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Synthesis and mesomorphic properties of fluorinated liquid crystals obtained from optically active 2-fluoro-octanol

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Several homologues of semi-fluorinated liquid crystals, 4'-(*n*-perfluoroalkyl)alkyloxy]phenyl 4-(2-fluoro-octyloxy)benzoates and 4'-(2-fluoro-octyloxy)phenyl 4-(*n*-perfluoroalkyl)alkyloxy]benzoates have been synthesized. One set of the compounds, with the central carbonyl group conjugated to the terminal position carrying the non-chiral perfluoroalkyloxy tail, showed enhanced chiral smectic C behaviour, while the other set, with the central carbonyl group conjugated to the terminal position carrying the chiral 2-fluoro-octyloxy tail, exhibited enhanced smectic A behaviour. The mesomorphic properties of these novel fluorinated materials are reported and the effects of extent of fluorination are discussed.

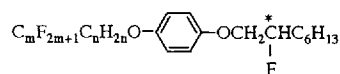
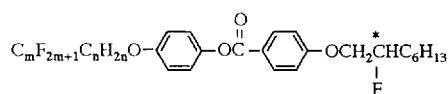
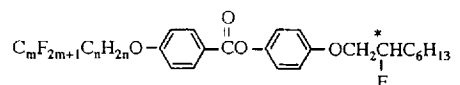
1. Introduction

Ferroelectric liquid crystal displays offer the possibility of a new type of flat-panel technology, which is based on a simple matrix structure but achieves a large screen area, high resolution, and excellent image quality [1-3]. However, the material requirements for ferroelectric liquid crystal displays are so exacting that the physical properties of the materials used need to be carefully optimized. For ferroelectric liquid crystals, a broad range chiral smectic C mesophase and a high spontaneous polarization are desirable. Therefore, enhancement of the smectic mesophase and improvement of spontaneous polarization are two important elements for molecular design.

It has been reported that ferroelectric liquid crystals obtained from (-)-2-fluoro-octanol present a large spontaneous polarization [4-6]. And earlier work by several groups on liquid crystals with a perfluoroalkyl or perfluoroalkyloxy tail have indicated that smectic mesophases were usually enhanced [7-12]. This led to the synthesis of a number of fluorinated liquid crystals from (-)-2-fluoro-octanol [13]. Recently, Tweig *et al.* have reported the effects on mesomorphic and ferroelectric properties of the extent of achiral tail fluorination for a series of thioesters [14]. In this paper, we will report the synthesis of the fluorinated liquid crystals shown in scheme 1 and the evaluation of their mesomorphic properties in order to investigate the effects of the extent of fluorination.

2. Synthesis

The fluorinated benzoic acids were synthesized as outlined in scheme 2. Ethyl 4-hydroxybenzoate was deprotected using sodium hydride in DMF. To the resulting



$m=3, 4$; $n=3, 4$

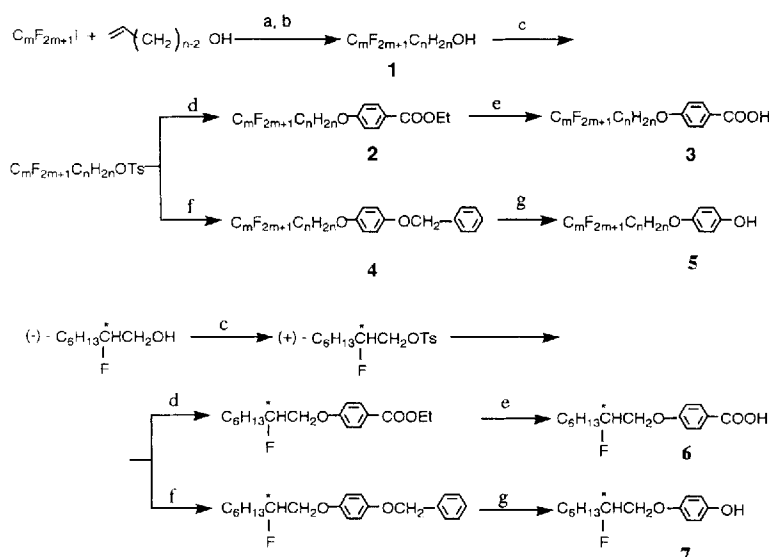
Scheme 1.

