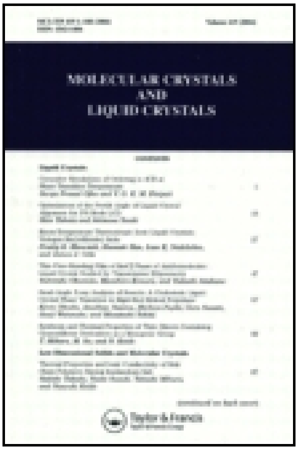

Molecular Crystals and Liquid Crystals

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Synthesis and Physical Properties of Novel Fluorinated Liquid Crystalline Compounds

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Synthesis and Physical Properties of Novel Fluorinated Liquid Crystalline Compounds

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Most twisted nematic liquid crystal displays (TN-LCD) uses liquid crystal mixtures with a positive dielectric anisotropy. In contrast, the recently introduced vertically aligned liquid crystal display (VA-LCD), which offers superior picture quality with a wide viewing angle, high contrast, and video-compatible switching times, is based on a liquid crystal mixture with negative dielectric anisotropy. We introduce here the synthetic route and physical and electro-optical properties of the liquid crystalline compounds with an ester group as linkage subsistent and with an alkyl chain as lateral subsistent. Also, we present physical and electro-optical properties of their mixture, and the LC-series for VA-LCD. Synthetic compounds exhibit broad range nematic phases up to 60 K degree and large negative dielectric anisotropies. And the viscosity of the LC-series is low in comparison with that of homologues with a lateral isothiocyanate group. The threshold voltage (Vth) was lower than that of a conventional mixture, enough so for it to be operated at a driving voltage. And the rising time of some LC-series improved to be faster than conventional LC mixtures. Our novel LC compounds are suitable materials for the improvement of the dielectric anisotropy of vertically aligned liquid crystal mixtures.

Keywords: fluorinated liquid crystalline compounds; negative dielectric constant; threshold voltage; transition temperature; viscosity

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INTRODUCTION

Thin film transistor liquid crystal displays (TFT-LCDs) are widely used information displays, especially in laptop computers, monitors, and TVs due to their excellent resolution. However, TFT-LCDs have several limitations, such as a narrow viewing angle and slow screen update time. Various methods to solve the viewing angle problem, such as the addition of birefringence films, the domain divided twisted nematic [1,2], the in-plane-switching (IPS) mode [3,4], and vertical alignment mode [5,6] have been proposed. Among these, the newly developed VA-LCD is expected to show improved wide-viewing angle and screen update time [7,8].

With the rapid change in the development of LCDs, demand for new liquid crystalline materials is increasing. For example, aliphatic tertiary nitrile compounds have a large negative dielectric anisotropy but a low phase transition temperature due to a decreased l/d. And the voltage holding ratio (VHR) values are insufficient for active matrix liquid crystal displays (AMLCDs) because the nitrile substituent is a property of conductivity and ion salvation [9,10]. And the laterally difluorinated phenylbicyclohexanes have large negative dielectric anisotropy, a high phase transition temperature and a sufficient VHR, but also a slow response time due to increased rotational viscosity [11]. Today, the applied materials use for VA modes are mainly 2,3-difluoro sub unit liquid crystalline compounds having low rotational viscosity and broad phase transition temperature range [12,13]. Super fluoro-substituted materials (SFMs) are known for their larger dipole moment, high stability, and high voltage holding ratio, low threshold voltage and low viscosity [14]. For this reason, many types of SFMs are in use and their properties have been investigated, despite the fact that they have low dielectric and optical anisotropy, which are known to deter high-speed response. In this study, we report the synthesis of novel fluorinated LCs with large negative dielectric anisotropy, characterizing their physical properties. In addition, we discuss the physical constants of new LCs in relation to the calculated molecular parameters.

