4. Liquid crystalline dendrimer: Towards intelligent functional materials

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Abstract. The structural organization of various types of dendritic systems that form liquid crystalline mesophases have been analysed with special emphasis on their relevance towards developing intelligent functional materials. Liquid crystalline dendrimers has been gaining considerable interest in recent years for development of newer functional materials because of their mesomorphic properties of the mesogenic subunits associated with the supermolecular versatile architecture. Combination of these features enhances their prospect as potential candidate for developing functional materials. Structural control achieved with such type of molecular architecture by tuning the terminal mesogenic groups, dendritic core and dendrimer generation, for appropriate molecular design are also reviewed. The influence of the dendritic matrix, particularly the factors like multivalency of the dendritic core, multiplicity of the branches etc. on their supramolecular organization are analysed. Some basic concepts about thermotropic liquid crystals as well as dendrimer along with various phases of liquid crystalline dendrimers are provided in the

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introductory chapter. Description on selected examples of liquid crystalline dendrimer such as side-chain, main-chain, fullerodendrimers, shape-persistent dendrimers, supramolecular dendromesogens and metallodendrimers etc. as representative families of liquid crystalline dendrimers along with their utility towards designing of intelligent functional materials are made in the proceeding sections. In conclusion an overall rational analysis has been made on the prospect of further development of liquid crystalline dendrimer.

Introduction

Liquid crystalline molecules are ‘soft materials’, representing a special states of matter (also called the fourth state of matter) which is recognized by it’s long range order (as in crystals) and mobility (as in liquid) [1-3]. These mesophases can occur in pure materials with dependence on temperature when it is referred to as thermotropic liquid crystals or can occur in multicomponent system with dependence on composition when it is referred to as lyotropic liquid crystals. This unusual feature of such molecules attribute anisotropic physical properties to liquid crystalline compounds and therefore have found enormous application in various fields, more specifically in electronics, display devise, mobile telecommunication and computing devices. Thermotropic liquid crystals are used in electrooptical displays, temperature sensors etc [4]. While lyotropic systems are mostly used in cosmetic industries [5] besides their use as templates for preparation of mesoporous materials.

Thermotropic liquid crystals are of three types namely nematic, cholesteric and smectic and all these are distinguished by the different kinds of molecular order they exhibit. For example nematic structure maintains a parallel or nearly parallel arrangement to each other along the long molecular axes. They can rotate about one axis and the structure is one dimensional. Cholesteric is in fact a chiral nematic liquid crystal where direction of the long axis of the molecule in a given layer is slightly displaced from the direction of the molecular axes of the molecules in an adjacent layer. All non nematic liquid crystals are included in smectic phase. In smectic phase liquid crystals retain some amount of orientational order that is present in nematic along with small amount of positional order. In smectic structures, the molecules are free to bounce around randomly and tend to point along a specific direction and arrange themselves in layers, either in neat rows or randomly distributed. Mesomorphism is exhibited by materials having liquid crystalline properties (which are referred to as mesogens) and shape of the mesogen, that form the mesophases like enantiotropic or monotropic mesophase may guide to the structure of liquid crystalline compound.
Also liquid crystalline materials can self organize into various nanostructured phases, such as layered, columnar, micellar, and bicontinuous cubic which are formed by segregation of immiscible parts in molecules on nanometer scale. Columnar phases are obtained by packing of disc like molecules into columns and are characterized by the symmetry of the arrangement, for example hexagonal (Col \(_h\)), rectangular (Col \(_r\)), square (Col \(_s\)) or oblique (Col \(_o\)). This phase is obtained with many non-discotic molecules such as polycatenar, polyphilic, and bent-shape mesogens. Diffusion between and within the column readily occurs and the phase are fluid. Chiral modifications for calamitic mesogens (rod like species) are also known which are referred to as chiral mesophase (for example SmC\(^*\), SmI\(^*\) etc.). These are exhibited by either a pure enantiomer or by a non chiral compound doped with little amount of chiral additives [6]. Additionally, less common liquid crystalline phases such as micelle cubic phases (Cub \(_b\)), bicontinuous cubic phases (Cub \(_c\)) are known to exhibit by some classical rod like mesogens. Laminated type phases (Lam) are also recognized with some smectic phases which are consists of sheets in which aromatic cores lie parallel to the layered planes, separated from each other by lipophilic sublayers [7]. Self organized structure of lyotropic liquid crystals are even compatible with those of living systems.

Liquid crystals have numerous functional utility such as information and mass transport, sensing, catalysis, templates, electro optic displays and so on. Therefore these materials have outstanding potential for advance application and therefore towards development of intelligent materials.

