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Synthesis of fluorinated terphenyl liquid crystals with 3-propylcyclopentane end group

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Synthesis of fluorinated terphenyl liquid crystals with 3-propylcyclopentane end group

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High performance liquid crystal (LC) displays require nematic mixtures with low rotational viscosity to reduce the response time and large dielectric anisotropy to reduce the threshold voltage. Furthermore, liquid crystals (LCs) with low melting temperature and high clearing temperature are particularly attractive for automobile and outdoor display applications. In this article, we report a series of new fluorinated terphenyl LCs with 3-alkylcyclopentane end group. The terphenyl mesogen is designed for high Δn value, and the lateral fluorine atom is used to reduce the melting temperature. In comparison with the terphenyl analogue containing a 4-alkylcyclohexyl end group, discussed in previous works, the obtained LCs show wider nematic temperature range and smaller rotational viscosity because 3-alkylcyclopentyl moiety is introduced. The effect of alkyl chain length and the lateral fluoro substituent on the mesomorphic properties of the obtained LC is discussed. The results show that the nematic temperature range increases with the alkyl chain length increase. The position of the lateral fluoro substituent also plays an important role; LC with the fluoro substitution on the central benzene ring provides the widest nematic temperature range. In conclusion, we have synthesised a new series of LCs with low melting point, wider nematic temperature range and high Δn value, which is promising in formulating eutectic mixture for display application.

Keywords: terphenyl liquid crystals; cyclopentyl end group; fluoro substituent; birefringence

1. Introduction

Wide mesophase range nematic liquid crystal (LC) with high birefringence (Δn) and low rotational viscosity are attractive materials for applications in reflective LC displays,[1,2] infrared spatial light modulators,[3] polymer-dispersed liquid crystals,[4] cholesteric LCDs,[5] holographic switching devices,[6] polarisers and directional reflectors [7] and laser beam steering.[8] High-Δn LCs can be achieved effectively by extending the conjugated π-bonding length of the molecule [9] by introducing multiple bonds or unsaturated (phenyl) rings,[10] such as diphenyldiacetylene,[11–13] tolane,[14] bistolane,[15–20] naphthalene tolanes,[21] thiophenyldiacetylene [22,23] and diacetylene systems.[24] However, the LC compounds containing highly conjugated double-bond and triple-bond units suffer from photo and thermal stabilities.[25] Therefore, phenyl ring serves as a more suitable building block for the highly conjugated for LCs for display application. The terphenyl mesogen aids in increasing Δn values because of its long molecular conjugation length. Nevertheless, as the molecular conjugation length increases, the melting point of the material also increases. Moreover, high birefringence LCs often exhibit high viscosity due to the increase of the moment of inertia.[1]

How to lower the melting temperatures and viscosities of these compounds is a major challenge. One approach to lower the melting point of a high Δn liquid crystal is to introduce a lateral alkyl group [1,15,26–29] or fluorine atom [25,26,28–30] onto its mesogenic core. We chose fluorine atom as the lateral substituent in this series because it not only lowers the melting point but also decreases the smectic tendency of LCs.[31] The other approach to lower the viscosity is to replace the flexible alkyl end group with 4-alkylcyclopentyl group on the mesogen. 4-Alkylcyclohexane end group has been proved to provide various impressive liquid crystalline properties such as low viscosity, good solubility and wide mesophase range.[32,33] Compared to abundant researches concerning cyclohexane, cyclopentane relatively remains unexplored.

There are several examples in the literature [33–36] to replace the cyclohexyl terminal group with cyclopentyl group. The obtained LCs show much lower melting temperatures and viscosities. In this article, we report the synthesis of fluorinated terphenyl LCs with 3-alkylcyclopantyl terminal group. The mesomorphic properties as well as optical anisotropies of the synthesised LCs are discussed. The general structure of the compounds is given in Figure 1. In this study, n was limited to 2–5 for low viscosity consideration.

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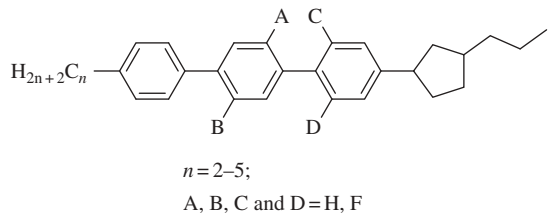


Figure 1. Chemical structure of fluorinated terphenyl liquid crystals.

transitions and thermodynamic parameters were measured by a TA Q200 differential scanning calorimeter (DSC), and thermogravimetric analysis was recorded on a Perkin Elmer Pyris under nitrogen atmosphere at a heating rate of 10°C min^{-1}. A Carl Zeiss Axiophot polarising optical microscope (POM) equipped with a Mettler FP 82 hot stage and a FP 80 central processor was used to observe the thermal transitions and analyse the anisotropic textures.

