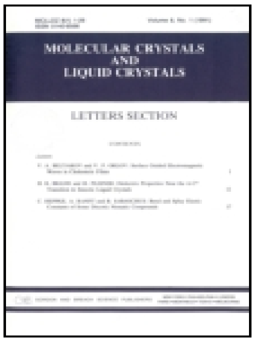

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Smectic C Mesogens with Terminal Perfluoroalkyl Chains

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The fluorocarbon derivatives were synthesized. Liquid crystalline states were studied by DSC and microscopic observation. T_{NI} of those compounds were from 161.2°C to 191.7°C, which represented those compounds had very good liquid crystalline stability. Smectic C temperature range was 91.7°C for F8H2OPMB, 54.9°C for F8H2OPCB, 41.1°C for F8H2OPMB-F, 36.2°C for F8H2OMB, 27.4°C for F8H2OPCB-F, and 10.8°C for F6H2OMB. The structures of F8H2OPCB and F8H2OPCB-F at room temperature were tilted herringbone packing of two aromatic ring ester cores (smectic K phase) and perfluoroalkyl chains were located up and down alternatively. Smectic K was proved by high intensity of 003 and 004 reflections in X-ray diffraction.

Keywords DSC; fluorocarbon; microscopic texture; smectic C; smectic K; XRD

Introduction

Fluorocarbons and hydrocarbons possess different properties and are incompatible with one another. Those are due to the different chemical structures of H and F atoms leading to different chain conformations; $(CH_2)_n$ segments arrange in the usual zigzag conformation with a cross-sectional area of 18.5 Å^2/molecule, whereas a $(CF_2)_m$ chain possesses a typical 15/7 helix conformation and cross-sectional area of 28 Å^2/molecule [1, 2]. When fluorocarbons are substituted for alkanes in calamitic liquid crystals (LCs), both the transition temperature and the temperature range of mesophase stability are increased. This is due to the increased rigidity of the fluorocarbon moieties, which enhances the linearity of molecules relative to their alkane counterparts [3]. However, the intrinsic incompatibility between the fluorocarbon tails and the hydrocarbon mesogenic core leads to a nanophase separation of the chemically distinct components which results in layered (smectic) structure composed of fluorocarbon-rich and hydrocarbon-rich strata [3–6].

To study this phenomenon, we have made F6H2OCB and F8H2OCB, which both compounds exhibit smectic C phase with wide temperature range, and showed smectic K phase, proved by X-ray diffraction (XRD) spectra at room temperature [7].

In this paper, we made many derivatives of F8H2OCB, which are compounds with methoxy terminal group for high smectic C phase stability, ester linkage for extending rigid group length and fluoro substitution in aromatic ring for reducing transition temperature

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were synthesized. These compounds are shown in Fig. 1. Ferroelectric smectic C* could be formed as a result of adding a chiral component as a dopant to smectic C matrix.

Experimental

4-(2-perfluorohexyl)-ethoxy-4′-methoxybiphenyl (F6H2OMB)

1H, 1H, 2H, 2H-perfluoro-1-octanol (3.64 g, 10 mmol), 4-hydroxy-4′-methoxybiphenyl (2.01 g, 10 mmol) and triphenylphosphine (2.62 g, 10 mmol) were dissolved in dry tetrahydrofuran (THF) (30 mL). Diisopropyl azodicarboxylate (2 cm^3, 10 mmol) was added dropwise to the solution for 30 min under N_2 at 0°C. The solution was stirred at 0°C overnight under N_2 atmosphere. After quenching with cold water (1 mL), the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluent 2.5:1 hexane and ethyl acetate), and recrystallized in 95% ethanol to produce 4-(2-perfluorohexyl)-ethoxy-4′-methoxybiphenyl (F6H2OMB) as a white crystal (0.27g) in 5% yield. ^{1}H NMR and IR confirmed the structure as (δ(ppm)) 7.50 (doublet, $J =$ 8.9 Hz, 4H), 6.98 (doublet, $J = 8.9$ Hz, 4H), 4.33 (triplet, $J = 6.8$ Hz, 2H), 3.87 (singlet, 3H), 2.67 (multiplet, $J = 6.7$ and 11.7 Hz, 2H), and IR(ν_{CF} and $\nu_{CO} = 1257, 1182, 1141,$ 1087 cm^{-1}).

4-(2-perfluorooctyl)-ethoxy-4′-methoxybiphenyl (F8H2OMB)

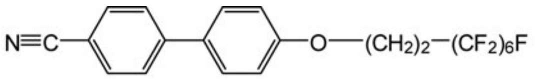
F8H2OMB was synthesized by the same method as F6H2OMB synthesis.

