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The effect of a single atom in the terminal position of a fluorocarbon chain on liquid crystalline properties

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Eight series of chiral compounds with semi-fluorocarbon chains have been synthesized. The compounds were characterized by IR, ^{1}H NMR, ^{19}F NMR and mass spectroscopies and elemental analysis. Their phase transition behaviour was investigated by differential scanning calorimetry and polarizing optical microscopy. Their clearing points increase with an increase of the length of fluorocarbon chain. For a certain compound, when the terminal hydrogen atom in the semi-fluoroalkyl chain was substituted by a chlorine atom, both the clearing point and melting point were increased, and the thermal stability of the chiral smectic C (SmC*) phase was enhanced. However, the clearing point decreased and the melting point increased with the introduction of a triple bond into the core.

1. Introduction

A variety of liquid crystalline compounds with fluorocarbon chains have been synthesized during the last decade [1–15]. Earlier work by different groups on liquid crystals with perfluoroalkyl or semi-perfluoroalkoxy chains showed that they form smectic mesophases and that their liquid crystalline thermal stabilities were enhanced. In particular, molecules with semi-perfluorinated chains exhibit tilted smectic phases and some are inherently ferroelectric. With the introduction of chiral centre, a smectic C* (SmC*) phase will be formed, which may be suitable for application in ferroelectric liquid crystal display (FLCD) mixtures. Therefore, the synthesis and study of liquid crystals with semi-perfluorocarbon chains and chiral centres has become more attractive [14, 15].

Previous results indicated that liquid crystals with wide SmC* phase range could be prepared by the introduction of semi-perfluorocarbon chains and chiral centres [14]. The liquid crystalline properties have also been preliminary studied by subtle modification of the fluorocarbon chain, e.g. a change of the terminal hydrogen atom in the semi-fluorocarbon chain to chlorine [13, 15]. In this paper we report a systematic study of the liquid crystalline properties of eight series of chiral liquid crystals by changing the terminal hydrogen atoms of the semi-fluorocarbon chains to chlorine.

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2. Experimental

2.1. *Characterization*

The structures of the final products and intermediates were determined by a variety of spectral methods. IR spectra were taken on a PE-983G spectrophotometer, using KBr pellets of the solids, or films of liquids. ^{1}H NMR spectra, with TMS as internal NMR standard, were recorded on a Varian EM 360L spectrometer (60 MHz) or a Fx-90Q (90 MHz) instrument. ^{19}F NMR spectra, with trifluoroacetic acid (TFA) as external standard, were recorded on a Varian EM 360L spectrometer (60 MHz). For ^{19}F NMR spectra the high field was positive. Mass spectra were measured with a Finnigan-4021 spectroscope.

The phase transition temperatures of the target compounds were measured by polarizing optical microscopy (POM) using a microscope (Olympus PM-6) fitted with a heating stage (Mettler FP-80) and control unit (FP-82), and by differential scanning calorimetry (DSC, Shimidazu DSC-50 calorimeter with a data system, heating and cooling rate 5°C min^{-1}). The transition temperatures reported in this paper are the peak values of the transition on DSC traces. Phase identification was made by comparing the observed textures with those reported in the literature.

2.2. *Synthesis*

All of the obtained liquid crystals were purified by column chromatography on silica gel using petroleum ether (b.p. 60–90°C)/ethyl acetate (20/1) as eluent and

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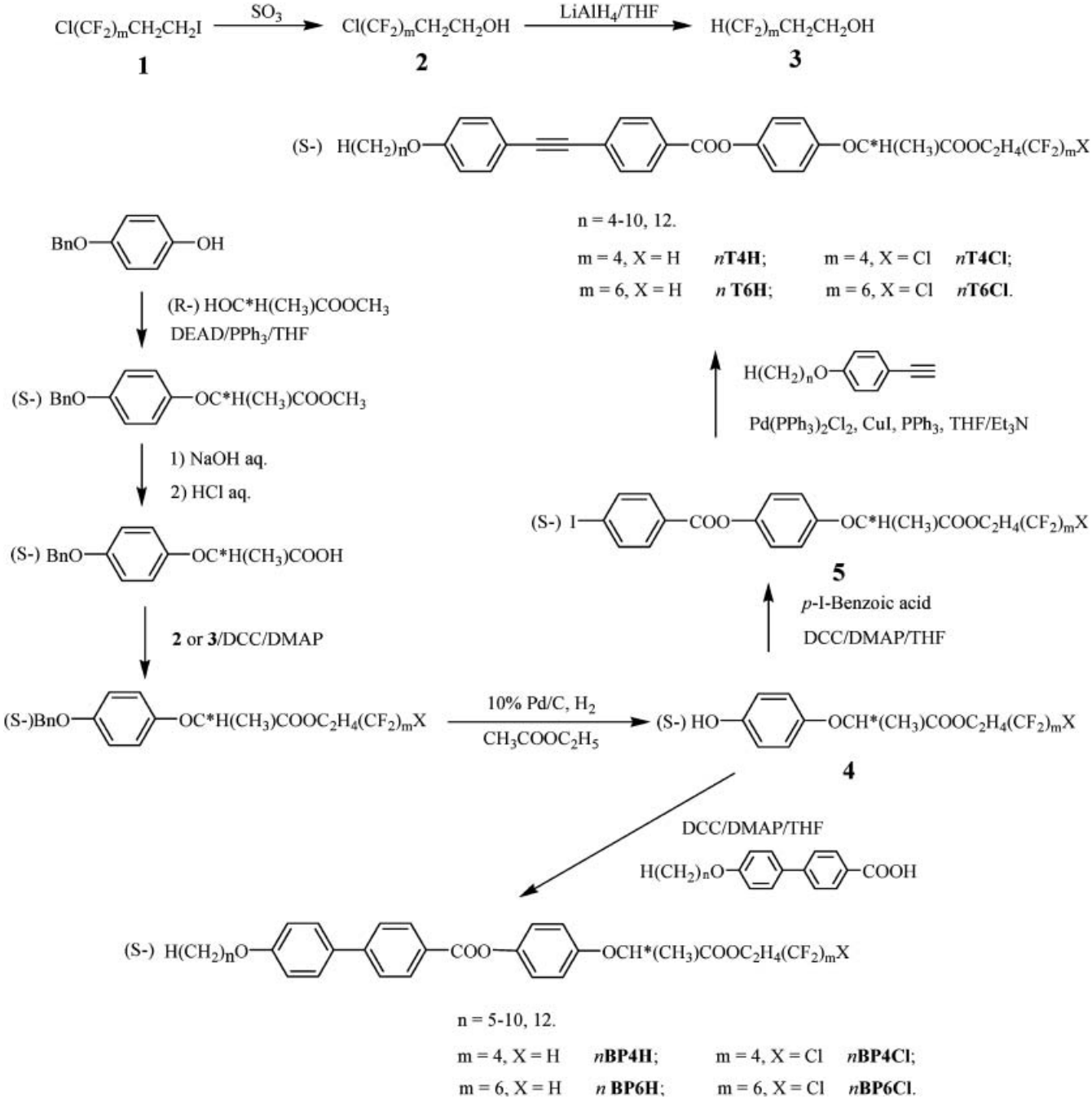
then recrystallized from petroleum ether (b.p. 60–90°C) and acetone/methanol.

