ChemComm

COMMUNICATION

RSCPublishing

View Article Online View Journal | View Issue

Cite this: Chem. Commun., 2013, 49, 8202

Received 10th July 2013, Accepted 1st August 2013

DOI: 10.1039/c3cc45207g

www.rsc.org/chemcomm

Tuning 'de Vries-like' properties in binary mixtures of liquid crystals with different molecular lengths[†]

Qingxiang Song,^a Andreas Bogner,^b Frank Giesselmann^b and Robert P. Lemieux*^a

Smectic liquid crystals with 'de Vries-like' properties are characterized by a maximum layer contraction of \leq 1% upon transition from the orthogonal SmA phase to the tilted SmC phase. We show that binary mixtures of 'de Vries-like' and conventional SmC mesogens with a molecular length ratio of 1.34 undergo a SmA–SmC phase transition with a maximum layer contraction ranging from 1.0 to 1.9% depending on the mixture composition.

Ferroelectric liquid crystals (FLC) are ordered fluids forming a chiral smectic C (SmC*) phase in which rod-like molecules are organized in diffuse layers with a period d corresponding to the layer spacing, and are tilted at an angle θ with respect to the layer normal. Alignment of a SmC* liquid crystal between glass slides with a rubbed alignment substrate gives a surface-stabilized FLC film with a spontaneous polarization oriented perpendicular to the glass slides.^{1–3} 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 used in high-resolution reflective color microdisplays. The components of FLC mixtures normally have a phase sequence with an orthogonal 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, the layer contraction (\sim 7–10%) that typically occurs upon cooling from the SmA to the SmC phase results in buckling of the smectic layers and the formation of zigzag defects that reduce the optical quality of the SSFLC film.⁴

To solve this problem, recent studies have focused on a unique class of chiral and achiral materials with layer contractions of \leq 1% upon SmA–SmC transition.⁵ 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.⁶ 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.^{7,8} We have developed a rational design strategy for achiral 'de Vries-like' liquid crystals based on a concept of frustration⁹ between a structural element promoting the formation of a SmA phase and one promoting the formation of a SmC phase.¹⁰⁻¹² For example, we recently showed that a mesogen with a phenylthiadiazole core (QL6-6) that combines a carbo-silane-terminated alkoxy chain (SmC-promoting) with a chloro-terminated alkyl chain (SmA-promoting) undergoes a SmA-SmC phase transition with a maximum layer contraction of only 0.4%. The compound forms a tilt angle of 21° at 10 K below the SmA-SmC transition temperature T_{AC} , which gives a reduction factor R of 0.20 (eqn (1))¹³ that is comparable to those calculated for the best 'de Vries-like' materials.11,14,15

$$R = \delta(T)/\theta_{\text{opt}}(T) = \cos^{-1}[d_{\text{C}}(T)/d(T_{\text{AC}})]/\theta_{\text{opt}}(T)$$
(1)

The layer spacing *d* of materials like **QL6-6** is characterized by a pronounced negative thermal expansion in the SmA phase that persists in the SmC phase (Fig. 1) and compensates for the layer contraction due to molecular tilt to such an extent that *d* expands well beyond the layer spacing at the SmA-SmC transition (d_{AC}).¹⁶



Fig. 1 Relative smectic layer spacing d/d_{AC} vs. reduced temperature $T - T_{AC}$ for compound **QL6-6**. From ref. 12.

^a Department of Chemistry, Queen's University, Kingston, Ontario, Canada.

E-mail: lemieux@chem.queensu.ca

^b Institute of Physical Chemistry, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany. E-mail: f.giesselmann@ipc.uni-stuttgart.de

[†] Electronic supplementary information (ESI) available: Synthetic procedures for compounds **QL13-6** and **QL14-8/8**, POM textures, tilt angle measurements and d_A vs. x_{13-6} plot. See DOI: 10.1039/c3cc45207g

In order to dampen this excessive layer expansion, we are investigating the effect of mixing 'de Vries-like' liquid crystals with conventional smectic liquid crystals by small angle X-ray scattering (SAXS). In this Communication, we report that mixtures of two SmC mesogens, **QL13-6** and **QL14-8/8**, form SmA and SmC phases in the mole fraction range $0.1 \le x_{13-6} \le 0.6$, with a maximum layer contraction in the range of 1.0-1.9% upon SmA–SmC transition. More importantly, we provide the first proof-of-principle that the reduction factor *R* can be tuned, and excessive negative thermal expansion of *d* can be dampened by mixing 'de Vries-like' and conventional smectic liquid crystals.



