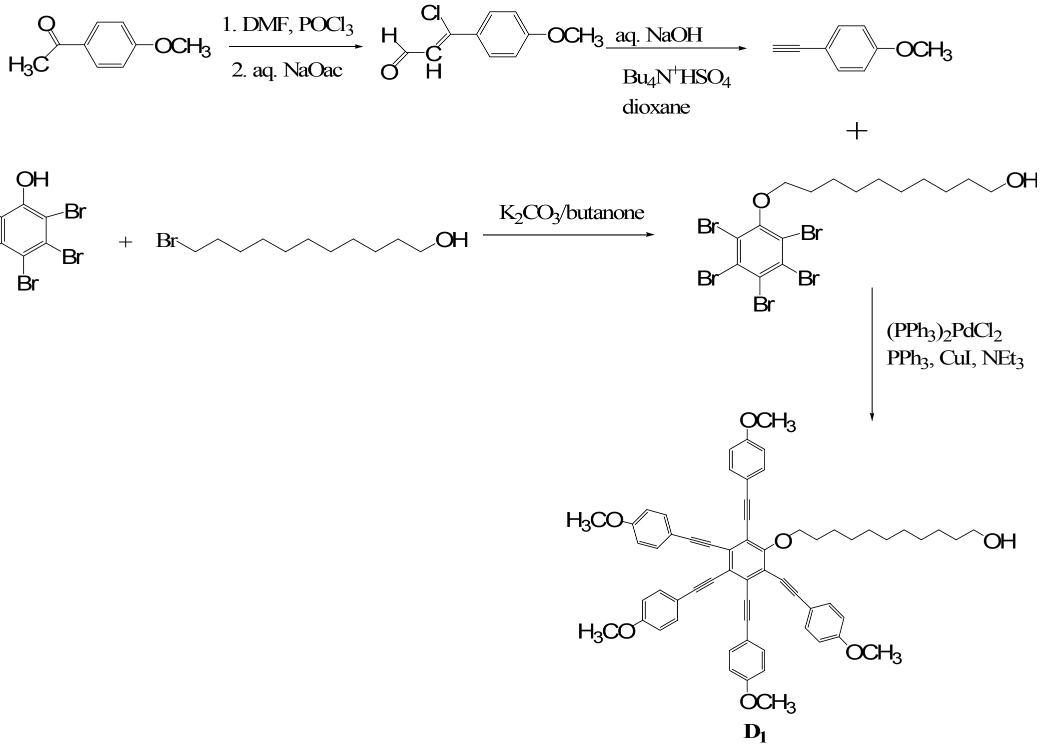
Nuclear magnetic resonance (NMR) spectra were recorded on a Jeol JNM-ECP 400 MHz FT-NMR spectrometer. Chemical shifts are reported in ppm relative to TMS. In some ^{13}C NMR spectra, multiple peaks are reported for because of the chemical dissimilarity of seemingly identical carbon atoms.

The data for the glass transitions and the nematic to isotropic transitions were recorded on cooling runs, as some of the transitions are monotropic, the data for the crystal to isotropic transitions stem from the first heats (all at 10 °C min^{-1}). The thermal properties were investigated using a Mettler Toledo differential calorimeter (DSC 822^e) in nitrogen against an indium standard. Transition temperatures were determined as the onset of the maximum in the endotherm or exotherm. The mesophases were studied on an Olympus BH-2 optical polarising microscope, equipped with a Mettler FP82 HT hot stage and a Mettler FP90 central processor. Pictures of the mesophases were taken using a JVC digital video camera connected to a PC. Software *Studio Capture*, supplied by Studio86Designs was used for image capturing.

X-ray diffraction measurements were performed on a MAR345 diffractometer with a 2D image plate detector (CuKα radiation, graphite monochromator, λ = 1.54 Å). The samples were placed in glass capillaries (Lindemann Tubes) and were heated in the presence of a magnetic field using a home-built capillary furnace.

Synthesis of the discs:

Synthesis of 11-[Pentakis-(4-methoxy-phenylethynyl)-phenoxy]-undecan-1-ol (D_1) was carried out according to the scheme 1 and was published before[15].



