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# Micro-segregation, molecular shape and molecular topology – partners for the design of liquid crystalline materials with complex mesophase morphologies†

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**This article gives an overview of recent progress in the design of novel materials, capable of forming liquid crystalline phases with non-conventional mesophase morphologies. The materials include dendritic molecules, ternary block-copolymers, rod–coil molecules and linear as well as non-linear polyphilic low molecular weight block molecules incorporating rigid segments with a specific shape. Changing the shape of the rigid segments from rod-like to disc-like or to a bent shape leads to additional possibilities for the directed design of mesophase forming materials. Many of these molecules are able to form quite unusual mesophase morphologies, distinct from the conventional lamellar (smectic) and columnar mesophases of classical rod-like and disc-like liquid crystals; they include mesophases which combine lamellar and columnar organisation, columnar mesophases incorporating three discrete sets of columns, biaxial smectic phases, such as the $\mathrm{SmA_b}$-phase (McMillan Phase), polar smectic phases and non-conventional layer structures in which rigid units are aligned parallel to the layers. These novel mesophase morphologies were realised by increasing the number of incompatible units combined in these molecules, by changing the volume fractions of the incompatible segments, by tailoring the shape of rigid segments and by controlling the molecular topology.**

## 1. Introduction

Liquid crystalline (LC) phases represent fascinating states of soft matter, combining order and mobility on a molecular and supramolecular level. This unique combination enables such systems to respond to external (magnetic, electric, chemical or mechanical) stimuli by finding a new configuration of minimum energy.[1] Therefore, liquid crystalline materials are of great importance for numerous applications. Low molecular weight thermotropic liquid crystals of rod-like molecules find wide application in optoelectronic devices, prerequisites for the development of mobile communication and information processing systems.[2] Numerous novel high-tech applications of rod-like and disc-like molecules, for example, as light modulators,[3] as photoconductors,[4] as polarised light emitting materials[5] and as intelligent lubricants[6] are in development. Additionally, processing polymeric materials in the LC state can improve their materials properties. Natural silk[7] and high tensile strength fibres such as Kevlar®[8] are important examples. Lyotropic liquid crystals[9] are important templates for the production of inorganic materials with well defined structures in sol–gel processes,[10] and mesogenic complexes of DNA with cationic and neutral lipids are discussed as potential carriers in gene delivery applications.[11] Finally, the combination of order and mobility is a basic requirement for self-organisation in living matter.

The mobility of these systems is provided by large amplitude motions[12] of the molecules or molecular parts, namely the flexible chains. The molecular order has two components: orientational and positional order. *Orientational order* can arise from the parallel alignment of anisometric molecules or supramolecules (*e.g.* hydrogen bonded supramolecules[1,13]). *Positional order*, on the other hand, is mainly the consequence of specific attractive forces and amphiphilicity.[14] These forces can contribute to the self-organisation of the molecules to a varying extend. Nematic phases (N), typically formed by rigid rod-like and disc-like molecules, have exclusively long-range orientational order. If anisometric units are appropriately combined with flexible chains, an amphiphilicity arises between these chemically and conformationally different molecular parts, and this leads to their segregation into different subspaces, separated by interfaces with well-defined shapes.[15] The organisation of these interfaces in space gives rise to a variety of positionally ordered mesophases, whereby in the case of rigid molecules the molecular shape and the molecular topology have a dominant impact on the shape of the interfaces: rod-like (calamitic) molecules with terminal alkyl chains preferentially arrange in layer structures (smectic mesophases, Sm),[16] whereas disc-like molecules, circularly surrounded by flexible chains, prefer an organisation in columns (columnar mesophases, Col).[17–19]

Flexible amphiphiles without anisometric segments, namely surfactants[9] and binary block copolymers,[20,21] represent another important class of mesophase forming materials. The mesophase morphologies of these flexible amphiphiles are mainly governed by the volume fractions of the two incompatible segments combined in such molecules. The phase sequence lamellar (smectic, SmA)–bicontinuous cubic ($\mathrm{Cub_V}$)–hexagonal columnar ($\mathrm{Col_h}$)–micellar cubic ($\mathrm{Cub_I}$) upon increasing the volume fraction of one component is typical for the morphologies of binary diblock copolymers and mesophases of surfactant–solvent systems (see Fig. 1).[9,20] The cubic phases, which are optically isotropic, have attracted special attention over recent years, because they can have different structures and lattice types. The bicontinuous cubic phases ($\mathrm{Cub_V}$), which represent intermediate states between lamellar and columnar organisation, are built up by two

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interpenetrating networks of branched cylinders containing one of the incompatible molecular parts within a continuum formed by the other one. Micellar (discontinuous) cubic phases (Cub$_I$) are the result of the regular organisation of closed spheroidic aggregates. In diblock copolymers the Cub$_V$ phases always have an *Ia*3*d*-lattice whereas spheroidic aggregates of Cub$_I$ phases are organised in *Im*3*m* lattices (see Fig. 1a). However, in lyotropic systems a greater diversity of lattice types is found (see Fig. 1b), which additionally depends on the relative volume fractions of the polar and apolar regions. In normal type lyotropic systems, where the polar regions represent the majority and form the continuum, the *Pm*3*n* lattice is the main lattice type for the micellar cubic phases (Cub$_{I1}$), but also *Im*3*m* and *Fm*3*m* lattices have been reported.[22] In contrast, in reversed type lyotropic mesophases (where the lipophilic chains form the continuum) only the *Fd*3*m* lattice has been found for the micellar cubic phases (Cub$_{I2}$), whereas for the bicontinuous phases (Cub$_{V2}$) *Pn*3*m* and *Im*3*m* lattices were reported in addition to the *Ia*3*d* lattice.[9]

In recent years amphiphilic polyhydroxy compounds[23–28] and carbohydrate derivatives[27–33] have received special attention, because these low molecular weight amphiphiles can form liquid crystalline phases in the presence of protic solvents (lyotropic phases), as well as in their absence (thermotropic phases). Hence, they represent an important class of amphotropic liquid crystals.[23–35] As shown in Fig. 2, the mesophase morphologies of the thermotropic mesophases can easily be tailored by variation of the number and position of the hydrogen bonding groups (OH groups) as well as by variation of the number, the length and the chemical structure of the lipophilic chains, leading to the phase sequence Cub$_{I2}$–Col$_{h2}$–Cub$_{V2}$–SmA–Cub$_{V1}$–Col$_{h1}$ with increasing volume fraction of the polar groups.[26,28] Hence, the same sequence of different mesophases as reported for diblock copolymers and lyotropic systems was obtained for the thermotropic phases of such amphiphiles.

In contrast to these polyhydroxy amphiphiles and other low molecular weight amphiphiles, where a strong incompatibility and in most cases additional attractive interactions (hydrogen bonding, Coulomb forces) are required for segregation,[36] in large molecules, such as block polymers, even minor chemical and structural differences are sufficient for mesophase formation.[20] This is due to the fact that segregation is disfavoured by the entropy of mixing and the entropy of mixing per unit volume decreases with the molecular weight. Hence, low molecular weight amphiphiles must possess a strong incompatibility between the different parts to produce the excess free energy contributions that are necessary for segregation. Consequently an increase in the molecular weight of the amphiphiles allows the reduction of the intramolecular incompatibility between the chemically distinct molecular parts. This concept was used by several groups for the design of novel mesophase forming materials at the borderline between low molecular weight amphiphiles and block copolymers.[15d,37–45]

Dendritic molecules were explored by Percec *et al.* A variety of molecular shapes, ranging from tapered *via* disc-like, conic, hemispheric to spherical have been realised with benzyl ether dendrons carrying alkoxy chains at the periphery (see

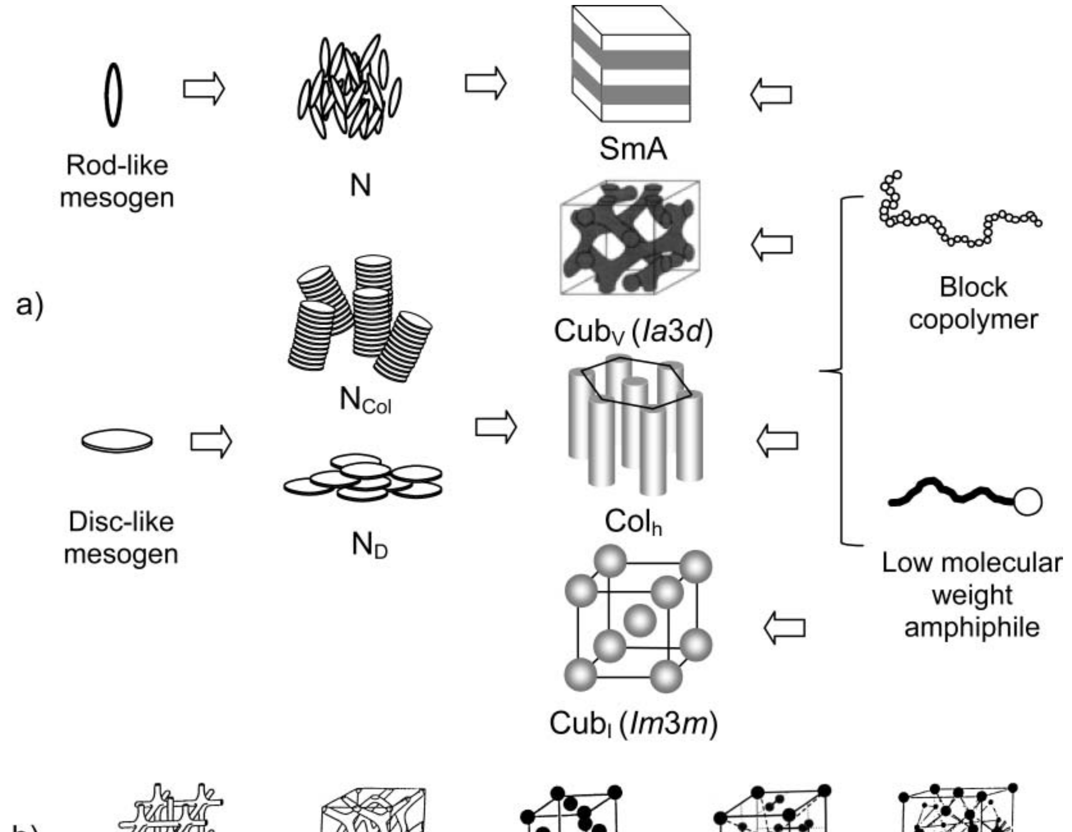


**Fig. 1** (a) Fundamental mesophase morphologies formed by the organisation of calamitic or disc-like molecules, binary amphiphiles and coil–coil AB diblock copolymers. Abbreviations: N = nematic mesophase formed by calamitic molecules (N), disc-like molecules (N$_D$) or columnar aggregates (N$_{Col}$), SmA = smectic A phase, Cub$_V$ = bicontinuous cubic phase, Col$_h$ = hexagonal columnar mesophase and Cub$_I$ = discontinuous (micellar) cubic mesophase. The shown cubic lattices (*Ia*3*d* and *Im*3*m*) correspond to those observed in coil–coil diblock copolymers. (b) Additional variants of cubic lattices of bicontinuous (Cub$_V$) and discontinuous cubic phases (Cub$_I$) occurring in the thermotropic and lyotropic phase sequences of binary amphiphiles. Remember, that the *Im*3*m* lattice can represent a bicontinuous structure as well as an array of spherical micelles.

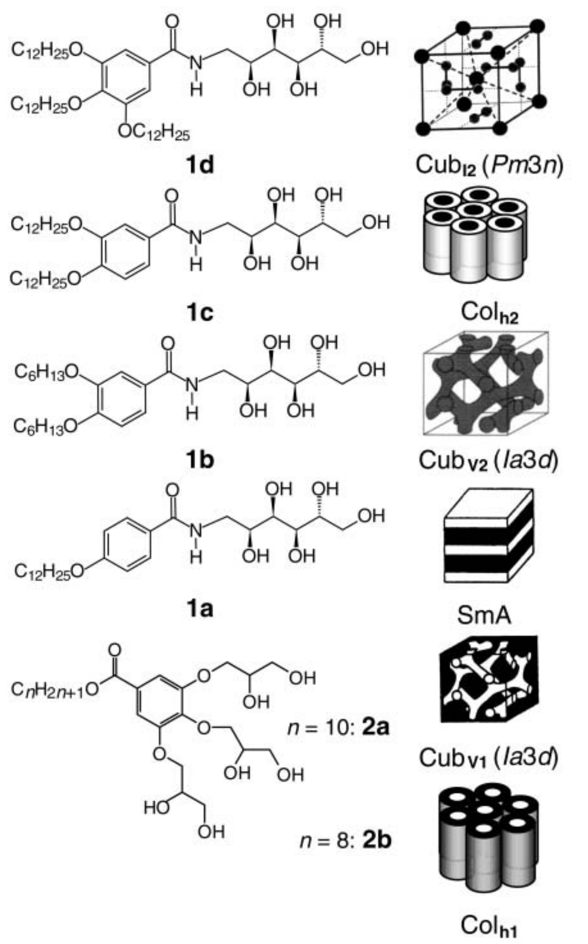


**Fig. 2** Dependence of the mesophase type of the polyhydroxy amphiphiles **1a–d**, **2a** and **2b** on the molecular structure. For the abbreviations see Fig. 1; the additional subscripts 1 and 2 describe normal type and reversed type mesophases, respectively.

Fig. 3).[37,38] Here, the main contribution to segregation arises from the incompatibility of the aromatic benzyl ether cores with the peripheral aliphatic chains, and the functional groups at the focal point are less important than in low molecular weight amphiphiles. Furthermore, the specific topology of connection of the molecular subunits within such molecules favours a tapered or cone-like average shape for most of these molecules. This rather specific shape and the larger volume fractions of the apolar periphery with respect to the polar dendritic core favour their organisation in columns or in spheroidic aggregates, leading to hexagonal columnar or micellar cubic phases over wide temperature ranges, whereas lamellar and bicontinuous cubic phases are disfavoured.

Also dendritic[39,40] and non-dendritic[41–45] molecules with no preference for a specific shape can form liquid crystalline phases based on micro-segregation. For example, the pentaerythritol tetrabenzoates (*e.g.* compound **4b** in Fig. 4a), in which the tapered segments are fixed to a tetrahedral central unit, show hexagonal columnar mesophases if two long alkyl chains are grafted on to each of the aromatic rings.[42] The stability of these mesophases was significantly increased by replacing the alkyl chains with semifluorinated chains (compound **4a**), due to the enhanced incompatibility of such chains with the aromatic cores.[43] With such compounds it was possible to change the mesophase morphology from lamellar (compound **3a**) *via* bicontinuous cubic (Cub$_V$, compound **3b**)[46] and hexagonal columnar (Col$_h$, compound **4a**) to micellar cubic (Cub$_I$, lattice: *Pm*3*n*, compound **5**) by changing the number and the length of the semifluorinated chains (Fig. 4a).[44]

Interestingly, the *Pm*3*n* lattice dominates the thermotropic micellar cubic phases (Cub$_{I2}$-phases[47]) for all low and medium molecular weight amphiphiles.[25] There is only one case of a dendritic molecule for which an *Im*3*m* lattice was confirmed.[38,48] This contrasts with the Cub$_I$ phases of block-copolymers which usually have *Im*3*m* lattices[20] and the reversed Cub$_{I2}$ phases of lyotropic systems which have the space group *Fd*3*m*.[9]

Another important observation is that the mesophase morphology of amphiphilic polyhydroxy compounds and

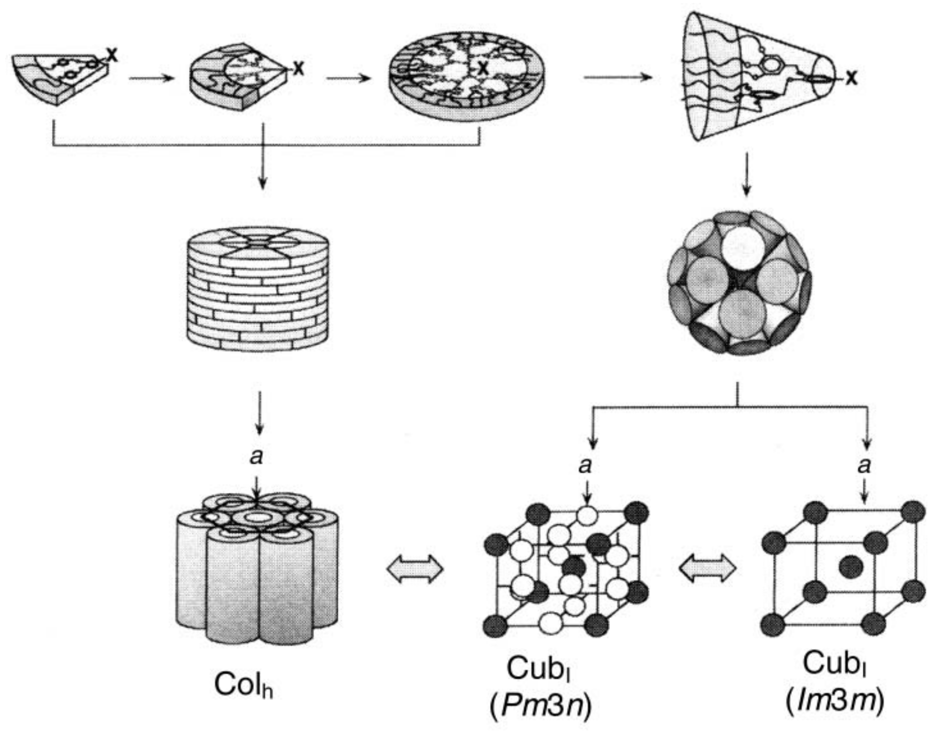
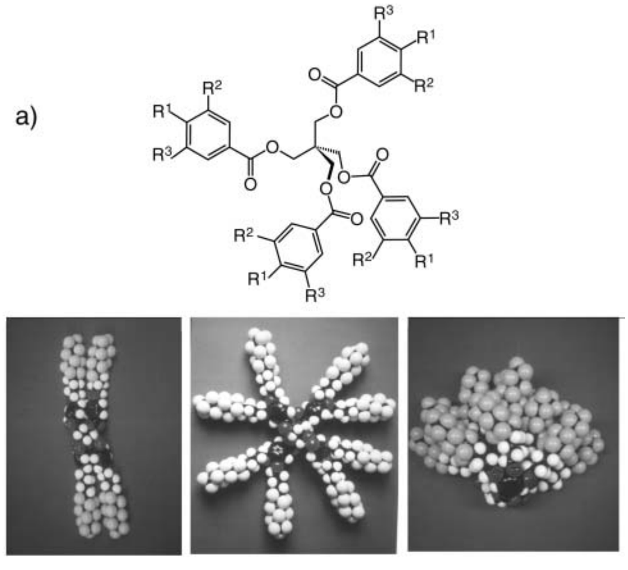


**Fig. 3** Self-assembly of benzyl ether dendrons in columnar and cubic mesophases (reprinted with permission from ref. 38 ©, 2001, American Chemical Society).



**3a:** SmA
**3b:** Cub$_V$

**4a, 4b:** Col$_h$

**5:** Cub$_I$
(*Pm*3*n*)

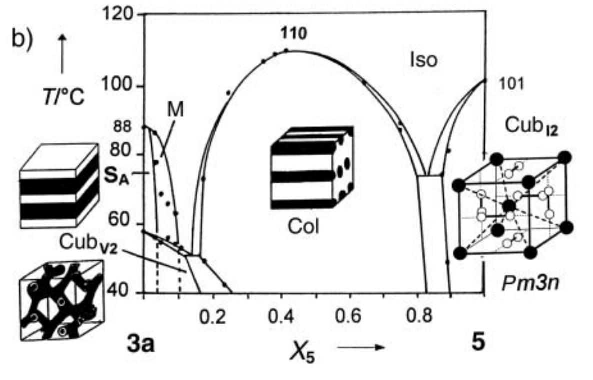


**Fig. 4** (a) Structures and mesophases of the pentaerythritol tetrabenzoates **3**–**5** (**3**: $R^1 = R$ and $R^2$, $R^3 = H$; **4**: $R^1$, $R^2 = R$ and $R^3 = H$; **5**: $R^1$–$R^3 = R$; **3a**, **4a** and **5**: $R = (CH_2)_4C_6F_{13}$; **3b**: $R = (CH_2)_6C_4F_9$; **4b**: $R = C_{10}H_{21}$) which are dependent on the number of chains and the degree of fluorination. The molecular models show the preferred average conformations of the compounds **3a**, **4a** and **5** in their mesophases.[44] (b) Binary phase diagram of the system **3a**/**5** (reprinted with permission from ref. 44 ©, 2000, Wiley-VCH). The abbreviations are explained in Fig. 1.

block molecules can be changed in a quite simple way by mixing structurally related molecules, which form different mesophase morphologies as pure materials.[26,28,44] For example, the binary system consisting of the two pentaerythritol tetrabenzoates **3a** (SmA) and **5** (Cub$_I$) is shown in Fig. 4b. Here, the phase sequence SmA–Cub$_V$–M–Col$_h$–Cub$_I$ was obtained by enhancing the concentration of **5** in **3a**.[44,49] This is the same sequence as obtained by the molecular design of the individual molecules. It shows that the realisation of the different mesophase morphologies requires only a correct tailoring of the average volume fractions of the incompatible molecular segments. However, this is only possible because these rather flexible molecules are miscible with each other. This is a significant advantage of these materials in comparison to rigid rod-like and disc-like mesogens, which are highly incompatible with each other and therefore do not allow the tailoring of their mesophase morphologies by physical mixing of rod-like and disc-like molecules.

Nevertheless, the variety of mesophases which can be realised with such simple binary amphiphiles is restricted to a few morphologies, namely layers (Sm), bicontinuous networks (Cub$_V$), columns (Col) and spheroidic aggregates (Cub$_I$). Only in special cases can additional intermediate phases occur in small temperature and concentration regions at the transition between these fundamental mesophase morphologies. So, non-cubic (rhombohedral or tetragonal) network structures,[9] modulated and undulated layer structures,[50] and different types of mesh phases[51,52] have been observed at the transition between lamellar and columnar organisation of polyelectrolyte–surfactant complexes[50] and in lyotropic systems.[9,51] Metastable hexagonally perforated layer structures are known in diblock copolymers[20,53] and a modulated columnar phase with a cubic lattice was reported as an intermediate phase between columnar and micellar cubic organisation of polyelectrolyte–surfactant complexes.[50]

An important task concerns the generation of self-organised systems with more complex mesophase morphologies. This can be achieved by (i) increasing the number of incompatible units combined in the molecules, by (ii) combination of microsegregation with the shape-dependent organisation of anisometric segments and by (iii) tailoring the molecular topology. In this report attention is focused on recent progress in the field of molecular design of non-conventional mesophase forming materials with new mesophase morphologies, which are different from simple smectic and columnar phases.

