

6. Electronic supplementary information

6.1. Evaluation of structure and purity. The confirmation of structure and purity of the prepared final liquid crystalline esters was made by using a Shimadzu HPLC prominence chromatograph with MS (API-ESI) detector 2010EV (mass analyzer) and UV-VIS detector (purity analyzer) as well as by IR spectrophotometry (FT-IR Spectrometer BIO-RAD FTS 175C and PMR apparatus (INOVA-500 “varian500”).

Positive and negative ions were analyzed. In the first case molecules catch Na^+ ion thus $[\text{M} + \text{Na}]^+$ and sometimes $[\text{M} + \text{H}]^+$ ion is detected, in the second case $[\text{M} - \text{H}]^-$ ion is detected. IR spectra were registered in CCl_4 solution.

The purity of the intermediate compounds like acids (**A**) was checked using a Hewlett-Packard HP-6890N chromatograph with MS detector HP5973N.

General method of preparation of the compounds $\text{I.r}(\text{X}_1\text{X}_2)$. It is given on the example of compound **I.3(HH)** ((S)-(+)-4'-4-(1-methylheptyloxycarbonyl)biphenyl-4-yl 4-[3-(2,2,3,3,4,4,4-heptafluorobutoxy)prop-1-oxy]benzoate).

To the suspension of 4-[3-(2,2,3,3,4,4,4-heptafluorobutoxy)prop-1-oxy]benzoic acid (**B**)²¹ (2.84 g; 7.5 mmol) in dry toluene ($\sim 100 \text{ cm}^3$), oxalyl chloride (0.75 cm^3 ; 8.25 mmol) and one drop of N,N-dimethylformamide were added. Vigorous reaction occurs. When the evolution of gases was stopped, mixture was heated at 30°C with stirring for 2 hours. The clear solution was then refluxed and the excess of oxalyl chloride was distilled off with toluene ($\sim 25 \text{ cm}^3$) using a Vigreux column. Then S-(+)-4-hydroxy-4'-4-(1-methylheptyloxycarbonyl)biphenyl (**C**)⁸ (2.45 g; 7.5 mmol) and pyridine (1.2 cm^3 ; 15 mmol) were added to the cold solution. The mixture was stirred at 60°C for 2 days, then it was cooled down to room temperature and poured into the solution prepared from concentrated hydrochloric acid ($\sim 2 \text{ ml}$) and water ($\sim 200 \text{ ml}$). The layers were separated, the organic layer was washed twice with water. The extract was filtered off by a layer of active carbon. Then it

was dried over anhydrous magnesium sulfate and the solvent was evaporated to dryness. The crude product was crystallized from anhydrous ethanol and acetone (2:1). The obtained solid was purified on silica gel using column chromatography and methylene chloride as eluent. After evaporation of the solvent the solid residue was then recrystallized from anhydrous ethanol and acetone. Yield: 3.1 g (60.3%); the phase transitions of ester are: Cr 54.5; 78.9 SmC_A* 116.2 Iso. Purity: 99.9%. MS: 685[M – H][–] (see Figure 9).

When positive charged ions were analyzed, molecular ion with captured sodium atom [M + Na]⁺ or weaker molecular ion captured hydrogen atom [M + H]⁺ was seen in every case and when negative charged ions were analyzed molecular ion with lost hydrogen atom [M – H][–] was seen respectively.

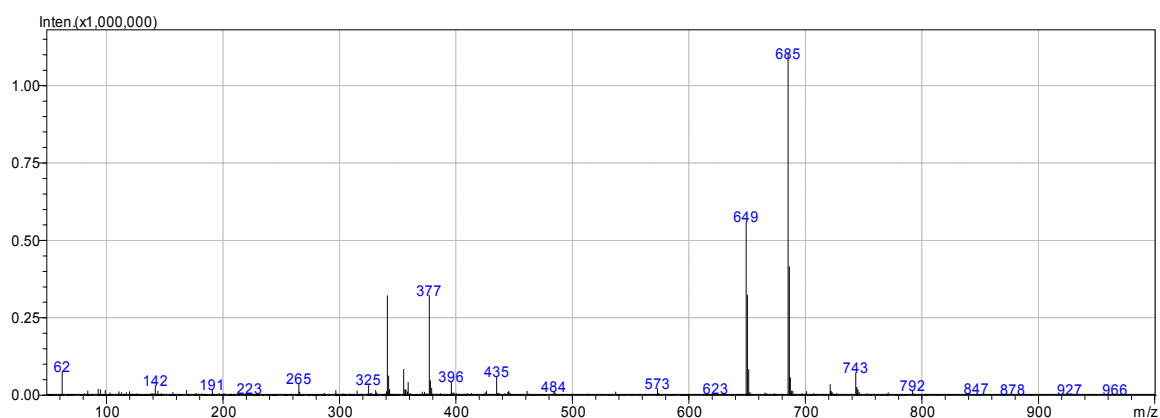
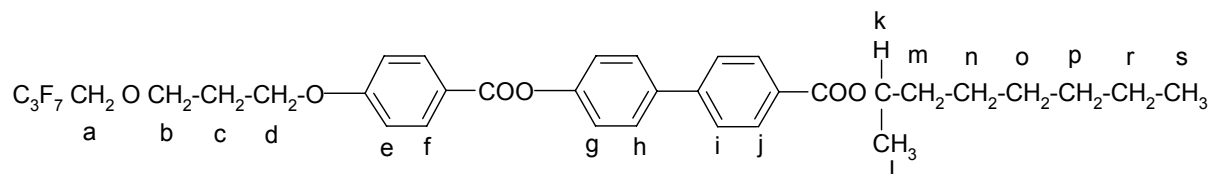


