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# Synthesis and Mesomorphic Properties of [4-((4-*n*-Alkoxy-2,3,5,6-Tetrafluorophenyl)Ethynyl)Phenyl] Fluoro-Substituted Benzoates

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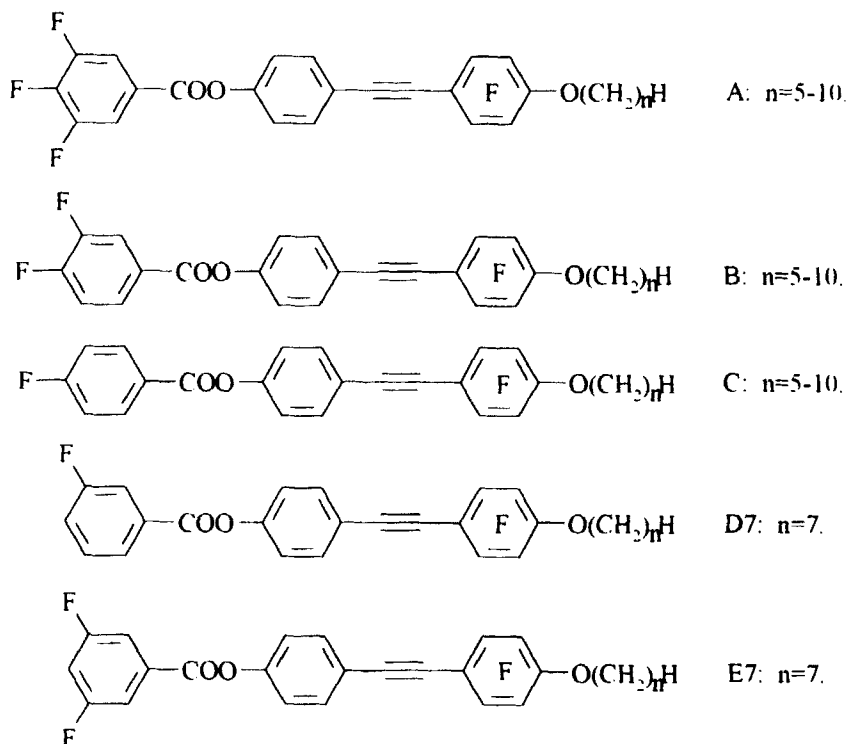
Five series of liquid crystals incorporating a 2,3,5,6-tetrafluorophenylene moiety and a terminal fluorosubstituted phenyl group have been prepared. The mesomorphic properties have been studied by polarizing microscopic textural observation and DSC measurements. The effect of terminal fluorosubstituent 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 research has been carried out on liquid crystals containing fluorine atoms in the backbone structure<sup>1-2</sup>, which are regarded as very useful in influencing the melting point, viscosity, birefringence and dielectric anisotropy. Therefore, a lot of liquid crystalline materials with monofluoro-, difluoro- or trifluoro-substituted aromatic rings have been extensively studied<sup>3-10</sup>. Nevertheless, only a limited number of liquid crystal materials with 1,4-disubstituted tetrafluorobenzene structures have been reported<sup>11-22</sup>. In our previous studies, we have synthesized liquid crystals with 2,3,5,6-tetrafluoro-1,4-phenylene in the core<sup>23-29</sup>. In this paper, we wish to report the synthesis and phase transitions of some novel fluorinated liquid crys-

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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 series **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 <sub>A</sub>	109.0	N	132.6	I	131.1	N	107.4	S <sub>A</sub>	57.8	Recr
A6	6	Cr 75.2	S <sub>A</sub>	1104	N	129.6	I	129.2	N	109.6	S <sub>A</sub>	56.7	Recr
A7	7	Cr 69.1	S <sub>A</sub>	109.2	N	121.1	I	119.5	N	107.7	S <sub>A</sub>	53.4	Recr
A8	8	Cr 62.7	S <sub>A</sub>	113.2	N	121.5	I	120.5	N	111.7	S <sub>A</sub>	44.5	Recr
A9	9	Cr 73.0	S <sub>A</sub>	114.5	N	117.8	I	115.9	N	112.3	S <sub>A</sub>	48.6	Recr
A10	10	Cr 68.5	S <sub>A</sub>	114.8	N	116.5	I	115.3	N	113.5	S <sub>A</sub>	45.2	Recr
B5	5	Cr 58.0	S <sub>A</sub>	75.4	N	152.0	I	149.6	N	72.5	S <sub>A</sub>	47.7	Recr
B6	6	Cr 61.1	S <sub>A</sub>	76.7	N	147.7	I	146.3	N	75.5	S <sub>A</sub>	51.0	Recr
B7	7	Cr 68.4	S <sub>A</sub>	84.9	N	138.3	I	136.9	N	84.2	S <sub>A</sub>	52.3	Recr
B8	8	Cr 64.7	S <sub>A</sub>	89.2	N	137.5	I	135.9	N	88.0	S <sub>A</sub>	48.4	Recr
B9	9	Cr 61.6	S <sub>A</sub>	93.1	N	126.7	I	124.7	N	90.9	S <sub>A</sub>	42.8	Recr
B10	10	Cr 63.0	S <sub>A</sub>	95.2	N	23.5	I	122.3	N	93.3	S <sub>A</sub>	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<sub>A</sub> = 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 length/breadth ratio, the wider the range. The *para*-substituted fluorine atom extends the length of the molecule, the length/breadth ratio and the molecular shape anisotropy.

