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Fuorinated hydrogen bonding liquid crystals based on Schiff base

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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, -CH₃, and -OCH₃, 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

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.

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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-1propanol was reacted with 4-chloronitrobenzene (2) to form 4-(2,2,3,3-tetrafluoropropoxy)nitrobenzene (3), which was further treated with hydrazine hydrate, FeCl₃ 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).

2.2. Identification

The structures of Schiff bases **A**, **B** and **C** were identified by IR, ¹H NMR, ¹³C NMR, ¹⁹F 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. 1. Infrared spectra of Schiff base (B8) and 4-n-octoxybenzoic acid (D8) and their supramolecular liquid crystal complex (LD-B8).

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Table 1



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

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; 1: isotropic liquid; SA: smectic A phase; N: nematic phase; the onset temperature of the phase transition from DSC of the second heating.



Fig. 3. POM textures of new supramolecular liquid crystal complexes: (a) **LD–A5**, heating to 122 °C, S_A phase; (b) **LD–B5**, heating to 135 °C, S_A phase; (c) **LD–C5**, heating to 124 °C, N phase (crossed polarizers, magnification 20×).

2.3. Liquid crystalline properties

The thermal behaviors of products Schiff bases, 4-*n*-alkoxybenzoic acids and supramolecular liquid crystal complexes were investigated by differential scan calorimetry (DSC), and polarizing optical microscopy (POM). The transition temperatures for all the new supramolecular liquid crystal complexes are shown in Table 1.

The two series of new supramolecular liquid crystal complexes (**LD–An** and **LD–Bn**) with the terminal fluoro-substituents, show good liquid crystal properties. Long alkoxy substituents anchored on the benzoic acids increased the transition temperature of the clearing point (Fig. 2). The melting points of **LD–An** are close to those of **LD–Bn** while the clear points of **LD–An** are higher than that of **LD–Bn**. Compared with **LD–Cn** bearing the terminal alkyl-substituent, all in all, the melting points and the clear points of **LD–An** are higher. It suggests that the two series of new

supramolecular liquid crystal complexes (**LD–An** and **LD–Bn**), with the terminal fluoro-substituents, show good stability. Mesomorphic phases with fluorinated tails are thermally more stable because fluorinated alkyl chains are stiffer than hydrocarbon alkyl chains [27,28].

Investigation of the optical textures by polarizing microscopy (POM) reveals that **LD-An** and **LD-Bn** show smectic A phase instead of nematic phase of **LD-Cn**. The typical texture change is shown in Fig. 3 for complex **LD-A5**, **LD-B5** and **LD-C5**. The substitution of the trifluoroethyoxyl and tetrafluoropropoxyl resulted in the high degree of order in a liquid crystal phase. The result was confirmed by DSC due to high melting points and clear points. Mesomorphic phases with fluorinated tails are much ordered because of strong affinity of fluoro-alkyl chains to neighboring fluoro-alkyl chains (fluorophilic effect), and the incompatibility with hydrocarbon chains and aromatic cores (fluorophobic effect). The fluorophilic and fluorophobic effects of fluorinated liquid crystals produce a micro-segregation and raise smectic phase stability, and suppress nematic phase [29].

All the POM pictures were taken at different temperatures on the second heating cycle according to DSC. Observations were made under 20-fold magnification. The initial heating rate of $10 \,^{\circ}\text{C min}^{-1}$ was slowed to $2 \,^{\circ}\text{C min}^{-1}$ when the temperature was close to the clearing point.

3. Conclusion

We have synthesized and characterized several novel supramolecular hydrogen bonding liquid crystals containing fluoroalkoxy as the terminal chains. The supramolecular liquid crystals displayed good liquid crystal properties that can be adjusted by the terminal substituent. They show a wide mesophase range and are mesophase stable compared with alkoxyl analogs. It was also found that terminal fluorinated substituents have a great impact on liquid crystal textures.

4. Experimental

4.1. General considerations

All the reagents were analytical grade, purchased from commercial sources and used as received. ¹H, ¹³C and ¹⁹F NMR were recorded on 400 MHz spectrometer (Avance III, Bruker) and chemical shifts were reported using tetramethylsilane as an internal reference. The solvent was CDCl₃ unless otherwise specified. The DSC was recorded on a differential scanning calorimeter at a scan rate of $10 \,^{\circ}$ C min⁻¹. Optical micrographs were observed with a polarizing optical microscope (POM) (Nikon LV100POL). Elemental analyses were performed on an EXETER CE-440 Elemental Analyzer.

4.2. General procedure for the preparation of A, B and C

Potassium hydroxide (1.16 g, 0.02 mol) was added to a solution of 2,2,2-trifluoroethanol or 2,2,3,3-tetrafluoro-1-propanol (0.02 mol) in *n*-methyl-2-pyrrolidone (NMP, 50 mL). P-chloronitrobenzene (3.14 g, 0.02 mol) was added to the solution after complete dissolution of potassium hydroxide at 60 °C. The mixture was stirred at 60 °C for 12 h. The reaction mixture was next poured into water and filtered to give solid. The solid was purified by column chromatography on silica gel with petroleum ether (60–90 °C)/acetic ether = 5/1 as the eluent. The second fraction was concentrated in vacuo to afford the target product **3** as pale yellow solid.

