Liquid crystalline dendrimers

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In recent years, there has been an increasing interest in the field of liquid crystalline dendrimers. Such a fast development is, among other things, driven by the multiple possibilities offered by combining the mesomorphic properties of single mesogenic subunits with the supermolecular and versatile architectures of dendrimers to yield a new class of highly functional materials. The induction and the control of the mesomorphic properties (phase type and stability) in dendrimers can be achieved by a dedicated molecular design which depends on the chemical nature and structure of both the functional groups and the dendritic matrix. In particular, the intrinsic connectivity of the dendrimer such as the multivalency of the focal core and the multiplicity of the branches, both controlling the geometrical rate of growth, or the dendritic generation, plays a crucial role and influences at various stages the subtle relationships between the supermolecular structure and the mesophase structure and stability. In this *critical review* article, an account of the various types of dendritic systems that form liquid-crystalline mesophases along with a description of the self-organization of representative case-study supermolecules into liquid crystalline mesophases will be discussed. Some basics of thermotropic liquid crystals and dendrimers will be given in the introduction. Then, in the following sections, selected examples including side-chain, main-chain, fullerodendrimers, shape-persistent dendrimers, supramolecular dendromesogens and metallodendrimers, as representative families of LC dendrimers, will be described. In the conclusion some further developments will be highlighted. This review will not cover liquid crystalline hyperbranched and dendronized polymers that might be considered as being somehow less structurally "perfect". (147 references.)

1. Introduction

1.1. Liquid crystals

The fluid liquid crystal (LC) state exists between the crystalline solid and the amorphous liquid.[1] In such a true discrete state of matter, molecules possess orientational and various degrees of translational/positional molecular orderings as in crystalline solids and the mechanical properties of liquids. The

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Bertrand Donnio

Bertrand Donnio was born in Bretagne (France) in 1967. He graduated from the University of Rennes (1991) and obtained his PhD from Sheffield University (1996) under the supervision of Professor D. W. Bruce. He moved to Neuchâtel (Institut de Chimie, Switzerland) in the group of Professor R. Deschenaux (1996–1997) and then to Freiburg (Institut für Makromolekulare Chemie, Germany) in the group of Professor H. Finkelmann (1997–1999) for two consecutive postdoctoral fellowships. Since 1999, he has been a fellow researcher of the CNRS. He is interested in the design and synthesis of functional self-assembling systems (metallomesogens and bent mesogens, liquid crystalline dendrimers, elastomers and dendronized organic–inorganic hybrids) and in the way they self-organise.

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combination of order and mobility results in the anisotropy of the physical properties, which have led to their widespread applications that have impacted on society in a major way. This is a multidisciplinary field of research, evidenced by the pervasive nature of LC science, constantly expanding and challenging with new applications, new molecular architectures design and new phase types discovery.

The LC state is generated as a function of temperature (*thermotropic*) *i.e.* when a compound passes between the crystal, LC and liquid states by a progressive loss of order on heating, or by a solvent (*lyotropic*) *i.e.* when the phase transitions are driven by the concentration of a LC in a solvent; *amphotropic* applies when mesomorphism is induced independently by both methods.[2,3] Only thermotropic low molar mass LCs will be considered here, and before proceeding further, some of the specific terminology currently used will be introduced. A material which has LC properties is referred to as a *mesogen* and is said to exhibit *mesomorphism*; although something which is *mesogenic*, is not necessarily *mesomorphic*. *Enantiotropic* mesophases are found in a reversible temperature phase-sequence, whilst *monotropic* mesophases may only appear on cooling (metastable phases).

A classification of the various mesophases based on the order and symmetry of the different molecular arrangements was suggested as early as 1922 by Friedel in a seminal report, '*Les états mésomorphes de la matière*'.[4] Conversely, LC structures may also be described on the basis of the shape of the mesogens that form the mesophases, as several types of molecules can induce mesomorphism. These two features, *i.e.* molecular shape anisometry and phase symmetry, not always specific to each other, are however inextricably linked,[5,6] and an interplay of both descriptions is not only more judicious but is indispensable.

Thermotropic LC mesophases are formed by molecules endowed with specific structural molecular criteria. Usually, a mesogen has a dichotomous molecular structure composed of at least two portions of contrasting structural and/or chemical character (*i.e. amphipathic* molecule), *e.g.* a rigid anisotropic moiety equipped with peripheral flexible segments. The amphipathic character is at the origin of the multiple step melting process[7] and it is believed that phase formation results from a phase separation process.[8] Thermotropic phases are stabilized by intermolecular interactions (dipolar, electrostatic, hydrogen bonding, van der Waals), anisotropic dispersion forces that result from the anisometry of the molecules and repulsive forces that result from its amphipathic character.[8] The rod-like (*calamitic*) and the disc-like (*discotic*) are the two most common anisotropic shapes used for LC phase formation.[1] A rod-like mesogen is much longer than it is broad and hence, possesses one unique, long axis (Fig. 1**a**). In contrast, a discogen is rather flat and hence possesses one, unique short axis (Fig. 1**e**). The rigid part consists in the specific arrangements of phenyl and/or heterocyclic (rigid or flexible) rings, fused or linked together through σ, double, triple bonds, or other functional linkers such as –COO–, –N=CH–, –N=N–, *etc.*, whereas the flexible moieties, often hydrocarbon chains but not systematically, are connected at one or several extremities of the rigid part.[1] Additionally, dipoles *e.g.* F, CN, NH_2, NO_2 can be incorporated within the anisometric

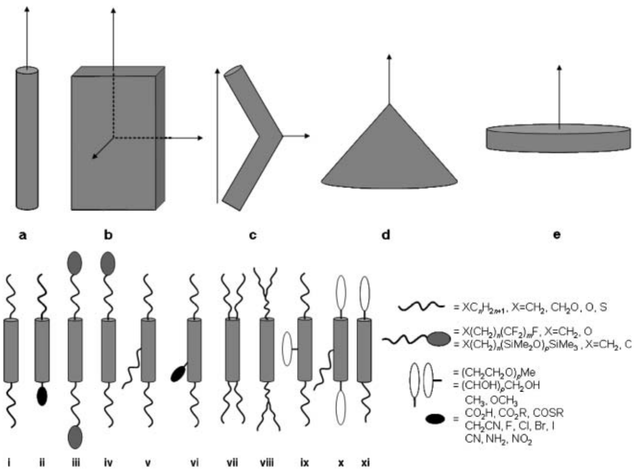

Fig. 1 Sketches of the main molecular anisotropies found in LC materials (+ symmetry axes): **a**: calamitic, **b**: sanidic, **c**: bent-core, **d**: bowlic, **e**: discotic motifs. Examples of derivatization of rod-like LC materials: **i**–**iv** (with terminal aliphatic chains, polar groups, segmented chains), **v**–**vi** (with laterally attached groups), **vii** (polycatenar), **viii** (swallow-tailed), **ix**–**x** (polyphilic ABC triblock molecules).

Izabela Bury

Izabela Bury graduated with a Master Degree of Chemistry at the University of Wroclaw (Poland) in 1996. She received her PhD, entitled "Design and synthesis of segmented 'Janus-type' dendrimers. Study of their supramolecular organization", in 2004 from the University Louis Pasteur (Strasbourg) under the supervision of Bertrand Donnio and Daniel Guillon. After a one-year postdoctoral fellowship at Rolic LTD in Basel, she joined the Rolic Research Group as a permanent researcher in 2006.

Daniel Guillon

Daniel Guillon received his PhD degree in Chemical Physics in 1976 from the Louis Pasteur University (Strasbourg). He has been director of research in CNRS, deputy director of the IPCMS since 2002. His main interests include the description at the molecular level of the mesomorphic structures exhibited by low molecular weight and polymer materials, the study of self-organisation processes in supramolecular chemistry, the bottom-up approach of organic and hybrid nanomaterials, and the structure of thin organic films. Since 2004 he has also been Vice-President of the International Liquid Crystal Society.

part to subtly modify some physical properties.[9] The need to control further macroscopic structures led to the exploration of mesogens with different shapes that bridge the gap between rods and discs. Following similar basic rules of construction, novel systems include sanidic mesogens (lath-like structure),[6] bent-core[10,11] and bowlic[12] LCs (polar mesogenic cores with reduced symmetry), polycatenars (LCs bearing more than two peripheral chains),[13] polyphilic block molecules (small ABC-like block molecules)[14,15] (Fig. 1), and dimers (and trimers).[16] Mixed oligomers combining rods with discs and/or bananas have also been prepared to form multicomponent molecules.[6] The design of amphotropic systems, such as carbohydrates[17] and amphiphiles,[3] metallomesogens[18] and supramolecular hydrogen-bonded LCs,[19] is rather specific to these materials.

1.1.1. The nematic phases. The nematic phase (N) has the simplest structure of all of the mesophases, and is characterized by one-dimensional orientational order of the molecules by virtue of correlations of the principal molecular axis, although this orientational order is not polar (Fig. 2), and molecules are free to flip.[1]

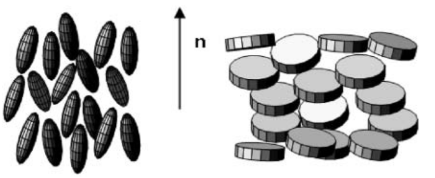

Fig. 2 Schematic representations of the molecular arrangement in the nematic phases (left: N from calamitics, right: N_D from discotics; **n** is the nematic director.)

This very fluid phase is commonly observed within calamitic LCs (Fig. 1: **i**, **ii**, **v**–**viii**), whilst remaining elusive in discotic materials (N_D).[20] As for the biaxial nematic phase (N_b),[21] claimed in sanidics, bananas, and mixed oligomers, it is believed to result from the hindered rotation around the main molecular axis on the macroscopic scale.

1.1.2. The smectic phases. The true smectic phases, formed principally by calamitic mesogens, consist of the superposition of equidistant molecular layers, and are characterized along orientational correlations of the principal axis, by partial translational ordering of the molecules within layers, but with no in-plane long-range positional order.[22] The simplest smectic phase is the smectic A phase (SmA), in which the long molecular axes are oriented on average in the same direction and parallel to the layer normal but with the molecules loosely associated into the layers (Fig. 3). If the molecular director is tilted with respect to the layer normal, then the SmC phase is obtained (correlation of the tilt). Hexatic smectic phases result from increasing the in-plane (short-range) positional and long-range bond orientational orders. In the SmB phase, the molecules sit at the nodes of a 2D hexagonal lattice. Two tilted variations of the SmB exist (Fig. 3): the SmI phase (the mesogens are tilted towards a *vertex* of the hexagonal net) and the SmF phase (the mesogens are tilted towards the *edge* of the hexagonal net).

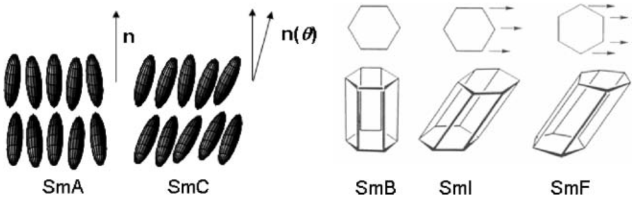

Fig. 3 Sketches of the SmA, SmC, SmB, SmI and SmF phases (ellipsoids represent the rod mesogens).

For hexatic phases, the rotation about the molecular long axes is concerted. In all cases, diffusion between the layers occurs readily and the phases are fluid. The soft crystalline smectic phases are derived from the true smectics, and characterized by the appearance of inter-layer correlations and, in some cases, by the loss of molecular rotational freedom. Thus, the B, G and J phases are SmB, SmF and SmI phases respectively with inter-layer correlations, while the E, H and K phases are B, G and J phases which have lost rotational freedom. These phases possess considerable disorder and are therefore properly intermediate between both crystal and liquid states. Smectic phases are also exhibited by sanidic[6] and bent-shape[10,11] molecules. For sanidics, the lath shape of the molecules restrict the rotation around the main axis to such an extent that smectic phases with a local biaxiality built up by parallel aligned lath molecules may form. The molecules can be non-tilted (SmA_b), or tilted with respect the layer normal (SmC_D, SmC_T).[6] As for bent-shape (achiral) systems,[10,11] they self-organize into a variety of smectic-like modifications, which are very different from the true smectic phases, since various polar orderings within the lamellae *e.g.* ferro-, ferri, and antiferroelectric, usually observed in chiral compounds, may be obtained. The origin of this polar order and macroscopic chirality is attributed to symmetry-breaking instabilities imposed by the polar-controlled packing, the tilt of the mesogens, and the steric constraints of the intrinsic bent shape.

