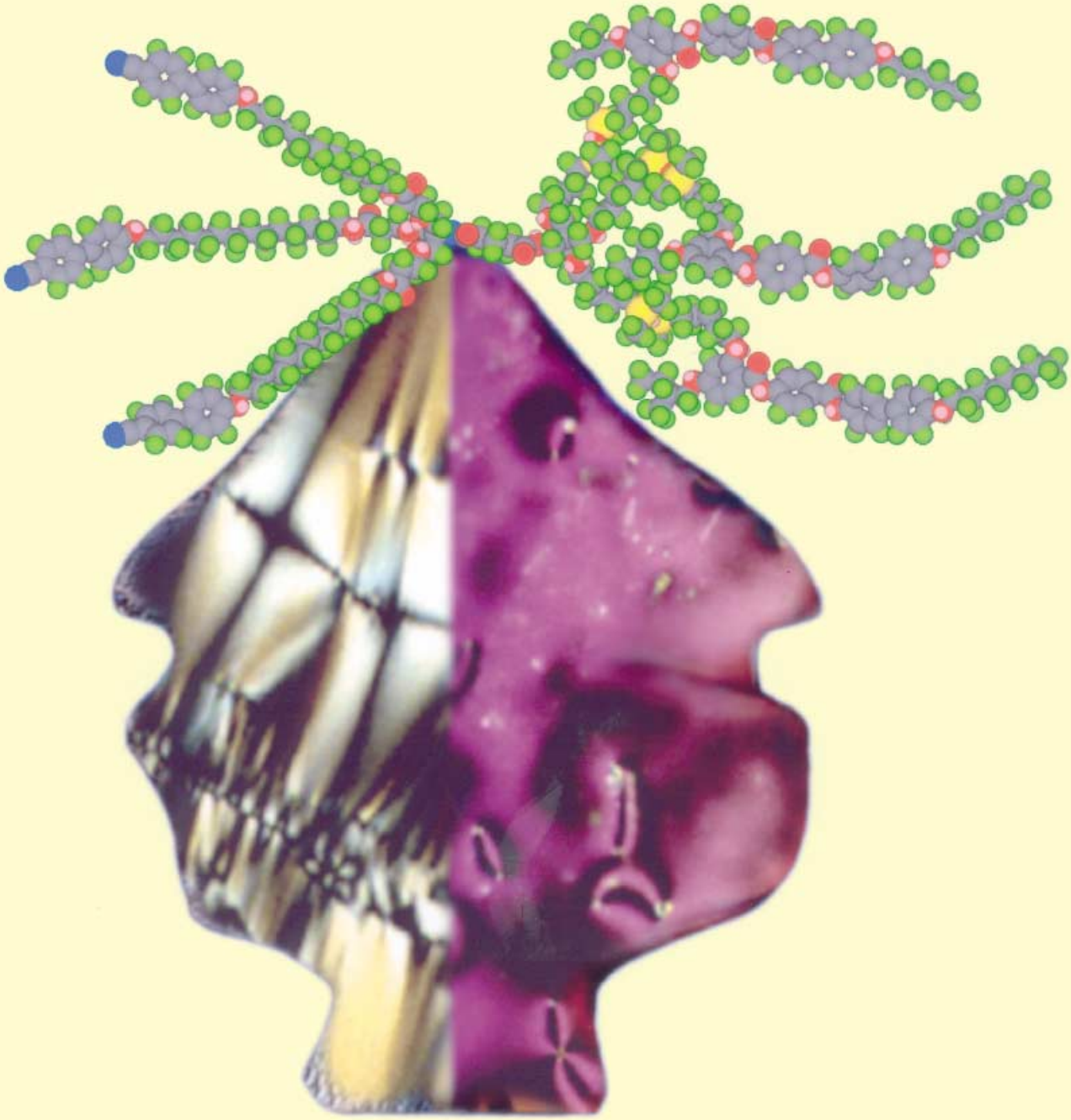
Janus Liquid Crystals



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 DOI: 10.1002/chem.200305100

"Janus" Supermolecular Liquid Crystals—Giant Molecules with Hemispherical Architectures

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Abstract: Liquid crystals represent a unique class of self-organising systems, which although found in many day-to-day practical material applications, such as displays, are also intimately entwined with living processes. They have the potential, just like living systems, to provide us with a unique vehicle for the development of self-ordering nano- and mesoscopic-engineered materials with specific functional properties. In this article we describe a new concept for the design of self-assembling functional liquid crystals as segmented or "Janus" liquid-crystalline supermolecular materials in the form of structures that contain two different types of mesogenic units, which favour different types of mesophase structure, grafted onto the same star-shaped scaffold to create supermolecules that contain different hemispheres. The materials exhibit chiral nematic and chiral smectic C phases.

Keywords: chirality · dendrimers · liquid crystals · self-assembly · supramolecular chemistry

Introduction

The engines of living systems are based on super- and supramolecular self-organising and self-assembling systems of discrete structure and topology. For example, proteins, although peptide polymers, have defined and reproducible primary compositions of amino acids, specified α-helical and β-pleated secondary constructions, and gross topological tertiary structures. Moreover, highly specific functionality, and thereby the ability to perform selective chemical processing, is in-built into such molecular machines. Concomitantly, the study of materials that self-assemble into supramolecular structures with desirable functionality and physical properties at nano- and mesoscopic length scales is currently an exciting area of intense research and provides a "bottom-up" approach to the design and synthesis of functional materials.[1]

Until recently, most liquid crystals have been designed to be either low molecular weight for displays or high molecular weight for prototypical high-yield-strength polymers.[2] Star-shaped liquid crystals, on the other hand, 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. Furthermore, dendrimers[3] 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 unprecedented level of control of the precise nature and location of specific functionalities and overall molecular architectures, as in proteins. As a consequence, the initial interest in dendrimer synthesis has shifted towards functional dendrimers, because of their rich supramolecular chemistry and self-assembling properties.[3] 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.[2] Therefore, star-shaped liquid crystals provide unique materials for the study of self-organising and self-assembling processes.[3–8]

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; these can yield supramolecular objects that may recognise and select left from right, or top from bottom, as described by de Gennes.[9] For example, block co-polymers in the form of Janus micelles,[10–14] segregated amphiphilic dendrimers[15–26] and shape-persistent macromolecules[27–31] are examples of such materials that self-organise, like proteins, in a pre-programmed fashion. Thus, we present the design, synthesis, characterisation and phase behaviour of complementary star-shaped hexamers **1** and **2**, based on a central scaffold made up of pentaerythritol and tris(hydroxymethyl)aminomethane units linked together, whereby one unit carries three cyanobiphenyl (CB) and the other three chiral phenyl benzoate (PB) mesogenic moieties or vice-

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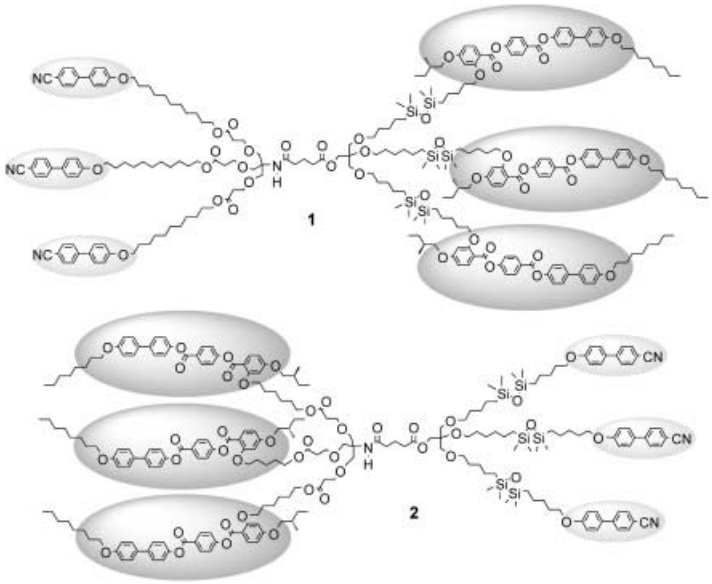
DOI: 10.1002/chem.200305100



versa. This group of amphiphilic star-shaped materials are thus formally related to the family of segregated AB block-copolymers.

