Synthesis and mesogenic property of new hockey-stick-like molecules

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ABSTRACT

In this study, new hockey-stick-like molecules were synthesized and characterized. The desired bent-core molecules consist of two arms with different numbers of aromatic rings, each with its own flexible chain with a different number of carbons: one arm contains four aromatic rings and a terminal propyloxy group, and the other arm contains an aromatic ring with a terminal hexyloxy or dodecyloxy group. To improve the net dipole of the bulk state, fluorine atoms were laterally substituted onto an aromatic ring within each molecule. The structures of the obtained compounds were characterized via FTIR and NMR spectrometry and elemental analysis. Their mesomorphic properties were investigated using DSC and polarizing optical microscopy.

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1. Introduction

Bent-core liquid crystal (LC) materials have attracted the attention of many researchers of late. Typical examples of such materials are the banana-shaped LC materials [1–4]. Particularly, in contrast to the conventional chiral rod-like LC materials, bent-core LC materials possess no chiral carbon centers but can generate ferroelectric and anti-ferroelectric characteristics. Moreover, the nematic phase of the latter LC materials can be considered a candidate for the next-generation LC materials for display applications [5,6]. One of the main topics in this research field is the establishment of relationships between the structure and properties. This can be achieved, however, only after many new materials are synthesized and correlated with properties. The formation of the bent-core LC phase is affected by various factors, including the molecular size, the number of aromatic rings, the resonance and inductive effects of the substituents, the length of the terminal alkyl groups, and the angle of the bent core [7–10]. Generally, bent-core LC structures that possess lateral substituents asymmetrically show lower molecular symmetry. There have been reports on the effects of the substituents positioned on the core or terminal aromatic groups during the formation of LC phases. First, adding substituents to the core aromatic group is less effective in directing the formation of the LC phase than adding substituents to the terminal groups [11–17]. Second, when the substituents are on the terminal aromatic groups, two main factors should be considered: the substituent size and polarity for packing, and the alignment of the molecules. For instance, it was reported that fluoro-substitution on the terminal aromatic group results in the formation of a more stable nematic phase while inhibiting the formation of the smectic phase [18].

In general, the structures of the two arms of bent-core molecules are essentially the same. If the two arms of these compounds are roughly different, however, hockey-stick-like (HSL) molecules are constructed. From a structural viewpoint, HSL-LCs are among the subclasses of asymmetric bent-core LC materials, while from the perspective of their molecular structures, they lie between rod-like and banana-shaped LCs. Furthermore, the formation of HSL-LC phases with intermediate molecular structures has caught the attention of many researchers [19,20]. It was reported that HSL-LCs generally gave rise to the conventional nematic and smectic phases, and sometimes bent-core LC phases [21–24]. It was recently reported, however, that HSL-LCs can show unique LC phases, such as the anticalinic structure in the smectic C phase [25] or the uncleared LC phase showing iridescence [26]. Moreover, because the HSL-LCs have significantly different structures with varying molecular lengths from the core to the terminal groups, an HSL-LC may induce the molecular asymmetry required to generate the polar mesophase associated with spontaneous polarization [27]. In addition, the HSL-LCs have relatively low...
rotation viscosities compared to their bent-core counterparts because of their more linear structures. These characteristics of HSL-LCs render them suitable for LCD applications because the fast-response characteristic of LCD technology requires low rotation viscosity, strong spontaneous polarization, proper tilt angle, and dielectric anisotropy of the molecules. Research on HSL-LCs was commenced only quite recently, and thus, the relationship between the structure and property of HSL-LCs is yet to be established [28–30]. Basically, the results of this type of study can be useful in the design of LC structures for broad application within the field of display technology.

In this study, new HSL molecules were designed and synthesized. The desired molecules consist of two arms with different numbers of aromatic rings. One arm has a propyloxy end group, and the other arm has a hexyloxy or dodecyloxy end group. To improve the net dipole of the bulk state, fluorine atoms were laterally substituted onto an aromatic ring within each molecule, as shown in Figure 1. The effects of the length of the alkyl terminal groups and the polarity of the molecular structures on the formation of HSL-LC phases were also examined.