1.1.3. The columnar phases. Columnar phases result from the stacking of disk-like (and bowlic) molecules into columns, which are packed parallel into 2D ordered lattices.[1,20,23] They are characterized by the symmetry of this arrangement, and hexagonal (Col_h), rectangular (Col_r), oblique (Col_o) or square (Col_s) columnar phases are formed (Fig. 4). Diffusion between and within the columns occurs readily and the phases are fluid. They are also exhibited by many non-discotic molecules such as polycatenar,[13] polyphilic,[14,15] and bent-shape mesogens[10,11] (polar columnar phases), with different processes of self-organization (stacking of molecular aggregates composed of 3 up to 6 molecules) driven by intermolecular microsegregation. The columnar-nematic phase, N_{Col}, only possesses an orientational ordering of cylindrical molecular aggregates (loss of 2D lattice).[8] As for the lamello-columnar phases, L_{Col} or Col_L, they result from the confinement of supramolecular columns within smectic layers, with or without interlayer correlations (2D lattice). The latter phases are often observed with sanidic and polyphilic molecules[14] or with oligomers combining rods and discs.[6]

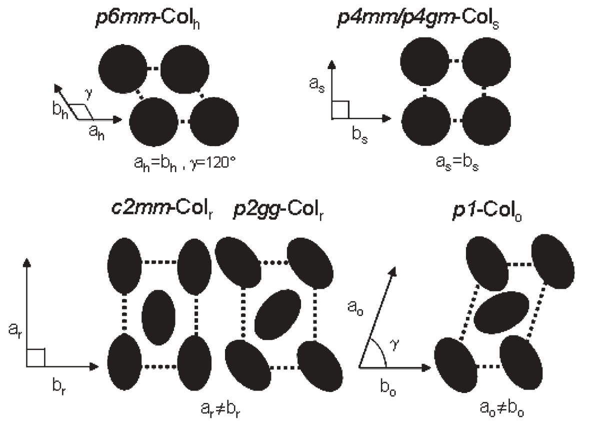

Fig. 4 The various 2D lattices found in LC columnar phases. The circles and ellipses represent the cross-sections of the columns with respect to the plane of symmetry.

1.1.4. The chiral mesophases. Chiral modifications of N and smectic phases also exist for calamitic mesogens *e.g.* N*, SmC*, SmI* and SmF* either in a pure enantiomer or with a non-chiral compound doped with a small amount of chiral additive.[24,25] Due to the packing constraints imposed by the materials being chiral, the director is forced to precess through the phase, describing a helix. Because of the low symmetry in the chiral smectic phases, the molecular dipoles align within the layers that are then ferroelectric. Chirality gives rise to a wide variety of other chiral frustrated supramolecular structures such as the twist grain boundaries phases (TGB)[26] and the blue phases (BP).[27] TGBs have an helical superstructure in which local smectic-like (A, C, C* types) blocks have their layer normals rotated to each other in a helicoidal fashion and separated by screw dislocations. BPs consist of the 3D arrangement of double-twisted columns in cubic symmetry. Ferroelectric columnar phases have been induced in discotic systems bearing chiral chains,[1] and in bent-shapes and bowlic mesogens.[10–12]

1.1.5. The other mesophases. There exist additional "exotic" mesophases, which are less commonly observed: the micellar cubic phases (Cub$_I$), which consist of ordered 3D arrays of micelles,[8,14] found with amphiphiles, the bicontinuous cubic phases (Cub$_V$) which is made of infinite, periodic, 3D molecular networks,[28,29] found for some classical rodlike mesogens or polycatenars, and the M$_{Tet}$ phase, a micellar organization with a tetragonal 3D symmetry found with rod-coil block molecules.[15] The laminated phases type (Lam) recently recognized in sanidics and polyphiles is a subgroup of smectic phases. They consist of sheets in which the aromatic cores lie parallel to the layer planes, separated from each other by lipophilic sublayers; various modifications are possible (Lam$_I$, Lam$_N$, Lam$_{Sm}$).[14]

1.2. Dendrimers

The word dendrimer comes from the Greek *dendros* meaning tree and *meros* meaning part.[30] Such an arborescent structure is one of the most pervasive, prolific, and influential natural patterns that can be observed on earth at all dimension length scales (from nm to km) at once in the inert, the virus and the living worlds. This hyperbranched architecture has reached an unrivalled level of perfection and provides maximum interfaces for efficient contacts and interactions, as well as for optimum information collection, transport and distribution. The elaboration and the synthesis of such aesthetically-challenging architectures have been driven by the need to mimic the macroscopic natural branching networks and to convey their functions at the molecular level.[31,32] These compartmentalized and hierarchical artificial supermolecules possess a regular and controlled three-dimensional branched topology, the result of sophisticated genealogical directed syntheses. Their construction is based on controlled and sequential reiterative synthetic elementary steps which are reproduced at each new generation (convergent or divergent directed sequential construction): at each new cycle, the molecule is incremented by an additional generation.[30] Their ultimate molecular architecture can be finely tuned by the intrinsic "dendritic connectivity" *i.e.* multiplicity of the core (N_C), degree of branching (N_B), number of junctions (J) and generations (G). This leads to hyperfunctionalized systems with a large number of peripheral groups (Z) per volume unit, which increases geometrically as $Z = N_C N_B{}^G$. Note that this starburst growth is not infinite for steric reasons (congestion effect) and, as a consequence, beyond a certain generation, the degree of branching and arborescence, defined by J, are no longer regular:[30] the creation of defects is accelerated and occurs at lower generation when the degree of branching (N_B) is high, since J increases exponentially with N_B and G according to $J = N_C[(N_B{}^G - 1)/(N_B - 1)]$.

2. Liquid-crystalline dendrimers

Molecular engineering of liquid crystals is an important issue for controlling the self-assembling ability and the self-organizing process of single moieties into periodically ordered meso- and nanostructures.[1] Moreover, ordered supramolecular assemblies can considerably enhance the functions of the single molecules.[33] Dendrimers and dendrons proved particularly versatile candidates as novel and original scaffoldings for the elaboration of new LC materials.[34,35] In particular, the dendritic structure is an interesting framework where mesomorphism can be modulated by very subtle modifications of the dendritic connectivity. LC dendrimers are now representative of an important class of mesogens where new types of mesophases and original morphologies may be discovered.[14,35]

2.1. Side-chain liquid-crystalline dendrimers

The most commonly studied LC dendrimers are the so-called side-group (terminology used by analogy to side-chain liquid crystal polymers). Their overall structure generally consists of mesogenic or pro-mesogenic promoters attached to the termini of the branches of the flexible dendritic network; these units may be laterally (side-on) or terminally (end-on) attached (Fig. 5). Induction and stabilization of mesophases result from both the anisotropic interactions winning over the tendency of the dendritic core to adopt a globular isotropic conformation, and microphase separation due to the chemical and structural incompatibilities between the flexible dendritic core and the

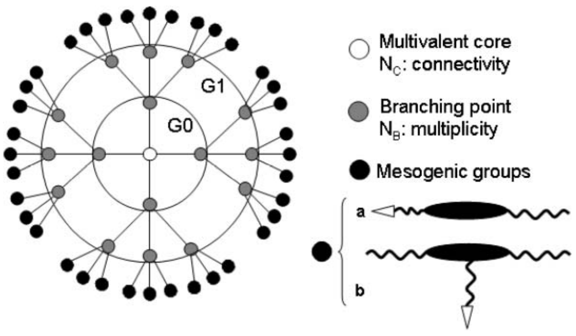

Fig. 5 Schematic 2D representation of a side-chain dendrimer (N_C = 4, N_B = 3, G = 1). The mesogen is terminally (**a**) or laterally (**b**) connected.

terminal groups. The type of mesogen and its topology of attachment to the dendritic core (Fig. 5) as well as the dendritic chemical nature and connectivity therefore strongly determine the mesomorphic properties of the entire supermolecule.

2.1.1. Silicon-containing LC dendrimers. The most studied systems are the silicon-containing dendrimers, which, 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. The carbosilane type represents the most important class of silicon-containing dendrimers essentially due to their excellent chemical and thermal stability, versatility of the core connectivity due to a rich Si–C chemistry and high flexibility.

The most complete study on silicon-containing LC dendrimers was carried out by Shibaev.[34,35] The dendritic motif is based on a tetravalent core (N_C = 4) coupled to a binary branching multiplicity (N_B = 2) (Fig. 6). The effect of the nature of the mesogen and the generation of the dendrimer has been systematically analyzed. Thus, dendrimers from the first to the fourth generation, functionalized by calamitic units (cyanobiphenyl,[36] methoxyphenylbenzoate,[37] or anisic acid derived[38] mesogens, Fig. 6), exhibit solely SmA and SmC phases between room temperature and *ca.* 90 °C, losing the N phase of the precursory mesomorphic monomers. The smectic phases stability and order was increased upon "dendrimerization" as a result of enhanced microphase separation between the mesogenic units and the flexible dendritic Si-containing skeleton. The quasi invariance of the layer periodicity with generation (*ca.* 4–6 nm) implies that the dendritic core is in a pronounced distorted conformation, with a 2D expansion in a plane parallel to the smectic layers. The model proposed is based on the cylindrical conformation of the dendrimer with strong segregation of the constitutive parts and consists of the parallel arrangement of the mesogens with one half extending on one side and the other half on the other side of the dendritic matrix forming mesogenic sublayers (see Fig. 9), in agreement with the cross-sectional area of each portion.

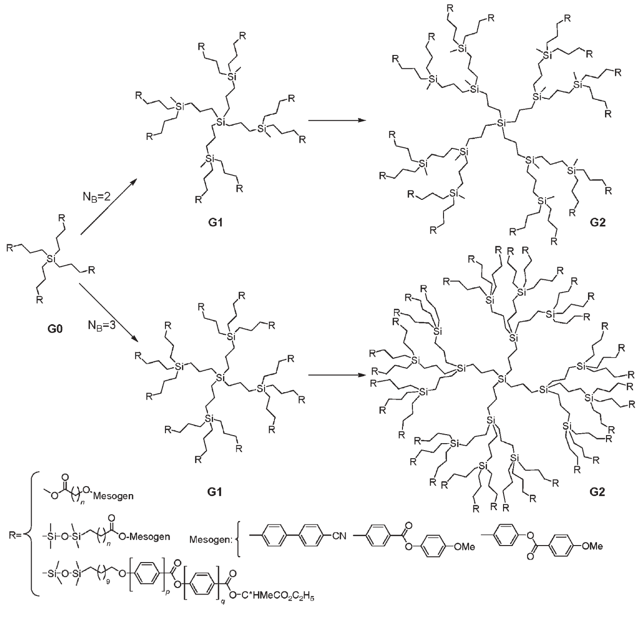

Fig. 6 Structure of R-functionalized carbosilane dendrimers (G0, G1, G2) with two different connectivity (N_B = 2 or 3), and the various mesogenic groups used. The higher generations (G3, G4 and G5) have not been reproduced.

As for the higher generation G5 compounds,[37,39] they self-organize into supramolecular columnar mesostructures.[40] Above the SmA phase, a $\mathrm{Col_r}$ phase is first formed, and on further heating, a $\mathrm{Col_h}$ phase. The explanation of this behaviour given by the authors is based on a drastic change of the supermolecular shape with the temperature: as it increases, the bulky carbosilane dendrimer continues its expansion in the third direction leading to the curvature of the mesogen/dendrimer interface as the mesogens must compensate the increase of the cross-sectional area of the core. Further increase of the temperature leads to a more cylindrical shape resulting in the layer breaking into columns. For both $\mathrm{Col_r}$ and $\mathrm{Col_h}$ phases, the silane dendrimer is embedded by a rigid shell formed by the mesogenic groups disposed radially. This study is a nice example of mesophase cross-over which results from a competition between the strengthening of the cooperative interactions of the increasing number of terminal mesogenic groups, and the decrease of the enthalpy due to a strong deformation of the core.