As part of an ongoing effort to tune 'de Vries-like' properties in chloro-terminated carbosilane mesogens,¹² we sought to prepare **QL13-6** as an analogue of **QL6-6** based on our observation that the model compound **QL14-8/8** forms a broad SmC phase (Table 1).¹⁷ Both **QL13-6** and **QL14-8/8** were derived from 2,5-dibromo-1,3,4-thiadiazole¹⁸ using a modification of the synthesis of 2-alkoxy-5- (4-cyanophenyl)-1,3-thiazole by Grubb *et al.*, as shown in Scheme 1 for **QL14-8/8** (see ESI[†] for details).^{19,20} Interestingly, **QL13-6** forms only a SmC phase (Table 1), which suggests that the SmC-promoting effect of the dialkoxy 5-phenyl-1,3,4-thiadiazole core completely overrides the SmA-promoting effect of the chloro-terminated chain in this new scaffold. Models of **QL13-6** and **QL14-8/8** minimized at the B3LYP/6-31G* level (Spartan'10, Wavefunction Inc.) give molecular lengths of 41.1 Å and 30.6 Å, respectively, and a molecular length ratio of 1.34.

Mixing the SmC mesogens **QL13-6** and **QL14-8/8** in varying proportions gave binary mixtures forming both SmA and SmC phases in the mole fraction range $0.1 \le x_{13-6} \le 0.6$, as shown in Fig. 2. This unusual phenomenon was previously observed by Kapernaum *et al.* for binary mixtures of 5-alkoxy-2-(4-alkoxy-phenyl)pyrimidine mesogens with molecular length ratios ranging from 1.4 to 1.8, and was attributed to a compensation of free volume by out-of-layer translational fluctuations, which are less hindered in the SmA phase.^{21,22} SAXS experiments on these 'bidisperse' mixtures showed a linear correlation between the



Fig. 2 Phase diagram of the binary mixture QL13-6–QL14-8/8. The phase transition temperatures were measured by POM on heating.

SmA layer spacing and the mole fraction, which is consistent with Diele's additivity rule.²³ Furthermore, the SmA–SmC transition of these mixtures showed a contraction of the layer spacing that is consistent with a classic model of hard spherocylinders,²⁴ and thus presented no evidence of 'de Vries-like' properties.²¹

In the present case, measurements of the layer spacing d as a function of temperature were carried out by SAXS for the binary mixtures with $x_{13-6} = 0.3, 0.4, 0.5$ and 0.6 as well as for the pure compounds QL13-6 and QL14-8/8. The relative layer spacing d/d^* is plotted as a function of the reduced temperature $T - T^*$, as shown in Fig. 3; d^* corresponds either to d_{AC} for the binary mixtures ($T^* = T_{AC}$), or to the layer spacing d_{CI} measured just below the clearing point for the pure compounds ($T^* = T_{CI}$). The $d/d^*(T)$ profile of QL13-6 shows a pronounced negative thermal expansion that is characteristic of 'de Vries-like' smectogens, whereas the profile of QL14-8/8 shows a layer contraction that is characteristic of conventional tilted smectogens. The negative thermal expansion is evident in the $d/d^*(T)$ profiles of mixtures with higher proportions of **QL13-6** ($x_{13-6} = 0.5, 0.6$) as it appears to compensate for the increasing molecular tilt, but it is not evident in mixtures with lower proportions of QL13-6 ($x_{13-6} = 0.3, 0.4$), either in the SmA or SmC phase. The maximum layer contraction is lowest for the mixture with $x_{13-6} = 0.4 (1.0\%)$ and d/d^* appears to level off with decreasing temperature, which suggests that a balance between the layer expansion and contraction behaviors of the two components is achieved around $x_{13-6} = 0.4$.

Table 1 Phase transition temperatures (°C) and enthalpies of transitions $(kJ \text{ mol}^{-1}, \text{ in parentheses})^{a,b}$

Cpd	Cr		SmC		SmA		Ι
QL6-6 ^c	•	14 (22)	•	61 (< 0.1)	•	71 (10)	
QL13-6	•	24 (18)	•			78 (13)	
QL14-8/8	•	60 (25)	•			94 (14)	

^{*a*} Measured on heating by differential scanning calorimetry (DSC). ^{*b*} The SmC phase was identified by polarized optical microscopy (POM) based on the appearance of broken fan and schlieren textures on cooling from the isotropic liquid phase (see Fig. S1 in ESI). ^{*c*} From ref. 12.



Scheme 1 Reagents and conditions: (a) Br₂, NaOAc, AcOH; (b) HBr, NaNO₂, CuBr; (c) CH₃(CH₂)₇OH, NaH, CuO, KI, THF; (d) 1-bromo-4-octyloxybenzene, *n*-BuLi, ZnCl₂(TMEDA), Pd(PPh₃)₄, THF.



