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Liquid Crystals

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INVITED ARTICLE

Dual frequency liquid crystals: a review

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We review the recent progress in developing high performance dual frequency liquid crystal (DFLC) materials. A new figure of merit is derived for evaluating the DFLC performance. The dielectric relaxation and electro-optical properties of several high performance compounds, which possess a positive dielectric anisotropy at low frequencies and a relaxation frequency in the kilohertz region, are presented. Potential applications of these compounds are discussed. Compounds with a negative dielectric anisotropy were also compared and discussed. Two experimental DFLC mixtures were demonstrated with one intended for room temperature operation and another for elevated temperature operation.

Keywords: dual-frequency liquid crystal; dielectric relaxation; figure of merit

1. Introduction

Nematic liquid crystals (NLCs) have been widely employed in numerous electro-optical devices, because the liquid crystal (LC) directors can be reoriented by an external voltage, which, in turn, changes the optical properties. However, in most NLC devices, only the turn-on process can be shortened by increasing the electric field; the turn-off or relaxation process is still governed by the surface anchoring (restoring elastic) energy. For a LC modulator operating at an infrared (IR) wavelength, a thicker cell gap is required in order to achieve the same phase change $\delta = 2\pi d\Delta n/\lambda$, where d is the LC cell gap, Δn is the LC birefringence, and λ is the wavelength. As the LC layer thickness increases, the response time also increases as d^x , where $x = 2$ for the case of strong anchoring and $x \rightarrow 1$ when the anchoring is weak (1–3). The demand for faster response time has brought dual frequency liquid crystals (DFLCs) into the limelight. The frequency reversible dielectric anisotropy makes it possible to align the DFLC molecules along or perpendicular to the electric field direction by varying the frequency of the driving signals (4, 5). This makes it possible to accelerate both the turning-on and turning-off processes by applying a high voltage pulse with different frequencies.

Many electro-optical devices utilising DFLCs have been developed. In the area of displays, a dual frequency cholesteric reflective display (6), a reflective display using dye-doped DFLC gel (7), and a bistable DFLC display have been introduced (8). For telecommunications and photonics, light shutters (9), variable

optical attenuators (10, 11), phase modulators (12, 13), tunable polarisation filters (14), and adaptive optics (15) have been demonstrated. Tunable focus lenses (16, 17) and microwave devices (18) also benefit from DFLCs for improving response time. The fast emergence of DFLC devices raises the demand for developing high performance DFLC materials.

2. Figure of merit of dual frequency liquid crystals

To design new DFLC materials, we need to analyse the governing factors that determine the DFLC response time and operating voltage. Let us use a vertical alignment DFLC cell with a strong anchoring boundary condition as an example. If we neglect the flow effect, the LC director's response time can be calculated as follows (19):

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

and

$$\tau_{off} \sim \frac{\tau_0}{(V_l/V_{th,l})^2 - 1}, \quad (2)$$

where

$$\tau_0 = \gamma_1 d^2 / K_{33} \pi^2. \quad (3)$$

In Equations (1)–(3), V_h and V_l are the driving voltages at high and low frequencies, $V_{th,h}$ and $V_{th,l}$ are the corresponding threshold voltages, γ_1 is the rotational

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viscosity, K_{33} is the bend elastic constant, and d is the cell gap. The response time of a homogeneous alignment DF LC cell has similar forms to those shown in Equations (1)–(3), although the corresponding elastic constant, the threshold voltages, and the frequency for turn-on/off needs to be changed accordingly.

Equations (1)–(3) provide the basis for evaluating the performance of DF LC mixtures. It is helpful to derive a figure of merit (FoM) from the response time in order to evaluate the performance of a LC material (19). In order to achieve a certain phase change, δ , in a homogeneous or homeotropic LC cell, the minimum cell gap is $d = \delta\lambda/2\pi\Delta n$. For such cells, the characterised relaxation time without an external field can be expressed as

$$\tau_0 = \gamma_1 \lambda^2 \delta^2 / \Delta n^2 K_{ii} 4\pi^4, \quad (4)$$

where K_{ii} is the splay (K_{11}) or bend (K_{33}) elastic constant depending on the cell configuration.

