

Synthesis and mesomorphic properties of some ferroelectric liquid crystals of lactate

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A semiperfluorinated chain has been introduced into three series of lactate-based molecules, and their mesomorphic properties have been studied by DSC and optical polarized microscope. An abnormal phenomenon has been found that the introduction of a triple bond in the core of the molecule, which lengthened the molecule, gave rise to a decrease in the thermal stability of chiral smectic C phase and smectic A phase. 2, 3-Difluoro substituents of the phenylenic structure hinder the formation of the chiral smectic C phase because of the steric effect.

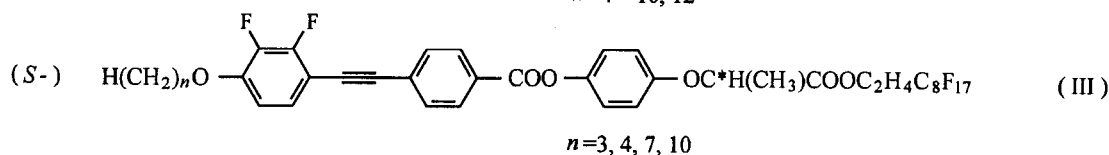
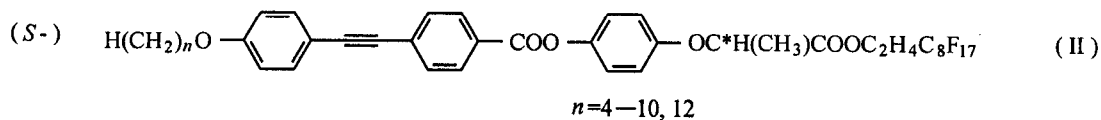
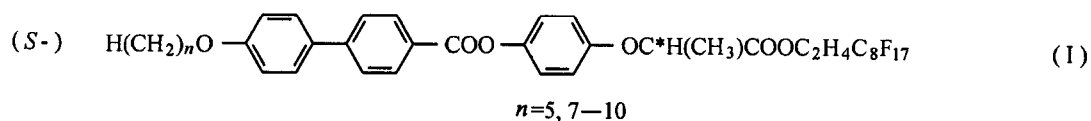
Keywords Liquid crystal, ferroelectric, semiperfluorinated

Introduction

Ferroelectric liquid crystals have been an active field of investigation in recent years in the expectation of achieving practical uses for new-age flat panel displays. To study the correlation between molecular structure and mesomorphic properties with the aim of preparing desir-

able materials, various molecular designs have been used and a great number of ferroelectric liquid crystals have been synthesized.¹ As has been pointed out, the replacement of hydrogen atoms with fluorine atoms in the hydrocarbon chains generally results in enhancement of smectic behaviour, which tends to be smectic A in type,² but in semiperfluorinated system, it seems that at a low fluorination extent, the smectic A phase is favoured and the smectic C phase is enhanced at a high fluorination extent. And the smectic C phase is always very broad.³⁻⁵ For getting new ferroelectric liquid crystals with wide chiral smectic C phase range, three series of them with long semiperfluorinated carbon tails at a high fluorination extent were synthesized (structure I, II and III), as shown in Scheme 1. In addition, only a few papers have been published in this field.⁶⁻⁸ For long fluorocarbon chains are favourable to stick together, and microphase separation may be formed in these three series, many new properties are found.

Scheme 1



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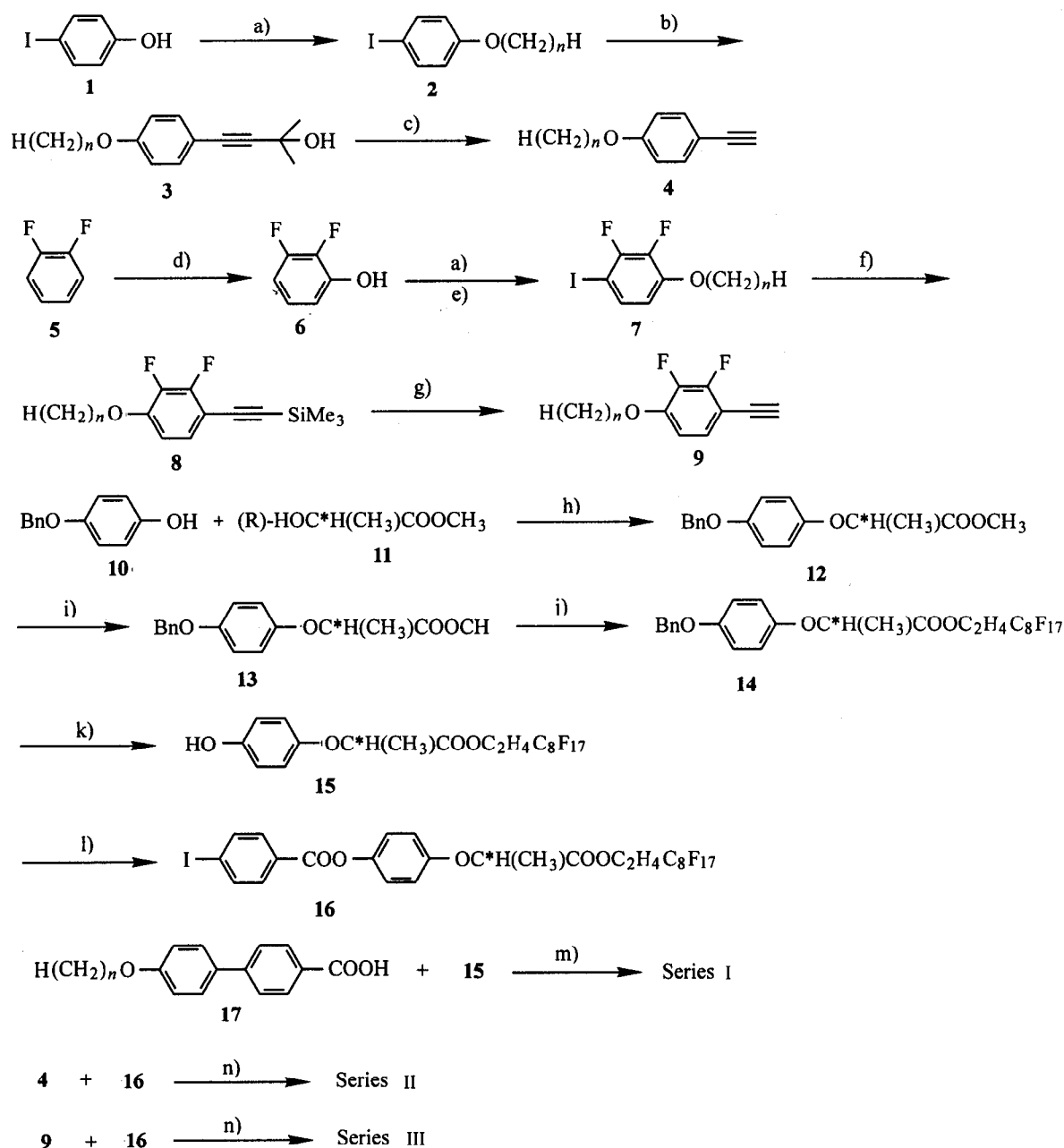
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Experimental

The compounds of series I, II and III were synthesized with the reactions shown in Scheme 2.

