

Design and properties of “Janus-like” supermolecular liquid crystals

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A new class of “Janus” liquid crystal compounds has been prepared with molecular weights in excess of 4000 D, but which have better temperature ranges with respect to room temperature than the revolutionary commercial material 4'-penty-1-4-cyanobiphenyl (5CB).

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 meso-scopic engineered materials with specific functional properties.

In this respect 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.¹ For example, block co-polymers in the form of Janus micelles,^{2–5} segregated amphiphilic dendrimers and shape-persistent macromolecules⁶ are examples of such materials that self-organise, like proteins, in a pre-programmed fashion.

Here we present the design, synthesis, characterisation and phase behaviour of complementary dendritic hexamers **1** and **2**, based on a central scaffold made up of pentaerythritol and tris(hydroxymethyl)amino methane units linked together,

where one of the units carries three cyanobiphenyl (CB) and the other three chiral phenyl benzoate (PB) mesogenic moieties or *vice-versa*. The materials prepared exhibit chiral nematic and chiral smectic C phases.

The basic design concept (Fig. 1) thus consists of creating a dendritic 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, *e.g.* hydrocarbon–fluorocarbon, hydrophobic–hydrophilic, units. To this end, the use of aliphatic spacers between the mesogenic moieties and the central scaffold follows the same concept as in traditional side-chain liquid crystalline polymers. In our model system we placed emphasis on studying the effect of attaching laterally appended chiral mesogenic units, which favour N* phases, to terminally appended polar mesogenic units favouring smectic phases.

The central scaffold **5** was constructed from sub-units **3** and **4**, based on pentaerythritol (PE) and tris(hydroxymethyl)amino methane (TRIS) respectively. The scaffold **5** was designed in this way to incorporate different end-groups, *i.e.* olefin and *tert*-butyl ester respectively, which could be functionalised independently of one another with different mesogenic moieties.

The mesomorphic properties of the supermolecular materials prepared were investigated by differential scanning calorimetry (DSC) and polarised light optical microscopy (POM). Both compounds were isolated in a glassy state at room temperature.

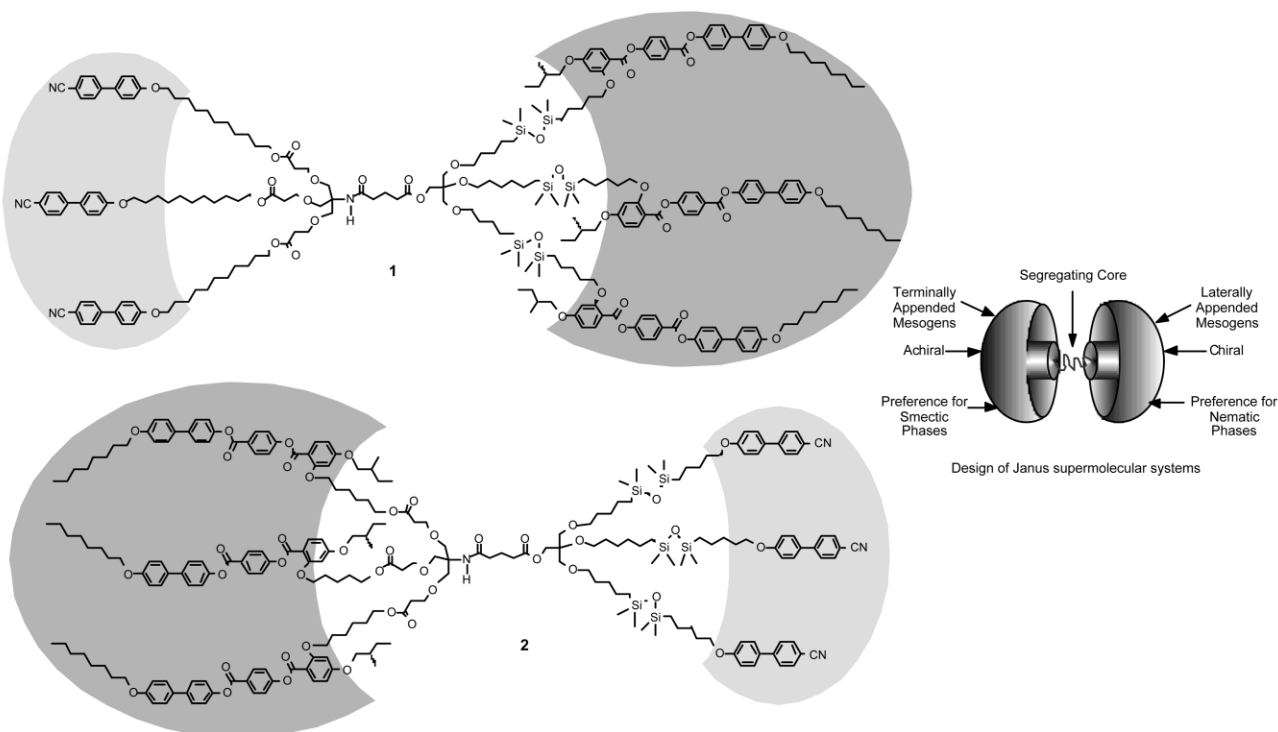
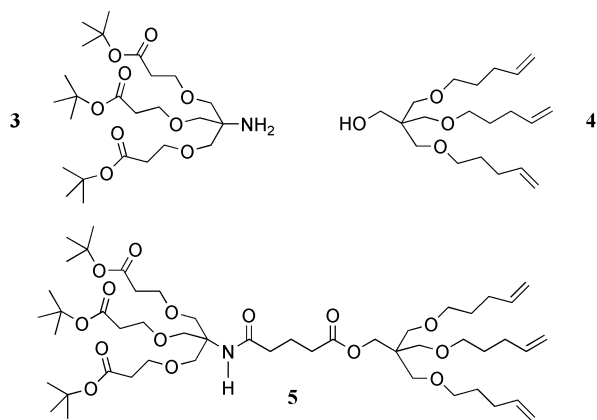


Fig. 1 Janus supermolecular architectures.



