2.1 BENT-CORE MOLECULES: A REVOLUTION

It was believed that molecules deviating from linearity could be liquid crystalline in nature [1] because rotation about the symmetry axis does not affect the order parameter so liquid crystal molecules rotate freely along this symmetry axis, unless there is no symmetry requirement. If non-linear molecules rotate freely about their long molecular axes, the excluded volume becomes large and violates the liquid crystallinity [1]. Until the discovery of polar order, only a few bent-shaped molecules have been reported. Vorlander reported some mesogenic bent-core liquid crystals in 1929 but the compounds seemed to be thermally less stable than their linear analogue. It was Matsunaga and co-workers [2,3] who revived the work on bent-core liquid crystals in 1991. One of the molecules 1,3-phenylene bis[4-(4-n-octyloxyphenyliminomethyl) benzoate] in Figure 2.1, was a major breakthrough as it led to the discovery of polar switching in bent-core liquid crystals. Compound A [4] in Figure 2.1 is the one synthesised by Vorlander and compound B [3,5,6] and compound C [7,8] are the ones in which polar switching was first discovered.

![Figure 2.1 Two historic bent-core compounds](image)

Simultaneously, Cladis and Pleiner [9] reported the possible emergence of polar phases in some board and bent-shaped molecules based on biaxial orders in side-chain [10] and main-chain polymers [11]. But it was due to Watanabe that polar switching gained importance [7,12]. Takezoe’s presentation at the international liquid crystal conference in Kent triggered extensive research on bent-core liquid crystals [8,13,14]. Besides polar order bent-core molecules have another important aspect to attract attention viz. chirality. Berlin group [15] and Sekine et al. [5,16] first reported spontaneous chiral resolution in a
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nontilted phase. It was pointed out that indistinguishable domains appear to be bright and dark by slightly decrossing the polarisers which are interchanged by decrossing the polarisers in opposite direction [15].

2.2 THE BANANA MANIA: QUEST FOR CHIRALITY IN ACHIRAL MOLECULE

Takezoe enlightening lecture at the 6th International liquid crystal conference in 1996 at Kent, Ohio in U.S. has sown the seeds for a new area of research of banana liquid crystals. He reported ferroelectric properties of a new type of liquid crystalline phase, in which chirality is manifested by achiral bent-shaped mesogens. Practically, their own shape is the origin of their permanent dipole moment. Those materials [7,16-18] possess C_{2V} symmetry, apart from exhibiting liquid crystalline polymorphism, also show distinct switching characteristics. They possess smectic stacking of molecules with hindered rotation exhibit polar order [13b,19-31], which resulted in a net spontaneous polarization and hence ferroelectricity (or antiferroelectricity). Further work on one of the liquid crystalline phases, which was first designated as B2 phase [32] revealed an antiferroelectric switching process. In the antiferroelectric switchable phase, the molecules arrange in anticlinical fashion in adjacent layers in such a way that the layer polarization alternates from layer to layer and the optical axis is tilted relative to the layer normal [26]. Hence this mesophase has been designated as SmCP_A, a tilted smectic phase (SmC) with a polar order of the molecules (P) within the layers and an antiferroelectric interlayer correlation (A). Further it was shown that the liquid like smectic layers of some of these molecules have a polar structure provided by the dense packing of the bent-core molecules [26,33,34]. These different arrangements are illustrated in Figure 2.2 below. By applying an electric field the molecules can be switched into a ferroelectric, i.e. non-centrosymmetric structure (SmCP_F). Further the polar order is equivalent to a non-centrosymmetric arrangement of molecules, and hence these molecules are also of interest to exhibit second order nonlinear optical (NLO) properties characterized by large first hyperpolarizability (β) values.
Recently, very large second-order NLO effects have been measured in these ferroelectric phases [35,36]. These distinct uncommon molecular structures, the unconventional mesomorphic properties, the occurrence of a spontaneous symmetry breaking in some cases, the biaxial smectic phases and the special switching behavior of some of their mesophases immediately attracted great interest to design and synthesize new materials having potential applicability in the fields like switchable nonlinear optical devices.

2.3 CHIRALITY IN ACHIRAL BENT-CORE MOLECULE

Interestingly, the chirality is exhibited only by banana-shaped achiral molecules exhibiting liquid crystalline behaviour and not by a linear or calamitic mesogenic compound. Jirakon et al. reported [29,37] a novel series of banana-shaped molecules with a central bent core based on a 2,7-dihydroxynaphthalene group, the side wings containing a Schiff’s based moiety, and alkoxy flexible tails. Among these, the molecules with $n = 8-16$ formed a novel smectic phase. The textures that developed from the isotropic melt was unconventional.

**Figure 2.2 Different arrangements in SmC**

![Diagram of SmC phases](image-url)
and had a liquid like association of the molecules similar to the SmA or SmC phase. Weissflog et al. [38] also observed that small fractal domains initially grew and then coalesced into several large domains with very weak birefringence and fine structure without any anisotropy. Natural occurrences of the helical arrangement of molecules in these materials were suggested. The molecule with n = 6 formed a frustrated smectic phase, which exhibited a simple fan-shaped texture. Similar studies of chiral domains of opposite handedness in banana liquid crystals is reported by Sadashiva et al. [39,40], Dantgrabler et al. [24b] and Weissflog et al. [38] in different five-ring bent core molecular systems. Field induced switching between states of opposite chirality have also been observed. However, the arrangement of the molecules in chiral domains of banana phases is not yet clear. Jirakon et al. [29,41] proposed three possible origins based on the banana shape.

1) Tilting of the molecule to the layer normal producing the mirror image
2) Helical twisting of the layers to escape the spontaneous polarization and
3) A chiral or twist conformation of the ester linkage groups.

They suggested two possibilities of helical twist and/or twist conformation leading to chirality. However, it has not been clarified which is the real origin for the chiral induction, and it has been thought that the banana shape is essential for absolute chiral induction in mesophase. On the other hand, it is well-known that absolute chiral induction in crystal takes place by freezing one chiral conformation of achiral molecules during the crystallizing process in which a banana shape is not essential. However Kishikawa et al. [42] reported generation of chiral mesophase in calamitic liquid crystal exhibiting smectic C phase and proposed the origin of helical conformation of the phenyl ester moiety in the molecules based on intermolecular interaction rather than the helical layered structure itself. Research is going on round the globe to pinpoint the origin of these specialties of bent core mesogens.
2.4 MOLECULAR ARCHITECTURE

The occurrence of novel phases, polarity and chirality in the mesophases of bent-core molecules strongly depends on the molecular structure and intermolecular interactions. The central bent unit, linking groups, rod-like wings, the substituents on the rings, number of rings together constitutes the molecular structure of a bent-core system. In Figure 2.3 the general structure of a bent-core molecule and some of the reported central bent unit is given. A brief discussion on the various factors affecting mesomorphism in a bent-core system.