The grafting of chiral ethyl-L-lactate-containing mesogenic groups (Fig. 6, with p/q = 2/1;1/2;1/1) led to ferroelectric dendrimers showing a SmC* phase, and a SmA phase for the most stable materials (p/q = 2/1).[41,42] The spontaneous polarization, P_s, measured at elevated temperature because of the high viscosity of the materials, showed values around 140 nC cm^{-2}. The increase in G led to a decrease in the P_s value and to an increase in the switching time. The analogous G4 and G5 dendrimers exhibit a single $\mathrm{Col_r}$ mesophase.[43]

Recently, a G2 carbosilane dendrimer functionalized by a bent-core unit was reported to exhibit a new polar phase, known as dark phase, which consists of a layered structure made of coexisting antiferro and ferroelectric clusters.[44]

To explore further the versatility offered by these carbosilanes, a photosensitive G1 dendrimer bearing azobenzene terminal groups (and showing a SmA phase) was studied with the aim of producing optical devices suitable for optical data storage.[45] It was shown that the *E*/*Z* photo-isomerisation of the azobenzene groups proceeds both in solution and in film under UV irradiation, and is photochemically and thermally reversible. In addition, UV irradiation destroys the SmA phase and gives rise to a transition to the isotropic liquid, due to the low anisometry of the *Z*-isomer. When 4-methoxycinnamoyl groups are attached instead, *E*/*Z* photo-isomerisation is also induced under UV radiation[46] in the SmA state, along photo-cycloaddition leading to the formation of a 3D polymeric network. These processes lead to a disordering effect and to an isothermal photo-induced SmA-to-I phase transition.

Highly functionalized carbosilane dendrimers (N_B = 3, Fig. 6) bearing pendant cholesteryl[47] or cyanobiphenyl groups[48] were also reported. G1 and G2 self-organize into smectic phases, whereas G3 is devoid of mesomorphism. This is likely due to the rapid densification of the dendritic frame leading to "compacted" molecules (elevated *J* value) restricting the deformation of the "pseudo-rigid" dendrimer (the number of peripheral groups, *Z*, varies from 36 to 108 from G2 to G3). A smectic-to-Col_h mesophases cross-over from G2 to G3 dendrimers was observed after the peripheral grafting of single perfluorinated alkyl chains,[49] showing that the rather bulky chains are, unlike the mesogens, able to compensate the great distortion of the dendritic core.

Thus, the direct grafting of peripheral groups (essentially mesomorphic) onto the Si-containing dendritic matrix was found to be a successful strategy to produce a wide range of novel materials whose properties can be tuned by the monomeric units and the connectivity of the dendrimer.

Siloxane-containing LC dendrimers are not as common,[34,35] and the mostly used dendritic framework initiator is the polyhedral octa(dimethylsiloxy)octasilsesquioxane core. Such a cage-like molecule provides eight radial primary branches ready for derivatization right at the G0 level. End-on functionalization by calamitic units essentially leads to broad SmA (and SmC) phase, directly at the ambient, whilst side-on grafting leads to N (or N*) phase.[35] Hexadecamer G1 homologues (Fig. 7) were obtained by grafting mesogenic groups onto the prefunctionalized G1 cage. As expected, SmC and SmA phases are seen for the G1 cyanobiphenyl end-on derivatives.[50] In contrast, changing the nature of the terminal mesogen (more anisometric and chiral) or its topology of attachment modifies drastically the behaviour: the formation of a SmC* is favoured for the end-on[51] compound, whilst Col_r and Col_h phases are formed for the side-on[52] isomer. In both cases, a small temperature range N* phase was also detected. To explain this behaviour, the decoupling of the mesogens and the siloxane-cage, thus acting independently, the cuboid core being surrounded by loosely packed mesogens, was proposed. For the columnar mesophases, the silsesquioxane core assists in the formation of the hexagonal and rectangular disordered structures, presumably through a good segregation between the siloxane core and the mesogenic units into distinct columns, enhanced by a high N_C and the important number of lateral groups.

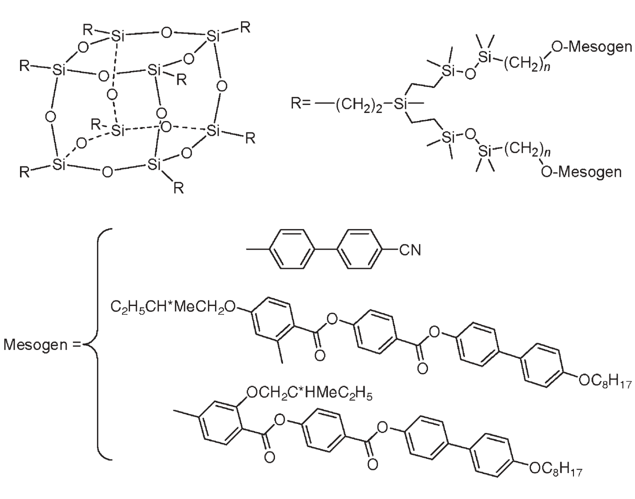

Fig. 7 Chemical structure of the mesomorphic LC silsesquioxanes.

As for the carbosilazane dendrimers (N_C = 3, N_B = 2), two series (G0–G2) with laterally attached mesogenic units were reported. Depending on the mesogenic unit, these dendrimers exhibit a single room temperature N phase[53] or a N–SmC and a N–Col dimorphism on increasing generation.[54]

Thus, the "side-on" attachment of mesogenic groups appears to be an excellent strategy to induce pure N systems, although, due to the strong tendency of the core to phase separate as the generation increases, the strongly segregated smectic and columnar supramolecular organizations were inescapably formed.

2.1.2. Polyamidoamine (PAMAM) and polypropyleneimine (PPI) LC dendrimers. The principal motif of these systems is based on a tetravalent core and a binary branching point (Fig. 8). In a pioneering work, Meijer *et al.*[55] described PPI dendrimers functionalized with cyanobiphenyl end-groups. All the dendrimers showed a SmA phase. In another pioneering work, Lattermann *et al.*[56] derivatized PPI dendrimers with the non-mesogenic 3,4-bis(decyloxy)benzoate groups. Induction of a Col_h phase was systematically observed from G0 to G4. A more thorough systematic study on both PPI and PAMAM side-chain LC dendrimers was carried out by Serrano *et al.*[57] As expected, dendrimers functionalized by anisotropic units bearing one terminal alkoxy chain (Fig. 8, R = L_1) led to the formation of smectic phases,[58] whilst the same dendritic matrices functionalized with mesogenic units bearing two or three terminal alkoxy chains (Fig. 8, R = L_2,L_3) exhibit solely a Col_h phase.[59,60]

As previously observed with carbosilane and PPI dendrimers, the phase parameters (*i.e.* layer periodicity and columnar diameter) do not vary significantly with the generation number (5 to 7 nm) suggesting a 1D (Col_h) or 2D (Sm) dendritic core deformation. Hence, the smectic organization resembles that described for silicon-containing LC dendrimers (Fig. 9) and is driven by both intramolecular segregation and lateral interactions between the mesogens; since the polyamine matrices are not as bulky as the carbosilane one, the formation of columnar phase is not favoured, at least not up to the fourth generation. However, for the series exhibiting the Col_h phase, the mesogens cannot be arranged parallel as in the rod model (smectic) since the cross-sectional area of the terminal chains is larger than the area occupied by the mesogenic units. The dendritic core is thus forced to deform anisotropically in one main direction, corresponding to that of the columnar axis, allowing the mesogenic groups to be radially distributed with uniform interfaces. With such a conformation, the dendrimers self-assemble into supramolecular discs or columns which

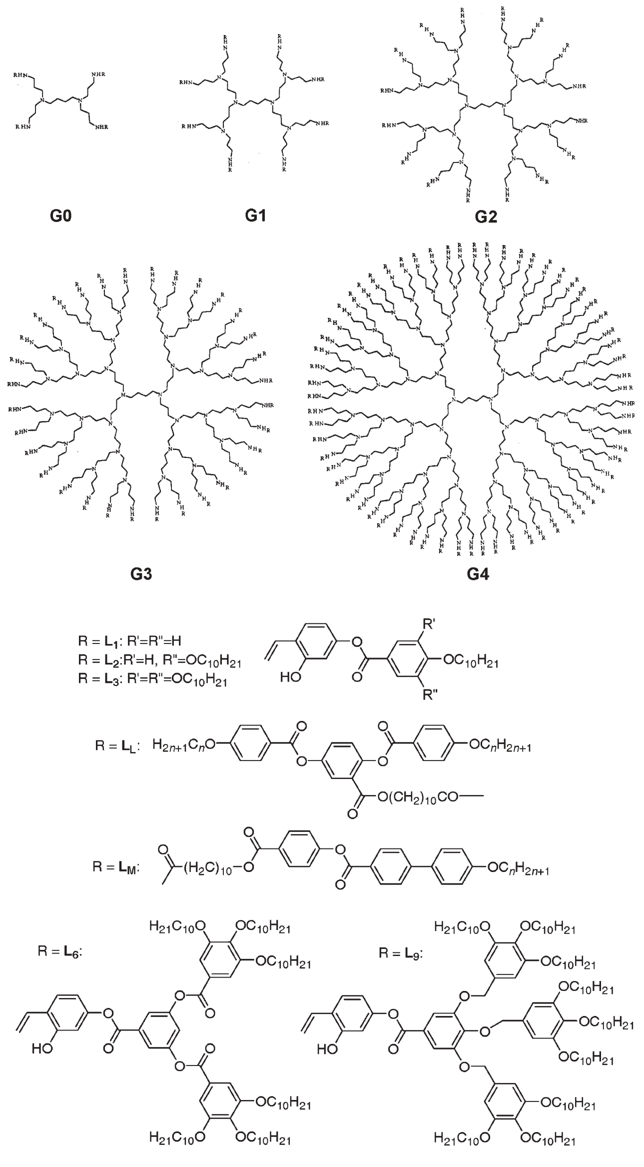

Fig. 8 Structures of the G0 to G4 PPI dendrimers and peripheral mesogens - R. PAMAM are structurally related, but between two junctions, the three CH_2 groups are replaced by a $(CH_2)_2$–CONH–$(CH_2)_2$ segment, and between the two central N, there are two CH_2 groups.

further self-organize into a hexagonal net (Fig. 9). Note that mesophases obtained by PAMAM-based LCs, and this was systematically observed, are thermodynamically more stable than those induced in PPI dendrimers. This is due to the presence of amide linkers in the PAMAM arborescence and, consequent to intra- and intermolecular hydrogen-bonds interactions, to some partial rigidifying of the structures.

Thus, either SmA and SmC or Col_h phases were obtained by such a molecular design, the structure of which is determined by the lateral (pro)mesogenic units nature. Mixing both types of mesogenic units (Fig. 8, $R = (1 - x)L_1 + xL_2$, x in mol%) within the same dendritic core (random codendrimers) revealed that, for intermediate compositions, SmC and Col_r phases are formed between the SmA and the Col_h phases of the two homodendrimers, respectively.[61] Codendrimers with a small content of the biforked comonomer (L_2) exhibit a SmC phase below the SmA phase, a consequence of the slight increase of the chain area with respect to that of the rigid part. Increasing further its contents favours the occurrence of the Col_r phase. As the number of terminal chains increases, the mesogen/chain interface is curved and the accommodation of the molecules within the cylindrical rod-like structure becomes unlikely (layer undulations), the layers break into columns. In another study, grafting bulkier units (Fig. 8, $R = L_3, L_6, L_9$) at the periphery of PAMAM and PPI did not lead to the ultimate spherical deformation of the dendritic matrix[62] and all the dendrimers showed a Col_h mesophase. A model of organization implies an elongated cylindrical molecular object, whose inner part is occupied by the dendritic core and the outer part by the bulky mesogenic units. This is possible due to the great flexibility (conformational freedom) of the PAMAM and PPI skeletons and also because the functionalization is not complete for steric constraints. Thus, the molecular model of thick disks proposed for the dendrimers with the L_2 mesogenic unit is transformed into a model consisting of a long cylinder, which is the result of the axial elongation of the oblate structure caused by the extended conformation adopted by the dendritic core in order to accommodate the bulky units all around. Columnar phases (Col_r and Col_h) were also obtained with PPI dendrimers bearing discotic triphenylene mesogenic units.[63] In these cases, sublattices were revealed by X-ray diffraction indicating segregation of the triphenylene units and dendrimers into separate columns.