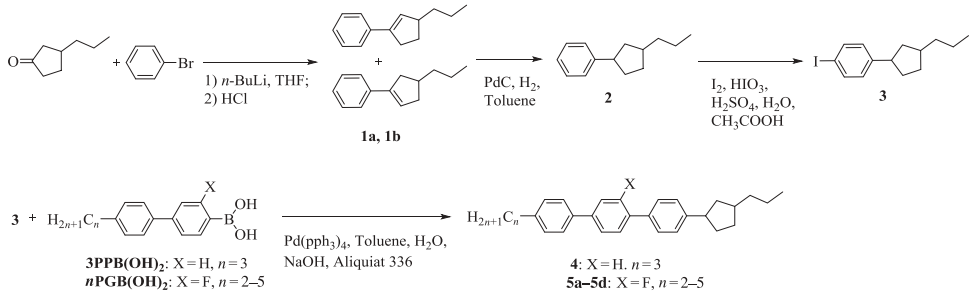
2. Experimental section

2.1 General measurement and characterisation

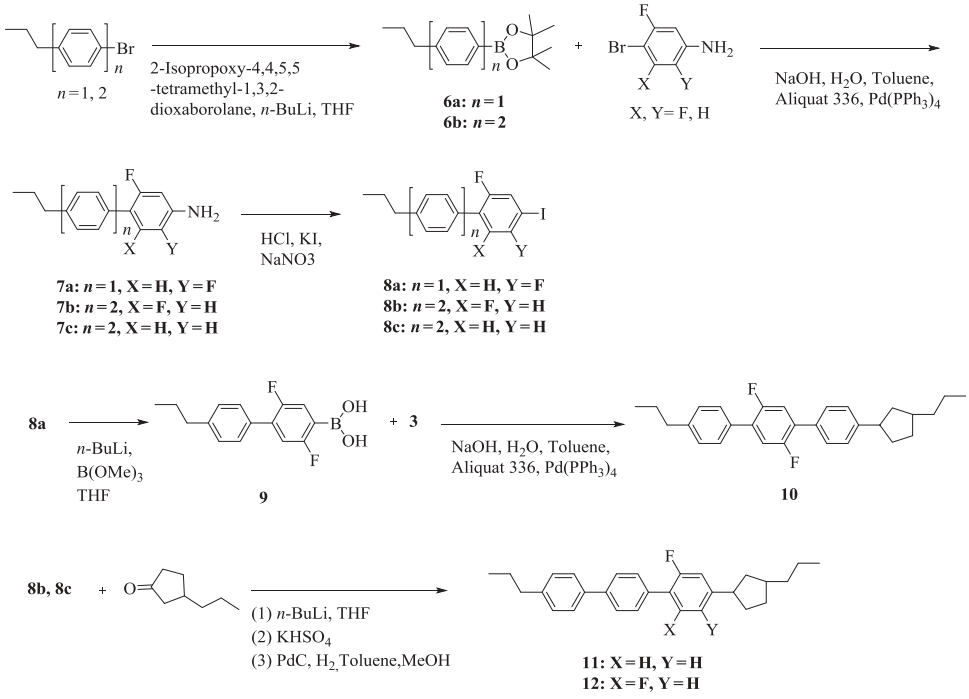
All chemicals were purchased from Aldrich or Acros and used as such unless otherwise specified. ^{1}H NMR spectra were measured using a Varian 300-MHz instrument spectrometer. Thermal

2.2 Synthetic procedures

Scheme 1 outlines the synthesis of 4-(4-propylphenyl)-4′-(3-propylcyclopentyl)-biphenyl (**4**) and 4-(4-alkylphenyl)-2-fluoro-4′-(3-propylcyclopentyl)-biphenyl (**5a–5d**), and Scheme 2 outlines the synthesis of



Scheme 1. The synthesis of compounds **4** (X = H, *n* = 3) and **5a–5d** (X = F, *n* = 2–5).



Scheme 2. The synthesis of compounds **10, 11** and **12.**

4-(4-propylphenyl)-2,5-difluoro-4′-(3-propylcyclopentyl)biphenyl (**10**), 4-(4-propylphenyl)-2′-fluoro-4′-(3-propylcyclopentyl)biphenyl (**11**) and 4-(4-propylphenyl)-2′,6′-difluoro-4′-(3-propylcyclopentyl)biphenyl (**12**).

*2.2.1 (3-propylcyclopent-1-enyl)benzene (**1a**) and (4-propylcyclopent-1-enyl)benzene (**1b**)*

Bromobenzene (3.73 g, 23.7 mmol) was dissolved in dry tetrahydrofuran (THF) and cooled to −78°C. A measure of 2.5 M n-butyl lithium (12.36 mL) was added to the mixture and stirred for 1 h at −78°C. 3-Propylcyclopentanone (3 g, 23.7 mmol) was then added to the reaction mixture and stirred for 1 h. The mixture was allowed to stir at room temperature for another hour. After the solvent was removed, the residue was washed twice with brine. The organic layer was dried with anhydrous magnesium sulphate and then the solvent was removed to obtain the crude product. Without further purification, the crude product was washed twice with brine and twice with 1 M hydrochloric acid (10 mL). The organic layer was dried with anhydrous magnesium sulphate. After the solvent was removed, the crude product was purified by column chromatography (silica gel, hexane as eluent) to yield 3.0 g (67%) of a white solid. The product was a mixture of compounds **1a** and **1b**. ^{1}H NMR($CDCl_3$, 400 MHz, ppm): δ 0.94 (t, J = 6.8 Hz, 3H, –CH_3), 1.30–1.62 (m, 4H, –CH_2CH_2–), 2.15–2.88 (m, 5H, C_3–H, C_4–H, C_5–H), 6.12 (t, J = 2 Hz, –C = CH– of **1b**), 6.15 (d, J = 2 Hz, –C = CH– of **1a**), 7.21 (t, J = 7.4 Hz, 1H, aromatic proton), 7.29 (t, J = 10 Hz, 2H, aromatic protons), 7.42–7.45 (m. 2H, aromatic protons). MS (EI, $C_{14}H_{18}$): calcd 186.14; found 186.30. HRMS (EI, $C_{14}H_{18}$): calcd 186.1409; found 186.1405.

*2.2.2 1-(3-propylcyclopentyl)benzene (**2**)*

A mixture of (3-propylcyclopent-1-enyl)benzene (**1a**) and (4-propylcyclopent-1-enyl)benzene (**1b**) (3.00 g, 16.10 mmol) was dissolved in a mixed solvent of methanol (50 mL) and toluene (20 mL). A measure of 10% Pd/C (30 mg) was then added. The mixture was stirred for 16 h at room temperature under H_2 atmosphere. The mixture was filtered to remove Pd/C. The solvent was removed under reduced pressure to obtain a colourless liquid (2.80 g) (92%). ^{1}H NMR($CDCl_3$, 400 MHz, ppm): δ 0.91 (t, J = 6.8 Hz, 3H, –CH_3), 1.28–1.43 (m, 5H, –CH_2CH_2CH–), 1.56–2.22 (m, 6H, C_2–H, C_4–H, C_5–H), 2.98–3.12 (m, 1H, Ph–CH–), 7.14–7.18 (m, 1H, aromatic proton), 7.23–7.30 (m, 4H, aromatic protons). ^{13}C NMR($CDCl_3$, 100 MHz, ppm): δ 14.35, 21.63, 21.72, 31.93, 33.36, 33.45, 35.12, 38.85, 39.03, 39.28, 39.92, 40.51, 42.26, 44.47, 45.85, 125.63, 127.00, 128.19, 146.49. MS (EI, $C_{14}H_{20}$): calcd, 188.16; found, 186.2. HRMS (EI, $C_{14}H_{20}$): calcd, 188.1565; found, 186.1560.

