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# Electrooptical properties of new type fluorinated phenyl-tolane isothiocyanate liquid crystal compounds

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## ABSTRACT

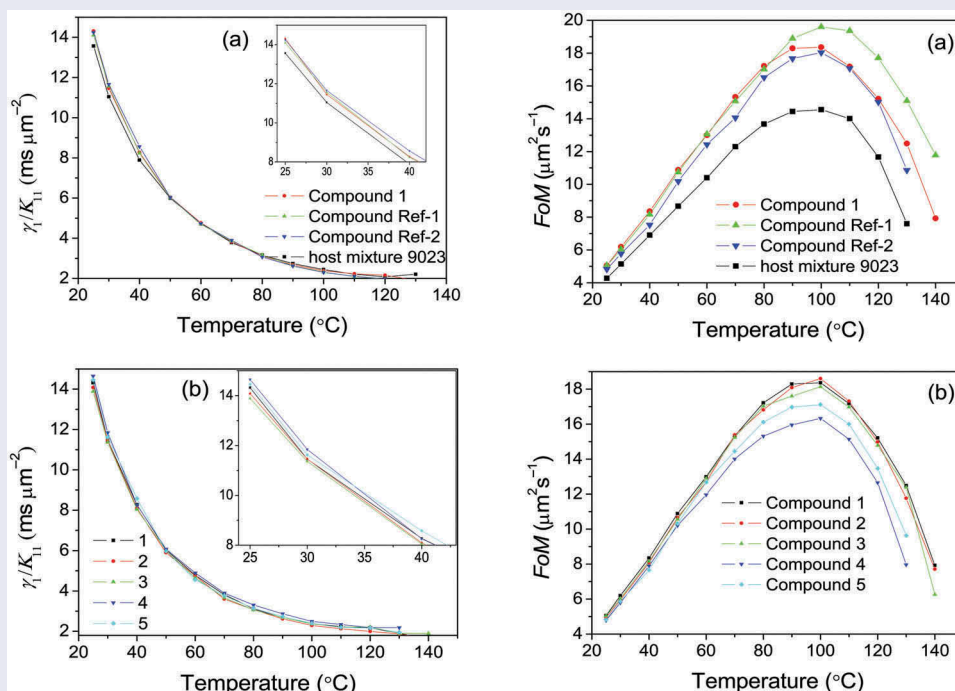
A series of 4'-(4-alkyl-phenyl)-2',6'-difluorotolane isothiocyanate liquid crystal (LC) compounds were synthesised, and their phase transitions and electrooptical properties were investigated. These compounds exhibit high birefringence, about 0.47–0.52. As the number of carbon atoms in the alkyl chains increases, these LC compounds can exhibit smectic phases. When these LCs were mixed into the commercial LCs, the birefringence values of LC mixtures become higher than pure commercial LCs, and the visco-elastic coefficients of five LC mixtures are very close to each other at every test temperature. The results of response properties indicate that the compounds with a tri-fluorine substitution and *n*-propyl end group possess better response performance than the others. These LC compounds are particularly attractive for achieving fast response times in LC optic devices.

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## 1. Introduction

High birefringence ( $\Delta n$ ) and low-viscosity liquid crystals (LCs) are important in so many different application fields such as spatial light modulator, reflective display and infrared scene projector. Fast response time is very desirable in device application and is sometimes pivotal.

The response time of an LC device is determined by the LC properties and device parameters. For a homogeneous nematic LC cell with strong anchoring energy, the decay response time is decisive, and can be expressed as [1]

$$\tau_{\text{decay}} = \gamma_1 d^2 / K_{11} \pi^2, \quad (1)$$

where  $\gamma_1$  is the rotational viscosity,  $d$  is the cell gap,  $K_{11}$  is the splay elastic constant. It is clear that response time is proportional to rotational viscosity ( $\gamma_1$ ) of LC materials and square of cell gap ( $d^2$ ). However, it is necessary to keep specific phase retardation ( $d\Delta n$ ) in the above LC devices, and then the cell gap can only be reduced to a limited value. Using high-birefringence LC materials can decrease the cell gap for the specific phase retardation, which will result in a shorter response time. Therefore, a figure-of-merit (*FoM*) value was defined by Gauza *et al.* to scale the response performance of LC materials [2]. LC material with high  $\Delta n$  and low viscosity will possess a higher *FoM* value, and can provide shorter response time.

$$FoM = K_{11}\Delta n^2/\gamma_1, \quad (2)$$

where  $\Delta n$  is the birefringence of LCs, and  $\gamma_1/K_{11}$  is defined as visco-elastic coefficient.