Dendrimers are highly branched three dimensional macromolecules with a branch point at each monomer unit and have attracted interest of both industrial and academic chemists. The most important feature of dendritic molecules is their well defined shape, symmetric nature and molecular architecture, which is not observed in case of hyper branched polymers [8]. Also unlike hyper branched polymers, dendrimers are obtained by careful stepwise growth of successive layers of generations. It is possible to functionalise dendrimers at the periphery of the globular structure instead of insulating a reactive site at the centre of a dendrimer. Besides amphiphilic dendrimers containing an extended rigid block represents a class of self assembling systems those are increasingly used for the construction of supramolecular architecture with well defined shape. Nowadays a broad range of dendrimers are available and some of them are even available commercially, and have found to be promising towards important chemical processes and also as drug or gene delivery devices, as carriers for catalytically active site in flow reactors and also as chiral auxiliaries for asymmetric synthesis. The field of research on the look for newer dendritic
species has also been boosted up by the enhanced possibility of their potential in wide spread application. Their resemblance and similar dimensions to some living components and to molecular functional materials projects them as potential candidate for even biological science too, provided these are suitably functionalised. High molecular weight monodisperse dendrimers are promising candidates for the development of new liquid-crystalline materials for specialized application.

The pervasive nature of liquid crystalline science along with the mesomorphic behaviour of dendritic architecture projects liquid crystalline dendrimers as interesting materials for basic studies and development of newer materials for organic molecular electronics and other allied fields of science. The notable features of liquid crystalline dendrimers is that the liquid crystalline properties of the compounds can be controlled as a function of dendrimer generation and can be tuned by careful selection of the mesogenic moiety. Therefore molecular engineering of liquid crystalline dendrimers through understanding of the structure-organization relationship is highly significant for design of mesomorphic with tailor made properties for application in various fields. Thus LC dendrimers projects them as most versatile dendritic architecture where mesomorphism can be modulated by very subtle modifications of the dendritic connectivities. These branch of science can be regarded as a multidisciplinary field of research with broader prospect for design of new novel molecular architecture.

1. Structural organization of liquid crystalline dendrimer

The evolutionary concept of dendritic architecture and more specifically dendritic nanostructure has already been able to introduce a new dimension in the hierarchical complexity of matter. The three dimensional branched macromolecular architecture is one of the most pervasive topologies observed in nature at the macro- and microdimensional length scales and consisting of three topologically distinct regions: multivalent surface, branched interior and encapsulated core (figure 1).

This has also been recognized as fourth major class of macromolecular architecture with distinct characteristic properties [9]. Numerous synthetic strategies developed so far has led to four architectural subclasses for dendritic polymers, namely random hyperbranched polymers, dendrigraft polymers, dendrons and dendrimers. Therefore dendrimers and dendrons are potentially useful versatile scaffolds for development of new liquid crystalline materials as the interesting structural framework which will allow modulation of the mesomorphism in the structural organization through appropriate modification of the dendritic connectivity. They thus constitute
an important class of mesogens where new types of mesophases and original morphologies may be discovered [7].

Overall structure of a liquid crystalline dendrimer influenced by the mesogenic or pro-mesogenic promoters attached to the peripheral groups of the flexible dendritic network, tendency of the dendritic core to adopt a globular isotropic conformation and also by the chemical and structural compatibilities between the dendritic core and the peripheral groups. Depending on the number of generation of the LC dendrimer, their structural organization may have different characteristics. For example higher generation dendrimers have strong tendency to self organize into supramolecular columnar mesostructure [10]. The strong tendency of the core to phase separate with increasing number of generation also led to formation of strongly segregated smectic structure for some LC dendrimers. These supramolecular organizations of LC dendrimers also changes with change in temperature.

1.1. Influence of dendritic matrix

The matrix of the liquid crystalline dendrimer is highly influential in determining the material properties of the complex structure. The complex
structure generated can be one dimensional (lamellar phases), two dimensional (columnar phases) or three dimensional (micellar or bicontinuous phases). It has been observed from X-ray crystallography and molecular modeling that 1st and 2nd generation dendrimers normally possess planar structure while structural complicacy arises for dendrimers with higher generations due to overcrowding of the terminal groups. With increasing generations the shape of the dendrimer become increasingly globular in order to occupy larger molecular structure with minimized repulsion between the segments [11]. In case of globular macromolecular structures, the core region of the dendritic matrix becomes increasingly shielded off from the surroundings by the dendritic wedges from large number of compartments created in the interior. For liquid crystalline dendrimers with increasing generation number the isotropization temperature increases and phase transition behaviour also changes. The strongest influence of spherical molecular architecture on the phase behaviour of the LC dendrimers appears at higher generations which regulates the structural organization of LC dendrimers.

Depending on the type and nature of intra molecular forces the resultant dendritic structure can be rigid or flexible. In case of flexible structures back-folding may occur as a consequence of weak forces between surface functionalities or dendrons and relatively higher mobilities leading to more disordered conformation where the molecular density is spread out over the entire molecular area. However back-folding may also resulted from attractive forces such as ion-pairing, hydrogen bonding etc. between functional groups at the inner part of dendrons and the surface functional groups. Thus the structural organization of LC dendrimers upon growing to higher generations depends upon its ability of the surface groups to form network with each other. In the case where hydrogen bonding is possible with the surface groups, a dendrimeric motif with a very dense periphery and hollow core may be resulted. Self assembly of such supramolecular dendritic architecture into bulk phase to produce periodic nanostructures renders possible the design of newer intelligent organic matter having multidimensional utility. This fact encourages further research activities on liquid crystalline bulk nanoscale organic matters.