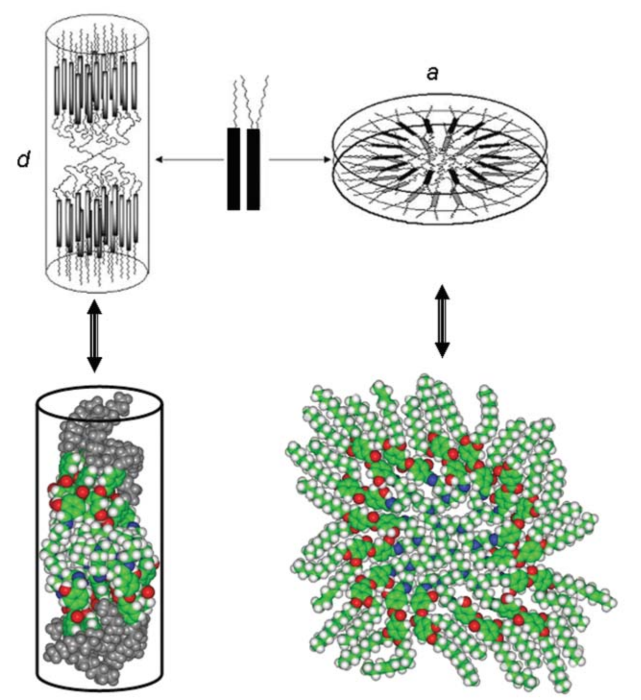

Fig. 9 Relationships between dendritic core deformation and mesogen for side-chain LC dendrimers (d: layer spacing, a: intercolumnar distance). Molecular dynamics of G3 PPI with $R = L_1$ and $R = L_2$ (see Fig. 8).

Dendritic nematogens were achieved in side-on and end-on dendrimers (providing L_1-type mesogens with short alkoxy chains)[64] or in codendrimers containing various proportions of laterally and terminally attached mesogenic units (Fig. 8, R = $(1 - x)L_L + xL_M$).[65] In these cases, the side-by-side molecular arrangement and the intramolecular segregation are not effective to promote the formation of smectic phases, but still sufficient to stabilize the N ordering. Decreasing the proportion of the side-on mesogens with respect to the end-on one contributes rapidly to the suppression of the N phase at the expense of the SmA and SmC phases.

In order to incorporate ferroelectric properties, PPI codendrimers bearing chiral and achiral end-on mesogens were also investigated (Fig. 8, R = $(1 - x)L_1 + xL_1{}^*$)[66] mimicking the situation occurring in classical mixtures of low molecular weight liquid crystals using chiral dopants. Small quantities of chiral mesogen favour the formation of the SmC* phase (and SmA); the pure chiral systems are not mesomorphic. Ferroelectric behaviour revealed to be very poor: switching was detected only in the small dendrimers (G0 and G1) and in codendrimers bearing a small number of chiral mesogenic units. Similarly, mixed end-on/side-on PPI codendrimers in various proportions (Fig. 8, R = $(1 - x)L_M + xL_M{}^*$) show a modulated SmC (or SmA), and a N* phases for high contents of side-on groups, a SmC* phase at intermediate composition, and a single SmA phase at high contents of end-on groups.[65]

Dendrimers bearing bent-core molecules at the periphery were also reported.[67] They exhibit a $\mathrm{Col_r}$ or a smectic-like phase with a relatively high viscosity, unfavourable for detailed investigation of the physical properties. No switching and thus ferroelectric behaviour could be observed for any of the dendrimers.

The large number of amino groups present at the periphery of PPI and PAMAM dendrimers appeared beneficial to generate ionic covalent and non-covalent materials. These studies were also motivated by the simple and rapid manner to generate a wide range of self-organized mesostructures. A first report concerned the straight protonation of non-mesomorphic terminally alkylated PPI G4 and G5 dendrimers by HBr. As a result, a bicontinuous thermotropic cubic phase, rarely observed in LCs, was induced.[68] The proposed structure consists of 24 nearly spherical, multicationic dendrimeric entities located in the axes constituting the skeletal graph of the gyroid, while the aliphatic chains are located on each side of the minimal surface.

Supramolecular ionic dendritic complexes were obtained by proton-transfer reaction of alkanoic acids to the primary amino groups of G0 to G5 of PAMAM and PPI dendrimers.[69–71] Most dendrimers (G0–G4) with a 1 : 1 molar ratio show lamellar phases. However, increasing the generation of PPI (G5) or the alkanoic acid content led to a change of mesomorphism from a SmA phase to a $\mathrm{Col_h}$ or a $\mathrm{Col_s}$ phase; the stability of the phases also depends on the chain length of the acids. Here, ionic interactions clearly play a key role in the formation of these thermotropic phases (no rigid mesogenic parts). The supramolecular organizations resemble those of lyotropic phases, the dendritic matrix playing the role of the polar solvent. Related ionic LC dendrimers formed with 4-decyloxy-, 3,4-didecyloxy-, and 3,4,5-tridecyloxybenzoic acids also form mesophases, a SmA phase for the first two series, $\mathrm{Col_r}$ and $\mathrm{Col_h}$ phases for the latter one. SmC* and SmA phases were induced by the protonation of PPI dendrimers with a cholesteryl-based carboxylic acid.[72]

G0 to G4 amphiphilic PPI dendrimers with facial amphiphilic carboxylic acids were also prepared. These acids are composed of three incompatible portions: a rigid terphenylic core, two terminal alkyl chains, and a lateral polar polyether segment and all form a SmA phase (Fig. 10, $n = 1$–4). Some of these original ionic dendrimers show a sequence with unconventional liquid crystalline phases, depending on the dendritic generation, the length of the polyether segments, the temperature and the molar ratio.[73] A single SmA phase is formed for materials with a short amphiphilic spacer between the terphenylene and the dendrimer (Fig. 10, R = CO_2H, n = 1,2, and 1 : 1 molar ratio), whereas $\mathrm{Col_h}$ and $\mathrm{Col_s}$ phases are formed for materials with long polar spacers Fig. 10, n = 3,4). For some of these blends (with long spacers) either two $\mathrm{Col_s}$ phases with different symmetries co-exist (*p*4*mm* and *p*4*gm*) or exclusively the *p*4*mm* $\mathrm{Col_s}$ phase is formed.

Thus, on increasing both the generation and the spacer length, the mesomorphism was found to evolve from SmA to an intermediate channel layered phase, *i.e.* a mesophase combining a layer structure with a hexagonal organization of columns, a $\mathrm{Col_h}$ and $\mathrm{Col_s}$ phases. The phases formation process resembles that of triblock copolymers, in that each of the incompatible constitutive molecular portions occupies specific zones in order to minimize their interactions: the ionic dendritic matrix, polar spacers and carboxylic functions are located within one column, the alkyl chains into another column, and the terphenyl groups between the two types of columns (Fig. 10). The ionic character of these dendrimers reinforces the intramolecular microsegregation and, the resulting segregated ''columnar'' structures are forced to be arranged into a registered packing of columns due to restricted rotation along the columnar axis, hence generating these new morphologies.

The sole example of hydrogen-bonding supramolecular complex dendrimers was reported for PPI dendrimers (G1 to G4) terminated by pyridyl moieties. When mixed with 3-cholesteryloxycarbonyl-propanoic acids,[74] they were found to be birefringent glasses at room temperature, and to form a viscous SmA phase at higher temperature.

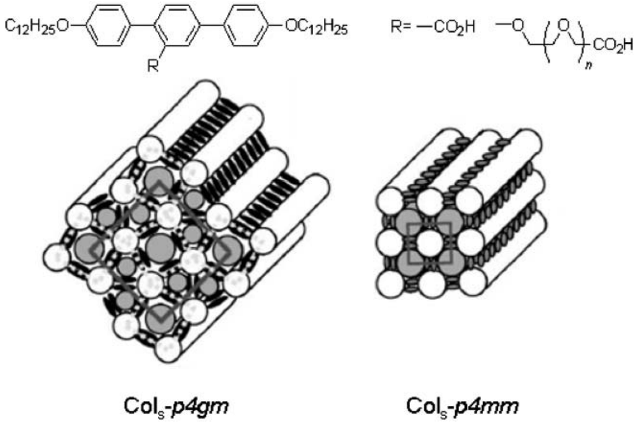

Fig. 10 Structure of the acids and model of organization of the PPI dendrimers-facial amphiphiles into square columnar phases: white = columns of alkyl chains; grey = H-bonding network of the polar groups (R); black = rod-like terphenyl cores; square lattices in dark grey lines.

The preparation of such supramolecular dendrimers held together by ionic interactions represents an interesting concept which can be viewed as a combinatorial approach based on dynamic combinatorial libraries.[75] It then allows an easy access to peripherally functionalized dendrimers in a thermodynamically controlled self assembly process. The mesomorphic properties can be tailored by the type of acid, the dendritic generation and the dendrimer-to-mesogen ratio.

2.1.3. Polyester and polyether LC dendrimers. Amphiphilic polyol monodendrons functionalized by alkyl chains connected to a linear polyethylene oxide chain self-assemble into various supramolecular architectures (Fig. 11). Such AB-block copolymers form crystalline lamellar, micellar cubic, Col_h, continuous cubic phases on increasing the polyethylene oxide portion and temperature.[76,77] Mesomorphism is induced in this case by microphase separation between the hydrophobic dendrons and hydrophilic linear polymer, the polar segments being embedded in a lipophilic coat. Ionic conductivity of ion-doped samples was monitored in these different phases. It appears to be strongly correlated to the mesomorphic behaviour.

Hult and coworkers reported the first ferroelectric LC dendrimers by attaching chiral mesogens onto an amphiphilic polyester dendritic core. This dendritic core is built by various generations of 2,2-bis(hydroxymethyl)propionic based-monodendrons that are coupled in the last stage of the reaction to 1,1,1-tris(hydroxyphenyl)ethane. The G0–G3 dendrimers end-capped with chiral calamitic units exhibit a SmC* and a SmA phase.[78,79] They all showed ferroelectric behavior upon the application of an external electric field, but electro-optical measurements did not reveal any cooperative effect since neither the spontaneous polarizations nor the tilt angles were found to be influenced by the generation number.

2.2. Main-chain liquid crystalline dendrimers

Regarding the dendrimers considered in the following section, the junctions are no longer single atoms but anisotropic molecular moieties instead. Within such architectures, anisotropic groups are present at every level of the dendritic hierarchy, and the dendrimers have less conformational freedom: the anisometric branches do not radiate isotropically as in side-chain LC dendrimers but, on the contrary, favor preferentially an anisotropic order by a gain in enthalpy. For equivalent generations, such systems also contain a larger number of functional units ($Z^* = Z + J$) than side-chain LC dendrimers (Z), and an amplification of the properties is expected. Up to now two families of such systems have been identified.

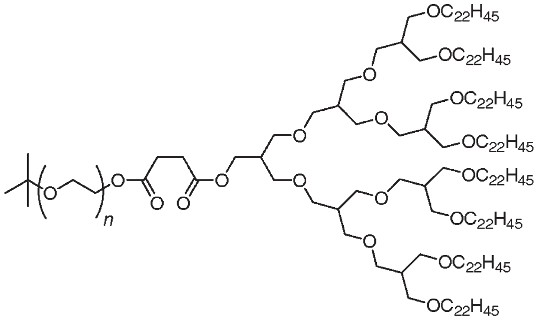

Fig. 11 Structure of the polyether dendrimers.

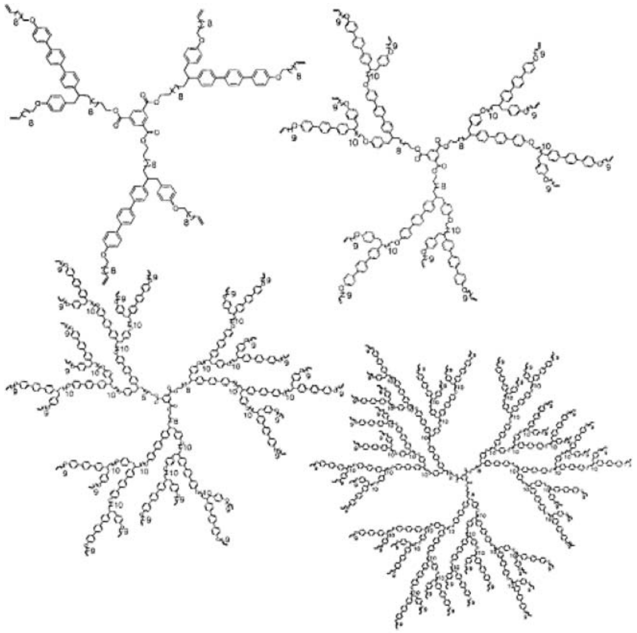

Fig. 12 Willow-like dendrimers G0 to G3.