## 2. Complex morphologies of ABC triblock copolymers

Polymer chemistry and physics have done pioneering work in the exploration of complex mesophase morphologies with polyphilic block copolymers, consisting of three or even more chemically different constituents.[20,21,54] For example, the phase behaviour of ABC-triblock copolymers, containing three incompatible segments, is not only governed by the two independent volume fractions $\phi_A$, $\phi_B$ and the three interaction parameters between the blocks ($\chi_{AB}$, $\chi_{AC}$ and $\chi_{BC}$), but additionally by the topology of the connection of the blocks. In the case of ternary ABC systems linear, cyclic and star-shaped polymer geometries are possible, and in the case of linear polymers the block sequence (ABC, BAC, ACB) is an additional variable.[55]

In earlier studies, triple layer structures, morphologies comprising two sets of different cylinders, spheres or interwoven networks in the continuum of the third block (Fig. 5a) as well as different core–shell morphologies (Fig. 5b) have been found.[20,54,56–61] In the core–shell morphologies the spherical, cylindrical or gyroid cores of the minority end component are separated from the continuum of the majority end block by a shell of the middle block.

A number of new morphologies have been discovered by the group of Stadler in linear poly(**s**tyrene)–poly(**b**utadiene)–poly(**m**ethyl methacrylate) (SBM) triblocks and the corresponding hydrogenated analogues poly(**s**tyrene)–poly(**e**thylene-*co*-**b**utylene)–poly(**m**ethyl methacrylate) (SEBM).[62–64] Reduction of the volume fraction of the middle block B in SBM triblocks with a similar volume fraction for S and M, gives rise to a transition from the lamellar triple layer morphology, *via* a lamellar morphology with cylinders of B at the interfaces between the S and M lamellae, to a morphology comprising spheres of B at the interfaces between the S and M lamellae (see Fig. 5c).[65] This means that with decreasing B-fraction, the layers of the B-component break with formation of columns and spheroids. This is closely related to the sequence lamellae–columns–spheroids in diblock systems, but in the triblock copolymers this phase sequence occurs in the confined environment between the S and M layers.

In an analogous way, starting with the *cylinder-in-cylinder* morphology (Fig. 6a) reduction of the volume fraction of the middle block leads to break up of the continuous B-shell of the cylinders along the main axis of the cylinders to form four isolated cylinders at the S-cylinder–M-continuum interface (Fig. 6d). If the B cylinders are turned around the core

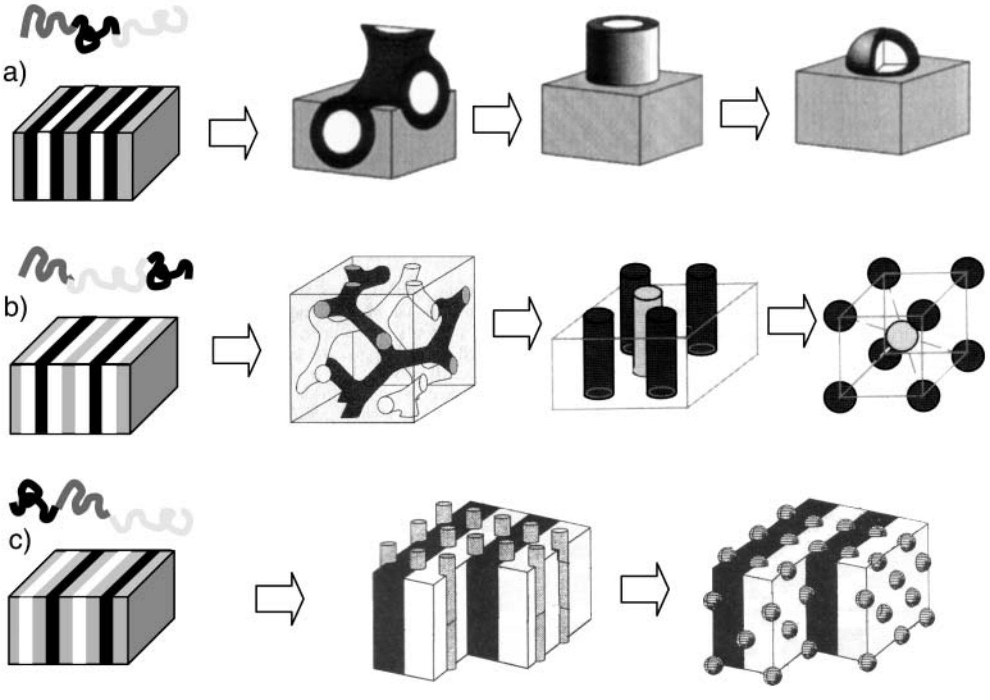


**Fig. 5** Selected morphologies of linear ABC triblock copolymers. (a) Triple-layer organisation and different core–shell morphologies, where the middle-block forms a shell around the minority end-block in the matrix of the majority end-block (reprinted with permission from ref. 71 ©, 2000, Wiley-VCH). (b) Triple-layer organisation and morphologies consisting of two types of bicontinuous networks, columns or spheres in the continuum of the middle-block. (c) Triple-layer organisation and morphologies with columns or spheres of the middle-block at the interfaces between the segregated regions of the end-blocks (reprinted with permission from ref. 64 ©, 1995, The American Chemical Society).

cylinders of S they form helices (Fig. 6e). This was the first example for a spontaneous assembly of a non-chiral block copolymer in a helical, *i.e.* chiral superstructure. In the related SEBM triblocks the cylinder shells break perpendicular to the main axis which leads to ring-like domains, instead (Fig. 6f).[63] The helical structures can be regarded as intermediate situations between the two "extreme" cylinder morphologies 6d and 6f. Undulated and perforated shells around the

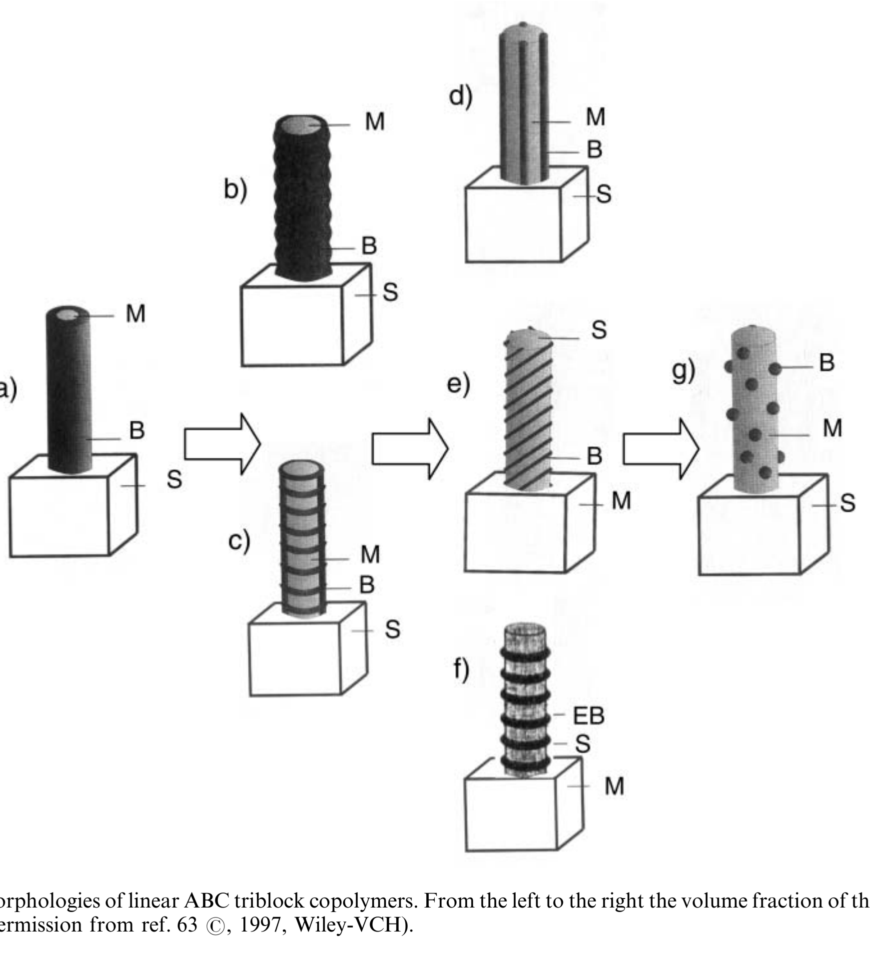


**Fig. 6** Various cylinder morphologies of linear ABC triblock copolymers. From the left to the right the volume fraction of the middle block (black) is reduced (reprinted with permission from ref. 63 ©, 1997, Wiley-VCH).

cylinders are additional morphologies (Fig. 6b,c) occurring at the transition between the *cylinder-in-cylinder* core–shell morphology 6a and the *cylinder-on-cylinder* morphologies 6d–6f.[63]

By further reducing the volume fraction of the middle block, the B-domains at the cylinder walls break and form isolated B-spheres on the surfaces of the cylinder cores (Fig. 6g). More recently, also *spheres-on-sphere* morphologies were obtained, and in these the middle block forms small spheres on the interfaces between the large spheres of the minority end block and the matrix of the majority end block.[66] Hence, the development of these morphologies is essentially based on the formation of hierarchically ordered arrays of layers, columns and spheres. However, even more complex morphologies, as for example the helical morphology (Fig. 6e) and the so-called knitting pattern (Fig. 7a) can be obtained with these linear triblock copolymers. In the knitting pattern, first reported for an SEBM triblock with nearly equal fractions of each block, the lamellar structure formed by the S- and M-blocks is wavy and is deformed by the elliptical EB-columns, which are arranged with their elliptic long axis parallel and also perpendicular to the lamellae.[67]

Mixing of different triblock copolymers or diblocks with triblocks (blending) can further enhance the possibilities. For example, non-centrosymmetric (*i.e.* macroscopically polar) arrangement of layers,[68] new "knitting patterns" and other new morphologies, such as the "ticker tape" morphology shown in Fig. 7b, have been obtained in this way.[69–71]

While a lot of work has been published on linear ABC triblock copolymers, only relatively few studies on related ABC ternary star copolymers have been reported.[20,72–75] In contrast to the linear ABC triblocks, where the sequence of the blocks is important, the molecular architecture of the stars enables the system to form the contacts between the phases independently. As a consequence of the changed molecular topology, morphologies distinct from those of linear block-copolymers result. Heteroarm star terpolymers exhibit distinct three-phase microdomain structures, among them tetragonal (Fig. 8b) and hexagonal morphologies (Fig. 8c) composed of three sets of different cylinders, each containing one of the different components. Also core-shell morphologies[59,74a] and lamellar structures with cylinders enclosed in one of the lamellae (Fig. 8a) were observed.[75]

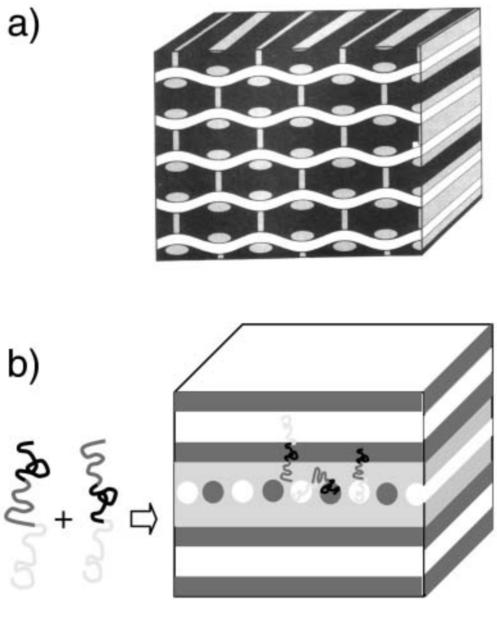


**Fig. 7** (a) The "knitting pattern" (reprinted with permission from ref. 67 ©, 1996, Wiley-VCH). (b) The "ticker-tape" morphology occurring in a blend of two different triblock copolymers.[71]

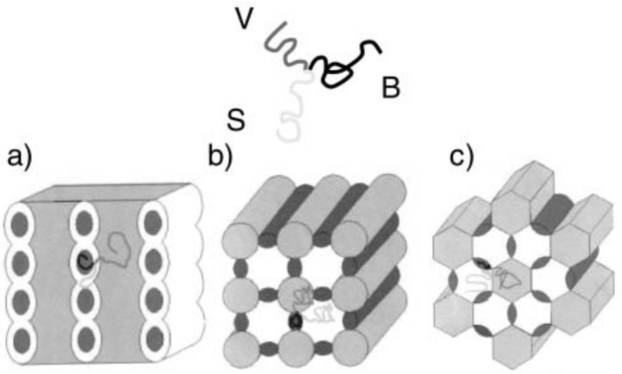


**Fig. 8** Selected morphologies of SBV [poly(styrene)–poly(butadiene)–poly(vinylpyridine)] star terpolymers. (a) Lamellar structure with lamellae comprising cylinders of the third component. (b) Tetragonal morphology. (c) Hexagonal morphology (reprinted with permission from ref. 75 ©, 2000, Wiley-VCH).

This shows that increasing the number of incompatible units and changing the topology of their connection is an appropriate way to form complex mesophase morphologies in block copolymers. The formation of these mesophase morphologies mainly results from the balance between the contribution of the interface energy and the elastic energy of chain stretching, which can be modified by the volume fractions of the blocks, their interaction parameter with each other and the position of the blocks with respect to each other.

## 3. Mesophase morphologies of low molecular weight block molecules

### 3.1. Low molecular weight materials *versus* polymers

Despite the great progress achieved with multiblock copolymers, polymer systems have some disadvantages in comparison to low molecular weight materials.

Firstly, polymers have a distribution of the molecular mass and polymers with a well-defined molecular structure are difficult to (re)produce.

Secondly, their ordered structures occur on a significantly longer length scale (*ca.* 100 nm) compared with the liquid crystalline phases (*ca.* 2–10 nm) of low molecular weight mesophase forming materials.

Finally, because of the high viscosity of the polymers, well-defined structures are difficult to obtain over large areas and they can respond only slowly to external stimuli. Therefore, to obtain macroscopically aligned samples, polymers are usually spread from solvents. Furthermore, optical textures typical for low molecular weight liquid crystals have only recently been observed for block-copolymers.[76] In other words, the molecular size not only gives rise to a longer *length scale* of the ordered structures, but also simultaneously leads to a significantly longer *time scale* for self-organisation and reorganisation. Because fast response times are important for many applications of mesophase forming materials, it is of interest to generate complex mesophase structures with low molecular weight molecules.

However, the larger impact of the entropy of mixing on such small-molecule systems requires a higher degree of incompatibility between the segments for their self organisation, whereas in the case of polymers even isotope effects can generate an incompatibility.[21] Therefore, the number of useful chemical structures available as building blocks for low molecular mass polyphilic block molecules is limited. Beside the well explored polar–apolar amphiphilicity (see Introduction), perfluoroalkyl groups and oligosiloxane fragments have become important. Another orthogonal set of incompatibilities arises from the rigid–flexible amphiphilicity. An additional advantage of rigid units is that they provide a quite specific molecular shape, often leading to orientational order. Furthermore, rigid molecular parts can lead to a specific molecular topology. This means that substituents at such rigid units have both a well-defined position and direction with respect to each other and to the rigid core units. This opens up additional possibilities for the design of mesophase forming materials.

Finally, the formation of uniformly tilted arrangements (such as SmC and $SmC_A$ phases and tilted columnar phases), which can arise from steric effects as well as from dipolar and quadrupolar interactions between the rigid segments,[77] is another useful specific property of such molecules.

### 3.2. Linear polyphilic block molecules incorporating rigid segments

The most investigated mesogenic molecules incorporating rod-like rigid units are the well known calamitic liquid crystals.[78] However, the cross-sectional areas of the terminally attached alkyl chains in such molecules are similar to those of the (mostly aromatic) rigid cores, and therefore, smectic phases dominate. Non-lamellar (columnar, cubic,[79] and other three-dimensionally ordered[80,81]) mesophases may result as a consequence of the onset and successive increase of the aromatic–aliphatic interface curvature by increasing the volume fraction of the alkyl chains. As shown in Fig. 9 these non-lamellar mesophases are the result of the organisation of ribbons of the collapsed layers into two- or three-dimensionally ordered lattices. Well-known examples are polycatenar mesogens,[82] swallow-tailed molecules,[83] long chain Ag(I) alkyl sulfate stilbazole complexes[84,85] and related metallomesogens.[86,87]

Also replacement of the alkyl chains by perfluoroalkyl chains[88,89] or oligo(dimethylsiloxane) chains[90–92] which have larger cross-sectional areas [$(CF_2)_n$: 0.27–0.31 nm$^2$; $(Me_2SiO)_n$: 0.43 nm$^2$] with respect to the aromatic cores (0.22 nm$^2$) can lead to cubic and columnar mesophases (*e.g.* compounds **7**[89] and **8**[93]). Rod–coil molecules, with extended rigid units and one or two coiled polymer chain(s), such as polybutadiene, poly(ethylene oxide) or poly(propylene oxide) at the terminal end(s) of the rods (*e.g.* compound **9**, Fig 10) represent another interesting class of mesogenic compounds forming not only smectic, but also bicontinuous cubic and columnar mesophases.[94–100] Even discrete micellar aggregates have been obtained with these calamitic molecules.[95] However, in contrast to the spheroidic micellar aggregates of flexible amphiphiles, which usually organise in micellar cubic mesophases, the closed micellar aggregates of the ABA coil–rod–coil molecules **9** represent disc-like segments, which organise to a three-dimensional body-centred tetragonal lattice (Tet, see Fig. 9).[95,101]

Polyphilic block molecules result, if chemically distinct groups (alkyl chains, polyether chains,[102] polar groups,[103–105] oligosiloxane segments,[106–108] perfluoroalkyl chains[88,109,110]) are attached to the opposite ends of calamitic molecules. Here, the incompatibility of the groups at the opposite terminal ends leads to layer structures composed of three distinct sublayers instead of only two in the smectic phases of the ABA compounds. However, in some cases steric effects can override the segregation of the different end-chains. For example, the tricatenar molecule **10a** with two bulky fluorocarbon chains at one end, and only one slim alkyl chain at the other end has a pronounced taper shape. This "steric dipole"[111] is strong enough to inhibit the segregation of the incompatible ends and leads to an antiparallel packing of the molecules in an SmA phase, built up by a sequence of aromatic sublayers and mixed fluoroaliphatic sublayers (Fig. 11a).[109] In the case of compound **10b**, in which the positions of aliphatic and fluorinated chains were exchanged (one perfluorinated chain at one end and two aliphatic chains at the other), the difference of the volume fractions of both ends is reduced. Here, segregation of the incompatible end-chains takes place and leads to a rectangular columnar phase built up of ribbons composed of three distinct sublayers.[109]

Similar effects have been found for ABC triblock molecules with a rigid end-block. For example, Tournilhac *et al.* reported that the SmE phase of the semifluorinated compound **11a** is characterised by the coexistence of three distinct sublayers, the layers of the crystallised and intercalated biphenyl cores, arranged in a herring-bone pattern, and the liquid-like layers of the aliphatic and the perfluorinated segments (Fig. 12a).[110] Remarkably, this mesophase combines highly ordered crystalline layers and disordered liquid-like layers in one structure. Analogous compounds with a reversed sequence of the aliphatic and perfluorinated segments (compound **11b**, Fig. 12b) form only an SmA-phase composed of sublayers of the fluorinated segments and sublayers of the intercalated aliphatic and aromatic regions. Hence, these molecules may be regarded as binary amphiphiles, in which only two incompatible parts are recognised.[110] This example additionally shows, that the *sequence* of the segments also has a large impact on the self-organisation of low molecular weight block molecules.

### 3.3. Calamitic molecules with terminal *and* lateral chains

**Lateral alkyl chains.** As shown above, the linear combination of three incompatible units in low molecular weight ABC triblock molecules predominately leads to layer structures and their modulated variants (columnar ribbon phases). A possible way to more complex structures with such low molecular weight block molecules should be provided by the non-linear combination of the incompatible units. Especially the non-linear connection of flexible chains with rigid segments should disturb the organization of the rigid cores in layers. This was first attempted with alkyl chains attached laterally to calamitic mesogens. The position of the lateral alkyl chain is very important. In the polycatenar molecules, the additional alkyl

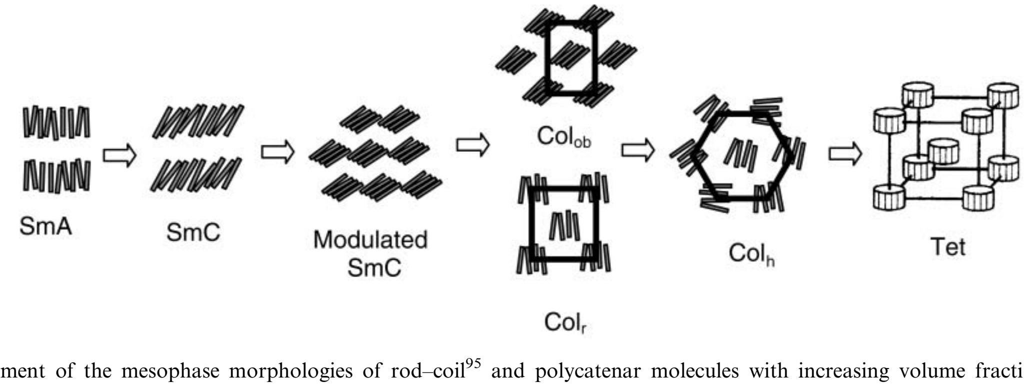


**Fig. 9** Development of the mesophase morphologies of rod–coil[95] and polycatenar molecules with increasing volume fraction of the flexible chains.[18,82] The chains which fill the space between the aggregates are not shown. Abbreviations: $Col_r$ = rectangular columnar phase, $Col_{ob}$ = oblique columnar phase, Tet = tetragonal mesophase, the other abbreviations are explained in Fig. 1.

