Electronic Supporting Information

The Design and Investigation of the Self-Assembly of Dimers with two Nematic Phases

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Experimental

Starting reagents and solvents were purchased from Fischer, Sigma Aldrich, Acros Organics and Fluorochem and used without further purification. Boronic acids were purchased from Kingston chemicals and were also used without further purification.

The structures after purification were confirmed by ^{1}H and ^{13}C and ^{19}F nuclear magnetic resonance spectroscopy. The experiments were performed with a Joel JNM-ECP 400 MHz FT-NMR. The chemical shifts reported in this section are relative to tetramethylsilane used as an internal standard and coupling constants *J* are reported in Hertz (Hz). ^{1}H experiments were performed at 400 MHz, ^{13}C at 100 MHz and ^{19}F 376 MHz.

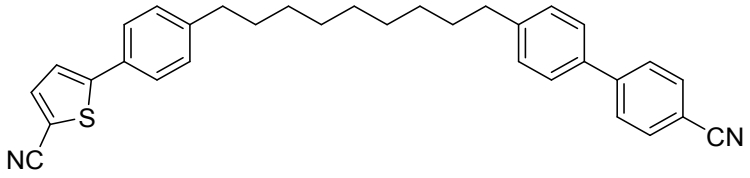
Low resolution electron ionisation (EI), electro-spray (ES), chemical ionisation (CI), matrix assisted laser deposition ionisation (MALDI) and high resolution mass spectrometry (HRMS) were obtained via the EPSRC National Mass Spectrometry Service Centre at Swansea University, Wales.

The purity of the final compounds was confirmed by high performance liquid chromatography. The HPLC setup consisted of Gilson 321 pump, Agilent/HP1100 detector with a Phenomex LUNA 18(2) reverse phase C18 column. The column dimensions are 250 mm x 4.6 mm, 5 µm particles and 100 Å pore size.

The thermal properties of the final compounds were investigated on Mettler-Toledo differential scanning calorimetry DSC822e. These experiments were performed under nitrogen and the enthalpies measured against an internal gold standard. The mesophase was optically observed on an Olympus BX-51 optical polarising microscope equipped with a Mettler FP82 hot stage and Mettler 5 central processing unit. The microscope was also equipped with Lumenera's Infinity X camera and images were captured using Studio86Design's studio capture. All experiments were carried out at 100X magnification unless stated otherwise. All transitions are reported in degrees Celsius.

The structure of the mesophase was also investigated by x-ray diffraction. CuKα radiation of wavelength 1.54 Å was generated using a copper tube at 35 KV and 30 mA. The beam is filtered through a 300 µm thick beryllium window and is further 2D shaped using Xenocs FOX2D12_INF optics. The samples are heated in the presence of a 0.5 T magnet in a home built graphite furnace consisting of Eurotherm heater. The x-rays were detected on Mar345 2D-image plate. The data was analysed using Paul Heiney's Datasqueeze software and was fitted using OriginLab's Origin pro 8 software. All experiments were conducted with the magnetic field perpendicular to the beam and capillary.

Synthesis of 5-(4-(9-(4'-cyano-[1,1'-biphenyl]-4-yl)nonyl)phenyl)thiophene-2-carbonitrile (1)



4'-(9-(4-Bromophenyl)nonyl)-[1,1'-biphenyl]-4-carbonitrile (0.20 g, 0.43 mmol), (5-cyanothiophen-2-yl)boronic acid (0.20 g, 1.3 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.025 g, 21.6 µmol) were dissolved in tetrahydrofuran (20 mL) under inert atmosphere. The reaction was stirred at room temperature, with nitrogen being bubbled through the solvent. After 1 hour an aqueous solution of sodium carbonate (0.070 g, 0.66 mmol) was added drop wise and the reaction was heated under reflux overnight. The solvent was removed under reduced pressure and the organics separated by silica column chromatography using a mixture of dichloromethane and hexane 1:1 to afford the title compound as a white solid (0.09 g, 42%).

Cr – (N_x 89) 90.4 – N – 101.1 - Iso

^{1}H NMR: δ_H (400 MHz, CD_2Cl_2) 7.62 (4H, m), 7.52 (1H, m), 7.44 (4H, dd, *J* 6.32, 1.94), 7.18 (5H, m), 2.55 (4H, m), 1.54 (4H, m), 1.33-1.12 (10H, m).

^{13}C NMR: δ_C (100 MHz, $CDCl_3$) 152.1, 145.6, 144.7, 143.8, 138.4, 136.5, 132.6, 129.8, 129.3, 129.2, 127.5, 127.1, 126.3, 122.7, 119.0, 114.5, 110.6, 107.7, 35.7, 35.6, 31.4, 31.3, 29.5, 29.3, 29.2.

MS: 488

m/z (CI) 489 ($M+H^+$)

HRMS Calc: $C_{33}H_{32}N_2S$+H requires = 489.2364

HRMS Found: 489.2349

Assay (HPLC, C18, MeCN:DCM 80:20) = 98.3 %

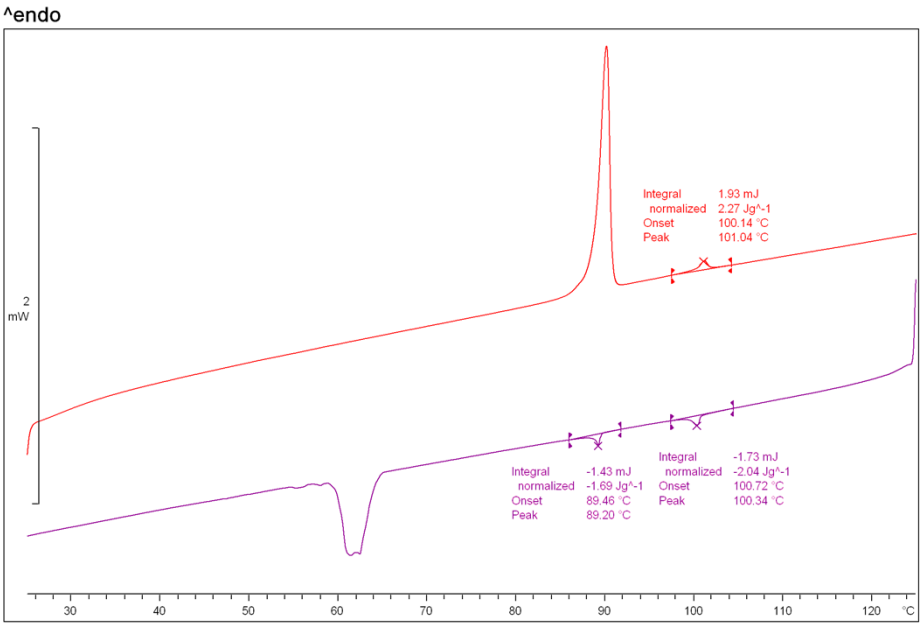


Figure 1: Calorimetric data of compound **1**.

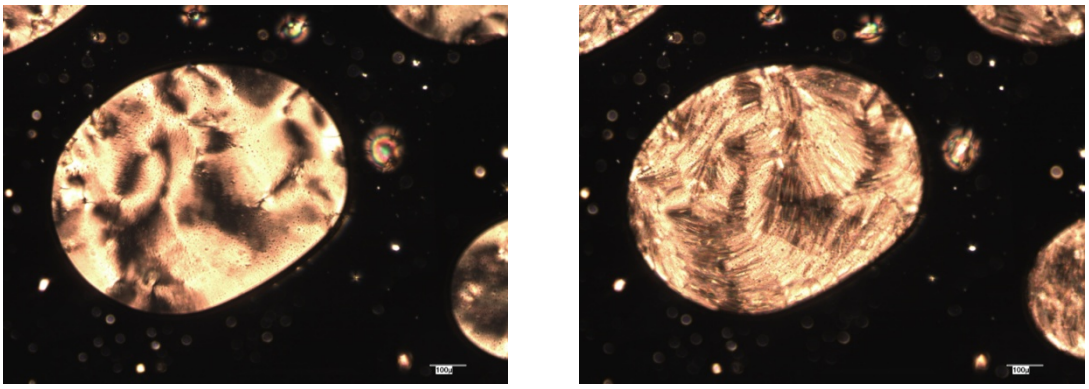


Figure 2: Micrographs of compound **1** at 91 °C (left) and 88 °C (right) under crossed polarizers and on untreated slides.

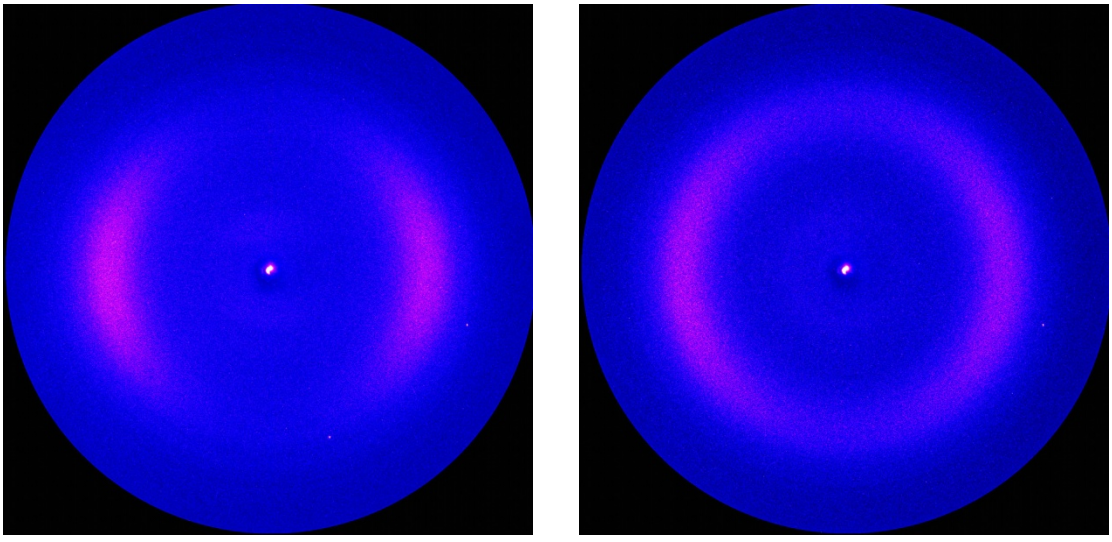
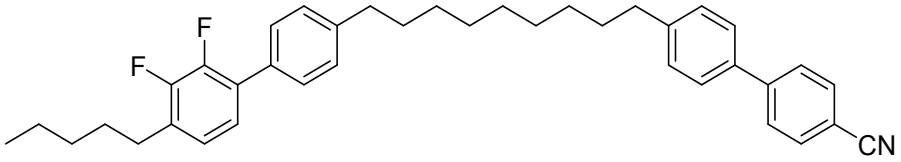


Figure 3 : XRD scattering data for compound **1** at 95 °C (left) and 85 °C (right).

Synthesis of 4'-(9-(2',3'-difluoro-4'-pentyl-[1,1'-biphenyl]-4-yl)nonyl)-[1,1'-biphenyl]-4-carbonitrile (2)



4'-(9-(4-Bromophenyl)nonyl)-[1,1'-biphenyl]-4-carbonitrile (0.23 g, 0.50 mmol), (2,3-difluoro-4-pentylphenyl) boronic acid (0.34 g, 1.5 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.028 g, 24.2 µmol) were dissolved in tetrahydrofuran (20 mL) under inert atmosphere. The reaction was stirred at room temperature, with nitrogen being bubbled through the solvent. After 1 hour an aqueous solution of sodium carbonate (0.080 g, 0.7 mmol) was added and the reaction was heated under reflux overnight. The solvent was removed under reduced pressure and the organics separated by silica column chromatography using a mixture of dichloromethane and hexane 1:2 to afford the title compound as a white solid (0.2 g, 71%).

Cr – (N_x 38.3) 40.6 – N – 43.8 – Iso

^{1}H NMR: δ_H (400 MHz, CD_2Cl_2) 7.68 (4H, m), 7.50 (2H, d, *J* 8.16), 7.44 (2H, dd, *J* 6.53, 1.53), 7.26 (4H, m), 7.08 (1H, dt, *J* 7.50, 1.63), 6.96 (1H, dt, *J* 7.50, 1.63), 2.65 (6H, m), 1.63 (6H, m), 1.42-1.26 (14H, m), 0.88 (3H, t, *J* 6.84).

^{13}C NMR: δ_C (100 MHz, $CDCl_3$) 145.6, 143.8, 142.7, 136.5, 132.6, 129.2, 128.70, 128.68, 128.6, 127.5, 127.0, 124.6, 124.1, 119.1, 110.5, 35.7, 35.6, 31.46, 31.38, 29.7, 29.5, 29.32, 29.28, 28.7, 22.5, 14.0.

^{19}F NMR: δ_F (376 MHz, $CDCl_3$) -143.7 (1F, dd, *J* 20.81, 6.94), -144.3 (1F, dd, *J* 20.81, 6.94).

