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# Fuorinated hydrogen bonding liquid crystals based on Schiff base

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ABSTRACT

Two new Schiff base compounds, tailed by the fluoroalkoxy, were synthesized in a three-step process. Those supramolecular structures constructed by hydrogen bonding show good liquid crystal properties with higher clear points and wider mesomorphic phase ranges than other analogs containing a terminal alkoxy chain. Investigation of the optical textures by polarizing microscopy reveals that terminal fluorinated substituents convert the nematic phase of supramolecular hydrogen-bonding complexes with terminal alkoxy chains into the smectic A phase of those with terminal fluoroalkoxy chains.

## 1. Introduction

Schiff base compounds are widely used in many fields, such as catalytic chemistry [1], organometallic chemistry [2], biochemistry [3], and photochemistry [4]. Schiff bases have attracted much attention in the field liquid crystal researches since the first report on the Schiff base liquid crystal compound 4-methoxybenzylidene-4′-butylaniline (MBBA) by Kelker et al. [5] in 1969. Over the past few decades, lots of Schiff bases with low molecular weight have been synthesized and investigated extensively toward applications of liquid crystal [6–15]. It has been found that the terminal or lateral groups, such as –F, –Cl, –CN, $-CH_3$, and $-OCH_3$, have a significant influence on the liquid crystalline properties of the Schiff bases especially in the cases of fluorine atoms. The small size of the fluoro-substituent enables its incorporation into liquid crystals' structures without undue disruption, and hence liquid crystalline phases can still be exhibited. However, it is the combination of the small size and high polarity which serves to modify melting point, mesophase morphology, transition temperatures, and other physical properties including optical anisotropy, dielectric anisotropy, and visco-elastic properties.

The use of molecular interactions caused by hydrogen bonding for the design of liquid crystals [16–20] has attracted attention because these materials involving non-covalent interactions have potential applications for dynamically functional molecular systems. Hydrogen bonding is one of the most important interactions in chemical and biological processes. In nature, hydrogen bonding plays a key role in molecular recognition and molecular assembly because of its stability, dynamics, directionality, and reversibility [21,22].

Herein we present synthesis and mesomorphic properties of hydrogen bonding liquid crystals based on Schiff bases with terminal fluoroalkoxy chains. For comparison, Schiff base liquid crystals with terminal alkoxy chains were also synthesized.

## 2. Results and discussion

### 2.1. Synthesis

The Schiff bases **A** and **B** with terminal fluoroalkoxy chains were synthesized in three steps (Scheme 1). 2,2,3,3-tetrafluoro-1-propanol was reacted with 4-chloronitrobenzene (**2**) to form 4-(2,2,3,3-tetrafluoropropoxy)nitrobenzene (**3**), which was further treated with hydrazine hydrate, $FeCl_3$ and activated carbon affording 4-(2,2,3,3-tetrafluoropropoxy)aniline (**4**). Reaction of **4** with 3-pyridinecarboxaldehyde (**5**) in ethanol at 85 °C for 12 h gave desired Schiff base **B**. The preparation of **A** is similar to that of **B**. The Schiff base **C** with terminal alkoxy chains was synthesized in one step with 4-propoxyaniline (**6**) and 3-pyridinecarboxaldehyde (**5**) in ethanol at 85 °C for 12 h.

4-*n*-Alkoxybenzoic acids (**Dn**) were synthesized as the literature [23]. The supramolecular hydrogen bonding liquid crystal

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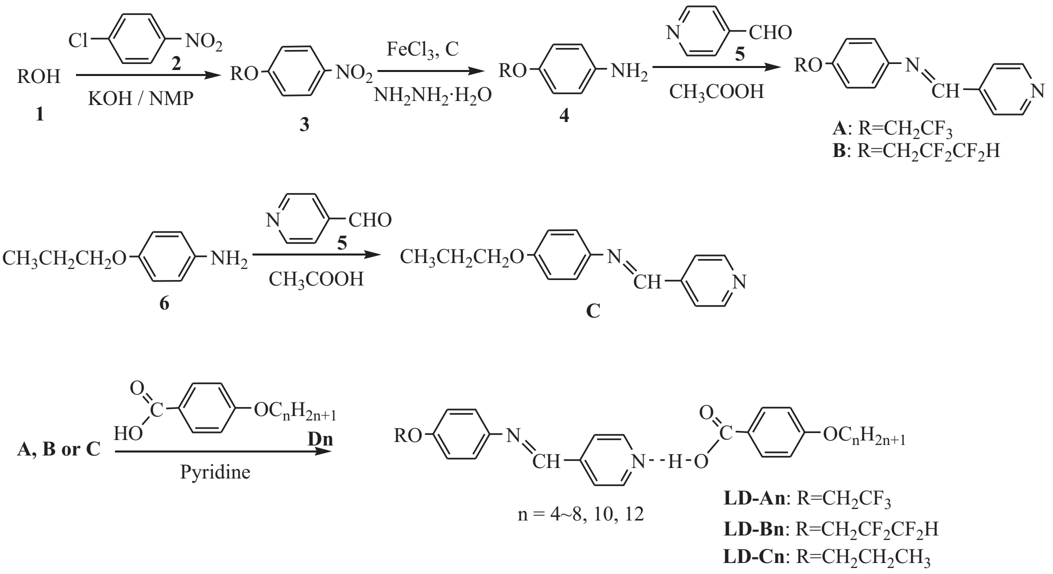

**Scheme 1.** Synthesis of Schiff bases and supramolecular liquid crystal complexes.

complexes (**LD–An**, **LD–Bn**, **LD–Cn**) were prepared with equimolar Schiff bases (**A**, **B** or **C**) and 4-*n*-alkoxybenzoic acids in pyridine. After evaporation of pyridine and drying under vacuum, the supramolecular liquid crystal complexes were obtained (Scheme 1).