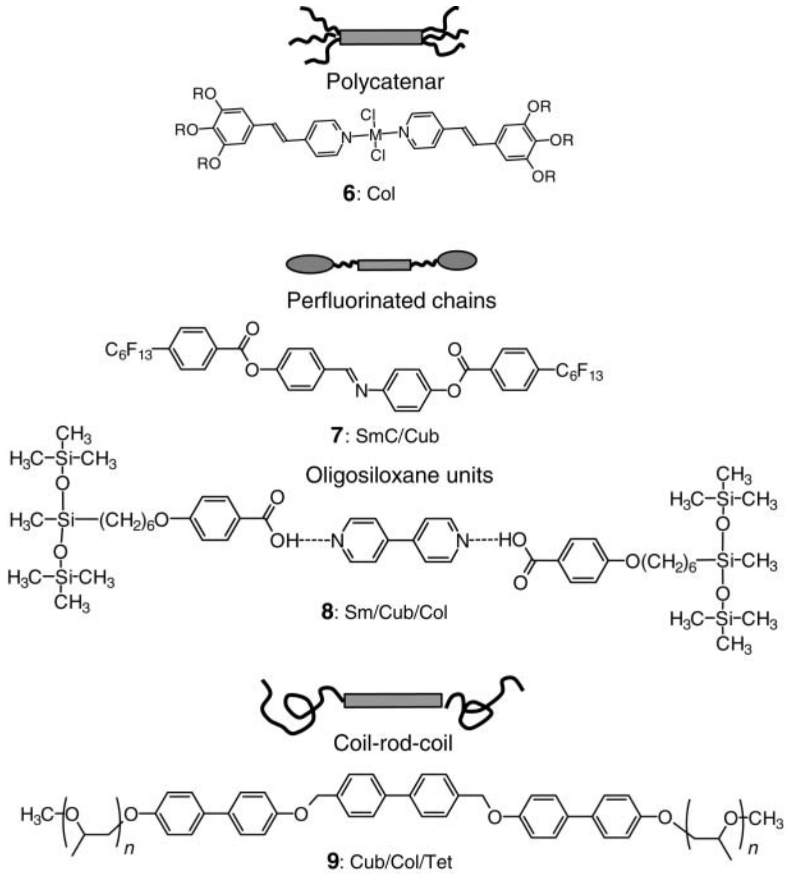


**Fig. 10** Selected examples of binary ABA block molecules forming columnar and cubic mesophases. A polycatenar molecule,[87] rod-like molecules with perfluorinated terminal chains[89] and oligosiloxane segments[93] and a coil–rod–coil molecule are shown.[97]

chains are grafted in lateral positions, directly beside the terminal alkyl chains (*ortho* to the terminal chains). In this way they can contribute to the volume fraction of the terminal chains, which due to space filling effects, leads to the above mentioned cubic and columnar phases.[82] In contrast, the connection of the aliphatic chain(s) to other lateral positions closer to the centre of the calamitic cores, gives rise to a complete collapse of the smectic layers, leading to nematic phases, accompanied by a drastic decrease of the isotropisation temperatures (see Fig. 13).[83,112] Hence, the position of the lateral alkyl chain has a large impact on the mesophase morphology of molecules with chemically identical or similar terminal and lateral chains. In such molecules, in addition to the steric effect of the lateral substituent, which disfavours the parallel alignment of the rigid cores, also the incompatibility of the lateral alkyl chains with the aromatic cores and especially their compatibility with the terminal alkyl chains are important. If the lateral chains are not located close to the terminal chains their segregation into distinct well-defined regions is disturbed and gives rise to disorder.

The situation becomes quite different, if the terminal and the lateral chains are incompatible with each other. Such ternary

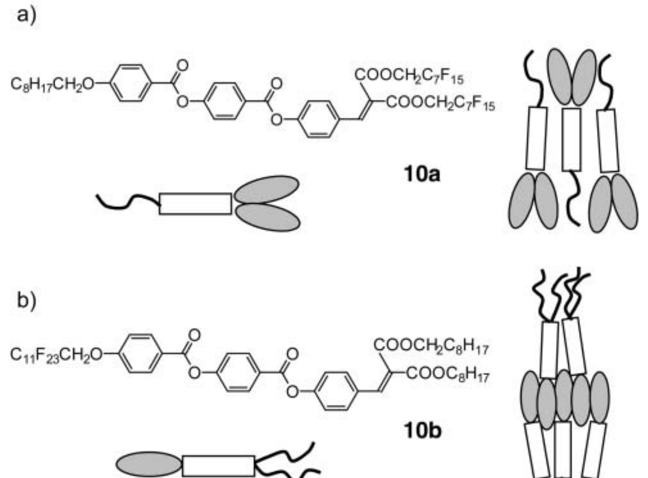


**Fig. 11** Influence of the position of the fluorinated chain(s) and the hydrocarbon chain(s) on the packing behaviour of the tricatenar compounds **10**.[109]

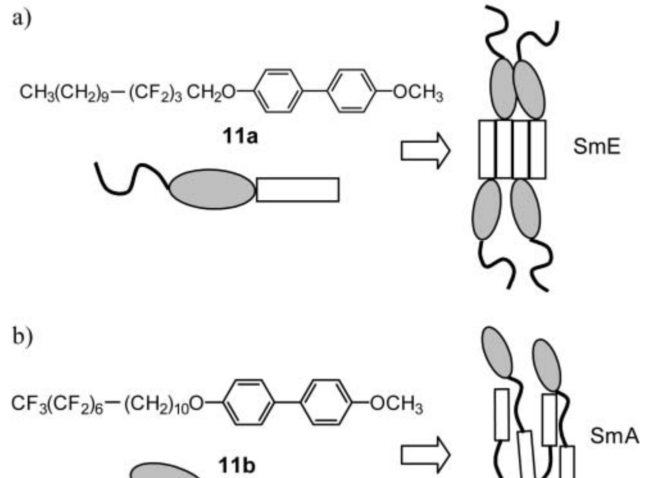


**Fig. 12** Influence of the block sequence on the packing behaviour of the linear ABC triblock molecules **11**.[110]

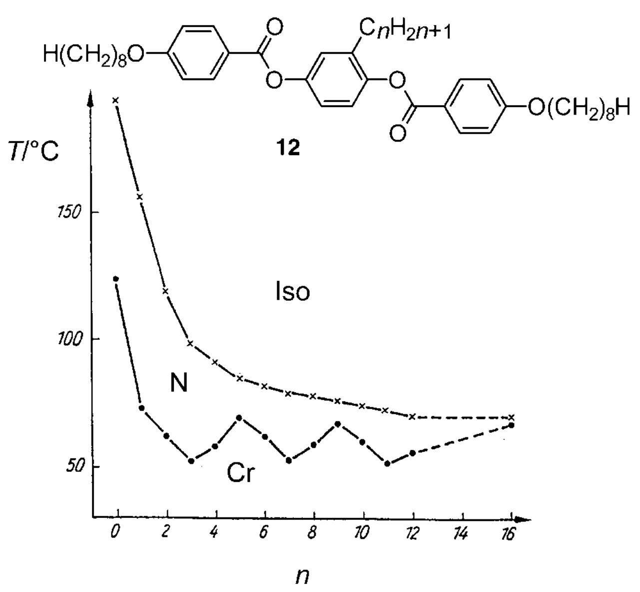
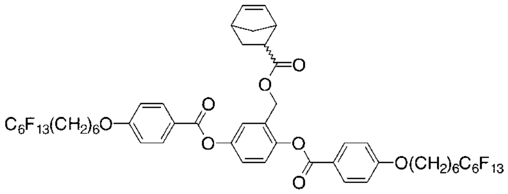


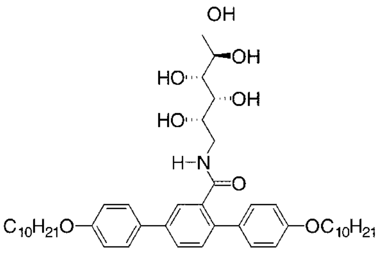
**Fig. 13** The effect of introduction and elongation of the lateral alkyl chain on the liquid crystalline properties of the calamitic mesogens **12** with aliphatic terminal chains. (reprinted with permission from ref. 83(*b*) ©, 1983, Wiley-VCH).

AB(C)A-triblock molecules may provide new mesophase morphologies.

Pugh *et al.* have shown that the smectic layer structures of calamitic mesogens with two semifluorinated terminal chains remain after introduction of aliphatic lateral substituents in a central position, even if they are very bulky (see compound **13**).[90,113] Because the fluorinated terminal segments are incompatible with the lateral groups as well as with the aromatic cores, the segregation of the central cores from the periphery remains in this case. Additionally, as the cross-section of the terminal fluorinated segments is larger than that of the aromatic parts, excess space becomes available to accommodate the lateral substituents between the aromatic cores. In this way the steric disturbance of the lateral substituents is less important. Moreover, the increased space filling within the non-fluorinated regions favours orthogonal SmA phases with respect to tilted (SmC) phases.[114]



**13**: Cr 78 (SmC 60) SmA 154 Iso



**14**: Cr 112 SmA 147 Iso

**Polar lateral substituents.** Weissflog *et al.* have demonstrated that large aromatic lateral substituents with electron acceptor properties can stabilise smectic A phases of calamitic molecules with two terminal alkyl chains, probably due to attractive polar interactions between the electron-rich aromatic cores and the electron-deficient substituents.[83]

A mesophase stabilising effect of lateral substituents was also achieved with functional groups that provide strong cohesive forces by hydrogen bonding, as shown in our laboratories for *p*-terphenyl mesogens with lateral diol groups, carboxy groups or carbohydrate units (*e.g.* compounds **14** and **16a**).[115] A wide variety of such compounds has been synthesised, and in all cases the smectic A phases are favoured over nematic phases (see for example compounds **15** and **16a** in Fig. 14). Here, the smectic layers are stabilised by (i) the preorganisation of the molecules by the intermolecular hydrogen bonding and (ii) by the increased polarity contrast between the central molecular

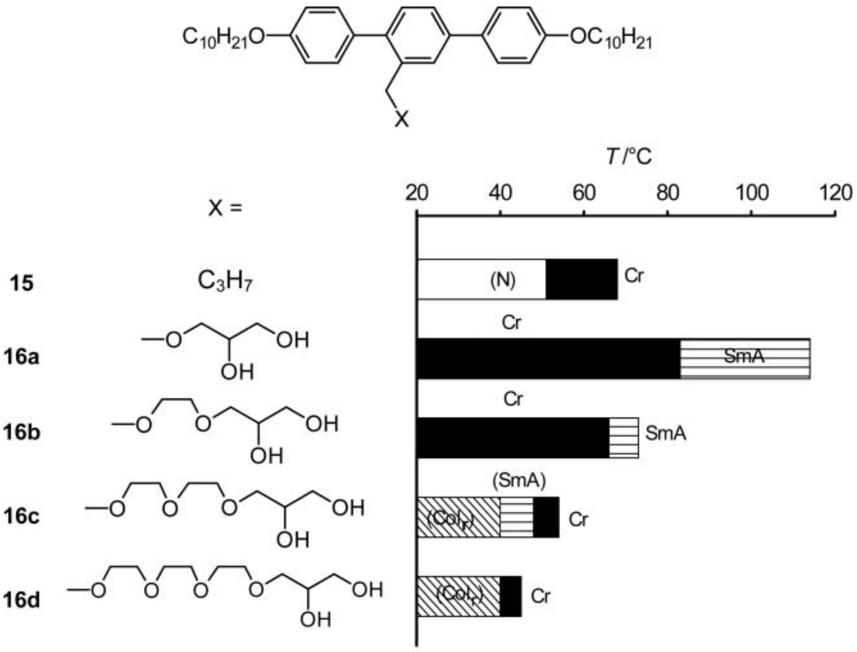


**Fig. 14** Mesomorphic properties of the facial amphiphiles **16** and their dependence on the length of the lateral chains.[116] Compound **15** is included as an example of an AB(A)A molecule with a lateral alkyl chain.

parts (rigid cores + polar lateral substituents) and the non-polar terminal chains, and this counterbalances the disturbance due to unfavourable steric effects.

Insertion of oxyethylene units between the hydrogen bonding functional groups and the rigid cores of such molecules increases the volume fraction of the lateral substituents without providing additional OH-groups for hydrogen bonding. As shown in Fig. 14, this leads to a destabilisation of the SmA phases and to the induction of non-centred rectangular columnar mesophases ($Col_{r1}$).[116] The formation of these columnar phases was explained as the onset of an additional segregation process between the rigid aromatic cores and the flexible as well as polar lateral groups. Thereby, the lateral groups become organised in separate cylinders, which interrupt the smectic layers in regular intervals with formation of infinite ribbons of parallel aligned *p*-terphenyl cores (*ca.* four in the cross section). The layers of the aliphatic chains remain largely intact and separate the adjacent arrays of alternating columns of polar groups and ribbons of the aromatic cores (see Fig. 15a). Hence, this phase combines a lamellar and a columnar organisation, whereby adjacent arrays of columns are positionally and orientationally correlated.[117]

Remarkably, addition of polar protic solvents, such as water, formamide or ethylene glycol gives rise to a significant stabilisation of the columnar mesophases. If the pure compounds exhibit exclusively smectic phases (small lateral substituents), then columnar mesophases can be induced by these solvents. In the case of molecules with lateral crown-ether units, such as **17**, the stability of the columnar phases can additionally be influenced by metal salts. Thereby, the stability of the induced columnar phases depends on the size of the alkali metal ion and it is highest for cations which perfectly fit with the size of the cavity of the crown-ether units (see Fig. 16).[118] These observations can be explained by the specific interaction of the polar solvents (and ions) with the lateral chains by hydrogen bonding (and coordination of the metal ions), and both of these interactions give rise to additional attractive intermolecular interactions. As a consequence, the incompatibility of the lateral groups with the aliphatic and the aromatic segments is further increased. This reinforces segregation and stabilises the columnar mesophases. Furthermore, the volume fraction of the polar segments is enlarged by the coordinated solvent molecules (and ions), which facilitates the collapse of the smectic layers for steric reasons and additionally contributes to the formation of columnar phases.

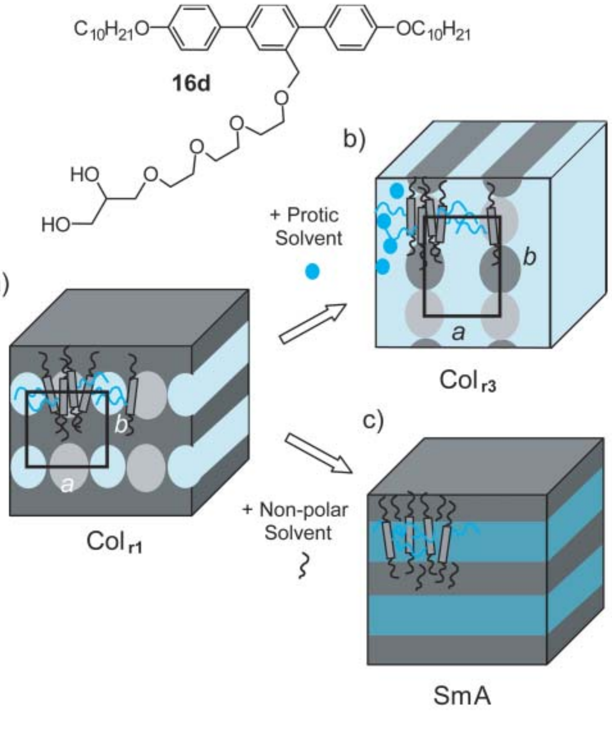


**Fig. 15** Models of the mesophase morphologies of the facial amphiphile **16d**. (a) $Col_{r1}$ phase of the pure compound.[116] (b) $Col_{r3}$ phase of the water-saturated sample.[119] (c) SmA-phase of the system **16d**–dodecane.[119]

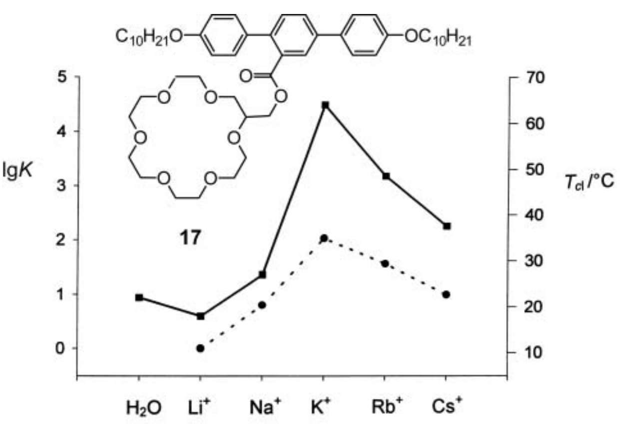


**Fig. 16** Dependence of the clearing temperatures $T_{cl}$. (——■——) of the induced columnar mesophases of the systems **17**–excess 1 M aqueous $M^+Cl^-$ on the type of cation and on the equilibrium constants lg*K* of the systems 18-crown-6–$M^+$ in water (…●…)(reprinted with permission from ref. 118 ©, 1997, Wiley-VCH). The transition temperatures of the pure compound **17** are: Cr 45 (SmA 13 N 15) Iso.

Compounds with long lateral polyether chains can coordinate more solvent molecules than those with shorter chains. For such compounds (**16c**,**d**), enhancing the concentration of the solvent can lead to phase transitions to other mesophases, which all have completely different optical textures.[119] Three different rectangular columnar phases have been observed for compound **16d** with increasing water concentration (see Fig. 17). The $Col_{r3}$ phase of the water saturated sample represents a non-centred rectangular columnar phase, which differs from the mesophase of the pure material only in the value of the lattice parameter *b*, which is attributed to the distance between adjacent arrays of columns (see Fig. 15a,b). The parameter *a*, corresponding to the lateral distance between identical columns, remains nearly the same in all columnar phases.[119] This was explained by an anisotropic swelling of the polar regions, which means that the polar regions expand

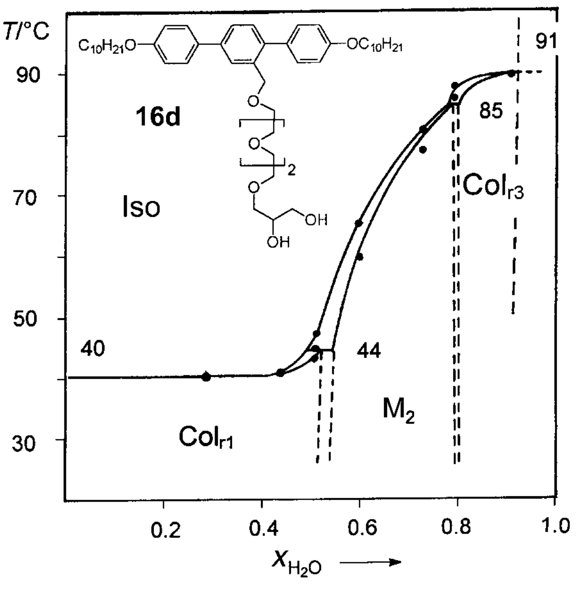
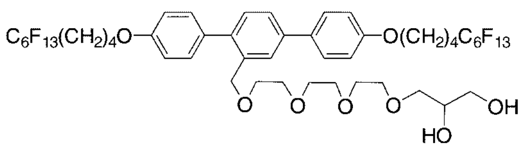


**Fig. 17** Binary phase diagram of the system **16d**–water (reprinted with permission from ref. 119 ©, 1998, The American Chemical Society).

perpendicular to the layer planes. In this way, the layers get disrupted and in the $\mathrm{Col}_{r3}$ phase, occurring at the highest water content (*ca.* 11 molecules per molecule **16d**), the polar regions should be fused to form polar layers which separate the hydrocarbon layers consisting of arrays of alternating ribbons of the parallel aligned aromatic cores and columns of fluid alkyl chains (see Fig. 15b). Hence, the columnar phases $\mathrm{Col}_{r1}$ and $\mathrm{Col}_{r3}$ should represent orthogonal sets of cylinder-layer morphologies, differing in the orientation of the calamitic cores with respect to the layer planes and also in the molecular parts which are localised within the uninterrupted layers of these mesophases.[119] $M_2$ seems to be an intermediate phase with a more complicated structure.

Lipophilic solvents have a reverse effect on the mesophase behaviour of such molecules, *i.e.* addition of such solvents (*e.g.* dodecane) destabilises the columnar phases and leads to SmA-phases.[119] This observation is also in accordance with the proposed models and can be explained as follows. The solvent molecules specifically interact with the terminal lipophilic chains and hence, they increase their volume fraction. In this way additional space becomes available between the aromatic cores and therefore the lateral groups can get distributed between the rigid cores, or the micro-segregated polar regions can become more disordered. As a consequence, the 2D lattice is lost, so that only the organisation in layers remains (see Fig. 15c).



**18**: Cr <20 SmA 161 Iso

**18** + Formamide: Cr <20 Col 135 SmA 137 Iso

The same effect is found if the terminal hydrocarbon chains of compound **16d** are replaced by more bulky semifluorinated chains (*e.g.* compound **18**).[120] Such molecules have a significantly enhanced mesophase stability due to the increased intramolecular incompatibility between the fluorinated chains and the central parts. However, they show exclusively smectic A phases. Columnar phases could only be induced with protic solvents, but only one columnar phase can be observed, instead of three. Additionally, it occurs at a rather high solvent concentration and it cannot completely replace the SmA-phase.[120] This shows that fluorinated facial amphiphiles like **18** require significantly larger lateral groups to disturb the layer arrangement to such an extent that columnar mesophases become possible. It should mainly be attributed to the larger cross sectional area of the fluorinated chains, which makes more space available between the rigid cores.