The compounds were obtained by routes depicted in scheme 1. Fluoroalkanols **1** and **2** were synthesized simply as shown; all the other intermediates and final compounds were synthesized according to literature methods [16].

2.2.1. Synthesis of compound *8*BP4H. A typical synthetic procedure is as follows. 4-*n*-Octyloxybiphenyl-4′-carboxylic acid (200′mg, 0.61′mmol), compound **4** (*m*=4, X=H) (250 mg, 0.61 mmol), *N*,*N*′-dicyclohexylcarbodiimide (125 mg, 0.61 mmol), catalytic DMAP and dry THF (10 ml) were stirred under N_2 at room temperature for 48 h. The mixture



Scheme 1. Synthesis route for compounds investigated.

was filtered and the residue was washed with THF. The collected filtrates were evaporated on a rotary evaporator. The residue was purified by flash chromatography and recrystallized from acetone/methanol to give 239 mg of white solid; yield 54.5%. $[\alpha]_D^{20} = -12.7$ (c 1.0, $CHCl_3$). IR (KBr) υ_{max} (cm^{-1}): 2931, 2854, 1731,1603, 1504, 1296, 1202, 872, 834. ^1H NMR (300 MHz, $CDCl_3$, TMS) δ (ppm): 0.96 (t, J=7.1 Hz, 3H, CH_3), 1.32–1.86 (m, 15H, aliphatic), 2.49 (tt, J_1=18.2, J_2=6.4 Hz, 2H, R_fCH_2), 4.02 (t, J=6.6 Hz, 2H, RCH_2O), 4.49 (t, J=6.3 Hz, 2H, RCH_2O), 4.79 (q, J=6.8 Hz, H, R_1R_2CHO), 6.07 (tt, J_1=49.3, J_2=5.2 Hz, H, CF_2H), 6.94 (d, J=9.1 Hz, 2H, ArH), 7.01 (d, J=8.7 Hz, 2H, ArH), 7.15 (d, J=9.1 Hz, 2H, ArH), 7.60 (d, J=8.7 Hz, 2H, ArH), 7.69 (d, J=8.4 Hz, 2H, ArH), 8.22 (d, J=8.3 Hz, 2H, ArH). ^{19}F NMR (56.4 MHz, $CDCl_3$, TFA) δ (ppm): 36.30 (m, 2F), 48.33 (s, 2F), 52.60 (s, 2F), 60.00 (d, J=50 Hz, 2F). MS m/z (rel. int.): 719 (M^++1, 1.63), 309 ($C_8H_{17}OC_6H_4C_6H_4CO^+$, 100.00), 197 ($HOC_6H_4C_6H_4CO^+$, 8.62). Elemental analysis: calculated (for $C_{36}H_{38}F_8O_6$), C 60.16, H 5.91, F 21.15%; found, C 60.39, H 5.30, F 20.37%.

2.2.2. Synthesis of compound *8*BP4Cl. $[\alpha]_D^{20} = -16.0$ (c 1.0, $CHCl_3$). υ_{max} (KBr, cm^{-1}): 2924, 2853, 1750, 1729, 1603, 1503, 1194, 1138, 834. ^1H NMR (300 MHz; $CDCl_3$; TMS) δ(ppm): 0.96 (t, J=7.1 Hz, 3H, CH_3), 1.32–1.86 (m, 15H, aliphatic), 2.49 (tt, J_1=18.2, J_2=6.4 Hz, 2H, R_fCH_2), 4.02 (t, J=6.6 Hz, 2H, RCH_2O), 4.49 (t, J=6.3 Hz, 2H, RCH_2O), 4.79 (q, J=6.8 Hz, H, R_1R_2CHO), 6.94 (d, J=9.1 Hz, 2H, ArH), 7.01 (d, J=8.7 Hz, 2H, ArH), 7.15 (d, J=9.1 Hz, 2H, ArH), 7.60 (d, J=8.7 Hz, 2H, ArH), 7.69 (d, J=8.4 Hz, 2H, ArH), 8.22(d, J=8.3 Hz, 2H, ArH). ^{19}F NMR (56.4 MHz, $CDCl_3$, TFA) δ(ppm): −9.30 (s, 2F), 36.50 (m, 2F), 42.80 (s, 2F), 45.80 (s, 2F). MS m/z (rel. int.): 753 (M^++1, 0.97), 309 ($C_8H_{17}OC_6H_4C_6H_4CO^+$, 100.00), 197 ($HOC_6H_4C_6H_4CO^+$, 8.38). Elemental analysis: calculated for $C_{36}H_{37}ClF_8O_6$, C 57.41, H 4.95, Cl 4.71, F 20.18%; found, C 57.55, H 4.98, Cl 4.67, F 20.06%.