Figure 2.3 General structure of bent-core molecules and positions of structural variations

2.4.1. INFLUENCE OF CENTRAL BENT UNIT

The length of the bent-core and the bending angle of the central unit play an important role in the formation of polar ordered mesophases. The minimum number of rings to stabilise the polar order is five [8,13b,14,43]. Generally six-
membered aromatic or hetero-aromatic rings have been used as the bent central unit and have been observed that bent-core units comprising of three aromatic rings conferred the highest thermal stability to the mesophases. In general, increasing the size of the rigid bent unit increases the transition temperatures and stabilises the columnar phases (Colr) which can be suppressed to obtain polar smectic phases by using longer terminal chains. Very few reports appeared in literature on compounds incorporating non-aromatic units in the rigid segments. Some of the compounds incorporating non-aromatic units like piperazine [44], tetrahydropyrans [45] have been shown below. 5-membered rings like 1,3,4-oxadiazole derivatives [46,47] 1,3-oxazoles [48] and 1,2,4-oxadiazoles [49] have a large bending angle and are at the borderline between bent-core and calamitic mesogens. Some reported compounds have been shown below in Figure 2.4.

**Figure 2.4** Examples of non-aromatic rings and oxadiazole moiety used as the bent-unit

<table>
<thead>
<tr>
<th>Table 2.1 Influence of central bent unit (BU) on liquid crystalline properties.</th>
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</thead>
<tbody>
<tr>
<td>1. Ph</td>
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<tr>
<td>2. Naph</td>
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<td>3. Biph</td>
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<td>5. Tol1</td>
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<tr>
<td>6. Tol2</td>
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<tr>
<td>7. PhSPh</td>
</tr>
<tr>
<td>8. PhCH₂Ph</td>
</tr>
</tbody>
</table>

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Modification of the bending angle is done by decreasing the size of the central bent unit or substituents at the bent central unit, close to the linking groups X and X’ [8,50]. Layer polarity in bent-core molecules can be achieved by varying the bending angle between 105° and 140° [50]. Molecules with bending angle outside these limits in most cases show non-polar mesophases.

2.4.2. INFLUENCE OF TERMINAL CHAINS

The length of the hydrocarbon chain at the terminal positions of the bent-core molecule also has an important role in determining the phase structures. *Cis*-double bond increases the flexibility of the chains and drastically reduces the melting point, leading to glassy polar smectic phases [51]. Branching in the chains can also reduce the melting points and favour the formation of glassy materials [52] besides leading to transition from AF to FE smectic phases [53]. Perfluorinated chains (RF) stabilise the SmCP_A mesophases, but increases the melting temperatures and requires more space than the alkyl chains [24(a),54]. However the steric effect disturbs the packing of the bent core molecules causing a transition from polar SmCP_A phase to non-polar SmA phase [54] at elevated temperature. Non-polar SmA phases are possible for molecules with only three rings due to the mesophase stabilising effect of the RF chains [54]. This may be due to the reason that a three-ring bent-core is too short for polar order or inhibition of a dense polar packing by the bulky RF chains. Oligo-(siloxane) and oligo-(carbosilane) units reduces the melting temperatures and give rise to FE switching phases with low viscosity[24(b),24(d)], mesophases with chiral superstructure and different modulated and undulated smectic phases showing field-induced switching of super-structural layer chirality [24(c)]. Their remarkable behaviour is attributed to their segregation into separate sub-layers and size effects of these bulky groups. A polyether chain however strongly reduces the thermal stability of the mesophases due to high flexibility in spite of the fact that broad mesomorphic regions around room temperature can be obtained due to reduction in the melting temperature [51]. Non-polar chains favour mesophase formation, whereas polar chains lowers mesophase stability.
due to disturbances created in the molecular organisation owing to their compatibility with the bent-core skeleton.

2.4.3. EFFECT OF LINKING GROUPS IN BENT-CORE MESOMORPHISM

A certain degree of flexibility of the bent core has to be maintained to prevent crystallisation and promote mesomorphism which can be done by introducing some linking groups in the bent-core system. The linking groups may be azomethine units (C=N), ester (COO), ethylene (C≡N), acetylene (HC≡CH), azo linkages (N=N). The problem with the Schiff’s base units is the hydrolytic instability which can be solved by introducing a hydroxyl group (-OH) in the ortho position of the azomethine unit thereby promoting intramolecular hydrogen bonding and hence stability [55-57]. Azobenzene units are photo-responsive in nature [58,59]. The direction of linking group also has a significant effect on mesomorphism as demonstrated by some of the compounds [24(a),40,60-63] in Figure 2.5.

Figure 2.5 Bent-core compounds showing the effect of direction of linking groups
The homologues series of the compounds in Series A exhibits two different types of smectic phases, a polar AF switching and a non-polar intercalated one, and a columnar phase, the sequence being SmC, Col, and SmCP\textsubscript{A} with increasing chain length. The corresponding thioester exhibit the same phase sequence. On reversing the direction of the ester linkage between the central and the middle phenyl rings as in series B, the liquid crystalline behaviour is suppressed. The analogous thioester showed in series C however shows only a non-polar SmC phase and a nematic phase. Reversing the direction of the ester linkage between the middle and the outer phenyl rings promotes a sequence of undulated FE (USmCP\textsubscript{FE}) and AF (USmCP\textsubscript{AF}) polar smectic phases. If all the -COO groups point in the same direction, then different columnar phases and FE switching polar smectic phases can be found.

Studies on the azo-functionalised bent-core compounds have introduced a new dimension called photochromism in bent-core liquid crystals [58(c),59,67]. Liquid crystalline compounds wherein the azo group is incorporated within the molecular framework have advantages over the doped systems. Nonlinear optical (NLO) properties have also been reported for such compounds [68-71]. It has been reported that the azobenzene moiety was introduced in the bent-core system to promote photochromic properties in addition to NLO activity and liquid crystalline order [71]. On exposing a molecule with an azo linkage to an UV light, a small kink is generated at the azo end of the molecule due to the cis-trans isomerisation, this being reflected in the electro-optical properties of the compounds [58(c)]. The compounds in series A in Figure 2.6 were not conducive to mesomorphism and exhibited a B1 phase. The compound VP-59 in Figure 2.6 however exhibited an enantiotropic B2 phase (SmC\textsubscript{A}P\textsubscript{A}). Other compounds in this series were also mesomorphic but the VN-392 in Figure 2.6 wherein a biphenyl ring was substituted in the azo arm was found to be non-mesomorphic [72]. Also, it was found that the position of the azo linkage affected the electro-optical properties of the compounds.
Nagaveni et al. studied another series of azo based bent-core compounds shown in Figure 2.7 by varying the molecular structure in a systematic way to investigate the effect of symmetrical and non-symmetrical molecules on the mesomorphic properties of the azo-substituted bent-core compounds [73].

