

# Polar Liquid Crystals for Highly Ordered Nematics

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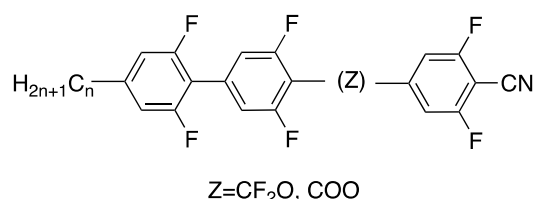
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## ABSTRACT

We report liquid crystals that show ferroelectric nematic phases. We have modified the bridged three-ring structure reported previously to investigate structure-property relationships. Small changes in the length of the flexible chain and variation of the bridge structure cause large differences in the phase sequence as well as in the ferroelectric-nematic transition temperatures. In addition, as a first step toward industrially relevant mixture design, a binary mixture has been formulated, and an enantiotropic ferroelectric nematic phase with a temperature range of 28 K was observed.

Based on this structure, we modified two elements in order to determine their influence on molecular properties. One is the alkyl chain length on the left side, the other is the bridging element, where we changed difluoromethoxy (CF<sub>2</sub>O) to ester (COO).



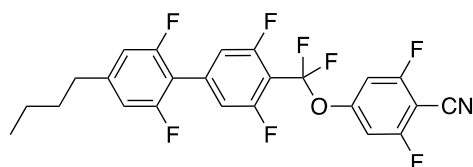
**Fig. 2.** General structure of the new materials investigated in this study.

## 1 Introduction

Compounds with ferroelectric nematic (FN) phases, as predicted by Max Born in 1916 [1], have been identified by Nishikawa [2] and Mandle [3] independently. Recently, we reported another compound that exhibits the FN phase at and below room temperature with a direct transition from the isotropic phase [4]. In this paper, we extend this study, focusing on modifications of molecular structure, namely the flexible alkyl chain and the bridging element between two of the three phenyl rings.

## 2 Singles and Characterization

The structure of the published material **1a** [4] is shown in Fig. 1. It contains fluorinated biphenyl- and phenyl units bridged by a difluoromethoxy (CF<sub>2</sub>O) group. The core structure is flanked by an n-butyl side chain and a terminal cyano group.



**Fig. 1.** The first compound with a monotropic FN phase close to room temperature.

Four combinations have been synthesized and investigated by Differential Scanning Calorimetry (DSC), microscopic texture observation, and dielectric spectroscopy. Observed phase sequences are shown in Table 1.

**Table 1.** Phase sequence of compounds **1** and **2**.

ID	side chain	bridge	phase
<b>1a</b>	n-butyl	CF <sub>2</sub> O	C 44 <b>FN</b> (21) I
<b>1b</b>	n-pentyl	CF <sub>2</sub> O	Tg -50 C 39 <b>FN</b> (-1) M2 (10) N (23) I
<b>2a</b>	n-butyl	COO	C 69 <b>FN</b> 89 M2 93 I
<b>2b</b>	n-pentyl	COO	C 80 <b>FN</b> (56) M2 (77) N 94 I

M2: mesophase, Tg: glass transition, temperatures in parentheses are monotropic transitions

All compounds show FN phases, but the transition temperature is quite variable, ranging from -1°C at **1b** to 89°C at **2a**.

Judging from the microscopic texture of **2a**, we cannot clearly identify whether the phase next to the isotropic one is a conventional nematic or an intermediate nematic phase (M2).

When the alkyl chain is changed from n-butyl **1a** to n-pentyl **1b**, a qualitative change in the phase sequence is observed. Instead of showing a direct transition to FN phase in **1a** upon cooling from the isotropic phase, **1b** shows a conventional nematic phase first, followed by an intermediate phase M2, and then the FN phase appears. This is similar to the phase sequence described by Nishikawa et al. [2].

**1a** and **1b** have FN transitions at comparably low temperatures of 21 °C and –1 °C respectively, which is monotropic. But due to the low melting points and stable supercooling behavior, these FN phases are easily observable, and their appearance is highly reproducible.

Compounds having the ester bridging elements (**2a**, **2b**) show much higher FN transition temperature of 89 °C and 56 °C for **2a** and **2b**.

The origin of the higher FN temperatures could partially be due to the stronger dipole moment of the ester bridge compared to difluoromethoxy one. Higher dipole moments should lead to stronger dipole-dipole interaction, resulting in higher FN transition temperature.