1-(2-perfluorooctyl)-ethoxy-4-methoxybenzene (F8H2OMP)

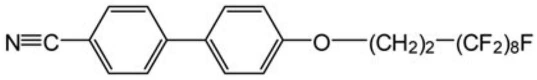
1H, 1H, 2H, 2H-perfluoro-1-decanol (11.6 g, 25 mmol), 4-methoxyphenol (3.1 g, 25 mmol) and triphenylphosphine (6.55 g, 25 mmol) were dissolved in dry tetrahydrofuran (THF) (35 ml). Diisopropyl azodicarboxylate (5 cm^3, 25 mmol) was added dropwise to the solution for 30 min under N_2 at 0°C. The solution was stirred at 0°C overnight under N_2 atmosphere. After quenching with cold water (1 mL), the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluent 2.5:1 hexane and ethyl acetate), and recrystallized in 95% ethanol to produce 1-(2-perfluorooctyl)-ethoxy-4-methoxybenzene as a white crystal (0.71g) in 5% yield. ^{1}H NMR confirmed the structure as (δ(ppm)) 6.87 (singlet, 4H), 4.25 (triplet, $J = 6.8$ Hz, 2H), 3.80 (singlet, 3H), 2.62 (multiplet, $J = 6.8$, and 11.7 Hz, 2H).

1-(2-perfluorooctyl)-ethoxy-4-hydroxybenzene

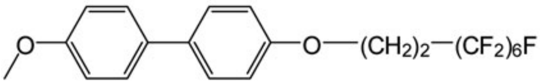
1-(2-Perfluorooctyl)-ethoxy-4-methoxybenzene (12.5 g, 22 mmol) was dissolved in dichloromethane (50 mL). Boron tribromide (5.1 cm^3, 53 mmol) in dichloromethane (50) was added dropwise to the solution at 0°C. The solution was stirred at room temperature overnight. After quenching with cold water (5 mL), the solvent was removed under reduced pressure. The residue was dissolved by the addition of 100 mL of ether. The organic layer was separated and extracted with water, 10% $NaHCO_3$ and water. The ether extract was dried over anhydrous magnesium sulfate and recrystallized in toluene to produce 1-(2-perfluorooctyl)-ethoxy-4-hydroxybenzene as a white crystal (10.6 g) in 87% yield. ^{1}H NMR confirmed the structure as (δ(ppm)) 6.83 (doublet, $J = 8.7$ Hz, 2H), 6.79 (doublet, $J = 8.7$ Hz, 2H), 4.78 (singlet, 1H), 4.24 (triplet, $J = 6.8$ Hz, 2H), and 2.62 (multiplet, $J = 6.8$ and 11.6 Hz, 2H).



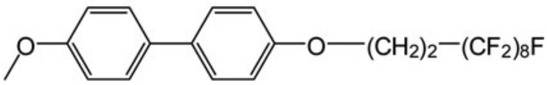
(1) F6H2OCB



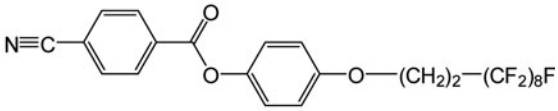
(2) F8H2OCB



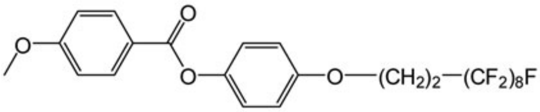
(3) F6H2OMB



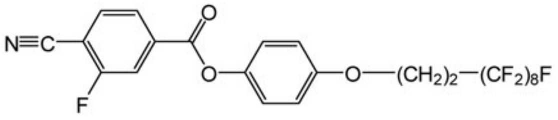
(4) F8H2OMB



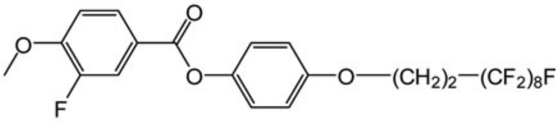
(5) F8H2OPCB



(6) F8H2OPMB



(7) F8H2OPCB-F



(8) F8H2OPMB-F

Figure 1. The structure of the liquid crystalline compounds with terminal perfluoroalkyl chains.