High-birefringence materials can be designed with highly conjugated molecular structure and polar end group, such as tolane [3], phenylethynyl thiophene [4] and terphenyl LCs [5]. In order to achieve  $\Delta n > 0.3$ , the LC compounds are always designed with benzene isothiocyanate group (NCS); meanwhile, these compounds also possess relatively low viscosity [6]. The LC compounds and mixtures with high birefringence have been reviewed by Dabrowski *et al.* in detail [7]; the chemical structures include isothiocyanato derivatives of biphenyl, terphenyl, quaterphenyl, tolane, phenyl tolane, phenyl ethynyl tolane and biphenyl tolane. Gauza *et al.* [2] have designed a high  $\Delta n$  eutectic LC mixture based on the biphenyl isothiocyanate compounds and tolane isothiocyanate compounds; the measured birefringence of the mixture is 0.45 at  $\lambda = 633$  nm and temperature = 23°C.

Parish [8] *et al.* investigated the LC properties of fluorinated terphenyl isothiocyanate LC compounds; these compounds have  $\Delta n = 0.35$ – $0.45$  in the visible spectral region at room temperature, and also have relatively low viscosity. Another kind of high-birefringence LCs is phenyl-tolane isothiocyanate, the  $\Delta n$  values of LC compounds are always greater than 0.4. Catanescu *et al.* [9] prepared phenyl-tolane isothiocyanate with fluorine substitution on terminal benzene ring the  $\Delta n$  values of these compounds are in the range 0.44–0.48 at  $\lambda = 589$  nm.

Some high-birefringence laterally fluorinated isothiocyanato phenyl-tolane LCs were synthesised and investigated by Gauza *et al.* These compounds exhibit narrow smectic phase, low melting point and low viscosity; their birefringence values are about 0.48 [10]. Many more laterally fluorinated isothiocyanato phenyl-tolane LC compounds were synthesised by Dziaduszek *et al.*, and the electro-optical properties of the compounds with different fluorinated positions were analysed [11].

Liao *et al.* had synthesised a few super high birefringence LC compounds containing isothiocyanato, biphenyl, alkyne and tolane groups; the value of  $\Delta n$  of the compounds could reach 0.73, but the viscosities of these compounds are relatively high [12]. This type of LC compounds was also synthesised and investigated by other researchers [13].

In this paper, we present five tri- and tetrafluorine bilaterally substituted 4'-(4-alkylphenyl) tolane isothiocyanate LC compounds with extrapolated birefringence of 0.47–0.52. The synthesis route of one of compounds has been given. The LC phase transition properties and electrooptical properties of these compounds are discussed.

## 2. Experimental

Differential scanning calorimetry (DSC, TA Instrument Model Q2000) was used to test the phase transition process of LC compounds. Results were obtained from ~3 mg samples in the heating and cooling cycles at a rate of 10° C min<sup>-1</sup>. The LC phase of each compound was confirmed by a polarised light microscope (Olympus, BX-51) with a thermal stage. The phase transition results of fluorine substituted compounds are listed in Table 1. At a specific temperature, the  $\Delta n$  and the visco-elastic coefficient ( $\gamma_1/K_{11}$ ) were determined using an optical method. Each compound was dissolved into a commercial medium- $\Delta n$  LC (SLC9023, Chengzhi Yonghua display materials Co.), respectively, with 10.00 wt% concentration for measurement. The  $\Delta n$  of SLC9023 is 0.241 at  $\lambda = 589$  nm, and the  $\gamma_1/K_{11}$  is 13.57 ms mm<sup>-2</sup> at room temperature. The measurement method of these parameters is shown as follows: each LC mixture was injected into a homogeneous cell of 4.90  $\mu\text{m}$  (pretilt angle of alignment film: ~1.0°). The LC cell was sandwiched between two crossed polarisers. The LC director without applied electric field was located 45° to the polarising direction of the polariser, whereas the incident light ( $\lambda = 589$  nm) direction was perpendicular to the substrate. When the applied voltage ( $\pm 10$  V, square wave, 1000 Hz) of LC cell was released, transient light intensity was recorded using a photomultiplier and an oscillograph. Then, the time-dependent transmittance was converted into the time-dependent optical phase retardation by the following formula,

$$\delta = 2\arcsin\sqrt{I}, \quad (3)$$

where  $\delta$  is the optical phase retardation, and  $I$  is the normalised light intensity [14]. The  $\Delta n$  value of the LC mixture was calculated from the total phase retardation ( $\delta_{\text{total}} = d\Delta n$ ) of the LC cell. The  $\gamma_1/K_{11}$  value was calculated from the equation derived by Wu *et al.* [15]