VN-567 is non-mesogenic, whereas the series A and B exhibits B1 (Colr) and B7, B1 (Colr) and B2 (SmC_AP_A) mesophases, respectively. The symmetrical molecules are less conducive to mesomorphism when compared to the non-symmetrical ones.

A reversible photo induced variation of the spontaneous polarization of the antiferroelectric state of the smectic phase has been reported for achiral bent-
core compounds shown in Figure 2.8 [58(c)]. The photo induced isomerization of the azo group leads to zig-zag shape due to which contributions of molecular dipoles partially cancel each other.

Srinivasan et al. [74] reported asymmetric azo based bent-core liquid crystals in Figure 2.8 exhibiting photo-switchable and electrically switchable B7 mesophase in the higher homologues, this being the first report of B7 phase in an azo based bent core molecule. The rigidity conferred by the biphenyl moiety, asymmetry and the higher length of the alkyl chain might have been responsible for the stabilization of the B7 phase in this type of molecule. The B7 phase shows the ferroelectric-anticlinic organization (SmC_{AP}) of molecules in the layers. Nematic phases have been reported in achiral unsymmetrical four-ring bent-core azo compounds possessing strongly polar cyano and nitro moieties as end substituents [75]. Viscoelastic studies on similar compounds with a polar fluoro or chloro moiety at one end revealed that the elastic bend-splay anisotropy $\delta K_{31} = K_{33} - K_{11}$ was negative. So these materials can be considered as dopants in formulating the wide range blue phase mixtures [76]. Prasad et al. reported [58(d),59] first examples of achiral bent-core molecules of five aromatic rings, linked through an azo linkage and with an imine and/or ester linkage shown in Figure 2.9, exhibiting B1 and B2 banana mesophases relatively at low transition temperatures and with wide temperature ranges. The B2 phase of these materials is identified to be the anticlinic–antiferroelectric, SmC_{AP} phase.
2.4.4. EFFECT OF POLAR GROUPS AT THE CENTRAL POSITION ON THE MESOMORPHISM

Novel five-ring bent-core compounds exhibiting a transition from the electro-optically non-switchable to a switchable B7 phase have been reported by Sadashiva et al. [64]  

![Diagram of bent-core compounds](image)

**Figure 2.10** Bent-core compounds reported by Sadashiva et al.

Achiral five-ring bent-core compounds derived from 2-cyano or 2-nitro resorcinol having terminal n-alkyl carboxylate groups have been reported by Sadashiva et al. to have exhibited enantiotropic mesophases. The compounds derived from 2-cyanoresorcinol exhibited two mesophases with the higher temperature mesophases showing unusual electro-optical properties in contrast to the nitro substituted compounds which exhibited only the mesophases with electro-optical switching properties. The aforesaid compounds represent the first example of a transition from the electro-optically non-switchable $B_{7x}$ phase to a switchable $B_{7FE}$ phase. B7 phases have been reported for various compounds containing polar groups like cyano and nitro at the bay position of the central
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phenyl ring [23,65]. One example of a compound, the higher homologue of which exhibited a helical filamentary growth patterns of B7 phase in Figure 2.11 [65(a)]. The compounds however did not exhibit any electro-optical switching on application of a triangular wave electric field.

![Figure 2.11: Bent core compound reported by Sadashiva et al. having cyano group at the bay position [65(a)]](image)

Two homologues series of five-ring Schiff’s base esters exhibiting the non-switchable B7 phase reported by Shreenivasa et al. have been shown in Figure 2.12. The compounds were derived from either 2-nitro- or 2-cyanoresorcinol. Three homologues of the nitro-substituted compounds undergo a transition from the non-switchable B7 phase to an antiferroelectric sub-phase (B7AF1), this being the first example of such a transition [66].

![Figure 2.12 Bent-core compounds from Schiff’s base exhibiting B7 phase](image)

2.4.5. INFLUENCE OF LATERAL SUBSTITUTION

Weissflog et al. [77] reported novel five ring bent core systems shown in Figure 2.13 possessing only ester connecting groups between the aromatic phenyl rings and different lateral substituents at the central phenyl ring. They demonstrated that the influence of the nature and position of lateral substituents on the banana mesophases behaviour is much more pronounced than in the calamitic compounds. Compounds which are derived from 4-cyano-, 4-chloro- and 4,6-dichloro-resorcinol, show polymorphism variants where polar phases (SmAP, SmCP) occur together with nematic and conventional smectic phases,
e.g. SmA–SmAP, SmA–SmC_3P_A–CoI_{ab}–SmC_3P_A, N–SmA–SmCP_A, SmA–SmC–SmCP_A and SmC–SmCP_A.

Figure 2.13 Five ring system reported by Weissflog at al. to study the effect of substituents

On the basis of the behaviour of two series of materials. It was demonstrated that polar switching can also take place by the director rotation around the tilt cone and through collective rotation of the molecules around their long axes in SmCP_A and SmCP_F phases. This corresponds to a field-induced switching of the layer chirality viz., coupling of reversal of layer chirality with field reversal. A remarkable finding is the polar switching in the crystalline modification of long-chain, bent-core compounds with a methyl group in 2-position, which is accompanied by a clear change of the optical texture and by a relatively high switching polarization (approx. 600 nC/cm^2). Above the transition temperature of a polar to a non-polar phase, the non-polar phase can be transformed to the polar phase by application of an electric field, which was proved for the transitions of isotropic–SmCP_F, SmA–SmCP_F and isotropic–CrII polar phase in some of the compounds. Orthogonal polar SmA phases have been reported [78,79] for two different types of homologues series of compounds containing 2-methylresorcinol as the central unit, nitro and/or chloro substituent’s in the outermost rings and a stilbene linking group between two outer phenyl rings as shown in Figure 2.14. Molecules of series 1 and series 2 possess only saturated terminal chains while those of series 3 have one or both unsaturated chain/s. All the compounds exhibit the isotropic to uniaxial orthogonal phase with ferroelectric properties SmAP_R phase transition and the B1_{RevTilted} phase at lower temperatures. For compounds with one olefinic terminal chain, the temperature range of the SmAP_R phase was found to be narrower in comparison to compounds with both saturated terminal chains. Dielectric investigation
inferred that both the SmAP_R and B1RevTilted phases and two different types of dynamical behaviour were observed.