solution of the anion, an appropriate *n*-perfluoroalkylalkyl *p*-toluenesulphonate, prepared using known procedures [15, 16], was added. The intermediate ethyl 4-(*n*-perfluoroalkylalkyloxy)benzoate was hydrolysed using aqueous base and the benzoic acid obtained after acidification.

The fluorinated phenols were synthesized by a similar procedure as outlined in scheme 2. To a suspension of sodium hydride in DMF was added 4-benzyloxyphenol. After the evolution of hydrogen ceased, the appropriate *n*-perfluoroalkylalkyl *p*-toluenesulphonate was added and the mixture stirred at 120°C for 6 h. The intermediate 1-benzyloxy 4-(*n*-perfluoroalkylalkyloxy) benzene was deprotected by hydrogenation to afford the desired phenol.

New semi-fluorinated liquid crystals **8** and **9** were readily synthesized from the corresponding fluorinated

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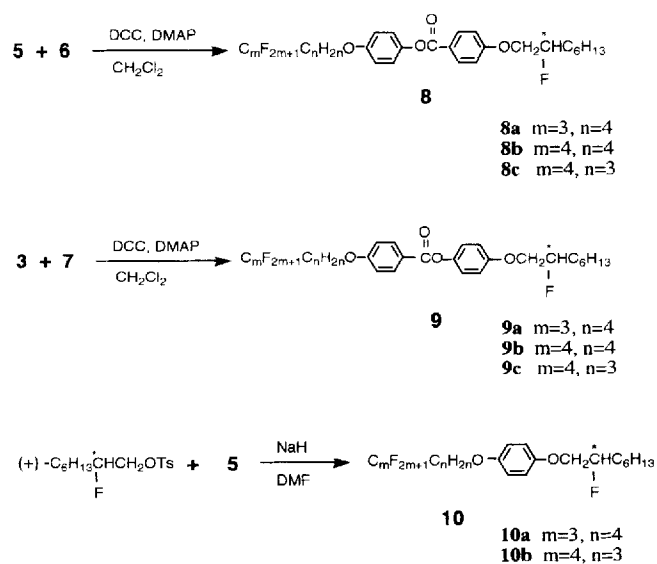
Scheme 2. (a) AIBN; (b) LiAlH_4 , dry ether; (c) TsCl , DABCO, CH_2Cl_2 ; (d) NaH , ethyl 4-hydroxybenzoate, DMF; (e) KOH , ethanol; (f) NaH , 4-benzyloxyphenol, DMF; (g) Pd/C , H_2 .

benzoic acids and phenols by esterification using dicyclohexylcarbodiimide (DCC) (scheme 3) [17]. Compounds **10** were obtained from (+)-2-fluorooctyl *p*-toluenesulphonate and the appropriate phenols by Williamson etherification.

3. Results and discussion

3.1. Phase diagram

It is interesting to note that, as shown in table 1, of the entire series of compounds **8**, only compound **8c** showed



Scheme 3. The synthetic routes to fluorinated phenyl benzoates and 1-(2-fluoro-octyl)-4-(*n*-perfluoroalkylalkoxy) benzenes.

a narrow, monotropic, chiral smectic C mesophase. The others showed only the smectic A phase. Compared to the non-fluorinated analogues [4], the smectic A mesophase was strongly enhanced.

