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Chiral nematic octasilsesquioxanes†

Isabel M. Saez* **and John W. Goodby**

Department of Chemistry, The University of Hull, Hull, UK HU6 7RX.
E-mail: I.M.Saez@chem.hull.ac.uk

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The octasilsesquioxane cage has been successfully derivatised by platinum-catalysed hydrosilylation reaction of the alkene functionality of appropriate laterally substituted, chiral mesogenic moieties to yield monodisperse multipodal octamers. The liquid-crystalline silsesquioxanes were characterised by multinuclear MR, SEC, TGA, POM and X-ray diffractometry. The giant supermolecular materials display remarkably wide temperature range enantiotropic chiral nematic phases and glass transitions near to room temperature. One of the materials is iridescent and has properties similar to a low molar mass material even though it has a size approaching that of a small globular protein. Thus these observations raise questions as to whether the materials act as singular molecular entities or as spherical side chain polymers.

Introduction

Important applications of thermotropic liquid crystals (LCs) are found in several forms of non-emissive electro-optic displays, thermochromic and fluid flow sensors for imaging devices, and for information storage.[1] Among these applications, LC displays based on light scattering and selective reflective modes have been an active area of research owing to their potential for use in large-area display technologies. In light scattering devices the scattering originates from either: (i) the spherical, solid particles of an inorganic aerosol or organic polymer dispersed in a continuous nematic LC phase, or (ii) from small droplets of nematic liquid crystals dispersed in a solid, continuous polymer matrix. In both cases, two-phase mixtures of the organic, low molecular weight liquid crystal and an inorganic or polymeric substrate are used.[2]

Organic–inorganic hybrid materials have also received enormous attention recently, essentially because they offer the potential to combine the properties of inorganic solids and the versatility of organic materials into a single nano-structured phase, with a high degree of control of the structure–properties relationships. Functionalised polyhedral silsesquioxanes[3] are a very appealing example of such organic–inorganic hybrids because all of the interactions between the organic and inorganic components of the hybrid are exclusively through covalent bonds, leading to precisely defined interfacial interactions and topologies.

Polyhedral silsesquioxanes can be considered as small, soluble chunks of silica, as their degree of oligomerisation is sufficient to result in Si–O frameworks that mimic crystalline forms of silica such as β-cristobalite and β-tridymite.[3b] When liquid crystal moieties are covalently grafted onto the core, the resulting LC silsesquioxane may provide a "molecular" analogue of the two-phase mixtures based on a dispersion of spherical particles of silica of very small diameter (<20 nm) in a low molecular weight LC phase.[4] This forms the basis for light scattering electro-optic switches, in the form of screens and switchable mirrors.[2] Moreover, they pose questions of a more fundamental importance; *i.e.* since the core framework (cage) imposes a restricted molecular topology, octasilsesquioxane based materials are promising candidates for the exploration of novel ways of controlling self-organisation in liquid crystals.[5]

A limited number of examples of monomeric LC polyhedral silsesquioxanes have been reported,[6] generally based on the derivatisation of the *exo*-cage functionality R of the core unit $(Si_8O_{12})R_8$. Most of the LC octasilsesquioxanes have been found to exhibit lamellar phases. Molecular modelling and optical studies agree with the observed X-ray diffraction results[6a,c,e] in suggesting that although the cubic topology of the core points to a globular or spherical disposition of the mesogens (see examples given by structure **I** for cages based on T_8H_8 and Q_8H_8) the supramolecular interactions between the LC units cause molecular deformation in order to accommodate the mesophase, and a smectic/lamellar arrangement is observed which is composed of rod-like molecules. Two approaches, however, have been pursued to produce nematic silsesquioxanes: (i) the first silsesquioxane nematogen, reported by Kreuzer,[6a] involved having lateral attachments of the mesogenic units to the silsesquioxane core, following a similar concept established for conventional side-chain liquid crystal polymers,[7] and (ii) a completely different approach used by Laine[6e] involved only partial substitution of the cubic octasilsesquioxane core. Interestingly, full substitution of the cubic core by esters of cholesterol has failed to provide cholesteric materials, and again smectic phases were obtained,[6a] and indeed no chiral nematic *monomeric* octasilsesquioxanes have been reported to date. More recently we have reported on the synthesis and liquid crystal properties of an hexadecamer LC silsesquioxane, **II**, which is a first generation *dendrimer* that exhibits chiral nematic, hexagonal columnar and rectangular columnar mesophases.[8]

In this article we describe the synthesis, characterisation, thermal and optical behaviour of monomeric chiral nematic octasilsesquioxanes. The induction of the N* phase in these materials is desirable because of its unique optical properties and potential applications to electro-optical devices.[9] Our approach to chiral nematic silsesquioxanes is based on the covalent lateral, or side-on, attachment of an appropriate mesogenic alkene precursor to the silsesquioxane core by hydrosilylation reaction, using a concept previously established for the related side-chain polysiloxanes.[10] A spacer group of moderate length as used here allows a certain degree of decoupling of the motions of the mesogenic units from the core in order to aid mesophase formation. However, the spacer is still short enough so that the mesogens do not act

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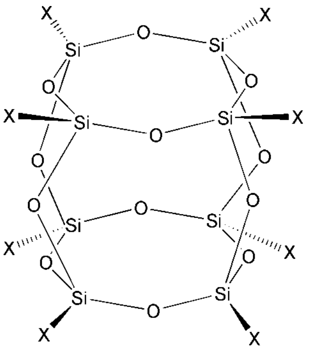
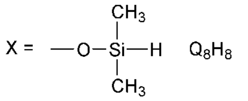




