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Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

High performance dual frequency liquid crystal compounds and mixture for operation at elevated temperature

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Online publication date: 10 December 2010

To cite this Article Xianyu, Haiqing , Liang, Xiao , Sun, Jie and Wu, Shin-Tson(2010) 'High performance dual frequency liquid crystal compounds and mixture for operation at elevated temperature', Liquid Crystals, 37: 12, 1493 — 1499

To link to this Article: DOI: 10.1080/02678292.2010.528803

URL: http://dx.doi.org/10.1080/02678292.2010.528803

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Liquid Crystals,
Vol. 37, No. 12, December 2010, 1493–1499

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(*Received 9 August 2010; final version received 29 September 2010*)

Dual frequency liquid crystal (DFLC) compounds with high birefringence and ultra-low crossover frequency have been developed. The long conjugated rigid core structure gives these compounds a high birefringence (0.3–0.4) and ultra-low Debye relaxation frequency. Using these compounds we have formulated a new DFLC mixture, designated UCF–02, for operation at elevated temperatures. The birefringence of the mixture is greater than 0.3 at 25°C and $\lambda = 633$ nm. Their initial ultra-low crossover frequency allows them to be used at elevated temperatures and significantly improves their utility.

Keywords: dual-frequency liquid crystal; fast response; high birefringence; dielectric relaxation

1. Introduction

Liquid crystals (LCs) have commonly been used in direct-view [1] and projection displays in the visible spectral region [2]. In the mid-1980s, certain linearly conjugated LCs were found to exhibit relatively high birefringence and weak absorption in some infrared (IR) regions [3–5]. Since that time a number of useful IR photonic devices have been developed, including dynamic scene projectors [6], laser beam steering [7] and adaptive optics [8]. The major deficiency of these IR LC devices has been their response time. Longer wavelengths demand a thicker cell gap, but this significantly increases the response time. In order to achieve fast response in IR devices a number of approaches have been developed, for example optimal operation temperature [9], high birefringence, the use of low viscosity LC materials [10–12], and overdrive and undershoot voltage methods [13, 14].

Among these approaches, dual frequency liquid crystals (DFLCs) [15, 16] offer a unique advantage in that they are able to accelerate both rise and decay processes. A DFLC mixture usually consists of LC compounds of both positive and negative dielectric anisotropy ($\Delta\varepsilon$). Compounds of positive dielectric anisotropy exhibit a strong Debye relaxation frequency, whereas their negative analogues are basically independent of frequency up to the megaHertz region. As a result, the $\Delta\varepsilon$ of a DFLC mixture gradually changes from positive at low frequencies ($\sim$1 kHz), to zero, and then becomes negative as the frequency increases at, say, 30 Hz. The frequency at which $\Delta\varepsilon = 0$ is described as the crossover frequency. In practical applications we can drive the device using a low frequency voltage burst to obtain a rapid rise time. On the other hand, during relaxation we can apply a voltage burst at high frequency to assist the decay process. In this manner both rapid rise and rapid decay times are achieved [17]. This characteristic is particularly helpful in speeding the response time of IR devices.

By analysing the response time we have devised a Figure of Merit (FoM) as a measure of the optimisation of performance of a DFLC device [18]:

$$\mathrm{FoM}_{\mathrm{DFLC}} \equiv \frac{(\Delta n)^2 K_{ii}}{\gamma_1 V_{\mathrm{th}}^2} = \frac{(\Delta n)^2 \Delta\varepsilon\varepsilon_0}{\gamma_1 \pi^2}, \qquad (1)$$

where Δn is the birefringence, K_{ii} the elastic constant corresponding to the LC alignment (K_{11} for homogeneous alignment and K_{33} for vertical alignment), γ_1 is the rotational viscosity, and V_{th} and $\Delta\varepsilon$ are, respectively, the threshold voltage and dielectric anisotropy at operating frequency. To enhance the FoM, high birefringence, low rotational viscosity, and large dielectric anisotropy are required. On the other hand, the formulation and operation of DFLC material is highly dependent on the crossover frequency. High crossover frequency demands a high frequency driving signal to address the DFLC, and in turn this increases the complexity and cost of the driving circuits, power consumption [18] and dielectric heating [19, 20].