SYNTHESIS

The synthetic procedure that is typically applied in preparing negative dielectric liquid crystalline compounds with a fluorine group is depicted in Figures 1 and 2. All homologues were prepared using the same methods. In Figure 1, the core structure (biphenyl group) was successfully introduced by the palladium-catalyzed cross-coupling

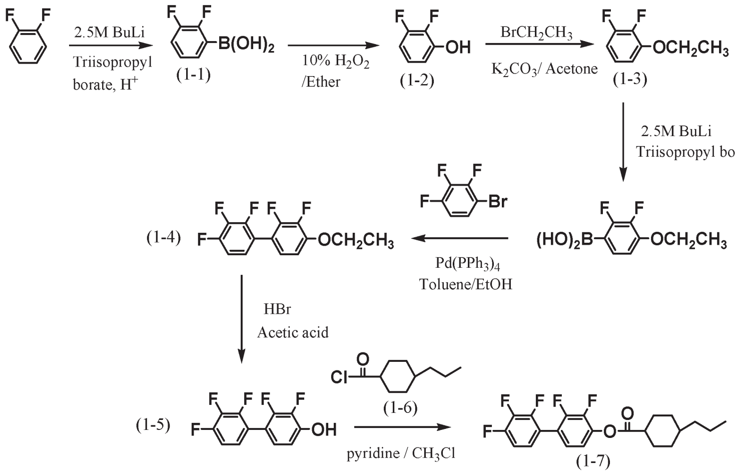


FIGURE 1 Synthetic method of an LC compound with Ester group as linking substitute.

reaction between boronic acid and aryl bromide [15], followed by the deprotection of alcohol and esterification reactions. In Figure 2, the core structure (phenylcyclohexyl group) was introduced by a carbon-carbon coupling reaction from the *trans*-alkylcylohexanone and organolithium reagent generated from the corresponding halide derivatives, followed by dehydration, the palladium-catalyzed cross-coupling reaction and reduction reactions. The pure *trans* compounds

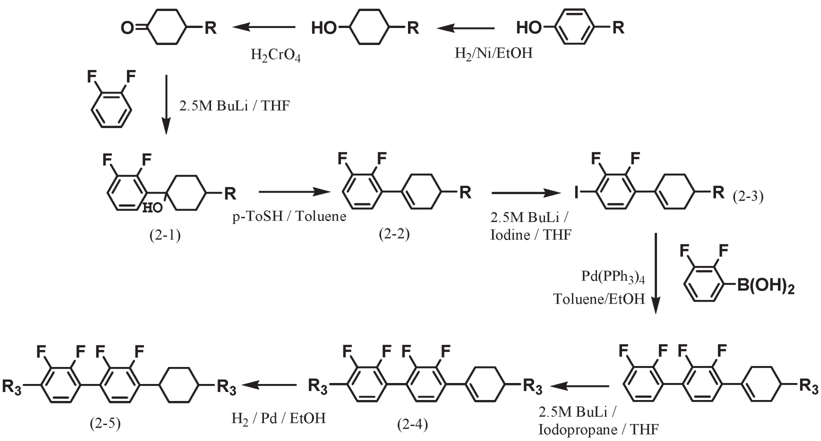


FIGURE 2 Synthetic route for an alkyl chain as terminal substitute.

were obtained in the final stage of the successive recrystallization process.

MEASUREMENTS

The chemical structures of products were confirmed by ^{1}H and ^{13}C NMR spectroscopy (Bruker Avance 400 Spectroscope) and GC/Mass spectrometer (Hewlett Packard 6890 series GC system and MSD). The liquid crystalline phase and phase transition temperature were observed through a polarizing microscope (Olympus BX51, BX60), equipped with a heating stage and a controller (Mettler FP90, STC 200D), and Differential Scanning Calorimeter (Perkin-Elmer DSC-7/TAC-7). The dielectric anisotropy ($\Delta\varepsilon$) was determined by the capacitive method, using an impedance analyzer (Hewlett Packard LF impedance analyzer 4172 A) at a frequency of 1 kHz. The optical birefringence (Δn) was measured by using an Abbe's refractometer and the flow viscosity (η) was obtained with a cannon micro viscometer at 20°C. All the measurements were carried out at a fixed temperature, 20°C, on 15 wt% solutions of the compound in standard host mixture (MJ 961213) and extrapolated to 100% concentrations, taking into account the variation of the physical parameters of the mixture under investigation. The molecular geometry was calculated using the semi empirical quantum chemical AM1 method (MOPEC 7.0 package).