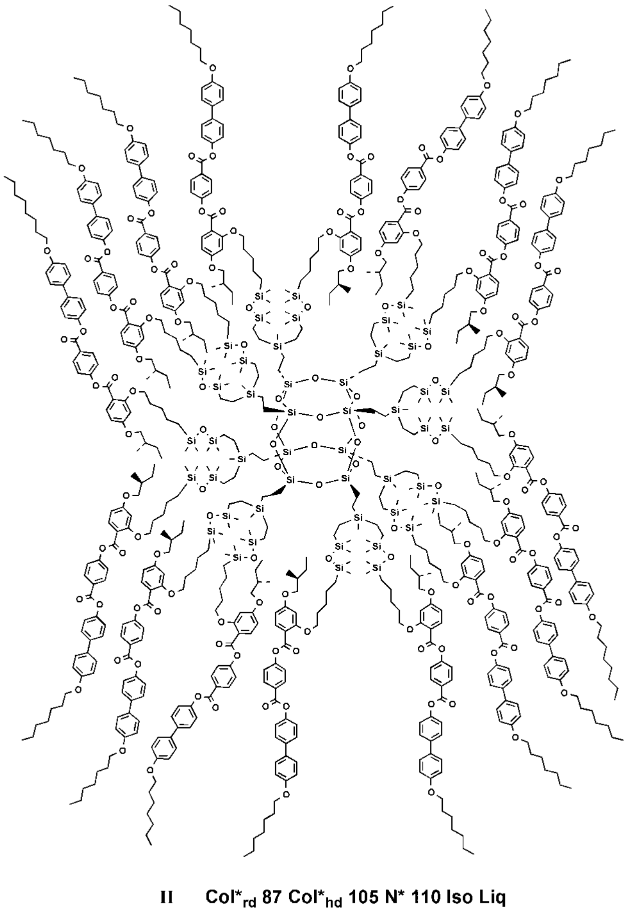
$$X = -O-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-H \quad Q_8H_8 \qquad \textbf{I}$$

X = H Cuboid Central Core Unit T_8H_8

independently of the core, and thus the effect of the core can be expressed, thereby hindering crystallisation of the mesogenic side chains.

Results and discussion

The liquid-crystalline octasilsesquioxanes **1** and **2** were prepared by platinum-catalysed hydrosilylation reaction of the laterally substituted mesogenic alkenes (*S*)-4′-octyloxybiphenyl-4-yl 4-[4-(2-methylbutoxy)-2-(pent-4-enyloxy)-benzoyloxy]benzoate, **3**,[10b] or (*R*)-4′-octyloxybiphenyl-4-yl 4-[4-(2-octyloxy)-2-(pent-4-enyloxy)benzoyloxy]benzoate, **4**, prepared from (*R*)-(−)-octan-2-ol following the procedure established for **3**, with octakis(hydridodimethylsiloxy)octasilsesquioxane, **5**, using Karstedt's catalyst at room temperature in toluene. A ratio of 1.3 : 1 of alkene per Si–H was used to ensure completion of the reaction. The progress of the reaction was followed by FT-IR spectroscopy, by the disappearance of the Si–H stretching, and TLC. Products **1** and **2** were purified by column chromatography over silica gel and isolated as glassy materials which were characterised by multinuclear MR (^{1}H, ^{13}C and ^{29}Si).