Compound **2** was prepared from etherification between **1** and $\text{Br}(\text{CH}_2)_n\text{H}$. Compound **3** was prepared from **2** and $\text{HO}(\text{CH}_2)_2\text{C}\equiv\text{CH}$ by the coupling reaction. Then compound **4** was obtained under the existence of

Scheme 2



Reagents and conditions: a) $\text{Br}(\text{CH}_2)_n\text{H}$, KOH, EtOH/KI; b) $\text{HO}(\text{CH}_2)_2\text{C}\equiv\text{CH}$, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI, $\text{Et}_3\text{N}/\text{THF}$; c) KOH, toluene; d) 1) BuLi, $\text{B}(\text{OMe})_3$; 2) H_3O^+ ; e) BuLi, I_2 ; f) $\text{Me}_3\text{SiC}\equiv\text{CH}$, CuI, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, $\text{Et}_3\text{N}/\text{THF}$; g) NaOH, MeOH, CH_3COCH_3 ; h) DEAD, PPh_3 , THF; i) NaOH, H_2O , THF; j) DCC/DMAP, $\text{HOC}_2\text{H}_4\text{C}_8\text{F}_{17}$; k) H_2 , 10% Pd/C; l) DCC/DMAP, *p*-I-benzoic acid; m) DCC/DMAP, THF; n) CuI, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, $\text{Et}_3\text{N}/\text{THF}$.

KOH. Compound **9** could also be obtained according to literatures.^{9,10} Compound **12** was synthesized by coupling ethyl (*R*)-2-hydroxypropanoate with *p*-(benzyloxy)phenol under standard Mitsunobu conditions. Basic hydrolysis of **12** followed by esterification with $\text{HOC}_2\text{H}_4\text{C}_8\text{F}_{17}$, in the presence of DCC/DMAP, led to the formation of the ester derivative **14**. Hydrogenolysis of **14** by palladium on activated carbon gave the phenol derivative **15**. The final series I, II and III were obtained according to the published procedure.¹¹

Infrared spectra were recorded on a PE-983G spectrophotometer. ¹H NMR spectra were recorded on a Bruker 300 NMR (300 MHz) spectrometer with TMS as internal standard. ¹⁹F NMR spectra with trifluoroacetic acid (TFA) as external standard were recorded on a Varian EM360L spectrometer (56.4 MHz). For ¹⁹F NMR spectra, high field is positive. Mass spectra were measured with a Finnigan 4021 spectrometer. Elemental analysis was performed on a Heraeus Rapid CHN-O (Germany) instrument. Specific rotation values were measured using a Perkin-Elmer 241MC polarimeter. The mesophase textures were observed on an Olympus BH2 polarized microscope in conjunction with a Mettler FP-52 heat-stage equipped with an FP-5 control unit. The transition temperatures were confirmed by differential scanning calorimetry at heating rate of 5°C/min and cooling down naturally under a nitrogen atmosphere on a Shimadzu DSC-50 system and data station, and the transition peaks were used as the transition temperatures.

(*S*)-4-[1'-(3'',3'',4'',4'',5'',5'',6'',6'',7'',7'',8'',8'',9'',9'',10'',10'',10''-Heptadecafluorodecyloxy-carbonyl) ethyloxy]phenyl 4-*n*-pentyloxybiphenyl-4'-carboxylate (**5BP8F**)

All the five compounds of series I were prepared by the esterification of the corresponding phenol **15** with **17**. A typical example of this procedure for synthesis of **5BP8F** was given as follows:

Typical procedure: Compound 4-*n*-octyloxybiphenyl-4'-carboxyl acid (88.5 mg, 0.311 mmol), compound **15** (200 mg, 0.311 mmol), DCC (96 mg, 0.465 mmol), catalytic DMAP and dry THF (5 mL) were stirred under N₂ atmosphere at room temperature for 48 h. The mixture was filtered and the residue was washed with THF. The collected filtrates were evaporat-

ed on rotary evaporator. The residue was purified by flash chromatography and recrystallized from acetone-methanol to give 90 mg of white solid (**5BP8F**). Yield 32.4%. $[\alpha]_D^{20} = -12.4$ (*c* 1.0, CHCl₃). mp 96.4°C. ν_{max} (KBr): 2938, 1748, 1729, 1605, 1202, 832 cm⁻¹. δ_{H} (300 MHz, CDCl₃, TMS): 0.96(t, *J* = 7.1 Hz, 3H, CH₃), 1.38—1.88 (m, 9H, aliphatic hydrogens), 2.49(tt, *J*₁ = 18.2, *J*₂ = 6.4 Hz, 2H, RFCH₂), 4.02(t, *J* = 6.6 Hz, 2H, RCH₂O), 4.49 (t, *J* = 6.3 Hz, 2H, RCH₂O), 4.79(q, *J* = 6.8 Hz, H, R¹R²CHO), 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). δ_{F} (56.4 MHz, CDCl₃, TFA): 3.60(s, 3F), 36.10(m, 2F), 44.70—46.30(m, 10F), 49.00(s, 2F). *m/z*(rel. int.): 895(M⁺ + 1, 0.67), 267(C₅H₁₁OC₆H₄C₆H₄C₈O⁺, 100.00), 197(HOC₆H₄C₆H₄CO⁺, 9.42). Anal. C₃₇H₃₁F₁₇O₆. Calcd: C, 49.68; H, 3.49; F, 36.10. Found: C, 49.96; H, 3.45; F, 35.95.

