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Synthesis and Mesomorphic Properties of Some Fluorinated Benzoate Liquid Crystals

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Three series of [4-(4′-*n*-alkyloxyphenyl)acetylenyl]-2,6-difluorophenyl fluorinated benezoates and one series of fluorinated benzoates with 2,3,5,6-tetrafluorophenylene group and semi-perfluorocarbon chain have been synthesized. Their phase transition temperatures have been measured by texture observation in a polarizing microscope and confirmed by DSC. For the series without fluorocarbon chains, increasing the quantity of fluorosubstituents on the terminal phenyl groups decreased nematic stability ($T_{N\text{-}I}$), but the breadth of the SmA phase range was increased. Lateral fluorosubstitution in the central group lowered the nematic stability ($T_{N\text{-}I}$) and decreased the breadth of the SmA phase range. The series with semiperfluorocarbon chains were more likely to form SmA phases than the series with hydrogencarbon chains, and with the increasing of fluorosubstituents quantity on the terminal phenyl groups nematic and SmA stability ($T_{N\text{-}I}$ and $T_{SmA\text{-}N}$) were both decreased.

Keywords: Fluorinated, liquid crystal, mesomorphic

INTRODUCTION

Fluorinated liquid crystals have been the focus of research in the liquid crystal field. The introduction of a fluorine atom generally leads to a subtle modification of properties and imparts many advantageous properties because it is the smallest substituent and has the highest electronegativity [1–7]. Up to now, thousands of liquid-crystalline molecules with monofluoro-, difluoro-, or trifluorosubstituted phenyls have been prepared [8]. However, on one hand the fluorosubstituted benzoate liquid crystals have not been carried

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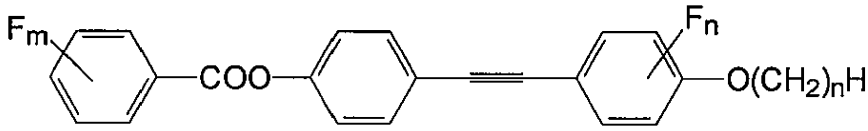
very well [9], especially the benzoates with the 2,6-difluorophenylene group. On the other hand, it was found that not only *para*-fluorosubstitution but also *meta*-fluorosubstitution of the terminal phenyl group enhances the formation of SmA phase in the series shown below [10–12]. This phenomenon may be due to the existence of microphase separation, which occurs when the number of the fluorine atoms increased beyond a certain level in the terminal aromatic ring.



m = 1, 2, 3. n = 0, 2, 4.

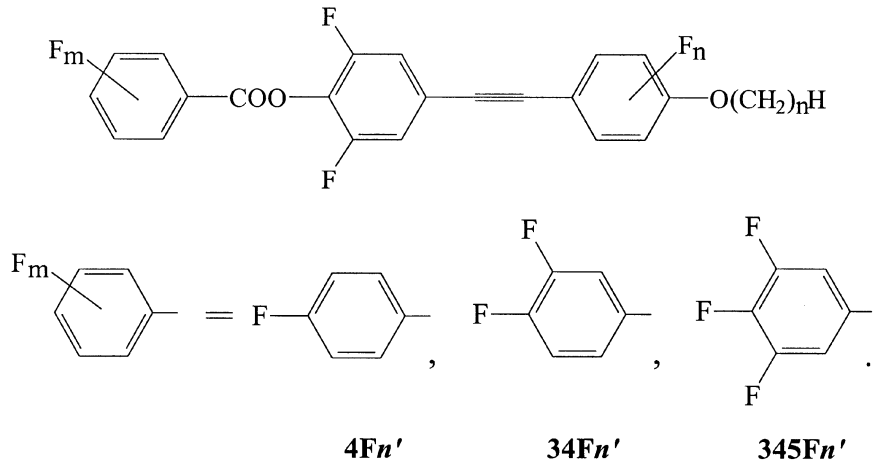
series **4F*n***: n = 0, m = 1. series **4F*n*″**: n = 4, m = 1.

series **34F*n***: n = 0, m = 2. series **34F*n*″**: n = 4, m = 2.

series **345F*n***: n = 0, m = 3. series **345F*n*″**: n = 4, m = 3.

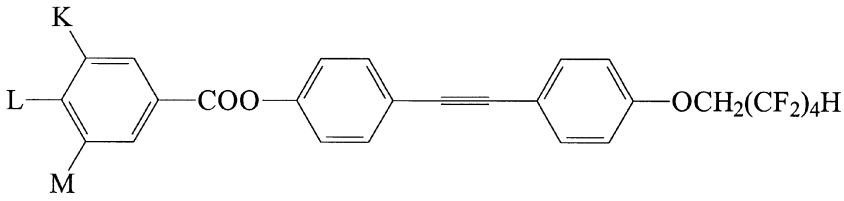
To further study this phenomenon, three series of *o*-, *m*-, *p*-fluoro-substituted benzoates with fluorosubstituents on the central phenylene groups (not on the terminal group as above) have been synthesized, the formula of which were shown in Scheme 1.

At the same time, the benzoates with highly fluorinated tails were also studied (see series A in Scheme 2). It is well-known that increasing the amount of fluorination, particularly in the terminal chains, favors the



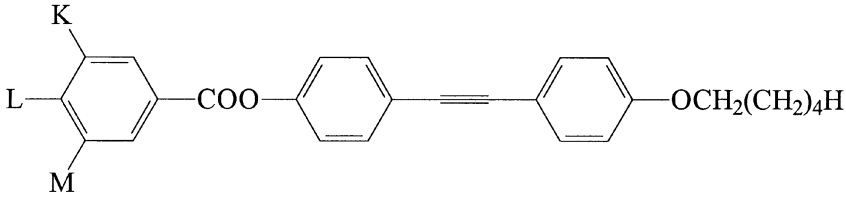
4F*n*′ **34F*n*′** **345F*n*′**

SCHEME 1 The molecular structure of **4F*n*′**, **34F*n*′** and **345F*n*′**.



