The influence of terminal chain on the formation of chiral nematic phase of non-symmetric liquid crystal dimers containing fluorinated units

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Abstract. In this study, we have synthesized four fluorine liquid crystals (LCs), termed FA-PD-UBA, FA-PD-PBA, FA-PD-ABA and FA-PD-BA. Through the research on thermal properties and mesophase type of the dimers, we can draw a conclusion that the non-symmetric structure type with flexible terminal chain of appropriate length, may help the dimers to form cholesteric fluorinated liquid crystals.

1. Introduction
Cholesteric (chiral nematic) liquid crystals [1-5] have attracted considerable attention for their etc. Fluorinated liquid crystals [6-10] have gradually aroused the interest of the researchers for the special physicochemical properties. In previous study [8], the symmetric and non-symmetric fluorinated liquid crystal (LC) dimer containing chiral core display smectic phases. This may be due to the strong molecular interaction force. In this study, the four non-symmetric dimers were synthesized to find appropriate structure for preparing fluorinated cholesteric LCs. The effect of the terminal structure on the properties of fluorinated dimers is discussed.

2. Synthesis
The synthesis of liquid crystal (LC) the dimers is shown in Scheme 1. The synthesis of FA-PD-UBA was synthesized according to Ref. [8]. The synthesis of FA-PD-PBA, FA-PD-ABA and FA-PD-BA was similar. The synthesis of FA-PD-ABA is shown below.

A solution of ABA (17.819 g, 0.1 mol), DCC (20.06 g, 0.1 mol), DMAP (12.22 g, 0.1 mol), 20 mL pyridine and 140 mL THF were put into the flask. The THF solution of FA-PD (44.4 g, 0.1 mol) was put
into the solution of ABA slowly. The solution was stirred at room temperature for 2 h and heated to 45 °C until the reaction is complete. Reaction mixture was filtered to remove N,N' -dicyclohexylurea (DCU). The filtrate was concentrated, put into water and neutralized. The white product powder was obtained by filtration and recrystallisation. Yield: 50.0%. m.p.: 110.0 °C

FA-PD-ABA: Infrared spectroscopy (IR) (KBr, cm⁻¹): 2975-2854 (-CH₃, -CH₂-), 1747, 1711 (C=O), 1642 (C=C), 1601, 1495 (Ar).

1H NMR (CDCl₃, d, ppm): 1.457-1.470 (m, 3H, -CH₃), 4.407-4.689 (m, 5H, -CH₂-, -CH-), 5.347-5.364 (d, J=10.20 Hz, 1H, CH₂=CHCH₂O), 5.446-5.477(d, J=18.60 Hz, 1H, CH₂=CHCH₂O), 6.050-6.123 (m, 1H, CH₂=CHCH₂O), 6.895-6.911 (m, 2H, Ar-H), 7.254-7.261 (m, 2H, Ar-H), 7.337-7.356 (m, 2H, Ar-H), 7.677-7.721 (m, 4H, Ar-H), 7.809-7.826 (m, 2H, Ar-H), 8.111-8.155 (m, 2H, Ar-H), 8.351-8.361 (m, 2H, Ar-H).

FA-PD-UBA: All data of FA-PD-UBA can be seen in [8].

FA-PD-PBA: All data of FA-PD-UBA can be seen in [11].

FA-PD-BA: Yield: 41.0%, m.p.: 154.9 °C.

Infrared spectroscopy (IR) (KBr, cm⁻¹): 2984-2898 (-CH₃, -CH₂-), 1741, 1722 (C=O), 1601, 1410 (Ar), 1412-1326 (C-F).

1H NMR (CDCl₃, d, ppm): 1.502-1.513 (d, J = 6.60 Hz, 3H, -CH₃), 4.512-4.573 (m, 2H, -CH₂-), 5.571-5.599 (m, 1H, -CH-), 7.332-7.347 (d, J = 9.00 Hz, 2H, Ar-H), 7.443-7.468 (t, J = 7.20 Hz, 2H, Ar-H), 7.561-7.568 (t, J = 7.20 Hz, 1H, Ar-H), 7.649-7.695 (dd, 4H, J₁ = 19.20 Hz, J₂ = 8.40 Hz, Ar-H), 7.805-7.819 (d, J = 8.40 Hz, 2H, Ar-H), 8.072-8.122 (m, 4H, Ar-H), 8.348-8.361 (d, J = 7.80 Hz, 2H, Ar-H).

3. Results and discussion

3.1. Thermal analysis. The LC performances of FA-PD-UBA, FA-PD-PBA, FA-PD-ABA and
FA-PD-BA were characterized using DSC, POM and XRD. The thermal performance data are summarized in Table 1. The results of DSC, POM and XRD are shown in Figure 1-3, respectively.

