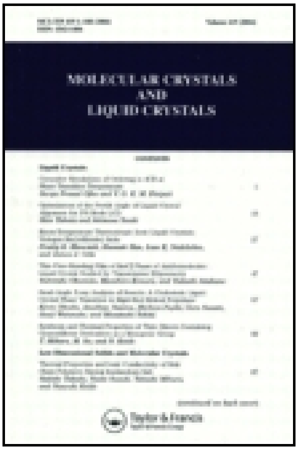

Molecular Crystals and Liquid Crystals

Synthesis and Mesomorphic Properties of Some Chiral Liquid Crystals with Semifluorinated Chains

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Synthesis and Mesomorphic Properties of Some Chiral Liquid Crystals with Semifluorinated Chains

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Three series of chiral compounds with semifluorinated chains have been synthesized. These compounds were characterized by IR, ^1H NMR, ^{19}F NMR, MS-mass spectrum, and elemental analysis. Their phase-transition behavior was investigated by DSC-differential scanning calorimetry and polarizing optical microscopy. Both the introduction of a triple bond and lateral difluorosubstitution in the core decrease the clearing points and suppress the formation of the SmC phase.*

Keywords: Ferroelectric; fluorocarbon; liquid crystal; mesomorphic

INTRODUCTION

Chiral smectic liquid crystals are some of the most interesting systems for future display devices, especially the liquid crystals that show the smectic C^* or the smectic C_A^* phases. Recently, a variety of liquid crystals with a SmC* phase have been synthesized [1–3]. Earlier work by different groups on liquid crystals showed that the formation of smectic mesophases and their liquid-crystalline thermal stabilities were enhanced with the introduction of perfluoroalkyl or semifluoroalkoxy chains [4–19]. In particular, molecules with semifluorinated chains exhibit tilted smectic phases, and some are inherently ferroelectric [4–6]. With the introduction of a chiral center, a smectic C^* phase will be formed, which may be suitable for application in ferroelectric liquid crystal display (FLCD) mixtures [20,21]. Therefore, the synthesis and study of liquid crystals with semifluorinated chains and chiral centers became more attractive.

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Several years ago, we obtained a liquid crystal with a broad (54°C) SmC* phase by the introduction of a semifluorinated chain and a chiral center [19]. Here we developed three new series of liquid crystals, some of which also show a broad SmC* phase range.

RESULTS AND DISCUSSION

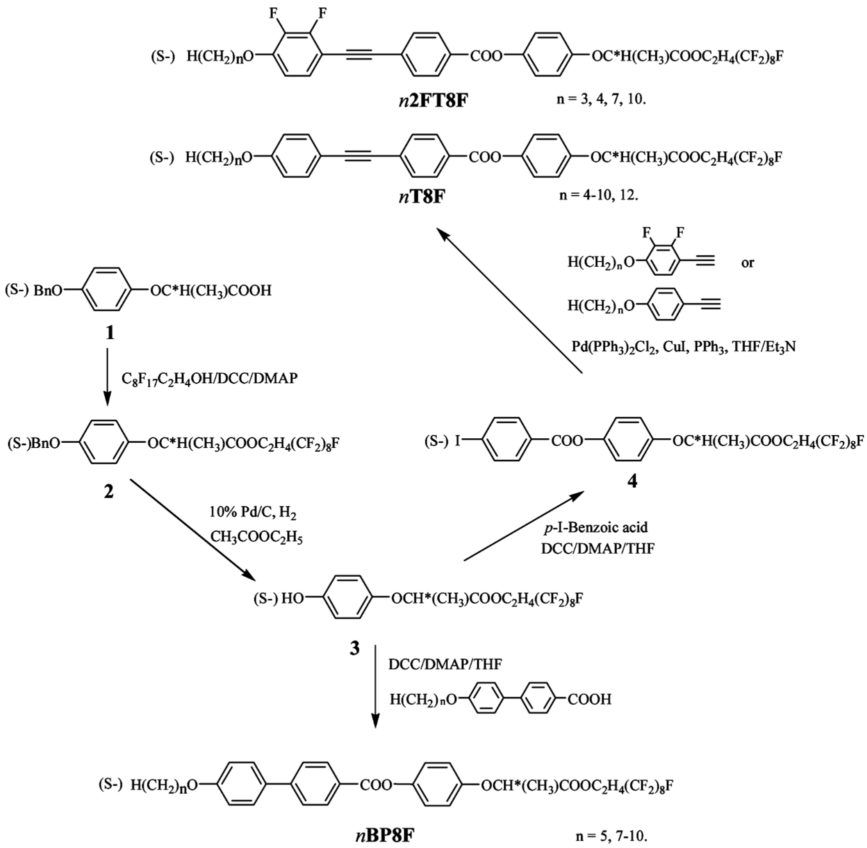
The phase-transition temperatures of all the compounds were determined by differential scanning calorimetry (DSC) with a heating rate of 5°C min^{-1}. The mesomorphic textures were observed on polarizing optical textures for determining the types of mesophases. The transition temperatures shown in all the tables are the maxima of the transition peaks on each DSC trace.

