

An introduction to Materials Discussion No. 4: Molecular topology in liquid crystals

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Liquid crystals have become the quintessential molecular electronic materials of the current era. As a consequence, they are thought of as high technology materials that are found in high content, low power, passive, flat-panel displays—known to the public as LCD's. Even for those who are relatively familiar with the subject there is a strong tendency to view liquid crystal mesophases as being composed of rod-like molecules that have relatively strong polar properties which respond to external fields like mini-magnets. However, it is not often realised that the term “liquid crystal” represents a number of separate states of matter which, like other states of matter, pervade all classes of materials and touch on a vast number of different topics of research, see Fig. 1. Thus, the multidisciplinary environment of the field of liquid crystals has provided a vehicle for research and training across a wide spectrum of activities, from physics and chemistry to biology and engineering. In the field of physics, as predicted by de Gennes, the discovery of the “liquid-crystalline equivalent of the Abrikosov flux phase”, the twist grain boundary phase, has unified liquid crystal phase transitions with those of superconductors. In biology, it is now realised that some proteins, most components of cell membranes, and even DNA are liquid-crystalline in nature, and in chemistry, the introduction of chirality has led to the discovery of non-linear effects such as thermochromism, electroclimism, ferroelectricity, antiferroelectricity and pyroelectricity in liquid-crystalline systems. Moreover, apart from applications in the area of displays, liquid crystals have also found practical uses in light modulators and gates for photonics, soaps and detergents, high yield strength polymers, artificial muscle, thermal, chemical and electrical sensors, drug delivery systems *etc.*, *etc.*

Molecular shape, reduced symmetry, microphase segregation, self-assembly and self-organisation are five important factors that drive the formation of various liquid crystal phases. The delicate interplay of the molecular interactions coupled with these factors can induce remarkable phase structures and behaviours, for example achiral banana-shaped molecules can pack together to generate helical macrostructures, a “Pasture effect in quasi-liquids”.

Over the past five years there has been a resurgence in the design, synthesis and characterisation of new and exciting liquid crystal systems where the shapes of molecules have been distorted, away from the classical rod-like convention, *e.g.*, dendrimers *etc.* Indeed many new phases have been found in such systems where the molecules have unusual shapes; for example, seven new so-called “banana-phases”, B₁ to B₇, have been discovered for mesogenic systems that have molecules with bent or non-linear-shapes.

The Discussion Meeting, which is the first liquid crystal

conference to be devoted entirely to chemical aspects of the subject, sought to investigate some of the latest results concerning the molecular design and engineering of non-conventional systems. The scientific programme of the Discussion Group was divided into the following eight sessions where one particular feature of molecular topology was put under the microscope.

- Twisting and Turning
- Poles Apart
- What is a Banana?
- Working with Bananas!
- Molecules on a Plate!

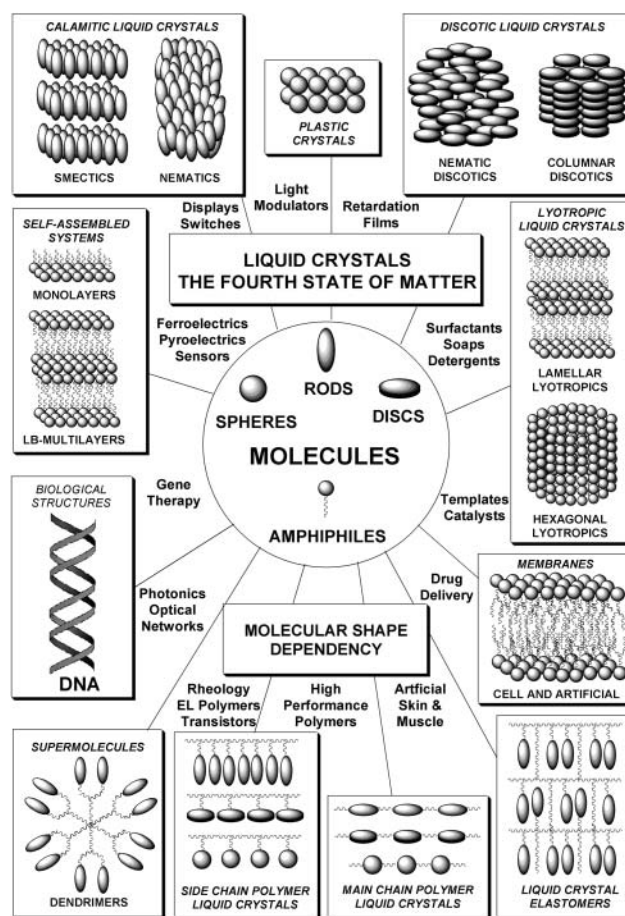


Fig. 1 The general shapes of the constituent molecules in mesogenic materials, the phases that they form and their applications.