Series **A** **A345**: K=F, L=F, M=F **A35**: K=F, L=H, M=F

A34: K=F, L=F, M=H **A4**: K=H, L=F, M=H



Series **B** **B345**: K=F, L=F, M=F **B35**: K=F, L=H, M=F

B34: K=F, L=F, M=H **B4**: K=H, L=F, M=H

SCHEME 2

formation of the SmA phase [10]. This is because there is a tendency to microphase separate—at least that is generally what the picture shows from X-ray diffraction studies [11–12]. In series **A**, the increase in fluoro-substituents in the terminal aromatic ring must affect the microphase separation generated by the fluorocarbon chain, and thus affect the breadth and thermal stability ($T_{SmA\text{-}N}$) of the smectic A phase. To evaluate the effect of fluorocarbon chains, we have designated the series **A** and **B** for comparison.

RESULTS AND DISCUSSION

The transition temperatures of compounds, **4F*n*′**[4-(4′-*n*-alkyloxyphenyl)-acetylenyl]-2,6-difluorophenyl-4′-fluorobenzoate, **34F*n*′** [4-(4′-*n*-alkyloxyphenyl)acetylenyl]-2,6-difluorophenyl 3,4-difluorobenzoate, **345F*n*′**

[4-(4′-*n*-alkyloxyphenyl)acetylenyl]-2,6-difluorophenyl 3,4,5-trifluorobenzoate are presented in Table 1. The transition temperatures are plotted against the number of carbon atoms in the alkoxy chain, *n*, in Figures 1, 2, and 3. The phase transition temperatures of compounds in series **A** and **B** are listed in Table 2, and shown as a bar graph in Figure 4.

The compounds of series **4F*n*′**, **34F*n*′**, and **345F*n*′** show enantiotropic *N* phases except for **345F4′**. With the increase in alkoxy chain length, the clearing point reduces and the width of the range of the nematic phase exhibits a maximum. Compounds **4F*n*′** exhibit enantiotropic nematic phases, and monotropic SmA phases are found when the carbon number of the alkoxy chain $n > 10$. Similar to series **4F*n*′**, compounds **34F*n*′** exhibit monotropic SmA phases when $n > 7$ and enantiotropic SmA phases when $n > 10$. The clearing point decreases gradually with the increase in the terminal chain length. Compared with compounds **34F*n*′**, compounds **345F*n*′** exhibit monotropic SmA phases when $n > 7$. This may due to the fact that two *meta*-fluorosubstituents broaden the molecule much more than

TABLE 1 Transition temperatures of compounds **4F*n*′**, **34F*n*′**, and **345F*n*′**

Compounds	*Name*	*n*	*Transition temperatures (°C)*
4F*n*′	**4F*5*′**	5	Cr 89.9 N 150.1 I 149.6 N 97.1 Recr
	4F*6*′	6	Cr 95.3 N 145.6 I 144.1 N 46.8 Recr
	4F*7*′	7	Cr 79.3 N 136.3 I 135.3 N 35.7 Recr
	4F*8*′	8	Cr 87.6 N 133.4 I 132.3 N 35.9 Recr
	4F*9*′	9	Cr 88.9 N 126.4 I 125.1 N 58.5 Recr
	4F*10*′	10	Cr 79.8 N 124.1 I 123.2 N 37.8 Recr
	4F*12*′	12	Cr 72.9 N 119.5 I 117.1 N 55.3 SmA 27.2 Recr
	4F*16*′	16	Cr 85.0 N 109.7 I 108.2 N 76.2 SmA 47.8 Recr
34F*n*′	**34F*4*′**	4	Cr 85.0 N 122.1 I 119.6 N 47.1 Recr
	34F*5*′	5	Cr 71.1 N 122.6 I 121.3 N 29.6 Recr
	34F*6*′	6	Cr 68.6 N 122.0 I 120.6 N 24.7 Recr
	34F*7*′	7	Cr 67.3 N 113.4 I 112.6 N 27.0 Recr
	34F*8*′	8	Cr 73.2 N 112.0 I 110.7 N 34.9 SmA 29.6 Recr
	34F*9*′	9	Cr 69.6 N 106.8 I 106.0 N 50.1 SmA 34.2 Recr
	34F*10*′	10	Cr 60.5 N 105.5 1104.4 N 60.4 SmA 28.2 Recr
	34F*12*′	12	Cr 50.5 SmA 75.0 N 101.0 I 99.3 N 73.4 SmA 24.5 Recr
	34F*16*′	16	Cr 64.7 SmA 83.3 N 95.2 I 93.8 N 82.7 SmA 49.1 Recr
345F*n*′	**345F*4*′**	4	Cr 120.0 I 103.8 N 56.1 Recr
	345F*5*′	5	Cr 95.8 N 97.3 I 96.7 N 56.4 Recr
	345F*6*′	6	Cr 86.1 N 98.1 I 97.3 N 60.8 Recr
	345F*7*′	7	Cr 76.1 N 91.2 I 90.5 N 52.8 Recr
	345F*8*′	8	Cr 76.1 N 89.9 I 89.0 N 61.1 SmA 46.3 Recr
	345F*9*′	9	Cr 80.1 N 87.2 I 86.1 N 61.9 SmA 42.3 Recr
	345F*10*′	10	Cr 80.1 N 89.9 I 88.8 N 74.4 SmA 54.5 Recr
	345F*12*′	12	Cr 80.2 N 87.5 I 86.5 N 78.8 SmA 44.7 Recr
	345F*16*′	16	Cr 81.4 N 82.8 I 81.4 N 79.6 SmA 61.9 Recr

Cr, Crystal; SmA, Smectie A phase; N, Nematic phase; I, Isotropic phase; Recr, Recrystal.

