

1. Methods

1.1. General Techniques

The silica supported platinum catalyst ($\text{Pt} @ \text{SiO}_2$) was prepared as described by Miao.¹ Alkene terminated alkoxycyanobiphenyls were prepared as described previously.² Pentamethyldisiloxane was purchased from Fluorochem and purified by short path distillation prior to use. Low sulphur toluene was prepared as by washing with sulphuric acid as described previously.³ Silica gel (purchased from Fluka), hexachloroplatinic acid (Acros Organics), triethoxyvinylsilane (Sigma Aldrich) were used as received, without purification. Yields refer to chromatographically (RP-HPLC) and spectroscopically (^1H NMR, ^{13}C { ^1H }, DEPT135 and ^{29}Si { ^1H } NMR) homogenous material. Spectral data for **2Si11OCB** was identical to that reported previously.³

1.2. Flow Setup

An Omnifit column with a variable end piece adapter and PTFE frits was packed with $\text{Pt} @ \text{SiO}_2$ ($\approx 4 \text{ cm}^3$). The packed column was connected to a pump and wetted with low sulphur toluene (10 ml, 0.5 ml min⁻¹). Separately the alkene (1 mol eq) pentamethyldisiloxane (1.1 mol eq) and low sulphur toluene (0.2M concentration) were combined and sonicated until homogenous. The solution was passed through the packed column at the specified flow rate. The column was washed with ethyl acetate (10 ml) and the combined organics concentrated *in vacuo* (70 °C, 5 mBar) to afford the title compounds as colourless liquids or liquid crystals which solidified on standing.

1.3. Nuclear Magnetic Resonance

NMR spectra were recorded on a JEOL ECS spectrometer operating at 400 MHz (^1H), 100.5 MHz (^{13}C { ^1H } and ^{13}C { ^1H } DEPT135) and 79.5 MHz (^{29}Si { ^1H } NMR) as solutions in deuterated chloroform. Spectra were referenced to the residual protic solvent for ^1H (7.26 ppm), ^{13}C { ^1H } to the resonance of CDCl_3 (77.16 ppm) and ^{29}Si { ^1H } were unreferenced.

1.4. Mass Spectrometry

Mass spectra were recorded on a Bruker compact time of flight mass spectrometer with both ESI and APCI sources, and we extend our gratitude to Mr. Karl Heaton of the University of York for obtaining MS data.

1.5. High Performance Liquid Chromatography

High-performance liquid chromatography was performed on a Shimadzu Prominence modular HPLC system comprising a LC-20A quaternary solvent pump, a DGU-20A₅ degasser, a SIL-20A autosampler, a CBM-20A communication bus, a CTO-20A column oven (maintained at 40 °C), and a SPO-20A dual wavelength UV-vis detector operating at 210/230 nm. The column used was an Supelco bonded silica column with a 5 µm pore size, an internal diameter of 10 mm and a length of 250 mm (cat. No 58513-U). The mobile phase was a gradient of hexane/DCM (0% > 100%, 30 min). Chromatograms with only one peak are quoted as >99.5% in both the SI and the manuscript. The injection volume was 20 µl

1.6. Polarised Optical Microscopy

Polarised optical microscopy was performed on a Zeiss Axioskop 40Pol microscope using a Mettler FP82HT hotstage controlled by a Mettler FP90 central processor. Photomicrographs were captured *via* an InfinityX-21 MP digital camera mounted atop the microscope.

1.7. Differential Scanning Calorimetry.

Differential scanning calorimetry was performed on a Mettler DSC822^e fitted with an autosampler operating with Mettler Star^e software and calibrated before use against an indium standard (onset = 156.55 ± 0.2 °C, ΔH = 28.45 ± 0.40 Jg⁻¹) under an atmosphere of dry nitrogen.

