Chapter 6
Effects of Hydrogen-Bonding on the Liquid Crystalline Properties of Dendritic Polymers

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Dendritic polymers have shape reminiscent of the braches of a tree. They may be symmetrical dendrimers, symmetrical fragments thereof called dendrons or their non symmetrical analogues, the hyperbranched polymers. All classes possess a nucleus or core, the inner branches which often form cavities and the external branches which are functionalized with characteristic groups. It is evident that in most cases the chemical environment of the core, the branches and the external groups is completely different. This anisotropy is among the most interesting properties of the dendritic polymers and makes them ideal candidates for formation of liquid crystalline phases. Dendritic mesogens or dendromesogens consist an interesting separate class of liquid crystalline polymers having different properties and behaviour from both main-chain and side chain liquid crystalline polymers (Matheus et al. 1998; Emrick and Fréchet 1999; Fischer and Vögtle 1999; Moore 1999; Schlenk and Frey 1999; Adronov and Frechet 2000; Smith and Diederich 2000; Grayson and Fréchet 2001; Ponomarenco et al. 2001; Tschierske 2001, 2002; Diele 2002; Guillon and Deschenaux 2002; Caminade et al. 2003; Lee et al. 2005).

An investigation of the mesomorphic properties of a very large number of dendritic polymers and a detailed characterization of their multiple liquid crystalline phases deriving from their diversified molecular architecture is developing as a consequence of the overall increasing scientific research for the prospected applications of these macromolecules during the previous two decades (Inoue 2000; Sun et al. 2001; Bergenudd et al. 2002; Burkinshaw et al. 2002; Arkas et al. 2003, 2005a, b, 2006, 2010; Kolhe et al. 2003; Seiler et al. 2003; Allabashi et al. 2007; Tsetsekou et al. 2008; Arkas and Tsiourvas 2009; Tsiourvas et al. 2011, 2013a, b; Arkas 2013). In order to build dendritic polymers exhibiting liquid crystal phases, a

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variety of strategies have been employed. The most typical method for the induction of mesophases is the functionalization of dendritic polymers in order to self assemble preferably into cylindrical (Percec et al. 1992, 1993a, b, c, 1994, 1995, 1996a, b, 1998a, c; Johansson et al. 1994, 1996; Percec and Schlueter 1997; Pesak and Moore 1997; Brewis and Clarkson 1998; Meier and Lehmann 1998; Prokhorova et al. 1998a, b; Suárez et al. 1998; Prokhorova et al. 1999) or spherical (Balagurusamy et al. 1997; Hudson et al. 1997; Percec et al. 1998b, c, 2008, 2009; Yin et al. 1998) shapes. The intrinsic property of dendritic macromolecules to form inner part (core) and an outer external surface with different properties mainly in terms of polarity and flexibility leads to microphase separation which is regarded as the main factor inducing the formation of these assemblies and governing their organization.

Inter and intra molecular hydrogen bonds may alter drastically the shape of dendritic molecules and/or the functionalization of the external groups. In addition they are reported to contribute to the rigidity of a particular part of the mesogenic molecules, most often its central core, resulting in more ordered and more thermally stable liquid crystalline properties with wider temperature range and higher transition temperatures (Donnio et al. 2002; Gehringer et al. 2005). By being weaker and by having different nature from the traditional conventional covalent bonding, hydrogen bonding is directional more versatile, reversible and allows very important biological processes such as molecular recognition. In addition by being dynamic in nature, hydrogen bonding presents a feasible way to prepare functional materials reacting to small changes of the external environment. In this context, the role of hydrogen bonding on microphase separation and mesophase formation of dendritic polymers became a very interesting field of research.

6.1 Dendromesogens Based on Hydrogen Bonds of the External Groups

The simplest method of generating liquid crystalline character via hydrogen bonding in dendritic polymers is the modification of the properties of the external surface. This can be achieved by various methods. The basic strategy consists of two stages (a) chemical modification of the external groups in order to render them capable of forming hydrogen bonds by certain complementary molecules having specific shape (rigid rod, disk) or properties (solubility) capable of inducing liquid crystalline character called mesogens and (b) interact the modified groups with the mesogens bearing the complementary moieties in the melt or in specific solvents in order to form supramolecular complexes.

6.1.1 Hydrogen Bonding with Rigid Rod Shaped Molecules

Felekis et al. (2005) functionalized diaminobutane poly(propyleneimine) dendrimers (DAB) of second to fifth generations with pyridyl moieties (Fig. 6.1a). Subsequent interaction of these modified dendrimers with 3-cholesteryloxycarbonylpropanoic acid through slow evaporation of DMF solutions formed supramolecular hydrogen-bonded complexes via intermolecular hydrogen bonding between the nitrogen of the pyridine ring and the hydroxyl group of the carboxylic acid exhibiting smectic A phases over a relatively broad temperature range.

In the same context Xu et al. (2008) starting from a of a series of cyclotriphosphazenes that were modified by stilbazolyl, Schiff bases and azopyridyl-type mesogenic groups, as central dendrimeric cores, functionalized them with mono, bis, and tris(alkyloxy)benzoic acids via hydrogen bonds by mixing them in chloroform (Fig. 6.1b). While the rigid core precursors did not exhibit liquid crystalline character most of them, when interacted with six monoalkyloxybenzoic acid molecules via intermolecular hydrogen bonding formed smectic or nematic mesophases. Weak single hydrogen bonds were proven strong enough to direct the star-shaped supramolecular assembly and induce liquid crystallinity.

Based on the same principle Didehban et al. (2009) obtained nematic and smectic liquid crystals from three generations of dendritic 5-hydroxyisophthalic acids when they reacted in the melt with an alkoxy-stilbazole bearing a pyridyl group due to the hydrogen bond interactions between the carboxylic acid of the dendron and the nitrogen of the pyridyl group (Fig. 6.2a).