MS: 563

m/z (CI) 564 ($M+H^+$)

HRMS Calc: $C_{39}H_{43}F_2N$+H requires = 564.3441

HRMS Found: 564.3425

Assay (HPLC, C18, MeCN:DCM 80:20) = 97.8 %

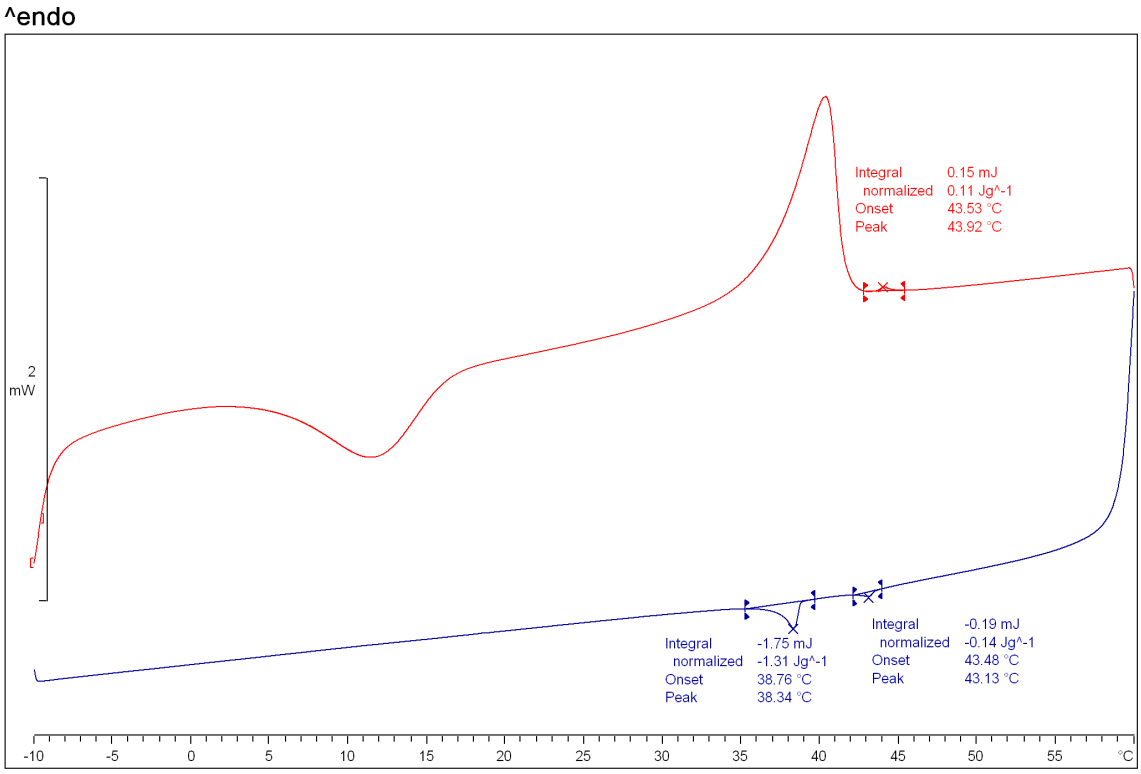


Figure 4: Calorimetric data for compound **2**.

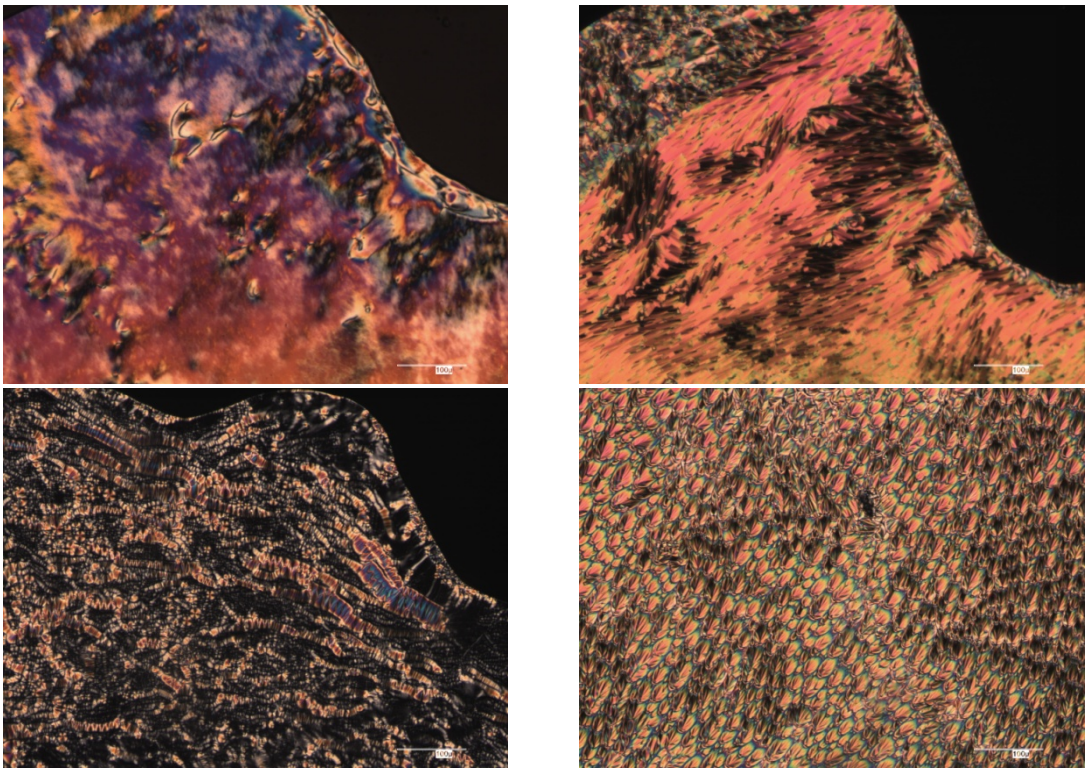


Figure 5: Micrographs of compound **2** at 41°C (top left), 36 °C (top right), upon sheering and at 33 °C after sheering. All micrographs were recorded on cooling under crossed polarizers and on untreated slides.

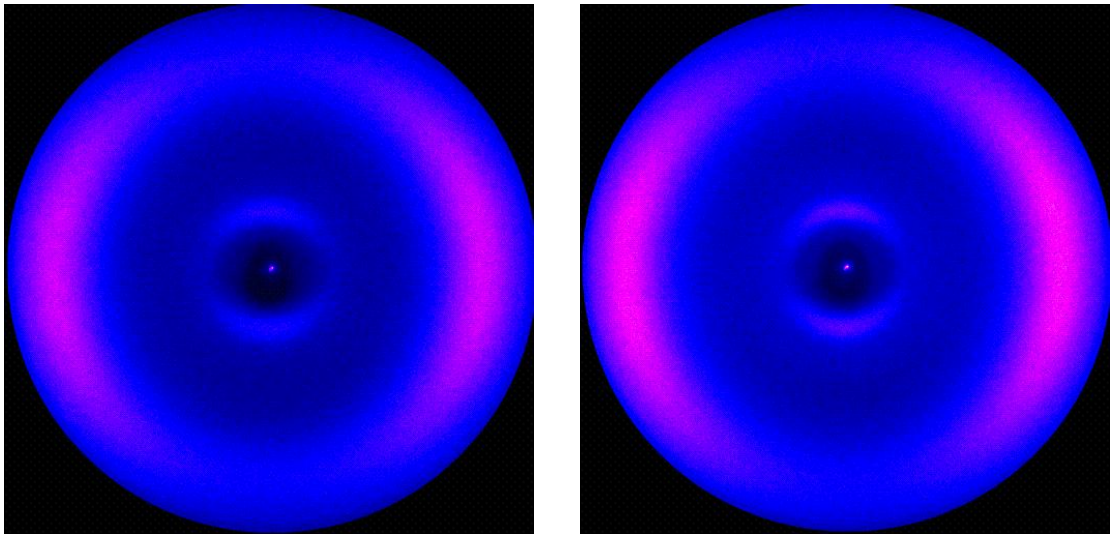


Figure 6: XRD scattering data for compound **2** at 41 °C (left) and 36 °C (right).

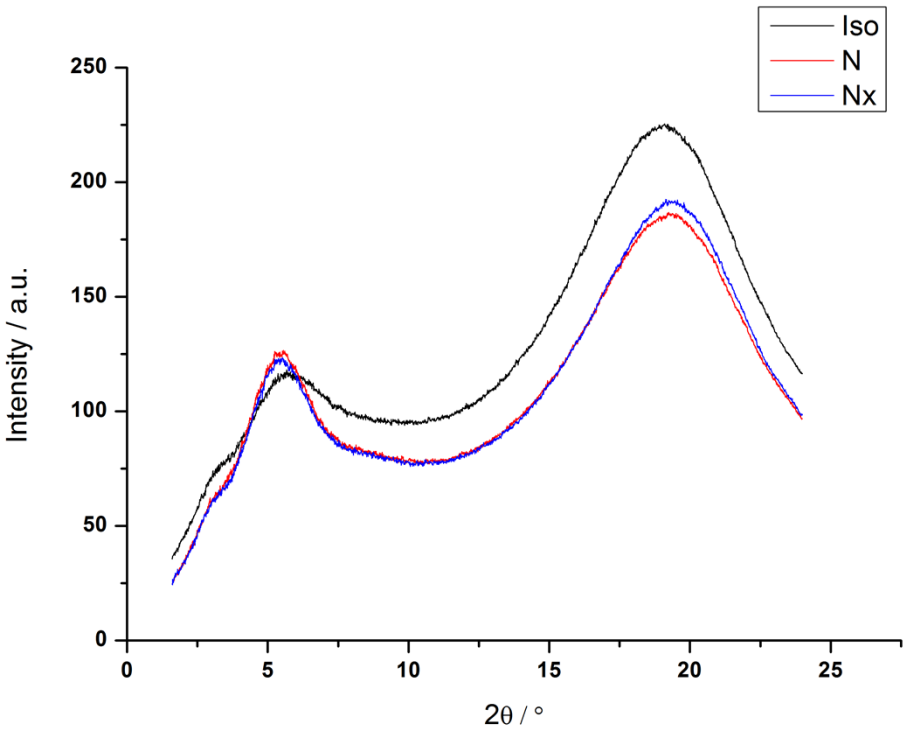
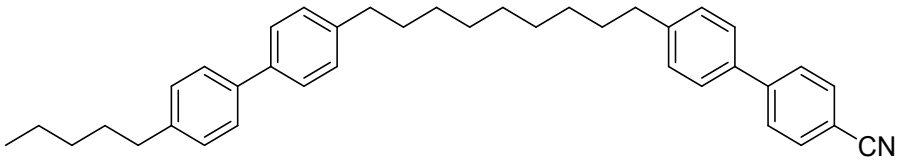


Figure 7: 2θ against intensity plot of compound **2**.

The change in wide angle is observed in the 2θ plot shown in Figure 7. A smectic phase is ruled out due to the very low small angle intensity. The small angle peak at 5.6 equals 15.8 Å, this value is roughly half the molecular length. This data points to considerable overlap with in the molecular arrangement of the mesophases.

Synthesis of 4'-(4'-pentyl-[1,1'-biphenyl]-4-ylnonyl)-[1,1'-biphenyl]-4-carbonitrile (3)



4'-(9-(4-Bromophenyl)nonyl)-[1,1'-biphenyl]-4-carbonitrile (0.23 g, 0.50 mmol), (4-pentylphenyl)boronic acid (0.28 g, 1.5 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.028 g, 24.2 µmol) were dissolved in tetrahydrofuran (20 mL) under inert atmosphere. The reaction was stirred at room temperature, with nitrogen being bubbled through the solvent. After 1 hour an aqueous solution of sodium carbonate (0.080 g, 0.7 mmol) was added drop wise and the reaction was heated under reflux overnight. The solvent was removed under reduced pressure and the organics separated by silica column chromatography using a mixture of dichloromethane and hexane 1:2 to afford the title compound as a white solid (0.15 g, 61%).

Cr – 81.9 – N – 85.8 – Iso

^{1}H NMR: δ_H (400 MHz, CD_2Cl_2) 7.66 (4H, m), 7.49 (6H, d, *J* 7.96), 7.27(2H, d, *J* 8.16), 7.22 (4H, dd, *J* 8.06, 2.34), 2.63 (6H, m), 1.64 (6H, m), 1.39-1.23 (16H, m), 0.91 (3H, t, *J* 6.94).

^{13}C NMR: δ_C (100 MHz, $CDCl_3$) 145.6, 143.8, 141.8, 141.7, 138.5, 138.4, 136.4, 132.5, 129.2, 128.75, 128.73, 127.5, 127.0, 126.79, 126.77, 119.0, 110.5, 35.61, 35.57, 31.56, 31.46, 31.4, 31.2, 29.5, 29.32, 29.26, 22.6, 14.0.