Molecular Balls?
Keeping Things Apart!
Bending and Shaping

Over the past 20 years molecular chirality has had a massive and dominating influence on the field of liquid crystals. Therefore it was entirely appropriate that the opening session started with the way in which helical macrostructures are formed in chiral liquid crystal phases. The first session entitled **Twisting and Turning** moved from theoretical modelling through to the practicalities of the induction of helical structures and inversions in their handedness. The discussion spent a great deal of time exploring the interplay between modelling, theory and real systems, and attention was drawn to the similarity of approaches to modelling and synthesis, *i.e.* design (parameterisation), synthesis (calculation), characterisation (evaluation). It was recognised that, in general, physicists had a strong appreciation of physical parameters and that in their simulations, they were able to control conformation—something which was not generally available to the synthetic chemist. This led to consideration of the case of solvent-independent helical twisting power (HTP) and the idea that helical twisting power does in fact depend on the solvent, where the solvent may “select” different conformations of the dopant on grounds of factors such as shape and polarity. Indeed, atomistic simulations show that conformations are rather different in the mesophase compared with, for example, the gas phase. However, although liquid crystals were viewed as fascinating and ideal systems to simulate, it was thought that there would be no immediate help in the way of aiding synthetic chemists with the rational/logical design of materials for applications. In terms of new materials, a novel phase which occurs in the isotropic liquid just above the transition to the liquid crystal state was reported for a chiral liquid crystal dimer, structure **I**. The presence of this phase implies a remarkable transition from one liquid state to another! Although exhibiting an isotropic microscopic defect texture characteristic of a cubic phase, X-ray diffraction studies of the liquid phase suggested the presence of weak layer ordering. For the racemic modification, a nematic to isotropic phase transition was found to occur at the same temperature as the liquid to liquid transition in the enantiomeric form. Thus, molecular chirality was shown to have a remarkably powerful effect on phase transition behaviour and temperatures. In the ensuing discussion there was a call for the use of consistent nomenclature, a suggestion that the new phase might be a layered Blue Phase (BPs) or a thermotropic phase that was analogous to one of the lyotropic “sponge” phases, and attention was drawn to the notion of “lattice melting” models proposed by Collings.¹

It is well-known that chiral systems not only induce the formation of helical structures, but they are also responsible for the induction of non-linear properties such as ferroelectricity and antiferroelectricity. In the second discussion entitled **Poles Apart** new aspects of chirality, ferroelectricity, antiferroelectricity and their relationship to microphase segregation were investigated, see Fig. 2.

The session began with discussions concerning the relationships between molecular structure and physical properties in banana-shaped liquid crystals. This was only the start of presentations and extensive discussions on banana systems which continued over the next two sessions. Several common structural features were identified including a molecular bend of *ca.* 105° and the presence of carbonyl groups in the molecular structure. It was thought that temperature dependent

