Supporting information

Development of polar order in a bent-core liquid crystal with a new sequence of two orthogonal smectic and an adjacent nematic phase.

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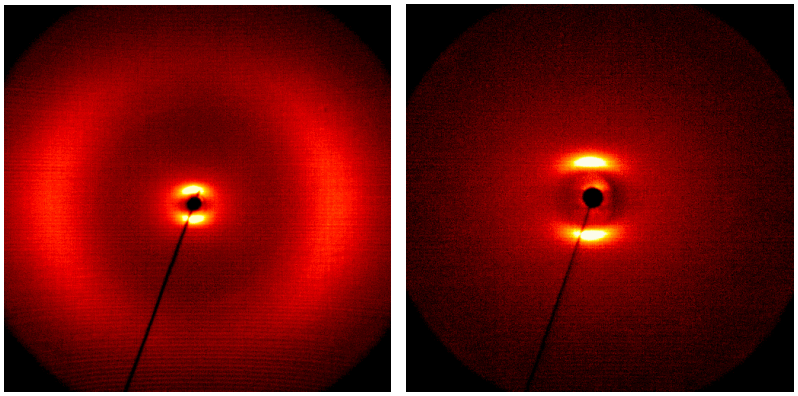
1. Synthetic procedure and analytical data

All the starting materials were obtained form either Aldrich, Alfa Aesar or Fluka companies and were used as received. Solvents were purified and dried by standard procedure prior to use. The crude samples were purified by column chromatographic technique using silica gel (230-400 mesh) as a stationary phase. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselgel 60, F254).

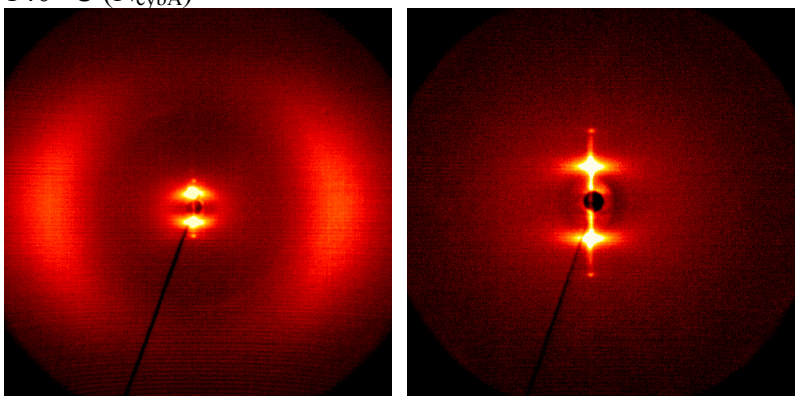
4-[4-(Undec-10-enyloxy)phenoxycarbonyl]benzoic acid (**2**) was obtained in analogy to the procedure reported previously[S1]; ^{1}H-NMR (DMSO-d6, 400MHz): δ 8.31 (d, 2H, *J* = 8.4, Ar-H), 8.23 (d, 2H, *J* = 8.4, Ar-H), 7.30 (d, 2H, *J* = 9.2, Ar-H), 7.10 (d, 2H, *J* = 9.2, Ar-H), 5.91 (m, 1H, C***H***=CH$_2$), 5.06 (m, 2H, CH=C***H$_2$***), 4.08 (t, 2H, *J* = 6.4, OCH$_2$), 2.01 – 1.36 (m, 16H, CH$_2$ × 8).