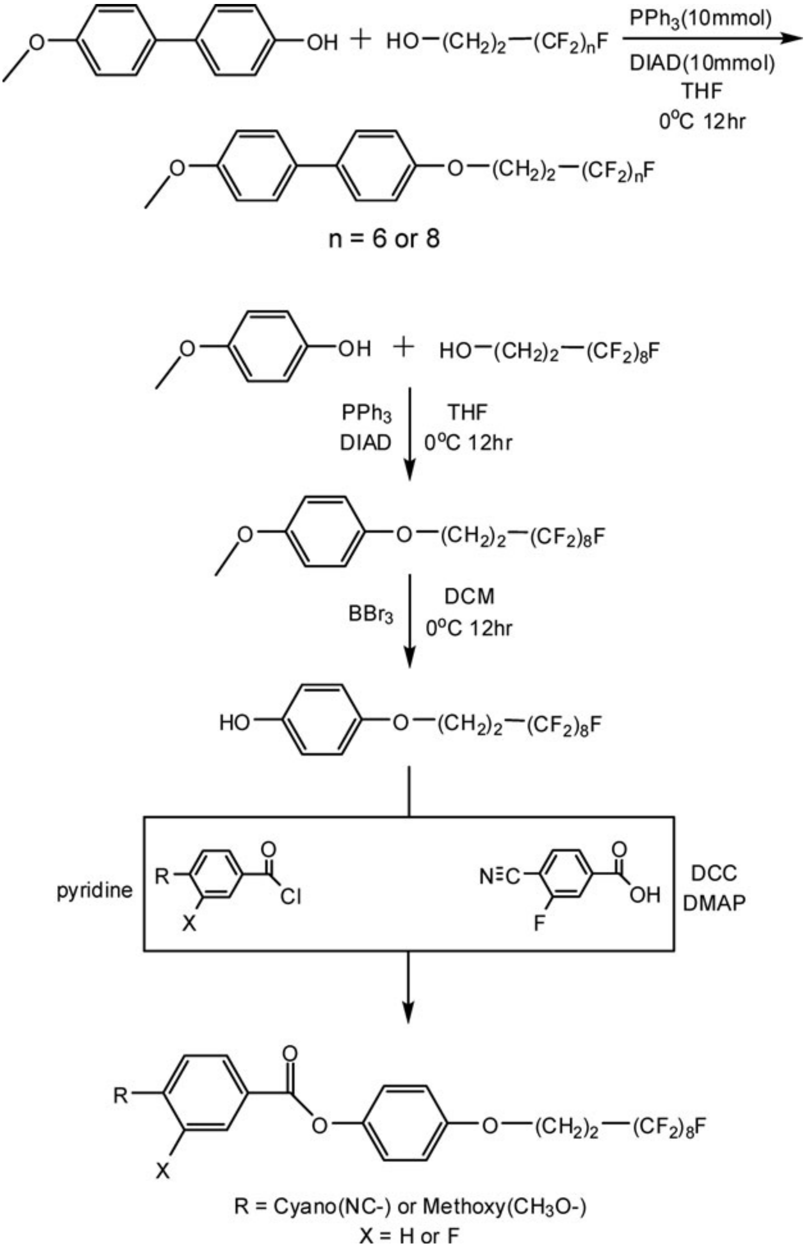


Figure 2. Synthesis of F-6H2OMB, F8H2OPCB and F8H2OPCB, F8H2OPMB and F8H2OPCB-F, F8H2OPMB-F.

4-(2-perfluorooctyl)-ethoxyphenyl-4′-cyanobenzoate (F8H2OPCB)

1-(2-Perfluorooctyl)-ethoxy-4-hydroxybenzene (0.56 g, 1 mmol), 4-cyanobenzoyl chloride (0.26 g, 1 mmol) and pyridine (0.16 cm^3, 2 mmol) were dissolved in chloroform (25 mL). The solution was stirred for 3 hr at room temperature. After quenching with cold water (1 mL), the solvent was removed under reduced pressure. The residue was purified by

Table 1. Thermal transitions of the liquid crystalline compounds (Fig. 3)

Compound	Transition temperatures (°C)										ΔH (J/g)
(1) F6H2OCB[7]	S_K	89.4	S_C	162.0	S_A	162.7	I				29.35 & 8.28
(2) F8H2OCB[7]	S_K	103.7	S_C	182.1	S_A	182.9	I				37.07 & 10.54
(3) F6H2OMB	Cr	124.5	S?	139.2	S_C	150.0	S_A	176.6	I		12.41 & 12.53 & 12.90
(4) F8H2OMB	Cr	104.3	S?	140.8	S_C	177.0	S_A	191.7	I		4.57& 5.61 & 5.60
(5) F8H2OPCB	S_K	129.1	S_C	184.0	S_A	189.5	I				36.90 & 10.58
(6) F8H2OPMB	Cr	82.3	S_C	174.0	S_A	182.4	I				16.50 & 3.98
(7) F8H2OPCB-F	S_K	121.6	S_C	149.0	S_A	161.2	I				48.19 & 10.48
(8) F8H2OPMB-F	Cr	104.9	S_C	146.0	S_A	162.3	I				35.34 & 6.37