**Bolaamphiphiles with lateral alkyl chains.** More recently the designing principle of ternary block molecules was reversed with the bolaamphiphiles **19**, shown in Fig. 18.[121,122]

Here, the positions of the alkyl chains and the polar hydrogen-bonding groups have been exchanged in comparison to the facial amphiphiles **16–18**. As a consequence, the strongest attractive forces (hydrogen bonding) are now positioned at the terminal ends of the rigid calamitic cores. This molecular topology and the strong segregation of the polar groups from the biphenyl cores into separate sublayers leads to a dramatic stabilisation of smectic phases. Hence, the parent compound of this series without any lateral substituent (compound **19/0**) forms an extremely stable SmA-phase with monolayer structure ($\mathrm{SmA}_1$).[123–125] Introduction of a lateral alkyl chain and successive increase of its length leads to a sequence of quite interesting mesophases. Smectic phases were observed for all molecules ***19/n*** with short lateral chains ($n \leqslant 7$). Though they all have the same typical focal conic texture which can easily be aligned homeotropically, the SmA-phases of compounds **19/3–19/7** are distinct from those of the shorter homologues. Here, in contrast to conventional SmA-phases, a diffuse scattering is found in the small-angle region, which, on increasing the chain length, becomes dominating and replaces the sharp scattering of the layer structure. It seems that these SmA-phases ($\mathrm{SmA}^+$) have strongly disturbed layer structures. Preliminary investigations of aligned samples suggest that the diffuse small-angle scattering occurs perpendicular to the layer reflections and this points to an electron density modulation perpendicular to the layers.[122]

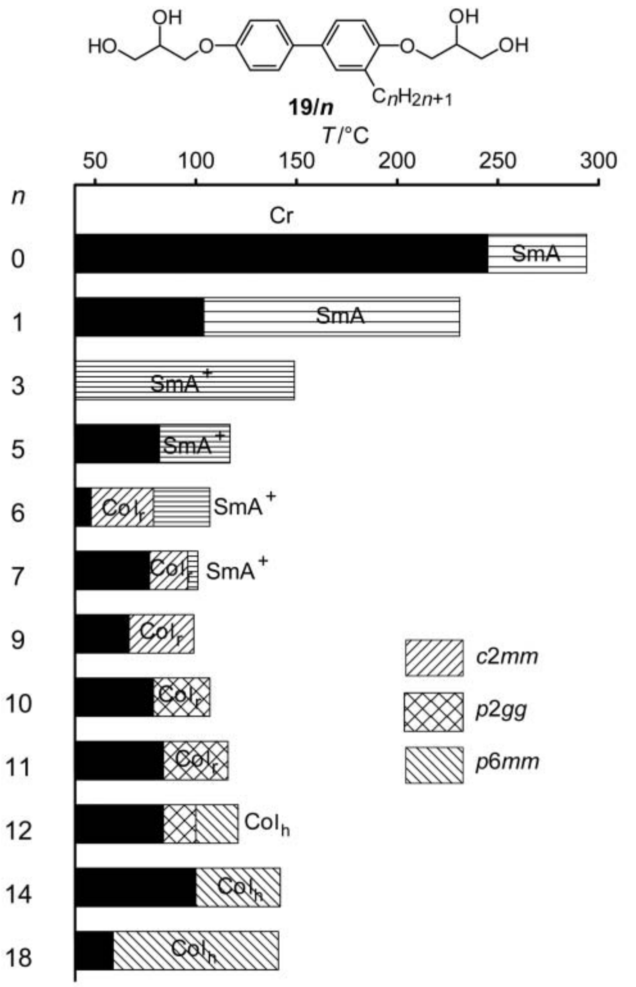


**Fig. 18** Influence of the length of the lateral alkyl chain on the mesomorphic properties of the bolaamphiphiles **19**.[122]

On further elongation of the lateral chains a quite interesting sequence of different columnar mesophases was found. At first, centred rectangular columnar phases with *c*2*mm*-lattices occur. They are replaced by non-centred rectangular columnar phases with *p*2*gg* lattices and the molecules with the longest alkyl chains exhibit hexagonal columnar phases ($\mathrm{Col}_h$, *p*6*mm*).

Fig. 19 gives an overview of the models proposed for the mesophases occurring and their dependence on the chain length. It seems that the lateral alkyl chains disturb the smectic monolayer structures (Fig. 19a) of the parent bolaamphiphiles and on elongation they segregate into well-defined distinct regions. The onset of this segregation obviously leads to the disordered structure of the $\mathrm{SmA}^+$ phase, at first. On further elongation the chains get organised in columns which register into the two-dimensional lattices of the *c*2*mm* phases. In these mesophases the bolaamphiphilic cores form networks of cylinders enclosing the lipophilic lateral chains (Fig. 19c). The cylinder walls are built up by the biphenyl cores which are

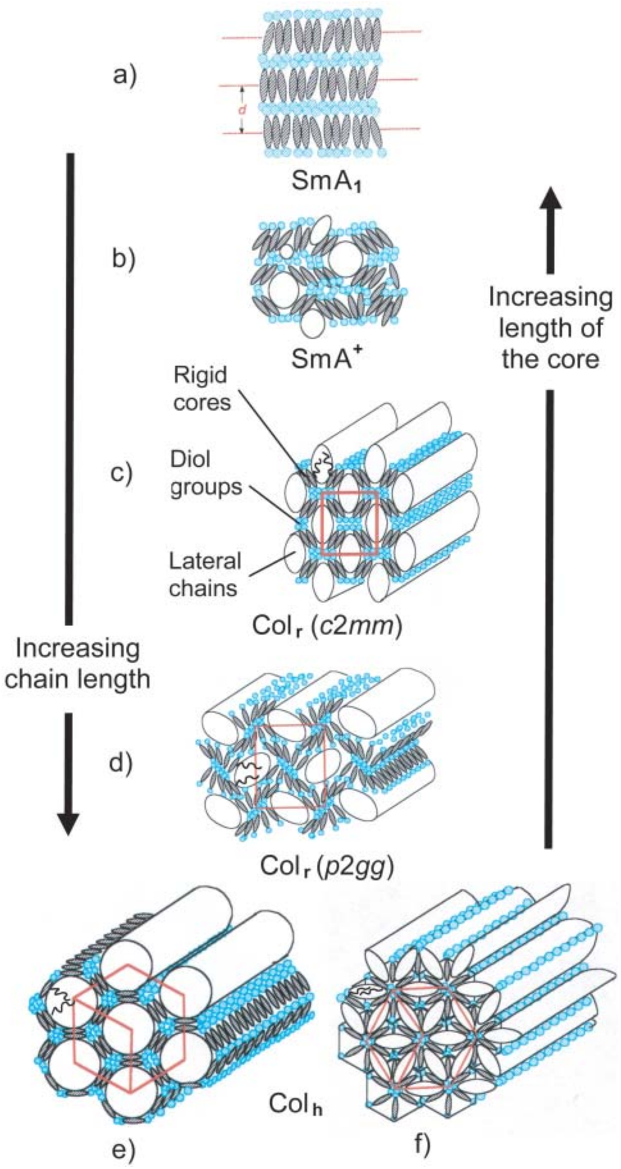


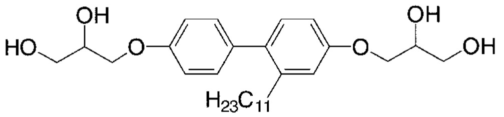
**Fig. 19** Proposed models of the molecular organisation in the mesophases of the bolaamphiphiles **19** and their dependence on the molecular structures.[122]

held together by ribbons of hydrogen bonding networks, acting as a kind of glue. Hence, the alkyl chains are enclosed in constrained environments and the space required by them with respect to the length of the bolaamphiphilic cores is limited. Therefore, enlarging the volume fraction of the lateral chains modifies the mesophase type. The transition from the *c*2*mm*-lattice ($n = 6$–9) to the *p*6*mm* lattice of the Col$_h$ phases ($n =$ 12–18) can take place by enhancement of the number of lipophilic columns, accompanied by the reduction of the number of calamitic cores in the cross-section of the aromatic ribbons, leading to the star-like arrangement shown in Fig. 19f. On the other hand, if the cross-sections of the lipophilic regions are increased and the number of calamitic cores surrounding the lipophilic columns is enhanced to six, the cylinder model shown in Fig. 19e results. Though this cylinder model seems more reasonable because of the minimized interfaces between the aliphatic and aromatic regions, a clear distinction between the two different models for the Col$_h$-phases is not yet possible.

For the organization of the compounds **19/10**–**19/12** with intermediate chain lengths ($n =$ 10–12) the herring-bone like organization within the *p*2*gg* lattice (Fig. 19d) seems to be the best possibility. Hence, the phase sequence SmA–SmA$^+$–Col$_r$(*c*2*mm*)–Col$_r$(*p*2*gg*)–Col$_h$, which is observed on increasing the length of the lateral chain, can be explained by rather simple geometric considerations.[122]

This explanation is also in line with the observation that the mesophase type depends not only on the length of the lateral chains, but also on the length of the bolaamphiphilic cores, which determines the amount of space available for the lateral chains. As shown in Fig. 20, the Col$_r$(*c*2*mm*) phase of **19/9** is replaced by the SmA$^+$-phase on elongation of the spacer unit. Because elongation of the bolaamphiphilic cores enlarges the space available for the accommodation of the lateral alkyl chains, this effect is opposite to the effect of elongation of the lateral chains. On the other hand, the phenol **24**, which has a shorter bolaamphiphilic core shows the Col$_h$ phase instead of the Col$_r$-phase of the related tetraol **19/9**.[122] This means that the Col$_h$ phase occurs with shorter chain length, if the length of the bolaamphiphilic core is diminished.

The fact that the mesophase type does not change with variation of the position of the lateral chain (**19/11** *versus* **25**) is also of significant importance. It shows that in such AB(C)A block molecules the position of the lateral chain has no significant influence on the mesophase morphology.[122] This is in sharp contrast to the behavior of the related AB(A)A molecules with compatible lateral and terminal chains.



**25:** Cr 78 (Col$_r$ [*p*2*gg*] 76) Iso

The same sequence of different mesophases, as shown in Fig. 19 was observed for the bolaamphiphiles **26**, with semifluorinated lateral chains (Fig. 21).[126] Again, the larger degree of incompatibility of the fluorinated chains with the other molecular segments gives rise to higher mesophase stabilities. Additionally, the volume fractions of the fluorinated chains are significantly larger than those of the analogous hydrocarbon chains with the same number of C-atoms. Therefore, the occurrence of the distinct columnar phase

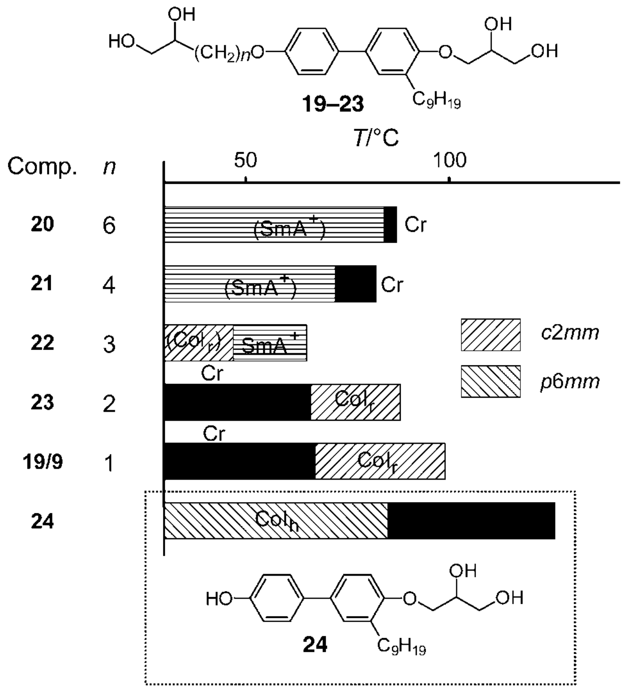


**Fig. 20** Influence of the length of the bolaamphiphilic core on the mesomorphic properties of compounds **19**–**24**.[122]

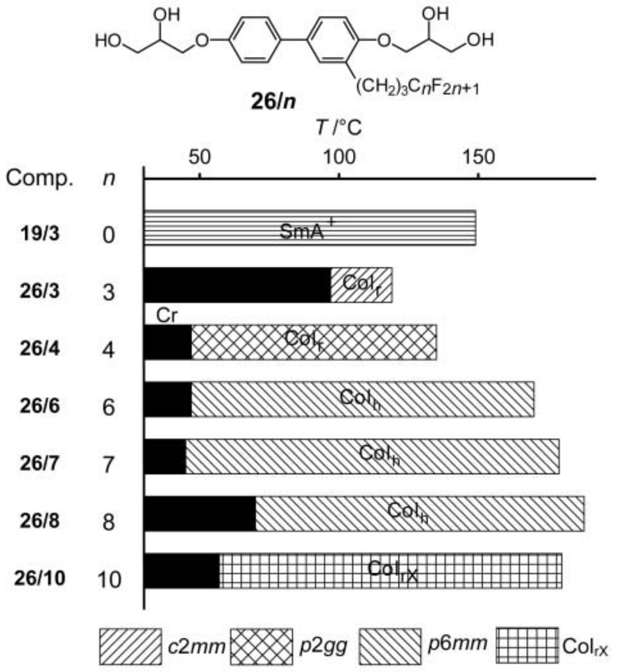


**Fig. 21** Influence of the length of the semifluorinated lateral chain on the mesomorphic properties of the bolaamphiphiles **26**.[126]

types is shifted to shorter chain length. Compound **26/6** with a semifluorinated lateral $C_9$-chain ($3CH_2+6CF_2$), for example, has a $Col_h$ phase instead of the *c2mm* lattice of the analogous hydrocarbon derivative **19/9** with the same number of C-atoms (compare Fig. 18 and 21). Additionally, compound **26/10**, which has the largest volume fraction of the lateral chain of all discussed compounds shows a novel rectangular columnar mesophase ($Col_{rX}$), distinct from the columnar phases of all other bolaamphiphiles with smaller lateral chains. Though the precise structure of this mesophase is not completely clear, this observation indicates that the mesophase type changes again on further enlargement of the lateral group,[126] which is in line with the suggested models of these columnar mesophases.

This shows that ternary AB(C)A block molecules provide access to a large number of mesophases with quite interesting structures. It should additionally be pointed out that the suggested mesophase morphologies of the columnar mesophases of the AB(C)A triblock compounds **16–26** are quite distinct from those observed for all other low molecular weight molecules. In the columnar phases of conventional amphiphiles,[9] disc-like molecules[17,18] or polycatenar molecules[82] the columns are surrounded by a *continuum*, in most cases consisting of fluid alkyl chains (or formed by solvent molecules as in the case of normal lyotropic systems). In the columnar mesophases of the bolaamphiphiles **16–26** the space is subdivided into three, instead of only two distinct subspaces. The columnar mesophases of the facial amphiphiles **16c** and **16d** are characterised by two different sets of columns embedded between the lamellae of the third component. In the columnar phases of the bolaamphiphiles **19** and **26**, space is subdivided into three distinct sets of columns – columns containing the fluid aliphatic chains, ribbons of aromatic units and ribbons of hydrogen bonding networks. Remarkably, the structures suggested for the $Col_r$(*c2mm*) phases and the $Col_h$ phases are closely related to the cylinder morphologies of the ABC star terpolymers, shown in Fig. 8b and 8c.[75] Additionally, the ordered structures formed by the bolaamphiphiles **19** and **26** have a significantly smaller length scale. Therefore, they have a low viscosity, similar to conventional smectic and columnar mesophases of other low molecular weight molecules.[127] Hence, the *competitive* combination of polar–apolar micro-segregation and rigid–flexible incompatibility turned out to be a successful designing principle for low molecular weight molecules, which are able to self-assemble to well organized states of soft matter with complex mesophase morphologies.

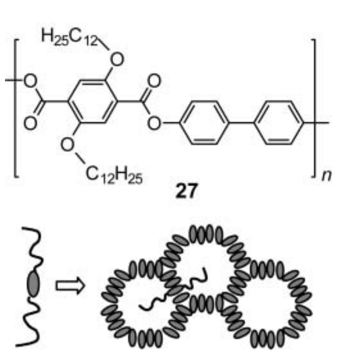


**Fig. 22** Organisation of the linear polymer **27** in the hexagonal columnar mesophase, the polymer chains lying perpendicular to the projection plane.[128]

Remarkably, a mesophase structure related to the cylinder model of the $Col_h$-phases of compounds **19/12–19/18** and **26/6-26/8** has been reported for the hexagonal columnar mesophase of the rigid polyester **27** with aliphatic side chains. As shown in Fig. 22, the extended rod-like aromatic polymer backbones aggregate with formation of a honeycomb-like network surrounding the cylindrical domains of the fluid lateral alkyl chains.[128] The main difference to the cylinder model of the bolaamphiphiles (Fig. 19e) is that the long axes of the polymers are arranged parallel to the main axes of these cylinders whereas the aromatic cores of the bolaamphiphiles are organised perpendicular to them.

### 3.4. Laminated mesophases – novel subgroups of smectic phases

Recently, several reports have appeared on special mesophases, formed by molecules with alkyl chains exclusively in the lateral positions at a rigid core. For example, SmA phases have been reported for the TTF-derivative **28**,[129] as well as for the high temperature mesophases of the 1,4,5,8-substituted anthracene **30** and the related anthraquinone **31**.[130] For the latter two compounds also monoclinic smectic low temperature mesophases (SmH and SmH′, see Fig. 23a–c) were observed. Palladium(II)–carbene complexes, such as **29**,[131] have highly ordered lamellar mesophases.[132] X-Ray investigations of the anthracene derivative **30** and the anthraquinone derivative **31** indicated that their low temperature mesophases are built up of defined sheets, in which the aromatic cores lie parallel to the

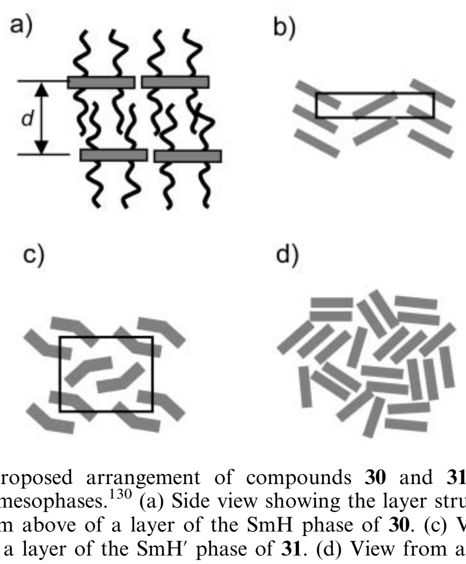
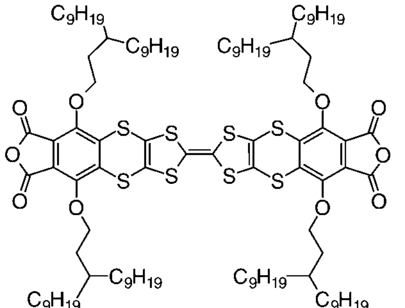
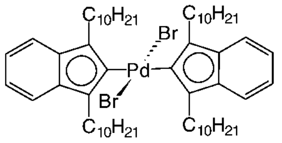


**Fig. 23** Proposed arrangement of compounds **30** and **31** in their lamellar mesophases.[130] (a) Side view showing the layer structure. (b) View from above of a layer of the SmH phase of **30**. (c) View from above of a layer of the SmH′ phase of **31**. (d) View from above of a possible arrangement of the molecules in the smectic layers of the high temperature phases.

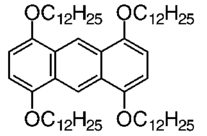
layer planes, adapting a herring bone arrangement with a face-to-face packing of the aromatic cores (Fig. 23). The sheets are separated from each other by the lipophilic sublayers of the fluid alkyl chains.[130] This structural model with well-defined alkyl and aryl sublayers should also be relevant for the mesophases of compounds **29** and the SmA phases of **28**, **30** and **31**. In contrast to the low temperature mesophases of **30** and **31**, in the SmA-phases the long axes of the cores should be randomly oriented within the aromatic layers,[133] but still aligned in average parallel to the layer planes (see Fig. 23d). This organisation is different from the arrangement of the molecules in the smectic phases of all conventional calamitic mesogens with terminal alkyl chains, where the rigid cores are organised perpendicular (SmA) or tilted (SmC) to the layers.



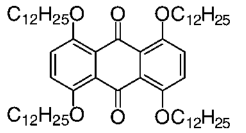
**28**



**29**



**30**



**31**

The organisation of the molecules in these novel mesophases is fundamentally based on the segregation of the aromatic cores from the aliphatic chains. Therefore, the necessary conditions for such an organisation should be (i) a sufficient incompatibility between the chains and the cores and (ii) an appropriate volume fraction of the chains, sufficiently large to allow the formation of discrete sublayers of fluid chains, but small enough to avoid a complete surrounding of the cores, which would lead to columnar phases. The nearly parallel and/or antiparallel preorganisation of flexible chains could additionally favour this organisation. The directed packing of the rigid segments is not a necessary condition for mesophase formation in such systems, but it could lead to additional order within the layers.

In principle, bolaamphiphiles with lateral chains should also fulfil the above mentioned requirements, especially, as the hydrogen bonds at the ends of the rigid cores give rise to a strong incompatibility of the central cores with the lipophilic chains and should facilitate an end-to-end organisation of the aromatic cores in the layers. Therefore, bolaamphiphiles comprising two semifluorinated lateral chains, such as **32** and bolaamphiphiles with reduced lengths of the bolaamphiphilic cores, such as **33** have been synthesised.[134] Though the pure compounds **32** and **33** have mesophases of unknown structures,[135] in binary mixtures with each other, a fluid optically biaxial smectic phase was detected over a wide concentration region.[134] This induced mesophase shows fan-like textures as well as schlieren textures (see for example Fig. 24), which cannot be homeotropically aligned. Furthermore, the schlieren texture is characterised by the absence of four brush disclinations, which would be expected for SmC-phases. This means that this mesophase should be distinct from conventional SmC-phases.[134] On the other hand, the observed textural features are quite similar to those recently found for biaxial SmA-phases ($SmA_b$) in binary systems of metallomesogens and TNF (see Fig. 37 in section 6).[136] On the basis of these observations a model in which the bolaamphiphilic cores are segregated from the semifluorinated lateral chains and simultaneously the calamitic cores of the bolaamphiphiles are arranged in average parallel to the smectic layers seems possible (Fig. 25a).[134] Also the layer thickness, determined by X-ray scattering is in accordance with this arrangement.[137]

As shown in Fig. 25 different structures are conceivable for such non-conventional smectic phases. Layer structures in which the calamitic cores have an orientational order, but no positional order, within the layers could be regarded as nematic phases which are laminated parallel to the long axes of the calamitic cores by the fluid layers of the non-polar chains (see Fig. 25a). Alternatively, they can be described as a special type of biaxial smectic phases (90°-tilted SmC-phases or $SmA_b$ phases). In these laminated nematic phases the adjacent layers are orientationally correlated. It can be expected that also laminated nematic phases without orientational correlation between the layers can occur (Fig. 25b), leading to optically uniaxial smectic phases. Furthermore, laminated analogues of smectic mesophases should be possible, where the molecules have an additional positional order within the layers (*e.g.* laminated SmA, SmC, $SmC_A$ phases).[138] Such laminated smectic phases could occur with or without correlation between adjacent layers. The orientationally correlated structure shown

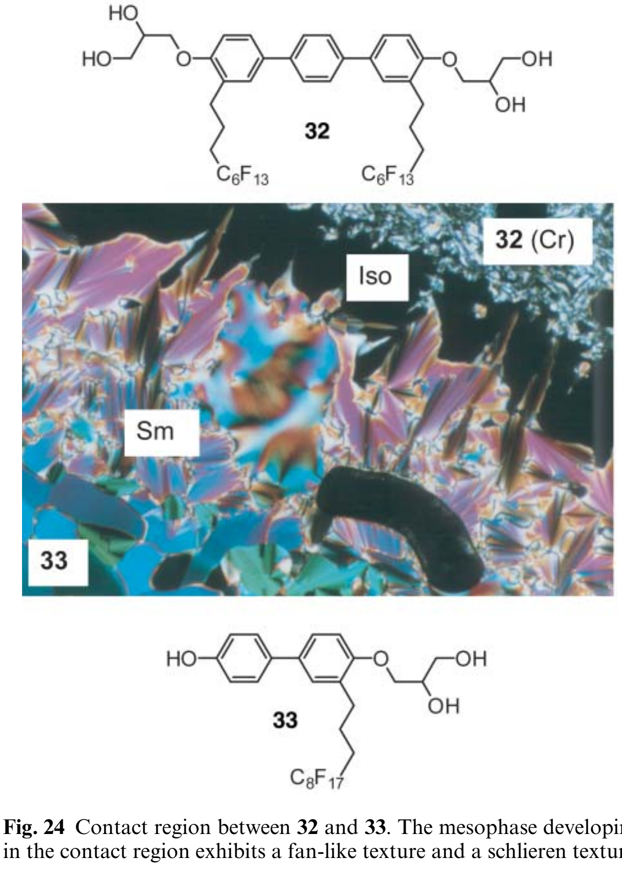


**Fig. 24** Contact region between **32** and **33**. The mesophase developing in the contact region exhibits a fan-like texture and a schlieren texture.