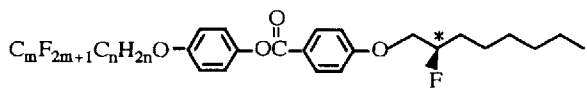
On the other hand, the compounds **9**, whose central ester linkage is conjugated with the terminal position carrying the non-chiral perfluoroalkoxy tail, the opposite situation to that for the compounds **8**, showed enantiotropic smectic A and chiral smectic C phases as presented in table 2. The cholesteric mesophase present in the non-fluorinated analogues [18] has been totally suppressed, and the smectic A and chiral smectic C phases have been enhanced. Compound **9c**, whose fluorination extent was the largest, showed the widest range chiral smectic C phase, while compound **9a**, which has the smallest fluorination extent, had the narrowest range chiral smectic C mesophase.

The compounds **10** do not show any mesophase. However, the lack of mesomorphism does not inhibit their usefulness as ferroelectric liquid crystal dopants. When mixed with the host liquid crystal whose constituents are shown in scheme 4, they do not greatly alter the phase diagrams of the mixtures, as can be seen from table 3.

Thus, phenyl benzoates with a fluorinated alkyloxy tail have strongly enhanced smectic properties and suppressed cholesteric behaviour. The direction of the central ester linkage influences greatly the phase diagram and the enhancement of the different smectic phases.

3.2. Mesomorphic properties

For ferroelectric liquid crystal devices, the spontaneous polarization P_s , response time and optical tilt angle of the materials are very important parameters.

Table 1. Transition temperatures (°C) of 4'-[*n*-perfluoroalkyl]alkyloxy]phenyl 4-(2-fluoro-octyloxy)benzoates (Compounds **8**).


Compound	<i>m</i>	<i>n</i>	Cr	<i>S_x</i>	<i>S_C</i> *	<i>S_A</i>	I
8a	3	4	●	83.5	—	●	113.3 ●
8b	4	4	●	79.8	—	●	128.8 ●
8c	4	3	●	79.4	● (69.5	● 75)	● 129.2 ●

The spontaneous polarization of the compounds **9** was measured as a function of temperature on cooling from the Curie point. The results are shown in figure 1. The magnitude of the spontaneous polarization of compound **9a** was found to be slightly larger than that of compound **9b** and **9c**, while the magnitude of the spontaneous polarization of **9b** was almost the same as that of **9c**. However, as shown in figure 2, the spontaneous polarizations of the ferroelectric liquid crystal mixtures obtained from the compounds **10** were greatly influenced by fluorination extent. The spontaneous polarization of the ferroelectric liquid crystal mixture obtained using 5 wt % of **10a** was even slightly larger than that of the ferroelectric liquid crystal mixture obtained with 10 wt % of **10b**. The large spontaneous polarization inducing power of **10a** may be due to the better miscibility with the host liquid crystal. And when 10 wt % of **10a** was mixed into the host liquid crystal, the spontaneous polarization of the mixture was almost twice that of a mixture containing 5 wt % of **10a**.

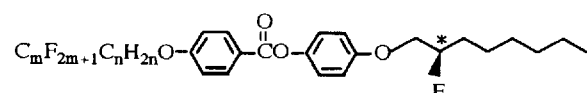
The characteristics of the electronically switched optical tilt angle for the compounds **9** are given in figure 3. The value of the optical tilt angle becomes greater with increasing extent of fluorination. The value of the tilt angle of compound **9c** at 42°C below the Curie point was found to be as large as 40°. The optical tilt angles of the compounds **9** are generally over 30° at 20°C below the Curie point; this is a surprisingly large value for a chiral

smectic C mesophase cooled from a smectic A phase. Detailed investigations are currently underway and the results will be reported later.

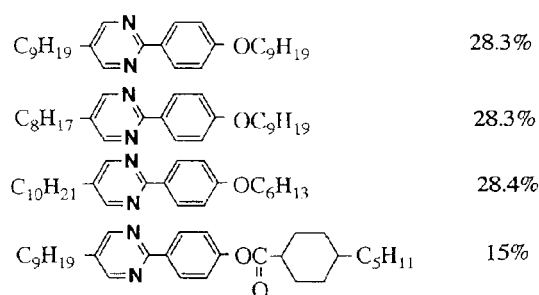
What is worthy of notice is the response time τ_{10-90} , which is defined as the time needed for the light transmission to change from 10% to 90%, of the ferroelectric liquid crystal mixtures. The results are presented in figure 4. Although only 10 wt % of **10a** was added to the host liquid crystal, the response time was as fast as 60 μ s; and what is more, this was invariant over the range of chiral smectic C mesophase. A similar result was also reported by Sakaigawa *et al.* [13]. It was considered that the fast response was due to the low viscosity of the ferroelectric liquid crystal mixture.