*2.2.3 1-iodo-4-(3-propylcyclopentyl)benzene (**3**)*

1-(3-Propylcyclopentyl)benzene (**2**) (2.80 g, 14.86 mmol) was dissolved in acetic acid (50 mL). A mixture of iodine (1.88 g, 7.40 mmol), iodic acid (0.88 g, 5.00 mmol), sulphuric acid (5 mL) and distilled water (10 mL) was added. The obtained solution was heated to 90°C and stirred for 16 h. After the mixture cooled to room temperature, 1 M sodium thiosulphate was added. Then, the solvent was removed and the residue was washed twice with brine and twice with distilled water. The organic layer was dried with anhydrous magnesium sulphate and then the solvent was removed to obtain the crude product. Further purification was performed using column chromatography to obtain a colourless liquid (4.50 g) (96%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.87–0.97 (m, 3H, –CH_3), 1.09–1.48 (m, 5H, –CH_2CH_2CH–), 1.56–2.24 (m, 6H, C_2–H, C_4–H, C_5–H), 2.89–3.02 (m, 1H, Ph–CH–), 6.89 (d, J = 8.1 Hz, 2H, aromatic protons), 7.57 (d, J = 8.1 Hz, 2H, aromatic protons). MS (EI, $C_{14}H_{19}I$): calcd, 314.05; found, 314.2. HRMS (EI, $C_{14}H_{19}I$): calcd, 314.0531; found, 314.0533.

*2.2.4 4-(4-propylphenyl)-4′-(3-propylcyclopentyl)-biphenyl (**4**), 4-(4-ethyllphenyl)-2-fluoro-4′-(3-propylcyclopentyl)biphenyl (**5a**), 4-(4-propylphenyl)-2-fluoro-4′-(3-propylcyclopentyl)biphenyl (**5b**), 4-(4-butylphenyl)-2-fluoro-4′-(3-propylcyclopentyl) biphenyl (**5c**) and 4-(4-pentylphenyl)-2-fluoro-4′-(3-propylcyclopentyl)biphenyl (**5d**)*

The methods for preparing compounds **4** and **5a–5d** are similar. The synthesis of compound **5a** is described as follows. To a 250-mL round-bottom flask, compound **3** (1 g, 3.2 mmol), (4′-ethyl-3-fluoro-[1,1′-biphenyl]-4-yl)boronic acid (2PGB$(OH)_2$) (0.8 g, 3.2 mmol), tetrakis(triphenylphospine)palladium(0) (0.1 g, 0.1 mmol), sodium hydroxide (0.4 g, 9.6 mmol), Aliquat 336 (0.1 mL), degassed toluene (50 mL) and degassed H_2O (10 mL) were added. The mixture was heated to 90°C under argon gas for 16 h. After cooling to room temperature, the mixture was washed twice with brine. The organic layer was dried with anhydrous magnesium sulphate. After the solvent was removed, the crude product was purified by column chromatography (silica gel, hexane as eluent) to yield 0.83 g (66%) of white crystals. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.89–0.94 (m, 3H, –CH_3 on 3-propylcyclopentyl), 1.25–1.39 (m, 8H, –CH_2CH_2CH– on 3-propylcyclopentyl protons and –

CH_3 on ethyl chain), 1.63–2.25 (m, 6H, cyclopentyl protons), 2.65 (q, J = 7.5 Hz, 2H, –$PhCH_2$–), 3.03–3.15 (m, 1H, –PhCH–), 7.28–2.54 (m, 11H, aromatic protons). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 14.37, 15.53, 21.75, 28.53, 31.97, 33.39, 39.09, 39.97, 42.29, 45.65, 114.21, 114.45, 122.65, 122.68, 126.85, 127.19, 128.43, 128.75, 128.78, 130.79, 130.83, 132.92, 141.91, 146.09. MS (EI, $C_{28}H_{31}F$): calcd, 386.24; found, 386.3. HRMS (EI, $C_{28}H_{31}F$): calcd 386.2410; found 386.2415.

Compound **4** yielded 36%. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.90–1.03 (m, 6H, –CH_3 on propyl terminal chain and –CH_3 on 3-cyclopentyl), 1.25–1.46 (m, 6H, 3-propylcyclopentyl protons), 1.61–1.79 (m, 3H, 3-propylcyclopentyl proton and –CH_2– on propyl terminal chain), 1.83–2.27 (m, 4H, cyclopentyl protons), 2.64 (t, J = 7.2 Hz, 2H, –$PhCH_2$–), 3.04–3.17 (m, 1H, –PhCH–), 7.26 (d, J = 5.6 Hz, 2H, aromatic protons), 7.32 (d, J = 7.2 Hz, 2H, aromatic protons), 7.55 (d, J = 7.6 Hz, 4H, aromatic protons), 7.64 (s, 4H, aromatic protons). MS (EI, $C_{29}H_{34}$): calcd, 382.26; found, 382.3.

Compound **5b** yielded 66%. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.89–1.00 (m, 6H, –CH_3 on propyl terminal chain and –CH_3 on 3-propylcyclopentyl), 1.35–1.39 (m, 6H, 3-propylcyclopentyl protons), 1.65–1.72 (m, 3H, 3-propylcyclopentyl protons and –CH_2CH_3), 1.89–2.25 (m, 4H, 3-propylcyclopentyl protons), 2.64 (t, J = 7.3 Hz, 2H, –$PhCH_2$–), 3.08–3.11 (m, 1H, –PhCH–), 7.28–7.55 (m, 11H, aromatic protons). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 13.85, 14.35, 21.73, 24.50, 31.95, 33.37, 37.68, 38.84, 39.95, 42.27, 45.63, 144.19, 114.42, 122.62, 122.65, 126.73, 127.17, 128.74, 128.77, 129.01, 130.76, 130.81, 132.90, 142.50, 146.08. MS (EI, $C_{29}H_{33}F$): calcd, 400.26; found, 400.5. HRMS (EI, $C_{29}H_{33}F$): calcd 400.2566; found 400.2564.