The so-called willow-like dendrons and dendrimers based on terphenylene monomeric units, were first reported.[80,81] The four generations of monodendrons (DH0–3) and the corresponding dendrimers (G0–3) (Fig. 12), obtained by the grafting of three dendrons onto a tribenzoic core, formed enantiotropic N and smectic phases. The formation of both phases was attributed to chain conformations implying that all the sub-units lie parallel to each other to give an overall rod-like shape, rather than a disc-like or spherical shape. This is possible since the racemic AB_2 monomer possesses conformational flexibility between the terphenylene and phenylene units (*anti* and *gauche* conformations) compatible with this assumption and the induction of both phases at rather accessible temperatures.

Octopus dendrimers result from the coupling of symmetrical dendritic branches containing mesogenic moieties onto a small tetra-podand core (Fig. 13).[82,83] These dendrimers are

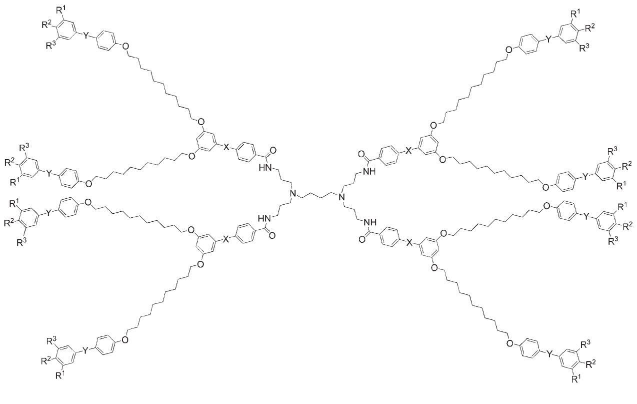

Fig. 13 G0 and G1 octopus dendrimers (X,Y: =/≡; R^1,R^2,R^3 = H/$OC_{12}H_{25}$).

mesomorphic and the morphology of the mesophases depends on the ratio number of terminal chains/end group. The dendrimers bearing one terminal aliphatic chain per unit adopt a *prolate* conformation and consequently exhibit smectic phases (A- and B-type), with rather large periodicities (10–12 nm), consistent with this elongated conformation. The formation of the smectic phases results from the parallel disposition of the mesogenic groups on both sides of the tetravalent core, the dendrimer adopting the shape of a giant elongated rod, and then organizing into layers. In this case, the structure of the smectic phases is quite unique and consists of a highly segregated molecular sublevels structure made of an internal sub-layer containing tilted rigid segments (with no correlation of the tilt), flanked by outer slabs inside which the mesogenic groups are arranged perpendicular to the layer (Fig. 14); these sublayers are separated by the aliphatic continuum.

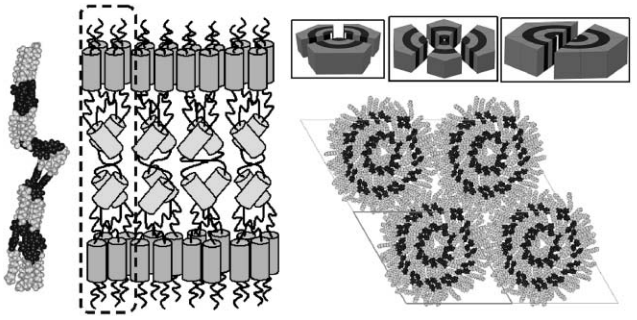

Fig. 14 Structures of the multilayer smectic and onion columnar phases: grey = aliphatic continuum; black = aromatic segments.

In contrast, the increase of the ratio prevents such a parallel disposition of the pro-mesogenic groups, and the dendrimers bearing two or three aliphatic chains per terminal unit adopt an oblate conformation, which leads to the induction of a $\mathrm{Col_h}$ phase.

The formation of these columnar superstructures is a consequence of the mismatch between the surface areas of the aromatic cores and the cross-section of the aliphatic chains, resulting in the curvature of all the interfaces. Consequently, the octopus adopts a wedge-like conformation allowing the mesogenic groups to be radially distributed with uniform interfaces. With such a conformation, the dendrimers self-assemble into (supra)molecular discs or columns which further self-organize into a hexagonal net, consistent with the lattice parameters (9–10 nm). Considering the diblock, alternated chemical nature of these dendrimers, an *onion* morphology for the columns is most likely (intracolumnar segregation) as evidenced by molecular dynamics (Fig. 14). Due to the modular construction used for their synthesis, a wide range of possible interesting structures for the elaboration of multicomponent supermolecules, including homolithic (Fig. 15, **A**) and alternated heterolithic (Fig. 15, **B**–**D**) dendrimers, were prepared.[33,51] Interestingly, it was found that the mesophase stability strongly depends on the localization of the various units within the heterolithic systems.

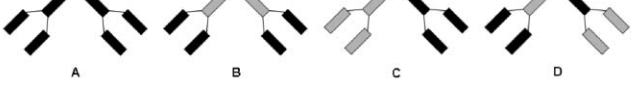

Fig. 15 Schematic representation of G1 octopus dendrimers with a homolithic (**A**), heterolithic alternated (**B**), segmented (**C**), and alternated-segmented (**D**) structure.

2.3. Shape persistent liquid crystalline dendrimers

The so-called "shape-persistent" LC dendrimers represent another original family of mesogens. The particularity of these systems is the nature of the dendritic matrices, which are completely rigid and conjugated, and intrinsically discotic. Moreover, due to their expanded and electron-rich core, they should find applications in materials science owing to their interesting photochemical and photophysical properties, and to their readily attainable nanoscale dimensions.

Three generations of tolane-based dendrimers (G1–G3) functionalized at the periphery by oligo(ethylene oxide) chains[84] were reported to exhibit wide temperature-range $\mathrm{Col_h}$ phases with clearing points increasing dramatically with the generation number (Fig. 16). The dendrimer of the fourth generation appeared to be amorphous. Similarly, G1 and G2 stilbenoid dendrimers showed columnar mesophases ($\mathrm{Col_h}$ and $\mathrm{Col_o}$), whilst higher generations failed to exhibit mesomorphism.[85,86]

X-ray diffraction and molecular modeling showed that the dendrimers of the first and second generation have a planar conformation without any steric hindrance and that they can stack into columns. In contrast, such a planar conformation is impossible for the largest dendrimers due to overcrowding of the terminal chains. The expansion of the molecule occurs in the molecular plane for the first generations to form megadiscs and the growth expands out of the molecular plane for higher generation to form protean objects. The stability of the columnar mesophases of these large unimolecular discs, which are formed by their face-to-face stacking, is primarily enhanced consequently to the increasing interactions between successive macrodiscs. Then, the mesomorphic properties are lost once this out-of-plane growth becomes too important due to steric repulsions and strong distortions of the molecular shape.

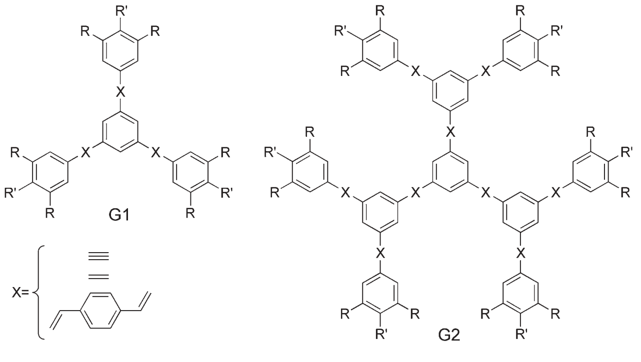

Fig. 16 Schematic structures of the G1 and G2 shape-persistent dendrimers (tolanoid: $R = CO_2(CH_2CH_2O)_3Me$, $R' = H$; stilbenoid: $R = R' = OC_nH_{2n+1}$, $n = 6,12$)

2.4. Liquid crystalline dendrimers containing active ferrocene and/or C_{60} sub-units

Deschenaux reported the first liquid-crystalline ferrocenyl dendrimers based on dendritic aromatic polyesters containing peripheral ferrocenomesogens (a ferrocene and a cholesteryl mesogenic promoter) grafted around a tribenzoic acid core with the view to designing dendrimer-based molecular switching devices. The ferrocenyl dendrimers with six[87] and twelve[88] terminal groups form a single SmA phase, though at rather elevated temperatures. Then, similar monodendrons were attached through a malonate spacer, giving the possibility of incorporating the active C_{60} unit within the dendritic frame. Both the malonates and corresponding mixed fullerene–ferrocene dendrimers were also found to self-organize into a SmA phase,[89] which was slightly destabilized upon the addition of C_{60}. This result showed that the association of fullerene (electron-acceptor unit) and ferrocene (electron-donor unit) within the same structure may be an attractive strategy to elaborate liquid-crystalline switches based on the photo-induced electron transfer occurring from ferrocene to fullerene. Moreover, the use of bulky dendritic addends to embed C_{60} was thought to be a suitable solution to avoid the aggregation of the C_{60} units.

Elaboration of fullerene-containing thermotropic dendrimers[90] was continued for a better understanding of how such a sphere-like structure could be inserted within liquid crystals in order to control the properties *via* the dendrimer generation. New dendritic malonate addends and the corresponding methanofullerodendrimers were then prepared (Fig. 17).[91] For all fullerodendrimers, a single SmA phase was formed, over large temperature ranges (from rt to 200–250 °C). In all cases, the stabilization of the mesophases was observed upon insertion of C_{60}. The only drastic change concerned the G1 compounds where the N phase was suppressed and replaced by the SmA phase upon the insertion of C_{60}. In such systems, C_{60} is buried within the large dendritic branches, and as a consequence the supramolecular organization of these fullerodendrimers is independent of the generation (*G* = 2,3,4). The supramolecular organization of G1 molecules consists of a bilayer structure, where lamellae interact through a layer of fullerene. Above G2, the branching part begins to have a significant lateral extension with respect to the layer normal, and the branches extend on both sides of the C_{60} nucleus: the lamellar structure is thus solely governed by the polar cyano groups. The central part of the layer is constituted by the fullerene moieties embedded by the large dendritic segments, and the layer interface is formed by partially interdigitated mesogenic groups. Similar trends were observed for the corresponding hemi-dendritic systems (one-sided).[91] Substituting the cyanobiphenyl derivatives by side-on chiral mesogens (see Fig. 7) leads to the induction of a rt N* phase.[92]

Fulleropyrrolidines constitute an important family of C_{60} derivatives which have the advantage over the methanofullerene systems of leading to stable reduced species, allowing the development of fullerene-based redox molecular switches. A family of LC fulleropyrrolidine dendrimers bearing the same dendrons as the malonates (Fig. 17, X = Me) also exhibited a SmA phase from G2 to G4,[93] the stability of which was found to increase with the generation (G1 was not mesomorphic), but slightly lower than that of the analogous methanofullerodendrimers. Except for the G2, a similar organization as that of the malonates was proposed for the SmA phase of G3 and G4. The G2 fulleropyrrolidine[93] was chosen as a representative reference for a systematic variation of the X group in order to evaluate the effects on the mesomorphic properties (Fig. 17). When X = H,[93] a broad temperature range SmA phase is formed. Modification of the X group by oligophenylenevinylene conjugates led also to similar results and indicated that the overall behavior is dominated by the dendritic framework.[94] Preliminary luminescence measurements in solution revealed a strong quenching of the OPV fluorescence by C_{60}, indicating that these donor–acceptor systems appeared suitable candidates for photovoltaic applications. When X is a ferrocene unit, a SmA phase is shown again, with a lower phase stability than in the other cases,[95] and a photo-induced electron transfer was observed with a lifetime of the charge-separated state of 560 ns in THF. Further, mixed ferrocenyl–fullerodendrimer