Synthesis of bent-core compound 1: The cyanoresorcinol monoester (**3**)[S2] (350 mg, 0.76 mmol, 1 equiv.), 4-[4-(undec-10-enyloxy)phenoxycarbonyl]benzoic acid (**2**)[S1] (312 mg, 0.76 mmol, 1 equiv.) and catalytic amount of DMAP were dissolved in dry CH_2Cl_2 (20 mL). *N,N'*-dicyclohexylcarbodiimide (DCC) (240 mg, 1.14 mmol, 1.5 equiv) was added and the solution was stirred for 10 h at room temperature. The reaction mixture was filtered and then evaporated, followed by column chromatography (230-400 silica gel) using CH_2Cl_2 : *n*-hexanes (3:7) as an eluent and further purified by crystallization from CH_2Cl_2/EtOH (1:9) to afford **1** colorless solid, 450 mg, 69% yield; ^{1}H-NMR ($CDCl_3$, 400MHz): δ 8.38 (d, 2H, *J* = 8.8, Ar-H), 8.35 (d, 2H, *J* = 8.6, Ar-H), 8.32 (d, 2H, *J* = 8.2, Ar-H), 8.28 (d, 1H, *J* = 8.0, Ar-H), 8.23 (d, 2H, *J* = 8.4, Ar-H), 8.14 (d, 1H, *J* = 6.4, Ar-H), 7.80 (d, 1H, *J* = 8.4, Ar-H), 7.40 (m, 4H, Ar-H), 7.14 (d, 2H, *J* = 8.8, Ar-H), 6.98 (d, 2H, *J* = 8.8, Ar-H), 5.83 (m, 1H, C***H***=CH$_2$), 4.99 (m, 2H, CH=C***H$_2$***), 3.95 (t, 4H, *J* = 6.4, OCH$_2$ × 2), 2.04 – 1.29 (m, 24H, CH$_2$ × 12), 0.91 (t, 3H, *J* = 6.8, CH$_3$); ^{13}C NMR (100 MHz, $CDCl_3$):164.22, 164.17, 163.89, 157.05, 144.03, 141.55, 139.21, 133.96, 132.45, 132.43, 132.25, 132.00, 131.39, 130.41, 130.56, 126.58, 122.42, 122.39, 122.34, 122.22, 122.18, 117.40, 115.19, 115.12, 114.43, 114.11, 102.42, 68.45, 68.40. 33.78, 32.36, 31.52, 30.75, 29.74, 29.49, 29.40, 29.34, 29.24, 29.09, 29.03, 28.91, 26.20, 26.01, 25.64, 25.34, 25.16, 24.51, 22.56, 14.00; EA, calc. for $C_{52}H_{53}O_{10}N$, 851.98 g/mol:, C 73.31, H 6.27, N 1.64, found: C 73.01, H 6.22, N 1.63.