RESULTS AND DISCUSSION

The chemical structures and abbreviations are listed in Table 1. Phase transition temperature data are given, in Table 2 and the calculated molecular parameters, such as the molecular dipole moment (μ),

TABLE 1 Chemical Structures and Abbreviations for the Biphenyl Cyclohenxane Liquid Crystal

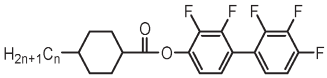
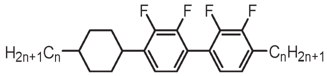
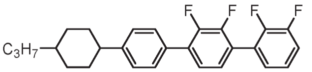
Abbreviation	Structure
nCcooPFFPFFF	
nCPFFPFFn	
R3CPPFFPFF	

TABLE 2 Phase Transition Temperatures and Length-to-Breadth Ratios of Biphenylcyclohenxane LC

Abbreviation	n X	m Y	l Z	Phase transition temperatures (°C)		Cr		Sm		N	Iso	ΔH_{NI}
3CPFFPFF3	3	0	0	Heat	•	–	–	–	–	43.9	•	–
	F	F	C_3H_7	Cool	•	22.7	–	–	–	–	•	
3CPFFPFF5	3	0	0	Heat	•	–	–	34.5	•	59.3	•	0.362
	F	F	C_5H_{11}	Cool	•	11.3	–	–	•	61.3	•	
5CPFFPFF3	5	0	0	Heat	•	43.2	•	–	–	79.4	•	–
	F	F	C_3H_7	Cool	•	14	•	78.6	–	–	•	
5CPFFPFF5	5	0	0	Heat	•	22.3	•	45.3	•	62.8	•	0.432
	F	F	C_5H_{11}	Cool	•	0.8	–	–	•	63.1	•	
3CcooPFFPFFF	3	1	0	Heat	•	–	–	63.0	•	108.6	•	0.206
	F	F	F	Cool	•	32.3	–	–	•	108.2	•	
5CcooPFFPFFF	5	1	0	Heat	•	–	–	72.4	•	109.8	•	0.579
	F	F	F	Cool	•	18.6	–	–	•	109.8	•	
3CPPFFPFF	3	0	1	Heat	•	–	–	130.2	•	190.2	•	0.371
	F	F	H	Cool	•	111.8	–	–	•	190.8	•	

anisotropy of molecular polarizability ($\Delta\alpha$) and the angle β between the molecular dipole moment and the long molecular axis of the molecule, and measured physical properties are summarized in Table 3.

As you can see in Tables 2, 3 CcooPFFPFF, 5CcooPFFPFF, 3CPFFPFF5, 5CPFFPFF3, and 5CPFFPFF5 were found to have enantiotropic nematic phases, whereas 3CPFFPFF3 compounds were non-mesogenic. For the 5CPFFPFF3 compounds, the smectic C phase was observed in the heating and cooling processes. It is known that thermal stability is

TABLE 3 Molecular Parameters from Molecular Modeling Calculations and the Measured Physical Properties of Biphenyl Cyclohexane Liquid Crystal

Abbreviation	μ^1 (Debye)	$\Delta\alpha^1$ (a.u)	$\Delta\alpha/M^1$	β^1	$\Delta\varepsilon^2$	Δn^2	η^2 (mm2/s)
3CPFFPFF3	4.822	181.8	0.4638	84.9	−4.43	0.0918	83.35
3CPFFPFF5	4.475	162.5	0.3869	84	−5.56	0.1095	66.41
5CPFFPFF3	4.438	163.3	0.3888	85.9	−4.43	0.1128	56.08
5CPFFPFF5	4.508	167.3	0.3734	81.8	−5.30	0.1197	49.88
3CcooPFFPFFF	5.469	166.1	0.4032	54.7	−3.83	0.1071	44.35
5CcooPFFPFFF	5.369	170.3	0.3874	40.6	−3.43	0.1093	45.48
3CPPFFPFF	5.018	287	0.6737	72.3	−5.56	0.1415	47.41

[1] For the calculations, we used the semi-empirical quantum method (AM1 in the MOPAC 7.0).

[2] Extrapolated values from 15 wt% host solutions.

greatly influenced by molecular parameters, such as rigidity, length-to-breadth ratio, packing density, polarizability and enhancement of polarity by conjugation. These factors can explain the effect of fluorine substitution on the thermal stability of liquid crystal molecules. And 3CcooPFFPFF and 5CcooPFFPFF have high phase transition temperatures due to the increase in l/d with the introduction of the ester group.

