

Liquid crystals with restricted molecular topologies: supermolecules and supramolecular assemblies

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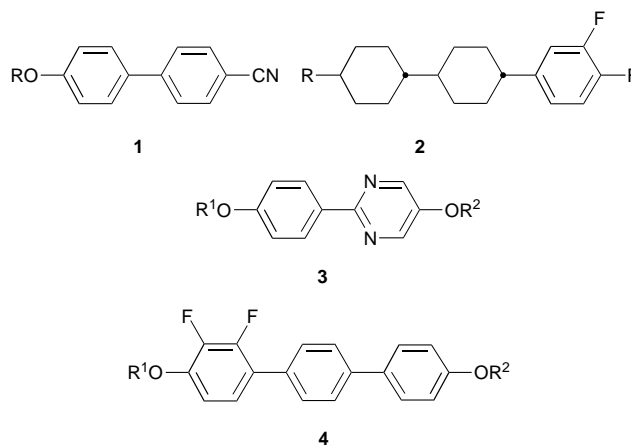
The term liquid crystal is often associated with fascinating compounds that exhibit unusual melting or solubilisation properties, however, it also represents a unique collection of mesophases that exist between the solid state and the amorphous liquid. As such, this unique state of matter can be accessed by a wide variety of materials from low molar mass to polymeric systems. In this Feature Article we describe some recent studies concerning the liquid-crystalline behaviour of 'in-between' materials that have discrete molecular structures, and which are oligomeric but not low molar mass or polymeric systems. Thus, these materials could be described as having supermolecular architectures. We examine some of their mesophase properties and their abilities to form supramolecular assemblies. The development of liquid crystals that have large molecular structures or consist of large scale assemblies is one step towards creating novel self-organising systems which are of a similar dimension to certain biological materials, such as proteins.

Introduction

Over the past two and a half decades low molar mass liquid crystals (LMMLCs) have been the quintessential molecular electronic materials. The invention of the twisted nematic display (TNLCD) in the early 1970s coupled with Gray and Harrison's development of stable room temperature nematogens based on cyanobiphenyls, **1**, ensured that liquid crystals would be synonymous, across the world, with flat-panel, low voltage visual display units (VDUs).¹ This association has continued with the invention and development of surface stabilised ferroelectric smectic C* displays (SSFLCDs)^{2,3} which are near to commercialisation, and the recent extension of this work to device configurations utilising antiferroelectric materials.⁴ All devices based on liquid crystal technology are, of course, non-emissive and depend on the reflection of incident light or an artificial light source for viewing. As a consequence, however, materials designed for, and utilised in, LCDs are not usually subject to optical damage. In addition, in-plane switching devices such as SSFLCDs, AFLCDs and bistable nematic displays possess wide viewing angles making them ideal candidates for exploitation in large area, high pixel density devices.

Ever more so, therefore, has the development of materials for use in display devices become a challenge of 'precision' molecular engineering.¹⁻⁵ Materials, thus, need to be designed to be chemically and optically stable, possess wide temperature ranges for their liquid crystal phases, have low melting points, low viscosities, suitable birefringences, desirable dielectric properties, low conductivities—in fact the demands on the quality and properties of organic liquid crystals approach those placed on conventional inorganic and semi-conductor materials used in the electronics industry. As a consequence, the design of

nematogens is now focused on creating materials based on fluorinated systems because they have low conductivities and viscosities, and suitable positioning of fluoro-substituents allows them to have appropriate dielectric anisotropies for applications,^{1,5} see **2**. Similarly, the development of ferroelectric materials is centred on the creation of materials with low viscosities, wide mesophase temperature ranges and low melting points.⁶ The design of fast switching low viscosity materials has therefore become akin to the utilisation of aerodynamics in the design of fast sports cars, *i.e.* narrow, stiff, rod-like molecules being the most suitable, *cf.* the phenyl



pyrimidines **3** and the difluoroterphenyls **4**.⁷ Although high technology applications of liquid crystals tend to catch the eye, it should be noted that by far and away the highest consumption of liquid crystals is by the soap and detergents industry,⁸ followed by that of companies involved in the production of structural polymers (PLCs), for example, poly(*p*-phenylene terephthalamide) is used commercially as the basis for spinning fibres such as Kevlar® (Du Pont) and Twaron® (Akzo).⁹ Cationic, anionic, and non-ionic surfactants (*e.g.* **5–7**) have been shown to be capable of exhibiting either thermotropic¹⁰ or lyotropic mesophases,¹¹ and in some cases materials have been shown to exhibit both forms of mesophase, thereby making them amphotropic. Glyco- and phospho-lipids, akin to those found in cell membranes, provide numerous examples of compounds that self-assemble to form lyotropic liquid crystals and self-organise to form thermotropic phases. Octyl 1-*O*- β -D-glucopyranoside, **8**, which is a commercially available non-ionic detergent (Sigma) exhibits a smectic A* phase upon heating, and lamellar, cubic and hexagonal lyotropic phases on progressive addition of water,¹² for example see Fig. 1.

Liquid crystals thus have many wide and varied applications apart from high profile uses in displays. However, because there is such a short amount of time between discovery/innovation

smectic/nematic and columnar phases, whereas hexacatenar materials tend to exhibit columnar phases.¹⁶ Similarly molecular structures that combine the features of both discs and spheres can have bowl-like shapes and can produce bowl-like or pyramidal mesophases. In most cases, the lowest energy static molecular shape defines mesophase type/formation, however, dynamical variations in molecular structure, such as conformational and geometrical changes, can also impinge on mesomorphic behaviour, particularly if the changes occur as a function of temperature or concentration of solvent.

When a large number of mesogenic units, be they spheroid, ellipsoid or discoid in shape, are linked together they form polymeric liquid crystals. Polymer systems, however, usually have associated problems of dispersity (γ) and degree of polymerization (DP) which impinge on their physical properties. A material that possesses more than one mesogenic unit but with a defined DP and a dispersity of one, *i.e.* a discrete molecular system, could be considered as a supermolecular system. The simplest architectural form of a supermolecular liquid crystal then is a dimer. Dimers may have a number of structural variants, for example the mesogenic units may be joined end to end, side to side, or they may be joined together as Siamese twins.¹⁷ Luckhurst and Imrie,¹⁸ in particular, have made many detailed investigations of dimeric systems, but principally of those where the mesogenic units are linked end to end. Trimers on the other hand can have their mesogenic units joined together in a linear chain, or they may be tethered to a central point, or they may be part of a cyclic system. From these simple examples it can be seen for a system which has available a defined number of structural moieties/units to be used in molecular construction, that a limited variety of molecular topologies are possible, see Fig. 2. However, once a supermolecular architecture has been defined, conformational, geometrical, and configurational factors have to be taken into account in the way a mesophase is formed and stabilised. In this Feature Article, the mesomorphic behaviour for systems that possess restricted molecular topologies and limited molecular flexibilities will be discussed; the first examples involve supermolecular mesogens where the mesogenic units are linked to a central focal point thereby limiting the molecular geometry and conformational structure.

Materials with defined molecular topologies

The possibility of creating liquid crystals that have large discrete molecular structures with defined molecular topologies is an intriguing prospect because the materials might be expected to exhibit unusual physical properties. For example, on paper an oligomeric material possessing mesogens tethered to a central point could be designed to have a spherical shape with its mesogenic units spread symmetrically about that point. However, if such a material were constrained in a liquid crystal environment, molecular distortion would be expected to occur in order to allow the mesogenic units to pack together.