Compound **5c** yielded 36%. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.88–0.97 (m, 6H, –CH_3 on butyl terminal chain and –CH_3 on 3-propylcyclopentyl), 1.21–1.46 (m, 8H, 3-propylcyclopentyl protons), 1.60–2.25 (m, 7H, 3-propylcyclopentyl protons and –CH_2CH_2–), 2.66 (t, J = 7.2 Hz, 2H, –$PhCH_2$–), 3.03–3.15 (m, 1H, –PhCH–), 7.28–2.54 (m, 11H, aromatic protons). MS (EI, $C_{30}H_{35}F$): calcd, 414.27; found, 414.5. HRMS (EI, $C_{30}H_{35}F$): calcd, 414.2723; found, 414.2717.

Compound **5d** yielded 40%. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.89–0.94 (m, 6H, –CH_3 on propyl terminal chain and –CH_3 on 3-propylcyclopentyl), 1.25–1.41 (m, 10H, 3-propylcyclopentyl protons –$CH_2CH_2CH_3$), 1.63–1.75 (m, 3H, 3-propylcyclopentyl protons and –$CH_2CH_2CH_2CH_3$), 1.97–2.25 (m, 4H, 3-propylcyclopentyl protons), 2.65 (t, J = 7.4 Hz, 2H, –$PhCH_3$–), 3.03–3.15 (m, 1H, –PhCH–), 7.28–2.54 (m, 11H, aromatic protons). MS (EI, $C_{31}H_{37}F$): calcd, 428.29; found, 428. HRMS (EI, $C_{31}H_{37}F$): calcd 428.2879; found 428.2884.

*2.2.5 4,4,5,5-tetramethyl-2-(4-propylphenyl)-1,3,2-dioxaborolane (**6a**) and 4,4,5,5-tetramethyl-2-(4'-propylbiphenyl-4-yl)-1,3,2-dioxaborolane (**6b**)*

The methods for preparing compounds **6a** and **6b** are similar. The synthesis of compound **6b** is described as follows. 4-Bromo-4′-propylbiphenyl (10 g, 36.4 mmol) was dissolved in dry THF (75 mL) and cooled to −78° C. To the mixture, 2.5 M n-butyl lithium (18 mL) was added, and stirred for 1 h at −78°C. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10 mL) is added to the reaction mixture and stirred for 1 h. The mixture was stirred at room temperature for another hour, and then the solvent was removed and the residue was washed twice with brine. The organic layer was dried with anhydrous magnesium sulphate. After the solvent was removed, 9.47 g (80%) of a yellow liquid was obtained. ^1H–NMR ($CDCl_3$, 300 MHz, ppm): 0.97 (t, J = 7.3 Hz, 3H, –CH_3), 1.36 (s, 12H, –$BOC(CH_3)_2C(CH_3)_2O$), 1.64–1.71 (m, 2H, –CH_2CH_3), 2.62 (t, J = 7.6 Hz, 2H, –CH2CH_2CH_3), 7.24 (d, J = 6.6 Hz, 2H, aromatic protons), 7.53 (d, J = 8.1 Hz, 2H, aromatic protons), 7.59 (d, J = 8.1 Hz, 2H, aromatic protons), 7.86 (d, J = 6.6 Hz, aromatic protons).

Compound **6a** yielded 98%. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.93 (t, J = 7.3 Hz, 3H, –CH_3), 1.33 (s, 12H, –$BOC(CH_3)_2C(CH_3)_2O$), 1.57–1.70 (m, 2H, –CH_2CH_3), 2.59 (t, J = 7.3 Hz, 2H, –CH2CH_2CH_3), 7.14 (d, J = 7.9 Hz, 2H, aromatic protons), 7.73 (d, J = 7.9 Hz, 2H, aromatic protons). MS (EI, $C_{13}H_{23}BO_2$): calcd, 246.18; found, 246.

*2.2.6 2,5-difluoro-4-(4'-propylphenyl)aniline (**7a**), 3,5-difluoro-4-(4'-propylbiphenyl-4-yl)aniline (**7b**) and 3-fluoro-4-(4'-propylbiphenyl-4-yl)-a niline (**7c**)*

The methods for preparing compounds **7a–7c** are similar. The synthesis of compound **7c** is described as follows. Compound **6b** (9.47 g, 29.4 mmol), 4-bromo-3-fluoroaniline (5.58 g, 29.4 mmol), tetrakis (triphenylphospine)palladium(0) (2.3 g, 1.47 mmol), potassium carbonate (12.2 g, 88 mmol), Aliquat 336 (0.5 mL), degassed toluene (80 mL) and degassed H_2O (15 mL) were added to a 250-mL flask. The mixture was heated to 90°C under argon gas for 16 h. After cooling to room temperature, the mixture was washed twice with brine. The organic layer was

dried with anhydrous magnesium sulphate. After the solvent was removed, the crude product was purified by column chromatography (silica gel, hexane as eluent) to obtain 7.0 g (78%) of a yellowish solid.

Compound **7a** yielded 67%. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 0.96 (t, J = 7.3 Hz, 3H, $-CH_3$), 1.63–1.73 (m, 2H, $-CH_2CH_3$), 2.60 (t, J = 7.6 Hz, 2H, $-CH_2CH_2CH_3$), 3.83 (s, 2H, $-NH_2$), 6.55 (dd, J_1 = 11.4 Hz, J_2 = 7.8 Hz, 1H, aromatic proton), 7.06 (dd, J_1 = 11.7 Hz, J_2 = 6.9 Hz, 1H, aromatic proton), 7.22 (d, J = 8.1 Hz, 2H, aromatic protons), 7.39 (d, J = 6.6 Hz, 2H, aromatic protons).