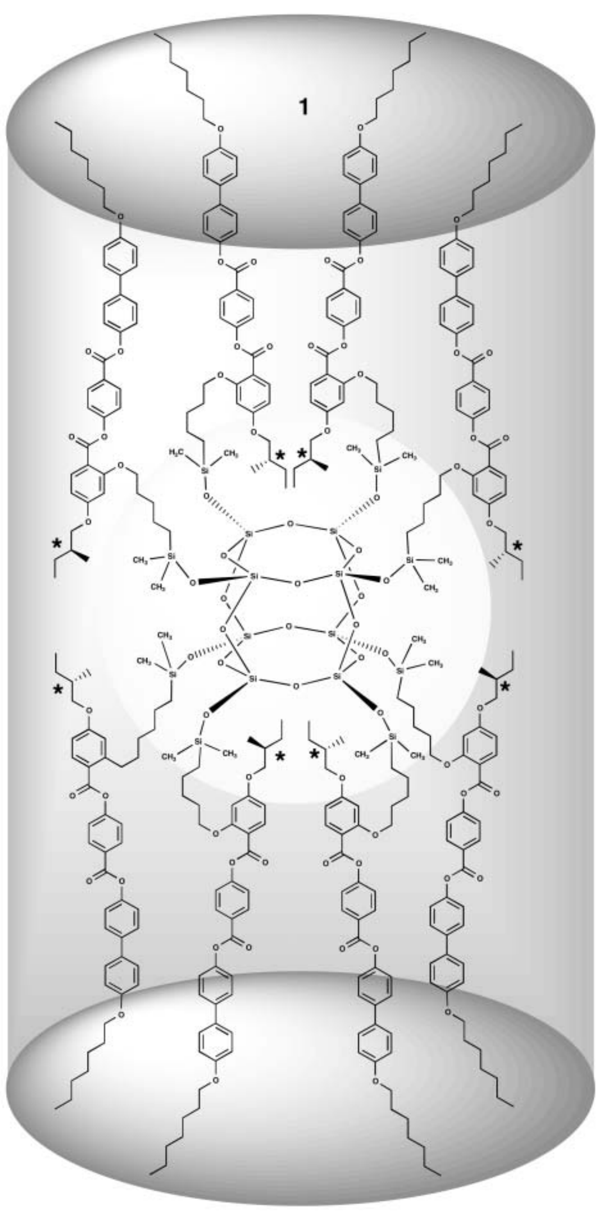


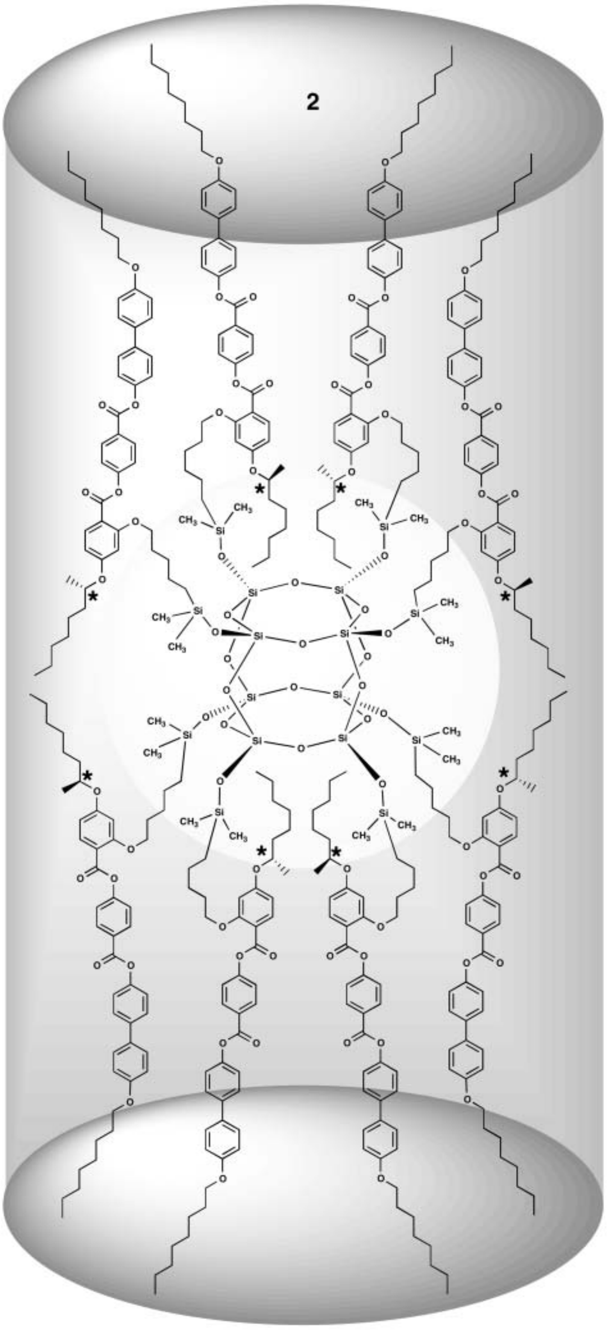
II Col*$_{rd}$ 87 Col*$_{hd}$ 105 N* 110 Iso Liq

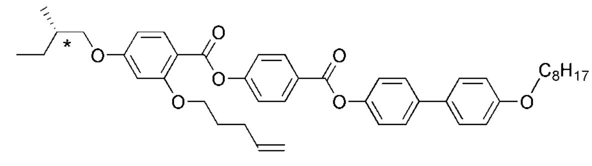
The ^{1}H NMR spectrum showed all the expected features (peaks and integrations), with well resolved resonances for the LC moieties, indicating full conformational freedom of the materials in solution. The Si–CH_2 pseudo-triplet in the region of ~0.5 ppm and the complete absence of signals at ~2.5 ppm (together with ^{13}C DEPT experiments) show that within the limit of detection, the addition of the Si–H bond to the alkene is regiospecific, affording only the β-addition product (the linear Si–CH_2–CH_2–R isomer). ^{29}Si NMR allowed further confirmation of the structure, showing a singlet at ~−108 ppm for the Q silicon atom of the cage and a singlet at ~12.8 for the M silicon atom of the spacer.

SEC showed that the two final products are monodisperse (Fig. 1), with very good agreement between the expected and the observed molecular weights. One notable feature of the hydrosilylation reaction is the high ratio of alkene isomerisation observed on the isolated unreacted olefin.

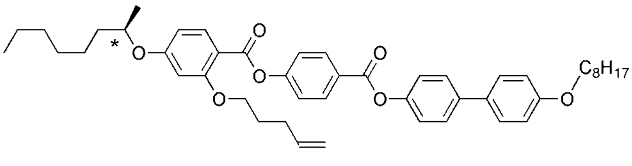
The mesomorphic properties of the materials were investigated by differential scanning calorimetry (DSC) and polarized



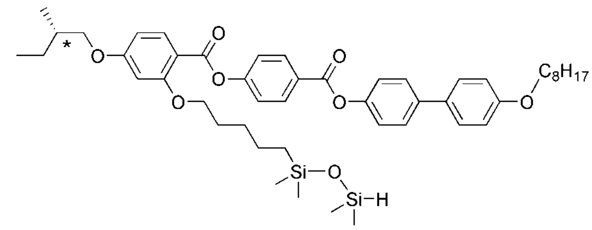




Cryst 111.3 N^* 153.5 Iso Liq **3**



Cryst 101.1 N^* 109.2 Iso Liq **4**



Cryst 73.6 N^* 88.2 Iso Liq **6**

light optical microscopy (POM). The DSC thermograms of the octasilsesquioxanes are shown in Fig. 2 and the transition temperatures are listed in Table 1. Both materials, which are in a glassy state at room temperature, exhibit a single enantiotropic transition between the LC state and the isotropic liquid; the only other thermal event being a glass transition near to room temperature.