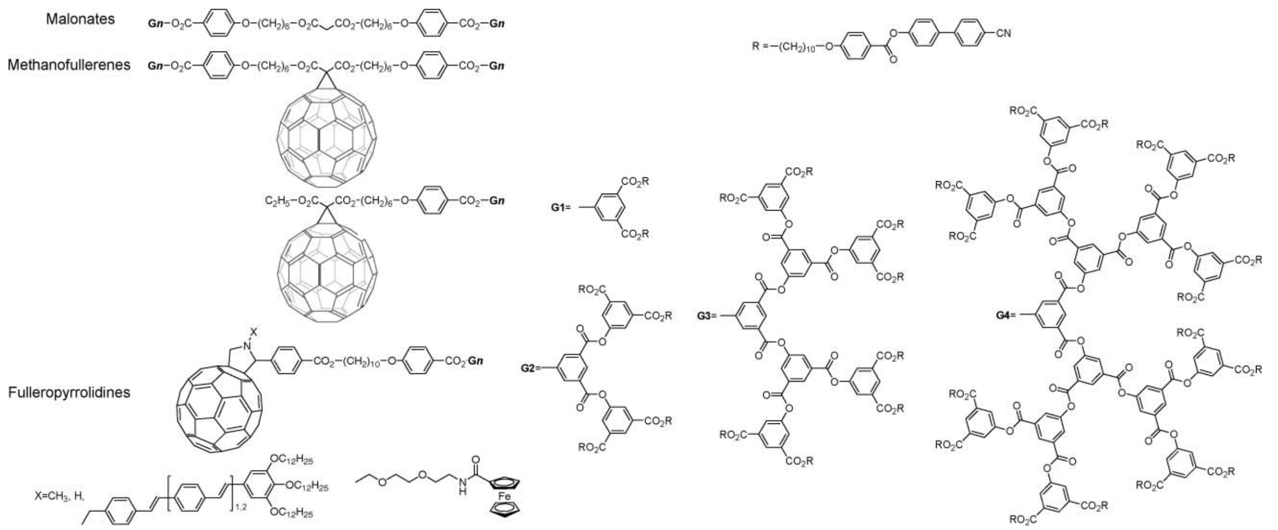

Fig. 17 LC fullerodendrimers.

dyads, containing a ferrocenyl dendrimer, with two and four ferrocene units as source of electrons, combined with a liquid-crystalline fullerodendrimer derivative of G2 polyarylester (Fig. 16, G2) formed an enantiotropic SmA phase and organized into bilayer structures within the smectic layers.[96] Oxidation and reduction processes were in agreement with the presence of both ferrocene and fullerene units, and an efficient photo-induced electron transfer from the ferrocenyl dendrimer to the fullerene was observed in solvent.

With the view to exploiting C_{60} as a synthetic platform for the design of liquid-crystalline materials with unconventional shapes, the mesomorphic properties of fulleropyrrolidine dendrimers based on the bis-addition pattern were investigated. Thus, a variety of new and interesting structures including *trans*-2, *trans*-3 and equatorial bisadducts were obtained by the condensation of the liquid crystalline promoter (derived from G2, Fig. 17) with the corresponding bisaminofullerene, and compared to the monoadduct.[97] All exhibit a SmA phase, with a bilayer and monolayer structures for the monoadduct and bisadducts, respectively.

The presence of a single smectic mesomorphism is imposed by the presence of the cyanobiphenyl derivative as liquid crystalline promoter grafted at the periphery of the dendrimers. Thus, to evaluate the possibility to generate other types of mesophases, related fulleropyrrolidines functionalized by polybenzylether dendrimers terminated by aliphatic chains were prepared. They were found to spontaneously self-organize into Col_r structures.[98] In such an organization, the molecules self-aggregate, through the C_{60} units which are confined within the spines of the columns.

2.5. Supramolecular dendromesogens

The supramolecular dendritic concept developed by Percec results from the self-assembly of structurally perfect dendrons with pre-programmed shapes into supramolecular cylindrical and spherical dendrimers, which then self-organize into various liquid crystalline mesophases. The originality of this approach (and its strength) is the simplicity of the molecular design and the versatility of the structural modification. The ramified skeleton of these self-assembling monodendrons is based on a benzyl ether dendritic arborescence which is obtained by the connection of AB benzyl ether junctions (referred to as AB building blocks) through ether links into successive rows. They are usually functionalized at the apex by various functions and at the periphery by flexible chains.

In order to assess the criteria that govern the shape and size of the supramolecular dendrimers and thus control the supramolecular assemblies, Percec *et al.* have investigated libraries of monodendrons whose architectures were rationally designed. At the periphery, the number of peripheral aliphatic chains and the position of grafting were varied (1 chain in the 4 position of the AB unit, 2 chains in the 3,4 or 3,5 positions of AB_2 units – constitutional isomers, and 3 chains in the 3,4,5 positions of the AB_3 unit), as well as its nature (Fig. 18, R = OC_nH_{2n+1}, $O(CH_2)_n(CF_2)_mF$). The apical functional group is usually hydrophilic (Fig. 18, X = CO_2H, CH_2OH, CO_2R, $CO_2(CH_2CH_2O)_pH$, $CO_2(CH_2CH_2O)_pMe$, crown ethers) but not always. As for the dendritic skeleton, the generation number (G = 1–5), the branching multiplicity of the arborescence ($N_B = 2$ for 3,4-AB_2 and 3,5-AB_2, and $N_B = 3$ for AB_3), and its symmetry (succession of identical synthons or mixed branching) were also varied. All these structural parameters allow subtle modulations of the rate of growth and deformation of the dendromesogens evaluated by the solid angle of the molecule, a parameter intimately linked to the mesophase structure. A plethora of dendrons with a single arborescence such as $(AB_3)^GX$ (G = 1–5)[99] or $(AB_2)^GX$ (G = 1–5),[100] or with a mixed connectivity such as $(AB_z)(AB_y)(AB_x)(AB_n)X$[100–104] (Fig. 17, n,x,y,z = 1,2,3) were thus synthesized and their thermal behaviours analyzed and compared. Generally, cylindrical or pseudo-cylindrical supramolecular dendrimers are obtained by the self-assembly of G2 monodendrons, and occasionally G3 dendrons or even a G4,[100,104] providing a low connectivity and one-chain terminal end-groups; essentially all G1 monodendrons are devoid of mesomorphism. On average, they exhibit a flat tapered fan, a semi-discoid or even discoid[104] shape. Mixed arborescence based on binary branching, and particularly the 3,5 positions, favour the formation of the Col_h phase, delaying the formation of cubic structures. For these low generation dendrons, the influence of the apical function is also crucial on the induction or stabilization of the mesophases, and follows the order $CO_2H > CH_2OH > CO_2Me/Et$. These tapered dendritic molecules aggregate 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 (Fig. 19).

As theoretically anticipated,[105] important 3D deformations of the molecules, from the flat conformations to conical up to pseudo-spherical shape, were found to occur upon increasing the dendritic connectivity and the number of terminal chains providing pseudo-spherical supramolecular entities and cubic self-assemblies. Indeed, from the structural combinations given above, various cone-shaped, hemi-sphere-like and spherical monodendrons were obtained, producing spherical supramolecular dendrimers, embedding the polar portions within, which in turn self-assemble into micellar cubic phases or other 3D phases.[99–104] The cubic liquid-crystalline phase have a $Pm3n$ or $Im3m$ space group symmetry (usually self-organization of small micelles will generate the primitive symmetry, whilst the large ones will favour the body-centred symmetry). Such a process is driven by intramolecular micro-segregation, steric constraints as well as in most cases H-bonding interactions. For instance, an AB_3-like arborescence allows only a restricted-cooperative rotation which requires the external benzyl ethers to be approximately orthogonal to the internal one, thus favouring the conical shape of the monodendron at earlier generation. Similarly, hindrance is observed for dendromesogens having a large number of chains. These two factors contribute to an increase of the solid angle and to the formation of 3D structures. Studies of electron density profiles and histograms computed from the X-ray diffraction data demonstrate that the cubic phases result from the self-assembly of these spheroid supramolecular dendrimers, according to the symmetry of the cubic phase, with the polar regions located at the crystallographic positions of the group.[106,107] Further studies by electron microscopy of the

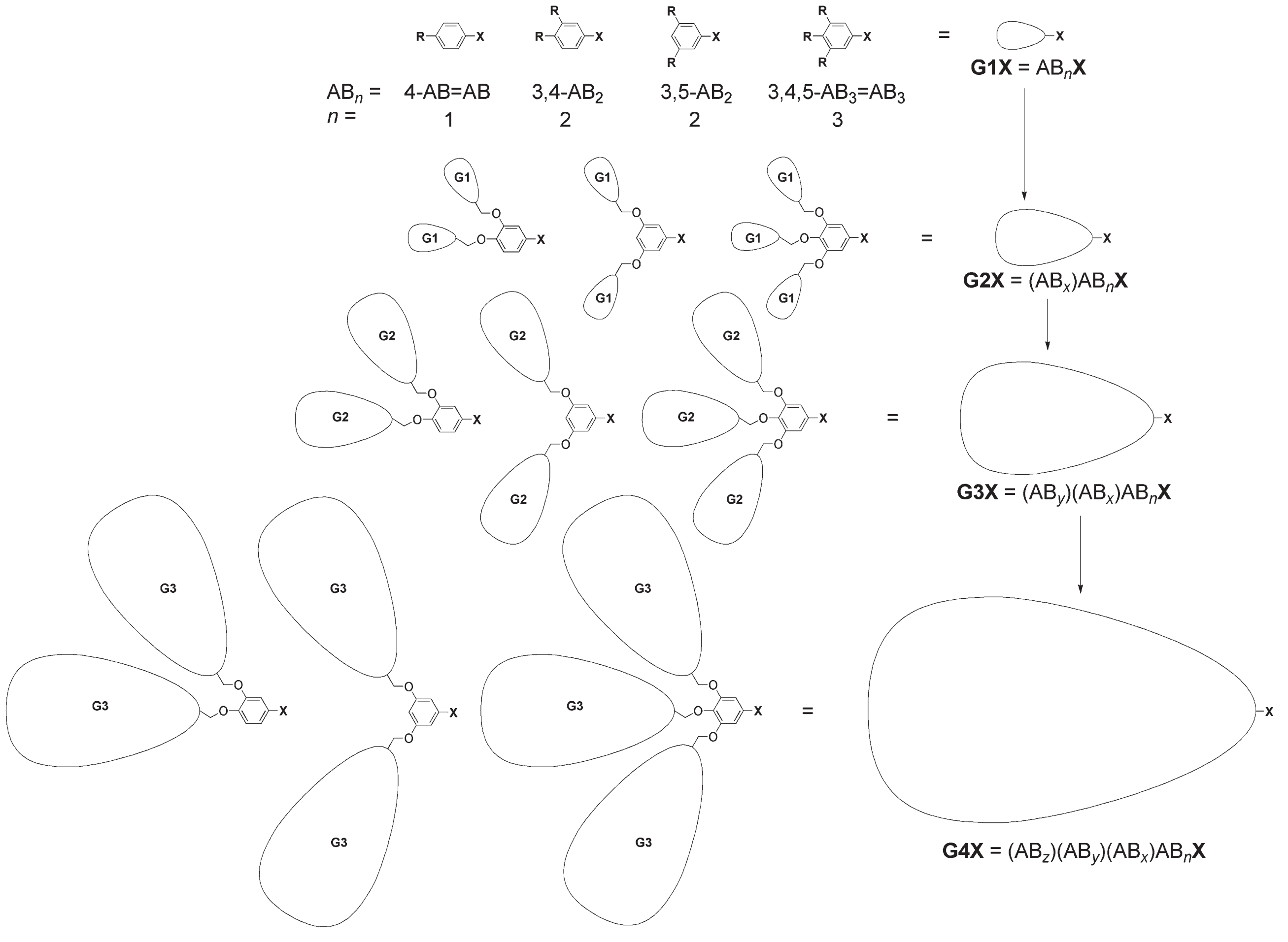

Fig. 18 Schematic representation of the library of Percec's dendromesogens up to the 4th generation. X, AB, *n*, *x*, *y*, *z* are defined in the text.

samples exhibiting the *Pm*3*n* cubic phase revealed the existence of grain boundaries and stacking faults.[108] These are all consistent with the presence of quasi-spherical assemblies or more precisely to polyhedral-like micelles, and moreover suggest that the supramolecular spheres are deformable, interacting one with the other through a relatively soft pair