1.2. Influence of multivalency of dendritic core on supramolecular organization

The core structure of dendrimer which is some times denoted as generation “zero” thus presents no focal point. The multiplicity of the
branched cell and directional characteristics of the core influences certain features of the dendritic architecture. Some details about core cell architectural components are available in literature [12]. The concentric monomer shells (generations) surrounding the core have well defined monomer shell saturation levels analogous to electron shells in atoms. Structural organization and building events in case of liquid crystalline dendrimer too is dependent on the architectural behaviour of the nucleus (core) including directional characteristics. Both the core multiplicity and branch multiplicity can be considered as a measure of precise number of terminal groups and mass amplification as a function of dendrimer generation. The core thus can be considered as the molecular information center containing the information about size, shape, multiplicity and directionality expressed as a function of covalent connectivity with the outer shells.

1.3. Influence of multiplicity of the branches

Each architectural component of a dendritic architecture manifests a special function characteristic of its own and at the same time also defines the properties of the whole structure. Interior of dendritic architecture can be considered as the branched cell amplification region and it also provides an idea of the type and volume of interior void space that may be enclosed by the terminal groups as the dendrimer is grown. Therefore the multiplicity of the branches of the interior region also influences the structural organization of dendritic liquid crystals since the multiplicity and nature of the interior region will influence the process of molecular self assembly and formation of quantized bundles of nano scale building units. Bulk nanoscale self-assembly of organic matter is promising for using as scaffolds for photonic materials and other intelligent components of molecular electronics. Dendrons and dendrimers are particularly versatile in generating such periodic nanostructures. Elemental compositions of the core as well as hydrophilic and hydrophobic nature of the core group are also decisive factors in the process of structural organization of liquid crystalline dendrimers.

1.4. Influence of terminal functional group

Surface groups in dendritic architecture manifests several characteristic functions. Appropriate functionalization of the surface groups might enable one to design newer intelligent functional material with novel utility. Further to this the surface functional groups also serve as a template polymerization
region as each generation is amplified and covalently attached to the precursor generation. For dendritic architecture, the terminal functional groups witness an exponential growth as the dendrimer generation increases which may lead to “tethered congestion” due to over crowding of the end groups. The consequence of such congestion is that while lower generation of the dendrimers are obtained as open floppy structures, the higher generations become increasingly robust. Molecular design of liquid crystalline dendrimer thus influenced by the chemical nature and structure of both the functional groups and the dendritic matrix. Intrinsic connectivity of the dendrimer such as the multivalency of the focal core, multiplicity of the branches has significant influence on the geometric growth of the dendrimer generation, supramolecular organization, stability and mesomorphic structure. Tuning of the mesomorphic structure can be achieved through appropriate design of molecular architecture with concomitant change of the terminal mesogenic groups and similar change in dendritic core and interior will produce analogous effect. Liquid crystalline dendrimers are attractive candidates for design of newer liquid crystalline materials containing active molecular units for specific physical properties.

Mesogenic group itself shows mainly a nematic phase which disappears quickly on getting attached to a dendritic scaffold. Also owing to the fact that the branched and the aromatic parts are chemically linked, the smectic phase represents the most stable thermodynamic state of organization in a lamellar morphology.

2. Selected examples of liquid crystalline dendrimers

2.1. Side-chain liquid crystalline dendrimer

The chain conformation of liquid crystalline dendrimers is an important factor controlling their phase behaviour as well as material properties. Side-chain liquid crystalline dendrimer is the term applied to those flexible dendritic network containing mesogenic or pro-mesogenic groups attached laterally (side-on) or terminally (end-on) to the termini of the branches. Both liquid crystalline dendrimers with terminal mesogenic groups and side chain liquid crystalline polymers consists of molecules possessing the following structural units: polymeric chain, spacer and terminal (or side chain) mesogenic groups. Of course liquid crystalline polymers possess linear polymer chain while liquid crystalline dendrimers possess dendritic architecture. A schematic representation of such side-chain liquid crystalline dendrimer is given in figure 2. The tendency of the dendritic core to adopt globular isotropic conformation and probable microphase separation due to
chemical and structural incompatibilities between the flexible dendritic core and the terminal groups collectively contribute towards stabilization of the mesogens and determines the mesomorphic properties of the entire molecule.

The type of mesophase of such compounds depends on the chemical nature of the mesogenic groups. It is important to know whether a dendrimer skeleton containing mesogenic group is able to impede liquid crystalline properties or whether the high concentration of mesogenic units in a dendritic molecule facilitate some pre-organization leading to the formation of mesophases.

2.1.1. Poly(propyleneimine) (PPI) LC dendrimers

Dendritic motif of poly(propyleneimine)(PPI) dendrimers contain a tetravalent core and a binary branching point and between two junctions there are three CH$_2$ groups. For this series of LC dendrimers (figure 3) Meijer et al. showed that for the two series of dendrimers functionalized with pentyloxy and decyloxy cyanobiphenyl mesogens, all the higher generation dendrimers with pentyl spacer exhibit liquid crystalline phases between glass transition temperature and the isotropic liquid, while those with decyloxy spacer also exhibit liquid crystalline behaviour but with the presence of a crystalline or semicrystalline state at low temperature and with higher transition temperatures [13].