As mentioned earlier, a DFLC mixture consists of compounds of positive and negative $\Delta\varepsilon$. The dielectric relaxation frequency of the positive compounds is the more important factor in determining the

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ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678292.2010.528803
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crossover frequency. Most positive compounds contain ester linking group(s) [21–23]. Ester linkages help to increase the rigid core length and they provide a dipole moment with projections both parallel and perpendicular to the direction of the long molecular axis. The orthogonal components of the dipole moment contribute to dielectric anisotropy at low and high frequencies, respectively. However, an ester linking group breaks the π-electron conjugation and in consequence limits the birefringence of compounds of positive $\Delta\varepsilon$.

We have recently developed DFLCs of ultra-low crossover frequency by the use of four-ring single ester cyanato compounds [24]. The long rigid core gives these compounds low relaxation frequency but the ester linking group limits their birefringence. The present study has shown that by replacing the ester link with a carbon–carbon triple bond the π-electron conjugation can be elongated without disturbing the low relaxation frequency [25]. In order to achieve higher birefringence, while maintaining an ultra-low relaxation frequency, we have replaced the ester group at the core of the four-ring single ester cyanato compounds with a conjugated carbon–carbon triple bond, and have derived a number of novel ultra-low relaxation frequency DFLC compounds of high birefringence. Their physical properties have been characterised and the results serve to validate the design concept. A DFLC mixture of high birefringence ultra-low crossover frequency has been formulated using these compounds and is found to exhibit a high FoM at elevated temperatures.

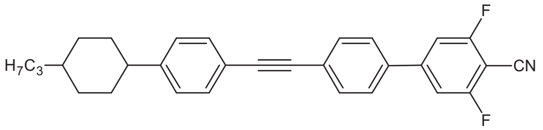
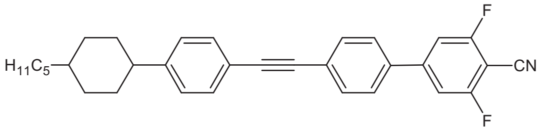
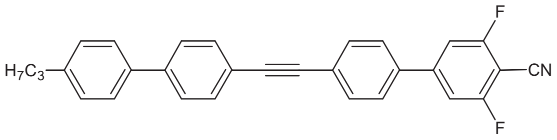
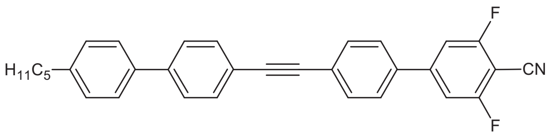
2. Properties of the novel compounds

Table 1 summarises the molecular structure of the compounds of high birefringence, ultra-low relaxation frequency and positive $\Delta\varepsilon$ which have been investigated. P denotes a phenyl ring, C a cyclohexanyl ring, T a carbon–carbon triple bond and CN a cyanato group. The symbol (3,5) indicates substituents in the 3 and 5 positions of a phenyl ring. The number preceding CN is the length of the alkyl chain at the opposite end of the molecule, and two digits separated by/ denote alternatives. The synthetic route is illustrated in Figure 1.

2.1 Mesomorphic properties

The DFLC material operates in the nematic phase. The mesomorphic properties of the individual compounds affect their solubility and adoption ratio in the DFLC mixture. The phase sequence and heat fusion enthalpy of these compounds were measured using a Q100 differential scanning calorimeter (DSC; TA

Table 1. Molecular structure and mesomorphic properties of the high birefringence ultra-low relaxation frequency compounds.

Compound	Structure	T_m (°C)	T_c (°C)	ΔH (cal mol^{-1})
CPTPP(3,5F)-3CN		136	343	5121
CPTPP(3,5F)-5CN		125	330	4971
PPTPP(3,5F)-3CN		224	346	7054
PPTPP(3,5F)-5CN		183	331	6697

Note: The symbols describing the compounds are explained in the text.