Scheme 1. Synthesis of disc structure D_1

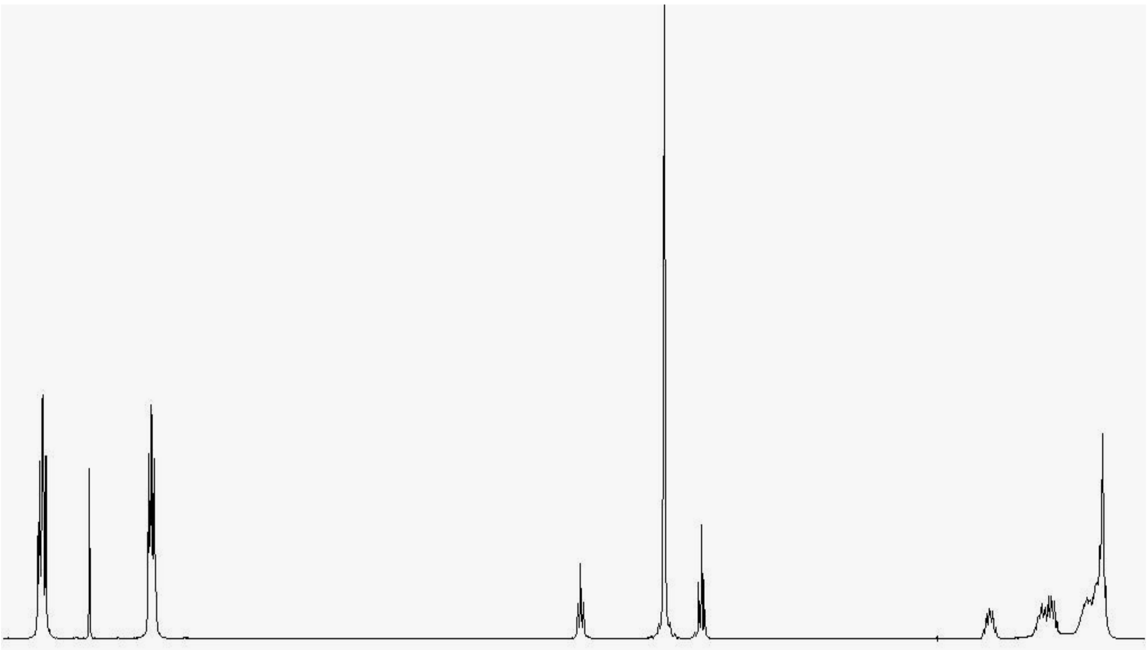


Figure 1. NMR spectra of 11-[Pentakis-(4-methoxy-phenylethynyl)-phenoxy]-undecan-1-ol (D_1)

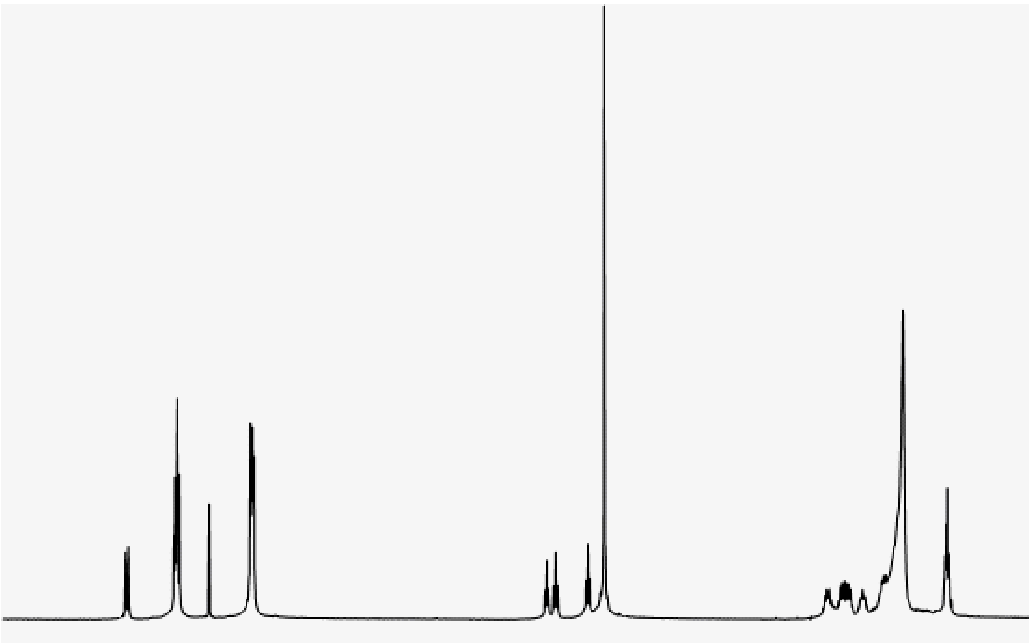


Figure 2. NMR spectra of 11-(2,3,4,5,6-pentakis(2-(4-methoxyphenyl)ethynyl)phenoxy)undecyl 4-(undecyloxy)benzoate (D_2)