column chromatography on silica gel (eluent 2.5:1 hexane and ethyl acetate), and recrystallized in 95% ethanol to produce 4-(2-perfluorooctyl)-ethoxyphenyl-4′-cyanobenzoate (F8H2OPCB) as a white crystal (0.4 g) in 58% yield. ^{1}H NMR and IR confirmed the structure as (δ(ppm)) 8.32 (doublet, $J = 8.4$ Hz, 2H), 7.84 (doublet, $J = 8.4$ Hz, 2H), 7.18 (doublet, $J = 9.0$ Hz, 2H), 6.99 (doublet, $J = 9.0$ Hz, 2H), 4.32 (triplet, $J = 6.8$ Hz, 2H), 2.67 (multiplet, $J = 6.7$ and 11.7 Hz, 2H), IR($\nu_{CN} = 2231$ cm^{-1}, $\nu_{C=O} = 1743$ cm^{-1}, ν_{CF} and $\nu_{CO} = 1251$, 1195, 1149, 1116 cm^{-1}).

4-(2-perfluorooctyl)-ethoxyphenyl-4′-methoxybenzoate (F8H2OPMB)

F8H2OPMB was synthesized by the same method as F8H2OPCB synthesis. ^{1}H NMR and IR confirmed the structure as (δ(ppm)) 8.17 (doublet, $J = 9.0$, 2H), 7.16 (doublet, $J = 9.0$, 2H), 7.00 (doublet, $J = 9.0$, 2H), 6.96 (doublet, $J = 9.1$, 2H), 4.31 (triplet, $J = 6.8$, 2H), 3.92 (singlet, 3H), 2.67 (multiplet, $J = 6.7$ and 11.7 Hz, 2H), and IR($\nu_{C=O} = 1735$ cm^{-1}, ν_{CF} and $\nu_{CO} = 1249$, 1203, 1164, 1116 cm^{-1}).

4-(2-perfluorooctyl)-ethoxyphenyl-3′-fluoro-4′-methoxybenzoate (F8H2OPMB-F)

F8H2OPMB-F was synthesized by the same method as F8H2OPCB synthesis. ^{1}H NMR and IR confirmed the structure as (δ(ppm)) 8.00 (doublet, $J = 9.3$, 1H), 7.92 (doublet, $J = 9.6$, 1H), 7.15 (doublet, $J = 9.2$, 2H), 7.07 (doublet, $J = 8.4$, 1H), 6.97 (doublet, $J = 9.1$, 2H), 4.31 (triplet, $J = 6.8$, 2H), 4.01 (singlet, 3H), 2.67 (multiplet, $J = 6.6$ and 12.0 Hz, 2H), and IR($\nu_{C=O} = 1732$ cm^{-1}, ν_{CF} and $\nu_{CO} = 1261$, 1203, 1145, 1101 cm^{-1}).

4-(2-perfluorooctyl)-ethoxyphenyl-3′-fluoro-4′-cyanobenzoate (F8H2OPCB-F)

4-(Dimethylamino)pyridine(DMAP) (0.08 g, 0.7 mmol) was added to a solution of 1-(2-perfluorooctyl)-ethoxy-4-hydroxybenzene (0.56 g, 1 mmol), 4-cyano-3-fluorobenzoic acid (0.18 g, 1 mmol) and *N*,*N*′-dicyclohexylcarbodiimide(DCC) (0.28 g, 1.4 mmol) in dichloromethane (25 mL). The solution was stirred for 26 hr at room temperature. After quenching with cold water (1 mL), the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluent 2.5:1 hexane and ethyl