1.8. Small Angle X-ray Scattering

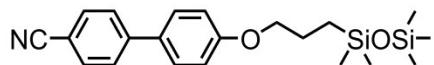
Small angle X-ray scattering was performed using a Bruker D8 Discover equipped with a temperature controlled, bored graphite rod furnace with two 1T magnets perpendicular to the incident beam for magnetic alignment, custom built at the University of York. The radiation used was copper Kα ($\lambda = 0.154056\text{ nm}$) from a 1 µS microfocus source. Diffraction patterns were recorded on a 2048x2048 pixel Bruker VANTEC 500 area detector set at a distance of 121 mm from the sample. Samples were filled into 0.9 mm I.D. capillary tubes. The samples were partially aligned by slowly cooling (0.1 °C min⁻¹) into the SmA phase from the isotropic liquid. Diffraction patterns were collected as a function of temperature and the data processed using Matlab as follows. Two-dimensional scattering patterns were collected on cooling from the isotropic liquid until crystallisation in ~ 1.2 °C intervals with a temperature

accuracy of +/- 0.1 °C. 2D SAXS patterns were radially averaged (0.05 ° step size) to give scattered intensity as a function of 2θ for each frame. Fitting of this integrated data (with either a Lorentzian, Gaussian or Voigt function as appropriate) allowed the peak position and FWHM to be determined for both the small-angle and wide-angle peaks.

1.9. Computational Chemistry

Quantum chemical calculations were performed using the Gaussian 09 revision e.01 suite of programmes.⁴

2.1. Chemical Analysis



2Si3OCB: 4'-(3-(1,1,3,3-pentamethyldisiloxanyl)propoxy)-[1,1'-biphenyl]-4-carbonitrile

¹H NMR: 0.09 (9H, S, SiOSi(CH₃)₃), 0.11 (6H, S, -CH₂Si(CH₃)₂OSi(CH₃)₃), 0.62 – 0.70 (2H, m, ArO-CH₂-CH₂-CH₂-Si), 1.78 – 1.90 (2H, m, ArO-CH₂-CH₂-CH₂Si), 3.98 (2H, t, *J* = 6.8 Hz, ArO-CH₂-CH₂), 6.99 (2H, ddd, *J* = 1.8 Hz, *J* = 2.3 Hz, *J* = 8.7 Hz, ArH), 7.53 (2H, ddd, *J* = 1.8 Hz, *J* = 2.3 Hz, *J* = 8.7 Hz, ArH), 7.63 (2H, ddd, *J* = 2.1 Hz, *J* = 2.3 Hz, *J* = 9.2 Hz, ArH), 7.69 (2H, ddd, *J* = 2.1 Hz, *J* = 2.3 Hz, *J* = 9.2 Hz, ArH)

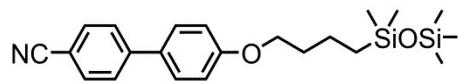
¹³C{¹H} NMR: 0.41 (S, *J*_{C-Si} = 58.7 Hz), 2.12 (S, *J*_{C-Si} = 54.7 Hz), 14.34, 23.31, 70.72, 100.07, 115.17, 119.21, 127.16, 128.42, 131.30, 132.66, 145.38, 159.87

¹³C DEPT135: 0.41 (+), 2.09 (+), 14.33 (-), 23.30 (-), 70.71 (-), 115.17 (+), 127.15 (+), 128.42 (+), 132.65 (+)

²⁹Si{¹H} NMR: 8.01 (S), 8.24 (S)

MS (ESI+): 406.1635 (calcd. for C₂₁H₂₉NNaO₂Si₂): 406.1629, M + Na)

Assay (HPLC): >99.5% (one peak detected, retention time = 5.6 min)



2Si4OCB: 4'-(4-(1,1,3,3,3-pentamethylsiloxy)butoxy)-[1,1'-biphenyl]-4-carbonitrile

¹H NMR: 0.08 (6H, S, -CH₂Si(CH₃)₂OSi(CH₃)₃), 0.09 (9H, S, SiOSi(CH₃)₃), 0.57 – 0.63 (2H, m, ArO-CH₂-CH₂-CH₂-CH₂-Si), 1.48 – 1.58 (2H, m, ArO-CH₂-CH₂-CH₂-CH₂-Si), 1.81 – 1.91 (2H, m, ArO-CH₂-CH₂-CH₂-CH₂-Si), 4.02 (2H, t, J = 6.8 Hz, ArO-CH₂-CH₂), 7.00 (2H, ddd, J = 2.1 Hz, J = 2.9 Hz, J = 9.2 Hz, ArH), 7.52 (2H, ddd, J = 2.1 Hz, J = 2.9 Hz, J = 9.2 Hz, ArH), 7.63 (2H, ddd, J = 1.8 Hz, J = 2.1 Hz, J = 8.7 Hz, ArH), 7.68 (2H, ddd, J = 1.8 Hz, J = 2.1 Hz, J = 8.7 Hz, ArH)