MS: 527

m/z (CI) 528 ($M+H^+$) 545 ($M+NH_4^+$)

HRMS Calc: $C_{39}H_{45}N+H$ requires = 528.3630

HRMS Found: 528.3620

Assay (HPLC, C18, MeCN:DCM 80:20) = 99.0 %

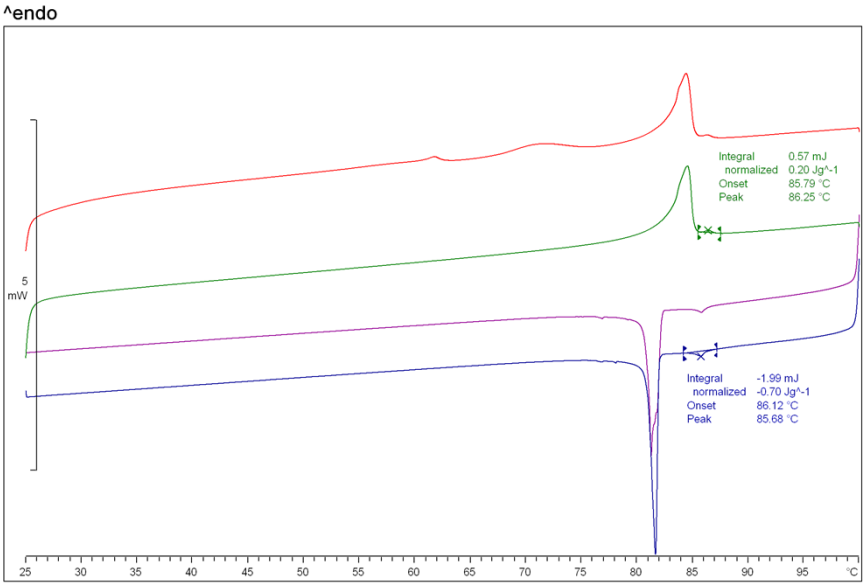


Figure 8: Calorimetric data for compound **3**.

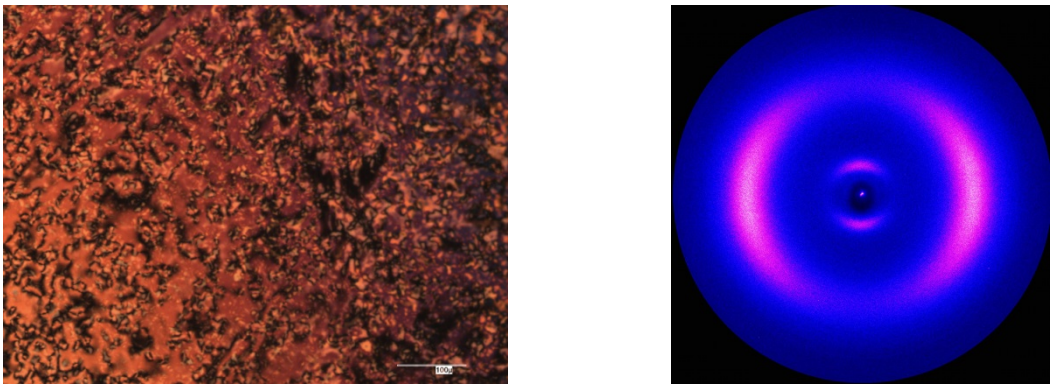
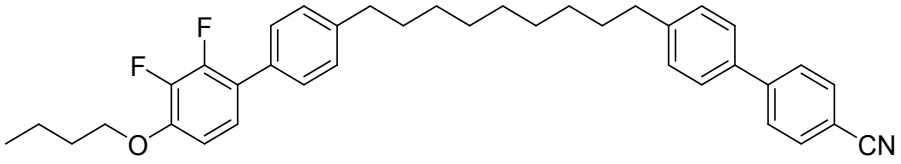


Figure 9: Nematic phase of compound **3** shown by OPM and XRD at 82 °C.

Synthesis of 4'-(9-(4'-butoxy-2',3'-difluoro-[1,1'-biphenyl]-4-yl)nonyl)-[1,1'-biphenyl]-4-carbonitrile (4)



4'-(9-(4-Bromophenyl)nonyl)-[1,1'-biphenyl]-4-carbonitrile (0.23 g, 0.50 mmol), (4-butoxy-2,3-difluorophenyl)boronic acid (0.34 g, 1.5 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.028 g, 24.2 µmol) were dissolved in tetrahydrofuran (20 mL) under inert atmosphere. The reaction was stirred at room temperature, with nitrogen being bubbled through the solvent. After 1 hour an aqueous solution of sodium carbonate (0.080 g, 0.7 mmol) was added drop wise and the reaction was heated under reflux overnight. The solvent was removed under reduced pressure and the organics separated by silica column chromatography using a mixture of dichloromethane and hexane 1:2 to afford the title compound as a white solid (0.16 g, 68%).

Cr – (N_x 54.9) 56.3 – N – 62.7 – Iso

^{1}H NMR: δ_H (400 MHz, $CDCl_3$) 7.69 (4H, m), 7.50 (2H, d, *J* 8.16), 7.41 (2H, dd, *J* 8.16, 1.43), 7.29 (2H, d, *J* 8.16), 7.24 (2H, d, *J* 8.16), 7.07 (1H, dt, *J* 8.47, 1.31), 6.78 (1H, dt, *J* 8.16, 1.84), 4.08 (2H, t, *J* 6.53), 2.64 (4H, m), 1.81 (2H, m), 1.63 (4H, m), 1.55 1.40-1.26 (10H, m), 0.88 (3H, t, *J* 7.34).

^{13}C NMR: δ_C (100 MHz, $CDCl_3$) 148.9, 145.6, 143.8, 142.4, 141.9, 136.4, 132.5, 132.2, 129.2, 128.6, 128.5, 127.4, 127.0, 123.5, 123.42, 123.39, 123.0, 122.9, 119.0, 110.5, 109.50, 109.48, 69.5, 35.62, 35.60, 31.37, 31.35, 31.2, 29.4, 29.28, 29.25, 19.1, 13.8.

^{19}F NMR: δ_F (376 MHz, $CDCl_3$) -141.8 (1F, dd, *J* 18.50, 6.94), -158.8 (1F, dd, *J* 20.81, 6.94).

MS: 565

m/z (CI) 566 ($M+H^+$) 583 ($M+NH_4^+$)

HRMS Calc: $C_{38}H_{41}F_2NO+H$ requires = 566.3234

HRMS Found: 566.3226

Assay (HPLC, C18, MeCN:DCM 80:20) = 99.5 %

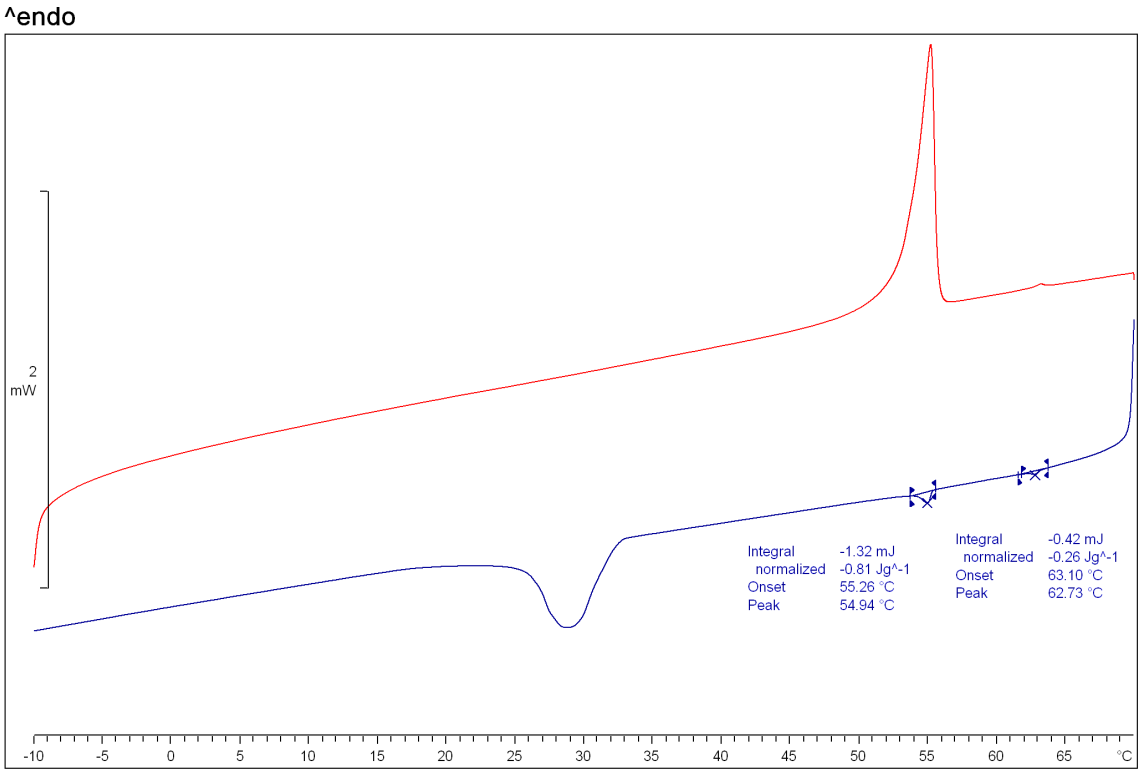


Figure 10: Calorimetric data of compound **4**.

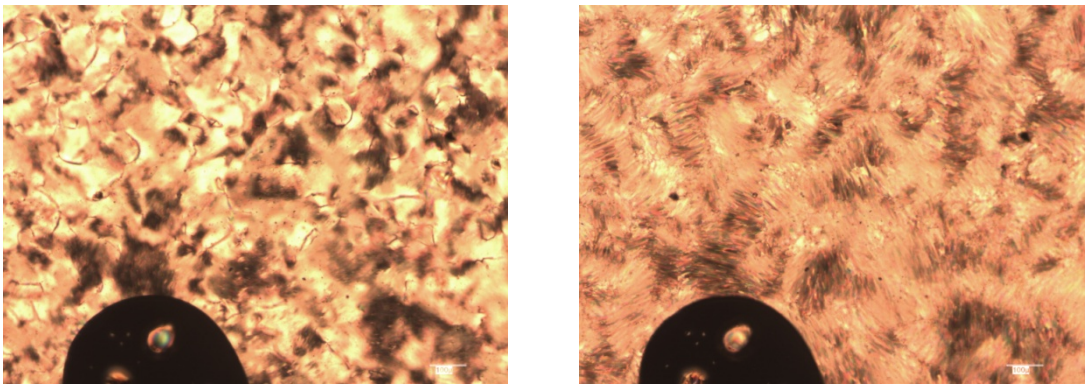


Figure 11: Micrographs of compound **4** at 56 °C (left) and 53 °C (right) under crossed polarizers and on untreated slides.

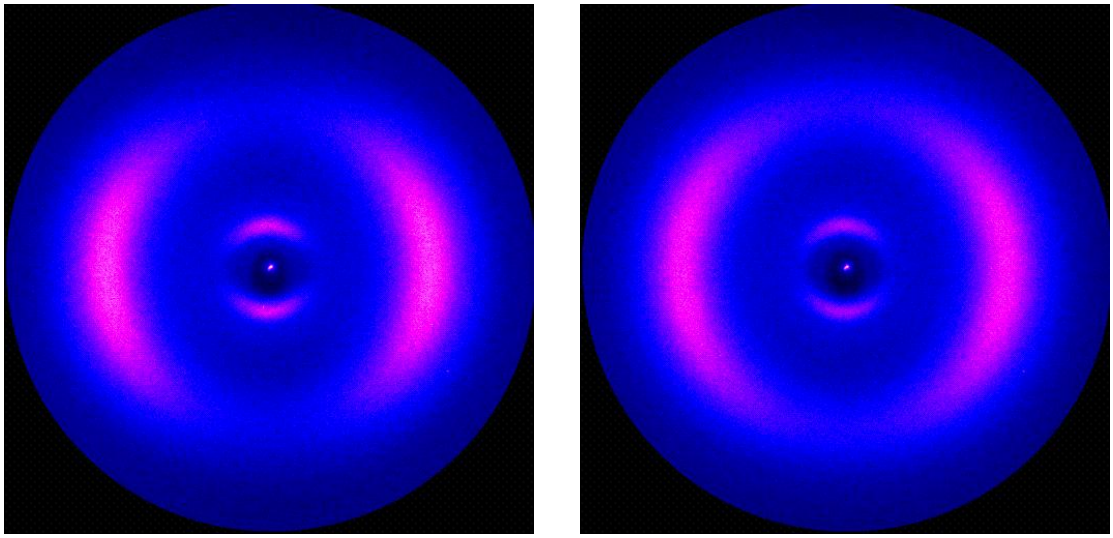


Figure 12: XRD scattering data of compound **4** at 58 °C (left) and 52 °C (right) on cooling from isotropic.

