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Self-assembled toron-like structures in inverse nematic gels[†]

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A novel form of nematic gel (N-gel) wherein bright flower-like domains (BFDs) rich in gelator fibres are embedded in a matrix of liquid crystal (LC) molecules has been reported. These gels which we denote as inverse N-gels are unlike typical N-gels in which the LC is encapsulated within an aggregated network of gelator molecules. The self-organization of the helical gelator fibres within the BFDs leads to the creation of localized toron-like structures that are topologically protected due to their skyrmion director profile. Optical and confocal microscopy have been used to deduce the LC director configuration, in order to understand possible intermolecular interactions that can lead to the formation of the twisted structures and the inverse N-gels.

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1 Introduction

Liquid crystal (LC) physical gels are usually formed by the encapsulation of the LC into an aggregated fibrous network induced by low molecular weight organo gelators (LMOGs), via non-covalent interactions such as hydrogen bonding, dipoledipole and $\pi - \pi$ interactions.¹ The self-assembly of LMOGs in LCs can lead to micro or nanostructured functional anisotropic gels. The mechanism and efficiency of the gelation process depends inherently on the chemical nature of the constituents. LC-gels formed with thermotropic LCs belong to a distinct class and exhibit thermoreversible phase transitions pertaining to isotropic (Iso) to LC and LC to LC-gel states. The nature of the LC and its self-assembling property coupled with that of the fibrous structures often leads to interesting types of phase separation. The molecular orientation in the LC phase can also influence the arrangement of the fibrous aggregates.² LC-gels are known to exhibit new and improved thermal, optical and electrical properties that are tunable. A few examples are (a) Nematic (N) gels (N-gels) formed by the self-assembly of hydrogen-bonded gelators and thermotropic NLCs composed of rod-like (R) molecules, that show improved electro-optic response³ (b) LC-gels composed of discotic LCs which exhibit enhanced hole mobilities⁴ and (c) photoresponsive LC-gels formed by the combination of LCs with hydrogen-bonded gelators possessing photoswitchable azobenzene moieties.⁵

LC-gels are mainly classified as Type I gels in which the transition temperature ($T_{\rm sol-gel}$) > ($T_{\rm iso-LC}$) and Type II gels in which ($T_{\rm sol-gel}$) < ($T_{\rm iso-LC}$).³ While Type I gels form randomly dispersed fibrous networks, the alignment of fibres in Type II gels can be influenced by the alignment of the LC. However, N-gels rarely form distinct and large domains with ordered arrangements of LC-rich and fibre-rich regions. More recently, a new form of self-ordering of gelator fibres resulting in a grating like pattern consisting of LC-rich and fibre-rich regions has been reported in a N-gel composed of the LC E7 and the organogelator 12-HSA.⁶

Gelation has also been obtained with lyotropic LCs (LLCs) and detailed investigations have been carried out on sol-gel transitions, phase microstructures and rheological behaviour.⁷⁻⁹ Depending on the LLC, both organo and hydrogelators are known to promote gelation.¹⁰ LLC-gels are also known to exhibit examples of orthogonal self-assembly¹¹⁻¹⁴ and can have applications ranging from drug delivery to the formation of templates for highly ordered nanostructured materials.

The NLC is characterized by an apolar director (n), about which the symmetry axes of the molecules are aligned. Topological defects occurring in NLCs are associated with the departure from N order and are a necessary requirement for attaining an equilibrium state when foreign particles are inserted into the LC and their surfaces locally align the LC in a preferred direction. Topological defects are also generated while rapidly cooling the LC across the Iso to N phase transition. A variety of defects occurring in LCs are easily revealed under the optical microscope due to the deviations of the director field initiated by them. The formation of defects can be influenced by boundary conditions, external stimuli, elastic constants or surface conditions of suspended colloidal particles. In spherical N droplets,

