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Introduction

Ionic liquid crystals (ILCs) form a class of liquid crystals (LCs) that contain anions and cations, and due to their ionic character, they differ significantly from the conventional neutral LCs.¹ They usually tend to stabilize layered phases due to the strong ionic character but are also known to stabilize several uncommon mesophases. Clearly, due to the ionic nature, they have the capability to transport ions and thus have the potential to be used as electrolytes for batteries, fuel cells, and dye-sensitized solar cells.² They merge the properties of ionic liquids and LCs, thus opening up a wide variety of applications to be utilized as designer solvents for the reactions due to the additional liquid crystalline order they bring about in comparison to ionic liquids, in addition to the tunability with respect to the change of cations and anions.³ Over the years, numerous ILCs based on the different types of ionic heads such as ammonium salts, phosphonium salts, imidazolium salts, pyridinium salts, viologens, pyrilium and thiopyrilium salts, dithiolium salts, vinamidinium salts, alkali metal alkanoates (soaps), phosphates, and phosphonates as well as several metal complexes have been developed.^{1,4}

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Metal-free C–H functionalization of pyrrolidine to pyrrolinium-based room temperature ionic liquid crystals[†]

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The development of ionic liquid crystals (ILCs) using pyrrolidinium cation has received considerable interest due to their higher electrochemical stability. However, high charge density associated with low charge distribution in the fully saturated pyrrolidine ring leads to the high melting temperature of the materials due to strong ionic interactions. Herein, the synthesis and evaluation of the structure-property relationship of a new class of pyrrolinium-based ionic liquid crystals has been reported. The metal-free direct C-H functionalization of pyrrolidine, followed by the *N*-alkylation of resulting pyrroline produced the pyrolinium moiety that serves as the unprecedented polar head of the mesogens. These ionic mesogens having a partially unsaturated pyrrolidine ring were found to stabilize numerous mesophases over a wide thermal range including room temperature.

However, ILCs built on aromatic cations such as imidazolium, pyridinium, and quinolinium have dominated the field. However, a few examples corresponding to pyrrolidiniumbased ILCs containing fully saturated N-heterocycle have been developed.⁵⁻⁸ The pyrrolidinium cation is a five-membered nonplanar N-heterocyclic nonaromatic ring system that lacks charge delocalization and displays higher electrochemical stability.9 However, high charge density associated with low charge distribution leads to a high melting temperature of the materials due to strong ionic interactions (Scheme 1). We anticipated that the increase in the charge delocalization by placing a partial unsaturation in the pyrrolidine ring would decrease the melting temperature. Herein, we report a new type of pyrrolinium-based ionic mesogens, which exhibited a broad range of LC phases at lower/room temperature that are common to calamitic (rod-shaped) and discotic (disc-shaped) LCs.



Scheme 1 Known pyrrolidinium-based ILCs.



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A metal-free direct β -(sp³) C–H functionalization of pyrrolidine has been developed for the synthesis of a series of pyrroliniumbased mesogens (Scheme 2).

Results and discussion

Synthesis and characterization

The synthesis of mesogens commenced with the preparation of aryl aldehyde bearing n-alkoxy groups with varying chain lengths. The desired pyrroline derivatives 2a-l were produced from the reactions of pyrrolidine and arylaldehydes 1 through the direct β-C-H functionalization of pyrrolidine under metalfree simple conditions (Scheme S1, ESI†).10,11 Selected pyrrolines possessing a polar head group and apolar aliphatic tails, which are often assumed as important structural features for a compound to show a mesophasic behavior, were evaluated under POM. Unfortunately, none of the tested pyrrolines showed LC properties. Then, we decided to prepare iminium ions from those imines by treating them with different alkyl halides. The treatment of different alkylating reagents such as methyl iodide, triethyloxoniumtetrafluoroborate, trimethyloxoniumtetrafluoroborate or benzyl bromide with the β-substituted secondary cyclic imines gave the corresponding iminium ions (Schemes 2 and S2, ESI[†]) with good to excellent yields. A series of ions comprising the cationic pyrroline-containing *n*-alkoxy aryl group as a head and different anions such as iodide, bromide, or tetrafluoroborate have also been synthesized. The number and positions of the alkoxy chains as well as the type of the anions were systematically varied to understand the effects of the structure on the thermotropic mesophase behavior of ions. Different alkyl groups such as methyl, ethyl, propyl, benzyl, and dodecyl with different counter anions (iodide, bromide, tetrafluoroborate, *etc.*) have been introduced. In the case of compounds with a long chain at the *N*-terminal, a low conversion (12/3/C12I, PhC12Br) was noticed.

Thermal behavior

All the ionic compounds were studied *via* polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD) studies to examine the thermal behavior. Table 1, bargraph shown in Fig. 1, Table S1, and S2 (ESI[†]) represent the thermal behavior of ILCs. The first four wedge-shaped compounds, namely 12/3/MI, 12/3/EI, 12/3/ProI, and 12/3/C12I, vary from each other only with the length of the alkyl chain attached to the nitrogen. Out of these, 12/3/MI and

Table 1 Phase transition temperatures^a (°C) and corresponding enthalpies (kJ mol⁻¹) of the ionic LCs

	Phase sequence		
Entry	2nd Heating	1st Cooling	
12/3/MI	Cr 9.2 (7.3) Col _r 108.8 (2.7) Col _b 173.6 (0.01) I	I 165.2 (0.01) Col _b 97.7 (2.6) Col _r 3.1 (8.6) Cr	
10/3/MI	Cr 55.7 (9.7) Col _h 167.9 (0.01) I	I 163.7 $\operatorname{Col_h}^c$ 39.1 (2.2) Cr_2 23.5 (0.7) Cr_1	
8/3/MI	Col _{ob2} 133.0 (7.2) Col _{ob1} 164.6 (0.1) I	I 161.5 (0.01) Col_{ob1} 124.1 (8.3) $\operatorname{Col}_{ob2}^{b}$	
12/3/EI	Cr 66.3 (1.4) Col _{h2} 82.3 (3.8) Col _{h1} 155.2 (0.01) I	I 144.1 (0.02) Col_{h1} 63.8 (12.7) Col_{h2} 16.4 (0.3) Cr	
12/3/ProI	$Cr_1 35.3 (3.0) Cr_2 93.5 (19.6) I$	I 80.9 (16.5) Cr ₂ 29.4 (2.7) Cr ₁	
12/3/C12I	Cr 78.6 (5.8) Col _h 98.5 (38.4) I	I 91.6 (0.5) Col _h 54.6 (32.2) Cr	
12/3/MBF	Cr 9.1 (1.2) Col _r 65.8 (5.5) Col _b 155 I	I 150 Col _{b1} 39.7 (11.5) Col _r -4.3 (0.5) Cr	
12/3/EBF	Cr ₁ 48.5 (2.3) Col _r 69.1 (14.5) Col _b 151.3 (0.1) I	I 148.3(0.3) $\operatorname{Col}_{b}49.2$ (14.4) $\operatorname{Col}_{r}^{b}$	
12/3/BnBr	$Cr_1 50 (11.1) Cr_2 73.4 (6.3) Cr_3 144.6 (46.4) I$	I 119 Cr ^c	

^{*a*} Peak temperatures in the DSC thermograms obtained during the first cooling and second heating cycles at 5 °C min⁻¹. ^{*b*} optical texture remains frozen. ^{*c*} the transition was observed only under POM and no transition was observed in DSC; (Cr = crystal; Col_h = Columnar hexagonnal phase; Col_r = Columnar rectangular phase; Col_r = Columnar oblique phase; I = Isotropic liquid.)



Fig. 1 Bargraph representation of the thermal behavior of ILCs (2nd heating scan in DSC is considered).

12/3/EI exhibited room temperature columnar (Col) phase, while compound **12/3/ProI** turned to be crystalline. Surprisingly, compound **12/3/C12I** with the *n*-C₁₂-chain exhibited a Col phase along with a crystalline phase (Fig. S4 and S11, ESI[†]).

Replacing the alkyl chain on *N* with a benzyl group (12/3/ **BnBr**) also led to a crystalline nature, although the counter ion was bromide. The variation of the counter ions, *i.e.*, BF₄⁻ as in the case of 12/3/MBF or 12/3/EBF instead of I⁻ exhibited the Col phase with a reduction in the isotropic temperature (Fig. S5 and S6, ESI†). Reduction in the length of the peripheral chain (with three *n*-decyloxy chains or *n*-octyloxy chains) as in the case of 10/3/MI and 8/3/MI led to the lowering of the clearing point, while the compound remained liquid crystalline (Fig. S1 and S2, ESI†).

Thus, the mesophase stabilization of these wedge-shaped ionic liquid crystals is more sensitive to the chain length of the *N*-alkyl group at the tip of the wedge, rather than the length of the peripheral chains. The dialkoxy derivatives 12/(3,4)/MI, 12/(3,4)/MBF, 12/(3,4)/EBF, and 12/(3,5)/MI were mesomorphic, whereas other dialkoxy derivatives 12/(2,3)/MI and 12/(2,4)/MI turned out to be crystalline. Surprisingly, among the monoalkoxy derivatives 12/p/MI, 14/p/MI, and 12/p/EBF, only the last compound was found to be liquid crystalline. This emphasizes the requirement of more peripheral tails as well as the type of counteranion in stabilizing the mesomorphic behavior in this class of compounds. The mesomorphic behavior of some of the representative compounds of each series is discussed in detail in the following section.

Among the trialkoxy derivatives, compound 12/3/MI, 12/3/ MBF, and 12/3/EBF were bimesomorphic exhibiting columnar rectangular (Col_r) phase and columnar hexagonal (Col_h) phases. Other trialkoxy derivatives 10/3/MI and 12/3/EI exhibited the Colh phase, while 12/3/C12I and 8/3/MI exhibited Col_r and columnar oblique (Col_{ob}) phases, respectively. Compound 12/3/MI, which is a sticky viscous sample at room temperature, was birefringent under POM. The compound showed a transition around 109 °C with an enthalpy change of 2.7 kJ mol⁻¹ (Fig. 2a, Table 1). Further heating led to a phase transition, where the birefringent mass converts to an isotropic liquid at 174 °C. The isotropic liquid on cooling yields a mosaic texture that is often obtained for Col phases (Fig. 2b). Further cooling leads to a transition at ≈ 98 °C ($\Delta H = 2.6$ kJ mol⁻¹) with a slight change in the optical texture (Fig. 2c), before showing the crystallization at 9 °C (Δ H = 8.6 kJ mol⁻¹), as noted in DSC. Thus, the compound was liquid crystalline at room temperature, as noted by POM and DSC observations. To investigate the phase structure, we have carried out the XRD studies well within the thermal ranges of the mesophase.

The XRD pattern obtained at 130 °C showed a single peak (*d*-spacing of 35.1 Å) with high intensity at a low angle along with a diffused peak in the wide-angle (Fig. 2d). The diffused peak at a wide angle corresponds to the packing of flexible alkyl chains. The mosaic pattern of the optical texture is often observed for columnar (Col) phases (Fig. 2b). However, the single peak at the low angle is often witnessed in the case of



Fig. 2 DSC thermograms obtained for 12/3/MI for the first cooling (blue trace) and second heating (red trace) scans (a); POM image obtained for compound 12/3/MI at 130 °C in the Col_h phase (b); at 30 °C in the Col_t phase (c); XRD profile of compound 12/3/MI depicting the intensity vs 2 θ obtained for the Col_h phase (d) and Col_r phase at 28 °C (e). Scale bar corresponds to 100 μ m.

columnar phases with the hexagonal symmetry (Col_h phase). Though the single peak in the low angle does not unambiguously prove the existence of the Col_h phase, there are several reports in the literature, where the Col_h phase with a single peak in the low angle are reported. Such a pattern has been ascribed to a minimum in the form factor.¹²

The hexagonal lattice parameter '*a*' was found to be 40.51 Å, which refers to the sides of a hexagonal unit cell. The molecular length (L) calculated for compound 12/3/MI was found to be ≈ 25 Å. From the calculations of the lattice area (S) and volume (V), we could arrive at the value, 'Z', i.e., the number of molecules forming a unit hexagonal cell, which was found to be \approx 4. Such discoid formation is possible if four such ionic LCs arrange with their ionic heads oriented towards the center, which eventually leads to the diameter of such a disk to be \approx 50 Å. Such disks can self-assemble to form long columns, which then self-organize to form the Col_h phase (Fig. 3). However, the value of a was around 20% less than the diameter of the disk, pointing to a possible interdigitation of the peripheral alkyl tails from the neighboring columns. Further, the low-temperature phase was investigated at 28 °C, showing the signatures of the Col_r phase. The diffraction pattern obtained at 28 °C showed an intense peak, followed by a peak of moderate intensity at a low angle region, corresponding to the *d*-spacings of 41 Å and 20.4 Å, which can be indexed to the

01, 10 planes of a rectangular lattice (Fig. 3). The lattice parameters for the rectangular unit cell was calculated to be a = 41 Å and b = 20.4 Å. Herein, the wide-angle, two diffused peaks were observed corresponding to the d-spacings of 4.4 Å and 3.73 Å, respectively. The first diffused peak corresponds to the packing of flexible alkyl chains, while the second one corresponds to the core-core stacking. This suggests that at low temperature the core-core interactions between the disks within the column has enhanced. Thus, the low-temperature phase can be unambiguously assigned the Col_r phase with the p2mm symmetry (Fig. 3). The number of molecules forming a disk in the rectangular unit cell was found to be around 2. The XRD studies carried out on the lower chain homologs of 12/3/MI, i.e., 10/3/MI and 8/3/MI showed that these compounds are monomesomorphic exhibiting Col_b and Col_{ob} phases, respectively (Fig. S1 and S2 ESI,† Table 1). Compound 8/3/MI exhibited a transition between Colob1 and Colob2 phases, where the Colob1 phase remains stable even at room temperature, as evidenced from POM, DSC, and XRD studies (Fig. S2 and Table S1, ESI⁺). It was very hard to detect the change in these two phases as the POM texture only showed a subtle change in birefringence. However, a significant enthalpy change corresponding to the phase transition was noted ($\Delta H = 8.3$ kJ) in DSC (Fig. S2 ESI⁺ and Table 1). Here again, almost four molecules form a disc, which self-assemble in a parallelogram lattice to give a Colob phase.



Fig. 3 Schematic showing the self-assembly of **12/3/MI** into Col_n and Col_r phases. The optical textures observed for the Col_n phase (at 130 °C) and Col_r phase (at 28 °C) is shown in the inset.

The substitution of the ethyl group in place of methyl as in the case of 12/3/EI stabilized the Col_h phase over a wide range (Fig. S3, ESI†). However, the same with the *n*-dodecyl group (compound 12/3/C12I) led to the stabilization of the Col_r phase over a short-range (Fig. S4, ESI†). The variation of the counter anion from iodide to tetrafluoroborate as in the case of 12/3/ MBF or 12/3/EBF led to the stabilization of both Col_h and Col_r phases (Fig. 4, Fig. S5 and S6, ESI†). In comparison to 12/3/MI, these compounds exhibited a reduction in the clearing points. However, in the case of 12/3/EBF, an increase in the melting point was noticed. These differences in the thermal behavior show that how a minute structural variation affects the selfassembly of ionic LCs.

The dialkoxy derivatives 12/(3,4)/MI, 12/(3,4)/MBF, 12/(3,4)/EBF and 12/(3,5)/MI were mesomorphic. Compound 12/(3,4)/MI exhibited a Col_h phase (Table 2). The optical texture showed a pseudo focal conic pattern (Fig. 5b). The XRD plot obtained at

120 °C showed a strong peak in the low angle with a *d*-spacing of 39.1 Å, followed by another reflection with a *d*-spacing of 19.5 Å (Fig. 5c and Table S2, ESI[†]). The *d*-spacing ratio of these two peaks is 1:0.5. Although it gives an impression of a layered phase, the POM textural observation supports this to be a Col phase, particularly a Col_h phase, where the *d*-spacing corresponding to the 11 planes of the hexagonal phase is missing. A diffused broad peak at wide-angle corresponding to a dspacing of 4.41 Å confirms the liquid crystalline nature of the sample (Fig. 5c). The calculated lattice constant a = 45.2 Å, which is less than the double of the molecular length (52 Å). This means that the individual disc is formed by more than one molecule, and from the calculation, it was found to be around eight molecules. It should be noted that the number of molecules that form a disc, *i.e.*, Z is more than trialkoxy derivatives, which is understandable as more number of dialkoxy derivatives are required to complete the disc formation. These molecules point

Table 2 Phase transition temperatures" (°C) and corresponding enthalpies (kJ mol *) of the ionic LCs			
Entry	Phase sequence		
	2nd Heating	1st Cooling	
12(3,4)/MI	Cr ₁ 69.7 (5.7) Cr ₂ 80.8 (10.4) Cr ₃ 141.1 (14.3) Col _b 177 ^b I	I 175 ^b Col _b 58.8 (5.1) Cr	
12(3,4)/MBF	Cr 139.3 (24.6) Col _b 212.1 (0.5) I	I 207.3 (0.3) Col _b 92.5 (24.7) Cr	
12(3,4)/EBF	Cr 120.1 (30.8) Col _b 163.6 (0.2) I	I 160.1 (0.4) Col _b 82.5 (30.0) Cr	
12(3,5)/MI	$Col_h 131.9 (0.2) I$	I 130 Col _h (0.3) M	
12(2,3)/MI	Cr 122.6 (49.2) I	I 107.1 (50.1) Cr	
12(2,4)/MI	Cr ₁ 9.2 (7.3) M2 108.8 (2.7) M1 173.6 (0.01) I	I 165.2 (0.01) M1 97.7 (2.6) M2 3.1 (8.6) Cr	
12/p/MI	$Cr_1 31.7 (0.6) Cr_2 136.5 (11) I^c$		
14/p/MI	$Cr_1 69.81(48.4) Cr_2 136 (60.1) I^c$		
12/p/EBF	$Cr_1 26.7 (4.7) Cr_2 43.5 (0.8) Cr_3 103.2 (10.2) Sm_2 162.1 (0.4) Sm_1 177^b I$	I 170.9 Sm ₁ 146.6 (0.3) Sm ₂ 21.1 (5.1) Sm ₃ ^d	

^{*a*} Peak temperatures in the DSC thermograms obtained during the first cooling and second heating cycles at 5 °C min⁻¹. ^{*b*} the transition was observed only under POM. ^{*c*} isotropic liquid freezes after a long time. ^{*d*} crystalliazation was not observed in DSC, but the optical texture remains frozen (Cr = crystal; Col_h = Columnar hexagonnal phase; Col_r = Columnar rectangular phase; Sm = Smectic phase; I = isotropic liquid.)



Fig. 4 POM image obtained for the Col_n phase (a) and Col_r phase (b) obtained for ILC 12/3/MBF. Scale bar corresponds to 100 $\mu m.$

their polar head towards the center and pack to form a disc, and such discs self-assemble to form columns, and these columns organize in a hexagonal symmetry to form a Col_h phase. The formation of such discs is expected due to the increased polarity of the ionic head, which makes two molecules to preferentially align with the polar parts pointing towards each other. The presence of two flexible chains per molecule drives them to self-assemble to form discs rather than layered structures.

The variation of the counterion to tetrafluoroborate (12/ (3,4)/MBF) led to the stabilization of the Col_h phase, which did not alter even with a change in the alkyl group from methyl to ethyl group (12(3,4)/EBF) (Fig. S8 and S9, ESI[†]). In these cases, the ratio of the first three *d*-spacings in the low angle was found to be in the ratio of 1: 0.57: 0.5, which is typical of a Col_h phase (Table S1, ESI[†]). However, the core–core peak was not found in these cases in comparison to corresponding trialkoxy derivatives. Notably, compound 12(3,5)/MI, where the alkoxy tails are substituted in 3 and 5 positions, stabilized the Col_h phase down to room temperature even with good core–core interactions, as evidenced from DSC and XRD studies (Fig. S10, ESI[†]). Other dialkoxy derivatives 12(2,3)/MI and 12(2,4)/MI were found to be crystalline (Fig. S11, ESI[†]) due to the unfavorable substitution pattern.

The monoalkoxy derivative **12/p/EBF** exhibited an interdigitated bilayer smectic phase (Sm₁ phase), as evidenced by the XRD studies carried out at 156 $^{\circ}$ C on cooling the isotropic liquid (Fig. 6). The POM image was typical of the SmA phase (Fig. S6b, ESI†). On further cooling, the POM texture did not change much except the birefringence, but a clear transition was noticed in the



Fig. 6 DSC thermograms obtained for **12/p/EBF** for the first cooling (blue trace) and second heating (red trace) scans (a); POM image obtained for the Sm₁ phase at 163 °C (b); for the Sm₂ phase at 104 °C (c) and for the Sm₂ phase at 28 °C on cooling from the isotropic state (d). Scale bar corresponds to 100 μ m.

DSC at ≈ 146.6 °C ($\Delta H = 0.3$ kJ mol⁻¹) (Fig. 6 and Fig. S12a–d, ESI[†]). The XRD studies carried out at 120 °C showed a similar diffraction pattern as in the Sm1 phase but with an additional reflection at a low angle. The *d*-spacing corresponding to the first reflection at a low angle is exactly the multiple of the second reflection, suggesting this to be a lamellar or layered phase (Fig. S12e–g, ESI⁺). The d/L ratio obtained was ≈ 1.5 , suggesting it to be an interdigitated bilayer smectic phase (Sm₂ phase) (Table S2, ESI^{\dagger}). Further cooling has shown a transition at 21 $^{\circ}$ C $(\Delta H = 0.3 \text{ kJ mol}^{-1})$, where the striations on focal conic fans were noted in the POM observation. The XRD studies just above this, *i.e.*, around 28 °C revealed additional reflections along with a sharp peak at a low angle. The first reflection was an exact multiple of other reflections, confirming the lamellar order. The d/L ratio was 1.8 confirming the interdigitated bilayer structure of the smectic phase (Fig. 7). The diffused reflection was seen at 4.64 Å along with another relatively sharp peak at 4.44 Å, which may be due to the core-core interaction.



Fig. 5 DSC thermograms obtained for 12(3,4)/MI for the first cooling (blue trace) and second heating (red trace) scans (a); POM image (b); XRD pattern obtained at 120 °C (c). Scale bar corresponds to 100 μm.

Fig. 7 Schematic showing the self-assembly of **12/p/EBF** into the interdigitated bilayer smectic phase (based on the XRD pattern obtained at 120 °C).

Conclusions

In summary, we synthesized a series of pyrrolinium-based mesogens via the metal-free C-H functionalization of pyrrolidine. In contrast to the pyrrolidinum-based LC, these mesogens containing a partially unsaturated pyrrolidine ring stabilizes LC phases at room temperature. Numerous molecular structures have been evaluated with reference to the variation in the number, length of the alkyl tails as well as the type of the counterion to understand the structure-property relationships. In particular, the trialkoxy and dialkoxy derivatives stabilized Col phases, while monoalkoxy derivatives stabilized the interdigitated bilayer smectic phase, which is due to the polarity of the ionic head and nanophase segregation of the incompatible molecular subunits. It is important to note that the type of counterion also plays a major role in the liquid crystalline self-assembly. The studies on the synthesis of chiral mesogens by incorporating a chiral center in the pyrroline ring are underway in our laboratory.

Author contributions

SM synthesized and characterized all the intermediates and final compounds; SP and RKG carried out the POM and DSC studies; DSSR and SKP conducted the XRD studies and analyses; AAS and CKJ conceptualized the project, supervised the execution and jointly wrote to the manuscript with the contribution from all coauthors.

Conflicts of interest

"There are no conflicts to declare".

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Notes and references

Selected reviews: (a) S. W. T. Chang and L. Huang, *Chem. Commun.*, 2008, 1957–1967; (b) T. Kato, T. Yasuda,
 Y. Kamikawaa and M. Yoshio, *Chem. Commun.*, 2009, 729–739; (c) K. Goossens, K. Lava, C. W. Bielawski and
 K. Binnemans, *Chem. Rev.*, 2016, **116**, 4643–4807;

(d) T. Ichikawa, T. Kato and H. Ohno, *Chem. Commun.*, 2019, 55, 8205–8214; (e) D. Devadiga and T. N. Ahipa, *RSC Adv.*, 2019, **9**, 23161–23228; (f) T. Kato, J. Uchida, T. Ichikawa and T. Sakamoto, *Angew. Chem., Int. Ed.*, 2018, 57, 4355; (g) K. V. Axenov and S. Laschat, *Materials*, 2011, **4**, 206–259; (h) M. Mansueto and S. Laschat, in *Handbook of Liquid Crystals*, ed. J. W. Goodby, P. J. Collings, T. Kato, C. Tschierske, H. Gleeson and P. Raynes, Wiley-VCH: Weinheim, Germany, 2nd edn, 2014, vol. 6: Nanostructured and Amphiphilic Liq. Cryst., pp.231.

- 2 (a) T. Kato, M. Yoshio, T. Ichikawa, B. Soberats, H. Ohno and M. Funahashi, *Nat. Rev.*, 2017, 2(17001), 1–20;
 (b) T. Onuma, E. Hosono, M. Takenouchi, J. Sakuda, S. Kajiyama, M. Yoshio and T. Kato, *ACS Omega*, 2018, 3, 159–166; (c) K. Salikolimi, A. S. Achalkumar and Y. Ishida, *Langmuir*, 2020, 36(40), 11702–11731.
- 3 (a) Y. Ishida, A. S. Achalkumar, S. Kato, Y. Kai, A. Misawa, Y. Hayashi, K. Yamada, Y. Matsuoka, M. Shiro and K. Saigo, J. Am. Chem. Soc., 2010, 132, 17435–17446; (b) Y. Ishida, H. Sakata, A. S. Achalkumar, K. Yamada, Y. Matsuoka, N. Iwahashi, S. Amano and K. Saigo, Chem. Eur. J., 2011, 17, 14752–14762; (c) Y. Ishida, H. Sakata, A. S. Achalkumar, K. Yamada, Y. Matsuoka, N. Iwahashi, S. Amano and K. Saigo, Chem. Eur. J., 2011, 17, 14752–14762; (c) Y. Ishida, N. Iwahashi, S. Amano and K. Saigo, Chem. Eur. J., 2011, 17, 14752–14762.
- 4 Selected reports on ionic liquid crystals: (a) Y. Z. Chiou, J. N. Chen, J. S. Lei and I. J. B. Lin, J. Mater. Chem., 2006, 16, 2972-2977; (b) W. Li, J. Zhang, B. Li, M. Zhang and L. Wu, Chem. Commun., 2009, 5269-5271; (c) J.-T. Lu, C.-K. Lee and I. J. B. Lin, Soft Matter, 2011, 7, 3491-3501; (d) T. Amann, C. Dold and A. Kailer, Soft Matter, 2012, 8, 9840-9846; (e) M. Zhou, J. Zhang, S. Wang, D. Boyer, H. Guo, W. Li and L. Wu, SoftMatter, 2012, 8, 7945-7951; (f) T. Ichikawa, M. Yoshio, S. Taguchi, J. Kagimoto, H. Ohno and T. Kato, Chem. Sci., 2012, 3, 2001-2008; (g) G. F. Starkulla, S. Klenk, M. Butschies, S. Tussetschläger and S. Laschat, J. Mater. Chem., 2012, 22, 21987-21997; (h) J. Song and B.-K. Cho, Chem. Commun., 2012, 48, 6821-6823; (i) A. A. Fernandez, L. T. de Haan and P. H. J. Kouwer, J. Mater. Chem. A, 2013, 1, 354-357; (*j*) L. A. Robertson, M. R. Schenkel, B. R. Wiesenauer and D. L. Gin, Chem. Commun., 2013, 49, 9407-9409; (k) T. Ichikawa, K. Fujimura, M. Yoshio, T. Kato and H. Ohno, Chem. Commun., 2013, 49, 11746-11748; (l) W. Jin, Q. Yang, Z. Zhang, Z. Bao, Q. Ren, Y. Yang and H. Xing, Chem. Commun., 2015, 51, 13170-13173; (m) S. K. Nayak, M. Amela-Cortes, C. Roiland, S. Cordier and Y. Molard, Chem. Commun., 2015, 51, 3774-3777; (n) H. Takeuchi, T. Ichikawa, M. Yoshio, T. Kato and H. Ohno, Chem. Commun., 2016, 52, 13861-13864; (o) T. Matsumoto, A. Ono, T. Ichikawa, T. Kato and H. Ohno, Chem. Commun., 2016, 52, 12167-12170; (p) W. Cao, B. Senthilkumar, V. Causin, V. P. Swamy, Y. Wang and G. Saielli, Soft Matter, 2020, 16, 411-420.
- 5 G. L. Burrell, N. F. Dunlop and F. Separovic, *Soft Matter*, 2010, **6**, 2080–2086.
- K. Goossens, K. Lava, P. Nockemann, K. Van Hecke, L. Van Meervelt, K. Driesen, C. Görller-Walrand, K. Binnemans and T. Cardinaels, *Chem. Eur. J.*, 2009, 15, 656–674.

- 7 K. Goossens, K. Lava, P. Nockemann, K. van Hecke, L. van Meervelt, P. Pattison, K. Binnemans and T. Cardinaels, *Langmuir*, 2009, 25, 5881–5897.
- 8 H. Li, M. J. Hollamby, T. Seki, S. Yagai, H. Moehwald and T. Nakanishi, *Langmuir*, 2011, **27**, 7493–7501.
- 9 (a) K. Matsumoto, R. Hagiwara and Y. Ito, *Solid State Lett.*, 2004, 7, E41; (b) S. Men, K. R. J. Lovelock and P. Licence, *Phys. Chem. Chem. Phys.*, 2011, **13**, 15244–15255.
- 10 For selected reviews on amine functionalization see

 (a) S. Doye, Angew. Chem., Int. Ed., 2001, 40, 3351-3353;
 (b) K. R. Campos, Chem. Soc. Rev., 2007, 36, 1069-1084;
 (c) K. M. Jones and M. Klussmann, Synlett, 2012, 159-162;
 (d) E. A. Mitchell, A. Peschiulli, N. Lefevre, L. Meerpoel and B. U. W. Maes, Chem. Eur. J., 2012, 18, 10092-10142;
 (e) L. Shi and W. Xia, Chem. Soc. Rev., 2012, 41, 7687-7697;
 (f) B. Peng and N. Maulide, Chem. Eur. J., 2013, 19, 13274-13287;
 (g) M. C. Haibach and D. Seidel, Angew. Chem., Int. Ed., 2014, 53, 5010-5036;
 (h) D. Seidel, Acc. Chem. Res., 2015, 48, 317-328;
 (i) S. Mahato and C. K. Jana, Chem. Rec., 2016, 16, 1477-1488.
- Selected reports of C-H functionalization of pyrrolidine: From our group (a) S. Mahato, S. Haldar and C. K. Jana, Chem. Commun., 2014, 50, 332-334; (b) S. Haldar, S. Mahato and C. K. Jana, Asian J. Org. Chem., 2014, 3, 44-47; (c) S. Mahato, M. A. Haque, S. Dwari and C. K. Jana, RSC Adv., 2014, 4, 46214-46217; (d) M. Rahman, A. K. Bagdi, S. Mishra and A. Hajra, Chem. Commun., 2014, 50, 2951-2953; (e) S. Haldar, S. K. Roy, B. Maity, D. Koley and C. K. Jana, Chem. - Eur. J., 2015, 21, 15290-15298; (f) S. Mandal, S. Mahato and C. K. Jana, Org. Lett., 2015, 17, 3762-3765; (g) D. T. Ahneman and A. G. Doyle, Chem.

Sci., 2016, 7, 7002-7006; (h) S. Mahato and C. K. Jana, Org. Biomol. Chem., 2017, 15, 1655-1660; (i) A. Purkait, S. K. Roy, H. K. Srivastava and C. K. Jana, Org. Lett., 2017, 19, 2540–2543; From others ; (j) J. A. Garden, A. R. Kennedy, R. E. Mulvey and S. D. Robertson, Chem. Commun., 2012, 48, 5265-5267; (k) W. Chen, Y. K. Kang, R. G. Wilde and D. Seidel, Angew. Chem., Int. Ed., 2014, 53, 5179-5182; (l) K. B. Manjappa, W. F. Jhang, S. Y. Huang and D. Y. Yang, Org. Lett., 2014, 16, 5690-5693; (m) L. He, L. Zhao, D. X. Wang and M. X. Wang, Org. Lett., 2014, 16, 5972-5975; (n) K. L. Zheng, W. M. Shu, J. R. Ma, Y. D. Wu and A. X. Wu, Org. Lett., 2016, 18, 3526-3529; (o) Y. Du, A. Yu, J. Jia, Y. Zhang and X. Meng, Chem. Commun., 2017, 53, 1684–1687; (p) L. Shi, M. Wang, L. Pan, Y. Li and Q. Liu, Chem. Commun., 2018, 54, 8721-8724; (q) R. Grainger, T. D. Heightman, S. V. Ley, F. Lima and C. N. Johnson, Chem. Sci., 2019, 10, 2264-2271.

12 (a) J. Barbera, R. Gimenez and J. L. Serrano, Chem. Mater., 2000, 12, 481-489; (b) A. Hayer, V. D. Halleux, A. Kohler, A. El-Garoughy, E. W. Meijer, J. Barbera, J. Tant, J. Levin, M. Lehmann, J. Gierschner, J. Cornil and Y. H. Geerts, J. Phys. Chem. B, 2006, 110, 7653-7659; (c) C. V. Yelamaggad, A. S. Achalkumar, D. S. S. Rao, M. Nobusawa, H. Akutsu, J. Yamada and S. Nakatsuji, J. Mater. Chem., 2008, 18, 3433-3437; (d) A. S. Achalkumar, U. S. Hiremath, D. S. Shankar Rao, S. Krishna Prasad and C. V. Yelamaggad, J. Org. Chem., 2013, 78, 527-544; (e) S. K. Pathak, B. Pradhan, R. K. Gupta, M. Gupta, S. K. Pathak, B. Pradhan, R. K. Pathak, B. Pradhan, M. Gupta, S. K. Pal and A. S. Achalkumar, J. Mater. Chem. C, 2016, 4, 6546-6561; (f) R. K. Gupta, S. K. Pathak, B. Pradhan, M. Gupta, S. K. Pal and A. S. Achalkumar, ChemPhysChem, 2016, 17, 859-872.