All these dendrimers showed a SmA phase. PPI dendrimer with the non-mesogenic 3,4-bis(decyloxy) benzoate end group, induction of a Col$_h$ phase was systematically observed from G0 to G4 [14]. The orientational order of
the peripheral mesogenic group also determines the possible interaction between terminal groups and thus influencing the layer spacing of the LC dendrimer. Layer spacing does not vary as a function of the number of peripheral mesogenic units.

2.1.2. Polyamidoamine (PAMAM) LC dendrimers

For this series of LC dendrimers also the dendritic motif is same as that of PPI dendrimers but between two junctions there are \(-(\text{CH}_2)_{2}-\text{CONH}(\text{CH}_2)_{2}-\) segment in place of three \(\text{CH}_2\) groups and between two central \(\text{N}\), there are two \(\text{CH}_2\) groups. Microphase separation between the mesogenic rigid unit and flexible dendritic skeleton leads to formation of smectic phases. True smectic phases are formed by calamitic mesogens through superposition of equidistant molecular layers and are characterized along orientational correlation of the principal axis. On the other hand columnar phases are
obtained by stacking of disc-like molecules into columns, which are packed parallel into 2D ordered lattice and are characterized by symmetry of the arrangement, for example for hexagonal case it is $\text{Col}_h$ [15]. It is to be noted that the arrangement of the mesogenic end groups is predominantly perpendicular with respect to the layer planes, with the dendritic core located between these mesogenic sublayers.

For PAMAM LC dendrimers (figure 4), the layer periodicity is almost independent of generation number and probably the molecular volume expands within the plane of the layer as we move from one generation to the next. Grafting of additional terminal chains at the periphery of the anisotropic matrix influences the phase behaviour of the liquid crystalline dendrimer. Dendrimers functionalized by anisotropic units bearing one terminal alkoxy chain led to formation of smectic phase whilst the same matrices functionalized with mesogenic units bearing two or three terminal alkoxy chains exhibit $\text{Col}_h$ phase (figure 4) [16]. This happens due to the fact that the terminal chains prevents parallel disposition of the pro-mesogenic group and are forced to arrange radially about the central moiety. The process of molecular self-assembly induces supramolecular columns which further self organize into columnar hexagonal phases. The dendritic core in such conformation forced to deform anisotropically in one main direction, corresponding to the molecular axis.

The presence of amide linkers in PAMAM based LC dendrimers enhances intra- and intermolecular hydrogen-bonds interactions and thereby accounting for greater thermodynamic stability.

2.1.3. Carbosilane liquid crystalline dendrimers

Silicon-containing dendrimers, depending on the nature of the linkage at each junction, can be derivatized into carbosilane (Si-C), siloxane (Si-O), and carbosilazane (Si-N) sub-systems. Among these carbosilane dendrimers constitute one of the most important class of dendrimers due to their excellent chemical and thermal stability and versatility of the core connectivity which gives rise to a rich Si-C chemistry. For carbosilane LC dendrimers [17] the dendritic motif is based on a tetravalent core ($N_c = 4$) coupled to a binary branching multiplicity ($N_b = 2$). Nature of the mesogen and generation number of the dendrimer are necessarily been involved in determining the phase of the LC dendrimer. Thus dendrimers up to 4th generation functionalized by calamitic units (for example cyanobiphenyl, methoxyphenyl benzoate or anisic acid derived mesogens) exhibit solely SmecticA and SmecticC phases between room temperature and 90°C and the smectic phases stability and order improve upon dendrimerization due because of enhanced microphase
Figure 4. Representative structure of PAMAM LC dendrimer and peripheral mesogens, R

separation between the mesogenic units and the flexible dendritic Si-containing skeleton. The dendritic core in such compounds is probably in a distorted conformation with a 2D expansion in a plane parallel to the smectic layers. The supramolecular shape of the dendrimer varies significantly with increase in temperature. Above the SmA phase, a Col₁ phase is first formed, and on further heating a Col₃ phase is formed. This happens because as the
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carbosilane dendrimer continues its expansion in the third direction leading to the curvature of the mesogen/dendrimer interface, mesogen must compensate the increase of the cross sectional area of the core. So further increase of temperature results more cylindrical shape leading to columnar structure [15].

Carbosilane LC dendrimers G-n(Und-CB)m (figure 5) of 1, 2, 3, 4, and 5 generations with 8, 16, 32, 64, and 128 terminal cyanobiphenyl mesogenic groups were synthesized via hydrosilylation reaction using Pt-catalyst [18].

