

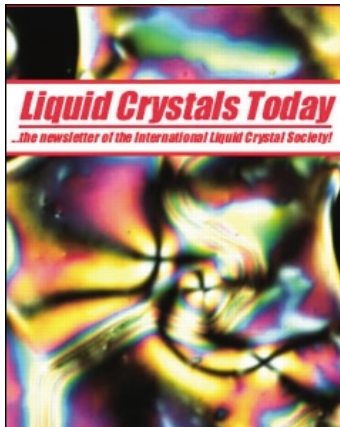
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Complex Liquid Crystals - Big is Beautiful

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Complex Liquid Crystals - Big is Beautiful

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Introduction

The manipulation of the non-covalent forces that hold the constituents of a system together, leading to the design of “smart” functional supramolecular materials, is expected to have a strong impact on the future development of materials science [1]. This area of research offers a powerful alternative for managing the awkward gap in the length scale which exists between top-down miniaturisation and bottom-up nanofabrication.

Through self-assembly and self-organisation processes, liquid crystalline phases have opened up new perspectives in materials science towards the design and engineering of supramolecular materials [1a,d,e]. The self-organisation in two- and three-dimensional space offered by the liquid crystalline medium is an ideal vehicle to explore and control the organisation of matter on the nanometer scale to the micrometer, which is key in the emerging development of nanotechnology.

Central to the development of new applications for LC is the search for new, non-conventional mesogenic materials. In many cases these new materials have molecular architectures that do not fall into the traditional categories of rod-like or disc-like but are characterised by intermediate shapes, which in turn contain several elements capable of being independently manipulated. Similarly, their mesogenic behaviour is not restricted to thermotropic or lyotropic but can display both types. This has led to the discovery of new types of mesophases with fascinating structures, which have been summarised in several recent papers [2].

As part of our ongoing work on non-conventional mesogens, we sought to develop *functional mesogenic materials* in the form of *dendritic liquid crystals and multipedes*. The structures of such materials possess large but discrete molecular systems created when many mesogenic feet are tied covalently to a central core (scaffold), with precisely defined molecular nature and topology. The resulting materials are thus expected to

exhibit unique physical properties dependent on the functionality. This group of materials combines the properties typically of low molar mass LC-like reduced melt viscosity, the glass-forming abilities [3] of conventional polymeric structures, and the fact that the materials are monodisperse, which ensures that the properties will possess reproducibility and independence on molar mass. This article focuses on our recent work in the field of liquid crystalline dendrimers and related multipedes, their design, synthesis and properties.

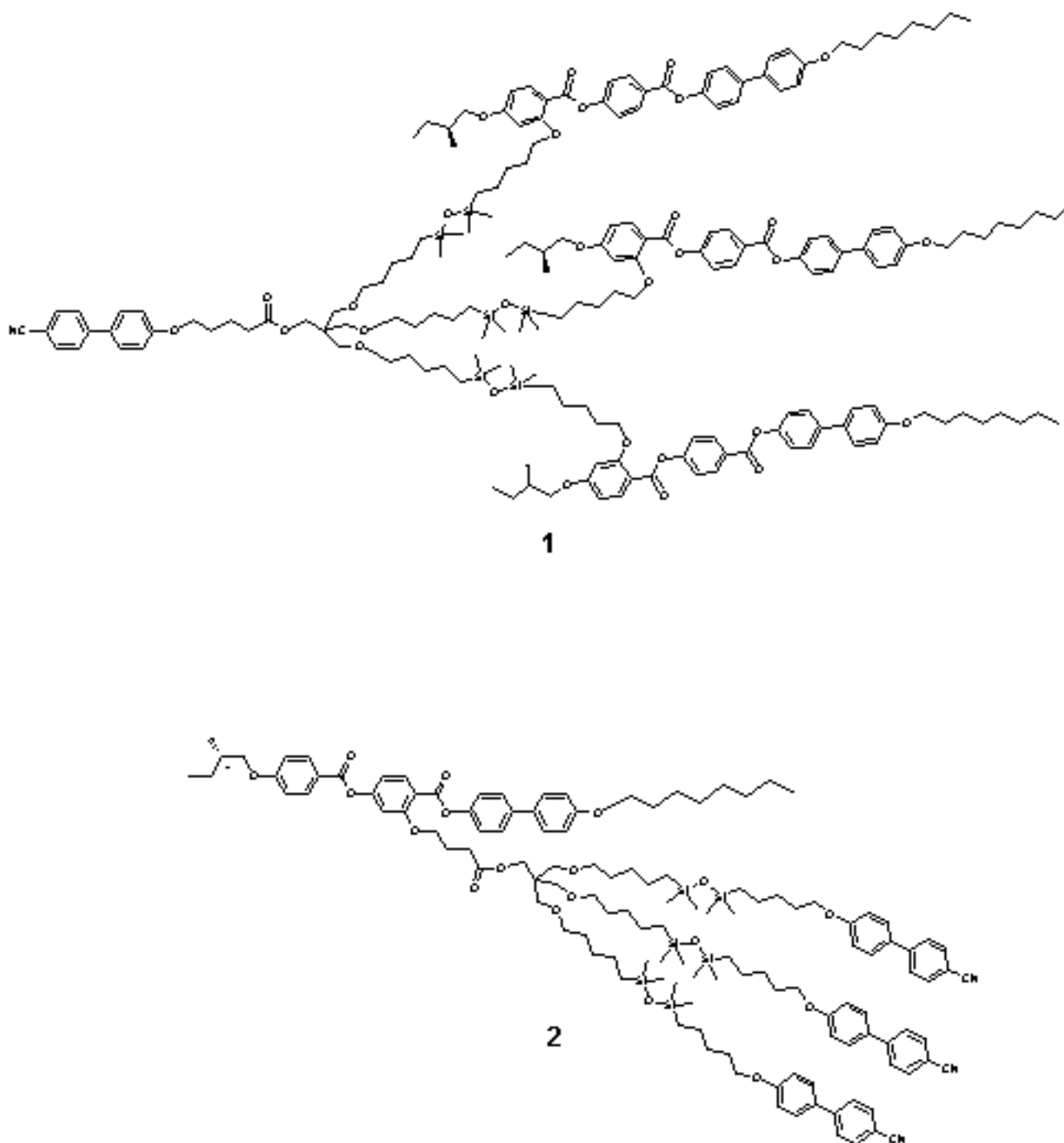
Multipedes and Polypedes

A group of chiral nematic multipedal unsymmetrical tetramers **1** and **2**, that contain two types of mesogenic sub-units based on pentaerythritol, covalently tied to the central scaffold, thereby forming a “molecular knot”, has been studied [4] (Figure 1). The nature of the mesogens (cyanobiphenyl and phenyl benzoate-types), chirality, the topology of the attachment to the core (end-on and side-on) and the chemical nature of the linking connection to the PE scaffold (ether, ester and tetramethyldisiloxane moieties) have been used to differentiate the quadrants of the PE-based core. We targeted the chiral nematic phase for its extensive applications in light driven devices and the possibility of fabricating cholesteric films for use as colour filters, reflective polarisers and polarised fluorescent films.

Supermolecular materials **1** and **2** exhibit the chiral nematic phase. The crystalline state was found to be suppressed in these materials once they had experienced a first isotropisation process, with glass transitions below room temperature and accompanying wide temperature range mesophases.

The symmetrical polypedal tetramers **3** and **4**, carrying only side-on mesogens, also display the N* mesophase, with a typical Grandjean plane texture. Mechanical shearing of the specimens shows that the samples have low viscosity, indicating that the materials have rheological properties similar to low molar mass mesogens. Conversely, the parent cyanobiphenyl-based tetramers **5** and **6** (all four identical) and the

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Figure 1. Multipedes **1** and **2**.

dendron-type trimer **7** (one arm missing) exhibit the smectic A phase.

In both sets of parent symmetrical tetramers (side-on and end-on), the mesophase stability of the tetraesters is higher than in the siloxy analogues; one important contributing factor may be that the presence of the flexible, but rather bulky tetramethyldisiloxane moiety

in the middle of the spacer chain considerably disrupts the interactions between the aromatic cores, decreasing the stability of the mesophase.

