PAPER

Intercalated soft-crystalline mesophase exhibited by an unsymmetrical twist-bend nematogen†

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A number of new states of matter have been reported in recent years for liquid crystal dimers, most notably the twist-bend nematic phase which exhibits spontaneous breaking of symmetry through the emergence of chiral structures in an achiral fluid. In this communication we report on an unsymmetrical liquid crystal dimer that exhibits a transition from the spontaneously chiral twist-bend nematic phase into a novel smectic liquid crystal phase.

Introduction

The observation of a lower temperature mesophase lacking lamellar or positional molecular order (*i.e.* a nematic-like mesophase),[1] later identified as the 'twist-bend nematic' phase (N_{TB}),[2–10] has motivated a great deal of study into the properties of this intriguing state of matter by a wide range of techniques.[11–18] In a typical nematic phase rod-like molecules are orientated, on average, parallel to one another along a vector termed the director, *n* (Fig. 1a). In the case where the rod-like molecules are chiral the structure twists forming a left or right-handed helix (Fig. 1c). Although the helicoidal model of the N_{TB} phase, proposed independently by Meyer and Dozov and depicted in Fig. 1b,[19,20] is supported by experimental data, alternate models have also been proposed.[21–24] The observation of direct isotropic liquid to N_{TB} phase transitions, first reported for a mixed dimer/chiral-dopant system[25] and then later in pure materials,[26] providing a challenge for future theoretical treatment.

That the N_{TB} phase has been observed in bent-core systems,[8] ether linked dimers,[27,28] trimers,[29–32] oligomers[33] and even polymers[34] hints at this mesophase being far more universal than was perhaps first thought. A comprehensive structure property relationship remains elusive despite the ever growing number of compounds reported in the literature to exhibit this state of matter.[35–44] The observation of spontaneous breaking of mirror symmetry in the twist-bend nematic phase leads to the emergence of helical nano-structures in an achiral fluid;[10,45,46] questions concerning the mechanism of this phenomenon are of fundamental importance to a range of scientific disciplines,[47–51] and are likely to motivate further study into the N_{TB} phase (and analogous states of matter such as splay-bend modulated phases[52] or possible smectic
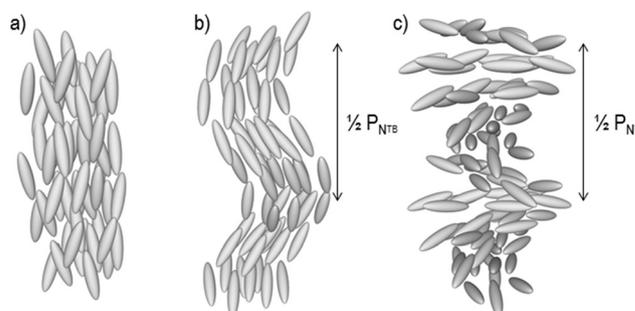
twist-bend mesophases) for some time to come. Possible applications of dimers and oligomesogens that exhibit twist-bend phases include tuneable selective reflection, presenting another motivation for study of these fascinating materials.[53,54]

In this work we report an unsymmetrical methylene linked bimesogen containing one polar rigid aromatic unit and one 'apolar' unit. In addition to exhibiting nematic and twist-bend nematic mesophases this material also exhibits what we believe to be a previously unobserved smectic mesophase.

Experimental

Compound **1** was synthesised, as shown in Scheme 1, *via* the EDAC/DMAP mediated Steglich esterification between (4-(9-(4-hydroxyphenyl)nonyl)phenyl 4-cyanobenzoate), prepared as described previously,[29] and 4-pentyloxybenzoic acid.