**Table 1.** Molecular structures, phase transition properties and birefringence of LC compounds.

| ID NO | Structure | Phase (°C)   | $\Delta H(\text{Cr-N})$<br>(kJ mol <sup>-1</sup> ) | $\Delta n$ |
|-------|-----------|--|--|------------|
| 1     |           | 1Cr 124.6 N 234.1 I<br>1Cr 107.7 N 233.8 I                           | 24.36  | 0.521      |
| 2     |           | 1Cr 137.4 N 249.1 I<br>1Cr 121.6 SmA 128.6 N 249.0 I                 | 26.11  | 0.471      |
| 3     |           | 1Cr 91.2 SmA 113.2 N 218.0 I<br>1Cr 85.4 SmA 114.2 N 218.0 I         | 19.56  | 0.478      |
| 4     |           | 1Cr 122.9 SmA 129.6 N 195.4 I<br>1Cr 106.0 SmA 127.0 N 196.8 I       | 25.61  | 0.480      |
| 5     |           | 1Cr 107.7 S 144.2 N 202.8 I<br>1Cr 86.5 SmB 90.4 SmA 144.3 N 202.8 I | 22.53  | 0.473      |
| Ref-1 |           | 1Cr 82.2 Sm 89.2 N 240.5 I   | 24.34*   | 0.498      |
| Ref-2 |           | 1Cr 89.0 N 216.0 I   | 27.30*   | 0.455      |
| Ref-3 |           | 1Cr 50.5 SmA 119.6 N 212.9 I   | 20.49*   | 0.510      |

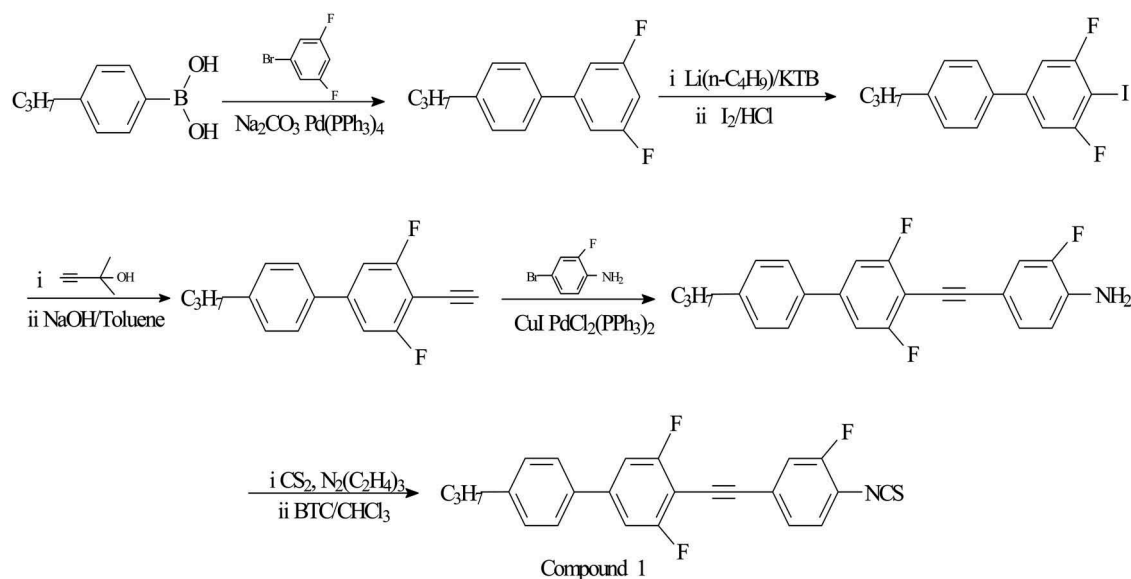
Note: \*The phase transition and birefringence data originate in literature [10,16]

**Scheme 1** illustrates the synthesis route of the compound 4'-(4-propylphenyl)-2',6',3-trifluoro-4-isothiocyanatobiphenyl. All reaction reagents were purchased from Alfa Aesar Co., and the purity is about 99%. The solvents of reactions were purchased from Shanghai Reagent Company (China), and the purity is AR. The synthesis of these LC compounds was similar to that of the compound 4'-phenyl-2',3'-difluoro-4-isothiocyanatobiphenyl [11].

**4'-Propyl-3,5-difluorobiphenyl:** 4-Propylbenzeneboronic acid (32.8 g, 0.20 mol), 3,5-difluoro-1-bromobenzene (38.6 g, 0.20 mol), sodium carbonate (42.4 g, 0.40 mol) and tetrakis (triphenylphosphine) palladium(0) (0.8 g) were added to a mixed solvent of water (100 mL), alcohol (200 mL) and toluene (300 mL), and the suspension was stirred at 90°C for 4 h. The suspension was cooled to room temperature naturally, and the organic phase layer was separated and washed with water. Anhydrous magnesium sulphate was added to the organic solution for drying, and the dried solution was

evaporated to obtain crude product. The crude product was purified by column chromatography using petroleum ether to give a clear transparent liquid; yield: 85.0%.