Figure 9 Mass spectrum of (S)-(+)-4'-(1-methylheptyloxycarbonyl)biphenyl-4-yl 4-[3-(2,2,3,3,4,4,4-heptafluorobutoxy)prop-1-oxyl]benzoate.

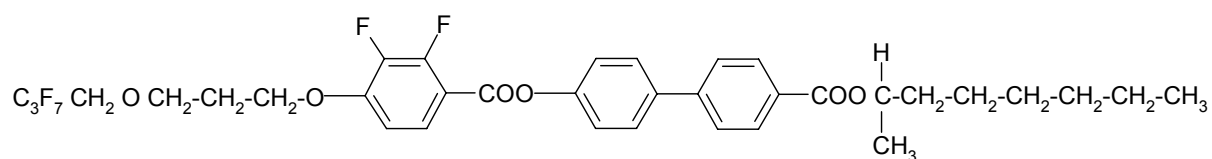
The remaining 24 liquid crystals were obtained in the same way and crystallized from anhydrous ethanol and acetone.

The value of chemical shift PMR results for four different substituted compounds of series **I.r(X₁X₂)** are given in Table 5. Protons are marked as below:

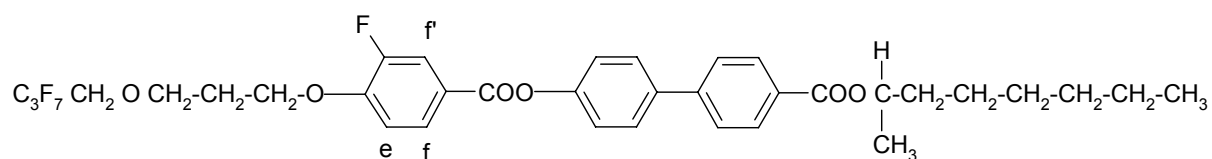
A) I.3(HH)



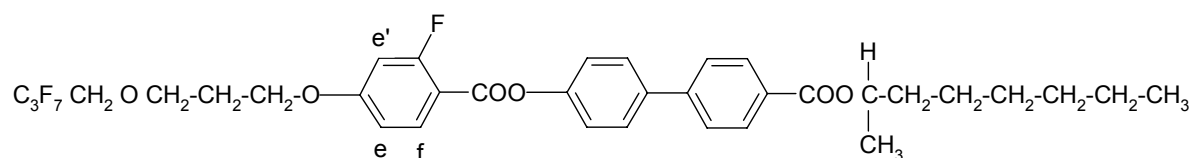
B) I.3(FF)



C) I.3(FH)



D) I.3(HF)



H = t

Table 5 PMR spectrum of compounds: I.3(HH) I.3(FF) I.3(FH) and I.3(HF) in CDCl₃ solution.

Chemical shifts [ppm]				
Protons	I.3(HH)	I.3(FF)	I.3(FH)	I.3(HF)
a	3.96 (2H, t of t)	3.97 (2H, t of t)	3.97 (2H, t of t)	3.96 (2H, t of t)
b	3.82 (2H, t)	3.83 (2H, t)	3.84 (2H, t)	3.8 (2H, t)
c	2.13 (2H, m)	2.17 (2H, m)	2.17 (2H, m)	2.12 (2H, m)
d	4.16 (2H, t)	4.26 (2H, t)	4.24 (2H, t)	4.15 (2H, t)

e	6.99 (2H, d)	6.86 (1H, t)	7.06 (1H, t)	6.80, 6.78, 6.72, 6.69 (2H, four d)
e'				
f	8.17 (2H, d)	7.87 (1H, t)	7.92, 7.93, 7.98, 8.00 (2H, four d)	8.09 (1H, t)
f'				
g	7.31 (2H, d)	7.32 (2H, d)	7.31 (2H, d)	7.32 (2H, d)
h	7.67 (2H, d)	7.67 (2H, d)	7.67 (2H, d)	7.67 (2H, d)
i	7.65 (2H, d)	7.65 (2H, d)	7.65 (2H, d)	7.65 (2H, d)
j	8.15 (2H, d)	8.12 (2H, d)	8.12 (2H, d)	8.12 (2H, d)
k	5.18 (1H, m)	5.18 (1H, m)	5.18 (2H, d)	
l m n r s	1.3÷1.76 (13H), group of signals of complex nature			
t	0.88 (t)	0.88 (t)	0.88 (t)	0.88 (t)