Results and Discussion

The basic design concept (see Figure 1) consists of creating a star-shaped scaffold that 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. The type of mesogen (CB- and PB-based), the geometry of the attachment of the mesogens to the central scaffold (end-on favouring smectic and side-on favouring nematic phase formation), and the nature of the connecting group (ester or tetramethydisiloxy) were explored as tools for creating supermolecular systems with different halves. To this end, the use of aliphatic spacers between the mesogenic moieties and the scaffold follows the same concept as in traditional side-chain liquid-crystalline polymers, that is, to decouple the motions of the mesogenic units from the scaffold thereby allowing their ordering in the creation of a mesophase. In this case we placed particular emphasis in studying the effect of segregation of chiral groups within the molecule on molecular recognition processes that ultimately lead to selective mesophase formation.

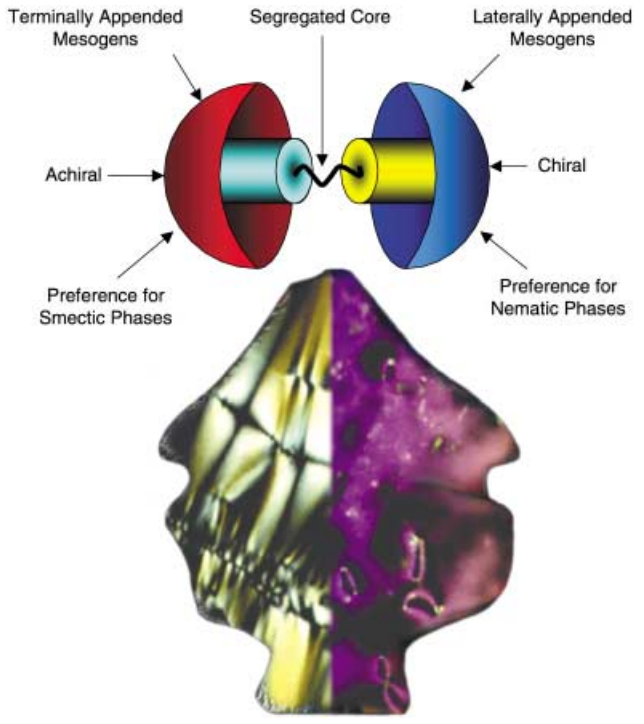
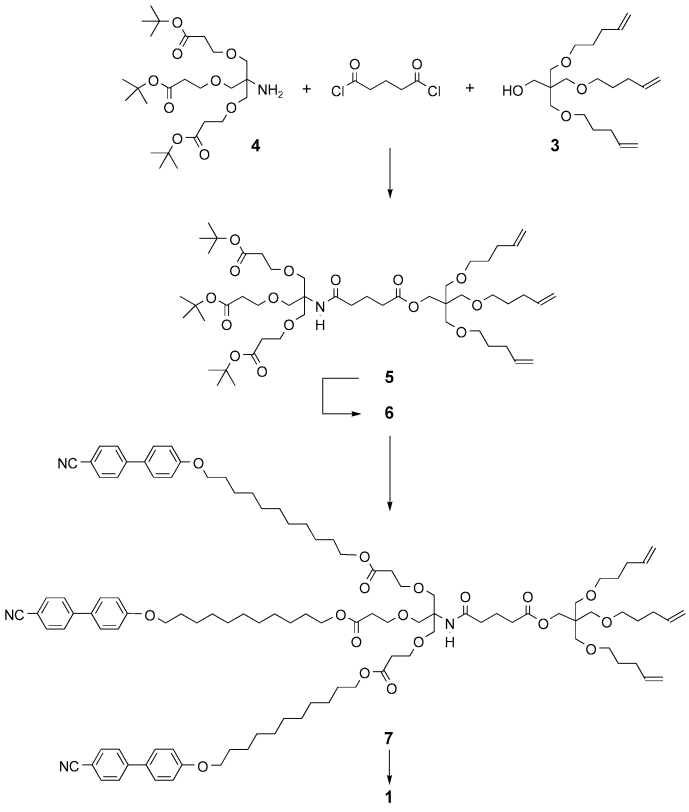


Figure 1. Design concept for "Janus" supermolecular liquid crystals with different hemispherical architectures.

The molecular sub-units or building blocks **3** and **4**, based on pentaerythritol (PE) and tris(hydroxymethyl)aminomethane (TRIS), respectively, were designed to incorporate different end-groups, olefin and *tert*-butyl ester, respectively, which can be functionalised independently with different mesogenic moieties (see Scheme 1 and Figure 2).



Scheme 1. Synthesis of compound **1**.

The strategy employed consists of 1) the divergent synthesis of the scaffold core **5** and 2) sequential functionalisation of the halves by mesogenic moieties. Of the several possible sequences, two complementary routes have been explored for this step:

a) Incorporation of end-on CB moieties on the TRIS side to yield the half-functionalised trimer **7**, which is subsequent-

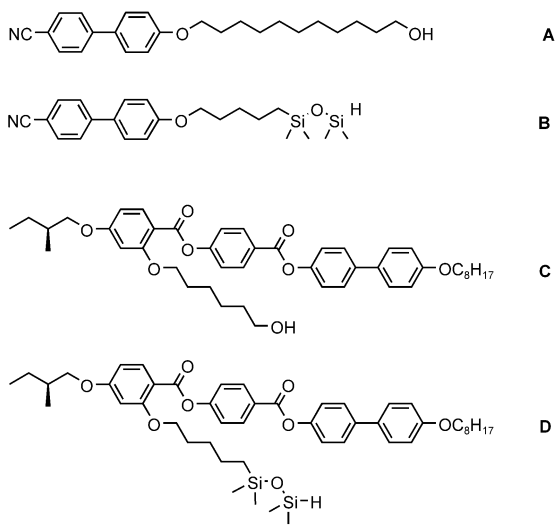


Figure 2. Mesogenic units used to derivatise central star-shaped scaffold.

ly reacted with side-on phenyl benzoate ester moieties on the PE hemisphere to yield hexamer **1**.

b) Incorporation of end-on CB moieties on the PE side to afford trimer **8**, which is reacted with side-on phenyl benzoate moieties on the TRIS hemisphere affording star-shaped hexamer **2**.

Branching unit **3** was synthesised by Williamson etherification of PE with 5-bromopentene in 50 % aqueous NaOH, with [N*n*Bu$_4$]Br as the phase-transfer agent, in 29 % yield. Branching unit **4**, structurally related to Lin's amine[32] and used extensively by Newkome and Diederich in dendrimer synthesis, was prepared by polyetherification of TRIS by Michael-type addition of *tert*-butyl acrylate.[33]

A high-dilution technique, using a three-component system, was employed to synthesise the desired scaffold **5** (Scheme 1). Thus, treatment of one equivalent of tris(5-pentenyloxy)pentaerythritol (**3**) with glutaryl dichloride in the presence of NEt$_3$ at 0 °C followed by amidation with **4** afforded **5** in 45 % yield. The characterisation of **5** was supported by ^{1}H NMR spectroscopy, with all seventeen different types of proton observed as unique signals, ^{13}C NMR spectroscopy, with absorptions at 172.88, 172.31 and 170.89 ppm for the three carbonyl groups and two different quaternary carbons in the structure clearly separated at 44.36 and 59.61 ppm, and the molecular ion peak at *m/z* 965 $[M+Na]^+$ (MALDI-TOF, HABA matrix).