Compound **7b** yielded 65%. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 0.97 (t, J = 7.3 Hz, 3H, $-CH_3$), 1.65–1.72 (m, 2H, $-CH_2CH_3$), 2.63 (t, J = 7.6 Hz, 2H, $-CH_2CH_2CH_3$), 3.9 (s, 2H, $-NH_2$), 6.29 (d, J = 9.6 Hz, 2H, aromatic protons), 7.26 (d, J = 8.0 Hz, 2H, aromatic protons), 7.48 (d, J = 8.0 Hz, 2H, aromatic protons), 7.54 (d, J = 8.0 Hz, 2H, aromatic protons), 7.63 (d, J = 8.0 Hz, 2H, aromatic protons); MS (EI, $C_{21}H_{19}F_2N$): calcd, 323.39; found, 323.

*2.2.7 2,5-difluoro-4-(4'propylphenyl)iodobenzene (**8a**) 3,5-difluoro-4-(4'-propylbiphenyl-4-yl) iodobenzene (**8b**) and 3-fluoro-4-(4'-propylbiphenyl-4-yl)iodobenzene (**8c**)*

The methods for preparing compounds **8a–8c** are similar. The synthesis of compound **8c** is described as follows. Compound **7c** (3 g, 9.8 mmol) was dissolved in THF (30 mL) and hydrogen chloride (10 mL) was added. After stirring for 1 h at −5°C, 5.5 M sodium nitrite (5 mL) was added slowly. The mixture was stirred for 1 h at −5°C and 5.5 M potassium iodide (5 mL) was then added and then again stirred for 1 h. The mixture was washed twice with brine and twice with 1 M sodium thiosulphate (30 mL), and the organic layer was dried with anhydrous magnesium sulphate. After the solvent was removed, the crude product was purified by column chromatography (silica gel, hexane as eluent) to obtain 1.5 g (50%) of white solid. ^{1}H–NMR ($CDCl_3$, 300 MHz, ppm): 0.98 (t, J = 7.3 Hz, 3H, $-CH_3$), 1.65–1.73 (m, 2H. $-CH_2-$), 2.64 (t, J = 7.4 Hz, 2H, $-PhCH_2-$), 7.14–7.28 (m, 3H, aromatic protons), 7.41–7.68 (m, 8H, aromatic protons). MS (EI, $C_{21}H_{18}FI$): calcd, 416.04; found, 416.

Compound **8b** yielded 43%. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 0.98 (t, J = 7.3 Hz, 3H, $-CH_3$), 1.65–1.73 (m, 2H, $-CH_2-$), 2.64 (t, J = 7.6 Hz, 2H, $PhCH_2-$), 7.27 (d, J = 4 Hz, 2H, aromatic protons), 7.38 (d, J = 6.8 Hz, 2H, aromatic protons), 7.49 (d, J = 8.1 Hz, 2H, aromatic protons), 7.55 (d, J = 8.1 Hz, 2H, aromatic protons), 7.67 (d, J = 8.4 Hz, 2H, aromatic protons); MS (EI, $C_{21}H_{17}F_2I$): calcd, 434.27; found, 434.

*2.2.8 2,5-difluoro-4-(4'-propylphenyl)phenylboronic acid (**9**)*

Compound **8a** (6 g, 16.7 mmol) was dissolved in dry THF and cooled to −78°C. To the mixture, 2.5 M n-butyl lithium (8.7 mL, 25.0 mmol) was added and stirred for 1 h at −78°C. Trimethyl borate (2 mL, 20.0 mmol) was added to the reaction mixture and stirred for 15 min. To the mixture, 5% hydrochloric acid (0.5 mL) was added. The mixture was stirred at room temperature for another hour, and then the solvent was removed and the residue was washed twice with brine. The organic layer was dried with anhydrous magnesium sulphate. After the solvent was removed, the crude product was purified by column chromatography (silica gel, hexane as eluent) to obtain 2.3 g (50%) of white solid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 0.97(t, J = 7.3 Hz, 3H, $-CH_3$), 1.64–1.72(m, 2H, $-CH_2CH_3$), 2.64 (t, J = 7.3 Hz, 2H, $-CH_2CH_2CH_3$), 7.14 (dd, J_1 = 4.8 Hz, J_2 = 5.7 Hz, 1H, aromatic proton), 7.27 (d, J = 6.5 Hz, 2H, aromatic protons), 7.48 (d, J = 6.5 Hz, 2H, aromatic protons), 7.56 (dd, J_1 = 4.9 Hz, J_2 = 5.4 Hz, 1H, aromatic proton).

*2.2.9 4-(4-propylphenyl)-2,5-difluoro-4'-(3-propylcyclopentyl)biphenyl (**10**)*

Compounds **3** (1.0 g, 8.0 mmol) and **9** (2.2 g, 8.0 mmol), tetrakis(triphenylphospine)palladium(0) (0.1 g, 0.1 mmol), sodium hydroxide (0.9 g, 24.0 mmol), Aliquat 336 (0.1 mL), degassed toluene (50 mL) and degassed H_2O (10 mL) were added to a 250-mL flask. The mixture was heated to 90°C under argon gas for 16 h. After cooling to room temperature, the mixture is washed twice with brine. The organic layer was dried with anhydrous magnesium sulphate. After the solvent was removed, the crude product was purified by column chromatography (silica gel, hexane as eluent) to obtain 1.8 g (54%) of white solid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 0.89–1.00 (m, 6H, $-CH_3$ on propyl terminal chain and $-CH_3$ on 3-propylcyclopentyl), 1.35–1.39 (m, 6H, 3-propylcyclopentyl protons), 1.65–1.72 (m, 3H, 3-propylcyclopentyl protons and $-CH_2-$ on propyl terminal chain), 1.89–2.25 (m, 4H, 3-propylcyclopentyl protons), 2.64 (t, J = 7.3 Hz, 2H, $-PhCH_2-$), 3.08–3.11 (m, 1H, –PhCH–), 7.19–7.35 (m, 6H, aromatic protons), 7.50 (d, J = 7.0 Hz, 4H, aromatic protons). MS (EI, $C_{29}H_{32}F_2$): calcd, 418.25; found, 418.4.

HRMS (EI, $C_{29}H_{32}F_2$): calcd, 418.2472; found, 418.2470.