2. Experiment

2.1. Materials and instruments

All the chemicals and solvents were commercially available and were used without any purification: 3-(benzyloxy)benzoic acid, 4-(benzyloxy)phenol, benzyl bromide, anhydrous dichloromethane, 1-bromopropane, 1-bromohexane, 1-bromododecane, and magnesium sulfate were purchased from Sigma-Aldrich; 4-(benzyloxy)benzoic acid, dicyclohexylcarbodiimide (DCC), dimethylaminopyridine (DMAP), and palladium 10% on carbon (Pd/C) from TCI; 4-hydroxy-3,5-difluorobenzoic acid and pyridine were purchased from Fluorochem and Duksan Chemical Co., respectively; and tetrahydrofuran (THF), potassium carbonate (K₂CO₃), cesium carbonate (Cs₂CO₃), potassium hydroxide (KOH), ethanol, sulfuric acid (H₂SO₄), methanol, n-hexane, dichloromethane (DCM), acetone, and hydrochloric acid (HCl) were from Daejung Chemical Co. All the obtained compounds were purified via column chromatography on silica gel (0.040–0.063 mm, Merck) using DCM and hexane as the eluents. The elemental analysis was performed using a Thermo Finnigan EA1108. ¹H NMR spectra were recorded using an NMR spectrometer (Bruker Biospin/Avance III 400 MHz) to identify the chemical structure of all the intermediate compounds as well as of the final compounds. A FT/IR spectrometer (Scinco Nicolet 6700) was used to record the infrared spectra. For the ¹H NMR spectra, the chemical shifts were reported in parts per million (ppm) relative to tetramethylsilane as an internal standard. The liquid crystalline behavior and thermal properties were investigated using a polarizing optical microscope (Nikon ME600) in conjunction with a hot stage (Linkam LTS420) and differential scanning calorimetry (Netzsch DSC 200 F3). DSC measurements were performed in a N₂ atmosphere, with 10°C/min heating and cooling rates.

2.2. Synthesis

2.2.1. Synthesis of compound 1
Sulfuric acid (3 mL) was added dropwise to a solution of 4-hydroxy-3,5-difluorobenzoic acid (10.0 g, 57.4 mmol) in methanol (50 mL) at room temperature. Then the mixture was stirred at 70°C for 24 h. The reaction mixture was concentrated under reduced pressure and was poured into water (200 mL). The crude product was filtered to yield white solid. Yield: 76.8%; IR (KBr pellet, cm⁻¹): 3221 (O–H stretch), 1701 (conjugated C=O stretch), 1611, 1457 (aromatic C=C), 1332 (–CH₃CH₃ bend), 1243, 1192 (C–O stretch), 1135, 1123 (C–F stretch); ¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.61–7.59 (m, 2H, Ar–H), 3.89 (s, 3H, OCH₃).

2.2.2. Synthesis of compound 2a
1-Bromohexane (1.17 mL, 8.36 mmol) was added dropwise to a solution of compound 1 (1.57 g, 8.36 mmol) and cesium carbonate (4.57 g, 14.0 mmol) in acetone (50 mL). The mixture was stirred at 100°C for 12 h, and the reaction mixture was poured into water (200 mL). The precipitate was filtered off. The residue was purified via column chromatography on silica gel using a mixture of hexane and DCM (1:1 v/v) as the eluent. The removal of the solvent afforded a white crystalline solid. Yield: 70.0%; IR (KBr pellet, cm⁻¹): 2917 (alkene C–H stretch), 1701 (conjugated C=O stretch), 1611, 1457 (aromatic C=C), 1332 (–CH₃CH₃ bend), 1243, 1192 (C–O stretch), 1135, 1123 (C–F stretch); ¹H NMR (400 MHz, CDCl₃, δ in ppm): 7.56 (d, J = 8.0 Hz, 2H, Ar–H), 4.22 (t, J = 6.8 Hz, 2H, Ar–OCH₂–C₅H₁₁), 3.89 (d, J = 4.0 Hz, 3H, –OCH₃), 1.78-1.71 (m, 2H, Ar–OCH₂–CH₂–C₄H₉).
2.2.3. Synthesis of compound 2b