Having obtained **5**, we functionalised it in the following way. Acid hydrolysis of the *tert*-butyl groups (CF_3COOH/Cl_2CH_2 1:1, RT) afforded the triacid **6**. Esterification of **6** with mesogen **A** (DCC/DMAP, Cl_2CH_2/THF, RT) gave the half-substituted trimer **7** in 37 % yield, which is supported by the appearance (^{13}C and ^{1}H NMR spectroscopy) of signals in the relevant aromatic regions of the spectra that correspond to the cyanobiphenyl moiety and the presence of a new signal for the carbonyl group formed in the reaction. Size exclusion chromatography (SEC) proved the complete substitution of **5**, through the presence of a single symmetrical peak of dispersity (γ) 1.02 (THF; $M_r = 2735$; $M_n = 2661$; M_r (calcd) = 1816).

Platinum-catalysed hydrosilylation of the olefinic functional group of **7** with the mesogenic hydridosiloxane **D** by using Karstedt's catalyst at room temperature in toluene afforded hexamer **1** in 51 % yield; the characterisation of this hexamer **1** was confirmed by ^{1}H NMR spectroscopy through the complete disappearance of the vinylic protons and the appearance of new signals in the aromatic region from the second mesogenic (PB) unit, the pseudo-triplet at 0.5 ppm assigned to the CH_2-CH_2-Si-O unit and the silicon methyl protons at 0.00 ppm. Similarly, ^{13}C NMR spectroscopy showed the expected signals of the new aromatic moieties, disappearance of the olefinic carbon signals and appearance of the new CH_2-CH_2-Si and Si-CH_3 of the tetramethyldisiloxane connector moiety. Furthermore, ^{29}Si NMR spectroscopy displayed two close singlets at 7.92 and 7.79 ppm, typical of M-type silicon. Gratifyingly, MALDI-TOF spectrometry showed the molecular ion (*m/z*: 4320 $[M+Na]^+$; calcd: 4320; HABA matrix) with the appropriate isotopic distribution (see Figure 3), indicating complete conversion of **7** to **1** by the

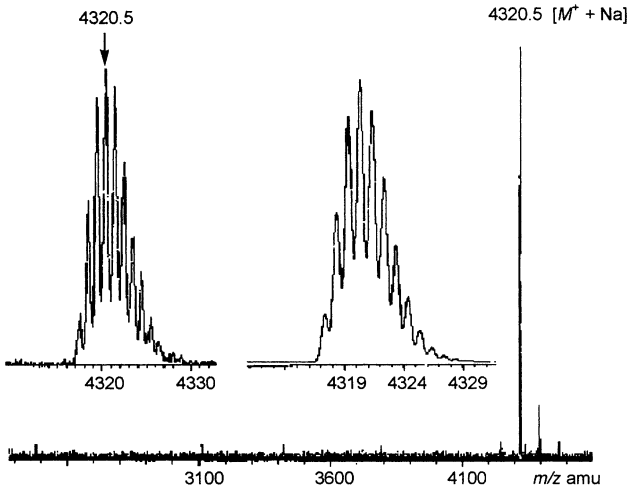
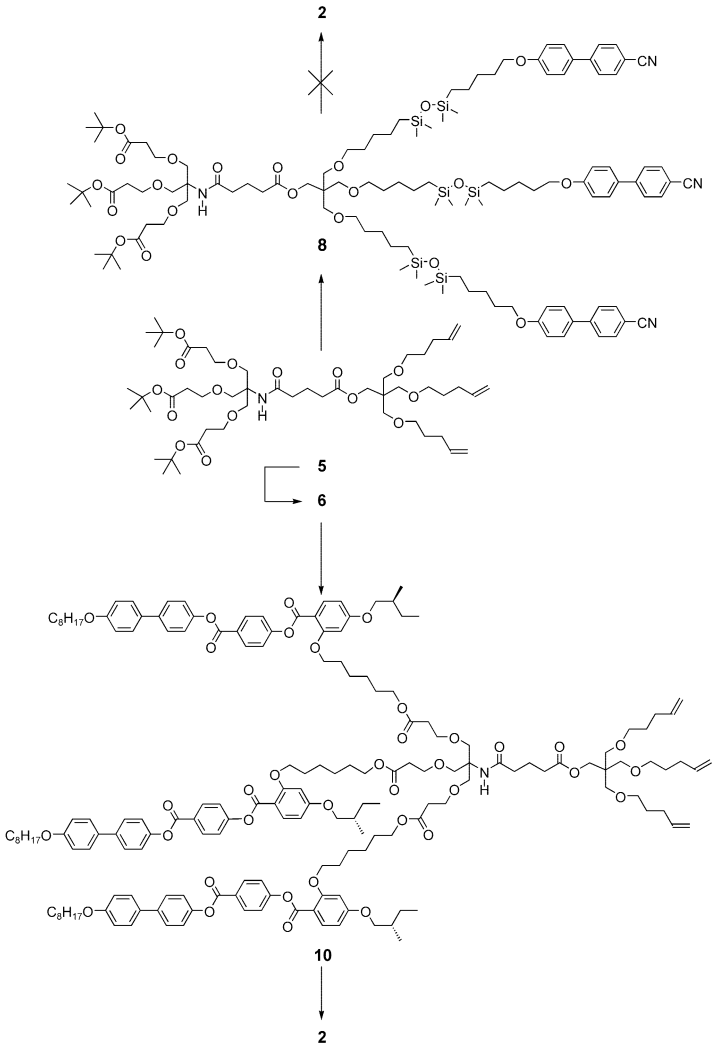


Figure 3. MALDI-TOF spectra for **1**, inserts show the predicted and measured isotope distribution for the mass ion.

absence of any other less substituted species. SEC was used to ascertain the monodispersity of **1** ($M_r = 5817$; $M_n = 5608$; $\gamma = 1.02$). However, the molecular weight was significantly overestimated by this technique, an indication of a bigger "apparent" hydrodynamic volume, which is most probably due to the globular shape of the molecule in contrast with that of the coiled PS standards used.

The analogous hexamer **2** was initially targeted for synthesis following the alternative route shown in Scheme 2; that is, derivatisation by hydrosilylation of the pentaerythritol-based hemisphere first, followed by derivatisation with the chiral phenylbenzoate mesogenic units on the TRIS hemisphere. Thus, hydrosilylation of **5** with mesogen **B** gave trimer **8** in 51 % yield; the formation of this product was confirmed by the disappearance of vinylic protons associated with **5** and the appearance of new aromatic H, CH_2-CH_2-Si and CH_3-Si signals in the ^{1}H NMR spectrum, as well as by ^{13}C and ^{29}Si spectroscopy. SEC confirmed the monodispersity of **8** ($M_r = 2994$; $M_n = 2851$; $\gamma = 1.02$; M_r(calcd) = 2135). However, de-



Scheme 2. Synthesis of compound **2**.

protection of the *tert*-butyl ester groups of **8** with CF_3COOH(excess)/Cl_2CH_2 (1:1) at room temperature resulted in considerable decomposition, affording impure triacid **9**, which failed to yield **2** when used to carry out the esterification with **C**.

Consequently we returned to the original protocol. The triacid **6** was esterified with the chiral mesogenic alcohol **C** to yield **10** (DCC/DMAP, Cl_2CH_2, RT) in 26% yield. Hydrosilylation of **10** with the cyanobiphenylhydridosiloxane (**B**) on the pentaerythritol side of the hemisphere (Karstedt's catalyst, toluene, RT) afforded **2** in 50% yield. Again, ^1H and ^{13}C NMR spectroscopy showed complete conversion of the carboxylic acid and the vinylic functionalities for **6** and **10**, respectively; the ^{29}Si NMR spectrum of **2** displayed two singlets (7.95, 7.76 ppm) as predicted. In all cases, within the limits of detection, the hydrosilylation reaction proceeded through β-addition to yield the linear (unbranched) Si-CH_2-CH_2- (*S*)-isomer. SEC of **2** showed that the product was monodisperse, with good agreement between the expected and observed molecular weights. As for **1**, the identity of **2** was confirmed MALDI-TOF spectrometry, with a peak at *m/z*: 4110.3 [M^++Na] (calcd: 4110 for [M^++Na]) with the expected isotopic distribution (see Figure 4).