6.1.2 Hydrogen Bonding of the Core with Dendrons

The basic strategy described in the previous chapter can be reversed. A dendritic core can be used as proton acceptor. For example trans-4-hexyloxy-4′-stilbazole a molecule with two pyridyl moieties by formation of hydrogen bonds with the carboxyl groups of two 3,5-dihydroxybenzoic acid dendrons which acted as proton donors exhibited nematic and smectic mesophases (Fig. 6.2b, Didehban et al. 2010). Using the same method and choosing tricarboxylic triphenylene bearing short pentyloxy chains as core and monopyridyl dendrons bearing long dodecyloxy chains as branches connected via complementary hydrogen-bonds Ishihara et al. (2007) obtained supramolecular complexes exhibiting columnar hexagonal mesophase only when all the carboxyl groups could form hydrogen bonds i.e., at 1:3 molar stoichiometry. Another attempt with a functionalized triphenylene derivative i.e., fluoroalkyl side chain-substituted 2,6,10-tris-carboxymethoxy-3,7,11-tris(4,4,5,5,6,6,7,7,7-nonafluoroheptyloxy)triphenylene provided again columnar hexagonal liquid crystal when this core compound formed a 1:3 complex with the second generation dendron 3,5-bis(3,4-bis-dodecyloxy-benzyloxy)-N-pyridin-4-yl-benzamide through complementary hydrogen bonding (Ishihara et al 2014).

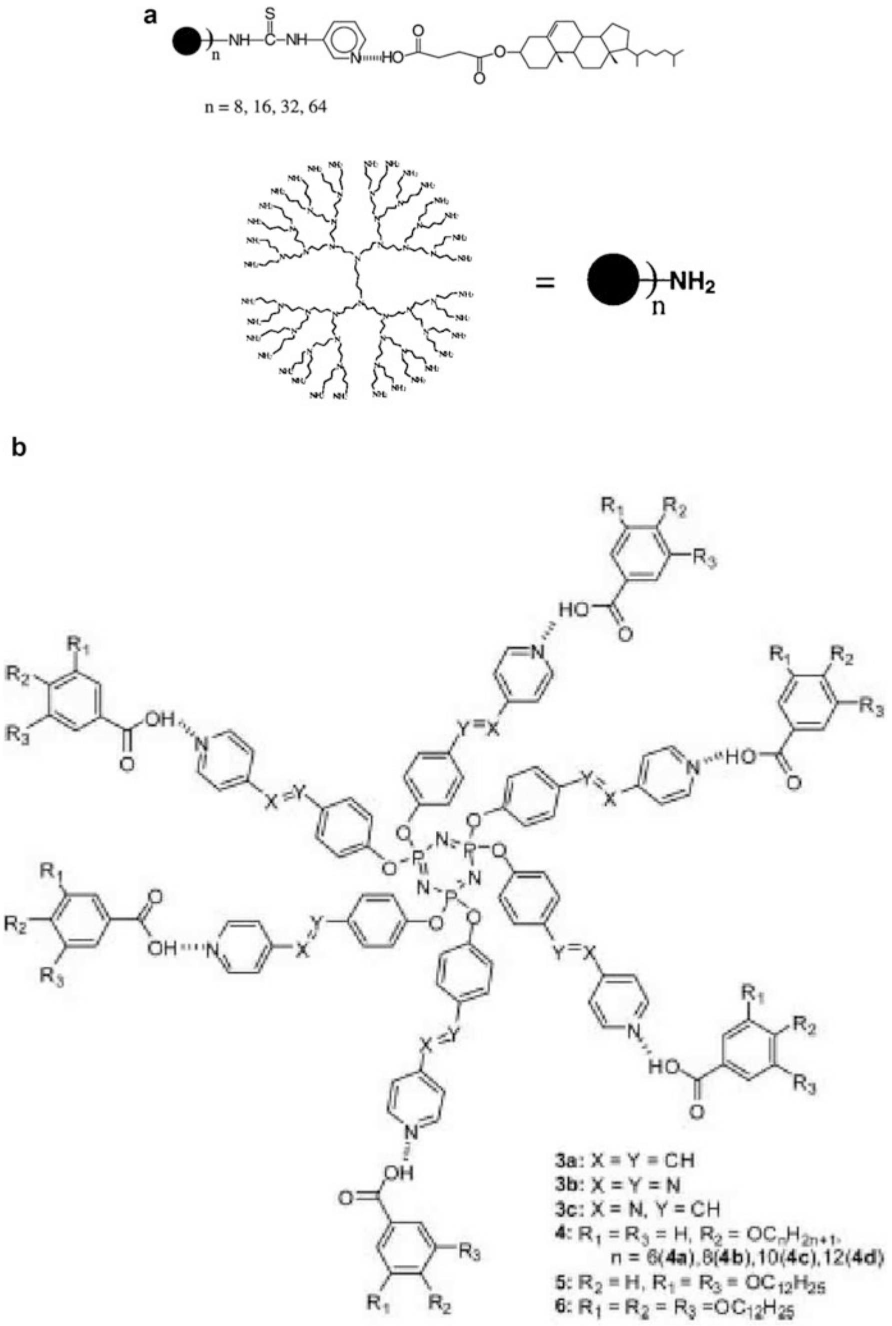


Fig. 6.1 (**a**) Diaminobutane poly(propyleneimine) dendrimers (DAB) of second to fifth generations functionalized with pyridyl moieties and their interaction with 3-cholesteryloxycarbonylpropanoic acid. **(b)** Cyclotriphosphazenes modified by stilbazolyl, Schiff bases and azopyridyl-type mesogenic groups, as central dendrimeric cores functionalized with mono, bis, and tris(alkyloxy)benzoic acids via hydrogen bonds