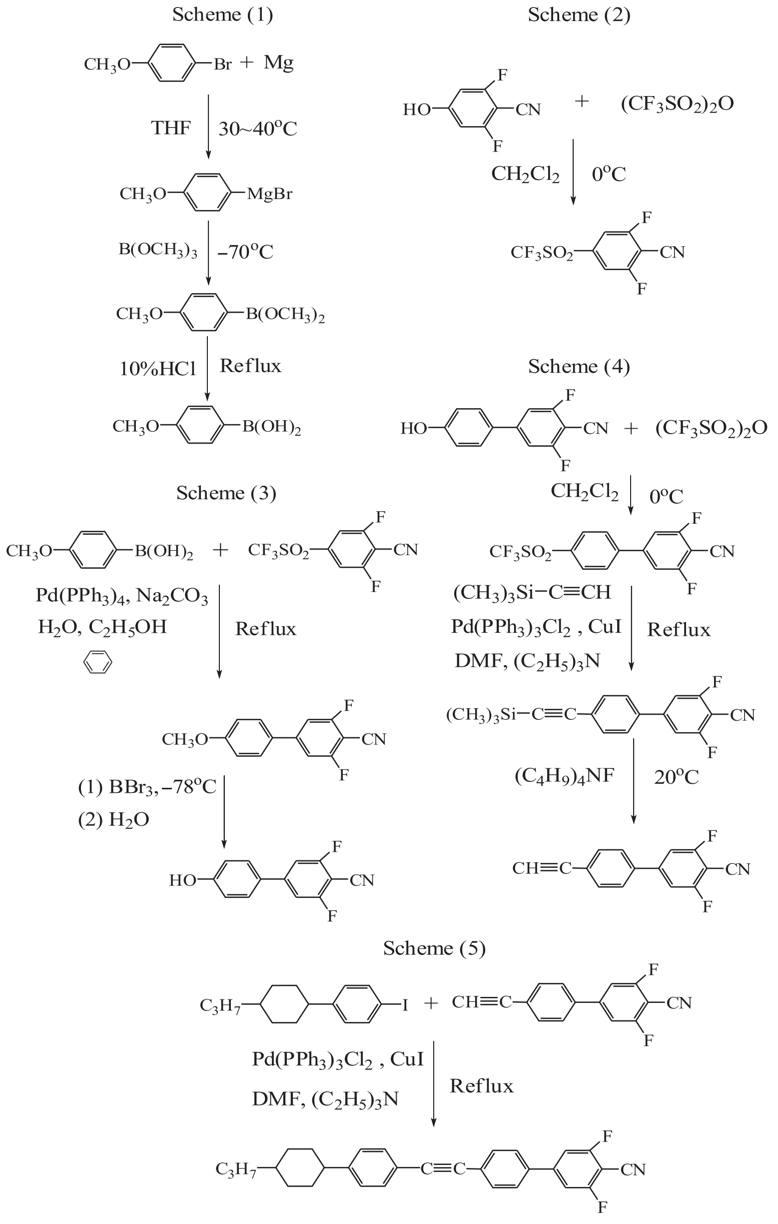


Figure 1. Schematic illustration of the synthesis route.

Instruments Inc.), and the results are summarised above in Table 1. Due to their long rigid core these compounds have high melting temperatures. Compounds with four phenyl rings, e.g. PPTPP(3,5F)-3/5CN, exhibit higher melting temperature and larger heat fusion enthalpy than those containing a single cyclohexanyl ring, e.g. CPTPP(3,5F)-3/5CN. For compounds with a similar rigid core structure, a longer alkyl chain helps to reduce melting temperature and heat fusion enthalpy. A high melting temperature and large heat fusion enthalpy limits the adoption ratio of PPTPP(3,5F)-3/5CN in DFLC mixtures.