**4'-Propyl-3',5'-difluoro-4-iodobiphenyl:** 4'-Propyl-3,5-difluorobiphenyl (34.8 g, 0.15 mol) and potassium tert-butoxide (33.7 g, 0.30 mol) were dissolved in tetrahydrofuran (150 mL), and cooled to -90 to -100°C; the reaction system was protected by a high-purity nitrogen flow. *n*-Butyllithium solution (0.16 mol, 2.25 M solution in *n*-hexane) was added drop-wise to the reaction solution, which was stirred for 30 min. The solution was stirred for 2 h at -90 to -100°C. The iodine (40.1 g, 0.158 mol) dissolved in tetrahydrofuran (80 mL) was added drop-wise to the reaction solution for 15 min at -90 to -100°C, and then the reaction solution was placed at room temperature. Deionised water was added to the reaction solution, and the liquid separated into two layers. The layer containing the water solution was washed using ethyl acetate, and the organic layer was separated, merged



**Scheme 1.** The synthesis route of Compound 1.

and dried using anhydrous  $\text{MgSO}_4$ . By evaporating the solvent, the crude product solid was obtained. The crude product was purified by column chromatography using petroleum ether. Yield: 51.0%

**4'-Propyl-3,5-difluorobiphenyl-4-acetylene:** The previous iodobenzene product (21.5 g, 0.06 mol), 2-methyl-3-butyn-2-ol (5.1 g, 0.06 mol) were dissolved in 60 mL triethylamine, bis(triphenylphosphine) palladium(II) chloride (0.02 g), copper iodide (0.02 g) and triphenylphosphine (0.04 g) were added to the solution as catalyst. The reaction solution was heated at reflux for 6 h, and then a white precipitate appeared in the reaction vessel. The reaction solution was filtered in hot state to obtain the organic solution. When the triethylamine was evaporated, slight yellow liquid is the crude intermediate product was 4'-propyl-3,5-difluorobiphenyl-1-(2-methyl-3-butyn-2-ol), a slight yellow-coloured liquid. The intermediate product was dissolved in 80 mL toluene, and 2.0 g NaOH was added to the reaction system. The solution was heated to  $95^\circ\text{C}$  for 4 h, stirring under high-purity nitrogen. The reaction solution was cooled naturally and washed with water. The organic layer was separated and dried. The solvent was evaporated from the solution; a crude solid product was obtained and purified by column chromatography using petroleum ether as eluent. Yield: 72.0%

**4-Amino-(4'-propylphenyl)-2',6',3-trifluorotolane:** The previous phenylacetylene product (10.3 g, 0.04 mol) and 4-bromo-2-fluoroaniline (9.5 g, 0.05 mol) were dissolved in 50 mL dried triethylamine, bis(triphenylphosphine) palladium(II) chloride (0.02 g), copper iodide (0.02 g) and triphenylphosphine (0.04 g) were added to the solution as catalyst. The reaction system was protected by high-purity nitrogen flow, and then it was

stirred at  $95^\circ\text{C}$  for 4 h. The reaction solution was filtered in hot state; then the solution was cooled to room temperature naturally, and the yellow crude product precipitated out. Then the product was filtered and dried. Yield: 50.0%

**4'-(4-Propylphenyl)-2',6',3-trifluoro-4-isothiocyanatotolane:** The previous aniline product (5.48 g, 0.015 mol) triethylenediamine (5.60 g, 0.05 mol) and carbon disulphide (3.80 g, 0.05 mol) were dissolved in 50 mL toluene, and the reaction solution was stirred for 24 h at room temperature. The precipitation was filtered and washed using toluene; a faint yellow intermediate product was obtained and dried in a vacuum oven. The intermediate product was dissolved in 30 mL chloroform; the solution of triphosgene (1.50 g, 0.005 mol) in chloroform was added drop-wise in the reaction solution in 15 min at stirring. The solution was stirred for 2 h, filtered, and the solution of final product was obtained. The product was evaporated from the solution and purified by column chromatography using petroleum ether as eluent; the pure product is a white solid crystal; yield, 68.0%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 0.970(t, 3H,  $J = 14.8$  Hz), 1.651–1.708(m, 2H), 2.641(t, 2H,  $J = 15.2$  Hz), 7.150–7.193(m, 3H), 7.267–7.287(d, 2H,  $J = 8.0$ ), 7.319–7.379(m, 2H), 7.474–7.494(d, 2H,  $J = 8.0$ ).

The other LC compounds (2, 3, 4 and 5 in Table 1) were synthesised using the similar reaction process. The NMR results are listed as follows:

**Compound 2**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 0.970(t, 3H,  $J = 14.8$  Hz), 1.652–1.708(m, 2H), 2.641(t, 2H,  $J = 15.2$  Hz), 6.986–7.047(m, 2H), 7.170–7.198(m, 2H), 7.268–7.289(d, 2H,  $J = 8.4$ ), 7.479–7.499(d, 2H,  $J = 8.0$ ), 7.525–7.565(t, 1H,  $J = 16.0$ ).



**Compound 3**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 0.947(t, 3H,  $J = 14.8$  Hz), 1.355–1.410(m, 2H), 1.533–1.652(m, 2H), 2.663(t, 2H,  $J = 15.6$  Hz), 7.149–7.190(m, 3H), 7.268–7.289 (d, 2H,  $J = 8.4$ ), 7.318–7.378 (m, 2H), 7.471–7.491 (d, 2H,  $J = 8.0$ ).