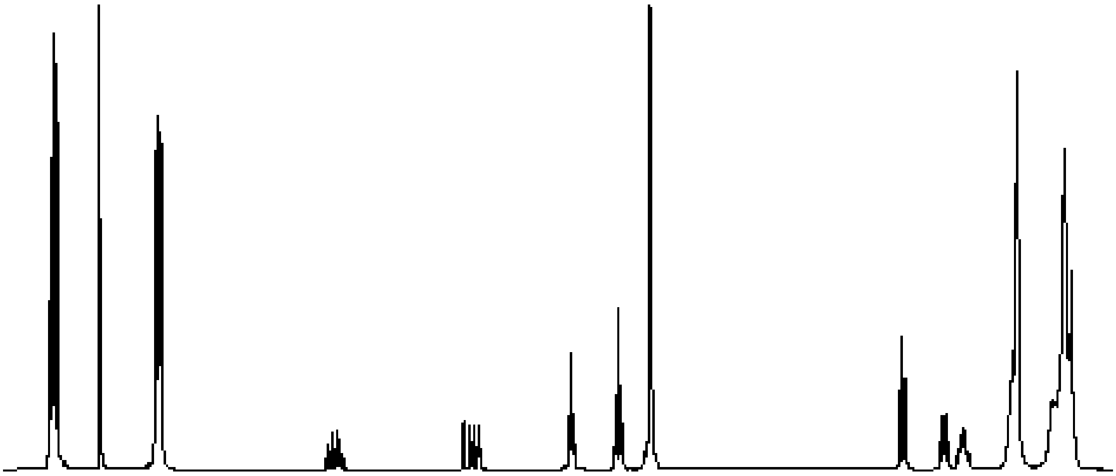


Figure 3. NMR spectra of 11-(2,3,4,5,6-pentakis(2-(4-methoxyphenyl)ethynyl)phenoxy)undecyl undec-10-enoate (D_3)

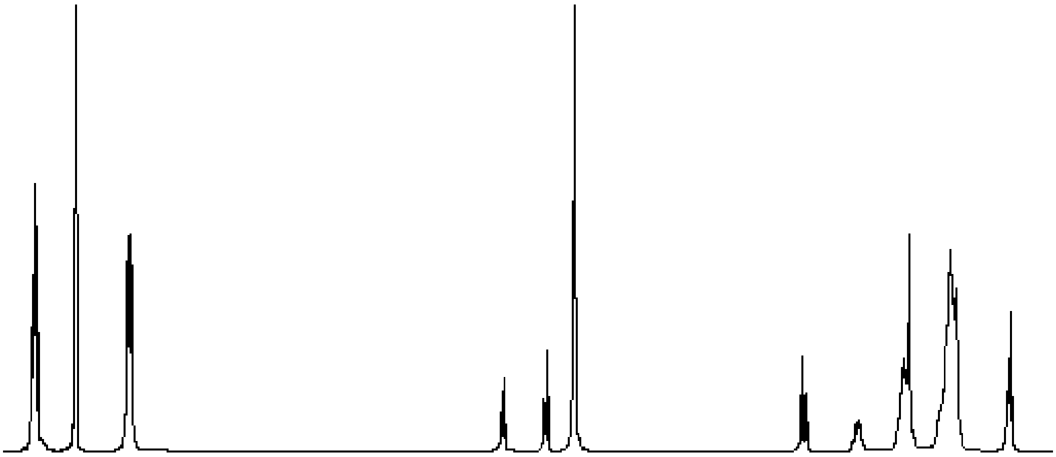


Figure 4 NMR spectra of 11-(2,3,4,5,6-pentakis(2-(4-methoxyphenyl)ethynyl)phenoxy)undecyl octanoate (D_4)

Synthesis of 11-(2,3,4,5,6-pentakis(2-(4- methoxyphenyl)ethynyl)phenoxy)undecyl 4-(undecyloxy)benzoate (D_2):

To a stirred solution containing 0.23g of 4-(undecyloxy)benzoic acid (0.786 mmol) and 0.6g of 11-(2,3,4,5,6-pentakis(2-(4-methoxyphenyl)ethynyl)phenoxy)undecan-1-ol (D_1) (0.655 mmol) (molar ratio 1.2 :1) and a catalytic amount of DMAP in anhydrous CH_2Cl_2, a solution of 0.12g of DIPC (0.983 mmol) in CH_2Cl_2 was added (final molar ratio acid : alcohol : DMAP: DCC = 1.2 : 1 : 0.5 : 1.5). After 6 days of stirring, diisopropyl urea was filtered off and the solution was concentrated in vacuo. The product was purified by column chromatography on silicagel (mesh 60Å) with mixture of CH_2Cl_2: hexane (4:1) as eluent. The pure product was recrystalised from acetone as a yellow powder. Yield:

62.5% (0.48g). Anal. Found: C,80.54, H,7.35, %. Calc. for $C_{80}H_{84}O_9$: C, 80.78, H, 7.12, %; m/z (MALDI): M+Na$^+$ 1211

^{1}H-NMR δ_H ($CDCl_3$): 7.97 (d, 2H, aromatic), 7.54 (m, 10H, aromatic), 6.89 (m, 12H, aromatic), 4.34 (t, 2H, -CH_2-), 4.26 (t, 2H, -CH_2-), 3.98 (t, 2H, -CH_2), 3.84 (s, 15H, -CH_3), 1.93-1.26 (m, 36 H, alkyl chain), 0.87 (t, 3H, -CH_3).