Comparison of transition temperatures between the unsymmetrical and the parent polypedal tetramers provides another insight into the effect of sequential substitution of one type of mesogen by a mesogen of a

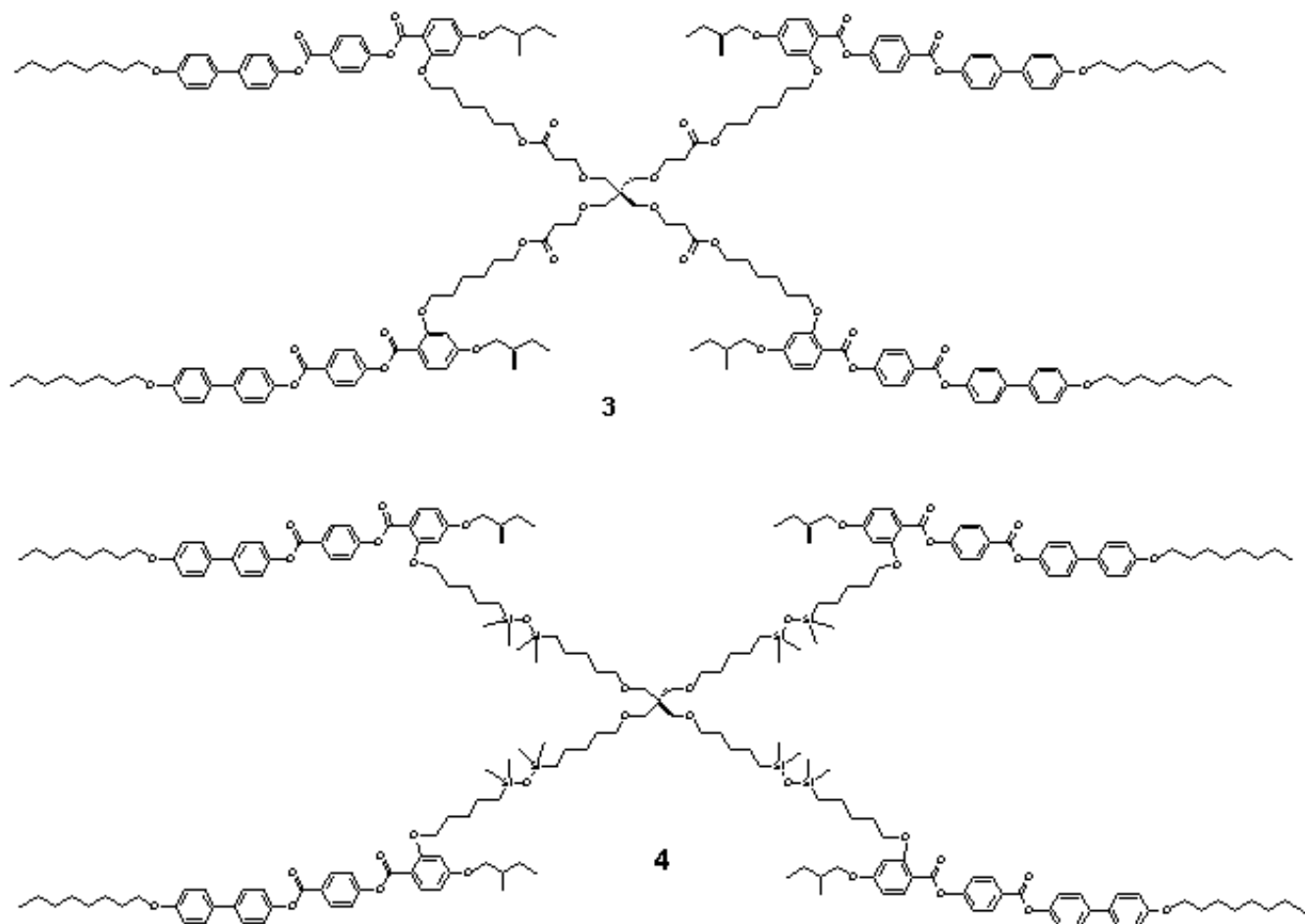


Figure 2. Parent polypedes with side-on mesogens.

different nature. Thus, replacement of one side-on siloxy mesogen in **4** by a terminally attached cyanobiphenyl to give **1** has the effect of suppressing crystallisation totally and reducing the clearing temperature (from 79.7 to 58.8°C), which is consistent with the fact that disordering has been introduced in the system, whereby the cyanobiphenyl moiety somewhat disrupts the cholesteric structure without totally suppressing the chiral nematic phase.

Comparison of **6** with **2** shows that substitution of one cyanobiphenyl unit by the large lateral mesogen is not enough to induce crystallisation, with the glassy state remaining. This is consistent with the fact that some disorder has been introduced in the system, which is enough for the lamellar arrangement (SmA phase) to be totally suppressed. Thus just one side-on mesogen out of four is enough to induce the chiral nematic phase in this group of materials, in keeping with the strong nematogenic tendency observed for this type of mesogen [5]. A similar conclusion is observed when comparing **7** with **2**. The introduction of one mesogenic

group that strongly favours nematic behaviour into a system which possesses SmA-promoting cyanobiphenyl unit as in **7**, the SmA phase is suppressed, resulting in the formation of an enantiotropic chiral nematic phase. This also enhances the tendency to form a glassy material and stabilises the mesomorphic state by 30°C, raising the isotropisation temperature from -11.3°C in **7** to 18.6°C in **2**.

Liquid Crystalline Dendrimers

Dendritic liquid crystals [6a-c] combine the unique traits of the self-organisation of discrete low molecular weight materials with those of polymers in their ability to form secondary and tertiary structures, providing unique materials for the study of self-organising and self-assembling processes.

Furthermore, dendrimers [6d-f] exhibit a variety of physical properties that make them attractive for applications in the fields of nanoscience, materials and biology. They offer a very elegant and effective way of adding functionalisation together with an exquisite and

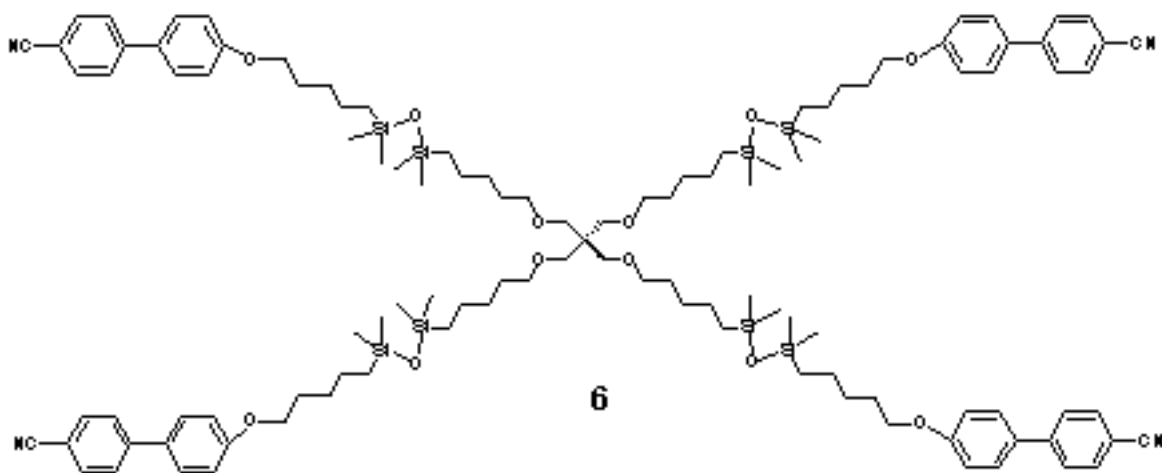
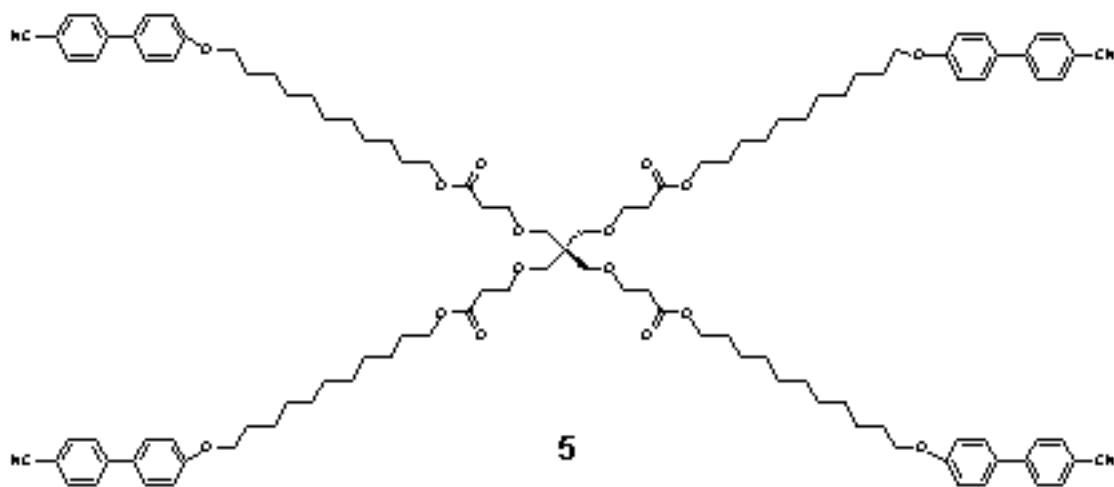


Figure 3. Parent polypeptides with end-on mesogens.

unprecedented level of control of the precise nature and location of specific functionalities and overall molecular architectures, as in proteins. As a consequence, the

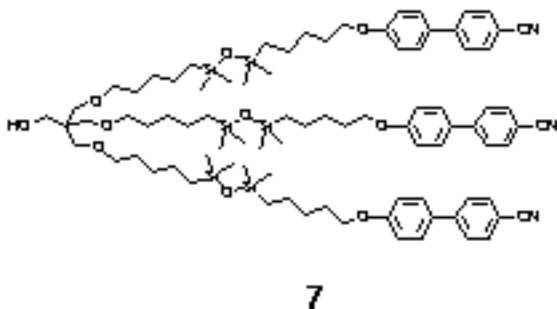


Figure 4.