Hydrazine hydrate (1.2 mL) was added dropwise to a stirred mixture of product 3 (1.66 g, 0.0087 mol), FeCl₃ (0.03 g), activated

carbon (0.31 g) and MeOH (29 mL) over the period of 1 h at 75 °C. The resulting mixture was stirred 12 h at 70–80 °C. After having been cooled, the mixture was filtered and the filtrate was evaporated in vacuo. The residue was extracted with AcOEthexane (1:1) for three times and then washed by water for three times to give **4** as pale brown solid.

4-Pyridinecarboxaldehyde **5** (1.9 mL, 0.02 mol) and acetic acid (2 mL) were added to a solution of **4** (or **6**, 0.02 mol) in ethanol (60 mL). The mixture was stirred at 85 °C for 12 h. After evaporation and dry in vacuo, pale brown solid (**A**, **B** or **C**) was obtained.

N-(pyridin-4-ylmethylene)-4-(2,2,2-trifluoroethoxy)benzenamine (**A**): Yield 44.6%, mp 63–64 °C. ¹H NMR (400 MHz, CDCl₃, *δ* ppm): 4.38 (t, 2H, –CH₂CF₃), 7.00 (d, 2H, Ar–H), 7.26 (d, 2H, Ar–H), 7.81 (d, 2H, Pyridine–H), 8.49 (s, H, –CH=N), 8.72 (d, 2H, Pyridine–H). ¹³C NMR (400 MHz, CDCl₃, *δ* ppm): 66.18 (q), 115.78, 122.47, 122.77, 124.37(q), 143.28, 145.40, 150.21, 156.52, 156.84. ¹⁹ F NMR (CDCl₃, *δ* ppm): –173.87 (s, 3F, –CH₂CF₃). HRMS ESI (*m*/*z*) Obsd 280.2452 Calcd 280.2452 (C₁₄H₁₁N₂F₃O). Anal. Calcd for C₁₄H₁₁N₂OF₃: C, 60.00; H, 3.96; N, 9.99. Found C, 60.02; H, 3.65; N, 9.96%.

N-(pyridin-4-ylmethylene)-4-(2, 2, 3, 3-tetrafluoropropoxy)benzenamine (**B**): Yield 42.8%, mp 61–62 °C. ¹H NMR (400 MHz, CDCl₃, δ ppm): 4.39 (t, 2H, –CH₂CF₂–), 6.21 (m, 1H, –CF₂H), 7.00 (d, 2H, Ar–H), 7.29 (d, 2H, Ar–H), 7.73 (d, 2H, Pyridine–H), 8.48 (s, H, – CH=N), 8.78 (d, 2H, Pyridine–H). ¹³ C NMR (400 MHz, CDCl₃, δ ppm): 65.57 (t), 106.64–111.95 (m), 114.32 – 117.07 (m), 115.51, 122.35, 122.76, 143.01, 145.35, 150.54, 156.66, 156.73. ¹⁹F NMR (CDCl₃, δ ppm): –139.11 (d, 2F, cCH₂CF₂CF₂H), –124.81 (t, 2F, –CH₂CF₂CF₂H). HRMS ESI (*m*/*z*) Obsd 312.2621 Calcd 312.2623 (C₁₅H₁₂N₂F₄O). Anal. Calcd for C₁₅H₁₂N₂F₄O: C, 57.70; H, 3.87; N, 8.97. Found C, 57.69; H, 3.88; N, 8.96%.

4-Propoxy-*N*-(pyridin-4-ylmethylene)benzenamine (**C**): Yield 77.2%, mp 93–94 °C. ¹H NMR (400 MHz, CDCl₃, *δ* ppm): 1.05 (t, 3H, –CH₂CH₂CH₃), 1.82 (m, 2H, –CH₂CH₂CH₃), 3.96 (t, 3H, – CH₂CH₂CH₃), 6.94 (d, 2H, Ar–H), 7.28 (d, 2H, Ar–H), 7.75 (d, 2H, Pyridine–H), 8.48 (s, H, –CH=N), 8.74 (d, 2H, Pyridine–H). ¹³ C NMR (400 MHz, CDCl₃, *δ* ppm): 10.63, 22.68, 69.87, 115.15, 122.19, 122.70, 143.29, 143.43, 150.55, 155.22, 158.91. HRMS ESI (*m/z*) Obsd 240.3006 Calcd 240.3004 (C₁₅H₁₆N₂O). Anal. Calcd for $C_{15}H_{16}N_2O;$ C, 74.97; H, 6.71; N, 11.66. Found C, 74.95; H, 6.72; N, 11.65%.

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