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# Introduction

Ferroelectric liquid crystals (FLC) define a class of polar materials forming a chiral tilted smectic phase such as the SmC\* phase in which rod-like molecules with a rigid aromatic core and two alkyl chains are self-organized in diffuse layers and tilted at an angle  $\theta$ with respect to the layer normal z. The chiral SmC\* phase forms a helical structure that unwinds between glass slides with a rubbed polymer substrate to give a surface-stabilized FLC film with a spontaneous polarization  $(P_s)$  oriented along the  $C_2$  symmetry axis (Fig. 1).<sup>1</sup> By coupling  $P_{\rm S}$  to an electric field E, the FLC film can be switched between opposite tilt orientations (Goldstone mode) to give a light shutter used in high-resolution color microdisplays that switch on a microsecond time scale.<sup>2,3</sup>

Unlike proper ferroelectrics (e.g., crystalline LiNbO<sub>3</sub>), in which  $P_{\rm S}$  originates from non-centrosymmetric dipole-dipole coupling, chiral SmC\* liquid crystals are improper or pseudoproper ferroelectrics because  $P_{\rm S}$  originates from the rotational order of the chiral mesogens about the director n, which is

# Ps

The design of smectic liquid crystals with an

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ferroelectric liquid crystal phase<sup>†</sup>

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measured by conventional methods.

axially chiral biphenyl core: in search of a proper

We report the results of a study in which we introduce a tricarbosilane end-group in a mesogenic scaffold derived from an axially chiral biphenyl with a large transverse dipole moment. This structural modification is intended to promote the formation of a chiral smectic C (SmC\*) phase, with the aim of discovering a mesogen with a virtual transition temperature to a proper ferroelectric phase ( $T_{o}$ ) that approaches the crystal-SmC\* melting point. We show herein that the combination of a 4-pentylbicyclo-[2.2.2]octane-1-carboxylate chain and a tricarbosilane-terminated 4-alkoxybenzoate chain gives a mesogen (R,S)-WL43 forming an enantiotropic orthogonal smectic A (SmA) phase and a higher order

tilted smectic phase. Substitution of the 4-pentylbicyclo[2.2.2]octane-1-carboxylate group with a trans-

4-pentylcyclohexane-1-carboxylate group gives a mesogen (R,S)-WL45 forming monotropic SmA and SmC phases. The SmC\* phase formed by the enantiomerically pure (R)-WL45 exhibits Goldstone-mode

switching characteristic of a surface-stabilized FLC, but its spontaneous polarization  $P_{\rm S}$  is too low to be

Fig. 1 Schematic representation of hard spherocylinders forming a SmC\* phase as a surface-stabilized ferroelectric liquid crystal film in a bookshelf geometry. The SmC\* phase is characterized by a uniform tilt  $\theta$  of the average direction of all molecular axes (the director **n**) with respect to the layer normal z.

imposed by the molecular tilt  $\theta$ .<sup>4,5</sup> Hence, coupling between  $P_{\rm S}$ and  $\theta$  normally results in  $P_{s}(\theta)$  being invariant of temperature. However, we recently found that the chiral mesogen E6 forms a SmC<sup>\*</sup> phase with a  $P_{\rm S}(T)$  profile showing an atypical convex curvature that does not correlate with the  $\theta(T)$  profile.<sup>6</sup> According to a molecular-statistical theory of ferroelectric ordering in

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WL45: X=H WL46: X=F

Scheme 2 Chiral mesogens WL43–46 prepared as racemic mixtures; WL45 was also prepared as the pure (*R*) enantiomer (correct stereochemistry shown).

Scheme 1 Chiral mesogens E6 and 2(*n*), and non-mesomorphic chiral dopant 1.

the SmC\* phase, this behavior may be explained by an increase in the virtual transition temperature to a proper ferroelectric phase ( $T_o$ ), which is normally well below the crystal-SmC\* melting point. In the case of **E6**, an unusually high  $T_o$  of 152 K was ascribed to stronger dipole–dipole coupling of the chiral epoxy units due to the high lamellar ordering imposed by the siloxane end-group, and the biaxial ordering of the epoxy unit (Scheme 1). These findings suggest that one might further increase  $T_o$  in a siloxane-terminated SmC\* mesogen featuring a chiral unit with a larger transverse dipole moment and higher biaxiality.