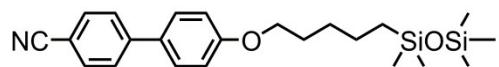
¹³C{¹H} NMR: 0.45 (S, J_{C-Si} = 58.6 Hz), 2.09 (S, J_{C-Si} = 59.5 Hz), 18.12 19.90 32.78, 67.84, 100.07, 115.16, 119.22, 127.14, 128.39, 131.27, 132.63, 145.36, 159.93

¹³C DEPT135: 0.46 (+), 2.10 (+), 18.13 (-), 19.91 (-), 32.79 (-), 67.85 (-), 115.17 (+), 127.15 (+), 128.40 (+), 132.65 (+)

²⁹Si{¹H} NMR: 7.88 (S), 7.90 (S)

MS (ESI+): 420.1791 (calcd. for C₂₂H₃₁NNaO₂Si₂): 420.1786, M + Na)

Assay (HPLC): 99.3% (retention time = 5.8 min)



2Si5OCB: 4'-(5-(1,1,3,3-pentamethyldisiloxanyl)pentyoxy)-[1,1'-biphenyl]-4-carbonitrile

¹H NMR: 0.09 (6H, S, -CH₂Si(CH₃)₂OSi(CH₃)₃), 0.10 (9H, S, SiOSi(CH₃)₃), 0.55 – 0.62 (2H, m, ArO-CH₂-(CH₂)₃-CH₂-Si), 1.39 – 1.47 (2H, m, ArO-CH₂-(CH₂)₂-CH₂-CH₂-Si), 1.49 – 1.57 (2H, m, (2H, m, ArO-CH₂-CH₂-CH₂-(CH₂)₂-Si), 1.78 – 1.88 (2H, m, ArO-CH₂-CH₂-CH₂-), 3.99 (2H, t, *J* = 6.6 Hz, ArO-CH₂-CH₂), 6.98 (2H, ddd, *J* = 2.0 Hz, *J* = 3.0 Hz, *J* = 8.4 Hz, ArH), 7.50 (2H, ddd, *J* = 2.0 Hz, *J* = 3.0 Hz, *J* = 8.4 Hz, ArH), 7.59 (2H, ddd, *J* = 1.5 Hz, *J* = 2.0 Hz, *J* = 8.8 Hz, ArH), 7.64 (2H, ddd, *J* = 1.5 Hz, *J* = 2.0 Hz, *J* = 8.8 Hz, ArH)

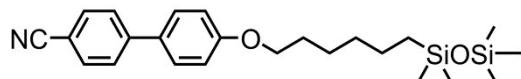
¹³C{¹H} NMR: 0.37, 2.00, 18.26, 23.11, 28.94, 29.66, 68.03, 109.94, 115.01, 118.99, 126.91, 128.22, 131.01, 132.44, 145.09, 159.78

¹³C DEPT135: 0.37 (+), 2.00 (+), 18.42 (-), 23.26 (-), 29.10 (-), 29.82 (-) 68.19 (-), 115.16 (+), 127.07 (+), 128.37 (+), 132.60 (+)

²⁹Si{¹H} NMR: 7.66 (S), 8.07 (S)

MS (ESI+): 434.1944 (calcd. for C₂₃H₃₃NNaO₂Si₂): 434.1942 M + Na)

Assay (HPLC): >99.5 % (only one peak, retention time = 4.7 minutes)



2Si6OCB: 4'-(6-(1,1,3,3,3-pentamethylsiloxy)hexyloxy)-[1,1'-biphenyl]-4-carbonitrile

¹H NMR: 0.07 (6H, S, -CH₂Si(CH₃)₂OSi(CH₃)₃), 0.10 (9H, S, SiOSi(CH₃)₃), 0.53 – 0.59 (2H, m, -CH₂-CH₂-Si), 1.35-1.55 (6H, m, -CH₂-(CH₂)₃-CH₂Si), 1.77 – 1.86 (2H, m, ArO-CH₂-CH₂-CH₂-), 4.00 (2H, t, *J* = 6.6 Hz, ArO-CH₂-CH₂), 6.99 (2H, ddd, *J* = 2.0 Hz, *J* = 3.4 Hz, *J* = 8.4 Hz, ArH), 7.51 (2H, ddd, *J* = 2.0 Hz, *J* = 3.4 Hz, *J* = 8.4 Hz, ArH), 7.61 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 8.8 Hz, ArH), 7.66 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 8.8 Hz, ArH)