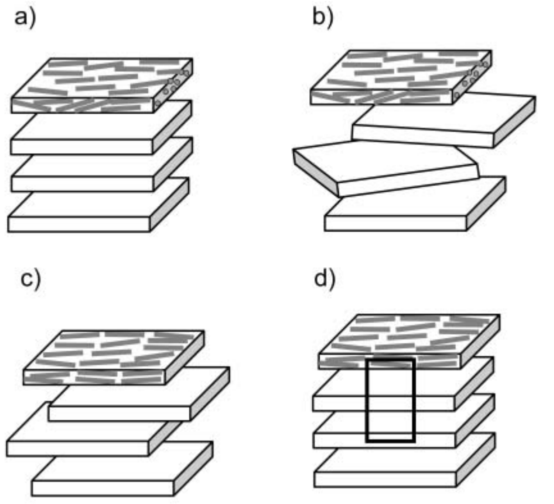


**Fig. 25** Laminated mesophases. (a) Laminated nematic phase with orientational correlation between the layers. (b) Laminated nematic phase without orientational correlation between the layers. (c) Laminated SmA phase with orientational, but no positional, correlation between adjacent layers. (d) Laminated SmA phase with orientational and positional correlation between adjacent layers ($Col_r$ phase).

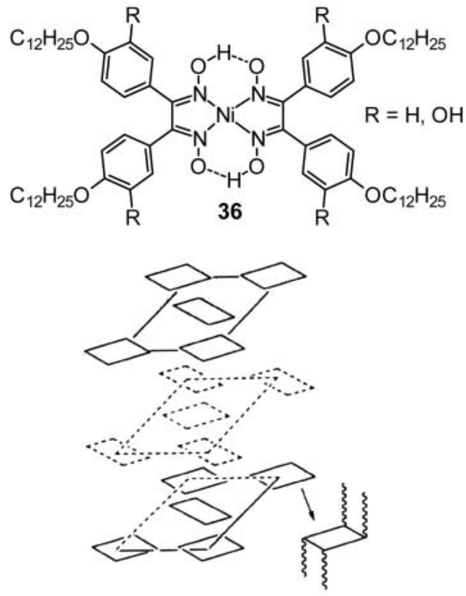
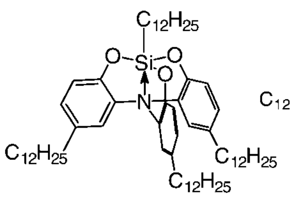


**Fig. 26** Structural model of the lamellar phase of the metallomesogen **36** comprising disc-like units arranged parallel to the layer planes (reprinted with permission from ref. 144 ©, 1998, The Royal Society of Chemistry).

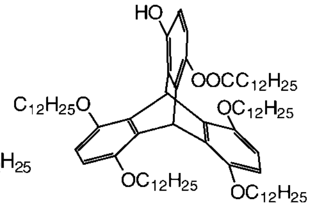
in Fig. 25(c) is in this respect related to lamellar columnar mesophases and to the sliding columnar phases of DNA–lipid complexes,[139] which will be discussed in section 6. The positional correlation between adjacent layers (Fig. 25d) would lead to different 2D-lattices (centred or non-centred rectangular columnar mesophases).

The induced smectic mesophase in the mixed system of the bolaamphiphiles **32**–**33** could correspond to a laminated nematic structure,[140] whereas the columnar phases of the pure compounds **32** and **33** and the structure proposed for the $Col_{r3}$-phase of the water saturated facial amphiphile **16d** (Fig. 15b) could possibly represent the first examples of laminated SmA phases with a positional and orientational correlation between the layers. However, additional investigations are necessary to further confirm the suggested mesophase structures.

If the aromatic cores are non-linear, then other organisations can occur within the layers. So, in the aromatic layers of the smectic phases of the tribenzosilatranes **34**[141] and the triptycenes **35**,[142] the $C_3$-symmetric cores are organised in two-dimensional hexagonal lattices ($Sm_h$ phases).



**34**



**35**

Smectic phases incorporating a tetragonal lattice ($Sm_t$-phases) have been reported for some quaternary ammonium amphiphiles.[143] In these mesophases the spherical or nearly spherical ionic groups (head groups and counter ions) are organised in tetragonal 2D-lattices within ionic sublayers, which are separated by the sublayers of the fluid alkyl chains. In some cases a three-dimensional tetragonal lattice was found, which means that there is an additional correlation between the layers.[143a]

A report by Ohta *et al.* claims a lamellar arrangement of disc-like molecules, organised with their disc-like cores parallel to the layer planes (see Fig. 26).[144] Here, the aromatic layers are built up by the edge-to-edge arranged disc-like cores. These sublayers are separated by sublayers of the fluid alkyl chains. Additionally, in this phase, there is a rectangular 2D-lattice within the layers and also a positional and orientational correlation between the adjacent layers, which leads to an in total three-dimensional structure of this mesophase.

Finally, conjugated aromatic polymers with flexible lateral chains have been shown to form smectic phases by the segregation of the rigid aromatic backbones from the flexible chains.[145]

These examples have shown that non-conventional molecular topologies can provide access to new mesophases with layer structures. These non-conventional lamellar phases differ from the fluid lamellar phases of simple binary amphiphiles (SmA, $L_\alpha$) by an additional orientational and/or positional order within one of the sublayers and from the classical smectic phases of rod-like molecules by the orientation of the rigid segments with respect to the smectic layers. Obviously, such laminated phases can be formed by a wide variety of molecules having quite different shapes. This shape-diversity and the numerous possible 2D arrangements in the layers as well as 3D correlations between the layers lead to a great diversity of possible mesophase structures. The design of novel laminated mesophases is a newly approaching topic in liquid crystal research and many new mesophase structures can be expected for such systems in the future.

## 4. Organisation at different length scales

Liquid crystals and block copolymers are two classes of materials that can undergo self organisation to mesophases at different length scales. Combining both in one molecule offers the opportunity to create well organised supramolecular systems with ordered structures at two different length scales, the LC-phase and the polymer morphology.[146–148] The broadest variety of such hierarchically ordered systems has recently been reported for diblock copolymers of polystyrene (S) and poly(4-vinylpyridine) where 4-*n*-nonadecylphenol is hydrogen bonded to the latter block, giving rise to supramolecular LC-segments (see Fig. 27). The LC-segments organise in an SmA-phase, which segregates from the

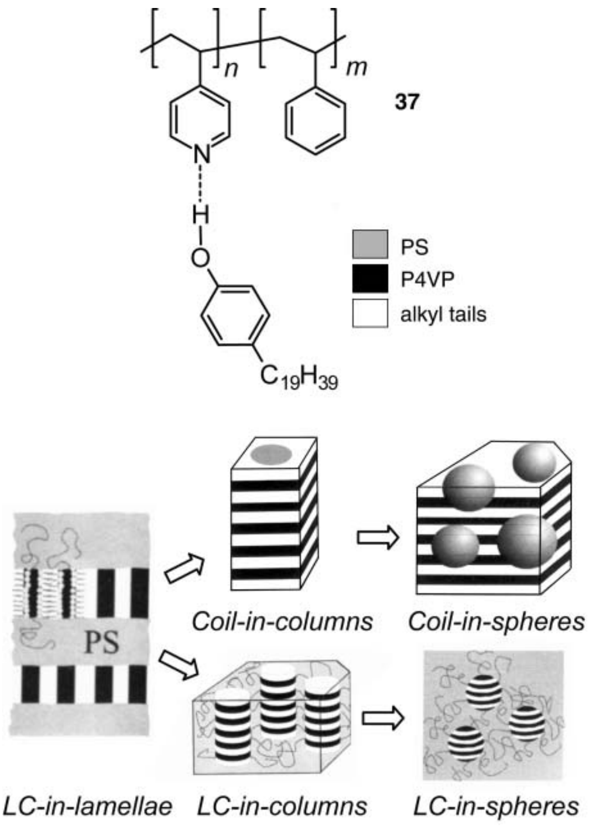


**Fig. 27** Different polymer morphologies comprising SmA domains formed by the LC-coil diblock copolymer **37** in dependence on the volume fraction of the coil segment (reprinted with permission from ref. 149 ©, 1999, Wiley-VCH.)

amorphous S-regions with formation of different polymer morphologies. In these morphologies the SmA-phase can fill the continuum surrounding S-columns or S-spheres or it can be enclosed within layers, columns or spheres, surrounded by the S-continuum.[149]

Additionally, there is a coupling between the confined geometry provided by the polymer morphology and the orientation of the individual mesogenic units relative to the LC-coil intermaterial interfaces. Within the columns and in the lamellae of the polymer morphology the layers of the mesogens preferably pack perpendicular to the interfaces. This is, because the polymer chains are stretched perpendicular to the interface and the orientation of the smectic layers is usually parallel to the stretching direction of the polymer backbones. If the supramolecular hydrogen bonded 4-nonadecylphenol–pyridine segments are regarded as calamitic mesogens, then, as sketched in Fig. 28, the topology of the polymer **37** is similar to the molecular topology of the facial amphiphile **16d**. In both cases flexible chains are fixed perpendicular with respect to the long axes of rigid segments and also perpendicular to a second, incompatible set of chains. Indeed, there are also some similarities of the *LC-in-lamellae* morphology of the polymer **37** with the organisation suggested for the lyotropic $\mathrm{Col}_{r3}$-phase of the facial amphiphile **16d** (see Fig. 15b). In both cases an SmA-phase is laminated perpendicular to the layer planes, but in the polymer system the layers have a larger thickness and distance, and they seem to be completely decoupled, *i.e.* there is no correlation between them.

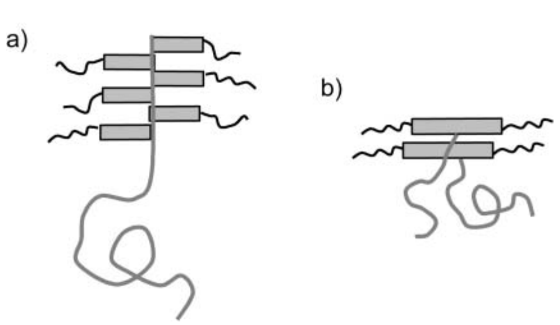


**Fig. 28** Comparison of the molecular topologies (a) of the LC-coil diblock copolymer **37** and (b) the facial amphiphile **16d**.

## 5. Impact of the molecular topology on the mesophases of oligomesogens and dendrimers incorporating calamitic rigid units

The covalent connection of two or more anisometric mesogenic units with each other is another way to influence mesophase morphologies.[83,150,151]

In such supramolecules the topology of connection (see Fig. 29) and the chemical structure of the spacer units which fix the rigid cores to each other have a large impact on the mesophase type. Oligomesogens[152] and dendritic liquid crystals,[153–155] in which the individual mesogenic units are connected in terminal positions to each other, give rise to materials that exhibit SmA and SmC phases, which are preferred over the nematic phases exhibited by many of the mesogenic monomers themselves. Generally, the stability of the mesophases increases with the number of mesogenic units combined in such molecules.[156] This is due to the fact that this molecular topology pre-organises the mesogenic units and the (chemically different) connecting units in distinct regions, and this favours their segregation and organisation in layers.

If, however, the mesogenic units are attached *laterally* to connecting units, which are highly incompatible with the calamitic mesogens, such as the siloxane core of compound **39**,[157] predominately nematic phases were found and the stability of the mesophases is only marginally influenced by the number of mesogenic units connected to each other. Smectic phases (SmC) were only obtained with oligomesogens with elongated rigid cores comprising at least four phenyl rings and long terminal alkyl chains. Though the mesogenic units are fixed side-by-side, which should favour an organisation in layers, the molecular topology is unfavourable for the segregation of the connecting units from the aromatic cores into distinct sublayers. Instead, the connecting units are forced to be largely located between the cores, and this disturbs any layer arrangement. Such oligomesogens are in some respect related to the AB(C)A block molecules with a rigid B-segment and incompatible lateral and terminal chains. Therefore, it can be expected that appropriate molecular design of such molecules could possibly also lead to novel non-conventional columnar and smectic phases, related to those of the facial amphiphiles **16** and the bolaamphiphiles **19** and **26**.

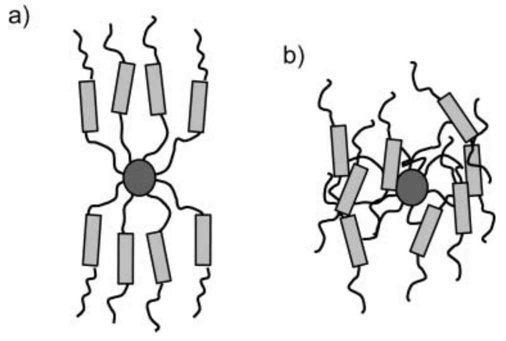
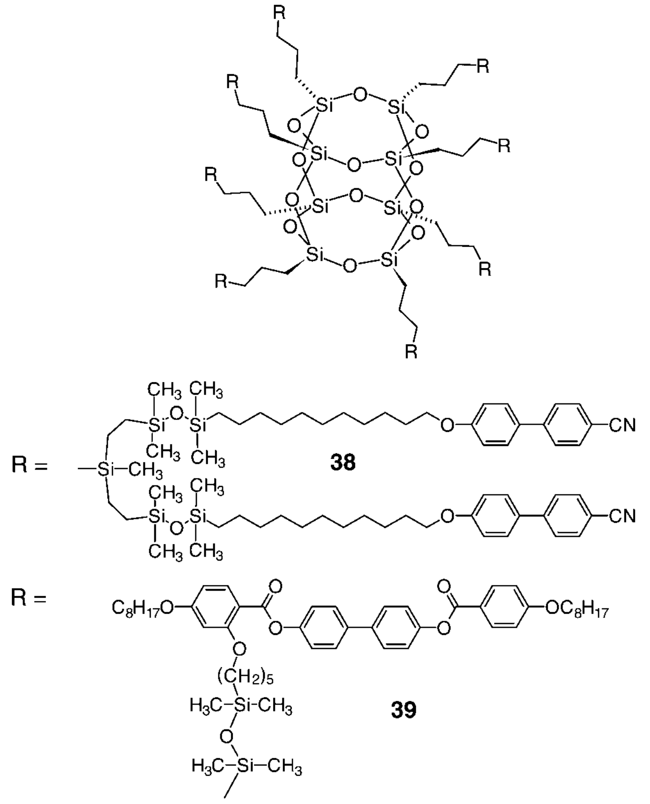
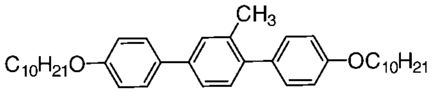


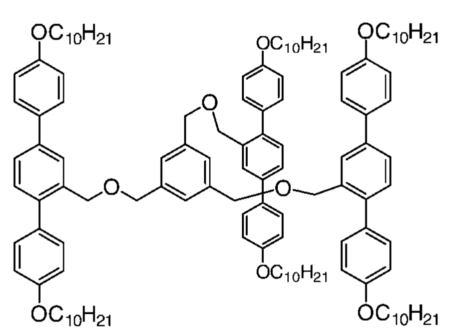
**Fig. 29** A schematic sketch of the molecular structures of oligomesogens, built up by calamitic mesogens attached terminally (a) and laterally (b) *via* spacer units to a central branching unit.



If the lateral connecting units are highly compatible with the rigid cores, the layer arrangement is not disturbed by the segregation of the connecting units from the aromatic cores, and the lamellar preorganisation of the cores is the dominating effect. In such cases nematic phases can be replaced by conventional smectic phases (SmA, SmC) and the mesophase stability can be increased as shown with compounds **40** and **41**.[158]



**40:** Cr 72 (SmC 70) SmA 104 N 109 Iso



**41:** Cr 73 SmA 124 Iso

## 6. New mesophase structures at the cross-over between lamellar and columnar organisation

In mesogenic systems formed by flexible amphiphiles the transition from lamellar to columnar organisation usually takes place *via* bicontinuous cubic mesophases.[9,15,26,28,44] Anisometric rigid segments have a large impact on the lamellar–columnar cross-over. So, in polycatenar molecules the cubic phases occur in quite unusual phase sequences, such as $\mathrm{Col_{ob}}$–SmC–*Cub* and SmC–*Cub*–SmA, and this cannot simply be explained on the basis of the development of an interface curvature.[79] Furthermore, the structures of the cubic phases, especially those with the *Im*3*m*-lattice are more complex than those formed by flexible amphiphiles,[159–164] and tetragonal or rhombohedral 3D phases can often be observed as companions of the cubic phases.[80,81]

An even larger impact on this transition can be expected for molecules with rigid cores extended in two dimensions (disc-like and sanidic rigid cores). The gradual change of the molecular shape from disc-like *via* sanidic to calamitic is shown in Fig. 30 for a series of porphyrin derivatives.[165,166] Here, the mesophase type changes from hexagonal columnar *via* rectangular columnar to lamellar, but no cubic phase was found as an intermediate phase at the transition between columnar and lamellar organisation.[167,168]

Also in the series of the multichain metallomesogens **46**[169] and related compounds (see Fig. 31),[170] the hexagonal columnar phases are replaced by SmA phases on reduction of the number of chains, whereas compound **46b** with an intermediate number of chains does not form any mesophase and again no cubic phase could be detected.[169] Hence, it seems that disc-shaped molecules use alternative pathways for this transition.

As shown in Fig. 32, this transition can take place *via* mesophases combining layer-like and columnar organisation in one structure. In a first step the flexible alkyl chains become unequally distributed around the aromatic regions. This can be due to a non-circular shape of the molecules, a reduced number of flexible chains or an unequal distribution of the chains around the rigid cores. In this structure the majority of chains

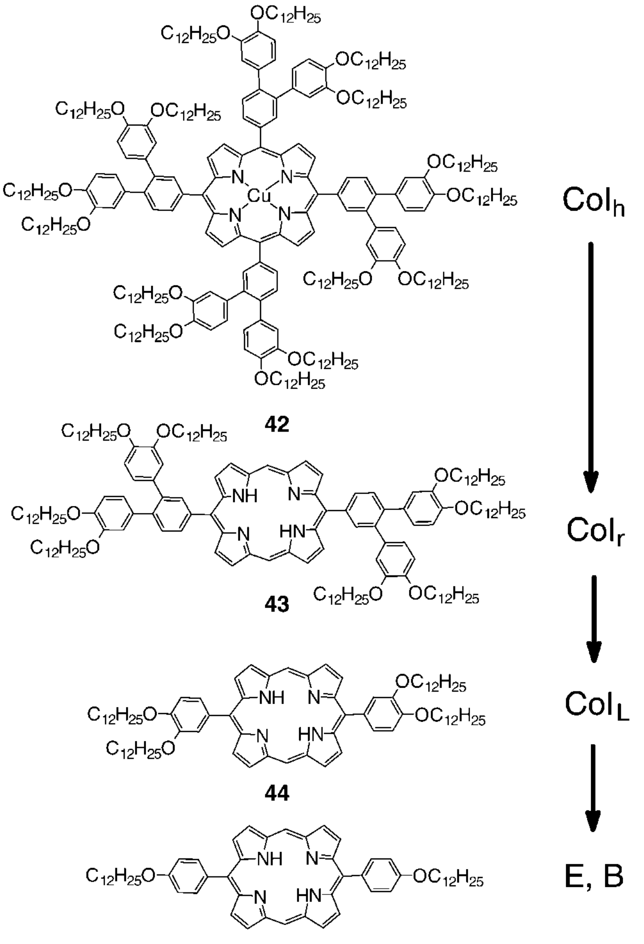
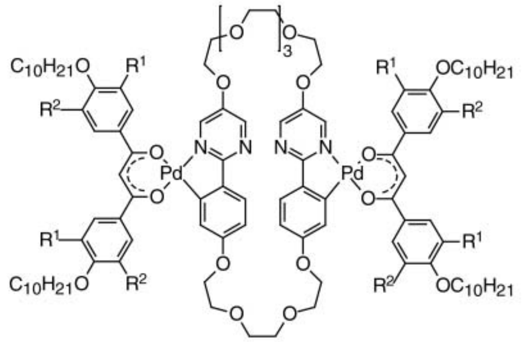


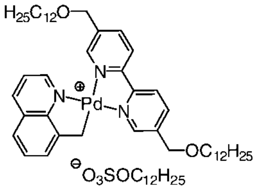
**Fig. 30** Change of the mesophase type by changing the molecular shape of porphyrin derivatives (reprinted with permission from ref. 165 ©, 1998, The Royal Society of Chemistry).[165]



| Comp. | $R^1$ | $R^2$ | Phase Transitions |
|---|---|---|---|
| **46a** | H | H | Cr 197 SmA 207 Iso |
| **46b** | $OC_{10}H_{21}$ | H | Cr 137 Iso |
| **46c** | $OC_{10}H_{21}$ | $OC_{10}H_{21}$ | Cr 110 $Col_h$ 178 Iso |