![Figure 2.14 Bent-core molecules showing polar orthogonal phases](image)

The symmetric compounds with 2-acetyl groups exhibited polarization randomised non-tilted smectic A (SmAP_R) and room temperature non-tilted smectic (SmAP_A) phases, a first example of polar biaxial Smectic A to polar uniaxial smectic A phase.

Five ring banana shaped molecules derived from isophthalic acids apart from different substituted compounds have been reported [4,61,80,81]. Combination of several linking groups and different selected substituents either on the outer ring or on the central ring promoted novel switchable mesophases thereby demonstrating the importance of the nature of lateral substituent and its position on the central ring in affecting the liquid crystalline properties which leads to new structural modifications. They also reported ferroelectric switching for a B7 phase in fluoro substituted bent-core molecules in peripheral positions on the aromatic core, ortho to each of the two terminal alkoxy chains. This special substitution pattern seems to be a quite useful structural unit for the formation of ferroelectric switchable banana phases, which was evidenced in fluoro substituted compounds [30,31].

Mieczkowski et al. reported [82] the synthesis of new bent-core derivatives with ethylene linkage in banana branches instead of an imine or ester linkage and incorporating lateral substituents like fluorine or iodine atoms. The compounds exhibited B7 and B2 phases with anticlinic (SmC_A) or synclinic (SmC_S) interlayer structures, depending on the central ligand and lateral substituent and also found lower transition temperatures than the
unsubstituted analogues. The SmC\textsubscript{AP} phase exhibited strong optical activity and chiral domain segregation could be induced by applying a weak electric field in these compounds. The homologous series of N,N/-bis[4-(4-n-alkoxybenzoyloxy)benzylidene] phenylene 1,3-diaminesexhibited interesting phase behavior \cite{81(b)}. The lower homologues (n = 1-6) form a intercalated B6 phases, the middle homologues (n = 5-10) form the two dimensional B1 phases, whereas the long chain members shows the switchable B2 phase. Therefore, systematic studies of homol agrues series are necessary for the clear understanding of the phase behavior.

![Figure 2.15 Bent-core compounds with lateral substituents](image)

There have been many reports on the effect of fluorine substitution in the lateral position in bent-core molecules. Fluorine substitution can induce mesomorphism in non-mesogenic molecules due to phase stabilization or reduction of the melting temperatures. The compound 1 is non-mesomorphic in Figure 2.16 but the compound 2 and 3 in Figure 2.16 with lateral fluorine substituted is mesomorphic \cite{83}.

![Figure 2.16 Fluorine substituted at the lateral position of 2,7-dihydroxy- naphthalene based bent-core molecule compounds](image)

One to three fluorine atoms in different positions at the central biphenyl unit of a six-membered ring shown in Figure 2.17 promotes Col\textsubscript{r} and SmCP\textsubscript{A} like the unsubstituted compounds. But fluorine substitution at the lateral position of the rod-like wing promotes novel mesophases.
Sadashiva *et al.* investigated the role of fluorine substitution on phenylbenzoate shown in *Figure 2.18*. The unsubstituted compound in *Figure 2.18* is mesomorphic with a phase sequence of SmC, Col, SmCP.

However, introducing fluorine atoms in positions A or C or A+C of the bent-core system in *Figure 2.18(b)* does not change the phase sequence. But fluorine in positions B or B+C and B+D suppresses mesomorphism. However, fluorine at the outer phenyl rings at D i.e. ortho position to the n-alkoxy chains promotes various interesting mesomorphism. Switchable tilted smectic phases have been observed in the C\textsubscript{12} - C\textsubscript{16} homologue and FE and AF switching columnar phases in the C\textsubscript{18} and C\textsubscript{20} terminal chains. But additional fluorine in position A mainly suppresses the columnar phase but promotes the FE switching SmCP\textsubscript{FE}[*]. Similar observation were reported for the 2,7-dihydroxynaphthalene based bent-core compounds containing only ester linkages shown in *Figure 2.19*.
Fluorine at the position C of a Schiff’s base derivative of compounds in series 1 shown in Figure 2.20 suppresses higher ordered mesophases and leads to broad regions of the SmCPA phase but substitution at the D position induces SmCPA[*] phase and B7 type of mesophases. Similarly substitution by Chloro (-Cl) at the periphery changes the SmCPA phase into a smectic phases having domains with opposite chirality. Studies have also been made on the effect of larger and polarizable groups like NO₂, CN, I on mesomorphism. It has been observed that a NO₂ or a CN group at the angular position of compounds in series 1 of Figure 1.20 promotes non-switchable B7 phase but CN at the 4-position as shown in series 2 in Figure 2.20 there is a transition observed from non-polar smectic phase to polar smectic phase. On the other hand CN group at the 5-position renders the molecule non-mesomorphic.

2.5. W-SHAPED COMPOUNDS:

A new corner developed in banana liquid crystal when a W-shaped molecule PBPBTB in Figure 2.21 exhibiting a sequence of different ferroelectric and antiferroelectric mesophases with anticlinical coupled double banana shape was reported by Kumar et al.[84].

Rao et al. has reported W-shaped molecule shown in Figure 2.22. The compound exhibited chiral filament like domains [85] and also chiral domains of opposite handedness. This compound exhibits an unusual smectic mesophase with additional in plane order (SmX₂).
2.6. NEMATIC PHASES IN BENT CORE MESOGENS

Pelzl et al. reported [81(c)] a novel achiral five-ring banana shaped mesogens, 4-chloro resorcinol bis[4-(4-n-dodecylbenzoyloxy) benzoate] in Figure 2.23, exhibiting nematic phase with unusual optical and electro-optical properties.

Niori et al. [86] and Goodby et al. [87] have reported N* phases which had a Schlieren and marble textural features, corresponding to non-chiral nematic phases and not to a cholesteric texture. This indicates that there is no helical superstructure or, if at all, there is such a structure, then its pitch is larger than the sample thickness. Also, no polar switching could be found in these nematic phases.

Yves et al. [88] have made theoretical studies on the phase behaviour of bent-core molecules which revealed that the nematic phase is thermodynamically stable for opening angle larger than 135° and that with decreasing opening angle, the region of stability of the nematic phase decreases, vanishing for opening angles smaller than ~135°.