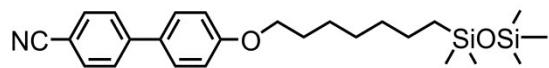
¹³C{¹H} NMR: 0.40, 2.04, 18.32, 23.25, 25.78, 29.19, 33.13, 68.14, 109.99, 115.06, 119.07, 127.00, 128.28, 131.12, 132.51, 145.19, 159.82

¹³C DEPT135: 0.51 (+), 2.15 (+), 18.42 (-), 23.26 (-), 25.88 (-), 29.29 (-), 33.23 (-) 68.25 (-), 115.17 (+), 127.09 (+), 128.39 (+), 132.62 (+)

²⁹Si{¹H} NMR: 7.64 (S), 8.05 (S)

MS (ESI+): 448.2104 (calcd. for C₂₄H₃₅NNaO₂Si₂: 448.2099, M + Na)

Assay (HPLC): >99.5 % (only one peak, retention time = 4.9 minutes)



2Si7OCB: 4'-(7-(1,1,3,3-pentamethyldisiloxanyl)heptyloxy)-[1,1'-biphenyl]-4-carbonitrile

¹H NMR: 0.06 (6H, S, -CH₂Si(CH₃)₂OSi(CH₃)₃), 0.9 (9H, S, SiOSi(CH₃)₃), 0.50 – 0.57 (2H, m, -CH₂-CH₂-Si), 1.30-1.52 (8H, m, -CH₂-(CH₂)₄-CH₂Si), 1.78 – 1.87 (2H, m, ArO-CH₂-CH₂-CH₂-), 4.01 (2H, t, *J* = 6.5 Hz, ArO-CH₂-CH₂), 7.00 (2H, ddd, *J* = 2.2 Hz, *J* = 3.0 Hz, *J* = 8.5 Hz, ArH), 7.52 (2H, ddd, *J* = 2.2 Hz, *J* = 3.0 Hz, *J* = 8.5 Hz, ArH), 7.62 (2H, ddd, *J* = 1.5 Hz, *J* = 1.8 Hz, *J* = 9.2 Hz, ArH), 7.67 (2H, ddd, *J* = 1.5 Hz, *J* = 1.8 Hz, *J* = 9.2 Hz, ArH)

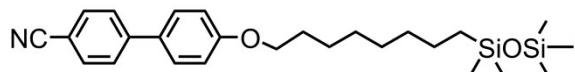
¹³C{¹H} NMR: 0.44 (S, *J*_{C-Si} = 58.4 Hz), 2.08 (S, *J*_{C-Si} = 59.5 Hz), 18.42, 23.29, 26.03, 29.18, 29.32, 33.37, 68.19, 110.05, 115.12, 119.16, 127.08, 128.35, 131.22, 132.59, 145.29, 159.87

¹³C DEPT135: 0.49 (+), 2.12 (+), 18.46 (-), 23.33 (-), 26.08 (-), 29.22 (-), 29.36 (-), 33.41 (-), 68.23 (-), 115.17 (+), 127.13 (+), 128.40 (+), 132.63 (+)

²⁹Si{¹H} NMR: 7.59 (S), 8.10 (S)

MS (ESI+): 462.2260 (calcd. for C₂₅H₃₇NNaO₂Si₂: 462.2255, M + Na)

Assay (HPLC): >99.5 % (only one peak, retention time = 5.1 minutes)



2Si8OCB: 4'-(8-(1,1,3,3-pentamethylsiloxy)octyloxy)-[1,1'-biphenyl]-4-carbonitrile

¹H NMR: 0.08 (6H, S, -CH₂Si(CH₃)₂OSi(CH₃)₃), 0.11 (9H, S, SiOSi(CH₃)₃), 0.51 – 0.57 (2H, m, -CH₂-CH₂-Si), 1.31-1.54 (10H, m, -CH₂-(CH₂)₅-CH₂Si), 1.76 – 1.85 (2H, m, ArO-CH₂-CH₂-CH₂-), 3.97 (2H, t, *J* = 6.5 Hz, ArO-CH₂-CH₂), 6.95 (2H, ddd, *J* = 2.0 Hz, *J* = 3.0 Hz, *J* = 8.5 Hz, ArH), 7.48 (2H, ddd, *J* = 2.0 Hz, *J* = 3.0 Hz, *J* = 8.5 Hz, ArH), 7.56 (2H, ddd, *J* = 1.5 Hz, *J* = 2.1 Hz, *J* = 9.2 Hz, ArH), 7.62 (2H, ddd, *J* = 1.5 Hz, *J* = 2.1 Hz, *J* = 9.2 Hz, ArH)