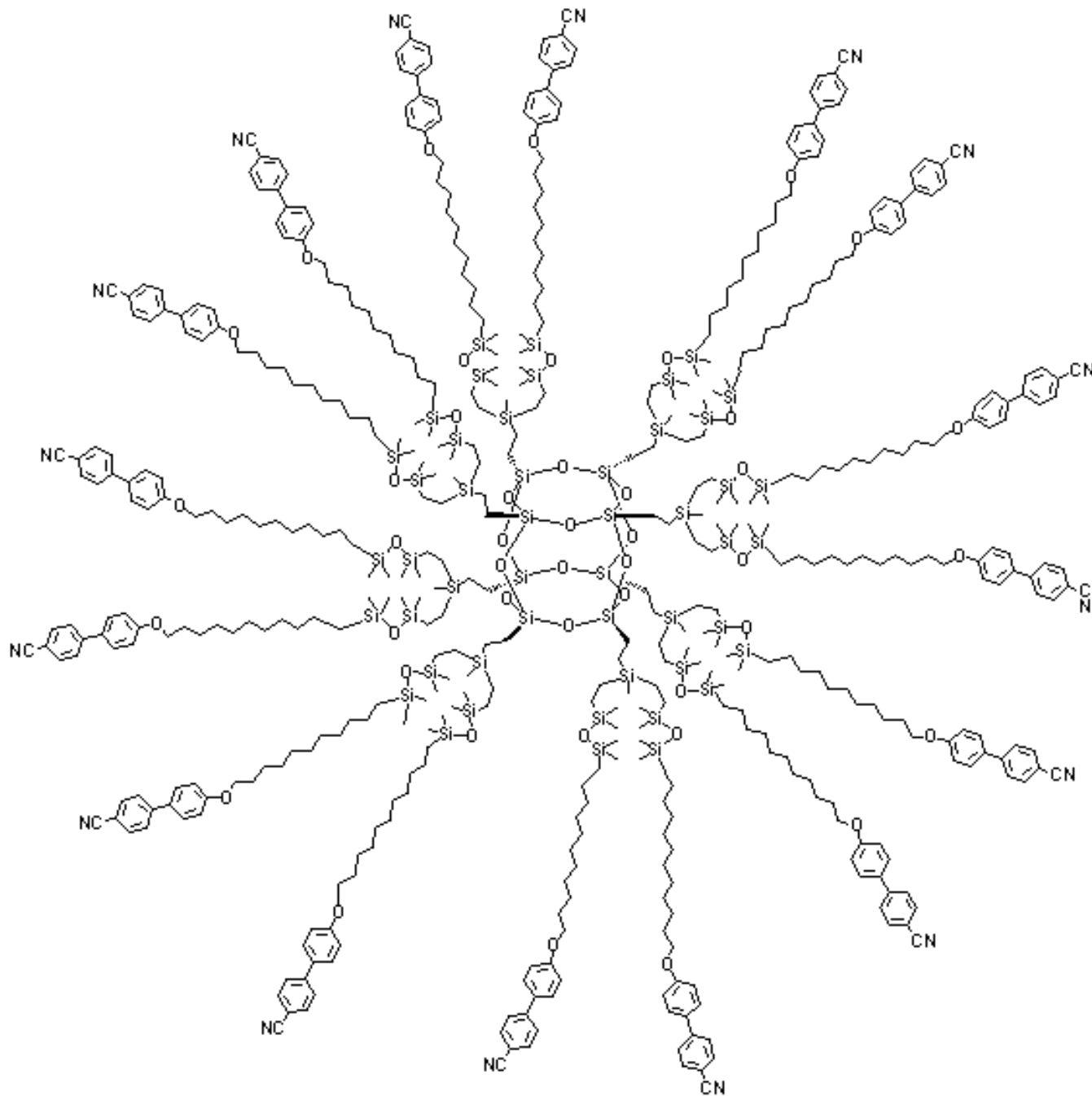
initial interest in dendrimer synthesis has shifted towards functional dendrimers because of their rich supramolecular chemistry and self-assembling properties [6]. The very properties of precise control of functionality and molecular architecture are also essential ingredients in the molecular engineering of liquid crystals for controlling and fine-tuning the physical properties that ultimately define the self-organising process that leads to mesophase formation [7].

Various morphologies have been documented for dendritic and hyperbranched LC polymers, and this topic has received intense interest recently [6]. Although the exhaustive revision of this area is outside the scope of this article, several types can be easily identified: a) hyperbranched polymers and LC dendrimers in which

the mesogenic groups form part of each branching unit; b) dendrimers without mesogenic groups that form LC phases, where the formation of the mesophases is due to the self-assembly process of the constituents dendrons, aided by microphase segregation; and c) LC

dendrimers formed by attachment of LC moieties to the periphery of a suitable core dendrimer, where the mesogenic units are located on the surface of the dendritic core.

Within the latter group, we have reported a group of



9

Figure 5. Hexadecamer dendrimer 9.

liquid crystalline dendrimers based on the octasilsesquioxane core, which provides eight primary (radial) branches for derivatisation, allowing an increased packing of the mesogens around the dendritic core at earlier generations; moreover, the rigid framework of the octasilsesquioxane core offers the possibility of a contrasting comparison with dendrimers derived from entirely flexible scaffolds, among others PPI, PAMAM, and carbosiloxanes [6a].

Among the factors that determine the type of mesophase exhibited in LC dendrimers are the nature of the mesogenic units, the topology of the attachment of the mesogens to the core, generation number and microsegregating properties of the dendritic core. In general, as in traditional side-chain liquid crystal polymers, end-on mesogens afford smectic phases whereas side-on mesogenic sub-units lead to nematic phases.

The hydrosilylation of the first generation hexadecavinyloctasilsesquioxane dendrimer **8** with cyanobiphenyl mesogens containing the terminal Si-H group affords the LC dendrimer **9**, which contains sixteen cyanobiphenyl groups attached to the dendritic core by undecylene aliphatic spacers [8]. ^1H NMR spectroscopy shows well-resolved resonances for all the protons of the CB groups, indicating complete conformational freedom of the mesogenic units in solution. The molecular weight of **9** was under-estimated by SEC, an effect frequently encountered in dendrimers, which is evidence of a globular conformation in solution.

Dendrimer **9** shows the phase sequence $g - 17.5 \text{ SmC}$

$63.1 \text{ SmA } 91.7 \text{ Iso } ^\circ\text{C}$. This mesophase behaviour implies that the dendrimer must have a rod-like shape in order that it can pack in layers, where the molecules within the layers are disordered and the layer structure diffuse, revealing that the mesogenic state deforms the globular environment of the dendrimer (Figure 6).

Comparison with the zeroth generation dendrimer **10**, that contains a linear (as opposed to branched) arm of the same spacer length, which also exhibits the SmC and SmA phases, in the sequence $g - 12.8 \text{ K } 4.66 \text{ K}' 39.0 \text{ SmC } 74.2 \text{ SmA } 102.9 \text{ Iso } ^\circ\text{C}$, suggests that the dendritic structure has the effect of lowering the clearing point, the SmC to SmA transition and the glass transition with doubling the number of mesogens per molecule. This thermal behaviour is in contrast with that found in LC dendrimers based on flexible dendritic cores, where the clearing points increase and the glass transitions remain almost constant with generation number [9].