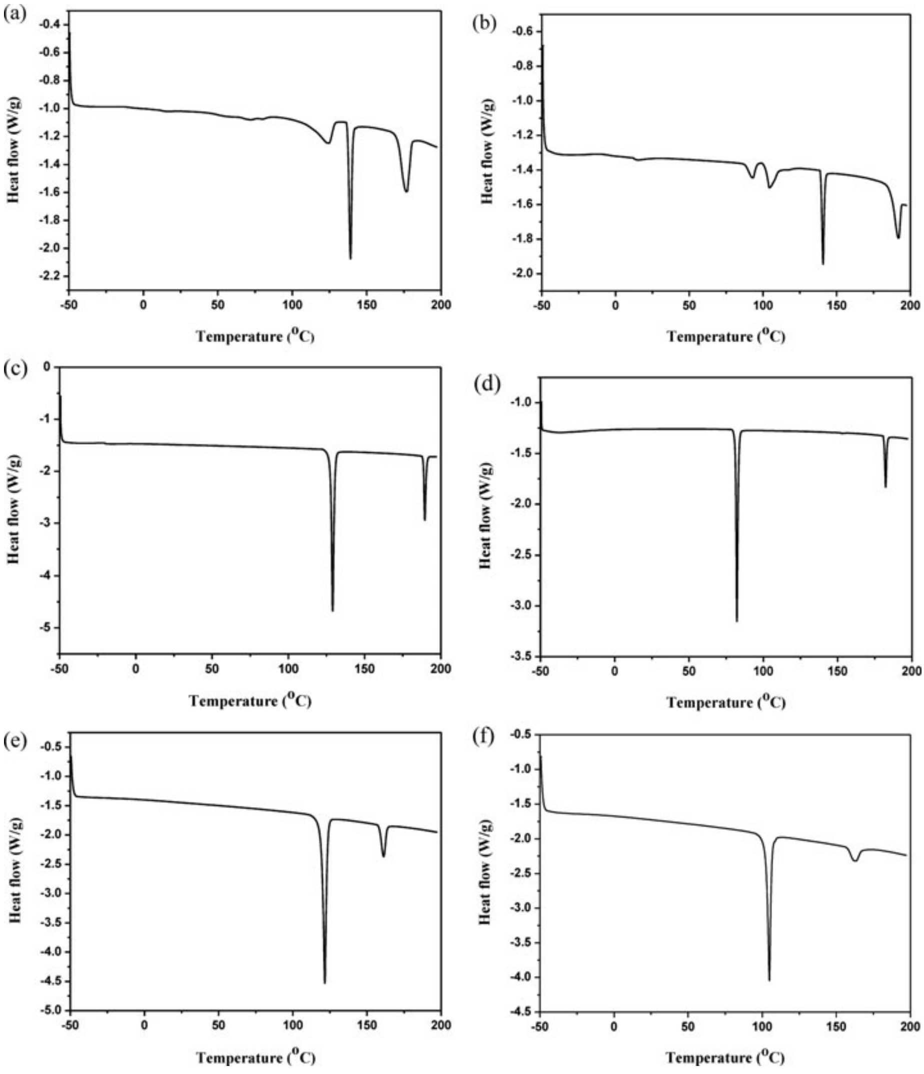


Figure 3. DSC thermogram of (a) F6H2OMB, (b) F8H2OMB, (c) F8H2OPCB, (d) F8H2OPMB, (e) F8H2OPCB-F, and (f) F8H2OPMB-F.

acetate), and recrystallized in 95% ethanol to produce 4-(2-perfluorooctyl)-ethoxyphenyl-3′-fluoro-4′-cyanobenzoate (F8H2OPCB-F) as a white crystal (0.42 g) in 60% yield. ^{1}H NMR and IR confirmed the structure as (δ(ppm)) 8.11 (doublet, $J = 6.6$ Hz, 1H), 8.05 (doublet, $J = 7.8$ Hz, 1H), 7.82 (doublet, $J = 6.1$ Hz, 1H), 7.17 (doublet, $J = 9.1$ Hz, 2H), 6.99 (doublet, $J = 9.2$ Hz, 2H), 4.31 (triplet, $J = 6.5$, 2H), 2.67 (multiplet, $J = 6.9$ and 11.4 Hz, 2H), IR($\nu_{\mathrm{CN}} = 2245$ cm^{-1}, $\nu_{\mathrm{C=O}} = 1732$ cm^{-1}, ν_{CF} and $\nu_{\mathrm{CO}} = 1257$, 1207, 1147, 1114 cm^{-1}).

Differential scanning calorimetry (DSC) was performed on a TA DSC Q20 (TA Instruments, New Castle, DE, USA) with ~10 mg sample using a scanning rate of 10°C min^{-1}.