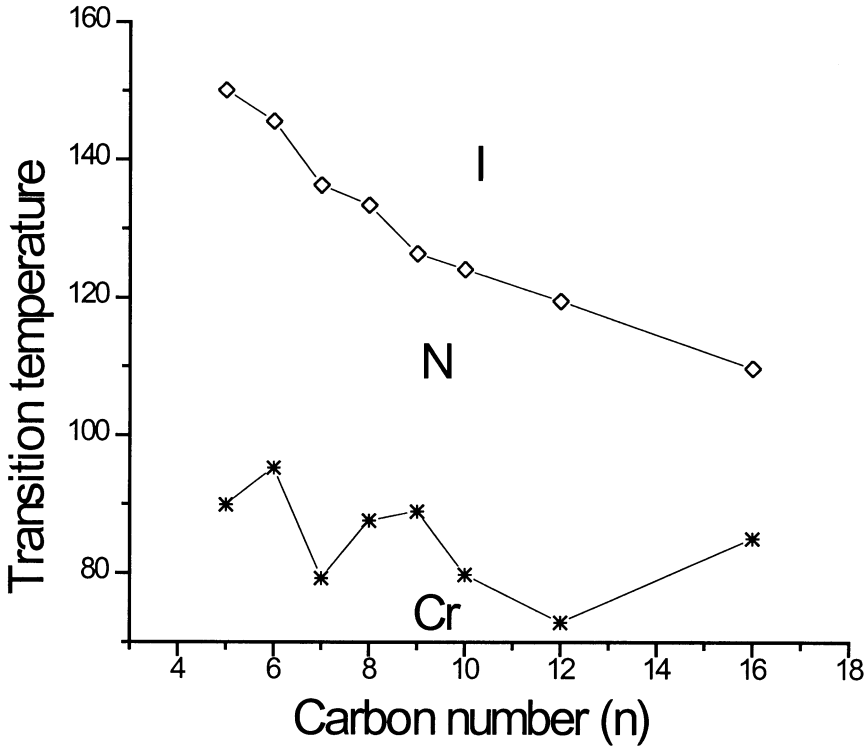


FIGURE 1 The transition behavior of series **HF*n*′**: dependence of transition temperatures on the number (*n*) of the aloxy chain.

one *meta*-fluorosubstituent does. From all these data listed in Table 1 the same result is obtained, namely that to increase the number of fluorosubstituents on the terminal phenyl group promotes the formation of the SmA phase. This means that with increasing fluorosubstitution in the terminal phenyl group, the terminal-terminal attractions are disrupted step by step. That the melting point of compounds **4F*n*′** or **345F*n*′** are higher than that of the corresponding compound **34F*n*′** may be due to molecular symmetry.

Comparing compounds **4F*8*′**, **34F*8*′**, and **345F*8*′** with the three compounds **4F*8***, **34F*8***, and **345F*8*** without lateral fluorosubstituents in the central phenylene group [10], respectively (see Figure 5), the lateral fluorosubstitution on the central phenylene group lowers the clearing point and narrows the breadth of the smectic phase range. This is because the lateral fluorosubstitution increases the breadth of molecules and reduces the lateral-lateral interaction. It is also because of this that the crystalline

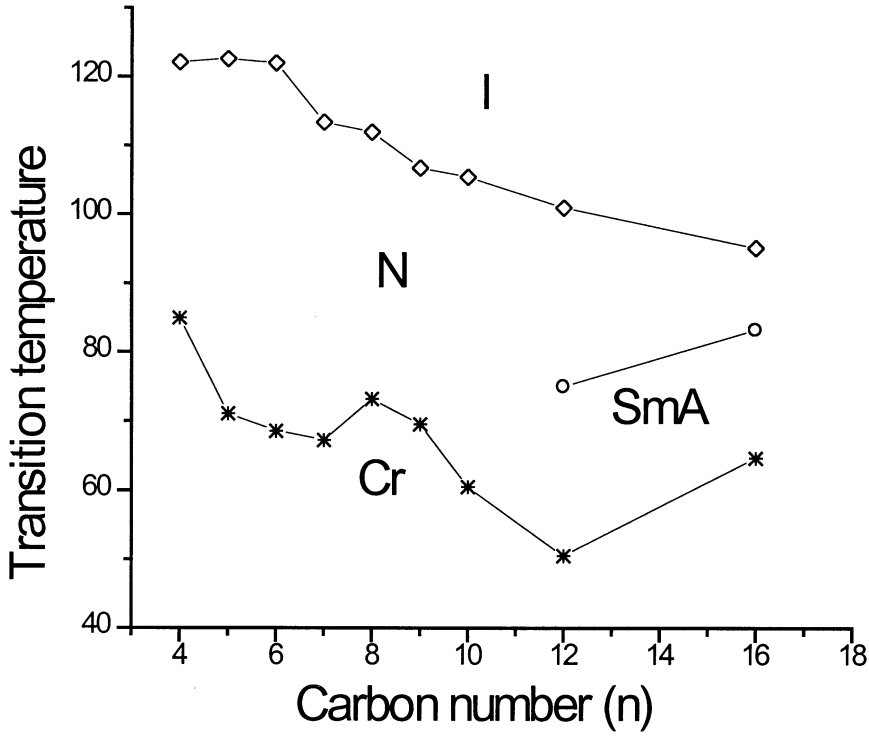


FIGURE 2 The transition behavior of series **34F*n*′**: dependence of transition temperatures on the number (*n*) of the alkoxy chain.

temperatures of compounds series **4F*n*′**, **34F*n*′**, and **345F*n*′** are lower than those of compounds **4F*n***, **34F*n***, and **345F*n*** respectively.

