Chapter 4(c)
Influence of methyl and chloro substituent at bay position of unsymmetrical achiral four-ring bent-core compounds: Synthesis and characterization.
4(c).1 Introduction:
Bent-core mesogens are generally made up of a bent aromatic core and two flexible side chains. Bent-core (BC) liquid crystals (LCs) show a range of interesting properties, they exhibit chiral superstructures even though the molecules are achiral, spontaneous polar ordering, unusual rheological properties and giant flexoelectricity [1-3]. The liquid crystalline phase behaviour of bent or banana-shaped compounds is dependent upon several factors, including the size of the molecule, the number of aromatic rings, the position and the magnitude of the bent angle, the size, number, position and nature of the substituents, the nature and direction of linkage groups and the length and nature of the terminal alkyl chains. In general, any minor change in these structural elements leads to a disproportionate change in phase behaviour. One important aspect is the nature and size of the substituent in the central core, which largely influences the mesophase behaviour [4–8]. Symmetrical bent-core molecules comprising an angular central core (for example: 1,3-substituted phenyl moiety), or mesogenic dimer with an odd-numbered acyclic alkylene unit, substituted with two identical linear rod-like mesogenic segments (arms) generally exhibit higher transition (melting and clearing) temperatures.

Molecules incorporating a rather rigid bent aromatic core, such as the resorcinol derived compound [1].

![Bent core molecule](image)

**Figure 4(c).1:** Bent core molecule
Mesogenic dimers with an odd-numbered non-cyclic (flexible) spacer unit [1]

![Bent mesogenic dimer](image)

**Figure 4(c).2:** Bent mesogenic dimer

To reduce the transition temperatures and to fill the gap between symmetrical bent-core LCs and rod like LCs (calamitic LC) unsymmetrical bent-core molecules have been designed and synthesized. In the search for unsymmetrical bent core systems the recent attempts have been directed by the combination of an angular 3,4'-disubstituted biphenyl central unit [7-10] with phenyl benzoate moieties possessing carbosilane or siloxyl groups in the end chains to realize the ferroelectric switchable liquid crystalline phase. In these unsymmetrical BC LC materials either the length of the two arms in the molecule are different or the two linking functional groups attached to angular central core are varied [7, 9–15]. Hence the modification of angular 3,4'-disubstituted biphenyl central unit with the introduction of an ester linkage viz., COO moiety between the phenyl units leads to structural variation of polar groups in bent core molecules and hence can promote a broad range of interesting variations [1, 2] in their mesogenic properties. The first reported parent compounds of the four-ring systems [16] exhibiting banana mesomorphism is presented in **Figure 4(c).3.** *The four ring molecule possesses two OH groups in two wings, located in unsymmetrical positions, which deviates significantly from the typical symmetrical and/or V-shape of other bent core molecules.* The parent compounds without any substituent in the central core, which promoted the bent structure, exhibited polarization modulated $B_{1rev}$ tilted phases when identical alkyl chains ($n \geq 10$) are present at both ends of the molecule.
Any substituent ortho to ester linkage separating the two phenyl rings may substantially change the conformation of the molecule depending on the size, polarity and direction of substituents. The introduction of a methyl or chloro moiety in the angular phenyl moiety at the 2-position (bay position of the central core) not only increases the bent angle but also disturbs the planarity in the molecule. The thermal stability and nature of the mesophase is determined by the contributions of the polarizability of different segments of the molecule and geometric anisotropy of the molecule. Hence the competing influences between core-core interactions, polarizability anisotropy and geometric anisotropy of molecular conformation contribute to the nature of the mesophase.