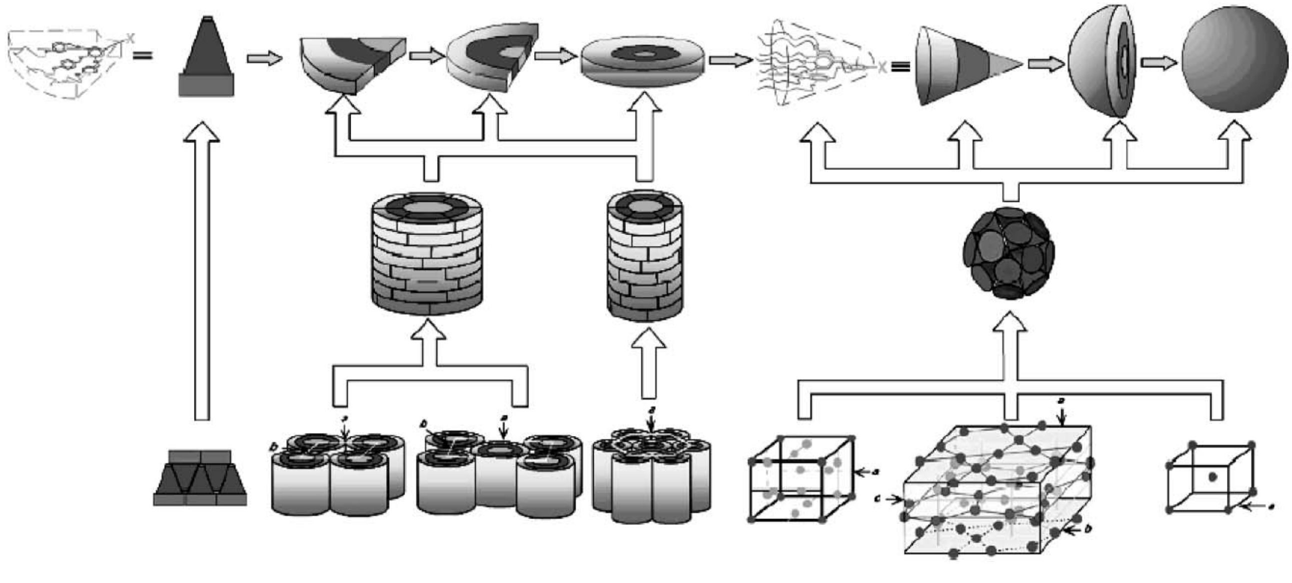

Fig. 19 Schematic representation of the self-assembly of dendromesogens into various mesophases (smectic, $\mathrm{Col_h}$, $\mathrm{Col_r}$, CubI, CubP, Tet, and LQC phases) by controlling the overall molecular shape conformation (from flat tapered to cylindrical to conical and to spherical shape). (Reprinted with permission from reference 127. Copyright 2004 American Chemical Society.)

potential.[109] The majority of such quasi-spherical assemblies are thus distorted into an oblate shape.

Comparing series based on AB_2 and AB_3 synthons showed that the use of the former unit *versus* the latter unit at the periphery leads to an increase of the diameter of the supramolecular dendrimer, consequent to a decrease of the solid angle of the dendron. Upon increasing the generation number, all the dendrimers increase their solid angle until they become a single sphere. This trend was generally confirmed for this class of materials. It is shown that the supramolecular dendrimers derived from 3,4-AB_2 arborescence quickly adopt a spherical shape (the monodendritic blocks have a cone-like shape) while the supramolecular dendrimers derived from the isomeric constitutional 3,5-AB_2 arborescence remain in a cylindrical conformation for several generations (the blocks have a disk fragment or a disk shape).[104] Let us remark that within all these libraries, that based on a 3,5-AB_2 arborescence provides the first example of supramolecular dendrimers able to change their shape in a reversible way as a function of temperature and also the first example of a spherical supramolecular dendrimer that self-organizes in a cubic phase of *Im*3*m* symmetry at elevated generations. Moreover, new mesophases were found. A LC phase with a tetragonal three-dimensional unit cell (Tet phase) was recently discovered between a cubic *Pm*3*n* and a Col_h phase.[110] Its structure consists of *ca* 30 globular supramolecular dendrimers (Voronoï polyhedra), each resulting from the self-assembling of *ca* 12 dendrons, and can be seen as an intermediate structure between Cub *Pm*3*n* and Cub *Im*3*m*. Interestingly, this tetragonal $P4_2/mmm$ phase is equivalent to the tetrahedral close packed Franck–Kasper structures[111] found with metals and metal alloys. The authors suggest that the analogy between dendrimers and metals lies in the role played by the "soft" d orbitals in the metals and the soft globular supramolecular dendrimers. Whereas the characteristic length of the self-assembled quasicrystals is of a few Å in metal alloys, it is nearly 10 nm in the case of self-assembled dendrons. Another 3D phase was found for a few other dendrimers. Its structure, which is an arrangement of micelles, is periodic in the direction of the 12-fold axis, but quasiperiodic in the plane perpendicular and is referred to as a liquid "quasi" crystal phase (LQC).[112]

Substitution of alkylated chains by perfluorinated chains was found to stabilize or induce mesomorphism,[113,114] as well as to change the nature of the mesophases. For instance, whilst the non-fluorinated ester $(AB_3)^2$ shows a monotropic cubic phase, the fluorinated analogue exhibits a pyramidal Col_h phase, resulting from a change of the dendron conformation; the clearing temperature was raised by *ca* 40 °C.[115] This modification proves to be an interesting alternative for the control of the molecular conformation and its mechanism of self-assembly into pre-designed morphologies.

The modification of the focal function of the dendrons (Fig. 18, X) to obtain functional materials (amphiphilic, bio- or electronic-inspired dendrons) has been demonstrated in various research topics, but also leads to interesting variations of the mesomorphism. Alkylated $AB(AB_3)$ (G2) dendrons equipped with oligo(ethylene oxide)[116] chains self-assemble into tubular columnar structures forming a Col_h phase which decreases in stability as the ethylene oxide chain increases (Fig. 18, X = $CO(OCH_2CH_2)OH$); enhancement of the stability temperature range was observed upon complexation of Li^+ ions. Absence of mesophase was systematic for end-methylated oligo(ethylene oxide) chains (Fig. 18, X = $CO(OCH_2CH_2)OMe$) or in the homologous series of AB_3 (G1) dendrons.[117] Similarly, crown ethers were incorporated at the focal points of a variety of these dendromesogens. The dendritic building blocks thus prepared self-assemble either spontaneously or after complexation with NaOTf into SmB, SmA, Col_h and *Pm*3*n* cubic phases, respectively, as the degree of branching and the generation number increases.[118,119] In the pure state, and for low generations, mesomorphism is either absent or monotropic, whilst self-assembly mediated by ionic interactions was facilitated upon complexation of the crown ether with NaOTf. These supramolecular columnar dendritic systems are equipped with ion channels, and may represent interesting materials for selective ion transport. Grafting larger polar groups such as bulky triols and hexols to produce "Janus-like" codendrimers was recently reported;[120] as for the dendritic frame, the 3,5-AB_2 arborescence, not optimal for LC properties, was chosen to evaluate the "LC inductive" effect; the 3,5 and 3,4,5-chain peripheral patterns were utilized as well as triforked chains. All the amphiphilic codendrimers, despite an *a priori* unfavourable shape, revealed mesophases, Col_h for the G1 and G2, and cubic for the G3; the triforked systems exhibit solely cubic phases. The symmetry of the cubic phase was changed according to the apex function: *Pm*3*n* was obtained with the triols and *Im*3*m* with the hexol compounds, the latter producing the larger micelles. A model for the *Pm*3*n* phase was proposed and consists of evenly pinched columns, 3 × 3 interlocked into a 3D network. Interestingly, G1 and G2 dendrons functionalized by dipeptides were found to self-assemble into helical porous columns through a complex recognition process; hexagonal and/or rectangular packing of columns was observed depending on the nature of the dendritic part.[121–124] Similarly, host molecules with U-shaped receptor cavities derived from diphenylglycoluril, functionalized at their apex by two $(AB_3)^2$ dendrons, exhibit a cubic phase resulting from a spherical supramolecular assembly with the host inside.[125] The corresponding 1 : 1 host–guest complex was found to form the same type of phase, with the guest included in the core of the spherical micelle. This class of biologically inspired self-assembling dendrimers provides powerful tools for programming structures and stability of porous proteins mimics, and may find applications in gene and viral therapies.[126]

In all the examples reported above concerning the self-assembly of dendrons based on AB_3, AB_2, and combinations of AB_3 and AB_2 building blocks, the shape and the diameter of the resulting supramolecular dendrimers were limited to less than 8 nm, mainly due to the solid angle of the dendron (maximum sphere radius). In fact, due to the shape change of the self-assembling dendron as a function of generation, the increase in generation is generally not accompanied by an excessive increase of the supramolecular assemblies dimensions, despite the fact the molecular weight increases fast. In order to produce supramolecular dendrimers of larger dimensions, new libraries of compounds based on various

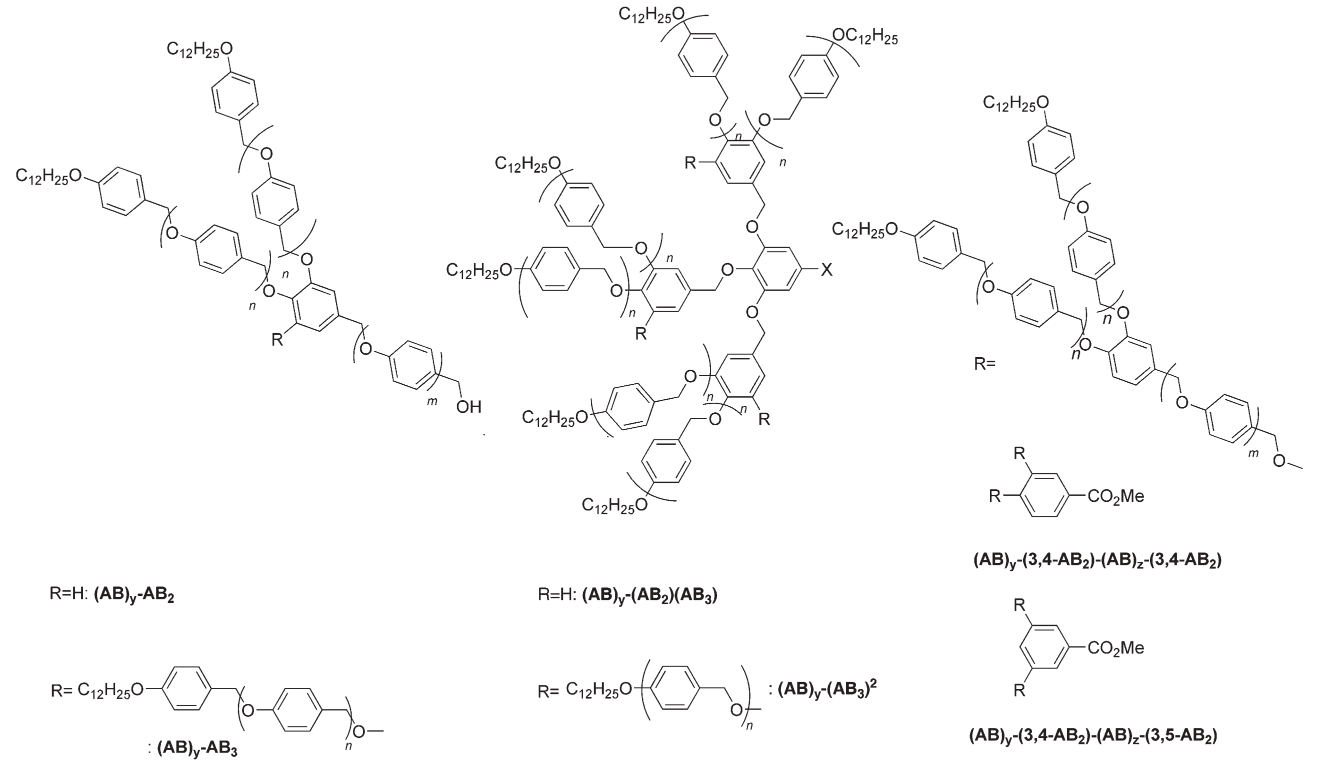

Fig. 20 Chemical structures of the $(AB)_y$–AB_3 and $(AB)_y$–AB_2 dendrons of the first generation (*y*: number of AB blocks, see text), the $(AB)_y$–$(AB_3)^2$ and $(AB)_y$–$(AB_2)(AB_3)$ hybrid dendrons of the second generation (*y*: number of AB blocks, see text, X = CH_2OH, CO_2Me), and of the two constitutional isomeric $(AB)_y$–$(3,4\text{-}AB_2)$–$(AB)_z$–$(3,4\text{-}AB_2)$ and $(AB)_y$–$(3,4\text{-}AB_2)$–$(AB)_z$–$(3,5\text{-}AB_2)$ hybrid dendrons of the second generation (*y* and *z*: number of AB blocks, see text).