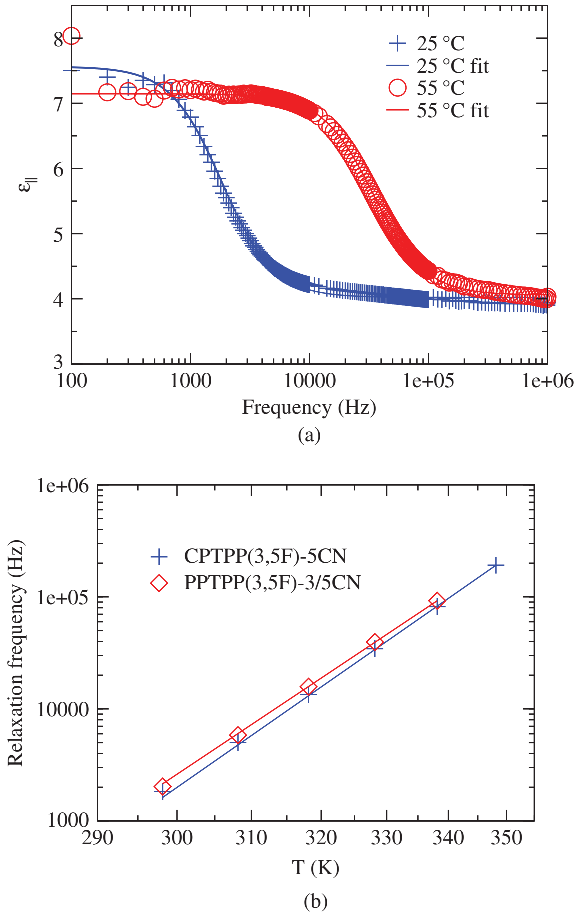
2.2 Dielectric relaxation

On account of their high melting temperature, the new positive $\Delta\varepsilon$ compounds were doped at 10 wt% into a negative host (LX–2, SliChem) before measuring their dielectric relaxation. Due to their identical core structure, CPTPP(3,5F)-3CN and CPTPP(3,5F)-5CN were expected to exhibit similar dielectric relaxation frequency, and therefore only CPTPP(3,5F)-5CN was assessed. The high heat fusion enthalpy limited the solubility of PPTPP(3,5F)-3/5CN in LX–2 and a eutectic mixture of the two compounds was therefore doped into the host. The dielectric relaxation of the positive compounds was measured in LX–2 over a range of temperatures. The dielectric permittivity of each mixture was derived by comparing the capacitance of an empty cell and one containing the mixture [26]. The parallel and perpendicular permittivities were measured using a homogeneous and a homeotropic aligned cell, respectively. The Debye model was employed to fit the relaxation frequency and dielectric permittivity at low and high frequency limits.

Figure 2(a) shows the parallel dielectric permittivity, measured as a function of driving frequency at 25°C and 55°C for the CPTPP(3,5F)-5CN doped mixture. Both the experimental data and fitting to the Debye equation are illustrated, and the fit is seen to be good at 25°C. If the ionic impurity effect at low frequency is excluded, the Debye equation also provides a good fit at elevated temperatures, and the 55°C data serve as an example. The perpendicular dielectric permittivity of the doped mixtures is constant when the frequency is below 1 MHz and a high temperature ionic effect is considered. Figure 2(b) shows the dielectric relaxation frequency as a function of temperature for these compounds. The relaxation frequency increased almost exponentially with increased temperature [16]:

$$f_c = A \exp\left(-E/kT\right), \tag{2}$$

where A is a material constant, k is the Boltzmann constant, E is the activation energy and T is the thermodynamic temperature. The activation energy of CPTPP(3,5F)-5CN and PPTPP(3,5F)-3/5CN were 836 and 817 meV, respectively. The parallel and perpendicular dielectric permittivities of the compounds were derived by extrapolation and the dielectric anisotropy was derived for both low and high frequency limits. The results are summarised in Table 2.



(a)

(b)

Figure 2. (a) Parallel permittivity of CPTPP(3,5F)-5CN (10 wt%) doped LX-2 as a function of frequency at 25°C and 55°C. The fitting curve using Debye model is also shown. (b) Relaxation frequency as a function of temperature of CPTPP(3,5F)-5CN and PPTPP(3,5F)-3/5CN in LX-2 (colour version online).