Small angle X-ray scattering was performed on a Bruker D8 Discover using copper Kα radiation (λ = 0.15418 nm) equipped with a temperature controlled, bored graphite rod furnace. Patterns were collected on a VANTEC 500 area detector (2048 × 2048 pixels) set at a distance of 121 mm from the

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ce02123a
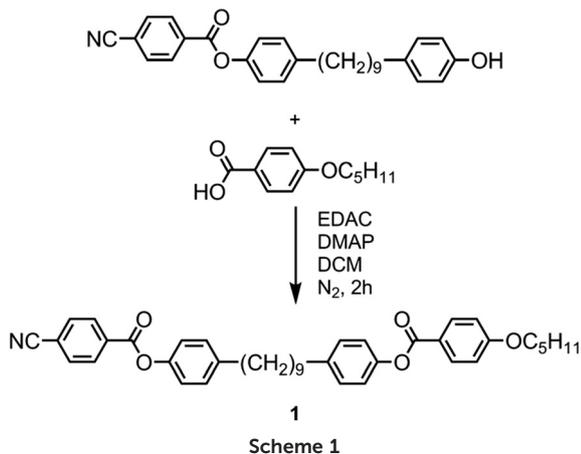

Fig. 1 Local structures and director arrangement in (a) the uniaxial nematic phase, (b) the oblique helicoidal model of the N_{TB} phase and (c) the chiral nematic phase.

Scheme 1

sample, allowing simultaneous observation of wide angle and small angle scattering data. Computational chemistry was performed at the B3LYP/6-31G(d) level of DFT in Gaussian G09 revision e01,[55] with Gaussian output files rendered using Qutemol.[56] Full experimental details, including chemical characterisation and descriptions of instrumentation used, are available in the ESI† to this article.

Results

The transition temperatures along with the associated enthalpies and entropies of transition for compound **1** are given in Table 1. Transition temperatures, along with associated enthalpies and entropies were determined by differential scanning calorimetry at a heat/cool rate of 10 °C min^{-1} and are the mean of 10 cycles; standard deviations are given in parenthesis. The associated enthalpies and entropies of transition are not especially characteristic and are of a comparable magnitude to those reported previously for methylene linked phenylbenzoate dimers.[38,39,41,43] Both the onset temperature and associated enthalpy of the SmX–N$_{TB}$ transition temperature were found to be invariant when subjected to different heat/cool rates in the range of 1–20 °C min^{-1}, indicating that the transition is not dependent on kinetic processes; contrast this to the N$_{TB}$–N transition which was previously shown to show a strong dependence on the heat/cool rate.[9] The magnitude of the enthalpy (Table 1) associated

with this transition to the SmX phase suggests that the phase is highly ordered. Whereas crystalline phases show thermal hysteresis (*i.e.* supercooling), liquid-crystalline or soft-crystalline states of matter do not, and cannot typically be supercooled more than a few tens of mK. In order to demonstrate that the SmX phase is a *bona fide* liquid-crystalline (or possibly soft-crystalline) phase a DSC study was performed whereby the sample was first heated into the isotropic liquid, then cooled into the SmX phase and reheated back into the N$_{TB}$ phase. The lack of thermal hysteresis (Fig. 2) confirms that the transition into the SmX phase is not simply a recrystallization event, but rather a transition to a mesophase.

On cooling from the isotropic liquid it is trivial to identify the first mesophase as the nematic, based on its fluidity and characteristic *schlieren* texture. The identification of the mesophase immediately below the nematic as the twist-bend nematic is also straightforward due to its characteristic optical textures (Fig. 3) and the shape of the peak obtained in DSC thermograms (Fig. 2).[9] As discussed by Zhu *et al.*,[13] small-angle X-ray scattering can be used to discriminate between the experimentally observed N$_{TB}$ phase and the theoretically predicted splay-bend nematic, N$_{SB}$, as the electron density modulation in the former does not lead to Bragg scattering whereas it is expected to in the later. We observe no Bragg scattering at Q values as low as 0.06 in the phase immediately below the nematic (Fig. SI-6 in the ESI†) and so we can be confident in our assignment of this mesophase as the twist-bend modulated nematic.

