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High birefringence and large negative dielectric anisotropy phenyl-tolane liquid crystals

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Two phenyl-tolane compounds with two pairs of (2,3) lateral difluoro substitutions were synthesized and their properties evaluated. These compounds exhibit a high birefringence ($\Delta n \sim 0.35$) and a large negative dielectric anisotropy ($\Delta\varepsilon \sim -8$). These two important features make the phenyl-tolane compounds useful as a dopant in a negative $\Delta\varepsilon$ liquid-crystal mixture to enhance the performance of the host mixture, or as a negative component in a dual-frequency liquid-crystal mixture to improve the dielectric anisotropy and birefringence and lower the crossover frequency.

1. Introduction

Nematic liquid crystals (LCs) with a large negative dielectric anisotropy ($\Delta\varepsilon<0$) play an important role in many electro-optical devices. For example, a vertical alignment (VA) cell using a negative $\Delta\varepsilon$ LC exhibits a high contrast ratio [1] which is particularly attractive for LCD TVs. In dual-frequency liquid-crystal (DFLC) devices, large negative $\Delta\varepsilon$ helps reduce the required driving voltage at a high frequency for achieving a fast response time [2]. A fast response time is desirable in almost all electro-optical devices and is sometimes critical. Therefore, it is important to know what factors determine the response time of a LC device.

The response time of a LC device is determined by the LC properties and the driving method. For a VA cell with strong anchoring energy, the rise time is given as [3]

$$\tau_{\text{rise}} \sim \tau_0\left((V/V_{\text{th}})^2-1\right), \tag{1}$$

and decay time is

$$\tau_{\text{decay}} \sim \tau_0 = \gamma_1 d^2/K_{33}\pi^2, \tag{2}$$

where V is the turn-on voltage, V_{th} is the threshold voltage, γ_1 is the rotational viscosity, K_{33} is the bend elastic constant and d is the cell gap. Equations (1) and (2) give us useful guidelines to optimize the LC properties in order to achieve a shorter response time. The upper limit of the phase modulation from a VA cell is $\delta = 2\pi d\Delta n/\lambda$, where Δn is the LC birefringence and λ is the operating wavelength. For a phase modulator at a given wavelength, the cell gap is determined by the birefringence of the LC. A larger birefringence would decrease the required cell gap, which helps to shorten the response time effectively. Reducing the rotational viscosity γ_1 or, to be more precise, decreasing the visco-elastic constant γ_1/K_{33} is another way to achieve a faster response. A larger dielectric anisotropy $\Delta\varepsilon$ may lead to a lower threshold voltage and may help to decrease the rise time when the overdrive and undershoot voltage method [4] is employed.

For a VA cell filled with a DFLC, equations (1) and (2) are modified as follows [6]:

$$\tau_{\text{on}} \sim \frac{\tau_0}{(V_{\text{h}}/V_{\text{th,h}})^2-1}, \tag{3}$$

and

$$\tau_{\text{off}} \sim \frac{\tau_0}{(V_{\text{l}}/V_{\text{th,l}})^2-1}. \tag{4}$$

In (3) and (4), V_{h} and V_{l} are the driving voltages for turning the cell on and off, $V_{\text{th,h}}$ and $V_{\text{th,l}}$ are the threshold voltages of the DFLC at high and low frequencies, respectively. In this situation, both on and off times are affected by the driving voltage. Therefore, the overdrive method [7] can be used to accelerate the response when turning the cell on or off. This property can be used to develop fast-response electro-optical devices.

From the above equations, we can see that a thinner cell gap [8] helps to shorten the response time because it is a quadratic effect. To take advantage of this, a large birefringence is needed. Elongating the π-electron conjugation of the LC compounds is the most effective way to increase the birefringence [9]. Common functional groups that contribute to the conjugation lengths

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include unsaturated rings, such as phenyl rings, and unsaturated bonds, such as carbon–carbon double [10] or triple bounds [11]. Including more linked functional groups with π-electrons can lead to a longer conjugation length and thereby a larger birefringence. For example, biphenyl and terphenyl compounds with neighbouring difluoro substitutions have been studied and widely adopted in commercial LC mixtures developed for VA mode displays [13]. Among unsaturated carbon–carbon bonds, stilbene [14], [15] and diacetylene [16], [17] are not stable under UV illumination. Therefore, the tolane structure is more favourable.