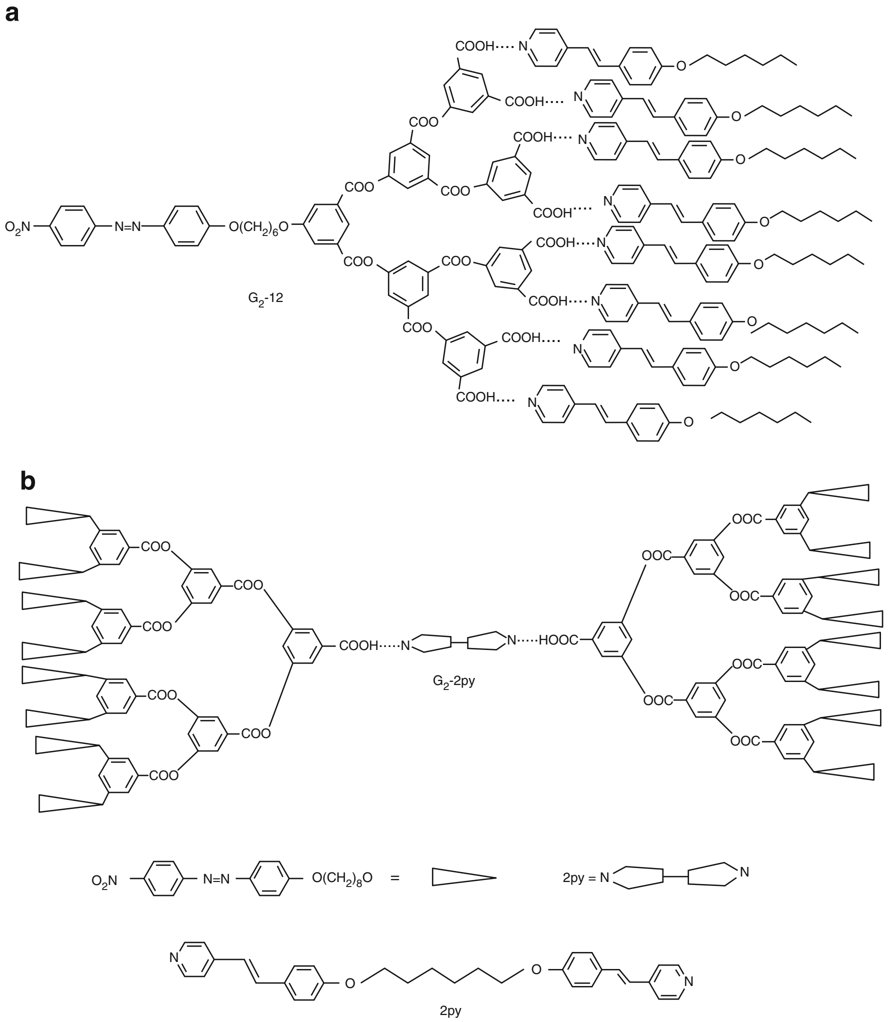


Fig. 6.2 (**a**) Hydrogen bonding between (**a**) dendritic 5-hydroxyisophthalic acids and alkoxy-stilbazoles bearing a pyridyl group. (**b**) trans-4-hexyloxy-4′-stilbazole bearing two pyridyl moieties with two 3,5-dihydroxybenzoic acid dendrons

Castelar et al. (2013) synthesized two families of supramolecular dedritic complexes. Using a triazine moiety as an electron-transporting central core they attached three peripheral dendrons of generations 1 and 2 derived from bis (hydroxymethyl)propionic acid by double hydrogen bonding of carboxylic acid groups with the amino groups and the aromatic nitrogens. The dendrons which were designed as hole-transporting moieties contained 5-[4-(4-butoxybenzoyloxy) phenyloxy]pentanoic acid (family A) or cholesteryl hemisuccinate (family B) as promesogenic units. The supramolecular complexes exhibited nematic and smectic A phases.

6.1.3 *Multiple Hydrogen Bonding and Molecular Recognition*

Though one hydrogen bond between complementary moieties seems enough to induce supramolecular complexes exhibiting mesophases the development of liquid crystalline aggregates through multiple hydrogen bonding and molecular recognition presents particular interest since it refers to the complex biological structures encountered in nature rendering these superstructures useful models for understanding the rules governing the organization through hydrogen bonding in nature. One such example is the columnar hexagonal phase resulting by hydrogen-bonding interactions between a 3-pentyl benzotri(imidazole) core and benzoic acids bearing acryloxy substituted dodexyloxy chains (Lee et al. 2001). Analogous results have been obtained by Kraft et al. (2000) for alkoxy-substituted benzoic acids forming supramolecular hydrogen bonded complexes around a tribasic core

6.1.4 *Hydrogen Bonding with Disk Shaped Molecules*

Poly(propylene-imine) dendrimer is also reported to exhibit columnar mesophases when the external amino groups form hydrogen bonds with acid functionalized discotic molecules. Fitié et al. (2008) synthesized supramolecular complexes from Poly(propylene-imine) and (((3,5-bis((decylamino)carbonyl)benzoyl)amino) undecanoic acid) at various ratios. All the complexes self-assembled into well-ordered oblique columnar liquid crystalline superlattices. These mesomorphic structures derive from the combination of an orthogonal pattern of hydrogen bonds with ionic interactions in a perpendicular plane which confine the dendrimers in columns.

6.2 Induction and/or Stabilization of Mesomorphism Based on Intra and Intermolecular Bonds

In series of systematic comparative studies (Barberá et al. 1999, 2005; Marcos et al. 2001; Donnio et al. 2002, 2007) liquid crystalline polypropylene imine (DAB) and polyamidoamine (PAMAM) dendrimers functionalized by terminal calamitic promesogenic units that carried alkoxy chains (Fig. 6.3a), the mesophases observed by functionalized PAMAM dendritic polymers were thermodynamically more stable than those exhibited by analogous PPI dendrimers. This was attributed to the presence of intra and inter molecular hydrogen bonds between the amide groups present only in PAMAM and the consequent rigidification of the inner dendritic structures. Moreover it was reported that the alteration of some geometrical parameters such as the surface of the calamitic mesogens caused by the addition of a second or a third alkoxy chain which leads them to radial disposition, in synergy with the presence of intra- and intermolecular hydrogen bonds which results in the stable aggregation of the central dendritic structure play a crucial role in the organization of the functionalized polymers into columnar hexagonal liquid crystalline phases instead of lamellar smectic A or C.

The same effect was observed in dendrimers with cyclotriphosphazene core and branches formed by polycatenar benzamide groups functionalized by dodecyloxy aliphatic chains (Barberá et al. 2006). IR measurements proved that the columnar mesophases observed over a range of temperatures derive from the stabilization of the stacking of the discotic structures by the intermolecular H-bonding of the benzamide groups.