*2.2.10 4-(4-propylphenyl)-2'-fluoro-4'-(3-propylcyclopentyl)biphenyl (**11**) and 4-(4-propylphenyl)-2',6'-difluoro-4'-(3-propylcyclopentyl) biphenyl (**12**)*

The methods for preparing compounds **11** and **12** are similar. The synthesis of compound **11** is described as follows. Compound **8c** (1.5 g, 3.6 mmol) was dissolved in dry THF (30 mL) and cooled to −78°C. A measure of 2.5 M n-butyl lithium (2.6 mL) was added to the mixture and stirred for 1 h at −78°C. 3-Propylcyclopentan-1-one (0.45 mL 4.6 mmol) was added to the reaction mixture and stirred for 1 h. The mixture was stirred at room temperature for another hour. After the solvent was removed and the residue was washed twice with brine, the organic layer was dried with anhydrous magnesium sulphate. After the solvent was removed, the crude product was transferred to a 150-mL round-bottom flask. Potassium bisulphate (0.5 g, 3.6 mmol) was added to the flask, and the mixture was heated to 100°C and stirred for 5 h. The mixture was purified by column chromatography (silica gel, hexane as eluent) to obtain 0.55 g (38%) of white solid. The white solid was dissolved in methanol (10 mL) and toluene (8 mL). A measure of 10% Pd/C (10 mg) was added to the mixture and stirred for 16 h at room temperature under H_2 atmosphere. The mixture was filtered to remove Pd/C powder. After the solvent was removed, 0.5 g (99%) of white solid was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): 0.87–0.98 (m, 6H, –CH_3 on 3-propylcyclopentane and –CH_3 on propyl chain), 1.23–1.39 (m, 6H, 3-propylcyclopentane protons), 1.63–2.19 (m, 7H, 3-propylcyclopentane protons and –CH_2– on propyl terminal chain), 2.62 (t, J = 10.4 Hz, 2H, –PhCH_2–), 3.72 (m, 1H, –PhCH–), 7.00–7.08 (m, 2H, aromatic protons), 7.22–7.26 (m, 2H, aromatic protons), 7.37 (t, J = 8.1 Hz, 1H, aromatic protons), 7.52–7.64 (m, 4H, aromatic protons). MS (EI, $C_{29}H_{33}F$): calcd, 400.26; found, 400. HRMS (EI, $C_{29}H_{32}F_2$): calcd, 400.2566; found, 400.2566.

Compound **12**: ^{1}H NMR (CDCl3, 300 MHz, ppm): 0.88–1.00 (m, 6H, –CH_3 on 3-propylcyclopentane and –CH_3 on propyl terminal chain), 1.19–1.28 (m, 2H, 3-propylcyclopentane protons), 1.34–1.40 (m, 4H, 3-propylcyclopentane protons), 1.62–1.73 (m, 3H, 3-propylcyclopentane protons and –CH_2– on propyl terminal chain), 1.96–2.11 (m, 3H, 3-propylcyclopentane protons), 2.21–2.24 (m, 1H, 3-propylcyclopentane proton), 2.64 (t, J = 7.2 Hz, 2H, –PhCH_2–), 2.99–3.11 (m, 1H, –PhCH–), 6.87 (d, J = 8.9 Hz, 2H, aromatic protons), 7.27 (d, J = 6.4 Hz, 2H, aromatic protons), 7.51–7.57 (m, 4H, aromatic protons), 7.66 (d, J = 8.4 Hz, 2H, aromatic protons). MS (EI, $C_{29}H_{32}F_2$): calcd, 418.25; found, 418. HRMS (EI, $C_{29}H_{32}F_2$): calcd, 418.2472; found, 418.2470.

3. Results and discussions

The synthetic procedure for the preparation of compounds **4** and **5a-5d** is outlined in Scheme 1. The terphenyl compounds containing 3-propylcyclopentyl end group were prepared by Suzuki coupling of 4-alkyl-2-fluorobiphenyl boronic acid with 1-iodo-4-(4-propylcyclopentyl)benzene. All obtained compounds were purified several times by column chromatography. The thermal and mesomorphic properties of the obtained compounds were characterised by DSC and POM. The representative DSC thermograms of compound **5c** are presented in Figure 2. Compound **5c** exhibits a melting transition at 7.5°C, a smectic C to smectic A transition at 32.9°C, a smectic A to nematic transition at 79.5°C and a nematic to isotropic phase transition at 132.9°C on the heating scan (curve A). The cooling scan (curve B) looks almost identical to the heating scan, except a very small supercooling (less than 5.5°C) is observed for the first three mesomorphic transitions. The supercooling for the crystallisation transition is larger as expected. Figure 3(a)–3(c) display the typical textures of nematic, smectic A and smectic C exhibited by **5c**, respectively.

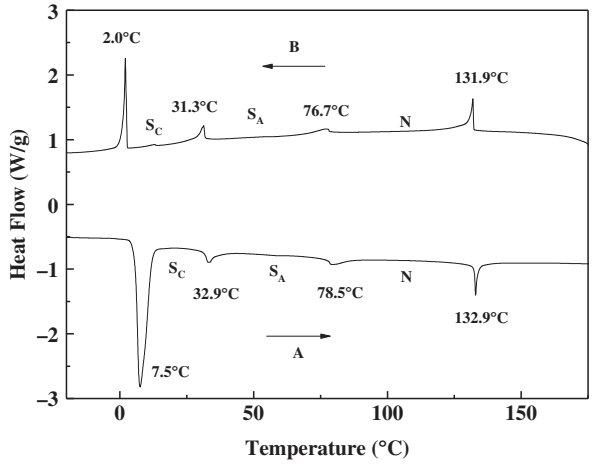


Figure 2. DSC thermograms of compound **5c**: heating scan (curve A) and cooling scan (curve B).