As shown in Fig. 3(a) and (b) a number of crossover points, reminiscent of braids in rope, were seen in the aligned rope texture of the N$_{TB}$ phase, with the 'length' of the rope defects being parallel to the rubbing direction of the cell. Insertion of a λ waveplate lead to different colours in adjacent stripes (Fig. 3b), indicating that the optical azimuthal angle alternates between stripes.[21] Additionally clear striations can be seen within the stripes (Fig. 3b), these being are offset from the length of the rope defects by an average of ±30° with the direction alternating in adjacent stripes. Further cooling of compound **1** below 56.1 °C leads to a reversible (see DSC trace in Fig. 2) transition from the N$_{TB}$ phase into to the unknown mesophase, denoted SmX presently. When confined in a 5 ± 0.1 μm cell with antiparallel buffed polyimide alignment layers the N$_{TB}$ phase of **1** gives a well

Table 1 Transition temperatures (°C), associated enthalpies of transition (kJ mol^{-1}) and dimensionless associated entropy of transition ($\Delta S/R$) for compound **1**. Note, the SmX–N$_{TB}$ transition is monotropic, *i.e.* it occurs below the melting point of the sample. Enthalpies and entropies were are the mean of 10 cycles as determined by DSC at a heat/cool rate of 10 °C min^{-1}, with standard deviations given in parenthesis. Tabulated DSC data is presented in the ESI

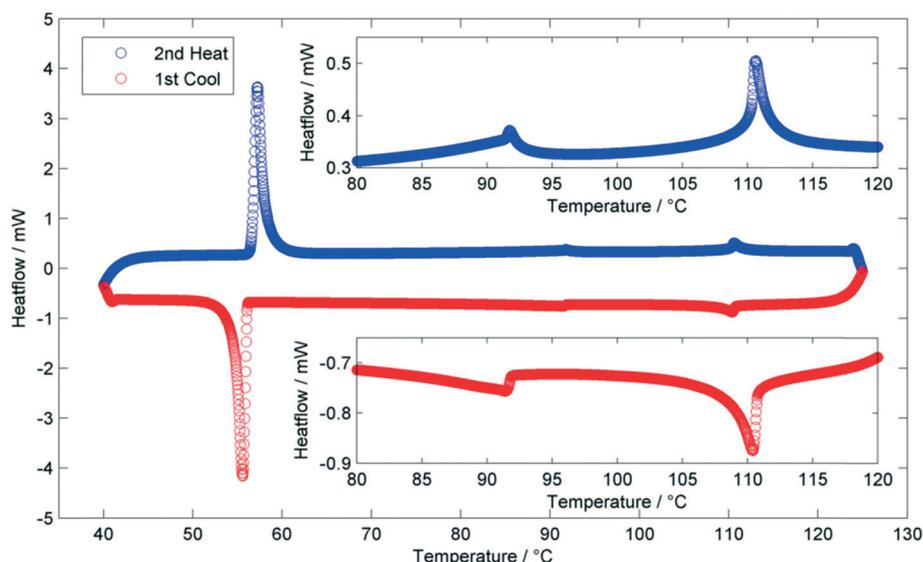|	MP	SmX–N$_{TB}$	N$_{TB}$–N	N–Iso
T (°C)	81.4 (0.027)	56.1 (0.009)	91.9 (0.007)	110.8 (0.007)
ΔH (kJ mol^{-1})	35.83 (0.194)	10.30 (0.004)	0.31 (0.002)	0.61 (0.002)
$\Delta S/R$	12.15 (0.065)	3.76 (0.001)	0.10 (0.001)	0.19 (0.001)

