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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

ISSN: 1058-725X (Print) (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl19

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To cite this article: J. X. Wen , G. Tang & Y. G. Yang (2000) Synthesis and Mesomorphic Properties of [4-((4-n-Alkoxy-2,3,5,6-Tetrafluorophenyl)Ethynyl)Phenyl] Fluoro-Substituted Benzoates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 338:1, 21-33, DOI: 10.1080/10587250008024417

To link to this article: http://dx.doi.org/10.1080/10587250008024417

Mol. Cryst. Liq. Cryst., Vol. 338, pp. 21-33
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Synthesis and Mesomorphic Properties of [4-((4-*n*-Alkoxy-2,3,5,6-Tetrafluorophenyl)Ethynyl)Phenyl] Fluoro-Substituted Benzoates

J.X. WEN*, G. TANG and Y.G. YANG

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Fenlin Lu 354, Shanghai, 200032, China

(Received January 20, 1999; In final form April 01, 1999)

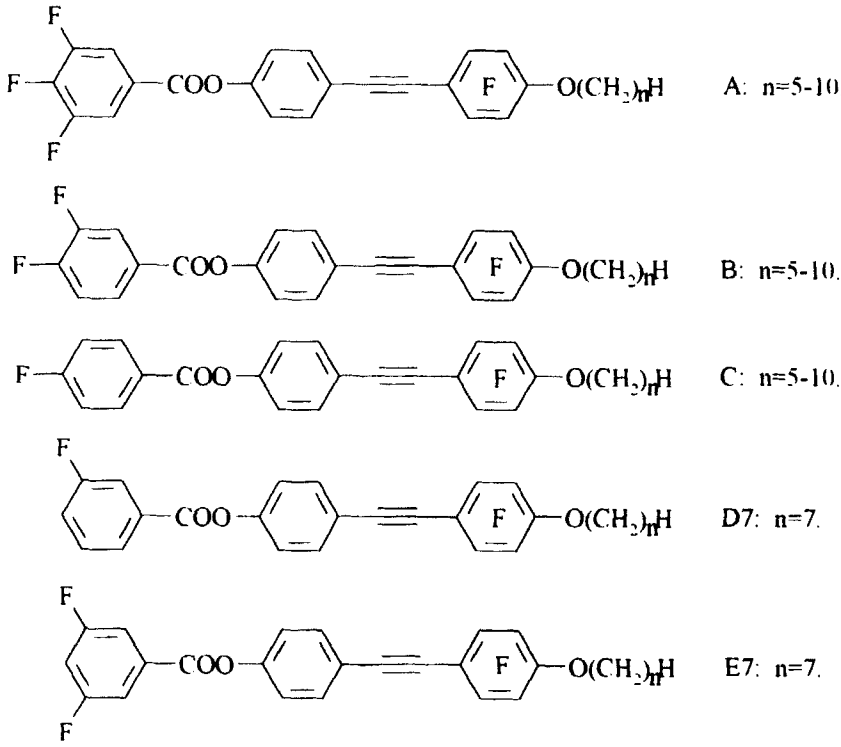
Five series of liquid crystals incorporating a 2,3,5,6-tetrafluorophenylene moiety and a terminal fluorosubstituted phenyl group have been prepared. The mesomorphic properties have been studied by polarizing microscopic textural observation and DSC measurements. The effect of terminal fluorosubstituent on mesomorphic behaviour has been discussed.

INTRODUCTION

Since the survey and synthesis of new liquid crystal compounds can bring about further development in the scientific understanding of liquid crystals and their device application, an increasing amount of reasearch has been carried out on liquid crystals containing fluorine atoms in the backbone structure[1–2], which are regarded as very useful in influencing the melting point, vicosity, birefringence and dielectric anisotropy. Therefore, a lot of liquid crystalline materials with monofluoro-, difluoro- or trifluoro-substituted aromatic rings have been extensively studied[3–10]. Nevertheless, only a limited number of liquid crystal materials with 1,4-disubstitutes tetrafluorobenzene structures have been reported[11–22]. In our previous studies, we have synthesized liquid crystals with 2,3,5,6-tetrafluoro-1,4-phenylene in the core[23–29]. In this paper, we wish to report the synthesis and phase transitions of some novel fluorinated liquid crys-

* Correspondence Author.

tals (series **A**, **B**, **C**, **D**, **E**) with terminal fluoro-substituted benzene and 2,3,5,6-tetrafluoro-1,4-phenylene.



RESULTS AND DISCUSSION

The phase transition temperatures of compounds in seires **A**, **B**, **C**, **D** and **E** are listed in the Table I below.