The compounds were obtained by routes depicted in Scheme 1. The intermediates and final compounds were synthesized according to literature methods [18,22–24]. The phase behavior of the final compounds is summarized in Tables 1 and 2 and was determined with DSC and polarizing optical microscopy.

The phase-transition temperatures of compounds *n***T8F** are summarized in Table 1. Figure 1 plots the transition temperature of compounds *n***T8F** as a function of the number of methylenic units (*n*) in the nonfluorinated chain. All of these compounds exhibit only smectic mesophases. When the alkoxy chains are short, only enantiotropic SmA and monotropic SmB phases are found. An enantiotropic SmC* phase appears only when the carbon numbers of the alkoxy chains are longer than 7. Generally, the SmC* phase ranges are around 20°C. By increasing the alkoxy chain length, the clearing points decrease gradually with a slight odd–even effect; however, the melting points are similar.

Compounds *n***BP8F** are similar to compounds *n***T8F** but without triple bonds in the cores. The phase-transition temperatures of compounds *n***BP8F** are summarized in Table 2. All of these compounds also exhibit smectic mesophases. When the alkoxy chain is short, a SmB phase is exhibited. When the carbon numbers are 8 and 9, broad ranges (more than 40°C) of the SmC* phase are seen, which may be suitable for FLCD mixtures. With the difluorosubstitution of compounds *n***T8F**, we obtained compounds *n***2FT8F**. The phase-transition temperatures of compounds *n***2FT8F** are also summarized in Table 2. Only an enantiotropic SmA phase is identified; the SmC* phase is strongly suppressed by lateral difluorosubstitution [23–25].

For a clear understanding of the effects of the introduction of the triple bond and lateral difluorosubstitution, the phase-transition properties of three compounds, **7BP8F**, **7T8F**, and **72FT8F**, are summarized in Figure 2. From the phase-transition properties of



SCHEME 1 Synthetic route.

7BP8F and **7T8F**, the introduction of a triple bond into the core, the clearing points, melting points, and the thermostability of SmC* phase are decreased. Possibly the triple bond interfered with the conjugation of the molecule; the lateral–lateral interactions were then weakened. Although the clearing points of **7T8F** and **72FT8F** are nearly the same, the clearing point of **7T8F** decreases by 24.5°C with lateral difluorosubstitution. The lateral difluorosubstitution strongly decreases the lateral interactions between the aromatic cores.

In summary, three series of chiral compounds with semifluorinated chains have been synthesized. Two of them show broad ranges (more than 40°C) of the SmC* phase. Both the introduction of a triple bond and lateral difluorosubstitution in the core decrease the clearing points and suppress the formation of the SmC* phase.

TABLE 1 Transition Temperature of Compounds

Compound	*n*	Transition temperature (°C)
_4_T8F	4	Cr, 115.4; SmA, 215.0; I, 213.0, SmA, 106.9; SmB; 99.1 Recr
_5_T8F	5	Cr, 123.0, SmA, 207.0; I, 204.6, SmA, 112.8 Recr
_6_T8F	6	Cr, 120.4; SmA, 202.0; I, 199.4; SmA, 110.2 Recr
_7_T8F	7	Cr, 121.6; SmA, 197.2; I, 195.3; SmA, 120.2; SmC*, 114.3 Recr
_8_T8F	8	Cr, 118.8; SmC*, 135.2; SmA, 191.6; I, 189.5; SmA, 134.5; SmC*, 112.1 Recr
_9_T8F	9	Cr, 119.7; SmC*, 142.5; SmA, 187.1; I, 185.2; SmA, 142.1; SmC*, 112.9 Recr
_10_T8F	10	Cr, 120.4; SmC*, 146.5; SmA, 183.1; I, 180.9; SmA, 146.1; SmC*, 113.6 Recr
_12_T8F	12	Cr, 122.0; SmC*, 142.0; SmA, 172.0; I, 169.1; SmA, 141.4; SmC*, 116.2 Rec

Note. Cr = crystal; SmA = smectic A; SmC* = chiral smectic C; SmB = smectic B; I = isotropic liquid; Recr = recrystal.