It has been generally observed that liquid crystalline phases exhibited by materials with severely bent structures have a lower thermodynamic stability than their straight-rod relatives [89]. Kishikawa et al. used a 2,5-substituted thiophene moiety as the central core of a bent-core molecule [90] shown in Figure 2.24. A 2,5-substituted thiophene moiety has a large bending angle as compared to other building blocks (154° for 2,5-disubstituted thiophene, 143°...
for 2,5-disubstituted furan, 141° for 2,5-disubstituted pyrrole and 120° for 1,3-disubstituted benzene) [90] in addition to its diverse chemistry, thereby allowing the scope for the synthesis of its numerous derivatives.

Figure 2.24 Bent core molecules containing 2,5-disubstituted thiophene as the central unit

A series of compounds given in Figure 2.24 have been reported to study the effect of the nature of the side chains and lateral dipole moments on the stability of liquid crystalline phases. Compound 1,2 and 3 have a small aspect ratio and limited liquid crystallinity. Compound 1 exhibited monotropic nematic phase but on replacing the hydrogen by bromide (-Br) or nitrile (-CN), the mesomorphism is disrupted, thereby, making the compounds 2 and 3 non-liquid crystalline. However, on increasing the aspect ratio of the compounds, the stability of the phases increased in compounds 4-7 but substitution by bromide and nitrile tends to decrease the phase stability. Bent-core molecules with an oxadiazole core shown in Figure 2.25 have been reported to exhibit the biaxial nematic phase [47,48].

Figure 2.25 Oxadiazole based bent-core molecule exhibiting biaxial nematic phase

2.7. BENT CORE LIQUID CRYSTALS CONTAINING BIPHENYL

Biphenyl derivatives have a strong tendency to form liquid crystals. Since the molecules contain no central group linking between the two phenyl rings, such
as the –CH=N- group in Schiff’s bases like MBBA or the –N=N- group in azo-compounds, etc., the compounds should be chemically and photochemically more stable. Biphenyl compounds have been reported to show potential applications in electrooptical devices with their crystal-nematic-isotropic phase transition close to room temperature. Gray [91,92] investigated a range of 4,4’-disubstituted biphenyls shown in Figure 2.26 to synthesise some room temperature liquid crystals.

![Figure 2.26 General structure of biphenyl compounds synthesised by Gray](image)

The group Y was either a nitro-group or a cyano-group, because both strongly promote nematic properties and are quite stable and might promote strong positive dielectric anisotropy for use in twisted nematic displays. The group X was an inert n-alkyl- or n-alkoxy-groups in order to lengthen the molecules. However the nitro compounds were unsatisfactory [91] as they exhibited only a short range monotropic liquid crystallinephases. But 4’-n-alkyl and 4’-n-alkoxy-cyano-biphenyls showed good results. The 4’n-alkyl-compounds (nCB, n=integer) have a lower melting points and N-I transition temperatures. The 5CB is a colourles compound, stable, single component, room temperature nematic with an enantiotropic range of 12.5°C and the ability to supercool in the nematic state for long periods down to about 4°C. The 4’-n-alkoxy compounds are higher melting with considerable higher N-I transition temperatures. All the compounds were chemically and photochemically stable. The cyanobiphenyls exhibited positive dielectric anisotropy and a resistivity of $10^{10}$-$10^{11}$ Ωcm at 100 Hz. Thus cyanobiphenyls seemed to be potential candidates for use in twisted nematic displays. All the eutectic mixtures of cyanobiphenyls supercooled strongly, and the nematic phase persisted for long periods at -20°C or below. The mixtures were colourless, stable like that of the pure mesogen with similar electrical properties and hence displays having these materials are unlikely to crystallise under ordinary conditions of use or storage. These works of Gray [91,92] motivated researchers to work on biphenyl compounds and incorporate them into bent-core molecules.
Four compounds of a series containing 2-cyanoresorcinol as the central core and a biphenyl derivative on one of the arm shown in Figure 2.11 have been reported to exhibit typical B7 phase with long single-spiral domains resembling telephone wires and double-spiral domains comparable to a chain. Equal number of right-handed and left-handed helices were also observed for these compound [65a].

![Figure 2.27 Five-ring bent-core system containing biphenyl as central core.](image)

Radhika et al. [65b] have reported two homologues series of isomeric achiral five-ring bent-core compounds containing 3,4-disubstituted biphenyl moiety Figure 2.27. Compounds of series 1 are obtained from 4-hydroxybiphenyl-3-carboxylic acid while those in series 2 are prepared by reversing the position of the hydroxyl and carboxylic groups, this being the first example of BC compounds derived from such moieties exhibiting a transition between two polar orthogonal smectic phases. The most interesting aspect is the occurrence of a transition between two polar partial bilayer orthogonal smectic phases.

Hird et al. reported [93,94,95] fluoro substituted four-ring bent-core material i.e. molecules with only four rings in the core with a biphenyl moiety, exhibiting mesomorphism Figure 2.28. The compound exhibited conventional SmA, ferro-, ferri-, and antiferroelectric SmC phases resulting from the molecular chirality and not due to the bent shape. The compound with conventional directions of ester groups based on banana-shape of parent compound is non-mesogenic, with a rather high melting point which may be masking liquid crystal phases and further the bend position is not in the right place for conventional mesomorphism.
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However when the chain length was increased and direction of ester moiety was changed, unusual optical textures of nematic phase was observed at low temperature which however was monotropic. When viewed between crossed polarizers domains of opposite handedness present in equal proportions were observed. Fan-like texture with an unusual switching behaviour was also observed on electro-optic switching of these nematic phases.

\[ \text{Series 1: } X=H \text{ Cryst 81.5 Iso} \]
\[ \text{Series 2: } X=F \text{ Cryst 38.0 (SmC*ferro 34.5) SmA* 49.8 Iso} \]

\[ \text{Series 3: } X=H \text{ Cryst 88.0 Iso} \]
\[ \text{Series 4: } X=F \text{ Cryst 48.7 (SmC*ferro 28.9 SmA* 31.9) Iso} \]

\[ \text{Series 5: } 4H, X=H \text{ Cryst 109.8 Iso} \]
\[ \text{Series 6: } 4F, X=F \text{ Cryst 84.6 Iso} \]
Govindaswamy et al. have reported end-to-end connected bent-core-rod couples and rod-bent-core-rod trimesogens incorporating a bent 3,5-diphenyl-1,2,4-oxadiazole core [96] shown in Figure 2.29.