Compounds in series **A** and **B** show both enantiotropic smectic A phase and nematic phase; whereas compounds **D**, **E** and compounds in series **C** shows only enantiotropic nematic phase. As shown in Figure 1, 2 and 3, with the increasing of the alkoxy chain length, the clearing points of compounds in series **A**, **B**, **C** tend to drop. And in series **A** and **B**, the tendency of a compound to form nematic decreases; whereas its tendency to exhibit smectic phase increases as the terminal chain extends longer. In Series **C**, its tendency to form nematic decreases with the increasement of the terminal chain.

TABLE I Transition temperatures of compounds of seires **A**, **B**, **C**, **D**, **E**

Compounds	*n*	*Transition temperatures/°C*											
A5	5	Cr 93.0	S_A	109.0	N	132.6	I	131.1	N	107.4	S_A	57.8	Recr
A6	6	Cr 75.2	S_A	1104	N	129.6	I	129.2	N	109.6	S_A	56.7	Recr
A7	7	Cr 69.1	S_A	109.2	N	121.1	I	119.5	N	107.7	S_A	53.4	Recr
A8	8	Cr 62.7	S_A	113.2	N	121.5	I	120.5	N	111.7	S_A	44.5	Recr
A9	9	Cr 73.0	S_A	114.5	N	117.8	I	115.9	N	112.3	S_A	48.6	Recr
A10	10	Cr 68.5	S_A	114.8	N	116.5	I	115.3	N	113.5	S_A	45.2	Recr
B5	5	Cr 58.0	S_A	75.4	N	152.0	I	149.6	N	72.5	S_A	47.7	Recr
B6	6	Cr 61.1	S_A	76.7	N	147.7	I	146.3	N	75.5	S_A	51.0	Recr
B7	7	Cr 68.4	S_A	84.9	N	138.3	I	136.9	N	84.2	S_A	52.3	Recr
B8	8	Cr 64.7	S_A	89.2	N	137.5	I	135.9	N	88.0	S_A	48.4	Recr
B9	9	Cr 61.6	S_A	93.1	N	126.7	I	124.7	N	90.9	S_A	42.8	Recr
B10	10	Cr 63.0	S_A	95.2	N	23.5	I	122.3	N	93.3	S_A	41.8	Recr
C5	5	Cr 91.9	N	170.1	I	168.6	N	63.7	Recr				
C6	6	Cr 84.2	N	164.4	I	162.9	N	52.6	Recr				
C7	7	Cr 81.7	N	155.7	I	154.2	N	55.9	Recr				
C8	8	Cr 74.8	N	149.3	I	147.3	N	47.8	Recr				
C9	9	Cr 78.7	N	143.9	I	142.5	N	49.0	Recr				
C10	10	Cr 78.2	N	139.6	I	138.1	N	46.7	Recr				
D7	7	Cr 58.8	N	91.3	I	89.7	N	38.7	Recr				
E7	7	Cr 71.4	N	76.5	I	74.5	N	61.6	Recr				

Cr = Crystal: S_A = Smectic A phase; N = Nematic phase; I = Isotropic phase; Recr = Recrystallization.

In order to investigate the effect of the fluorine atoms in the terminal phenyl, we pay attention to these five compounds **A7**, **B7**, **C7**, **D7**, **E7**, in which the number of carbon in the terminal hydroxycarbon chain is seven .

As shown in Figure 4, the clearing point of **C7** is the highest, 155.7°C: however, the clearing point of **E3** is the lowest, 76.5°C. As for compounds **A7** and **B7**, **B7** and **C7**, **D7** and **E7**; we can found that *m*-fluorosubstitution shortens the temperature range of liquid crystal phase. The protrusion of *meta*-substitution fluorine atom forces the long molecular axes apart and reducing the lateral-lateral interaction of molecules, thus lowering liquid crystal thermal stability. As for compounds **B7** and **D7**, **A7** and **E7**, the *p*-fluorosubstitution extends the temperature range of liquid crystal phase. We suggest that the larger the lengh/breadth ratio, the wider the range. The *para*-substituted flurine atom extends the length of the molecule, the lengh/breadth ratio and the molecular shape anisotropy.