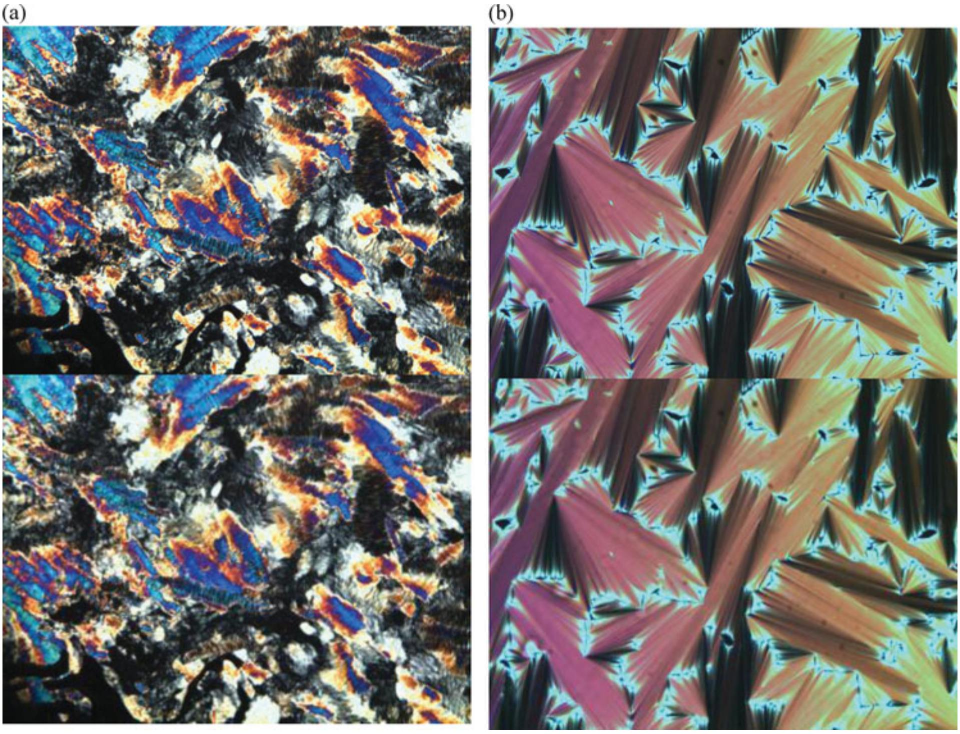


Figure 4. (a) Broken fan-shaped texture of the S_C phase of F8H2OPCB at 130°C (200×). (b) Fan-shaped texture of the S_A phase of F8H2OPCB at 186°C (200×).

Optical microscope evaluation was carried out using Olympus BX41 (Olympus Co., Shinjuku, Tokyo, Japan) polarizing microscope equipped with a Mettler FP82HT (Mettler Toledo AG, Im Langacher, Greifensee, Switzerland) hot stage.

The XRD data were collected between 5° and 60° 2θ with a step increment of 0.02° 2θ and a count time of 2 s/step. The well-known Bragg's equation ($\lambda = 2d \sin \theta$) was used to calculate the d spacing, wherein λ is a wavelength of 0.154 nm, d is the distance between each adjacent crystal plane (d spacing), and θ is the Bragg angle.

Results and Discussion

Synthesis

F8H2OMB and F8H2OMP were synthesized by Mitsunobu reaction as shown in Fig. 2. Boron tribromide was used for demethylation of methoxyphenyl, and fortunately 2-perfluorooctyl-ethoxy group was stable in this condition. Esterification was carried by conventional method, and the reaction scheme is shown in Fig. 2.

Mesomorphic Properties

The mesomophic properties of fluorocarbon compounds were investigated by DSC and optical microscopy. The smectic C to smectic A transition is second-order transition. The transition temperature was not appeared in DSC. The temperature was detected by