In a word, the lateral fluorosubstituents on the central group of series **4F*n*′**, **34F*n*′**, and **345F*n*′** reduce the nematic stability and the melting point. Similar to other series with fluorosubstituents on the terminal phenylene group [10–12], increasing the number of fluorosubstituents on the terminal group will promote the formation of smectic phases.

In series **A**, the system with a fluorinated tail, it is found that the clearing point of **A4** is the highest, 156.9°C. Meanwhile, the clearing point of **A35** is the lowest, 98.2°C. This is related to the steric and electronic effects of fluorine atoms. Considering the steric effect, the protrusion of the *meta*-fluorosubstituent in **A35** will tend to disrupt the side-to-side intermolecular forces of attraction which reduce the clearing point. As to compounds **A35** and **A345**, it is found that the *para*-fluorosubstitution increases the clearing point and

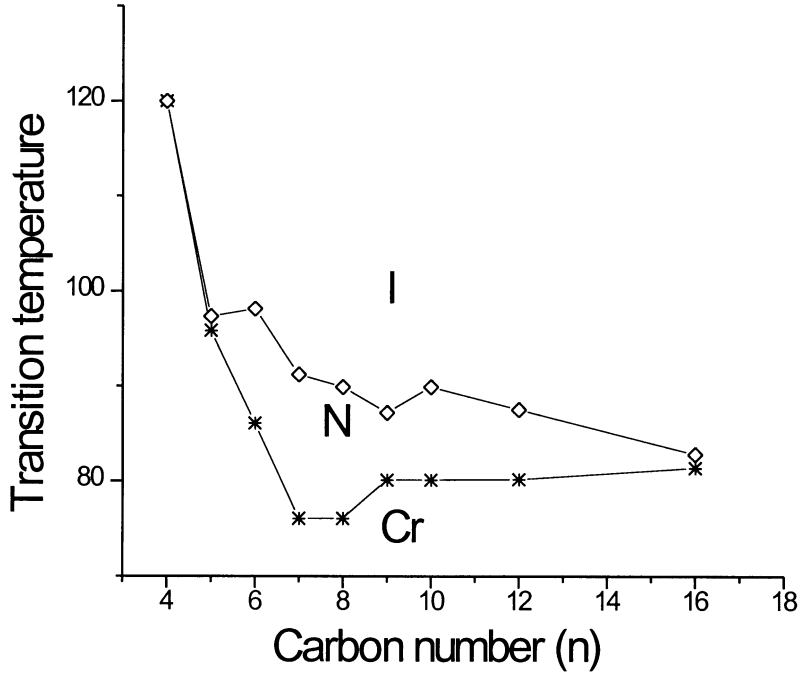


FIGURE 3 The transition behavior of series **345F*n***′: dependence of transition temperatures on the number (*n*) of the alkoxy chain.

enhances the formation of the nematic phase. This may be due to the electronic effect of the fluorosubstitution, which might enhance the formation of pairwise associations [13, 14]. As for compounds **A4, A34**, and **A345**, it is found that the *meta*-fluorosubstitution affects the tendency to form the SmA

TABLE 2 The transition temperatures of compounds in series **A** and **B**

Compounds	*Transition temperatures/°C*
A345	Cr 103.3 N 103.7 I 101.6 N 62.1 Recr
B345	Cr 93.0 SmA 109.0 N 132.6 I 131.1 N 107.4 SmA 57.8 Recr
A35	Cr 97.6 SmA 98.2 I 97.6 SmA 64.6 Recr
B35	Cr 65.3 N 68.8 I 66.6 N 55.0 Recr
A34	Cr 94.4 SmA 106.6 N 129.4 I 126.9 N 103.0 SmA 51.1 Recr
B34	Cr 58.0 SmA 75.4 N 152.0 I 149.6 N 72.5 SmA 47.7 Recr
A4	Cr 102.0 SmA 140.2 N 156.9 I 155.4 N 138.4 SmA 72.1 Recr
B4	Cr 91.9 N 170.1 I 168.6 N 63.7 Recr

Cr, Crystal; SmA, Smectic A phase; N, Nematic phase; I, Isotropic phase; Recr, Recrystallization.