Examples of simple model tetrahedral systems with cubic symmetry were created by reacting tetrakis(dimethylsil-

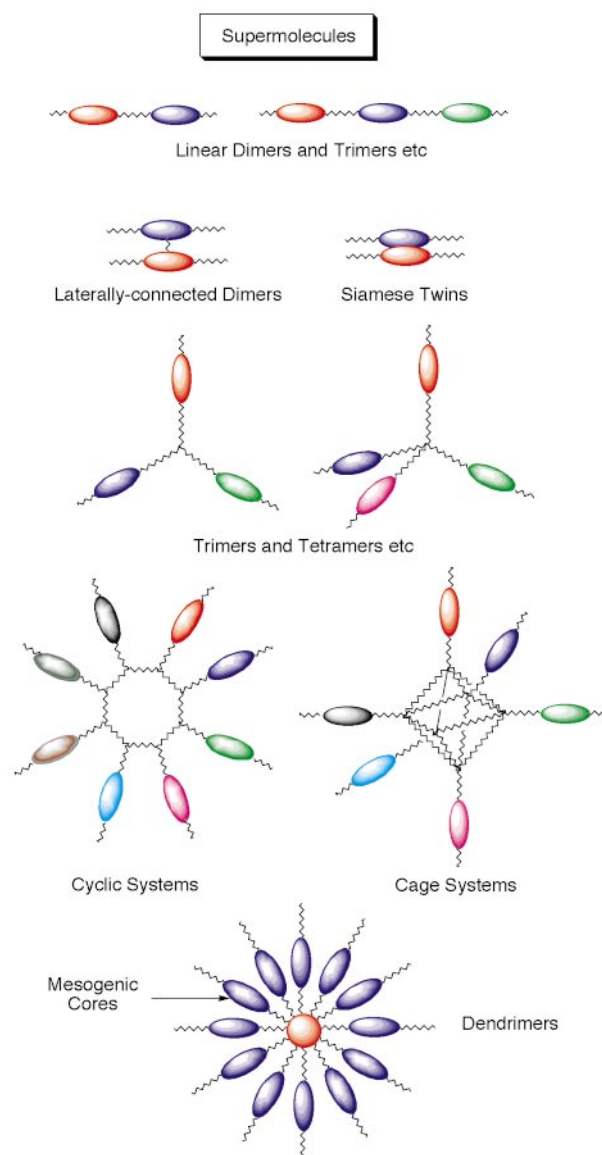


Fig. 2 Various molecular scaffolds for the design of large discrete supermolecules

oxy)silane with a variety of alkenyloxy-cyanobiphenyls,¹⁹ thereby generating a set of tetrahedrally substituted mesogenic supermolecules, *e.g.* **9a–c**, where four mesogenic units are tethered to a central point. Although such a molecular shape would be expected to disfavour mesophase formation, Table 1 shows that the tetramers exhibit smectic A liquid crystal phases. It is also interesting to note that smectic A phases are preferred over the nematic phase exhibited by the mesogenic monomers themselves. In this sense, these supermolecules are similar in

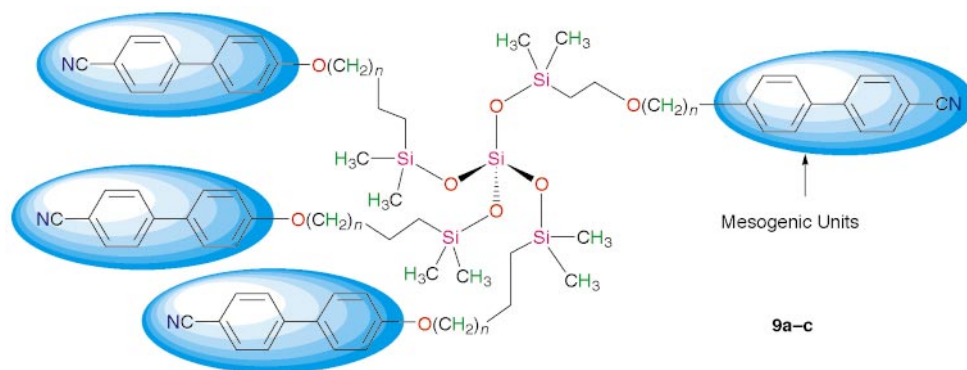


Table 1 Transition temperatures (°C) for the tetramers of structure **9a–c**

Compound	<i>n</i>	tg	SmX–SmA	SmA–Iso Liq
9a	2	–9.6	—	88.7
9b	4	–14.7	—	118.7
9c	9	–6.3	38.7	129.7
Cyclic	6	57	—	118.0

mesophase behaviour to conventional side-chain liquid crystal polysiloxanes which have cyanobiphenyl moieties as the mesogenic side group.

In general the smectic A phase has a structure where rod-like molecules pack in diffuse layers where there is no positional ordering of the molecules in the plane and out of the plane of the layers.¹⁵ The only way in which the tetramers can form such a phase is by molecular distortion away from a spherical shape

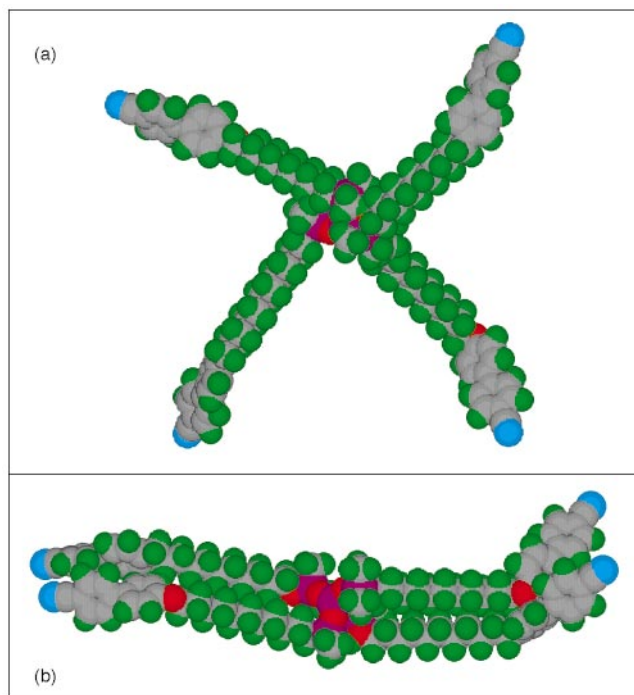


Fig. 3 The molecular shape of tetramer **9c**, (a) shows the shape of the molecule where the four arms were symmetrically positioned about the core; (b) shows the minimised structure in the gas phase at absolute zero using a Silicon Graphics system operating with Quanta and CHARMM software

[see Fig. 3(a)] to give a rod-like conformational structuring. Molecular modelling studies reveal that, even in the gas phase at absolute zero, the conformation where the mesogenic side-chains are aligned is the more energetically favoured conformation [Fig. 3(b)], thereby allowing the supermolecules to achieve rod-like molecular shapes.

Materials **9a** and **9b** exhibit only a smectic A phase, whereas **9c** shows, upon heating, a transition to an additional unidentified phase at 38.7 °C. When the number of methylene units is increased, the isotropization temperatures increase accordingly. Furthermore, the isotropization temperatures of the materials were found to be comparable with those of cyclic siloxanes bearing four side-chains of a similar structure.²⁰ However, the solidification temperatures of the tetrahedrally substituted systems were found to be much lower. For example, the cyclic analogue of compound **9b** exhibits a glass transition or recrystallisation well above room temperature (*ca.* 50–60 °C), whereas the tetrahedrally substituted equivalent material produces a non-crystalline material that has a low solidification temperature (–14.7 °C). Thus the symmetrically substituted systems show low melting behaviour and primarily

glass formation on cooling. This effectively widens the relative temperature ranges of the liquid crystal mesophases.

X-Ray diffraction shows that the trichotomous nature of the tetramers allows for different packing characteristics to exist for the molecules in the smectic A phase. Thus, the separate interactions of the mesogenic units, the alkyl spacers and the silicon cores have to be considered in the formation of the A phase. For the shorter methylene spacer lengths, **9a** and **b**, internal phase separation leads to the smectic A phase being described as a smectic A_d phase with respect to the mesogens and a monolayer smectic A₁ phase with respect to the silicon cores, see Fig. 4. In the smectic A_d phase the mesogenic units are partially interdigitated giving a layer spacing *d*, where $l < d < 2l$, and *l* is the molecular length. The smectic A₁ phase is a disordered layered phase where the layer spacing is approximately equal to the molecular length. For the longer methylene spacer lengths, **9c**, the co-existence of smectic A_d and smectic A₂ phases is probable (the smectic A₂ phase is a bilayer system where the layer periodicity is twice the molecular length). The occurrence of these structures can be explained by the presence of biphasic or incommensurate smectic A phases, or even a smectic A anti-phase.