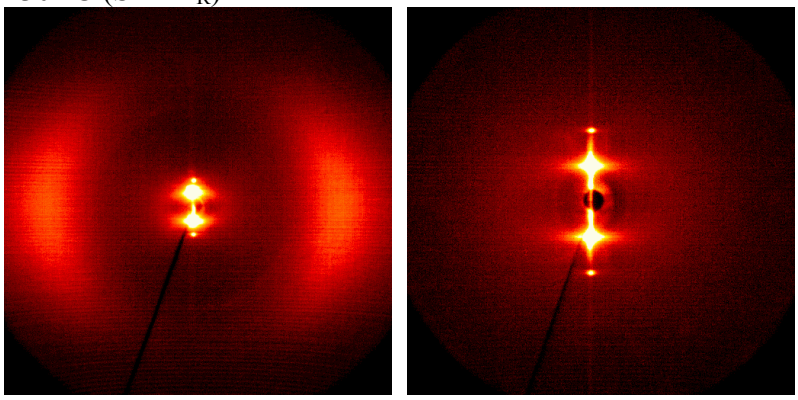
2. Additional XRD data



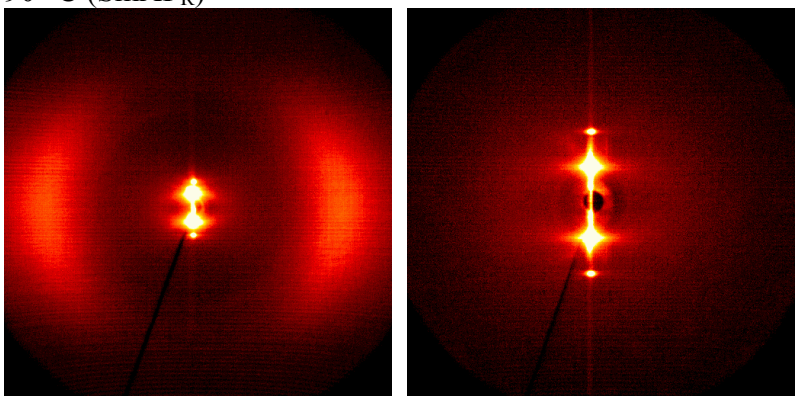
140 °C (N_{cybA})



130 °C ($SmAP_R$)



90 °C ($SmAP_R$)



70 °C ($SmAP_A$)

Figure S1: XRD patterns at different temperatures, wide-and small angle scattering at the left, small angle region at the right.

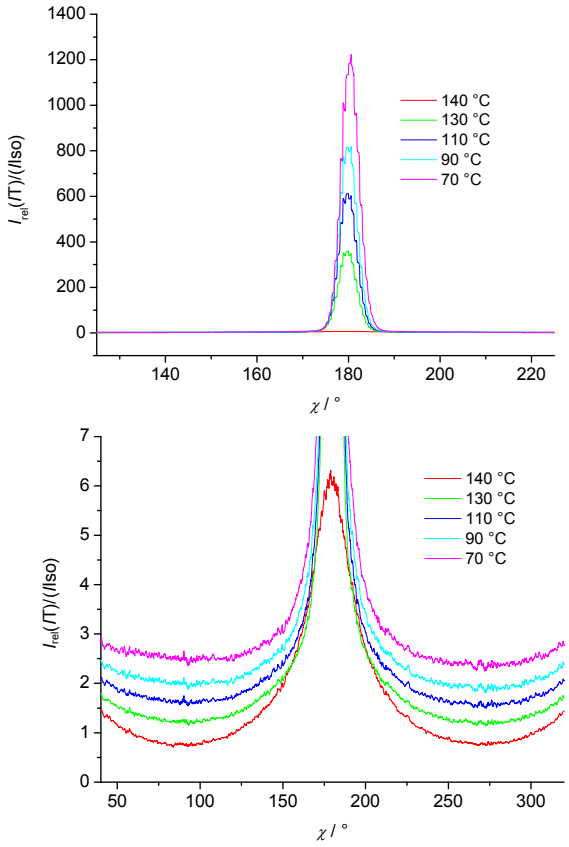


Figure S2. χ-scans over the small angle scattering (2θ = 1-3°) at different temperatures, confirming the absence of a splitting.

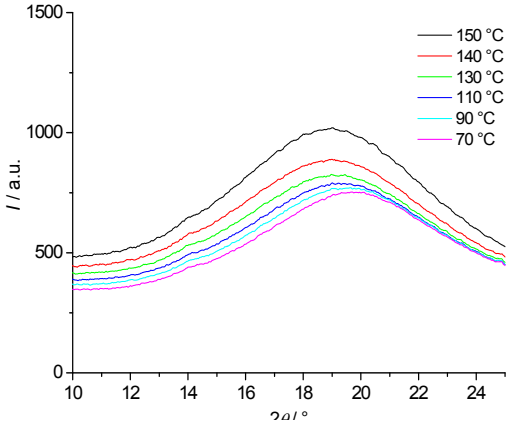


Figure S3. θ-scans over the wide angle scattering at different temperatures.

References

S1 C. Keith, M. Prehm, Y. P. Panarin, J. K. Vij, and C. Tschierske, *Chem Commun*. 2010, **46**, 3702.
S2 C. Keith, A. Lehmann, U. Baumeister, M. Prehm and C. Tschierske, *Soft Matter*, 2010, **6**, 1704.