4. Conclusion

A series of fluorinated phenyl benzoates, 4'-[(*n*-perfluoroalkyl)alkyloxy]phenyl 4-(2-fluoro-octyloxy)benzoates and 4'-(2-fluoro-octyloxy)phenyl 4-[(*n*-perfluoroalkyl)alkyloxy]benzoates, have been prepared. Investigation of their mesomorphic properties showed that the extent of fluorination of the alkyloxy tail influenced the stability of the smectic mesophase, but had little effect on the spontaneous polarization. 1-(2-fluoro-octyl) 4-(*n*-perfluoroalkyl)alkyloxy]benzenes were found suitable as ferroelectric liquid crystal dopants although they showed no mesophase.

Table 2. Transition temperatures (°C) of 4'-(2-fluoro-octyloxy)phenyl 4-[(*n*-perfluoroalkyl)alkyloxy]benzoates (Compounds **9**).


Compound	<i>m</i>	<i>n</i>	Cr	<i>S_x</i>	<i>S_C</i> *	<i>S_A</i>	I
9a	3	4	●	85.7	—	● 93	● 106.3 ●
9b	4	4	●	93.8	—	● 107	● 119.4 ●
9c	4	3	●	62.6	● 65.3	● 103	● 119.6 ●



Scheme 4. Constituents of the achiral host liquid crystal.

5. Experimental

The structures of the intermediates and products were confirmed by ^1H NMR and ^{13}C NMR (Bruker AX400), infrared (IR) spectroscopy (Perkin-Elmer 1640) and mass spectroscopy (JEOL DX303). The progress of reactions was monitored frequently using gas chromatography or thin layer chromatography. Transition temperatures were measured using a Mettler 32HT hot stage and central processor in conjunction with a NIKON OPTIPHOTOL-POL polarizing microscope and the results were confirmed by differential scanning calorimetry (MAC Science DSC 3100). The purity of each final compound was checked by HPLC analysis. The P_s was measured using the triangular wave method under a field of $4\text{ V}_{\text{pp}}\mu\text{m}^{-1}$ and a $18\mu\text{m}$ cell. The response time τ_{10-90} was measured using a rectangular wave under a field of $10\text{ V}_{\text{pp}}\mu\text{m}^{-1}$ with a $1.4\mu\text{m}$ cell.

5.1. 4-Perfluoropropyl-1-butanol (**1**; $m=3$, $n=4$)

α' -Azobis(isobutyronitrile) (AIBN) (0.058 g, 0.35 mmol) was added to a mixture of perfluoropropyl iodide (8.88 g, 0.35 mmol) and but-3-en-1-ol (2.16 g, 30.0 mmol) at 0°C . The mixture was heated to 70°C for 4 h to give 3-iodo-4-perfluoropropyl-1-butanol. An ethereal solution of 4-perfluoropropyl-1-butanol was then added dropwise to a suspension of lithium aluminium hydride in ether at 0°C . After boiling for 6 h, the mixture was cooled and ice water and 6 M sulphuric acid were added fully. The product was extracted into ether ($\times 3$). The combined ethereal extracts were successively washed

with water and then dried over anhydrous sodium phosphate. The solvent was removed *in vacuo* and the crude product was purified by reduced pressure distillation (b.p. $76^\circ\text{C}/20\text{ mmHg}$). Yield: 73.3%; IR (cm^{-1} , neat): 3318, 2952, 2883, 1465, 1356, 1206, 1132, 1038, 879; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 1.74–1.64 (4H), 1.86 (s, 1H), 2.18–2.0 (m, 2H), 3.69 (t, $J=6.0$ 2H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 125–120 (m), 61.9, 31.8, 30.5 (t, $^2J_{\text{C-F}}=22.3$ Hz), 16.7.