The optical textures of the compounds were examined by POM. On cooling from the isotropic state material **1** rapidly develops small focal-conic domains that evolve and then coalesce to give a Grandjean plane texture at 114 °C (see Fig. 3). The iridescent texture appeared to have oily streaks (floating edge-dislocations) and was blue in colour indicating that the pitch of the helix of the phase was approximately 0.2–0.3 µm. The presence of this texture unequivocally identifies the mesophase as a chiral nematic phase. No further change in texture was observed on cooling down to room temperature, except for the iridescent texture becoming green in colour as the pitch of the helix increased. Mechanical shearing of the specimen shows that the sample has low viscosity; in addition, the rapid development of the typical Grandjean defect texture and the very short annealing time indicate that **1** has properties more akin to low molar mass (LMM) materials than to conventional polymers.

In contrast, on cooling from the isotropic state material **2** forms a grainy, unidentifiable texture where the edges of the domains are highly birefringent, and even after long periods of annealing the texture did not evolve further. Mechanical

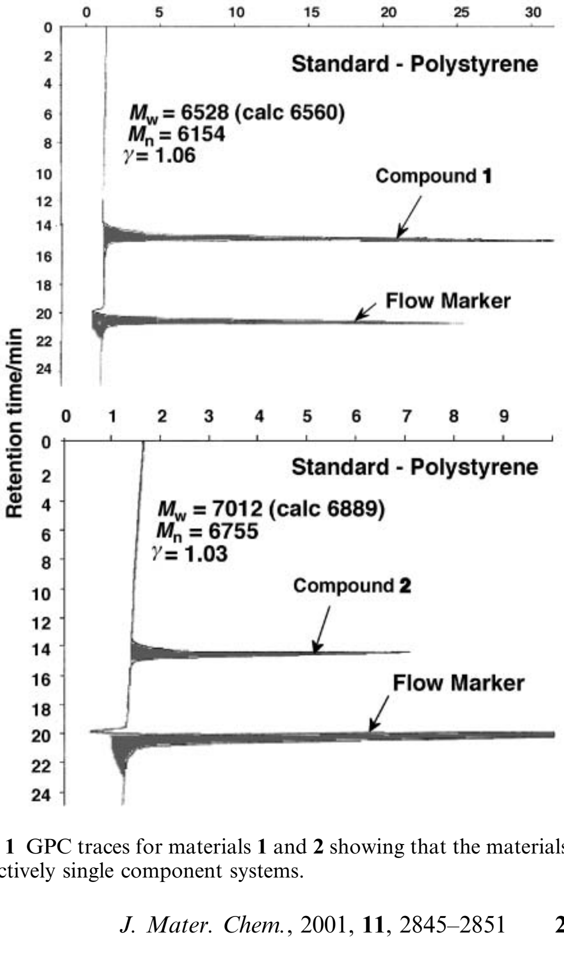


Fig. 1 GPC traces for materials **1** and **2** showing that the materials are effectively single component systems.

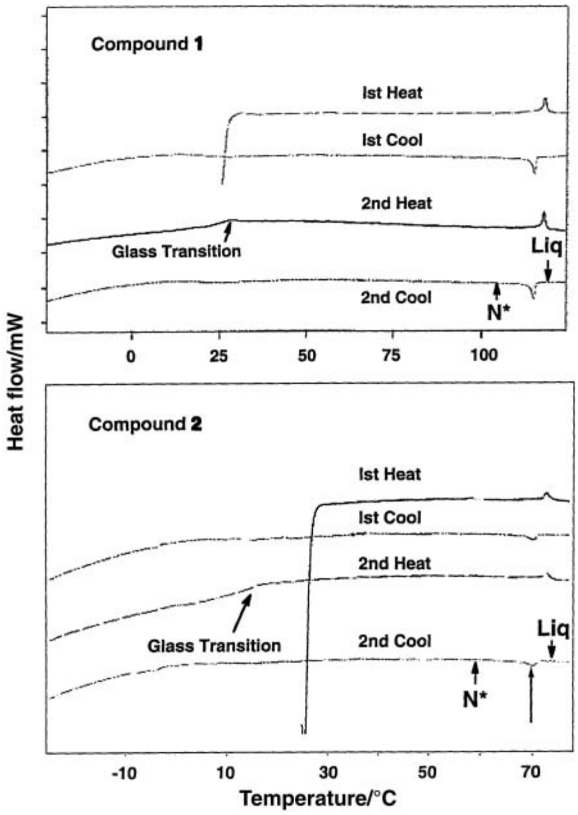


Fig. 2 Differential scanning thermogram (heating and cooling rates taken at 10 °C min^{-1}) of octasilsesquioxanes **1** and **2**.

shearing of the specimen shows that the sample was relatively fluid. However, very thin preparations of material **2** allowed for the formation of small focal-conic domains which coalesced to give *schlieren* and oily streak textures which are characteristic of a chiral nematic phase (Fig. 4). The pitch of the helix of the phase was found to be very short and thus the phase was not iridescent; on cooling a blue iridescence was observed as the pitch of the phase increased.