EXPERIMENTAL

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

TABLE 2 Transition Temperatures of Compounds

Compound	*n*	Transition temperature (°C)
_5_BP8F	5	Cr, 96.4; CrE, 104.1; SmB, 115.7; SmA, 217.7; I, 214.8; SmA, 114.7; SmB, 98.5; Cr, E75.4 Recr
_7_BP8F	7	Cr, 108.0; SmC*, 138.1; SmA, 204.0; I, 202.4; SmA, 137.3; SmC*, 107.6; SmB, 100.3 Recr
_8_BP8F	8	Cr, 109.9; SmC*, 152.7; SmA, 197.3; I, 194.1; SmA, 152.1; SmC*, 103.9 Recr
_9_BP8F	9	Cr, 113.4, SmC*, 155.0; SmA, 190.8; I, 188.8; SmA, 154.3; SmC*, 108.6 Recr
_10_BP8F	10	Cr, 121.7; SmC*, 126.0; SmA, 176.4; I, 173.5; SmA, 125.4; SmC*, 114.0 Recr
_3_2FT8F	3	Cr, 118.8; SmA, 188.2; I, 185.8; SmA, 101.1 Recr
_4_2FT8F	4	Cr, 119.7; SmA, 188.3; I, 185.8; SmA, 101.5 Recr
_7_2FT8F	7	Cr, 121.4; SmA, 172.7; I, 170.2; SmA, 109.2 Recr
_10_2FT8F	10	Cr, 123.7; SmA, 161.0; I, 157.4; SmA, 115.7 Recr

Note. Cr = crystal; SmA = smectic A; SmC* = chiral smectic C; SmB = smectic B; CrE = crystal E; I = isotropic liquid; Recr = recrystal.

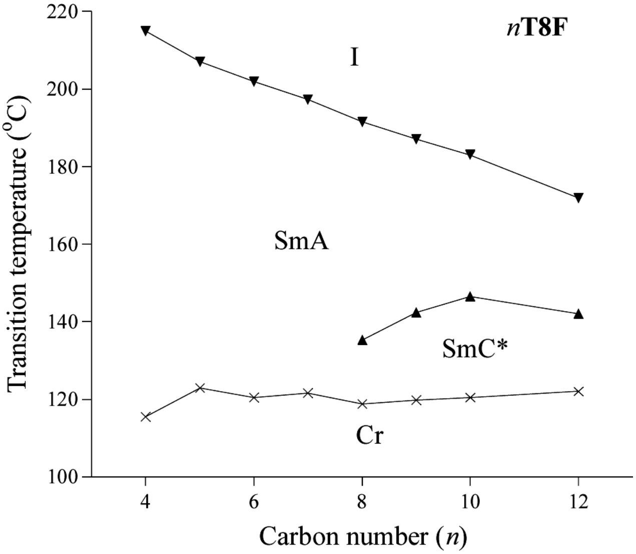


FIGURE 1 Transition behavior of the compounds *n***T8F**: dependence of the transition temperatures on the number (*n*) of methylene units of the nonfluorinated chain.

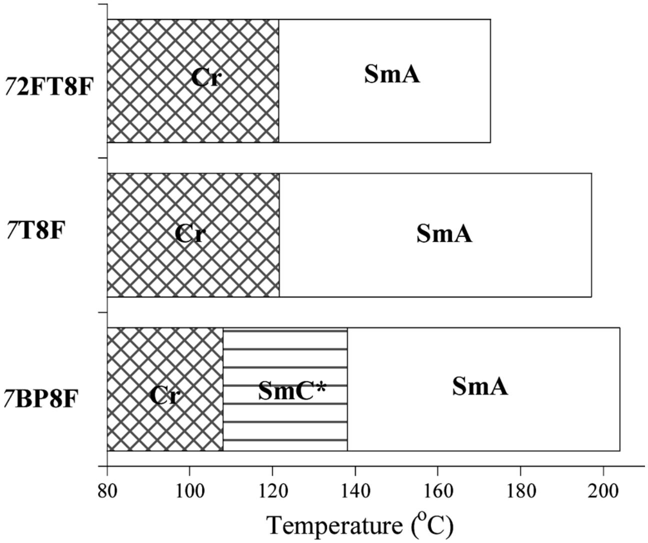


FIGURE 2 Comparison of mesomorphic properties of compounds **7BP8F**, **7T8F**, and **72FT8F**.

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 spectra spectrum ^{19}F NMR, the high field was positive. MS spectra were measured with a Finnigan-4021 spectroscope.