Another example of liquid crystalline phase induction due the enhanced rigidity of the dendritic molecules attributed to hydrogen bonding is hyperbranched polyethylene imine functionalized with long aliphatic chains. These functionalized hyperbranched poly(ethylene imine) polymers exhibit columnar rectangular and lamellar (SmA and SmB) mesophases in contrast to their symmetric analogs i.e., propylene imine dendrimers. (Tsiourvas and Arkas 2013) This profound difference is attributed to the fact that the former due to their asymmetry possess secondary amino groups which reside not only close to the periphery but even near the core of the molecule. Since both secondary and primary amino groups are functionalized (alkylated) the subsequent creation of urea groups results in hydrogen bonding formation throughout the interior of the hyperbranched polymer. These hydrogen bonds enhance the rigidity of the inner part of the molecules and in synergy with the difference in polarity due to the polar character of the same urea groups lead to segregation between the rigid polar segments of the core and the flexible non polar segments of the aliphatic chains and thus to the induction of liquid crystalline properties. Analogous results have been obtained by Stebani and Lattermann (1995) (Fig. 6.3b) with smaller polyethylene imine symmetrical dendrimers where external amino groups of the first generation are functionalized by benzoyl groups substituted by two decyloxy chains. In this case microphase separation from the flexible non polar alkyl chains is achieved by the enhancement of the dendrimer polarity by amide groups and its rigidity by the formation of hydrogen bonds between the same. For this compound a spherulitic texture was recognized and was attributed to a columnar mesophase structure. Intramolecular H-bonding between the urea groups has also been reported to stabilize thermotropic mesophases with homeotropic orientation observed for poly(propylene imine) dendrimers modified peripherically with urea oligo(p-phenylene vinylene)s bearing a 3,4,5-tri(dodecyloxy)phenyl mesogenic units (Precup-Blaga et al. 2003) The increased temperature range of the liquid crystalline phases of the higher generation dendrimers was attributed to stronger hydrogen-bonding interactions due to the more dense-shell packing and the closer proximity of the urea groups.

H-bonding interactions deriving from a combination of different groups such as ureas and amides can also enhance the stability of the mesophases. Zhou et al. (2008) (Fig. 6.3c) confirmed that symmetrical dendritic trisureas such as cyanophenylazo tributyl and tridecyl-1,3,5-(benzene-1,3,5-triyl)tris-3-phenylureas mixed with symmetrical trisamide gelators such as N^1,N^3,N^5-trioctadecylbenzene-1,3,5-tricarboxamide (G1) display liquid crystalline properties in the form of thermotropic liquid crystals and liquid crystalline gels. Both trisureas have lamellar

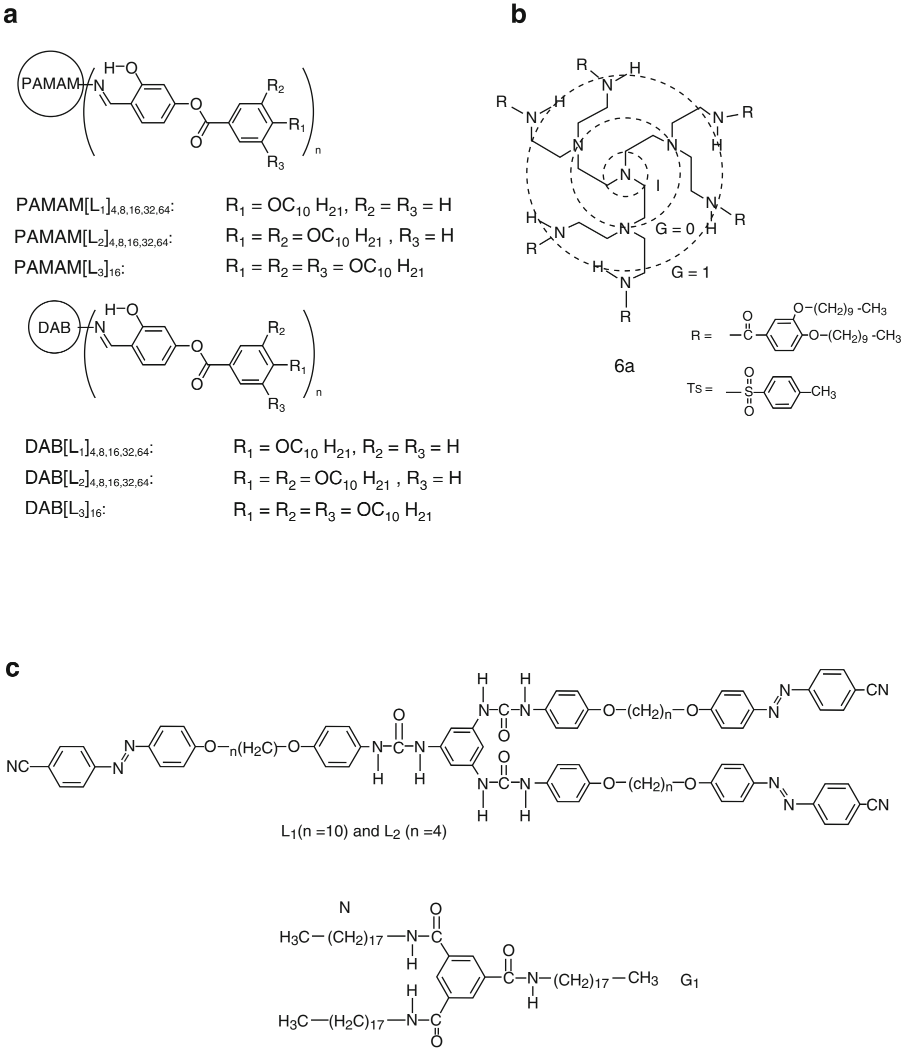


Fig. 6.3 (**a**) Polypropylene imine (DAB) and polyamidoamine (PAMAM) dendrimers functionalized by terminal calamitic promesogenic bearing chains. (**b**) Polyethylene imine symmetrical dendrimers where external amino groups of the first generation are functionalized by benzoyl groups substituted by two decyloxy chains. (**c**) Symmetrical dendritic trisureas cyanophenylazo tributyl and tridecyl-1,3,5-(benzene-1,3,5-triyl)tris-3-phenylureas (L_1 or L_2) and symmetrical trisamide gelator N^1,N^3,N^5-trioctadecylbenzene-1,3,5-tricarboxamide (G_1)

structures in high temperatures whereas their mixtures with the gelator exhibited columnar rectangular and hexagonal mesophases with thermal stability up to 240 °C. The role of the hydrogen bonds was ascertained by temperature dependent FTIR spectroscopy which revealed that the hydrogen bonding network between ureas and amides was much more organized than the respective urea and amide analogues.

Rigidification of the cores of dendritic molecules leading to the formation of non-tilted discotic columnar hexagonal mesophases has also been reported by Shu et al. (2013). Hydrazone molecules functionalized with flexible dendritic groups containing linear hexyloxy, octyloxy, and decyloxy chains, formed mesophases where the hydrazone discs were rigidified by intramolecular hydrogen bonds. In another example monodendrons consisting of L-alanine at their core and long alkyl chains at the periphery exhibited thermotropic columnar hexagonal and columnar rectangular liquid-crystalline phases stabilized by hydrogen-bonded clusters (Anokhin et al. 2012).