We targeted the induction of the chiral nematic phase in this class of materials by employing mesogens laterally attached to the core, using the same strategy as in traditional side-chain liquid crystal polymers. Thus, the hexadecamer, first generation octasilsesquioxane dendrimer **11**, that contains sixteen side-on attached mesogenic units and has monodispersity of 1.01, was prepared following the hydrosilylation reaction described above; it was found to exhibit chiral nematic, hexagonal disordered columnar and rectangular disordered columnar phases, in the

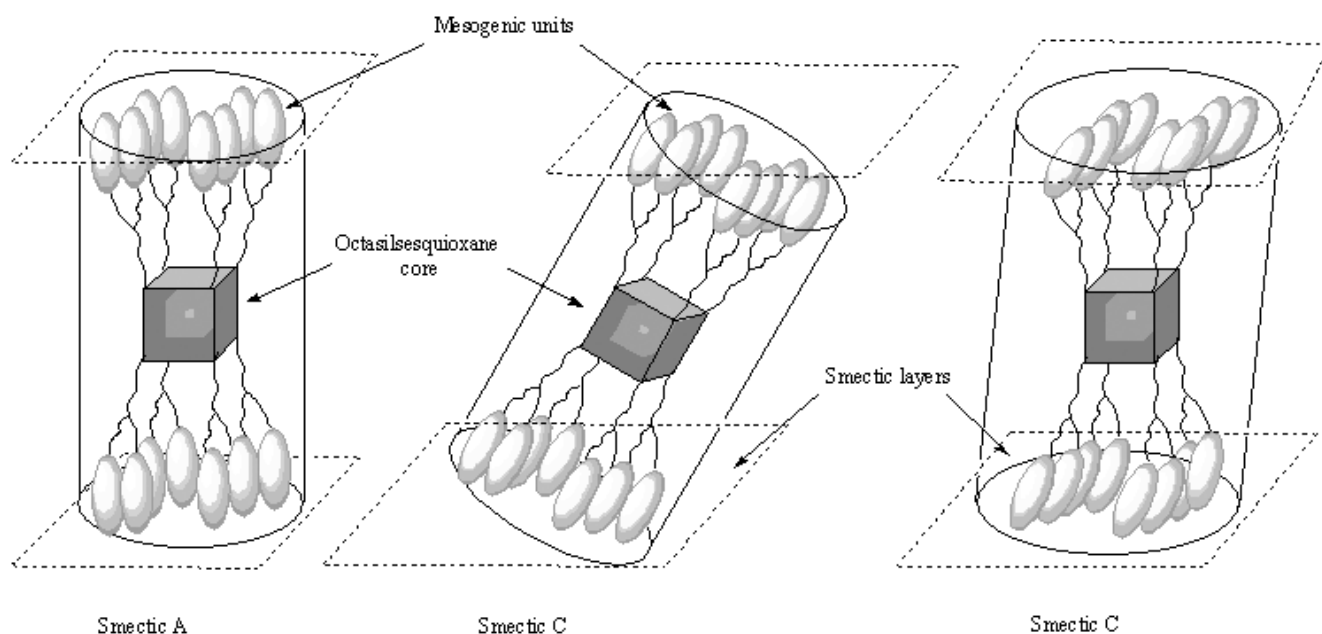


Figure 6. Possible molecular topologies enforced by the liquid crystalline environment in **9**.

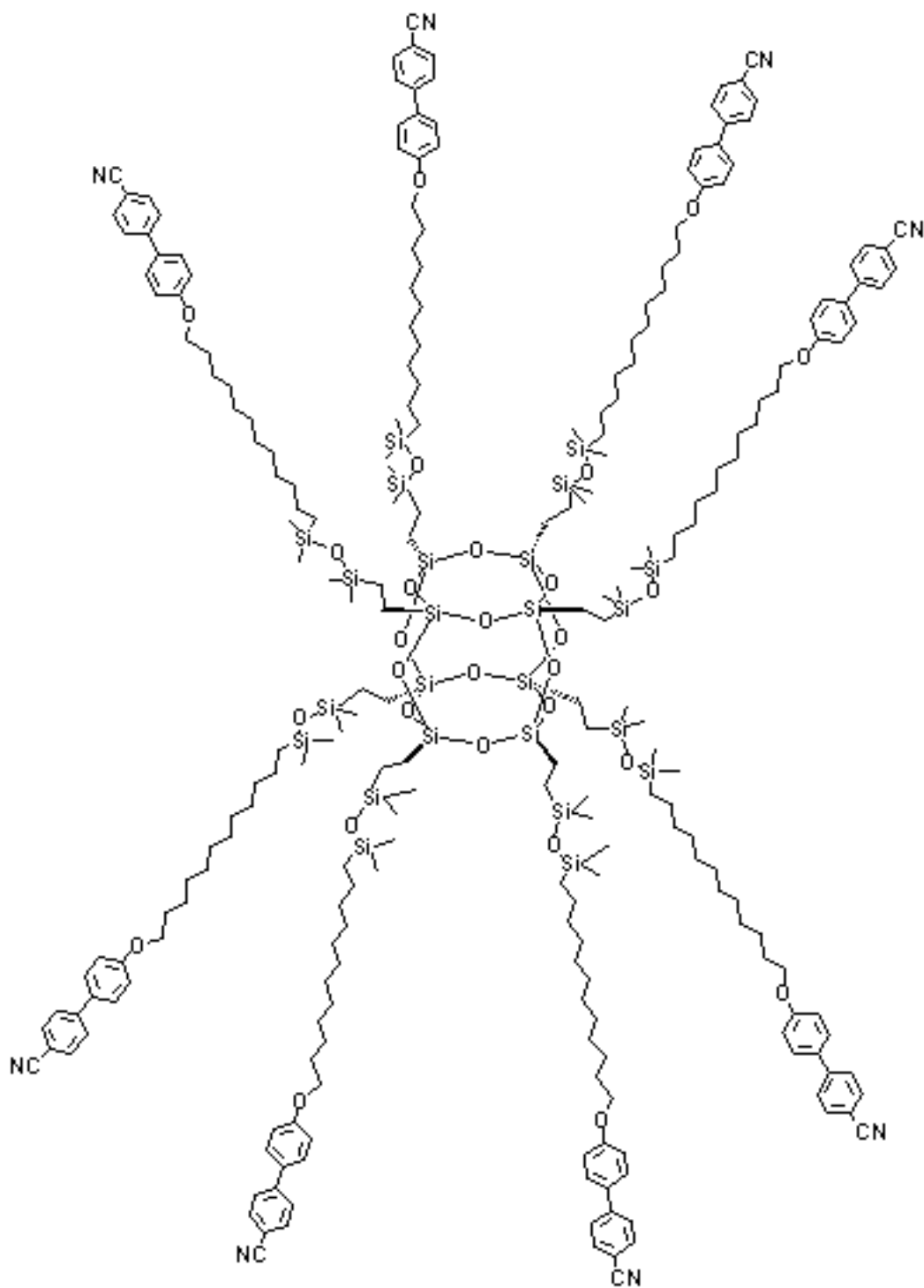
**10**

Figure 7. Octamer 10.

sequence g 5.4 Col*_{rd} 30 Col*_{hd} 102.3 N* 107.7 Iso °C [10].

From the point of view of the mesophase structure,

the best fit to the X-Ray data is obtained with the “cotton-reel” model, which suggests that in the hexagonal columnar phase the dendrimer assumes a