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constraints imposed by the surface anchoring conditions lead to a variety of defects ranging from point defects and surface disclinations to more intricate structures.^{15,16} Normal or homeotropic boundary orientation of the N director on the surface leads to a radial hedgehog defect in its interior. On the other hand, in a droplet with planar or degenerate anchoring the point defects remain at the surface because of the tangential boundary conditions and can result in a pair of surface defects called boojums. The complexity of the defects is further enriched by the introduction of chirality in the system. Chiral N (N*) droplets have been found to exhibit analogues of 2D skyrmions and torons¹⁷ and topological defect constellations.¹⁸ A variety of solitonic structures including torons and hopfions have also been observed.¹⁹

Evidence has now been shown for a new type of gelation involving LCs, wherein fibres formed by gelator molecules are mainly confined within micrometer sized bright flower-like domains (BFDs) dispersed in the N phase. This is contrary to the usual N-gels where the LC is confined within the fibre assemblies formed by gelator molecules. We therefore denote the gels reported here as inverse N-gels because in this case it is the fibre-rich regions that are surrounded by an LC. Under the polarizing optical microscope (POM) the BFDs appear somewhat similar to spherical N droplets dispersed in the Iso phase. The LC director configuration within the BFDs is found to be influenced by the mutual orientation of the gelator fibres and the N director in the surrounding region. The BFDs can also have anisotropic shapes or exhibit surface faceting and sometimes contain a collection of defect-like cores. Furthermore, in homeotropic cells, the chiral gelator fibres within the BFDs induce toron-like (bubble-like) structures, that seem to be topologically protected. Based on the experimental evidence obtained from optical and confocal microscopy, reasons that can account for the formation of inverse N-gels and the BFDs will be discussed.

2 Experimental

Materials and methods

The binary system used in the study consists of the two liquid crystalline compounds 4'-butyl-4-heptyl-bicyclohexyl-4-carbonitrile (CCN-47) and 4,4'-dipentyl-bicyclohexyl-4-carbonitrile (CCN-55) (Nematel, GmbH & Co., Germany). The molecules corresponding to both these compounds have an identical core with a transverse cyano group but differ in the lengths of their terminal alkyl chains. While CCN-47 exhibits the phase sequence N and smectic-A (SmA) phases, CCN-55 exhibits N and smectic-B (SmB) phases. The molecular structures and phase transition temperatures are shown in Fig. 1. A specific mixture CCN-mn consisting of CCN-47 and CCN-55 in the ratio of 1:1 which exhibits only a N phase from 61 °C down to room temperature (\sim 25 °C) has been used in the studies. Nematic gels (N-gels) were prepared by the addition of the gelator 12-hydroxystearic acid (12-HSA) (Tokyo Chemical Industry Co.) to the mixture CCN-mn. The LC-gelator mixture was first homogenized in the isotropic phase and subsequently cooled to



Fig. 1 Molecular structures and phase transition temperatures (in $^\circ\text{C}$) of the liquid crystalline compounds used in the study.

form the N-gels. The minimum concentration of 12-HSA required to form a gel is 0.5 wt%. However, in this case it takes a few days to form the gel. The optimum concentration was 0.75 wt% of 12-HSA, in which case the gelation occurs almost immediately on cooling from the N phase. The N-gels were found to be thermally reversible and did not flow when the sample cup was turned upside down, which confirms the formation of a strong gel.

The experimental studies described below have been carried out for mixtures with varying concentrations of the gelator, henceforth designated as [CCN-mn (*X*)] where *X* denotes the wt% of 12-HSA. For Fluorescence Confocal Polarizing Microscopy (FCPM) studies, a low concentration (0.1 wt%) of the N,N'-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-

perylenedicarboximide (BTBP) fluorescent dye dissolved in acetone was doped into the [CCN-mn (X)] samples. The acetone was evaporated at room temperature from the LC gelator mixture overnight and then heated to 80 °C for two hours. As the CCN-mn mixture exhibits a very low birefringence of 0.03, it is suitable for FCPM as it minimizes artefacts due to defocussing and polarization guiding of both excitation and detected light.¹⁷ BTBP was particularly chosen as the transition dipole associated with its molecules align along the LC director.