Most innovatively, the symmetry of the bent-cores has also been reduced effectively by introducing various lateral substituents such as fluoro (F), chloro (Cl), bromo (Br), cyano (CN), nitro (NO₂) and methyl (CH₃) groups into either the central 1,3-phenylene ring at the 2-, 4- and 6-position(s) or the aromatic cores of the two arms attached to the central angular core [17,18]. Owing to the large electronegativity of the fluorine (F) atom, functional entities like F, CF₃, CF₂O, etc. are electron withdrawing and find many applications in

Figure 4(c).3: Parent compound
materials [19]. Fluoro substitution has in particular been used in LC materials, in which the electronic effects of a C–F bond in the form of inductive and resonance effects helps in modifying properties like melting point, transition temperatures, mesophase and other physical properties of the parent system [20, 21]. Fluoro substituents have been successfully and usefully incorporated into liquid crystal molecules because of the combination of small size and high polarity [22]. However the use of fluoro substituent in bent-core compounds synthesis and the study of its influence on mesogenic and electro-optical properties in these bent-core compounds are meagre [1]. Further the investigations on the importance of central core possessing a polar linking group in the bent direction that can contribute to the magnitude of polarization and also influence the phase structure are meagre [1, 2].

The recent experimental investigations also support in favour of a biaxial nematic phase that is exhibited by bent-core mesogens composed of two rod-like mesogenic wings coupled to a central linking moiety has been debated very well. The central linking moiety is mainly thiadiazole or oxadiazole derivatives with a large transverse dipole and an obtuse bent angle between the two arms. This represents a banana or V-shaped molecule composed of two uniaxial arms with a central transverse dipole. The study of the influence of dipole–dipole correlations on the stability of the biaxial nematic phase, in the two-particle-cluster approximation [23, 24], revealed that (a) the stabilization of biaxial nematic phases are substantially favoured by the molecular-shape dependent polar correlations between neighbouring molecules, and (b) the electrostatic interactions between permanent transverse dipoles of bent-core molecules also significantly stabilize the biaxial nematic phases. The introduction of a 2-chloro group in the 1,3-disubstituted phenyl ring of a bent-core molecular architecture can generate an obtuse bond angle of ~145°, which gives rise to an increase in bend angle as well as a strong dipole in the bending direction. Incorporation of chloro group in the 2-position of 1,3-phenyl moiety reduced the bend from 120 to ~145° and with the decrease the number of rings from five or more to four in molecular unit, places these compounds at the borderline between classical rood like LCs and bent-core mesogens. The
realization of such a molecular architecture leads to a reduction in rotational 
disorder as well as a strong dipole in the bent direction. If molecular 
interactions are strong enough then the molecular structure can also promote 
polar biaxial nematic phases.

In this chapter, few homologues \textbf{n-2F-2Me-m} and \textbf{n-2F-2Cl-m}, where \textbf{n} and 
\textbf{m} (\textbf{n} = \textbf{m} = 5 or 10, \textbf{n} = 5, \textbf{m} = 10; and \textbf{n} = 10, \textbf{m} = 5) represent the number of 
methylene units in end alkyloxy chains, have been designed following the 
hypothesis described above and synthesized successfully following the simple 
synthetic procedures. The characterization of these materials are described in 
order to study the effect of substituent as well as the length of the terminal 
chain and in turn the importance of interlayer interaction in bent-core liquid 
crystals containing four aromatic rings with ester and imine linkages where two 
lateral hydroxyl group in both the wings, ortho to imine linkage participate in 
termolecular H-bonding to stabilize the imine linkage of the molecule.

\textbf{4(c).2 List of target compounds designed and synthesized:}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image1.png}
\caption{Modified structure of bent-core molecule having non-polar substituent at the bent direction.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image2.png}
\caption{Modified structure of bent-core molecule having polar substituent at the bay position.}
\end{figure}
Experimental:
The starting material 4-n-alkyloxysalicylaldehyde was prepared by Williamson etherification of 2,4-dihydroxybenzaldehyde with appropriate n-alkyl bromide in presence of KHCO₃ as base and potassium iodide as catalyst in dry acetone. 2-methyl-3-nitrobenzoic acid/2-chloro-3-nitro benzoic acid was converted into corresponding amine by reduction using 4% Pd-C, which was condensed with 4-n-alkoxy 2-hydroxybenzaldehyde (4-n-pentyloxy and 4-n-decyloxy 2-hydroxy benzaldehyde) in presence of few drops of glacial acetic acid. 2-fluoro-N-[4-((2-hydroxy-4-(pentyloxy (or n-decyloxy)benzylidene)amino)]phenol was prepared by condensation with 4-n-pentyloxy (or 4-n-decyloxy) 2-hydroxy benzaldehyde in presence of glacial acetic acid. The synthesis of individual segments can lead to desired unsymmetrical end alkyl chain lengths. Further esterification reaction of the designed compounds n-2F-2Me-m (n = m = 5, 10; n = 5, m = 10; n = 10, m = 5) and n-2F-2Cl-m (n = m = 5, 10; n = 5, m = 10; n = 10, m = 5) are presented in scheme 4(c).1.