Fig. 3 Relative smectic layer spacing d/d^* vs. reduced temperature $T - T^*$ for the binary mixtures **QL13-6–QL14-8/8** with $x_{13-6} = 0.3$, 0.4, 0.5 and 0.6 (open symbols) and for the pure compounds **QL13-6** and **QL14-8/8** (filled symbols); d^* for the mixtures is the layer spacing d_{AC} measured at the SmA–SmC transition ($T^* = T_{AC}$) and d^* for the pure compounds is the layer spacing d_{CI} measured just below the clearing point ($T^* = T_{CI}$).



Fig. 4 Reduction factors *R vs.* reduced temperature $T - T_{AC}$ for the mixtures **QL13-6–QL14-8/8** with $x_{13-6} = 0.3$ (\bigcirc), 0.4 (\blacksquare), 0.5 (\square) and 0.6 (\blacktriangle).

Optical tilt angles θ_{opt} were measured as a function of temperature in the absence of an electric field by measuring the angle of rotation between dark states in domains of opposite tilt orientation in 4 µm films aligned in glass cells with rubbed polyimide alignment layers (see Fig. S2 in ESI†). The $\theta_{opt}(T)$ profiles are virtually identical for the mixtures $x_{13-6} = 0.4$, 0.5 and 0.6, with θ_{opt} levelling off at *ca.* 24°, whereas θ_{opt} for the mixture $x_{13-6} = 0.3$ levels off at *ca.* 20°; these values are near the optimum θ_{opt} of 22.5° for SSFLC display applications. The corresponding reduction factors *R* were calculated using eqn (1) and plotted as a function of $T - T_{AC}$, as shown in Fig. 4. The R(T) profiles for the four binary mixtures reveal that the 'de Vries-like' character of the binary mixtures is optimized at $x_{13-6} = 0.4$, with a *R* value of 0.31 at $T - T_{AC} = -10$ K that remains more or less constant on further cooling.

Interestingly, a plot of the SmA layer spacing d_A as a function of x_{13-6} gives a linear correlation that is consistent with Diele's additivity rule based on a model of hard spherocylinders (see Fig. S3 in ESI†).²³ Extrapolation of the $d_A(x_{13-6})$ plot to $x_{13-6} = 0$ and 1 gives *d* values of 31.8 Å and 49.9 Å, which correspond to the layer spacings of the *virtual* SmA phases of pure **QL14-8/8** and **QL13-6**, respectively. The former is near the molecular length of **QL14-8/8** (*vide supra*), whereas the latter is *ca*. 1.2 times the molecular length of **QL13-6**, which may be consistent with an intercalated bilayer structure with relatively low orientational ordering.¹⁶ However, it is unclear at this juncture how one can reconcile this apparent adherence to Diele's rule with 'de Vries-like' behavior.

We have shown that binary mixtures of a SmC mesogen with 'de Vries-like' character (**QL13-6**) and a shorter conventional SmC mesogen (**QL14-8/8**) form SmA and SmC phases in the mole fraction range $0.1 \le x_{13-6} \le 0.6$, which is consistent with the behavior of bidisperse liquid crystal mixtures previously reported by Kapernaum *et al.*²¹ More importantly, we have shown that the tuning of 'de Vries-like' properties can be achieved by varying x_{13-6} , and provided the first proof-of-principle that the excessive negative thermal expansion characteristic of a pure 'de Vries-like' liquid crystal can be dampened by mixing with a conventional smectic liquid crystal. A detailed study of the scope of this formulation strategy will be reported in due course. We thank the Natural Sciences and Engineering Research Council of Canada (Discovery and CREATE grants) and the Deutsche Forschungsgemeinschaft (NSF/DFG *Materials World Network* program DFG Gi 243/6) for support of this work.