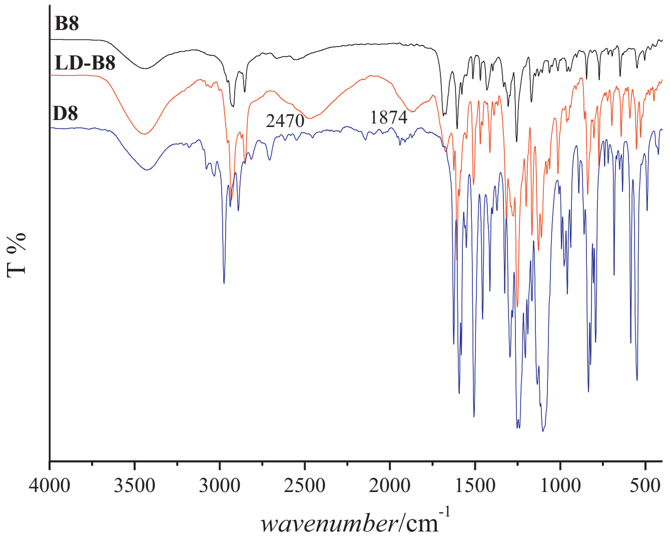

**Fig. 1.** Infrared spectra of Schiff base (**B8**) and 4-*n*-octoxybenzoic acid (**D8**) and their supramolecular liquid crystal complex (**LD–B8**).

### 2.2. Identification

The structures of Schiff bases **A**, **B** and **C** were identified by IR, $^1$H NMR, $^{13}$C NMR, $^{19}$F NMR, mass spectra and elemental analyses. The hydrogen bonds in the supramolecular complexes (**LD–An**, **LD–Bn**, **LD–Cn**) were identified by infrared spectra for the two new peaks centered at 2470 and 1874 cm$^{-1}$ compared with Schiff bases and 4-*n*-alkoxybenzoic acids (Fig. 1, **LD–B8** for example) [24–26].

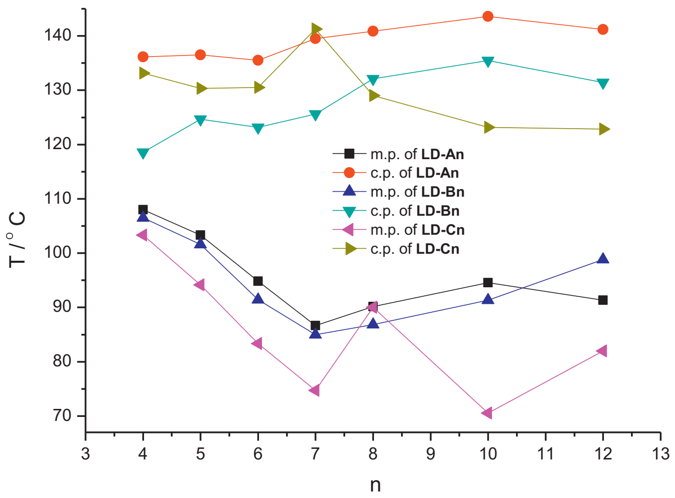

**Fig. 2.** Melting points (m.p.) and clear points (c.p.) of new supramolecular liquid crystal complexes.

**Table 1**
Transition temperatures (°C) of new supramolecular liquid crystal complexes.

| Compound | Transition temperature [a] | Compound | Transition temperature [a] | Compound | Transition temperature [a] |
|---|---|---|---|---|---|
| **LD–A4** | Cr 108 $S_A$136 I | **LD–B4** | Cr 107 $S_A$119 I | **LD–C4** | Cr 103 N133 I |
| **LD–A5** | Cr 103 $S_A$137 I | **LD–B5** | Cr 102 $S_A$125 I | **LD–C5** | Cr 94 N130 I |
| **LD–A6** | Cr 95 $S_A$136 I | **LD–B6** | Cr 91 $S_A$123 I | **LD–C6** | Cr 83 N131I |
| **LD–A7** | Cr 87 $S_A$140 I | **LD–B7** | Cr 85 $S_A$126 I | **LD–C7** | Cr 75 N141 I |
| **LD–A8** | Cr 90 $S_A$141 I | **LD–B8** | Cr 87 $S_A$132 I | **LD–C8** | Cr 90 N129 I |
| **LD–A10** | Cr 95 $S_A$144 I | **LD–B10** | Cr 91 $S_A$135 I | **LD–C10** | Cr 71 N123 I |
| **LD–A12** | Cr 91 $S_A$141 I | **LD–B12** | Cr 99 $S_A$131 I | **LD–C12** | Cr 82 N123I |

[a] Cr: crystal state; I: isotropic liquid; $S_A$: smectic A phase; N: nematic phase; the onset temperature of the phase transition from DSC of the second heating.