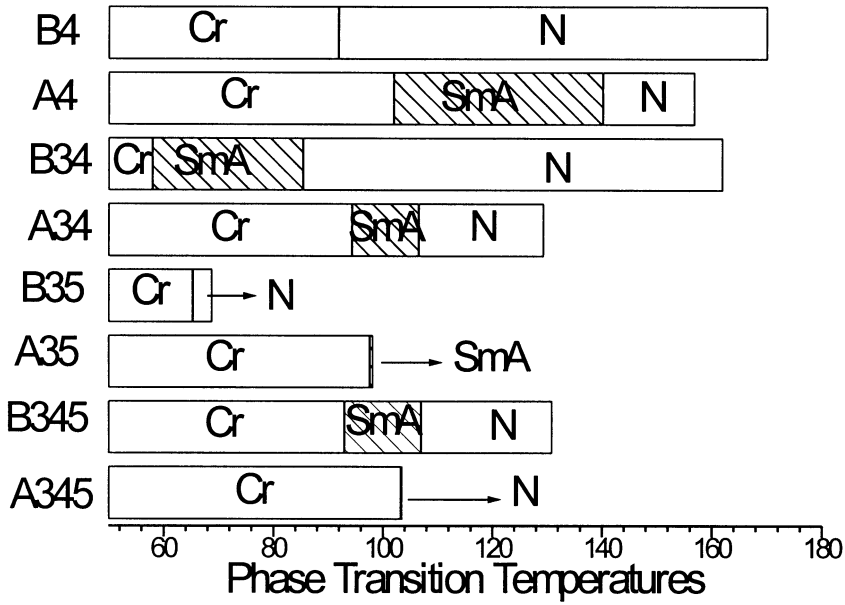


FIGURE 4 The mesomorphic properties of compounds in series **A** and **B**. Cr = Crystal; SmA = Smectic A phase; N = Nematic phase.

phase. This is different from the phenomenon in series **B** in which the *meta*-fluorosubstituent enhances the tendency to form the SmA phase [11].

In series **A**, both the fluorocarbon chain and the fluorosubstituted terminal aromatic ring show low cohesive energy density, which is the main reason for microphase separation in fluorinated compounds. Thus, similar to fluorocarbon chains, the fluorosubstituent in the terminal aromatic rings may also change the polyphilic property of the whole molecule. In series **A**, two terminals were both fluorinated, and the whole molecule may lose the polyphilic property. Therefore, with the increase in *meta*-fluorosubstituents in the terminal phenyl group, the thermal stability of the smectic A phase, which is stabled by the polyphilic property of fluorocarbon chains, is decreased. But due to the strong microphase separation of series **A**, compound of series **A** is more favorable to form smectic A phase than that in the series **B**.

Comparing the two series, series **A** with the fluorinated tail generally decreases the clearing point and increases the melting point. The increasing of melting points of the compounds in series **A** is probably due to the rigidity of the fluorocarbon chain.

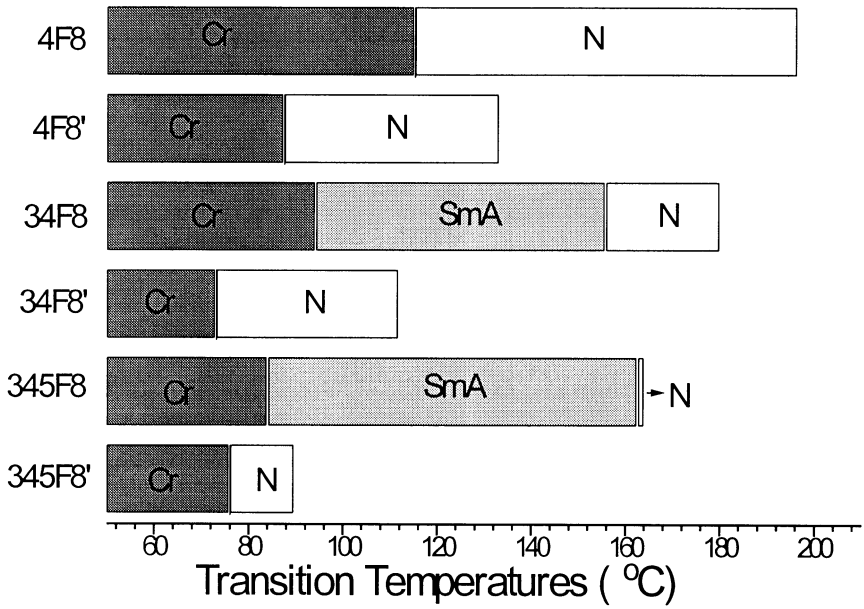


FIGURE 5 Comparison of mesomorphic properties of selected compounds. Cr = Crystal; SmA = Smectic A phase; N = Nematic phase.

Considering the compounds studied above, we know that the *para*-fluorosubstitution *meta*-fluorosubstitution in the terminal phenyl group in combination with the fluorosubstitution in the tail tend to form the SmA phase. However, they might disturb each other during the formation of microphase separation due to the same low cohesive energy density.

EXPERIMENTAL

Compound **3** can be easily obtained according to the published procedure [15]. Compound **4** was prepared from compound **3** directly through a bromosubstitution step. Then compound **6** was synthesized via a mild one-pot esterification procedure, between **4** and **5** in the presence of both dicyclohexylcarbodiimide (DCC) and DMAP catalyst in dried THF. Compound **10** can be obtained according to our published procedure [16]. Finally, the coupling reaction between compounds **6** and **10** under the catalysis of