It should be clarified that the key reason a DF LC device can get a fast response time is because of the relatively high operating voltage. From the mixture viewpoint, DF LC materials exhibit a larger viscosity than a typical nematic because a DF LC mixture often consists of highly polar positive $\Delta\varepsilon$ LC compounds in a negative $\Delta\varepsilon$ LC host. The dielectric anisotropy of positive LC compounds (e.g. ester compounds) relaxes quickly as the frequency increases, while the negative compounds remain inert to the applied frequency up to the megahertz region. These highly polar positive $\Delta\varepsilon$ compounds are viscous. To compensate for the increased viscosity while obtaining a large gain in response time, we need to apply a high voltage ($V \gg V_{th}$) as shown in Equations (1) and (2). Let us see an example where we need to achieve a 0.5 ms response time for a 2π phase change at $\lambda = 1.55 \mu\text{m}$ with a DF LC mixture. Let us assume the DF LC has the following properties: $\Delta n = 0.25$, $\gamma_1/K_{33} \sim 20 \text{ ms } \mu\text{m}^{-2}$ (similar to that of E7 at room temperature), $\Delta\varepsilon = 6$ at $f = 1 \text{ kHz}$ and $\Delta\varepsilon = -4.5$ at $f = 50 \text{ kHz}$. The minimum cell gap for getting a 2π phase change is $d = 6.2 \mu\text{m}$. However, surface layers are strongly anchored and difficult to reorient. Thus, we choose an $8 \mu\text{m}$ cell gap. From Equation (3), the resulting τ_0 is $\sim 130 \text{ ms}$. In order to shorten this response time to 0.5 ms, a voltage switching ratio $V/V_{th} \sim 16$ is necessary according to Equations (1) and (2). If the threshold voltage is $3 V_{\text{rms}}$, then we need to apply a $48 V_{\text{rms}}$ pulse in order to obtain the targeted response time. If the threshold voltage is $2.5 V_{\text{rms}}$, then the required voltage is dropped to $40 V_{\text{rms}}$. A lower threshold voltage, i.e. larger $|\Delta\varepsilon|$, helps to reduce the switching voltage and is therefore preferred.

To simplify the discussion without losing generality, let us assume the DF LC has an equal $|\Delta\varepsilon|$ at low

and high frequencies, which means $V_{th,h} = V_{th,\ell} = V_{th}$. Under such a circumstance, the response time, both for turn-on and turn-off times, is simplified to:

$$\tau \sim \frac{\gamma_1 d^2 / K_{ii} \pi^2}{(V/V_{th})^2} = \frac{\gamma_1 \lambda^2 \delta^2 V_{th}^2}{\Delta n^2 K_{ii} 4\pi^4 V^2}. \quad (5)$$

If we compare the device performance at the same voltage (say $V = 50 V_{\text{rms}}$), wavelength, and phase change (say, $\delta = 2\pi$) in Equation (5), then the contribution solely from material properties can be evaluated by a new FoM:

$$\text{FoM}_{\text{DFLC}} \equiv \frac{(\Delta n)^2 K_{ii}}{\gamma_1 V_{th}^2}. \quad (6)$$

Similar results can be derived for DF LCs in cells with a large pretilt angle (12). In comparison to the conventional definition for a nematic (20), the FoM of DF LCs involves the V_{th}^2 term in the denominator, where the threshold voltage is defined as $V_{th} = \pi\sqrt{K_{ii}/|\Delta\varepsilon|\varepsilon_0}$, when the driving voltage is sinusoidal (19). A mixture with a higher FoM exhibits a faster response time.

The dielectric anisotropy of DF LCs is frequency dependent. Thus, the threshold voltage and, consequently, the FoM, also depend on the frequency and waveform of the driving voltage. If the driving signal is sinusoidal, the elastic constant in Equation (6) can be cancelled and the FoM leads to:

$$\text{FoM}_{\text{DFLC}} = \frac{(\Delta n)^2 \Delta\varepsilon \varepsilon_0}{\gamma_1 \pi^2}. \quad (7)$$

If the driving signal is not sinusoidal, the Fourier component at various frequencies should also be taken into consideration. The FoM cannot maintain the form as Equation (7) shows. On the other hand, the visco-elastic constant and threshold voltage can be easily measured experimentally. Therefore, Equation (6) is more practical in this sense. As mentioned earlier, if a DF LC mixture has symmetric $|\Delta\varepsilon|$ at low and high frequencies, its V_{th} is the same. However, if the DF LC has asymmetric $|\Delta\varepsilon|$, then its FoM would be somewhat different at low and high frequencies.

The new FoM provides a way to compare the performance of various DF LC mixtures at different operating conditions. It also gives us directions in materials development to achieve a fast response time. Increasing birefringence boosts the FoM effectively and thereby decreases the response time. Low rotational viscosity is always desirable. Large dielectric anisotropy helps to reduce the threshold voltage and therefore is favourable.