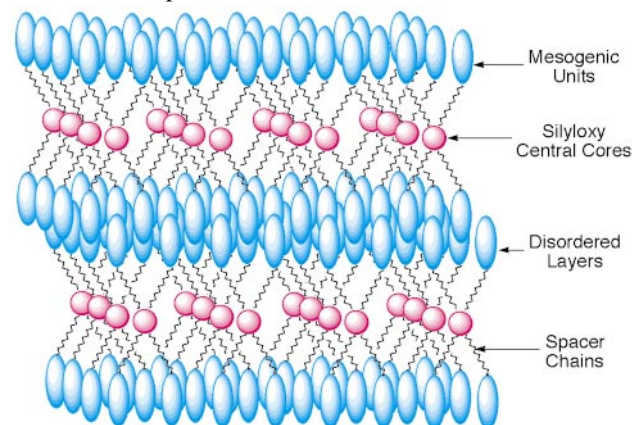
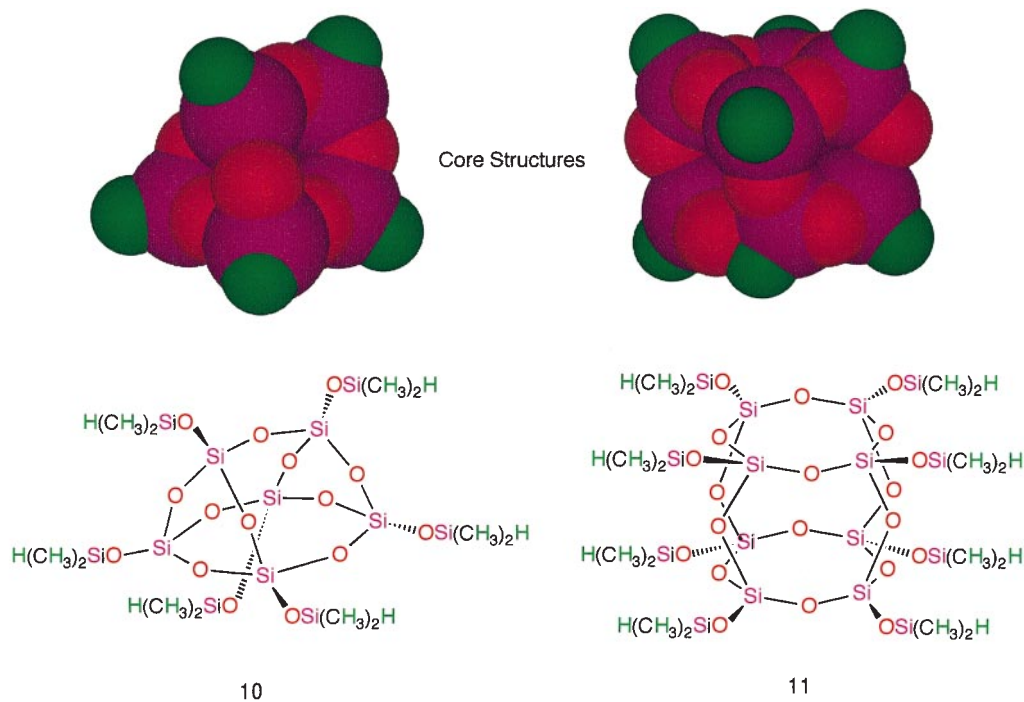


Fig. 4 The structure of the interdigitated smectic A_d phase of tetramers **9a** and **b**. The mesogenic units form an interdigitated bilayer, whereas the silyloxy cores have a monolayer arrangement.

For the tetramers there is adequate free volume for the cyanobiphenyl ‘mesogenic arms’ to rotate so as to give a distorted rod-like molecular shape. Increasing the number of mesogenic units attached to the central point, however, has the effect of reducing the free volume for the packing of the mesogenic groups, which in turn reduces their freedom of movement and suppresses the ability of the supermolecular system to generate a rod-like conformational form. Increasing the number of mesogens attached to a central point is difficult to achieve without moving in the direction of dendrimer formation, but the substitution of polyhedral core units with mesogenic groups can provide an alternative route to packing a larger number of mesogenic units about a central focal point. The use of various polyhedral siloxane-substituted systems as the central cores of the supermolecular systems allows for meaningful comparisons to be made as the free volume available to the mesogens is reduced as the degree of substitution about the polyhedral core is increased.²¹

The hexakis(dimethylsiloxy)silsesquioxane, **10**, and octasilsesquioxane, **11**, core systems are caged polyhedral units, where silicon atoms are situated at the corners of the cage and oxygen atoms in between. The hexakis-core can be substituted with up to six mesogenic units, whereas the octasilsesquioxane core can be substituted with up to eight mesogenic groups. Comparative materials with similar mesogenic cyanobiphenyl side chains have been prepared. In both cases the cores are not much different in size to the tetrakis(dimethylsiloxy)silane core discussed in the synthesis of the tetramers, optical microscopy shows that, on cooling from the amorphous liquid, smectic A



liquid crystal phases are formed for the hexakis(dimethylsiloxy)silsesquioxane and octasilsesquioxane systems. Table 2 shows that for the octasilsesquioxane based systems, compounds **12a–c**, the clearing temperatures are in a similar temperature regime to those found for the tetrahedrally substituted materials **9a–c**. However, the rise in the clearing temperatures, with increasing spacer length, was less steep.²²

Table 2 Transition temperatures (°C) for the octamers **12a–c** based on the octasilsesquioxane core unit

Compound	<i>n</i>	tg	Cryst– Sm3	Sm2– Sm3	Sm3– SmA	Sm1– SmA	SmA– Iso Liq
12a	4	11.0	—	—	—	—	93.9
12b	6	3.0	—	—	—	22.5	116.5
12c	11	–7.5	34.4	54.6	64.5	—	128.5

As with the tetramers, the mesogenic arms of the octasilsesquioxane based materials again rotate so that they lie parallel to one another. This creates a rod-like structure where

the supermolecules can pack together in layers to form a smectic A phase. Molecular simulations in the gas phase at absolute zero serve to reinforce this point of view. Fig. 5 shows the minimised structure of the cyanobiphenyl substituted octasilsesquioxane

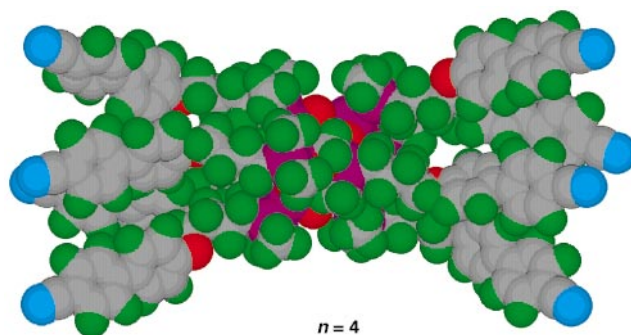
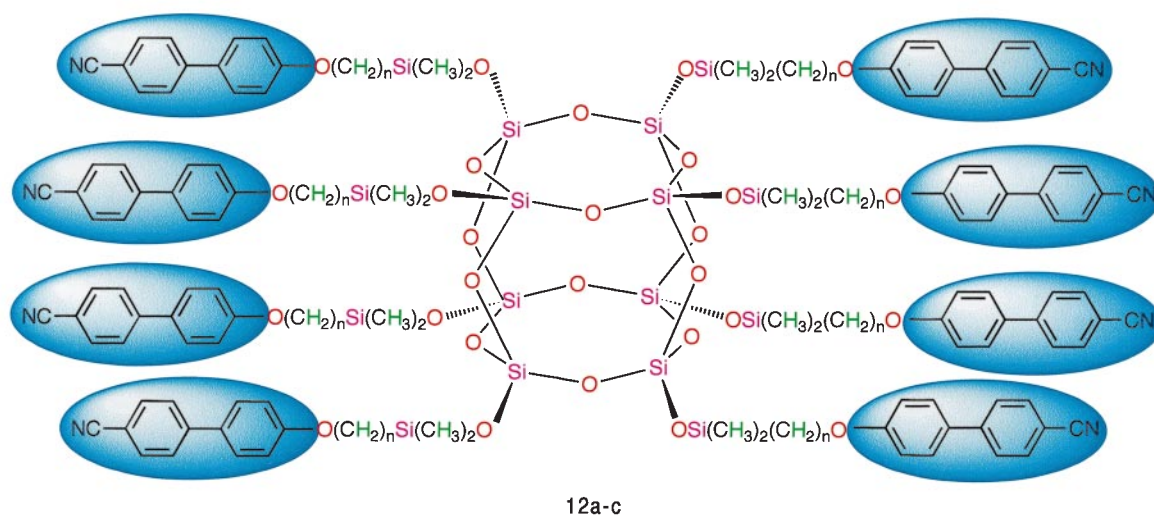
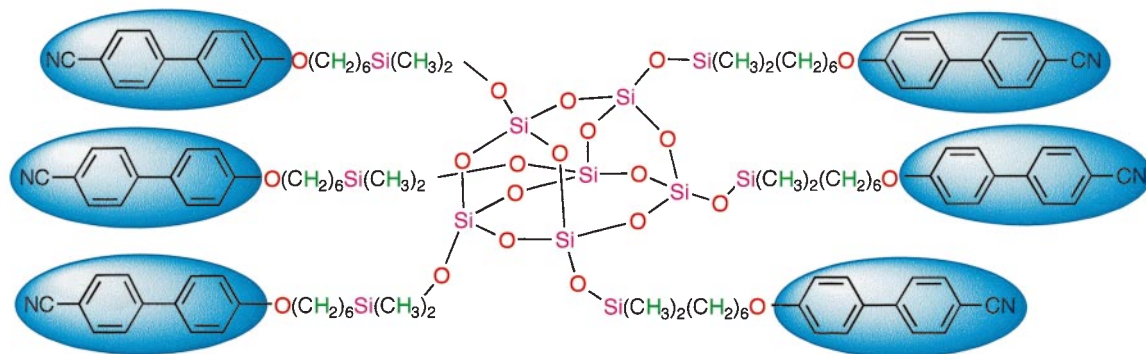


Fig. 5 The minimised structure of the octamer **12a** in the gas phase at absolute zero using a Silicon Graphics system operating with Quanta and CHARMM software





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with a tetramethylene spacer unit. In this structure the cyanobiphenyl 'mesogenic arms' pack together in a parallel arrangement thereby producing a supermolecular system that has a rod-like gross shape which is conducive to the formation of smectic A phases.