Both XRD scattering patterns are typical for nematic phases. The lack of an intense small angle peak points to the phase not being smectic as layer correlations are very strong. The narrowing of the wide angle in the N_X phase is more obvious in this compound showing the increase in macroscopic order.

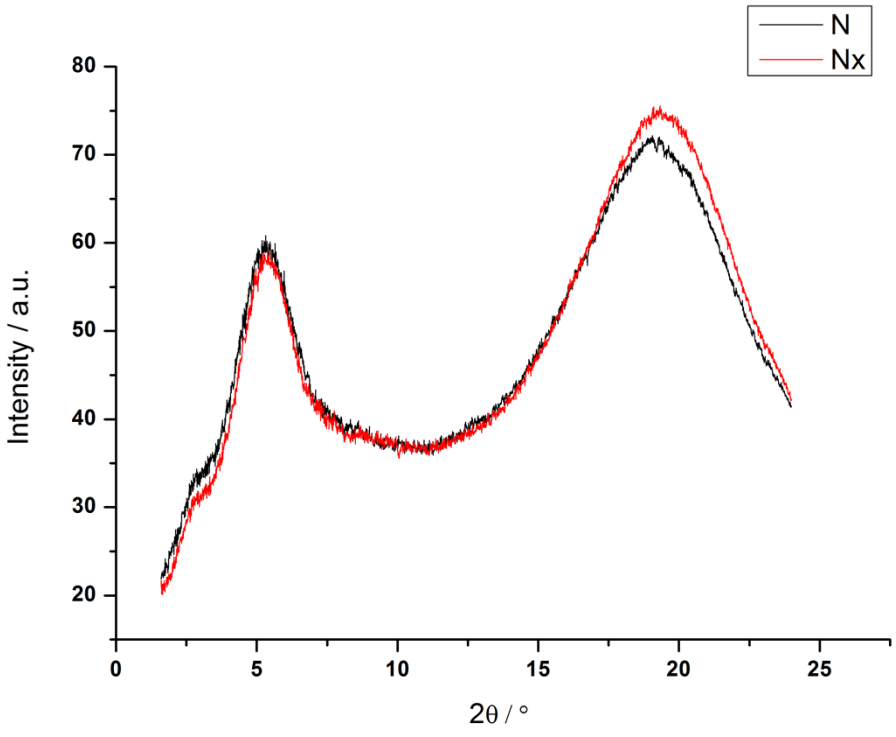
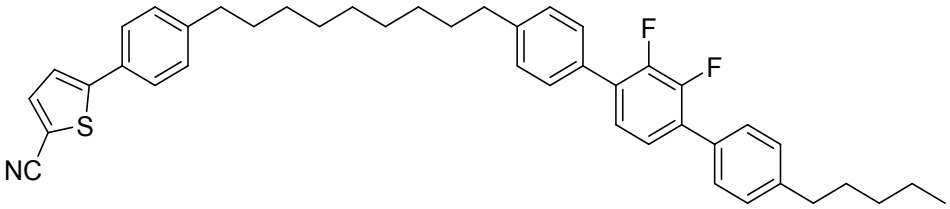


Figure 13: 2θ against intensity plot of compound **4** in the nematic and N_X phase.

Shown in Figure 13 are the 2θ plots of the two nematic phases of compound **4**. The difference in the height of the peak is noticeable. As the spread of the wide angle is narrower more molecules are closer to the value represented by the peak, giving an overall increase in the signal. The small angle peak at 5.3 equals 16.6 Å.

Synthesis of 5-(4-(9-(2',3'-difluoro-4''-pentyl-[1,1':4',1''-terphenyl]-4-yl)nonyl)phenyl)thiophene-2-carbonitrile (5)



4-(9-(4-Bromophenyl)nonyl)-2',3'-difluoro-4''-pentyl-1,1':4',1''-terphenyl (0.20 g, 0.32 mmol), (5-cyanothiophen-2-yl)boronic acid (0.15 g, 0.98 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.020 g, 17.3 µmol) were dissolved in tetrahydrofuran (20) mL under inert atmosphere. The reaction was stirred at room temperature, with nitrogen being bubbled through the solvent. After 1 hour an aqueous solution of sodium carbonate (0.052 g, 0.49 mmol) was added drop wise and the reaction was heated under reflux overnight. The solvent was removed under reduced pressure and the organics separated by silica column chromatography using a mixture of dichloromethane and hexane 1:5 to afford the title compound as a white solid (0.09 g, 44%).

Cr – (N_x 83.9) 89.7 – N -114.7– Iso

^{1}H NMR: δ_H (400 MHz, CD_2Cl_2) 7.50 (1H, d, *J* 3.88), 7.46-7.40 (6H, m), 7.21 (4H, dd, *J* 8.16, 2.96), 7.18-7.15 (5H, m), 2.60-2.53 (6H, m), 1.55 (6H, m), 1.34-1.18 (14H, m), 0.83 (3H, t, *J* 6.94).

^{13}C NMR: δ_C (100 MHz, $CDCl_3$) 149.0, 144.8, 143.1, 143.0, 138.4, 132.0, 129.7, 129.3, 128.69, 128.68, 126.3, 124.6, 122.7, 114.5, 35.7, 31.6, 31.4, 31.3, 31.1, 29.4, 29.3, 29.2, 22.6, 14.0.

^{19}F NMR: δ_F (376 MHz, $CDCl_3$) -143.2 (2F, s).

MS: 645

m/z (CI) 646 ($M+H^+$)

HRMS Calc: $C_{43}H_{45}F_2NS$ +H requires = 646.3319

HRMS Found: 646.3305

Assay (HPLC, C18, MeCN:DCM 80:20) = 98.6 %

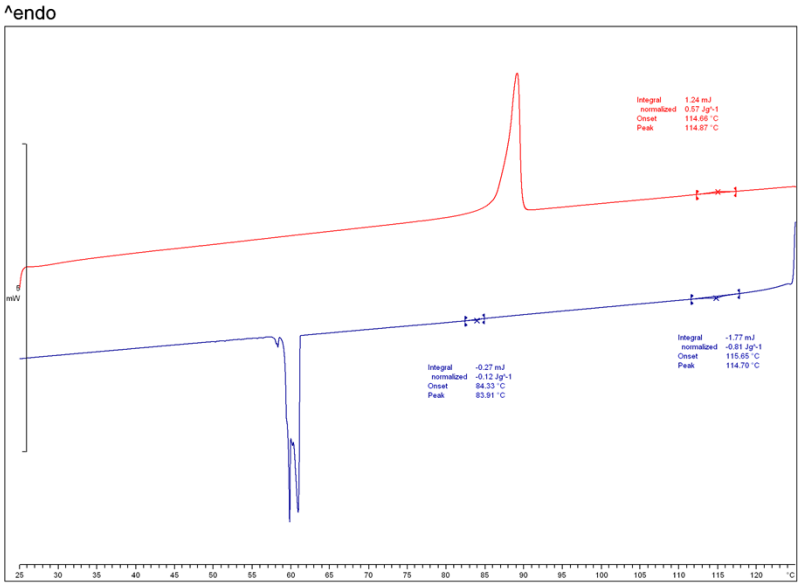


Figure 14: Calorimetric data for compound **5**.

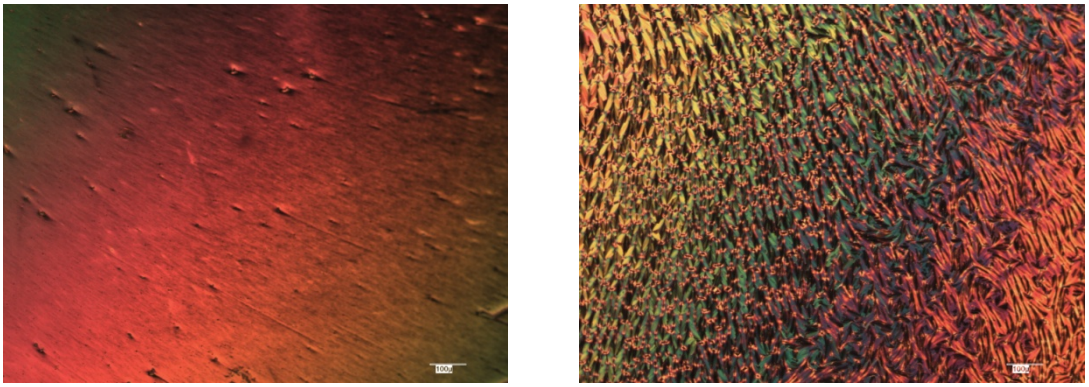


Figure 15: Micrographs of compound **5** at 90 °C (left) and 78 °C (right) under crossed polarizers and on untreated slides.

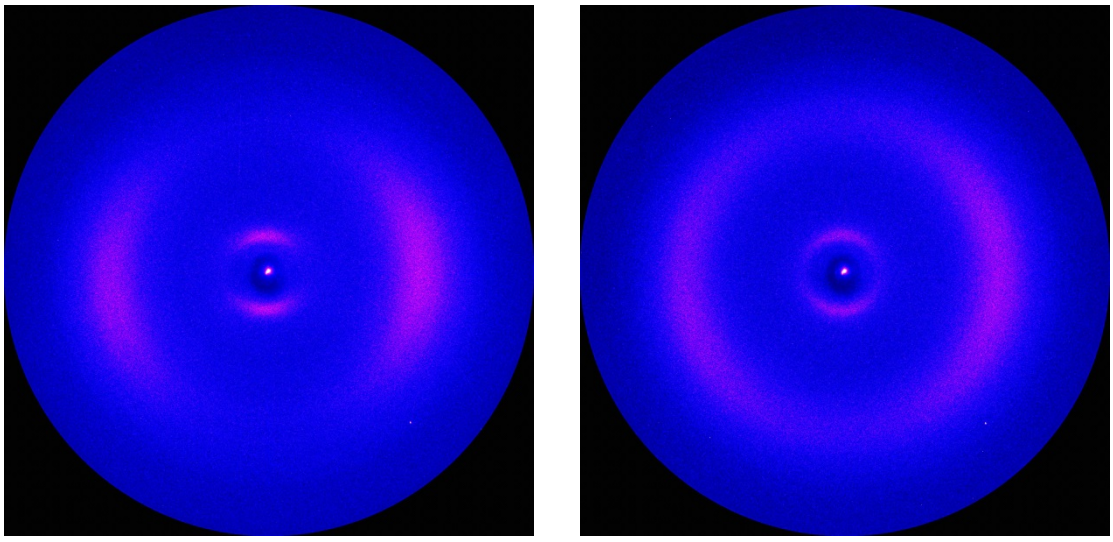


Figure 16: XRD scattering data of compound **5** at 100 °C and 80 °C

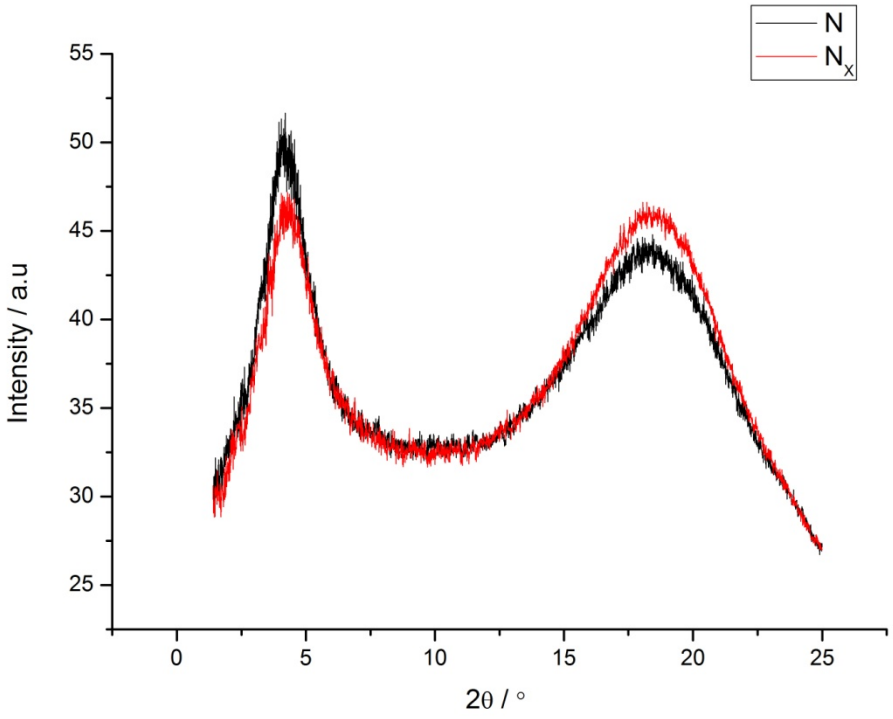
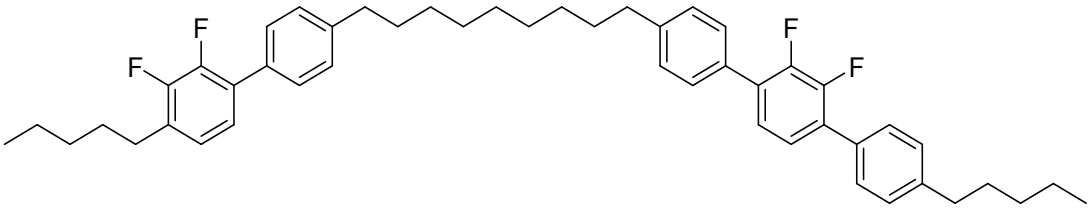


Figure 17: Plot of 2θ against intensity of compound **5** in both nematic phases.