Powder X-ray diffraction studies confirmed the structural classification of the mesophase observed *via* POM. On cooling from the isotropic state, an unaligned sample of **2** shows no Bragg peaks at all in the smectic layer region, only displaying diffuse scattering associated with that of a nematic phase.

Comparison of the transition temperatures shows that a decrease in isotropisation temperature is observed from the alkene precursors to the octasilsesquioxanes, thereby decreasing the thermal stability of the mesophase. This is in accordance with the depression in clearing point observed in the related polysiloxanes.[10b] Remarkably, the decrease in isotropisation temperature is nearly identical for both materials **1** and **2**, in comparison with mesogenic precursors **3** and **4** respectively (36 °C for **1** and 37 °C for **2**). However, the chiral nematic mesophase range is greatly enhanced in both cases (from 42 °C for compound **3** to 99 °C for **1** and from 8 °C for compound **4** to 60 °C for **2**) since the octamers show absence of crystallisation, with glass transitions at or slightly below room temperature.

Table 1 Transition temperatures and enthalpies of the transitions

Compound	Transition temperatures/°C [ΔH/kJ mol^{-1} per mesogen][a]
3	K 111.3 [42.3] N* 153.5 [0.9] Iso
4	K 101.1 [40.19] 109.2 N* [0.58] Iso
1	g 23.7 N* 116.9 [0.46] Iso
2	g 11.2 N* 72.0 [0.18] Iso
6	K 73.6 [32.2] N* 88.2 [0.59] Iso

[a] The transition temperatures were determined at 10 °C min^{-1}.

Fig. 3 The Grandjean plane texture of material **1** (× 100).

A further comparison of material **1** with compound **6**,[8b] which possesses a tetramethyldisiloxane terminal group, provides another view of the double role of the octasilsesquioxane core; firstly it is the incorporation of the compact, but bulky, dimethylsiloxane connector group that is responsible for the large decrease of isotropisation temperature observed (*e.g.* comparing compounds **3** and **6**), but secondly on grafting the mesogenic unit onto the silsesquioxane core the stability of the mesophase recovers, although only partially. Moreover, the multiple substitution of the inorganic core appears to suppress the crystalline behaviour, thereby enhancing the mesomorphic temperature range. This behaviour is in contrast with that displayed by related silsesquioxanes.[6h] However in the cited case the mesogenic group used is constitutionally different and the total spacer length considerably longer than for the materials reported here; these facts could account for the different behaviour, particularly the longer spacer length which would effectively decouple the mesogenic groups from the octasilsesquioxane core.

From the point of view of the formation of the chiral nematic mesophase, two extreme situations can be envisaged for the molecular conformation, one where the mesogenic units are decoupled from the octasilsesquioxane core and as a consequence they act relatively independently, and another where the materials act as giant molecular systems, see Fig. 5. In the second case the giant molecules could have either disc-like or rod-like shapes. In the first case the octasilsesquioxane molecules adopt a conformation where the long axes of the mesogens are arranged perpendicular or nearly perpendicular to the central cubic core, thereby embedding the octasilsesquioxane unit. This arrangement confers a disc-like conformational shape on the giant molecules, thus they have a cotton reel-like structure where the central cage is surrounded by loosely packed mesogens. Therefore the "pseudo-discs" could

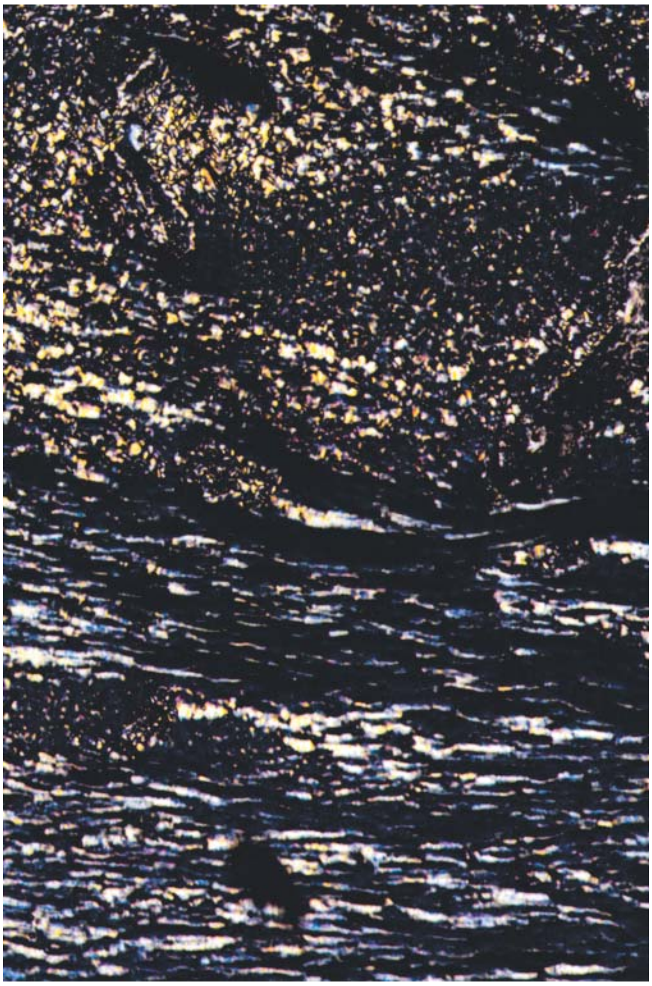


Fig. 4 The oily-streak and Grandjean plane texture of material **2** (×100).