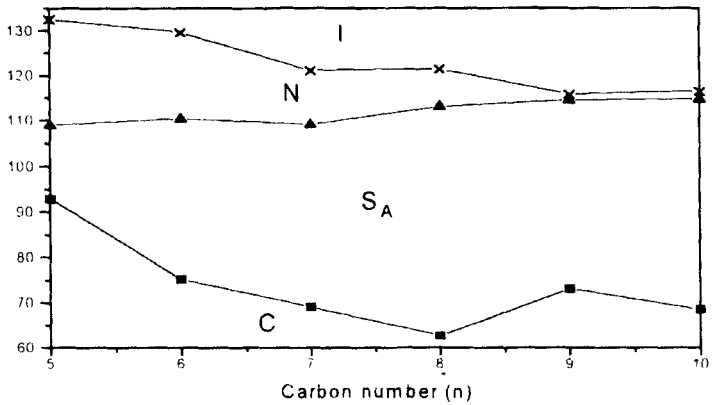


FIGURE 1 Series A C = crystal; S_A = Smectic A phase; N = Nematic phase: I = Isotropic phase

Now we discuss the effect of fluoro-substitution in compounds **A7**, **B7** and **C7** With the increasement of *m*-fluorosubstitution in the terminal phenyl, the tendency forming SmA phase is strengthened and the ability of forming nematic phase is weakened. This may be the reason of that the *meta*-fluorine atom occupy an outer edge position of the terminal phenyl. It affects not only the terminal-terminal interaction but also the lateral-lateral interaction, and it must decreases the former much than the later. Then the smectic phase is favorable with increasing the degree of fluoro-substitution at the outer edge position.

For seires **B** and series **C**, the former is more favorable to from smectic phase than the later. It can be explained as usual[30]. That the radius of fluorine atom is very small, and it will be shield by the phenol. Then the lateral dipolarity O molecule is noticeable. But it can not explain the different between series B and series C as this.

Professor J.W.Goodby explained this phenomena as this[31]. It is well-known that increasing the amount of fluorination, particularly in the terminal chains, favours the formation of smectic A phase[32]. (Although in semiperfluorinated systems, it seems that SmA phase and SmC phase are all enhanced[33–36].) This is because there is a tendency to microphase separate – at least that is generally the picture that is produced from X-ray diffraction studies[37,38]. This means that the fluorocarbon bits stick together, the aromatic bits also stick together etc[39,40]. The strong fluorine-fluorine interactions tend then to limit the phases to smectic A –

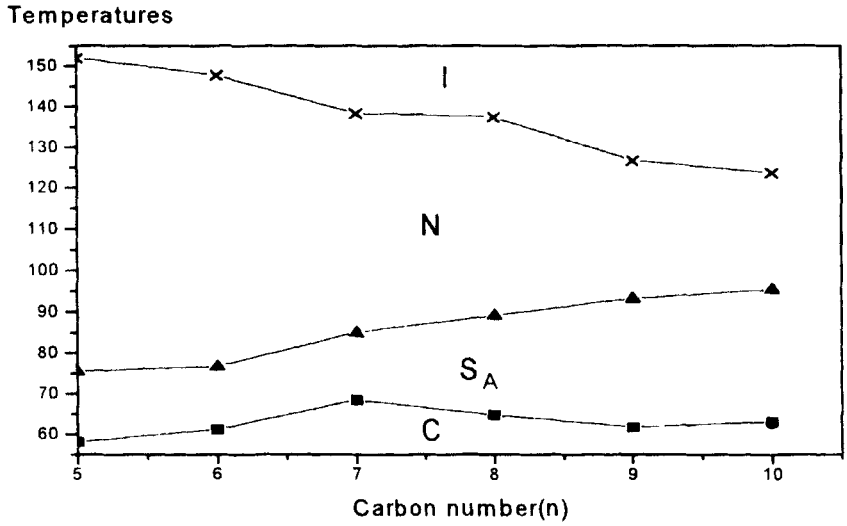
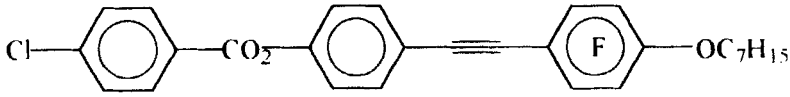


FIGURE 2 Series B C = Crystal; S_A = Smectic A phase: N = Nematic phase: I = Isotropic phase

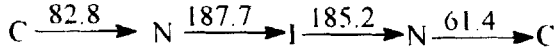
ie generally we don't get nematics as this would require the breaking up of the microphase separated regions.

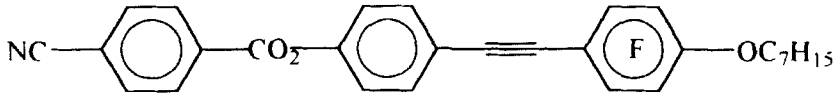
For fluoro-substitution in aromatics in this paper have the added problem of polarisability and conjugation. For a limited number of fluoro-substituents conjugation reduces the intermolecular interactions so that microphase separation does not occur and nematic phases can form. Increase the number of fluorine atoms to apoint where microphase separation can occur and then we get smectics again.