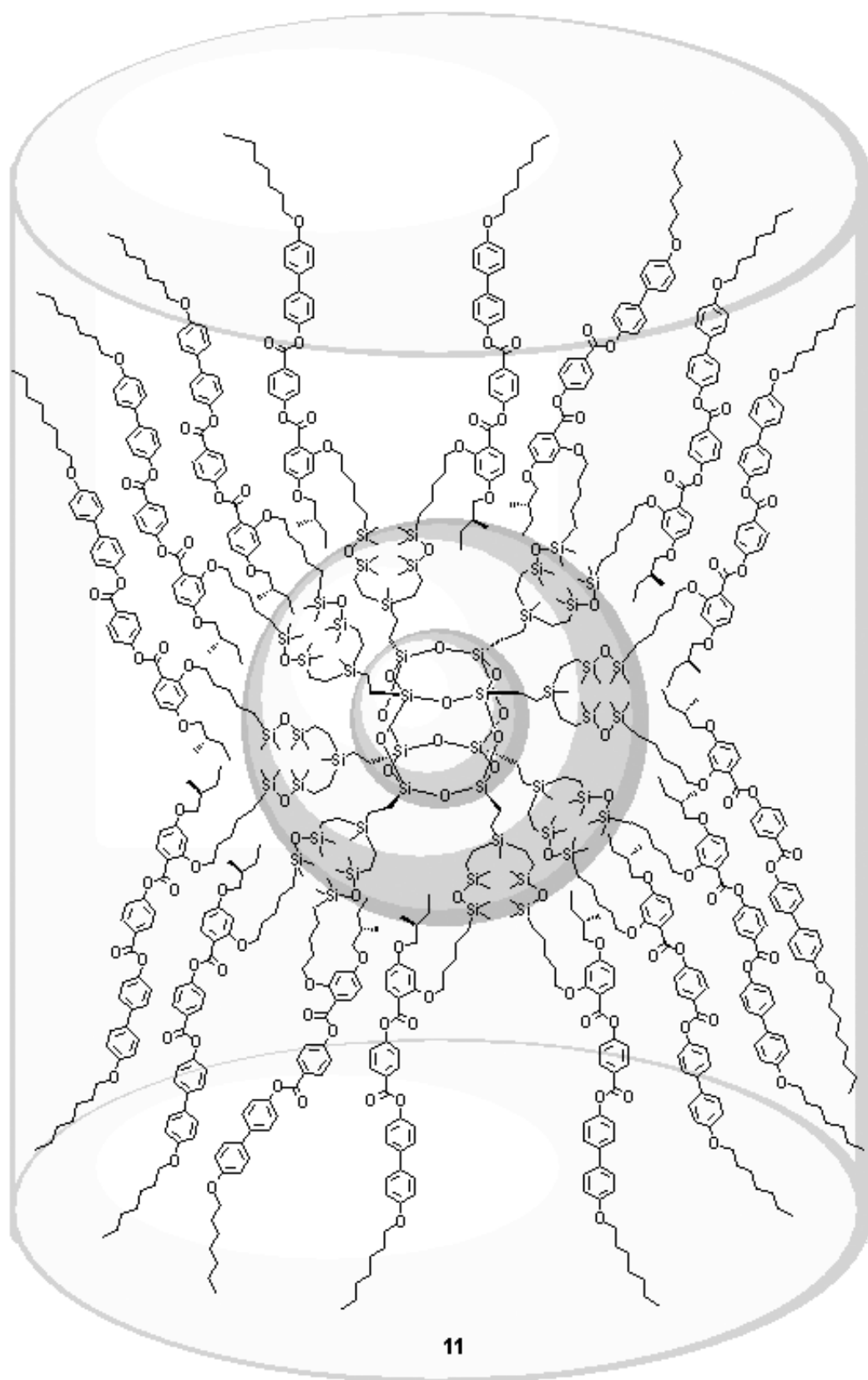
**11**

Figure 8. Hexadecamer dendrimer 11.

cylindrical shape that has approximately the same height as its diameter (Figure 9). The long axes of the mesogenic units are roughly parallel to or slightly tilted with respect to the rotational axis that is normal to the cylinder, and they are packed together side by side on the outer surface of the cylinder, in a disordered fashion. The mesogenic behaviour of **11** emphasizes the role played by the octasilsesquioxane core when comparing with the related side-chain LC polysiloxanes [5]. It is remarkable that the thermal stability of the chiral nematic phase is similar in both materials, suggesting that the cubic core does not significantly perturb the associations between the mesogens necessary to support the chiral nematic phase, as the columns are organised parallel to the long axes of the calamitic segments, which form a nematic continuum around them (Figure 9). Similarly, the formation of the columnar phases in the dendrimer **11** but not in the side-chain polysiloxanes indicates that the silsesquioxane core assists in the interaction of neighbouring units resulting in the formation of the hexagonal and rectangular disordered structures, presumably through segregation of the siloxane cores from the mesogenic units in distinct columns. This remarkable phase structure is favoured by the spacer length used to attach the mesogen to the dendrimer core since it has been kept relatively short (5 methylene units) in order to prevent full decoupling of the mesogenic motions from the inner core and by forcing the mesogens to pack closely together around the dendritic core.

The related silsesquioxane octamers **12** and **13**, which carry eight side-on chiral mesogens, display wide temperature range enantiotropic chiral nematic phases and glass transitions near room temperature [11]. **13** is highly iridescent and both have properties similar to low molar mass mesogens, even when their size approaches that of a small globular protein. The chiral nematic phase range is greatly increased with respect to their monomeric precursors, since the crystallisation process is suppressed, resulting in glassy materials at or near room temperature. The use of octasilsesquioxane as a central core unit essentially incorporates a knot or a region of reduced flexibility into the system, which has the effect of retaining a substantial amount of disorder in the system as the mesogenic groups cannot pack quite so easily together. This results in a depression in the melting point and for these materials glassy states are found rather than conventional crystal forms.

The concept of creating functional materials by incorporating a certain functionality within a liquid crystalline molecule, through covalent attachment, in a bottom-up approach to self-organising functional materials, was further explored in the study of chiral nematic fullerenes, in collaboration with R. Deschenaux.

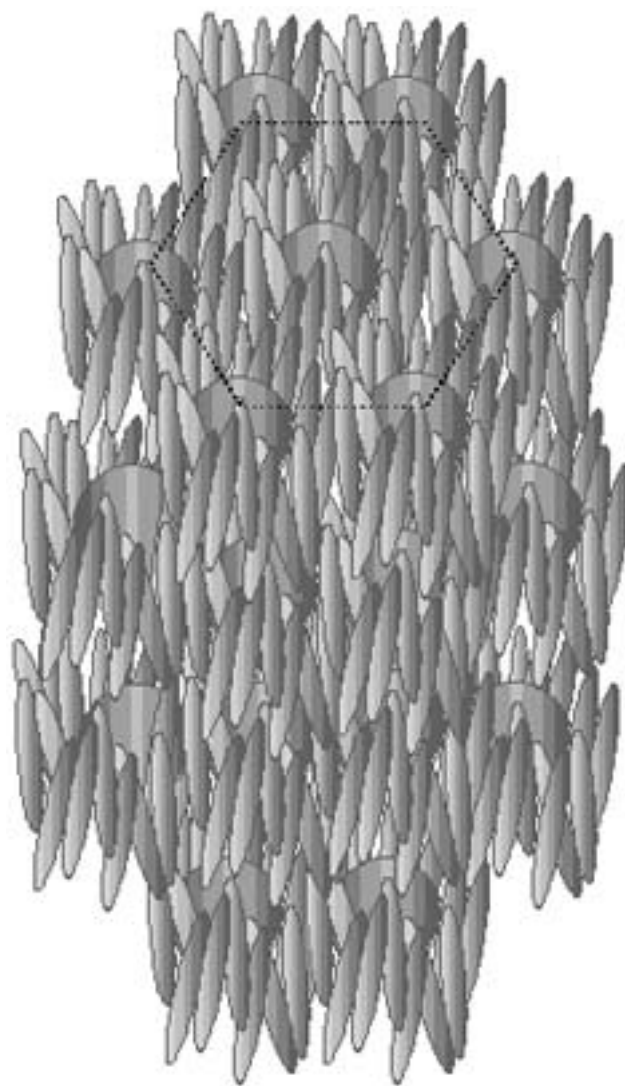
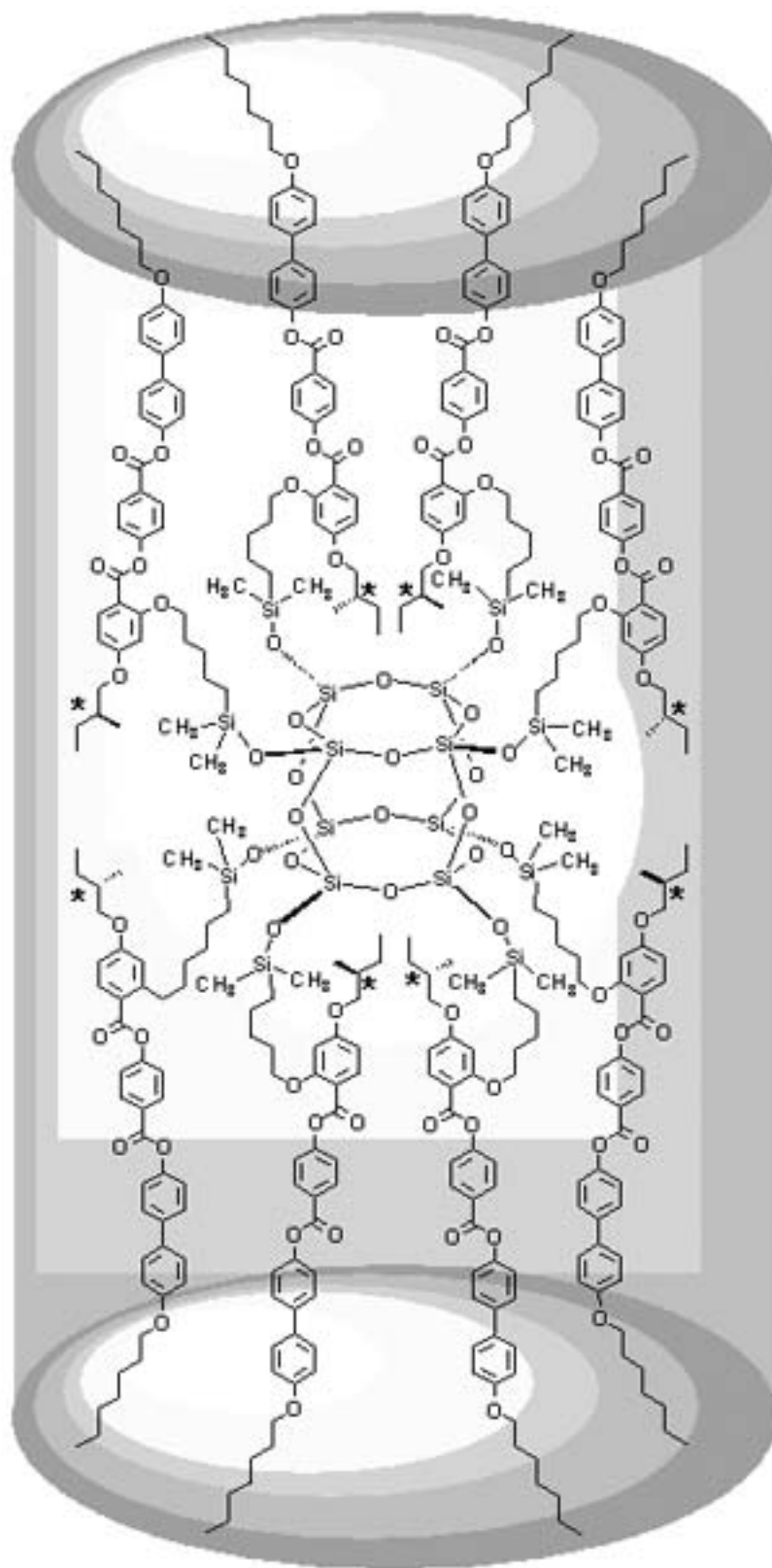


Figure 9. A schematic representation of the structure of the disordered hexagonal columnar phase of **11**. The octasilsesquioxane core is shown as the top of a ball with the mesogens disordered, forming a “cloud” around them.