**Compound 4**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 0.950(t, 3H,  $J = 14.8$  Hz), 1.336–1.429(m, 2H), 1.594–1.670(m, 2H), 2.662(t, 2H,  $J = 15.2$  Hz), 7.162–7.191(m, 4H), 7.268–7.289 (d, 2H,  $J = 8.4$ ), 7.468–7.488 (d, 2H,  $J = 8.0$ ).

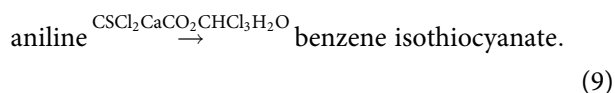
**Compound 5**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 0.906(t, 3H,  $J = 14.0$  Hz), 1.335–1.383(m, 4H), 1.612–1.686(m, 2H), 2.654(t, 2H,  $J = 15.6$  Hz), 7.165–7.194(m, 4H), 7.269–7.289 (d, 2H,  $J = 8.0$ ), 7.470–7.490 (d, 2H,  $J = 8.0$ ).

Three laterally fluorinated isothiocyanato phenyltolane LC compounds (Ref-1, Ref-2, Ref-3) were also prepared by a similar reaction route, and the NMR data of these compounds can be found in our previous work [16]. When the phase transition properties and electro-optical properties were discussed, these compounds were used as reference.

### 3. Results and discussions

#### 3.1. Synthesis of LC compounds

In the final synthesis step of NCS compounds, an indirect reaction route was selected. The aniline reactant was first treated with triethylenediamine and  $\text{CS}_2$ , and then with triphosgene. This reaction route can avoid using the highly toxic  $\text{CSCl}_2$ . Meanwhile, a relatively purer product can be obtained by this route compared to the direct method



When the intermediate precipitation product was filtered, the impurity without amino group in the aniline could be removed, which would result in a pure final NCS product.

#### 3.2. Phase transitions and mesomorphic properties

Table 1 shows phase transition temperatures and fusion enthalpy ( $\Delta H$ ) values of five LC compounds investigated and three reference compounds. These compounds possess different alkyl end groups and different fluorinated positions in the central benzene ring. First, a comparison of bilaterally and laterally fluorinated compounds is carried out. The fusion enthalpy values of bilaterally fluorinated compounds (Compound 1 and Compound 3) are approximately equal to those of laterally fluorinated

compounds (Compound Ref-1 and Compound Ref-3). However, the bilaterally fluorinated compounds have higher melting points, which probably come from the larger dipole moment of this type of compounds.

Compound 1 > Compound Ref-1; Compound 3 > Compound Ref-3.

When the melting points of LC compounds were compared among tetrafluorine-substituted compounds, bilaterally fluorinated compounds (4, 5) show higher melting point of  $\sim 100^\circ\text{C}$  than that of laterally fluorinated LCs (Compound Ref-2) because of the different dipole moments.

Compound 4, 5 > Compound Ref-2

In addition, the phase transition property is compared among the bilaterally fluorinated compounds. The three-position fluorine substituted compound (Compound 1) has a lower melting point than the two-position fluorine substituted compound (Compound 2). The fusion enthalpy of Compound 1 is also less than that of Compound 2,

Compound 1 ( $124.6^\circ\text{C}$ ) < Compound 2 ( $137.4^\circ\text{C}$ ).

When the middle phenyl ring of LC compound is substituted by fluorine at the same position, the compound with the last phenyl ring fluorinated in the (3, 5) positions has a higher melting point than that of fluorinated in the 3 position, as following,

Compound 4 ( $122.9^\circ\text{C}$ ) > Compound 3 ( $91.2^\circ\text{C}$ );

Compound Ref-2 ( $89.0^\circ\text{C}$ ) > Compound Ref-1 ( $82.2^\circ\text{C}$ ).

When compared to LC compounds with different terminal alkyl groups and the same rigid core structure, the melting point and  $\Delta H$  decrease with increasing carbon atom number, for example:

Compound 1 > Compound 3; Compound 4 > Compound 5.

Moreover, with the carbon atom number increasing, the LC compounds begin to exhibit smectic phase between the crystal phase and the nematic phase; the smectic phase has an adverse effect on the application of nematic LC devices.

#### 3.3. Electrooptical properties

When the  $\Delta n$  value of LC mixture is determined by an optical method, the  $\Delta n$  value of single LC compound at  $25^\circ\text{C}$  can be extrapolated according to the following guest–host equation,

$$(\Delta n)_{gh} = x(\Delta n)_g + (1 - x)(\Delta n)_h, \quad (4)$$

where  $gh$ ,  $g$  and  $h$  denote the guest–host LC solution, guest compound and host LCs, respectively, and  $x$  is the concentration of the guest LC compound. The extrapolated

**Table 2.** Calculated polarisability of compounds with *n*-propyl end group.

|                | $\Delta\alpha$ | $\bar{\alpha}$ | $\alpha_{xx}$ | $\alpha_{yy}$ | $\alpha_{zz}$ |
|----------------|----------------|----------------|---------------|---------------|---------------|
| Compound 1     | 492.4          | 417.4          | 745.7         | 298.7         | 207.7         |
| Compound 2     | 490.2          | 416.9          | 743.8         | 299.8         | 207.3         |
| Compound Ref-1 | 485.3          | 415.1          | 738.7         | 299.5         | 207.2         |

$\Delta n$  values of target bilaterally fluorinated LC compounds are in the range 0.47–0.52, as shown in Table 1.