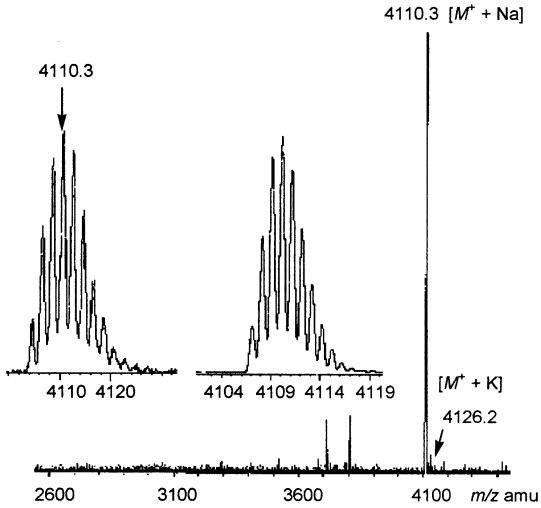


Figure 4. MALDI-TOF spectra for **2**, inserts show the predicted and measured isotope distribution for the mass ion.

The mesomorphic properties of the materials were investigated by differential scanning calorimetry (DSC) and polarised light optical microscopy (POM). The DSC data for compounds **1** and **2** and the transition temperatures are listed in Table 1. Both materials were isolated in a glassy state at room temperature. On heating a pristine sample of **1**, a broad melting endotherm with onset at 33.8 °C was followed by a weaker endotherm with onset at 60.7 °C associated with the transition from the liquid-crystal state to the isotropic liquid. The cooling cycle from the isotropic state showed a similarly broad, weak exotherm, with onset at 64.3 °C, marking the transition between the isotropic liquid and the liquid-crystalline state, and a second exotherm with onset at approximately 36.1 °C, marking a second-order transition to another mesophase. Further cooling induced a glass transition

Table 1. Phase transition temperatures[a] of compounds **1**, **2**, **7**, **8** and **10** in °C. In parenthesis, the enthalpy changes ΔH in kJ mol^{-1}.

	Tg	Cr		SmA		SmC*		N*		Iso
1	– 2.8		–	–	–	•	33.8 (6.26)	•	60.8 (2.73)	•
2	– 7.9		–	–	–	–	–	•	38.2 (0.87)	•
7		•	– 19.4 K′ – 7.5	•	31.0	–	–	–	–	•
8	– 22.2	–	–	–	–	–	–	–	–	–
10	– 9.8	•	58.4 (63.1)	–	–	–	–	•	64.8 (0.69)	•

[a] Tg = glass transition, Cr = crystal, K′ = crystal′, SmA = smectic A, SmC* = chiral smectic C, N* = chiral nematic (cholesteric), Iso = isotropic liquid. Temperatures are given as the onset of the peak observed during the second heating run; glass transitions are determined during the first cooling cycle.

below room temperature, at approximately 2.8 °C. This sequence of events was perfectly reproducible in subsequent heating and cooling cycles. It is noteworthy that the transitions have 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 (see Figure 5), hinting at possibly different transitions for the two mesogenic blocks and two spacer units. This result is indicative of a degree of microphase separation that is present in the system.[37]

In contrast, hexamer **2** shows only one enantiotropic transition by DSC between the liquid-crystalline state and the isotropic liquid, in the form of a weak, broad peak at 38.2 °C. The only other thermal event present was a glass transition below room temperature (see Figure 6). Only when the sample was left standing at room temperature for three weeks did a broad, strong endotherm with onset at 31.6 °C with a shoulder at 42.6 °C occur. However, these thermal events were not present in successive heating and cooling cycles, suggesting that crystallisation only occurs on standing for long periods of time.

The defect textures of the compounds were examined by thermal polarised light microscopy. On cooling from the isotropic state, both compounds **1** and **2** rapidly developed a Grandjean-plane texture with oily streak defects (floating edge dislocations), both being deep blue in colour (see Figure 7 for compound **1**); the presence of this texture unequivocally identifies the phase as a chiral nematic phase.

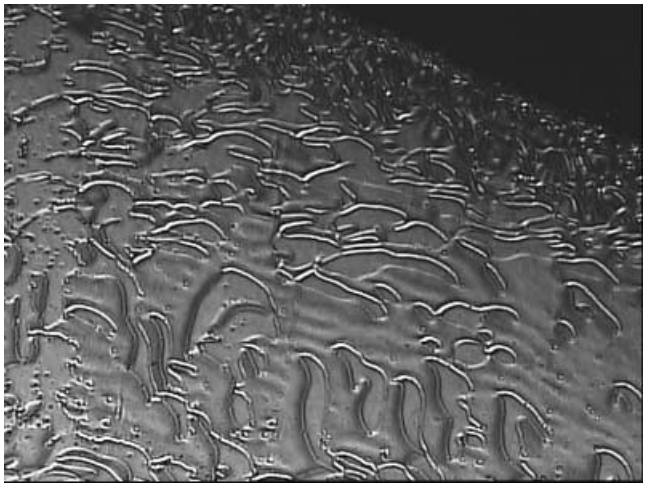


Figure 7. The Grandjean plane texture of the chiral nematic phase of compound **1** (× 100).

Rotation of the analyser showed that in both cases the helical macrostructure of the mesophase was left-handed. Further cooling of **1** to 30.8 °C (corresponding to the transition at 33.8 °C by DSC) sharply induced the formation of the schlieren and marbled texture (see Figure 8) characteristic of the chiral smectic C phase. Mechanical shearing of the specimen induced the formation of numerous, very small focal-conic domains, characterised by their elliptical and hyperbolic lines of optical discontinuity, and oily streak defects that coalesced, reverting rapidly to the schlieren texture of the SmC* phase. No further textural changes were observed upon cooling. Remarkably upon further cooling, the sample froze into a glass, but it still retained its mesophase texture, that is, a glassy chiral smectic C phase was formed. Reheating a sample of **1** from the SmC* phase, a transition to a highly iridescent, very mobile schlieren texture with oily streak defects was formed; this is typical of the chiral nematic phase. The easy formation of typical low-molecular-mass defect textures plus the mobility of the materials seen in the microscope is indi-

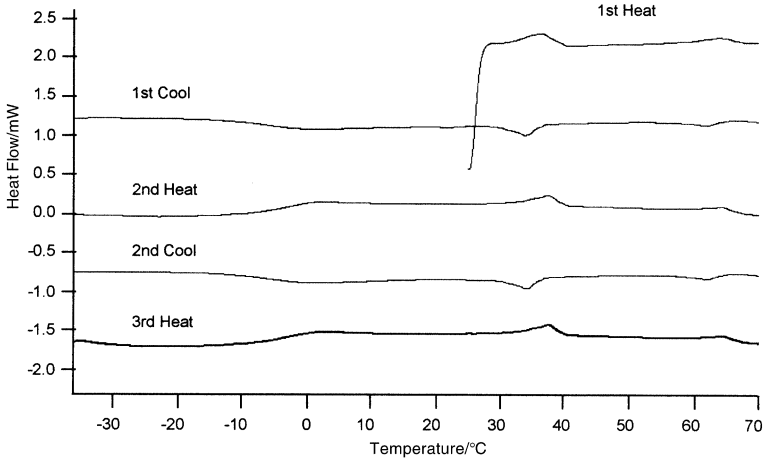


Figure 5. DSC traces of **1** (rate 10 °C min^{-1}) showing heating and cooling cycles.