5.2. Ethyl (4-perfluoropropylbutyloxy)benzoate (**2**; $m=3$, $n=4$)

A solution of the ethyl 4-hydroxybenzoate (0.955 mmol) in DMF was added to a suspension of sodium hydride (0.24 g, 6.0 mmol) in DMF at 0°C . After stirring at room temperature for one hour, 4-perfluoropropyl butyl *p*-toluenesulphonate (1.98 g, 5.0 mmol) was added. The mixture was then heated to 130°C for 6 h. When the mixture had cooled to room temperature, ice water was added and the product extracted into ether ($\times 3$). The combined ethereal extracts were dried over sodium sulphate. The crude product ethyl (4-perfluoropropyl butyloxy)benzoate was purified by column chromatography (silica gel/*n*-hexane–ethyl acetate, 3:1). Yield: 98.4%; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 1.38 (t, $J=7.2$, 3H), 1.80–1.92 (m, 4H), 2.11–2.20 (m, 2H), 4.11 (t, $J=5.8$, 2H), 4.35 (q, $J=7.2$, 2H), 6.90 (d, $J=8.0$, 2H), 8.0 (d, $J=8.0$, 2H).

5.3. 4-(4-Perfluoropropylbutyloxy)benzoic acid (**3**; $m=3$, $n=4$)

Aqueous potassium hydroxide was poured into an ethanolic solution of ethyl (4-perfluoropropyl butyloxy)benzoate (1.92 g, 4.92 mmol). After stirring at 70°C for 3 h, ethanol was removed and water and ether were added. The aqueous layer was acidified with 1 M hydrochloric acid. Then ether was added to extract the product. The organic layer was dried over sodium sulphate. Removal of the solvent gave 1.61 g (4.44 mmol) of the final product. Yield: 90.2%, IR (cm^{-1} , KBr): 1616, 1607, 1560, 1512, 1436, 1356, 1257, 1038, 850, 770, 710.

Table 3. Transition temperatures ($^\circ\text{C}$) of FLC mixtures doped with 1-(2-fluoro-octyl)-4-(*n*-perfluoroalkylalkyloxy)benzenes (Compounds **10**).

Compound	m	n	mp/ $^\circ\text{C}$	wt %	Cr	S_{C}^*	S_{A}	Ch	I				
10a	3	4	44.3	5	●	< r.t.	●	60	●	68	●	74.5	●
				10	●	< r.t.	●	56	●	65	●	71	●
10b	4	3	53.0	10	●	< r.t.	●	55	●	67	●	71	●

* Host liquid crystal is a mixture of a series of phenylpyrimidines whose constituents are shown in scheme 3. Phase diagrams

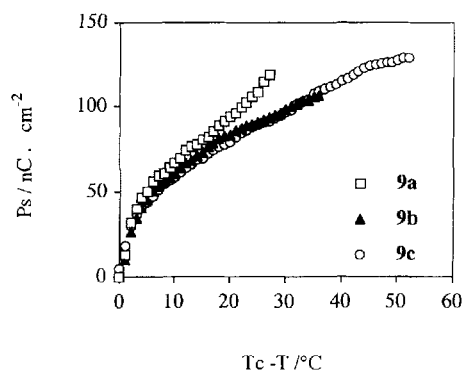


Figure 1. Temperature dependence of P_s of 4'-(2-fluoro-octyloxy)phenyl 4-[(*n*-perfluoroalkyl)alkyloxy]benzoates, **9**.