2.3 *Birefringence and viscoelastic constant*

Due to their relatively low melting temperature, the birefringence of CPTPP(3,5F)-5CN and PPTPP(3,5F)-5CN were measured. These compounds were filled using a capillary into indium–tin oxide glass cells with anti-parallel alignment layers. The cells were then placed between two crossed polarisers, with their optic axis 45° to the polariser axes. The transmittance of the system as a function of applied voltage was measured at a series of temperatures using a 633 nm He–Ne laser, and the optical birefringence deduced as a function of reduced temperature, as shown in Figure 3(a). CPTPP(3,5F)-5CN exhibited $\Delta n > 0.3$, and the corresponding figure for PPTPP(3,5F)-5CN was ~0.4. The latter has longer conjugation length and therefore exhibits greater birefringence.

Table 2. Dielectric relaxation properties of the new compounds over a range of temperatures.

	25°C	35°C	45°C	55°C	65°C
CPTPP(3,5F)-5CN					
$\Delta\varepsilon(0)$	29.3	27.2	24.9	23.2	21.3
$\Delta\varepsilon(\infty)$	−3.4	−3.6	−3.9	−4.4	−4.8
f_r (kHz)	2.0	5.8	15.8	39.5	92.3
PPTPP(3,5F)-3/5CN					
$\Delta\varepsilon(0)$	37.4	36.5	34.2	31.8	29.2
$\Delta\varepsilon(\infty)$	0.8	0.8	0.5	−0.1	−0.7
f_r (kHz)	1.8	5.0	13.4	34.5	81.8

Notes: f_r indicates dielectric relaxation frequency; the other symbols are explained in the text.

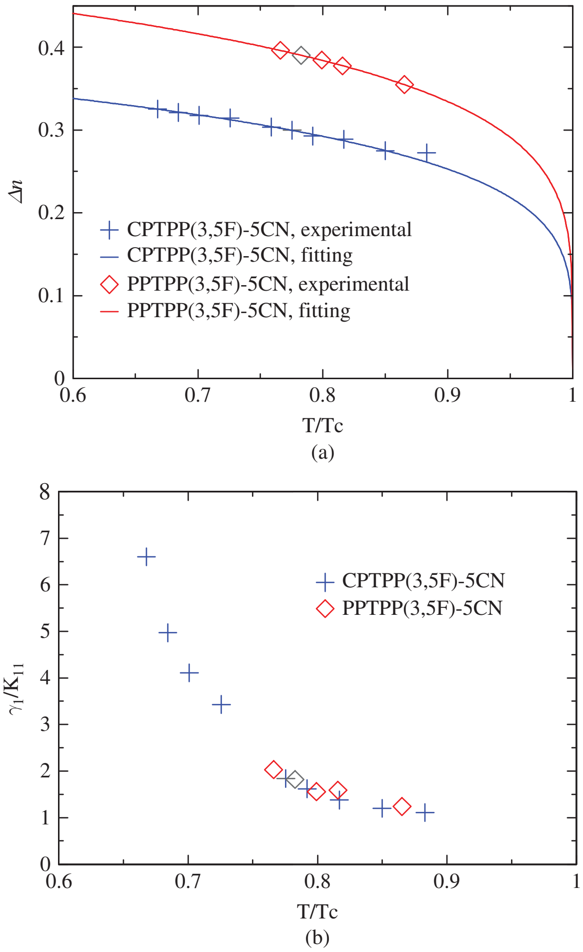


Figure 3. (a) Measured birefringence and (b) viscoelastic coefficient of CPTPP(3,5F)-5CN and PPTPP(3,5F)-5CN as a function of reduced temperature (colour version online).

The viscoelastic constant of the two compounds was also measured, and the results are presented in Figure 3(b). As the temperature increased, the viscoelastic constant decreased. This trend is to be expected for CPTPP(3,5F)-3CN on account of its relatively low melting point and wide nematic range.