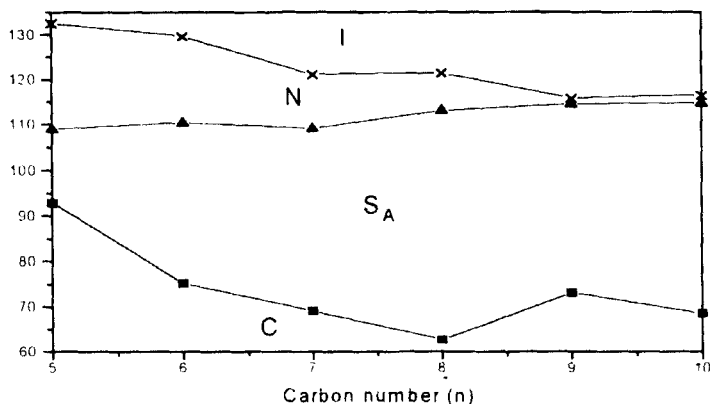
Temperatures/ $^{\circ}\text{C}$ 

FIGURE 1 Series A C = crystal; S<sub>A</sub> = 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 increase of *m*-fluorosubstitution in the terminal phenyl, the tendency to form the SmA phase is strengthened and the ability to form the nematic phase is weakened. This may be the reason that the *meta*-fluorine atom occupies 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 decrease the former much more than the latter. Then the smectic phase is favorable with increasing the degree of fluoro-substitution at the outer edge position.

For series **B** and series **C**, the former is more favorable to form the smectic phase than the latter. It can be explained as usual<sup>30</sup>. That the radius of the fluorine atom is very small, and it will be shielded by the phenol. Then the lateral dipolarity of the molecule is noticeable. But it cannot explain the difference between series **B** and series **C** as this.

Professor J.W. Goodby explained this phenomenon as this<sup>31</sup>. It is well-known that increasing the amount of fluorination, particularly in the terminal chains, favors the formation of the smectic A phase<sup>32</sup>. (Although in semiperfluorinated systems, it seems that the SmA phase and the SmC phase are both enhanced<sup>33–36</sup>.) 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<sup>37,38</sup>. This means that the fluorocarbon bits stick together, the aromatic bits also stick together etc<sup>39,40</sup>. The strong fluorine-fluorine interactions tend then to limit the phases to smectic A –

## Temperatures

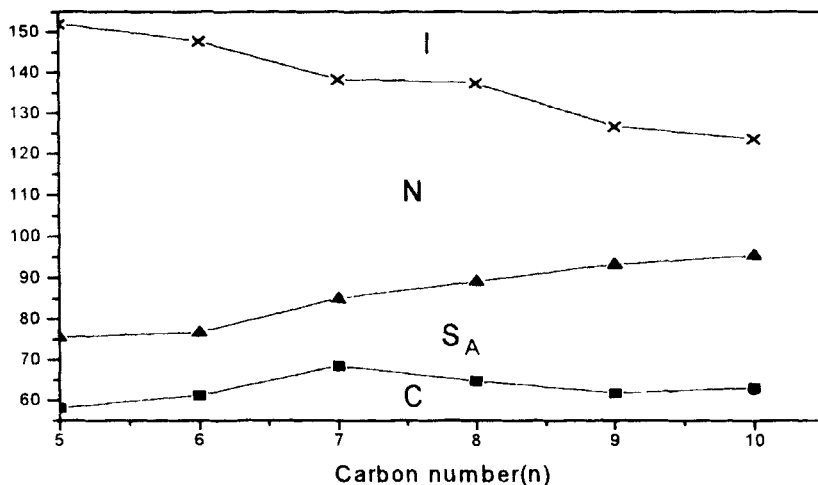
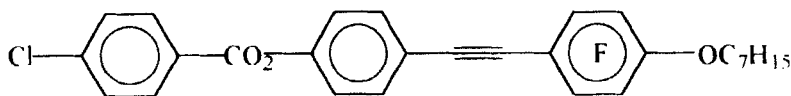


