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ARTICLE TYPE

Chiral nematic organo-siloxane oligopodes based on an axially chiral binaphthalene core

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Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX 5 DOI: 10.1039/b000000x

The synthesis of a novel class of organosiloxane oligopodes, based on an axially chiral binaphthalene core, is described and their mesogenic properties are fully characterised.

The development of axially chiral systems has received a ¹⁰ considerable amount of attention in recent years. Such structures are widely employed in chiral catalysis,¹ natural product synthesis,² non-linear optics^{3, 4} and as chiral templates.^{5, 6} Axially chiral systems are particularly useful due to their ability to effectively transfer chirality, and the relative ease of obtaining ¹⁵ materials of high optical purity, when compared to centrally chiral molecular structures. This feature has made them of significant interest for liquid crystal research.⁷⁻¹⁰

Work on axially chiral systems, which show liquid crystalline phase behaviour (vs chiral dopants), has focused on atropisomers ²⁰ of oligophenyls,¹⁰⁻¹² allenes,⁸ and chiral binaphthalenes.¹³⁻¹⁷ Chiral binaphthalene and its derivatives, such as 1,1'-bi(2-

- naphthol) **3** (Scheme 1), are widely employed to induce a substantial helical superstructure upon solvation in a non-chiral liquid crystal host (chiral dopant), inducing the chiral nematic ²⁵ (N^{*}) phase.¹⁸⁻²² Whilst the excellent structural compatibility of chiral binaphthalene derivatives towards liquid crystal host solvents has led to the successful development of powerful chiral
- dopants, these materials generally show little, if any, mesophase behaviour.^{13, 14} This makes the development of powerfully chiral ³⁰ liquid crystal mesogens highly attractive and desirable. Surprisingly, efforts to induce liquid crystalline behaviour in
- binaphthalene derivatives have proven limited. Notable exceptions are concerned with the mesogenic functionalisation of the binaphthalene core.¹⁴⁻¹⁷ The problems associated with ³⁵ inducing mesogenic behaviour in binaphthalene derivatives can be easily rationalised. The three-dimensional non-planar
- orientation of the naphthyl planes hinders molecular ordering. Mesogenic functionalisation is required to compensate for this disordering effect. Functionalisation at the 2,2' and 6,6'-positions
- ⁴⁰ is commonly employed to introduce mesogenic groups via a flexible spacer. Smectic¹⁴ and monotropic blue and chiral nematic phases¹⁵⁻¹⁷ have been observed in materials possessing terminally linked mesogenic units in the 2,2',6,6' and 2,2'-positions respectively. However, materials exhibiting an enantiotropic
- ⁴⁵ chiral nematic phase have yet to be realised. Previous work focused on the development of liquid crystalline organosiloxane tetrapode systems, bearing laterally connected mesogenic units, provided a strategy towards realising nematic phase behaviour.²³⁻



50 Fig. 1 Schematic illustration of binaphthalene oligopodes bearing laterally linked organo-siloxane mesogens

²⁵ A conceptually related organosiloxane-binaphthalene system was expected to induce mesophase properties.

In this article we report the synthesis and full characterisation ⁵⁵ of analogous organosiloxane oligopode materials, based on a chiral binaphthalene molecular core.

Control of the mesogenic properties was an important factor in the structural design. Essentially, the attachment of laterally linked mesogenic units was predicted to suppress higher ordered ⁶⁰ LC phases. Indeed, the mesogenic precursor **8** exhibits only the nematic phase. The inclusion of organo-siloxane moieties within the flexible spacer would provide convenient access to the target compounds, whilst additionally contributing to reduce the viscosity and melting point of the target systems.

The binaphthalene intermediates 4 and 7 were prepared from optically pure (S)-1,1'-bi(2-naphthol) 3 as shown in Scheme 1. Alkylation of the hydroxyl functionalities with 5-bromopentene, under Williamson ether conditions, afforded precursor 4. Initial bromination of 3 and subsequent alkylation of the hydroxyl ⁷⁰ groups provided dibromide 6. Suzuki-Miyaura cross-coupling with allylboronic acid pinacol ester afforded precursor 7. Hydrosilylation of the olefinic intermediates, using Karstedt's catalyst, and siloxane mesogen 8,^{26,27} with a long lateral spacer, designed to promote nematic phase behaviour produced the target ⁷⁵ oligopode systems 1 and 2 in 63% and 57% yields respectively (Scheme 2).

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i) 5-Bromopentene / K_2CO_3 / MeCN; ii) Br₂ / DCM / -78 °C; iii) Allylboronic acid pinacol ester / PdCl₂(dppf) / CsF / DME / 60 °C

Scheme 1 Synthesis of olefinic oligopode precursors.



Published on 18 May 2012 on http://pubs.rsc.org | doi:10.1039/C2CC33050D

10

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Scheme 2 Binaphthalene oligopode synthesis

 Table 1
 Thermal properties of oligopode materials and organosiloxane mesogen.



Fig. 2 OPM texture and DSC thermograph of tetramer $2 (10^{\circ} \text{ min}^{-1})$

Oligopode purity was confirmed by gel permeatation chromatography (GPC).

¹⁵ Phase assignments and thermal transitions were initially determined by optical polarizing microscopy (OPM) and differential scanning calorimetry (DSC). Mesogenic properties were observed in both dimer **1** and tetramer **2** (Table 1). Dimer **1**, comprising two liquid crystal mesogens linked to the central



Fig. 3 Optical microscopy of dimer **1** (a) contact experiment on cooling at 96 °C with nematic mesogen **8** (left); (b) contact experiment on cooling at 85 °C; (c) planar aligned cell on cooling; (d) HTP measurement using Grandjean-Cano wedge cell in nematic host 5CB at ambient temperature.