On heating a pristine sample of **1**, a broad melting endotherm with onset at 33.8 °C ($\Delta H = 6.26 \text{ kJ mol}^{-1}$) was followed by a weaker endotherm with onset at 60.7 °C ($\Delta H = 2.73 \text{ kJ mol}^{-1}$) associated with the transition from the liquid crystal state to the isotropic liquid. The cooling cycle from the isotropic liquid showed a similar broad, weak exotherm, with onset at 64.3 °C marking the transition between the liquid and the liquid crystalline state. A second exotherm occurred on cooling, with onset at approximately 36.1 °C, marking a second order transition to another mesophase. Further cooling induced a glass transition 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 extremely low ΔH values, suggesting that the system is relatively disordered and highly flexible.

In contrast, compound **2** exhibits only one enantiotropic transition by DSC which occurs between the liquid crystalline state and the isotropic liquid, in the form of a weak and broad peak at 38.2 °C ($\Delta H = 0.87 \text{ kJ mol}^{-1}$). The only other thermal event present was a glass transition below room temperature. 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 after a long period of time.

The defect textures of the compounds were examined by thermal polarised light microscopy (POM). On cooling from the isotropic state, both compounds **1** and **2** rapidly developed a Grandjean-plane texture with both being deep blue in colour (Fig. 2) the presence of this texture unequivocally identifies the phase as a chiral nematic phase. 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 induced the

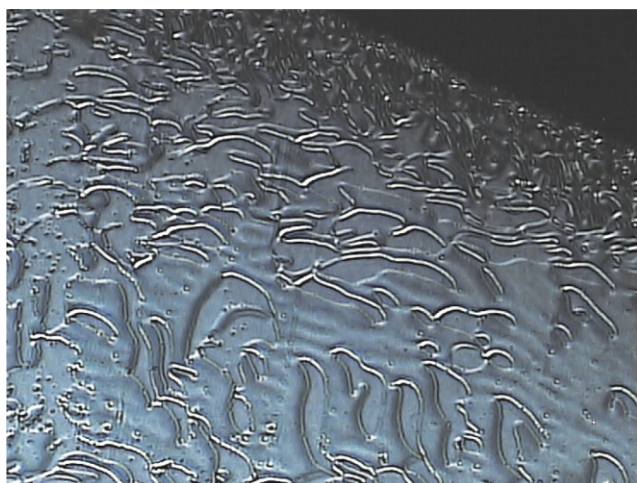


Fig. 2 The Grandjean-plane texture of the chiral nematic phase of compound **1** ($\times 100$).

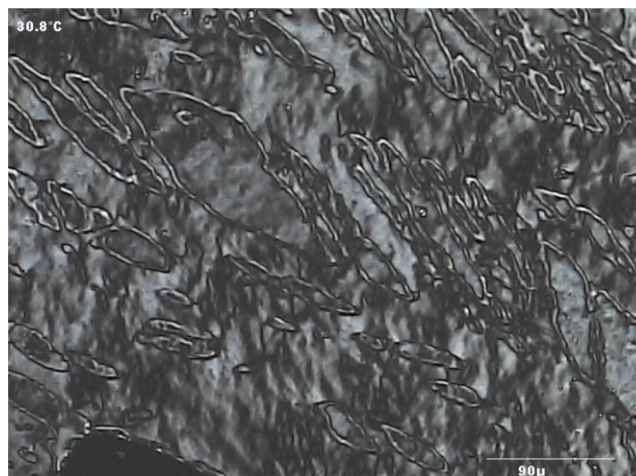


Fig. 3 The *schlieren* texture of the chiral smectic C* phase of compound **1** ($\times 100$).

formation of a *schlieren* texture (Fig. 3) 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. Oily streak defects which also occurred coalesced and reverted 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, *i.e.* a glassy chiral smectic C phase was formed. Glassification probably occurs due to the disordering influence of the central scaffold preventing the mesogenic units readily packing together to form a crystalline solid. Reheating a sample of **1** from the SmC* phase produced a transition to a highly iridescent, very mobile Grandjean texture typical of the chiral nematic phase. The speed and easy formation of typical low molar mass defect textures, plus the mobility of the materials seen in the microscope, is indicative of low viscosity approaching that of conventional low molar mass materials, rather than would be found in conventional side-chain polymers. Furthermore, it is important to note that the formation of chiral mesophases also means that the nematic phase selectively reflects light and therefore filters light, and the smectic C* phase is ferroelectric and pyroelectric and will exhibit electrostrictive properties, which will be discussed in future reports. In addition, the glassy chiral phases could thus have applications as optical notch 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 orientation of the inner core 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.

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Notes and references

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