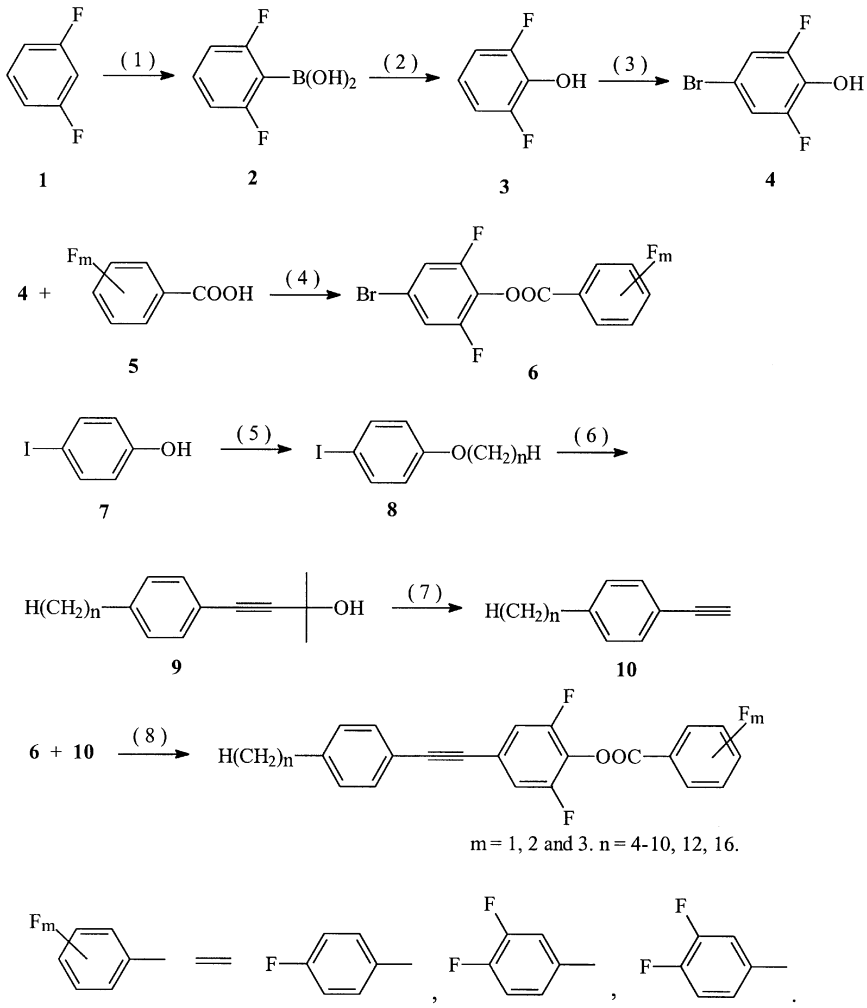
bis(triphenylphosphine) palladium dichloride, triphenylphosphine and copper(I) iodide in dried triethylamine and THF gave the compounds **4F*n*′**, **34F*n*′**, and **345F*n*′**.

Infrared spectra were scanned on a PE-983G spectrophotometer. ^{1}H NMR spectra were recorded on a FX-90Q (90 MHz), a Varian 360L (60 MHz) or a Brucker 300 NMR (300 MHz) spectrometer with TMS as the internal standard. ^{19}F NMR spectra, with trifluoroacetic acid (TFA) as external standard and $CDCl_3$ as the solvent, were recorded on a Varian EM 360L (56.4 MHz) spectrometer (high field positive). Mass spectra were measured with a Finnigan 4021 spectrometer. Elemental analyses were performed on a Heraeus Rapid CHN-O (Germany) instrument. The mesophase textures were observed on the Olympus BH2 polarized microscope in conjunction with a Mettler FP-52 heat-stage, equipped with a FP-5 control calorimetry at the heating rate of 5°C/min and cooling down naturally under a nitrogen atmosphere on a Shimadzu DSC-50 system and data station. The transition peaks were used as the transition temperatures.

The liquid crystal molecules studied were synthesized following the route as shown in Scheme 3 [17].

2,6-Difluorophenol (3) [15]

Butyl-lithium (1.6 mol/L in hexane, 33 mL, 52.8 mmol) was added dropwise to a stirred, cooled (−78°C) solution of compound (**1**) (5.8 g, 46.3 mmol) in dry THF (65 mL) under dry nitrogen. The reaction mixture was maintained under these conditions for 2.5 h, and then a previously cooled solution of trimethyl borate (10.4 g, 100.0 mmol) in dry THF (25 mL) was added dropwise at −78°C. The reaction mixture was allowed to warm to r.t. overnight and was then stirred for 1 h with 10% hydrochloric acid (30 mL). The product was extracted into ether (twice), then the combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield colorless crystals (8.0 g). 10% Hydrogen peroxide (50 mL, 146.7 mmol) was added dropwise to a stirred solution of these colorless crystals in ether (50 mL) heated under reflux. The stirred mixture was heated under reflux for 2.5 h and then cooled. The ether layer was separated and the aqueous layer was washed with ether. The combined ethereal layers were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was purified by flash chromatography to give an off-white solid (5.59 g). Yield: 85.3%. δ_F ($CDCl_3$): 59.1(s, 2F) ppm. m/z(%): 130(100.00), 82(55.78), 110(23.32).



SCHEME 3 The synthesis route of series **4F*n′***, **34F*n′*** and **345F*n′***. *Reagents and condition*: (1) a) *n*-C_4H_9Li/THF; $B(OMe_3)$/THF, −78°C to r.t.; b) H_3^+O, r.t.; (2) H_2O_2, Et_2O, r.t.; (3) Br_2, CH_3COOH, 0°C; (4) DCC, DMAP, r.t. THF; (5) *n*-$H(CH_2)_nBr$, CH_3COCH_3, K_2CO_3, reflux; (6) $Pd(PPh_3)_2Cl_2$, $HC{\equiv}CC(CH_3)_2OH$, CuI, Et_3N, 70°C; (7) KOH, $C_6H_5CH_3$, reflux; (8) $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, reflux.

2,6-Difluoro-4-bromophenol (4)

A solution of bromine (15.0 g, 92.6 mmol) in glacial acetic acid (6 mL) was added slowly, dropwise to a stirred solution of 2, 6-difluorophenol (**3**) (10.0 g, 76.9 mmol) in glacial acetic acid (20 mL), keeping the temperature

below 0°C. The mixture was stirred at r.t. for 4 h, and then sodium thiosulphate (5 g), sodium acetate (12.5 g) and water (50 mL) were added and the mixture was cooled in a refrigerator overnight. The product was extracted into ether (twice), then the combined ethereal extracts were washed with 10% sodium hydroxide water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was purified by flash chromatography to give a yellow solid (11.5 g). Yield: 71.7%. δ_F ($CDCl_3$): 54.8(s, 2F) ppm. m/z(%): 210(100.00), 208(99.69), 162(24.92), 160(25.76), 81(52.05).