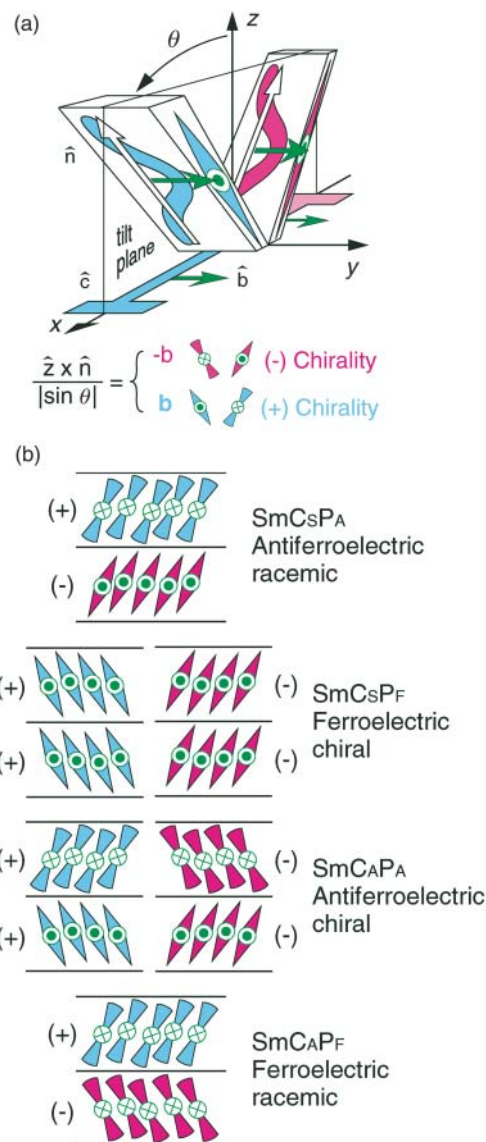
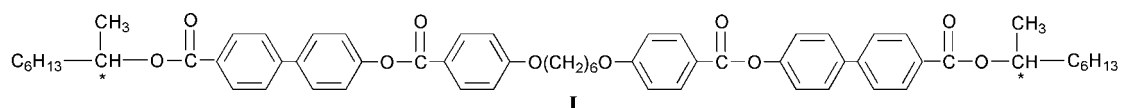


Fig. 2 (Takezoe, DOI: 10.1039/b103506c) Definition of layer chirality and possible molecular orientation arrangements in bent-core mesogens. (a) In a smectic layer with layer normal along the *z*-axis and polar order along *b* parallel to the *y*-axis, two possible chiral layer structures are defined by the director *n* tilting by θ either along the positive (blue) or negative *x*-axis (red). (b) The suffix S or A added to SmC in the nomenclature SmC_{S,A}P_{F,A} indicates either a synclinc or anticlinic tilt structure and suffix F or A added to P specifies either ferroelectric or antiferroelectric polar ordering in adjacent layers. Two racemic layer structures and four (two positive and two negative) homochiral layer structures are also specified by the combinations of ferroelectric or antiferroelectric in polar order and synclinc or anticlinic in layer tilt.

conformational changes were important in determining phase behaviour as there were no known examples of banana-shaped mesogens with rigid structures. The rôle of carbonyl functional groups was also discussed and specifically whether the arrangement of the dipoles parallel to the layers was a consequence of packing effects or whether this was part of the driving force in phase formation. The possibility of forming biaxial smectic A phases composed of banana-shaped molecules was also discussed as a way towards developing materials that might exhibit the elusive biaxial nematic phase. The mesomorphic



properties of bent and linear dimers containing siloxane moieties were presented with the ensuing discussion centring on the rôle played by the siloxane unit in determining phase behaviour. Views were expressed that there could be an incompatibility between the siloxane and alkyl regions leading to microphase segregation. However, this was disputed as it was noted that dimethylsiloxane was actually miscible with alkanes! Instead it was proposed that differences in shape were at the root of smectic phase formation. In addition, novel dimers were shown to exhibit helical structures and to have strong flexoelectric properties. This made the materials ideal candidates for very fast responding electrooptic switches and displays.

The programme then moved on from chirality at the molecular level to chirality in broken space. Here the focus was totally on molecules that have bent molecular structures and which self-organise to give mesophases with reduced symmetries. This aptly titled third discussion group **What is a Banana?** centred on the driving forces which cause the self-organisation of bent achiral molecules to give chiral and mixed helical mesophases. A new smectic Sm1 phase was reported, and the importance of shape in establishing the properties of oligomeric liquid crystals was highlighted. A lively debate then followed a presentation on polyfluorinated hockey-stick shaped systems. Two particularly surprising observations were made; the first centred on the formation of columnar phases by an apparently rigid, rod-like mesogenic material, and the second concerned the remarkable observation of a racemic compound forming a chiral phase with a helical structure of one hand only, see structure **II** and Fig. 3. Many suggestions were made for the induction of chirality into such systems, including the possibility of enriching of one enantiomer over an other. However, it was concluded that this was unlikely as the pitch of the helix in the phase was relatively short indicating that enrichment would have had to have been substantial. Thus it appears that macroscopic chiral induction from a microscopic achiral system had been achieved—*i.e.* parity breaking on a macroscopic scale!