As shown in Table 3, the dielectric anisotropy values vary according to core structure, terminal group and alkyl spacer length. The Eq. (1) can be explained by the Maier-Meier theory [16] which is based on the Onsager model. The dielectric anisotropy is given by

$$\Delta\varepsilon = \frac{NFh}{\varepsilon_o}\left\{\Delta\alpha + \frac{F\mu^2}{2k_BT}(1 - 3\cos^2\beta)\right\} \bullet S \tag{1}$$

Here, S is the order parameter, N is the molecular packing density, h is the cavity field factor, F is the Onsager reaction field factor, and μ is the dipole moment forming an angle β with the major inertial axis of the molecule. n is the average refractive index of the substance. Δn is determined by molecular polarizability anisotropy ($\Delta\alpha$), order parameter (S), and crystal density (ρ), as follows.

$$\Delta n = (2\pi/3n)(n^2 + 2)N_A(\Delta\alpha/M)\rho S \tag{2}$$

From Figure 3, we can deduce that it is a typical behavior for Δn to increase with an increase in $\Delta\varepsilon$ in each group because of the relationship between two parameters. As shown in Eqs. (1) and (2), dielectric anisotropy, $\Delta\varepsilon$, and birefringence, Δn, are in proportion to the anisotropy of molecular polarizability, $\Delta\alpha$, and order parameter S. Figure 4 shows the viscosity tendency of LC compounds.

Introduction of the fluorine group as a lateral substituent in the phenyl ring, affords a lower kinetic viscosity compared with homologues with the isothiocyanate-substituent (Fig. 4). This is explained by the fact that the molecular polarizability anisotropy ($\Delta\alpha$) of the isothiocyanato group with three non-bonding electron pairs is higher than that of fluorine. This factor enhances the Van der Waal's attraction in molecules.

As shown in Table 4, LC-006, LC-007, LC-008 and LC-009 have faster rising times than the host due to increase negative dielectric anisotropy and low threshold voltage. In the case of falling time, LC-006, LC-007, LC-008 and LC-009 have slower falling times than the host due to increase kinetic viscosity and decrease elastic constants. LC-010 and LC-011 have slower falling times nevertheless, having large elastic constants due to large kinetic viscosity. Especially, LC-012 has the fastest rising time (6.3 msec) and falling

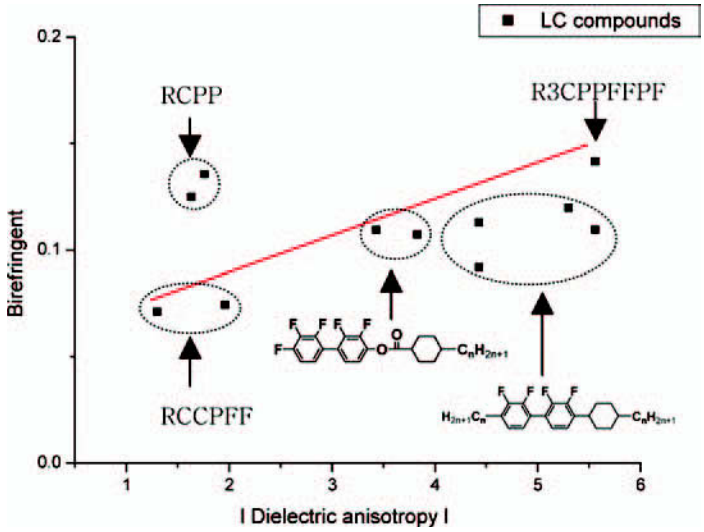


FIGURE 3 Relationship between Δn and Δε for new LCs for the experiments.

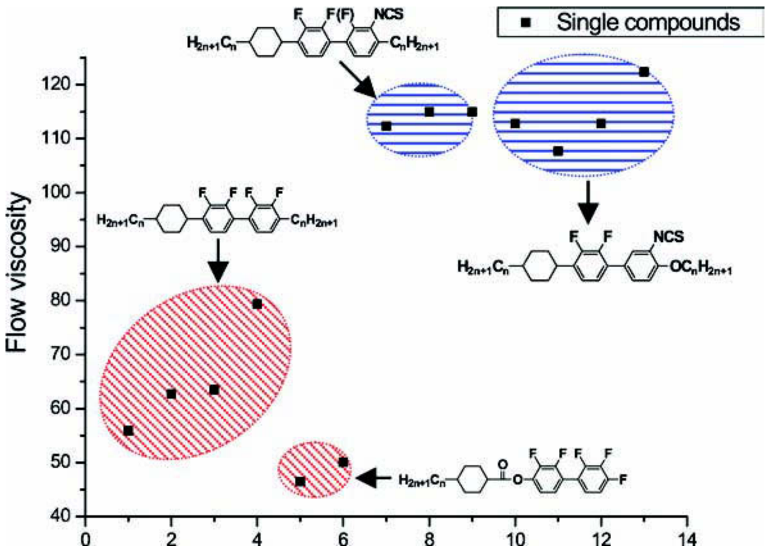


FIGURE 4 Comparison of flow viscosity between LC of isothiocianate and LC of fluorine. LC of fluorine (red) and LC of isothiocyanate (blue).