The details of the experimental procedures along with the spectroscopic data for the compounds are presented in the experimental part of Chapter 3. The liquid-crystalline behaviour of the synthesised compounds has been investigated by polarising optical microscope and differential scanning calorimetry (DSC).

Scheme 4(c).1: Reagents and condition (i) Ethanol, drops of glacial AcOH, Δ4h. (ii) DCC, DMAP, DCM, 48h.
4(c).3 Results and discussion:
The unsymmetrical four-ring molecules possess an alkoxy chain attached at both ends of the bent core molecule, with a highly polar fluoro moiety in the second ring of long arm of the molecule, and methyl or chloro group transverse to the molecular axis in the central ring of the molecule. The highly polarizable aromatic parts which have conjugated electrons contribute to the anisotropic dispersion potential between them. The molecule consists of two linkages viz., salicylidene linkage, an ester linkage and salicylidene linkage between the four phenyl rings. The salicylidene linkage instead of benzylidene linkage was preferred due to the presence of ortho hydroxyl group in benzylidene moiety which enhances the transverse dipole-moment as well as the stability of the imines through intramolecular H-bonding to overcome the hydrolytic instability of the molecules towards moisture. The homologues n-2F-2Me-m possesses a methyl group in the transverse direction of the molecule and fluoro substituent is positioned adjacent to ester linkage in the central core. The homologues n-2F-2Cl-m possesses a chloro group in the transverse direction of the molecule and fluoro substituent is positioned adjacent to ester linkage in the central core. The salicylidene aniline core, present in these compounds, apparently seems superior to the benzylidene aniline core with respect to mesogenicity, and is more stable towards hydrolysis.

The chemical structures of the final compounds were confirmed by spectral techniques and elemental analysis. The analytical data is in good agreement with their chemical structures. The main observed FTIR peaks confirmed the intramolecular H-bonding of OH--N at 3184~3186 cm\(^{-1}\), C=O stretching of an ester at 1737~1741 cm\(^{-1}\), C=N stretching of an imine at 1602~1606 cm\(^{-1}\), C=C stretching of an aromatic ring 1490 cm\(^{-1}\), and C-O-C stretching of an ester ~1290 and ~1170 cm\(^{-1}\). The chemical shift values of representative compound 5-2F-2Me-5, at \(\delta = 13.51\) and 13.39 in \(^1\)H NMR spectrum confirmed the hydrogen bonded hydroxyl groups with the nitrogen in the imine linkages. The values of \(\delta = 8.45\) and 8.39 confirmed the formation of imines. The aromatic
protons with characteristic signals confirmed the molecular formation and its purity. All other compounds also gave satisfactory NMR spectra.

Mesomorphic properties: Polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) studies:

The transition temperatures, enthalpies and entropies associated with the phase transitions of all the compounds of the two homologues series n-2F-2Me-m (n = m = 5, 10; n = 5, m = 10; n = 10, m = 5) and n-2F-2Cl-m (n = m = 5, 10; n = 5, m = 10; n = 10, m = 5) obtained from DSC at a scan rate of 5°C/min in the second heating and cooling scans are presented in Table 4(c).1. Differential scanning calorimetry (DSC) spectra of two representative compounds 10-2F-2Me-10 and 5-2F-2Cl-10 are presented in Figure 4(c).6 and Figure 4(c).7 respectively. DSC spectrum of 10-2F-2Me-10 (Figure 4(c).6) exhibited five transitions at 86.4°C (ΔH = 44.5 kJ/mol, ΔS = 124.0 J/mol/K), 90.2°C (ΔH = 0.3 kJ/mol, ΔS = 1.0 J/mol/K), 98.8°C (ΔH = 0.1 kJ/mol, ΔS = 0.2 J/mol/K), 137.8°C (ΔH = 2.2 kJ/mol, ΔS = 5.4 J/mol/K), 139.8°C (ΔH = 0.3 kJ/mol, ΔS = 1.8 J/mol/K) in heating cycle and five transitions at 53.9°C (ΔH = 36.3 kJ/mol, ΔS = 111.1 J/mol/K), 87.4°C (ΔH = 0.3 kJ/mol, ΔS = 0.9 J/mol/K), 97.8°C (ΔH = 0.1 kJ/mol, ΔS = 0.4 J/mol/K), 137.0°C (ΔH = 2.6 kJ/mol, ΔS = 6.5 J/mol/K), 139.1°C (ΔH = 0.9 kJ/mol, ΔS = 2.3 J/mol/K) in the cooling cycle.