As for the compounds studied above, we get to know that both *p*-fluorosubstitution and *m*-fluorosubstitution are the abundant condition of forming S_A phase. However, *p*-fluorosubstitution or *m*-fluorosubstitution alone can not ensure the formation of S_A phase. In our previous study, we also prepared such molecules as below:



Q1 Phase transition temperature:





Q2 Phase transition temperature:

$$C \xrightarrow{109.9} N \xrightarrow{225.1} I \xrightarrow{222.7} N \xrightarrow{101.9} C$$

Among **C7**, **Q1** and **Q2**, the clearing point of **C7** is the lowest and the temperature range of nematic phase in **C7** is the narrowest. Compared with **Cl** atom and **CN** group, fluorine atom largely decreases the clearing point and shrinks the range of nematic phase. This is the reason of that the terminal group which extends the molecule along the molecular axis without increasing the molecular breath too much increases the thermal stability of a mesophase. And it is also the reason of that the terminal group which increases the anisotropy of molecular polarizability, particularly if they conjugate with the aromatic ring increases the thermal stability of a mesophase.

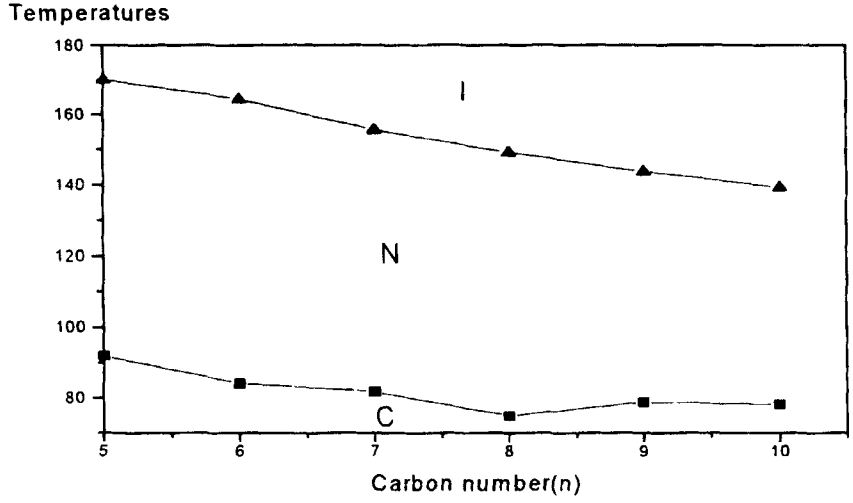


FIGURE 3 Series C C = Crystal: N = Nematic phase; I = Isotropic phase

Experimental

The structures of the intermediates and the final compounds were elucidated by spectral mathods. IR spectra were determined on a Shimadzu IR-440 spectral

spectrometer using a KBr disc pellet. ^1H NMR spectra, with TMS as the internal standard and $CDCl_3$ as the solvent, were run in FX-90Q (90 MHz) or Bruker 300 (300 MHz) spectrometer. ^{19}F NMR spectra, with trifluoroacetic acid(TFA) as external standard and $CDCl_3$ as the solvent, are recorded on a Varian EM 360L (60 MHz) spectrometer (high field positive). MS spectra were measured with a Finnigan 4021 Spectroscope. The phase transtion temperatures of the target compounds were measured visually by optical microscopy using a polarizing microscope fitted with a Mettler FP 82 heating stage. The phase identification was made by comparing the observed textures with those in the literature.