FIGURE 2 Series B C = Crystal; S<sub>A</sub> = Smectic A phase; N = Nematic phase; I = Isotropic phase

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

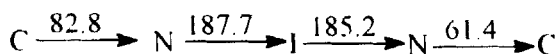
For fluoro-substitution in aromatics in this paper have the added problem of polarisability and conjugation. For a limited number of fluoro-substituents conjugation reduces the intermolecular interactions so that microphase separation does not occur and nematic phases can form. Increase the number of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

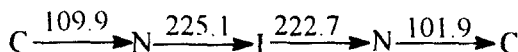
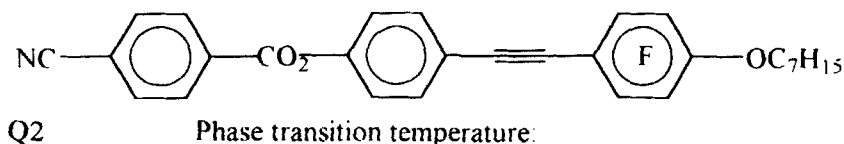
As for the compounds studied above, we get to know that both *p*-fluorosubstitution and *m*-fluorosubstitution are the abundant condition of forming S<sub>A</sub> phase. However, *p*-fluorosubstitution or *m*-fluorosubstitution alone can not ensure the formation of S<sub>A</sub> phase. In our previous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



Q1

Phase transition temperature:





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.

### Temperatures

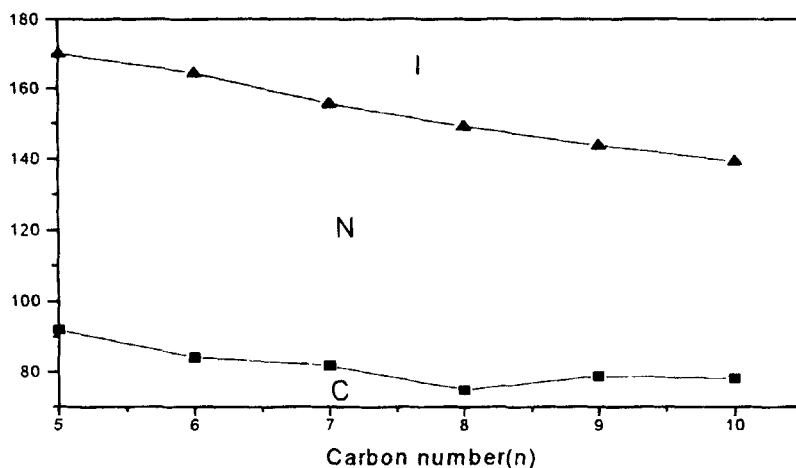


FIGURE 3 Series C C = Crystal; N = Nematic phase; I = Isotropic phase

### Experimental

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



spectrometer using a KBr disc pellet.  $^1\text{H}$  NMR spectra, with TMS as the internal standard and  $\text{CDCl}_3$  as the solvent, were run in FX-90Q (90 MHz) or Bruker 300 (300 MHz) spectrometer.  $^{19}\text{F}$  NMR spectra, with trifluoroacetic acid (TFA) as external standard and  $\text{CDCl}_3$  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 transition 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.