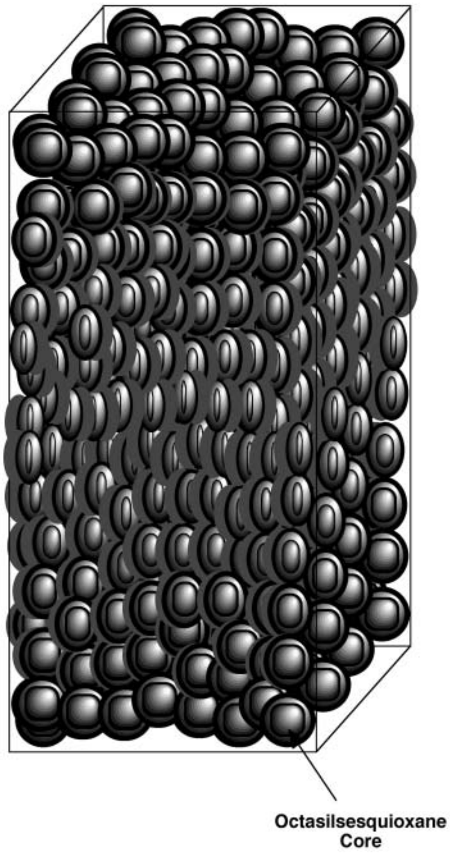


Fig. 6 The alternative model of the octamers with the mesogens surrounding the core to form a disk-like shaped system which is conducive to forming a nematic discotic phase.

self-organise like a chiral nematic *discotic* mesophase, see Fig. 6. Alternatively, if the mesogens are packed around the central core in a more rod-like conformation, the resulting "bundles" would self-organise into a chiral nematic *calamitic* phase, as shown in Fig. 5. Kreuzer, however, has reported the only conoscopy study to date on silsesquioxanes, indicating that the nematic phase of the material with a similarly

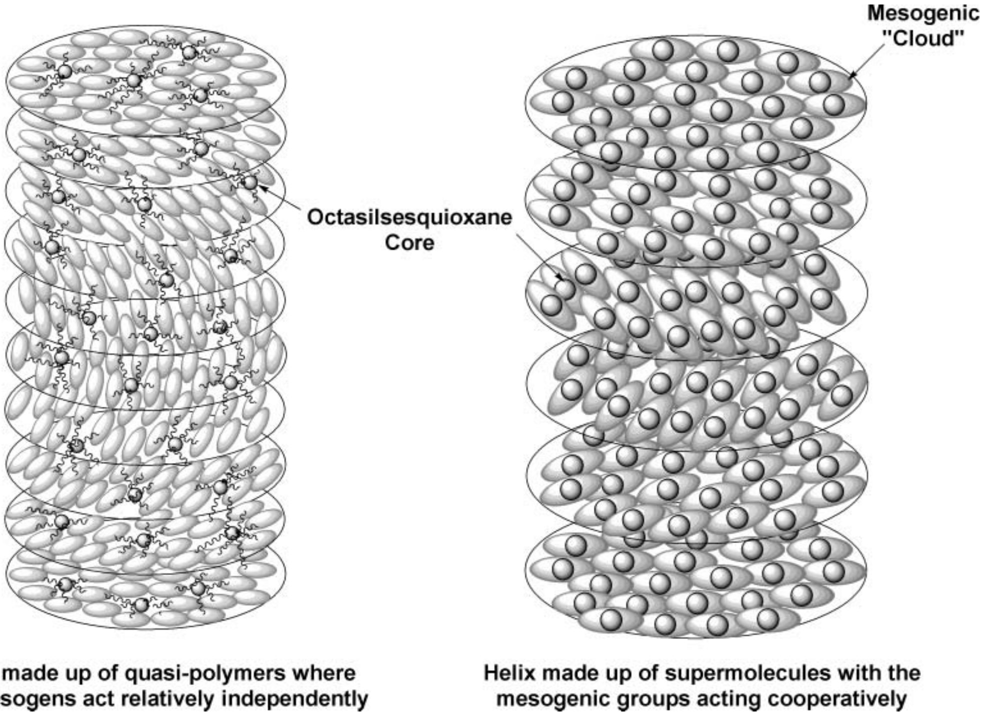


Fig. 5 A schematic representation of the structure of the chiral nematic phase of the octamers as (left) octasilsesquioxane cores with the mesogenic units decoupled from the core, and (right) octasilsesquioxane cores with the mesogenic units forming a rod-like or tactoidal "cloud" about them.

(laterally) attached mesogen is uniaxially positive, and therefore calamitic in nature, thus the rod-like conformation appears to be the more favoured.