![Diagram of carnosilane LC dendrimer G-n(Und-CB)m](image)

**Figure 5.** Carbosilane LC dendrimer G-n(Und-CB)m; In the formula $n$ is the generation number and $m$ is the number of terminal groups.
Mesogenic groups were linked to the carbosilane dendritic matrix through an undecylenic spacer and that facilitate mesophase formation. Consideration of the influences of the factors such as generation number of the dendritic matrix, spacer length between the mesogenic units and the dendritic matrix and chemical nature of the terminal mesogenic group are very important in assigning the phase behaviour of such compounds. Thus in case of carbosilane LC dendrimers, for higher generations the influence of spherical molecular architecture become more significant which might pursue even formation of different supramolecular nanostructures of columnar type in addition to the smectic type arrangement.

2.1.4. Polyester and polyether LC dendrimers

LC dendrimers of these types are obtained by functionalizing amphiphilic polyol monodendrons with alkyl chain and then connecting those dendrons to a linear polyethylene oxide chain (figure-6). These dendrimers on increasing the polyethylene oxide portion and temperature, self assemble into various supramolecular architecture such as lamellar, micellar cubic, Colh etc. [19].

Mesomorphism can be induced in such dendrimers through microphase separation between the hydrophobic dendron and hydrophilic linear polymer. Dendritic core is built by various generations of 2,2-bis(hydroxyphenyl) ethane. Ferroelectric behaviour is known to exhibit by such LC dendrimers when appropriate chiral mesogenic groups are being attached to the amphiphilic polyester dendritic core [20]. Ionic conductivity of ion doped samples of such dendrimers in different phases can eventually be correlated with the mesomorphic behaviour.

![Figure 6. Structure of the polyether dendrimer.](image-url)
2.2. Main-chain liquid crystalline dendrimer

Unlike side-chain liquid crystalline dendrimers, where the junctions are consisting of single atoms, main chain liquid crystalline dendrimers contain anisotropic molecular moieties at every branching points, i.e. within such dendritic architectures at every level of dendritic hierarchy anisotropic groups are present. Consequently these molecular architectures possess less conformational freedom and also presence of these anisotropic segments forces the dendrimer to adopt more extended conformation. Conformational restriction occur due to squeezing of the dendritic part within the peripheral cell. Branches for such architectures do not radiate isotropically as we observe with side-chain LC dendrimers and rather they favour an anisotropic order by a gain in enthalpy. Such system possess larger number of functional units compared to side-chain LC dendrimers and a proportionate amplification of properties also expected.

B. Donnio et. al. have synthesized main chain LC dendrimers with homolithic systems containing building blocks of identical dendritic branch [21] and heterolithic systems with different anisotropic cores [22]. They have synthesized the dendrimers by a convergent/divergent approach consisting in synthesizing first the acidic branches and then grafting onto the anisotropic core in presence of diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate. (scheme 1) [23]. The perspective structures of few such LC dendrimers are represented in figure 7. Main chain LC dendrimers with eight functional arms are also some times referred to as ‘octopus dendrimer’.

**Scheme 1.** Synthesis of main chain LC dendrimers A, B, C and D (refer to fig. 7 for structure of A, B, C and D)
Depending on the chain substitution pattern of the terminal units, octopus dendrimers with terminal mesogenic groups may exhibit smectic mesomorphism (SmB and SmA phases) due to parallel disposition of the mesogenic groups on both sides of the tetravalent core, or columnar mesophase. Dendrimers with one terminal aliphatic chain per unit adopt a prolate conformation and this unique structural pattern with highly segregated molecular sublevels favours formation of smectic mesophases. On the other hand dendrimers with two or more than two aliphatic chains disfavours parallel disposition of the terminal mesogenic groups. The dendrimer adopts an oblate conformation which leads to induction of a Col\textsubscript{h} phase which can arguably possess onion morphology. The situation can pictorially be represented as shown in scheme 2. The columnar mesostructure in case of the later are indeed resulted from mismatch between the surface areas of the aromatic cores and the cross section of the aliphatic chains and thereby imparting a wedge-like conformation to the octopus dendrimer with the mesogenic groups radially distributed.

**Figure 7**
With such a conformation the dendrimer can self-assemble into supramolecular discs or columns and even to hexagonal net consistent with the lattice parameters (9-10 nm). These dendrimers having onion morphology for the columns in fact can have a wide range of possible interesting structures. Several of such dendrimers were prepared in practice [24-25] with the multicomponent supermolecules including homolithic systems (i.e. the building blocks constituting the dendritic branch are all identical) [figure 8(A)] and alternate heterolithic systems (i.e. containing different anisotropic units) [figure 8(B-D)].
2.3. Liquid crystalline fullerodendrimers

The covalent attachment of dendritic addends to the [60] fullerene (C\textsubscript{60}) was first reported by Frechet \textit{et al.} [26] and that was proved to be an effective method for the design of C\textsubscript{60} dendrimers with liquid crystalline properties. Fullerene has interesting physical properties and therefore fullerene containing liquid crystalline dendrimers can encourage enthusiastic studies in the field of supramolecular chemistry and materials science through design of newer self organized structures containing the fullerene unit. Especially this process of self-assembly using supramolecular interactions, might help generation of nanoscale architecture from functional groups which are otherwise not well adapted. Although the large C\textsubscript{60} unit disturbs the mesogenic interactions,
presence of enough mesogenic subunits in the dendritic addend, can compensate these effect to obtain self-assembled structures with liquid crystalline properties. This necessitates proper understanding of the structure-organization relationship for fullerene based supramolecular assemblies. Control of dendritic generations will help tuning of the properties for such supramolecular architecture.