^{13}C-NMR δ_C ($CDCl_3$): 166.49, 162.82, 159.97, 159.88, 133.25, 133.11, 131.59, 128.48, 123.94, 122.72, 119.99, 115.83, 115.64, 115.59, 114.21, 114.18, 114.09, 99.26, 99.13, 97.02, 86.73, 86.21, 83.65, 74.76, 68.29, 64.92, 55.45, 32.0, 31.05, 30.70, 29.70, 29.44, 29.22, 28.88, 26.49, 26.18, 26.08, 22.79, 14.23.

Synthesis of 11-(2,3,4,5,6-pentakis(2-(4-methoxyphenyl)ethynyl)phenoxy)undecyl undec-10-enoate (D_3):

To a stirred solution containing 0.12 g of undec-10-enoic acid (0.655 mmol) and 0.5 g of 11-(2,3,4,5,6-pentakis(2-(4-methoxyphenyl)ethynyl)phenoxy)undecan-1-ol (D_1) (0.546 mmol) (molar ratio 1.2 :1) and a catalytic amount of DMAP in anhydrous CH_2Cl_2, a solution of 0.10g of DIPC (0.819 mmol) in CH_2Cl_2 was added (final molar ratio acid : alcohol : DMAP: DCC = 1.2 : 1 : 0.5 : 1.5). After 7 days of stirring, diisopropyl urea was filtered off and the solution was concentrated in vacuo. The product was purified by column chromatography on silicagel (mesh 60Å) with mixture of CH_2Cl_2: hexane (5:2) as eluent. The pure product was recrystalised from acetone/alcohol as a yellow powder. Yield: 53% (0.31g); m/z (MALDI): M+Na$^+$ 1118 ^{1}H-NMR δ_H ($CDCl_3$): 7.54 (m, 10H, aromatic), 6.88 (d, 10H, aromatic), 5.8 (m, 1H, -CH=CH_2); 5.00-4.89 (m, 2H, -CH=CH_2); 4.35 (t, 2H, -CH_2-), 4.0 (t, 2H, -CH_2-), 3.85 (t, 15H, -CH_3), 2.27 9t, 2H, -CH_2-); 2.17 (t, 2H, -CH_2-) ; 2.03 (t, 2H, -CH_2-); 1.59 (m, 10 H, alkyl chain), 1.27 (m, 20H, -CH_2-); ^{13}C-NMR δ_C ($CDCl_3$): 160.00; 159.90; 159.80; 139.19; 133.27; 133.11; 128.38; 119.87; 115.72; 115.55; 115.48; 114.10; 114.06; 104.80; 99.13; 98.99; 86.60; 83.53; 64.41; 55.34; 34.37; 33.77; 30.57; 29.61; 29.56; 29.28; 29.20; 29.12; 29.04; 28.86; 28.63; 26.36; 25.94; 24.98.

Synthesis of 11-(2,3,4,5,6-pentakis(2-(4-methoxyphenyl)ethynyl)phenoxy)undecyl octanoate (D_4):

To a stirred solution containing 0.0467 g of octanoic acid (0.32 mmol) and 0.27 g of 11-(2,3,4,5,6-pentakis(2-(4-methoxyphenyl)ethynyl)phenoxy)undecan-1-ol (D_1) (0.29 mmol) (molar ratio 1.1 :1) and a catalytic amount of DMAP in anhydrous CH_2Cl_2, a solution of 0.055 g of DIPC (0.44 mmol) in CH_2Cl_2 was added (final molar ratio acid : alcohol : DMAP: DCC = 1.1 : 1 : 0.5 : 1.5). After 10 days of stirring, diisopropyl urea was filtered off and the solution was concentrated in vacuo. The product was purified by column chromatography on silicagel (mesh 60Å) with mixture of CH_2Cl_2: hexane (4:1) as eluent. The pure product was recrystalised from acetone as a yellow powder. Yield 74.9% (0.23 g); m/z (MALDI): M+Na$^+$ 1064; ^{1}H-NMR δ_H ($CDCl_3$): 7.53 (m, 10H, aromatic), 6.88 (m, 10H, aromatic), 4.33 (t, 2H, -CH_2-), 4.03 (t, 2H, -CH_2-), 3.84 (s, 15H, -CH_3), 2.27 (t, 2H, -CH_2-), 1.90 (m, 2H, -CH_2-), 1.59 (m, 10H alkyl chain), 1.27 (m, 18 H, alkyl chain), 0.86 (t, 3H, -CH_3). ^{13}C-NMR δ_C ($CDCl_3$): 160.11, 160.01, 141.08, 133.40, 133.23, 128.49, 123.94, 119.99, 115.66, 114.18, 99.25, 86.72, 83.65, 64.51, 55.46, 34.50, 31.77, 30.68, 29.68, 29.40, 29.21, 29.04, 28.76, 26.47, 26.06, 25.12, 22.70, 14.18.

