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COMMUNICATION

Tuning the frustration between SmA- and SmC-promoting elements in liquid crystals with 'de Vries-like' properties†

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Smectic liquid crystals with 'de Vries-like' properties are characterized by a maximum layer contraction of ≤1% upon transition from the non-tilted SmA phase to the tilted SmC phase. We show herein that one can systematically increase the 'de Vries-like' character of a smectic liquid crystal by tuning the frustration between SmA- and SmC-promoting elements according to established structure–property relationships.

Ferroelectric liquid crystals (FLC) define a class of polar materials forming a chiral smectic C* (SmC*) phase in which rod-like molecules are self-organized in diffuse layers described by a density wave with a period d corresponding to the layer spacing,[1] and tilted at an angle θ with respect to the layer normal. Alignment of a SmC* liquid crystal between glass slides with rubbed polymer alignment layers gives a *surface-stabilized* FLC film with a spontaneous polarization (P_S) oriented perpendicular to the alignment layers.[2–4] By coupling the polarization to an electric field, the FLC film can be switched between opposite tilt orientations to give an electro-optical shutter that is currently used in high-resolution reflective color microdisplays. FLC materials used in display applications normally consist of a mixture of achiral liquid crystals (*e.g.*, **2-PhP8**)[5] and a chiral dopant with an appropriate polarization power.[6] The achiral liquid crystal components of FLC mixtures normally have a phase sequence with a nematic phase and a non-tilted smectic A (SmA) phase above the tilted SmC phase in order to achieve a high quality alignment upon cooling the material from the isotropic liquid phase. However, a significant problem with surface-stabilized FLC films is the layer contraction (~7–10%) that occurs upon cooling from the SmA* to the SmC* phase, which results in buckling of the smectic layers into a chevron structure, and the formation of zigzag defects that reduce the optical quality of the film (*vide infra*).[7]

To solve this problem, recent studies have focused on a unique class of chiral and achiral materials with maximum layer contractions of ≤1% upon cooling from the SmA to the SmC phase.[8] The SmA phase formed by these so-called 'de Vries-like' liquid crystals was originally described as a lamellar structure in which molecules have a tilted orientation and a degenerate azimuthal distribution; according to this model, the SmA–SmC transition is described as an ordering of the azimuthal distribution that results in zero layer contraction.[9] In fact, the structure of this unusual phase has yet to be fully elucidated, but recent theoretical studies suggest that materials combining low orientational order and high lamellar order are likely to exhibit this behavior.[10,11] We recently reported results of the first rational design strategy for achiral 'de Vries-like' liquid crystals based on a concept of *frustration*[12] between a structural element promoting the formation of a SmA phase and one promoting the formation of a SmC phase.[13–15] For example, we have shown that a mesogen **1** with a 2-phenylpyrimidine core that combines a trisiloxane-terminated alkoxy side-chain (SmC-promoting) with a chloro-terminated alkoxy side-chain (SmA-promoting)[16] undergoes a SmA–SmC phase transition with a maximum layer contraction of 1.3%,[15] which is significantly less than that of 7.1% observed with the parent compound **2-PhP8**.[5] Despite this improvement, the reduction factor R (eqn (1))[17] of compound **1** at 10 K below the SmA–SmC transition temperature T_{AC} (R = 0.47) is still well above those reported for the best 'de Vries-like' materials (R = 0.14–0.20).[15,18,19]

$$R = \delta(T)/\theta_{\mathrm{opt}}(T) = \cos^{-1}[d_C(T)/d(T_{AC})]/\theta_{\mathrm{opt}}(T) \qquad (1)$$

$$\theta \propto |T - T_{AC}|^{\beta} \qquad (2)$$

In this communication, we report small angle X-ray scattering (SAXS) and optical tilt angle (θ_{opt}) measurements on isometric analogues of compound **1** which suggest that the frustration between the trisiloxane-terminated 2-phenylpyrimidine element and the chloro-terminated alkoxy element in **1** is unbalanced towards the latter, and that one can 'tune' the frustration—and further reduce R—by increasing the SmC-promoting character of the former. This is achieved by replacing the 2-phenylpyrimidine core in **1** with one of two cores known to be stronger SmC-promoters, either 6-phenylpyridazine (**2**) or 2-phenyl-1,3,4-thiadiazole (**3**).[20]