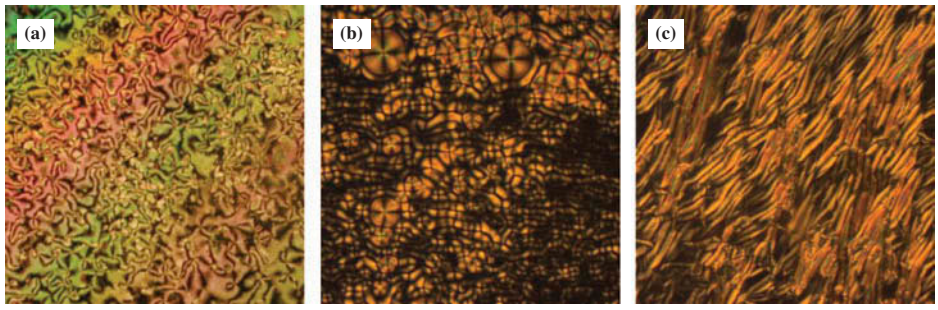


Figure 3. Optical micrographs of (a) nematic texture obtained at 110°C, (b) smectic A texture obtained at 54°C and (c) smectic C texture obtained at 25°C for compound **5c**.

3.1 Effect of terminal alkyl chain

The phase transition temperatures and mesomorphic properties of compounds **5a–5d** are listed in Table 1. All of them possess the same mesogenic core except that the left-handed terminal alkyl chains vary from ethyl to pentyl group. Compound **5a**, which contains an ethyl end group, reveals an enantiotropic nematic phase. Bearing a propyl terminal alkyl chain, compound **5b** possesses an enantiotropic nematic phase and two monotropic smectic A and smectic C phases. Compounds **5c** and **5d** contain a butyl terminal alkyl chain and a pentyl terminal alkyl chain, respectively, and both compounds present enantiotropic nematic, smectic A and smectic C phases. The result demonstrates that the length of terminal alkyl group affects the mesomorphic properties of this series of compounds profoundly. Compounds with longer alkyl chain ends have an obvious tendency to form more ordered smectic phases. In our previous studies, [11,37] we have found that the symmetry of alkyl chain on the both sides of the mesogen has a strong effect in the melting and isotropisation temperatures. In general, asymmetric compounds generally exhibit much lower melting and isotropisation temperatures than the symmetric analogues. The phenomenon can be observed in these terphenyl compounds as well. Compound **5d** which contains symmetric propyl terminal alkyl chains shows a much higher melting temperature and isotropisation temperature than those of compounds **5c** and **5d**. If one end of the molecule is a considerably short alkyl chain, the phenomenon is not obvious; for instance, the melting temperature of **5a** is higher than that of **5b**. What is worth noting is the enthalpy change in compounds **5a**–**5d**. Generally, during the transition to isotropic phase, nematic phase exhibits a small enthalpy change that is approximately 1–2 kJ mol^{-1}; however, that of **5b** and **5c** is obviously larger than expected.[38–40]

3.2 Effect of lateral fluoro substituent

To study the effect of lateral fluoro substituent on the mesomorphic phase behaviour of these terphenyl compounds, compounds **4** and **10–12** were prepared.

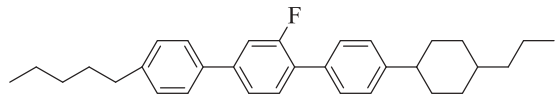
Table 1. The phase transitions and corresponding enthalpy changes of compounds **4, 5a–5d** and **10–12**.

Compound	Phase transition temperature (°C) and enthalpy in parenthsis (kJ mol^{-1})
4	Cr 164.3 (37.3) I
	I 160.9 (36.8) Cr
5a	Cr 50.9 (92.4) N 71.3 (1.1) I
	I 68.7 (0.8) N 47.4 (1.4) Cr
5b	Cr 36.1 (72.9) N 144.3 (4.0) I
	I 143.0 (7.0) N 18.4 (3.7) S_A −2.3 (1.5) S_C −13.2 (15.5) Cr
5c	Cr 7.5 (45.8) S_C 32.9 (2.8) S_A 79.5 (2.4) N 132.9 (4.1) I
	I 131.9 (5.2) N 76.7 (1.6) S_A31.3 (2.4) S_C 2.0 (8.6) Cr
5d	Cr 1.8 (39.7) S_C 36.6 (4.9) S_A 68.3 (2.1) N 89.8 (1.2) I
	I 83.9 (1.9) N 68.9 (3.0) S_A 32.4 (3.5) S_C 1.0 (7.9) Cr
10	Cr 52.5 (119.4) N 76.9 (3.2) I
	I 74.1 (4.4) N 2 (35.6) Cr
11	Cr 61.8 (109.7) N 142.5 (5.4) I
	I 141.1 (5.2) N 42.0 (4.81) S 29.0 (8.4) S 12.3 (52.1) Cr
12	Cr 76.4 (139.2) I
	I 74.4 (4.3) N 36.9 (45.7) Cr

Compound **4** containing no lateral fluoro substituent exhibits only crystalline phase and its melting point is much higher than the melting point compounds **5a–5d**. The result indicates that the lateral fluoro substituent has a significant effect on lowering the melting point and formation of mesophases. To study the different positions of fluoro substituents and the fluoro-substituent number on the mesomorphic properties of the obtained compounds, we also synthesised compounds **10–12** (Scheme 2). Compounds **10–12** bear symmetry propyl groups on both terminal ends. Compound **10** contains two fluoro substituents on 2 and 5 positions of central phenyl ring of the terphenyl compounds, whereas compounds **11** and **12** contain, respectively, a fluoro substituent and two fluoro substituents on the phenyl ring close to cyclopentyl end group. Comparing mesomorphic properties of compound **10** with those of **5b**, compound **10** merely exhibits an enantiotropic nematic phase, whereas compound **5b** displays an enantiotropic nematic phase and two monotropic smectic A and C phases. The results indicate that addition of a second fluoro substituent onto the 5 position of central phenyl ring inhibits the formation of smectic phases. Nevertheless, its nematic temperature range also decreases. The phenomena can be attributed to the fact that the stability of mesophase is interrupted by the inter-annular twisting caused by lateral fluorine atom.[41] Both compounds **11** and **5b** contain only one fluorine atom, but the fluorine substituent for compound **11** locates on the phenyl ring close to cyclophenyl group. Their mesomorphic behaviours are similar except that compound **11** exhibits a narrower mesomorphic temperature range. Compound **12** contains two fluoro substituents on the phenyl ring close to cyclophenyl group, and it reveals only a monotropic nematic phase. By comparing the mesomorphic properties of compound **12** with that of compound **10**, it seems that phenyl ring next to the cyclopentyl end group bearing two fluoro substituents will decrease the stability of nematic phase. The slightly large enthalpy changes on the transition of nematic and isotropy phase for compounds **10** and **12** are unusual and noteworthy.[38–40]