6.3 Intermolecular Hydrogen Bonds Defining the Shape of Mesomorphic Dendritic Molecules and the Organization of the Liquid Crystalline Phases

One of the most important works in this particular field has been performed by Takashi Kato and his group. Through a series of studies in dendritic polymers they managed to prove direct correlation between the hydrogen bonding patterns, the shapes of the molecules and the nature of liquid crystalline phases. Firstly they focused on the derivatives of folic acid, an important biologically active molecule. By increasing the length of the alkyl chains of the 2-(3,4-dialkoxyphenyl)ethyl derivatives and by inducing ion–dipolar interaction between the pterin ring and metal cations they managed to direct hydrogen-bonding network into forming dendritic disk-like aggregations of tetramers of pterin ring of folic acid resulting in hexagonal columnar and nematic columnar instead of lamellar mesophases (Kanie et al. 2001a, Fig. 6.4a). The same derivatives produced identical effect when they formed lyotropic mesophases in organic solvents. A change of the liquid crystalline phases from lamellar to columnar nematic has been observed in more hydrophobic solvents attributed to the change of the hydrogen bonding patterns from ribbon to disk (Kanie et al. 2001b). Furthermore when 2-(3,4-dialkoxyphenyl) ethyl moieties were replaced by respective dialkoxyoligo(glutamic acid) moieties (Fig. 6.4b) hexagonal columnar and *P*m3n cubic LC phases were formed (Kato et al. 2004).

Moreover since the dialkoxyoligo(glutamic acid) derivatives possess three chiral centers they examined the possibility of chiral mesomorphic behavior. Indeed formation of chiral hexagonal columnar and *P*m3n cubic liquid crystalline phases were observed in the presence of sodium triflate ($NaOSO_2CF_3$) in all three γ-Bis(L-glutamoyl) N-[N^{10}-(trifluoroacetyl)pteroyl] L-glutamic acid tetra{2-[3,4-di (alcyloxy)phenyl]ethyl} esters.

The tetra{2-[3,4-di(hexyloxy)phenyl]ethyl} compound together with its D-glutamoyl D-glutamic acid enantiomer and the L-glutamoyl D-glutamic acid diastereomer also exhibited respective thermotropic chiral *P*m3n cubic and chiral hexagonal columnar mesophases (Kamikawa et al. 2005) and also lyotropic chiral

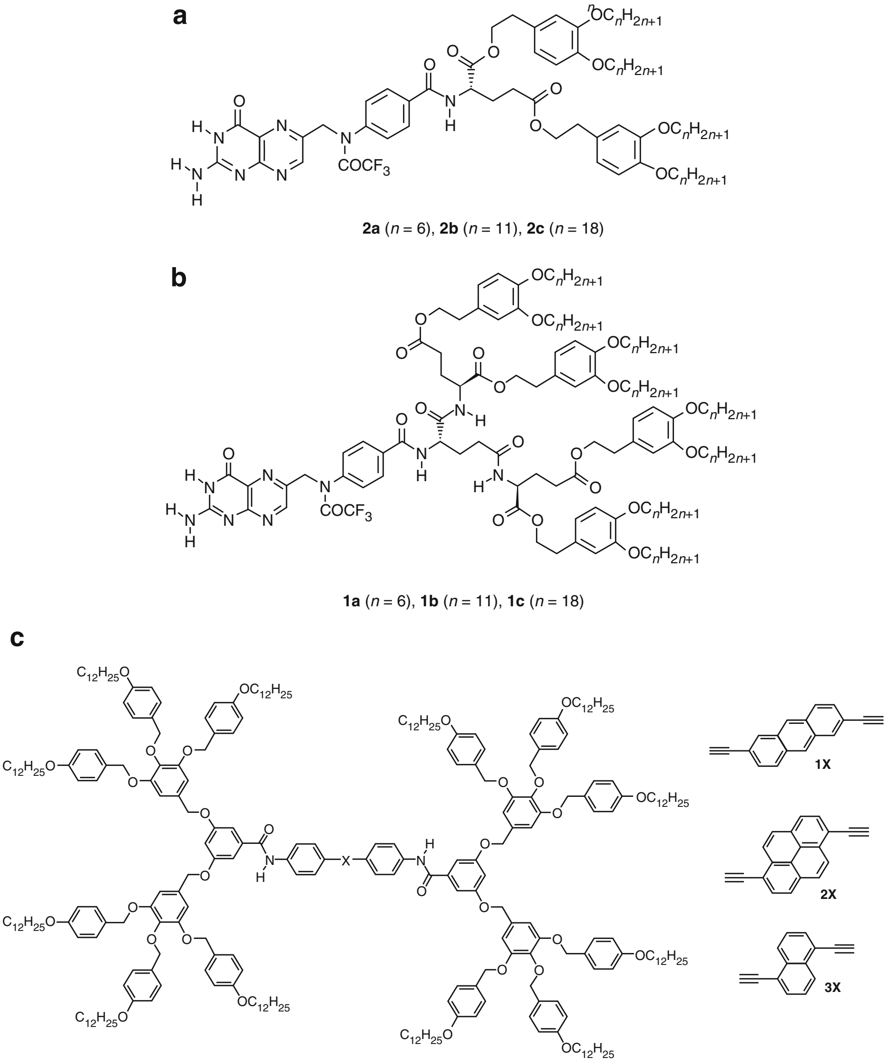


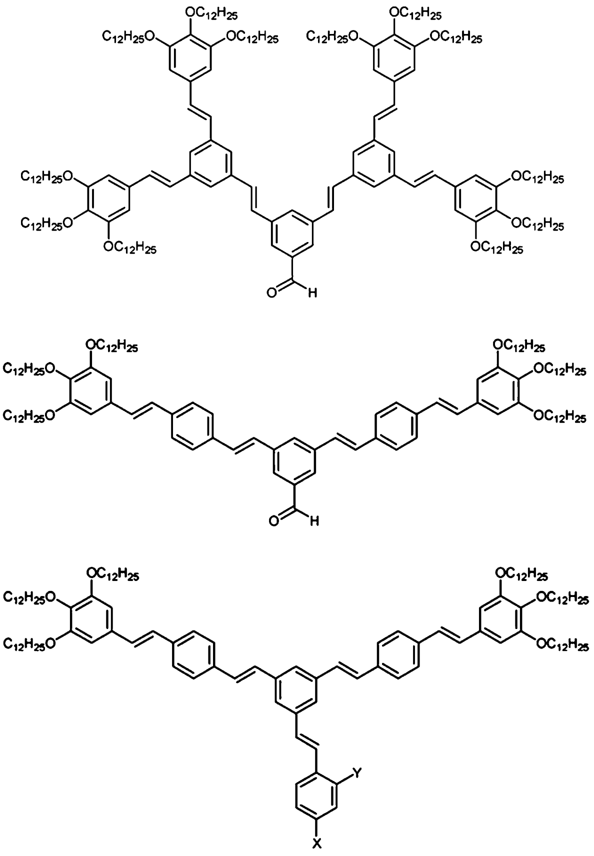
Fig. 6.4 **(a)** 2-(3,4-dialkoxyphenyl)ethyl and **(b)** dialkoxyoligo(glutamic acid) derivatives of folic acid. **(c)** Dendrimers from benzyloxy derivatives of pyrene anthracene and naphthalene functionalized by dodedyloxy chains