(*S*)-4-[1'-(3'',3'',4'',4'',5'',5'',6'',6'',7'',7'',8'',8'',9'',9'',10'',10'',10''-Heptadecafluorodecyloxy-carbonyl) ethyloxy]phenyl 4-*n*-heptyloxybiphenyl-4'-carboxylate (**7BP8F**)

$[\alpha]_D^{20} = -12.3$ (*c* 1.0, CHCl₃). mp 108.0°C. ν_{max} (KBr): 2933, 1748, 1729, 1603, 1505, 1202, 832 cm⁻¹. δ_{H} (300 MHz, CDCl₃, TMS): 0.92(t, *J* = 6.6 Hz, 3H, CH₃), 1.34—1.87(m, 13H, aliphatic hydrogens), 2.49(tt, *J*₁ = 18.2, *J*₂ = 6.4 Hz, 2H, RFCH₂), 4.02(t, *J* = 6.6 Hz, 2H, RCH₂O), 4.49 (t, *J* = 6.3 Hz, 2H, RCH₂O), 4.79(q, *J* = 6.8 Hz, H, R¹R²CHO), 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). δ_{F} (56.4 MHz, CDCl₃, TFA): 3.60(s, 3F), 36.10(m, 2F), 44.70—46.30(m, 10F), 49.00(s, 2F). *m/z*(rel. int.): 923(M⁺ + 1, 0.51), 295(C₇H₁₅OC₆H₄C₆H₄CO⁺, 100.00), 197(HOC₆H₄C₆H₄CO⁺, 9.66). Anal. C₃₉H₃₅F₁₇O₆. Calcd: C, 50.77; H, 3.82; F, 35.00. Found: C, 50.90; H, 3.90; F, 34.77.

(S)-4-[1'-(3'', 3'', 4'', 4'', 5'', 5'', 6'', 6'', 7'', 7'', 8'', 8'', 9'', 9'', 10'', 10'', 10''-Heptadecafluorodecyloxy carbonyl)-ethyloxy]phenyl 4-*n*-octyloxybiphenyl-4'-carboxylate (**8BP8F**)

$[\alpha]_D^{20} = -11.4$ (*c* 1.0, CHCl₃). mp 109.9°C. ν_{\max} (KBr): 2925, 2854, 1748, 1729, 1603, 1504, 1201, 834 cm⁻¹. δ_H (300 MHz, CDCl₃, TMS): 0.96 (t, *J* = 7.1 Hz, 3H, CH₃), 1.32—1.86 (m, 15H, aliphatic hydrogens), 2.49 (tt, *J*₁ = 18.2, *J*₂ = 6.4 Hz, 2H, RFCH₂), 4.02 (t, *J* = 6.6 Hz, 2H, RCH₂O), 4.49 (t, *J* = 6.3 Hz, 2H, RCH₂O), 4.79 (q, *J* = 6.8 Hz, H, R¹R²CHO), 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). δ_F (56.4 MHz, CDCl₃, TFA): 3.60 (s, 3F), 36.10 (m, 2F), 44.70—46.30 (m, 10F), 49.00 (s, 2F). *m/z* (rel. int.): 937 (M⁺ + 1, 0.38), 308 (C₈H₁₇OC₆H₄C₆H₄CO⁺ - 1, 100.00), 197 (HOC₆H₄C₆H₄CO⁺, 10.19). Anal. C₄₀H₃₇F₁₇O₆. Calcd: C, 51.29; H, 3.98; F, 34.48. Found: C, 51.57; H, 4.11; F, 34.17.

(S)-4-[1'-(3'', 3'', 4'', 4'', 5'', 5'', 6'', 6'', 7'', 7'', 8'', 8'', 9'', 9'', 10'', 10'', 10''-Heptadecafluorodecyloxy carbonyl)-ethyloxy]phenyl 4-*n*-nonyloxybiphenyl-4'-carboxylate (**9BP8F**)

$[\alpha]_D^{20} = -12.6$ (*c* 1.0, CHCl₃). mp 113.4°C. ν_{\max} (KBr): 2921, 1748, 1730, 1603, 1505, 1201, 836 cm⁻¹. δ_H (300 MHz, CDCl₃, TMS): 0.91 (t, *J* = 6.5 Hz, 3H, CH₃), 1.44—1.87 (m, 17H, aliphatic hydrogens), 2.49 (tt, *J*₁ = 18.2, *J*₂ = 6.4 Hz, 2H, RFCH₂), 4.02 (t, *J* = 6.6 Hz, 2H, RCH₂O), 4.49 (t, *J* = 6.3 Hz, 2H, RCH₂O), 4.79 (q, *J* = 6.8 Hz, H, R¹R²CHO), 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). δ_F (56.4 MHz, CDCl₃, TFA): 3.60 (s, 3F), 36.10 (m, 2F), 44.70—46.30 (m, 10F), 49.00 (s, 2F). *m/z* (rel. int.): 951 (M⁺ + 1, 0.37), 322 (C₉H₁₉OC₆H₄C₆H₄CO⁺, 100.00), 197 (HOC₆H₄-C₆H₄CO⁺, 10.45). Anal. C₄₁H₃₉F₁₇O₆. Calcd: C, 51.80; H, 4.13; F, 33.97. Found: C, 51.57; H,

4.25; F, 33.54.

(S)-4-[1'-(3'', 3'', 4'', 4'', 5'', 5'', 6'', 6'', 7'', 7'', 8'', 8'', 9'', 9'', 10'', 10'', 10''-Heptadecafluorodecyloxy carbonyl) ethyloxy]phenyl 4-*n*-decyloxybiphenyl-4'-carboxylate (**10BP8F**)

$[\alpha]_D^{20} = -11.8$ (*c* 1.0, CHCl₃). mp 121.7°C. ν_{\max} (KBr): 2921, 2852, 1748, 1729, 1603, 1505, 1200, 831 cm⁻¹. δ_H (300 MHz, CDCl₃, TMS): 0.96 (t, *J* = 7.1 Hz, 3H, CH₃), 1.30—1.88 (m, 17H, aliphatic hydrogens), 2.49 (tt, *J*₁ = 18.2, *J*₂ = 6.4 Hz, 2H, RFCH₂), 4.02 (t, *J* = 6.6 Hz, 2H, RCH₂O), 4.49 (t, *J* = 6.3 Hz, 2H, RCH₂O), 4.79 (q, *J* = 6.8 Hz, H, R¹R²CHO), 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). δ_F (56.4 MHz, CDCl₃, TFA): 3.60 (s, 3F), 36.10 (m, 2F), 44.70—46.30 (m, 10F), 49.00 (s, 2F). *m/z* (rel. int.): 965 (M⁺ + 1, 0.28), 336 (C₁₀H₂₁OC₆H₄C₆H₄CO⁺, 100.00), 197 (HOC₆H₄C₆H₄CO⁺, 9.33). Anal. C₄₂H₄₁F₁₇O₆. Calcd: C, 52.29; H, 4.28; F, 33.48. Found: C, 52.06; H, 4.19; F, 33.34.