In VA modes displays and electro-optical devices, LCs with a negative dielectric anisotropy are necessary so that the device can be activated by an electric field. A large negative dielectric anisotropy helps to lower the threshold voltage and therefore decrease the response time when overdriven by a voltage, as indicated by (2). Moreover, it helps to decrease the driving voltage of the device. Negative dielectric anisotropy can be achieved by lateral polar substituents that introduce a dipole moment perpendicular to the principal axis of the LC molecule. A widely adopted structure is the lateral (2,3) difluoro substitutions on the phenyl ring, which can be found in negative Δε compounds employed in many commercial LC mixtures for VA mode displays [18], [19]. Inclusion of more (2,3) difluorinated phenyl rings in the rigid core helps to increase the negative dielectric anisotropy at the expense of increased viscosity.

In this paper, we report a series of laterally fluorinated phenyl-tolane compounds, their physical properties and potential applications. The phenyl-tolane core has an elongated conjugation which bestows these compounds with a large birefringence. The two (2,3) difluorinated phenyl rings leads to a large negative Δε. For the purposes of comparison, we also studied the properties of phenyl-tolane compounds with only one (2,3) difluorinated phenyl ring. These compounds can serve as dopants in a negative Δε LC host to substantially enhance the mixture's performance. They can also be used in a DFLC mixture to decrease the crossover frequency and to boost the mixture's performance.

2. Compound properties

Table 1 lists the molecular structures of the two homologues we studied, PP(23F)TP(23F)-3O2 and PP(2,3F)TP(2,3F)-5O2, where P represents the phenyl ring, T the carbon–carbon triple bond, (2,3F) the difluoro substitutions and O the alkoxy chain. The phenyl-tolane rigid core is chosen because of its long conjugation length. The two phenyl rings connected by the carbon–carbon triple bound each have two fluoro substitutions in the (2,3) positions in order to obtain a large negative dielectric anisotropy. In comparison, we also investigated the phenyl-tolane compounds with difluoro substitutions only on the phenyl ring connected to the alkoxy group. The lateral difluoro group, enhanced by the alkoxy, provides a dipole moment perpendicular to the principal molecular axis. The alkoxy group also helps to increase the conjugation

Table 1. Molecular structures and abbreviations of the four laterally difluorinated phenyl-tolane liquid crystals studied.

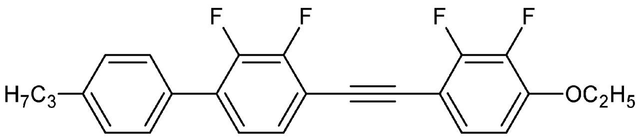
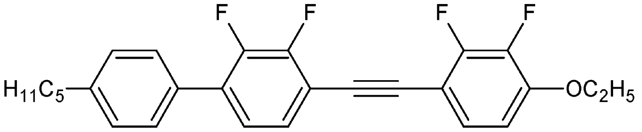
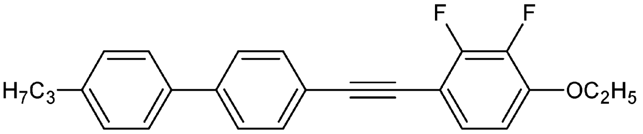
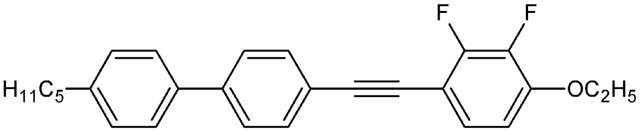
No.	Notation	Molecular structures
1	PP(2,3F)TP(2,3F)-3O2	
2	PP(2,3F)TP(2,3F)-5O2	
3	PPTP(2,3F)-3O2	
4	PPTP(2,3F)-5O2	

Table 2. Phase transition temperatures and heating fusion enthalpy of the fluorinated phenyl-tolane compounds.

	T_m (°C)	T_c (°C)	ΔH (cal/mol)
PP(2,3F)TP(2,3F)-3O2	82	210	6618
PP(2,3F)TP(2,3F)-5O2	75	194	6267
PPTP(2,3F)-3O2	146	240	7260
PPTP(2,3F)-5O2	116	222	6226

length, but at the price of increased melting temperature.