hexagonal columnar liquid crystalline phases (Kamikawa et al. 2004). More specifically the two enantiomers in polar chloroform in the presence of sodium triflate self-organize into the same chiral columnar assemblies but with reversed helicity. In this case the transfer of the chirality from the molecular level of the oligo (glutamate) parts to the supramolecular chirality was attributed to the cooperative ion–dipolar interactions and hydrogen bonds. Most impressively all three diastereomers in a lipophilic environment such as dodecane produced chiral assemblies even in the absence of sodium triflate. In this case the chiral aggregates were formed solely through lipophilic interactions of the alkyl chains of the solvent with the smaller aliphatic chains of the dendritic tetramers resulting to the increase of the lipophilic fraction. This in turn, in cooperation with the hydrogen bonds, enhances microphase segregation resulting in the induction of chirality at the supramolecular aggregates without the presence of a metal ion.

In another example where materials with photoluminescent properties are concerned, the role of the intermolecular hydrogen bonds is not limited to the stabilization or even the formation of liquid crystalline phase but also induces a change in the self-assembled structures at a molecular level when shearing is applied (Yamane et al. 2012). Dendrimers from benzyloxy derivatives of pyrene (Fig. 6.4c) functionalized by dodedyloxy chains undergo a transition from a micellar *P*m3n cubic to a P2/a columnar rectangular phase with subsequent change of the photoluminescence color from yellow to blue-green upon mechanical shearing (Sagara and Kato 2008). IR measurements indicated that in the cubic phase hydrogen bonds of the amide groups were weaker whereas in the columnar phase a downshift of the C=O groups revealed a stronger H-bonds network in a completely different pattern. Respective derivatives of anthracene (Fig. 6.4c) apart from piezochromic exhibit thermochromic properties too. On rapid cooling from the isotropic phase by putting the isotropic sample onto a metal substrate at room temperature exhibited a metastable *Pm3n* cubic phase and yellow photoluminescence (Sagara et al. 2009). Conventional slow cooling i.e., up to 10 °C/min produced columnar rectangular phase with emission of blue light. The metastable cubic phase in turn can undergo transition to the stable columnar phase through heating or mechanical shearing. This behaviour was attributed to the differences in the hydrogen bond patterns. Longer intermolecular hydrogen bonds between the amide groups of adjacent molecules in combination with π–π stacking of the anthracene cores lead to segmented columnar structures and a cubic phase whereas stronger shorter, up to 5 Å, hydrogen bonds in a linear pattern result in the more ordered longer columns of the columnar rectangular phase. Analogous results are obtained when anthracene is replaced by naphthalene (Sagara and Kato 2011a, Fig. 6.4c) whereas mixtures 1:1 of two 9,10-bis(phenylethynyl)anthracene derivatives, each bearing different benzyloxy dendron functionalized by trimethyldodecyloxy aliphatic chains exhibit three mesophases with three different hydrogen patterns and a three-colored luminescence (Sagara and Kato 2011b). When the benzyloxy derivatives of pyrene were replaced by oligopeptides supramolecular chiral columnar liquid crystals are produced. The synergy intermolecular hydrogen bonding of the peptide bonds and electron donor–acceptor interactions is controlling supramolecular chirality (Kamikawa and Kato 2006).

Alteration between columnar hexagonal and cubic mesophases due to hydrogen bond interactions is also described by Lehmann and his co-workers (2005) for stilbenoid dendrons (Fig. 6.5) bearing long dodecyloxy chains at their periphery. Stable ordered cubic mesophase was observed only when the dendron possessed amide groups and thus was capable of intermolecular hydrogen bonding. Replacement of the amide functionality even with groups capable of other type of

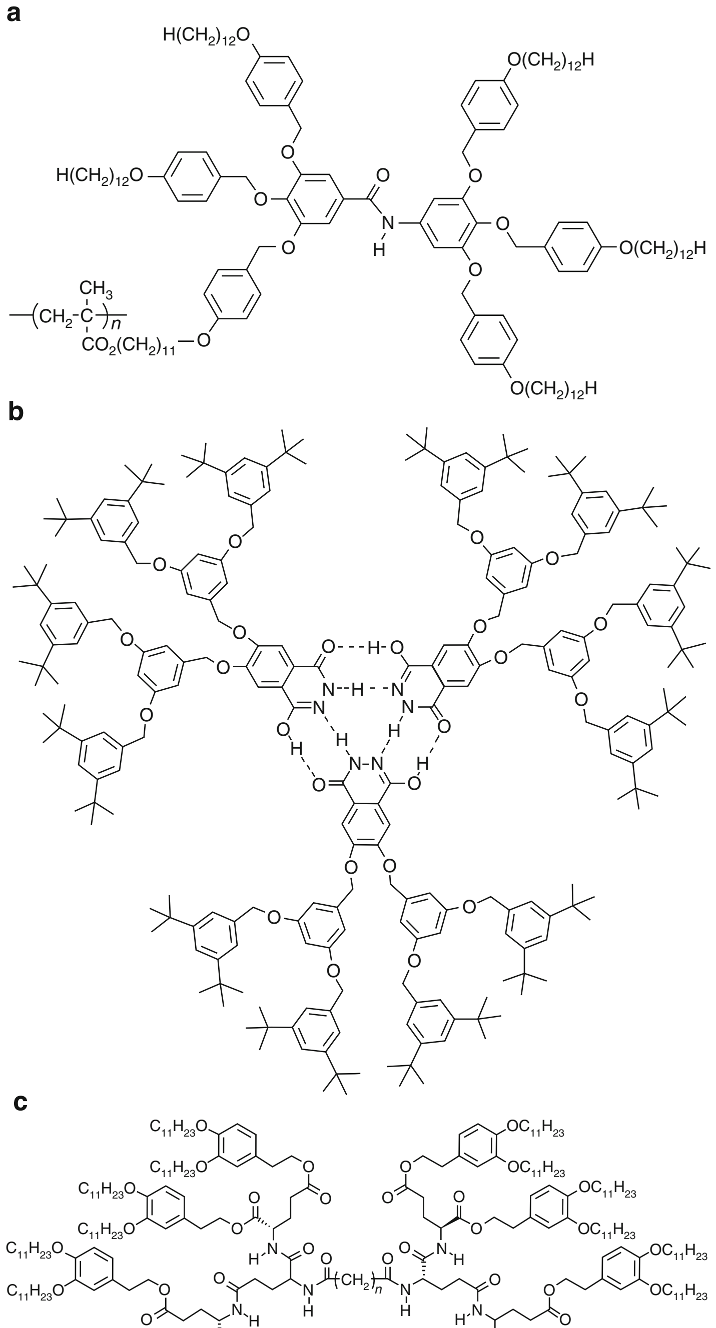
Fig. 6.5 Stilbenoid dendrons bearing long dodecyloxy chains at their periphery