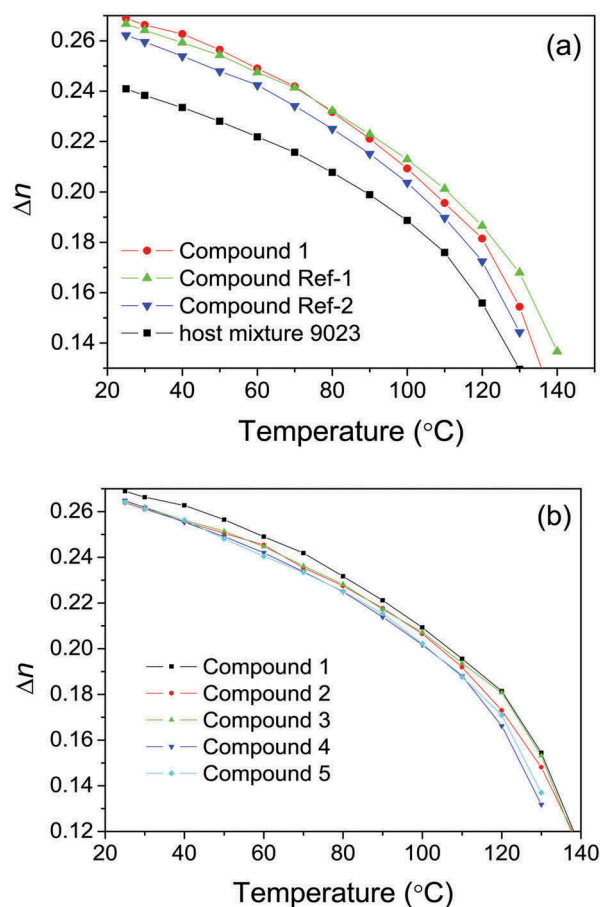
When the  $\Delta n$  values were compared among LC compounds with *n*-propyl end group, the  $\Delta n$  value of Compound 1 is larger than the values of Compound 2, Compound Ref-1 and Compound Ref-2, the reason is analysed by calculating the molecular polarisability. The polarisability values ( $\Delta\alpha$ ,  $\bar{\alpha}$ ) of each compound were calculated from  $\alpha_{xx}$ ,  $\alpha_{yy}$ , and  $\alpha_{zz}$  that come from the semi-empirical AM1 method acting on the relevant chemical structure, as shown in Table 2. These compounds almost have the same  $\bar{\alpha}$  values, but Compound 1 has the largest  $\Delta\alpha$  value among these compounds because of bilateral 2',6'-difluorine substitution. Consequently, it will possess a higher  $\Delta n$  value according to the Vuks formula [17]. When  $\Delta n$  values are compared among the bilaterally fluorinated compounds, Compound 1 has the largest  $\Delta n$  value (0.521) because of the highest molecular packing density. When a longer alkyl chain is introduced to the LC compound, such as Compound 3 and Compound 5, the  $\Delta n$  values will slightly decrease for the lower molecular packing density, for instance,

Compound 3 (0.478) < Compound 1 (0.521);

Compound 5 (0.473) < Compound 4 (0.480).

The  $\Delta n$  value of Compound 3 is very similar to that of Compound 4, the result suggests that the number of fluorine substitution adjacent to the NCS group do not affect the  $\Delta n$  value of bilaterally fluorinated compounds.