(S)-4-[1'-(3'', 3'', 4'', 4'', 5'', 5'', 6'', 6'', 7'', 7'', 8'', 8'', 9'', 9'', 10'', 10'', 10''-Heptadecafluorodecyloxy carbonyl) ethyloxy]phenyl 4'-[(4-*n*-butyloxyphenyl) ethynyl] benzoate (**4T8F**)

All the twelve compounds of series II and series III were prepared by the coupling reaction of the corresponding compounds **16** with **4** or **9**. A typical example of this procedure for synthesis of **4T8F** was given as follows:

Typical procedure: Under dry nitrogen, into a mixture of compound 4-*n*-butyloxyphenylacetylene (43 mg, 0.247 mmol), compound **16** (150 mg, 0.175 mmol), Pd(PPh₃)₂Cl₂ (5 mg) and CuI (4 mg), was added 10 mL of anhydrous triethylamine. The resulting mixture was refluxed while it was stirred. Analysis by TLC revealed completion of the reaction in 2 h. Then the formed precipitate was filtered and washed with ether and the filtrate washed with water, dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* and

the residue was purified by column chromatography on silica gel using petroleum ether (bp 60–90°C)-ethyl acetate (20:1) as eluent to give a pale yellow solid which was recrystallized from acetone-methanol to yield white solids of compound **4T8F**. Yield: 141 mg (92.2%). $[\alpha]_D^{20} = -13.4$ (c 1.0, CHCl₃). mp 115.4°C. ν_{\max} (KBr): 2961, 2214, 1748, 1726, 1599, 1506, 1250, 1201, 836 cm⁻¹. δ_H (300 MHz, CDCl₃, TMS): 0.99 (t, $J = 7.4$ Hz, 3H, CH₃), 1.45–1.84 (m, 7H, aliphatic hydrogens), 2.49 (tt, $J_1 = 18.2$, $J_2 = 6.4$ Hz, 2H, RFCH₂), 4.00 (t, $J = 6.6$ Hz, 2H, RCH₂O), 4.49 (t, $J = 6.3$ Hz, 2H, RCH₂O), 4.79 (q, $J = 6.8$ Hz, H, R¹R²CHO), 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). δ_F (56.4 MHz, CDCl₃, TFA): 3.50 (s, 3F), 36.00 (m, 2F), 44.50–46.00 (m, 10F), 48.70 (s, 2F). m/z (rel. int.): 905 (M⁺ + 1, 2.93), 277 (C₄H₉OC₆H₄-≡-C₆H₄CO⁺, 100.00), 221 (HOC₆H₄-≡-C₆H₄CO⁺, 7.29). Anal. C₃₈H₂₉F₁₇O₆. Calcd: C, 50.45; H, 3.23; F, 35.70. Found: C, 50.71; H, 3.16; F, 35.69.

(S)-4-[1'-(3'',3'',4'',4'',5'',5'',6'',6'',7'',7'',8'',8'',9'',9'',10'',10'',10''-Heptadecafluorodecyloxy) ethyloxy] phenyl 4'-[(4-n-pentylloxyphenyl) ethynyl] benzoate (**5T8F**)

$[\alpha]_D^{20} = -12.1$ (c 1.0, CHCl₃). mp 123.0°C. ν_{\max} (KBr): 2937, 2213, 1747, 1725, 1599, 1506, 1251, 1201, 834 cm⁻¹. δ_H (300 MHz, CDCl₃, TMS): 0.95 (t, $J = 7.0$ Hz, 3H, CH₃), 1.34–1.86 (m, 9H, aliphatic hydrogens), 2.49 (tt, $J_1 = 18.2$, $J_2 = 6.4$ Hz, 2H, RFCH₂), 4.00 (t, $J = 6.6$ Hz, 2H, RCH₂O), 4.49 (t, $J = 6.3$ Hz, 2H, RCH₂O), 4.79 (q, $J = 6.8$ Hz, H, R¹R²CHO), 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). δ_F (56.4 MHz, CDCl₃, TFA): 3.50 (s, 3F), 36.00 (m, 2F), 44.50–46.00 (m, 10F), 48.70 (s, 2F). m/z (rel. int.): 919 (M⁺ + 1, 2.94), 291 (C₅H₁₁OC₆H₄-≡-C₆H₄CO⁺, 100.00), 221 (HOC₆H₄-≡-C₆H₄CO⁺, 7.74). Anal. C₃₉H₃₁F₁₇O₆. Calcd: C, 50.99; H, 3.40; F, 35.16. Found: C, 50.92; H, 3.39; F,

35.44.

(S)-4-[1'-(3'',3'',4'',4'',5'',5'',6'',6'',7'',7'',8'',8'',9'',9'',10'',10'',10''-Heptadecafluorodecyloxy) ethyloxy] phenyl 4'-[(4-n-hexyloxyphenyl) ethynyl] benzoate (**6T8F**)

$[\alpha]_D^{20} = -12.9$ (c 1.0, CHCl₃). mp 120.4°C. ν_{\max} (KBr): 2937, 2213, 1748, 1726, 1599, 1506, 1250, 1201, 834 cm⁻¹. δ_H (300 MHz, CDCl₃, TMS): 0.92 (t, $J = 6.9$ Hz, 3H, CH₃), 1.31–1.85 (m, 11H, aliphatic hydrogens), 2.49 (tt, $J_1 = 18.2$, $J_2 = 6.4$ Hz, 2H, RFCH₂), 4.00 (t, $J = 6.6$ Hz, 2H, RCH₂O), 4.49 (t, $J = 6.3$ Hz, 2H, RCH₂O), 4.79 (q, $J = 6.8$ Hz, H, R¹R²CHO), 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). δ_F (56.4 MHz, CDCl₃, TFA): 3.50 (s, 3F), 36.00 (m, 2F), 44.50–46.00 (m, 10F), 48.70 (s, 2F). m/z (rel. int.): 933 (M⁺ + 1, 2.67), 304 (C₆H₁₃OC₆H₄-≡-C₆H₄CO⁺ - 1, 100.00), 221 (HOC₆H₄-≡-C₆H₄CO⁺, 8.06). Anal. C₄₀H₃₃F₁₇O₆. Calcd: C, 51.51; H, 3.57; F, 34.63. Found: C, 51.70; H, 3.46; F, 34.85.