All the molecules exhibited broad regions nematic phases. The heterotrimesogens with two CB units (CB-Ox-CB/n) form exclusively nematic phases, whereas related dimesogens with only one CB unit (Ox-CB/n) show an additional CybA phase. The nematic phases of these dimesogens represent cybotactic nematic phases[97,94,99] composed of small SmA-like clusters, which is an important observation as restricted rotation around the long axes of the molecules would in this case lead to biaxial nematic phase of the orthorhombic type [99(b),100]. In contrast biaxial nematic phase of the monoclinic type is expected for the cybotactic nematic phases composed of...
tilted SmC clusters where biaxiality is additionally influenced by the tilt of the molecules. Therefore the \( N_{cybA} \) [101] phases are important in the search for biaxial nematic phases [100]. Nematic phases of some 3,5-bis(4-hydroxyphenyl)-1,2,4-oxadiazole bis(4-alkyloxybenzoates) have been reported to be ferroelectric-like switching cybotactic nematic phases[102]where the molecules are tilted by 40-50° but the combination of 2,5-dipheyl-1,2,4-oxadiazole core with one CB unit in dimesogen leads to the removal of the tilt and promotes an orthogonal organization of the molecules. However replacing the CB group by a 2-phenyl-1,3,4-thiadiazole core retains the tilted SmC-like organization of the simple 1,2,4-oxadiazole bent core mesogens [103]. Alkoxy biphenyl have been incorporated into the four ring compounds which exhibited ferroelectric SmC*, SmA* phases. Csorba et al. have reported a series of five-ring compounds shown in Figure 2.30 wherein the effect of polar substituent’s on a series of bent-core compounds incorporating biphenyl derivative is focussed on [104]. The compounds without substituent’s or having electron-donating groups on their central aromatic ring are nonmesomorphic.

![Figure 2.30 Bent-core series demonstrating effect of polar groups](image)

However electron-withdrawing substituent like chloro (–Cl) or nitro (–NO₂) on their central aromatic ring promoted B phases or nematic phases supporting the earlier observations that introducing of dipolar groups like -NO₂ in the 2-position favours the occurrence of B phases [23]. The rigid biphenyl carboxylate structures on both arms might have discouraged the richer variety of mesophases. The introduction of a large chlorine (-Cl) substituent at the 4-position widens the bend angle of the unsubstituted 1,3-phenylene ring (120°) to 135° thereby decreasing the polar packing in layers. This ability is more depressed in 4,6-dichloro-substituted molecules, in which the bend angle is
further enlarged resulting in a rod like conformation [105]. Consistent with the above interpretation IVa and IVb formed an enantiotropic, high clearing nematic phase as compared to IIIa and IIIb for which the nematic phase is monotropic. Also it was observed that IIIb was difficult to crystallise and the nematic phase could be frozen in the glassy state on cooling below the glass transition temperature at $T_g = 74^\circ C$.

2.8. PORPHYRINS AS PHOTOVOLTAIC SOLAR MATERIALS:
Organic solar cells have very poor power-conversion efficiencies. However substantial advances have been made in terms of power-conversion efficiencies in dye-sensitised solar cells (DSSCs) [106] and bulk-hetero-junction solar cells [107]. A dye-sensitised solar cell is a low-cost solar cell based on a semiconductor formed between a photo-sensitised anode and an electrolyte, a photo-electrochemical system. The modern version of a dye solar cell, also known as the Gratzel cell, was originally co-invented in 1988 by O’Regan and Gratzel with an award of the 2010 millennium technology prize. In dye-sensitised solar cells, ultrafast light-induced charge separation and slow charge recombination takes place at the interface between the dye and the nanocrystalline semiconductor TiO$_2$ which has a very large surface area to promote an efficient light-harvesting system. The detailed mechanism has been discussed in chapter 1. The light harvesting efficiency is dependent upon the area of the window covered by the dye film. Using the right linker and binding group, the performance of porphyrin-based solar cells can be greatly improved. Dye sensitised solar cells having an efficiency 12% have been reported [106(a),108]. The performance of the device also depends on the dye chemisorbed on the semiconducting oxide surface. But the design and synthesis of efficient green photo sensitizers is a formidable task because of the limited availability of ruthenium (Ru) dyes (efficiency ~11%) and undesirable environmental impact. Coumorin dyes, indoline dyes, carbazole dyes, triarylamine dyes, hemicyanine dyes, squaraine dyes, thiophene dyes have been proved to have moderate efficiencies in DSSCs.
However porphyrins have been attracted attention in this regard due to their major role in photosynthesis with a strong Soret and moderate Q-bands. The LUMO of the porphyrin molecules are above the conduction band of TiO$_2$ required for electron injection and the HOMO lies below the redox potential of $\Gamma^-/I_3^-$ required for the dye regeneration. Many porphyrin sensitizers have been successfully applied in DSSCs [109]. However Zn porphyrins bearing a malonic acid substituted at the β-pyrrole position with power conversion efficiency (PCE) of 7.1% was a major breakthrough in this respect [110]. Zinc porphyrins with a push-pull system (D-π-A) are attracting attention due to the ease of structural modifications on the electron-donating and anchoring sites which facilitates the modifications of their optical, photo-physical and electrochemical properties to increase the efficiency of DSSCs.

Campbell et al. [110] reported unprecedented overall conversion efficiency of ~7% for novel dark green porphyrin based sensitizers Figure 2.31 under standard global solar conditions. The studies revealed that the nature of the aryl group is not a major factor in determining overall cell performance. Also the similarity in the opto-electrical properties and HOMO-LUMO levels of the dyes explains that the variations in cell performance are not due to electronic effects exerted by the benzene substituents. The electronic structure of the dye which depends on the peripheral substituents, the anchoring group, the type of central metal, the bridging distance between dye and TiO$_2$ affects the efficiency of a dye. Carboxyl group (-COO) is being popularly used in sensitizers as an anchoring group and is believed to bind to the TiO$_2$ in a bidentate bridging mode and significantly affects the electronic coupling between dye and TiO$_2$ conducting band thereby affecting the performance of the device. Studies on Ruthenium dyes suggested that at least two carboxyl groups are required for a strong binding with the TiO$_2$ surface [111]. But there are very few reports on porphyrins with more than one carboxyl phenyl group at meso or β-pyrrole positions [111(c),112]. Ambre et al. reported effects of porphyrin meso-substituents on the photovoltaic performance of dye-sensitised solar cells highlighting the significance of the number and positions of p-carboxyl-phenyl and thieryl groups on Zinc porphyrins.
Figure 2.31 Zn porphyrins reported by Campbell et al. [110]

Porphyridin group bearing thienyl and at least three carboxyl in Figure 2.32 groups have been reported. Thienyl group can increase the donor property and is believed to induce coplanarity to the porphyrin system [113]. The results of dye-loading and the photovoltaic properties are consistent with those of the ATR-FTIR study and suggest that a stronger attachment to TiO₂ occurs with compounds having two meso-p-carboxyl phenyl at the cis-position which ultimately leads to a better device performances. IS3A and cis-2S2A in Figure 2.32 with a minimum of two arms attached on TiO₂ prove to be more efficient than the trans-2S2A and 3S1A. 1S3A showed the maximum power conversion efficiency due to the maximum number of carboxyl phenyl groups and minimum number of heavy metal atoms effect. The study also revealed that the cis 2S2A with better binding to the TiO₂ in a bidentate mode is a better candidate than its trans counterpart with mono binding mode.