3 Results

Differential scanning calorimetry

Thermal analysis was carried out using DSC in particular for [CCN-mn (*X*)] mixtures with X = 0.75, 1 and 1.5 wt% of 12-HSA. Fig. S1(a) (ESI[†]) shows the DSC scans obtained on cooling from the Iso phase, as this ensures better homogenization of the sample. It is observed that as X increases, the Iso to N transition temperature (T_{IN}) decreases, whereas the temperature at which N transforms to N-gel (T_{N-Ngel}) increases (Fig. S1(b), ESI[†]). This shows that the addition of the gelator essentially decreases the N range.

Optical microscopy

Textural observations were performed under the POM on [CCNmn (*X*)] taken in different types of cells (Instec Inc) having a thickness of 9 μ m with substrates pre-treated to impose a homeotropic or planar alignment of the N director.

Homeotropic alignment

As the sample [CCN-mn (0.75)] taken in a cell treated for homeotropic alignment is cooled from the Iso phase, a well aligned N phase is formed at 61 °C and the sample appears completely dark



Fig. 2 Optical textures of [CCN-mn (0.75)] taken in a homeotropic cell viewed between crossed polarizers in the N-gel phase at 30 °C. (a) BFDs obtained in the first cooling cycle. The inset shows an enlarged view of a single BFD with a defect-like core (b) BFDs obtained after repeated thermal recycling, (c) enlarged view of a single BFD as in (b) with sharp dark brushes emanating from defect-like cores (indicated by red arrows), polarizers at 0 and 90°, (d) same BFD as in (c) with polarizers rotated by 45°. Scale bar corresponds to 100 μ m in (a) and (b) and 25 μ m in (c) and (d).

between crossed polarizers. In the first cooling cycle, a large number of small BFDs with a defect-like core at the centre and four sharp dark brushes can be observed (Fig. 2(a)). These appear at the temperature corresponding to the transition from the N to N-gel phase identified by the second peak in the DSC thermogram. The defect-like dark cores present at the centre of the BFDs appear very similar to the radial hedgehog point defects in spherical N droplets. If the sample is subjected to repeated thermal recycling, the BFDs, that eventually form, are bigger and fewer in number and often have a six-fold faceted structure (Fig. 2(b)). Several thin sharp dark brushes can also be observed. With a further decrease in temperature the size of the BFDs increases to some extent after which they remain unaltered. On careful observation, it can be seen that the multiple dark brushes actually originate from different defect-like cores present within the BFDs (Fig. 2(c) and (d)).

On rotation of the crossed polarizers the dark lines also rotate suggesting that these owe their origin to the N director in a plane parallel to the substrates. The sense of rotation of the dark brushes corresponding to the defect-like cores in all the BFDs is similar and matches the sense of rotation of the crossed polarizers. The optical appearance of the BFDs between crossed polarizers suggests that the director distribution within each BFD is effectively radial. On the other hand, in the case of hyperbolic distribution, the sense of rotation of the dark brushes would have been opposite to the sense of the rotation of the crossed polarizers.

The detailed director distribution within the BFDs can be deciphered by placing the sample between crossed polarizers in

conjunction with a lambda (λ) plate, placed with its slow axis (γ) at 45° to the polarizer axis. It is well established that the regions in which the director is parallel to the slow axis of the λ plate appear blue (quadrants of addition) and the regions in which the director is perpendicular to it appear yellow (quadrants of subtraction). On the other hand, the appearance of the firstorder red (magenta) colour implies that the λ plate does not affect the optical path in this region. Such a colour scheme is possible if the director is homeotropically aligned as in the present sample. Unlike in spherical N droplets with either radial or tangential director configurations, where two opposite quadrants of blue and yellow are observed, in most of the BFDs more than two alternate domains of blue and yellow can be visualized (Fig. 3(a)). This may be attributed to the combined effect of the director distribution pertaining to multiple defectlike cores present within the BFDs (Fig. 3(b)).

Another noteworthy feature is that when the BFDs are observed without the analyser, a radial cluster of fibres of 12-HSA is clearly visible (Fig. 3(c)). The orientation direction of the fibres has a correlation with the N director as revealed by the λ plate (see Fig. 3(a)). These fibres are mainly restricted only to the region of the BFDs and cannot be observed in the outer regions which continue to remain smooth and homeotropically aligned. The fibres appear to have a curvature in the regions surrounding the defect-like cores influencing the director configuration within different sectors.

As the fibres develop better with repeated thermal recycling the director configuration in the BFDs formed after this process has a different nature to that in BFDs formed during the first cooling run. This can also affect the strength of the gel. It was indeed found that the N-gel formed on first cooling is quite weak and starts flowing when the sample cup is disturbed, whereas the N-gel formed after repeated thermal recycling is stable and remains unaltered for several days. An increase in the concentration of the gelator leads to an increase in the size of the BFDs (Fig. S2(a)–(c), ESI†) due to the further growth of the fibres, as the number of gelator molecules increases. A corresponding increase in the number of fibrous strands can also be observed (Fig. S2(d)–(f), ESI†).

When an ac electric field is applied between the substrates to the homeotropic sample of [CCN-mn (0.75)], regions outside



Fig. 3 Enlarged view of a single BFD in the same sample as in Fig. 2. (a) Between crossed polarizers with a λ plate placed with its slow axis at 45° to the polarizers. Blue lines show the average director orientation in different sectors (b) between crossed polarizers when multiple sharp dark lines corresponding to different defect-like cores can be observed (c) with only one polarizer when the fibres are revealed. Scale bar corresponds to 25 μm in all figures.



Fig. 4 Formation of defects under the application of an ac electric field (1 kHz) in the homeotropic regions outside the BFDs, with the fibres and director orientation remaining intact within the BFDs (a)–(c) between crossed polarizers and (d)–(f) with an additional λ plate placed with its slow axis at 45° to the polarizers. (a) and (d) V = 0 (b), (e) $V = 0.07 V_{rms} \mu m^{-1}$ and (c) and (f) $V = 0.08 V_{rms} \mu m^{-1}$. Scale bar = 100 μm .

the BFDs reorient orthogonal to the field direction due to the negative dielectric anisotropy ($\Delta \varepsilon$) of the LC. This results in a schlieren texture due to the degenerate planar alignment (Fig. 4(a)–(c)). It can be noted that the BFDs are themselves not affected and remain distinct even at high fields with the BFDs and some fibres also clearly visible. This again confirms that the fibres are mainly present within the BFDs and that the director within the BFDs is already orthogonal to the field direction. The creation of defects and similarity of the colours of addition/subtraction within and outside the BFDs reveal that the director configuration outside the BFDs after the reorientation under the field is to some extent influenced by the director configuration within the BFD (Fig. 4(d)–(f)).

Planar alignment

The sample [CCN-mn (0.75)] was also filled in cells made of glass plates treated for planar alignment and observed under the optical microscope. In this case, the BFDs that are formed at the temperature corresponding to the N to N-gel transition have four elongated lobes emanating from the centre (Fig. 5(a)). The colour scheme obtained when a λ plate is used in combination with the crossed polarizers shows that the director is parallel to the



Fig. 5 Optical textures of [CCN-mn (0.75)] taken in a planar cell. (a) Enlarged image of a single BFD obtained by repeated thermal recycling viewed between crossed polarizers in the N-gel phase at 30 °C. The same BFD as in (a) with an additional λ plate. *R* denotes the rubbing direction. Scale bar corresponds to 20 μ m.





Fig. 6 (a) Top view of possible director configuration within a BFD in a planar aligned sample. (b and c) Collection of BFDs observed between crossed polarizers when [CCN-mn (0.75)] taken in a cell treated for planar alignment is subject to thermal recycling and eventually cooled down to room temperature. (b) Immediately after formation and (c) after a few hours. Scale bar corresponds to 100 μ m in both (b) and (c).

plane of the substrates within the BFDs and is mainly oriented radially (Fig. 5(b)). Although the four lobes in this case appear smooth between crossed polarizers, fibrous strands can clearly be seen in the direction of the lobes when only the analyser is present. On close examination these appear to be twisted (Fig. S3, ESI[†]).

A possible director configuration which can account for the optical observations is shown in Fig. 6(a). If the planar sample is left undisturbed for a few hours at room temperature, this promotes the formation of a stripe-like pattern oriented orthogonal to the rubbing direction due to the lining up of the BFDs (Fig. 6(b) and (c)).

Application of an electric field orthogonal to the substrates results in a field induced response similar to electro hydrodynamic instability (EHD) only in the region between the lined up BFDs (Fig. S4, ESI†). However, the BFDs themselves are not affected by the field and remain distinct even at relatively high fields.

With the increase in the concentration of the gelator the fibrous structures increase in number and orient randomly. Their distribution and hence the LC director become haphazard and no specific patterns are observed (Fig. S5, ESI[†]).

Based on the POM observations it can be concluded that the defect-like cores and dark brushes in both the homeotropic and planar samples owe their origin to the distribution of fibres which promotes the formation of a localized (flower-like) structure with a cylindrical symmetry of the director distribution. This structure is embedded into the uniform far field director. Consequently, the regions containing the fibres appear bright resulting in the BFDs.

Confocal microscopy

As suggested by the optical texture studies the fibres appear to form a radial distribution in homeotropic cells, when viewed along the far-field director. In order to obtain an insight into the three dimensional structure of the BFDs in this case and probe the effect of the chiral fibres, FCPM imaging studies were carried out with the [CCN-mn (0.75)] doped with the dye BTBP taken in cells treated for homeotropic alignment. The strength of the FCPM signal depends on the angle between the transition dipole of the dye (fluorescent) molecules and the polarizer P. The intensity of fluorescence is maximum when P is parallel to the director and at a minimum when P is perpendicular to it. The orientation dependence of the fluorescence signal can



Fig. 7 FCPM images of slices close to the microscope objective for two orthogonal polarizations of excitation and detected light (a and b), indicated in the top-right corners. A fibre-like structure is oriented in a radial direction relative to the axis of the structure within a BFD of diameter 18 μ m in a cell of thickness 12 μ m. Scale bar corresponds to 12 μ m.

therefore be used to decipher the 3D orientation pattern of the LC director based on the FCPM observations.^{17,20} The studies were carried out using linearly polarized excitation (488 nm) and detection (515–575 nm).

Confocal images reveal that the LC/dye molecules are locally oriented because the images taken at different polarizations of the excitation and emitted light are different, as illustrated in Fig. 7. The fluorescence pattern emitted from the 3D structure of the BFDs shows some rotation with the director oriented radially at the top and bottom substrates relative to the axis of the structure but rotated by 90° in the central plane of the cell. The presence of fibres which influences the director orientation and to some extent the local concentration of the fluorescent dye is also clearly evident in the FCPM images of the slices close to the objective (Fig. 7).

To get more insight about the director structure within the BFDs, we analysed the patterns of emitted fluorescent light taken at different polarizations of the excitation beam, which is presented in Fig. 8. We see that the BFDs are rotationally



Fig. 8 Intensity of detected fluorescent light taken at different polarization of excitation and detected light. (a) Polarization of excitation and detection is parallel to the *y*-axis as indicated in upper-right corner of (a). The main panel shows the intensity pattern captured at the mid-plane of the BFD structure. The panel on the right is the vertical cross section taken along the A-A direction. The panel at the bottom is the vertical cross section taken along the along the *B*-*B* direction. (b) The polarization of excitation and detected light is along the *x*-axis (upper-right corner of (b)). Note the alternation of bright patterns in (a) and (b).



Fig. 9 Two possible director structure configurations of BFDs that will give fluorescence emission patterns, as observed in the experiment. (a) Radial structure with higher symmetry, (b) umbilic-like structure with lower symmetry.

symmetric about the normal (*z*-axis) to the cell surfaces. There is also clear alternation of the bright fluorescent regions, when the polarization is rotated 90° , which leads us to two hypothetical structures of BFDs, as presented in Fig. 9.

Both structures in Fig. 9 are axially symmetric about the A-A axis. We call them radial-like and hyperbolic-like and they differ by the direction of the initial tilt, as indicated by the two red-coloured and tilted molecules in Fig. 9(a) and (b). Both structures are non-singular, which means there are no topological defects in the sense of vanishing order parameter. Any discontinuity of the director field is avoided by local twist, which is similar to what is realized in lambda and tau line defects in cholesterics. The hyperbolic-like structure is to a certain level similar to the well-known toron structure,²¹ and the difference is that it does not have any singularity or topological defect. The expected FCPM intensity for the radial structure is presented in Fig. 10 for two orthogonal polarizations and there is a qualitative agreement with the experiments. However, the proposed structures are only hypothetical and their stability needs to be confirmed by numerical modelling.

Both radial and hyperbolic toron-like structures presented in Fig. 9 are inherently stabilized by the presence of the skyrmion director profile in their cross section. If we take a look at the *B–B* director profile in the schematic in Fig. 9, we see that the director twists by 180° as we go from the edge of the structure to its centre. This is realized for all directions perpendicular to the symmetry axis *A–A* of the structures. The resulting 2D director pattern in this mid-plane cross section is a skyrmion profile, which is ubiquitous in N* LCs. The skyrmion profile (or more accurately, the half-skyrmion or "meron" profile)²² is best known from Blue Phases I and II, where the



Fig. 10 Fluorescent light intensity captured in the vertical cross-section for two different polarizations of the excitation and detected light. (a) The excitation and detected light is polarized within the plane of the cross-section. (b) Light is polarized perpendicular to the plane of the cross-section.

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cross section of the double-twisted cylinders shows a vortex-like profile of the director. Skyrmions are topologically protected structures, which cannot be made uniform by any continuous transformation of the director profile. Indeed, if one looks at the cylindrical, 180° twisted vortex-like profile across the *B–B* line in Fig. 9, it is clear that this profile is stable and can be made uniform only by cutting the director field. Cutting the director field means adding energy to the system, and skyrmions are thereby protected by a large energy barrier derived from the homogeneous state. Skyrmions are known to pack into lattices and structures of skyrmions in 2D without any singularities. It seems that this natural smoothness of the skyrmion profile is also demonstrated in our structures, which appear to be smooth and free of singularities.

The sense of rotation in all the BFDs observed under the confocal microscope is left handed. The twisting can be asymmetric sometimes, with the plane in which the orientation is rotated by 90° being displaced from the mid-plane of the cell. In this case either the bottom or the top half of the structure becomes larger. However, the sense of rotation is always left handed. A stack of fluorescent images corresponding to a BFD formed in a homeotropic cell of [CCN-mn (0.75)] as observed with FCPM is shown in Movie S1 (ESI†).

Morphology of fibres

The morphology of the fibres formed within the N-gels was also examined by Cryo-SEM after the extraction of the LC. The presence of well-defined left handed twisted helical fibres formed by the gelator molecules is shown in Fig. 11.

4 Discussion

The efficiency of gelation in general depends on the solventsolvent and gelator–gelator interactions and various intermolecular forces.^{23–28} When the solvent–gelator interaction is minimal, the gelator–gelator interactions can become stronger and lead to the formation of self-assembled fibrillar networks (SAFiNs). An enantiomerically pure form of 12-HSA is also known to form helical aggregates with the hydroxyl groups at the chiral center linking *via* unidirectional hydrogen bonds.²⁹



Fig. 11 Fibres of 12-HSA observed with a SEM after the extraction of the LC.

The SAFiNs are then formed by the dimerization of carboxylic acid head groups and the formation of hydrogen bonds between the secondary hydroxyl groups.³⁰ Detailed studies have shown that the racemic form of 12-HSA does not form gels.³¹ The used 12-HSA shows evidence for optical activity which is left handed. The melting point is found to be 79.5 °C similar to that reported for the (R) form of 12-HSA.³¹ These studies have also shown that the twist of the fibres is related to the chirality of the 12-HSA molecule and that the (R)-form of 12-HSA forms left-handed fibres as also evidenced by freeze fracture electron microscopy studies. As the fibres formed by the present N-gel samples show only a left handed twist, it can further be concluded that the used 12-HSA is enantiopure and hence promotes only one type of twisted fibres. The clear formation of twisted fibres as shown by Cryo-SEM (see Fig. 11) confirms that such a process is taking place even in the present system. Spontaneous self-organization into periodic and well separated LC-rich and fibre-rich regions in N-gels has previously been observed in a mixture of E7 composed of cyanobiphenyls and the gelator 12-HSA.⁶ In this case, the distinct segregation of the fibrous aggregates and LCs was attributed to the strong association between the molecular dimers formed by the LC molecules due to the highly polar cyano end group.³² This promotes enhanced gelator-gelator interactions via intermolecular hydrogen bonding rather than LC-gelator interactions. However, in the present system the CCN molecules possess a transverse cyano group. DFT based ground state electronic structure calculations have shown that the molecules are not linear and their 2D projections are bent-shaped with the dipoles in the transverse direction.33 The presence of alkyl chains on either side of the aromatic core leads to a new form of selfassembly in the CCN-mn gels. As the sample is cooled towards the N to N-gel transition the gelator molecules diffuse from the bulk LC and collect together and start forming fibres. As the chiral gelator fibres extend radially within the homeotropic sample, due to the bent conformation of the LC molecules, the interaction between the alkyl chains of the LC and gelator molecules leads to an out of plane tilting of the LC molecules in the vicinity of the fibres. This leads to their interpenetration between the chiral fibres (Fig. 12(a)), eventually becoming parallel to the plane of the substrates. This results in a disturbance of the LC alignment in the near vicinity of the fibres (Fig. 12(b)) causing these regions to appear bright between crossed polarisers. The dimensions of these regions, which have a flower-like appearance and hence are referred to as BFDs, depend on the extent to which the fibres grow. Furthermore, the helical fibres influence the LC director leading to twisted structures resulting in the formation of toron-like structures. The formation of the distinct fibre rich regions surrounded by aligned N regions in both the homeotropic and planar aligned samples corresponds to a new form of gelation process resulting in the formation of inverse N-gels. Topological defects are often created when an LC forms a dispersed system as in a colloid with solid particles,³⁴ water droplets³⁵ and even droplets of a second type of LCs.36 Depending on the boundary conditions at the interface between the well aligned surrounding LC medium



Fig. 12 (a) Schematic representation of inter-molecular hydrogen bonding within the helical fibres and the orientation of the LC molecules in the proximity of the fibres. Red arrows show the growth direction of the fibres. (b) Schematics of the elastically distorted field around the fibre for different orientations of the fibre with respect to the far-field uniform director. The anchoring at the surface of the fibre is tilted, which follows the model shown in (a). Note that the elastic distortion in this particular plane of view is minimal, when the fibre is tilted with respect to the far-field director.

and the dispersed entities, as mentioned earlier, most often radial hedgehog point defects or surface boojums can be created. On the other hand, the formation of the inverse N-gel and its rigidity in the CCN-mn system can be attributed to the creation of defect-like cores and twisted structures originating from the collection of fibres within the BFDs embedded in a uniform N matrix.