Fig. 2 DSC thermogram of compound **1** obtained at 10 °C min^{-1} on the first cooling cycle (red circles) and second heating cycle (blue circles), with two expansions showing the region between 80–120 °C which contains the N_{TB}–N and N–Iso transitions.
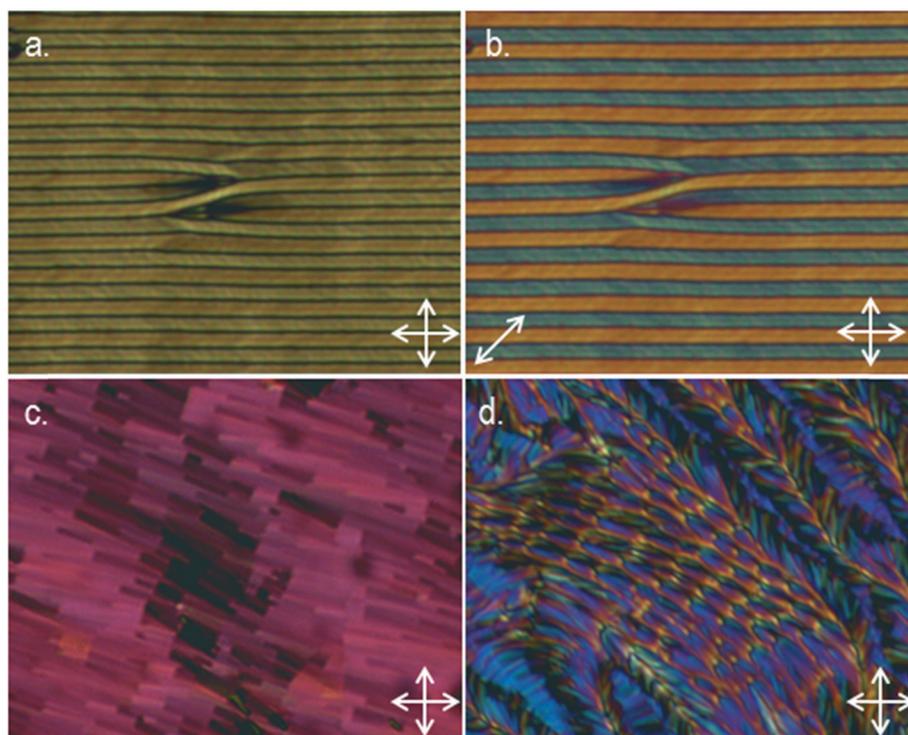

Fig. 3 Photomicrographs (×100) of the twist bend phase of compound **1**. (a) The well-aligned rope texture of the N_{TB} phase at 86.5 °C confined in a 5 ± 0.1 μm cell with antiparallel buffed polyimide alignment layers, (b) the same conditions as (a) but with a λ waveplate inserted, (c) the 'blocky' texture of the N_{TB} phase at 89.4 °C in a sample on untreated glass, (d) parabolic defects and the 'blocky' texture on untreated glass at 87.3 °C.

aligned rope texture (Fig. 3a and 4a), and at the phase transition the rope texture is partially preserved, either through paramorphosis or this being a characteristic texture of the SmX phase, however the birefringence changes markedly (Fig. 4b and c). If the sample is reheated across the SmX–N_{TB} phase transition then the original rope texture returns (Fig. 4d), however, the interface between adjacent stripes now

appear buckled and the striations set at 30° to the rope length, which persist after cooling into the SmX phase, are more pronounced than they are in the virginal texture (compare Fig. 4a–d).

The behaviour of **1** in a cell was studied under applied electric fields. In the nematic phase at 95 °C a Fréedericksz transition could be observed at low frequency (<50 Hz) with

an applied field of above 1 V_{RMS}. The sample was cooled into the N_{TB} phase to 85 °C where it was possible to observe some form of electrooptic response at an applied voltage of 60 V_{RMS}. With a higher applied voltage (100 V_{RMS}) the sample was reversibly into a reasonably uniform homeotropic state, removal of the field lead to the regrowth of the rope-texture over a period of minutes. When cooled into the SmX mesophase we did not observe any electrooptic response at amplitudes of up to 100 V_{RMS} across a range of frequencies (1 mHz to 100 KHz). Therefore we conclude that the SmX phase does not exhibit any electrooptic behaviour in the voltage regime used in this work.