3.3 Effect of 3-propylcyclopentane end group

In the literature, the cyclohexyl group is more popular than cyclopentyl group to be used as a building block for LCs. However, there are still several examples [33–36] that demonstrate compounds replacing cyclohexyl terminal group with cyclopentyl group. Those compounds with cyclopentyl end group show much lower melting temperatures than those compounds with cyclohexyl end group. The phenomenon



13
C 99.0 N 293.9 I

Figure 4. Chemical structure of compound **13**.[42]

is also verified in the terphenyl system we have synthesised in this article. Figure 4 shows the chemical structure and mesomorphic property of compound **13**.[42] Both compounds **13** and **5d** have identical mesogenic core except the terminal group. Compound **13** that has a cyclohexyl terminal group shows only an enantiotropic nematic phase, whereas compound **5d** that possesses a cyclopentyl end group shows three enantiotropic nematic, smectic A and smectic C phases. The melting temperature of **5d** is lower than that of **13** by approximately 90°C. The decrease in melting temperature can be attributed to the mixture of cis- and trans-forms of 1,3-substitued cyclopentyl end group and the non-linear molecular structure of both cis- and trans-forms.[43,44] We use proton NMR and nuclear Overhauser effect spectroscopy (NOESY) to determine the cis/trans isomers ratio. The proton NMR peak of C1 proton (connecting to the phenyl ring) on cis-cyclopentyl group presents at δ 2.98–3.02 ppm and that of C1 proton on trans-cyclopentyl group presents at δ 3.04–3.11 ppm. The ratio of cis/trans-forms of the synthesised compounds is 1:0.31. It depicts that there are more cis-forms than trans-forms. Figure 5 shows the simulated molecular structures of cis-form of **5b**, which presents a much curved molecular skeleton and cyclohexyl analogue that shows a more linear structure.

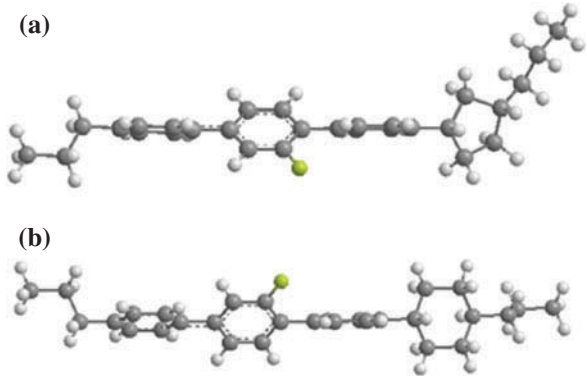


Figure 5. (colour online) The molecular structures of (a) cis-form of **5b** and (b) analogue with a cyclohexane end group.

Table 2. The electro-optical properties of compounds **5b** and **10–12.**

Compound	Δn	$\Delta\varepsilon$	γ_1 (mPa·s)
5b	0.227	1.31	123
10	0.216	0.34	312
11	0.224	0.22	228
12	0.197	1.23	244

3.4 Electric and optical properties

Table 2 lists the birefringence (Δn), dielectric anisotropy ($\Delta\varepsilon$) and rotational viscosity (γ_1) of compounds **5b** and **10–12**. The Δn, $\Delta\varepsilon$ and γ_1 are measured using guest–host method.[45] The birefringence is measured by Abbe refractometer. The dielectric anisotropy and rotational viscosity are measured by Instec automatic liquid crystal tester ALCT4. All four compounds show moderate values of Δn around 0.2. Both compounds **5b** and **11** containing only one fluoro substituent reveal a higher value of Δn than those of compounds **10** and **12**, which contain two fluoro substituents. It can be attributed to the fact that fluoro substituent is an electron-withdrawing group.[9,46,47] The $\Delta\varepsilon$ value is strongly related to the molecular dipole moment of the molecule. All four compounds show low $\Delta\varepsilon$ value because they contain no strong dipole substituents besides fluoro substituent. Compound **5b** contains a lateral fluoro substituent, and the $\Delta\varepsilon$ is 1.31, which is the highest among four compounds. Compound **10** contains two fluoro substituents. Both fluoro substituents are located at para position of central phenyl ring, and their dipoles cancel each other. Therefore, it shows a smaller $\Delta\varepsilon$ value of 0.34. Compound **11** contains only one fluoro substituent on the phenyl ring close to the cyclopentyl ring. We speculate that its fluoro dipole is cancelled by the terminal cyclopentyl group, the reason for the smallest $\Delta\varepsilon$ value of 0.224. Compound **12** also contains two fluoro substituents. Both fluoro substituents are located at meta position of phenyl ring close to cyclopentyl group, and their dipoles do not cancel each other, the reason for the medium value of $\Delta\varepsilon$ of 1.23. Finally, all four compounds possess rather large rotational viscosities. The rotational viscosity is related to the linearity of molecular structure. Those compounds containing cyclopentyl group exhibit bend molecular structures. This is the reason why these compounds show large γ_1 values. Compound **10** with two kink fluoro substituents shows the largest γ_1 value of 312.

4. Conclusion

We have synthesised a series of fluorinated terphenyl LCs containing cyclopentyl end group. All compounds in this series show wide mesomorphic temperature range. As anticipated, introduction of fluoro substituent and cyclopentyl end group decreases the melting point of these terphenyl compounds. Most of the terphenyl compounds discussed in previous literature always show very high melting points. Our study provides an efficient way in molecular design to achieve the moderate birefringence LCs with low melting points. The obtained LC, such as compound **5b**, that possess moderate birefringence, wide nematic temperature range, low melting point and moderate γ_1 value is suitable to formulate eutectic mixture for LC applications.

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