	Y	X	Yield
3a	H	OCH_3	(29 %)
3b	CH_3	H	(28 %)
3c	H	H	(36 %)
3d	H	Br	(37 %)
3e	H	CN	(31 %)
3f	H	$CONH_2$	(27 %)
3g	H	CHO	(35 %)

interactions such as dipole–dipole led to monotropic disordered columnar hexagonal phases.

In another example of mixtures of two similar dendritic polymers Percec et al. (2003) studied the self assembly of two benzamide derivatives i.e., N-[3,4,5-Tris(4′-dodecyloxybenzyloxy)phenyl]-3,4,5-tris(4′-dodecyloxybenzyloxy) benzamide which forms a columnar hexagonal mesophase and its polymethacrylate (Fig. 6.6a) which presents a columnar nematic phase with short-range hexagonal order, in different ratios. Again intermolecular hydrogen bonds form between amide groups which reside in the core of both dendritic compounds. In this way supramolecular columns deriving from the coassembly of these two dendritic building blocks



1-3 (**1**: *n* = **3**; **2**: *n* = **4**; **3**: *n* = **10**)

Fig. 6.6 **(a)** N-[3,4,5-Tris(4′-dodecyloxybenzyloxy)phenyl]-3,4,5-tris(4′-dodecyloxybenzyloxy) benzamide polymethacrylate. **(b)** self-assembly of phthalhydrazides into trimeric disks through hydrogen bonding. **(c)** Dendritic peptides from glutamic acid monomers functionalized by undecyl benzalo lipophilic segments are bonded along their center with the polymethacrylic analog acting as a matrix (host) and the monomer as a guest to create novel liquid crystalline “superlattices”. Apart from the liquid crystalline phases observed for the pure compounds when polymethacrylate is present at high molar ratios a columnar hexagonal superlattice is formed which is replaced by simple-rectangular columnar superlattice, and a centered-rectangular columnar superlattice, at mixtures with about equimolar quantities. Replacement of N-[3,4,5-Tris(4′-dodecyloxybenzyloxy)phenyl]-3,4,5-tris (4′-dodecyloxybenzyloxy)benzamide by benzamide dendrons with alkyl chains of different lengths affords bisdendritic benzamides (Percec et al. 1999). Dodecyloxy benzamides coupled with benzamides with dissimilar but long alkyl tails with at least 6 up to 18 carbon atoms self-assemble in hexagonal columnar lattices. The respective N-methylated benzamides did not exhibit liquid crystalline phases demonstrating thus the crucial role of hydrogen bonding in the organization of these molecules at high temperatures.

Apart from the formation of column axes hydrogen bonds can also be employed for the achievement oligomeric disk like conformations. Taking advantage of the capability of phthalhydrazide to self-assemble through hydrogen bonding into trimeric disks in their lactim-lactam tautomerization Suárez et al. (1998, Fig. 6.6b) obtained columnar hexagonal and rectangular liquid crystalline phases from 6,7-Bis(alkyloxy)-2,3-dihydrophthalazine-1,4-diones with 8, 12 and 16 carbon atoms.

In a biomimetic approach Kamikawa et al. 2010 (Fig. 6.6c), prepared a series of dendritic peptides from glutamic acid monomers functionalized by undecyl benzalo lipophilic segments Thermally stable columnar rectangular (p2gg, c2mm) and hexagonal phases (p6mm) were obtained when all the peptide groups contributed to the formation of intra and intermolecular hydrogen bonds. In contrast when half of the glutamate moieties were in the dissociated state a dynamic equilibrium of hydrogen bonds was observed by IR spectroscopy and a less thermally stable columnar hexagonal phase was produced. Apart from the stabilization of the hexagonal and rectangular columnar structures the hydrogen bonds also play an important role to the transfer of the molecular chirality to the supramolecular structures via intermolecular interactions. Another similar example establishing the importance of hydrogen bonds in the formation of chiral supramolecular aggregates from chriral dendritic monomers based on peptides is the work of (Gao et al. 2011). Starting by perylene bisimides at the core they introduced peptides on its two ends functionalized by dodecyloxy branches. The resulting dendrimers presented ordered columnar mesophases even at room temperature. Optical activity was observed and was attributed to helical conformation of the columns due to the hydrogen bonds of the peptide groups at the periphery of the bisimides.