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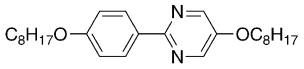
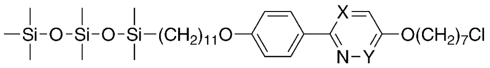
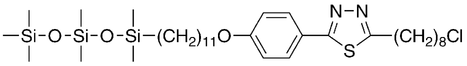

2-PhP8: Cr 53 SmC 93 SmA 101 N 102 I


1: X=N, Y=CH
2: X=CH, Y=N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Compound **2** was obtained by a Pd-catalyzed cross-coupling of 3-chloro-6-iodopyridazine[21] with the MOM-protected 4-hydroxyphenylboronic acid, followed by a nucleophilic aromatic substitution reaction with the sodium salt of 7-chloroheptanol, deprotection, and alkylation *via* a Mitsunobu reaction with 11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecanol. Compound **3** was obtained by acylation of 4-methoxybenzohydrazide with 9-chlorononanoyl chloride,[22] followed by reaction with Lawesson's reagent to give 2-(8-chlorooctyl)-5-(4-methoxyphenyl)-1,3,4-thiadiazole, which was demethylated with BBr_3 and alkylated *via* a Mitsunobu reaction with 11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecanol (see ESI† for details). The mesophases formed by compounds **2** and **3** were characterized by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). Both compounds form SmA and SmC phases (Table 1), as shown by the characteristic fan and homeotropic textures of the SmA phase that turn into broken fan and Schlieren textures upon transition to the SmC phase (ESI†). Unlike **1**, compounds **2** and **3** undergo SmA–SmC phase transitions with measurable enthalpies of transition ΔH_{AC} that are consistent with weakly first-order transitions (*vide infra*).

Accurate measurements of the smectic layer spacing d as a function of temperature were carried out by SAXS. As shown in Fig. 1, the normalized $d/d_{AC}(T)$ profiles of **2** and **3** are very similar to that of **1**, showing a negative thermal expansion in the SmA phase that persists in the SmC phase and counteracts the layer contraction caused by tilting in the SmC phase. Other 'de Vries-like' materials have been reported to show a similar negative thermal expansion in their $d(T)$ profiles.[8,13–15] Maximum layer contractions of 1.1% and 1.3% are observed at *ca.* 10 K below T_{AC} for **2** and **3**, respectively, and the layer spacing at the SmA–SmC transition d_{AC} is restored upon further cooling to *ca.* 30 K below T_{AC}. This behavior is also manifested by the appearance and disappearance of zigzag defects on cooling either material from the isotropic liquid phase to $T - T_{AC} = -32$ K in ITO glass cells with rubbed Nylon alignment layers and a spacing of 5 μm, as shown in Fig. 2.

Table 1 Phase transition temperatures (°C) and enthalpies of transitions (kJ mol^{-1}, in parentheses),[a] optical tilt angles (°) and reduction factors at $T - T_{AC} = -10$ K for compounds **1–3**

cpd	Cr		SmC		SmA		I	θ_{opt}	R
1[b]	•	26 (37)	•	84 (<0.1)[c]	•	98 (9)	•	20	0.47
2	•	44 (14)	•	78 (0.16)	•	90 (8)	•	26	0.32
3	•	30 (25)	•	72 (0.48)	•	77 (10)	•	29	0.32

[a] Measured on heating by DSC. [b] From ref. 15. [c] Measured by polarized optical microscopy.

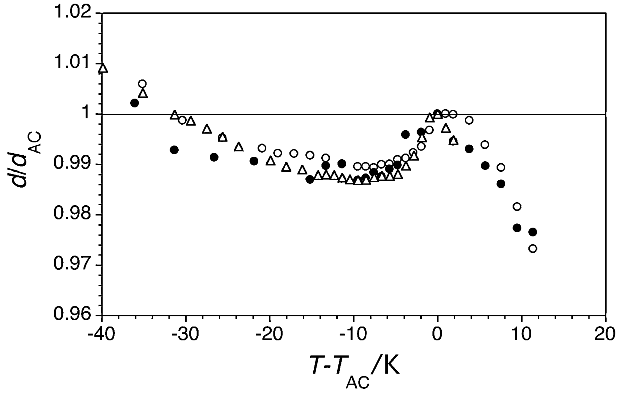

Fig. 1 Relative smectic layer spacing d/d_{AC} *versus* reduced temperature $T - T_{AC}$ for compounds **1** (●), **2** (○) and **3** (△). Data for **1** are from ref. 15.