$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ (ppm): 0.89–0.96 (m, 2H), 1.05–1.11 (m, 2H), 1.46–1.60 (m, 2H), 3.32 (t, $J=6.0$, 2H), 6.24 (d, $J=8.7$, 2H), 7.12 (d, $J=8.7$, 2H), 11.83 (s, 1H). $^{13}\text{C NMR}$ (100 MHz, $\text{DMSO-}d_6$) δ (ppm): 167.01, 162.17, 131.35, 122.95, 114.23, 108.37–120.58 (m), 67.24, 29.22 (t, $^2J_{\text{C-F}}=22.1$), 27.66, 16.62.

5.4. 4'-(2-Fluorooctyloxy)phenyl

4-(4-perfluoropropylbutyloxy)benzoate (**9**; $m=3$, $n=4$)

To a solution of 4-(4-perfluoropropylbutyloxy)benzoic acid (0.44 g, 1.2 mmol), 4-(2-fluoro-octyloxy)phenol (0.29 g, 1.2 mmol) and 4-dimethylaminopyridine (DMAP) in 5.0 ml of dichloromethane was added a solution of *N,N'*-dicyclohexylcarbodiimide (DCC) (0.29, 1.4 mmol) in dichloromethane at 0°C. The mixture was then stirred at room temperature until reaction was complete (monitored by TLC). Filtration and removal of the solvent gave the crude product which was then purified by column chromatography (silica gel/*n*-hexane–ethyl acetate, 3:1) and recrystallization from *n*-hexane/

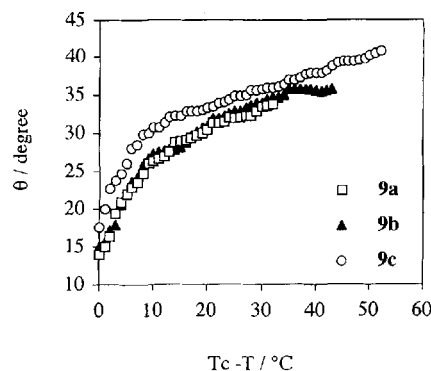


Figure 3. Temperature dependence of tilt angles of 4'-(2-fluoro-octyloxy)phenyl 4-[(*n*-perfluoroalkyl)alkyloxy]benzoates, **9**.

ethanol to give a white solid. Yield: 95.6%; IR(cm^{-1} , KBr): 2936, 2878, 1728, 1607, 1512, 1356, 1259, 1197, 1171, 1118, 907, 853, 766, 728; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm): 0.90 (t, $J=8.0$, 3H), 1.24–1.47 (overlapping peaks, 8H), 1.62–1.97 (overlapping peaks, 6H), 2.11–2.25 (m, 2H), 4.00–4.14 (m, 4H), 4.82 (dm, $^1J_{\text{H-F}}=49.0$, 1H), 6.93–6.97 (m, 2H), 7.11 (d, $J=9.0$, 2H), 8.13 (d, $J=8.8$, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm): 165.82, 163.44, 157.15, 145.3, 132.94, 123.23, 115.74, 115.05, 92.36 (d; $^1J_{\text{C-F}}=173.2$), 70.58 (d, $^2J_{\text{C-F}}=24.2$), 68.27, 32.25, 32.18 (t, $^2J_{\text{C-F}}=26.2$), 31.08 (t, $^2J_{\text{C-F}}=24.2$), 29.71, 29.36, 23.21, 17.92 (t, $^3J_{\text{C-F}}=8.05$), 14.69; MS $m/z=585$ (M^+), 345, 240.