Once having established what a banana was, the next discussion group focused on the properties of self-assembled systems of molecules that have bent structures. This intriguingly named session called **Working with Bananas!** probed the physical properties of those phases; the generation of ferroelectricity and antiferroelectricity; the defects that are formed and the structures that they possess. The papers of Walba and Weissflog triggered the debate surrounding the nomenclature and classification of the seven “banana” (B₁ to B₇) phases. It was recognised that the current designations are based on textural observations, and it is clear that the same label is sometimes being used for structurally different phases. X-Ray

diffraction suggested that some banana-phases were in fact soft crystals, and order–disorder transitions could occur with the less ordered phase occurring below the ordered phase on cooling! It was agreed that situation concerning the designation of banana phases was similar to that which pervaded the classification, in the early 1970’s, of smectic phases, and thus a new and consistent system was required. A discussion ensued about the structural features needed to observe banana phases and how surprisingly exacting these are. Fascinating hockey-stick molecules based on benzofuran were also described. These new materials were shown to have potentially interesting nematic and smectic properties making them of interest in devices. However, the materials were shown to be not fully light stable, which was thought to be due to the materials undergoing a [2+2] cycloaddition across the furan ring system.

Having explored chiral rod-like systems and materials with bent molecular shapes, the meeting moved on to discuss liquid crystal phases formed by conventional disc-like systems through to metal-containing and polyaromatic materials—**Molecules on a Plate!** Disc-like molecules have been known for a long time to be able to stack in disordered and ordered columns. Moreover disc-like molecules have also been shown to form negative uniaxial nematic phases. Theoretic modelling of mixtures of positive and negative uniaxial nematic has shown that under certain circumstances a biaxial phase might be formed. This part of the programme investigated the detailed structure of columnar phases, guest–host interactions and the induction of columnar phases in systems that are not mesogenic, and the potential for the formation of biaxial phases in mixtures of board-like and rod-like molecular systems. Mixed thiol ether and ether-substituted triphenylene-based materials were thought to form helical columnar phases with the sulfur atoms, through steric constraints on their packing arrangements, causing a unidirectional rotation of the molecular discs along the column axes. The characterisation of such phases was realised to be extremely difficult. However, if twisted columns do in fact exist, as with banana systems, chiral induction in a macroscopic system is caused by the packing of achiral molecular units at the microscopic level. New triphenylene-based materials were described which contained carbazole moieties; the induced liquid crystallinity in these systems was achieved by the addition of TNF. Discussion focused on possible photorefractive effects in these systems, the specificity of the interaction between TNF and these molecules and the observation that the interaction was predominantly with the triphenylene units. So far the discussion programme had centred on the self-organisation of discrete disc-like molecules, but the design and synthesis of new hyperbranched polymers utilising phthalocyanine as the disc-like unit gave new insights into the development of novel microporous materials. The nature of the porosity in these systems, with the possibility of incorporating various metals into the pores, prompted much discussion as did comparisons of their properties with zeolites and templated inorganic materials. Lastly in this session the work was presented on the syntheses of novel octa- and tetra-substituted systems based on tetrabenz[*a,c,h,j*]anthracene. The disc-shaped octa-substituted material was shown to exhibit a columnar mesophase, whereas the tetra-substituted material was found to exhibit a lamellar phase. Binary mixtures of the two materials were examined in