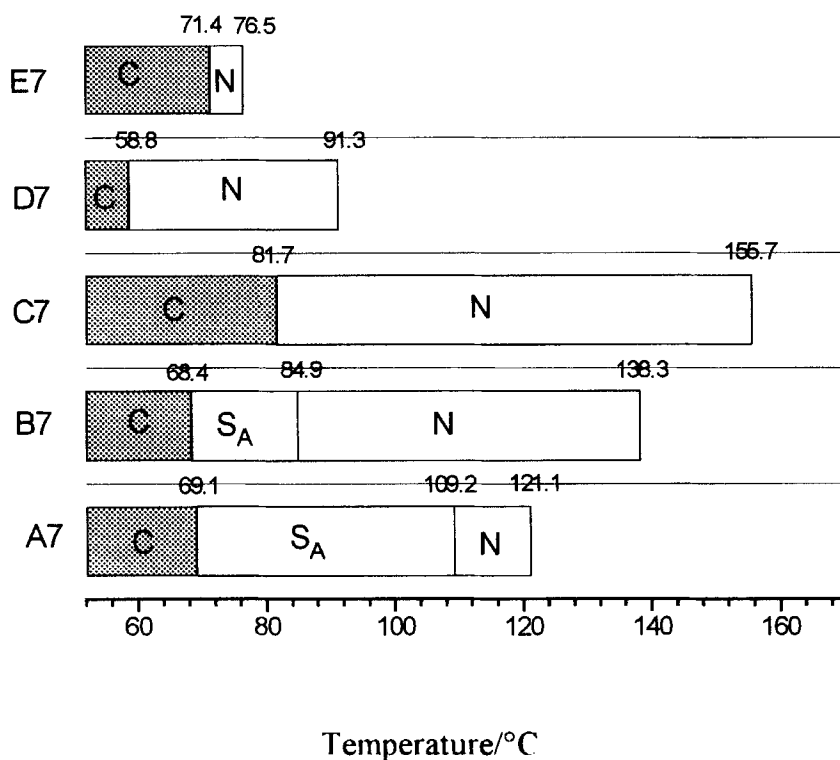
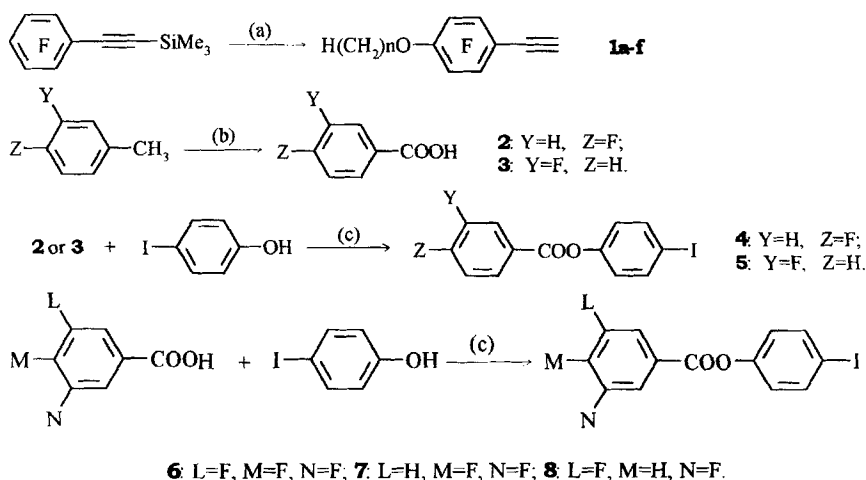


FIGURE 4 C = Crystal; S<sub>A</sub> = Smectic A phase; N = Nematic phase

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<sup>41</sup>. And the oxidation of 1-fluoro-4-methylbenzene and 1-fluoro-3-methylbenzene by the  $\text{K}_2\text{Cr}_2\text{O}_7$  in concentrated  $\text{H}_2\text{SO}_4$ /water solu-

tion afforded 4-fluorobenzoic acid **2** and 3-fluorobenzoic acid **3**<sup>42</sup>. Then the mild one pot esterification between 4-iodophenol 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 synthesized 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.



SCHEME 1 (a) DMF,  $\text{K}_2\text{CO}_3$ , ROH; (b)  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ ; (c) DCC, DMAP, THF; (d)  $\text{Pd(PPh}_3)_2\text{Cl}_2/\text{CuI}$ ,  $\text{NEt}_3$