As the bridging groups between the octasilsesquioxane core and the mesogenic groups are relatively short, the mesogenic units cannot be totally decoupled, and therefore the model of the materials acting as giant molecular entities seems feasible. Conversely, the short pitch lengths obtained for the chiral nematic phase are of a similar magnitude to those that would be expected for the mesogenic units themselves which suggests that the materials are acting as clusters of mesogenic groups and not as giant single entities. However, each giant molecule has eight chiral centres and so one might expect the twisting power to scale with the number of mesogenic units/chiral centres with the overall outcome being that the twisting power is similar to the mesogens themselves.

The use of octasilsesquioxane as a central core unit essentially incorporates a knot or a region of reduced flexibility into the system. This 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 technique of introducing molecular disorder through covalent tethering could have great advantages in depressing melting point while at the same time maintaining clearing points.

Conclusions

In this paper we have presented a rational design of chiral nematic octasilsesquioxanes, implemented through the lateral attachment of the chiral mesogen to the cubic core. The materials prepared display wide temperature range enantiotropic iridescent chiral nematic phases and strong depressions in melting point. First indications are that the materials act as giant supermolecular entities, thereby giving us access to a new design concept for liquid crystal systems.

Experimental

Solvents were rigorously dried over appropriate drying agents and distilled prior to use. Low sulfur content, dry, degassed toluene (Fluka) and Karstedt's catalyst (Fluorochem) were used as received. All atmosphere-sensitive reactions were carried out under dry nitrogen using standard Schlenk techniques. Analytical TLC was performed on Kieselgel F-254 pre-coated silica gel plates (Merck). Visualisation was accomplished with UV light or cerium and ammonium molybdate stain.

Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR. NMR spectra were recorded on a Jeol JNM-LA (400 MHz) spectrometer; chemical shifts are reported in ppm (δ) with reference to internal $SiMe_4$ or residual protonated species of the deuteriated solvent used for ^1H analysis. Elemental analysis was performed on a Fisons Instruments Carlo Erba EA 1108 CHN analyser using acetanilide as the reference standard. Mass spectra were recorded on a Finnigan 1020 GC-MS spectrometer (EI mode/70 eV). Gel permeation chromatography was performed using a set of 2 × 25 cm PL Gel Mixed-D columns (Polymer Laboratories), RI detector (Erma) 7510; the mobile phase was THF eluting at a flow rate of 1 mL min^{-1}, with toluene as flow marker. The molecular weight characteristics were established using monodisperse polystyrene standards, with Polymer Laboratories Caliber software.

The mesomorphic properties of the materials were investigated by a combination of thermo-optical polarised light microscopy using an Olympus BH-2 polarised light microscope together with a Mettler FP52 microfurnace and FP5 temperature controller. The temperature controller was calibrated to an accuracy of ±0.1 °C in the range 50–250 °C. Phase transitions were determined by differential scanning calorimetry (DSC) using a Perkin Elmer DSC 7-Series with Unix DSC data acquisition and analysis software at a scan rate of 10 °C min^{-1}. The instrument was calibrated against pure indium metal (Mp = 156.6 °C, ΔH = 28.5 J g^{-1}). Phase transition temperatures are reported as the endothermic onset temperature from differential scanning calorimetry traces. The diffraction measurements were made by using CuKα radiation from a sealed tube with other wavelengths removed by using a nickel filter and a graphite monochromator. The diffraction pattern was detected by a multi-wire area detector.[11] It was placed at 840 nm from the sample with an evacuated path so that a Q (scattering vector) range from 0.03 to 0.5 Å^{-1} was covered. The sample to detector distance was calibrated by using silver behenate standard.[12] Since the sample was not aligned, the scattering was regrouped so that pixels at the same radius were averaged, and the center of gravity of each diffraction peak was determined numerically and used to calculate its scattering vector. The precision of the Q values was generally better than 1%. The software for viewing and analysing the X-ray scattering was developed by PV-WAVE.[13] The measurements were made at temperatures from 80 °C to room temperature.

(*R*)-4′-Octyloxybiphenyl-4-yl 4-[4-(2-octyloxy)-2-(pent-4-enyloxy)benzoyloxy]benzoate 4

Material **4** was prepared from (*R*)-(−)-octan-2-ol following the established procedure for **3**[10b] and isolated as white crystals.

^1H NMR (400 MHz, $CDCl_3$, 24 °C, internal $CHCl_3$) δ ppm: 8.27 (m, 2H, aromatic), 8.03 (m, 1H, aromatic), 7.59 (m, 2H, aromatic), 7.51 (m, 2H, aromatic), 7.35 (m, 2H, aromatic), 7.25 (m, 2H, aromatic), 6.97 (m, 2H, aromatic), 6.51 (m, 2H, aromatic), 5.82 [d (J *trans* = 17 Hz) d (J *cis* = 10 Hz) t (J = 7 Hz), 1H, $CH_2{=}CH$], 5.03 [d (J *trans* = 17 Hz) d (J *cis* = 10 Hz) m, 1H, *trans* $CH_2{=}CH$], 4.98 [d (J *cis* = 10 Hz) m, 1H, *cis* $CH_2{=}CH$], 4.46 (m, 1H, CH_3-C*H*-O), 4.05 [t (J = 6 Hz), 2H, CH_2-O-Ph], 3.99 [t (J = 6 Hz), 2H, CH_2-O-Ph], 2.30 (m, 2H, CH_2-CH-O), 1.95 (m, 2H, CH_2-CH=), 1.80 (m, 2H, -CH_2-), 1.61 (m, 2H, -CH_2-), 1.51 (m, 2H, $(CH_2)_n$), 1.36 (m, 19H, CH_3, $(CH_2)_n$), 0.89 [t (J = 7 Hz), 6H, CH_3-CH_2].