Table 4(c).1: DSC data of n-2F-2Me-m and n-2F-2Cl-m homologues. Phase transition temperatures (°C) and mesomorphic thermal range of the compounds n-2F-2Me-m (n = m = 5, 10; n = 5, m = 10; n = 10, m = 5) and n-2F-2Cl-m (n = m = 5, 10; n = 5, m = 10; n = 10, m = 5), recorded for second heating and second cooling cycles at 5°C/min from DSC and confirmed by polarized optical microscopy. The enthalpies (ΔH in kJ/mol) and entropies (ΔS in J/mol/K) respectively are presented in parentheses.
5-2F-2Cl-5  Cr 100.7 (12.4, 33.3) N 122.8 (0.08, 0.20) Iso
          Cr 90.7 (10.7, 29.5) N 121.3 (0.08, 0.20) Iso
5-2F-2Cl-10  Cr 96.2 (4.5, 12.2) SmX 112.2 (6.7, 17.5), N 123.1 (0.3, 0.8) Iso
          Cr 73.9 (6.4, 18.4) SmX 110.6 (7.1, 18.6), N 122.0 (0.3, 0.9) Iso
10-2F-2Cl-5  Cr 98.8 (5.8, 15.8) SmX 100.5 (0.28, 0.75), N 126.3 (0.34, 0.85) Iso
          Cr 87.5 (7.0, 19.4) SmX 98.7 (2.66, 7.15), N 125.2 (0.29, 0.73) Iso
10-2F-2Cl-10* Cr 92.7 (10.2, 28.0), SmX1 128.2 (1.36, 3.39), SmX2 135.6 (4.84, 11.8) Iso
          Cr 71.9 (14.6, 42.3) SmX1 126.6 (0.29, 0.72), SmX2 132.9 (3.26, 8.03) Iso

Note: * compounds exhibited a crystal–crystal transition during the first heating cycle which disappeared in the second heating cycle.

DSC spectrum of 5-2F-2Cl-10 (Figure 4(c).7) shows three transitions in the heating cycle at 96.2°C (ΔH = 4.5 kJ/mol, ΔS = 12.2 J/mol/K), 112.2°C (ΔH = 6.7 kJ/mol, ΔS = 17.5 J/mol/K), 123.1°C (ΔH = 0.3 kJ/mol, ΔS = 0.6 J/mol/K), and three transitions in the cooling cycle at 73.9°C (ΔH = 6.4 kJ/mol, ΔS = 18.4 J/mol/K), 110.6°C (ΔH = 7.1 kJ/mol, ΔS = 18.6 J/mol/K), 122.0°C (ΔH = 0.3 kJ/mol, ΔS = 0.9 J/mol/K).

Figure 4(c).6: DSC thermogram of 10-2F-2Me-10 on second heating and cooling at 5°C/min.
All the compounds exhibit enantiotropic mesomorphic behaviour. The molecule is made up of three parts, where (i) both the wings comprises of same n-alkoxy chain, $5\text{-2F-2X-5}$ and $10\text{-2F-2X-10}$, ($X = \text{Me or Cl}$) (ii) longer wing contains lower n-alkoxy chain containing five methylene units i.e. 4-n-pentyloxy salicylaldimine, while the shorter wing contains longer n-alkoxy chain containing ten methylene units i.e. 4-n-decyloxy salicylaldimine, $5\text{-2F-2X-10}$, ($X = \text{Me or Cl}$) (iii) longer wing contains ten methylene units in n-alkoxy chain i.e. 4-n-decyloxy salicylaldimine, while the shorter wing contains smaller n-alkoxy chain with five methylene units i.e. 4-n-pentyloxy salicylaldimine $10\text{-2F-2X-5}$, ($X = \text{Me or Cl}$).