TABLE 4 Physical Properties of Liquid Crystal Mixtures

		LC-006	LC-007	LC-008	LC-009	LC-010	LC-011	LC-012
		85%	85%	85%	85%	85%	85%	3%
No	Host	R3CPFF	R3CPFF	R3CPFF	R3CPFF	R3CcooPFF	R3CcooPFF	R3CPPFF
Host dopant	100%	PFFR3 (15%)	PFFR3 (15%)	PFFR3 (15%)	PFFR3 (15%)	PFFF (15%)	PFFF (15%)	PFF (3%)
Tni[°C]	72.9	62.8	70.7	73.4	71.3	75.8	77.3	75.2
Δn^2	0.0815	0.0833	0.0857	0.0862	0.0862	0.0853	0.0857	0.0833
$\Delta\varepsilon$[1 kHz]	–3.23	–3.39	–3.58	–3.42	–3.54	–3.32	–3.26	–3.30
η^2[mm^2/s]	21.08	30.42	27.88	26.33	25.4	24.57	24.74	21.87
V_{th}[V]	2.66	2.47	2.43	2.44	2.50	2.58	2.59	2.56
K_{eff}[pN]	12.8	11.11	11.79	11.95	11.9	13.06	13.15	12.59
VHR[%]	97.8	96.71	97.24	96.83	95.94	95.98	95.98	95.2
τ^1_{on} [ms]	9	8.95	8.6	8.62	8.21	9.3	8.97	6.3
τ^1_{off} [ms]	11	15.6	12.9	12.6	14.1	13	13.5	9.26
τ^1_{total} [ms]	20	24.55	21.5	21.22	22.22	22.3	22.47	15.56

[1] It measured at room temperature 3.75 um cell.
[2] It measured at 20°C.

time (9.26 msec) than all other mixtures and hosts because of increase negative dielectric anisotropy and low kinetic viscosity.

Experimental

The *trans*-2,3,2′,3′-tetrafluoro-4′-alkyl-4-(4-alkyl-cyclohexyl)-biphenyl were prepared according to the synthetic route in Figure 2. The representative procedures for the propyl derivative are described below.

1-(2,3-Difluoro-phenyl)-4-propyl-cyclohexanol (2-1)

A solution of 1,2-difluorobenzene (9.2 g, 0.08 mol) in dry THF (200 mL) was cooled to −78°C, and then 2.5 M n-BuLi (38.4 mL 0.096 mol) was slowly added to this solution. After maintaining it at –78°C for 4 hrs, 4-propylcyclohexanone (11.3 mL, 0.08 mol), which was dissolved in THF (100 mL), was added; the reaction mixture was warmed to room temperature and neutralized with 10% hydrochloric acid. The mixture was washed with saturated sodium chloride aqueous solution and Ether. The organic layer was dried over anhydrous $MgSO_4$ and removed in vacuo to give a yellow liquid product (20.03 g, 0.079 mol, yield 98%). Mass: 254(M^+) 236, 193, 179, 165

1,2-Difluoro-3-(4-propylcyclohex-1-enyl)-benzene (2-2)

The solution of compound (2-1) (10.4 g, 0.041 mol) and p-toluenesulfornic acid 1-hydrate (7.78 g, 0.0041 mol) in toluene (250 mL) were placed in a three-neck flask. After the mixture was heated under reflux at 115°C for 6hrs, the product was washed with saturated sodium bicarbonate and water. Then, the organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated in vacuo to give a dehydration product in a yellow solid form. The product was purified by column chromatography (hexane) to give a colorless liquid product (8.12 g, 0.034 mol 84% yield). Mass: 236(M^+) 193, 179, 127

2,3-Difluoro-1-iodo-4-(4-propyl-cyclohex-1-enyl)-benzene (2-3)