Axially chiral biaryl compounds have proven to be very effective in the induction of chiral bulk properties in calamitic liquid crystals, including the helical pitch of the chiral nematic (N\*) phase or the spontaneous polarization of the SmC\* phase.<sup>7,8</sup> For example, we have shown that the dopant **1**, which has an axially chiral biphenyl core with a transverse dipole moment of 6.9 D, induces a remarkably high  $P_{\rm S}$  in the SmC phase of 2-phenylpyrimidine liquid crystal hosts as a result of chirality transfer via core-core interactions.<sup>9</sup> Yet, despite the ubiquitous qualities of these molecules as strong chiral inducers, there are only a few examples of axially chiral biaryl mesogens.<sup>10–13</sup> Compounds such as **1** are not liquid crystalline due to the unfavorable lateral bulk of the biphenyl core caused by the four ortho substituents, which maintain the configurational integrity of the core by imposing a torsional angle of ca. 90° between the phenyl rings.<sup>9,14,15</sup> However, we have shown that substituting one 4-alkoxyphenyl benzoate chain with a 4pentylbicyclo[2.2.2]octane-1-carboxylate chain results in the formation of an enantiotropic N\* phase (e.g., 2(8)-2(14)),<sup>16</sup> which has been attributed to the bicyclo[2.2.2]octane segment effectively 'shielding' the unfavorable lateral bulk of the axially chiral biphenyl core.17,18

We and others have also shown that carbosilane end-groups promote the lamellar ordering of calamitic mesogens due to their tendency to nanosegregate from hydrocarbon segments into distinct sub-layers, which normally results in the formation of partially interdigitated smectic bilayers.<sup>19–21</sup> As such, they behave similarly to siloxane end-groups, but are hydrolytically and electrochemically far more stable.<sup>22</sup> Tricarbosilane-terminated mesogens tend to form very stable SmC phases, which may be due to a suppression of out-of-layer fluctuations that reduces the entropic cost of molecular tilt. In this paper, we report the results of a study in which we introduce tricarbosilane end-groups in the 2(n) molecular scaffold to promote the formation of a chiral SmC\* phase, and explore further structural modifications with the aim of discovering a mesogen with a virtual transition temperature to a proper ferroelectric phase ( $T_o$ ) that approaches the crystal-SmC\* melting point (Scheme 2).

## Results and discussion

### Synthesis

The first structural modification to the 2(n) scaffold was to replace the alkoxy chain with a tricarbosilane-terminated undecenyloxy chain to give the new derivative **WL43**. Two additional structural modifications were investigated: (i) substitution of the benzoate group with a 2,3-difluorobenzoate group, which is known to promote the formation of a SmC phase,<sup>23</sup> and (ii) substitution of the laterally bulky 4-pentylbicyclo[2.2.2]octane-1-carboxylate, which is a strong nematogenic unit,<sup>17,18</sup> with a *trans*-4-pentylcyclohexane-1-carboxylate unit.

The axially chiral core 4,4'-dihydroxy-3,3'-dinitro-2,2',6,6'tetramethylbiphenyl (3) was synthesized as a racemic mixture according to Hartley *et al.*,<sup>24</sup> and converted to the THP-protected derivative **4** in 29% yield, as shown in Scheme 3 (see ESI† for details). Esterification of **4** with either 4-pentylbicyclo[2.2.2]octane-1-carboxylic acid or *trans*-4-pentylcyclohexane-1-carboxylic acid using DIC and DMAP followed by deprotection gave the precursors **5** and **6** in 80% and 63% yield, respectively. The target compounds were then obtained as racemic mixtures ((*R*,*S*)-WL43-WL46) by esterification of **5** and **6** with the appropriate tricarbosilane-terminated 4-undecyloxybenzoic acid (7 or **8**) using DIC and DMAP in yields ranging from 56 to 87% yield. Compound (*R*)-WL45 was obtained in enantiomerically pure form by resolution of **3** using preparative chiral phase HPLC (Chiralpak AS column) according to Hartley *et al.*<sup>24</sup>



Scheme 3 Reagents and conditions: (a) 3,4-dihydro-2H-pyran, pyridinium *p*-toluenesulfonate, CH<sub>2</sub>Cl<sub>2</sub>; (b) 4-pentylbicyclo[2.2.2]octane-1-carboxylic acid, DIC, DMAP, CH<sub>2</sub>Cl<sub>2</sub>; (c) TsOH, 1:1 MeOH/CH<sub>2</sub>Cl<sub>2</sub>; (d) *trans*-4-pentylcyclohexane-1-carboxylic acid, DIC, DMAP, CH<sub>2</sub>Cl<sub>2</sub>; (e) **7** or **8**, DIC, DMAP, CH<sub>2</sub>Cl<sub>2</sub>; (f) 1-bromo-12,12,14,14,16,16-hexamethyl-12,14,16-trisilylheptadecane, K<sub>2</sub>CO<sub>3</sub>, acetone, reflux; (g) NaOH, MeOH/THF/H<sub>2</sub>O, reflux.