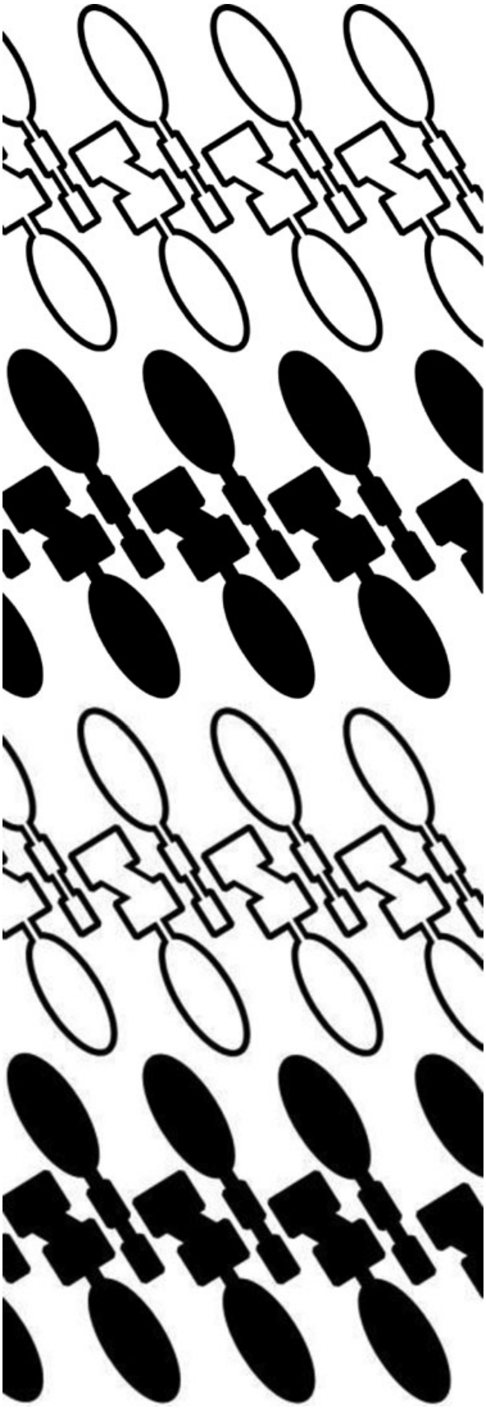


Figure 5. Schematic representation of the crystalline structure of F8H2OPCB and F8H2OPCB-F at room temperature.

Table 2. Structural parameters of the compounds with cyano terminal group

Parameter	F6H2OCB[7]	F8H2OCB[7]	F8H2OPCB	F8H2OPCB-F
L (±1Å)	36.5	41.7	43.6	43.6
d (±1Å)	28.9	32.7	36.9	37.3
	$d(002) = 14.45$	$d(002) = 16.35$	$d(003) = 12.30$	$d(003) = 12.45$
	$d(003) = 9.71$	$d(003) = 10.94$	$d(004) = 9.22$	$d(004) = 9.33$
	$d(004) = 7.32$	$d(004) = 8.29$		
θ (±1°)	37.7	38.5	32.2	31.2

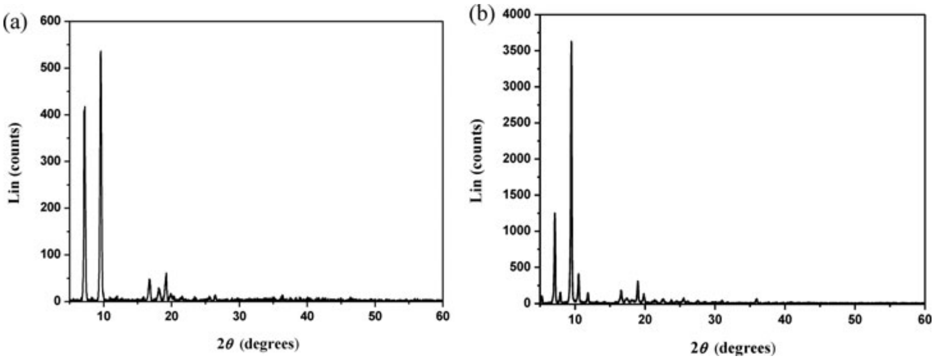


Figure 6. X-ray diffraction patterns of (a) F8H2OPCB and (b) F8H2OPCB-F.

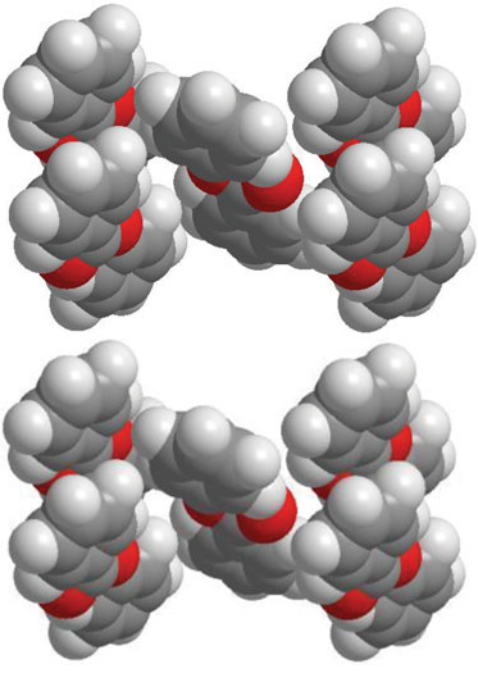


Figure 7. Tilted herringbone packing of phenyl benzoate cores (S_K, tilted S_E).

Table 3. Experimental values of intensities of 00*l* reflections in the S_K (tilted S_E) and SC phases and calculated values from the model of Fig. 5 [10]

	hkl	001	002	003	004
Calculated[10]	S_K	100	17	30	1
	S_C	100	13	13	0.2
Measured	F6H2OCB[7]	?	20	63	71
	F8H2OCB[7]	?	21	39	12
	F8H2OPCB	?	?	40	52
	F8H2OPCB-F	?	?	40	116

polarized microscope. For the methoxy terminated LC, it was difficult to detect the transition temperature due to high viscosity.