Defects and structures occurring in chiral NLCs can be more complex than in achiral NLCs. Some notable examples are that of twisted structures analogous to torons³⁷ and skyrmions^{17,37} Interestingly in the CCN-mn system in spite of the N being achiral, FCPM studies show evidence for toron-like structures within the BFDs which can be associated with the chiral gelator fibres. It should be noted that the quality of our FCPM images in the case of BFDs is not good enough to make accurate director reconstruction, following the recently developed method for reconstructing the 3D director structures using the annealing algorithm.^{17,18} The reason for this is in the presence of fibres and local variations of fluorescence intensity nearby the gelator fibres which are not directly correlated to changes in director orientation. Since the method uses the measured values of the light intensity at a particular voxel for a particular light polarization, these structural non-uniformities prevent reliable reconstruction. Earlier studies had shown evidence for the induction of a bulk electro-clinic effect when a small quantity of carbon nanotubes (CNTs) was dispersed in an achiral NLC. A measurable helical pitch was also found to be induced in such a mixture.³⁸ The most likely reason to which these effects were attributed was the transfer of surface chirality of the CNTs to the surrounding LC. The presence of the twisted director configuration within the BFDs in the CCN-mn gels may have a somewhat analogous reason where the chiral gelator fibres affect the director configuration of the surrounding LC. As the gelator fibres do not extend into the surrounding LC-rich regions beyond the BFDs, the chiral effects are localized and are restricted to the BFDs with the N in the surrounding aligned region remaining achiral. The dark appearance of the N outside the BFDs when viewed between crossed polarizers confirms this further. Also the dark brushes associated with the defects in the schlieren texture appearing under the action of the electric field in the outer regions are oriented parallel and perpendicular to the polarizers showing no trace of a twisted structure.

The formation of well separated BFDs in the case of the homeotropic sample and their lining up to form stripe-like patterns in the case of the planar samples can be understood as follows. In the homeotropic sample the N director progressively tilts on moving from the outer N region rich in CCN-mn molecules towards the fibre rich BFD, resulting in a boundary region. In the case of the planar samples the director twists only in a direction orthogonal to the rubbing direction in order to match with the average molecular orientation in the far field (see Fig. 6(a)). The BFDs can then self-assemble linearly leading to the stripe-like patterns with a continuous evolution of the N director between the BFDs.

It can also be noticed that when there are multiple defectlike cores originating from individual fibre clusters in the homeotropic samples, independent clusters of twisted fibres can be identified. However, interestingly the dark brushes associated with each of these exhibit the same sense of rotation on rotating the sample between crossed polarizers (see Movie S2, ESI⁺).

The N-gel composed of the BFDs embedded in the N matrix may be considered as a form of orthogonal self-assembly¹¹ as the 12-HSA and CCN-mn molecules retain their individual characteristics and predominantly form fibres within the BFDs and the N phase in the surrounding regions, respectively. However, in this system the coexisting self-assembled structures corresponding to the BFDs and the N are not totally independent as the N phase is also found within the BFDs.

5 Conclusion

Inverse N-gels formed by a binary system of two NLCs belonging to a series of alkyl-bicyclohexyl-carbonitriles along with a simple organo gelator 12-HSA have been investigated by optical and confocal microscopy. The bent-shape of the LC molecules with alkyl chains at both ends leads to a new form of self-assembly of the LC and gelator molecules. This results in the formation of fibre rich BFDs confined within an aligned N with incorporated twisted structures. Interestingly, although the N is achiral in the outer regions, the observed twisted structures owe their origin to the helical gelator fibres.

The formation of BFDs shows an interesting interplay of fibre-induced chirality and self-assembly of fibres and in localized, toron-like LC-fibre structures, which are topologically protected. It is known that such structures can be induced in chiral liquid crystals by strong and localized Laquerre-Gaussian vortex beams,³⁷ or by the quench of the LC across the Iso-N phase transition.

Our results demonstrate a new way of engineering stable N-gels, which are stabilized by topologically protected superstructures formed by the self-assembly of LCs and fibres.

Such inverse N-gels with the embedded BFDs can be considered as a new form of soft solid which retains the properties of an LC but can have enhanced rigidity and altered rheological properties.

Conflicts of interest

The authors declare no conflict of interest.

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