Addition reaction of mesomorphic malonate-based dendrimers with fullerene (C\textsubscript{60}) produces liquid-crystalline fullerodendrimers where the terminal cyanobiphenyl units act as liquid crystalline promoter. The dendrimers were prepared by applying a convergent synthetic methodology [27]. Except the second generation dendrimer, all the fullerenes showed only smectic A phases. Figure 9 (A) and (B) represents the perspective structures of the first generation and second generation of methanofullerenes obtained from the addition of malonate based dendrimers to C\textsubscript{60} while figure 9 (C) constitutes a representative example of a fulleropyrrolidines. Fulleropyrrolidines are important class of C\textsubscript{60} derivatives which are even advantageous than the methanofullerenes as they can produce a stable reduced species having potential towards development of fullerene based redox molecular switches. This family of LC dendrimers also exhibit smectic A phases and stability of the dendrimers increases with increasing number of generations. Of course fulleropyrrolidines have slightly lower stability than that of the analogous methanofullerodendrimers.

Studies carried out on the supramolecular organization of these class of LC dendrimers indicated that in case of lower generation of dendrimers, the supramolecular organization is determined by the steric factors. To account for the steric constraint and efficient space filling we need to take into account the cross sectional areas of the fullerene moiety and terminal mesogenic group.

The fullerene moiety has a cross sectional area of about 90-100 Å\textsuperscript{2} whereas the mesogenic group has a cross sectional area of about 22-25 Å\textsuperscript{2}. Apart from these other factors like strong attraction between the fullerene moieties, dipolar interaction between the mesogenic groups, amphilic nature of the macromolecules and natural tendency of the mesogenic groups to form anisotropic organization within micro-domains must have to be emphasized to describe the supramolecular organization.

For higher generations the supramolecular organization is being influenced by the mesogenic groups which arrange in a parallel fashion, analogous to classical smectic A phase. This happens due to lateral extension of the branching part of the molecules. The rest of the macromolecules being located between the mesogenic sub layers [28]. Thus functionalization of C\textsubscript{60}
Figure 9. Examples of LC fullerodendrons.
with liquid crystalline addends constitutes an appropriate method for the elaboration of fullerene containing thermotropic liquid crystals. Although the bulky size and shape of the fullerene moiety have a tendency to decrease the liquid crystalline tendency as it can act as bulky spacer between the molecular units, this effect can be counteracted by providing a large number of mesogenic units through an increase in the generation number of the dendrimer. Therefore appropriate selection of the dendritic addends can provide a mean to prepare tailor made fullerodendrons through proper control of the dendrimer generation.

### 2.4. Shape-persistent liquid crystalline dendrimers

Shape persistent liquid crystalline dendrimers are another interesting family of liquid crystalline compounds which should find important applications in the field of material science. The dendritic matrix consisting of a conjugated rigid structure with electron-rich core. This family of dendritic matrix possess interesting photochemical and photophysical properties due to the presence of conjugate structure and electron rich core [15]. The matrices are intrinsically discotic in nature.

**Tolanoid:** $R=\text{CO}_2(\text{CH}_2\text{CH}_2\text{O})_3\text{Me}, R'=\text{H};$

**Stilbenoid:** $R=R'=\text{OC}_n\text{H}_{2n+1}, n=6,12$

**Figure 10.** Structure of G-1 and G-2 shape persistent dendrimer.
Tolane-based dendrimers up to third generation, with oligo(ethylene oxide) chain as the surface groups were reported to exhibit wide temperature range Col\textsubscript{h} phases while fourth generation were found to be amorphous [29]. Stilbenoid dendrimers up to second generation showed Col\textsubscript{h} and Col\textsubscript{o} mesophases [30]. These dendrimers up to second generation, consisting of trans stilbene building blocks and synthesized through a convergent synthetic pathway [30], are shown in figure 10.

Lower generation of these dendrimers (first and second generation) possess a planar conformation which can be stacked into columns without any steric hindrance as revealed by XRD pattern and molecular modeling [31]. In case of the higher generations steric crowding of the terminal groups restricts the dendrimers from such planar structure. The columnar mesophases are formed by face to face stacking of the unimolecular discs and an increased interaction between successive macrodiscs offers positive contribution towards the collective stability of the columnar mesophase.