Similar results are obtained for systems based on the hexakis(dimethylsiloxy)silsesquioxane core system, **13**. Again smectic A phases are formed indicating that the molecules must adopt a rod-like structure. Mehl and Saez²¹ have reported several other variants of liquid crystals based on polyhedral core

units, and where cyanobiphenyl moieties were used as the source of mesogenic units smectic A phases were found. Kreuzer *et al.*²³ have reported that silsesquioxane cores with six, eight and ten mesogenic units, with structures based on that of cholesterol, still appear to exhibit smectic A phases, thus demonstrating the power of the mesogenic environment to inflict conformational changes on the supermolecules so as to distort their shapes from being spherical to being tactoidal, and preventing the formation of nematic, or in the last example from Kreuzer *et al.*²³ chiral nematic phases.

Table 3 Transition temperatures (°C) and enthalpies (in parentheses, J g⁻¹) of transition for a variety of materials that combine the 4'-(2-methylbutylbenzoyloxy)biphenyl-4-carboxylate mesogenic unit, **A**, with siloxy moieties based on the tetramer, **B**, octasilsesquioxane, **E**, cyclic siloxanes, **C** and **D**, and polysiloxane, **F**, systems

Mesogenic Monomer	
Reactants	Transition temperatures and calorimetric data
A (Monomer)	cryst 78.5 SmC 106.1 (0.7) SmA 157.2 (2.9) N 168.9 (1.51) Iso Liq
A + B (Tetramer)	tg -8.4 (0.5) SmCa 125.0 (0.1) SmC 154.4 (0.1) SmA 164.4 (-) Iso Liq
A + C (Cyclic Tetramer)	tg 10.3 (0.5) SmX 69.5 (1.0) SmC 184.2 N 193.3 (8.0) Iso Liq
A + D (Cyclic Pentamer)	tg 11.2 (0.4) SmC 182.5 (-) SmA 188.7 (6.8) Iso Liq
A + E (Caged Octamer)	cryst 143.0 (21.1) SmC 208.0 (0.2) SmA 214.0 (6.4) Iso Liq
A + F (Linear Polymer)	tg 19.0 (0.2) SmC 223.5 (0.1) SmA 234.3 (5.3) Iso Liq

Substitution of the silsesquioxane cores with mesogenic groups that are more conducive to smectic mesophase formation, as with the other systems described above, yields supermolecular materials that as expected exhibit smectic phases. However, for the many cases studied, the formation of smectic phases and mesophase temperature ranges are considerably enhanced. For example the use of the 4'-(2-methylbutylbenzoyloxy)biphenyl-4-carboxylate mesogenic unit, which favours the formation of orthogonal smectic A and tilted smectic C, I and F phases, results in the preference for tilted smectic C phases, see compounds **14** and **15**. For compound **14** the smectic C phase is present from 11.5 to 191.5 °C, *i.e.* a temperature range of over 180 °C, whereas it is only present over a temperature range of 22–23 °C for the mesogenic monomer unit. The coupling of the potential stability of the smectic C phase with chirality built into the mesogenic units allows for the possibility of synthesising supermolecular ferroelectric materials which may have interesting non-linear physical properties, *e.g.* antiferroelectric, pyroelectric and piezoelectric properties.

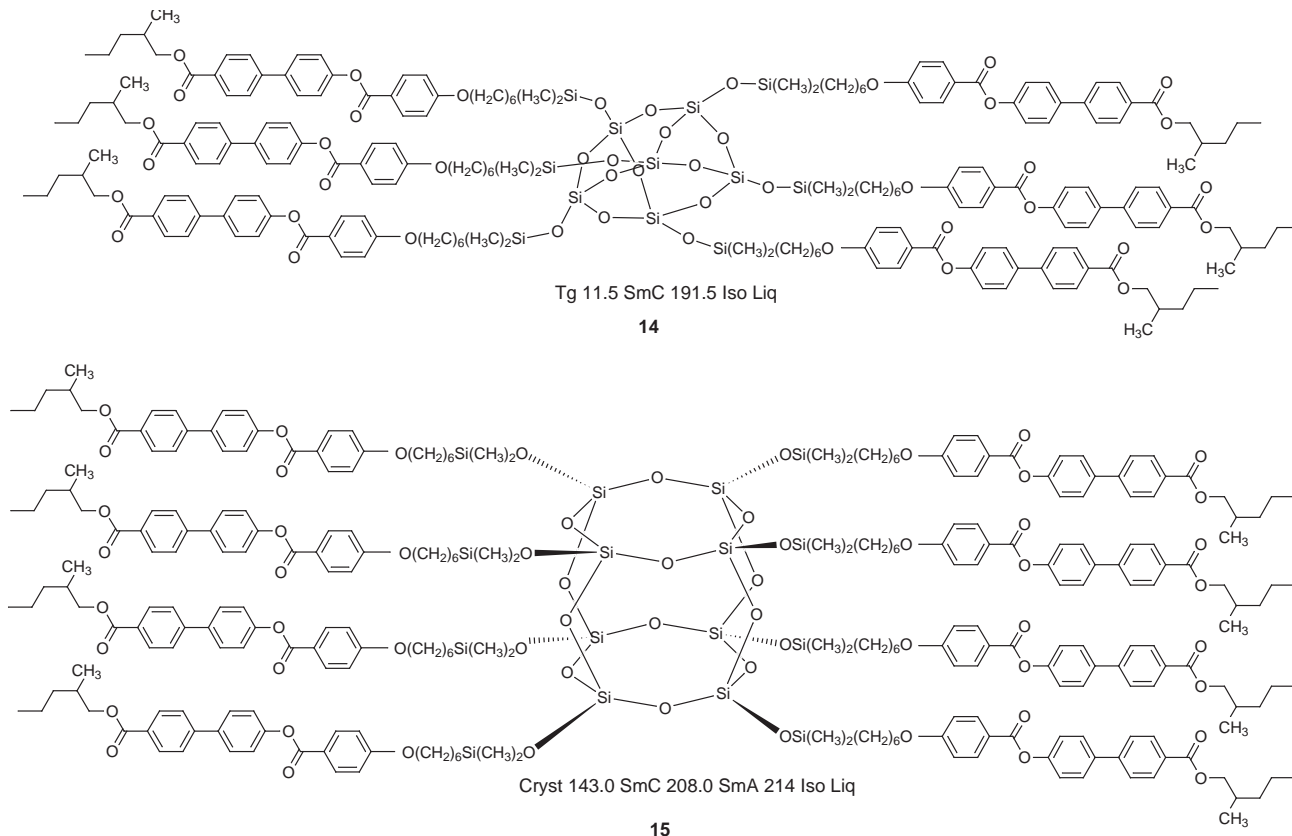
Table 3 shows a comparison of the mesomorphic behaviour for a variety of materials that combine the 4'-(2-methylbutylbenzoyloxy)biphenyl-4-carboxylate mesogenic unit with siloxy moieties based on the tetramer, octasilsesquioxane, cyclic siloxane and polysiloxane systems. It can be seen from the table that in all cases for the supermolecules and the side chain polymer, considerable stabilisation of the liquid crystal properties, and in particular the tilted smectic C phase, is found. However, although the polymer version exhibits similar phase behaviour to the supermolecular systems, its viscosity is very much higher. Conversely, the viscosities of the supermolecular materials are similar to low molar mass liquid crystals.