2.2.3. Synthesis of compound *8*BP6H. $[\alpha]_D^{20} = -14.9$ (c 1.0, $CHCl_3$). υ_{max} (KBr, cm^{-1}): 2930, 2853, 1730, 1603, 1504, 1200, 1140, 834. ^1H NMR (300 MHz; $CDCl_3$; TMS) δ(ppm): 0.96 (t, J=7.1 Hz, 3H, CH_3), 1.32–1.86 (m, 15H, aliphatic), 2.49 (tt, J_1=18.2, J_2=6.4 Hz, 2H, R_fCH_2), 4.02 (t, J=6.6 Hz, 2H, RCH_2O), 4.49 (t, J=6.3 Hz, 2H, RCH_2O), 4.79 (q, J=6.8 Hz, H, R_1R_2CHO), 6.07 (tt, J_1=49.3, J_2=5.2 Hz, H, CF_2H), 6.94 (d, J=9.1 Hz, 2H, ArH), 7.01 (d, J=8.7 Hz, 2H, ArH), 7.15 (d, J=9.1 Hz, 2H, ArH), 7.60 (d, J=8.7 Hz, 2H, ArH), 7.69 (d, J=8.4 Hz, 2H, ArH), 8.22 (d, J=8.3 Hz, 2H, ArH). ^{19}F NMR (56.4 MHz, $CDCl_3$, TFA) δ(ppm): 36.40 (m, 2F), 44.70–46.60 (m, 6F), 52.50 (s, 2F), 60.0(d, J=50 Hz, 2F). MS m/z (rel. int.): 753 (M^+, 0.97), 309 ($C_8H_{17}OC_6H_4C_6H_4CO^+$, 100.00), 197 ($HOC_6H_4C_6H_4CO^+$, 8.38). MS m/z (rel. int.): 820 (M^++2, 0.27), 308 ($C_8H_{17}OC_6H_4C_6H_4CO^+$–1, 100.00), 197 ($HOC_6H_4C_6H_4CO^+$, 7.79). Elemental analysis: calculated for $C_{38}H_{38}F_{12}O_6$, C 55.75, H 4.68, F 27.85%; found, C 55.86, H 4.66, F 27.60%.

2.2.4. Synthesis of compound *8*BP6Cl. $[\alpha]_D^{20} = -13.7$ (c 1.0, $CHCl_3$). IR (KBr, cm^{-1}) υ_{max}: 2929, 2854, 1748, 1729, 1603, 1504, 1200, 834. ^1H NMR (300MHz; $CDCl_3$; TMS) δ(ppm): 0.96 (t, J=7.1 Hz, 3H, CH_3), 1.32–1.86 (m, 15H, aliphatic), 2.49 (tt, J_1=18.2, J_2=6.4 Hz, 2H, R_fCH_2), 4.02(t, J=6.6 Hz, 2H, RCH_2O), 4.49 (t, J=6.3 Hz, 2H, RCH_2O), 4.79 (q, J=6.8 Hz, H, R_1R_2CHO), 6.94 (d, J=9.1 Hz, 2H, ArH), 7.01 (d, J=8.7 Hz, 2H, ArH), 7.15 (d, J=9.1 Hz, 2H, ArH), 7.60 (d, J=8.7 Hz, 2H, ArH), 7.69 (d, J=8.4 Hz, 2H, ArH), 8.22(d, J=8.3 Hz, 2H, ArH). ^{19}F NMR (56.4 MHz, $CDCl_3$, TFA) δ(ppn): −9.30(s, 2F), 35.90(m, 2F), 42.80–43.75 (m, 6F), 46.50(s, 2F). MS m/z (rel. int.): 853 (M^++1, 0.38), 308 ($C_8H_{17}OC_6H_4C_6H_4CO^+$–1, 100.00), 197($HOC_6H_4C_6H_4CO^+$, 9.74). Elemental analysis: calculated for $C_{38}H_{37}ClF_{12}O_6$, C 53.50, H 4.37, Cl 4.16, F 26.72%; found, C 53.68, H 4.38, Cl 4.18, F 26.55%.

2.2.5. Synthesis of compound *8*T4H. A typical synthetic procedure is as follows. To a mixture of 4-octyloxyphenylacetylene (100 mg, 0.43 mmol), compound **5**(m=4, X=H) (250 mg, 0.39 mmol), bis(triphenylphosphine)-palladium dichloride (20 mg) and CuI (60 mg), under dry N_2, was added 20 ml of anhydrous triethylamine. The obtained mixture was heated under reflux while stirring for 2 h. Analysis by TLC revealed completion of the reaction. The precipitate formed was then filtered off and washed with ether. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane as eluent. The obtained compound was recrystallized from petroleum ether (b.p. 60–90°C) and acetone/methanol. $[\alpha]_D^{20} = -14.5$ (c 1.0, $CHCl_3$). IR υ_{max} (KBr, cm^{-1}): 2928, 2853, 2215, 1731, 1600, 1505, 1248, 1176, 836. ^1H NMR (300 MHz; $CDCl_3$; TMS) δ(ppm): 0.91 (t, J=6.7 Hz, 3H, CH_3), 1.26–1.83 (m, 15H, aliphatic), 2.49 (tt, J_1=18.2, J_2=6.4 Hz, 2H, R_fCH_2), 4.00 (t, J=6.6 Hz, 2H, RCH_2O), 4.49 (t, J=6.3 Hz, 2H, RCH_2O), 4.79 (q, J=6.8 Hz, H, R_1R_2CHO), 6.07 (tt, J_1=49.3, J_2=5.2 Hz, H, CF_2H), 6.87–6.94 (m, 4H, ArH), 7.13

(d, J=6.7 Hz, 2H, ArH), 7.50 (d, J=8.7 Hz, 2H, ArH), 7.62 (d, J=8.5 Hz, 2H, ArH),), 8.16 (d, J=8.4 Hz, 2H, ArH). ^{19}F NMR (56.4 MHz, $CDCl_3$, TFA) δ(ppm): 36.30 (m, 2F), 48.33 (s, 2F), 52.60 (s, 2F), 60.00 (d, J=50 Hz, 2F). MS m/z (rel. int.): 742 (M^+, 1.82), 333 ($C_8H_{17}OC_6H_4$–≡–$C_6H_4CO^+$, 100.00), 221 (HOC_6H_4–≡–$C_6H_4CO^+$, 5.84). Elemental analysis: calculated for $C_{38}H_{38}F_8O_6$, C 61.45, H 5.16, F 20.46%; found, C 61.57, H 4.95, F 20.62%.