Synthesis of the rods shaped molecules R_1 and R_2:

The rods R_1 and R_2 were synthesized according to procedures reported in the literature. the literature data [2d],[3]

DSC Data

c(%) refers to molar concentrations, only the value of the concentration of the rod shaped mateirlas is given, the reminder is made up of the disc shaped materials.

T_{NI} –refers to the transition detected from DSC curves on the 3rd cooling to the nematic phase

$T_{(Cr\text{-}I)}$ – the transition detected from DSC curves on the first heating

T_{Cr} – temperature of crystallization on the 3rd cooling

T_g – glass transition

ΔH (kJ/mole) = M_m ΔH (J/g); $M_m = (n_1M_1 + n_2 M_2)/(n_1 + n_2)$; n_1, n_2 = moles of compounds 1 and 2; $M_{1,2}$ = molar mass of the pure compounds, M_m = medium molar mass of the mixture. All values are negative as the data was taken on cooling.

Table 1. DSC data of the mixtures D_2/R_1:

	Thermal Transtions (°C)			
Composition c(%) R_1	$T_{(N\text{-}I)}$	$T_{(Cr\text{-}I)}$	T_g	$\Delta H_{(N\text{-}I)}$ (kJ/mol)
0	81.4	92.3	2.4	-0.09
7.11	49.8	86	1.2	
9.23	45.1	86.2	1.2	-0.03
12.72	45.0	86.2	1.6	-0.04
16.37	22.9	79.2	-3.5	-0.04
17.49	23.7	81.3	-3.0	-0.03
17.52	26.7	81.0	-2.8	-0.03
18.78	22.3	80.4	-3.9	-0.02
19.4	22.2	80.5	-4.1	-0.03
21.39	18.1	77.1	-5.4	-0.03
26.82	21.7	74.8	-8.2	-0.22
32.5	25.7	72.7		-0.33
34.99	29.0	72.8		-0.39
41.84	35.1	67.9		-0.45
43.75	34.9	67.9		-0.44
51.45	41.6	65.9		-0.73
56.46	45.3	65.4		-0.79
80.36	61.5	47.3		-1.29
100	72.8	48.1		-1.30

Table 2. DSC data of the mixtures **D_2/R_2:**

Thermal Transtions (°C)

Composition c(%) R_2	$T_{(N-I)}$	$T_{(Cr-I)}$		T_g	$\Delta H_{(N-I)}$ (kJ/mol)
0	81.4	93.2		2.4	-0.09
7.69	49.3	87.7			-0.1
8.09	45.3	87.7			-0.07
10.21	41.0	85.4		0.4	-0.01
12.03	42.1	84.9		0.4	-0.04
15.87	32.6	83.1		-1.1	-0.003
19.34	34.6	82.5		-2.0	-0.05
23.13	38.2	78.3			-0.05
29.83	44.7	82.2			-0.11
34.47	59.4	78.5			-0.12
38.52	62.7	80.2			-0.16
50.56	81.9	79.3			-0.5
59.52	95.6	82.5	11.6		-0.61
80.14	116.5	82.1	34.1		-0.97
100	140.8	91.9	93		-1.52

Table 3. DSC data of the mixtures **D_3/R_2:**

Thermal Transtions (°C)

Composition c(%) R_2	$T_{(N-I)}$	$T_{(Cr-I)}$	T_{cr}	$\Delta H_{(N-I)}$ (kJ/mol)
0	140.11	79.78	17.47	-0.12
9.88	78.19	73.47	10.25	-0.18
13.54	66.35	69.15	8.85	-0.15
21.15	41.6	70.97	7.88	0
25.24	33.56	71.63	7.31	-0.05
30.43	43.46	71.67	7.15	0.076
40.54	66.19	65.73	-0.65	-0.092
51.88	83.51	64.12	27.73	-0.3
70.53	107.04	83.15	33.81	-0.57
80.61	121.54	84.37	40.63	-0.78
100	140.82	91.86	3.66	-1.86

Table 4. DSC data of the mixtures **D_4/R_2:**

Thermal Transtions (°C)

Composition c(%)R_2	T_{NI}	$T_{(Cr-I)}$	T_{Cr}	Δ H (kJ/mol)
0	157.56	95.11	49.06	-0.11
6.61	128	92.05	15.08	0
11.27	92.4	88.73	12.27	0
22.12	42.7	85.31	9.79	0
30.5	35	84.5		0
39.84	37.7	80.94		-0.11
51.24	74.01	81.41		-0.23
60.74	93.09	80.63		-0.47
78.55	116.08	80.71		-1.37
100	140.82	91.86	3.66	-1.86

The data for the glass transitions and the nematic to isotropic transitions were recorded on cooling runs, as some of the transitions are monotropic, the data for the crystal to isotropic transitions stem from the first heats (all at 10 °C min^{-1}). The thermal properties were investigated using a Mettler Toledo differential calorimeter (DSC 822^{e}) in nitrogen against an indium standard. Transition temperatures were determined as the onset of the maximum in the endotherm or exotherm. The mesophases were studied on an Olympus BH-2 optical polarising microscope, equipped with a Mettler FP82 HT hot stage and a Mettler FP90 central processor. Pictures of the mesophases were taken using a JVC digital video camera connected to a PC. Software *Studio Capture*, supplied by Studio86Designs was used for image capturing.