The experimental procedure was the same as described for the preparation of compound 2a. Quantities: compound 1 (1.02 g, 5.42 mmol), cesium carbonate (5.00 g, 14.2 mmol), and 1-bromododecane (1.30 mL, 5.42 mmol) in 50 mL acetonitrile. Yield: 72.1%; IR (KBr pellet, cm⁻¹): 2917 (aliphatic C–H stretch), 1701 (conj. C=O stretch), 1611, 1457 (aromatic C=C stretch), 1332 (-CH3 CH3 bend), 1243, 1192 (C–O stretch), 1135, 1123 (C–F stretch); ¹H NMR (400 MHz, CDCl3, δ in ppm): 7.56 (d, J = 8.0 Hz, 2H, Ar–H), 3.89 (t, J = 6.8 Hz, 2H, Ar–OCH2–), 1.78–1.71 (m, 2H, Ar–OCH2–CH2–), 1.44–1.41 (m, 2H, -CH2–CH3), 1.32–1.16 (m, 16H, -(CH2)8–C2H3), 0.86 (t, J = 6.4 Hz, 3H, -CH3). (KBr pellet, cm⁻¹): 2917, 2850 (aliphatic C–H stretch), 1517 (aromatic C=C stretch), 1332 (-CH3 CH3 bend), 1243, 1192 (C–O stretch), 1135, 1123 (C–F stretch); ¹H NMR (400 MHz, CDCl3, δ in ppm): 7.61 (t, J = 8.0 Hz, 2H, Ar–H), 4.27 (t, J = 6.4 Hz, 2H, Ar–OCH2–), 1.80–1.73 (m, 2H, Ar–OCH2–CH2–), 1.53–1.45 (m, 2H, -CH2–CH3), 1.32–1.30 (m, 4H, -(CH2)2–C2H3), 0.83 (t, J = 6.0 Hz, 3H, -CH3). (KBr pellet, cm⁻¹): 2917, 2850 (aliphatic C–H stretch), 1517 (aromatic C=C stretch), 1332 (-CH3 CH3 bend), 1243, 1192 (C–O stretch), 1135, 1123 (C–F stretch); ¹H NMR (400 MHz, CDCl3, δ in ppm): 7.85 (s, 1H, Ar–OH), 6.75 (d, J = 1.6 Hz, 2H, Ar–H), 3.84 (t, J = 6.8 Hz, 2H, Ar–OCH2–), 1.74–1.70 (m, 2H, Ar–OCH2–CH2–), 1.00 (t, J = 7.2 Hz, 3H, -OCH2–CH2–). (KBr pellet, cm⁻¹): 2917, 2850 (aliphatic C–H stretch), 1727 (C=O stretch), 1606, 1509 (aromatic C=C stretch), 1457 (aromatic C=C stretch), 1332 (-CH3 CH3 bend), 1243, 1192 (C–O stretch), 1135, 1123 (C–F stretch); ¹H NMR (400 MHz, CDCl3, δ in ppm): 8.0 (s, 1H, Ar–OH), 7.56 (d, J = 8.0 Hz, 2H, Ar–H), 4.45 (t, J = 6.4 Hz, 2H, Ar–OCH2–), 1.96–1.89 (m, 2H, Ar–OCH2–CH2–), 1.48–1.40 (m, 2H, -CH2–CH3), 1.32–1.30 (m, 4H, -(CH2)8–C2H3), 1.02 (t, J = 6.8 Hz, 3H, -CH3). 1-Bromopropane (5.00 mL, 55.1 mmol) was added dropwise to a mixture of 4-benzoyloxyphenol (5.00 g, 25.0 mmol) and potassium carbonate (5.00 g, 36.2 mmol) in acetonitrile (50 mL). The mixture was stirred at 100°C for 6 h, and the reaction mixture was poured into water (200 mL). The precipitate was filtered off. The residue was purified via column chromatography on silica gel using a mixture of hexane and DCM (1:1 v/v) as the eluent. The removal of the solvent afforded a white crystalline solid. Yield: 85.6%; IR (KBr pellet, cm⁻¹): 2917 (aliphatic C–H stretch), 1511 (aromatic C=C stretch), 1240 (C–O stretch); ¹H NMR (400 MHz, acetone-d₆, δ in ppm): 7.46 (t, J = 4.4 Hz, 2H, Ar–H), 7.40–7.31 (m, 3H, Ar–H), 6.93 (t, J = 2.4 Hz, 2H, Ar–H), 5.05 (s, 2H, Ar–OCH2–), 3.87 (t, J = 6.4 Hz, 2H, Ar–OCH2–), 1.78–1.70 (m, 2H, Ar–OCH2–CH2–), 1.01 (t, J = 7.2 Hz, 3H, -OCH2–CH2–).
1193 (C–O stretch); $^1$H NMR (400 MHz, CDCl$_3$, $\delta$ in ppm): 8.13 (d, $J = 6.0$ Hz, 2H, Ar–H), 7.37–7.31 (m, 5H, Ar–H), 7.10–7.01 (m, 4H, Ar–H), 6.90 (d, $J = 4.8$ Hz, 2H, Ar–H), 5.14 (s, 2H, –OCH$_2$–Ar), 3.90 (t, $J = 6.4$ Hz, 2H, Ar–OCH$_2$–), 1.84–1.75 (m, 2H, Ar–OCH$_2$–CH$_2$–), 1.02 (t, $J = 7.2$ Hz, 3H, –C$_2$H$_4$–CH$_3$).