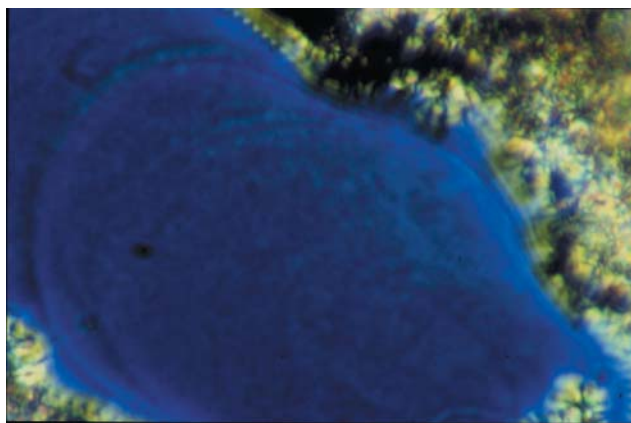
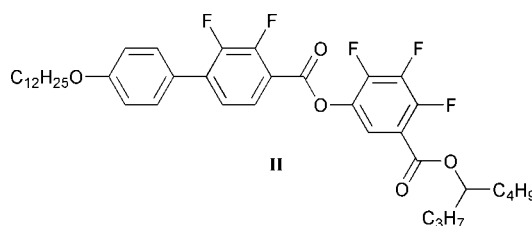


Fig. 3 (Hird, DOI: 10.1039/b102988f) A free-standing film showing the iridescent texture exhibited by the SmX* phase of racemic compound **II**.



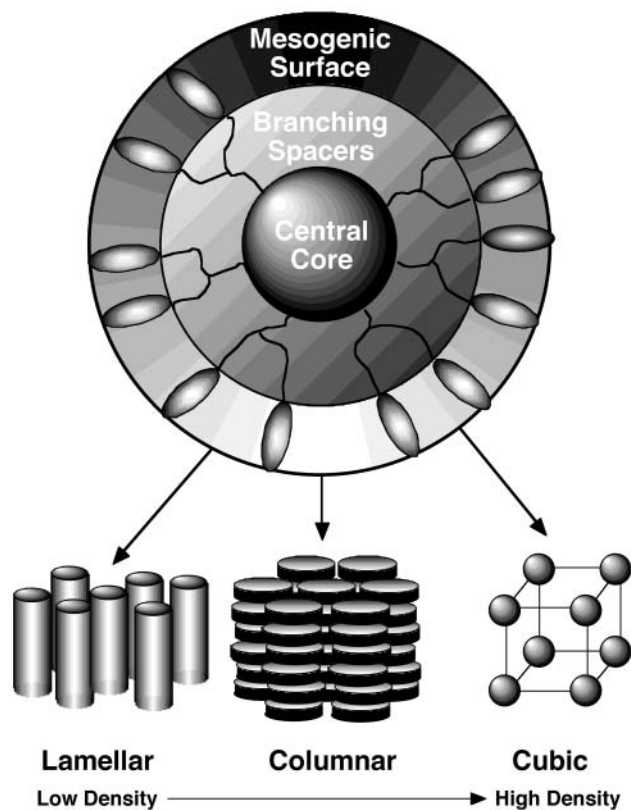


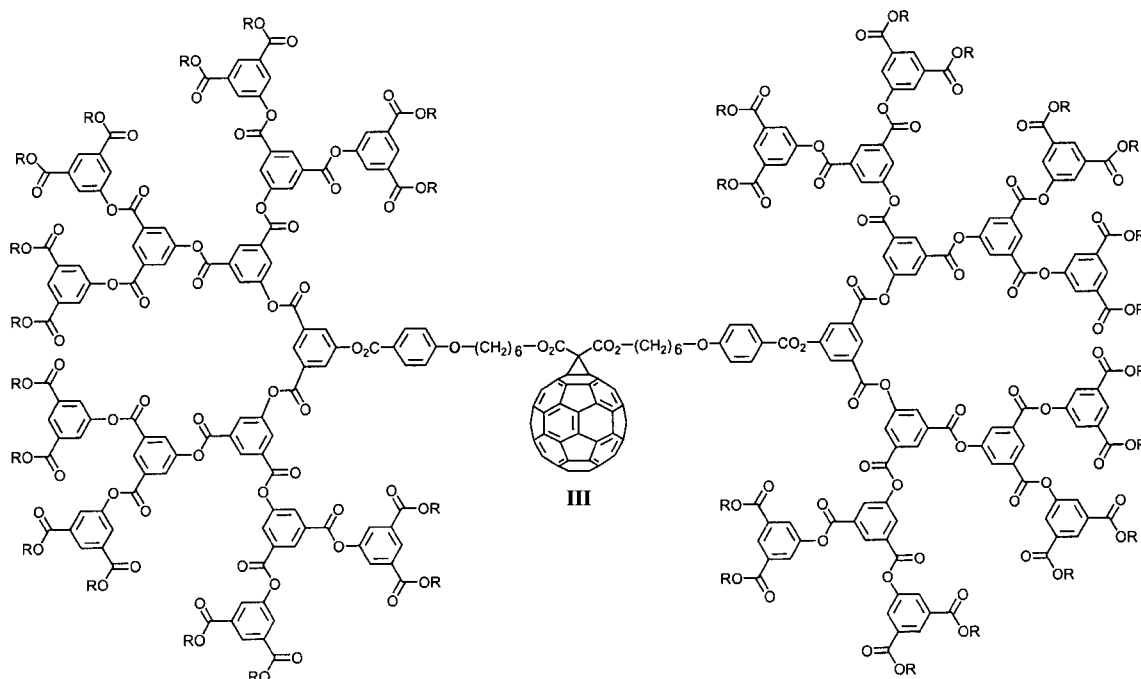
Fig. 4 The effect of the density of mesogenic groups on mesophase formation in liquid crystal dendrimers.