Figure 5. Examples of DSC diagrams for **D_2/R_1** and **D_2/R_2** mixtures

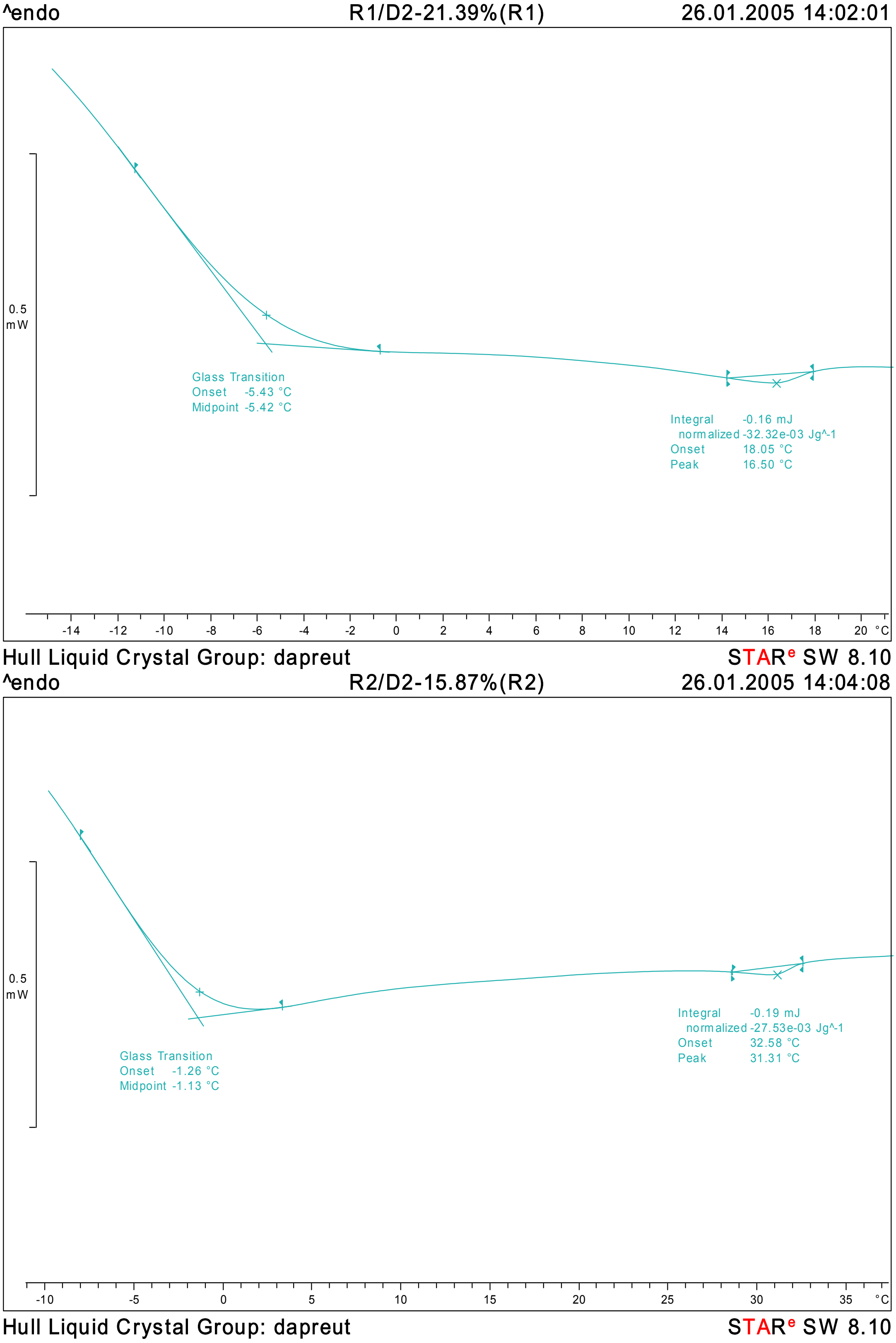