2.2.6. Synthesis of compound *8*T4Cl. $[\alpha]_D^{20} = -12.2$ (c 1.0, $CHCl_3$). IR υ_{max} (KBr, cm^{-1}): 2922, 2853, 2213, 1748, 1725, 1599, 1507, 1252, 1200, 834. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ(ppm): 0.91 (t, J=6.7 Hz, 3H, CH_3), 1.26–1.83 (m, 15H, aliphatic), 2.49 (tt, J_1=18.2, J_2=6.4 Hz, 2H, R_fCH_2), 4.00 (t, J=6.6 Hz, 2H, RCH_2O), 4.49 (t, J=6.3 Hz, 2H, RCH_2O), 4.79 (q, J=6.8 Hz, H, R_1R_2CHO), 6.87–6.94 (m, 4H, ArH), 7.13 (d, J=6.7 Hz, 2H, ArH), 7.50 (d, J=8.7 Hz, 2H, ArH), 7.62 (d, J=8.5 Hz, 2H, ArH),), 8.16 (d, J=8.4 Hz, 2H, ArH). ^{19}F NMR (56.4 MHz, $CDCl_3$, TFA) δ(ppm): −9.30 (s, 2F), 36.50 (m, 2F), 42.80 (s, 2F), 45.80 (s, 2F). MS m/z (rel. int.): 776 (M^+, 0.79), 333($C_8H_{17}OC_6H_4$–≡–$C_6H_4CO^+$, 100.00), 221(HOC_6H_4–≡–$C_6H_4CO^+$, 5.75). Elemental analysis: calculated for $C_{38}H_{37}ClF_8O_6$, C 58.73, H 4.80, Cl 4.56, F 19.56%; found, C 58.91, H 4.97, Cl 4.65, F 19.60%.

2.2.7. Synthesis of compound *8*T6H. $[\alpha]_D^{20} = -13.4$ (c 1.0, $CHCl_3$). IR υ_{max} (KBr, cm^{-1}): 2924, 2853, 2213, 1748, 1725, 1599, 1506, 1251, 1199, 834. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ(ppm): 0.91 (t, J=6.7 Hz, 3H, CH_3), 1.26–1.83 (m, 15H, aliphatic), 2.49 (tt, J_1=18.2, J_2=6.4 Hz, 2H, R_fCH_2), 4.00 (t, J=6.6 Hz, 2H, RCH_2O), 4.49 (t, J=6.3 Hz, 2H, RCH_2O), 4.79 (q, J=6.8 Hz, H, R_1R_2CHO), 6.07 (tt, J_1=49.3, J_2=5.2 Hz, H, CF_2H), 6.87–6.94 (m, 4H, ArH), 7.13 (d, J=6.7 Hz, 2H, ArH), 7.50 (d, J=8.7 Hz, 2H, ArH), 7.62 (d, J=8.5 Hz, 2H, ArH), 8.16 (d, J=8.4 Hz, 2H, ArH). ^{19}F NMR (56.4 MHz, $CDCl_3$, TFA) δ(ppm): 36.40 (m, 2F), 44.70–46.60 (m, 6F), 52.50 (s, 2F), 60.00 (d, J=50 Hz, 2F). MS m/z (rel. int.): 842 (M^+, 0.53), 333

Table 1. Transition temperatures of the *n***T4H**, *n***T4Cl**, *n***T6H** and *n***T6Cl** compounds (Cr=crystal; SmA=smectic A phase; SmC*=chiral smectic C phase; SmB=smectic B phase; I=isotropic liquid; CrE=crystal E phase; CrX=unclear crystal phase).

Compound	*n*	Transition temperatures/°C
***4*T4H**	4	Cr 83.2 CrE 87.4 SmB 96.0 SmA 158.1 I 156.3 SmA 95.1 SmB 86.4 CrE 59.3 Cr
***5*T4H**	5	Cr 77.3 SmB 85.7 SmA 146.9 I 143.6 SmA 84.5 SmB 64.4 CrE
***6*T4H**	6	CrE 66.3 SmB 90.4 SmA 147.4 I 143.9 SmA 88.7 SmB 64.0 CrE
***7*T4H**	7	Cr 47.3 CrE 59.0 SmB 84.7 SmA 140.1 I 135.9 SmA 83.2 SmB 57.8 CrE
***8*T4H**	8	Cr 57.7 SmB 88.0 SmA 138.5 I 135.9 SmA 86.9 SmB 54.6 CrE
***9*T4H**	9	Cr 52.0 SmB 84.4 SmC* 86.0 SmA 132.5 I 129.8 SmA 85.6 SmC* 83.1 SmB 38.4 CrE
***10*T4H**	10	Cr 81.3 SmB 87.8 SmC* 94.0 SmA 129.9 I 127.8 SmA 92.9 SmC* 86.3 SmB 47.7 CrE 43.4 Cr
***12*T4H**	12	Cr 91.0 SmC* 99.6 SmA 121.8 I 120.0 SmA 99.3 SmC* 85.0 SmB 64.0 Cr
***4*T4Cl**	4	Cr 83.1 CrE 91.7 SmB 99.6 SmA 158.0 I 155.6 SmA 98.5 SmB 90.7 CrE 70.1 CrX 66.7 Cr
***5*T4Cl**	5	Cr 90.6 SmA 147.8 I 145.9 SmA 89.5 SmB 73.0 CrE
***6*T4Cl**	6	Cr 90.3 SmB 94.3 SmA 147.7 I 145.2 SmA 93.1 SmB 75.0 CrE 68.1 CrX 59.5 Cr
***7*T4Cl**	7	Cr 89.4 SmA 140.5 I 138.6 SmA 88.8 SmB 74.4 Cr
***8*T4Cl**	8	Cr 87.1 SmB 93.0 SmC* 95.1 SmA 139.0 I 136.9 SmA 94.7 SmC* 91.6 SmB 67.4 CrX 66.2 Cr
***9*T4Cl**	9	Cr 88.2 SmC* 102.5 SmA 132.6 I 130.6 SmA 101.8 SmC* 86.7 SmB 75.9 Cr
***10*T4Cl**	10	Cr 81.0 SmB 89.6 SmC* 104.7 SmA 130.0 I 128.0 SmA 104.1 SmC* 88.2 SmB 65.3 Cr
***12*T4Cl**	12	Cr 91.4 SmC* 108.6 SmA 123.0 I 120.6 SmA 107.3 SmC* 85.3 SmB 79.7 Cr
***4*T6H**	4	Cr 74.7 CrE 89.1 SmB 96.5 SmA 166.9 I 165.5 SmA 95.7 SmB 88.0 CrE 62.3 Cr
***5*T6H**	5	Cr 84.7 SmB 87.4 SmA 157.5 I 154.6 SmA 85.8 SmB 68.4 CrE
***6*T6H**	6	Cr 84.3 SmB 92.3 SmA 157.4 I 155.6 SmA 91.1 SmB 70.9 CrE
***7*T6H**	7	Cr 81.1 SmB 88.0 SmA 150.8 I 148.3 SmA 86.7 SmB 63.2 CrE
***8*T6H**	8	Cr 79.1 SmB 91.9 SmA 149.0 I 147.0 SmA 90.6 SmB 62.1 CrE
***9*T6H**	9	Cr 82.8 SmB 88.7 SmC* 97.0 SmA 143.3 I 141.5 SmA 95.1 SmC* 87.6 SmB 50.3 Cr
***10*T6H**	10	Cr 90.9 SmC* 101.8 SmA 140.4 I 138.1 SmA 101.5 SmC* 89.2 SmB 50.2 Cr
***12*T6H**	12	Cr 98.6 SmC* 107.4 SmA 131.9 I 129.6 SmA 105.7 SmC* 89.2 SmB 67.6 Cr
***4*T6Cl**	4	CrE 94.3 SmB 102.3 SmA 173.4 I 170.4 SmA 101.2 SmB 93.1 CrE
***5*T6Cl**	5	Cr 107.2 SmA 164.6 I 161.8 SmA 97.6 Cr
***6*T6Cl**	6	Cr 106.0 SmA 162.5 I 159.3 SmA 96.6 SmB 91.4 Cr
***7*T6Cl**	7	Cr 104.6 SmA 156.1 I 153.7 SmA 96.1 Cr
***8*T6Cl**	8	Cr 102.4 SmC* 105.5 SmA 152.1 I 149.3 SmA 104.8 SmC* 94.5 Cr
***9*T6Cl**	9	Cr 103.8 SmC* 115.6 SmA 148.5 I 146.7 SmA 115.1 SmC* 97.3 Cr
***10*T6Cl**	10	Cr 103.4 SmC* 119.2 SmA 144.8 I 142.5 SmA 118.6 SmC* 98.9 Cr
***12*T6Cl**	12	Cr 104.3 SmC* 121.1 SmA 136.4 I 133.6 SmA 120.0 SmC* 100.0 Cr