Further increase in the number of mesogenic units positioned around a central core unit can be achieved only *via* the synthesis of dendrimers. Examples of liquid crystalline dendrimers, however, are surprisingly scarce. The first thermochromic

liquid crystalline dendrimer was reported by Percec and Kawasumi for a hyperbranched polyether structure that consists of an AB₂ monomer.²⁴ Recently, however, the groups of Shivaev and Frey reported simultaneously the synthesis of liquid crystalline carbosilane dendrimers,^{25,26} which are similar in structure to the silsesquioxane liquid crystals described above. Some of the reported dendrimers combine a flexible, dendritic carbosilane inner core with an outer region that is functionalised on the surface with cyanobiphenyl mesogenic groups, see Fig. 6. As discussed previously this structural concept appears to be at odds with the formation of liquid crystal phases at first sight, because the rod-like mesogenic units are attached to a molecular scaffolding of globular geometry. Thus, it might be expected that the densely packed mesogenic groups in the outer shell of the dendrimer would ensure a spherical disposition of the supermolecule. However, the dendrimers formed exhibit smectic A phases which again requires that the giant molecules must have conformational rod-like shapes which pack in disordered layers. This suggests that the shapes of the dendritic molecules must be deformed by being in a liquid crystal environment. The possibility of being able to control molecular deformation could lead towards novel applications.

Supermolecules with reduced molecular flexibility

So far the materials discussed have had structures where there is reduced flexibility caused by the tethering of the mesogens to a central point and filling the space about this point with mesogenic groups. Internal flexibility, however, can also be reduced by increasing the number of bridging chains between the mesogenic units; which have so far been limited to one in the above discussion. Fig. 7 for example shows the architectural situation for dimers. When one flexible chain links two mesogenic units together, the odd or even parity of the chain can affect the orientation of the mesogenic units relative to one



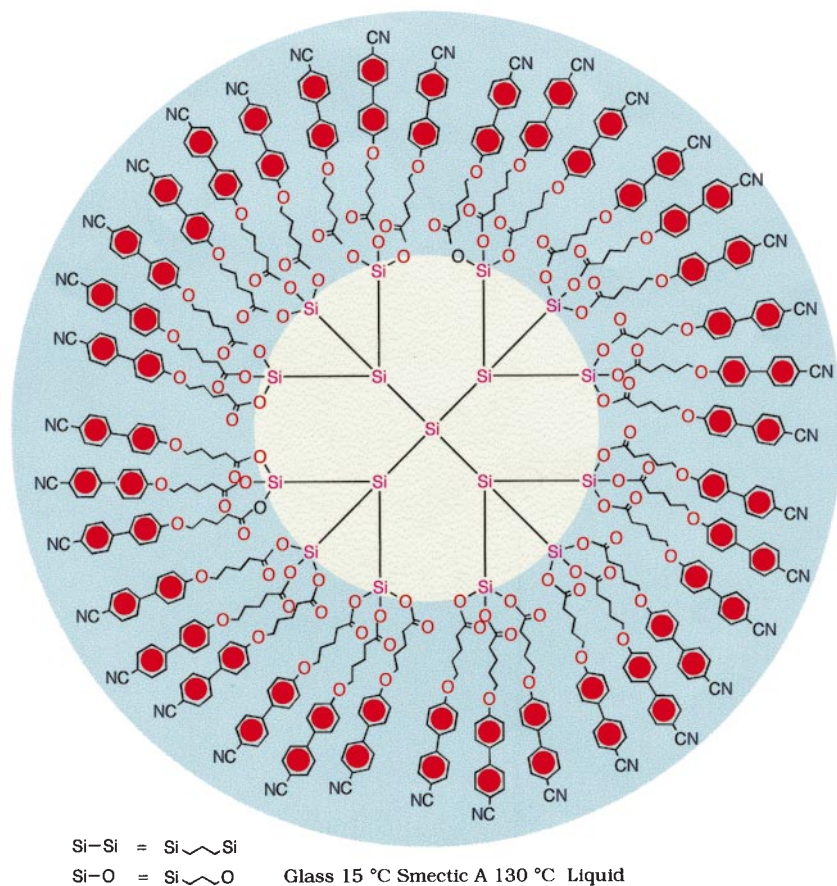


Fig. 6 The structure of a dendrimer that possesses 32 cyanobiphenyl units. The dendrimer exhibits a smectic A phase.

another. For an odd number of methylene units the mesogenic groups will lie at an angle to one another, whereas for an even number of methylene units they will be in line with one another. Thus, the transition temperatures for the even members will be much higher than those of the odd because the even members will have approximately a linear shape rather than a bent one.¹⁸ This effect on molecular shape is particularly important for shorter spacer lengths where the flexibility of the spacer chain is less and the dependency of liquid crystal properties on shape is more pronounced. For dimers where two bridging chains are used to link the mesogenic groups together the degree of flexibility around the centre of the supermolecular structure is further reduced. For instance, if carbocyclic ring systems are introduced between the mesogenic groups, as shown in the middle part of Fig. 7, they will be able to bend in and out of the page, but not so easily in the plane of the page. Carbocyclic rings that are appropriately substituted with mesogenic groups are difficult to synthesise, however, for the purposes of producing model systems it is easier to prepare liquid crystals where two mesogenic groups are attached to a macrocyclic aza-crown ether ring as shown in Fig. 7. Tuffin has taken this approach forward in such a way that she has been able to replicate all forms of liquid crystal behaviour in materials that possess a macrocyclic ring.²⁷

When a macrocyclic ring is inserted between two mesogenic units, then the liquid crystal groups do not need necessarily to be symmetrically positioned on the ring, and they can be located asymmetrically. This allows control of molecular shape so that bent or linear systems can be produced. Materials with bent structures will of course exhibit different mesophase properties to those of linear systems.²⁸ For example compounds **16** and **17** have identical mesogenic groups, but linear compound **16**

exhibits a nematic phase, whereas **17** has an additional smectic C phase, and interestingly, because **17** is bent ferroelectric or antiferroelectric properties become a possibility.

Not only can the position of the substituents be varied on the central ring, but so too can the flexibility of the aza-crown ring. For instance, by increasing the size of the aza-crown ring the degree of flexibility can be increased, and as a consequence the mesogenic units become increasingly decoupled from one another.²⁹ Table 4 clearly demonstrates the effect of increasing the size of the macrocyclic ring. For small ring sizes, nematic phases predominate because the macrocyclic ring acts as part of the rigid central core of the mesogen. As the material 'thinks' it is a 'seven ring' mesogen, high transition temperatures are obtained. When the ring is increased in size the aromatic mesogenic groups start to become decoupled, and smectic phases are introduced. As the ring size is increased further to the extent that the macrocyclic ring can flex and bend more easily, and the mesogenic groups become further decoupled from one another, the smectic phases become destabilised. At this point the motions and orientations of the mesogenic units are relatively independent of one another and the material 'thinks' it is now a quasi-dimer. The flexibility was increased further by substituting oxygen for sulfur in the macrocyclic ring unit, and slightly lower clearing points were obtained and further destabilisation of the smectic state occurred. NMR studies in dilute solution as a function of temperature confirm that the macrocyclic moiety can bend and flex easily about its middle. At low temperatures the molecules were shown to have linear rod-like structures, however when the temperature was raised the population of molecules with hair-pin shaped conformational structures grew.²⁷ Preliminary X-ray diffraction experiments on the neat mesophases exhibited by a selection of the