![Figure 1](image1.png)

**Figure 1.** Thermal analysis results: (a) FA-PD-UBA; (b) FA-PD-PBA; (c) FA-PD-ABA; (d) FA-PD-BA.

For FA-PD-UBA, FA-PD-PBA, FA-PD-ABA and FA-PD-BA, they have the same rigidity group, but the terminal flexible chains are different. In general, the flexibility of the molecule decreases with the length of terminal flexible chain decreasing, resulting the melting temperature increasing. For FA-PD-UBA, FA-PD-ABA and FA-PD-BA, the melting temperature increases from 90.6 °C to 110.0 °C to 154.9 °C with the length of the terminal flexible decreasing, while the mesomorphic region decreased (as shown in Table 1)

FA-PD-PBA and FA-PD-ABA displayed different thermal properties, although they have the similar terminal flexible chains which the only difference is the structure of the terminal bond. The terminal bond of non-fluorinated unit of FA-PD-PBA is C-C, while that of FA-PD-ABA is C=C. The melting point of FA-PD-ABA is lower than that of FA-PD-PBA because isolated double bond may decrease the rigidity of the molecule.

These results indicated that the structure of the terminal group played important roles on the performance of the target products.
Table 1. List of performance of target products.
*The transition temperature obtained from POM; SmA*, smectic A*; N, nematic; ch, cholesteric.

| Product   | Heating/cooling | T_m/T_k (°C) | ΔH_m/ΔH_k (J·g⁻¹) | T_c/T_k (°C) | ΔH/ΔH_c (J·g⁻¹) | ΔT1 (°C) | Meso phase | SROT (°) |
|-----------|-----------------|--------------|--------------------|--------------|------------------|----------|------------|----------|
| FA-PD-UBA | Heating         | 90.6         | 6.7                | 109.0        | 1.2              | 18.4     | SmA*      | -39.9    |
|           | Cooling         | 13.4         | -2.2               | 103.2        | -1.9             | 89.8     | SmA*      |          |
| FA-PD-PBA | Heating         | 128.4        | 60.9               | 137.0        | 1.1              | 8.6      | N         |          |
|           | Cooling         | 92.2         | -36.3              | 112.6        | -1.8             | 20.4     | N         |          |
| FA-PD-ABA | Heating         | 110.0        | 55.9               | -            | -                | -        | -         | -7.3     |
|           | Cooling         | 96.0*        | -                  | 166.0        | -5.2             | 70.0     | Ch        |          |
| FA-PD-BA  | Heating         | 154.9        | 75.3               | -            | -                | -        | -         | -6.6     |
|           | Cooling         | 87.9         | -54.6              | -            | -                | -        | -         |          |

3.2. LC properties analysis. FA-PD-BA showed no texture during heating and cooling process. FA-PD-BA is a non-LC compound.

FA-PD-UBA containing ten alkyl units in the terminal group displayed chiral smectic A phase [8]. The representative texture is presented in Figure 2 (a).

FA-PD-PBA displayed typical nematic schlieren texture with twofold and fourfold brushes (as presented in Figure 2 (b)).

FA-PD-ABA displayed fan-shaped texture (Figure 2 (c)). Figure 3 is the XRD result of FA-PD-ABA. These results state that FA-PD-ABA is a cholesteric LC. FA-PD-ABA only displayed cholesteric fan-shaped texture on cooling process. Thus FA-PD-ABA is a monotropic cholesteric LC.

Figure 2. Optical textures of the target product (200×): (a) FA-PD-UBA (b) FA-PD-PBA (c) FA-PD-ABA.
In this study, short alkyl terminal chain was adopted to obtain cholesteric dimer. The shorter flexible terminal chain successfully prevented the formation of lamellar phase. FA-PD-PBA and FA-PD-ABA containing three alkyl units in the terminal group did not display lamellar phase, while exhibited nematic phase and cholesteric phase, respectively. Although FA-PD-PBA and FA-PD-ABA all have three alkyl units in the terminal group, FA-PD-PBA and FA-PD-ABA displayed different thermal properties and mesophase type, suggesting that bonding type had an obvious influence in mesomorphic behaviour. FA-PD-BA is not a LC, which indicated that flexible terminal chain was necessary to form mesophase, which played a stabilizing effect on mesophase. The results indicated that the non-symmetric structure type, which contained fluorinated mesogenic unit and non-fluorinated mesogenic unit with flexible terminal chain of appropriate length, is advantageous to form cholesteric fluorinated liquid crystals.

4. Conclusion
Four non-symmetric dimers, FA-PD-UBA, FA-PD-PBA, FA-PD-ABA and FA-PD-BA, were synthesised. The structure of terminal chain of the non-fluorinated mesogenic unit had obvious effects on not only stabilizing mesophase but also the mesophase type. The non-symmetric structure type, which contained fluorinated mesogenic group and non-fluorinated mesogenic unit with flexible terminal chain of appropriate length, may help the dimers to form cholesteric fluorinated liquid crystals.

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