A solution of 1,2-difluoro-3-(4-propylcyclohex-1-enyl)-benzene (10 g, 0.042 mol) in dry THF (200 mL) was cooled to −78°C, and then 2.5 M n-BuLi (20.2 mL, 0.05 mol) was slowly added. After maintaining at –78°C for 4 hrs, 2 M I_2 solution (21 mL, 0.05 mol), which was dissolved in dried THF, was added; the reaction mixture was warmed to room temperature and neutralized with 10% hydrochloric acid. The product was extracted into ether (twice), and the combined ethereal extracts were washed with water and dried ($MgSO_4$). The organic layer was dried over anhydrous $MgSO_4$ and removed in vacuo to give a dark brownish crude product. The product was purified by column chromatography (hexane) to produce a yellow liquid product (12.92 g, 0.0357 mol, yield 85%). Mass: 362(M^+), 305, 266, 165 ^{1}H NMR (400 MHz, $CDCl_3$): 0.7(2H, m), 1.86 (2H, m), 2.23 (3H, m), 5.96 (1H, s), 6.75(1H, m), 7.36(1H, m)

2,3,2′,3′-Tetrafluoro-4′-propyl-4-(4-propyl-cyclohex-1-enyl)-biphenyl (2-4)

A solution of 2,3,2′,3′-Tetrafluoro-4-(4-propyl-cyclohex-1-enyl)-biphenyl (4.16 g, 0.012 mol) in dry THF (200 mL) was cooled to −78°C, and then 2.5 M n-BuLi (12.4 mL, 0.015 mol) was slowly added. After it was maintained at −78°C for 2.5 hrs, iodopropane (3 mL, 0.03 mol), which was dissolved in THF (10 mL), was added; the reaction mixture was warmed to room temperature and neutralized with 10% hydrochloric acid. The product was extracted into ether (twice), the organic layer was dried over anhydrous $MgSO_4$ and removed in vacuo to give a brownish crude product. The product was purified by column chromatography (hexane) to produce a colorless liquid product (3.9 g, 0.01 mol, yield 83%). Mass: 390 (M^+), 347, 333, 294

Trans-2,3,2′,3′-Tetrafluoro-4′-propyl-4-(4-propyl-cyclohexyl)-biphenyl (2-5)

The reaction mixture of compound (2-4) (3.3 g, 0.0084 mol) and palladium on activated carbon (0.5 g, 10% Pd) in ethanol (150 mL)/toluene (50 mL) was maintained for 12 h under an H_2 stream (pressure: 60 psi). The Pd/C was filtered off and the residue was evaporated in vacuo to yield a colorless liquid product. The product was purified by column chromatography (hexane) and separated by recrystallization (Ethanol and E.A.) to give trans-2,3,2′,3′-tetrafluoro-4′-propyl-4-(4-propyl-cyclohexyl)-biphenyl (1.36 g, 40% yield). Mass: 392($M^{+\cdot}$) 363,294,265 ^{1}H NMR (400 MHz, $CDCl_3$): 0.8(3H,m), 0.98 (3H, m), 1.0 (2H,m), 1.1 (9H,m), 1.32(9H,m), 1.5(4H,m), 1.67(2H,m), 1.85(4H,m), 2.87(1H,t), 6.9(4H,m)

CONCLUSION

The development of vertically aligned thin film transistor liquid crystal displays (VA TFT-LCDs) has created a greater demand for the development of new and improved liquid crystalline materials. In this study, we synthesized novel LC compounds, trans-2,3,2′,3′-tetrafluoro-4-alkyl-4′-(4-alkyl-cyclohexyl)-biphenyl and 4-alkyl-cyclohexane carboxylic acid 2,3,2′,3′,4′-pentafluoro-biphenyl-4-yl ester and 2,3,2′, 3′,tetrafluoro-4″-(4-propyl-cyclohexyl) triphenyl measured the physical properties for the purpose of high phase transition temperature, large negative dielectric constants, and low viscosity. We found that the synthesized LC showed relatively low viscosity and large negative dielectric anisotropy and the threshold voltage Vth was low enough to operate in TFT-LCD at the driving voltage. And LC-012 is the fastest response time than host because of increase negative dielectric anisotropy and low kinetic viscosity. The proposed LC compounds are deemed to be suitable materials for the improving dielectric anisotropy of vertically aligned liquid crystal displays (VA-LCDs).

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