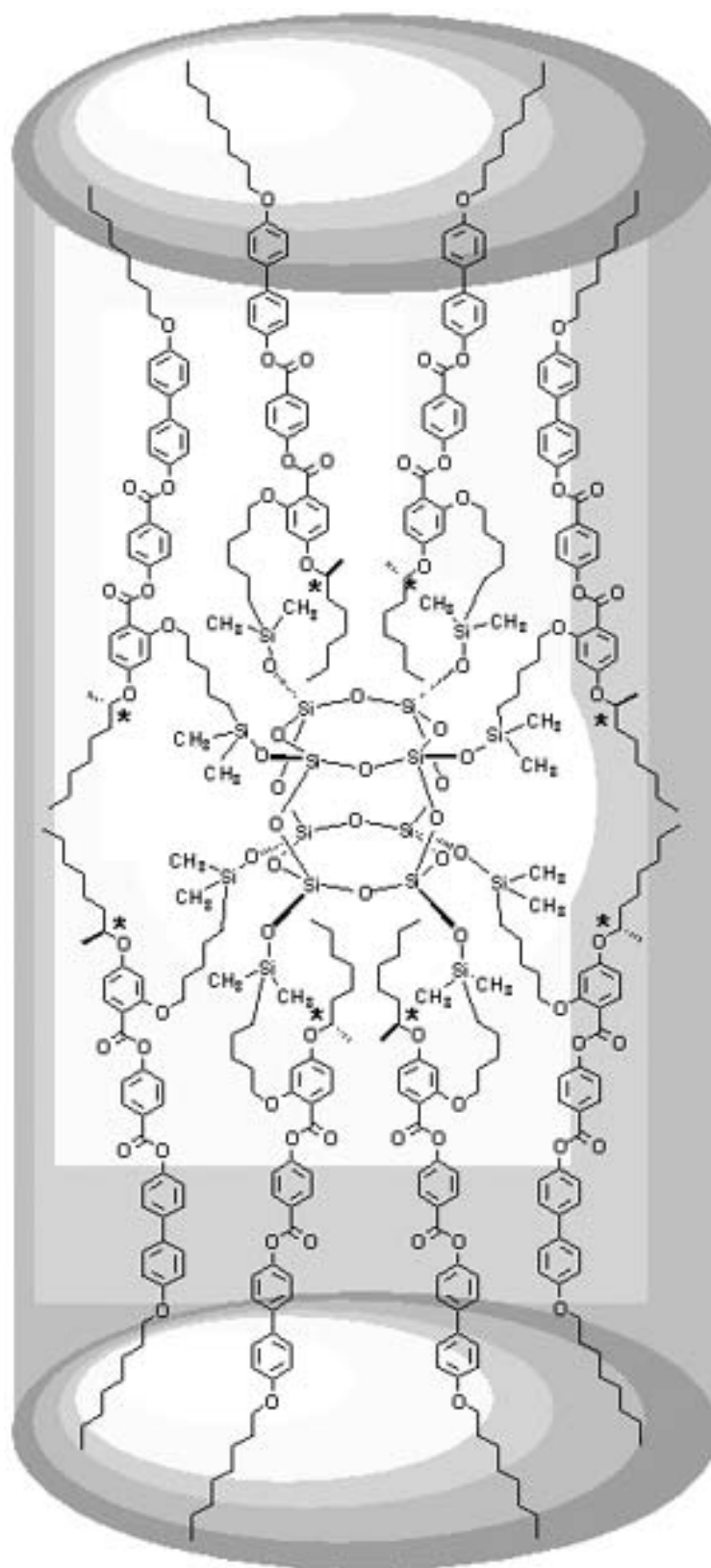
The synthesis of fullerene-containing liquid crystals has opened new avenues in the design of self-organised structures containing the fullerene unit [12]. These materials combine the exceptional electrochemical and photophysical properties of fullerenes with those of self-organising and self-assembling media. This approach appears particularly interesting for functional groups such as fullerenes, which are not well adapted to be organised in nanoscale architectures.

The three-dimensional structural analogy between fullerenes and the octasilsesquioxane was exploited, designing chiral nematic fullerene dendrimers [13]. The Bingel reaction of fullerene and dendritic malonates of



12

Figure 10. Octamer 12.



13

Figure 11. Octamer 13.

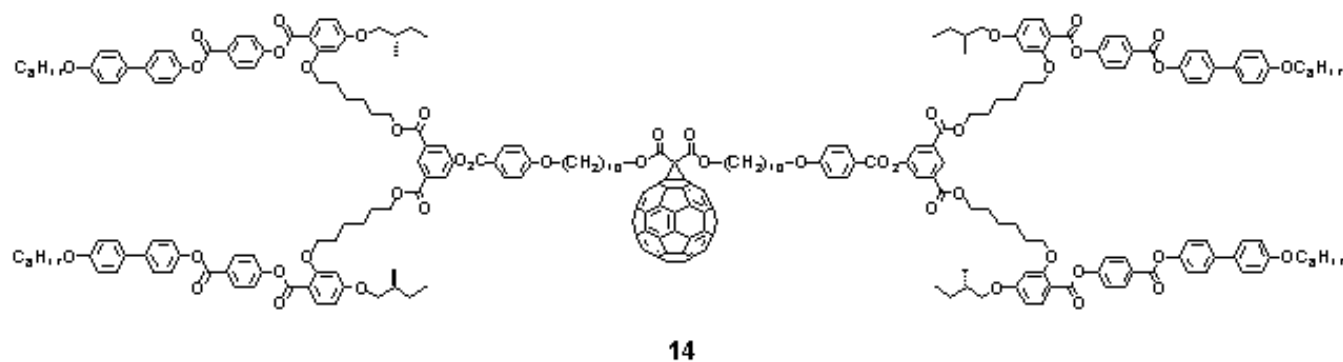
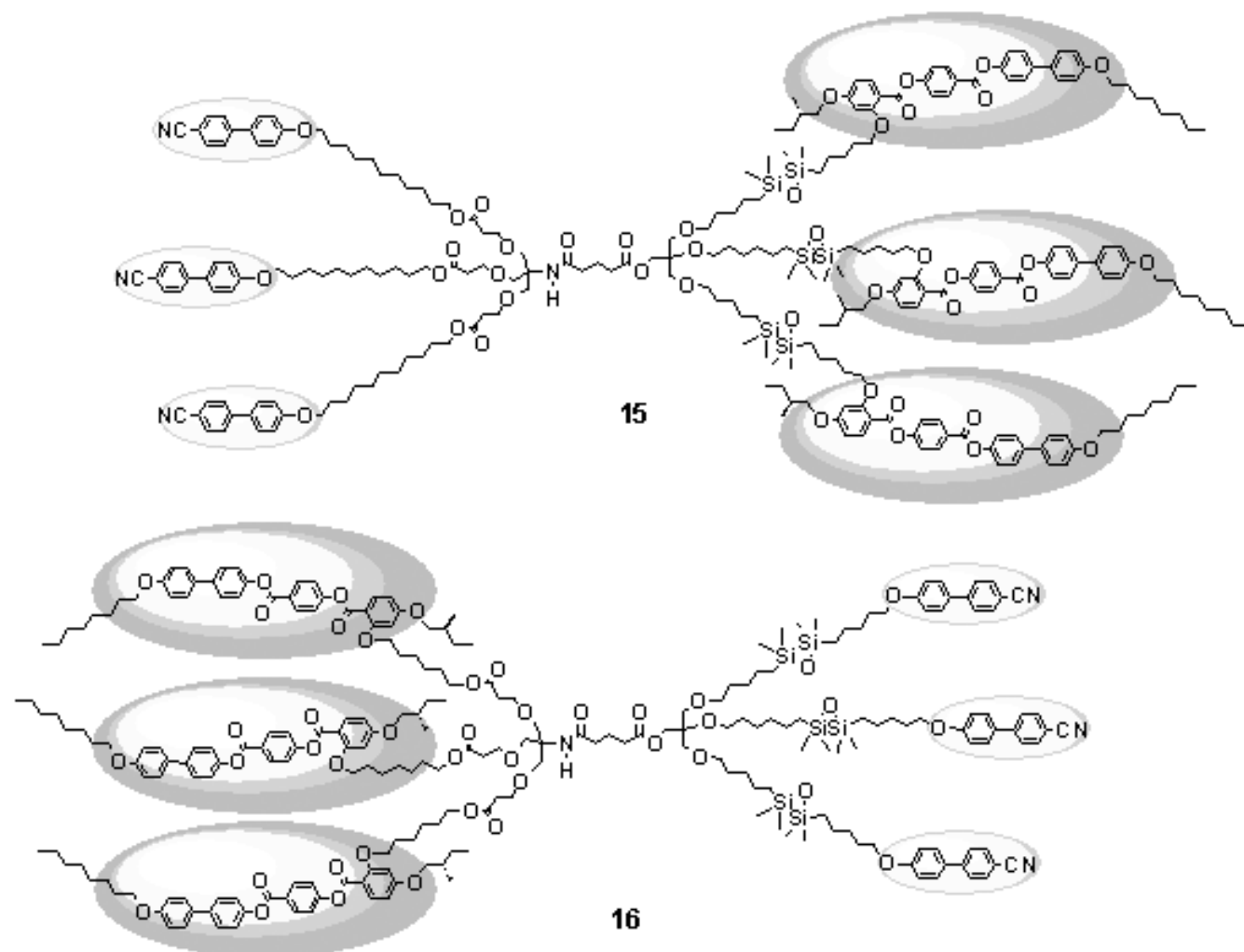