The rotational viscosity of LCs decreases exponentially with the increase of operating temperature. On the other hand, the birefringence and dielectric anisotropy decrease as the temperature increases. The combinational effect is still positive in a large temperature range. Therefore, operating the DFCLs at elevated temperatures is a favourable approach from the viewpoint of achieving a fast response time. However, the crossover frequency of DFCLs increases almost exponentially as the temperature increases (5). Of course, we can increase the operating frequency to compensate for the increased crossover frequency at an elevated temperature. However, operating a DFCL device at a too high frequency, say 100 kHz, causes at least two undesirable effects: 1) high power consumption; and 2) dielectric heating.

The power consumption P of a DFCL device is proportional to the operating frequency f , the capacitance of the LC device C , and the applied voltage V as $P = (1/2)fCV^2$. As the operating frequency or voltage increases, the power consumption increases. The consumed power will generate heat and warm up the LC device, which, in turn, causes the crossover frequency to increase. Another negative impact of high frequency operation is on the dielectric heating due to the imaginary part (absorption) of the dielectric constant. The generated heat will raise the temperature of the LC device and then shift the crossover frequency (21, 22). Therefore, it is highly desirable to design a DFCL mixture with a low crossover frequency (say, 1 kHz) and to operate the DFCL device so as not to exceed a certain limit (say, 50 kHz) in a real system.

Such requirements put a bar to the high side of the operating temperature, which is helpful for lowering the viscosity of the DFCL materials. In order to exploit the negative dielectric anisotropy at high frequencies, we need the high driving frequency to be larger than the saturation frequency, where the dielectric relaxation is close to its saturation level. Understanding the relationship between the high driving frequency and the upper limit of the relaxation frequency (or crossover frequency) of the DFCL mixture is therefore essential for optimising the device operation.

3. Relaxation frequency

The relaxation of dielectric permittivity along the long molecular axis can be described by the Debye equation:

$$\varepsilon_{||}(f) = \varepsilon(\infty) + \frac{\varepsilon(0) - \varepsilon(\infty)}{1 + (f/f_r)^2}, \quad (8)$$

when only one relaxation frequency exists. In Equation (8), $\varepsilon(0)$ and $\varepsilon(\infty)$ are the dielectric permittivity at the low frequency and high frequency limits, respectively; f is the driving frequency, and f_r is the relaxation frequency. In most DFCL mixtures, the careful choice of positive compounds ensures that there is only one relaxation frequency. The dielectric permittivity along the short molecular axis is constant when the driving frequency is below 1 MHz. Therefore, the dielectric anisotropy has the same form as Equation (8):

$$\Delta\varepsilon(f) = \Delta\varepsilon(\infty) + \frac{\Delta\varepsilon(0) - \Delta\varepsilon(\infty)}{1 + (f/f_r)^2}, \quad (9)$$

where $\Delta\varepsilon(0)$ and $\Delta\varepsilon(\infty)$ represent the dielectric permittivity at the low frequency and high frequency limits, respectively.

If we set the criteria for the high driving frequency to be higher than the frequency f_h at which the decrease of dielectric anisotropy reaches $x\%$ of its saturation level, i.e. $\Delta\varepsilon(f_h) = \Delta\varepsilon(\infty) + (\Delta\varepsilon(0) - \Delta\varepsilon(\infty)) \cdot (1 - x\%)$, then the critical frequency f_h should satisfy:

$$f_h = f_r \sqrt{\frac{1}{1 - x\%} - 1}. \quad (10)$$

On the other hand, at the crossover frequency f_c ,

$$\Delta\varepsilon(f_c) = \Delta\varepsilon(\infty) + \frac{\Delta\varepsilon(0) - \Delta\varepsilon(\infty)}{1 + (f_c/f_r)^2} = 0. \quad (11)$$

Solving Equation (11), we find:

$$f_r = f_c \sqrt{(|\Delta\varepsilon(\infty)|/|\Delta\varepsilon(0)|)}. \quad (12)$$

Therefore, when dielectric relaxation finishes at $x\%$ we find:

$$f_h = f_c \sqrt{\left| \frac{\Delta\varepsilon(\infty)}{\Delta\varepsilon(0)} \right|} \sqrt{\frac{1}{1 - x\%} - 1}. \quad (13)$$

Equations (10) and (13) show how the choice of high driving frequency sets a limit to the relaxation frequency or crossover frequency of the DFCL mixture. Table 1 shows the limit to relaxation with different saturation criteria $x\%$ when the high driving frequency is set at 30 kHz. If we choose more than 90% decrease in $\Delta\varepsilon$ to be the criteria for choosing a high operation frequency, Equation (10) tells us that f_h should be more than three times f_r , i.e. $f_r < f_h/3$. If the dielectric anisotropy is symmetric at low and high frequency limits, then f_c should also be less than a

Table 1. Upper limit of relaxation frequency f_r with different choices of $x^0\%$ when the high driving frequency f_h is set at 30 kHz.