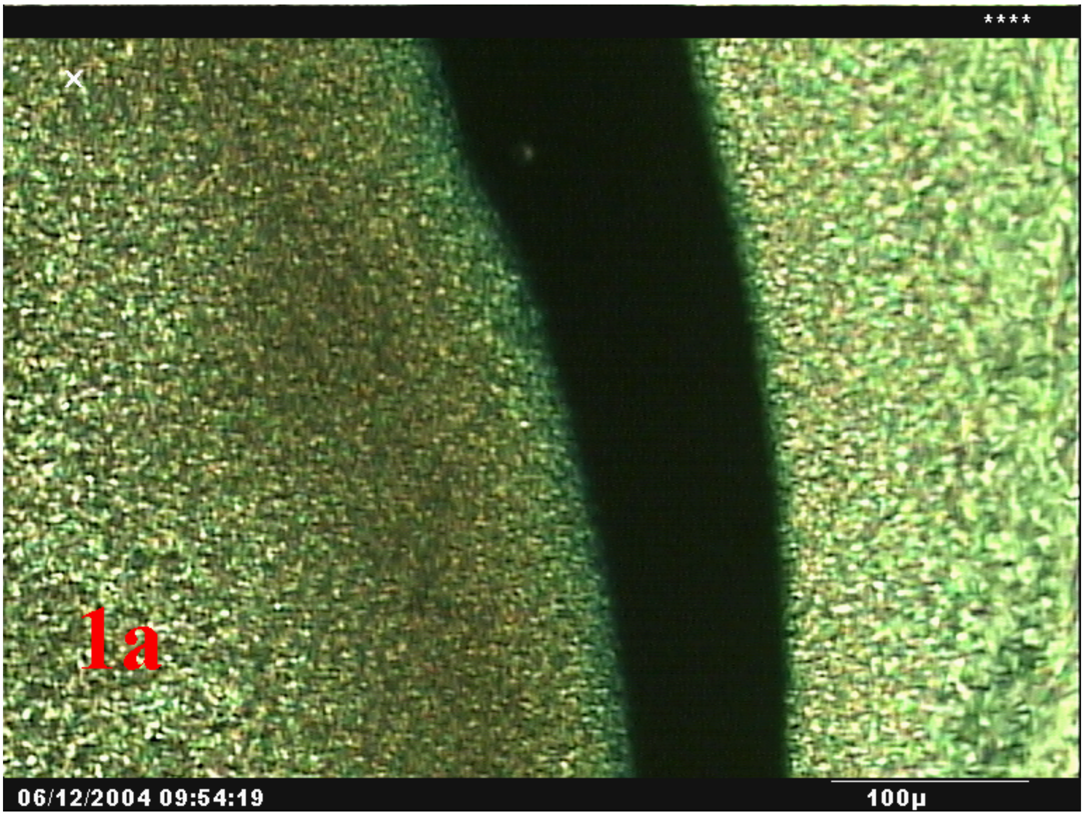
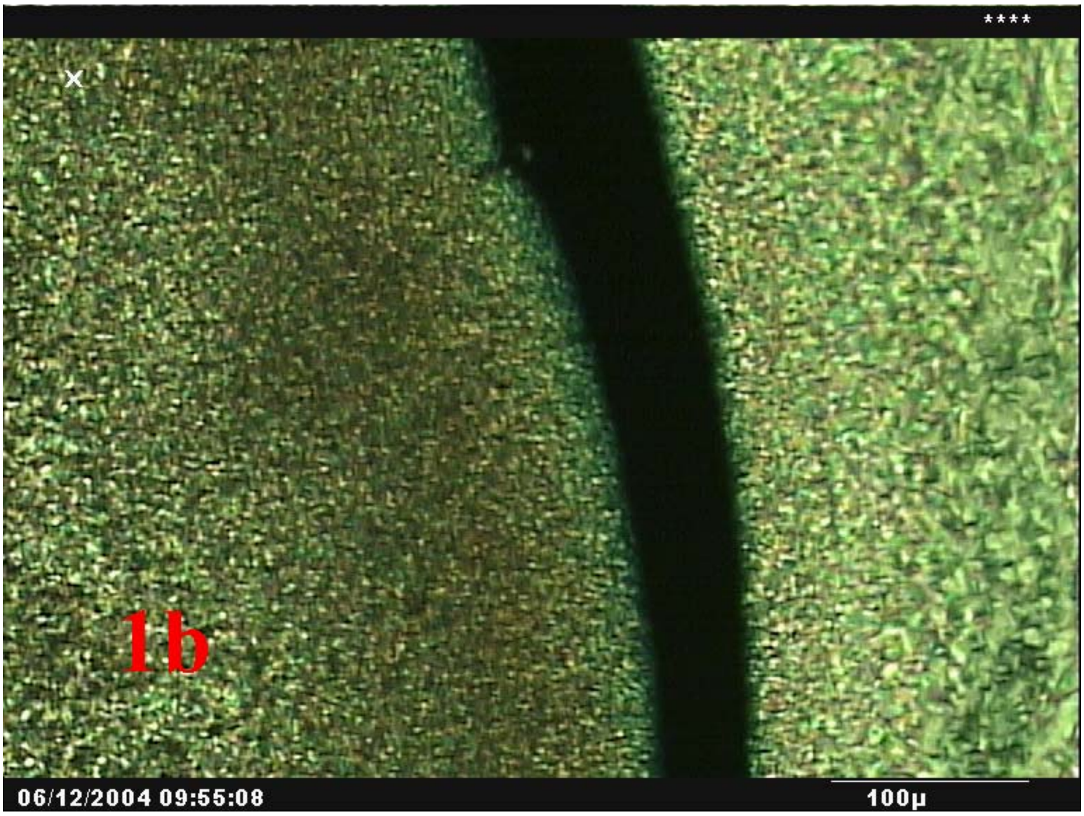