Polarising optical microscope were carried out on different types of substrates viz., glass plate and cover slip, commercial ITO coated cell of $3.2\mu$ HG cell and $5.0\mu$ HT cell.

$5\text{-2F-2Me-5}$: The lower homologue $5\text{-2F-2Me-5}$ was found to exhibit marble texture characteristic of nematic phase in heating and cooling cycles when viewed using glass plate and cover slip. A large supercooling effect is observed in the cooling cycle. The nematic phase is identified by the appearance of droplet texture followed by marble textures exhibited by the
sample 5-2F-2Me-5, as shown in Figure 4(c).8a and Figure 4(c).8b. Moreover the compound displays a wide thermal range of nematic phase in cooling cycle.

5-2F-2Me-10: When the pentyloxy chain in one of the wings (shorter wing) is changed to decyloxy moiety the compound 5-2F-2Me-10 was also found to exhibit marble texture characteristic of nematic phase in heating and cooling cycles when viewed using glass plate and cover slip. A large supercooling effect is also observed in the cooling cycle driving the mesomorphism to ambient temperature close to room temperature. The longer terminal end alkyl chains govern the interlayer molecular order and hence the interlayer steric interactions might have played an important role to realize a variety of phase structures [25]. The sample 5-2F-2Me-10 on further cooling from nematic phase, undergo a phase transition to with a characteristic fan texture exhibited by smectic phase as shown in Figure 4(c).8d. Hence the characteristic marble texture Figure 4(c).8c in high temperature region confirmed the nematic phase while the fan texture (Figure 4(c).8d) resembles banana phases exhibited by the five-ring bent-core compounds.

Figure 4(c).8: Textures of n-2F-2Me-m contained between normal glass plate
and cover slip (a) Growth of Nematic phase at 146°C of $5\text{-}2\text{F}\text{-}2\text{Me}\text{-}5$. (b) Nematic phase of $5\text{-}2\text{F}\text{-}2\text{Me}\text{-}5$ at 132°C. (c) Marble texture at 133°C of $5\text{-}2\text{F}\text{-}2\text{Me}\text{-}10$. (d) Smectic phase exhibited by $5\text{-}2\text{F}\text{-}2\text{Me}\text{-}10$ at 64°C.

**10-2F-2Me-5:** When the pentyloxy chain in one of the wings (longer wing) is changed to decyloxy moiety the compound $10\text{-}2\text{F}\text{-}2\text{Me}\text{-}5$ exhibits nematic phase in the heating cycle and nematic and smectic phases in the cooling cycle similar to the compound $5\text{-}2\text{F}\text{-}2\text{Me}\text{-}10$. A large supercooling effect is also observed in the cooling cycle driving the mesomorphism to ambient temperature close to room temperature. Hence both these compounds with longer and shorter terminal end chains almost exhibit similar mesophase behaviour of enantiotropic nematic phase and monotropic smectic phase of banana type. The chemical incompatibility between the aromatic mesogenic cores and the flexible end aliphatic (methylene units) chains leads to micro-segregation. Such micro-segregation has been supported by the presence of molten state of alkyl chains in liquid crystalline (LC) states leading to strong super cooling effect. Moreover such incompatible units lead to the formation of one dimensional (1-D) uniform smectic layers or two dimensional modulated phases of mesogenic aromatic cores and aliphatic regions and with the interlayer boundary regions prominently occupied by the alkyl chains. Further work is in progress to confirm the banana phase as a part of future programme.
At 71.0°C

Figure 4(c).9: Microphotographs of **10-2F-2Me-5** under 20X magnification, temperature is shown below the figure.

Polarising optical microscope were carried out on different types of substrates viz., glass plate and cover slip, commercial ITO coated cell of 3.2µ HG cell and 5.0µ HT cell.