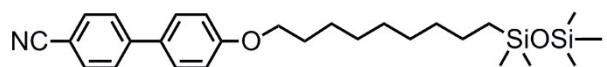
¹³C{¹H} NMR: 0.33 (S, *J*_{C-Si} = 58.4 Hz), 1.95 (S, *J*_{C-Si} = 59.4 Hz), 18.29, 23.21, 26.02, 29.19, 29.25, 29.30, 33.28, 67.97, 109.90, 114.94, 118.87, 126.80, 128.12, 130.89, 132.35, 144.96, 159.74

¹³C DEPT135: 0.33 (+), 1.95 (+), 18.29 (-), 23.21 (-), 26.01 (-), 29.18 (-), 29.25 (-), 29.30 (-), 33.28 (-), 67.96 (-), 114.94 (+), 126.80 (+), 128.12 (+), 132.35 (+)

²⁹Si{¹H} NMR: 7.57 (S), 8.07 (S)

MS (ESI+): 476.2420 (calcd. for C₂₆H₃₉NNaO₂Si₂: 476.2412 M + Na)

Assay (HPLC): >99.5 % (only one peak, retention time = 5.1 minutes)



2Si9OCB: 4'-(9-(1,1,3,3-pentamethyldisiloxanyl)nonyloxy)-[1,1'-biphenyl]-4-carbonitrile

¹H NMR: 0.04 (6H, S, -CH₂Si(CH₃)₂OSi(CH₃)₃), 0.7 (9H, S, SiOSi(CH₃)₃), 0.47 – 0.52 (2H, m, -CH₂-CH₂-Si), 1.25 - 1.52 (12H, m, -CH₂-(CH₂)₆-CH₂Si), 1.76 – 1.83 (2H, m, ArO-CH₂-CH₂-CH₂-), 3.97 (2H, t, *J* = 6.8 Hz, ArO-CH₂-CH₂), 6.94 (2H, ddd, *J* = 2.2 Hz, *J* = 3.1 Hz, *J* = 8.8 Hz, ArH), 7.46 (2H, ddd, *J* = 2.2 Hz, *J* = 3.1 Hz, *J* = 8.8 Hz, ArH), 7.54 (2H, ddd, *J* = 1.8 Hz, *J* = 2.1 Hz, *J* = 8.4 Hz, ArH), 7.60 (2H, ddd, *J* = 1.8 Hz, *J* = 2.1 Hz, *J* = 8.4 Hz, ArH)

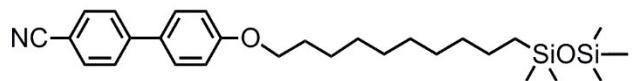
¹³C{¹H} NMR: 0.48 (S, *J*_{C-Si} = 58.4 Hz), 2.10 (S, *J*_{C-Si} = 58.3 Hz), 18.47, 23.38, 26.15, 29.33, 29.43, 29.54, 29.62, 33.51, 68.26, 110.09, 115.16, 119.24, 127.15, 128.41, 131.29, 132.65, 145.37, 159.90

¹³C DEPT135: 0.47 (+), 2.10 (+), 18.47 (-), 23.37 (-), 26.14 (-), 29.33 (-), 29.43 (-), 29.53 (-), 29.62 (-), 33.51 (-), 68.25 (-), 115.15 (+), 127.13 (+), 128.40 (+), 132.65 (+)

²⁹Si{¹H} NMR: 7.55 (S), 8.15 (S)

MS (ESI+): 490.2579 (calcd. for C₂₇H₄₁NNaO₂Si₂: 490.2568 M + Na)

Assay (HPLC): >99.5 % (only one peak, retention time = 4.9 minutes)



2Si10OCB: 4'-(10-(1,1,3,3,3-pentamethyldisiloxanyl)decyloxy)-[1,1'-biphenyl]-4-carbonitrile