(2,6-Difluoro-4-bromophenol) 4-fluorobenzoate (6a)

2,6-Difluoro-4-bromophenol (3.9 g, 18.6 mmol), 4-fluorobenzoic acid (2.8 g, 20 mmol), N,N′-dicyclohexylcarbodiimide (4.0 g, 19.2 mmol), catalytic DMAP and dry THF (40 mL) were stirred under dry nitrogen at room temperature for 24 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 to give a white solid (3.3 g). Yield: 53.2%. δ_F ($CDCl_3$): 46.5(s, 2F), 25.5(s, 1F) ppm. m/z(%): 330(1.41), 123(71.13), 95(100.00).

(2,6-Difluoro-4-bromophenol) 3,4-difluorobenzoate (6b)

The experiment procedure was as described for the preparation of compound (**6a**). δ_F ($CDCl_3$): 57.9(m, 1F), 49.9(m, 1F), 46.1(s, 2F) ppm. m/z(%): 348(0.42), 141(100.00).

(2,6-Difluoro-4-bromophenol) 3,4,5-trifluorobenzoate (6c)

The experiment procedure was as described for the preparation of compound (**6a**). δ_F ($CDCl_3$): 72.6(m, 1F), 54.5(m, 2F), 46.5(s, 2F) ppm. m/z(%): 367(1.05, M + 1), 365(1.07), 159(100.00).

[4-(4′-n-Pentoxyphenyl)acetylenyl]-2,6-difluorophenyl 4-fluorobenzoate (4F5′)

A typical procedure: Under dry nitrogen, into a mixture of compound 4-*n*-pentoxyphenylacetylene (**10**) (190 mg, 1.02 mmol), compound **6a** (300 mg, 0.909 mmol), bis(triphenylphosphine)palladium dichloride (30 mg) and copper (I) iodide (50 mg) were added 15 mL of anhydrous triethylamine. The resulting mixture was refluxed while it was stirred. Analysis by TLC revealed completion of the reaction within 8 h. Then the formed precipitate was filtered and the solvent was removed *in vacuo*. The residue was purified

TABLE 3 The M.P., IR, MS, and E.A. of the compounds synthesized in this paper

Comp.	*M.P. (°C)*	*IR*	*MS*	*E.A.*	
				Calcd	*Found*
1PTP*6′* ($C_{27}H_{23}F_3O_3$)	95.3	2958, 2206, 1751, 1603, 1208, 1045	452, 123	C, 71.67; H, 5.12; F, 12.60	C, 71.69; H, 5.02; F, 12.36
1PTP*7′* ($C_{28}H_{25}F_3O_3$)	79.3	2925, 2207, 1751, 1604, 1209, 1155	466, 123	C, 72.09; H, 5.40; F, 12.22	C, 72.00; H, 5.30; F, 12.22
1PTP*8′* ($C_{29}H_{27}F_3O_3$)	87.6	2920, 2211, 1755, 1605, 1208, 1157	480, 123	C, 72.49; H, 5.66; F, 11.86	C, 72.41; H, 5.56; F, 11.51
1PTP*9′* ($C_{30}H_{29}F_3O_3$)	88.9	2920, 2211, 1757, 1603, 1208, 1157	494, 123	C, 72.86; H, 5.91; F, 11.52	C, 73.04; H, 5.86; F, 11.23
1PTP*10′* ($C_{31}H_{31}F_3O_3$)	79.8	2915, 2209, 1755, 1603, 1207, 1155	508, 123	C, 73.21; H, 6.14; F, 11.21	C, 73.24; H, 6.35; F, 11.30
1PTP*12′* ($C_{33}H_{35}F_3O_3$)	72.9	2918, 2208, 1756, 1604, 1209, 1156	536, 123	C, 73.86; H, 6.57; F, 10.62	C, 73.87; H, 6.35; F, 10.35
1PTP*16′* ($C_{37}H_{43}F_3O_3$)	85.0	2917, 2207, 1755, 1604, 1208, 1155	592, 123	C, 74.97; H, 7.31; F, 9.62	C, 75.00; H, 7.27; F, 9.54
2PTP*5′* ($C_{26}H_{20}F_4O_3$)	71.1	2935, 2213, 1749, 1606, 1209, 1046	456, 141	C, 68.40; H, 4.42; F, 16.66	C, 68.46; H, 4.38; F, 16.53
2PTP*6′* ($C_{27}H_{22}F_4O_3$)	68.6	2943, 2209, 1760, 1604, 1249, 1184	470, 141	C, 68.91; H, 4.72; F, 16.16	C, 68.73; H, 4.57; F, 16.36
2PTP*7′* ($C_{28}H_{24}F_4O_3$)	67.3	2934, 2213, 1759, 1606, 1301, 1180	484, 141	C, 69.40; H, 5.00; F, 15.70	C, 69.49; H, 5.03; F, 15.46
2PTP*8′* ($C_{29}H_{26}F_4O_3$)	73.2	2923, 2213, 1759, 1606, 1179, 1044	498, 141	C, 69.85; H, 5.26; F, 15.25	C, 69.83; H, 4.90; F, 14.94
2PTP*9′* ($C_{30}H_{28}F_4O_3$)	69.6	2917, 2215, 1756, 1606, 1307, 1173	512, 141	C, 70.29; H, 5.51; F, 14.84	C, 70.34; H, 5.59; F, 14.87
2PTP*10′* ($C_{31}H_{30}F_4O_3$)	60.5	2919, 2213, 1758, 1606, 1212, 1174	526, 141	C, 70,69; H, 5.75; F, 14.44	C, 70.85; H, 5.70; F, 14.59
2PTP*12′* ($C_{33}H_{34}F_4O_3$)	50.5	2920, 2215, 1766, 1604, 1249, 1182	554, 141	C, 71.45; H, 6.18; F, 13.71	C, 71.20; H, 5.91; F, 13.45
2PTP*16′* ($C_{37}H_{42}F_4O_3$)	64.7	2919, 2215, 1760, 1605, 1250, 1183	610, 141	C, 72.77; H, 6.93; F, 12.44	C, 72.79; H, 6.85; F, 12.50
3PTP*5′* ($C_{26}H_{19}F_5O_3$)	95.8	2950, 2200, 1760, 1610, 1250, 1190	474, 159	HRMS: 474.1255	HRMS: 474.1249
3PTP*6′* ($C_{27}H_{21}F_5O_3$)	86.1	2931, 2214, 1760, 1605, 1250, 1196	488, 159	C, 66.39; H, 4.33; F, 19.45	C, 66.56; H, 4.22; F, 19.62
3PTP*7′* ($C_{28}H_{23}F_5O_3$)	76.1	2931, 2213, 1761, 1605, 1252, 1197	502, 159	C, 66.93; H, 4.61; F, 18.90	C, 66.99; H, 4.95; F, 17.99
3PTP*8′* ($C_{29}H_{25}F_5O_3$)	76.1	2930, 2214, 1760, 1604, 1250, 1197	516, 159	C, 67.44; H, 4.88; F, 18.39	C, 67.57; H, 4.95; F, 17.99
3PTP*9′* ($C_{30}H_{27}F_5O_3$)	80.1	2928, 2214, 1761, 1605, 1250, 1196	530, 159	C, 67.92; H, 5.13; F, 17.90	C, 68.08; H, 5.11; F, 17.68
3PTP*10′* ($C_{31}H_{29}F_5O_3$)	80.1	2930, 2213, 1764, 1605, 1249, 1196	544, 159	C, 68.37; H, 5.37; F, 17.44	C, 68.13; H, 5.31; F, 17.48
3PTP*12′* ($C_{33}H_{33}F_5O_3$)	80.2	2919, 2214, 1762, 1605, 1249, 1198	572, 414, 246	C, 69.22; H, 5.81; F, 16.59	C, 68.99; H, 5.90; F, 17.06
3PTP*16′* ($C_{37}H_{41}F_5O_3$)	81.4	2900, 2215, 1770, 1605, 1250, 1200	628, 404, 159	C, 70.68; H, 6.57; F, 15.11	C, 70.69; H, 6.70; F, 14.68