$x^0\%$	f_r/f_h	f_r
90%	33.33%	10.00
95%	22.94%	6.88
98%	14.29%	4.29

third of f_h . It is known that the relaxation frequency (and the crossover frequency) of a DF LC mixture increases almost exponentially with the increasing temperature. Thus, the selection of high driving frequency puts an upper limit to the operating temperature of the DF LC device, although elevated temperature helps to boost the FoM.

4. Dual frequency liquid crystal compounds

A DF LC mixture is usually composed of two categories of materials (23): 1) Compounds exhibit a positive dielectric anisotropy at low frequencies, but their dielectric anisotropy decreases with the increase of driving frequency. We refer to these compounds as positive compounds. These compounds are responsible for the frequency dependence of the DF LC mixture. 2) Compounds exhibit a negative dielectric anisotropy and their dielectric anisotropy remains almost constant when the driving frequency is below the megahertz range. We refer to these compounds as negative compounds. These compounds ensure that the whole mixture shows a large negative dielectric anisotropy in the high frequency region. Compounds in a DF LC mixture may or may not have a liquid crystalline phase, but at least some compounds should have an enantiotropic nematic phase, so that the DF LC mixture has a wide nematic range.

The crossover frequency, the frequency at which the dielectric anisotropy changes sign, is largely determined by the relaxation frequency of the positive compounds. The relaxation frequency of a positive compound is determined by various factors. Molecular length (24, 25), in particular the length of the rigid core (26), plays a key role in determining the relaxation frequency. However, complexity in molecular interaction makes the relaxation frequency also dependent on various physical conditions, such as the viscosity and order parameter (27).

In order to realise a low relaxation frequency in $\epsilon_{||}$, the employed positive compounds usually have at least three rings (cyclohexane, phenyl, or other ring structure (28)) in the rigid core. Most DF LC compounds

also have an ester-linking group. Ester helps to increase the molecular length and provides a permanent dipole that has components parallel and perpendicular to the principal molecular axis, which will contribute to the dielectric anisotropy at low and high frequencies, respectively. Lateral polar substitutions are included in positive compounds, helping to increase the dielectric anisotropy and mesomorphic properties (23, 28). Various polar groups have been added on one end of the rigid core to increase the dielectric anisotropy at low frequencies.

4.1 Positive compounds

Table 2 lists some high performance positive compounds for DF LCs (29). The rigid core of these compounds is composed of phenyl/cyclohexane rings with at least one ester-linking group. Almost all of these compounds have lateral fluoro substitution on the phenyl ring(s). This helps to improve the mesomorphic properties and increase the dielectric anisotropy, while not increasing the rotational viscosity too much. All of these compounds have a cyano (CN) or isothiocyanato (NCS) terminal group, which helps to enhance both birefringence and dielectric anisotropy.

These positive compounds can be divided into four categories by their rigid core structures: 1) three-ring single ester cyanate; 2) three-ring double-ester cyanate; 3) three-ring single ester isothiocyanate; and 4) four-ring single ester cyanate.

The mesomorphic properties determine the concentration of a compound in a DF LC mixture and also have strong impact on the electro-optical properties of the mixture. The phase sequence and heat fusion enthalpy of the positive compounds are presented in Table 3. All of these compounds are in the crystalline phase at room temperature (23°C). By comparing the melting points of the double ester compounds 3, 4 and 5, we find that the lateral fluoro substitution helps to decrease the melting point and thereby greatly improves the solubility of the compounds. The large heat fusion enthalpies of some compounds limit their solubility in the DF LC mixtures. Homologues and positive compounds with different core structures are necessary to formulate a DF LC mixture with a practically useful nematic range.

The temperature dependent dielectric relaxation of these compounds is the key property for application in DF LC mixtures. The dielectric relaxation of these compounds when doped into a negative $\Delta\epsilon$ LC host mixture was characterised at a series of temperatures. The host mixture, N-2, is commercially available from SliChem (China). Its birefringence is 0.15 (at $\lambda = 589$ nm and 20°C) and its dielectric anisotropy is -4.1

Table 2. Molecular structures and abbreviations of the positive compounds.

Group	Abbreviation	Structure
3-ring single ester CN	CPEP(3F)-3CN	
	PPEP(3F)-3CN	
3-ring double ester CN	PEPEP-5CN	
	PEPEP(3F)-5CN	
	PEP(3F)EP(3F)-5CN	
3-ring single ester NCS	CPEP(3F)-5NCS	
	PPEP(3F)-5NCS	
4-ring single ester CN	CPEPP(3F)-5CN	
	PPEPP(3F)-5CN	

P stands for phenyl ring, C for cyclohexane ring, E for ester, and 3F for the fluoro group at the three-position of the phenyl ring.