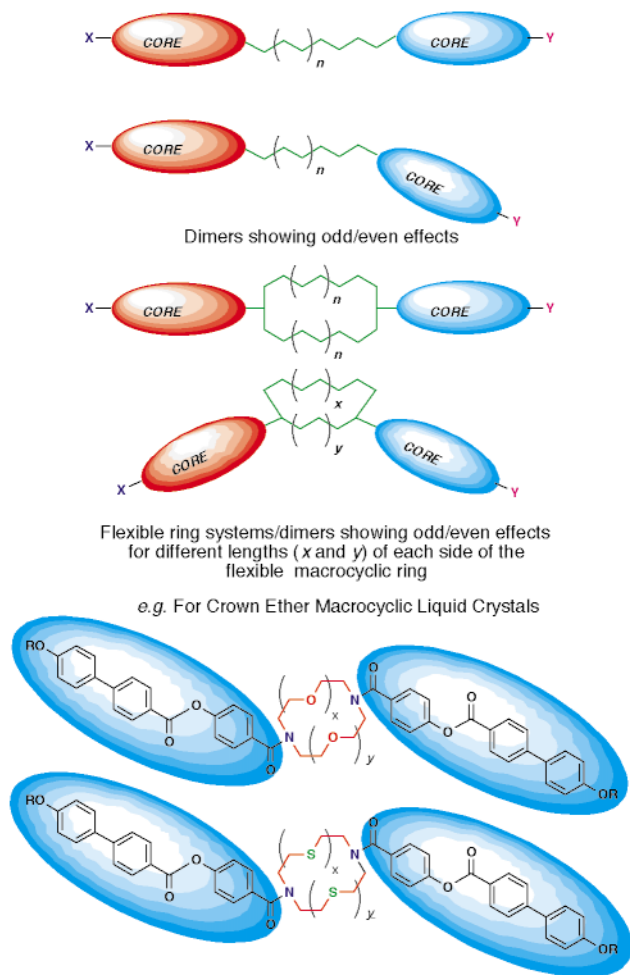


Fig. 7 Schematic representation of mesogenic dimers containing either identical or different mesogenic groups. The linking units between the mesogenic moieties can be either single methylene chains or macrocyclic units. The macrocyclic ring can be an aza-crown *etc.*, and the mesogenic groups need not be positioned symmetrically on the ring, *i.e.* $x \neq y$.

materials confirm the presence of a number of sub-phases which have structures based on either linear or bent molecular conformations. Bilayer phases based on molecules that have bent conformational structures, and monolayer phases where the molecules have fully extended rod-like structures were observed, see Fig. 8. In addition, phases where the long axes of the molecules are either orthogonal (SmA_1 and SmA_2) or tilted (SmC_1 and SmC_2) with respect to the layer planes were found, and in the case of bent molecular conformations even 'antiferroelectric-like' phases ($SmCalt$) were detected.

Supramolecular assemblies of supermolecules

The shapes of the above systems can be varied further by increasing the number and lengths of terminal aliphatic chains attached to the mesogenic aromatic cores. By varying the number and the length of the peripheral aliphatic chains, hair-pin shaped molecular structures can be advantaged over stretched-out conformational structures. Table 5 shows the transition temperatures for a series of compounds based on the tetracatenar macrocyclic liquid crystal structure **18**.³⁰ It can be seen from the table that as the terminal aliphatic chain length is increased lamellar smectic phases give way to disordered columnar mesophases, and for the hexadecyl homologue, at least, both calamitic and columnar phases are exhibited by the

Table 4 Dependency of the transition temperatures ($^{\circ}C$) on macrocyclic ring type **G**, monotropic phase transition given in parentheses

Macrocyclic Core G	Transition Temperatures ($^{\circ}C$)
	Cryst 215 N 323 Iso Liq
	Cryst 195 (SmA 142 N 172.6) Iso Liq
	Cryst 151 (SmC 140.2) N 171.6 Iso Liq
	Cryst 194 (N 186.3) Iso Liq
	Cryst 199 (N 174) Iso Liq

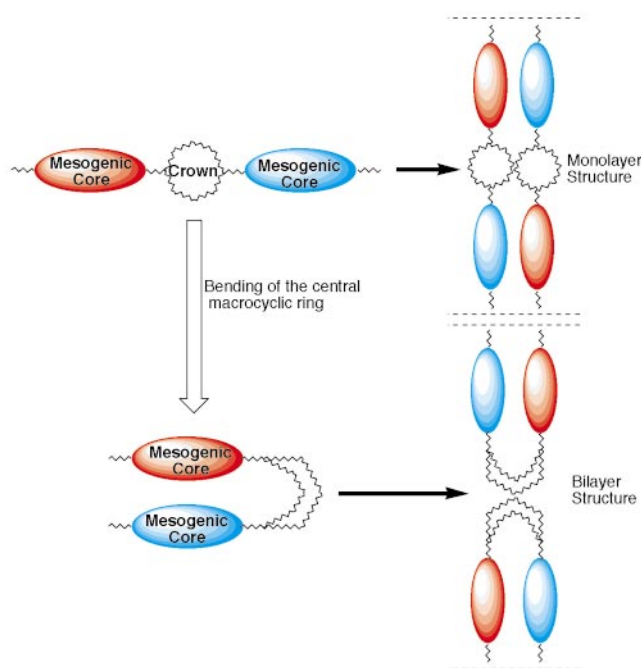
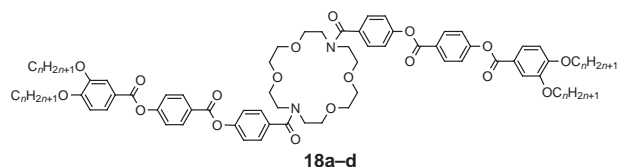
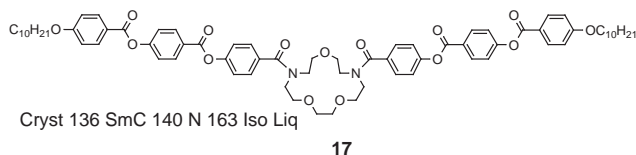
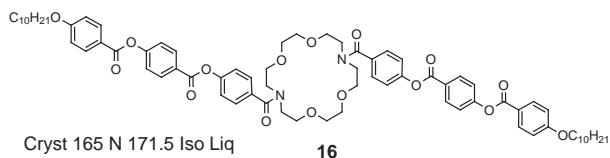


Fig. 8 Packing of the fully extended molecules produces a layered smectic phase, whereas molecular folding about the macrocyclic ring can produce a smectic bilayer structure. As the layer spacing is approximately the same for both conformers mixtures of both structures probably exist.

same material. How then can this be rationalised in terms of molecular shape? One possibility is that clusters of rod-like molecules in their most extended conformations come together, usually in numbers of three, to form disc-like clusters, as postulated for hexacatenar materials.¹⁶ The supramolecular disc-like clusters aggregate and stack in a disordered way to form a columnar architecture. Alternatively, as noted earlier, it is possible that compounds of general structure **18** bend to give hair-pin gross molecular shapes. The bent molecules can

Table 5 Transition temperatures (°C) for the tetracatenar compounds **18a–d**, monotropic phase transition given in parentheses

Compound	Cryst–Liq Cryst	SmC–Iso Liq	SmC–Col	Col–Iso Liq
18a	137.8	(88.0)	—	—
18b	134.9	(129.8)	—	—
18c	134.0	—	(114.0)	(119.0)
18d	120.0	—	—	(90.0)

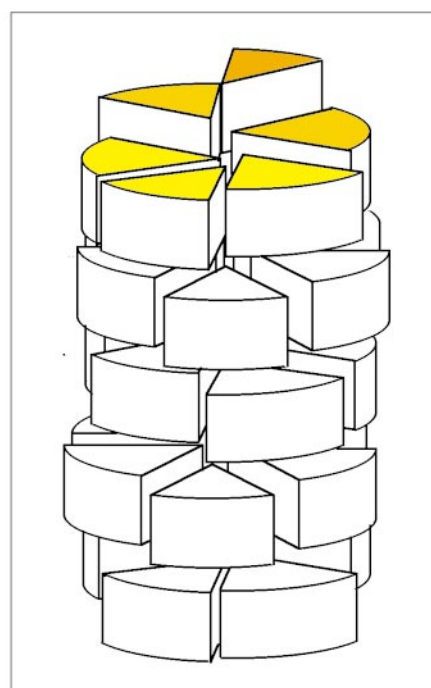
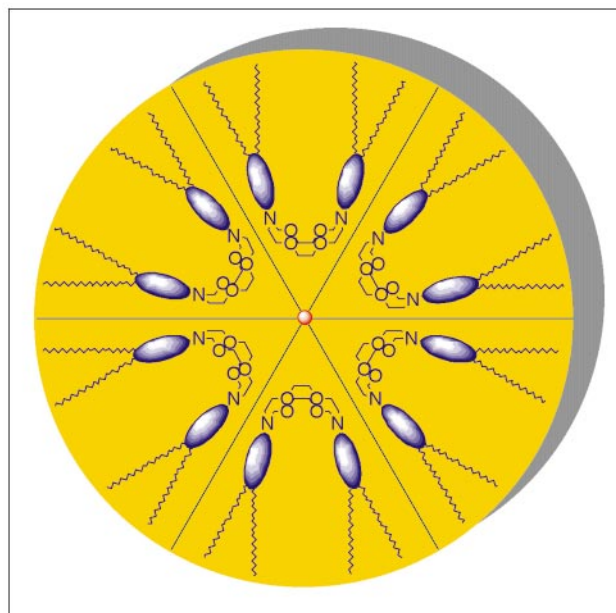


effectively assemble together in clusters to give quasi-discs which are the basis for column formation. Thus, in this case we have a supermolecular system, where the conformational structure can change from being linear to being bent in order to support the formation of supramolecular assemblies, which in turn generate a columnar mesophase,³⁰ as shown in Fig. 9. It is not necessary that the molecules cluster to form flat discs, and in fact the molecules probably remain disordered along the column axes. In this arrangement of the molecules there will be ‘pores’ running down the column axes, thereby indicating the possibility that such systems might act as ion channels. This arrangement is not too dissimilar to the one proposed previously by Percec *et al.* for synthetic mimics of tobacco mosaic virus.³¹