### 2.2.9. Synthesis of compound 7

Compound 6 (1.00 g, 2.76 mmol) was dissolved in 50 mL THF, and then 10% Pd/C (0.22 g, 2.08 mmol) was added to the solution. The mixture was stirred at 70°C for 12 h in a hydrogen atmosphere until the required quantity of hydrogen was absorbed. After the reaction, the mixture was filtered off, and the filtrate was concentrated under reduced pressure. The crude product dissolved in acetone was re-precipitated from excessive hexane. The removal of the solvent afforded a white solid. Yield: 95.2%; IR (KBr pellet, cm$^{-1}$): 3367 (O–H stretch), 2916, 2850 (aliphatic C–H stretch), 1732 (conj. C=O stretch), 1606, 1514 (aromatic C=C stretch), 1280, 1194 (C–O stretch); $^1$H NMR (400 MHz, CDCl$_3$, $\delta$ in ppm): 8.30 (d, $J = 20.0$ Hz, 2H, Ar–H), 7.87 (d, $J = 2.8$ Hz, 2H, Ar–H), 7.58–7.53 (m, 7H, Ar–H), 7.45–7.42 (m, 2H, Ar–H), 7.41 (d, $J = 2.0$ Hz, 2H, Ar–H), 7.37–7.22 (m, 2H, Ar–H), 7.03–7.00 (m, 2H, Ar–H), 5.27 (s, 2H, Ar–OCH$_2$–O–), 3.99 (t, $J = 6.4$ Hz, 2H, Ar–OCH$_2$–), 1.83–1.78 (m, 2H, Ar–OCH$_2$–CH$_2$–), 1.04 (t, $J = 7.2$ Hz, 3H, –C$_2$H$_4$–CH$_3$).

### 2.2.10. Synthesis of compound 8

DCM (200 mL) was dissolved in 4-(benzylxoy)benzoic acid (1.00 g, 3.10 mmol), and then compound 7 (1.00 g, 3.67 mmol), DCC (1.00 g, 4.85 mmol), and DMAP (0.400 g, 3.28 mmol) were added to the solution. The mixture was stirred at room temperature for 24 h. After the reaction, the N,N′-dicyclohexylurea precipitate was filtered off, and the filtrate was diluted with DCM (50 mL). This solution was washed with water (3 × 100 mL) and was then dried over anhydrous MgSO$_4$. After the removal of the solvent, the residue was purified via column chromatography on silica gel using a mixture of hexane and DCM (1:1 v/v) as the eluent. The removal of the solvent afforded a white solid. Yield: 88.7%; IR (KBr pellet, cm$^{-1}$): 3069 (aromatic C–H stretch), 2920, 2850 (aliphatic C–H stretch), 1729 (conj. C=O stretch), 1603, 1511 (aromatic C=C stretch), 1277, 1194 (C–O stretch); $^1$H NMR (400 MHz, CDCl$_3$, $\delta$ in ppm): 8.30 (d, $J = 20.0$ Hz, 2H, Ar–H), 8.15 (d, $J = 20.0$ Hz, 2H, Ar–H), 7.38–7.32 (m, 7H, Ar–H), 7.12–7.04 (m, 4H, Ar–H), 6.94–6.90 (m, 2H, Ar–H), 5.16 (s, 2H, Ar–CH$_2$–O–Ar), 3.90 (t, $J = 2.4$ Hz, 2H, Ar–OCH$_2$–), 1.85–1.76 (m, 2H, Ar–CH$_2$–CH$_2$–), 1.03 (t, $J = 7.2$ Hz, 3H, –C$_2$H$_4$–CH$_3$).