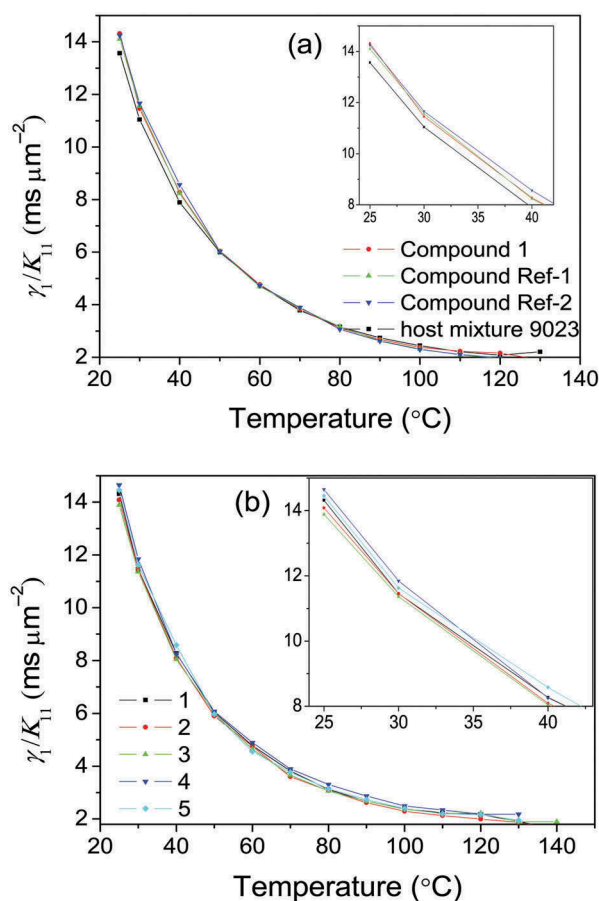
Figure 1(a) shows the experimental data of  $\Delta n$  which includes the host mixture and host LCs doped with bilaterally and laterally fluorinated compounds with propyl end group depending on the temperature. Obviously, the  $\Delta n$  values decrease with increase in the temperature, and reach zero at the clear point of the LC mixture. The  $\Delta n$  values of host LCs doped with these compounds are larger than the pure SLC9023 LCs at each temperature, because LC compounds investigated possess higher  $\Delta n$  values than host LCs. Among host LCs doped with LC compounds, tetra-fluorine-laterally substituted Compound Ref-2 possesses the lowest  $\Delta n$  value at each temperature. The LCs doped with bilaterally fluorinated Compound 1 display the highest value at the low temperature region (<80°C), while laterally fluorinated Compound Ref-1 displays the highest value in the high temperature region (>80°C), perhaps the results come from the higher melting point of Compound Ref-1.



**Figure 1.** (colour online) Temperature-dependent  $\Delta n$  value of different LC mixtures. (a) results of pure host LC (SLC9023) and host LCs doped with Compounds 1, ref-1, ref-2, respectively, (b) results of host LCs doped with Compounds 1, 2, 3, 4, 5, respectively. The symbols are experimental data, and the lines are connecting lines.

In the comparison of bilateral substituted compounds, the host LC doped with Compound 1 always displays the highest  $\Delta n$  value at every temperature; the host LCs doped with Compounds 2, 3, 4, 5 possess approximately the same  $\Delta n$  value in the low-temperature region (<60°C), as shown in Figure 1(b), this phenomenon is similar to the results at 25°C in Table 1. In the high-temperature area (>60°C), the  $\Delta n$  values of host LCs doped with Compounds 2, 3 are larger than those doped with Compounds 4, 5, and are close to the  $\Delta n$  value of Compound 1. Compounds 2, 3 possess higher clear points than Compounds 4, 5; the clear points of host LCs doped with Compounds 2, 3 become higher, which results in higher  $\Delta n$  values in the high-temperature area.

Figure 2(a) shows the visco-elastic coefficient values of host mixture SLC9023 and host LCs doped with Compound 1, Ref-1, Ref-2, which possess the same propyl end group and different fluorine-substituted positions. In general, the visco-elastic coefficient decreases with increasing temperature, and reaches a constant



**Figure 2.** (colour online) Temperature-dependent  $\gamma_1/K_{11}$  value of different LC mixtures. (a) results of pure host LC (SLC9023) and host LCs doped with Compounds 1, ref-1, ref-2, respectively, (b) results of host LCs doped with Compounds 1, 2, 3, 4, 5, respectively. The symbols are experimental data, and the lines are connecting lines.

value once close to the clear point. We find that the visco-elastic coefficient of mixture with LC compound is slightly larger than that of pure host LC. The rotational viscosity of the LC mixture can be approximately expressed as the arithmetic average of the components in low concentration, and the elastic constant of LC materials with same rigid core structure is similar [18]. Therefore, the above result indicates that LC compounds (1, Ref-1, Ref-2) have slightly larger viscosities than host LCs. When the viscosities are compared among host LCs doped with these compounds respectively, the viscosity of Compound 1 is equal to that of Compound Ref-1, and lesser than that of Compound Ref-2 in the low temperature region ( $<50^{\circ}\text{C}$ ), as shown in the enlarged figure of Figure 2(a). The result indicates that the overmuch fluorine substitution ( $\geq 4$ ) in LC compounds would probably increase the viscosity,

Compound 1  $\sim$  Compound Ref-1  $<$  Compound Ref-2.

In the high-temperature region ( $>50^{\circ}\text{C}$ ), the viscosity of each host LCs doped with the investigated compound is approximately equal.

In Figure 2(b), the visco-elastic coefficients of host LCs doped with different bilaterally fluorinated compounds were compared. The host mixture doped with tetra-fluorine-substituted Compound 4 has the highest value, while the host LCs doped with Compounds 2, 3 possess lower viscosity value, and the host LCs doped with Compounds 1, 5 have medium viscosity values; the sequence can be expressed as,

Compound 3  $\sim$  Compound 2  $<$  Compound 1  $\sim$  Compound 5  $<$  Compound 4.

Such a result suggests that di-fluorine substitution adjacent to the NCS group will increase the viscosity of the LC compound.