2.4 *Absorption spectra*

The photostability of a LC material is vital in the application and fabrication of electro-optical devices. The absorption properties of the C/PTPP(3,5F)-xCN series were investigated. The high melting temperature and large heat fusion enthalpy reduced the solubility of the new compounds in many solvents. Among the solvents examined, only dichloromethane (DCM) was found to dissolve sufficient amounts of these compounds for their spectral measurement. CPTPP(3,5F)-5CN and PPTPP(3,5F)-5CN were dissolved in DCM at a concentration of ~4 × 10^{-5} mol L^{-1} and filled into a 5 mm thick quartz cell. A similar quartz cell was filled with pure DCM for baseline measurement, and assessment conducted using a Cary 500 spectrophotometer. DCM exhibits strong absorption at wavelengths below 240 nm and also shows absorption peaks in the region 1100–2000 nm. Only the data between 350 nm and 1100 nm were therefore relevant. Both compounds showed no obvious absorption in the range 450–1100 nm; their UV absorption is illustrated in Figure 4. The long π-electron conjugation shifts the absorption tail of the compounds towards longer wavelengths.

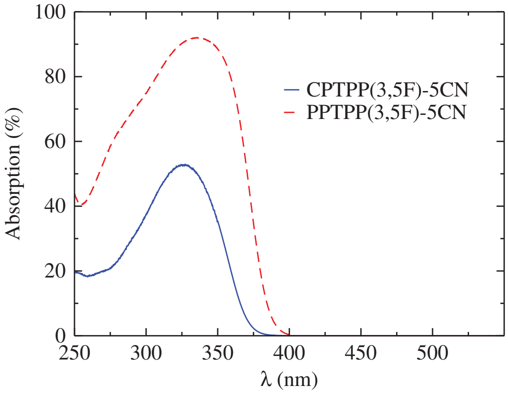


Figure 4. UV absorption of CPTPP(3,5F)-5CN and PPTPP (3,5F)-5CN (colour version online).

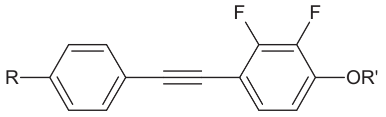
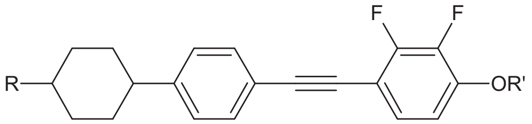
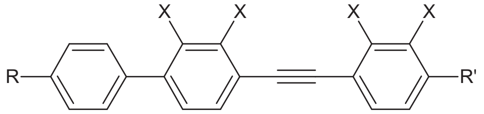
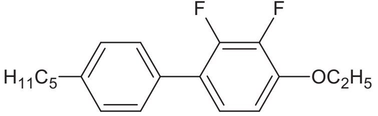
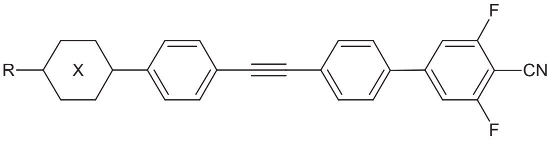
PPTPP(3,5F)-5CN has a longer conjugation length and therefore showed an absorption tail up to 400 nm, whereas CPTPP(3,5F)-5CN had a shorter absorption tail, up to 370 nm. The long UV absorption tails of the new positive $\Delta\varepsilon$ compounds may reduce their stability under UV exposure, implying that these compounds may therefore not be suitable for UV applications. Materials using them may similarly require to avoid UV exposure during processing and device fabrication. On the other hand, the compounds are stable at wavelengths longer than 450 nm.

3. Performance in mixtures

A DFLC mixture with high birefringence and ultra-low crossover frequency, UCF–02, was formulated based on the new positive $\Delta\varepsilon$ compounds. The composition of the mixture is listed in Table 3. Tolane and phenyl tolane compounds with negative $\Delta\varepsilon$ were adopted due to their high birefringence. On account of their high melting temperature and large heat fusion enthalpy, the practicable ratio of PPTPP(3,5F)-3CN and PPTPP(3,5F)-5CN was somewhat restricted.

The dielectric relaxation and electro-optical properties of the mixture were determined and the results are summarised in Table 4. The crossover frequency of UCF–02 was only 1.2 kHz at 25°C, and was even lower than 10 kHz at 45°C, making it possible to

Table 3. Composition of the high birefringence ultra-low crossover frequency DFLC mixture, UCF–02.