order to explore the changeover from discotic to calamitic behaviour as a function of concentration. At the crossover point, the possibility of the formation of a biaxial phase was investigated.

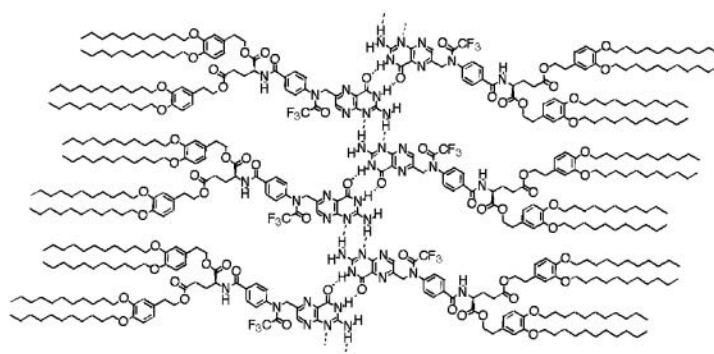
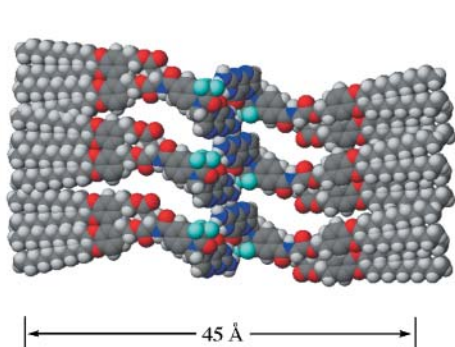
Having discussed the self-organising properties of rods, bananas and discs the next obvious molecular shape to investigate was the self-organisation of molecular spheres, *i.e.* dendritic liquid crystals. In this session on **Molecular Balls?** an examination of how the liquid crystal environment deforms the structure of spherical dendritic molecules from balls to disks to

rods was investigated as a function of the density of packing of the mesogenic groups on the outer surface of the dendritic structure, see Fig. 4. It was demonstrated how, by increasing the density of mesogenic groups terminally attached to flexible dendritic cores such as PAMAM, rod-like conformational molecular shapes were obtained that preferred the formation of lamellar phases, as the density was increased to 64 mesogenic groups, the supermolecular structure switched to being disc-like, thereby preferring the formation of columnar phases. By laterally attaching the mesogenic groups, nematic phases were achieved. These giant single molecular entities were shown to exhibit properties more akin to low molar mass materials than to polymeric systems. This theme was continued in research reported on the synthesis and properties of fullerene-containing liquid crystal dendrimers, see structure **III**. The discussion focused on the extent to which the unique properties of fullerene were attenuated by the liquid-crystalline dendritic environment and whether or not the fullerene unit was easily accessible for the purposes of application. Theoretical modelling provided a molecular description of the mesomorphic behaviour of radial, propeller-like dendritic globular supermolecules; this generated considerable discussion, particularly how the propeller-like supermolecules would pack together like cog-wheels, and how these ideas might be transferred to real molecular systems.