Figure 12. Fullerene dendrimer 14.

several generations, carrying the chiral nematic mesogens attached in an end-on fashion, synthesized these. Fullerene dendrimer **14** (Figure 12) shows an entiotropic chiral nematic phase, in the sequence $g\ 26\ N^* 69$

Iso °C. The values of the pitch of the cholesteric helix obtained indicate that C_{60} fits within the helical structure formed by the mesogens themselves without causing any significant perturbation of the pitch.

Figure 13. Dendritic hexamers **15** and **16**.

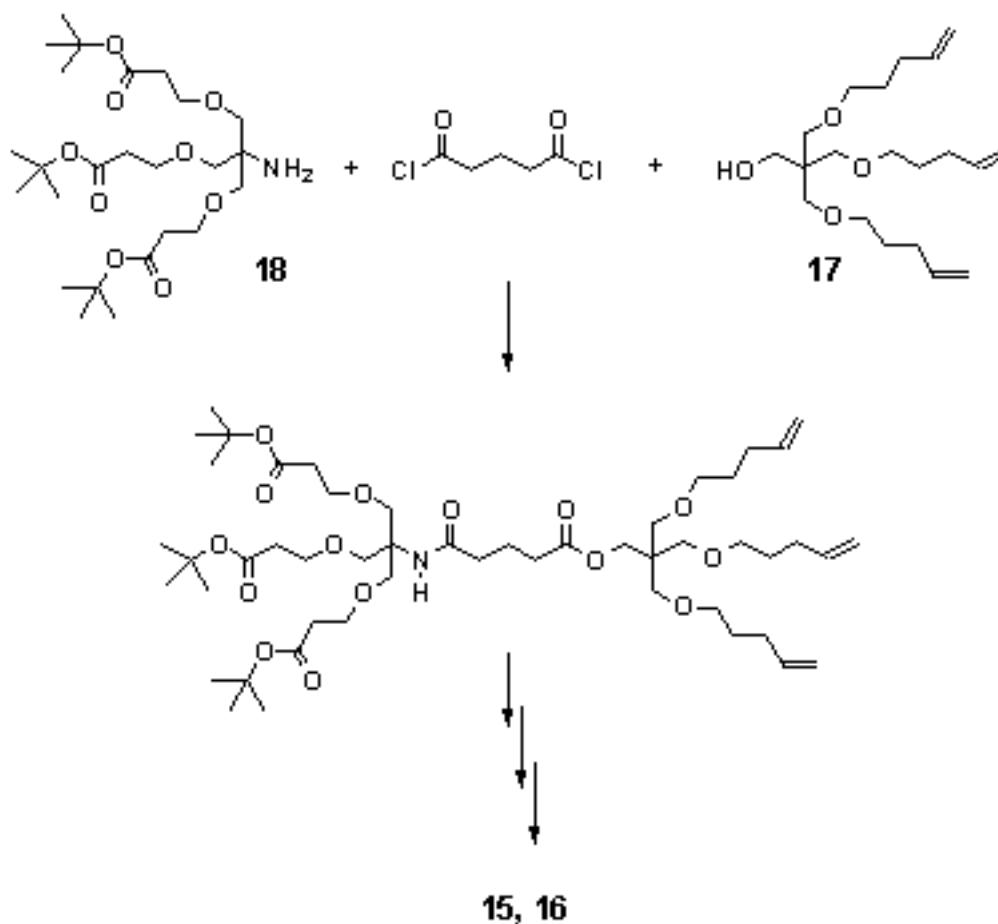


Figure 14. Synthesis of “Janus” dendritic hexamers 15 and 16.

This, in turn, implies that although the large C_{60} unit disturbs the mesogenic interactions, therefore lowering the clearing point, it can be effectively camouflaged within the self-organising cholesteric medium, provided that enough mesogenic sub-units are available in the dendritic addend, without markedly suppressing the liquid crystalline state.

Janus Liquid Crystals

The universal principles of self-assembly, based on symmetry, relative size, shape and interactions between the components can be found all over the biological world, and the very existence of life (and disease) depends upon them. The lipid bilayer membrane for example, an essential structural and functional element of the biological cells, is a beautiful exponent of these principles, whereas the coating of viruses like HIV represents a sinister, although very effective, side of these principles. The same self-assembly principles govern the behaviour of synthetic micelles, complex polymers and liquid crystals. LC has the potential, just

like living systems, to provide us with a unique vehicle for the development of self-ordering materials with specific functional properties.

One of the more intriguing and challenging aspects in materials science is understanding the molecular recognition and self-assembling processes in materials with diversely functionalised faces or sides, which can yield supramolecular objects that may recognise and select left from right, or top from bottom, as described by de Gennes [14]. For example, Janus grains [15a], block co-polymers in the form of Janus micelles [15b], segregated amphiphilic dendrimers [15c–e], shape-persistent macromolecules [15e, f] and polar colloidal particles [15g] are examples of such materials that self-organise, like proteins, in a pre-programmed fashion.

We have described a new concept for the design of self-assembling functional liquid crystals as “Janus” liquid crystalline molecular materials in the form of segmented structures that contain two different types of mesogenic units, which favour different types of mesophase structure, grafted onto the same scaffold,

to create giant molecules that contain different hemispheres. ("Janus" refers to materials with two faces, such as hydrophilic/hydrophobic, fluorocarbon/hydrocarbon, etc.) Thus, we studied the complementary dendritic hexamers **15** and **16**, based on a central scaffold made up of pentaerythritol and tris(hydroxymethyl)amino methane units linked together, where one unit carries three cyanobiphenyl (CB) and the other three chiral phenyl benzoate (PB) mesogenic moieties or *vice-versa* [16].

The basic design concept consists of creating a dichotomous dendritic scaffold, which contains two chemically different halves, capable of being independently manipulated to which appropriately functionalised mesogenic sub-units (or any other functional group for that matter) may be covalently attached [17]. The molecular sub-units or building blocks **17** and **18**, based on pentaerythritol (PE) and tris(hydroxymethyl)amino methane (TRIS) respectively, were designed to incorporate different end-groups, olefin and t-butyl ester respectively, that can be functionalised independently with different mesogenic moieties (Figure 14).

Dendritic hexamers **15** and **16** are monodisperse materials, isolated in the glassy state. **15** display enantiotropic chiral SmC* and chiral nematic phases, with typical Grandjean-plane texture and *Schlieren* texture respectively, with left-handed helical structure; it is noteworthy that the transitions have very low ΔH values, suggesting that the system is relatively disordered and highly flexible. Also noticeable is the fact that the transitions in the DSC thermograms are unsymmetrical, perhaps hinting a certain degree of microphase separation. Furthermore, compound **15** is one of the rare examples to date where side-on attachment of the mesogen to the core allows the formation of (tilted) smectic phases, since this topology strongly suppresses the tendency to form lamellar phases, with only the nematic phase being formed [18]. On the other hand, **16** is purely chiral nematic.

Comparison of the phase behaviour of compounds **15** and **16** shows clearly that the overall topology of the molecule in respect to the inner core (*ie* which hemisphere carries what mesogen) plays a significant role in determining the type of mesophase formed, since in both cases the number of mesogens of each type and the core are the same and simply placing them in different hemispheres changes the mesophase exhibited.