### [[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;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3/\text{TMS}$ ): 0.87–0.90(m, 3H), 1.31–1.83(m, 10H), 4.27(t, 2H,  $J=6.6\text{Hz}$ ), 7.23–7.26(m, 2H), 7.64–7.67(m, 2H), 7.84–7.88(m, 2H) ppm;  $^{19}\text{F}$  NMR (60MHz,  $\text{CDCl}_3/\text{TFA}$ ): 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  $\text{cm}^{-1}$ ; MS(m/z): 159(100.00), 440(44.15), 538( $\text{M}^+$ , 12.27); Elem. anal. Calcd for  $\text{C}_{28}\text{H}_{21}\text{O}_3\text{F}_7$ : 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  $\text{cm}^{-1}$ ; MS(m/z): 159(100.00), 440(44.15), 510( $\text{M}^+$ , 6.37); Elem. anal. Calcd for  $\text{C}_{26}\text{H}_{17}\text{O}_3\text{F}_7$ : 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  $\text{cm}^{-1}$ ; MS(m/z): 159(100.00), 440(52.73), 524( $\text{M}^+$ , 17.35); Elem. anal. Calcd for  $\text{C}_{27}\text{H}_{19}\text{O}_3\text{F}_7$ : 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  $\text{cm}^{-1}$ ; MS(m/z): 159(100.00), 440(21.76), 552( $\text{M}^+$ , 2.70); Elem. anal. Calcd for  $\text{C}_{29}\text{H}_{23}\text{O}_3\text{F}_7$ : 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  $\text{cm}^{-1}$ ; MS(m/z): 159(100.00), 440(43.67), 566( $\text{M}^+$ , 7.38); Elem. anal. Calcd for  $\text{C}_{30}\text{H}_{25}\text{O}_3\text{F}_7$ : 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  $\text{cm}^{-1}$ ; MS(*m/z*): 159(100.00), 440(47.69). 580( $\text{M}^+$ , 5.36); Elem. anal. Calcd for  $\text{C}_{31}\text{H}_{27}\text{O}_3\text{F}_7$ : 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;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3/\text{TMS}$ ): 0.91–0.96(t, 3H), 1.35–1.84(m, 6H), 4.28(t, 2H,  $J=6.5\text{Hz}$ ), 7.23–7.26(m, 3H), 7.64–7.67(m, 2H), 7.84–7.88(m, 2H) ppm;  $^{19}\text{F}$  NMR (60MHz,  $\text{CDCl}_3/\text{TFA}$ ): 51.60(m, 1F), 59.00(m, 1F), 61.40(m, 2F), 80.80(m, 2F) ppm; IR (KBr): 2922, 2852, 2226, 1736, 1611, 1516, 1443, 1299, 1206, 1112, 1070  $\text{cm}^{-1}$ ; MS(*m/z*): 141(100.00), 422(21.28), 492( $\text{M}^+$ , 12.70); Elem. anal. Calcd for  $\text{C}_{26}\text{H}_{18}\text{O}_3\text{F}_6$ : 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  $\text{cm}^{-1}$ ; MS(*m/z*): 141(100.00), 422(27.63), 506( $\text{M}^+$ , 11.66); Elem. anal. Calcd for  $\text{C}_{27}\text{H}_{20}\text{O}_3\text{F}_6$ : 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  $\text{cm}^{-1}$ ; MS(*m/z*): 141(100.00), 422(29.92), 520( $\text{M}^+$ , 15.08); Elem. anal. Calcd for  $\text{C}_{28}\text{H}_{22}\text{O}_3\text{F}_6$ : 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  $\text{cm}^{-1}$ ; MS(*m/z*): 141(100.00), 422(21.41), 534( $\text{M}^+$ , 10.34); Elem. anal. Calcd for  $\text{C}_{29}\text{H}_{24}\text{O}_3\text{F}_6$ : 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  $\text{cm}^{-1}$ ; MS(m/z): 141(100.00), 422(17.15), 548( $\text{M}^+$ , 4.02); Elem. anal. Calcd for  $\text{C}_{30}\text{H}_{26}\text{O}_3\text{F}_6$ , 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  $\text{cm}^{-1}$ ; MS(m/z): 141(52.56), 422(100.00), 562( $\text{M}^+$ , 26.50); Elem. anal. Calcd for  $\text{C}_{31}\text{H}_{28}\text{O}_3\text{F}_6$ : 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;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3/\text{TMS}$ ): 0.92–0.96(t, 3H), 1.37–1.82(m, 6H), 4.27(t, 2H,  $J=6.5\text{Hz}$ ), 7.18–7.27(m, 4H), 7.63–7.66(m, 2H), 8.21–8.25(m, 2H) ppm;  $^{19}\text{F}$  NMR (60MHz,  $\text{CDCl}_3/\text{TFA}$ ): 27.00(m, 1F), 61.50(m, 2F), 81.00(m, 2F) ppm; IR (KBr): 2962, 2923, 2853, 1739, 1599, 1517, 1442, 1266, 1199, 1157, 1068  $\text{cm}^{-1}$ ; MS(m/z): 123(100.00), 404(4.25), 474( $\text{M}^+$ , 8.33); HRMS: Calcd for  $\text{C}_{26}\text{H}_{19}\text{O}_3\text{F}_5$ : 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  $\text{cm}^{-1}$ ; MS(m/z): 123(100.00), 404(5.00), 488( $\text{M}^+$ , 7.27); Elem. anal. Calcd for  $\text{C}_{27}\text{H}_{21}\text{O}_3\text{F}_5$ : 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  $\text{cm}^{-1}$ ; MS(m/z): 123(100.00), 404(5.64), 502( $\text{M}^+$ , 5.87); HRMS: Calcd for  $\text{C}_{28}\text{H}_{23}\text{O}_3\text{F}_5$ : 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  $\text{cm}^{-1}$ ; MS(m/z): 123(100.00), 404(2.26), 516( $\text{M}^+$ , 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.

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