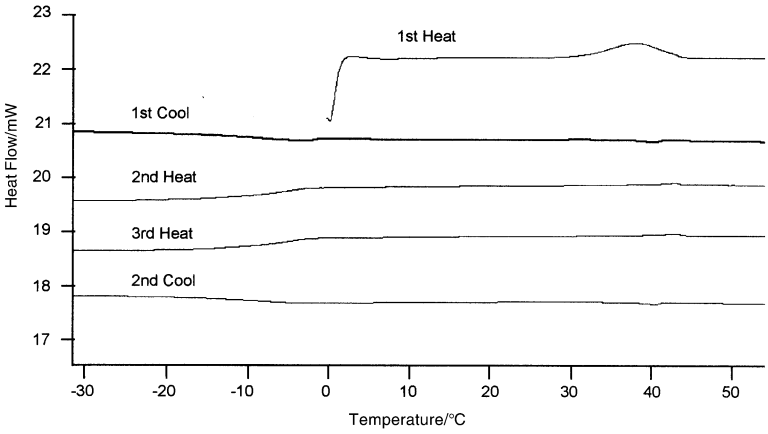


Figure 6. DSC traces of **2** (rate 10 °C min^{-1}) showing heating and cooling cycles.

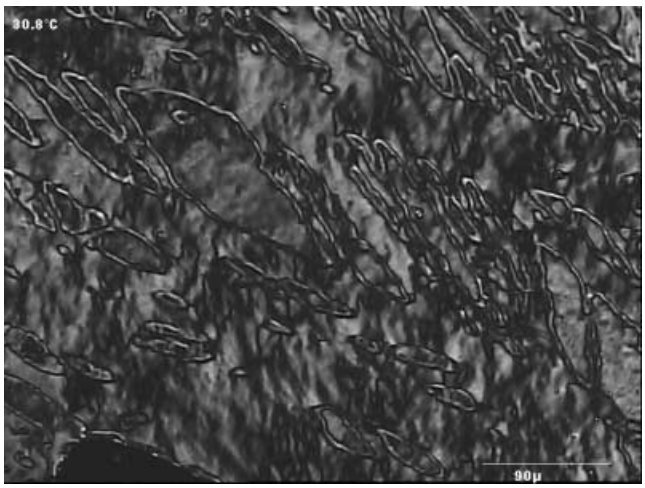


Figure 8. The schlieren texture of the chiral smectic C* phase of compound **1** (×100).

cative of low viscosity. Furthermore, it is important to note that the formation of chiral mesophases also means that the nematic phase is thermochromic, and the smectic C* phase is ferroelectric and pyroelectric, and will exhibit electrostrictive properties, which will be discussed in the future. In addition, the glassy chiral phases have applications as optical filters and reflectors.

Comparison of the phase behaviour of compounds **1** and **2** shows clearly that the overall topology of the molecule in respect to the inner core (i.e., 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. Furthermore, compound **1** is one of the extremely rare examples to date in which 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.[2]

Comparison of the phase behaviour of hexamer **1** and precursor trimer **7** shows the dramatic change that takes place upon the incorporation of laterally appended mesogenic units. Compound **7** displays a smectic A phase at room temperature (Table 1); however, incorporation of the three side-on phenylbenzoate/tetramethyldisiloxy moieties on the unreacted olefinic chains totally suppresses the smectic A phase, generating the chiral nematic phase and a tilted chiral smectic C phase. Moreover lateral substitution significantly reduces the glass transition temperature, probably because of the increased molecular disordering, with the overall effect of increasing dramatically the temperature range and stability of the liquid-crystalline state.

Due to the strong tendency of laterally attached mesogenic moieties to support the formation of nematic phases, trimer **10** as predicted exhibits a chiral nematic phase. The derivatisation of **10** with three cyanobiphenyltetramethyldisiloxy moieties to yield compound **2** results in a reduction of the temperature range and thermal stability of the chiral nematic phase, decreasing the isotropisation temperature for **10** from 64.8 °C to 38.2 °C for **2**, whereas the glass transition remains almost unaltered (−9.8 °C for **10** to −7.9 °C for **2**).

Comparison of cyanobiphenyl-based trimers **7** and **8** also highlights the role of the nature and structure of the scaffold on mesophase formation. Compound **7** displays the SmA phase, whereas no liquid crystal properties were observed for **8**, which has three *tert*-butyl groups, even on cooling down to −50 °C. In comparison, the fully substituted parent cyanobiphenyl mesogen-based pentaerythritol tetramers,[34] with either ester or tetramethyldisiloxane linking groups, display the SmA phase. Therefore, the absence of liquid-crystal properties in **8** is presumably related to the presence of the three, bulky *tert*-butyl groups that preclude mesophase formation by disrupting the effective packing of the promesogenic units.

Conclusion

In conclusion, we have created a new class of "Janus" liquid-crystal compounds with molecular weights in excess of 4000 D, but which have better thermal stabilities and temperature ranges about room temperature than the revolutionary commercial material 4′-pentyl-4-cyanobiphenyl (5CB). Furthermore, the materials appear to have physical properties more in keeping with low-molecular-mass materials than polymers or dendrimers.

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.

Experimental Section

Solvents were rigorously dried over appropriate drying agents and distilled prior use. Low sulphur content, dry, degassed toluene (Fluka), Karstedt's catalyst (Fluorochem), tetramethyldisiloxane (Fluorochem), and all remaining reagents (Aldrich) 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 precoated silica gel plates (Merck). Visualisation was accomplished with UV light and cerium and ammonium molybdate stain.[35]

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 deuterated solvent used for ^1H analysis. Elemental analysis was performed on a Fisons Instruments Carlo Erba EA 1108 CHN analyser by using acetanilide as the reference standard. Mass spectra were recorded on a Shimadzu GCMS 5050A spectrometer (EI mode/70 eV). MALDI-TOF MS was performed on a Bruker Reflex IV instrument, N_2 laser operating at 337 nm, with 2-(4-hydroxyphenylazo)-benzoic acid matrix, 1 µL saturated solution in CH_2Cl_2 and 1 µL solution of sample in CH_2Cl_2, 45 laser shots averaged per spectrum. Size exclusion chromatography (SEC) was performed by 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 $\pm 0.1\,^{\circ}C$ in the range 50–250 °C. Phase transitions were determined by differential scanning calorimetry (DSC) by using a Perkin–Elmer DSC 7-Series with Unix DSC data acquisition and analysis software at a scan rate of $10\,^{\circ}C\,min^{-1}$. The instrument was calibrated against pure indium metal (m.p. = 156.6 °C, $\Delta H = 28.5\,J\,g^{-1}$). Phase-transition temperatures are reported as the endothermic onset temperature from differential scanning calorimetry traces.