At the centre of each supermolecular mesogen, of course, is a cavity associated with the aza-crown macrocyclic unit. This cavity is capable of accepting a guest ion, and such resulting guest–host systems have remarkably different phase behaviour to the host system. The guests tested included various metal ions associated with a number of different counter ions.²⁷ From these studies it is possible to compare the effects produced on sequentially changing the metal ions, *e.g.* Li⁺, Na⁺, K⁺ *etc.*, with respect to a common counter ion, such as triflate. Similarly it is also possible to maintain the same metal ion but vary the counter ion. Table 6 shows the variation in mesophase types and transition temperatures for 1:1 mixtures obtained in doping studies on the tetradecyloxy tetracatenar material **18b**, and Fig.

Table 6 Dependency of the transition temperatures (°C) on the nature of the metal ion in 1:1 mixtures of compound **19a** with the listed metal triflates

Metal salt	Phase behaviour on cooling
None	Iso liq 129.8 SmC 120.0 Cryst
Lithium triflate	Glassy
Sodium triflate	Iso liq 156.0 col 147.0 lamellar 119.0 glass
Potassium triflate	Iso liq 138.0 col 93.0 lamellar 93.0 glass



Packing of V-shaped molecules into disc-shaped aggregates and columns

Fig. 9 Self-assembly of folded macrocyclic materials can lead to the formation of disc-like structures which in turn self-organise to give columns. The molecules are disordered along the column axes.

10 shows a schematic representation of the structure of the self-assembled columnar phase of **18b** when doped with K⁺. The results for the transition temperatures show a strong dependency on the metal ion (and although not shown here, the counter ion). The transition temperatures are markedly affected by the addition of guests, and in some cases mesophases were found to be introduced where other phases exist for the pure host material. The full phase diagrams show there is a strong dependency of phase type and transition temperatures on concentration of the dopant, and therefore these systems could be used as qualitative or quantitative sensors for certain dopants.

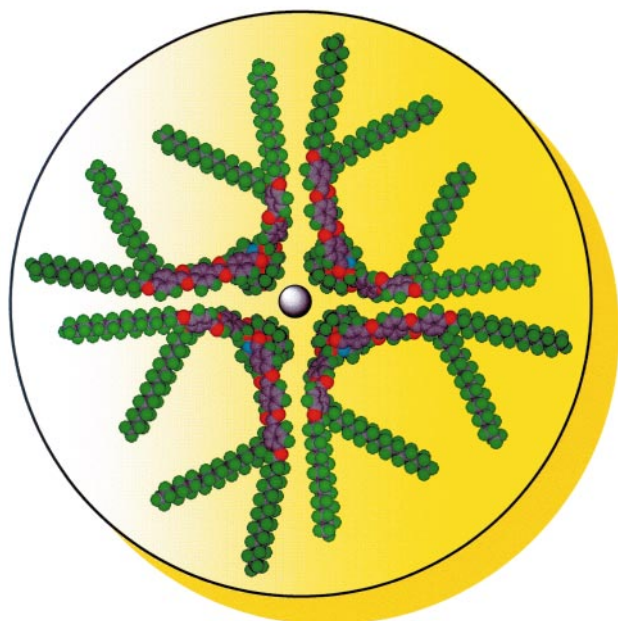
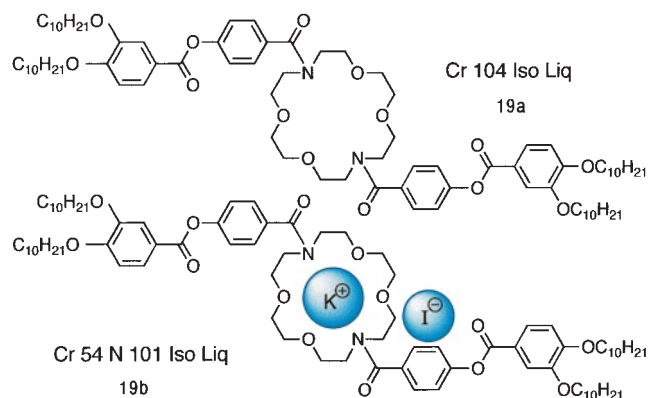


Fig. 10 The self-assembly and self-organisation of folded macrocyclic materials into columns. The inclusion of metal ions stabilises the structure and increases the clearing point of the mesophase.

For some macrocyclic systems mesomorphic properties can be injected into guest–host systems where for the host material alone no liquid crystal properties are found. Tetracatenar compound **19a** exhibits no liquid crystal phases because the aromatic groups responsible for inducing mesomorphic proper-



ties are too short, however the material will still have latent tendencies to produce liquid crystal phases. Upon the addition of potassium triflate, the resulting guest–host supramolecular system, **19b**, exhibits a nematic phase.²⁷ One explanation for such remarkable behaviour is that the host tetracatenar material has a folded or globular structure that is not conducive to mesophase formation because the rigid aromatic cores are too short. However, upon inclusion of potassium ions into the cavities of the macrocyclic unit the molecular structure of the host either unfolds to give a combined guest–host assembly which is much longer and narrower than that of host, or else it forms a rod-like hair-pin complex, see Fig. 11. Either way, the guest–host assembly is now much more rod-like in shape and

now more capable of supporting mesomorphic phase behaviour. Thus, as with the other systems described above, this potential guest–host assembly could be used as a sensor because the introduction of liquid crystal properties are sensitive to the concentration of the ionic guest species.

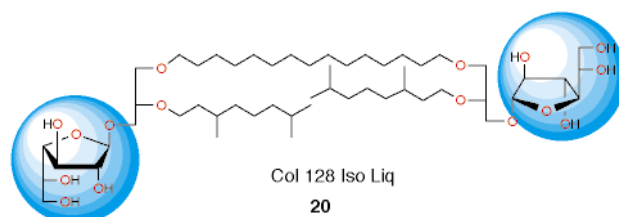
Chiral macrocyclic systems which exhibit chiral nematic phases have also been investigated. The resulting chiral nematic liquid crystals have the property of being able to selectively reflect light of a relatively narrow wave band, *c.f.* non-invasive LC thermometers,⁵ and it has been found that when chiral macrocyclic hosts are doped with chiral ionic species, such as amino acids, the wavelength of the reflected light and the degree of circular polarization is dependent on the concentration and spatial configuration of the dopant. Hence the macrocyclic liquid crystal is capable of distinguishing qualitatively and quantitatively between certain types of enantiomers.

Biological systems

Molecular self-assembly and self-organization are becoming increasingly significant in the elucidation of life processes, and to the generation of new supramolecular structures/ensembles and molecular materials.^{32–40} As a consequence, the most important inspirations for the conceptual development of such structures and materials are those provided by biological cells, which exemplify the assembly of a variety of microstructures of different sizes and functions. Archaeobacteria, with their resistance to extreme conditions, are one class of organisms that have been found to provide a rich source of inspiration. Of particular interest to our studies on molecular topology are lipids derived from thermophilic Archaea. These molecules are characterized by a bipolar architecture with two polar heads linked together by two C₄₀ polyisoprenoid chains which are thought to span the membrane, and therefore determine the lipid layer thickness. Although such lipids are classified as bolaphiles, in relation to the glycolipids discussed earlier (and shown in Fig. 1) they are essentially dimers. A unique feature of tetraether-based lipids lies with (i) the high proportion of glycosylated lipids in the membranes of both methanogenic and sulfur depending thermophiles and (ii) the occurrence of unusual carbohydrate moieties, *i.e.* β-D-galactofuranosyl units.^{41–43} These structural units may further stabilise the membrane structure through cooperative inter-glycosyl hydrogen bonding, *i.e.* via the formation of supramolecular assemblies.^{44,45}

However, in spite of growing attention to archaeal glycolipid structure and function, very few studies have been performed so far to elucidate the relationships between the molecular structure of the glycolipids and the architecture of their supramolecular aggregates. This is in part due to the difficulty of obtaining sufficient amounts of chemically pure compounds from natural sources or by synthetic methods. Some synthetic mimics, however, have been prepared⁴⁶ and their self-assembling properties investigated. For instance, compound **20** is a typical representative member of a number of quasi-macrocyclic bolaphiles that have prepared by Auzély-Velty.⁴⁷ This material is very similar in structural design to those found in the membranes of archaeobacteria and in essence it is an amphiphilic dimer.