In the previous topics for discussion we discussed the self-organisation of systems that have various types of molecular shape; in the next session an examination was made of how materials might pack together where the constituent molecules have dichotomous and trichotomous structures. In such systems the self-organisation process is driven by the associations of like parts of the materials which will run away from the dissimilar parts of the molecules. This view on structural aspects of microphase segregation gave the title of **Keeping Things Apart!** for this session. Two contributions were made in this session, one following on from the discussion on molecular balls and the other on biologically relevant liquid crystals. Firstly it was shown how the octasilsesquioxane cage could be derivatised by laterally substituted, chiral mesogenic moieties to yield monodisperse multipodal octamers. The liquid-crystalline silsesquioxane giant supermolecular materials were shown to display remarkably wide temperature range enantiotropic



(A) Smectic aggregation



(B) Discotic aggregation

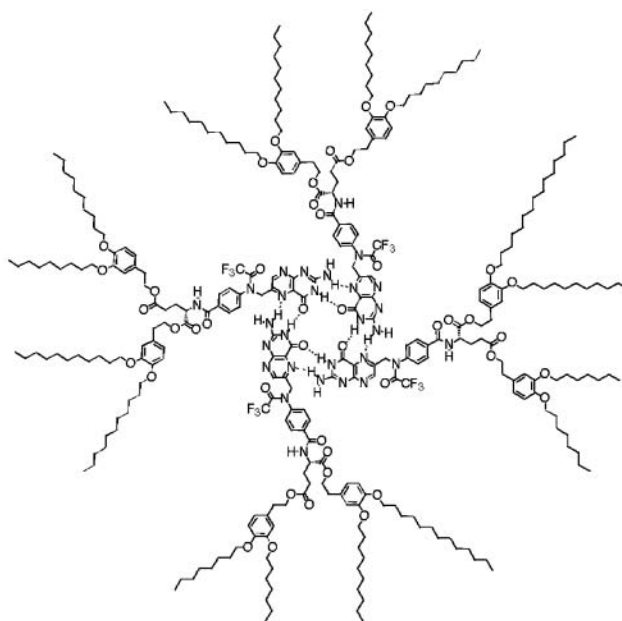
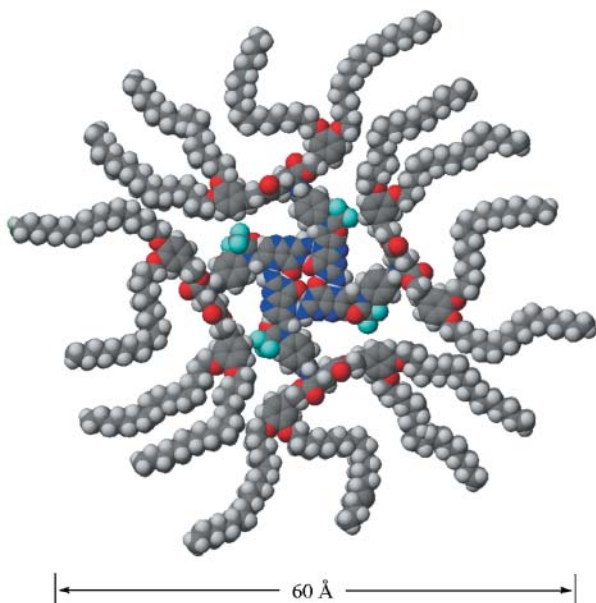


Fig. 5 (Kato, DOI: 10.1039/b103168f) Self-assembled smectic (A) and discotic (B) structures of folic acid derivatives.

chiral nematic phases and glass transitions near to room temperature. The materials were similar to low molar mass materials even though they had a size approaching that of small globular proteins. These observations stimulated the questions as to whether the materials act as singular molecular entities or as spherical side chain polymers. In a complete change of direction, the session continued with a description of how the variation in the position of attachment of an aliphatic chain to a disaccharide sucrose unit can markedly influence the self-organising properties of a sucrose ester. The location of the attachment can introduce curvature into the system thereby stabilising certain structures over others. The results obtained for the thermotropic liquid crystalline properties of the mono-*O*-(2-hydroxydodecyl)sucroses show a similar dependency on molecular shape and curvature as those found in general for lyotropic systems. Debate ensued over whether or not a complete phase diagram relating curvature of packing to transition temperature could be achieved for thermotropic systems in a similar way to that obtained for lyotropic systems.