($C_8H_{17}OC_6H_4$–≡–$C_6H_4CO^+$, 100.00), 221 (HOC_6H_4–≡–$C_6H_4CO^+$, 6.67). Elemental analysis: calculated for $C_{40}H_{38}F_{12}O_6$, C 57.01, H 4.55, F 27.05%; found, C 56.89, H 4.61, F 26.95%.

2.2.8. Synthesis of compound *8*T6Cl. IR υ_{max} (KBr, cm^{-1}): 2922, 2853, 2213, 1748, 1725, 1599, 1506, 1251, 1200, 834. ^1H NMR (300 MHz; $CDCl_3$; TMS) δ(ppm): 0.91 (t, J=6.7 Hz, 3H, CH_3), 1.26–1.83 (m, 15H, aliphatic), 2.49 (tt, J_1=18.2, J_2=6.4 Hz, 2H, R_fCH_2), 4.00 (t, J=6.6 Hz, 2H, RCH_2O), 4.49 (t, J=6.3 Hz, 2H, RCH_2O), 4.79 (q, J=6.8 Hz, H, R_1R_2CHO), 6.87–6.94 (m, 4H, ArH), 7.13 (d, J=6.7 Hz, 2H, ArH), 7.50 (d, J=8.7 Hz, 2H, ArH), 7.62 (d, J=8.5 Hz, 2H, ArH),), 8.16 (d, J=8.4 Hz, 2H, ArH). ^{19}F NMR (56.4 MHz, $CDCl_3$, TFA) δ(ppm): −9.40 (s, 2F), 36.20(m, 2F), 43.00–44.30 (m, 6F), 46.30 (s, 2F). MS m/z (rel. int.): 877 (M^++1, 1.79), 332 ($C_8H_{17}OC_6H_4$–≡–$C_6H_4CO^+$–1, 100.00), 221(HOC_6H_4–≡–$C_6H_4CO^+$, 6.82). Elemental analysis: calculated for $C_{40}H_{37}ClF_{12}O_6$, C 54.77, H 4.25, Cl 4.04, F 25.99%; found, C 54.91, H 4.21, Cl 3.85, F 25.87%.

