Tuning the Mesogenic Properties of 5-Alkoxy-2-(4-alkoxyphenyl)pyrimidine Liquid Crystals: Mixtures with ‘de Vries-like’ Properties using Fluoro-Substituted Phenoxy End-Groups

M. Thompson1,* N. Kapernaum1,2 and R. P. Lemieux1

1 Chemistry Department, Queen’s University, Kingston, Ontario, Canada
2 Institute of Physical Chemistry, Universität Stuttgart, Stuttgart, Germany

The trisilane end-group is a strong SmC-promoting element because it promotes lamellar ordering by nanosegregation; by combining a trisilane end-group with a strong SmA-promoting element (e.g., a chloro-terminated alkyl chain or a 5-phenylpyrimidine core), our group has developed new liquid crystalline materials with ‘de Vries-like’ properties.1 These unusual materials undergo a SmA-SmC phase transition with a maximum layer contraction of < 1%. A figure of merit often used to characterize ‘de Vries-like’ properties is the reduction factor $R$ according to eq. 1, where $\delta(T)$ is the tilt angle required to give the observed layer contraction $d_C(T)/d_{AC}$ assuming a model of hard spherocylinders in which the layer contraction scales with the cosine of the tilt angle, and $\theta_{opt}$ is the observed tilt angle measured by polarized optical microscopy. According to eq. 1, a SmA-SmC transition would approach that described by de Vries’ diffuse cone model as $R \rightarrow 0$.

$$R = \frac{\delta(T)/\theta_{opt}(T)}{\cos^{-1} \left[ \frac{d_C(T)/d_{AC}}{\theta_{opt}(T)} \right]}$$ (1)

It has been shown using monodomain 2D X-ray scattering analysis that 5-alkoxy-2-(4-alkoxyphenyl)pyrimidine liquid crystals with phenoxy end-groups form intercalated bilayers in which the phenoxy end-groups are nanosegregated, but they do not exhibit ‘de Vries-like’ properties.2 We also showed that the mesogenic properties of these materials could be tuned by fluoro- or difluorosubstitution of the phenoxy end-group, and that ortho-fluoro substitution has a strong SmC-promoting effect.2

In this presentation, we report the mesogenic property of binary mixtures of the normal and inverted 2,6-difluorophenoxy isomers $\text{QL22-8/8-2,6F}_2$ and $\text{QL23-8/8-2,6F}_2$, respectively, and the effect of mixing these two compounds on the layer contraction at the SmA-SmC transition according to small-angle X-ray scattering (SAXS) analyses. As shown in Fig. 1, the maximum layer contraction of a 1:1 mixture of the two isomers (Cr <0 SmC 56 SmA 83 N 85 I) upon SmA-SmC transition is on the order of 1%, although optical tilt angle measurements show that this can be explained on the basis of a conventional model of hard spherocylinders (i.e., $R \sim 1$). However, unlike conventional SmA/SmC materials, the negative thermal expansion of the smectic layer in the SmA phase persists in the SmC phase, which is characteristic of ‘de Vries-like’ materials. In this poster, a full phase diagram of the binary mixture will be presented, as well as the investigation of ternary mixtures in which a SmC component with high tilt will be added to tune the optical tilt to values that are useful for display applications.

References:
* Matthew Thompson; E-mail: Matthew.Thompson@chem.queensu.ca