Mesomorphic characterization. Compounds (R,S)-WL43-46 were first analyzed by differential scanning calorimetry (DSC) and polarized optical microscopy (POM), but characterization of the mesophases formed by these compounds proved difficult due to our inability to produce textures with unambiguous characteristics (see Fig. S1 in ESI,† for example). We therefore relied on additional evidence from small angle X-ray scattering (SAXS) and 2D X-ray scattering to confirm the mesomorphic properties of these new compounds. As shown in Table 1, the addition of a tricarbosilane end-group to the 2(n) scaffold resulted in suppression of the nematic (N) phase, and the formation of an orthogonal smectic A (SmA) phase and a higher order tilted smectic phase, with no evidence of a crystalline phase upon cooling down to -20 °C. The assignment of a SmA phase is based on a X-ray scattering pattern that shows a sharp scattering peak at small-angle corresponding to the periodicity along the layer normal z, and a diffuse wide-angle scattering from both carbosilane and hydrocarbon sub-layers (Fig. 2a).<sup>20</sup> The orthogonal structure of the SmA phase was confirmed by 2D X-ray scattering on a sample aligned on cooling, which shows an azimuthal intensity distribution of the wide angle scattering with maxima perpendicular to that of the small-angle scattering (see inset in Fig. 2a). On heating towards the clearing

point, the small-angle scattering peak broadens and decreases

in intensity whereas the azimuthal intensity distribution of the wide-angle scattering evens out, which is inconsistent with the formation of a nematic phase.

The X-ray scattering pattern of the lower temperature phase obtained prior to heating to the SmA phase shows sharp fundamental and higher-order scattering peaks at small-angles and a sharp peak at wide-angle, which is consistent with a smectic phase with hexagonal ordering of the hydrocarbon sub-layer, while a diffuse inner ring corresponding to the carbosilane sublayer persists (see Fig. 2b). We were unable to obtain a 2D X-ray scattering pattern of this phase due to persistent supercooling of the SmA phase, which precluded observation of any azimuthal shift of the wide-angle scattering. However, a decrease in layer spacing measured by SAXS, as well as the corresponding change from homeotropic to Schlieren textures observed by POM (see Fig. S1 in ESI†) are consistent with the formation of a tilted SmF or SmI phase (Fig. 3).

Substitution of the benzoate group in (R,S)-WL43 with a 2,3-difluorobenzoate group did not affect the mesomorphic properties other than cause an increase in transition temperatures. On the other hand, substitution of the 4-pentylbicyclo-[2.2.2]octane-1-carboxylate group in (R,S)-WL43 with a *trans*-4-pentylcyclohexane-1-carboxylate group to give (R,S)-WL45 completely suppressed the enantiotropic mesomorphism, although

Table 1 Transition temperatures (°C) and enthalpies of transitions (kJ mol <sup>-1</sup> , in parentheses) on heating											
Compound	Cr		SmX		SmC		SmA		Ν		I
2(12) <sup>a</sup> (R,S)-WL43 (R,S)-WL44 (R,S)-WL45 (R,S)-WL46 (R)-WL45	• •	108 (31) 67 (13) 77 (16)	• (• •	$\begin{array}{c} 69 \ (9.4) \\ 81 \ (7.8) \\ 28 \ (3.5))^b \\ 45 \ (5.9))^b \\ 61 \ (4.5) \end{array}$	(• (•	$60)^{b,c}$ 59 (4.0)) <sup>b</sup>	• (• (•	95 (2.6) 100 (3.0) 66 (3.3)) <sup>b</sup> 74 (3.8)) <sup>b</sup>	•	156 (1.6)	• • • •

<sup>*a*</sup> From ref. 16. <sup>*b*</sup> Monotropic phase transition; transition temperature measured on cooling. <sup>*c*</sup> Second order phase transition; transition temperature measured by polarized microscopy.