The manipulation of the structural fragments (mesogenic units, central scaffold, and linking units) in the molecular design of such supermolecular systems potentially allows us to vary mesophase type and therefore the physical properties and potential applications of materials. Thus the molecular design of these systems is flexible and potentially capable of

incorporating functional units, thereby allowing us to take some steps towards the molecular and functional complexity found in living systems.

We are looking further now, designing more rigid systems to create materials with better-defined interfacial geometries, so that functional units can be incorporated in a precisely positioned three-dimensional environment. The aim is to create materials with selective features, like those found in proteins.

Acknowledgements

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References

- [1] a) LEHN, J.-M., 1995, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, Germany; b) LEHN, J.-M., 2002, *Science*, **295**, 2400; c) WHITESIDES, G. M., GRZYBOWSKI, B., 2002, *Science*, **295**, 2418; d) KATO, T., 2002, *Science*, **295**, 2414; e) ELEMANS, J. E., ROWA, A. E., NOLTE, R. J. M., 2003, *J. Mater. Chem.*, **13**, 2661.
- [2] a) BUNNING, T. J., KREUZER, F. H., 1995, *Trends Polym. Sci.*, **3**, 318. b) GOODBY, J. W., MEHL, G. H., SAEZ, I. M., TUFFIN, R. P., MACKENZIE, G., AUZELY-VELTY, R., BENVIGNU, T., PLUSQUELLEC, D., 1998, *Chem. Commun.*, 2057. c) TSCHIERKE, C., 1998, *J. Mater. Chem.*, **8**, 1485. d) GOODBY, J. W., 1999, *Current Opinion in Solid State and Materials Science*, **4**, 361. e) TSCHIERKE, C., 2001, *J. Mater. Chem.*, **11**, 2647. f) TSCHIERKE, C., 2002, *Current Opinion in Colloid and Interface Science*, **7**, 69. g) GOODBY, J. W., 2002, *Current Opinion in Colloid and Interface Science*, **7**, 326. h) PERCEC, V., BERA, T. K., GLODDE, M., FU, Q., BALAGURUSAMY, V. S., HEINEY, P. A., 2003, *Chem. Eur. J.*, **9**, 921 and references therein.
- [3] For glassy LC see for example a) BUNNING, T. J., KREUZER, F. H., 1995, *Trends Polym. Sci.*, **3**, 318, b) WEDLER, W., DEMUS, D., ZASCHKE, H., MOHR, K., SCHÄFER, W., WEISSFLOG, W., 1991, *J. Mater. Chem.*, **1**, 347. c) KREUZER, F.-H., ANDRZEJWSKI, D., HAASE, W., HÄBERLE, N., RIEPL, G., SPES, P., 1991, *Mol. Cryst. Liq. Cryst.*, **199**, 345. d) VAN DE WITTE, P., LUB, J., 1999, *Liq. Cryst.*, **26**, 1039. e) CHEN, H. P., KATSIKIS, D., MASTRANGELO, J., CHEN, S. H., JACOBS, S., HOOD, P., 2000, *Adv. Mater.*, **12**, 1283. f) PFEUFFER, T., HANFT, D., STROHRIEGL, P., 2002, *Liq. Cryst.*, **29**, 1555.
- [4] SAEZ, I. M., and GOODBY, J. W., 2003, *J. Mater. Chem.*, **13**, 2727.
- [5] a) LEWTHWAITE, R. A., GRAY, G. W., TOYNE, K. J., 1992, *J. Mater. Chem.*, **2**, 119. b) LEWTHWAITE, R. A., GRAY, G. W., TOYNE, K. J., 1993, *J. Mater. Chem.*, **3**, 241.
- [6] For selected examples of liquid crystalline and functional dendrimers see: a) PONOMARENKO, S. A., BOIKO, N. I., SHIBAIEV, V., 2001, *Polym. Sci. Ser. C*, **43**, 1; b) PERCEC, V., GLODDE, M., BERA, T. K., MIURA, Y., SHIYANOVSKAYA, I., SINGER, K. D., BALAGURUSAMY, V. S. K., HEINEY, P. A., SCHNELL, I., RAPP, A., SPIESS, H.-W., HUDSON, S. D., DUANK, H., 2002, *Nature*, **419**, 384; c) TOMALIA, D. A., 2003, *Nat. Mater.*, **2**, 711; d)

- NEWKOME, G. R., MOOREFIELD, C. N., VÖGTLE, F., 2000, in *Dendrimers and Dendrons. Concepts, Syntheses, Applications*, Wiley-VCH, Weinheim; e) *Dendrimers and Other Dendritic Polymers*, FRÉCHET, J.-M., TOMALIA, D. A., Eds., Wiley, Chichester, 2001; f) FRÉCHET, J.-M., 2003, *J. Polym. Sci. Part A: Polym. Chem.*, **41**, 3713.
- [7] *Handbook of Liquid Crystals, Vols. 1-3*, (Eds. D. Demus, J. W. Goodby, G. W. Gray, H. W. Spiess, V. Vill), Wiley-VCH, Weinheim, 1998.
- [8] SAEZ, I. M., and GOODBY, J. W., 1999, *Liq. Cryst.*, **26**, 1101.
- [9] See for example a) BAARS, M. W. P. L., SÖNTJENS, S., FISCHER, H. M., PEERLINGS, H. W. I., MEIJER, E. W., 1998, *Chem. Eur. J.*, **4**, 2456; b) PONOMARENKO, S. A., BOIKO, N. I., SHIBAEV, V. P., RICHARDSON, R. M., WHITEHOUSE, I. J., REBROV, E. A., MUZAFAROV, A. M., 2000, *Macromolecules*, **33**, 5549; c) DONNIO, B., BARBERÁ, J., JIMÉNEZ, R., GUILLON, D., MARCOS, M., SERRANO, J. L., 2002, *Macromolecules*, **35**, 370; d) RUEFF, J. M., BARBERÁ, J., DONNIO, B., GUILLON, D., MARCOS, M., SERRANO, J. L., 2003, *Macromolecules*, **36**, 8368.
- [10] SAEZ, I. M., GOODBY, J. W., and RICHARDSON, R. M., 2001, *Chem. Eur. J.*, **7**, 2758.
- [11] SAEZ, I. M., and GOODBY, J. W., 2001, *J. Mater. Chem.*, **11**, 2845.
- [12] a) EVEN, M., HEINRICH, B., GUILLON, D., GULDI, D. M., PRATO, M., DESCHENAUX, R., 2001, *Chem. Eur. J.*, **7**, 2595; b) CHUARD T., DESCHENAUX R., 2002, *J. Mater. Chem.*, **12**, 1944; c) CAMPIDELLI, S., DESCHENAUX, R., ECKERT, J. F., GUILLON, D., NIERENGARTEN, J.-F., 2002, *Chem. Commun.*, 656; d) SAWAMURA, M., KAWAI, K., MATSUI, Y., KANIE, K., KATO, T., NAKAMURA, E., 2002, *Nature*, **419**, 702.
- [13] CAMPIDELLI, S., ENG, C., SAEZ, I. M., GOODBY, J. W., and DESCHENAUX, R., 2003, *Chem. Commun.*, 1520.
- [14] DE GENNES, P.-G., 1992, Nobel Lecture in *Angew. Chem. Int. Ed. Engl.*, 842.
- [15] a) CASSAGRANDE, C., VEYSSIÉ, M., 1988, *R. Acad. Sci. (Paris)*, II-306, 1423; b) ERHARDT, R., ZHANG, M., BÖKER, A., ZETTL, H., ABETZ, C., FREDERIK, P., KRAUSCH, G., ABETZ, V., MÜLLER, A. H. E., 2003, *J. Am. Chem. Soc.*, **125**, 3260; c) HAWKER, C. J., WOOLEY, K. L., FRÉCHET, J. M. J., 1993, *J. Chem. Soc. Perkin Trans. 1*, 1287-1297. d) GRAYSON, S. M., FRÉCHET, J. M. J., 2000, *J. Am. Chem. Soc.*, **122**, 10335-10344; e) PESAK, D., MOORE, J. S., 1997, *Tetrahedron*, **53**, 15331-15347; f) ZHAO, D., MOORE, J. S., 2003, *Chem. Commun.*, 807; g) CAYRE, O., PAUNOV, V. N., VELEV, O. D., 2003, *J. Mater. Chem.*, **13**, 2445.
- [16] SAEZ, I. M., and GOODBY, J. W., 2003, *Chem. Commun.*, 1726.
- [17] SAEZ, I. M., and GOODBY, J. W., 2003, *Chem. Eur. J.*, **9**, 4869.
- [18] a) GRAY, G. W., HILL, J. S., LACEY, D., 1989, *Angew. Chem. Int. Ed. Engl.*, **28**, 1120; b) LECOMMANDOUX, S., ARCHARD, M. F., HARDOUIN, F., 1998, *Liq. Cryst.*, **25**, 85.