The N_X phase can be seen clearly from the narrowing of the wide angle scattering shown in Figure 16 and Figure 17.

Synthesis of 4-(9-(2',3'-difluoro-4'-pentyl-[1,1'-biphenyl]-4-yl)nonyl)-2',3'-difluoro-4''-pentyl-1,1':4',1''-terphenyl (6)



4-(9-(4-Bromophenyl)nonyl)-2',3'-difluoro-4''-pentyl-1,1':4',1''-terphenyl (0.22 g, 0.35 mmol), (2,3-difluoro-4-pentylphenyl)boronic acid (0.24 g, 1.05 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.020 g, 17.3 µmol) were dissolved in tetrahydrofuran (20 mL) under inert atmosphere. The reaction was stirred at room temperature, with nitrogen being bubbled through the solvent. After 1 hour an aqueous solution of sodium carbonate (0.052 g, 0.49 mmol) was added drop wise and the reaction was heated under reflux overnight. The solvent was removed under reduced pressure and the organics separated by silica column chromatography using a mixture of dichloromethane and hexane 1:5 to afford the title compound as a white solid (0.13 g, 52%).

Cr – 47.4 – X– 62.2 – SmA – 71.6 – N – 81.3 – Iso

^{1}H NMR:

δ_H (400 MHz, CD_2Cl_2) 7.50 (4H, d, *J* 7.96), 7.343(2H, dd, *J* 8.26, 1.73), 7.30 (4H, d, *J* 8.16), 7.27 (4H, m), 7.11 (1H, dt, *J* 8.16, 1.70), 7.00 (1H, dt, *J* 7.45, 1.63), 2.66 (8H, m), 1.64 (8H, m), 1.38-1.31 (18H, m), 0.91 (6H, m).

^{13}C NMR:

δ_C (100 MHz, $CDCl_3$) 149.5, 148.5, 148.00, 143.4, 143.06, 142.7.0, 132.3, 132.0, 130.6, 130.5, 129.5, 128.70, 128.68, 128.4, 128.3, 124.7, 124.6, 124.2, 35.7, 31.6, 31.5, 31.4, 31.1, 29.7, 29.5, 29.3, 28.7, 22.6, 22.5, 14.04, 14.00.

^{19}F NMR: δ_F (376 MHz, $CDCl_3$) -143.2 (2F, s), -143.8 (1F, dd, *J* 20.81, 6.94), -144.2 (1F, dd, *J* 20.81, 6.94).

MS: 720 *m/z* (CI) 721 ($M+H^+$)

HRMS Calc: $C_{49}H_{56}F_4$ +H requires = 721.4396 HRMS Found: 721.4385

Assay (HPLC, C18, MeCN:DCM 80:20) = 98.6 %

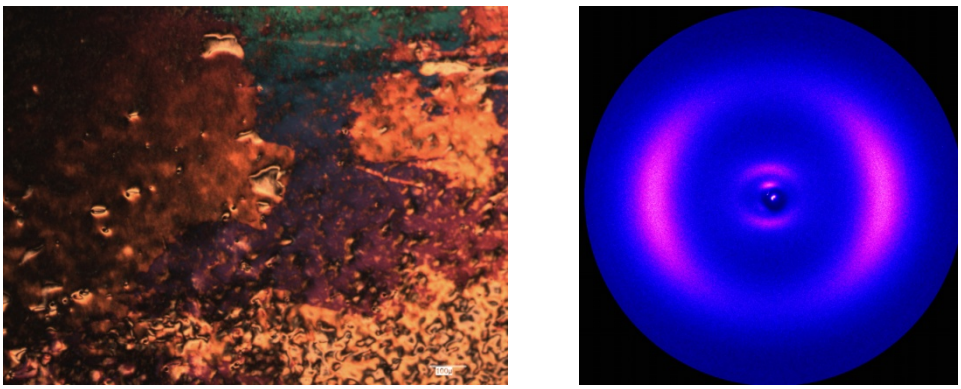


Figure 18: Micrograph and XRD scattering data of compound **6** at 70 °C.

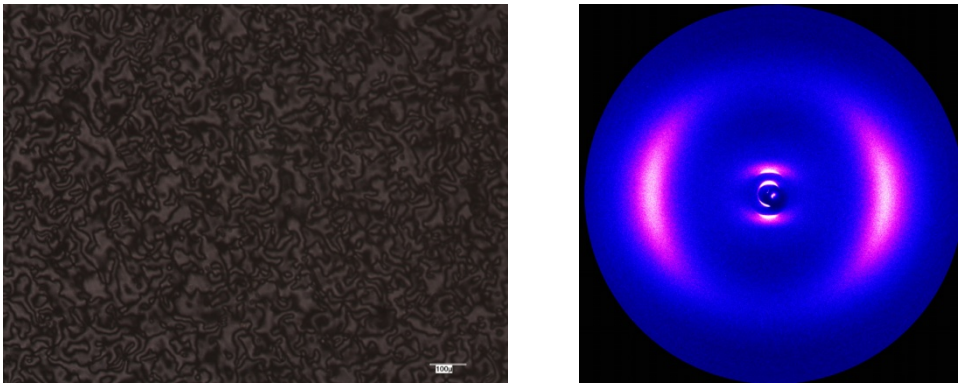


Figure 19: Micrograph and XRD scattering data of compound **6** at 50 °C

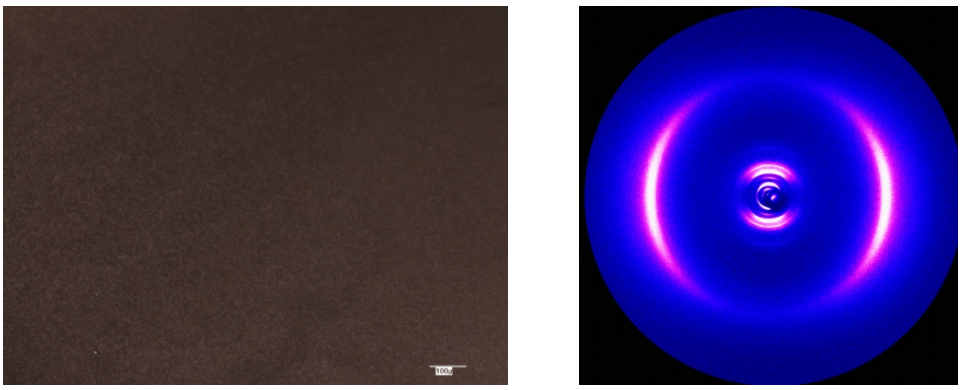


Figure 20: Micrograph and XRD scattering data of compound **6** at 30 °C

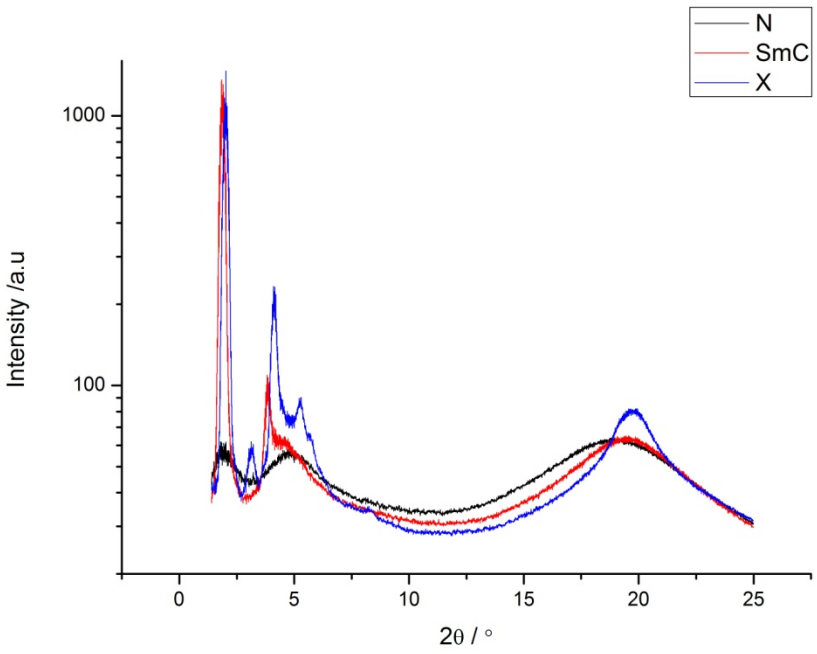
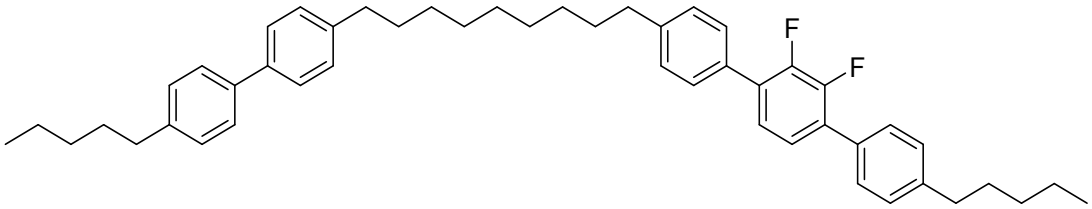


Figure 21: 2Theta against intensity plot of compound **6**.

Synthesis of 2',3'-difluoro-4-pentyl-4''-(9-(4'-pentyl-[1,1'-biphenyl]-4-yl)nonyl)-1,1':4',1''-terphenyl (7)



4-(9-(4-Bromophenyl)nonyl)-2',3'-difluoro-4''-pentyl-1,1':4',1''-terphenyl (0.16 g, 0.26 mmol), (pentylphenyl)boronic acid (0.15 g, 0.78 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.020 g, 17.3 µmol) were dissolved in tetrahydrofuran (20 mL) under inert atmosphere. The reaction was stirred at room temperature, with nitrogen being bubbled through the solvent. After 1 hour an aqueous solution of sodium carbonate (0.052 g, 0.49 mmol) was added drop wise and the reaction was heated under reflux overnight. The solvent was removed under reduced pressure and the organics separated by silica column chromatography using a mixture of dichloromethane and hexane 1:4 to afford the title compound as a white solid (0.14 g, 77%).

Cr- 78.2- N_x – 86.4 – N – 105.5 – Iso

^{1}H NMR: δ_H (400 MHz, $CDCl_3$) 7.50 (8H, m), 7.28 (4H, dd, *J* 8.25, 1.94), 7.23, (6H, m), 2.65 (8H, m), 1.66 (8H, m), 1.35 (18H, m), 0.91 (6H, m).

^{13}C NMR: δ_C (100 MHz, $CDCl_3$) 148.5, 143.09, 143.08, 141.8, 141.7, 138.50, 138.48, 132.0, 129.5, 128.75, 128.72, 128.68, 128.4, 128.2, 126.8, 125.5, 124.6, 35.72, 35.71, 35.60, 35.58, 31.6, 31.5, 31.4, 31.2, 31.1, 29.5, 29.4, 22.6, 14.0.

^{19}F NMR: δ_F (376 MHz, $CDCl_3$) -143.2 (2F, s).