Fig. 2 X-ray scattering profiles of (*R*,*S*)-WL43 (a) at 82 °C in the SmA phase (left, inset shows the azimuthal intensity of the wide-angle scattering relative to the small-angle scattering peak) and (b) at 29 °C in the SmF/I phase prior to first heating (right).



**Fig. 3** Layer spacing *d versus* temperature *T* for **(***R***,***S***)-WL43** measured by SAXS on heating; the open symbols correspond to the diffuse peak maxima in the isotropic phase.

both SmA and SmC phases formed on cooling below the melting point. The derivative (R,S)-WL46 featuring both structural modifications formed only a monotropic SmA phase. The SmC phase in (R,S)-WL45 was characterized by the formation of contrasting domains of opposite tilt orientation observed by POM in a sample aligned between rubbed polyimide glass slides on cooling from the SmA phase, as shown in Fig. 4.

The enantiomerically pure (R)-WL45 forms only a SmC\* phase on cooling, together with a higher order smectic phase. It is not entirely clear why the orthogonal SmA\* phase is suppressed upon resolution, although it is possible that non-covalent interactions



Fig. 4 Photomicrographs of (*R*,*S*)-WL45 as a thin film between rubbed polyimide glass slides (4  $\mu$ m spacing) in the SmA phase at 65 °C (left) and in the SmC phase at 55 °C (right).

between axially chiral cores of the same handedness are stronger in a lamellar organization, which would favor the tilted SmC\* phase.<sup>25</sup> As a consequence of enantiomeric resolution, Goldstonemode switching was observed in the SmC\* phase and the optical tilt angle  $\theta_{opt}$  was measured as a function of temperature on a sample aligned between rubbed polyimide ITO glass slides (1.6 µm spacing), as shown in Fig. 5. The sharp rise in tilt angle and relative temperature invariance of  $\theta_{opt}$  on cooling is consistent with a first-order transition from the isotropic phase and confirms the absence of a SmA\* phase above the SmC\* phase. However, we were unable to measure a spontaneous polarization via the triangular wave method (detection limit of  $\sim 0.5$  nC cm<sup>-2</sup>) over a broad temperature range below the SmC\*-I transition point (see ESI† for details). The absence of a measurable P<sub>S</sub> may be ascribed to a lack of biaxial ordering of the 'stereo-polar unit' by virtue of the orthogonal geometry of the axially chiral biphenyl core, as well as the subtle asymmetric conformational bias about the ester C-O bonds of the biphenyl core, which is not enhanced by chiral perturbations from corecore interactions with mesogenic host molecules that are dynamically racemic, such as those featuring a 2-phenylpyrimidine



Fig. 5 Optical tilt angle  $\theta_{opt}$  measured as a function of temperature *T* for (*R*)-WL45 by applying a field of 6 V  $\mu$ m<sup>-1</sup> across an aligned film between rubbed polyimide ITO glass slides with a spacing of 1.6  $\mu$ m; the optical tilt is saturated at this applied field.

core.<sup>8,26</sup> Another possible explanation may be that any biaxial ordering of the polar core imposed by the SmC\* phase may cause the transverse dipole moment to lie in the n, z tilt plane, which would minimize its contribution to  $P_{\rm S}$ .

# Conclusions

In this study, we have shown that the introduction of a tricarbosilane end-group in a nematogenic scaffold with an axially chiral biphenyl core does induce smectogenic properties, albeit not to the extent that it does in more conventional mesogenic scaffolds, which may be ascribed to unfavorable steric repulsion of the laterally bulky biphenyl cores in a lamellar organization.<sup>19-21</sup> Indeed, we were unable to produce a material forming an enantiotropic SmC phase, although one did form a monotropic SmC phase. Interestingly, the SmC\* phase formed by the enantiomerically pure (R)-WL45 does not exhibit a measurable spontaneous polarization. These results suggest that the design features of a SmC\* mesogen with proper ferroeletric properties should include a large transverse dipole moment and exhibit strong biaxial ordering. Further investigation will therefore focus on mesogenic structures derived from axially chiral biphenyl cores with a bridge structure such as 11-dimethyl-5,7-dihydrodibenz[c,e]thiepin,<sup>27</sup> which restricts the dihedral angle formed by the two phenyl rings to ca. 65 degrees and reduces the unfavorable lateral bulk that may hinder the formation of a SmC phase. Such a core structure, appropriately derivatized to give a large transverse dipole moment, should also exhibit enhanced biaxial ordering in the SmC\* phase.

# Conflicts of interest

There are no conflicts to declare.

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