Preparation of compound 5: Glutaryl dichloride (0.300 g, 1.77 mmol) in dry THF (8 mL) was cooled to 0 °C, and a solution of **4** (0.900 g, 1.73 mmol) and NEt_3 (0.179 g, 1.73 mmol) in THF (8 mL) was added dropwise over a period of 1 h and stirred for further 2 h. A solution of **3** (0.602 g, 1.73 mmol) and NEt_3 (0.179 g, 1.73 mmol) in THF (5 mL) was added at once. The mixture was left to reach room temperature slowly and stirred for 18 h. The precipitate formed was filtered off and the residue obtained after evaporation of the solvent purified by column chromatography (flash-grade silica gel; gradient Cl_2CH_2/20% EtAcO) to yield **5** as a clear oil (0.755 g, 45%). Elemental analysis calcd (%) for $C_{50}H_{87}NO_{15}$: C 63.74, H 9.31, N 1.49; found: C 63.25, H 9.72, N 1.49; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, TMS): $\delta = 6.06$ (brs, 1H; CO-N*H*); 5.75 (ddt, $^3J(H,H_{trans}) = 17$ Hz, $^3J(H,H_{cis}) = 10$ Hz, $^3J(H,H) = 7$ Hz, 3H; CH_2=C*H*), 4.98 (ddm, $^3J(H,H_{trans}) = 17$ Hz, $^2J(H,H) = 10$ Hz, 3H; *trans*-C*H*$_2$=CH), 4.91 (dm, $^3J(H,H) = 10$ Hz, 3H; *cis*-C*H*$_2$=CH), 4.08 (s, 2H; C^4-C*H*$_2$-OCO), 3.65 (s, 6H; C^4-C*H*$_2$-O), 3.59 (t, $^3J(H,H) = 6$ Hz, 6H; O-C*H*$_2$-CH$_2$-CH$_2$), 3.32 (s, 6H; NC^4-C*H*$_2$-O), 3,32 (t, $^3J(H,H) = 6$ Hz, 6H; O-C*H*$_2$-CH$_2$-CH$_2$), 2.40 (t, $^3J(H,H) = 6$ Hz, 6H; *t*BuOCOC*H*$_2$), 2.30 (t, $^3J(H,H) = 6$ Hz, 2H; NH-CO-C*H*$_2$), 2.16 (t, $^3J(H,H) = 6$ Hz, 2H; C*H*$_2$-COO), 2.05 (m, 6H; C*H*$_2$-CH=CH$_2$), 1.86 (m, 2H; NHCO-CH$_2$-C*H*$_2$-CH$_2$-COO), 1.57 (m, 6H; -C*H*$_2$-), 1.40 ppm (s, 27H; C*H*$_3$-^{4}C); ^{13}C NMR (100.4 MHz, $CDCl_3$, 24 °C, external TMS): $\delta = 172.88, 172.31, 170.89, 138.37, 114.53, 80.39, 70.64, 69.36, 69.09, 66.96, 63.87, 59.61, 44.36, 36.06, 36.00, 33.44, 30.25, 28.75, 28.03, 20.84$ ppm; MALDI-TOF MS (HABA matrix): *m/z* calcd for $C_{50}H_{87}NO_{15}$Na: 964.8; found: 965.2 $[M+Na]^+$.

Preparation of compound 6: Compound **5** (0.400 g, 0.41 mmol) was stirred with CF_3COOH (5 mL) and Cl_2CH_2 (5 mL) at room temperature. The reaction was monitored by TLC until no **5** was present in the reaction mixture (5 h). The solvents were evaporated to dryness to yield a colourless syrup that was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, TMS): $\delta = 7.90$ (brs, 3H; COO*H*), 6.49, 6.46 (brs, 1H; CO-N*H*), 5.80 (ddt, $^3J(H,H_{trans}) = 17$ Hz, $^3J(H,H_{cis}) = 10$ Hz, $^3J(H,H) = 7$ Hz, 3H; CH_2=C*H*), 4.98 (ddm, $^3J(H,H_{trans}) = 17$ Hz, $^2J(H,H) = 10$ Hz, 3H; *trans*-C*H*$_2$=CH), 4.94 (dm, $^3J(H,H) = 10$ Hz, 3H; *cis* C*H*$_2$=CH), 4.14 (s, 2H; C^4-C*H*$_2$-OCO), 3.72 (s, 6H; C^4-C*H*$_2$-O), 3.59 (t, ^{3}*0*(H,H) = 6 Hz, 6H; O-C*H*$_2$-CH$_2$-CH$_2$), 3.38 (s, 6H; NC^4-C*H*$_2$-O), 3.38 (t $^3J(H,H) = 6$ Hz, 6H; O-C*H*$_2$-CH$_2$-CH$_2$), 2.58 (t, $^3J(H,H) = 6$ Hz, 6H; *t*BuOCOC*H*$_2$), 2.30 (t, $^3J(H,H) = 6$ Hz, 2H; NH-CO-C*H*$_2$), 2.16 (t, $^3J(H,H) = 6$ Hz, 2H; C*H*$_2$-COO), 2.05 (m, 6H; C*H*$_2$-CH=CH$_2$), 1.86 (m, 2H; NHCO-CH$_2$-C*H*$_2$-CH$_2$-COO), 1.57 ppm (m, 6H; -C*H*$_2$-).

Preparation of compound 7: Compound **6** (0.100 g, 0.127 mmol), mesogenic alcohol **A** (0.153 g, 0.419 mmol), DCC (88 mg, 0.419 mmol) and DMAP (62 mg, 0.209 mmol) were dissolved in dry THF (20 mL), and the solution stirred three days at room temperature. The solvent was evaporated to dryness, the residue extracted with Cl_2CH_2 (50 mL) and the solvent evaporated to dryness. The crude solid was recrystallised three times from Cl_2CH_2/EtOH to yield **C** as opaque droplets (85 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, TMS): $\delta = 7.57$ (m, 12H; aromatic), 7.44 (m, 6H; aromatic), 6.90 (m, 6H; aromatic), 5.97 (brs, 1H; CO-N*H*), 5.75 (ddt, $^3J(H,H_{trans}) = 17$ Hz, $^3J(H,H_{cis}) = 10$ Hz, $^3J(H,H) = 7$ Hz, 3H; CH_2=C*H*), 4.98 (ddm, $^3J(H,H_{trans}) = 17$ Hz, $^2J(H,H) = 10$ Hz, 3H; *trans*-C*H*$_2$=CH), 4.91 (dm, $^3J(H,H_{cis}) = 10$ Hz, 3H; *cis*-C*H*$_2$=CH), 4.03 (s, 2H; C^4-C*H*$_2$-OCO), 3.99 (t, $^3J(H,H) = 6$ Hz, 6H; Ph-O-C*H*$_2$-), 3.91 (t, $^3J(H,H) = 6$ Hz, 6H; COO-C*H*$_2$-), 3.65 (s, 6H; C^4-C*H*$_2$-O), 3.60 (t, $^3J(H,H) = 6$ Hz, 6H; O-C*H*$_2$-CH$_2$-CH$_2$), 3.29 (s, 6H; NC^4-C*H*$_2$-O), 3.29 (t, $^3J(H,H) = 6$ Hz, 6H; O-C*H*$_2$-CH$_2$-CH$_2$), 2.47 (t, $^3J(H,H) = 6$ Hz, 6H; CH$_2$-OCOC*H*$_2$), 2.28 (t, $^3J(H,H) = 6$ Hz, 2H; NH-CO-C*H*$_2$), 2.13 (t, $^3J(H,H) = 6$ Hz, 2H; C*H*$_2$-COO), 2.01 (m, 6H; C*H*$_2$-CH=CH$_2$), 1.85 (m, 2H; NHCO-CH$_2$-C*H*$_2$-CH$_2$-COO), 1.55 (m, 6H; -C*H*$_2$-), 1.38 (m, 6H; -CH$_2$-), 1.21 ppm (m, 48H; -(CH$_2$)$_8$-); ^{13}C NMR (100.4 MHz, $CDCl_3$, 24 °C, external TMS): $\delta = 172.91, 172.37, 171.62, 159.76, 145.23, 138.38, 132.53, 131.21, 128.28, 127.02, 119.07, 115.03, 114.57, 110.00, 70.68, 69.38, 69.15, 68.11, 66.75, 64.66, 59.62, 44.39, 29.52, 29.50, 28.78, 26.01, 25.87, 20.88$ ppm; SEC: $M_r = 2735$, $M_n = 2661$, $\gamma = 1.02$.