Figure 4(a) showed a broken fan-shaped texture characteristics of smectic C phase of F8H2OPCB at 130°C, Fig. 4(b) showed a fan-shaped texture characteristics of smectic A phase of F8H2OPCB at 186°C [8, 9]. All the compounds in this paper showed similar texture as that of F8H2OPCB. The transition temperatures are reported in Table 1 and Fig. 3. Methoxy terminated biphenyl compounds ((3) F6H2OMB and (4) F8H2OMB) had higher isotropic temperature (13.9°C and 8.8°C respectively) compared with that of cyano terminated biphenyl compounds ((1) F6H2OCB and (2) F8H2OCB), but smectic C temperature range was greatly reduced from 72.8°C to 10.8°C and 78.2°C to 36.2°C in that of (1) F6H2OCB to (3) F6H2OMB and (2) F8H2OCB to (4) F8H2OMB, respectively. The addition of ester linking group ((5) F8H2OPCB) extends the core group length compare with biphenyl core ((2) F8H2OCB). T_{NI} temperature was slightly higher (6.6°C), but smectic C temperature range was slightly reduced from 78.4°C in (2) F8H2OCB to 54.9°C in (5) F8H2OPCB. Compound ((6) F8H2OPMB) with methoxy terminal group and ester linking group had most wide smectic C temperature range (91.7°C).

The use of lateral fluoro substituents ((7) F8H2OPCB-F and (8) F8H2OPMB-F) is helpful in the design of ferroelectric because they usually tend to reduce melting point markedly, and the lateral polarity tends to favor the smectic C phase. Compounds (7) and (8) reduced T_{NI} 27.3°C and 20.1°C compared to that of compounds (5) and (6), respectively. The smectic C temperature range was greatly reduced from 54.9°C to 27.4°C and 91.7°C to 41.1°C in that of (5) F8H2OPCB to (7) F8H2OPCB-F and (6) F8H2OPMB to (8) F8H2OPMB-F, respectively. The fluorocarbon LCs in this paper had great LC stability based on T_{NI}. The rate of smectic C temperature range of the LCs was in the following order.

1. (6) F8H2OPMB (91.7°C) 2. (5) F8H2OPCB (54.9°C) 3. (8) F8H2OPMB-F (41.1°C) 4. (4) F8H2OMB (36.2°C) 5. (7) F8H2OPCB-F (27.4°C) 6. (3) F6H2OMB (10.8°C)

Structure of the Smectic K

The molecular lengths of F8H2OPCB and F8H2OPCB-F with fully extended conformation were about 26.6Å, which were significantly smaller than the interlayer distance, 36.9Å and 37.3Å, respectively. A bimolecular structure should be considered since the cross-sectional area of perfluoroalkyl and aromatic ring, the tilt model as shown in Fig. 5, was reasonable for these compounds.

The tilt angle (θ) was calculated by the comparison of *d* and *L* (Table 2): calculated values were $\theta = 32.2^o$ for F8H2OPCB and $\theta = 31.2^o$ for F8H2OPCB-F. Herringbone structure of two aromatic ring ester cores was identified by X-ray scattering studies (Fig. 6 and Table 3) [4, 10]. The characteristic peaks of herringbone structure in X-ray showed strong intensity in 003 and 004 reflections (Fig. 6). Even though there is no data for 001 and 002 reflections, the strong intensity of 003 and 004 reflections proved that the structure of F8H2OPCB and F8H2OPCB-F were tilted herringbone packing (smectic K phase) (Fig. 7) [10].

Conclusion

LCs with fluorocarbon exhibited smectic C phase with wide temperature range. This was proved by broken fan-shaped texture characteristics of smectic C phase in an optical microscope. Liquid crystal stability base on T_{NI} from 161.2°C to 191.2°C was very good. Smectic C temperature range was 91.7°C for F8H2OPMB, 54.9°C for F8H2OPCB, 41.1°C for F8H2OPMB-F, 36.2°C for F8H2OMB, 27.4°C for F8H2OPCB-F, and 10.8°C for F6H2OMB. Smectic K phase was observed at room temperature for both F8H2OPCB and F8H2OPCB-F up and down alternatively. Smectic K was proved by the comparison of *d* (interlayer distance) and *L* (calculated dimer molecular length) and high intensity of 003 and 004 reflections in XRD.

Acknowledgments

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