K 101.1 (ΔH = 32.2 kJ mol^{-1}) N* 109.2 Iso °C (ΔH = 0.58 kJ mol^{-1}).

1,3,5,7,9,11,13,15-Octakis{(*S*)-4′-octyloxybiphenyl-4-yl 4-[4-(2-methylbutoxy)-2-(5-pentyloxydimethylsiloxy)-benzoyloxy]benzoate}-substituted pentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane, 1

(*S*)-4′-Octyloxybiphenyl-4-yl 4-[4-(2-methylbutoxy)-2-(pent-4-enyloxy)benzoyloxy]benzoate **3**[10b] (0.40 g; 0.57 mmol) in toluene (10 mL) was placed in a small Schlenk tube under nitrogen atmosphere. Karstedt's catalyst (3% Pt solution in xylene, 10 µL) was added and the solution stirred at room temperature 15 min; a solution of octakis(hydridodimethylsiloxy)octasilsesquioxane **5**[14] (0.055 g; 0.0054 mmol) in 8 ml of toluene was added over a period of 1 h and the solution stirred 18 h at room temperature. The solvent was evaporated under vacuum and the residue was purified by column chromatography (flash grade silica gel, dichloromethane, R_f = 0.1). After evaporation of the solvent the residue was filtered (0.45 µm) and the product dried under vacuum at room temperature to yield **1** as a glassy material (0.242 g; 68%).

Elemental analysis calcd (%) for $C_{368}H_{472}O_{76}Si_{16}$: C 67.37, H 7.24; found: C 67.21, H 6.96.

Phase transitions: g 23.7 N* 116.9 [0.46 kJ mol^{-1} per mesogen] Iso Liq.

IR (KBr plates, thin film, ν cm^{-1}): 1742, 1732 (s, C=O), 1073 (vs, Si–O–Si).

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, internal CH_2Cl_2) δ ppm: 8.17 (m, 2H, aromatic), 7.96 (m, 1H, aromatic), 7.55 (m, 2H, aromatic), 7.48 (m, 2H, aromatic), 7.28 (m, 2H, aromatic), 7.20 (m, 2H, aromatic), 6.93 (m, 2H, aromatic), 6.49 (m, 2H, aromatic), 3.96 [t ($J = 6$ Hz), 4H, CH_2-O-Ph], 3.78 (m, 2H, O-CH_2-CH), 1.79 (m, 5H, CH_2-CH_2-O, CH, CH_2-CH_2-Si), 1.46 [m, 4H, $(CH_2)_n$], 1.31 [m, 12H, $(CH_2)_n$], 0.99 [d ($J = 6$ Hz), 3H, CH_3-CH], 0.90 (2 × t, 6H, CH_3-CH_2, CH_3-CH_2), 0.55 (m, 2H, CH_2-SiOSi), 0.08 [s, 6H, $(CH_3)_2$Si-O]. ^{29}Si NMR (79.3 MHz, $CDCl_3$, 24 °C, external TMS) δ ppm: 12.83 [s, 8Si, $(CH_3)_2$-*Si*OSi], −108.83 (Si_8O_{12}).

1,3,5,7,9,11,13,15-Octakis{(*S*)-4′-octyloxybiphenyl-4-yl 4-[4-(2-octyloxy)-2-(5-pentyloxydimethylsiloxy)benzoyloxy]benzoate}-substituted pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane, 2

Compound **2** was prepared by a procedure similar to that described for **1**, from **4** (0.400 g; 0.54 mmol) and **5** (0.053 g; 0.0052 mmol) as a glassy material (0.112 g; 31%).

Elemental analysis calcd (%) for $C_{392}H_{520}O_{76}Si_{16}$: C 68.26, H 7.59; found: C 67.98, H 7.65.

Phase transitions: g 11.2 N* 72.0 [0.18 kJ mol^{-1} per mesogen] Iso Liq.

IR (KBr plates, thin film, ν cm^{-1}): 1742, 1732 (s, C=O), 1073 (vs, Si–O–Si).

^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, internal CH_2Cl_2) δ ppm: 8.20 (m, 2H, aromatic), 7.99 (m, 1H, aromatic), 7.54 (m, 2H, aromatic), 7.47 (m, 2H, aromatic), 7.29 (m, 2H, aromatic), 7.21 (m, 2H, aromatic), 6.93 (m, 2H, aromatic), 6.47 (m, 2H, aromatic), 4.46 (m, 1H, CH_3-CH-O), 3.96 (m, 4H, CH_2-O-Ph), 1.79 (m, 4H, CH_2-CH_2-O, CH_2-CH_2-Si), 1.46 [m, 4H, $(CH_2)_n$], 1.29 [m, 22H, $(CH_2)_n$], 0.87 (2 × t, 6H, CH_3-CH_2), 0.55 (m, 2H, CH_2-SiOSi), 0.08 [s, 6H, $(CH_3)_2$Si-O]. ^{29}Si NMR (79.3 MHz, $CDCl_3$, 24 °C, external TMS) δ ppm: 12.83 [s, 8Si, $(CH_3)_2$-*Si*OSi], −108.83 (Si_8O_{12}).

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