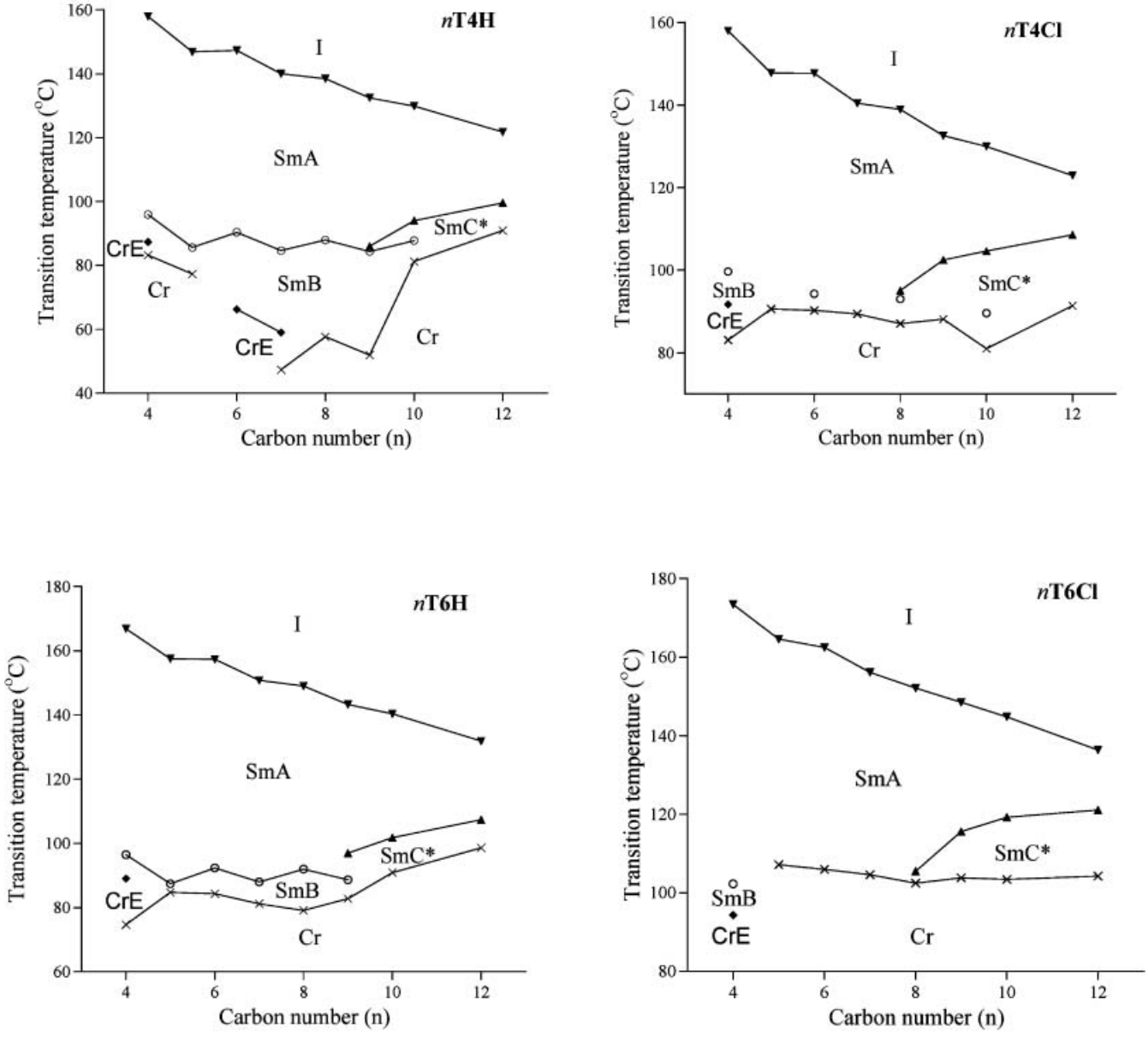


Figure 1. Transition behaviour of the *n***T4H**, *n***T4Cl**, *n***T6H** and *n***T6Cl** series: dependence of the transition temperatures on the number (*n*) of methylene units of the non-fluorinated chain.

3. Results and discussion

The phase transition temperatures of all the compounds were determined by DSC with a heating rate of $5^{\circ}C\,min^{-1}$. POM textures were observed to determine the types of mesophases. The transition temperatures shown in all the tables are the maxima of the transition peaks on each DSC trace.

The phase transition temperatures of *n***T4H**, *n***T4Cl**, *n***T6H** and *n***T6Cl** compounds are summarized in table 1. Figure 1 plots the transition temperatures of these four series with triple bonds as a function of the number of methylene units (*n*) in the non-fluorinated chain. All of these compounds exhibit smectic mesophases. For compounds *n***T4H**, when the alkoxy chains are short, only enantiotropic smectic B (SmB) and smectic A (SmA) phases are found. An enantiotropic SmC* phase appears only when the alkoxy chain is longer than eight carbons. In general, the clearing points decrease with increasing alkoxy chain length. The clearing points and the temperatures of the SmB–SmA (or SmC) transition show a clear odd–even effect.

Compounds *n***T4Cl** are formed by changing the hydrogen atoms in the semi-fluorocarbon chains of compounds *n***T4H** to chlorine. Compounds *n***T4Cl** show similar liquid crystalline properties to those of *n***T4H**. However, when the alkoxy chain numbers are even, compounds *n***T4Cl** show enantiotropic SmB phases. When the alkoxy chain numbers are odd, compounds *n***T4Cl** show monotropic SmB phases. Figure 2 plots the clearing points of compounds *n***T4H**, *n***T4Cl**, *n***T6H** and *n***T6Cl** versus the number of the carbon atoms in the alkoxy chains. In general, when the numbers of the carbon atoms in the alkoxy chains are the same, with change of the terminal hydrogen atom in the semi-fluorocarbon chain to chlorine, the clearing points increase by around 0.1–0.5°C.

By increasing the length of fluorocarbon chain of *n***T4H**, compounds *n***T6H** were synthesized. They also show similar liquid crystalline properties as *n***T4H**. However, comparing these two series, when the number of the carbon atoms in the alkoxy chains is same, the clearing points are 10°C increased and the thermal stability of the SmB phase is around 3°C increased with an increase of the fluorocarbon chain length. When the terminal hydrogen atoms in the semi-fluorocarbon chain of *n***T6H** were substituted by chlorine atoms, the clearing points of *n***T6Cl** increased around 5°C. This increase is higher than that of the clearing points of *n***T4H** to *n***T4Cl**. When the fluorocarbon segments are long enough, at least six to eight carbons, due to the incompatibility of fluorocarbon- and hydrocarbon-segments, lamellar phases tend to be formed [17–19]. Moreover, because fluorocarbon chains are rigid, when the carbon number increases to 6, we may consider the fluorocarbon chain as a liquid crystalline core. It is well known that the substitution of hydrogen in the terminal of liquid crystalline core by other atoms may increase the length or enhance the polarity of the compounds [20–23]. Therefore, the clearing points of the obtained compounds would increase. For compounds *n***T4H** and *n***T4Cl**, because their fluorocarbon chains are too short to form stable fluorocarbon phase, when the carbon numbers (*n*) of the alkoxy chains are same, the clearing points are nearly same.

Comparing all four series of compounds shown in figure 1, the substitution of the terminal hydrogen atom in the semi-fluorocarbon chain by chlorine can enhance the thermal stability of SmC* and SmA phases, suppress the formation of the SmB phase, increase melting points and broaden the SmC* phase range. Moreover, the increase of the length of fluorocarbon chain can simplify phase transition sequence. However, the SmC* phase range does not change.