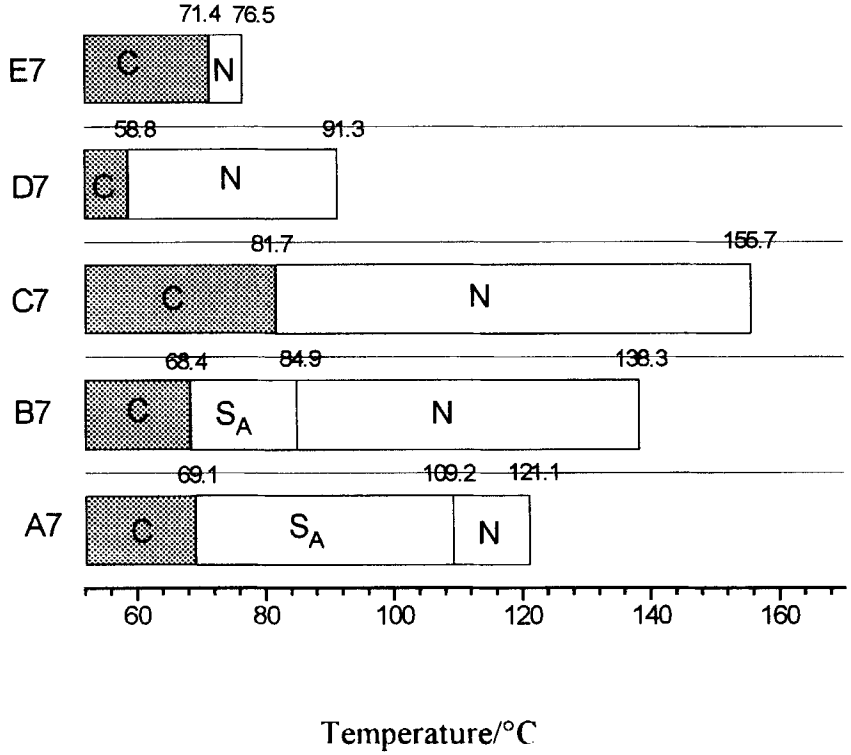
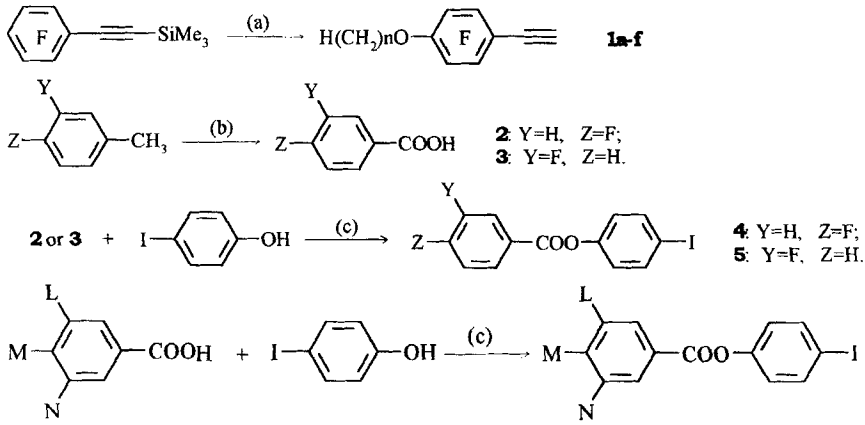


FIGURE 4 C = Crystal: S_A = Smectic A phase: N = Nematic phase

The target molecules were prepared according to Scheme 1. The 4-n-alkoxy 2,3,5,6-tetrafluorophenylacetylenes **1a-f** were obtained by nucleophilic substitution on the starting material 1-pentafluorophenyl-2-trimethylsilylacetylene at room temperature[41]. And the oxiadation of 1-fluoro-4-methylbenzene and 1-fluoro-3-methylbenzene by the $K_2Cr_2O_7$ in concentrated H_2SO_4/water solu-

tion afforded 4-fluorobenzoic acid 2 and 3-fluorobenzoic acid 3[42]. Then the mild one pot esterification between 4-idiophenol and 2, and 3, and 3,4,5-trifluorobenzoic acid, and 3,4-difluorobenzoic acid, and 3,5-difluorobenzoic acid in the presence of both dicyclohexylcarbodiimide(DCC) and DMAP catalyst in dried THF gave the compounds 4, 5, 6, 7, 8. Finally, the desired compounds in series **A**, **B**, **C**, **D**, **E** were easily synthsized by the coupling reaction between compounds 1a-f and 4, 5, 6, 7, 8 under the catalysis of bis(triphenylphosphine)palladium dichloride and copper(I) iodide in dried triethylamine.



6: L=F, M=F, N=F; **7**: L=H, M=F, N=F; **8**: L=F, M=H, N=F.

1a-f + **4**, **5**, **6**, **7** or **8** —(d)→ Series A(n=5-10), B=(n=5-10), C (n=5-10), D(n=7), E(n=7).

SCHEME I (a) DMF, K_2CO_3, ROH; (b) $K_2Cr_2O_7$, H_2SO_4/H_2O; (c) DCC, DMAP, THF; (d) $Pd(PPh_3)_2Cl_2/CuI$, NEt_3

[(4-(4-n-Heptyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 3,4,5-trifluoro benzoate (A7)