2.1 *Mesomorphic properties*

The mesomorphic properties of the compounds affect the solubility of the compounds in forming eutectic mixtures. We used a TA Instrument Inc. Q100 differential scanning calorimeter (DSC) to measure the phase sequence of the compounds. Results are presented in table 2.

All the phenyl-tolane compounds we studied have high melting temperatures. Compounds with two lateral fluoro substitutions (compounds 3 and 4) show much higher melting temperatures than those with four lateral fluoro substitutions. The high melting temperature and large heat fusion enthalpy limits the solubility of the phenyl-tolane compounds in LC mixtures. Owing to their lower melting temperatures, compounds 1 and 2 can serve as dopants for enhancing the birefringence of LC mixtures. Compound 4 can also work as a dopant in LC mixtures, but its concentration is rather limited. On the other hand, the solubility of compound 3 is very poor, which strongly restricts its application in eutectic LC mixtures.

2.2 *UV absorption*

LC materials are widely used in electro-optical devices operating at various wavelengths. From a device viewpoint, a basic requirement of the LC materials is their chemical, photo and thermal stabilities. We measured the absorption spectra of the phenyl-tolane compounds with four lateral fluoro substitutions in the UV and visible region using a Cary 500 spectrometer. As these compounds are in crystal phase at room temperature, we dissolved them into cyclohexane for the experimental measurements. Figure 1 shows the UV absorption spectra of compounds 1 and 2. Their absorption spectra are nearly the same because the only difference between these two homologues is in the alkyl chain length. The absorption tail ends at around 375 nm. The compounds appear white in the crystalline phase. For projection displays a UV cut-off filter blocks any wavelength below 420 nm. For direct-view LCDs, the employed polarizers transmit wavelength longer than ~380 nm. Therefore, these compounds should be reasonably stable as long as we avoid direct UV exposure during hermetic sealing process.

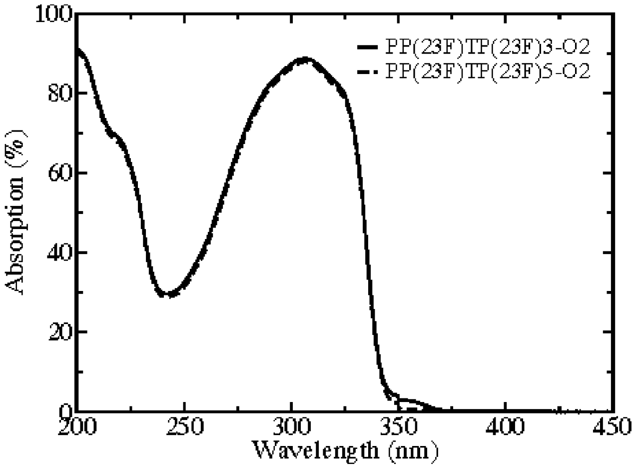


Figure 1. Measured UV absorption spectra of PP(2,3F)TP(2,3F)-3O2 and PP(2,3F)TP(2,3F)-5O2. Each compound is dissolved in cyclohexane solvent with 2×10^{-4} mol l^{-1} concentration and 1 mm cell gap.

2.3 *Polarizability, birefringence and dielectric anisotropy*

The birefringence of a LC is determined by the differential polarizability of the LC molecules. We used HyperChem, molecular modelling software, to calculate

Table 3. Calculated polarizabilities of PPTP(2,3F)-5O2 and PP(2,3F)TP(2,3F)-5O2.

	$\Delta\alpha$	α	Polarizability tensor			
PPTP(2,3F)-5O2	353.75	287.31		x	y	z
			x	148.46	24.66	14.58
			y	24.66	190.33	20.85
			z	14.58	20.84	523.15
PP(2,3F)TP(2,3F)-5O2	352.62	290.50		x	y	z
			x	147.41	24.57	1.68
			y	24.57	198.50	25.82
			z	1.67	25.83	525.58

Table 4. Measured birefringence and dielectric anisotropy of three phenyl-tolane compounds.