Preparation of compound 1: Mesogenic unit **D** (*S*)-4′-octyloxybiphenyl-4-yl 4-[4-(2-methylbutoxy)-2-(5-tetramethyldisiloxypentyloxy)benzoyloxy]benzoate[8] (0.104 g, 0.125 mmol) in toluene (6 mL) was placed in a small Schlenk tube under nitrogen atmosphere and Karstedt's catalyst (3% Pt solution in xylene, 8 μL) added. A solution of **7** (59 mg, 0.032 mmol) in toluene (6 mL) was added to the above solution dropwise over a 30 min period, and the solution stirred 18 h at room temperature. The solvent was evaporated under vacuum and the residue purified by column chromatography (flash grade silica gel, Cl_2CH_2/hexane 4:1 to elute unreacted **D**, and then changed to Cl_2CH_2 to elute **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 white tacky material (71 mg, 51%). Elemental analysis calcd (%) for $C_{254}H_{348}N_4O_{42}Si_6$: C 70.98, H 8.16, N 1.30; found: C 70.79, H 8.06, N 1.40; ^{1}H NMR (400 MHz, CD_2Cl_2, 24 °C, residual CH_2Cl_2): $\delta = 8.25$ (m, 6H; aromatic), 8.03 (m, 3H; aromatic), 7.67–7.56 (m, 18H; aromatic), 7.50 (m, 12H; aromatic), 7.34 (m, 6H; aromatic), 7.24 (m, 6H, aromatic), 6.96 (m, 12H; aromatic), 6.50 (m, 6H; aromatic), 6.00 (brs, 1H; CO-N*H*), 4.08–3.95 (m, 30H; C^4-C*H*$_2$-OCO, Ph-O-C*H*$_2$-, CH-C*H*$_2$-O-Ph, COO-C*H*$_2$-), 3.82 (m, 6H; CH-C*H*$_2$-O), 3.67 (s, 6H; C^4-C*H*$_2$-O), 3.66 (t, $^3J(H,H) = 6$ Hz, 6H; O-C*H*$_2$-CH$_2$-CH$_2$), 3.34 (s, 6H; NC^4-C*H*$_2$-O), 3.34 (t, $^3J(H,H) = 6$ Hz, 6H; O-C*H*$_2$-CH$_2$-CH$_2$), 2.51 (t, $^3J(H,H) = 6$ Hz, 6H; CH$_2$-OCOC*H*$_2$), 2.33 (t, $^3J(H,H) = 6$ Hz, 2H; NH-CO-C*H*$_2$), 2.18 (t, $^3J(H,H) = 6$ Hz, 2H; C*H*$_2$-COO), 1.85 (m, 22H; NHCO-CH$_2$-C*H*$_2$-CH$_2$-COO, C*H*$_2$-CH$_2$-Si-), 1.60, 1.49, 1.27 (m, 116H; CH$_3$-C*H*$_2$-CH, -(CH$_2$)$_n$-), 1.02 (d, $^3J(H,H) = 6$ Hz, 9H; C*H*$_3$-CH), 0.95 (t, $^3J(H,H) = 6$ Hz, 9H; C*H*$_3$-C*H*$_2$), 0.88 (t, $^3J(H,H) = 6$ Hz, 9H; C*H*$_3$-CH$_2$), 0.47 (2pseudo-t, 12H; C*H*$_2$-SiOSi-C*H*$_2$), 0.00 ppm (2s, 36H; (C*H*$_3$)$_2$Si-O); ^{13}C NMR (100.4 MHz, $CDCl_3$, 24 °C, external TMS): $\delta = 172.89, 172.38, 171.59, 164.89, 164.60, 163.71, 161.89, 159.74, 158.74, 155.57, 149.77, 145.20, 138.69, 134.52, 132.66, 132.51, 131.68, 131.17, 128.25, 128.06, 127.67, 126.99, 126.52, 122.20, 121.85, 119.06, 115.01, 114.06, 110.41, 109.97, 105.38, 100.09, 73.08, 71.61, 69.44, 69.13, 68.87, 68.09, 68.06, 66.74, 64.36, 63.99, 59.62, 44.39, 36.03, 34.84, 34.62, 33.42, 31.79, 29.88, 29.59, 29.52, 29.50, 29.41, 29.37, 29.33, 29.25, 29.21, 29.19, 28.81, 28.58, 26.03, 26.01, 25.87, 23.18, 22.99, 22.63, 20.85, 18.35, 18.26, 16.46, 14.08, 11.29, 0.34, 0.17$ ppm; ^{29}Si NMR (79.3 MHz, CD_2Cl_2, 24 °C, external TMS): $\delta = 7.92, 7.79$ ppm (2s; (CH$_3$)$_2$-*Si*O*Si*(CH$_3$)$_2$); MALDI-TOF MS (HABA matrix): *m/z* calcd for $C_{254}H_{348}N_4O_{42}Si_6$Na: 4321.0; found: 4320.5 $[M+Na]^+$; SEC: $M_r = 5817$, $M_n = 5608$, $\gamma = 1.02$.

Preparation of compound 8: A solution of **5** (0.343 g, 0.364 mmol) and 15 μL of Karstedt's catalyst (xylene) in toluene (8 mL) was added dropwise over a period of 1.5 h to a solution of 4′-(5-tetramethyldisiloxypentenyloxy)-4-cyanobiphenyl (**B**, 0.555 g, 1.40 mmol) in toluene (12 mL), and the solution stirred at room temperature for 20 h. The solvent was evaporated to dryness and the resulting syrup purified by column chromatography (flash-grade silica gel, Cl_2CH_2/4% diethyl ether) to afford **8** as a clear oil (0.391 g, 51%). ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C, residual $CHCl_3$): $\delta = 7.64$ (m, 12H; aromatic), 7.49 (m, 6H; aromatic), 6.95 (m, 6H; aromatic), 6.06, 6.03 (2brs, 1H; CO-N*H*), 4.07 (s, 2H; C^4-C*H*$_2$-OCO), 3.96 (t, $^3J(H,H) = 6$ Hz, 6H; Ph-O-C*H*$_2$-), 3.65 (s, 6H; C^4-C*H*$_2$-O), 3.62 (t, $^3J(H,H) = 6$ Hz, 6H; O-C*H*$_2$-CH$_2$-CH$_2$), 3.33 (s, 6H; NC^4-C*H*$_2$-O), 3.30 (t, $^3J(H,H) = 6$ Hz, 6H; O-C*H*$_2$-CH$_2$-CH$_2$), 2.40 (t, $^3J(H,H) = 6$ Hz, 6H; CH$_2$-OCOC*H*$_2$), 2.31 (t, $^3J(H,H) = 6$ Hz, 2H; NH-CO-C*H*$_2$), 2.17 (t, $^3J(H,H) = 6$ Hz, 2H; C*H*$_2$-COO), 1.87 (m, 2H; NHCO-CH$_2$-C*H*$_2$-CH$_2$-COO), 1.47 (m, 6H; -C*H*$_2$-), 1.42–1.23 (m, 57H; -(CH$_2$)-, C*H*$_3$-^{4}C), 0.51, 0.46 (2pseudo-t, 12H; C*H*$_2$-SiOSi-C*H*$_2$), 0.01, 0.00 ppm (2s, 36H; (C*H*$_3$)$_2$Si-O); ^{13}C NMR (100.4 MHz, $CDCl_3$, 24 °C, external TMS): $\delta = 172.89, 172.38, 170.92, 159.77, 145.24, 132.53, 131.18, 128.27, 119.08, 115.02, 109.97, 80.42, 71.61, 69.46, 69.11, 68.10, 66.99, 64.00, 59.64, 53.40, 44.41, 36.09, 29.89, 29.68, 29.43, 28.94, 28.07, 23.19, 23.10, 18.36, 18.29, 0.37$ ppm; ^{29}Si NMR (79.3 MHz, CD_2Cl_2, 24 °C, external TMS): $\delta = 7.95, 7.76$ ppm (2s; (CH$_3$)$_2$-*Si*O*Si*(CH$_3$)$_2$).