MS: 684

m/z (CI) 685 ($M+H^+$) 702 ($M+NH_4^+$)

HRMS Calc: $C_{49}H_{58}F_2$ +H requires = 685.4584

HRMS Found: 685.4570

Assay (HPLC, C18, MeCN:DCM 80:20) = 96.3 %

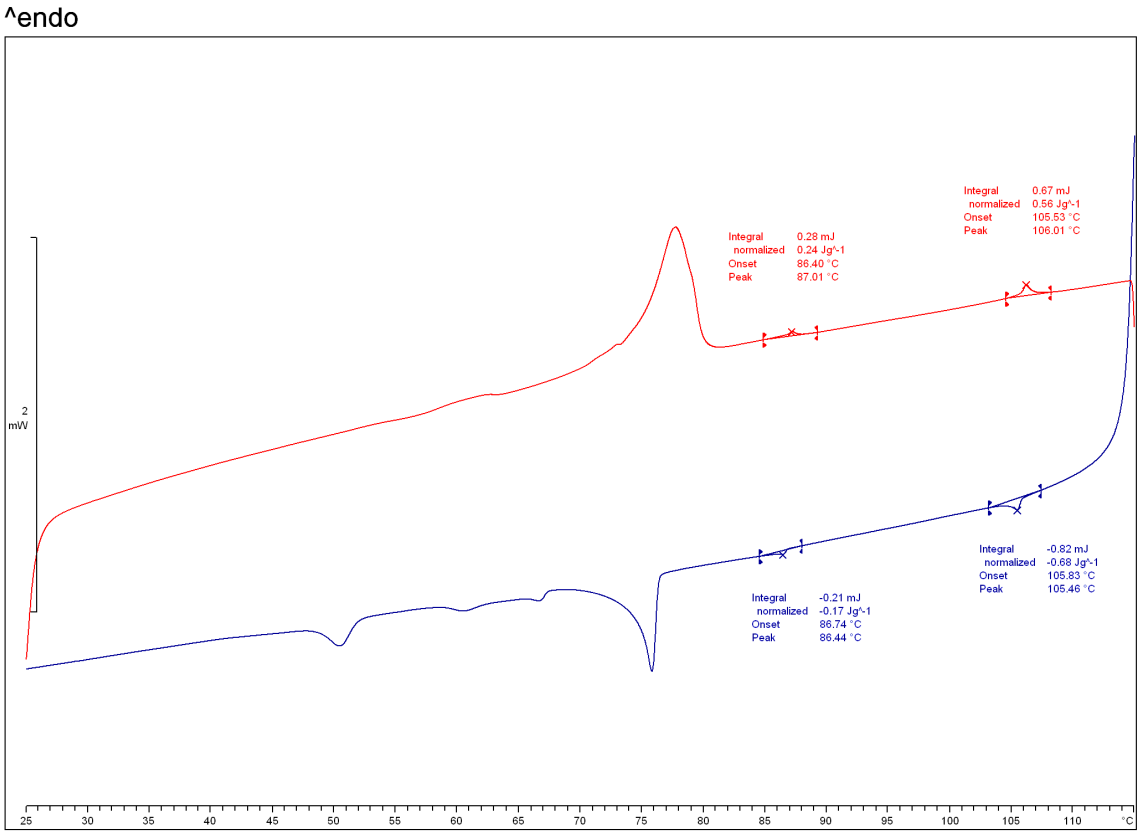


Figure 22: Calorimetric data for compound **7**

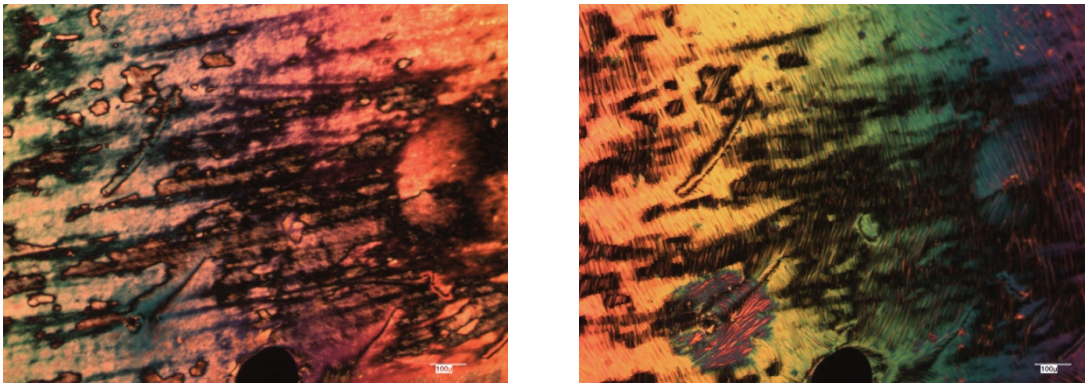


Figure 23: Micrographs of compound **7** at 101 °C (left) and 85 °C (right) under crossed polarizers and on untreated slides.

Figure 23 shows the marble texture of the nematic phase at 101 °C and shows the plated texture of the nematic twist bend phase at 85 °C immediately after the transition. After cooling a further 10 °C the plated textures develops into the polygonal fish scale texture as shown in Figure 24 of the same area. A rope like texture can also be observed which has developed spontaneously without any rubbing.

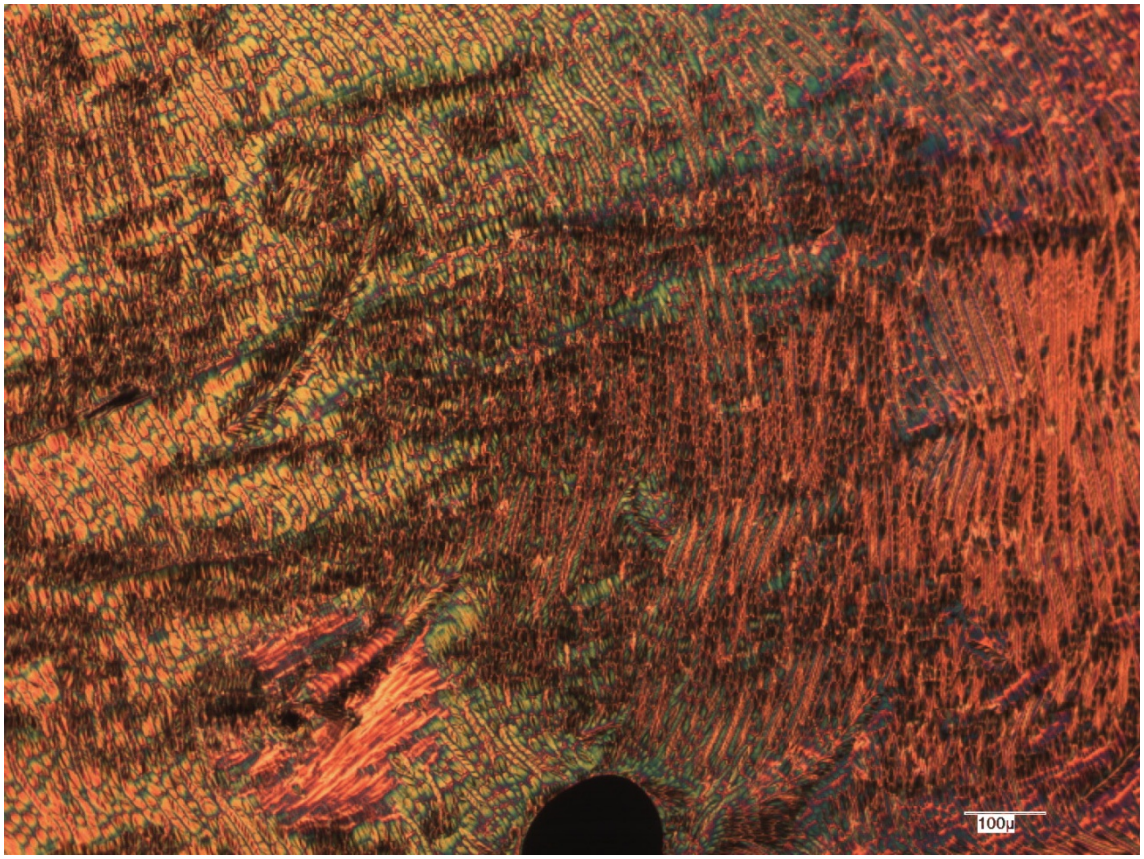


Figure 24: Micrograph of compound **7** at 75 °C.

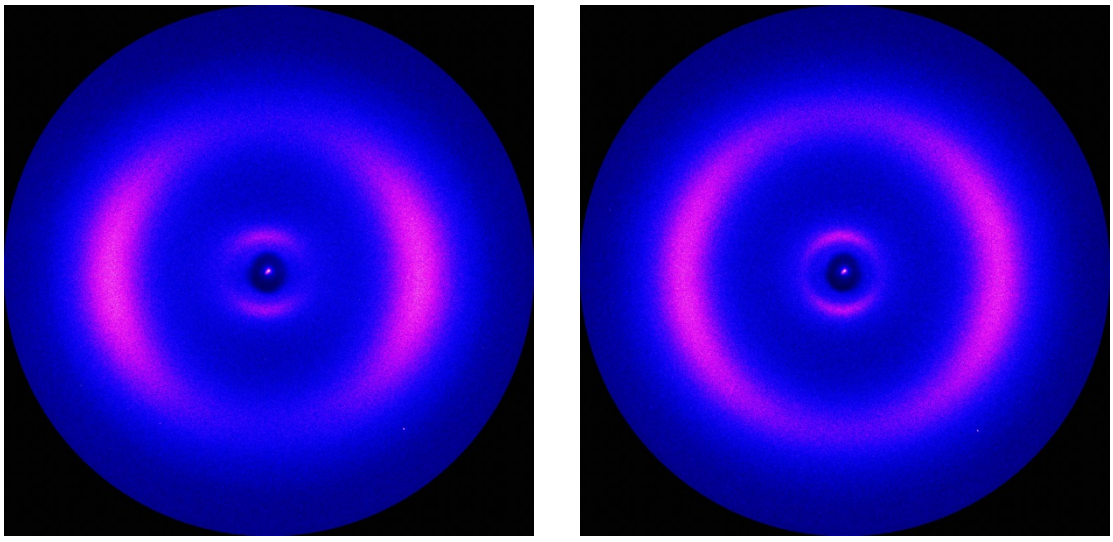
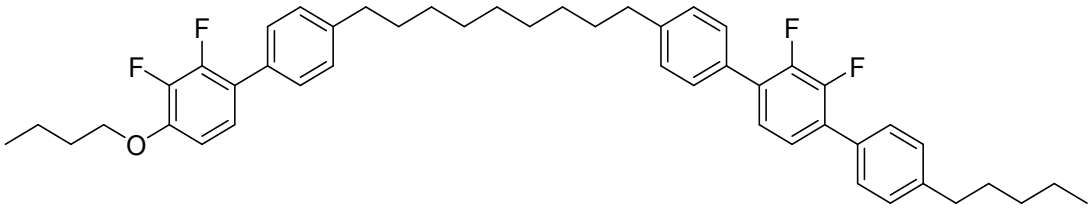


Figure 25: XRD scattering data for compound **7** at 103 °C (left) and 83 °C (right).

Figure 25 shows the scattering data for the nematic and the N_X phase. The narrowing of the wide angle is visible in the N_X phase. The small angle peak at 4.5 equals to 19.6 Å. 19.6 Å is approximately half the molecular length.

Synthesis of 4-(9-(2',3'-difluoro-4'-butyloxy-[1,1'-biphenyl]-4-yl)nonyl)-2',3'-difluoro-4''-pentylterphenyl (8)



4-(9-(4-bromophenyl)nonyl)-2',3'-difluoro-4''-pentyl-1,1':4',1''-terphenyl (0.16 g, 0.26 mmol), (2,3-difluoro-4butyloxyphenyl)boronic acid (0.18 g, 0.78 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.020 g, 17.3 µmol) were dissolved in tetrahydrofuran (20 mL) under inert atmosphere. The reaction was stirred at room temperature, with nitrogen being bubbled through the solvent. After an hour an aqueous solution of sodium carbonate (0.052 g, 0.49 mmol) was added drop wise and the reaction was heated under reflux overnight. The solvent was removed under reduced pressure and the organics separated by silica column chromatography using a mixture of dichloromethane and hexane 1:5 to afford the title compound as a white solid (0.11 g, 57%).

Cr – (SmX 61.7) 69.5 – N_x – 82.8 – N – 103.4 – Iso

^{1}H NMR: δ_H (400 MHz, CD_2Cl_2) 7.50 (4H, d, *J* 7.96), 7.40 (2H, dd, *J* 8.16, 1.43), 7.27 (4H, d, *J* 7.14), 7.23 (4H, d, *J* 8.36), 7.06 (1H, dt, *J* 8.46, 2.24), 6.76 (1H, dt, *J* 8.16, 1.63), 4.05 (2H, t, *J* 6.53), 2.64 (6H, m), 1.82 (2H, m), 1.65 (6H, m), 1.51 (2H, m), 1.38-1.31 (14H, m), 0.98 (3H, t, *J* 7.45), 0.91 (3H, t, *J* 6.94).

^{13}C NMR: δ_C (100 MHz, $CDCl_3$) 148.8, 148.4, 143.1, 143.0, 142.4, 132.2, 132.0, 129.5, 128.69, 128.66, 128.6, 128.5, 124.5, 123.4, 123.0, 122.9, 109.51, 109.49, 69.6, 35.69, 35.68, 35.6, 31.5, 31.39, 31.37, 31.2, 31.1, 29.5, 29.3, 22.5, 19.1, 14.0, 13.8.

^{19}F NMR: δ_F (376 MHz, $CDCl_3$) -141.8 (1F, dd, *J* 20.81, 6.94), -143.2 (2F, s), -158.8 (1F, dd, *J* 20.81, 6.94).