5.5. 4'-(4-Perfluoropropylbutyloxy)phenyl 4-(2-fluoro-octyloxy)benzoate (**8**; $m=3$, $n=4$)

A similar preparative procedure to that for compound **9** was used to synthesize compound **8**. The product was obtained as a white solid. Yield: 91.2%; IR(cm^{-1} , KBr): 2928, 2859, 1724, 1608, 1508, 1356, 1263, 1172, 1120,

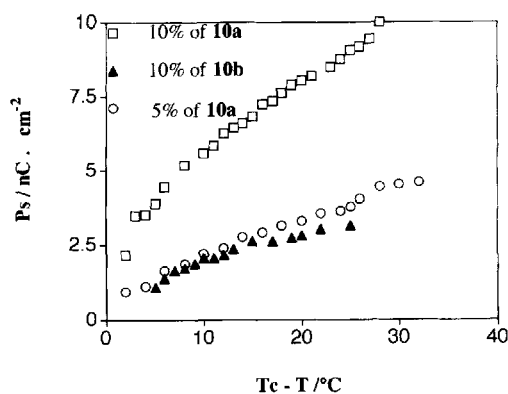


Figure 2. Temperature dependence of P_s of FLC mixtures obtained from 1-(2-fluoro-octyl)-4-(*n*-perfluoroalkyl)alkyloxybenzenes, **10**.

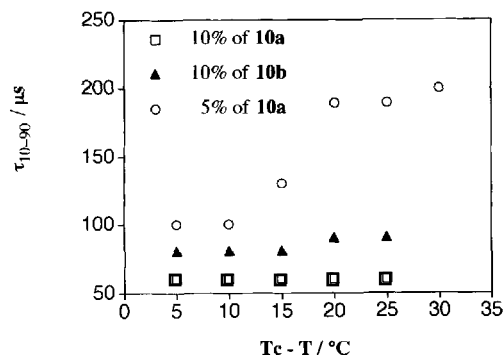


Figure 4. Characteristics of optical response time of FLC mixtures obtained from 1-(2-fluoro-octyl)-4-(*n*-perfluoroalkyl)alkyloxybenzenes, **10**, as dopants used in the different wt % values shown.

1038, 910, 849, 764, 728; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 0.90 (t, $J=6.8$, 3H), 1.21–1.48 (overlapping peaks, 8H), 1.64–1.93 (m, 6H), 2.11–2.24 (m, 2H), 4.00 (t, $J=5.6$, 2H), 4.08–4.22 (m, 2H), 4.86 (dm, $^1J_{\text{H-F}}=49.0$, 1H), 6.92 (d, $J=9.2$, 2H), 7.00 (d, $J=9.2$, 2H), 7.11 (d, $J=8.8$, 2H); 8.15 (d, $J=8.8$, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 165.84, 163.44, 157.16, 145.31, 132.96, 123.25, 115.76, 115.07, 92.38 (d; $^1J_{\text{C-F}}=173.2$), 70.60 (d, $^2J_{\text{C-F}}=23.2$), 65.64, 32.27, 32.20 (d, $^2J_{\text{C-F}}=23.2$), 31.27 (t, $^2J_{\text{C-F}}=24.2$), 29.72, 29.39, 25.50 (d, $^3J_{\text{C-F}}=5.0$), 23.22, 17.96 (t, $^3J_{\text{C-F}}=8.05$), 14.71; MS $m/z=584$ (M^+), 334, 251, 231.

5.6. 1-(2-Fluoro-octyl)-4-(3-perfluorobutylpropyloxy) benzene (**10**; $m=4$, $n=3$)

To a suspension of sodium hydride in DMF was added 4-(3-perfluorobutylpropyloxy)phenol. After reacting at room temperature for one hour, 2-fluoro-octyl *p*-toluenesulphonate was added and the mixture was stirred at 130°C for 4 h to give the crude compound **10**, which was then purified by column chromatography (*n*-hexane/ethyl acetate, 3:1) and recrystallization from *n*-hexane/ethanol to afford a white solid. Yield: 91.7%; IR (cm^{-1} , neat): 2932.0, 2857.7, 1508.0, 1475.4, 1452.4, 1356.6, 1131.9, 1028.1, 825.1, 770.0, 741.4, 719.9; ^1H NMR (400 MHz, CDCl_3) δ (ppm): 0.89 (t, $J=6.7$, 3H), 1.75–1.31 (overlapping peaks, 10H), 2.11–2.04 (m, 2H), 2.37–2.24 (m, 2H), 4.10–3.95 (m, 4H), 4.80 (dm, $^1J_{\text{H-F}}=49.1$, 1H), 6.87–6.81 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 153.13, 115.75, 115.51, 92.07 (d; $^1J_{\text{C-F}}=171.5$), 70.66 (d, $^2J_{\text{C-F}}=22.0$), 67.01, 31.65, 31.59 (d, $^2J_{\text{C-F}}=20.4$), 29.07, 27.89 (t, $^2J_{\text{C-F}}=22.4$), 24.84 (d, $^3J_{\text{C-F}}=4.4$), 22.54, 20.66, (t, $^3J_{\text{C-F}}=3.8$), 14.0; MS $m/z=620$ (M^+), 370, 251, 231.