	Δn (25°C, 633 nm)	$\Delta\varepsilon$ (23°C)
PP(2,3F)TP(2,3F)-3O2	0.35	−8.5
PP(2,3F)TP(2,3F)-5O2	0.32	−8.5
PPTP(2,3F)-5O2	0.35	−6.8

the polarizability of these compounds. The polarizability anisotropy is defined as [9], [20]

$$\Delta\alpha = \alpha_x - \left(\alpha_y + \alpha_z\right)/2, \tag{5}$$

where α_x is polarizability along the long molecular axis, and α_y and α_z are the polarizabilities along the short molecular axes. We calculated the polarizability of PP(2,3F)TP(2,3F)-5O2 and PPTP(2,3F)-5O2. The results are displayed in table 3.

From table 3, the phenyl tolane with two neighbouring fluoro substitutions (PPTP(2,3F)-5O2) shows a slightly larger polarizability anisotropy than PP(2,3F) TP(2,3F)-5O2, phenyl tolane with four neighbouring fluoro substitutions. As a result, PPTP(2,3F)-5O2 should have a larger Δn than PP(2,3F)TP(2,3F)-5O2. A similar trend should also appear between PPTP(2,3F)-3O2 and PP(2,3F)TP(2,3F)-3O2.

All of the fluorinated phenyl-tolane compounds studied exhibited fairly high melting temperatures. In addition, they do not align well in VA cells. Therefore, we have to dope these compounds into host mixtures to measure their electro-optical properties. The host mixture we chose is Merck MLC-6608 (a negative $\Delta\varepsilon$ TFT mixture). The birefringence and dielectric anisotropies of PP(2,3F)TP(2,3F)-3O2 and PP(2,3F)TP(2,3F)-5O2 were derived from extrapolation and results are shown in table 4. For comparison, the data of PPTP(2,3F)-5O2 are also included in table 4. Compound PPTP(2,3F)-3O2 is not characterized because of its poor solubility.

All of these compounds show a relatively high birefringence because of the elongated π-electron conjugation. PPTP(2,3F)-5O2 exhibits a larger birefringence than compound PP(2,3F)TP(2,3F)-5O2, which is in good agreement with the simulated polarizability anisotropy data. The first two compounds show a larger negative dielectric anisotropy than the third because of the additional pair of (2,3) difluoro substitutions.

3. Dopants in negative Δε LC mixtures

Although the fairly high melting point and large heat fusion enthalpy of the phenyl-tolane compounds with four lateral fluoro substitutions limit the solubility of these compounds in LC mixtures, they are still useful as dopants in a LC mixture.

3.1 *Physical and electro-optical properties*

We chose MLC-6608 as the host mixture to study the performance of the phenyl-tolane compounds with four lateral fluoro substitutions. We prepared two mixtures, each doped with 15 wt% of a phenyl-tolane compound. The physical and electro-optical properties of these mixtures were studied and results are presented in table 5. The properties of the host, MLC-6608, are also included for comparison.

A substantial increase in the optical birefringence is observed in the doped mixtures. The increased birefringence enables a thinner cell gap to be used to achieve the same phase change. The decreased cell gap in turn leads to a faster response time. In addition, the dielectric anisotropy of the doped mixtures is higher than that of the host mixture, but the visco-elastic coefficient is also increased. To take cell gap and visco-elastic coefficient into consideration, we compare their figure of merit (FoM), which is defined as [21]

$$\mathrm{FoM} \equiv K_{33}(\Delta n)^2 \Big/ \gamma_1. \tag{5}$$

Table 5. Physical and electro-optical properties of two doped mixtures in the MLC-6608 host.

	MLC-6608+15% PP(2,3F)TP(2,3F)-3O2	MLC-6608+15% PP(2,3F)TP(2,3F)-5O2	MLC-6608
Δn (633 nm, 25°C)	0.124	0.117	0.0818
V_{th}	3.22	3.22	3.23
$\varepsilon_\perp$	7.9	7.9	7.1
$\varepsilon_\parallel$	3.4	3.5	3.3
$\Delta\varepsilon$	−4.5	−4.5	−3.8
K_{11} (pN)	24.2	24	20.3
K_{33} (pN)	28.6	28.3	22.3
K_{33}/K_{11}	1.18	1.18	1.1
γ_1/K_{33} (25°C)	11.56	11.22	11.1
T_c (°C)	106.8	105.3	90
FoM (μm^2 s^{-1})	1.33	1.22	0.60