²⁵ binaphthyl unit, was found to display only monotropic liquid crystalline phase behaviour, as observed on cooling from the isotropic at 78.2 °C (0.24 J g⁻¹), with the onset of slow crystallisation observed below 48.8 °C.

In contrast, the tetrameric material, constructed with four ³⁰ mesogenic units linked to the binaphthyl central core, revealed an enantiotropic (thermodynamically stable) chiral nematic phase, as confirmed by OPM and DSC studies (Fig. 2). On heating, a chiral nematic phase was observed at 90.7 °C, preceded by crystalcrystal transitions at lower temperatures, turning to an isotropic ³⁵ liquid at 98.0 °C (0.12 J g⁻¹). Formation of the chiral nematic phase at 98.2 °C (0.24 J g⁻¹) was observed on cooling from the isotropic state, with slow crystallisation below occurring 68.2 °C.

The observed OPM textures were somewhat unspecific, with characteristics of oily streak textures, with similar appearance to ⁴⁰ planar textures previously reported for organosiloxane elastomers containing chiral binaphthalene units.²⁸ Thus, electro-optical cells, of a 2µm thickness, with a polyimide coating favouring planar alignment were prepared for compounds **1** and **2**, and the characteristic Grandjean texture for a chiral nematic phase was ⁴⁵ observed (Fig. 3c).[‡] However, as the greyish colour texture did not change much over the stability range of the chiral nematic phase, the question remained as to whether short or long pitch helical structures were formed.

A contact experiment, between dimer **1** and the nematic ⁵⁰ precursor mesogen **8**, was therefore prepared to further classify the nature of the phase (Fig. 3a-b). The materials were placed between glass substrates and allowed to freely mix in the isotropic state, with no discernable phase boundary observed on cooling from the isotopic liquid. The solvation of dimer **1** (as an ⁵⁵ isotropic liquid) into the nematic material formed an oily streak texture. Further cooling led to the co-existence of the chiral nematic texture and the oily streak texture in the area of the pure mesogen. Crystallisation of **1** and the onset of phase separation occurred at lower temperatures. The observed texture and ⁶⁰ appearance of colour, with the decreasing concentration of dimer **1** in the mixed region, suggested that the pure material had a short pitch length beyond the visible region of the spectrum.

To investigate the degree of helical twist further the helical twisting powers of compounds **1** and **2** were recorded. The ⁶⁵ relationship between the molecular structure of chiral binaphthalenes and their ability to induce the chiral nematic Published on 18 May 2012 on http://pubs.rsc.org | doi:10.1039/C2CC33050D

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75



Fig. 4 XRD pattern and 2θ profile of tetramer 2

phase (helical twisting power - HTP) is well documented, if not ⁵ fully understood.^{11, 18, 20, 29} Despite the nature of the system, with the naphthyl planes remaining unlinked and relatively flexible, the HTP of compounds **1** and **2** were expected to be moderately high. The HTP of compounds **1** and **2** were determined using a Grandjean-Cano wedge cell with 4-pentyl-4'-cyanobiphenyl ¹⁰ (5CB) as the nematic host (Figure 3d).[‡] The HTPs were found to be 27.9 μ m⁻¹ and 40.2 μ m⁻¹ for compounds **1** and **2** respectively, and higher than the majority of the conformationally flexible dopants previously reported.^{19, 28} Significantly, the pitch lengths were found to in the order of 6.4-6.5 μ m for a ~5% w/w ¹⁵ concentration in 5CB. This further indicates that the pitch lengths for both compounds **1** and **2**, in their respective chiral nematic phases, are substantially shorter.

Characterisation of compounds 1 and 2 was completed by Xray diffraction (XRD). Fig. 4 shows the 2θ scan of the recorded ²⁰ intensities in the chiral nematic phase and the original diffraction pattern. It is noted that the experimental set-up, using capillaries in a micro furnace with a magnetic field perpendicular to the direction of the X-ray beam, did not allow for a distinction between chiral nematic and nematic phase structures. However

²⁵ the alignment in the external field was very limited, with only two intensities at $2\theta = 3.17$ (2.77 nm) and $2\theta = 18.73$ (0.47 nm) were detected. The position of the reflection did not change to any extent over the stability range of the liquid crystal phase. The intensities can be associated with the approximate length of the ³⁰ aromatic groups and the lateral distances of the molecules.

In summary, we have prepared a novel class of organosiloxane oligopodes, based on an axially chiral binaphthalene core, and fully characterised their liquid crystalline properties. The integration of laterally substituted mesogenic units results in the

- ³⁵ complete suppression of higher ordered liquid crystal phases. The tetrapodal system **2** represents the first binaphthalene derivative to display enantiotropic chiral nematic phase behaviour. The systems also display high helical twist in their respective chiral nematic phase.
- ⁴⁰ We thank the EPSRC National Mass Spectrometry Service Centre for their support. This work was supported through the EU 7th Framework Program NANOGOLD.

Notes and references

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[†] Electronic Supplementary Information (ESI) available: Full experimental procedures, data and liquid crystal properties. See DOI: 10.1039/b000000x/

- 50 ‡ Electro-optical polyimide test cell –KSRO-02/A111N1NSS05, cell gap 2μm; Grandjean-Cano wedge KCRK-03, 0.3 mm, tanθ 0.0083. E.H.C. Co. Ltd.
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