Notes and references

- 1 N. A. Clark and S. T. Lagerwall, Appl. Phys. Lett., 1980, 36, 899-901.
- 2 Ferroelectric Liquid Crystals: Principles, Properties and Applications, ed. J. W. Goodby, R. Blinc, N. A. Clark, S. T. Lagerwall, M. A. Osipov, S. A. Pikin, T. Sakurai, K. Yoshino and B. Zeks, Gordon & Breach, Philadelphia, 1991.
- 3 S. T. Lagerwall, Ferroelectric and Antiferroelectric Liquid Crystals, Wiley-VCH, Weinheim, 1999.
- 4 T. P. Rieker, N. A. Clark, G. S. Smith, D. S. Parmar, E. B. Sirota and C. R. Safinya, *Phys. Rev. Lett.*, 1987, **59**, 2658–2661.
- 5 J. P. F. Lagerwall and F. Giesselmann, *ChemPhysChem*, 2006, 7, 20–45, and references cited therein.
- 6 A. de Vries, J. Chem. Phys., 1979, 71, 25-31.
- 7 M. V. Gorkunov, M. A. Osipov, J. P. F. Lagerwall and F. Giesselmann, *Phys. Rev. E*, 2007, **76**, 051706.
- 8 K. Saunders, D. Hernandez, S. Pearson and J. Toner, *Phys. Rev. Lett.*, 2007, **98**, 197801.
- 9 R. D. Kamien and J. V. Selinger, J. Phys.: Condens. Matter, 2001, 13, R1-R22.
- 10 L. Li, C. D. Jones, J. Magolan and R. P. Lemieux, J. Mater. Chem., 2007, 17, 2313–2318.
- 11 J. C. Roberts, N. Kapernaum, Q. Song, D. Nonnenmacher, K. Ayub, F. Giesselmann and R. P. Lemieux, J. Am. Chem. Soc., 2010, 132, 364–370.
- 12 Q. Song, D. Nonnenmacher, F. Giesselmann and R. P. Lemieux, J. Mater. Chem. C, 2013, 1, 343–350.
- 13 The reduction factor R is a measure of 'de Vries-like' character defined as the ratio of the tilt angle $\delta(T)$ required to give the observed layer spacing contraction $d_{\rm C}(T)/d_{\rm AC}$ at a given temperature T below the SmA-SmC transition temperature $T_{\rm AC}$, assuming a classic model of hard spherocylinders, over the tilt angle $\theta_{\rm opt}(T)$ measured directly by polarized optical microscopy. According to eqn (1), a SmA-SmC transition would approach the idealized de Vries model as $R \to 0$. Y. Takanishi, Y. Ouchi, H. Takezoe, A. Fukuda, A. Mochizuki and M. Nakatsuka, *Jpn. J. Appl. Phys.*, 1990, **2**, L984–L986.
- 14 M. D. Radcliffe, M. L. Brostrom, K. A. Epstein, A. G. Rappaport, B. N. Thomas, R. Shao and N. A. Clark, *Liq. Cryst.*, 1999, 26, 789–794.
- 15 M. S. Spector, P. A. Heiney, J. Naciri, B. T. Weslowski, D. B. Holt and R. Shashidhar, *Phys. Rev. E*, 2000, 61, 1579–1584.
- 16 Recent SAXS analyses of smectic monodomains have shown that similar 'de Vries-like' organosiloxane liquid crystals exhibit unusually large molecular tilt fluctuations, and that the layer contraction due to molecular tilt at the SmA-SmC transition is almost fully compensated by an increase in orientational order as the tilt fluctuations decrease with decreasing temperature. D. Nonnenmacher, S. Jagiella, Q. Song, R. P. Lemieux and F. Giesselmann, *ChemPhysChem*, DOI: 10.1002/ cphc.201300358.
- 17 By comparison, the model compound corresponding to **QL6-6**, 2-nonyl-5-(4-octyloxyphenyl)-1,3,4-thiadiazole, forms a SmC phase with a narrower temperature range: Cr 77 SmC 90 I. Ref. 12.
- 18 D. Xiao, A. Palani, M. Sofolarides, Y. Huang, R. Aslanian, H. Vaccaro, L. Hong, B. McKittrick, R. E. West Jr., S. M. Williams, R.-L. Wu, J. Hwa, C. Sondey and J. Lachowicz, *Bioorg. Med. Chem. Lett.*, 2011, 21, 861–864.
- 19 A. M. Grubb, C. Zhang, A. Jakli, P. Sampson and A. J. Seed, *Liq. Cryst.*, 2012, **39**, 1175–1195.
- 20 Z. M. Hudson, X.-Y. Liu and S. Wang, Org. Lett., 2011, 13, 300-303.
- 21 N. Kapernaum, C. S. Hartley, J. C. Roberts, F. Schoerg, D. Krueerke,
- R. P. Lemieux and F. Giesselmann, *ChemPhysChem*, 2010, 11, 2099–2107.
 F. Yan and D. J. Earl, *J. Chem. Phys.*, 2012, 136, 124506.
- 23 According to Diele's additivity rule, the layer spacing d of a binary mixture of smectogens A and B is calculated as $d = d_A x_A + d_B x_B$, where d_A , d_B are the layer spacings of the pure smectogens. S. Diele, *Ber. Bunsen-Ges. Phys. Chem.*, 1993, **97**, 1326–1336.
- 24 L. Onsager, Ann. N. Y. Acad. Sci., 1949, 51, 627-659.