**10-2F-2Me-10**: The optical textures of sample **10-2F-2Me-10** using four different preparation methods (i) untreated glass plate and coverslip (ii) commercial cells made up of poly imide treated indium tin oxide coated glass plates for homogenous alignment (cell gap = 3.2µ HG planar cell) and (iv) commercial cells made up of polymer treated indium tin oxide coated glass plates for homeotropic alignment (cell gap = 5.0µ homeotropic cell) are studied. The examination of the pristine samples for **10-2F-2Me-10** sandwiched between a untreated slide and a coverslip gave usual marble texture of nematic phase and unusual textures of smectic phases when examined on POM attached with a hot stage. On cooling from the isotropic phase exhibited distinctly well-known characteristic textures of nematic phase viz. 2- and 4-brush schlieren texture, planar and marble textures with threads as boundaries throughout the nematic phase temperature range. The growth of Schlieren texture is accompanied by Brownian motion. The unusual textures could not be identified and hence homogenous cell of thickness 3.2 µm (assembled with polyimide coated parallel rubbed ITO coated glass plates such that the rubbing directions are anti-parallel to promote homogenous molecular alignment) are filled with **10-2F-2Me-10** by capillary action in isotropic phase. The growth of smectic phase (SmX3) on slow cooling from nematic phase **figure 4(c).10a** and **b** in addition to two other different types of smectic phases.
are shown in Figure 4(c).10c and d) of SmX2 followed by SmX1 (Figure 4(c).10e) before crystallization below 53°C (Figure 4(c).10f).

Figure 4(c).10. POM textures of 10-2F-2Me-10 in a 3.2μm HG cell under 20X magnification, temperature is shown below the figure.

5-2F-2Cl-5: The lower homologue 5-2F-2Cl-5 was found to exhibit marble texture shown in Figure 4(c).11a characteristic of nematic phase in heating and cooling cycles when viewed using glass plate and cover slip. Even though a small supercooling effect is observed in the cooling cycle it is not comparable with the supercooling observed in 5-2F-2Me-5. It may be due to the polar
chloro group in the transverse direction of the molecule which might have influenced the supercooling. Moreover the nematic-isotropic transition temperature is also found to be lowered by ~25°C in spite of the replacement of methyl by chloro substituent in the transverse direction of the molecule. In a commercial PI coated parallel rubbed sandwich cell filled with the sample 5-2F-2Cl-5, when the director (optic axis) of the nematic phase was aligned with one of the polarizer’s direction in POM studies, the sample appeared black, Figure 4(c).11b, a defect free planar texture, such that the high temperature phase resembled a birefringent plate of a crystal with the optic axis in the plane of the substrate. With the variation of the sample in azimuthal angle the transmitted light intensity between crossed polarisers continuously increased to a maximum (Figure 4(c).11c), when the optic axis was oriented at 20°. The nematic phase was confirmed by characteristic flickering upon tapping the sample caused by Brownian motion. Hence the compound 5-2F-2Cl-5 exhibits enantiotropic nematic phase only.

5-2F-2Cl-10: When the pentyloxy chain in one of the wings (shorter wing) is changed to decyloxy moiety the compound 5-2F-2Cl-10 was also found to exhibit marble texture characteristic of nematic phase in heating and cooling cycles when viewed using glass plate and cover slip. The supercooling effect is also observed in the cooling cycle driving the mesomorphism to a lower temperature but not like the methyl substituted homologues. Further the compound also exhibited smectic phase both in heating and cooling cycles. The longer terminal end alkyl chains govern the interlayer molecular order and hence the interlayer steric interactions might have played an important role to realize a variety of phase structures [25]. The sample 5-2F-2Cl-10 on further cooling from nematic phase, undergo a phase transition to with a characteristic fan texture exhibited by smectic phase. In a commercial PI coated parallel rubbed sandwich cell (5.0µ HG cell) filled with the sample 5-2F-2Cl-10, it exhibited characteristic fan texture (Figure 4(c).11d) resembling banana phases exhibited by the five-ring bent-core compounds.