MS: 722

m/z (CI) 723 ($M+H^+$) 740 ($M+NH_4^+$)

HRMS Calc: $C_{48}H_{54}F_4O$+H requires = 723.4189

HRMS Found: 723.4178

Assay (HPLC, C18, MeCN:DCM 80:20) = 99.0 %

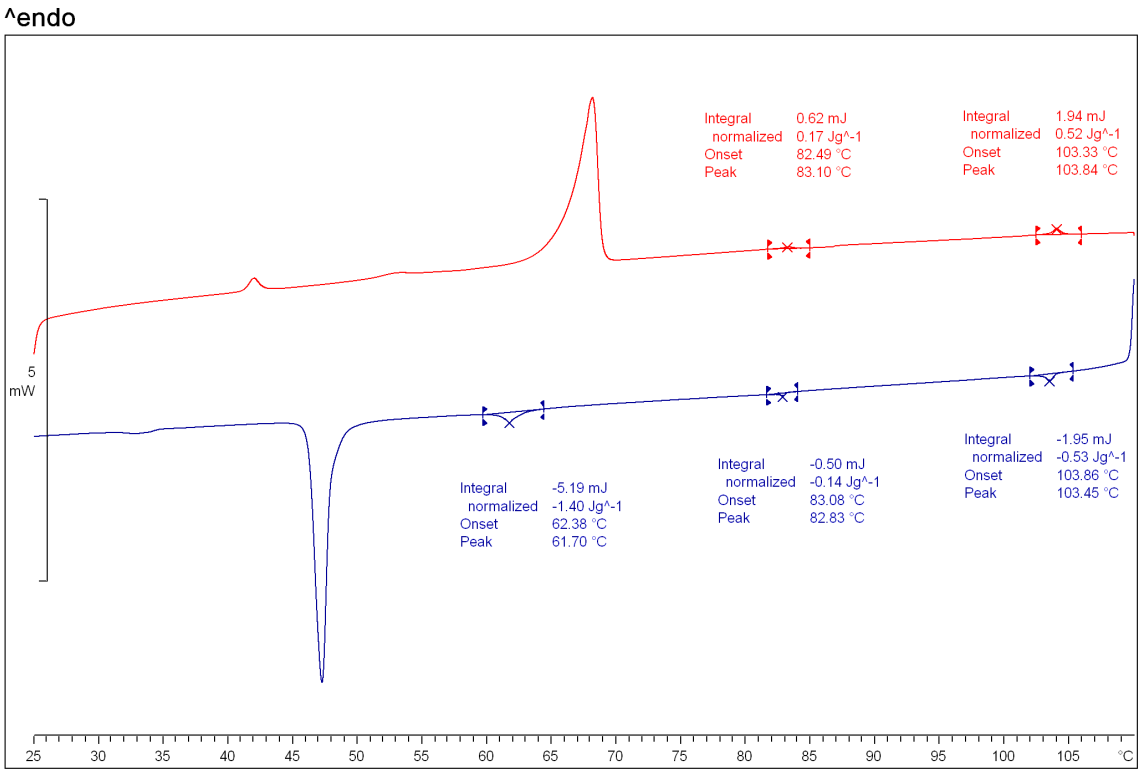


Figure 26: Calorimetric data for compound **8.**

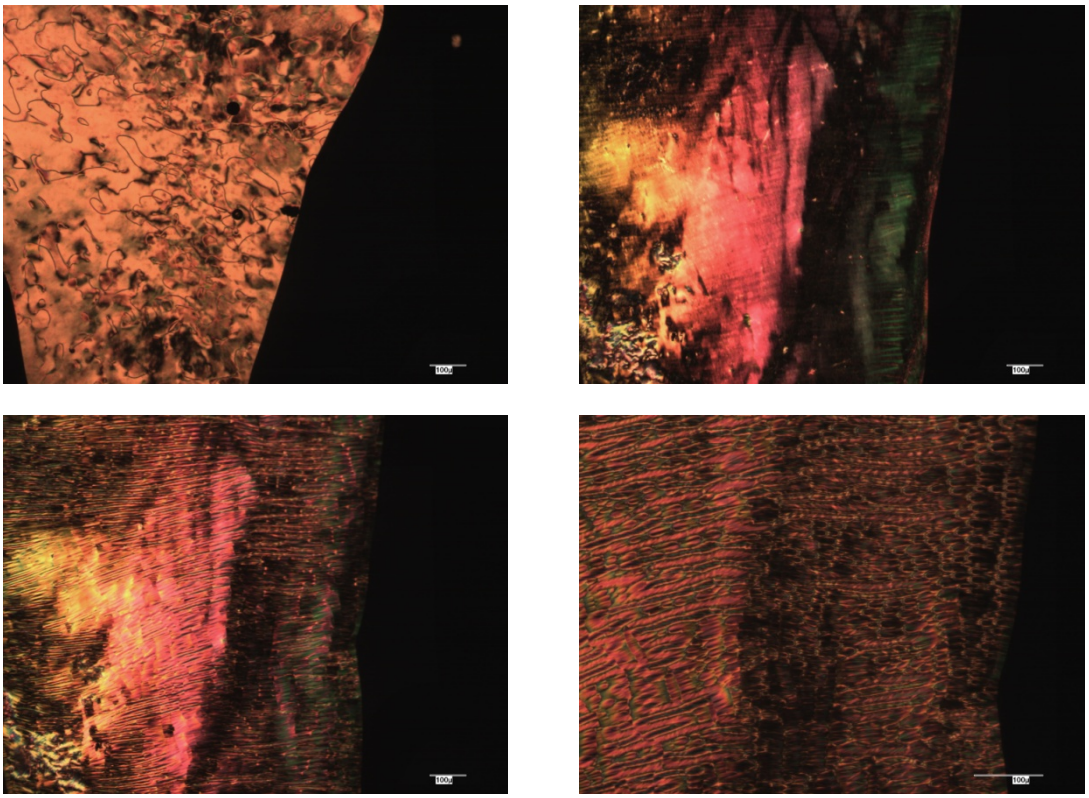


Figure 27: Micrographs of compound **8** at 100 °C (top left), 84 °C (top right), 81 °C (bottom left) and 78 °C (bottom right) under crossed polarizers and on untreated slides.

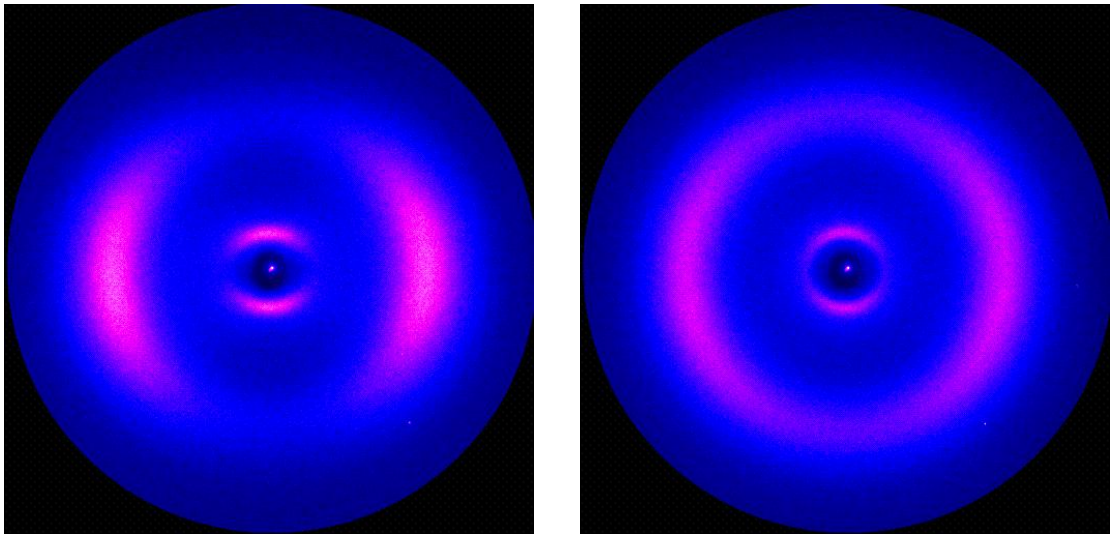


Figure 28: XRD scattering data for compound **8** at 90 °C and 70 °C.

The data shown in Figure 28 shows the two patterns expected for the conventional nematic phase and the N_X phase exhibited by compound **8**. The peak in the small angle is at 4.7 which equals to 18.8 Å.

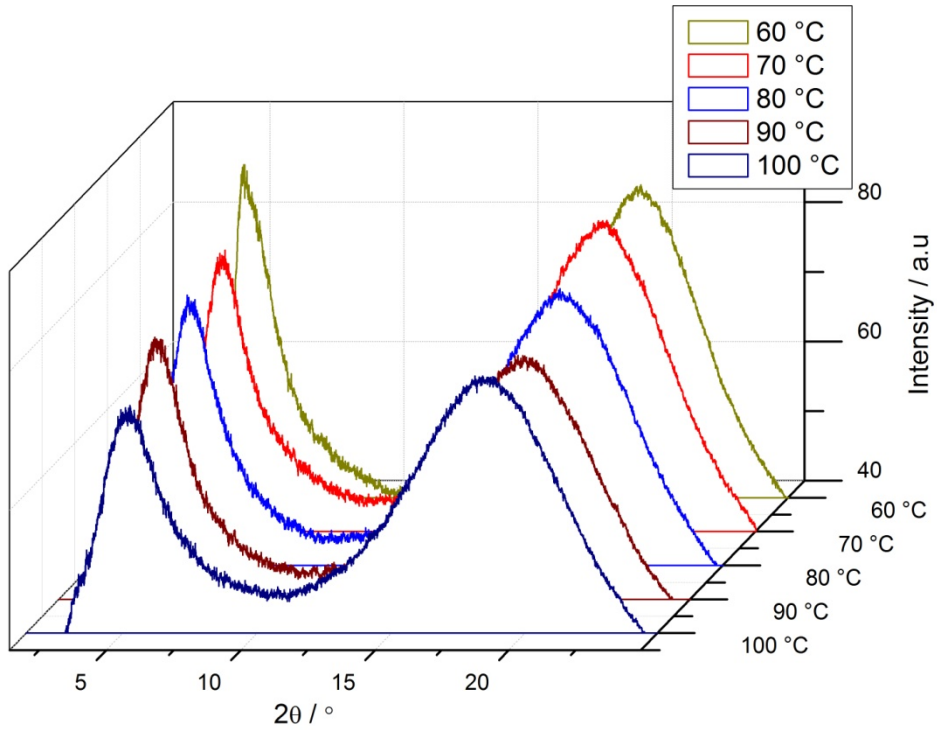


Figure 29: Plot of 2θ against intensity for compound **8** at various temperatures.

Figure 29 shows the plot of 2θ against intensity for compound **8** in all the mesophases on cooling from the isotropic. The narrowing effect of the N_X in the wide angle is most evident in this example with a sizeable difference in peak height. Another interesting thing to note is the plot of the unknown phase.

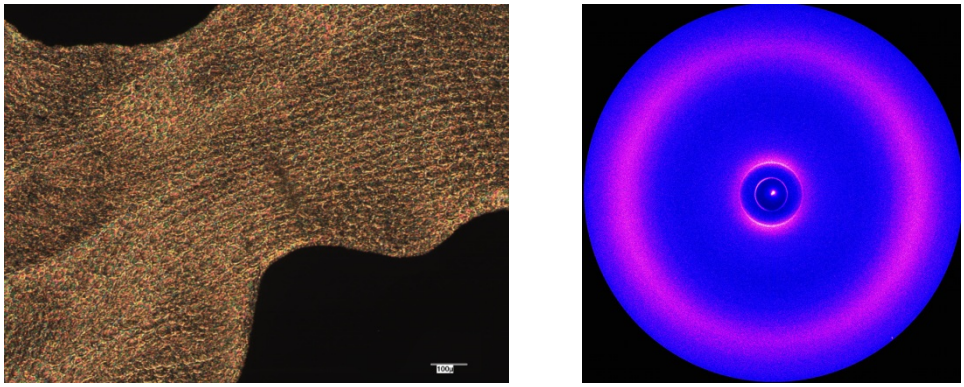
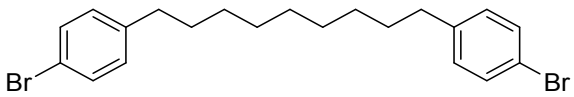


Figure 30: Micrograph and XRD scattering data of compound **8** at 60 °C.

The Two signals in the small angle at 2.1 and 4.3 equal 42 Å and 20.5 Å respectively. As the signal is near the limit of the instrumentation it is important to collect the complete data set before a conclusion can be made regarding the assignment of this phase. A recent report[i] has shown evidence of a smectic twist bend phase. This is under further investigation.

Synthesis of 1,9-bis(4-bromophenyl)nonane (I1)



1,9-Bis(4-bromophenyl)nonane-1,9-dione (21.4 g, 45.9 mmol) and hydrazine hydrate (5.51 g, 0.11 mol) were dissolved in diethylene glycol by stirring at 130 °C for 1 hour. Potassium hydroxide (15.4 g, 0.27 mol) was added carefully and stirred at 130 °C for 4 hours. The condenser was removed and the reaction was stirred at 200 °C to remove the excess hydrazine overnight. Upon completion the reaction was cooled and diluted with water and poured onto a mixture of concentrated hydrochloric acid and ice. The organics were extracted into dichloromethane and washed with water and brine. After drying over magnesium sulphate the solvent was removed under reduced pressure. The organics separated by silica column chromatography using hexane afford the title compound as a white solid (18.2 g, 91%).

^{1}H NMR: δ_H (400 MHz, CD_2Cl_2) 7.38 (4H, d, *J* 8.36), 7.04 (4H, d, *J* 8.36), 2.54 (4H, t, *J* 7.76), 1.54 (4H, m), 1.27 (10H, m).

^{13}C NMR: δ_C (100 MHz, $CDCl_3$) 141.8, 131.2, 130.2, 119.2, 35.3, 31.3, 29.41, 29.39, 29.1.

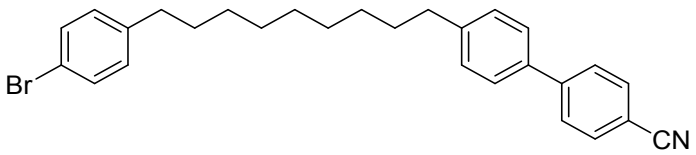
MS: 438

m/z (CI) 439 ($M+H^+$)

HRMS Calc: $C_{21}H_{26}Br_2+_4$ requires = 437.0479

HRMS Found: 437.0477

Synthesis of 4'-(9-(4-bromophenyl)nonyl)-[1,1'-biphenyl]-4-carbonitrile (I2)



1,9-Bis(4-Bromophenyl)nonane (1.80 g, 4.1 mmol), (4-cyanophenyl)boronic acid (0.20 g, 1.4 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.030 g, 26.0 µmol) were dissolved in tetrahydrofuran (40 mL) under inert atmosphere. The reaction was stirred at room temperature, with nitrogen being bubbled through the solvent. After 1 hour an aqueous solution of sodium carbonate (0.21 g, 2.0 mmol) was added drop wise and the reaction was heated under reflux overnight. The solvent was removed under reduced pressure and the organics separated by silica column chromatography using a mixture of dichloromethane and hexane 1:3 to afford the title compound as a white solid (0.41 g, 65%).

Cr – (N 20) 48 – Iso

^{1}H NMR: δ_H (400 MHz, CD_2Cl_2) 7.69 (4H, q, *J* 8.56), 7.51 (2H, d, *J* 8.16), 7.38 (2H, d, *J* 8.36), 7.29 (2H, d, *J* 8.16), 7.04 (2H, d, *J* 8.36), 2.65 (2H, t, *J* 7.75), 2.54 (2H, t, *J* 7.65), 1.65-1.55 (4H, m), 1.40-1.20 (10H, m).

^{13}C NMR: δ_C (100 MHz, $CDCl_3$) 145.6, 143.8, 141.8, 136.4, 132.6, 131.2, 130.1, 129.2, 127.5, 127.1, 119.2, 119.0, 110.5, 35.6, 35.3, 31.4, 31.3, 29.43, 29.39, 29.3, 29.1.

MS: 460

m/z (CI) 461 ($M+H^+$)

HRMS Calc: $C_{28}H_{30}BrN$+H requires = 460.1634

HRMS Found: 460.1625

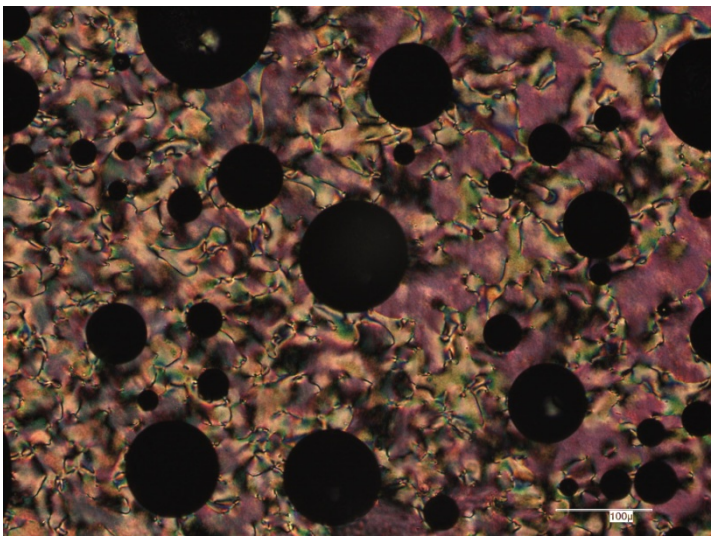
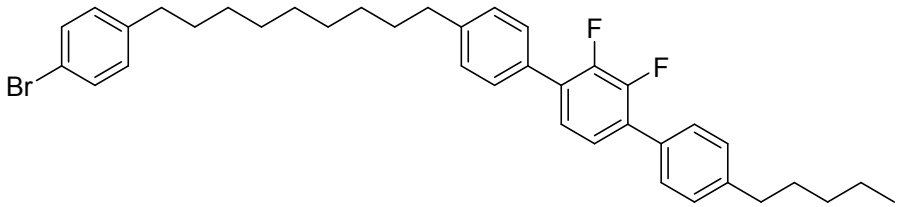


Figure 31: Monotropic Nematic phase of intermediate **I2** at 20 °C under crossed polarizers and on untreated slide.

Synthesis of 4-(9-(4-bromophenyl)nonyl)-2',3'-difluoro-4''-pentyl-1,1':4',1''-terphenyl (I3)



1,9-bis(4-Bromophenyl)nonane (4.3 g, 9.8 mmol), (2,3-difluoro-4'-pentyl-[1,1'-biphenyl]-4-yl)boronic acid (1.0 g, 3.3 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.076 g, 65.7 µmol) were dissolved in tetrahydrofuran (100 mL) under inert atmosphere. The reaction was stirred at room temperature, with nitrogen being bubbled through the solvent. After 1 hour an aqueous solution of sodium carbonate (0.52 g, 4.9 mmol) was added drop wise and the reaction was heated under reflux overnight. The solvent was removed under reduced pressure and the organics separated by silica column chromatography using a mixture of dichloromethane and hexane 1:5 to afford the title compound as a white solid (2.03 g, 65%).

Cr – 42 – SmA – 61 – N – 85 – Iso

^{1}H NMR: δ_H (400 MHz, CD_2Cl_2) 7.51 (4H, d, *J* 7.75), 7.38 (2H, d, *J* 8.36), 7.31 (2H, d, *J* 2.45), 7.29 (2H, d, *J* 2.45), 7.27 (2H, dd, *J* 1.74, 3.37), 7.07 (2H, d, *J* 8.57), 2.66 (4H, dt, *J* 2.04, 7.14), 2.56 (2H, t, *J* 7.75), 1.70-1.50 (4H, m), 1.38-1.31 (16H, m), 0.91 (3H, t, *J* 6.94).

^{13}C NMR: δ_C (100 MHz, $CDCl_3$) 149.8, 149.6, 147.3, 147.2, 143.4, 143.1, 143.0, 141.8 , 132.0, 131.2, 130.2, 129.5, 129.4, 128.69, 128.66, 124.5, 119.2, 35.7, 35.3, 31.5, 31.36, 31.29, 31.1, 29.5, 29.4, 29.3, 29.1, 22.5, 14.0.

MS: 617

m/z (CI) 618 ($M+H^{=}$)

HRMS Calc: C38H43BrF2 +H requires = 617.2594

HRMS Found: 617.2591

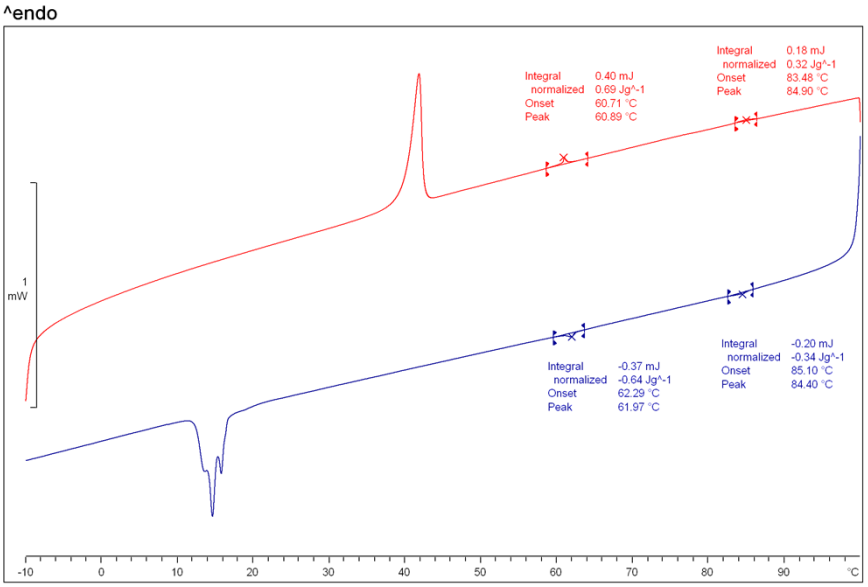


Figure 32: Calorimetric data for intermediate **I3**.

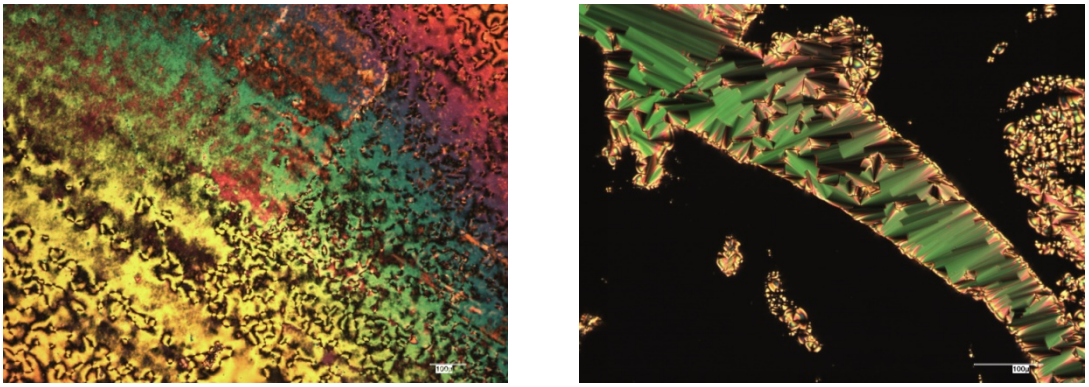


Figure 33: Micrographs of intermediate **I3** at 77 °C Nematic (left) and 60 °C Smectic A (right) under crossed polarizers and on untreated slides.

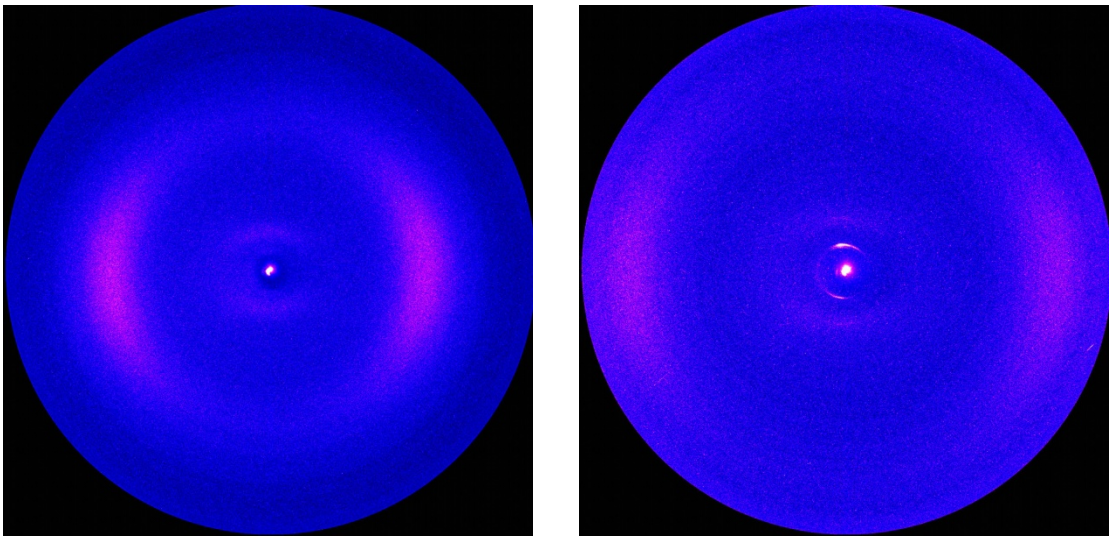


Figure 34 : XRD scattering data for **I3** at 70 °C (left) and 56 °C