### 2.2.11. Synthesis of compound 9

Compound 8 (1.00 g, 2.07 mmol) was dissolved in 50 mL THF, and then 10% Pd/C (0.22 g, 2.08 mmol) was added to the solution. The mixture was stirred at 70°C for 12 h in a hydrogen atmosphere until the required quantity of hydrogen was absorbed. After the reaction, the mixture was filtered off, and the filtrate was concentrated under reduced pressure. The crude product dissolved in acetone was re-precipitated from excessive hexane. The removal of the solvent afforded a white solid. Yield: 91.8%; IR (KBr pellet, cm$^{-1}$): 3367 (O–H stretch), 2917, 2850 (aliphatic C–H stretch), 1732 (conj. C=O stretch), 1606, 1514 (aromatic C=C stretch), 1280, 1194 (C–O stretch); $^1$H NMR (400 MHz, CDCl$_3$, $\delta$ in ppm): 8.13 (d, $J = 6.4$ Hz, 2H, Ar–H), 7.47–7.42 (m, 7H, Ar–H), 7.38–7.32 (m, 5H, Ar–H), 7.12–7.04 (m, 4H, Ar–H), 6.94–6.90 (m, 2H, Ar–H), 5.16 (s, 2H, Ar–CH$_2$–O–Ar), 3.90 (t, $J = 2.4$ Hz, 2H, Ar–OCH$_2$–), 1.85–1.76 (m, 2H, Ar–CH$_2$–CH$_2$–), 1.03 (t, $J = 7.2$ Hz, 3H, –C$_2$H$_4$–CH$_3$).

### 2.2.12. Synthesis of compound 10

3-(Benzylxoy)benzoic acid (1.00 g, 4.38 mmol) was dissolved in 200 mL DCM, and then compound 9 (1.00 g, 2.62 mmol), DCC (1.00 g, 4.85 mmol), and DMAP (0.400 g, 3.28 mmol) were added to the solution. The mixture was stirred at room temperature for 24 h. After the reaction, the N,N′-dicyclohexylurea precipitate was filtered off, and the filtrate was diluted with DCM (50 mL). This solution was washed with water (3 × 100 mL) and was then dried over anhydrous MgSO$_4$. After the removal of the solvent, the residue was purified via column chromatography on silica gel using a mixture of hexane and DCM (1:1 v/v) as the eluent. The removal of the solvent afforded a white solid. Yield: 88.7%; IR (KBr pellet, cm$^{-1}$): 3069 (aromatic C–H stretch), 2920, 2850 (aliphatic C–H stretch), 1729 (conj. C=O stretch), 1603, 1511 (aromatic C=C stretch), 1277, 1194 (C–O stretch); $^1$H NMR (400 MHz, acetone-d$_6$, $\delta$ in ppm): 8.25–8.21 (m, 4H, Ar–H), 7.87 (d, $J = 2.2$ Hz, 2H, Ar–H), 7.58–7.53 (m, 7H, Ar–H), 7.45–7.42 (m, 2H, Ar–H), 7.41 (d, $J = 2.0$ Hz, 2H, Ar–H), 7.37–7.22 (m, 2H, Ar–H), 7.03–7.00 (m, 2H, Ar–H), 5.27 (s, 2H, Ar–CH$_2$–O–), 3.99 (t, $J = 6.4$ Hz, 2H, Ar–OCH$_2$–), 1.83–1.78 (m, 2H, Ar–OCH$_2$–CH$_2$–), 1.04 (t, $J = 7.2$ Hz, 3H, –C$_2$H$_4$–CH$_3$).

### 2.2.13. Synthesis of compound 11

Compound 10 (1.00 g, 1.95 mmol) was dissolved in 50 mL THF, and then 10% Pd/C (0.22 g, 2.08 mmol) was added to the solution. The mixture was stirred at 70°C for 12 h in a hydrogen atmosphere until the required quantity of hydrogen was absorbed. After the
reaction, the mixture was filtered off, and the filtrate was concentrated under reduced pressure. The crude product dissolved in acetone was re-precipitated from excessive hexane. The removal of the solvent afforded a white solid. Yield: 95.2%; IR (KBr pellet, cm\(^{-1}\)): 3369 (O–H stretch), 3065 (aromatic C–H stretch), 2917, 2850 (aliphatic C–H stretch), 1739 (conj. C=O stretch), 1603, 1514 (aromatic C=C stretch), 1283, 1207 (C=O stretch); \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\) in ppm): 8.30–8.26 (m, 4H, Ar–H), 7.80 (d, \(J = 8.00\) Hz, 1H, Ar–H), 7.65 (s, 1H, Ar–H), 7.42–7.35 (m, 5H, Ar–H), 6.93 (d, \(J = 8.00\) Hz, 2H, Ar–H), 5.28 (s, 1H, Ar–OH), 3.92 (t, \(J = 6.4\) Hz, 2H, Ar–OCH\(_2\)–), 1.83–1.78 (m, 2H, Ar–OCH\(_2\)–CH\(_2\)–), 1.03 (t, \(J = 7.2\) Hz, 3H, –C\(_2\)H\(_4\)–CH\(_3\)).