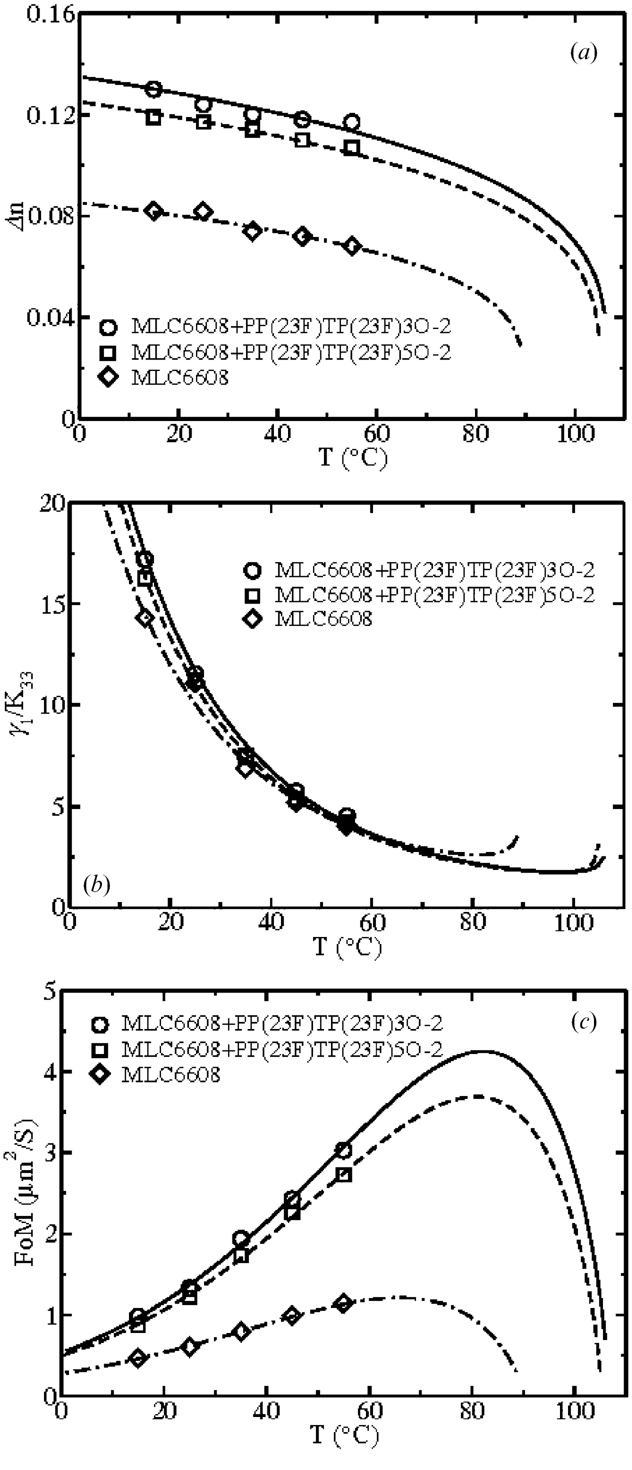


Figure 2. Measured temperature-dependent (a) birefringence, (b) visco-elastic coefficient and (c) FoM of two phenyl tolane (15 wt%) doped in MLC-6608 and host mixture MLC-6608. Here $\lambda=633$ nm.

As table 5 shows, doping the phenyl-tolane compounds with four lateral fluoro substitutions in MLC-6608 improves the FoM by around a factor of two. This is because the birefringence effect in FoM is quadratic, but the K_{33}/γ_1 effect is linear.

3.2 *Temperature effect*

The physical properties of a thermotropic LC, such as birefringence, elastic constants, dielectric constants and viscosity, are all dependent on the temperature. A LC device could be operated at elevated temperatures. For example, in an LCD TV the LC temperature could go up to ~35°C owing to the backlight heating, while in a projector the chassis temperature could go up to 50°C because of the thermal effect from the high-power lamp. Therefore, the temperature effects should be studied in order to optimize the LC device performance [22].

We investigated the performance of the negative $\Delta\varepsilon$ LC mixtures doped with PP(2,3F)TP(2,3F)-3O2 and PP(2,3F)TP(2,3F)-5O2. The birefringence, visco-elastic coefficient and *FoM* of the mixtures were measured from 15 to 60°C. Results are plotted in figures 2(a)–(c). Dots in figure 2 represent measured data while lines are fitting curves.