Preparation of compound 10: Triacid 6 (94 mg, 0.119 mmol), mesogenic alcohol **C**[36] (0.276 g, 0.38 mmol), DCC (86 mg, 0.41 mmol) and DMAP (56 mg, 0.1 mmol) in dry Cl_2CH_2 (20 mL) were stirred at room temperature for 3 days. The precipitate formed was filtered off and the solvent evaporated to dryness. The residue obtained was purified by column chromatography (flash-grade silica gel, Cl_2CH_2 100% followed by Cl_2CH_2/4% EtAcO) to afford **10** as a white solid (89 mg, 26%). ^{1}H NMR (400 MHz, CD_2Cl_2, 24 °C, residual CH_2Cl_2): $\delta = 8.18$ (m, 6H; aromatic),

7.98 (m, 3H; aromatic), 7.48 (m, 12H; aromatic), 7.18 (m, 12H; aromatic), 6.88 (m, 6H; aromatic), 6.43 (m, 6H; aromatic), 5.94 (br s, 1H; CO-N*H*), 5.71 (ddt, $^3J(H,H_{trans}) = 17$ Hz, $^3J(H,H_{cis}) = 10$ Hz, $^3J(H,H) = 7$ Hz, 3H; CH_2=C*H*), 4.91 (ddm, $^3J(H,H_{trans}) = 17$ Hz, $^2J(H,H) = 10$ Hz, 3H; *trans*-CH_2=CH), 4.84 (dm, $^3J(H,H) = 10$ Hz, 3H; *cis*-CH_2=CH), 4.03 (s, 2H, C^4-CH_2-OCO), 3.97–3.90 (m, 18H; Ph-O-CH_2-, COO-CH_2-), 3.76 (m, 6H; CH-CH_2-O), 3.59 (s, 6H; C^4-CH_2-O), 3.60 (t, $^3J(H,H) = 6$ Hz, 6H; O-CH_2-CH_2-CH_2), 3.29 (s, 6H; NC^4-CH_2-O), 3.29 (t, $^3J(H,H) = 6$ Hz, 6H; O-CH_2-CH_2-CH_2); 2.43 (t, $^3J(H,H) = 6$ Hz, 6H; CH_2-OCOCH_2), 2.25 (t, $^3J(H,H) = 6$ Hz, 2H; NH-CO-CH_2), 2.10 (t, $^3J(H,H) = 6$ Hz, 2H; CH_2-COO), 2.01 (m, 6H; CH_2-CH=CH_2), 1.85 (m, 18H; NHCO-CH_2-CH_2-CH_2-COO,-CH_2-CH_2-O, CH_2-CH, CH_2-CH_2-CH=), 1.64–1.16 (m, 64H; $(CH_2)_n$), 1.02 (d, $^3J(H,H) = 6$ Hz, 9H; CH_3-CH), 0.96 (t, $^3J(H,H) = 6$ Hz, 9H; CH_3-CH_2), 0.87 ppm (t, $^3J(H,H) = 6$ Hz, 9H; CH_3-CH_2); ^{13}C NMR (100.4 MHz, $CDCl_3$, 24 °C, external TMS): $\delta = 172.89$, 172.38, 171.57, 164.93, 164.61, 163.10, 161.84, 158.76, 155.56, 149.78, 138.71, 138.39, 134.53, 132.67, 131.72, 128.06, 127.68, 126.57, 122.20, 121.86, 114.79, 114.56, 110.39, 105.47, 100.12, 73.11, 70.66, 69.36, 69.15, 68.65, 68.08, 66.72, 64.44, 63.90, 59.62, 44.38, 36.00, 34.79, 34.64, 33.90, 33.44, 31.79, 30.27, 29.34, 29.26, 29.22, 28.98, 28.77, 28.49, 26.03, 25.63, 25.58, 24.90, 22.63, 20.88, 16.46, 14.07, 11.28 ppm.

Preparation of compound 2: 4′-(5-tetramethyldisiloxypentenyloxy)-4-cyanobiphenyl (**B**, 50 mg, 0.120 mmol) in toluene (5 mL) was placed in a small Schlenk tube under nitrogen atmosphere and Karstedt's catalyst (3% Pt solution in xylene, 8 μL) added. A solution of **10** (85 mg, 0.003 mmol) in toluene (6 mL) was added to the above solution dropwise over a 30 min period, and the resulting solution stirred for 18 h at room temperature. The solvent was evaporated under vacuum and the residue purified by column chromatography (flash grade silica gel, Cl_2CH_2/4% EtAcO). After evaporation of the solvent, the residue was dissolved Cl_2CH_2, filtered (0.45 μm) and the product dried under vacuum at room temperature to yield **2** as a white tacky material (57 mg, 45%). Elemental analysis calcd (%) for $C_{239}H_{318}N_4O_{42}Si_6$: C 70.23, H 7.84, N 1.37; found: C 69.94, H 7.90, N 1.53; ^{1}H NMR (400 MHz, CD_2Cl_2, 24 °C, residual CH_2Cl_2): $\delta = 8.24$ (m, 6H; aromatic), 8.01 (m, 3H; aromatic), 7.65–7.52 (m, 18H; aromatic), 7.47 (m, 12H; aromatic), 7.34 (m, 6H; aromatic), 7.24 (m, 6H; aromatic), 6.96 (m, 12H; aromatic), 6.50 (m, 6H; aromatic), 5.97 (br s, 1H; CO-N*H*), 4.06 (s, 2H; C^4-CH_2-OCO), 4.02–3.94 (m, 28H; Ph-O-CH_2-, CH-CH_2-O-Ph, COO-CH_2-), 3.81 (m, 6H; -CH_3CH-CH_2-O), 3.64 (s, 6H; C^4-CH_2-O), 3.62 (t, $^3J(H,H) = 6$ Hz, 6H; O-CH_2-CH_2-CH_2), 3.32 (s, 6H; NC^4-CH_2-O plus t, $^3J(H,H) = 6$ Hz, 6H; O-CH_2-CH_2-CH_2), 2.49 (t, $^3J(H,H) = 6$ Hz, 6H; CH_2-OCOCH_2), 2.30 (t, $^3J(H,H) = 6$ Hz, 2H; NH-CO-CH_2), 2.15 (t, $^3J(H,H) = 6$ Hz, 2H; CH_2-COO), 1.90–1.74 (m, 22H; NHCO-CH_2-CH_2-CH_2-COO, CH_2-CH_2-Si-), 1.60, 1.49, 1.27 (m, 92H, CH_3-CH_2-CH, -$(CH_2)_n$-), 1.01 (d, $^3J(H,H) = 6$ Hz, 9H; CH_3-CH), 0.93 (t, $^3J(H,H) = 6$ Hz, 9H, CH_3-CH_2), 0.87 (t, $^3J(H,H) = 6$ Hz, 9H; CH_3-CH_2), 0.51, 0.46 (2 pseudo-t, 12H; CH_2-SiOSi-CH_2), 0.01, 0.00 ppm (2s, 36H; $(CH_3)_2$Si-O); ^{13}C NMR (100.4 MHz, $CDCl_3$, 24 °C, external TMS): $\delta = 172.89$, 172.38, 171.56, 164.93, 164.60, 163.0, 161.85, 159.77, 158.77, 155.55, 149.78, 145.20, 138.71, 134.55, 132.66, 132.53, 131.72, 131.18, 128.27, 128.06, 127.68, 127.02, 126.57, 122.20, 121.87, 119.08, 115.03, 114.79, 110.38, 109.97, 105.45, 100.13, 73.11, 71.61, 69.30, 69.10, 68.65, 68.10, 66.73, 64.44, 59.60, 44.30, 34.79, 34.64, 33.2, 31.80, 29.89, 29.68, 29.43, 29.35, 29.27, 29.23, 28.96, 28.94, 28.20, 26.04, 25.63, 25.59, 23.19, 23.11, 22.63, 18.37, 18.30, 16.47, 14.09, 11.30, 0.38 ppm; ^{29}Si NMR (79.3 MHz, CD_2Cl_2, 24 °C, external TMS): $\delta = 7.95$, 7.76 ppm (2s; $(CH_3)_2$-*Si*O*Si*$(CH_3)_2$); MALDI-TOF MS (HABA matrix): *m/z* calcd for $C_{239}H_{318}N_4O_{42}Si_6Na$: 4110.0; found: 4110.3 $[M+Na]^+$ SEC: $M_r = 5070$ (calcd $M_r = 4087.6$), $M_n = 4894$, $\gamma = 1.03$.

Acknowledgement

The authors are very grateful to The Leverhulme Trust for support.

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Received: May 6, 2003 [F5100]