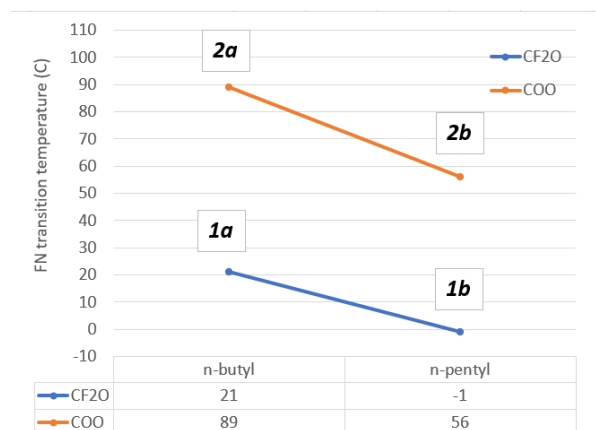
The calculated dipole moments and their angles with the molecular long axes (defined as rotation axes with smallest moment of inertia) are shown in Table 2.

**Table 2.** Calculated dipole moments (B3LYP/6-31G(d)).

ID	dipole moment	angle to molecular axis
<b>1a</b>	11.3 Debye	2.4°
<b>2a</b>	11.9 Debye	2.1°

The difference in dipole moments is quite small and cannot fully explain the huge difference of FN transition temperatures. Maybe the stronger local dipole of the ester group leads to stronger specific intermolecular interactions.

The influence of alkyl chain and bridging component on the FN transition temperature for all four singles are summarized in Fig. 3.



**Fig. 3.** Influence of alkyl chain length and bridge structure on FN transition temperatures.

The structure with an ester bridge (**2a**, **2b**) is another lead structure for FN phase formation. Moreover, compound **2a** shows an enantiotropic ferroelectric nematic phase, thanks to the combination of high FN transition temperature and a relatively low melting point. To our knowledge, this is the first single compound reported to possess enantiotropic behavior.

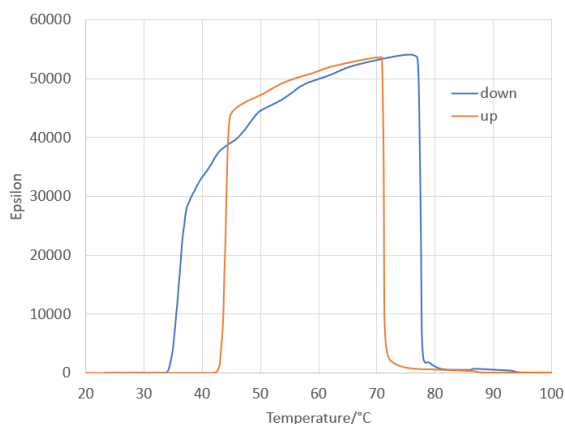
The monotropic FN phase of **2b** can be easily and reproducibly observed, similar to the case of **1a** and **1b**.

### 3 Binary Mixture Experiment

In order to utilize this unique property for actual devices, the liquid crystal should have a wide-range enantiotropic FN phase, including room temperature. Although single **2a** shows enantiotropic behavior, the phase range is only 20 K and it lies just outside room temperature. To lower the melting point and widen the phase range, mixture design is the logical next step.

As a first attempt toward a mixture with practical operating temperature range, **2a** and **2b** were mixed 1:1 and the properties were determined by DSC, microscopic observation, and dielectric spectroscopy.

Fig. 4 shows dielectric spectroscopy of the 1:1 mixture **2a** and **2b**, both upon cooling down (blue) and heating up (orange).



**Fig 4.** Dielectric spectroscopy of a 1:1 homologue mixture of **2a** and **2b** at 1kHz.

The FN range (epsilon from 10000 to over 50000) is 43 K wide in the cooling down process, and 28 K during heating up.

#### 4 Summary and Outlook

We have presented new single materials that exhibit ferroelectric nematic phases. Small modification of the structure leads to drastic change of material properties, including the phase sequence and FN transition temperatures. With more suitable single materials, the realization of FN mixtures should be possible including room temperature.

One remaining obstacle for device design will be the fabrication of defect-free, homogeneous monodomains. More work on the interaction between an orientation layer and the FNLC would be necessary to achieve strong surface anchoring. Finally, the possibility to drive the LC in the FN phase with DC voltage is highly attractive but challenging at the same time.

After only a few years, ferroelectric nematic materials are no longer an academic curiosity, but are close to becoming a rich and fascinating object of study in applied soft matter research. Materials that show extremely high dielectric constants while keeping full fluidity are unique and attractive. Many potential applications can be envisioned in the field of display and beyond-display technologies.

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