Table 3. Phase transition temperatures and heat fusion enthalpies of the positive compounds. Data taken from (29).

Compounds	T_m (°C)	T_c (°C)	ΔH (kcal mol ⁻¹)
1. CPEP(3F)-3CN	100	201	4.7
2. PPEP(3F)-3CN	96	201	5.5
3. PEPEP-5CN	122	240	7.3
4. PEPEP(3F)-5CN	100	214	6.3
5. PEP(3F)EP(3F)-5CN	89	202	6.7
6. CPEP(3F)-5NCS	86	219	5.0
7. PPEP(3F)-5NCS*	88	220	3.2
8. CPEPP(3F)-5CN	105	361	6.9
9. PPEPP(3F)-5CN	91	346	5.9

*PPEP(3F)-5NCS has a smectic phase. The smectic to nematic transition temperature is 175°C. Reprinted with permission from (29). Copyright © 2008, Taylor & Francis Ltd.

(1 kHz, 20°C). The doping ratio is 10 wt%. The solubility of PEPEP-5CN is poor due to its high melting point and large heat fusion enthalpy. Therefore, a binary mixture of PEPEP-5CN (46 wt%) and its homologue PEPEP-3CN (54 wt%) was prepared and then doped in N-2 with 10 wt% concentration.

The parallel permittivity and perpendicular permittivity of the doped mixture were measured using homeotropic and homogeneous cells, respectively. The dielectric permittivity of the host was measured the same way. $\epsilon_{||}$ and ϵ_{\perp} of the host mixture stay constant when the frequency is below 1 MHz. The dielectric permittivity of the compound was obtained by extrapolation. $\epsilon_{||}$ as a function of the frequency of

each compound was fitted to the Debye equation and the fitted curves agree well with the experimental data. The relaxation frequency increases with the temperature almost exponentially (5):

$$f_r = A \exp(-E/kT), \quad (14)$$

where A is a material constant, k is the Boltzmann constant, E is the activation energy, and T is the thermal dynamic temperature. The activation energy is obtained by fitting the relaxation frequency versus temperature data to Equation (14).

Figure 1 shows the temperature dependent relaxation frequency of the positive compounds studied. The rigid core structure, which has the strongest impact on molecular length, plays the most important role in determining the relaxation frequency. The four-ring single ester CN compounds show the lowest relaxation frequency. The three-ring single ester NCS compounds and the three-ring double ester CN compounds exhibit similar relaxation frequencies, all higher than the four-ring single ester CN compounds. The three-ring single ester CN compounds show the highest relaxation frequencies among the compounds investigated.

Table 4 lists the dielectric anisotropy at low and high frequency limits, relaxation frequencies, and the activation energy of the nine positive compounds studied. The three-ring NCS compounds exhibit the smallest dielectric anisotropy at low frequency. The cyano compounds show a much larger $\Delta\epsilon$ because of the strong dipole moment of the CN polar group. The fluoro substitutions contribute to the dielectric anisotropy and help to lower the melting point, but also increase the rotational viscosity.

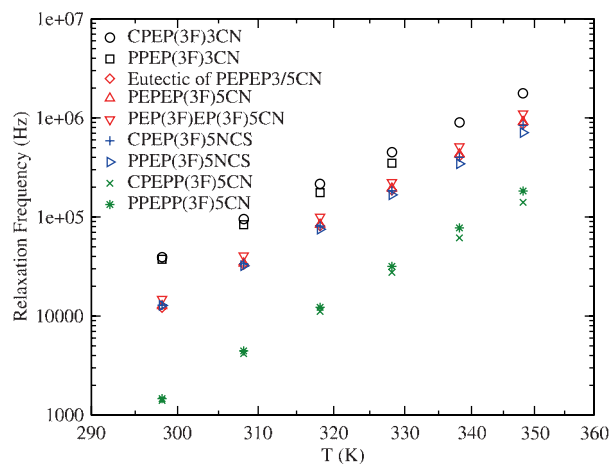


Figure 1. Relaxation frequency as a function of temperature of the positive compounds. Note that the relaxation frequency is on a logarithmic scale, and the temperature is in Kelvin and on a reciprocal scale. Reprinted with permission from (29). Copyright © 2008, Taylor & Francis Ltd.

Table 4. Measured dielectric relaxation properties, relaxation frequency (f_r), and activation energy (E) of the positive compounds. Reprinted with permission from (29). Copyright © 2008, Taylor & Francis Ltd.