In an analogy with the session on microphase segregation, the final session moved on to working with such systems in novel ways so that the molecular shapes can be bent or curved.

In this session called **Bending and Shaping** we examined polycatenar and block copolymer systems where, if one chain or segment can do it for you, we were sure that two or three chains or segments would be better. The session centred on two themes, one on the self-assembly of mesomorphic systems which then exhibited self-organisation and the other concerned tri-block copolymers in lyotropic systems. In the first theme the self-assembly of polycatenar systems based on metal complexation or the hydrogen bonding of folic acid was described. Lamellar, columnar and cubic phases, the full range, were obtained in polycatenar systems and lamellar and columnar phases in derivatives of folic acids. This research illustrated the difference between self-assembly and self-organisation; *self-assembly* being the process of the assembly of the component parts of a larger molecular system, which does not necessarily have orientational order, and *self-organisation* applying to systems where the molecular entities are in dynamic motion but also have long range orientational ordering. Non-mesogenic moieties can therefore self-assemble to give a discrete entity or complex which can then self-organise to give an orientationally ordered system—a liquid crystal, see Fig. 5. In the second theme, tri-block copolymers were shown to self-organise in

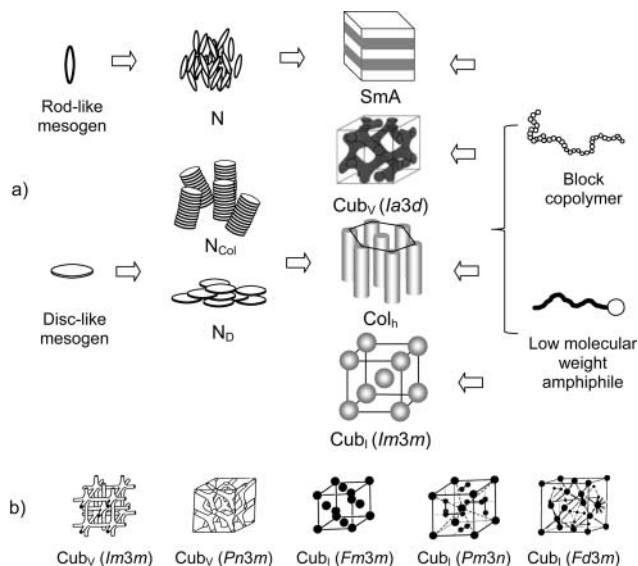


Fig. 6 (Tschierske, DOI: 10.1039/b102914m) (a) Fundamental mesophase morphologies formed by the organisation of calamitic or disc-like molecules, binary amphiphiles and coil-coil AB diblock copolymers. Abbreviations: N=nematic mesophase formed by calamitic molecules (N), disc-like molecules (N_D) or 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 (Ia3d and Im3m) 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 Im3m lattice can represent a bicontinuous structure as well as an array of spherical micelles.

lyotropic systems and to give the full range of lamellar, columnar and cubic mesophases, thereby unifying the underlying physics of block co-polymers with that of liquid crystals, see Fig. 6.

The following plenary lectures covered aspects of simulations and modelling, and synthesis and characterisation of materials: *Molecular Design and Computer Simulations of Novel Mesophases* by Claudio Zannoni and *Micro-segregation, Molecular Shape and Molecular Topology – Partners for the Design of Liquid Crystalline Materials with Complex Mesophase Morphology* by Carsten Tschierske.

The Discussion Group lively debated the full range of the effects of molecular topology on mesophase formation. Even though the biaxial nematic phase remained elusive, many new phases were reported that had unusual structures which demonstrated that the field of structure and bonding in liquid crystals is very much alive. The effects of the liquid crystal environment on the shapes of supermolecules were debated, and strong similarities were drawn between the structures and properties of liquid crystals, block copolymers and biological membranes, indicating that these subjects share the same underlying physics. A paradigm shift appears evident in the understanding of chiral interactions and the induction of chirality into liquid crystal phases by achiral materials—raising a question over the equivalency of the laws for left and right in such macroscopic systems.

References

- 1 “Lattice Melting at the Clearing Point in Frustrated Systems”, J. W. Goodby, D. A. Dunmur and P. J. Collings, *Liq. Cryst.*, 1995, **19**, 703.