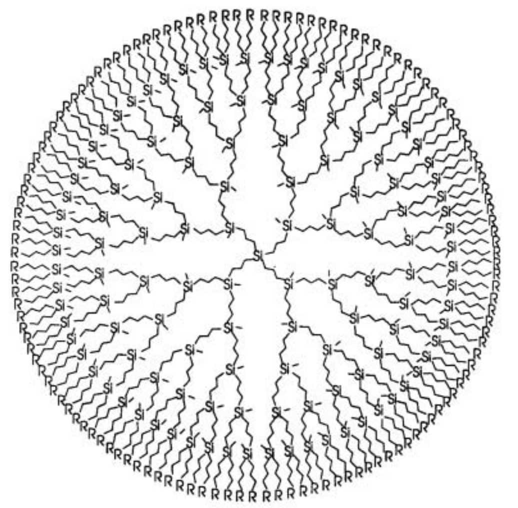
**Fig. 31** Dependence of the liquid crystalline properties of the metallomesogens **46** on the number of alkyl chains.[169]

segregate in layers, whereas in the perpendicular direction the density of alkyl chains between the columns is reduced. This leads to a transition from hexagonal to rectangular columnar phases ($Col_r$). Such rectangular columnar phases represent lamellar arrangements of parallel aligned columns, whereby the columns in neighbouring layers are positional and orientational correlated with each other. The mesophases of the porphyrin derivatives of type **43**,[165] and the metallomesogens **47**[171] are examples for this type of organisation.[172]

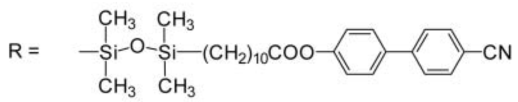


**47**

Another example of such an organisation has recently been reported for the fifth generation carbosilane dendrimer **48** with a shell of 128 cyanobiphenyl mesogens (Fig. 33).[173] On raising the temperature a lamellar (SmA), a rectangular columnar ($Col_r$) and a hexagonal columnar mesophase ($Col_h$) were detected. X-Ray diffraction and calorimetric investigations indicated that two levels of structural organisation coexist in



**48**



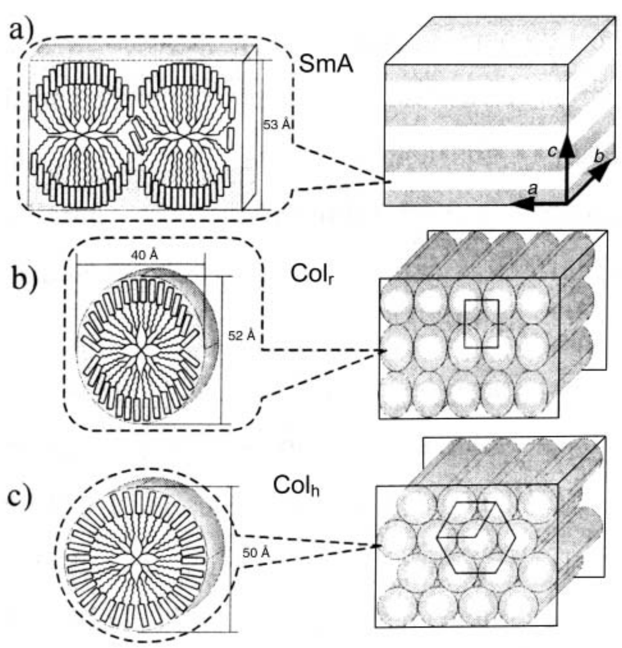


**Fig. 33** Mesophases formed by the fifth generation carbosilane dendrimer **48**, carrying 128 cyanobiphenyl units at the core. (Reprinted with permission from ref. 173 ©, 2000, American Chemical Society.)

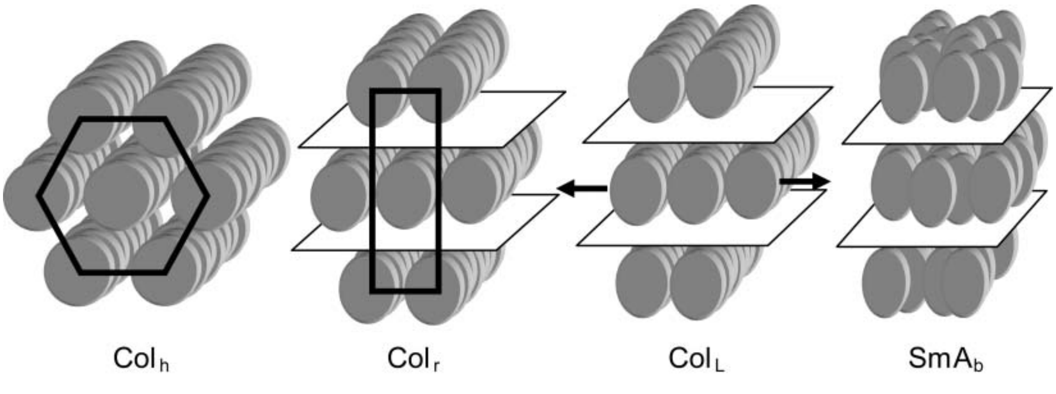
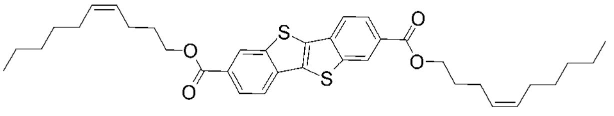


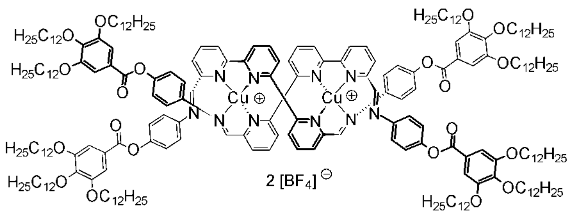
**Fig. 32** Mesophases occurring at the transition from columnar to lamellar organisation of flat molecules (reprinted with permission from ref. 17 ©, 2001, The Royal Society of Chemistry). Beside the non-tilted mesophases shown, the corresponding tilted variants are also possible. Abbreviations: $Col_L$ = lamellar columnar phase; $SmA_b$ = biaxial smectic A phase (McMillan phase).

the Col$_r$ phase. Here, the supramolecular columnar arrangement of the dendrimer molecules as a whole gives rise to the columnar structure, whereas the smectic layers are due to the interaction between the calamitic end groups. In the hexagonal columnar phase the assembly of the whole dendrimers in columns dominates the mesophase morphology.[173] Though the molecular structure of these dendrimers is distinct from the disc-like mesogens discussed above, their organisation is based on essentially the same principles: a central unit (dendritic core) which favours a columnar organisation is in competition with a periphery which prefers a lamellar organisation (calamitic cores).

As shown in Fig. 32, in the next step of the transition from columnar to lamellar organisation, the positional correlation between the adjacent layers can get lost. Evidence for this organisation, designated as lamellocolumnar or lamellar columnar (Col$_L$), was at first given by Levelut *at al.* for the mesophase formed by a charge transfer complex.[174] Lamellar columnar mesophases were also reported for the sanidic molecule **49**[175] and metallomesogens with only four alkyl chains.[176,177] Modifications of this lamellar columnar structure have been reported for tridentate azamacrocyclic metallomesogens,[178] long-chain tetraphenylporphyrins,[179] a copper(II) pentacosadiynoate[180] and the mesophase of the metallohelicate **50**.[181] The metallohelicate **50** has a quite unusual shape. It can be regarded as a short cylinder, laterally surrounded by alkyl chains. These cylinders organise into rows which are parallel aligned within the layers and without positional correlation between the layers (see Fig. 34).[181]



**49**



**50**

This organisations of columns in layers is quite similar to the sliding columnar phase proposed for two-dimensional smectic arrays of linear DNA strands, organised between lipid bilayers (see Fig. 35).[139,182]

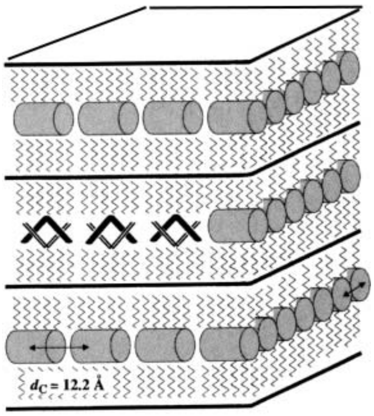


**Fig. 34** Organisation of the metallohelicate **50** in its lamellar columnar phase. (Reprinted with permission from ref. 181 ©, 2000, Wiley-VCH.)

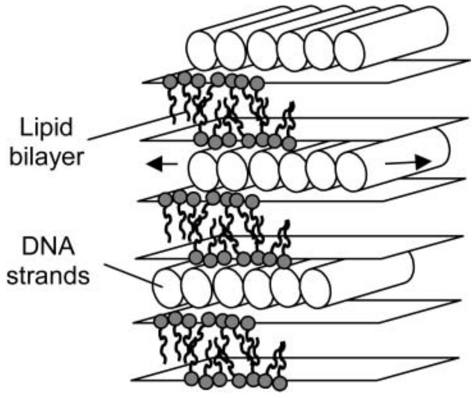


**Fig. 35** The sliding columnar phase of DNA–lipid complexes.[139] The linear DNA strands (shown as cylinders) are organised in 2D-smectic arrays which are arranged between the lipid bilayers. Between neighbouring arrays there is an orientational, but no positional correlation.

In the next step from columnar to lamellar organisation, the long range positional order of the molecules within the layers may get lost, and this means that the columnar aggregates disappear and only the individual molecules are organised in layers. In other words, the segregation remains in only one direction leading to truly smectic phases. However, the flat shape of the molecules could restrict the rotation around their long axes to such an extent that biaxial smectic phases built up by parallel aligned flat molecules could occur[183] before this rotational order is lost in a final step with the formation of the conventional smectic phases.

Within these biaxial smectic phases, the flat molecules can be non-tilted (SmA$_b$, see Fig. 36) or tilted with respect to the layer normal (designated here as SmC$_D$, D = disc-like refers to the flat molecular shape, see Fig. 36).

Layer structures built up by discrete disc-like molecules (disc-like lamellar phases) have been suggested by Shimizu *et al.* and Ohta *et al.* for several disc-like metallomesogens with only four long alkyl chains.[184–186] A tilted arrangement of the disc-like cores was reported,[187] and this corresponds to the SmC$_D$ structure shown in Fig. 36, but further structural investigations are necessary.

If the flat sanidic cores are arranged, on average, perpendicular to the layers, this layer structure should represent a biaxial smectic A phase (McMillan phase).[188] The existence of such an SmA$_b$ phase has very recently been indicated by textural investigations as well as by X-ray investigations in a binary system of the metallomesogen **51** and TNF (see Fig. 37).[136] Though the metallomesogen **51** itself has the molecular shape necessary for the formation of the SmA$_b$

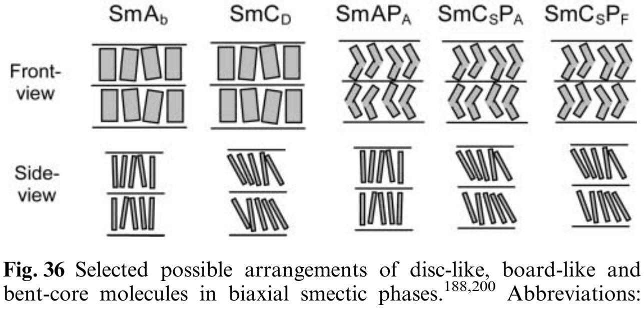
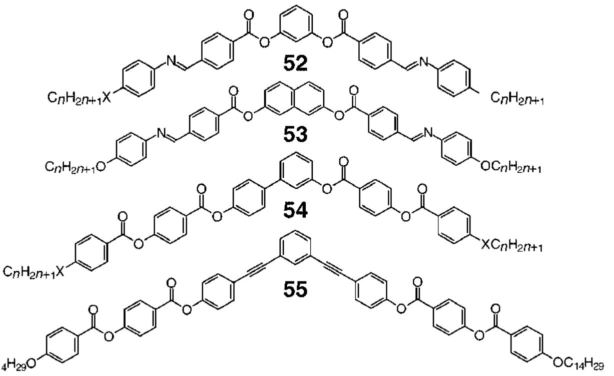


**Fig. 36** Selected possible arrangements of disc-like, board-like and bent-core molecules in biaxial smectic phases.[188,200] Abbreviations: SmA$_b$ = biaxial smectic A-phase (the molecules are aligned perpendicular to the layer planes, McMillan phase, C$_M$[183]), SmC$_D$ = (SmC phase built up by uniformly tilted **d**isc-like or board-like flat molecules); SmAP$_A$ = **a**ntiferroelectric switchable **p**olar SmA phase, SmC$_S$P$_A$ = **a**ntiferroelectric switchable **p**olar SmC phase with **s**ynclinic correlation between adjacent layers, SmC$_S$P$_F$ = **f**erroelectric switchable **p**olar SmC phase with **s**ynclinic correlation between adjacent layers. The tilted phases can also occur with anticlinic interlayer-correlation (the tilt-direction changes from layer to layer).

phase, the rotation around the molecular long axis is fast, and only a uniaxial SmA phase and a conventional SmC phase are observed.[170] However, in mixed systems with a sufficiently large concentration of the electron acceptor 2,4,7-trinitrofluorenone (TNF)[189,190] the attractive face-to-face interactions between TNF and the flat aromatic cores of compounds **51** strongly reduce the molecular rotation around the long axis leading to the biaxiality of this SmA$_b$ phase.[191]

## 7. Bent-core molecules

More recently a new feature was added to the organisation of rigid molecules. Molecules incorporating a bent rigid core (banana-shaped molecules) have been synthesised[192] and investigated.[193] Compounds **52**–**55** represent selected examples of typical bent-core molecules.[194–199]



The reduced symmetry of the rigid segments of such molecules leads to a directed stacking of the molecules within layers.[200] The important consequence of the directed packing of such molecules is the occurrence of a polar order parallel to the smectic layers. In order to escape from a macroscopic polarisation, the layer structures are modified, and this leads to new mesophases. The formation of columnar mesophases, built up by antiparallel aligned ribbons of collapsed layers seems to be the simplest way to escape from a macroscopic polar order (see Fig. 38, Col$_r$).[195c,201] However, this organisation is only possible if the core–core interactions are dominant. It becomes unstable for molecules with elongated alkyl chains or semifluorinated terminal chains, where the unfavourable interfaces between the chains and the aromatic cores at the ribbon–ribbon interfaces disfavour this arrangement.[195c] In this case polar biaxial smectic phases are formed in which the polarisation of adjacent layers cancels out from layer to layer by adaptation of an antiferroelectric correlation between the layers, leading to antiferroelectric switchable smectic phases (SmP$_A$-phases, see Fig. 38).[202] Such bent core molecules and a special polymer system[203] were the first examples which have experimentally shown that antiferroelectric switching with large spontaneous polarisation is indeed possible in a liquid crystalline phase composed of *non-chiral* materials. More recently, also ferroelectric switchable mesophases have been reported for some special bent-core molecules.[204–206] In most of these phases the molecules are additionally tilted (SmCP$_A$ phases),[207] and this leads to a further reduction of the phase symmetry. An inherent handedness of such SmCP$_A$-phases is observed, and this handedness is geometrical in nature and does not result from a molecular chirality.[204,208] This inherent chirality can lead to mesophases with chiral supramolecular structures, even though the molecules themselves are *achiral*. The formation of helical suprastructures in order to escape from a macroscopic polarisation, as shown in the lower part of Fig. 38, is another way to chirality in such supramolecular systems composed of achiral molecules.[209,210] Moreover, in some cases macroscopic regions of opposite handedness are spontaneously formed.[209,210] All these findings stimulated intensive research in the field of these banana-shaped mesogens, and has led to the discovery of a series of new mesophases, unknown in

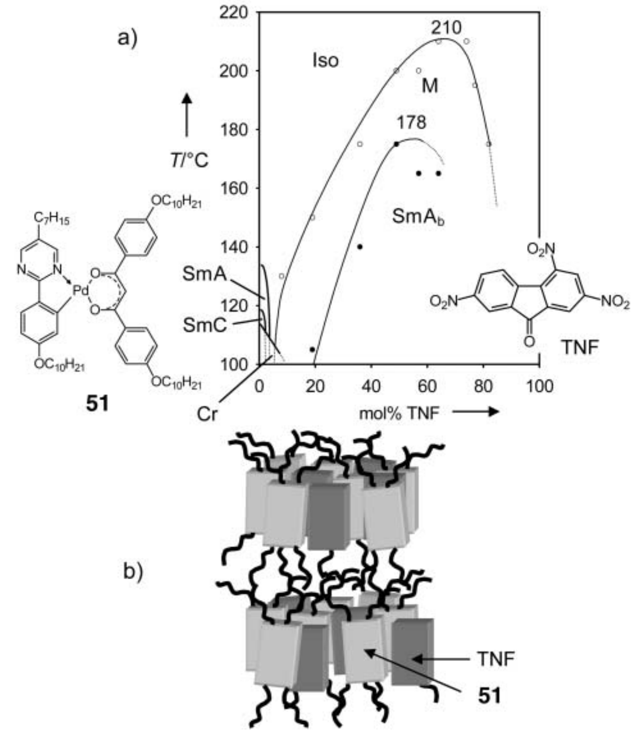


**Fig. 37** Formation of a biaxial smectic A phase (SmA$_b$ phase, McMillan phase) in the system **51**–TNF. (a) Binary phase diagram of the binary system **51**–TNF. M is most probably a lamellar columnar phase. (b) Arrangement of the molecules in the SmA$_b$-phase (reprinted with permission from ref. 136 ©, 2001, Wiley-VCH).

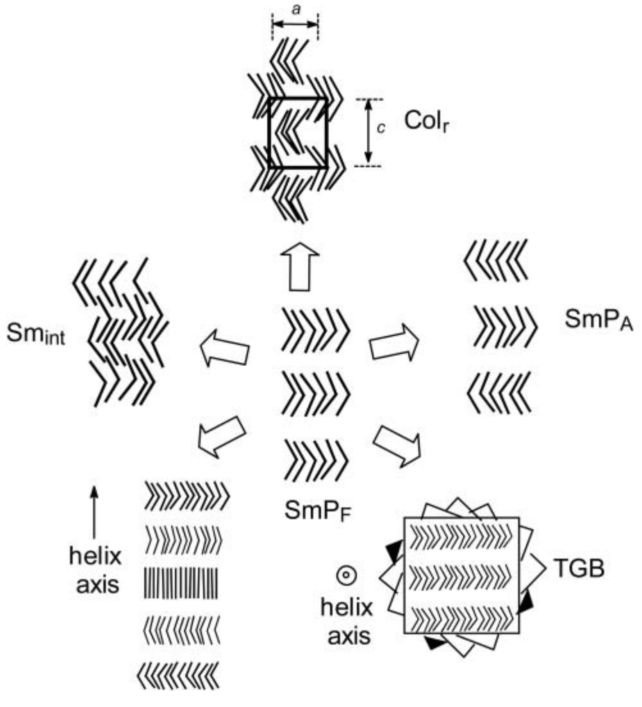


**Fig. 38** Possible ways to escape a macroscopic polarisation in mesophases built up by bent-core molecules (adapted from ref. 209 ©, 1998, Japan Society of Applied Physics). Abbreviations: Sm$_{int}$ = intercalated smectic phase; SmP$_A$ = smectic phase with antiferroelectric correlation between adjacent layers; SmP$_F$ = smectic phase with ferroelectric correlation between adjacent layers (macroscopically polar ordered); TGB = twisted grain boundary structure.

conventional mesogenic materials. Amongst them, mesophases comprising a helical organisation (so-called $B_7$-phases).[211–214] To date, the precise structure of these mesophases and of several other mesophases is not completely understood. Nevertheless, such bent-core molecules open the door to novel complex types of molecular self-organisation and to the new field of supramolecular stereochemistry.[204] More details concerning this subject are summarised in recent reviews[19,194] and are given in the above cited references.

## 8. Summary

The selected examples summarised in this review have shown that significant progress has been achieved over recent years in the design of mesogenic materials with quite unusual and complex types of supramolecular organisation. This was possible by (i) the combination of several levels of incompatibility within the molecules, (ii) by using rigid segments with well-defined shapes, by (iii) changing the molecular topology and by (iv) variation of the volume fractions of the incompatible segments. Anisometric rigid units represent important tools for the tailoring of the molecular order of such low molecular weight molecules. Their important impact results from the strong incompatibility of such segments with flexible molecular parts and the possibility to tailor specific molecular shapes and topologies. Therefore, the appropriate design of polyphilic block molecules incorporating rigid segments can lead to novel mesophase morphologies. These include columnar structures composed of three sets of different columns, combinations of columns and layers, as well as non-conventional layer structures, in which rigid segments are organised with their long axes parallel to the layer planes. It turned out that mesophases with lamellar structures can be formed by molecules with quite different shapes (rod-like, disc-like and spheroidic). The diversity of molecular structures, the numerous possible arrangements of rigid molecular segments within the layers and the different correlation between adjacent layers can lead to a great diversity of possible structures. Some of them are summarised in Fig. 39. This figure also shows that the transition between the different layer structures can take place on different pathways. Several unusual columnar phases can represent stages of the transition between orthogonal sets of layered mesophases if the position and the structure of flexible chains is modified.

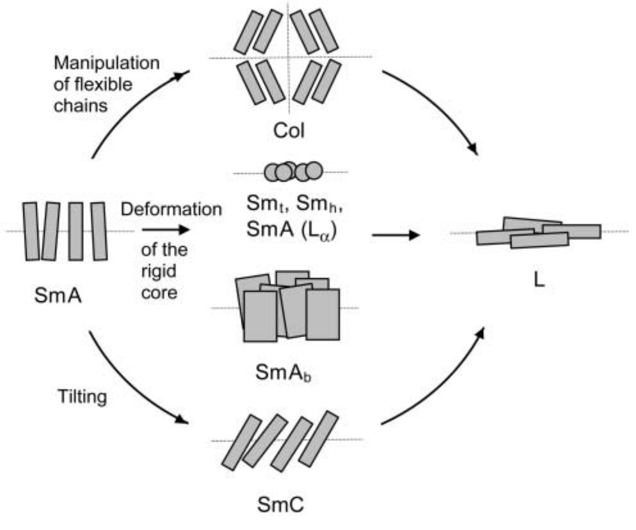


**Fig. 39** Possible pathways of the transitions from conventional smectic phases (*e.g.* SmA) to laminated mesophases (L). The flexible chains, which are liquid-like disordered, are not shown and only one of the possible columnar phases (Col) is displayed. Abbreviations: $Sm_h$ = smectic phase with a hexagonal 2D-lattice within the layers; $Sm_t$ = smectic phase with a tetragonal 2D-lattice within the layers; SmA($L_\alpha$) = fluid smectic phases of binary amphiphiles without additional order within the polar layers.