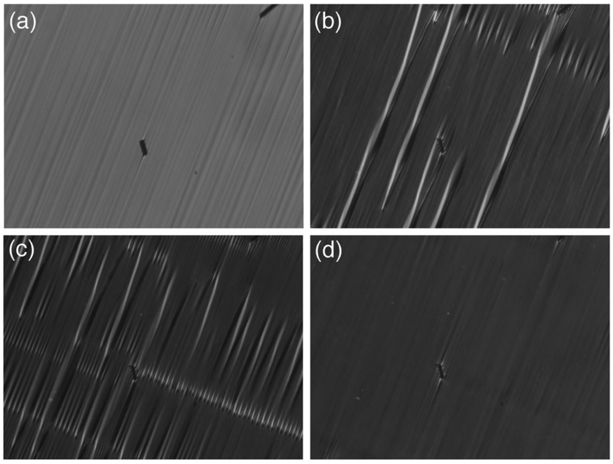

Fig. 2 Polarized photomicrographs (400×) of a 5 μm film of **3** doped with a chiral additive (1 mol%)[23] in an ITO glass cell with rubbed Nylon alignment layers. The film is cooled at 10 K min^{-1} while applying a 10 V dc field across the cell: (a) $T - T_{AC} = +1$ K, (b) $T - T_{AC} = -15$ K, (c) $T - T_{AC} = -25$ K and (d) $T - T_{AC} = -32$ K.

Although there is no appreciable change in the normalized $d/d_{AC}(T)$ profiles relative to that of **1**, the introduction of stronger SmC-promoting cores in **2** and **3** has the effect of increasing the optical tilt angle θ_{opt}, as shown in Fig. 3, which results in significantly lower reduction factors R (Table 1). Fitting of the $\theta_{opt}(T)$ profiles to the power law shown in eqn (2), where β is the order parameter related to the nature of the SmA–SmC phase transition, suggests that the phase transition is weakly first-order for **2** ($\beta = 0.18$) and **3** ($\beta = 0.19$), which is consistent with the ΔH_{AC} measurements.[24] These results are also consistent with theoretical models associating 'de Vries-like' behavior to smectic phases with a high lamellar and low orientational order, which are predicted to undergo a SmA–SmC transition that is either tricritical or weakly first-order.[10,11]

In summary, the results reported herein strongly suggest that one can systematically increase the 'de Vries-like' character of a smectic liquid crystal by tuning the frustration between SmA- and SmC-promoting elements according to

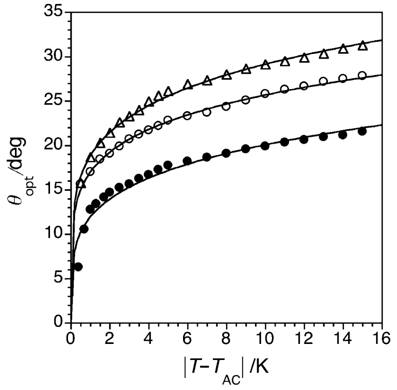

Fig. 3 Optical tilt angles θ_{opt} *versus* reduced temperature $T - T_{AC}$ for compounds **1** (●), **2** (○) and **3** (△). The solid lines represent the fits to eqn (2) (**1**: $\beta = 0.22$, $R^2 = 0.947$; **2**: $\beta = 0.18$, $R^2 = 0.996$; **3**: $\beta = 0.19$, $R^2 = 0.994$). The data for **1** are from ref. 15.

established structure–property relationships. This new rational approach represents a powerful means of optimizing FLC molecular design and mixture formulation to produce chevron-free FLC displays. A detailed study of structure–property relationships for homologous series of liquid crystals based on **2** and **3**, including the measurements of orientational and lamellar order parameters, is under way and will be reported in due course.

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