We next elected to study the nematic, N_{TB} and SmX mesophases of **1** by small angle X-ray scattering using copper K alpha radiation on magnetically aligned samples. The nematic phase was well aligned by the external magnetic field and gave the expected diffuse scattering pattern shown in Fig. 5a. This alignment was partially lost on entering the N_{TB} phase (Fig. 5b). For the nematic phase the orientational order parameter P_2 (Fig. 5c) was calculated as follows: integration of the wide-angle scattering as a function of the angle χ followed by averaging of the two signals gave Fig. 5d, from this the order parameter could be calculated according to Davidson

et al.[57] The alignment of the N_{TB} phase was not sufficient to obtain order parameters, however in the nematic phase the order parameter increases from a value of 0.30 to a maximum of 0.39, these values being comparable to those measured for the nematic phase of methylene linked bimesogens.[11]

As shown in Fig. 6, in the nematic and twist-bend mesophases only diffuse scattering peaks are seen, with a single wide angle peak and a single small angle peak. These scattering peaks corresponding to the side-to-side and end-to-end separation of molecules respectively, however, as the nematic and N_{TB} phases lack positional ordering the small angle peak occurs at roughly $\frac{1}{2}$ of the molecular length (37.2 Å at the B3LYP/6-31G(d) level of DFT). Upon cooling into the SmX phase the diffraction pattern changes markedly in both the small and wide angle regions. The