In predominately rigid systems the efficient packing of the rigid segments becomes a dominating ordering force. Hence, changing the shape of rigid segments between a rod-like and a disc-like shape is an alternative way to mesophases which combine lamellar and columnar organisation, such as ribbon phases and lamellar columnar arrangements. It can also lead to biaxial SmA-phases ($SmA_b$), whereas bent shaped molecules provide access to mesophases with polar order and supramolecular chirality.

Molecular chirality is another important tool for the design of novel mesophase structures, which was not covered in this review.[19,160,215]

Increasing the number of incompatible units, changing the symmetry of the rigid segments, controlling the segregation at different length scales and using the additional possibilities provided by molecular and supramolecular chirality could lead to novel hierarchically ordered mesophase structures. Such systems should be of significant interest, not only because of potential applications, but also because they could provide an important step to self-organised states of soft matter which have a complexity approaching that of biological relevant structures.

## References

1 M. Suarez, J.-M. Lehn, S. C. Zimmerman, A. Skoulios and B. Heinrich, *J. Am. Chem. Soc.*, 1998, **120**, 9526.

2 I. C. Sage, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, Vol. 1, p. 731.

3 W. A. Crossland and T. D. Wilkinson, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, Vol. 1, p. 763.

4 H. Eichhorn, *J. Porphyrins Phthalocyanines*, 2000, **4**, 88.

5 (*a*) D. Katsis, H. P. Chen, S. H. Chen, L. J. Rothberg and T. Tsutsui, *Appl. Phys. Lett.*, 2000, **77**, 2982; (*b*) S. H. Chen, D. Katsis, A. W. Schmid, J. C. Mastrangelo, T. Tsutsui and T. N. Blanton, *Nature*, 1999, **397**, 506; (*c*) M. Grell and D. D. C. Bradley, *Adv. Mater.*, 1999, **11**, 895.

6 R. Eidenschink and A. M. Hager, *Mol. Cryst. Liq. Cryst.*, 1997, **304**, 513.

7 J. Magoshi, Y. Magoshi and S. Nakamura, *Silk Polym.*, 1994, **544**, 292.

8 A. Greiner and H.-W. Schmidt, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, Vol. 3, p. 3.

9 J. M. Seddon and R. H. Templer, in *Handbook of Biological Physics*, ed. R. Lipowsky and E. Sackmann, Elsevier, Amsterdam, 1995, Vol. 1, p. 97.

10 (*a*) C. G. Göltner and M. Antonietti, *Adv. Mater.*, 1997, **9**, 431; (*b*) G. S. Attard, C. G. Göltner, J. M. Corker, S. Henke and R. H. Templer, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1315.

11 I. Koltover, T. Salditt, J. O. Rädler and C. R. Safinya, *Science*, 1998, **281**, 78.

12 W. Chen and B. Wunderlich, *Macromol. Chem. Phys.*, 1999, **200**, 283.

13 T. Kato, in *Structure and Bonding, Vol. 96, Molecular Self-Assembly Organic Versus Inorganic Approach*, ed. M. Fujita, Springer, Berlin, 2000, p. 95.

14 Also rod-like oligo(phenylenes) without terminal chains, such as sexiphenyl can form a smectic mesophase (R. Pummerer and L. Seligsberger, *Ber. Dtsch. Chem. Ges.*, 1931, **64**, 2477), even though they are usually regarded as non-amphiphilic. In such molecules the terminal ends are different from the central core and a minimization of the excluded volume and an optimization of the intermolecular interactions can obviously be achieved if the ends segregate from the central cores with formation of separate layers.

15 (*a*) Y. Hendrikx and A. M. Levelut, *Mol. Cryst. Liq. Cryst.*, 1988, **165**, 233; (*b*) J. Charvolin, *J. Chim. Phys. Phys.-Chim. Biol.*, 1983, **80**, 15; (*c*) A. Skoulios and D. Guillon, *Mol. Cryst. Liq. Cryst.*, 1988, **165**, 317; (*d*) C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 1485.

16 J. W. Goodby, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, Vol. 2A, p. 3.

17 A. N. Cammidge and R. J. Bushby, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, Vol 2B, p. 693.

18 D. Guillon, in *Structure and Bonding, Vol 95, Liquid Crystals II*, ed. D. M. P. Mingos, Springer, Berlin, 1999, p. 41.

19 Overview of recent developments in the field of mesophase forming materials: C. Tschierske, *Annu. Rep. Prog. Chem. Sect. C Phys. Chem.*, 2001, **97**, 191.

20 I. W. Hamley, *The Physics of Block Copolymers*, Oxford University Press, Oxford, 1998, p. 24.

21 F. S. Bates and G. H. Fredrickson, *Phys. Today*, 1999, 32.

22 (*a*) P. Sakya, J. M. Seddon, R. H. Templer, R. J. Mirkin and G. J. T. Tiddy, *Langmuir*, 1997, **13**, 3706; (*b*) V. Luzzati, H. Delacroix and A. Gulik, *J. Phys. II*, 1996, **6**, 405.

23 C. Tschierske, *Prog. Polym. Sci.*, 1996, **21**, 775.

24 G. Staufer, M. Schellhorn and G. Lattermann, *Liq. Cryst.*, 1995, **18**, 519.

25 K. Praefcke, D. Blunk and J. Hempel, *Mol. Cryst. Liq. Cryst.*, 1994, **243**, 323.

26 (*a*) K. Borisch, S. Diele, P. Göring and C. Tschierske, *Chem. Commun.*, 1996, 237; (*b*) K. Borisch, S. Diele, P. Göring, H. Müller and C. Tschierske, *Liq. Cryst.*, 1997, **22**, 427; (*c*) K. Borisch, S. Diele, P. Göring, H. Kresse and C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 529.

27 H. A. van Doren, E. Smith, J. M. Pestman, J. B. F. N. Engberts and R. M. Kellogg, *Chem. Soc. Rev.*, 2000, **29**, 183.

28 (*a*) K. Borisch, C. Tschierske, P. Göring and S. Diele, *Chem. Commun.*, 1998, 2711; (*b*) K. Borisch, C. Tschierske, P. Göring and S. Diele, *Langmuir*, 2000, **16**, 6701.

29 (*a*) H. Prade, R. Miethchen and V. Vill, *J. Prakt. Chem.*, 1995, **337**, 427; (*b*) R. Miethchen, J. Holz, H. Prade and A. Liptak, *Tetrahedron*, 1992, **48**, 3061.

30 (*a*) J. W. Goodby, *Liq. Cryst.*, 1998, **24**, 25; (*b*) J. W. Goodby, M. J. Watson, G. Mackenzie, S. M. Kelley, S. Bachir, P. Bault, P. Gode, G. Goethals, P. Martin, G. Ronco and P. Villa, *Liq. Cryst.*, 1998, **25**, 1390.

31 M. Veber, E. Cheylan, S. Czernecki and J. Xie, *Liq. Cryst.*, 1996, **21**, 197.

32 U. Beginn, S. Keinath and M. Möller, *Liq. Cryst.*, 1997, **23**, 35.

33 S. Fischer, H. Fischer, S. Diele, G. Pelzl, K. Jankowski, R. R. Schmidt and V. Vill, *Liq. Cryst.*, 1994, **17**, 885.

34 C. M. Paleos and D. Tsiourvasaleos, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1696.

35 D. Blunk, K. Praefcke and V. Vill, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, Vol. 3, p. 306.

36 Though numerous combinations of chemically distinct subunits give rise to amphiphilicity, only a few small molecules can self-assemble in the absence of solvents with formation of thermotropic liquid crystalline phases. Beside the well known ionic amphiphiles and amphiphilic polyhydroxy compounds, some long chain fatty acid esters (J. E. Baldvins and R. G. Weiss, *Liq. Cryst.*, 1999, **26**, 897) and hydrocarbons comprising perfluorinated segments have been reported to form thermotropic smectic phases: (*a*) G. Ungar, K. Noble, V. Percec and G. Johansson, *J. Mater. Sci.*, 2000, **35**, 5241; (*b*) M. Duan, H. Okamoto, V. F. Petrov and S. Takenaka, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 1637; (*c*) P. Marczuk, P. Lang and M. Möller, *Colloids Surf. A*, 2000, **163**, 103; (*d*) J. Wang and C. K. Ober, *Liq. Cryst.*, 1999, **26**, 637.

37 (*a*) V. Percec, W.-D. Cho, G. Ungar and D. J. P. Yeardley, *Angew. Chem., Int. Ed.*, 2000, **39**, 1597; (*b*) V. Percec, W.-D. Cho and G. Ungar, *J. Am. Chem. Soc.*, 2000, **122**, 10273; (*c*) V. Percec, W.-D. Cho, P. E. Mosier, G. Ungar and D. J. P. Yeardley, *J. Am. Chem. Soc.*, 1998, **120**, 11061; (*d*) V. Percec, W.-D. Cho, M. Möller, S. A. Prokhorova, G. Ungar and D. J. P. Yeardley, *J. Am. Chem. Soc.*, 2000, **122**, 4249; (*e*) V. S. K. Balagurusamy, G. Ungar, V. Percec and G. Johansson, *J. Am. Chem. Soc.*, 1997, **119**, 1539; (*f*) G. Ungar, V. Percec, M. N. Holerca, G. Johansson and J. A. Heck, *Chem. Eur. J.*, 2000, **6**, 1285.

38 V. Percec, W.-D. Cho, G. Ungar and D. J. P. Yeardley, *J. Am. Chem. Soc.*, 2001, **123**, 1302.

39 Poly(propyleneimine) dendrimers surrounded by a shell of 3,4-dialkoxybenzoyl groups: J. H. Cameron, A. Facher, G. Lattermann and S. Diele, *Adv. Mater.*, 1997, **9**, 398.

40 Carbosilane dendrimers surrounded by a shell of fluorinated chains: K. Lorenz, H. Frey, B. Stühn and R. Mühlhaupt, *Macromolecules*, 1997, **30**, 6860.

41 (*a*) U. Stebani, G. Lattermann, M. Wittenberg and J. H. Wendorff, *J. Mater. Chem.*, 1997, **7**, 607; (*b*) U. Stebani, G. Lattermann, M. Wittenberg and J. H. Wendorff, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1858; (*c*) U. Stebani, G. Lattermann, R. Festag, M. Wittenberg and J. H. Wendorff, *J. Mater. Chem.*, 1995, **5**, 2247.

42 (*a*) A. Pegenau, P. Göring and C. Tschierske, *Chem. Commun.*, 1996, 2563; (*b*) A. Pegenau, T. Hegmann, C. Tschierske and S. Diele, *Chem. Eur. J.*, 1999, **5**, 1643.

43 A. Pegenau, X. H. Cheng, C. Tschierske, P. Göring and S. Diele, *New J. Chem.*, 1999, **23**, 465.

44 X. H. Cheng, S. Diele and C. Tschierske, *Angew. Chem., Int. Ed.*, 2000, **39**, 592.

45 Tetrahedral copper(I) complexes of multichain pyridine ligands: (*a*) A. El-ghayoury, L. Douce, A. Skoulios and R. Ziessel, *Angew. Chem., Int. Ed.*, 1998, **37**, 2205; (*b*) L. Douce, A. El-ghayoury, A. Skoulios and R. Ziessel, *Chem. Commun.*, 1999, 2033.

46 A. Pegenau and C. Tschierske, unpublished work.

47 With the exception of compounds **2** the stronger cohesive forces are located inside the aggregates of the columnar and cubic mesophases formed by compounds **1**, **3–5** and the dendritic molecules. This means that these mesophases can be regarded as reversed type (Cub$_{V2}$, Col$_{h2}$, Cub$_{I2}$) phases.

48 An $Im3m$-type micellar cubic phase was also reported for a poly(ethyleneimine) containing 3,4,5-tri(dodecyloxy)benzoyl side groups: D. J. P. Yeardley, G. Ungar, V. Percec, M. N. Holerca and G. Johansson, *J. Am. Chem. Soc.*, 2000, **122**, 1684.

49 M is a birefringent intermediate phase.

50 M. Antonietti and C. Göltner, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 910.

51 M. C. Holmes, *Curr. Opin. Colloid Interf. Sci.*, 1998, **3**, 485.

52 S. Puntambekar, M. C. Holmes and M. S. Leaver, *Liq. Cryst.*, 2000, **27**, 743.

53 Only recently a reversible transition to a hexagonal perforated layer structure was reported: S. Mani, R. A. Weiss, M. E. Cantino, L. H. Khairallah, S. F. Hahn and C. E. Williams, *Eur. Polym. J.*, 2000, **36**, 215.

54 V. Abetz, in *Supramolecular Polymers*, ed. A. Ciferri, Marcel Dekker Inc., New York, 2000, p. 215.

55 H. Hückstädt, A. Göpfert and V. Abetz, *Polymer*, 2000, **41**, 9089.

56 Y. Mogi, H. Kotsuji, Y. Kaneko, K. Mori, Y. Matsushita and I. Noda, *Macromolecules*, 1992, **25**, 5408.

57 Y. Matsushita, M. Tamura and I. Noda, *Macromolecules*, 1994, **27**, 3680.

58 T. A. Shefelbine, M. E. Vigild, M. W. Matsen, D. A. Hajduk, M. A. Hillmyer, E. L. Cussler and F. S. Bates, *J. Am. Chem. Soc.*, 1999, **121**, 8457.

59 H. Hückstädt, T. Goldacker, A. Göpfert and V. Abetz, *Macromolecules*, 2000, **33**, 3757.

60 S. Brinkmann, R. Stadler and E. L. Thomas, *Macromolecules*, 1998, **31**, 6566.

61 Y. Mogi, M. Nomura, H. Kotsuji, K. Ohnishi, Y. Matsushita and I. Noda, *Macromolecules*, 1994, **27**, 6755.

62 U. Krappe, R. Stadler and I. Voigt-Martin, *Macromolecules*, 1995, **28**, 4558.

63 U. Breiner, U. Krappe, V. Abetz and R. Stadler, *Macromol. Chem. Phys.*, 1997, **198**, 1051.

64 R. Stadler, C. Auschra, J. Beckmann, U. Krappe, I. Voigt-Martin and L. Leibler, *Macromolecules*, 1995, **28**, 3080.

65 J. Beckmann, C. Auschra and R. Stadler, *Macromol. Rapid Commun.*, 1994, **15**, 67.

66 U. Breiner, U. Krappe, T. Jakob, V. Abetz and R. Stadler, *Polym. Bull.*, 1998, **40**, 219.

67 U. Breiner, U. Krappe and R. Stadler, *Macromol. Rapid Commun.*, 1996, **17**, 567.

68 T. Goldacker, V. Abetz, R. Stadler, I. Erukhimovich and L. Leibler, *Nature*, 1999, **398**, 137.

69 T. Goldacker and V. Abetz, *Macromolecules*, 1999, **32**, 5165.

70 T. Goldacker and V. Abetz, *Macromol. Rapid Commun.*, 1999, **20**, 415.

71 V. Abetz and T. Goldacker, *Macromol. Rapid Commun.*, 2000, **21**, 16.

72 K. Ishizu and S. Uchida, *Prog. Polym. Sci.*, 1999, **24**, 1439.

73 F. L. Beyer, S. P. Gido, C. Büschl, H. Iatrou, D. Uhrig, J. W. Mays, M. Y. Chang, B. A. Garetz, N. P. Balsara, N. B. Tan and N. Hadjichristidis, *Macromolecules*, 2000, **33**, 2039.

74 (*a*) S. Sioula, N. Hadjichristidis and E. L. Thomas, *Macromolecules*, 1998, **31**, 5272; (*b*) S. Sioula, N. Hadjichristidis and E. L. Thomas, *Macromolecules*, 1998, **31**, 8429.

75 H. Hückstädt, A. Göpfert and V. Abetz, *Macromol. Chem. Phys.*, 2000, **201**, 296.

76 W. Wang, *Abstr. Pap. Am. Chem. Soc.*, 2000, **219**, U465.

77 G. Barbero and G. Durand, *Mol. Cryst. Liq. Cryst.*, 1990, **179**, 57.

78 D. Demus, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, Vol. 1, p. 133.

79 S. Diele and P. Göring, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, Vol. 2B, p. 887.

80 A.-M. Levelut, B. Donnio and D. W. Bruce, *Liq. Cryst.*, 1997, **22**, 753.

81 J. Kain, S. Diele, G. Pelzl, C. Lischka and W. Weissflog, *Liq. Cryst.*, 2000, **27**, 11.

82 H.-T. Nguyen, C. Destrade and J. Malthete, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, Vol. 2B p. 865.

83 (*a*) W. Weissflog, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, Vol 2B, p. 835; (*b*) W. Weissflog and D. Demus, *Cryst. Res. Technol.*, 1983, **18**, K21.

84 B. Donnio, K. E. Rowe, C. P. Roll and D. W. Bruce, *Mol. Cryst. Liq. Cryst.*, 1999, **332**, 383.

85 D. W. Bruce, *Acc. Chem. Res.*, 2000, **33**, 831.

86 B. Donnio and D. W. Bruce, in *Structure and Bonding, Vol. 95, Liquid Crystals II*, ed. D. M. P. Mingos, Springer, Berlin, 1999, p. 193.

87 B. Donnio and D. W. Bruce, *J. Chem. Soc., Dalton Trans.*, 1997, 2745.

88 F. Guittard, E. Taffin de Givenchy, S. Geribaldi and A. Cambon, *J. Fluorine Chem.*, 1999, **100**, 85.

89 M.-A. Guillevic and D. W. Bruce, *Liq. Cryst.*, 2000, **27**, 153.

90 C. Pugh, J.-Y. Bae, J. Dharia, J. J. Ge and S. Z. D. Cheng, *Macromolecules*, 1998, **31**, 5188.

91 D. Creed, J. R. D. Gross, S. L. Sullivan, A. C. Griffin and C. E. Hoyle, *Mol. Cryst. Liq. Cryst.*, 1987, **149**, 185.

92 (*a*) P. Lehmann, W. K. Robinson and H. J. Coles, *Mol. Cryst. Liq. Cryst.*, 1999, **328**, 221; (*b*) W. K. Robinson, C. Carboni, P. Kloess, S. P. Perkins and H. J. Coles, *Liq. Cryst.*, 1998, **25**, 301.

93 (*a*) E. Nishikawa and E. T. Samulski, *Liq. Cryst.*, 2000, **27**, 1457; (*b*) E. Nishikawa and E. T. Samulski, *Liq. Cryst.*, 2000, **27**, 1463.

94 (*a*) S. I. Stupp, V. LeBonheur, K. Walker, L. S. Li, K. E. Huggins, M. Keser and A. Amstutz, *Science*, 1997, **276**, 384; (*b*) S. I. Stupp, *Curr. Opin. Colloid Interf. Sci.*, 1998, **3**, 20; (*c*) S. I. Stupp, M. U. Pralle, G. N. Tew, L. Li, M. Sayar and E. R. Zubarev, *MRS Bull.*, 2000, 42.

95 M. Lee, B.-K. Cho, Y.-G. Jang and W.-C. Zin, *J. Am. Chem. Soc.*, 2000, **122**, 7449.

96 (*a*) M. Lee, B.-K. Cho, H. Kim and W.-C. Zin, *Angew. Chem., Int. Ed.*, 1998, **37**, 638; (*b*) M. Lee, B.-K. Cho, H. Kim, J.-Y. Yoon and W.-C. Zin, *J. Am. Chem. Soc.*, 1998, **120**, 9168; (*c*) B.-K. Cho, J.-H. Ryu, W.-C. Zin and M. Lee, *Polym. Bull.*, 2000, **44**, 393; (*d*) M. Lee, B.-K. Cho, Y.-S. Kang and W.-C. Zin, *Macromolecules*, 1999, **32**, 8531.

97 M. Lee, D.-W. Lee and B.-K. Cho, *J. Am. Chem. Soc.*, 1998, **120**, 13258.

98 T. Ohtake, M. Ogasawara, K. Ito-Akita, N. Nishina, S. Ujiie, H. Ohno and T. Kato, *Chem. Mater.*, 2000, **12**, 782.

99 B. Perly, A. Douy and B. Gallot, *Makromol. Chem.*, 1976, **17**, 2569.

100 J. T. Chen, E. L. Thomas, C. K. Ober and G.-P. Mao, *Science*, 1996, **273**, 343.

101 A disordered micellar structure was found for an ABC coil–rod–coil molecule, see ref. 97.

102 (*a*) B. Neumann, C. Sauer, S. Diele and C. Tschierske, *J. Mater. Chem.*, 1996, **6**, 1087; (*b*) N. Lindner, M. Kölbel, C. Sauer, S. Diele, J. Jokiranta and C. Tschierske, *J. Phys. Chem. B*, 1998, **102**, 5261.

103 H. Müller and C. Tschierske, *J.Chem. Soc., Chem. Commun.*, 1995, 645.

104 D. F. Ewing, M. Glew, J. W. Goodby, J. A. Haley, S. M. Kelly, B. U. Komanschek, P. Letellier, G. Mackenzie and G. H. Mehl, *J. Mater. Chem.*, 1998, **8**, 871.

105 S. Ujiie and Y. Yano, *Chem. Commun.*, 2000, 79.

106 M. Ibn-Elhaj, H. Möhwald, M. Z. Cherkaoui and R. Zniber, *Langmuir*, 1998, **14**, 504.

107 P. Sebastiao, S. Mery, M. Sieffert, J. F. Nicoud, Y. Galerne and D. Guillon, *Ferroelectrics*, 1998, **212**, 133.

108 H. J. Coles, S. Meyer, P. Lehmann, R. Deschenaux and I. Jauslin, *J. Mater. Chem.*, 1999, **9**, 1085.

109 D. Lose, S. Diele, G. Pelzl, E. Dietzmann and W. Weissflog, *Liq. Cryst.*, 1998, **24**, 707.

110 S. Pensec, F.-G. Tournilhac, P. Basssoul and C. Durliat, *J. Phys. Chem. B*, 1998, **102**, 52.

111 A. G. Petrov, *The lyotropic state of matter: Molecular physics and living matter physics*, Gordon and Breach, Amsterdam, 1999.