A typical procedure: Under nitrogen, 20 ml of dried triethylamine was added to a mixture of compound 1c (n=7) (90 mg, 0.31 mmol), 6 (115 mg, 0.30 mmol), bis(triphenyl phosphine)palladium dichloride (30 mg, 0.04 mmol) and copper(I) iodide (15 mg, 0.08 mmol). The resulting mixture was refluxed while stirring until analysis by TLC revealed a complete reaction. The cooled mixture was filtered and the filtrate was washed with anhydrous ether. The solvent was removed under vacuum and residue was purified by column chromatography on silica gel using petroleum ether (b.p. 60–90 °C) and ethyl acetate (20:1) as eluent to give

pale-yellow crystals which were recrystallized from acetone-methanol to yield white crystals of compound A7. Yield: 103 mg (62.8%) m.p 69.1°C; ^{1}H NMR (300 MHz, $CDCl_3$/TMS): 0.87–0.90(m, 3H), 1.31–1.83(m, 10H), 4.27(t, 2H, J=6.6Hz). 7.23–7.26(m, 2H), 7.64–7.67(m, 2H), 7.84–7.88(m, 2H) ppm; ^{19}F NMR (60MHz, $CDCl_3$/TFA): 55.40(m, 2F), 61.50(m, 2F), 74.70(m, 1F). 80.90(m, 2F) ppm; IR (KBr): 2966, 2920, 2853, 2232, 1737, 1627, 1530, 1440, 1290, 1129, 1217, 1048 cm^{-1}; MS(m/z): 159(100.00), 440(44.15), 538(M^+, 12.27); Elem. anal. Calcd for $C_{28}H_{21}O_3F_7$: C, 62.47%; H, 3.90%; F, 24.71%; Found: C, 62.35%; H, 3.88%; F, 24.87%.

The same procedure was used to prepare the other compounds. The other compounds in series A had the same type of NMR spectrum.

[(4-(4-n-Pentyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 3,4,5-trifluoro benzoate (A5)

m.p 93.0°C; IR (KBr): 2966, 2920, 2853, 2233, 1737, 1627, 1530, 1440, 1290, 1129, 1217, 1048 cm^{-1}; MS(m/z): 159(100.00), 440(44.15), 510(M^+, 6.37); Elem. anal. Calcd for $C_{26}H_{17}O_3F_7$: C, 61.20%; H, 3.33%; F, 26.06%; Found: C, 61.08%; H, 3.35%; F, 26.06%.

[(4-(4-n-Hexyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 3,4,5-trifluoro benzoate (A6)

m.p. 75.2°C; IR (KBr): 2966, 2920, 2853, 2231, 1737, 1627, 1530, 1440, 1290, 1129, 1217, 1048 cm^{-1}; MS(m/z): 159(100.00). 440(52.73). 524(M^+, 17.35); Elem. anal. Calcd for $C_{27}H_{19}O_3F_7$: C, 61.85%; H, 3.62%; F, 25.37%; Found: C, 61.95%; H, 3.58%; F, 25.35%.

[(4-(4-n-Octyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 3,4,5-trifluoro benzoate (A8)

m.p. 62.7°C; IR (KBr): 2966, 2920, 2853, 2233, 1737, 1627, 1530, 1440, 1290, 1129. 1217, 1048 cm^{-1}; MS(m/z): 159(100.00), 440(21.76), 552(M^+, 2.70); Elem. anal. Calcd for $C_{29}H_{23}O_3F_7$: C, 63.06%; H, 4.16%; F, 24.08%; Found: C, 63.35%; H, 4.42%; F, 23.85%.

[(4-(4-n-Nonyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 3,4,5-trifluoro benzoate (A9)

m.p. 73.0°C; IR (KBr): 2966, 2920, 2853, 2233, 1737, 1627, 1530, 1440, 1290, 1129, 1217, 1048 cm^{-1}; MS(m/z): 159(100.00), 440(43.67), 566(M^+, 7.38): Elem. anal. Calcd for $C_{30}H_{25}O_3F_7$: C, 63.63%; H, 4.41%; F, 23.48%; Found: C, 63.17%; H, 4.30%; F, 23.47%.

[(4-(4-n-Decyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 3,4,5-trifluoro benzoate (A10)

m.p. 68.5°C; IR (KBr): 2966, 2920, 2853, 2233, 1737, 1627, 1530, 1440, 1290, 1129, 1217, 1048 cm^{-1}; MS(m/z): 159(100.00), 440(47.69). 580(M^+, 5.36); Elem. anal. Calcd for $C_{31}H_{27}O_3F_7$: C, 64.16%; H, 4.65%; F, 22.92%; Found: C, 63.99%; H, 4.643%; F, 22.76%.