(S)-4-[1'-(3'',3'',4'',4'',5'',5'',6'',6'',7'',7'',8'',8'',9'',9'',10'',10'',10''-Heptadecafluorodecyloxy) ethyloxy] phenyl 4'-[(4-n-heptyloxyphenyl) ethynyl] benzoate (**7T8F**)

$[\alpha]_D^{20} = -13.4$ (c 1.0, CHCl₃). mp 121.6°C. ν_{\max} (KBr): 2929, 2857, 2214, 1748, 1726, 1599, 1506, 1250, 1201, 834 cm⁻¹. δ_H (300 MHz, CDCl₃, TMS): 0.91 (t, $J = 6.7$ Hz, 3H, CH₃), 1.45–1.84 (m, 13H, aliphatic hydrogens), 2.49 (tt, $J_1 = 18.2$, $J_2 = 6.4$ Hz, 2H, RFCH₂), 4.00 (t, $J = 6.6$ Hz, 2H, RCH₂O), 4.49 (t, $J = 6.3$ Hz, 2H, RCH₂O), 4.79 (q, $J = 6.8$ Hz, H, R¹R²CHO), 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). δ_F (56.4 MHz, CDCl₃, TFA): 3.50 (s, 3F), 36.00 (m, 2F), 44.50–46.00 (m, 10F), 48.70 (s, 2F). m/z (rel. int.): 947 (M⁺ + 1, 2.04), 318 (C₇H₁₅O-C₆H₄-≡-C₆H₄CO⁺ - 1, 100.00), 221 (HOC₆H₄-≡-

$C_6H_4CO^+$, 7.13). Anal. $C_{41}H_{35}F_{17}O_6$. Calcd: C, 52.02; H, 3.73; F, 34.12. Found: C, 51.92; H, 3.43; F, 33.83.

(S)-4-[1'-(3'',3'',4'',4'',5'',5'',6'',6'',7'',7'',8'',8'',9'',9'',10'',10'',10''-Heptadecafluorodecyloxy)carbonyl] ethyloxy] phenyl 4'-[(4-n-octyloxyphenyl) ethynyl] benzoate (8T8F)

$[\alpha]_D^{20} = -12.0$ (c 1.0, $CHCl_3$). mp 118.8°C. ν_{max} (KBr): 2924, 2853, 2214, 1748, 1726, 1599, 1506, 1251, 1202, 834 cm^{-1} . δ_H (300 MHz, $CDCl_3$, TMS): 0.91(t, $J = 6.7$ Hz, 3H, CH_3), 1.26—1.83(m, 15H, aliphatic hydrogens), 2.49(tt, $J_1 = 18.2$, $J_2 = 6.4$ Hz, 2H, $RFCH_2$), 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). δ_F (56.4 MHz, $CDCl_3$, TFA): 3.50(s, 3F), 36.00(m, 2F), 44.50—46.00(m, 10F), 48.70(s, 2F). m/z (rel. int.): 961 ($M^+ + 1$, 2.56), 332 ($C_8H_{17}O-C_6H_4-C_6H_4CO^+ - 1$, 100.00), 221 ($HOC_6H_4-C_6H_4CO^+$, 8.12). Anal. $C_{42}H_{37}F_{17}O_6$. Calcd: C, 52.51; H, 3.88; F, 33.62. Found: C, 51.51; H, 3.65; F, 34.06.

(S)-4-[1'-(3'',3'',4'',4'',5'',5'',6'',6'',7'',7'',8'',8'',9'',9'',10'',10'',10''-Heptadecafluorodecyloxy)carbonyl] ethyloxy] phenyl 4'-[(4-n-nonyloxyphenyl) ethynyl] benzoate (9T8F)

$[\alpha]_D^{20} = -12.7$ (c 1.0, $CHCl_3$). mp 119.7°C. ν_{max} (KBr): 2921, 2852, 2213, 1747, 1728, 1599, 1506, 1250, 1202, 834 cm^{-1} . δ_H (300 MHz, $CDCl_3$, TMS): 0.89(t, $J = 6.7$ Hz, 3H, CH_3), 1.29—1.87(m, 17H, aliphatic hydrogens), 2.49(tt, $J_1 = 18.2$, $J_2 = 6.4$ Hz, 2H, $RFCH_2$), 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). δ_F (56.4 MHz, $CDCl_3$, TFA): 3.50(s, 3F), 36.00(m, 2F), 44.50—46.00(m, 10F), 48.70(s, 2F). m/z (rel.

int.): 975 ($M^+ + 1$, 1.97), 346 ($C_9H_{19}OC_6H_4-C_6H_4CO^+ - 1$, 100.00), 221 ($HOC_6H_4-C_6H_4CO^+$, 7.84). Anal. $C_{43}H_{39}F_{17}O_6$. Calcd: C, 54.34; H, 4.46; F, 33.13. Found: C, 54.47; H, 4.39; F, 33.42.

(S)-4-[1'-(3'',3'',4'',4'',5'',5'',6'',6'',7'',7'',8'',8'',9'',9'',10'',10'',10''-Heptadecafluorodecyloxy)carbonyl] ethyloxy] phenyl 4'-[(4-n-decyloxyphenyl) ethynyl] benzoate (10T8F)

$[\alpha]_D^{20} = -11.6$ (c 1.0, $CHCl_3$). mp 120.4°C. ν_{max} (KBr): 2920, 2852, 2214, 1748, 1725, 1599, 1506, 1251, 1202, 834 cm^{-1} . δ_H (300 MHz, $CDCl_3$, TMS): 0.89(t, $J = 6.6$ Hz, 3H, CH_3), 1.23—1.82(m, 19H, aliphatic hydrogens), 2.49(tt, $J_1 = 18.2$, $J_2 = 6.4$ Hz, 2H, $RFCH_2$), 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). δ_F (56.4 MHz, $CDCl_3$, TFA): 3.50(s, 3F), 36.00(m, 2F), 44.50—46.00(m, 10F), 48.70(s, 2F). m/z (rel. int.): 989 ($M^+ + 1$, 1.77), 360 ($C_{10}H_{21}O-C_6H_4-C_6H_4CO^+ - 1$, 100.00), 221 ($HOC_6H_4-C_6H_4CO^+$, 8.28). Anal. $C_{44}H_{41}F_{17}O_6$. Calcd: C, 53.45; H, 4.18; F, 32.66. Found: C, 53.35; H, 4.04; F, 31.69.