When the thermal properties of compound **20** were investi-



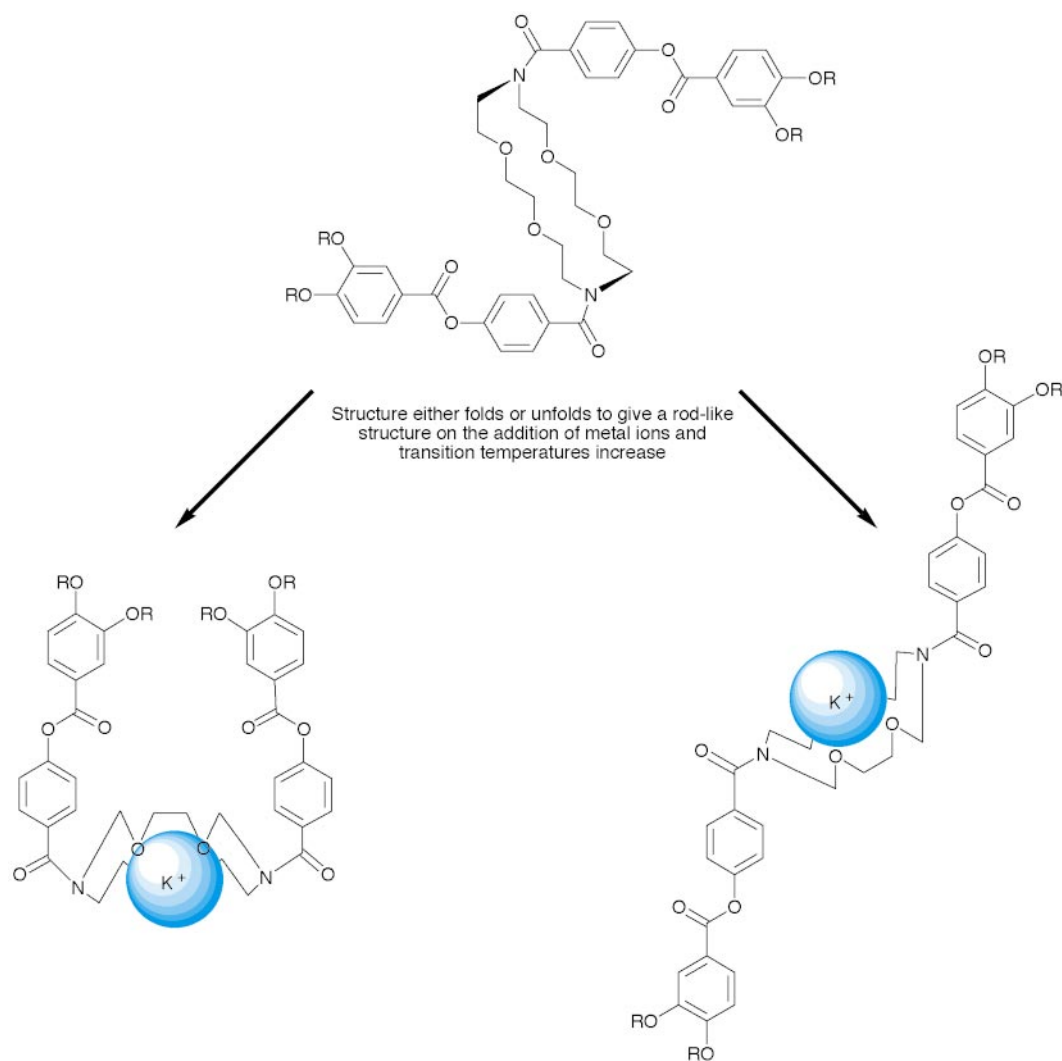


Fig. 11 A globular shaped macrocyclic system undergoes conformational changes upon inclusion of a metal ion. The resulting complex is rod-like in shape and hence the complex is mesomorphic and exhibits a nematic phase.

gated, the material was found to melt just above room temperature from a glassy state directly into a liquid crystal phase which persisted up to a temperature of 128 °C before the isotropic liquid was formed. Upon cooling from the liquid state, the liquid crystal phase was retained *via* supercooling to temperatures well below 0 °C (and under certain conditions down to -50 °C). Thermal cycling served to demonstrate the stability of the mesophase. Thermal optical microscopy showed that the mesophase formed had a columnar structure, Fig. 12(a). The addition of water to the material, plus heating from room temperature, revealed the formation of a lyotropic hexagonal mesophase, Fig. 12(b). The fact that the hexagonal columnar thermotropic phase was found not to be continuously miscible with the hexagonal lyotropic phase indicates that the two columnar structures are not the same. A model for the thermotropic phase based on mixture studies is shown in Fig. 13. In this model the aliphatic chains are on the outside of the columns and the polar head groups are on the inside. This implies that the bolaphiles, just like the macrocycles described earlier, must bend in the centre so that the polar head groups of each end of the glycolipid can interact with one another through hydrogen bonding. Again the hair-pin shaped molecules, just like those shown in Fig. 9 for the macrocyclic systems, cluster together to form quasi-discs which pack in columns (in fact

Figs. 9 and 13 could be easily interchanged). In addition, the molecules have no positional order along the column axis. Much the same situation applies for the lyotropic phase structure except for the probability that the columns are composed of double layers with head groups positioned on the outside and on the inside of the columns in order to allow access of water through the system.

In addition to forming thermotropic and lyotropic liquid crystals these bolaphiles also form large scale aggregates on sonication in water, *i.e.* they form vesicles and tubules. These structures are on a much larger scale than those of the columnar structures of lyotropic and thermotropic liquid crystals, however, their existence serves to demonstrate that the process of self-assembly can extend far beyond the level of simple one on one intermolecular interactions.

Conclusions

In conclusion, we have shown that oligomeric materials with unusual discrete large scale molecular structures can exhibit mesomorphic phase behaviour. In order to exhibit such properties molecular deformation takes place. In certain

(a)



(b)



Fig. 12 The defect texture of (a) the thermotropic columnar mesophase and (b) the hexagonal lyotropic mesophase formed by compound **18** ($\times 100$)

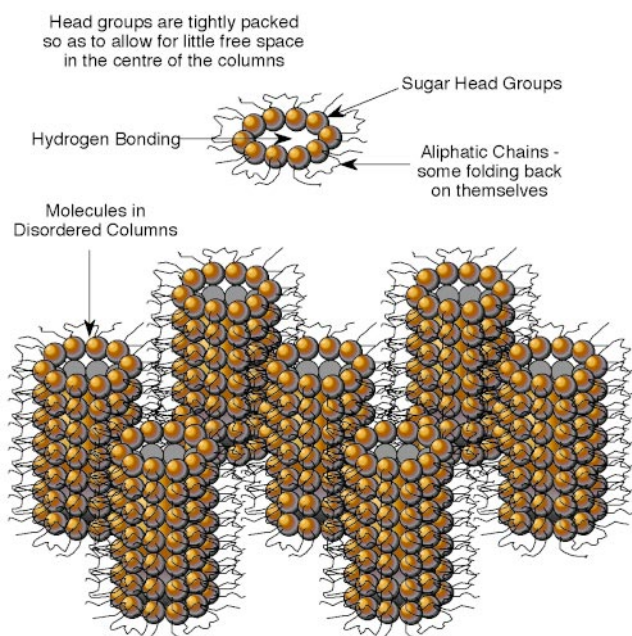


Fig. 13 The disordered hexagonal columnar structure formed by bolaphiles that mimic those found in archaeobacteria. The bolaphiles fold in half so that the sugar residues can hydrogen bond. Clustering leads to the formation of disc-like complexes which then self-organise to give a columnar mesophase.

circumstances molecular deformation stabilises the formation of mesophases through a clustering process where the molecules form supramolecular assemblies. The so-formed assemblies self-organise to give mesophases of various types, for example molecules with rod-like molecular structures can fold in the middle to give wedge-shaped conformers which in turn can self-assemble into discs that self-organise into columns. Thus it is possible that materials of this type will have unique properties and hence applications.

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