The  $FoM$  value can be used to compare the response performance of LC materials, which is calculated according to Equation (2) using  $\Delta n$  and  $\gamma_1/K_{11}$  and taking the effect of birefringence and visco-elastic coefficient into consideration. First, a comparison of  $FoM$  values between laterally fluorinated (1) and bilaterally fluorinated (Ref-1, Ref-2) compounds was carried out; the result is shown in Figure 3(a). The  $FoM$  value of each LC mixture first increases and then decreases at about  $100^{\circ}\text{C}$ . The  $FoM$  values of host LCs doped with investigated compound are larger than that of pure host LCs at every detecting temperature because of the high  $\Delta n$  values of these compounds. In the low-temperature region ( $<80^{\circ}\text{C}$ ), the host LC doped with Compound 1 displays the highest  $FoM$  value for its higher  $\Delta n$  value; the sequence can be expressed as,

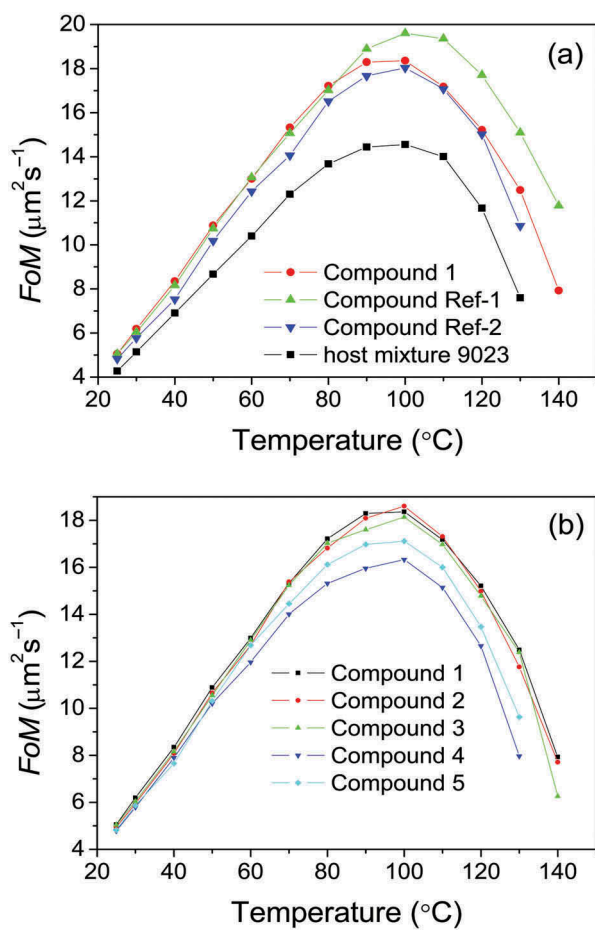
Compound 1  $>$  Compound Ref-1  $>$  Compound Ref-2.

In the high-temperature region ( $>80^{\circ}\text{C}$ ), the host LC doped with Compound Ref-1 displays the highest response performance because of the high clear point of the LC mixture.

When comparing host LCs doped with bilaterally fluorinated LC compounds, it can be seen that the host mixture doped with Compound 4 has the lowest  $FoM$  value, as shown in Figure 3(b), because it has a relative low birefringence and a large viscosity value in the whole of test temperature region. The host mixtures doped with Compound 1, Compound 2 almost have the same  $FoM$  values in every measured temperature, which comes from the combined effect of  $\Delta n$  and visco-elastic coefficient. The host LCs doped with Compounds 3, 5 display medium  $FoM$  value. The response performance of LC mixtures can be expressed as the following sequence,

Compound 1  $\sim$  Compound 2  $>$  Compound 3  $>$  Compound 5  $>$  Compound 4.





**Figure 3.** (colour online) Temperature-dependent  $FoM$  value of different LC mixtures, (a) results of pure host LC (SLC9023) and host LCs doped with Compounds 1, ref-1, ref-2, respectively, (b) results of host LCs doped with Compounds 1, 2, 3, 4, 5, respectively. The symbols are experimental data, and the lines are connecting lines.

#### 4. Conclusions

In this paper, we synthesised five 4-(4-alkyl-phenyl)-2,6-difluorotolane isothiocyanate LC compounds and investigated their phase transition properties and response properties. The LC compound has a higher melting point than the corresponding laterally fluorinated compound. The LC compounds are inclined to exhibit smectic phase when the alkyl carbon atom number increases. The extrapolated  $\Delta n$  of LC compounds is determined by a guest–host method in a commercial LC solution; the  $\Delta n$  value is in the range 0.47–0.52, and Compound 1 has the highest  $\Delta n$  value. The visco-elastic coefficients of five LC mixtures are very close to each other at every temperature, and the host LC doped Compound 4 possesses the largest visco-elastic coefficient. The response performance of

the host LCs doped with Compound 1 is very similar to that of Compound 2, and better than that of the host LCs doped with Compound 3 (or 4, 5). Therefore, these bilaterally substituted phenyl-tolane isothiocyanate LCs will find useful application in fast LC optic devices and display devices.

#### Disclosure statement

No potential conflict of interest was reported by the authors.

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