(S)-4-[1'-(3'',3'',4'',4'',5'',5'',6'',6'',7'',7'',8'',8'',9'',9'',10'',10'',10''-Heptadecafluorodecyloxy)carbonyl] ethyloxy] phenyl 4'-[(4-n-dodecyloxyphenyl) ethynyl] benzoate (12T8F)

$[\alpha]_D^{20} = -11.7$ (c 1.0, $CHCl_3$). mp 122.0°C. ν_{max} (KBr): 2920, 2850, 2213, 1748, 1728, 1599, 1506, 1250, 1202, 831 cm^{-1} . δ_H (300 MHz, $CDCl_3$, TMS): 0.91(t, $J = 6.7$ Hz, 3H, CH_3), 1.28—1.85(m, 23H, aliphatic hydrogens), 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). δ_F (56.4

MHz, CDCl₃, TFA): 3.50(s, 3F), 36.00(m, 2F), 44.50—46.00(m, 10F), 48.70 (s, 2F). *m/z* (rel. int.): 1017(M⁺ + 1, 1.94), 388(C₁₂H₂₅OC₆H₄-≡-C₆H₄CO⁺ - 1, 100.00), 221(HOC₆H₄-≡-C₆H₄CO⁺, 6.71). Anal. C₄₆H₄₅F₁₇O₆. Calcd: C, 54.34; H, 4.46; F, 31.76. Found: C, 54.47; H, 4.39; F, 31.63.

(S)-4-[1'-(3'',3'',4'',4'',5'',5'',6'',6'',7'',7'',8'',8'',9'',9'',10'',10'',10''-Heptadecafluorodecyloxy)carbonyl] ethyloxy] phenyl 4'-[(4-*n*-propyloxy-2,3-difluorophenyl) ethynyl] benzoate (**32T8F**)

$[\alpha]_D^{20} = -12.1$ (c 1.0, CHCl₃). mp 118.8°C. ν_{\max} (KBr): 2971, 2213, 1750, 1729, 1603, 1505, 1252, 1199, 827 cm⁻¹. δ_H (300 MHz, CDCl₃, TMS): 1.06(t, *J* = 7.5 Hz, 3H, CH₃), 1.64(d, *J* = 6.9 Hz, 3H, CH₃), 1.81—1.93(m, 2H), 2.49(tt, *J*₁ = 18.2, *J*₂ = 6.4 Hz, 2H, RFCH₂), 4.00(t, *J* = 6.6 Hz, 2H, RCH₂O), 4.49 (t, *J* = 6.3 Hz, 2H, RCH₂O), 4.79 (q, *J* = 6.8 Hz, H, R¹R²CHO), 6.69—7.25(d, *J* = 8.5 Hz, 6H, ArH), 7.64(d, *J* = 8.5 Hz, 2H, ArH), 8.16(d, *J* = 8.4 Hz, 2H, ArH). δ_F (56.4 MHz, CDCl₃, TFA): 3.60(s, 3F), 36.33(m, 2F), 44.90—46.50(m, 10F), 49.20(s, 2F), 56.30(d, *J* = 18.8 Hz, F), 81.30(d, *J* = 18.8 Hz, F). *m/z* (rel. int.): 928(M⁺ + 2, 1.64), 299 (C₃H₇OC₆H₂F₂-≡-C₆H₄CO⁺ - 1, 100.00), 257 (HOC₆H₂F₂-≡-C₆H₄CO⁺, 11.73). Anal. C₃₇H₂₅F₁₉O₆. Calcd: C, 47.96; H, 2.72; F, 38.96. Found: C, 47.73; H, 2.46; F, 38.63.

(S)-4-[1'-(3'',3'',4'',4'',5'',5'',6'',6'',7'',7'',8'',8'',9'',9'',10'',10'',10''-Heptadecafluorodecyloxy)carbonyl] ethyloxy] phenyl 4'-[(4-*n*-butyloxy-2,3-difluorophenyl) ethynyl] benzoate (**42T8F**)

$[\alpha]_D^{20} = -11.4$ (c 1.0, CHCl₃). mp 119.7°C. ν_{\max} (KBr): 2962, 2213, 1750, 1727, 1602, 1505, 1252, 1199, 827 cm⁻¹. δ_H (300 MHz, CDCl₃, TMS): 0.99(t, *J* = 7.3 Hz, 3H, CH₃), 1.46—1.87(m, 7H, aliphatic hydrogens), 2.49(tt, *J*₁ = 18.2, *J*₂ = 6.4 Hz, 2H, RFCH₂), 4.00(t, *J* = 6.6 Hz, 2H, RCH₂O), 4.49(t, *J* = 6.3 Hz, 2H, RCH₂O), 4.79 (q, *J* = 6.8 Hz, H, R¹R²CHO), 6.69—7.25(d, *J* = 8.5 Hz, 6H, ArH), 7.64(d, *J* = 8.5 Hz, 2H,

ArH), 8.16(d, *J* = 8.4 Hz, 2H, ArH). δ_F (56.4 MHz, CDCl₃, TFA): 3.60(s, 3F), 36.33(m, 2F), 44.90—46.50(m, 10F), 49.20(s, 2F), 56.30(d, *J* = 18.8 Hz, F), 81.30(d, *J* = 18.8 Hz, F). *m/z* (rel. int.): 941(M⁺ + 1, 1.34), 313(C₄H₉OC₆H₂F₂-≡-C₆H₄CO⁺, 100.00), 257 (HOC₆H₂F₂-≡-C₆H₄CO⁺, 13.39). Anal. C₃₈H₂₇F₁₉O₆. Calcd: C, 48.52; H, 2.89; F, 38.38. Found: C, 48.59; H, 2.71; F, 37.96.