Figure 6. Contact microscopy pictures of **1.)** $\mathbf{D_2/R_1}$; **2.)** $\mathbf{D_2/R_2}$; **3.)** $\mathbf{D_3/R_2}$ and **4.)** $\mathbf{D_4/R_2}$. The pure disc is on the left side and pure rod on the right side of the photomicrographs.

The contact samples have been prepared by positioning the pure disc and pure rod on each side of the microscope slides and heating to the isotropic state so that both compounds flows until there is a contact between them in the middle. The appearance of the nematic phase has been observed on each side on cooling and the nematic regions increase and meet at a minimum temperature, forming a continuous nematic phase.

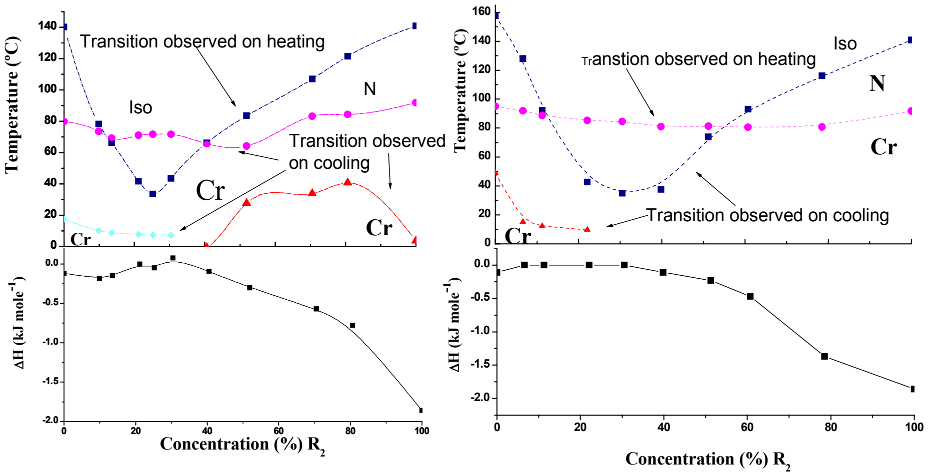


1. a) T=25.5 °C. Left side: Pure D_2, right side: Pure R_1. In the middle is an isotropic region.



b) T=22.8 °C. Pure D_2, right side: Pure R_1. In the middle is an isotropic region With decreasing temperature the nematic regions become larger.

c) T=18 °C. Pure D_2, right side: Pure R_1. The nematic regions have grown and have met without a phase boundary. There is the appearance of a continuous nematic phase from the pure disc to the pure rod, indicative of complet miscibility.



a.

b.

Figure 7. Phase diagrams of **a.) D_3/R_2** and **b.) D_4/R_2**. The upper plots refer to the mixtures of discs and rods as determined by DSC measurements. The compositions are plotted as molar concentrations of the rods. Data shown in magenta refers to enantiotropic N-I transitons obtainaed on heatung, data shown in blue refers to N-I transitons reorded on cooling. Data shown in red or light blue indicates crystallisation emperatures reorded on cooling. Glass transitions are omitted. The sketched lines are guides for the eyes only. The lower plots refer to the enthalpy changes associated with the N-I transitions reorded on cooling.

References

1 P. H. J. Kouwer, W. F. Jager, W. J. Mijs, S. J. Picken, *Macromolecules* 2002, **35**, 4322.

2 (a) P. H. J. Kouwer, G. H. Mehl, *J. Am. Chem. Soc.* 2003; **125**, 11172. b) D. Apreutesei, G. H. Mehl, *Brit Liq. Cryst Soc. Conf.*, O14, Exeter, 22. 03. 2005; c) V. Vill, LiqCryst Database Version 3.0. d) L. Cseh, G. H. Mehl, to be published.

3 S. Diez, D.A. Dunmur, M. R. De la Fuente, P. K. Karahaliou , G. H. Mehl, T. Meyer , M. A. P. Jubindo, D. J. Photinos , *Liq. Cryst.* (2003), **30**, 1021.