2.2.14. Synthesis of compound 12a
3,5-Difluoro-4-(hexyloxy)benzoic acid (0.800 g, 3.10 mmol) was dissolved in 200 mL DCM, and then compound 11 (0.80 g, 3.10 mmol), \(N,N'\)-dicyclohexyl carbodiimide (DCC) (1.00 g, 4.85 mmol), and 4-dimethylaminopyridine (DMAP) (0.400 g, 3.28 mmol) were added to the solution. The mixture was stirred at room temperature for 24 h. After the reaction, the \(N,N'\)-dicyclohexylurea precipitate was filtered off, and the filtrate was diluted with DCM (50 mL). This solution was washed with water (3 × 100 mL) and was then dried over anhydrous MgSO\(_4\). After the removal of the solvent, the residue was purified via column chromatography on silica gel using a mixture of hexane and DCM (1:1 v/v) as the eluent. The removal of the solvent afforded a white solid. Yield: 73.7%; IR (KBr pellet, cm\(^{-1}\)): 3075 (aromatic C–H stretch), 2917, 2850 (aliphatic C–H stretch), 1739 (conj. C=O stretch), 1603, 1511 (aromatic C=C stretch), 1273, 1193, 1166 (C–O, C–F stretch); \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\) in ppm): 8.31–8.26 (m, 4H, Ar–H), 8.15–8.13 (m, 1H, Ar–H), 8.05 (t, \(J = 2.0\) Hz, 1H, Ar–H), 7.75 (d, \(J = 8.00\) Hz, 2H, Ar–H), 6.82 (d, \(J = 8.00\) Hz, 2H, Ar–H), 5.28 (s, 1H, Ar–OH), 3.92 (t, \(J = 6.4\) Hz, 2H, Ar–OCH\(_2\)–CH\(_2\)–), 1.83–1.78 (m, 2H, Ar–OCH\(_2\)–CH\(_2\)–), 1.03 (t, \(J = 7.2\) Hz, 3H, –C\(_2\)H\(_4\)–CH\(_3\)).

2.2.15. Synthesis of compound 12b
The experimental procedure was the same as described for the preparation of compound 12a. Quantities: compound 11 (1.00 g, 2.92 mmol), 3,5-difluoro-4-(dodecyloxy)benzoic acid (1.00 g, 2.92 mmol), DCC (1.00 g, 4.85 mmol), and DMAP (0.400 g, 3.28 mmol) in 200 mL DCM. Yield: 78.7%; IR (KBr pellet, cm\(^{-1}\)): 3075 (aromatic C–H stretch), 2917, 2850 (aliphatic C–H stretch), 1739 (conj. C=O stretch), 1603, 1511 (aromatic C=C stretch), 1273, 1193, 1166 (C–O, C–F stretch); \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\) in ppm): 8.31–8.26 (m, 4H, Ar–H), 8.15–8.13 (m, 1H, Ar–H), 8.05 (t, \(J = 2.0\) Hz, 1H, Ar–H), 7.75 (d, \(J = 8.00\) Hz, 2H, Ar–H), 7.63–7.52 (m, 1H, Ar–H), 7.51–7.40 (m, 1H, Ar–H), 7.39–7.35 (m, 4H, Ar–H), 7.12–7.10 (m, 2H, Ar–H), 6.94–6.91 (m, 2H, Ar–H), 4.30 (t, \(J = 6.8\) Hz, 2H, Ar–OCH\(_2\)–C\(_6\)H\(_5\)), 3.92 (t, \(J = 6.8\) Hz, 2H, Ar–OCH\(_2\)–C\(_2\)H\(_5\)), 1.83–1.76 (m, 4H, Ar–OCH\(_2\)–CH\(_2\)–), 1.46 (t, \(J = 7.6\) Hz, 2H, Ar–OCH\(_2\)–CH\(_2\)–), 1.40–1.10 (m, 16H, –(CH\(_2\))\(_8\)–CH\(_3\)) 1.03 (t, \(J = 7.6\) Hz, 3H, –C\(_2\)H\(_4\)–CH\(_3\)), 0.86 (t, \(J = 6.8\) Hz, 3H, –C\(_11\)H\(_{22}\)–CH\(_3\)); Anal. Calcd for C\(_{49}\)H\(_{50}\)F\(_2\)O\(_{10}\): C 70.32, H 6.02; found: C 70.93, H 6.15.