(s)-4-[1'-(3'',3'',4'',4'',5'',5'',6'',6'',7'',7'',8'',8'',9'',9'',10'',10'',10''-Heptadecafluorodecyloxy)carbonyl] ethyloxy] phenyl 4'-[(4-*n*-heptyloxy-2,3-difluorophenyl) ethynyl] benzoate (**72T8F**)

$[\alpha]_D^{20} = -11.3$ (c 1.0, CHCl₃). mp 121.4°C. ν_{\max} (KBr): 2925, 2213, 1750, 1728, 1602, 1505, 1252, 1198, 827 cm⁻¹. δ_H (300 MHz, CDCl₃, TMS): 0.90(t, *J* = 6.7 Hz, 3H, CH₃), 1.45—1.84(m, 13H, aliphatic hydrogens), 2.49(tt, *J*₁ = 18.2, *J*₂ = 6.4 Hz, 2H, RFCH₂), 4.00(t, *J* = 6.6 Hz, 2H, RCH₂O), 4.49(t, *J* = 6.3 Hz, 2H, RCH₂O), 4.79 (q, *J* = 6.8 Hz, H, R¹R²CHO), 6.69—7.25(d, *J* = 8.5 Hz, 6H, ArH), 7.64(d, *J* = 8.5 Hz, 2H, ArH), 8.16(d, *J* = 8.4 Hz, 2H, ArH). δ_F (56.4 MHz, CDCl₃, TFA): 3.60(s, 3F), 36.33(m, 2F), 44.90—46.50(m, 10F), 49.20(s, 2F), 56.30(d, *J* = 18.8 Hz, F), 81.30(d, *J* = 18.8 Hz, F). *m/z* (rel. int.): 983 (M⁺ + 1, 1.19), 354 (C₇H₁₅-OC₆H₂F₂-≡-C₆H₄CO⁺ - 1, 100.00), 257 (HOC₆H₂F₂-≡-C₆H₄CO⁺, 14.51). Anal. C₄₁H₃₃F₁₉O₆. Calcd: C, 50.11; H, 3.38; F, 36.83. Found: C, 50.20; H, 3.25; F, 36.60.

(S)-4-[1'-(3'',3'',4'',4'',5'',5'',6'',6'',7'',7'',8'',8'',9'',9'',10'',10'',10''-Heptadecafluorodecyloxy)carbonyl] ethyloxy] phenyl 4'-[(4-*n*-decyloxy-2,3-difluorophenyl) ethynyl] benzoate (**102T8F**)

$[\alpha]_D^{20} = -10.4$ (c 1.0, CHCl₃). mp 123.7°C. ν_{\max} (KBr): 2921, 1750, 1728, 1603, 1505, 1252, 1199, 827 cm⁻¹. δ_H (300 MHz, CDCl₃, TMS): 0.89 (t, *J* = 6.6 Hz, 3H, CH₃), 1.23—1.82(m, 19H, aliphatic hydrogens), 2.49(tt, *J*₁ = 18.2, *J*₂ = 6.4 Hz, 2H, RFCH₂), 4.00 (t, *J* = 6.6 Hz, 2H, RCH₂O), 4.49(t, *J* = 6.3 Hz, 2H, RCH₂O), 4.79 (q, *J* = 6.8 Hz, H, R¹R²CHO), 6.69—7.25(d, *J*

= 8.5 Hz, 6H, ArH), 7.64(d, $J = 8.5$ Hz, 2H, ArH), 8.16(d, $J = 8.4$ Hz, 2H, ArH). δ_F (56.4 MHz, $CDCl_3$, TFA): 3.60(s, 3F), 36.33(m, 2F), 44.90–46.50(m, 10F), 49.20(s, 2F), 56.30(d, $J = 18.8$ Hz, F), 81.30(d, $J = 18.8$ Hz, F). m/z (rel. int.): 1027 ($M^+ + 3$, 0.88), 396 ($C_{10}H_{21}OC_6H_2F_2 \equiv -C_6H_4CO^+$, 100.00), 257 ($HOC_6H_2F_2 \equiv -C_6H_4CO^+$, 14.89). Anal. $C_{44}H_{39}F_{19}O_6$. Calcd: C, 51.57; H, 3.84; F, 35.22. Found: C, 51.94; H, 3.74; F, 35.28.

Results and discussion

Transition temperatures of series I, II and III were measured by DSC, and phase identification was made by comparing the observed textures with those reported in the literatures.^{8,12,13} The results were summarized in Table 1. The transition temperatures of series II were plotted against the number of carbon atoms in the alkoxy chain, n , in Fig 1.

Table 1 Transition temperatures of series I, II, III

Compounds	n	Transition temperatures (°C)
5BP8F	5	Cr96.4CrE104.1SmB115.7SmA217.7 I 214.8SmA114.7SmB 98.5CrE 75.4 Recr
7BP8F	7	Cr 108.0SmC* 138.1SmA204.0 I 202.4SmA137.3SmC* 107.6SmB100.3Recr
8BP8F	8	Cr 109.9SmC* 152.7SmA197.3 I 194.1SmA152.1SmC* 103.9Recr
9BP8F	9	Cr 113.4SmC* 155.0SmA190.8 I 188.8SmA154.3SmC* 108.6Recr
10BP8F	10	Cr 121.7SmC* 126.0SmA176.4 I 173.5SmA125.4SmC* 114.0Recr
4T8F	4	Cr 115.4 SmA 215.0 I 213.0 SmA 106.9 SmB 99.1 Recr
5T8F	5	Cr 123.0 SmA 207.0 I 204.6 SmA 112.8 Recr
6T8F	6	Cr 120.4 SmA 202.0 I 199.4 SmA 110.2 Recr
7T8F	7	Cr 121.6 SmA 197.2 I 195.3 SmA 120.2 SmC* 114.3 Recr
8T8F	8	Cr 118.8 SmC* 135.2 SmA 191.6 I 189.5 SmA 134.5 SmC* 112.1 Recr
9T8F	9	Cr 119.7 SmC* 142.5 SmA 187.1 I 185.2 SmA 142.1 SmC* 112.9 Recr
10T8F	10	Cr 120.4 SmC* 146.5 SmA 183.1 I 180.9 SmA 146.1 SmC* 113.6 Recr
12T8F	12	Cr 122.0 SmC* 142.0 SmA 172.0 I 169.1 SmA 141.4 SmC* 116.2 Recr
32FT8F	3	Cr 118.8 SmA 188.2 I 185.8 SmA 101.1 Recr
42FT8F	4	Cr 119.7 SmA 188.3 I 185.8 SmA 101.5 Recr
72FT8F	7	Cr 121.4 SmA 172.7 I 170.2 SmA 109.2 Recr
102FT8F	10	Cr 123.7 SmA 161.0 I 157.4 SmA 115.7 Recr

Cr = crystal, CrE = crystalline E phase, SmA = smectic A phase, SmB = smectic B phase, SmC* = smectic C* phase, I = isotropic, Recr = recrystallization.