combinations of AB, AB_2 and AB_3 building blocks have been designed and synthesized (Fig. 20).[127] The introduction of linear AB fragments within the arborescence produces dramatic effects in that smectic phases are stabilized, along new columnar phases such as Col_r phases of various symmetries, preferentially to cubic structures. This led to a large number of compounds where the length of the branches, the number of terminal chains, the degree of branching and the apex group multiplicity were systematically varied. Thus, most of the dendritic mesogens of the first generation such as the $(AB)_y$–AB_3 dendrons (Fig. 20; *y*: number of AB blocks; for the $(AB)_y$–AB_3 system, $y = 3n + 3 + m = 3$–11, and for the $(AB)_y$–AB_2 system $y = 2n + 3 + m = 2$–7) self-organize into lamellar ($n = 1$–2; $m = 0$), Col_r and Col_h ($n = 0$–2; $m = 0$–1) and *Pm*3*n* cubic phases ($n = 0$; $m = 1$–3), whereas those derived from the AB_2 series ($(AB)_y$–AB_2) form lamellar ($n = 1$–2; $m = 0,3$) and columnar ($n = 0$–2; $m = 1$–3) phases. The mesostructures are much larger (up to three times) than those of the phases of same symmetry exhibited by the highest generations of the supramolecular dendrimers obtained through the self-assembling of dendrons based on AB_3, AB_2, and combinations of AB_3 and AB_2 building blocks.

The corresponding second generation of the AB_3 hybrid dendrons of the type $(AB)_y$–$(AB_3)^2$ (Fig. 20, $y = 0,9,18,27$) and $(AB)_y$–$(AB_2)(AB_3)$ (Fig. 20, $y = 0,6,12$) were also prepared by varying the total number of benzyl AB groups *n* and *m*. A Col_h was obtained for the first series $(AB)_y$–$(AB_3)^2$ (Fig. 20, $n = 1$–2), except for $n = 0$ which shows a *Pm*3*n* cubic phase and $n = 3$ which is crystalline. As for the mixed hybrid series $(AB)_y$–$(AB_2)(AB_3)$, a *Pm*3*n* cubic phase was obtained for all *n* (Fig. 20, $n = 0$–2), with an additional Col_h phase for $n = 2$. Unlike the previous series of the first generation, no smectic phases were detected.

Other compounds with mixed hybrid structures could be prepared. The constitutional isomeric dendrimers based on the (AB_2) unit with the 3,4 and 3,5 arborescence were synthesized. The AB_2 hybrid dendrons $(AB)_y$–$(3,4\text{-}AB_2)$–$(AB)_z$–$(3,4\text{-}AB_2)$ (Fig. 20, $y + z = 4,6,12$, $z = 0,2,4$) yielded 3D cubic structures with an additional Col_h phase for the compound with $m = 1$ and $n = 0$. In contrast, the isomeric series $(AB)_y$-$(3,4\text{-}AB_2)$-$(AB)_z$-$(3,5\text{-}AB_2)$ yielded mainly 2D columnar phases, namely a Col_h, then both Col_r and Col_h, and finally a single Col_r phase for the three compounds with $m = n = 0$, $m = 1$ and $n = 0$, and $m = 2$ and $n = 1$, respectively.

All the above examples show that supramolecular dendromesogens of various shapes and dimensions (in the nanometre scale) can be obtained through a large variety of AB building blocks connected together according to various topologies, and through an efficient three-dimensional self-assembling process (Fig. 19). The structural diversity of self-assembling dendrons was further explored and expanded through the combination of AB, constitutional isomeric AB_2 and AB_3 biphenyl ether[128] and phenylpropyl ether building blocks.[129] These novel libraries modelled on that of the phenyl series (Fig. 18) offer new LC dendrons which regardless of *G*, the periphery, and the arborescence, self-assemble into supramolecular dendrimers that self-organize into periodic or quasiperiodic mesostructures with large dimensions including smectic,

Col_h, Col_r (*p*2*mm*, c2mm), and cubic *Pm*3*n* phases for the biphenyl series,[128] and smectic, Col_h, Col_r (*p2mm*, *c2mm*), LQC, Tet, and cubic *Pm*3*n* phases for the phenylpropyl series.[129] Unexpectedly, porous columnar lattices and hollow spheres were characterized for some of these structures.[128,129]

Such supramolecular nanostructures are of particular interest in complex soft matter in general, but represent also promising materials for optoelectronics and electronics, as the semifluorinated dendrons connected to electron-donor groups that mediate helical pyramidal columns formation,[130,131] as well as in biology in which the principles of organization to 3D tertiary structures of bioinspired supramolecular dendrimers such as dendritic dipeptides[121–124,126] or dendritic folic acid derivatives (that show Col_h and Cub-*Pm*3*n* phases),[132] can help modelling and understanding biological processes or used in gene and viral therapies.

2.6 Metallodendromesogens

Liquid-crystalline metal complexes or metallomesogens constitute an important class of mesomorphic materials as they offer wider structural diversity (types of coordination geometry) and functional behavior (metal–ligand synergy) than their organic counterparts. They may have a covalent (neutral) or an ionic character, and both thermotropic[18] and lyotropic[133] systems have been reported. While in general the vast majority of dendrimers are purely organic systems,[30] there is also a great interest in metallodendrimers.[134,135] Their incorporation within a dendritic matrix may find many applications in various areas of science as for example efficient catalysts due to the high concentration of active sites, electro-active molecules due to the multiredox centers, sensors due to their multivalent and selective binding ability, or as molecular antennas due to their particular photo-physical properties.[134] The properties of these "suprasupermolecules"[135] can be tuned and modulated by the specific location of the active moieties within the dendrimer: the metals can be incorporated at the core, within the structure or at the periphery of the dendrimer. Surprisingly, very few studies on liquid crystalline metallodendrimers have been reported. Except the ferrocenyl dendrimers (*vide supra*), most of LC metallodendrimers consist of minidendrons of first generation grafted around various coordinative sites. Induction of columnar mesomorphism was observed upon complexation of the oxovanadyl metal ion to salen-based ligands (ML type, Col_r and Col_h)[136] or copper atoms to enaminoketone derivatives[137] (M_2L_2 type, Col_h), as none of the dendritic ligands were themselves mesomorphic (Fig. 20). The stability of the mesophases was found to depend on structural parameters such as the spacer Y (for the salen) and the length and number of chains. The occurrence of the mesophase is likely due to the rigidifying of the central chelating part.

Coordination of MX_2 salts (M = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, and X = Cl, SCN, NO_3) to dendritic PPI ligands D1 and D2 (Fig. 22) led also to MX_2Di dendrometallomesogens.[138] Depending on the salt, ionic (trigonal bipyramidal geometry, $[MXDi]^+[X]^-$, M = Cu^{II}, Co^{II}) or neutral (octahedral geometry, MX_2Di, M = Ni^{II}) complexes were formed; the structure of the Zn^{II} complex was not elucidated. A Col_h phase was induced for all the complexes with D1 except $[Ni(NO_3)_2(D1)]$ and was stabilized upon coordination of $CuCl_2$ with D2 ($[CuCl(D2)]Cl$).[139] Thus, stabilization of mesomorphism upon metal coordination was systematically observed. Note that related quasi metallodendrimers involving one, two or three metallic centres, were obtained from a mesomorphic multicoordinative G0 dendritic imine ligand, D, derived from tris-(2-aminoethyl)amine (as D1 Fig 22, functionalized by R = L_1, Fig. 8).[140]

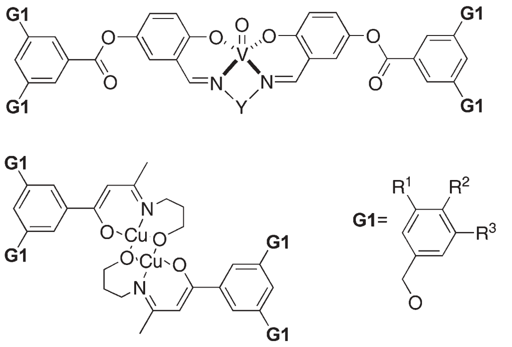

Fig. 21 Structure of the dendritic oxovanadyl (Y = $–(CH_2)_2–$, $–(CH_2)_3–$, $–CH_2CMe_2CH_2–$) and dicopper dendritic complexes (R^1,R^2,R^3 = H/OC_nH_{2n+1}).

Dendritic lanthanidomesogens were prepared following the same molecular design successfully used for liquid crystalline fullerodendrimers, but with a central tridentate 2,6-bis(benzimidazole)pyridine unit replacing the malonate spacer (Fig. 17). Peripheral cyanobiphenyl dendrimers impose a microphase organization forcing the lanthanidomesogens to form fluid thermotropic smectic mesophases (the dendritic ligands formed a N phase only).[141] The bulky nine-coordinate lanthanide core is located between the decoupled mesogenic sublayers made up of parallel cyanobiphenyl groups. Finally, zeroth- and first-generation PPI dendrimers end-functionalized by mesogenic salicylaldimine (Fig. 8, R = L_1) were considered as potentially multicoordinative organic ligands too.[142] Whereas the organic ligands exhibited SmC and SmA phases,[60] mesomorphism was either suppressed or strongly destabilized in the corresponding dimetallic (G0) and tetrametallic (G1) copper(II) dendrimers. Only SmC phases were formed.

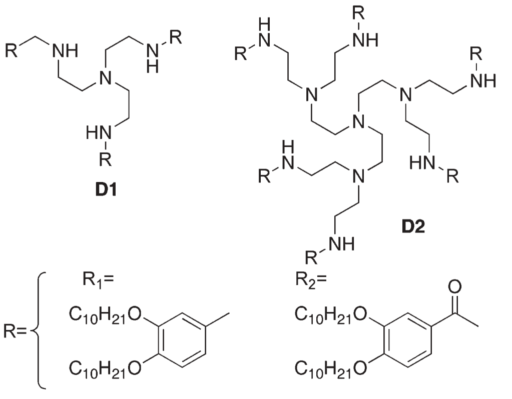

Fig. 22 Dendritic ligands D1 and D2 forming $[MXDi]^+[X]^-$ and MX_2Di metal complexes.

3. Conclusions

Thus, the above examples show that liquid-crystalline phases can been produced with high molecular weight monodisperse dendrimers and dendrons. Nematic, lamellar, columnar, cubic phases as well as less conventional mesophases (Tet and LQC phases, onion, segregated and porous columnar phases, hollow cubic phases, multilayered and dark smectic phases) were obtained depending upon the dendritic chemical nature and connectivity and the type of mesogenic groups. Enhancement of mesophases stability was almost systematically observed, due to reinforced microsegregation. This control of the mesomorphic structure by an appropriate molecular design makes possible the development of new liquid-crystalline materials containing active molecular units (metals, Fc, C_{60}) with specific physical properties (magnetic, optical, electronic) which may find uses in nano- and bio-technology. The high sensitivity of LC dendrimers with the surrounding environment (properties *versus* molecular structure) could be, in principle, beneficial to access some kinds of molecular sensors *i.e.* to use such supermolecules as tools to test how properties in general may be altered or modulated upon delicate external stimuli. The fabrication of self-assembling organic–inorganic nanohybrids by combining the magnetic, electronic and/or optical properties of metallic clusters, oxides and nanoparticles with the soft nature of organic dendrons represents an interesting perspective in this area. In this case, the nanoparticle plays the role of a hard and multivalent core,[143] and recently LC materials based on gold,[144,145] TiO_2,[146] and Fe_2O_3[147] nanoparticles were obtained by grafting mesogenic organic addends. Such interesting and innovative developments lead us to predict an exciting future in this area.

Acknowledgements

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