[(4-(4-n-Pentyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 3,4-difluoro benzoate (B5)

m.p. 58.0°C; ^1H NMR (300 MHz, $CDCl_3$/TMS): 0.91–0.96(t, 3H), 1.35–1.84(m, 6H), 4.28(t, 2H, J=6.5Hz), 7.23–7.26(m, 3H), 7.64–7.67(m, 2H), 7.84–7.88(m, 2H) ppm; ^{19}F NMR (60MHz, $CDCl_3$/TFA): 51.60(m, 1F), 59.00(m, IF), 61.40(m, 2F), 80.80(m, 2F) ppm; IR (KBr): 2922, 2852, 2226, 1736, 1611, 1516, 1443, 1299, 1206, 1112, 1070 cm^{-1}; MS(m/z): 141(100.00), 422(21.28), 492(M^+, 12.70); Elem. anal. Calcd for $C_{26}H_{18}O_3F_6$: C, 63.44%: H, 3.66%; F, 23.16%; Found: C, 63.49%; H, 3.68%; F, 23.07%.

The other compounds in series B had the same type of NMR spectrum.

[(4-(4-n-Hexyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 3,4-difluoro benzoate (B6)

m.p. 61.1°C; IR (KBr): 2922, 2856, 2227, 1736, 1611, 1515, 1443, 1299, 1205, 1112, 1070 cm^{-1}; MS(m/z): 141(100.00), 422(27.63), 506(M^+, 11.66): Elem. anal. Calcd for $C_{27}H_{20}O_3F_6$: C, 64.05%; H, 3.95%; F, 22.52%; Found: C, 64.04%; H, 3.88%; F, 22.21%.

[(4-(4-n-Heptyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 3,4-difluoro benzoate (B7)

m.p. 68.4°C; IR (KBr): 2900, 2825, 2222, 1737, 1617, 1515, 1443, 1299, 1207, 1111, 1069 cm^{-1}; MS(m/z): 141(100.00), 422(29.92), 520(M^+, 15.08); Elem. anal. Calcd for $C_{28}H_{22}O_3F_6$: C, 64.64%; H, 4.23%; F, 21.91%; Found: C, 64.40%; H, 4.19%: F, 22.25%.

[(4-(4-n-Octyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 3,4-difluoro benzoate (B8)

m.p 64.7°C; IR (KBr): 2922, 2855, 2227, 1736, 1611, 1515, 1442, 1299, 1205, 1112, 1070 cm^{-1}; MS(m/z): 141(100.00), 422(21.41), 534(M^+, 10.34); Elem. anal. Calcd for $C_{29}H_{24}O_3F_6$: C, 65.19%; H, 4.49%; F, 21.34%; Found: C, 64.92%; H, 4.49%; F, 21.66%.

[(4-(4-n-Nonyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 3,4-difluoro benzoate (B9)

m.p. 61.6°C; IR (KBr): 2922, 2852, 2225, 1736, 1611, 1516, 1443, 1299, 1206, 1112, 1070 cm^{-1}; MS(m/z): 141(100.00), 422(17.15), 548(M^+, 4.02); Elem. anal. Calcd for $C_{30}H_{26}O_3F_6F$, 20.79%; Found: F, 20.44%.

[(4-(4-n-Decyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 3,4-difluoro benzoate (B10)

m.p. 63.0°C; IR (KBr): 2922, 2854, 2225, 1736, 1618, 1516, 1443, 1299, 1206, 1112, 1070 cm^{-1}; MS(m/z): 141(52.56), 422(100.00), 562(M^+, 26.50): Elem. anal. Calcd for $C_{31}H_{28}O_3F_6$: C, 66.21%; H, 4.98%; F, 20.27%; Found: C, 65.94%; H, 5.03%; F, 19.99%.

[(4-(4-n-Pentyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 4-fluoro benzoate (C5)

m.p. 91.9°C; ^1H NMR (300 MHz, $CDCl_3$/TMS): 0.92–0.96(t. 3H), 1.37–1.82(m, 6H), 4.27(t, 2H, J=6.5Hz), 7.18–7.27(m, 4H), 7.63–7.66(m, 2H), 8.21–8.25(m, 2H) ppm; ^{19}F NMR (60MHz, $CDCl_3$/TFA): 27.00(m, IF), 61.50(m, 2F), 81.00(m, 2F) ppm; IR (KBr): 2962, 2923, 2853, 1739, 1599, 1517, 1442. 1266, 1199, 1157, 1068 cm^{-1}; MS(m/z): 123(100.00), 404(4.25), 474(M^+, 8.33); HRMS: Calcd for $C_{26}H_{19}O_3F_5$: 474.4380; Found: 474.1248.

The other compounds in series C had the same type of NMR spectrum.