by flash chromatography and recrystallized from acetone-methanol to give a white solid (210 mg). Yield: 50.4%. Mp 150.1°C. ν_{max} (KBr): 2940, 2200, 1750, 1610, 1520, 1380, 1300, 1280, 1170, 1050, 840, 760 cm^{-1}. $\delta_H(CDCl_3)$: 0.90–1.30(m, 3H), 1.30–2.23(m, 6H), 4.10(t, 2H, J = 6.8 Hz), 6.83–8.60(m, 10H) ppm. δ_F ($CDCl_3$): 48.1(d, 2F, J = 7.8 Hz), 25.0(s, 1F) ppm. m/z(%): 438(13.91), 373(41.44), 234(64.27), 123(100.00). HRMS: $C_{26}H_{21}O_3F_3$. Calcd: 438.1443. Found: 438.1448.

[4-(4′-n-Butoxyphenyl)acetylenyl]-2,6-difluorophenyl 3,4-difluorobenzoate (34F4′)

Mp 122.1°C. ν_{max} (KBr): 2963, 2210, 1753, 1603, 1520, 1375, 1298, 1248, 1184,1050, 926, 751, 570 cm^{-1}. δ_H ($CDCl_3$): 0.90–1.28(m, 3H), 1.26–2.13(m, 4H), 4.20(t, 2H, J = 6.0 Hz), 6.97–8.40(m, 9H) ppm. δ_F ($CDCl_3$): 57.61–57.75(m, 1F), 49.76–49.91(m, 1F),48.14(d, 2F, J = 6.8 Hz) ppm. m/z(%): 442(33.29), 141(100.00). Anal. $C_{25}H_{18}F_4O_3$. Calcd: H, 4.10; C, 67.87; F, 17.18. Found: H, 4.40; C, 68.09; F, 16.64.

[4-(4′-n-Butoxyphenyl)acetylenyl]-2,6-difluorophenyl 3,4,5-trifluorobenzoate (345F4′)

Mp 120.0°C. ν_{max} (KBr): 2950, 2200, 1760, 1610, 1520, 1440, 1360, 1250, 1190, 1040, 940, 830, 760 cm^{-1}. $\delta_H(CDCl_3)$: 0.90–1.25(m, 3H), 1.25–2.10(m, 4H), 4.18(t, 2H, J = 6.0 Hz), 6.90–8.20(m, 8H) ppm. δ_F ($CDCl_3$): 72.0–73.3(m, 1F), 53.3–54.7(m, 2F), 48.5(d, 2F, J = 7.8 Hz) ppm. m/z(%): 460(37.30), 159(100.00). HRMS: $C_{25}H_{18}F_4O_3$. Calcd: 460.1098. Found: 460.1113.

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