The phase transition temperatures of compounds *n***BP4H**, *n***BP4Cl**, *n***BP6H** and *n***BP6Cl** are summarized in table 2. All of these compounds exhibit smectic mesophases. Generally, these four series show similar phase transition properties. Figure 3 plots the transition temperature of *n***BP6Cl** as a function of the number of methylene units (*n*) in the non-fluorinated chain. With increasing the number of methylene units (n) in the non-fluorinated chain, the clearing points decrease gradually with a somewhat small odd–even effect. The SmB phase

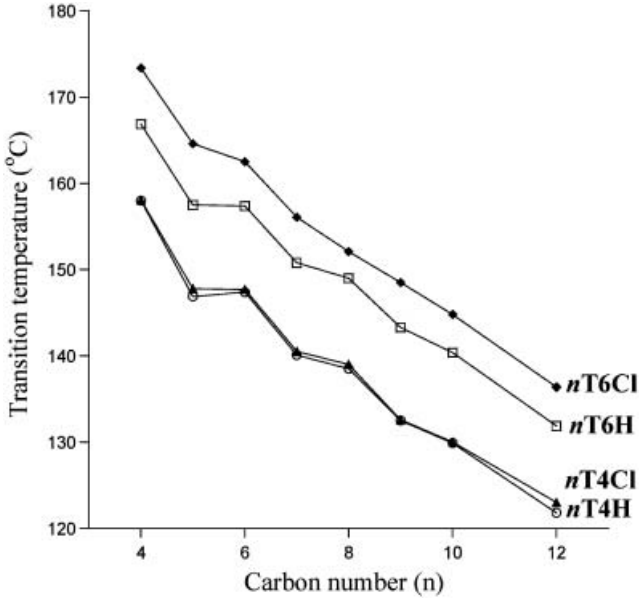


Figure 2. The clearing points of the four series of compounds listed in table 1 versus the number of the carbon atoms in the alkoxy chain.

Table 2. Transition temperatures of the *n***BP4H**, *n***BP4Cl**, *n***BP6H** and *n***BP6Cl** compounds (definitions as in table 1).

Compound	*n*	Transition temperatures/°C
*5***BP4H**	5	CrE 92.6 SmB 102.7 SmA 159.9 I 157.3 SmA 100.8 SmB 90.3 CrE
*7***BP4H**	7	Cr 69.3 SmB 91.8 SmA 147.1 I 145.5 SmA 90.8 SmB 58.4 CrE
*8***BP4H**	8	Cr 71.4 SmB 87.9 SmC* 96.0 SmA 142.1 I 139.9 SmA 95.6 SmC* 86.6 SmB 44.6 CrE
*10***BP4H**	10	Cr 77.8 SmC* 103.8 SmA 130.0 I 128.3 SmA 102.0 SmC* 73.6 SmB 43.2 Cr
*5***BP4Cl**	5	CrE 94.5 SmB 105.1 SmA 163.8 I 161.5 SmA 102.8 SmB 91.8 CrE
*7***BP4Cl**	7	Cr 63.7 CrE 74.3 SmB 94.9 SmC* 100.9 SmA 152.6 I 150.2 SmA 93.6 SmC* 100.4 SmB 62.7 CrE
*8***BP4Cl**	8	Cr 75.4 SmB 90.0 SmC* 110.7 SmA 147.2 I 144.8 SmA 109.3 SmC* 87.9 SmB 49.6 CrE
*9***BP4Cl**	9	Cr 85.2 SmC* 114.8 SmA 140.6 I 139.2 SmA 113.1 SmC* 79.8 SmB 68.3 Cr
*10***BP4Cl**	10	Cr 85.6 SmC* 117.0 SmA 136.7 I 135.0 SmA 115.2 SmC* 75.2 Cr
*5***BP6H**	5	CrE 91.9 SmB 103.2 SmA 170.0 I 168.1 SmA 102.3 SmB 90.5 CrE
*7***BP6H**	7	Cr 60.9 SmB 94.3 SmA 157.1 I 154.7 SmA 92.9 SmB 59.8 Cr
*8***BP6H**	8	Cr 76.1 SmB 90.5 SmC* 105.9 SmA 151.2 I148.9 SmA 105.1 SmC* 87.7 SmB 48.2 CrE
*9***BP6H**	9	Cr 80.4 SmB 83.0 SmC* 109.3 SmA 144.9 I 142.9 SmA 107.5 SmC* 82.0 SmB 55.1 Cr
*10***BP6H**	10	Cr 88.7 SmC* 112.3 SmA 140.2 I 137.8 SmA 110.4 SmC* 79.5 SmB 62.4 Cr
*5***BP6Cl**	5	CrE 95.4 SmB 108.6 SmA 179.5 I 177.0 SmA 107.4 SmB 94.1 CrE
*6***BP6Cl**	6	CrE 89.1 SmB 107.6 SmA 174.9 I 172.6 SmA 106.4 SmB 87.6 CrE
*7***BP6Cl**	7	Cr 87.4 SmB 99.0 SmA 166.3 I 164.5 SmA 98.3 SmB 72.8 Cr
*8***BP6Cl**	8	Cr 87.7 SmB 95.7 SmC* 125.3 SmA 161.8 I 159.3 SmA 124.2 SmC* 94.6 SmB 76.2 Cr
*9***BP6Cl**	9	Cr 95.9 SmC* 128.2 SmA 155.0 I 153.4 SmA 127.3 SmC* 89.9 Cr
*12***BP6Cl**	12	Cr 102.9 SmC* 127.5 SmA 140.4 I 138.7 SmA 125.6 SmC* 97.3 Cr

is suppressed and SmC* phase tends to be formed. Comparing compounds *n***T6Cl** with *n***BP6Cl** (figures 1 and 3), it is found that with the introduction of a triple bond the clearing points and the thermal stability of SmC* phase decrease, the tendency of the formation of SmB phase is suppressed.

For a clear understanding the effect of the H/Cl change in the terminal of fluorocarbon chain, the fluorocarbon chain length, and the introduction of a triple bond, the phase transition properties of eight compounds, *8***BP4H**, *8***BP4Cl**, *8***BP6H**, *8***BP6Cl**, *8***T4H**, *8***T4Cl**, *8***T6H**, and *8***T6Cl** are summaried in figure 4. From the phase transition properties of the four pairs *8***T4H**/*8***T4Cl**, *8***T6H**/*8***T6Cl**, *8***BP4H**/*8***BP4Cl** and *8***BP6H**/*8***BP6Cl**, it is found that the substitution of chlorine atom can enhance the tendency of the formation and the thermal stability of SmC* phase and increase the clearing and melting points. However,

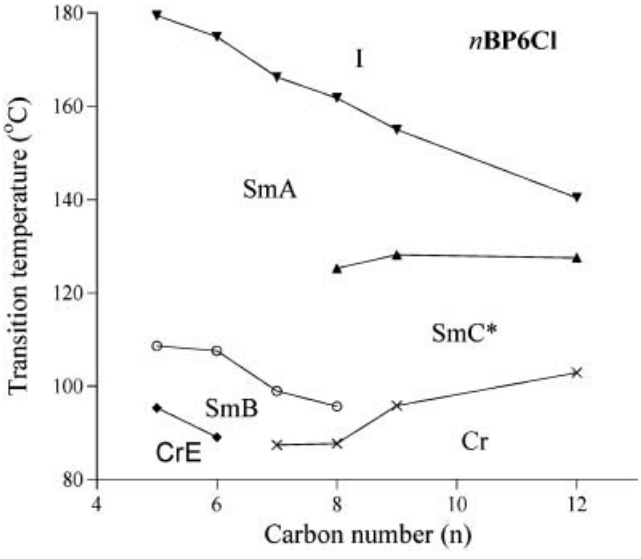


Figure 3. Transition behaviour of the *n***BP6Cl** series: dependence of the transition temperatures on the number (*n*) of methylene units of the non-fluorinated chain.