3. Results and discussion
New HSL molecules were synthesized through the synthetic route shown in Scheme 1. To synthesize compounds 12a and 12b, compounds 3 and 11 were first synthesized. In the HSL-mesogenic unit, compound 3 formed the head of the unit with a difluorophenyl group, and compound 11 formed the body of the unit with a tri-benzyloxy group. In the synthesis of compound 3, the starting material was 4-hydroxy-3,5-difluorobenzoic acid. To prevent the reaction of the carboxyl group, it was protected through esterification. Subsequently, the alkoxy group was substituted for the p-position of difluoroaniseate through the reaction of 1-bromohexane or 1-bromododecane with the hydroxyl group via a nucleophilic substitution reaction. Finally, the carboxylic acid group was deprotected via acid hydrolysis to yield compound 3. For the synthesis of compound 11, the starting material was 4-benzylphenoxypen. First, using the nucleophilic substitution reaction, the propyloxy group was substituted for the p-position of the phenyl ring through the reaction of 1-bromopropane with the hydroxyl group. Second, two synthesis methods were mainly used: hydrogenation with palladium, with carbon as the catalyst; and Steglich esterification, with DCC as a coupling agent and DMAP (4-dimethylaminopyridine) as the catalyst. Upon reaching the target, compound 9 was reacted with 3-(benzyloxy)benzoic acid to yield compound 10, which had a bent-core structure. Finally, hydrogenation was carried out to obtain compound 11, which reacted with compound 3 through the DCC method to yield compound 12, the desired molecule in this study.

Figure 2 displays the DSC thermograms of the two compounds at the first heating, first cooling, and second heating runs. The transition temperatures and enthalpy...
Scheme 1. Synthetic route to hockey-stick-like molecules.

Figure 2. DSC thermograms of compounds 12a (a) and 12b (b) (heating and cooling rate: 10°/min).
Table 1. Transition temperatures (°C) and enthalpy changes (kJ/mol).

| Compound | DSC scan | $T_{s,k}$ | $\Delta H_{s,k}$ | $T_{m}$ | $\Delta H_{m}$ | $T_{c}$ | $\Delta H_{c}$ | $T_{i}$ | $\Delta H_{i}$ |
|----------|----------|-----------|-----------------|--------|----------------|--------|----------------|--------|----------------|
| 12a ($n = 6$) | 1-h | 106, 113, 122 | 6.7 | 158 | 27.3 | 128 | 25.6 | 162 | 0.9 |
| | 1-c | 95, 110 | 7.3 | 157 | 19.9 | – | – | – | – |
| | 2-h | 104, 112, 122 | 6.4 | 157 | 19.9 | 168 | 1.1 | 171 | 1.0 |
| 12b ($n = 12$) | 1-h | 112 | 4.5 | 155 | 40.2 | – | – | – | – |
| | 1-c | 105 | 5.7 | 135 | 32.3 | 142 | 1.4 | – | – |
| | 2-h | 111 | 6.0 | 154 | 29.5 | – | – | – | – |

*Abbreviations: 1-h: first heating; 1-c: first cooling; 2-h: second heating.

*Solid-to-solid transition temperature.

*Crystallization temperature.

changes for compounds 12a and 12b are given in Table 1. Interestingly, in the heating and cooling DSC cycles, these two compounds showed multiple melting phenomena. Generally, three types of transitions can be defined: the solid-to-solid, melting, and isotropization transitions. On the first heating, compound 12a showed solid–solid transitions at 106°C, 113°C, and 122°C, melting at 158°C, and isotropization at 162°C. Successively, on cooling, it exhibited isotropization at 168°C and crystallization at 128°C, 110°C, and 95°C. On the first heating, compound 12b showed a solid–solid transition at 112°C and melting at 155°C, but no isotropization. On cooling, it exhibited isotropization at 142°C and crystallization at 135°C and 105°C. On the second heating, compound 12a had solid–solid transitions at 104°C, 112°C, and 122°C, melting at 157°C, and isotropization at 171°C. On the second heating, compound 12b had a solid–solid transition at 111°C and melting at 154°C. This indicates that most of the transitions were reversible both in the heating and cooling DSC cycles, whereas exceptionally the isotropization for compound 12b was observed only in the cooling DSC cycle. Accordingly, compound 12a was an enantiotropic LC, whereas compound 12b was determined to be a monotropic LC. It seems that, apparently, most of the transition behaviors hardly depended on the thermal treatment condition. Nevertheless, practically all the enthalpy changes for the melting transitions were affected by the DSC scan cycle. As given in Table 1, on the first