112 P. Berdagué, M. Munier, P. Judeinstein, J.-P. Bayle, C. S. Nagaraja and K. V. Ramanathan, *Liq. Cryst.*, 1999, **26**, 211.

113 (*a*) S. V. Arehart and C. Pugh, *J. Am. Chem. Soc.*, 1997, **119**, 3027; (*b*) A. C. Small, D. K. Hunt and C. Pugh, *Liq. Cryst.*, 1999, **26**, 849.

114 This may be due to the equal space filling of the fluoroaliphatic and hydrocarbon regions or a consequence of the reduction of the quadrupole interactions between the rigid cores due to their larger distance between each other. A related effect, the induction of SmA phases by addition of small rod-like molecules to the columnar and SmC phases of polycatenar mesogens was also observed (filled phases): S. Diele, G. Pelzl, W. Weissflog and D. Demus, *Liq. Cryst.*, 1988, **3**, 1047.

115 (*a*) F. Hildebrandt, J. A. Schröter, C. Tschierske, R. Festag, R. Kleppinger and J. H. Wendorff, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1631; (*b*) R. Plehnert, J. A. Schröter and C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 2611.

116 F. Hildebrandt, J. A. Schröter, C. Tschierske, R. Festag, M. Wittenberg and J. H. Wendorff, *Adv. Mater.*, 1997, **9**, 564.

117 With respect to the presence of two different columns, the mesophase structure is related to the lamellar columnar mesophase reported for a charge transfer complex, but in this case no 2D-order was found, see ref. 174.

118 J. A. Schröter, C. Tschierske, M. Wittenberg and J. H. Wendorff, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1119.

119 J. A. Schröter, C. Tschierske, M. Wittenberg and J. H. Wendorff, *J. Am. Chem. Soc.*, 1998, **120**, 10669.

120 R. Plehnert and C. Tschierske, unpublished results.

121 M. Kölbel, T. Beyersdorff, I. Sletvold, C. Tschierske, J. Kain and S. Diele, *Angew. Chem., Int. Ed.* , 1999, **38**, 1077.

122 M. Kölbel, T. Beyersdorff, X. H. Cheng, C. Tschierske, J. Kain and S. Diele, *J. Am. Chem. Soc.*, 2001, **123**, 6809.

123 (*a*) F. Hentrich, C. Tschierske and H. Zaschke, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 440; (*b*) F. Hentrich, S. Diele and C. Tschierske, *Liq. Cryst.*, 1994, **17**, 827.

124 Columnar mesophases have been found for bolaamphiphiles, in which the head groups are connected with each other by flexible alkyl chains. The self-organization of these compounds is related to those found for conventional amphiphiles: (*a*) A. Gulik, V. Luzzati, M. De Rosa and A. Gambacorta, *J. Mol. Biol.*, 1985, **182**, 131; (*b*) H. Gutman, A. Loewenstein, Z. Luz, R. Poupko and H. Zimmermann, *Liq. Cryst.*, 1991, **9**, 607; (*c*) R. Auzély-Velty, T. Benvegnu, D. Plusquellec, G. Mackenzie, J. A. Haley and J. W. Goodby, *Angew. Chem., Int. Ed.*, 1998, **37**, 251.

125 F. Hentrich, C. Tschierske, S. Diele and C. Sauer, *J. Mater. Chem.*, 1994, **4**, 1547.

126 X. H. Cheng, C. Tschierske, J. Kain and S. Diele, *Chemistry and Characterization of Mesophase Materials, Book of Abstracts*, Bayreuth, 2000, P17.

127 It should be pointed out that the hydrogen bonding networks between the hydroxy groups are highly dynamic, allowing a high degree of fluidity in these systems. Also the alignment of the biphenyl cores is not as perfect as suggested by the models. This is confirmed by the diffuse wide angle scattering found in the X-ray diffraction pattern of these mesophases.

128 J. Watanabe, N. Sekine, T. Nematsu, M. Sone and H. R. Kricheldorf, *Macromolecules*, 1996, **29**, 4816.

129 R. A. Bissell, N. Boden, R. J. Bushby, C. W. G. Fishwick, E. Holland, B. Movaghar and G. Ungar, *Chem. Commun.*, 1998, 113.

130 S. Norvez, F. G. Tournilhac, P. Bassoul and P. Herson, *Chem. Mater.*, 2001, **13**, 2552.

131 C. K. Lee, J. C. C. Chen, K. M. Lee, C. W. Liu and I. J. B. Lin, *Chem. Mater.*, 1999, **11**, 1237.

132 It is not really clear if these mesophases represent soft crystals or real liquid crystals.

133 Most probably, the smectic layers can be formed by disordered clusters of parallel aligned aromatic cores.

134 C. Tschierske, T. Beyersdorff, X.-H. Cheng, S. Diele, J. Kain and M. Kölbel, presented at the 18th International Liquid Crystal Conference, Sendai, 2000, 27M-7-I.

135 The textural features are characteristic for columnar phases, whereas the X-ray diffraction pattern suggests a layer structure.

136 T. Hegmann, J. Kain, S. Diele, G. Pelzl and C. Tschierske, *Angew. Chem., Int. Ed.*, 2001, **40**, 887.

137 S. Diele, X. H. Cheng and C. Tschierske, unpublished results.

138 The formation of laminated smectic phases can be expected for rod-like molecules with distinct terminal and lateral groups (*e.g.* facial amphiphiles and bolaamphiphiles with lipophilic lateral

chains). Here, the segregation of the lateral chains should lead to the layer structure and the segregation of the terminal chains from the rigid cores can give rise to the 2D smectic structure within the layers.

139 J. O. Rädler, I. Koltover, T. Salditt and C. R. Safinya, *Science*, 1997, **275**, 810.

140 It seems that the different length of the molecules **32** and **33** disfavors a positional order within the aromatic layers in these mixed system.

141 P. Bassoul, J. Simon and C. Soulie, *J. Phys. Chem.*, 1996, **100**, 3131.

142 S. Norvez and J. Simon, *Liq. Cryst.*, 1993, **14**, 1389.

143 (*a*) M. Arkas, D. Tsiourvas, C. M. Paleos and A. Skoulios, *Chem. Eur. J.*, 1999, **5**, 3202; (*b*) K. Ohta, T. Sugiyama and T. Nogami, *J. Mater. Chem.*, 2000, **10**, 613.

144 K. Ohta, R. Higashi, M. Ikejima, I. Yamamoto and N. Kobayashi, *J. Mater. Chem.*, 1998, **8**, 1979.

145 (*a*) M. Stone, T. Wade, B. Harkness and J. Watanabe, *Macromolecules*, 1998, **31**, 8865; (*b*) L. Kloppenburg, D. Jones, J. B. Claridge, H. C. zur Loye and U. H. F. Bunz, *Macromolecules*, 1999, **32**, 4460; (*c*) A. F. Thünemann, S. Janietz, S. Anlauf and A. Wedel, *J. Mater. Chem.*, 2000, **10**, 2652.

146 (*a*) S. Poser, H. Fischer and M. Arnold, *Prog. Polym. Sci.*, 1998, **23**, 1337; (*b*) G. Mao and C. K. Ober, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, Vol. 3, p. 66.

147 E. L. Thomas, J. T. Chen, M. J. E. O'Rourke, C. K. Ober and G. Mao, *Macromol. Symp.*, 1997, **117**, 241.

148 M. Muthukumar, C. K. Ober and E. L. Thomas, *Science*, 1997, **277**, 1225.

149 J. Ruokolainen, G. ten Brinke and O. Ikkala, *Adv. Mater.*, 1999, **11**, 777.

150 (*a*) C. T. Imrie and G. R. Luckhurst, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, Vol. 2B, p. 801; (*b*) C. T. Imrie, in *Structure and Bonding, Vol 95, Liquid Crystals II*, ed. D. M. P. Mingos, Springer, Berlin, 1999, p. 149.

151 J. Watanabe, T. Niori, S. W. Choi, Y. Takanishi and H. Takezoe, *Jpn. J. Appl. Phys.*, 1998, **37**, L-401.

152 J. W. Goodby, G. H. Mehl, I. M. Saez, R. P. Tuffin, G. Mackenzie, R. Auzely-Velty, T. Benvegnu and D. Plusquellec, *Chem. Commun.*, 1998, 2057.

153 K. Yonetake, T. Masuko, T. Morishita, K. Suzuki, M. Ueda and R. Nagahata, *Macromolecules*, 1999, **32**, 6578.

154 K. Suzuki, O. Haba, R. Nagahata, K. Yonetake and M. Ueda, *High Perform. Polym.*, 1998, **10**, 231.

155 M. W. P. L. Baars, S. H. M. Sötjens, H. M. Fischer, H. W. I. Peerlings and E. W. Meijer, *Chem. Eur. J.*, 1998, **4**, 2456.

156 G. H. Mehl and J. W. Goodby, *Chem. Ber.*, 1996, **129**, 521.

157 R. Elsäßer, G. Mehl, J. W. Goodby and M. Veith, *Angew. Chem., Int. Ed.*, 2001, **40**, 2688.

158 (*a*) J. Andersch, C. Tschierske, S. Diele and D. Lose, *J. Mater. Chem.*, 1996, **6**, 1297; (*b*) J. Andersch, S. Diele and C. Tschierske, *J. Mater. Chem.*, 1996, **6**, 1465; (*c*) J. Andersch and C. Tschierske, *Liq. Cryst.*, 1996, **21**, 51.

159 Y. Fang, A. M. Levelut and C. Destrade, *Liq. Cryst.*, 1990, **7**, 265.

160 B. Pansu, *Mod. Phys. Lett. B*, 1999, **13**, 769.

161 D. W. Bruce, B. Donnnio, S. A. Hudson, A.-M. Levelut, S. Megtert, D. Petermann and M. Veber, *J. Phys. II*, 1995, **5**, 289.

162 A.-M. Levelut and M. Clerc, *Liq. Cryst.*, 1998, **24**, 105.

163 M. Imperor-Clerc, P. Sotta and M. Veber, *Liq. Cryst.*, 2000, **27**, 1001.

164 S. Kutsumizu, T. Ichikawa, M. Yamada, S. Nojima and S. Yano, *J. Phys. Chem. B*, 2000, **44**, 10196.

165 K. Ohta, N. Yamaguchi and I. Yamamoto, *J. Mater. Chem.*, 1998, **8**, 2637.

166 D. W. Bruce, D. A. Dunmur, L. S. Santa and M. A. Wali, *J. Mater. Chem.*, 1992, **2**, 363.

167 W. D. J. A. Norbert, J. W. Goodby, M. Hird and K. J. Toyne, *Liq. Cryst.*, 1997, **22**, 631.

168 Nevertheless, cubic phases can occur as high temperature mesophases in the phase sequences of disc-like molecules. However, the structure of these cubic phases is not clear: (*a*) B. Kohne, K. Praefcke and J. Billard, *Z. Naturforsch.*, 1986, **41b**, 1036; (*b*) J. Billard, H. Zimmermann, R. Poupko and Z. Luz, *J. Phys.*, 1989, **50**, 539; (*c*) K. Hatsusaka, K. Ohta, I. Yamamoto and H. Shirai, *J. Mater. Chem.*, 2001, **11**, 423.

169 T. Hegmann, B. Neumann, J. Kain, S. Diele and C. Tschierske, *J. Mater. Chem.*, 2000, **10**, 2244.

170 T. Hegmann, F. Peidis, S. Diele and C. Tschierske, *Liq. Cryst.*, 2000, **27**, 1261.

171 A. El-ghayoury, L. Douce, A. Skoulios and R. Ziessel, *Angew. Chem., Int. Ed.*, 1998, **37**, 1255.

172 A related three-dimensional organization was reported for perylene diimides: C. W. Struijk, A. B. Sieval, J. E. J. Dakhorst, M. van Dijk, P. Kimbes, R. B. M. Koehorst, H. Donker, T. J. Schaafsma, S. J. Picken, A. M. van de Craats, J. M. Warman, H. Zuilhof and E. J. R. Sudhölter, *J. Am. Chem. Soc.*, 2000, **122**, 11057.

173 S. A. Ponomarenko, N. I. Boiko, V. P. Shibaev, R. M. Richardson, I. J. Whitehouse, E. A. Rebrov and A. M. Muzafarov, *Macromolecules*, 2000, **33**, 5549.

174 P. Davidson, A. M. Levelut, H. Strzelecka and V. Gionis, *J. Phys. Lett.*, 1983, **44**, L-823.

175 D. Haristoy, S. Mery, B. Heinrich, L. Mager, J. F. Nicoud and D. Guillon, *Liq. Cryst.*, 2000, **27**, 321.

176 A. C. Ribeiro, A. F. Martins and A. M. Giroud-Godquin, *Mol. Cryst. Liq. Cryst. Lett.*, 1988, **5**, 133.

177 A. M. Levelut, M. Ghedini, R. Bartolino, F. P. Nicoletta and F. Rustichelli, *J. Phys. (Paris)*, 1989, **50**, 113.

178 G. Lattermann, S. Schmidt, R. Kleppinger and J.-H. Wendorff, *Adv. Mater.*, 1992, **4**, 30.

179 Y. Shimizu, H. Monobe, S. Mima, T. Higanhiyama, T. Fuchita and T. Sugino, *Res. Soc. Symp. Proc.*, 1999, **559**, 211.

180 G. S. Attard and R. H. Templer, *J. Mater. Chem.*, 1993, **3**, 207.

181 R. Ziessel, L. Douce, A. El-ghayoury, A. Harriman and A. Skoulios, *Angew. Chem., Int. Ed.*, 2000, **39**, 1489.

182 T. C. Lubensky and C. S. O'Hern, in *Slow Dynamics in Complex Systems: Eighth Tohwa University International Symposium*, ed. M. Tokuyama and I. Oppenheim, The American Institute of Physics, Woodbury, NY, 1999, p. 105.

183 The existence of such phases was proposed by DeGennes: P. G. DeGennes, *The Physics of Liquid Crystals*, Clarendon, Oxford, 3rd edn., 1982.

184 Y. Shimizu, M. Miya, A. Nagata, K. Ohta, A. Matsumura, I. Yamamoto and S. Kusabayashi, *Chem. Lett.*, 1991, 25.

185 K. Ohta, N. Ando and I. Yamamoto, *Liq. Cryst.*, 1999, **26**, 663.

186 A. Akai and Y. Shimizu, *Liq. Cryst.*, 2000, **27**, 437.

187 H. Sakashita, A. Nishitani, Y. Sumiya, H. Terauchi, K. Ohta and I. Yamamoto, *Mol. Cryst. Liq. Cryst.*, 1988, **163**, 211.

188 H. R. Brand, P. E. Cladis and H. Pleiner, *Macromolecules*, 1992, **25**, 7223.

189 K. Praefcke and J. D. Holbrey, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1996, **24**, 19.

190 K. Praefcke and D. Singer, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, vol. 2b, p. 945.

191 An optical biaxial SmA-phase with double-layer structure (SmA$_{b2}$) was recently suggested for a binary systems of a bent-core molecule with a calamitic mesogen. Here, the biaxiality should be caused by the alignment of the large bent-core guest molecule parallel to each other and parallel to the layers of the uniaxial smectic matrix of the SmA$_2$ phase of the calamitic host. However, the reported schlieren texture comprises not only two-brush, but also four-brush disclinations, which should be absent in an SmA$_b$ phase: R. Pratibha, N. V. Madhusudana and B. K. Sadashiva, *Science*, 2000, **288**, 2184.

192 Y. Matsunaga and S. Miyamoto, *Mol. Cryst. Liq. Cryst.*, 1993, **237**, 311.

193 T. Niori, F. Sekine, J. Watanabe, T. Furukawa and H. Takezoe, *J. Mater. Chem.*, 1996, **6**, 1231.

194 G. Pelzl, S. Diele and W. Weissflog, *Adv. Mater.*, 1999, **11**, 707.

195 (*a*) D. Shen, S. Diele, G. Pelzl, I. Wirth and C. Tschierske, *J. Mater. Chem.*, 1999, **9**, 661; (*b*) D. Shen, S. Diele, I. Wirth and C. Tschierske, *Chem. Commun.*, 1998, 2573; (*c*) D. Shen, A. Pegenau, S. Diele, I. Wirth and C. Tschierske, *J. Am. Chem. Soc.*, 2000, **122**, 1593.

196 (*a*) H. T. Nguyen, J. C. Rouillon, J. P. Marcerou, J. P. Bedel, P. Barois and S. Sarmento, *Mol. Cryst. Liq. Cryst.*, 1999, **328**, 177; (*b*) J. P. Bedel, H. T. Nguyen, J. C. Rouillon, J. P. Marcerou, G. Sigaud and P. Barois, *Mol. Cryst. Liq. Cryst.*, 1999, **332**, 163.

197 (*a*) J. P. Bedel, J. C. Rouillon, J. P. Marcerou, M. Laguerre, M. F. Achard and H. T. Nguyen, *Liq. Cryst.*, 2000, **27**, 103; (*b*) W. Weissflog, C. Lischka, S. Diele, G. Pelzl, I. Wirth, S. Grande, H. Kresse, H. Schmalfuss, H. Hartung and A. Stettler, *Mol. Cryst. Liq. Cryst.*, 1999, **333**, 203; (*c*) W. Weissflog, L. Kovalenko, I. Wirth, S. Diele, G. Pelzl, H. Schmalfuss and H. Kresse, *Liq. Cryst.*, 2000, **27**, 677; (*d*) L. Kovalenko, W. Weissflog, S. Grande, S. Diele, G. Pelzl and I. Wirth, *Liq. Cryst.*, 2000, **27**, 683.

198 (*a*) R. A. Reddy and B. K. Sadashiva, *Liq. Cryst.*, 2000, **27**, 1613; (*b*) B. K. Sadashiva, V. A. Raghunathan and R. Pratibha, *Ferroelectrics*, 2000, **243**, 249; (*c*) B. K. Sadashiva, H. N. S. Murthy and S. Dhara, *Liq. Cryst.*, 2001, **28**, 483.

199 (*a*) J. Watanabe, T. Niori, S. W. Choi, Y. Takanishi and H. Takezoe, *Jpn. J. Appl. Phys.*, 1998, **37**, L-401; (*b*) S. W. Choi, M. Zennyoji, Y. Takanishi, H. Takezoe, T. Niori and J. Watanabe, *Mol. Cryst. Liq. Cryst.*, 1999, **328**, 185.

200 P. E. Cladis, H. R. Pleiner and H. Brand, *Ferroelectrics*, 2000, **243**, 221.

201 J. Watanabe, T. Niori, T. Sekine and H. Takezoe, *Jpn. J. Appl. Phys.*, 1998, **37**, L139.

202 D. R. Link, G. Natale, R. Shao, J. E. Maclennan, N. A. Clark, E. Körblova and D. M. Walba, *Science*, 1997, **278**, 1924.

203 E. A. Soto Bustamante, S. V. Yablonskii, B. I. Ostrovskii, L. A. Beresnev, L. M. Blinov and W. Haase, *Liq. Cryst.*, 1996, **21**, 829.

204 D. M. Walba, E. Körblova, R. Shao, J. E. Maclennan, D. R. Link, M. A. Glaser and N. A. Clark, *Science*, 2000, **288**, 2181.

205 (*a*) P. A. Kumar, M. L. N. Madhu-Mohan and V. G. K. M. Pisipati, *Liq. Cryst.*, 2000, **27**, 1533; (*b*) V. Prasad, D. S. S. Rao and S. K. Prasad, *Liq. Cryst.*, 2000, **27**, 585.

206 E. Gorecka, D. Pociecha, F. Araoka, D. R. Link, M. Nakata, J. Thisayukta, Y. Takanishi, K. Ishikawa, J. Watanabe and H. Takezoe, *Phys. Rev. Lett. E*, 2000, **62**, R4524.

207 Bent-core molecules in which the central 1,3-disubstituted benzene ring is replaced by an odd-numbered alkylene spacer form mesophases in which the bent dimers are not tilted with respect to the layer normal (SmAPA), see ref. 199. This phase is related to the antiferroelectric switchable mesophase of the side chain polymer reported by Soto Bustamante.[203] More recently, an $\mathrm{SmA_{PA}}$ phase was also reported for a rigid bent-core molecule: A. Eremin, S. Diele, G. Pelzl, H. Nadasi, W. Weissflog, J. Salfetnikova and H. Kresse, *6th European Conference on Liquid Crystals*, Halle, 2001, Abstracts 4-P4.

208 G. Heppke and D. Moro, *Science*, 1998, **279**, 1872.

209 T. Sekine, T. Niori, M. Sone, J. Watanabe, S.-W. Choi, Y. Takanishi and H. Takezoe, *Jpn. J. Appl. Phys.*, 1997, **36**, 6455.

210 (*a*) J. Thisayukta, Y. Nakayama and J. Watanabe, *Liq. Cryst.*, 2000, **27**, 1129; (*b*) J. Thisayukta, Y. Nakayama, S. Kawauchi, H. Takezoe and J. Watanabe, *J. Am. Chem. Soc.*, 2000, **122**, 7441.

211 (*a*) G. Pelzl, S. Diele, A. Jakli, C. Lischka, I. Wirth and W. Weissflog, *Liq. Cryst.*, 1999, **26**, 135; (*b*) A. Jakli, C. Lischka, W. Weissflog, G. Pelzl and A. Saupe, *Liq. Cryst.*, 2000, **27**, 1405.

212 C.-K. Lee and L.-C. Chien, *Liq. Cryst.*, 1999, **26**, 609.

213 (*a*) G. Heppke, D. D. Parghi and H. Sawade, *Ferroelectrics*, 2000, **243**, 269; (*b*) G. Heppke, D. D. Parghi and H. Sawade, *Liq. Cryst.*, 2000, **27**, 313.

214 J. P. Bedel, J. C. Rouillon, J. P. Marcerou, M. Laguerre, H. T. Nguyen and M. F. Achard, *Liq. Cryst.*, 2000, **27**, 1411.

215 (*a*) J. W. Goodby, in *Handbook of Liquid Crystals*, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, vol. 1, p. 115; (*b*) J. W. Goodby, in *Structure and Bonding, Vol. 95, Liquid Crystals II*, ed. D. M. P. Mingos, Springer, Berlin, 1999, p. 83; (*c*) T. Matsumoto, A. Fukuda, M. Johno, Y. Motoyama, T. Yui, S.-S. Seomun and M. Yamashita, *J. Mater. Chem.*, 1999, **9**, 2051.