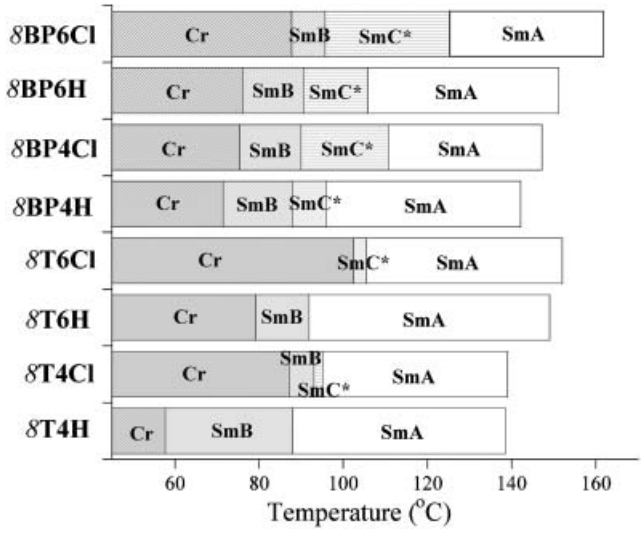


Figure 4. Comparison of mesomorphic properties of compounds investigated.

the width of the SmB phase range becomes narrower. The introduction of a chlorine atom seems to enhance the formation of fluorocarbon phase. Because of the phase separation between fluorocarbon and hydrocarbon phase, the thermal stability of lamellar phases are enhanced. Turning to the four pairs *8***T4H**/*8***T6H**, *8***T4Cl**/*8***T6Cl**, *8***BP4H**/*8***BP6H** and *8***BP4Cl**/*8***BP6Cl**, the increase of the length of the fluorocarbon chain increases the clearing points by around 10°C and the thermal stability of the SmC* phase. For the four pairs *8***BP4H**/*8***T4H**, *8***BP4Cl**/*8***T4Cl**, *8***BP6H**/*8***T6H** and *8***BP6Cl**/*8***T6Cl**, the introduction of a triple bond into the core decreases the clearing points, melting points and the thermal stability of the SmC* phase. Possibly the triple bond interfers with the conjugation of the molecule; the lateral–lateral interactions are then weakened.

In summary, eight series of chiral compounds with semi-fluorocarbon chains have been synthesized. The increase of the fluorocarbon chains length can increase their clearing points and thermal stability of the SmC* phase. For a particluar compound, when the terminal hydrogen atom in the semi-fluoroalkyl chain was substituted by a chlorine atom, both the clearing point and melting point are increased and the thermal stability of SmC* phase is enhanced. Meanwhile, it was also found that the clearing point decreased and melting point increased with the introduction of a triple bond into the core.

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References

[1] F.G. Tournilhac, L.M. Blinov, J. Simon, S.V. Yablonsky. *Nature*, **359**, 621 (1992).
[2] P. Kromm, M. Cotrait, J.C. Roullon, P. Barois, H.T. Nguyen. *Liq. Cryst.*, **21**, 121 (1996).
[3] P. Kromm, M. Cotrait, H.T. Nguyen. *Liq. Cryst.*, **21**, 95 (1996).
[4] B. Chen, Y. Yang, J. Wen. *Liq. Cryst.*, **24**, 539 (1998).
[5] F.G. Tournilhac, L. Bosio, L. Simon, L.M. Blinov, S.V. Yablonsky. *Liq. Cryst.*, **14**, 405 (1993).
[6] H. Liu, H. Nohira. *Liq. Cryst.*, **22**, 217 (1997).
[7] H.T. Nguyen, G. Sigaud, M.F. Archard, F. Hardouin, R.J. Twing, K. Betterton. *Liq. Cryst.*, **10**, 389 (1991).
[8] G. Johansson, V. Percec, G. Ungar, K. Smith. *Chem. Mater.*, **9**, 164 (1997).
[9] S. Takenaka. *J. chem. Soc., Chem. Commun.*, 1748 (1992).
[10] H. Okamoto, H. Murai, S. Takenaka. *Bull. chem. Soc. Japan*, 3163 (1997).
[11] S.V. Arehart, C. Pugh. *J. Am. chem. Soc.*, **119**, 3027 (1997).
[12] Y. Yang, G. Tang, J. Wen. *Mol. Cryst. liq. Cryst.*, **373**, 25 (2002).
[13] Y. Yang, J. Wen. *Liq. Cryst.*, **28**, 1735 (2001).
[14] Y. Yang, J. Wen. *Liq. Cryst.*, **29**, 159 (2002).
[15] Y. Yang, J. Wen. *Liq. Cryst.*, **29**, 161 (2002).
[16] H. Li, Y. Yang, J. Wen. *Chin. J. Chem.*, **18**, 900 (2000).
[17] J. Höpken, M. Möller. *Macromolecules*, **25**, 2482 (1992).
[18] W. Mahler, D. Guillon, A. Skoulios. *Mol. Cryst. liq. Cryst.*, **2**, 111 (1985).
[19] C. Viney, R.J. Twieg, T.P. Russell, L.E. Deprero. *Liq. Cryst.*, **5**, 1783 (1989).
[20] G. Tang, K. Wang, Y. Yang, J. Wen. *Liq. Cryst.*, **28**, 1623 (2001).
[21] Y. Yang, K. Wang, J. Wen. *Liq. Cryst.*, **28**, 1553 (2001).
[22] Y. Yang, H. Chen, G. Tang, J. Wen. *Liq. Cryst.*, **29**, 255 (2002).
[23] Y. Yang, H. Chen, G. Tang, J. Wen. *Mol. Cryst. liq. Cryst.*, **373**, 1 (2002).