Compounds	$\Delta\epsilon(0)$, 25°C	$\Delta\epsilon(\infty)$, 25°C	f_r (kHz), 25°C	E (meV)
1. CPEP(3F)-3CN	41.5	-4.3	39.2	677
2. PPEP(3F)-3CN	43.5	-5.5	37.4	623
3. PEPEP-3/5CN binary	45.0	-4.4	12.2	759
4. PEPEP(3F)-5CN	56.5	-6.3	12.7	761
5. PEP(3F)EP(3F)-5CN	69.1	-4.0	14.8	776
6. CPEP(3F)-5NCS	20.3	-1.7	12.9	749
7. PPEP(3F)-5NCS	21.4	-2.6	12.8	720
8. CPEPP(3F)-5CN	33.6	-3.5	1.4	817
9. PPEPP(3F)-5CN	35.6	-5.3	1.5	865

The response time of a DFCLC device highly depends on the birefringence (through the cell gap effect) and the visco-elastic coefficient of the DFCLC. The birefringence of most positive compounds was measured in their nematic phase despite their high melting temperatures. The birefringence of PPEP(3F)-5NCS was extrapolated by the guest-host method because of its high smectic-to-nematic transition temperature. The birefringence as a function of reduced temperature (T/T_c) is visualised in Figure 2. The LC birefringence depends mostly on the π electron conjugation length (30, 31). Therefore, compounds with a cyclohexane ring exhibit a lower birefringence than similar compounds with a phenyl ring. Similarly, the isothiocyanate compounds exhibit a higher birefringence than the corresponding cyano compounds. To give a more realistic comparison, the birefringence exhibited by the compounds at a reduced temperature of 0.72, or in other words at 25°C when

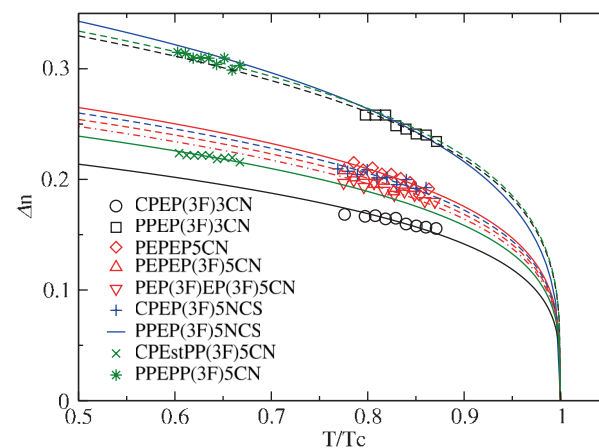


Figure 2. Birefringence of the positive compounds as a function of reduced temperature T/T_c . T and T_c are both Kelvin temperatures. Reprinted with permission from (29). Copyright © 2008, Taylor & Francis Ltd.

Table 5. Δn exhibited by the positive compounds at 25°C when employed in a nematic mixture with clearing point 140°C; γ_1/K_{11} of the E44 doped with 10% compound at 25°C. Reprinted with permission from Ref. (29). Copyright © 2008, Taylor & Francis Ltd.

Compounds	Δn at 25°C	γ_1/K_{11} (ms μm^{-2}) (25°C)
1. CPEP(3F)-3CN	0.184	28.7
2. PPEP(3F)-3CN	0.284	29.8
3. PEPEP-5CN	0.228	32.3
4. PEPEP(3F)-5CN	0.219	32.1
5. PEP(3F)EP(3F)-5CN	0.213	28.9
6. CPEP(3F)-5NCS	0.224	23.5
7. PPEP(3F)-5NCS	0.290	24.6
8. CPEPP(3F)-5CN	0.206	24.7
9. PPEPP(3F)-5CN	0.288	31.4
10. E44	0.242	23.1

functioning in a nematic mixture with a clearing point of 140°C, is presented in Table 5. The effect of the positive compounds on the visco-elastic coefficients was evaluated by doping them into E44 (Merck) and observing the change in the visco-elastic constant brought by the dopants. The results are also listed in Table 5. The rotational viscosity depends on the moment of inertia of the LC compound, the molecular conformation, and the inter-molecular interactions (32). The NCS compounds and CPEPP(3F)-5CN bring the least increase to γ_1/K_{11} , while PPEPP(3F)-5CN and the double ester compounds cause a significant increase.