An exotic class of Janus-like (from the roman god of beginnings and transitions who was depicted as having two faces looking at the future and the past) diblock codendritic polymers which are formed by combination of two independent

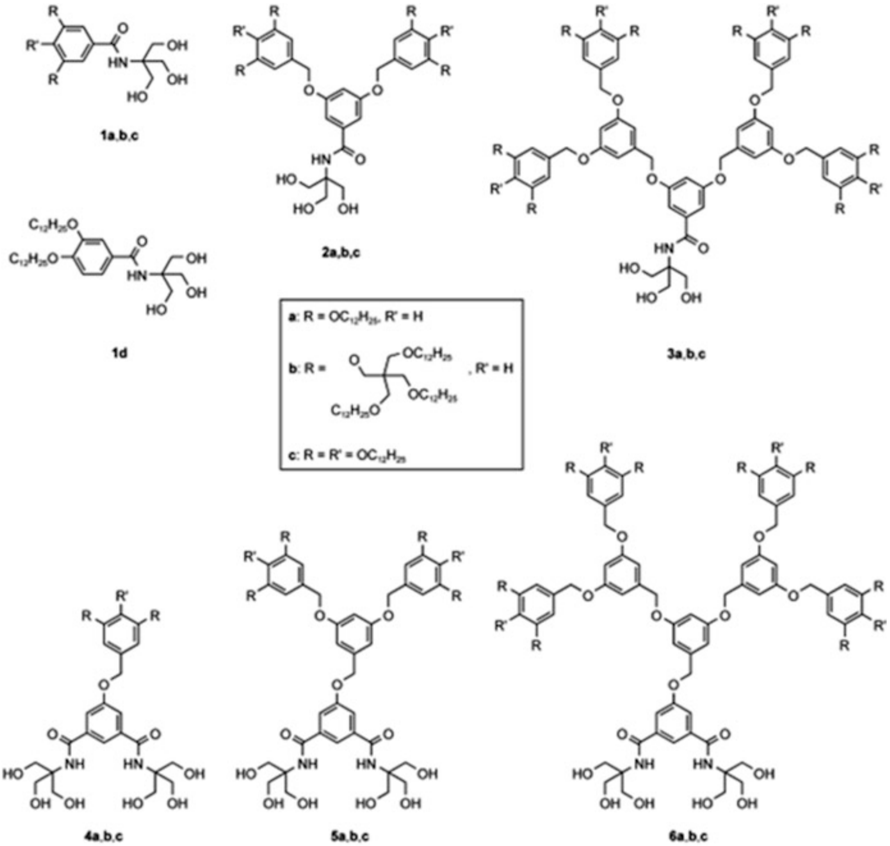


Fig. 6.7 Janus-like diblock codendritic polymers that present mesomorphism through hydrogen bonding interactions

dendrons of different chemical nature can also present mesomorphism through hydrogen bonding interactions. Guillon and his group synthesized three series of amphiphilic compounds containing two discrete segments one hydrophilic containing hydroxyl groups and the other hydrophobic, containing poly(benzyl ether) branches bearing linear or branched dodecyloxy chains by combining different generations of these two dendrons (Bury et al. 2006). The nature of the resulting liquid-crystalline phases was governed by the ability to form strong intermolecular hydrogen bonding network and the hydrophilic/hydrophobic balance. When a dense and interlocked hydrogen-bonding pattern of the hydroxyl groups is stereochemically favored dendritic copolymers self-assemble into Colh-p6mm phases with stable hydrogen bonded cores comprising the polar segments whereas when this is not possible Cub-*Imm and* Cub-*Pmn emerge* (Fig. 6.7).

6.4 Conclusion and Future Perspective

It is evident from all the examples presented that a wide variety of chiral or non-chiral liquid crystalline structures, such as lamellar smectic A, B and C, columnar hexagonal and rectangular and cubic can derive from dendritic polymers with functional groups capable of hydrogen bonding. These examples cover almost the entire range of mesophases observed for liquid crystalline monomers. Hydrogen bonding can induce or influence liquid crystallinity of dendrimers in three major ways.

1. By molecular assembly. A variety of structural units such as dendritic polymers, dendritic cores, dendrons and mesogens of specific shape and properties can be interconnected to form supremolecular complexes exhibiting liquid crystalline phases. As a general rule dendritic polymers of higher generations forming hydrogen bonds with calamitic mesogens and dendrons with calamitic branches hydrogen bonded with dendritic central cores present nematic and lamellar i.e., smectic phases whereas multiple hydrogen bonding, small rigid dendrons connected with a dendritic polyaromatic core and disk shaped mesogens favor columnar hexagonal mesophases.
2. By stabilizing the shape of the supramolecular complex by rigidifying certain parts, most frequently the central core. The development of hydrogen bonding network between functional groups such as ureas and amides allows to dendritic polymers that do not posses rigid calamitic or disk structural units to exhibit mesomorphism. This kind of hydrogen bonding interactions result mainly in the thermodynamic stabilization of the mesophase rendering for example monotropic mesophases (i.e., mesophases emerging only on cooling compounds from the melt) to enantiotropic or enhancing the thermal stability and the temperature range of the mesophases. Furthermore in the cases where, often in synergy with other factors, the extend of rigidification of the dendritic structures leads to the formation of disk shaped molecules interconnected through rigid axes, the organization of supramolecular assemblies is enhanced and nematic or lamellar mesophases are converted to columnar hexagonal or rectangular.
3. By defining of modifying the shape of dendritic monomers and supramolecular aggregates. Alterations of the hydrogen bonding network that take place either by supramolecular interactions, such as electrostatic interactions with dipoles or ions, interactions with appropriate polymeric matrices, and lipophilic π–π interactions of aromatic rings or long aliphatic chains either by external stimuli such as thermal treatment, pH, light, electric and magnetic field or mechanical. Usually this kind of interactions enhances the organization and the stability of the hydrogen bonding pattern which in turn leads to more organized mesophases. As a general result lamellar and cubic mesophases are transformed to columnar hexagonal. In addition though the same interactions the chirality of the dendritic monomers can be transferred to supramolecular aggregation by the formation helicoid columns.

Self-assembled amphiphilic dendritic polymers are considered to be model compounds for biological systems like liposomes vesicles or micelles. Hydrogen bonding, is a non-covalent and thus weaker selective, reversible and more flexible intermolecular interaction and it is considered as the most important driving force to the formation of these versatile supramolecular architectures. In addition, functional groups capable of multiple hydrogen bonding formation from complementary components such as DNA bases, or amino acids can be used for programmed generation of nanoscale architectures through molecular recognition. Understanding thus and control of the self assembly of such dendritic polymers via hydrogen bonding is of crucial importance not only for the research in the field of liquid crystals but also in many areas where supramolecular organizates are involved such as cell membranes and organic–inorganic nanohybrids. Functional materials for biological applications based on specifically designed dendritic molecules with tailor made hydrogen bonding patterns can be developed.

In another connection the weak and flexible nature of the hydrogen bonds renders the liquid crystalline dendritic polymers very interesting candidates for applications in materials science. Dynamic and complex properties are deriving since the dendrimers undergo structural changes as a result of external stimuli or in synergy with secondary supramolecular interactions. These compounds have possible applications in the areas of sensors, and displays.

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