6.2. Purity and structure confirmation

In Table 6 IR bands of carbonyl bond (C=O) and mass purity analysis for prepared compounds (**I**) are listed. Characteristic absorption bands from the valence oscillations of –C=O– bond in –COO– ester bridging groups depend on the substitution of rigid core. Wavelength of absorption band of the carbonyl group in the chiral chain has the same value 1716÷1717 cm⁻¹ for all esters. The C=O bond in the central position has a singular band with value 1740 cm⁻¹ only for (**HH**) and (**FH**) substituted compounds and it is splitted into two bands: 1736 and 1757 cm⁻¹ for (**FF**) disubstituted compounds or 1731 and 1752 cm⁻¹ for (**HF**) monosubstituted ones, see Fig. 10. There CO bonds for compounds **I.7** having seven carbon atoms in the oligomethylene spacer are composed. Splitting the band of carbonyl group into two bands may be explained by Fermi resonance, but this option needs more advanced further studies.

Table 6 Mass analysis, values of IR C=O bands in ester –COO– groups (in CCl₄), chromatographic purity, helical pitch length *p* and its temperature dependence.

	MS(mz)		CO bonds [cm ⁻¹]		Purity [%]	<i>p</i> at 20°C [nm]	Temp. dep. <i>p</i>
	[M + Na] ⁺ , [M + H] ⁺	[M – H] ⁻	side	central			
I.2(HH)	695	671	1716	1740	99.6	131 ^a	+
I.2(FF)		707	1717	1736 1755	99.9	163 ^a	++
I.2(HF)	713	689	1716	1731 1752	99.9	374 ^a	+
I.2(FH)	713	689	1717	1742	99.3	62 ^a	+
I.3(HH)		685	1716	1740	99.9	56 ^a	+
I.3(FF)		721	1717	1736 1755	99.9	204 ^a	++
I.3(HF)		703	1716	1731 1752	99.9	229 ^a	++
I.3(FH)		703	1717	1742	99.9	57 ^a	++
I.4(HH)		699			99.4	143	++
I.4(FF)	759				99.3	443	++
I.4(HF)	741	719			99.9	499 ^a	++
I.4(FH)		717			99.3	287 ^a	++
I.5(HH)	737	715	1716	1740	99.7	102 ^a	++
I.5(FF)	773		1717	1736 1755	98.1	305 ^a	++
I.5(HF)	755		1716	1731 1752	99.9	847 ^b	-- ++
I.5(FH)	755		1717	1742	99.4	210 ^a	--
I.6(HH)	751	727	1716	1740	99.9	1256	+/-
I.6(FF)	787	765	1717	1736 1755	98.5	966	+/-
I.6(HF)	769	747	1716	1731 1752	98.95	506	+/-
I.6(FH)	769		1717	1742	99.35	1452 ^a	+/-
I.7(HH)	765		1716	1740	97.5	1253 ^a	--
I.7(FF)	801		1717	1736 1755	99.6	1643 ^a	--
I.7(HF)	783	761	1716	1731 1752	99.4	809 ^a	-
I.7(FH)	783	761	1717	1742	99.0	8529 ^a	--

(+) – growing; (++) – strongly growing with temp.; (+/-) – small temp. dependence; (-) – decreasing; (--) – strongly decreasing with temperature. *a* – extrapolated to 20°C; *b* – changes of temperature dependence and sign of helix is observed at about 50°C

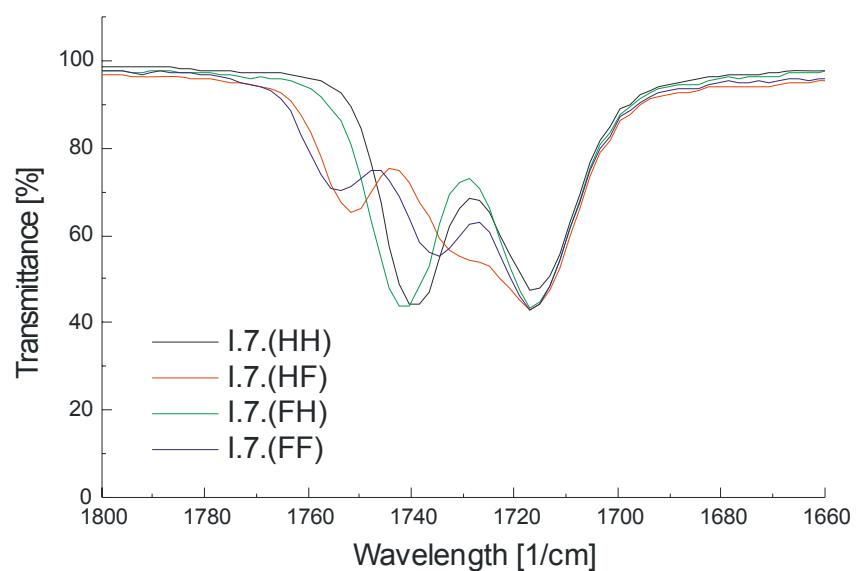


Figure 10 Comparison of absorption bands of the carbonyl group for differently substituted esters in CCl_4 solution.