These experimental results shed light on the optimal use of these compounds. The four-ring single ester cyano compounds exhibit the lowest relaxation frequencies and a large dielectric anisotropy. These compounds are therefore suitable for formulating DF LC mixtures operating at elevated temperatures to benefit from the greatly reduced visco-elastic constant. The three-ring single ester isothiocyanate compound exhibits a low relaxation frequency, a small visco-elastic coefficient, and a high birefringence. They are suitable for high performance DF LC mixtures operating at room temperature. The three-ring double ester CN compounds exhibit a large dielectric anisotropy, similar to the relaxation frequency of the three-ring single ester NCS compounds, but suffer from a relatively low birefringence and relatively large visco-elastic coefficient. They can be utilised in DF LC mixtures to achieve a large dielectric anisotropy. The three-ring single ester CN compounds show a large dielectric anisotropy and a moderate birefringence, but their relaxation frequencies are the highest among the compounds we compared. These compounds can be used in DF LC mixtures that require a large dielectric anisotropy and high birefringence.

4.2 Negative compounds

The negative compounds are employed in DF LC mixtures in order to maintain a large negative dielectric anisotropy at high frequencies. In most DF LC mixtures, the negative compounds make up the most part (~70 wt%). Therefore, high performance negative $\Delta\epsilon$ LC compounds are very important to the DF LC mixtures.

In most popular negative $\Delta\epsilon$ LC compounds, the permanent dipole perpendicular to the long molecular axis is bestowed by neighbouring fluoro substitutions on phenyl rings (33). Many negative LC compounds have been developed for display applications (34–36). Compounds with one or two phenyl rings exhibit a fairly low birefringence ($\Delta n < 0.15$) (33) and therefore are not attractive for IR applications. The terphenyl compounds, some of which are shown in Table 6, show a modest birefringence ($\Delta n \sim 0.23$) (33, 37–39), but their rotational viscosity is relatively high, as shown in Table 6. We need a better material with a higher Δn and lower viscosity.

In order to achieve higher birefringence, tolane and phenyl tolane compounds have been considered (37, 40–42), some of which are shown in Table 7. The long π -electron conjugation leads to a high birefringence ($\Delta n > 0.3$). Tolane compounds, with neighbouring fluoro substitution on the phenyl ring connected to the alkoxy end, show a high birefringence, large dielectric anisotropy, and relatively low melting temperature, and are therefore favoured for high performance DF LC mixtures. The phenyl tolane compounds, which show an even higher birefringence ($\Delta n > 0.35$), are also preferable. However, they either have a relatively small dielectric anisotropy or have a high melting point. Therefore, their possible adoption ratio in DF LC mixtures is limited.

5. Dual frequency liquid crystal mixtures

For demonstration purposes, we have prepared two experimental DF LC mixtures aiming at room temperature and elevated temperature operation, respectively. We will discuss their composition and physical properties in the following sections.

5.1 High performance DF LC mixture for room temperature

An experimental DF LC mixture, designated as DF-2, was formulated for room temperature operation using the three-ring single ester NCS and CN compounds (43). The electro-optical properties of this mixture are shown in Table 8. This mixture is also favoured for its low dielectric heating.

Table 6. Molecular structures and physical properties of some terphenyl compounds.

	Phase sequence	$\Delta\epsilon$	Δn	γ_1
PP(23F)P2-3	C 73 N 115.2 I	-2.5	0.233	90
PP(23F)P(23F)3-4	C 85 N (50.5) I	-5.5	0.201	277
PP(23F)P(23F)5-O2	C 92.5 N 122.3 I	-5.9	0.199	N/A
P(23F)PP(23F)P5-5 [†]	C 88 N 89.2 I	-4.3	0.156	210

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Table 7. Molecular structures and properties of some tolane and phenyl tolane compounds.

	Phase sequence	$\Delta\epsilon$	Δn
PTP(23F)5-O2	C 57 N 61 I	-4.4	0.25
PPTP(23F)5-O2 [†]	C 116 N 222 I	-6.8	0.35
PP(23F)TP3-3*	C 96 N 190 I	-1.29	0.32
P(23F)TP(23F)5-O2 [†]	C 75 N 194 I	-8.5	0.32

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Table 8. Electro-optical properties of DF-2.

Δn	γ_1/K_{11} (ms μm^{-2})	V_{th}	FoM _{DFLC}	$\Delta\epsilon(0)$	$\Delta\epsilon(\infty)$	Crossover frequency (kHz)
0.27	17.8	2.2	0.85	7.5	-4.1	10

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5.2 High performance DF LC mixture for elevated temperatures

A super low crossover frequency DF LC mixture was developed for operating at elevated temperatures to take advantage of the greatly reduced visco-elastic constant (44). Such a low crossover frequency was realised by employing the four-ring single ester CN compounds. Tolane and phenyl tolane compounds with negative dielectric anisotropy were chosen as the negative components. The electro-optical properties of the mixture are listed in Table 9.