[(4-(4-n-Hexyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 4-fluoro benzoate (C6)

m.p. 84.2°C; IR (KBr): 2962, 2923, 2853, 1739, 1599, 1517, 1442, 1266, 1199, 1157, 1068 cm^{-1}; MS(m/z): 123(100.00), 404(5.00), 488(M^+, 7.27); Elem. anal. Calcd for $C_{27}H_{21}O_3F_5$: C, 66.41%; H, 4.30%; F, 19.45%; Found: C, 66.59%; H, 4.50%; F, 19.63%.

[(4-(4-n-Heptyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 4-fluoro benzoate (C7)

m.p. 81.7°C; IR (KBr): 2962, 2923, 2853, 1739, 1599, 1517, 1442, 1266, 1199, 1157, 1068 cm^{-1}; MS(m/z): 123(100.00), 404(5.64), 502(M^+, 5.87); HRMS: Calcd for $C_{28}H_{23}O_3F_5$: 502.4840; Found: 502.1575.

[(4-(4-n-Octyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 4-trifluoro benzoate (C8)

m.p 74.8°C; IR (KBr): 2962, 2923, 2853, 1739, 1599, 1517, 1442, 1266, 1199, 1157, 1068 cm^{-1}; MS(m/z): 123(100.00), 404(2.26), 516(M^+, 7.92); Elem. anal.

Calcd for $C_{29}H_{25}O_3F_5$: C, 67.46%; H, 4.84%; F, 18.40%; Found: C, 67.73%; H, 4.85%; F, 18.65%.

[(4-(4-n-Nonyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 4-fluoro benzoate (C9)

m.p. 78.7°C; IR (KBr): 2962, 2923, 2853, 1739, 1599, 1517, 1442, 1266, 1199, 1157, 1068 cm^{-1}; MS(m/z): 123(100.00), 404(7.79), 474(M^+, 6.12); Elem. anal. Calcd for $C_{30}H_{27}O_3F_5$: C, 67.94%; H, 5.09%; F, 17.91%; Found: C, 67.88%; H, 4.95%; F, 17.53%

[(4-(4-n-Decyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 4-fluoro benzoate (C10)

m.p. 78.2°C; IR (KBr): 2962, 2923. 2853. 1739. 1599, 1517, 1442, 1266, 1199, 1157, 1068 cm^{-1}; MS(m/z): 123(100.00), 404(3.36), 544(M^+, 10.74); Elem. anal. Calcd for $C_{31}H_{29}O_3F_5$: C, 68.40%; H, 5.33%; F, 17.45%; Found: C, 68.06%; H, 5.24%; F, 17.66%.

[(4-(4-n-Heptyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 3-fluoro benzoate (D7)

m.p. 58.8°C; ^1H NMR (300 MHz, $CDCl_3$/TMS): 0.88–0.92(t, 3H), 1.25–1.87(m, 10H), 4.28(t. 2H, J=6.5Hz), 7.24–7.37(m, 3H), 7.48–7.55(m, 1H), 7.63–7.67(m, 2H), 7.87–7.91(m, 1H), 8.00–8.02(m, 1H) ppm; ^{19}F NMR (60MHz, $CDCl_3$/TFA): 34.80(m, 1F), 60.90(m, 2F), 80.50(m, 2F) ppm; IR (KBr): 2950, 2924, 2855, 1736, 1595, 1517, 1440, 1290, 1136, 1076 cm^{-1}; MS(m/z) 123(100.00), 404(14.86), 502(M^+, 6.85); Elem. anal. Calcd for $C_{28}H_{23}O_3F_5$: C, 66.95%: H, 4.58%; F, 18.91%; Found: C, 67.07%; H, 4.53%; F, 19.18%.

[(4-(4-n-Heptyloxy-2,3,5,6-tetrafluorophenyl)ethynyl)phenyl] 3,5-difluoro benzoate (E7)

m.p 71.4°C; ^1H NMR (300 MHz, $CDCl_3$/TMS): 0.87–0.92(t, 3H), 1.31–1.81(m, 10H), 4.27(t, 2H, J=6.5Hz), 7.09–7.15(m, 3H), 7.23–7.26(m, 2H), 7.63–7.75(m, 2H) ppm; ^{19}F NMR (60MHz, $CDCl_3$/TFA): 30.30(m, 2F), 60.80(m, 2F), 80.40(m, 2F) ppm; IR (KBr): 2959, 2928, 2858, 2219, 1745, 1602, 1516, 1443, 1235, 1124, 1211, 1085 cm^{-1}; MS(m/z): 141(100.00), 422(21.38), 520(M^+. 3.53); HRMS Calcd for $C_{28}H_{22}O_3F_6$: 520.4744; Found: 520.1488.

Acknowledgements

The authors acknowledge grarefully the National Natural Science Foundation of China for partially financial support.

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