	Molecular structure	
Tolane		12%
Cyclohexanyl tolane		25%
Phenyl tolane	 R, R′: alkyl or alkoxy end–groups; X: at least 2 neighbouring X atoms on the phenyl rings are fluorine, the others are hydrogen.	40%
PP(2,3F)-5O2		5%
C or PPTPP(3,5F)-xCN	 R: C_3H_7 or C_5H_{11};  : phenyl or cyclohexanyl	20%

operate it at elevated temperatures. In comparison, the crossover frequency of MLC–2048 was already 18.9 kHz at 20°C; as the temperature increased, its crossover frequency would be increased exponentially, making it unsuitable for elevated temperatures.

We also measured the birefringence, viscoelastic constant and FoM of UCF–02 over a range of temperatures, and the results are also shown in Table 4. The properties of MLC–2048 are included for comparison.

The rotational viscosity of a liquid crystal decreases as the temperature increases, thereby substantially improving the response time. Figure 5 illustrates the FoM of UCF–02 *vs* crossover frequency. UCF–02 exhibited a lower crossover frequency at 55°C than that of MLC–2048 at 20°C. As mentioned earlier, the maximum achievable FoM is limited by the crossover frequency, and from Figure 5 it is seen that under a similar crossover frequency limitation UCF–02 can

Table 4. Dielectric relaxation and electro-optical properties of UCF–02.

	UCF–02				MLC–2048
T (°C)	25	35	45	55	20
Δn	0.305	0.299	0.295	0.294	0.210
γ_1/K_{11} (ms μm^{-2})	27.2	16.8	11.1	8.8	18.97
$\mathrm{FoM}_{\mathrm{DFLC}}$ (μm^2 s V^{-2})	0.63	1.06	1.55	2.11	0.385
$\Delta\varepsilon$ (0)	4.98	4.51	4.21	4.22	2.87
$\Delta\varepsilon$ (∞)	−3.12	−2.92	−2.76	−2.57	−3.35
f_c (kHz)	1.2	3.2	7.7	17.0	18.9

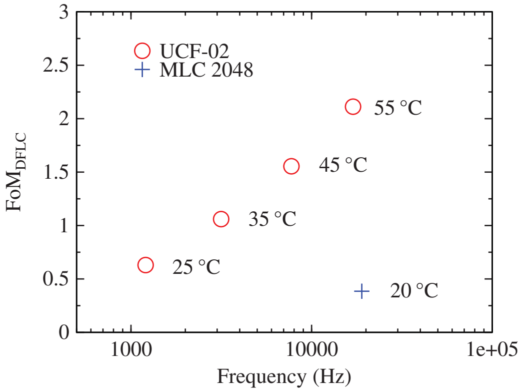


Figure 5. Figure of Merit vs. crossover frequency of UCF-02 and MLC-2048.

achieve a response time more than five times faster than MLC–2048.

4. Conclusions

Novel compounds with high birefringence, positive $\Delta\varepsilon$ and ultra-low relaxation frequency have been developed for the formulation of DFLC mixtures. Their long π-electron conjugation contributes to the high birefringence of these compounds, and the long rigid core provides ultra-low relaxation frequency. Utilising these compounds a DFLC mixture with high birefringence ultra-low crossover frequency, UCF–02, has been formulated. When operated at the elevated temperature enabled by the ultra-low crossover frequency, this mixture exhibited a much better performance than that of MLC–2048. The new mixtures help to reduce the response time of IR LC devices where elevated temperature operation is demanded.

On the other hand there are a number of concerns regarding the application of these new compounds. The long conjugation length shifts their UV absorption tails into a region of longer wavelength. These compounds are therefore more vulnerable to UV irradiation than are ester-based compounds, and electro-optical devices making use of them may need to avoid radiation at wavelength shorter than 400 nm during their fabrication and operation. Their high melting temperature and large heat fusion enthalpy also limits the adoption ratio of these compounds, particularly PPTPP(3,5F)-3/5CN. Modification of their molecular structure may serve to improve their mesomorphic properties.

Acknowledgement

The authors are indebted to AFOSR for financial support under Contract No. FA95550–09–1–0170.

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