As the temperature increases, the visco-elastic constant of the mixture decreases substantially. Even though the crossover frequency increases almost exponentially with the increase of temperature, the initially ultra-low crossover frequency makes it still possible to operate the mixture at high temperatures and enjoy the benefit of greatly reduced rotational viscosity. The frequency of the high frequency signal to drive the DF LC mixture as a negative $\Delta\epsilon$ LC remains low enough when the operating temperature reaches $\sim 50^\circ\text{C}$. During experiments, we used square waves to drive the mixture. Therefore, the effective $\Delta\epsilon$ at a low frequency at low temperatures should be lower than the value shown in Table 9 because of the high frequency components in the driving signal, resulting in a higher threshold voltage in this case.

5.3 Performance of the DF LC mixtures

The FoM of the two experimental DF LC mixtures increases as the operating temperature increases in a wide temperature range that is not too close to the clearing point. On the other hand, the crossover frequency increases almost exponentially with the increase of temperature, which puts an upper limit on the operating temperature and thereby on the maximum achievable FoM. In Section 2, we learnt how the choice of high driving frequency limits the crossover and relaxation frequency of the DF LC mixture. For simplicity of discussion, let us set more than 90% of total decrease in dielectric anisotropy as the criteria for

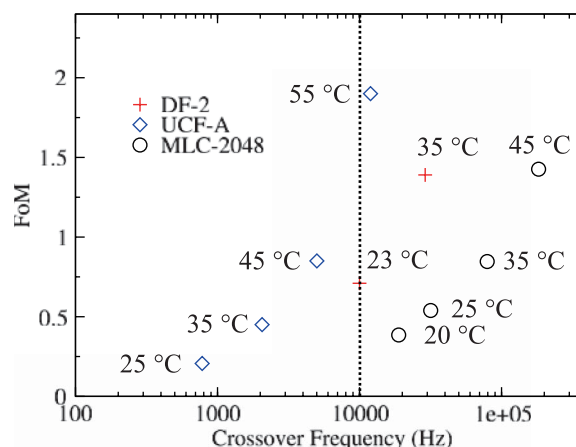


Figure 3. FoM versus crossover frequency of DF-2, UCF-A, and Merck MLC-2048.

a high driving frequency. When the difference between low frequency and high frequency dielectric anisotropy is not very large, we can roughly neglect this difference. Therefore, the crossover should be less than a third of the high driving frequency. This makes it possible to compare the FoM that can be achieved by different DF LC mixtures.

Figure 3 displays the FoM versus crossover frequency of DF-2, UCF-A, and Merck MLC-2048. This figure tells us that the upper limit of FoM can be achieved using each mixture. If we choose the high driving frequency to be 30 kHz, the crossover frequency of the DF LC should be less than 10 kHz. Under this restriction, MLC-2048 does not work appropriately even at 20°C . It should be operated at a lower temperature, which implies an even lower performance, or the high operating frequency should be raised, which will raise the cost of driving circuit and power consumption. DF-2 is just barely drivable at 23°C with its FoM much higher than that of MLC-2048. On the other hand, UCF-A can be operated even at 50°C . If high temperature operation is not an issue, UCF-A can achieve the highest FoM of all three mixtures compared. However, if the operating temperature is restricted to room temperature, then DF-2 is the best choice in terms of response time.

Table 9. Electro-optical properties of DF LC-A.

	25°C	35°C	45°C	55°C
Δn	0.292	0.288	0.286	0.282
γ_1/K_{11} ($\text{ms } \mu\text{m}^{-2}$)	31.88	18.1	12.89	8.88
V_{th}	3.60	3.19	2.73	2.17
FoM_{DFLC}	0.21	0.45	0.85	1.90
$\Delta\epsilon(0)$	6.48	6	5.39	5
$\Delta\epsilon(\infty)$	-4.13	-3.89	-3.68	-3.45
Crossover frequency (kHz)	0.78	2.06	5.01	11.95

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6. Conclusion

The ever-increasing need for faster response time in LC electro-optical devices generates a strong demand for high performance DF LC materials. Several high performance positive and negative compounds were developed and two experimental DF LC mixtures with promise for achieving a fast response time were formulated. Operating a DF LC device at an elevated

temperature benefits substantially from reduced viscosity. However, this approach is ultimately limited by the crossover frequency, which increases exponentially with the increased temperature. In order to further enhance the performance of DFCLC mixtures, new compounds need to be developed. For DFCLC mixtures operating at room temperature, positive compounds with a higher birefringence, lower rotational viscosity, and larger dielectric anisotropy, while keeping a low relaxation frequency, are desired. For DFCLC mixtures intended for elevated temperature operation, positive compounds with higher birefringence, lower viscosity and smaller activation energy are preferred. In either case, negative compounds with higher birefringence, larger dielectric anisotropy, and lower viscosity are critically needed.

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