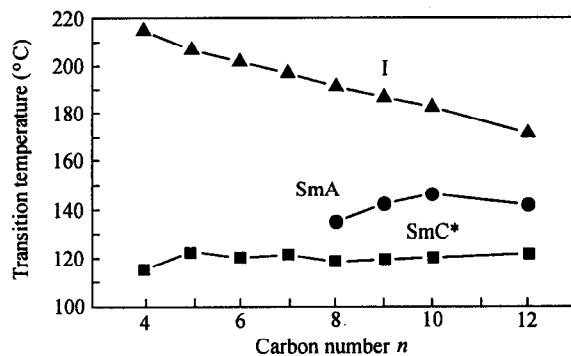


Fig. 1 Transition temperatures as a function of the number of carbon atoms in the alkoxy chain of series II.

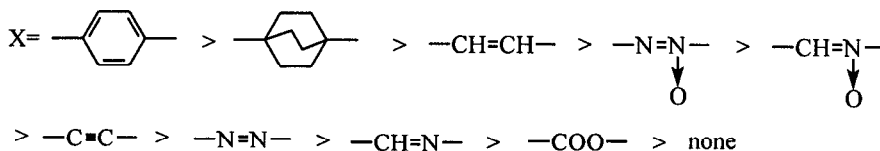
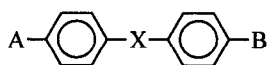
All the three series show enantiotropic smectic A

phase. In series I and series II, enantiotropic chiral smectic C phase is emerged when the hydrocarbon chain is a little longer. But when the hydrocarbon chain is very short, smectic B and crystalline E phases are found.

For series II, generally speaking, there is a decrease of the clearing point when the number of carbon atoms in alkoxy chain increases, corresponding to the transition from a rigid system (short chains) to a more flexible one (long chain). The odd-even effects were not found. Chiral smectic C phase is favourable to form when the alkoxy chain is long enough, but the thermal stability is a little decreased when the alkoxy chain is too long.

Gray discussed the role of the central group in sim-

ple mesogens,

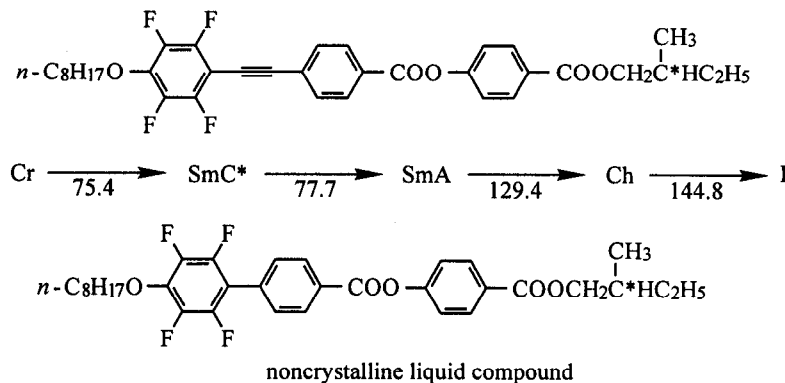


He showed that the relatively low position in the order for $X = -\text{C}\equiv\text{C}-$ was surprising. Coates showed that the high birefringency of tolans was due to the excellent conjugation throughout the molecule.^{15,16} It is possible, however, that when crystal forces are removed on melting the rings become noncoplanar. This may be less se-

where A and B are suitable terminal substituents, and X is the central group.¹⁴ With minor exceptions, dependent upon the end group A and B in this case, the order is:

rious than in Schiff's bases, since the cylinder of electron density of $-\text{C}\equiv\text{C}-$ may still permit conjugative interaction to occur even when the ring is noncoplanar.

In previous study,¹⁷ we have published the results of the following two compounds,



A comparison of the effect on thermostability of the liquid crystals, shown in Table 1 exhibits an abnormal phenomenon. The insertion of triple bond into the biphenyl group in series II is found to be unfavourable to the formation of SmA and SmC* phases. The abnormal phenomenon should be ascribed to the semiperfluorinated tails.

As for the effect of 2, 3-difluoro substituents of phenylenic structure on the formation of SmA phase and tilted SmC* phase concerned. The lateral fluorosubstituents usually exert two opposing effects on the thermal stability of the mesophase, that is, the polar effect and the steric effect. The laterally introduced fluorosubstituent decreases the length/breadth ratio of the mesogenic molecules, and this broadening effect tends to decrease the thermostability of both nematic and smectic mesophases. However, a 2, 3-difluoro substituted phenylenic structure can increase and reinforce the lateral interaction of molecules, owing to the dipole moment

acting across the molecular long axes, giving rise to the formation of stable smectic C phase.^{18,19} In viewing of the high SmC* tendency of the 2, 3-difluoro-substituted mesogen,^{18,19} it was surprising that the 2, 3-difluoro-substituted series III compounds did not show an SmC phase and the thermal stability of SmA phase was weaker than those of the corresponding parent compounds as shown in the Table. The results of this paper can not be explained by McMillan's model which is so called a dipolar theory. In order to explain the results, we would consider the steric effect. Probably the most well-known theory based on molecular stacking conformation is Wulfs zigzag model of the phase in which molecules that have a zigzag conformation pack together in a tilted arrangement to produce a phase.¹ The series III compounds exhibit only A phase but no C* phase, whereas their unfluorinated parent compound exhibit A and C* phases. One explanation for this behaviour is that when the *ortho*-difluoro-substituents are in a position on the

edge of the core, the structure tends to hinder the formation of an overall zigzag shape, so the steric repulsive interaction is greater in difluorosubstituted compounds than in their corresponding parent compound.

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