2.5. Supramolecular dendromesogens

Supramolecular dendromesogens are consisting in dendritic branches which self-assembled together into supramolecular columns (cylindrical) and/or spherical dendrimers which further self-organize into various liquid crystalline mesophases. Since because unlike dendritic branches (which grow linearly with increasing generation number of the dendrimer) the number of promesogenic unit grows geometrically, therefore there is a limit for the growth of the diameter of the supramolecule. To avoid exceeding this limit, which is marked by the length of the repeating unit of the dendrimer and the branch multiplicity, the supramolecule undergoes conformational changes leading to various phases. Supramolecular dendritic concept was developed by Percec through exploration of self-assembling nature of perfect dendritic moieties [32]. In his attempt to find out the criteria those governing the shape and size of supramolecular dendromesogens he investigated libraries of monodendrons whose structures were rationally designed. He observed that variation of the number of peripheral aliphatic chains and the position of grafting influences the rate of growth or deformation of the dendromesogens and hence the structural organization. The structural organization also depends up on the generation number of the dendrimer. Generally cylindrical or pseudo-cylindrical supramolecular dendromesogens are obtained by the self assembly of the G2 monodendrons and some times with G3 and even with G4 depending on the connectivity of the terminal end-groups while G1 monodendrons are devoid of mesomorphism [32]. On an average they exhibit a flat tapered fan or semi-discoid shape. The influence of the apical function,
which is usually hydrophilic in nature, is also crucial for the stabilization of the mesophase. These tapered dendritic molecules through a process of self assembly may organize into infinite supramolecular columns with a polar interior. These columns, separated from each other by the aliphatic medium, then self-organize into rectangular and/or hexagonal lattices (figure 11).

Upon increasing dendritic connectivity and the number of terminal chains the flat tapered conformation might deform to important 3D structures like conical or even to pseudo-spherical supramolecular entities and cubic self-assemblies.

These spherical motives contain the polar portions within which in turn self assemble into miceller cubic phase. By controlling the overall molecular shape various mesophases like smectic, ColH, ColR, CubH, CubP, Tet (a LC phase with a tetragonal three dimensional unit cell), LQC (Liquid quasi crystal) etc. can be obtained from these dendromesogens [33].

**Figure 11.** Schematic representation of the self-assembly of dendromesogens from flat tapered to cylindrical shape.
Eventually these supramolecular self-organizations are driven by intramolecular micro-segregation, steric factors as well by H-bonding interactions. X-ray crystallographic data revealed that the cubic phases result from the self-assembly of these spheroid dendrimers with Polar Regions embedded at the crystallographic position of the group [34]. These supramolecular spheres are also deformable, interacting one with the other through relatively soft pair potential and thus can be distorted into an oblate shape.

The skeleton of these self-assembling monodendrons are valuable building blocks used in the construction of nanoscale objects with novel functional utility and more complex functional architectural motives where micro segregation between polar and apolar regions plays a significant role in attributing the observed mesophase along with flexibility of the backbone [35]. The intermolecular interactions among the promesogenic units also determine the conformation of the dendromesogens which adapts to their requirements as long as it is conformationally and sterically possible. For example a cylindrical symmetry in the molecule might lead to supramolecular columnar arrangement.

### 2.6. Liquid crystalline metallodendrimers

Although vast majority of dendrimers are purely organic systems, but metallodendrimers are not few in numbers. Incorporation of the metal into the dendritic matrix opens up the possibility of application of metallodendrimers in various areas of science. Examples of such applications includes as efficient catalysts due to the high concentration of active sites, electro-active molecules due to the multiredox center, sensor applications and other photo-physical applications. Therefore metallodendrimers are supramolecular entities with greater potential for multidisciplinary areas [36]. More interestingly the properties of such macromolecules can be tuned and modulated by the specific location of the active moieties within the dendrimer. The metal can be incorporated at the core or even at the periphery of the dendrimer.

LC metallodendrimers are very few in numbers and usually contain minidendrons of first generation with exception to ferrocenyl dendrimers. A few of such liquid crystalline metallodendrimers are known and upon complexation with suitable ligands they can exhibit mesomorphic behaviour. Structure of a dendritic oxovanadyl compound complexed with salen based ligand is shown in figure 12, which exhibits columnar mesophase (Col\textsubscript{r} and Col\textsubscript{h}) [37]. Rigidification of the central chelating part probably leads to occurrence of mesophase.
Coordination of other metal centers such as Co(II), Ni(II), Cu(II), Zn(II) etc. to dendritic imine ligands also produces dendrometallomesogens with stabilized mesomorphism [38]. Examples of lower generation PPI dendrimers involved in the formation of such metallo dendrimers through coordination with MX$_2$ (M is the metal center) type of salts are shown in figure 13. These dendrimers those are end functionalized with mesogenic salicylaldimine are considered as potential multicoordinative organic ligands

![Figure 12. Structure of an oxovanadyl dendritic complex.](image)

![Figure 13. Structure of dendritic imine ligands D1 and D2 involved in metalloidendrimer formation.](image)
for obtaining LC metallodendrimers. Quasi metallodendrimers involving one, two or three metallic centers were thus obtained from a mesomorphic multicoordinative adequately functionalized dendritic imine ligands [39].