small-angle scattering peak grows in intensity and becomes significantly more defined, with the average full-width at half-maximum (FWHM) being an order of magnitude larger in the N_{TB} phase than in the SmX phase (0.348 Å^{-1} and 0.035 Å^{-1} respectively). The out-of-plane correlation length (ξ, defined as $\xi = 2\pi/\Delta Q$ increases from an average of 18.1 Å in the N_{TB} phase to 182.1 Å in the SmX mesophase. The SmX phase also exhibits an scattering peak at $Q \approx 0.17$ Å^{-1} ($d \approx 3.7$ nm) that is both more
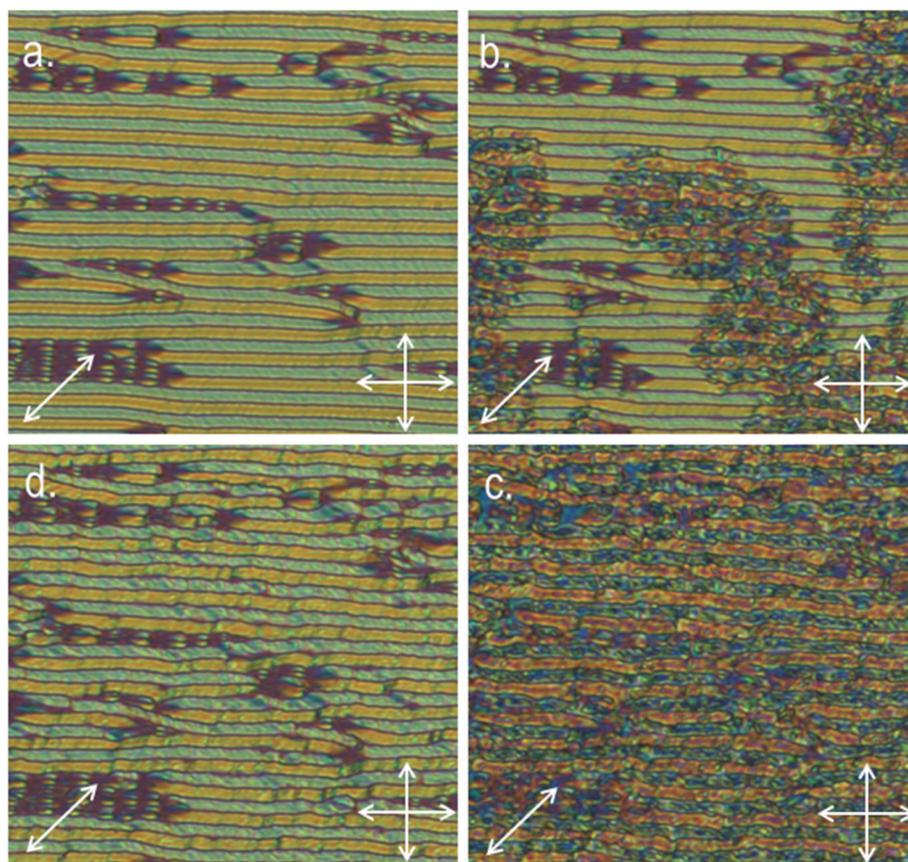
Fig. 4 Photomicrographs, taken with a λ waveplate inserted, of compound **1** (×100) confined in a 5 ± 0.1 μm cell with antiparallel buffed polyimide alignment layers. The rope texture of **1** at 60.0 °C (a), the onset of the SmX–N_{TB} transition at 56.0 °C (b), the rope texture of the SmX phase at 54.5 °C (c), the rope texture of the N_{TB} phase restored after heating through the SmX–N_{TB} transition, 59.2 °C (d). Photomicrographs correspond to approximately the same area of the sample.
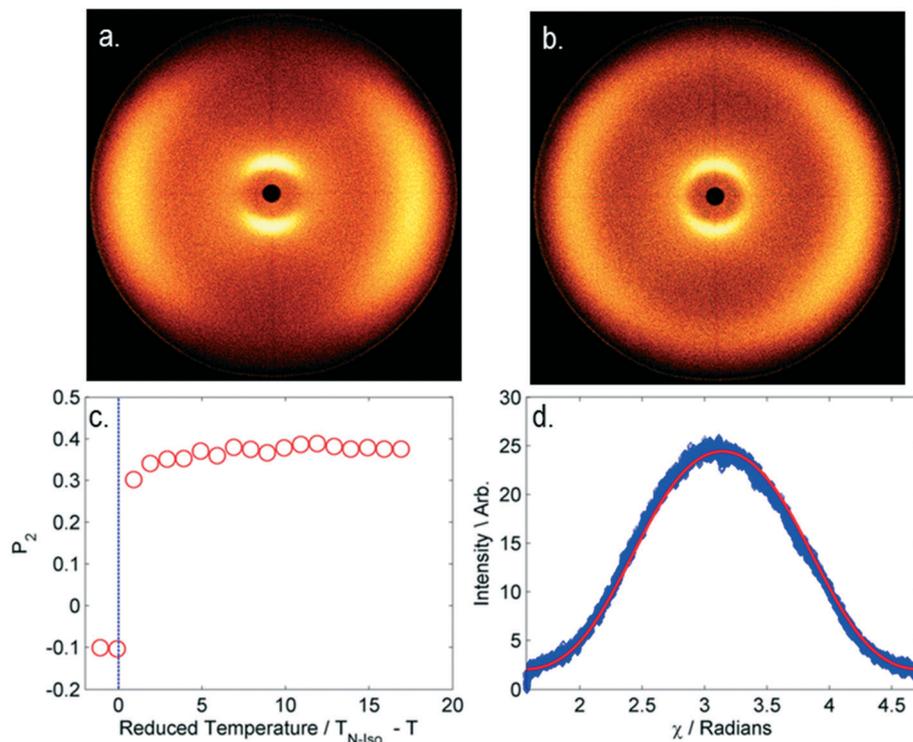
Fig. 5 Two dimensional small-angle X-ray scattering patterns for the nematic phase of **1** at 109 °C (a), the N_{TB} phase of **1** at 89 °C (b), plot of the order parameter P_2 vs. reduced temperature (c), plot of scattered X-ray intensity (blue diamonds) fitted using as described by Davidson et al. (red line) as a function of the angle χ for the wide-angle ($2\theta = 15$–25) region of compound **1** in the nematic phase at 99 °C (d).

diffuse and less intense than the larger of the two small angle peaks ($Q \approx 0.34$ Å^{-1}, $d \approx 2.0$ nm).

The diffuse wide-angle peak present in the twist-bend phase sharpens and splits into two peaks that are not fully resolved at the SmX–N_{TB} transition. The increase in scattered intensity in this region at the SmX–N_{TB} phase transition is further evidence for the large increase in the in-plane correlation length. The wide-angle scattering data, which corresponds to the average lateral separation between molecules, was deconvoluted into two Lorentzian peaks with maxima (Fig. 7) at $Q = 1.3296$ Å^{-1} ($d \approx 4.73$ Å) and $Q = 1.4114$ Å^{-1} ($d \approx 4.45$ Å). In the more ordered SmX phase we propose that there are two different average lateral intermolecular distances, one for the polar phenyl 4-cyanobenzoate unit and one for the 'apolar' phenyl 4-pentyloxybenzoate group.

From experimental data it is known that the SmX phase is intercalated, with a layer spacing of $\frac{1}{2}$ the molecular length (i.e. d/l ratio of 0.5). The in-plane correlation length is relatively large (average of 18 nm) and although we do not observe evidence of hexagonal close packing of molecules this cannot be excluded as the sample is not aligned during SAXS on the SmX phase (Fig. 6b). Assuming the polar phenyl 4-cyanobenzoate units form antiparallel correlated pairs with adjacent polar units, mirroring what is observed in calamitic systems such as 8CB,[58,59] interdigitated smectic layers will result. The antiparallel correlation between adjacent polar phenyl 4-cyanobenzoates is possibly also the origin of the two distinct spacings seen in the wide angle X-ray scattering ex-

periment (Fig. 7). Additionally this mixed polar/apolar molecular structure will lead to segregation of polar and apolar mesogenic units into adjacent layers. We propose that the scattering peak in the small angle at $Q \approx 0.17$ Å^{-1} ($d \approx 3.7$ nm) is the distance between two 'like' (e.g. polar–polar and apolar–apolar) layers, which is roughly the molecular length, while the layer spacing at $Q \approx 0.34$ Å^{-1} ($d \approx 2.0$ nm) is the average layer spacing of the two layers and is approximately $\frac{1}{2}$ of the molecular length.