¹H NMR: 0.06 (6H, S, -CH₂Si(CH₃)₂OSi(CH₃)₃), 0.09 (9H, S, SiOSi(CH₃)₃), 0.50 – 0.57 (2H, m, -CH₂-CH₂-Si), 1.26 - 1.54 (14H, m, -CH₂-(CH₂)₇-CH₂Si), 1.77 – 1.86 (2H, m, ArO-CH₂-CH₂-CH₂-), 4.00 (2H, t, *J* = 6.6 Hz, ArO-CH₂-CH₂), 6.99 (2H, ddd, *J* = 2.0 Hz, *J* = 2.8 Hz, *J* = 8.5 Hz, ArH), 7.49 (2H, ddd, *J* = 2.0 Hz, *J* = 2.8 Hz, *J* = 8.5 Hz, ArH), 7.60 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 9.2 Hz, ArH), 7.66 (2H, ddd, *J* = 1.8 Hz, *J* = 2.4 Hz, *J* = 9.2 Hz, ArH)

¹³C{¹H} NMR: 0.45 (S, *J*_{C-Si} = 58.4 Hz), 2.11 (S, *J*_{C-Si} = 58.3 Hz), 18.44 (S, *J*_{C-Si} = 60.3 Hz), 23.36, 26.12, 29.30, 29.46, 29.49, 29.62, 29.70, 33.50, 68.20, 110.05, 115.12, 119.16, 127.08, 128.35, 131.21, 132.59, 145.28, 159.87

¹³C DEPT135: 0.49 (+), 2.12 (+), 18.48 (-), 23.40 (-), 29.34 (-), 29.50 (-), 29.53 (-), 29.66 (-), 29.74 (-), 33.54 (-), 68.23 (-), 115.16 (+), 127.12 (+), 128.49 (+), 132.63 (+)

²⁹Si{¹H} NMR: 7.53 (S), 8.14 (S)

MS (ESI+): 504.2729 (calcd. for C₂₈H₄₃NNaO₂Si₂: 504.2725 M + Na)

Assay (HPLC): >99.5 % (only one peak, retention time = 4.8 minutes)

3.1. Supplemental SAXS Data

We present additional two dimensional SAXS patterns obtained for **2Si11OCB** prepared both in flow and in a batch reaction.

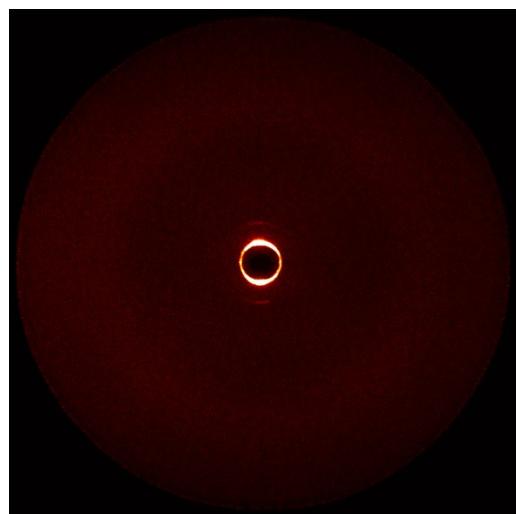


Figure SI-1: Unaligned SAXS pattern of the SmA phase of **2Si11OCB** prepared in flow at 30 °C

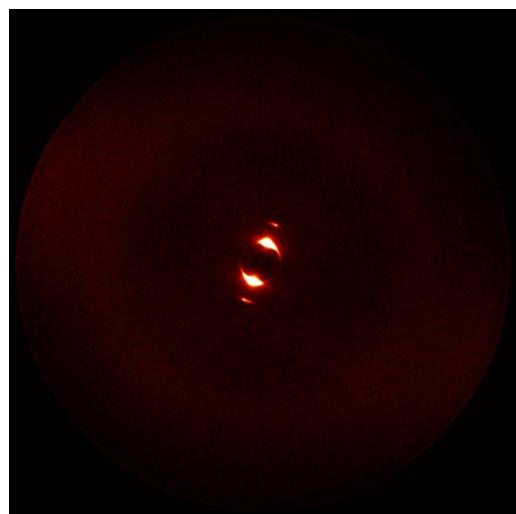


Figure SI-2: Partially SAXS pattern of the SmA phase of **2Si11OCB** prepared in batch at 31 °C

6. References

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3. R. J. Mandle, E. J. Davis, C. C. A. Voll, D. J. Lewis, S. J. Cowling and J. W. Goodby, *J Mater Chem C*, 2015, **3**, 2380-2388
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