3. Utility of LC dendrimers as functional materials

Dendritic architecture, the most pervasive topology has been assigned as the unique one in terms of its capability for total control over molecular design structural parameters, control over branching pattern, molecular size, structure and morphology. These features project them as a newer class of potential material for development of intelligent functional material. The ability of dendritic motifs to self assemble to well defined and nanosized dendritic macromolecules will continually increase their importance in material science and serve as an interesting and fascinating motif in nanoscience, nanotechnology and other interdisciplinary field. Current investigation on LC dendrimers mainly focuses on the application prospects. For example due to micro phase separation between polar and apolar regions different mesophases are observed for ionic derivatives of linear carboxylic acid with PAMAM or PPI liquid crystalline dendrimers. Such dendrimers are modified to obtain birefringent glasses at room temperature and viscous smectic A phase at higher temperature [40]. These dendrimers possess terminal flexible alkyl carboxylic acids separated by a region of high density of the ionic ammonium carboxylates and these LC dendrimers may find interesting application as anisotropic ionic conductive material [41].

The spin functional soft dendritic materials capable of undergoing spin transition at specific temperature range have potential for sensor application because of their quick response of the spin cross over phenomena to temperature change. Fujigaya et al. has reported about some dendritic triazole Fe(II) complex [obtained from Fe(II) ion, dendritic triazole ligands with polybenzyl ether dendrons] having alkyl sulphonate as counter ion, which can undergo thermal induced discoulouration – colouration cycle and that can be repeated without any sign of deterioration [42]. Phenomena of self-assembly in some of these dendrimers can attribute characteristic texture due to liquid crystalline mesophase. For such dendrimers the spin-transition and phase-transition events are perfectly synchronous to each other and show quick response to temperature change and hence are projected as promising materials for sensor application. Astruc et al. has reviewed the application prospects of liquid crystalline dendrimer [43].

Percec and his group observed the fact that when electron acceptor or donor organic groups are placed at the focal point of suitable dendrons, the supramolecular organization in such cases produced liquid crystalline
dendrimer with high charge carrier mobilities. The materials produced could have interesting electronic and opto-electronic applications [44]. Deschenaux et al. have argued that properties of fullerene-containing thermotropic liquid crystals could be of interest for applications like molecular switches; solar cells etc. and hence find importance in nanotechnology. They designed fulleropyrrolidines representing family of electroactive macromolecules. Different substituents, for example ferrocene units, can be attached to the N-atom of the fulleropyrrolidine which can make them suitable candidates for photovoltaic applications or supramolecular switches [45]. The ferrocene and the fullerene groups constitute a well known redox system with marked electrochemical properties. The supramolecular organization promoted by the mesogenic group enhances the photophysical and electrochemical properties of the supramolecule. We can generalize that fullerenes covalently functionalized with mesomorphic dendrimers can produce self assembled liquid crystalline architecture that can be tuned by molecular design to obtain tailor made characteristics for application purpose.

Thermotropic liquid crystals are already been used in most of our daily used items like watches, calculators, mobile telephones etc. Therefore liquid crystalline dendrimers are certainly interesting materials for application studies. The beauty of such compounds is that liquid crystalline properties can be controlled as a function of dendrimer generation and can be tuned by careful selection of mesogenic group. For example ferroelectric properties were obtained for dendrimers functionalized with chiral mesogenic moieties [46]. Metallocenyl dendrimers due because of their electrochemical properties have attracted much attention in the field of molecular electronics. Thus smectic C and smectic A liquid crystalline phase has also been observed with LC dendrimers such as ferrocenyl and C₆₀ terminated dendrimer [47]. Photosensitive ionic nematic liquid crystal complexes are also known [48]. PAMAM and PPI dendrimers can be decorated with appropriated groups to obtain liquid crystalline dendrimers having smectic and columnar mesophase and with interesting photophysical properties [49]. The development attained so far in the field of liquid crystalline dendrimers throws light on the bright prospect of emergence of newer intelligent opto-electronic materials for novel applications.

Furthermore dendrimers containing electroactive groups at the center or on the periphery can help understanding biological electron transfer and are excellent candidates for applications like as catalyst, electron transfer mediator, ion sensors etc. Proper understanding of the connection between structure and function will provide deeper insight into the behaviour of biological systems too, so that the scope of the application can also be extended to real world problems.
Conclusion

Liquid crystalline dendrimers constitute the most interesting topology for generation of varieties of nanoscopic devices, intelligent materials with designer structural and functional properties. This molecular architecture might lead to newer ideas for the development of materials for which their design is only limited by human imagination. With the high molecular weight monodisperse dendrimers and dendrons, liquid crystalline dendritic motifs can be generated containing the conventional liquid crystalline phases like nematic, lamellar, columnar, cubic phase as well less conventional mesophases such as onion, segregated and porous columnar mesophases, multilayered and dark smectic phases. Chemical nature and connectivity of the mesogenic groups greatly influence the mesomorphic properties and appropriate selection of such mesogenic groups will make possible the design of newer functional materials with tailor made properties. The self-organization of these polymeric structures are gaining significant importance for obtaining intelligent nanoscale architectures with specific physical properties like magnetic, electronic or optoelectronics which in turn find important application in the fields like supramolecular chemistry, nanotechnology, biotechnology and other relevant fields.

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