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

Synthesis

All of the obtained liquid crystals were purified by column chromatography on silica gel using petroleum ether (bp 60–90°C)/ethyl acetate (20:1) as eluent and then recrystallized from petroleum ether (bp 60–90°C) and acetone/methanol.

*Synthesis of Compound 7*BP8F

A typical synthetic procedure is as follows. 4-*n*-Heptyloxybiphenyl-4′-carboxylic acid (0.60 mmol), compound **3** (0.60 mmol), *N,N*′-dicyclohexylcarbodiimide (0.7 mmol), catalytic 4-(dimethylamino)pyridine (DMAP), and dry THF (10 ml) were stirred under N_2 at room temperature for 48 h. The mixture 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 a white solid. $[\alpha]_D^{20} = -12.3$ (c 1.0, $CHCl_3$). Mp 108.0°C. IR (KBr) υ_{max}: 2933, 1748, 1729, 1603, 1505, 1202, 832 cm^{-1}. ^{1}H NMR δ_H (300 MHz; $CDCl_3$; TMS): 0.92 (t, $J = 6.6$ Hz, 3H, CH_3), 1.34–1.87 (m, 13H, aliphatic hydrogens), 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) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 3.60 (s, 3 F), 36.10 (m, 2 F), 44.70–46.30 (m, 10 F), 49.00 (s, 2F) ppm. MS m/z (rel. int.): 923 ($M^+ + 1$, 0.51), 295 ($C_7H_{15}OC_6H_4C_6H_4CO^+$, 100.00), 197 ($HOC_6H_4C_6H_4CO^+$, 9.66). Elemental analysis: calculated (for $C_{39}H_{35}F_{17}O_6$) C, 50.77; H, 3.82; F, 35.00%; found C, 50.90; H, 3.90; F, 34.77%.

Synthesis of Compound 7T8F

A typical synthetic procedure is as follows. To a mixture of 4-heptyloxyphenylacetylene (0.44 mmol), compound **4** (0.4 mmol), bis(triphenylphosphine)palladium dichloride (20 mg), and CuI (60 mg) under dry N_2, 20 mL of anhydrous triethylamine were added. The obtained mixture was heated under reflux with stirring for 2 h. Analysis by thin-layer chromatography (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 elucent. The obtained compound was recrystallized from petroleum ether (bp 60–90°C) and subsequently acetone/ methanol. $[\alpha]_D^{20} = -13.4$ (c 1.0, $CHCl_3$). Mp 121.6°C. IR (KBr) υ_{max}: 2929, 2857, 2214, 1748, 1726, 1599, 1506, 1250, 1201, 834 cm^{-1}. ^1H NMR δ_H (300 MHz; $CDCl_3$; TMS): 0.91 (t, $J = 6.7$ Hz, 3H, CH_3), 1.45–1.84 (m, 13H, 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) ppm. ^{19}F NMR δ_F (56.4 MHz, $CDCl_3$, TFA): 3.50 (s, 3 F), 36.00 (m, 2F), 44.50–46.00 (m, 10F), 48.70 (s, 2F) ppm. MS m/z (rel. int.): 947 ($M^+ + 1$, 2.04), 318 ($C_7H_{15}OC_6H_4{-}{\equiv}{-}C_6H_4CO^+{-}1$, 100.00), 221 ($HOC_6H_4{-}{\equiv}{-}C_6H_4CO^+$, 7.13). Elemental analysis: calculated (for $C_{41}H_{35}F_{17}O_6$) C, 52.02; H, 3.73; F, 34.12%; found C, 51.92; H, 3.43; F, 33.83%.

Synthesis of Compound 72FT8F

$[\alpha]_D^{20} = -11.3$ (c, 1.0, $CHCl_3$). Mp 121.4°C. υ_{max}(KBr): 2925, 2213, 1750, 1728, 1602, 1505, 1252, 1198, 827 cm^{-1}. ^1H NMR δ_H (300 MHz, $CDCl_3$, TMS): 0.90 (t, $J = 6.7$ Hz, 3H, CH_3), 1.45–1.84 (m, 13H, 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), 6.69–7.25 (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) ppm, ^{19}F NMR 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) ppm. MS m/z (rel. int.): 983 ($M^+ + 1$, 1.19), 354 ($C_7H_{15}OC_6H_2F_2{-}{\equiv}{-}C_6H_4CO^+{-}1$, 100.00), 257 ($HOC_6H_2F_2{-}{\equiv}{-}C_6H_4CO^+$, 14.51). Elemental analysis: calculated (for $C_{41}H_{33}F_{19}O_6$) C, 50.11; H, 3.38; F, 36.73%; found C, 50.20; H, 3.25; F, 36.60%.

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