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References

- [1] MEYER, R. B., LIEBERT, L., STRZELECKI, L., and KELLER, P., 1975, *J. Phys. Lett., Paris*, **36**, 69.
- [2] CLARK, N. A., and LAGERWALL, S. T., 1980, *Appl. Phys. Lett.*, **36**, 899.
- [3] GOODBY, J. W., BLINC, R., CLARKE, N. A., LAGERWALL, S. T., OSIPOV, M. A., PIKIN, S. A., SAKURAI, T., YOSHINO, K., and ZEKS, B., *Ferroelectric Liquid Crystals*, (Gordon & Breach Science Publisher), p. 409.
- [4] NOHIRA, H., NAKAMURA, S., and KAMEI, M., 1990, *Mol. Cryst. liq. Cryst.*, **108B**, 379.
- [5] NAKAMURA, S., NOHIRA, H., and KAMEI, M., 1990, *Mol. Cryst. liq. Cryst.*, **185**, 199.
- [6] NOHIRA, H., 1991, *J. syn. Org. Chem. Jpn*, **49**, 105.
- [7] GRIFFIN, A. C., and BUCKLEY, N. W., 1978, *Mol. Cryst. liq. Cryst.*, **41**, 141.
- [8] MISAKI, S., TAKAMURA, S., SUFUJI, M., MITOTE, T., and MATSUMURA, M., 1981, *Mol. Cryst. liq. Cryst.*, **66**, 123.
- [9] IVASHCHENKO, A. V., KOVSHEV, E. I., LAZAREVA, V. T., PRUDNIKOVA, E. K., TITOV, V. V., ZVERKOVA, T. I., BARNIK, M. I., and YAGUPOLSKI, L. M., 1981, *Mol. Cryst. liq. Cryst.*, **67**, 235.
- [10] JANULIS, E. P., JR., NOVACK, J. C., PAPAPOLYMEROU, G. A., TRISTANI-KENDRA, M., and HUFFMAN, W. A., 1988, *Ferroelectrics*, **85**, 375.
- [11] NGUYEN, H. T., SIGAUD, G., ACHARD, M. F., HARDOUIN, F., TWIEG, R. J., and BETTERTON, K., 1991, *Liq. Cryst.*, **10**, 389.
- [12] KODEN, M., NAKAGAWA, K., ISHII, Y., FUNADA, F., MATSUURA, M., and AWANE, K., 1989, *Mol. Cryst. liq. Cryst. Lett.*, **6(6)**, 185.
- [13] SAKAIGAWA, A., and NOHIRA, H., 1993, *Ferroelectrics*, **148**, 71.
- [14] TWIEG, R. J., BETTERTON, K., DIPIETRO, R., GRAVERT, D., NGUYEN, C., NGUYEN, H. T., BABEAU, A., and DESTRADE, C., 1991, *SPIE, Liq. Cryst. Devices Mater.*, **1455**, 86.
- [15] BRACE, N. O., 1962, *J. org. Chem.*, **27**, 4491.
- [16] SAKAIGAWA, A., PhD thesis (1994).
- [17] HASSNER, A., and ALEXANIAN, V., 1978, *Tetrahedron Lett.*, **46**, 4475.
- [18] NAKAMURA, S., PhD thesis (1992).