Figure 3. Cross-polarizing optical micrographs of compound 12a (magnification ×200): (a) on cooling at 164°C; (b) on cooling at 120°C; (c) on heating at 163°C; and (d) on heating at 121°C.
heating, the melting endotherms ($\Delta H_m$) for compounds 12a and 12b were about four or nine times higher than the endotherms for the solid–solid transition ($\Delta H_{k-k}$), respectively. Then the exotherms for the crystallization ($\Delta H_c$) of compounds 12a and 12b were about 3.5 or 5.6 times higher than the exotherms for the solid–solid transition ($\Delta H_{k-k}$), respectively. Finally, on the second heating, the $\Delta H_{mfs}$ for compounds 12a and 12b were about 3 or 5 times higher than the $\Delta H_{k-k}$s, respectively. In contrast, the enthalpy changes for isotropization ($\Delta H_i$) were scarcely affected by the DSC scan cycles. In addition, the $\Delta H_s$ for compounds 12a and 12b were not much different. This result supports the conclusion that compounds 12a and 12b formed a mesophase with similar thermal stability both in the heating and cooling DCS cycles.

The LC phases formed by the compounds were investigated via cross-polarizing optical microscopy. The textures that occurred at the transition temperatures determined via DSC analysis were observed. The transition temperatures were in accordance with the DSC data. Figures 3 and 4 show the cross-polarizing optical micrographs of compounds 12a and 12b obtained during the heating and cooling runs. Compound 12a showed a Schlieren texture for the nematic phase on heating at 163°C and on cooling at 164°C (Figure 3(a, c)), while on heating at 121°C and cooling at 120°C, the textures for the solid state were observed (Figure 3(b, d)). Compound 12b showed a crystalline texture on heating (Figure 4(b)) and an unknown texture on cooling, suggesting the occurrence of a smectic phase (Figure 4(a)). Accordingly, compounds 12a and 12b were determined to be a nematogen and a smectogen, respectively. Due to the low fluidity of the texture that occurred at a very short temperature range, however, to confirm the smectic mesophase, a follow-up study may be required.

In conclusion, two new HSL molecules were successfully designed and synthesized. The molecular structures of these two compounds were identified via FTIR and $^1$H NMR spectroscopy and elemental analysis. The results are in accordance with the expected molecular formula of the compounds. Compound 12a, with $n = 6$, had an enantiotropic LC structure showing an optical texture consistent with a nematic mesophase on heating and cooling. Compound 12b, with $n = 12$, had a monotropic LC optical structure showing an unknown texture probably for a smectic mesophase. Compound 12a had a propyloxy group at one end of the molecule and a hexyloxy group at the other end, while compound 12b had a propyloxy group at one terminal and a dodecyloxy group at the other. As shown in Figure 5, the results of this study suggest that compounds can show different characteristics and orientations depending on whether there is a hexyloxy or dodecyloxy group at the ends of the molecules. As the end groups in compound 12a were relatively short, a roughly asymmetrical bent-core mesogen and a hockey-stick-shaped molecule can have beneficial orienting roles. In the case of compound 12b, the difference in the lengths of the two flexible terminal chains is extremely large, and therefore a molecular orientation reduction may be induced due to the severely low interaction between the aromatic and aliphatic moieties. This was also attributed to the significant asymmetrical bent-core mesogenic structures or the so-called ‘HSL mesogens.’ In short, for the compounds with an HSL mesogen (i.e. significantly asymmetrical bent-core compounds whose two arms have different lengths), small differences in the lengths of the flexible, terminal chains were more favorable for mesophase formation than large differences. It was not clear from this study, however, how important the role of the fluorine substituents was in the formation of the mesophases. Also, it is not clear if these findings are applicable to all HSL molecule cases. Further
studies are therefore required to make firm conclusions about this.

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