Figure 2.32 Zn-porphyrins reported by Ram et al
Non-carboxylic acid groups as anchoring group is being studied to be used in solar cells because anchoring groups play an important role in deciding the performance of the device. Lu et al. reported [114] donor-π-acceptor zinc-porphyrins dyes with a pyridine ring as an anchoring group exhibiting overall PCE of about 4.0% under full sunlight (AM 1.5G, 100 mW cm\(^{-2}\)). Wrobel et al. reported [115] photovoltaic studies on halogenated porphyrins. The compound TPPCl\(_{12}\) exhibited the highest current value of about 16 nA/cm\(^2\) compared to that of TPPF\(_{12}\) (2 nA/cm\(^2\)) and TPP (9 nA/cm\(^2\)). The fluorine and chlorine atoms can modify the electronic properties due to resonance effects. The enhancement of photocurrent in PEC with TPPCl\(_{12}\) versus TPP could be due to the electronic distribution of π-electrons due to the mesomeric effect or inductive effects (or both) in addition to other effects like aggregation [116], changes in conformation and steric effects [117]. The amount of photocurrent produced is however lower than 120 nA/cm\(^2\) exhibited by ZnPcF\(_{16}\) and ZnPcCl\(_{16}\) which are symmetrically substituted by 16 Fluorine and chlorine atoms. ZnPc and CuPc however exhibited a photocurrent of about 30 nA/cm\(^2\) and 2 nA/cm\(^2\) [118]. The high photo-conversion of light energy into electric energy could be assigned to the unique character of interaction between the π-electrons in the main ring and electronegative atoms. The results indicate dominance of the positive mesomeric effect whereas the negative inductive one seems to be less essential. The higher photocurrent in TPPCl\(_{12}\) than that of the TPP and TPPF\(_{12}\) suggest the occurrence of the stabilizing mesomeric effect, which dominates over the inductive effect in TPPCl\(_{12}\) whereas the inductive effect is important in TPPF\(_{12}\) leading to photovoltaic declining reflecting the importance of halogenations in the modification of the photovoltaic performance. Recently Mathew et al. reported a dye in **Figure 2.33** which maximises electrolyte compatibility and improves light-harvesting properties. In cells based on the Co(II/III) redox shuttle, the dye exhibited \(V_{OC}\) value of 0.91 V, \(J_{SC}\) value of 18.1 mA cm\(^{-2}\), fill factor of 0.78 corresponding to an efficiency of 13%, which in fact revealed a great potential of porphyrins as natural green solar materials [119].
Most of the organic sensitizers have a narrow absorption bands entailing incomplete visible light collection. So in order to overcome the problem several efforts have been made like co-sensitising with complementary absorbing dyes which requires the design and synthesis of two efficient dyes instead of one and a fine tuning of the sensitising conditions [108(b),120]. A combination of zinc porphyrin (ZnP) and a diketopyrrolopyrrole (DPP) fragments could be one of the examples of two sensitizers displaying complementary absorption features. Few compounds of these types were prepared by Favereau et al [121] and have been shown in Figure 2.34. DPP exhibits an intense absorption at 500nm which perfectly matches the lack of absorption of the ZnP and is reported to have been exhibiting interesting performances in organic solar cells and DSCs [122,123]. On the other hand ZnP is a potential sensitizer in DSCs [124]. The compound D1 in Figure 2.34 exhibited an efficiency of 5.25% but the substitution of the phenyl group by an electron rich moiety dianisylamine to facilitate the injection of electrons into the conduction band of TiO₂, however reduced the efficiency to 2.55%. Bichromophore sensitizers DPZ1 end-capped with methoxyphenyl and DPZ2 end-capped with carbazole group were also studied. The substituents are electron donating and have an oxidation potential anodically shifted compared to dianisylamine. Substituents 2,6-didodecyloxyphenyl is hydrophobic and allow better protection to the TiO₂ surface from the approach of the electrolyte, thereby impeding the charge recombination [125] in addition to protecting the zinc atom from a presupposed assemblage with I₃⁻ responsible for increasing the
dark current [125,126]. Another dye CPZ devoid of the DPP moiety was reported to evaluate the effect of the DPP in the device performance.

Figure 2.34 Various Zinc porphyrin (ZnP) to evaluate the effect of diketopyrrolopyrrole (DPP) fragments on photovoltaic device reported by Ludovic and co-workers.

The $V_{OC}$, $J_{SC}$, fill factor (FF) and the efficiency of the compounds have been shown in Table 2.2 along with a comparison with a Ru(II) dye (N719) which has a great potentiality in solar devices.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$V_{OC}$ (mV)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPZ1</td>
<td>625</td>
<td>17.70</td>
<td>70</td>
<td>7.74</td>
</tr>
<tr>
<td>DPZ2</td>
<td>525</td>
<td>9.11</td>
<td>70</td>
<td>3.40</td>
</tr>
<tr>
<td>CPZ</td>
<td>565</td>
<td>7.34</td>
<td>71</td>
<td>2.93</td>
</tr>
<tr>
<td>N719</td>
<td>645</td>
<td>21.31</td>
<td>64</td>
<td>8.75</td>
</tr>
</tbody>
</table>