The temperature-dependent birefringence can be expressed as [23]

$$\Delta n=\Delta n_0(1-T/T_c)^{\beta}, \tag{6}$$

where Δn_0 is the birefringence at $T=0$ K and β is a material constant. From (6), it can be seen that the LC birefringence decreases as the temperature increases. The curves in figure 2(a) show that the doped mixtures and the host mixture follow the same trend as the temperature increases. Meanwhile, the visco-elastic coefficient decreases sharply and gradually saturates as the temperature increases, as shown in figure 2(b). Therefore, the *FoM* increases gradually before reaching the optimal operation temperature and then decreases sharply as the temperature approaches the clearing point, as figure 2(c) shows. From figure 2(c), the doped LC mixtures exhibit a factor of two to three higher *FoM* than the host MLC-6608 because of the enhanced birefringence, although their visco-elastic coefficients are also increased.

4. DFLC mixtures

The negative phenyl-tolane compounds we obtained were employed to form DFLC mixtures in order to keep a large negative $\Delta\varepsilon$ in the high-frequency region. High birefringence of these compounds is also favourable because it benefits the response time.

We replaced a tolane compound with PP(2,3F)TP(2,3F)-5O2 in one of our previous DFLC mixtures designated as DFLC-01 and derived a new mixture DFLC-02. The weight percentage of the

Table 6. The physical and electro-optical properties of DFLC-01 and DFLC-02.

	DFLC-01	DFLC-02
Δn (25°C, 633 nm)	0.274	0.288
$\Delta\varepsilon$ (1 kHz, 23°C)	11.2	11.1
$\Delta\varepsilon$ (100 kHz, 23°C)	-3.98	-4.41
γ_1/K_{11} (ms μm^{-2}) (25°C)	22.96	24.41
V_{th} (V)	1.97	2.21
FoM (μm^{2}s^{-1}) (25°C, 1 kHz)	3.27	3.39
Crossover frequency (kHz)	~28.5	~18.5

compound is around 10% in the mixture. The physical and electro-optic properties of the DFLC-01 and DFLC-02 were characterized and results compared in table 6.

By introducing the phenyl-tolane compound PP(2,3F)TP(2,3F)-5O2 to the host mixture, a noticeable increase in birefringence is observed. Thus, a thinner cell gap can be used for achieving a shorter response time. This thin cell gap effect is especially important for infrared devices, such as laser beam steering [25], where the LC birefringence is decreased [26] and wavelength is increased.

From table 6, the modified mixture DFLC-02 exhibits a substantially lower crossover frequency ($f_c \sim 18.5$ kHz) than DFLC-01 ($f_c \sim 28.5$ kHz). This lowered crossover frequency is particularly desirable because a DFLC mixture usually has a relatively high viscosity. In order to reduce viscosity, the device is normally operated at a mild elevated temperature, e.g., 35–40°C. However, as the temperature increases, the crossover frequency increases exponentially [27]. Therefore, it is essential to design a DFLC mixture with a low crossover frequency at room temperature so that its crossover frequency at 35–40°C will not be too high. If the operating frequency is too high, then the dielectric heating effect [28] becomes important which will cause crossover frequency to drift.

5. Conclusions

We have investigated phenyl-tolane compounds with neighbouring difluoro substitutions on the phenyl rings connected by the carbon–carbon triple bound. These compounds show large optical birefringence, which is attributed to their long π-electron conjugation length. The large negative dielectric anisotropy of these compounds is brought by the two neighbouring difluoro substitutions on the phenyl rings.

These compounds can serve as dopants in negative LC mixtures to improve the performance, which is mainly achieved by the increase of the Δn. In a large temperature range, the performance of the doped mixture increases with the increase in operating temperature.

Another application of these compounds is to serve in the negative part in the DFLC mixtures. An increase in birefringence enables a thinner cell gap, which leads to a shortened response time and lowered operating voltages. This is much appreciated in devices operating in the infrared range of the spectrum, where a thicker cell gap is necessary to achieve a certain phase modulation. In addition, we can decrease the crossover frequency substantially by introducing the phenyl-tolane compounds with four lateral fluoro substitutions. This helps to improve the temperature stability of the devices using DLFC mixtures.

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