Conclusions

We have prepared and characterised a novel unsymmetrical liquid crystalline dimer which consists of one polar and one non-polar mesogenic unit. In addition to exhibiting the highly topical twist-bend nematic phase this compound also exhibits a smectic mesophase. Transitions from the N_{TB} phase to smectic mesophases still remain rare (we are aware of only a handful of examples) and present rich opportunities for physical study and theoretical treatment of both the local structure, and the processes occurring at the phase transition between, these two mesophases. We note that the lower-temperature phase observed in compound **1** appears unique – based on small angle X-ray scattering data we propose that the local structure is lamellar, with alternating blocks of 'polar' and 'apolar' mesogenic units. It is believed that this mesophase arises due to the strong intermolecular self-association of nitrile units. With this point in mind it seems
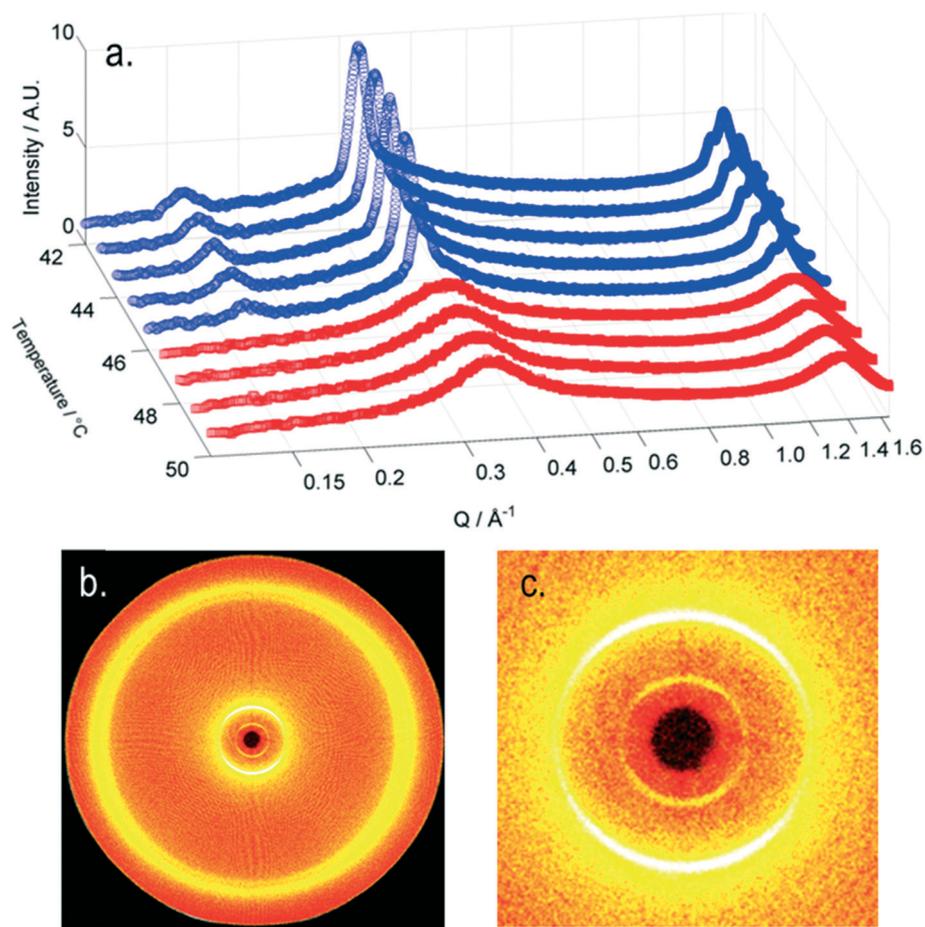
Fig. 6 Small angle X-ray scattering data for compound **1**. (a) Plot of diffraction intensity (arbitrary units) *versus* Q ($Å^{-1}$) as a function of temperature (42–50 °C, 1 °C steps), with red circles corresponding to the N_{TB} phase and blue circles to the SmX phase. (b) two dimensional diffraction pattern of the SmX mesophase exhibited by **1** at 47 °C and (c) an expansion of the two-dimensional diffraction pattern showing scattering at small angles ($2\theta = 3$–10, $Q = 0.1$–0.6 $Å^{-1}$).
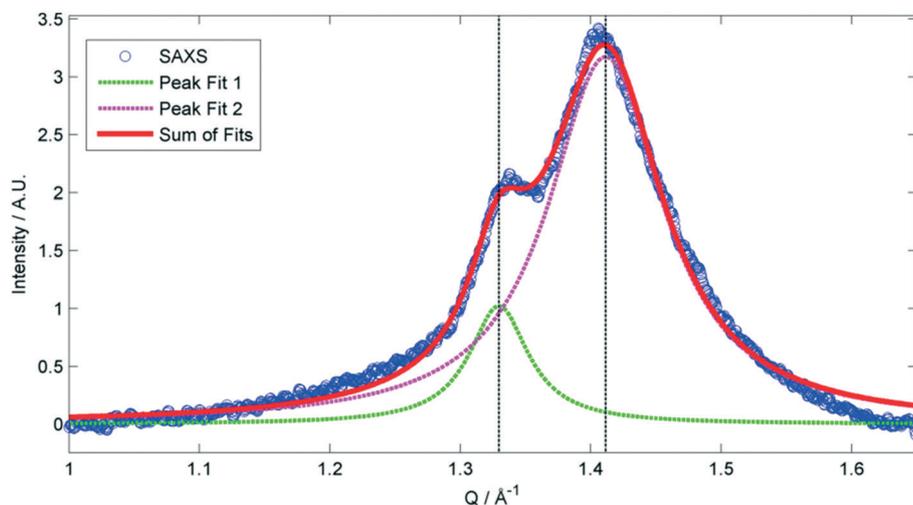
Fig. 7 Plot of scattered X-ray intensity for compound **1** in the SmX mesophase at 50 °C between Q 1.0 and Q 1.65. The overlapping peaks were deconvoluted into two Lorentzian peaks (dashed lines, I_{max} at $Q = 1.3296$ $Å^{-1}$ and $Q = 1.4114$ $Å^{-1}$ respectively) which sum to give the solid red line, giving an R^2 value of >0.99.

logical that other groups prone to self-association will also support the formation of this mesophase. Studies of the phase by microscopy, calorimetry, SAXS and under applied fields indicate it is soft-crystalline in nature; however the phase does not exhibit thermal hysteresis and thus can be classified as a mesophase rather than a true crystalline state of matter.

Acknowledgements

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