Thus DPZ1 proved to be the best performing sensitizer followed by DPZ2 and then CPZ. Also CPZ, which was prepared by replacing the dihexylphenylamine moiety of the dye YD2 or YD2-o-C8 by a carbazole moiety [121(b)] exhibited a low performance as compared to YD2. The structure is shown in Figure 2.35 [127]
Polymer solar cells (PSC) and bulk hetero-junction (BHJ) as photovoltaic devices have been a hot topic of research due to low cost, flexibility, eco-friendly use, facile processing etc [107(c), 128]. Usually a polymer BHJ solar cell consists of a conjugated polymer donor and a fullerene derivative as acceptor as the active component. Suitable HOMO and LUMO energy levels, broad and strong absorption, good film-forming property and high hole mobility in polymer blend are important prerequisites for conjugated polymers [129]. Donor-acceptor (D-A) copolymers has been proven to be one of the most effective design in this respect. PCEs over 7% have been reported for the D-A copolymers [130]. The PCEs of photovoltaic devices significantly depends on a broad absorption of the solar spectrum, a planar molecular structure, a good stacking property between molecules and a good charge transport properties etc [131]. So porphyrin molecules have been extensively used as donors due to their large planar-conjugated structure, unique electrochemical property and good thermal and photochemical stability [132]. Some D-A polymers with porphyrins as donor and fullerenes as acceptor have been reported to exhibit efficient electron transfer due to the fullerenes containing an extensively conjugated three-dimensional π system [133]. The remarkable photocurrent generation is due to the π-π interaction between the porphyrin and fullerene [134]. But fullerenes directly connected to porphyrin do not form an efficient conjugation due to steric hindrance. So conjugated polyacetylenes having pendant fullerene and/or porphyrin groups with less steric hindrance and extended conjugation were synthesized and studied [135]. Thiophene derivatives have been reported to have been successfully incorporated in the solar cells. Imahori et al. reported
porphyrin-thiophene copolymer (PZnPT) with an efficiency of 0.027% for the PZnPT: PCBM device [136]. However all these porphyrin polymers exhibited narrow absorption with low PCE. With an idea to get a broader absorption spectrum of porphyrins, a star-shaped polythiophene with porphyrin core was synthesised which exhibited a strong and broad absorption in the range 350-650nm and an efficiency of 0.61% for the BHJ solar cells [137]. Deng et al. synthesised two D-A porphyrin-based copolymers P1 and P2 shown in Figure 2.36 with different co-polymeric units to tune the absorption and molecular energy levels. P1 contains a benzo [1, 2-b:4,5-b’] dithiophene (BDT) unit and P2 contains 4,7-di(4-hexylthiophen-2-yl)benzothiadiazole (T-DTBT) [138]. The compounds exhibited absorption spectra in the range of 300-650 nm. P2 exhibited a good thermal stability, broad absorption and deep HOMO energy level. P2 exhibited a low energy gap of 1.86 eV which led to a broadened spectrum leading to higher Jsc and the D-A structure of the main chain led to an effective charge and energy transfer.

![Figure 2.36](image)

Figure 2.36 D-A porphyrin-based copolymers synthesised by L. Deng et al.

Thus copolymer P2 exhibited an efficiency of 1.26% and P1 an efficiency of 0.32 %. Xiang et al. reported π-conjugated porphyrin copolymers P-PTT and P-POT in Figure 2.37 containing a terthiophene and oligothiophene moiety into the polymer main chain respectively [139]. Terthiophene has been used to extend conjugation, enhance absorption and improve charge transport property in addition to the fact that it has a better light-harvesting characteristics and lower oxidation potential than thiophene [140]. Oligothiophene units broaden the Soret band and Q-band of porphyrin polymer and the long octyloxy chains at the meta-position of 5,15-phenyl
groups helps in improving the solubility of the copolymer [139]. The PSCs were fabricated with a traditional sandwich structure (denoted as ITO/PEDOT: PSS/polymer: PCBM/Al). The electrochemical properties indicated that the energy levels of the polymers were suitable for efficient charge transfer and separation at the interface between the polymer donor and PCBM acceptor. P-POT has a lower value of PCE (0.18 %) due to low IPCE value than the P-PTT PCE value (0.32%) [139].

![Figure 2.37 Zn-porphyrins containing thiophene moiety reported by N. Xiang et al.](image)

Recently a porphyrin sensitizer, LD31 incorporating an ethynyl-anthracenyl moiety between the dioctylaminophenyl group and porphyrin core to extend the conjugation for better light harvesting has been reported. The dye which exhibited a large harvesting ability beyond 800 nm had a $J_{SC} = 20.3 \text{ mA cm}^{-2}$, $V_{OC} = 704 \text{ mV}$, FF= 0.72 and an PCE of 10.3% when combined with an organic dye AN-4 [141].

2.9 MOTIVATION OF THE PHD PROPOSAL

Occurrence of new mesophases in banana liquid crystals and their explanations on the basis of structure opens up newer ideas for designing newer molecules. The study of mesomorphism in biphenyl and terphenyl based molecules was a major breakthrough since it could lead to design of new molecules which were stable and suitable for use in LCDs. However suitable bent-core molecules incorporating a biphenyl or terphenyl moiety for display applications are yet not much explored. Five-, six-, or seven-ring bent-core molecules incorporating a biphenyl moiety have been reported but four-ring bent-core systems incorporating a biphenyl moiety in one of the wings exhibiting banana phases or cybotactic nematic phases are yet to be reported. Four-ring bent core
systems exhibiting banana mesomorphism has been a challenge to researchers. The structure property relationship for the four-ring banana shaped liquid crystals has not yet been understood, although numerous number of bent-core materials were synthesized and extensively studied. Till date nematic phases in four-ring bent-core systems have been rare due to the core-core interactions, incompatibility of the aromatic and aliphatic moieties and prevention of the flip-flop rotation by the shape factor of the molecules. Spontaneous polarity and chirality of bent-core liquid crystals provoked interest for research in liquid crystals because of its potential applications owing to their polar packing which in turn account for their polar switching. But there are very few reports of polar order in four-ring bent-core systems and in particular in four-ring systems it is a challenging task. Also strong polar groups like cyano, nitro are reported to exhibit nematic phase no polar order has been reported till date.

Furthermore, an idea to study the *supramolecular aggregate of a four ring system led to the direction of designing porphyrins to study their material properties and their use as photovoltaic materials*. Porphyrins have attracted the attention as light harvesting materials due to its presence of chlorophyll. Recently many porphyrin compounds have been synthesized and reported to be potential candidates for OPV even though reasonable power conversion efficiency values are yet to be attained to match the inorganic silicon based solar cells.

Therefore in this thesis, design and synthesis of novel unsymmetrical four-ring bent-core compounds incorporating the biphenyl moiety with a polar substituent like fluoro and chloro atoms shall be presented along with their characterisation and investigation of their material properties so as to focus on the structure-property relationship. Influence of substituents on the mesomorphism of four-ring bent-core liquid crystals shall be presented. Design and synthesis of some porphyrin molecules shall also be presented along with their characterisation and photovoltaic studies. Further a study on the emissive properties of all the compounds shall be presented in order to ascertain the potentialities of the compounds for their applications in relevant areas.
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b) The nomenclature of the mesophases of the banana-shaped molecules as B1, B2, etc. was recommended at the Workshop “Banana-Shaped Liquid Crystals: Chirality by Achiral Molecules”, Berlin, Dec 1997.


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