10-2F-2Cl-5: When the pentyloxy chain in one of the wings (longer wing) is changed to decyloxy moiety the compound 10-2F-2Cl-5 was also found to
exhibit two enantiotropic phases. The higher temperature phase exhibited schlieren texture (Figure 4(c).11e) characteristic of nematic phase, while the lower temperature phase is a smectic phase with characteristic textures resembling the other homologues.

10-2F-2Cl-10: The optical textures of sample 10-2F-2Cl-10 using untreated glass plate and cover slip gave 4-brush defect schlieren texture as shown in Figure 4(c).11f characteristic of smectic phase. On further cooling the schlieren texture transformed into a smooth texture resembling smectic C (anti) phase. The lower temperature phases exhibited unknown smectic type phase and are shown in Figure 4(c).11g and h. Hence the compound 10-2F-2Cl-10 exhibited only two enantiotropic phases unlike its methyl analogue 10-2F-2Me-10 which exhibited four phases.
Figure 4(c).11. Defect texture of the compound n-2F-2Cl-m during cooling from isotropic phase (a) Marble texture at 114°C of 5-2F-2Cl-5, (b) complete extinction at 123°C of 5-2F-2Cl-10 in a 5.0µ HG cell, (c) same temperature as in (b) with optic axis rotated 20° from polarizer direction, (d) POM texture at 102°C of 5-2F-2Cl-10 in a 5.0µ HG cell under 20X magnification. (e) 2 and 4 brush defect texture at 120°C of 10-2F-2Cl-5, (f) SmC like phase at 132°C of 10-2F-2Cl-10, (g) Texture during transition at 126.6°C of 10-2F-2Cl-10, (h) POM texture at 120°C of 10-2F-2Cl-10 after phase transformation.

4(c).4 Absorption and emission spectral analysis:
The UV-visible absorption spectra of the compounds n-2F-2Me-m (n = m = 5, 10; n = 5, m = 10; n = 10, m = 5) (c = 10⁻⁵ M solution in CHCl₃) are shown in Figure 4(c).12 revealed strong absorption at 343 nm with a large molar extinction coefficient (ε~ 692000-565000 Lmol⁻¹cm⁻¹) and the compounds n-2F-2Cl-m (n = m = 5, 10; n = 5, m = 10; n = 10, m = 5) (c = 10⁻⁵ M solution in CHCl₃) are shown in Figure 4(c).13 exhibited strong absorption peak at 347 nm with a large molar extinction coefficient (ε~ 668000-598000 Lmol⁻¹cm⁻¹), which reflected the symmetry allowed π-π* transition of chromophore in the molecule [26].
The fluorescence spectra of these compounds n-2F-2Me-m (n = m = 5, 10; n = 5, m = 10; n = 10, m = 5) and n-2F-2Cl-m (n = m = 5, 10; n = 5, m = 10; n =
10, m = 5) (Figure 4(c).14, Figure 4(c).15) were studied in chloroform solution (conc. 10⁻⁵ M) and it was found that both homologous series exhibit Stokes shift (~92 nm), which reflects the structural relaxation of the excited molecule, is significantly larger than in reported push-pull systems exhibiting liquid crystal behaviour [27], indicating that the molecular conformation changes upon excitation.

**Figure 4(c).12:** UV-visible spectra of n-2F-2Me-m in chloroform (C =10⁻⁵ M)

**Figure 4(c).13:** UV-visible spectra of n-2F-2Cl-m in chloroform (C =10⁻⁵ M)
Figure 4(c).14: Fluorescence spectra of the series n-2F-2Me-m in chloroform (C = 10^{-5} M)

Figure 4(c).15: Fluorescence spectra of the series n-2F-2Cl-m in chloroform (C = 10^{-5} M)
4(c).5 Conclusions:
Unsymmetrical four-ring bent-core compounds possessing unequal chain lengths and different substituents in the central core in the molecule have been designed, successfully synthesized and characterized. All the compounds were found to be liquid crystalline and exhibit a wide variety of nematic and smectic polymorphism. It was found that, the formation of different mesophase is not solely determined by the position of the substituent but also type of the substituent. Substitution by methyl, fluoro and chloro group on the bent-core system produced liquid crystals with a wide variety of mesophases. Further work is in progress to confirm the banana phase as a part of future programme.
References:


