High Birefringence Fluoro-Terphenyls for Thin-Cell-Gap TFT-LCDs

Yuan Chen, Jie Sun, Haiqing Xianyu, Shin-Tson Wu, *Fellow, IEEE*, Xiao Liang, and Hong Tang

***Abstract*—Two series of high birefringence fluoro terphenyl compounds are investigated. A binary mixture M1, instead of each individual compound, is found to have predictable properties when mixed with other host mixtures. Doping M1 to a low birefringence thin-film transistor (TFT) mixture improves the figure of merit by 2× to 3×. Based on M1, a high birefringence and large dielectric anisotropy TFT mixture was formed and its properties evaluated.**

***Index Terms*—Liquid crystals, birefringence, dielectric anisotropy, fast response, thin cell gap, thin-film transistor (TFT) display.**

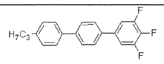
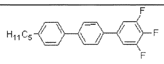
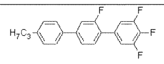
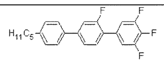
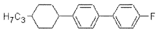
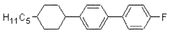
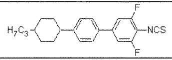
I. Introduction

A HIGH birefringence (Δn) and low viscosity liquid crystal (LC) enables a thin cell gap to be used for achieving fast response time while keeping necessitated phase retardation. The LC birefringence is governed primarily by the molecular conjugation. The most effective approach for increasing birefringence is to elongate the π-electron conjugation of the LC compounds [1]–[3]. Conjugation length can be extended by either unsaturated bonds or phenyl rings in the rigid core structure. Due to UV instability of double bonds and carbon-carbon triple bonds, conjugated phenyl rings have been commonly used for obtaining high birefringence because of their excellent stability. However, using too many phenyl rings will cause two undesirable drawbacks: 1) its melting point will be too high which leads to a poor solubility and 2) its viscosity will increase resulting in an increased response time. Therefore, terphenyl could be an optimal structure. For active matrix LCDs, high resistivity and sufficiently large dielectric anisotropy ($\Delta\varepsilon$) are two additional requirements. Fluoro group provides an excellent resistivity, modest dipole moment, and low viscosity. Therefore, fluorinated terphenyls seem to meet all the desirable properties mentioned.

Several fluorinated terphenyl compounds including positive [4]–[6] and negative [7], [8] $\Delta\varepsilon$ have been synthesized and their properties studied. However, most of positive $\Delta\varepsilon$ fluoro-terphenyl compounds do not have nematic phase. Therefore, their properties in a eutectic mixture can only be extrapolated, which often lead to a fairly large discrepancy.

TABLE I

Chemical Structures and Properties of the Compounds Studied. C Stands for Crystalline Phase; S for Smectic Phase; and I for Isotropic Phase

Compound	Chemical Structure	PTT (°C)	ΔH(cal/mol)
1. PPP-3FFF		C118.72 I	4039
2. PPP-5FFF		C95.01 S98.52 I	2975
3. PP(3F)P-3FFF		C63.85 I	5673
4. PP(3F)P-5FFF		C57.3I	7167
5. CPP-3F		C106.53N156.17	5214
6. CPP-5F		C102.27N154.42I	5337
7. CPP(3,5F)-3NCS		C54.97N199.48I	6028

In this paper, we report the physical properties of two series of fluorinated terphenyls. Surprisingly, a binary mixture (designated as M1) exhibits a narrow (~4 °C) but enantiotropic nematic phase during heating process and a fairly wide nematic range (including room temperature) during super cooling. This enables us to measure its Δn, $\Delta\varepsilon$, and γ_1/K_{11} (visco-elastic coefficient) directly. Besides, M1 has excellent solubility with some other positive $\Delta\varepsilon$ TFT-grade mixtures. We doped 30 wt% and 50 wt% of M1 into MLC-6815 and measured their physical properties. After doping, the figure of merit is improved by 2× to 3×. More importantly, the final mixture's clearing temperatures can be predicted reliably. Furthermore, we formed a eutectic mixture (designated as M4) with M1 and other compounds, which exhibits nematic phase from 0 °C to 83.9 °C. As a TFT material, M4 has a fairly high birefringence ($\Delta n = 0.21$ at $\lambda = 633$ nm) and large dielectric anisotropy ($\Delta\varepsilon = 16.8$). The latter helps to reduce the operating voltage, which is particularly desirable for low power mobile displays.

II. Experiment

We prepared two series of fluoro terphenyl compounds with chemical structures shown in Table I. Compounds 1 and 2 have a fairly high melting point and do not have nematic phase. Their mixtures also do not show any nematic phase. Therefore, their properties are not measured. With an extra fluoro substitution in the middle ring, compounds 3 and 4 exhibit a much lower melting point, but still no LC phase. Due to their relatively low melting points, we formed a binary eutectic mixture (designated as M1) consisting of 50.34 wt% PP(3F)P-3FFF and 49.66 wt% PP(3F)P-5FFF. Unexpectedly, M1 shows an enantiotropic nematic phase. Its nematic phase range is from 27.82°C to

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TABLE II
PROPERTIES OF LC HOST MLC-6185 BEFORE AND AFTER DOPING M1

Sample	Compositions		T_c (°C)	Δn	γ_1/K_{11} (ms/μm^2)	Δε	FoM (μm^2/s)
	MLC 6815	M1					
Host	100%	0	67	0.0529	13.21	2.53	0.212
M2	70%	30%	60	0.0888	16.52	5.86	0.477
M3	50%	50%	51.8	0.1073	18.42	7.95	0.625

31.06°C, but the super-cooling effect lowers the melting point to -5.9 °C. Thus, M1 remains liquid crystal at room temperature (~24 °C). The dielectric anisotropy ($\Delta\varepsilon$) of M1 was measured to be 13.7 at the room temperature, corresponding to a reduced temperature $T/T_c \sim 0.97$. Therefore, at a normal operating condition of $T/T_c \sim 0.8$, $\Delta\varepsilon$ could be much larger.

The Δn of M1 was measured through phase retardation of a LC cell sandwiched between two crossed polarizers. Homogeneous cells with strong anchoring, small pretilt angle of 2°–3° and cell gap d~5 μm were prepared. Indium-tin-oxide (ITO) electrodes were coated on the inner surfaces of the LC cell. The LC mixtures were filled into these cells at ~50 °C. To obtain maximum transmittance, the LC director was oriented at 45 ° with respect to the polarizers' transmission axis. The cell was mounted in a Linkam LTS 350 Large Area Heating/Freezing Stage controlled by a Linkam TMS94 Temperature Programmer. A 1-kHz square-wave AC signal was applied to the LC cell. A linearly polarized He–Ne laser ($\lambda = 632.8$ nm) was used as probing light source. The light transmittance was measured by a photodiode detector (New Focus Model 2031) and recorded digitally by a LabVIEW data acquisition system (DAQ, PCI 6110). The VT curve and then the phase retardation (δ) of the homogeneous cells were then measured by the LabVIEW system. The LC birefringence at wavelength λ and temperature was obtained from the phase retardation (δ) using the following equation [9]:

$$\delta = 2\pi d\Delta n/\lambda \tag{1}$$

where d is the cell gap.

By measuring the free relaxation (decay) time for a controlled phase change, visco-elastic coefficient (γ_1/K_{11}) was obtained according to the following equations [10]:

$$\delta(t) = \delta_0 \exp(-2t/\tau_0) \tag{2}$$

$$\tau_0 = \gamma_1 d^2/(K_{11}\pi^2) \tag{3}$$

where δ_0 is the total phase change, γ_1 is rotational viscosity, and K_{11} is the splay elastic constant. The $\Delta\varepsilon$ was determined through the capacitance measurements of parallel- and perpendicular-aligned LC cells [10]. An HP-4274 multi-frequency LCR meter was employed for the capacitance measurements.

III. RESULTS

A. Birefringence of M1

The temperature dependent birefringence of M1 was measured from 30 °C to 12 °C. Results are fitted by the following equation:

$$\Delta n = \Delta n_o S = \Delta n_o (1 - T/T_c)^{\beta} \tag{4}$$

where Δn_o is the birefringence at $T = 0$ K, S is the order parameter, β is a material constant, T is the operating temperature in Kelvin, and $T_\mathrm{c} (= 304.21\ \mathrm{K})$ is the clearing point of M1. Equation (4) fits the experimental data well. Thru fittings, we find $\Delta n_0 = 0.309$ and $\beta = 0.217$. Due to low clearing point, the data measured correspond to a reduced temperature $T/T_\mathrm{c} > 0.94$, where the order parameter is small. Thus, the birefringence is relatively low. However, with a normal operating condition $T/T_\mathrm{c} \sim 0.8$, the Δn of M1 is close to 0.22 ($\lambda = 633$ nm). At $\lambda = 550$ nm, the expected Δn should be ~0.24. For a 90° TN cell, to satisfy Gooch-Tarry first minimum condition the required dΔn~0.48 μm. Thus, a 2-μm cell gap is sufficient. This example illustrates the principle of using a high birefringence LC in a thin cell for achieving fast response time.

B. Dopant Effect

Here, we use M1 as a dopant for enhancing the figure of merit (FoM) of other low birefringence TFT materials. In our experiment, we doped M1 into a commercial TFT LC host MLC-6815 (Merck) at 30 wt% and 50 wt% ratios. These two mixtures are designated as M2 and M3, respectively. The measured properties are listed in Table II. The overall performance of the samples was evaluated based on the FoM defined as [11]

$$\mathrm{FoM} = \frac{(\Delta n)^2}{\gamma_1/K_{11}}. \tag{5}$$

FoM is commonly used to compare the performance of a LC compound or mixture because it is independent of the cell gap employed. The MLC-6815 LC host has a relatively low birefringence ($\Delta n = 0.0529$ at $\lambda = 633$ nm and 23°C). When we mix 30 wt% M1 with 70 wt% MLC-6185 (called M2), the birefringence is increased to 0.0888. Although its $\gamma_1/_{11}$ is also increased slightly, the FoM is improved by 2.25×.

For M3 (50% M1 and 50% MLC-6815), its Δn is increased to 0.1073. Nevertheless, the FoM is almost 3× higher than that of MCL-6815. Moreover, with a large dielectric constant, M2 and M3 both have a larger $\Delta\varepsilon$ than MLC-6815, which is helpful for reducing operating voltage. It deserves mention here is the predictability of M1 while forming eutectic mixtures with MLC-6815. As shown in Table I, compounds 3 and 4 do not have any LC phase. Therefore, their properties, especially the clearing point in a mixture is often difficult to predict. By forming the M1 binary mixture, the clearing points of M2 and M3 are predictable. For instances, the calculated and measured clearing points of M2 and M3 are 57 °C versus 60 °C, and 50 °C versus 51.8 °C, respectively. The small difference is because we simply use the weight percentage in the calculations. To be more precise, we should use molar fractions instead of weight percentages.

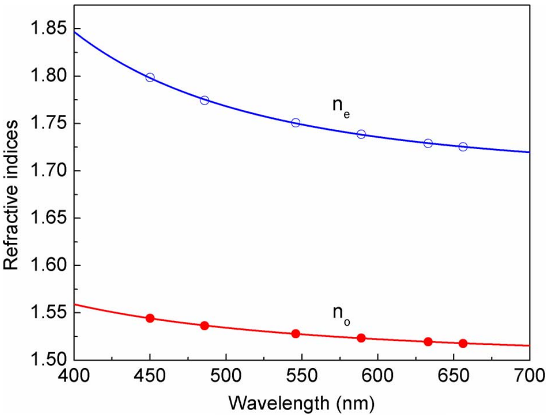

Fig. 1. Refractive indices of M4 at different wavelengths: dots are measured data and lines are fittings with (6).

C. High Birefringence TFT Mixture M4

To formulate a wide nematic range mixture using these terphenyl compounds, we need to mix more compounds with higher clearing temperature.

As Table I shows, compound 7 [CPP(3,5F)-3NCS] has a very wide nematic range from 55 °C to 199 °C. Usually, isothiocyanate group has lower resistivity than fluoro group, which would result in a lower voltage holding ratio in TFT-addressed liquid crystal displays. However, fluorinated $-\mathrm{NCS}$ compounds can still maintain a high resistivity [12], [13]. Besides, with two phenyl rings and -NCS group, the conjugation length is elongated and the birefringence should also be high. A eutectic mixture is formed with 62.6 wt% of M1, 21.2 wt% of CPP(3,5F)-3NCS, 7.6 wt% of CPP-3F, and 8.6 wt% of CPP-5F. This new mixture, denoted as M4, has a wide nematic range from 0 °C to 83.9 °C. Moreover, the super cooling effect brings the melting point lower than -60 °C. (The lower limit of our DSC is -60 °C). Moreover, together with a large polarizability of fluorinated NCS compounds [13] and relative high clearing temperature, M4 has a large dielectric anisotropy of 16.8 at room temperature (23°C).

The extraordinary and ordinary refractive indices of M4 at different wavelength were measured at room temperature (23 °C). The results are shown in Fig. 1. The blue open circles denote the extraordinary refractive indices (n), while the red solid circles represent the ordinary refractive indices (n_o). These data are well fitted by the following extended Cauchy equation [14]:

$$n_{e,o} = A_{e,o} + \frac{B_{e,o}}{\lambda^2} + \frac{C_{e,o}}{\lambda^4}. \qquad (6)$$

The birefringence was also measured at different temperature within the nematic range at $\lambda = 633$ nm. The temperature dependent Δn was fitted with (4). The experimental data and fitting results are shown in Fig. 2. Through fitting, we obtained $\Delta n_{\mathrm{o}} = 0.315$ and $\beta = 0.23$. The Δn_o of M4 is even higher than M1. With these two parameters, the birefringence at any temperature can be extrapolated. At room temperature of 23°C, $\Delta n = 0.21$ at 633 nm.

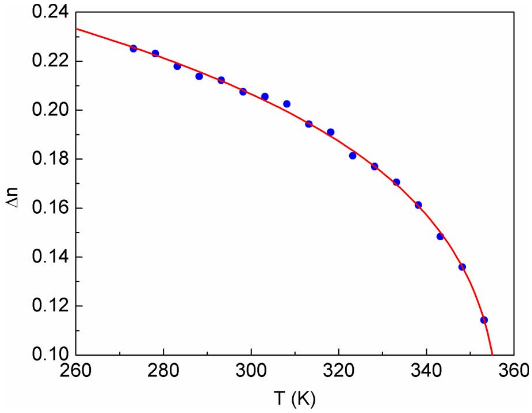

Fig. 2. Birefringence of M4: dots stand for measured data and solid line for fitting curve. $\lambda = 633$ nm.

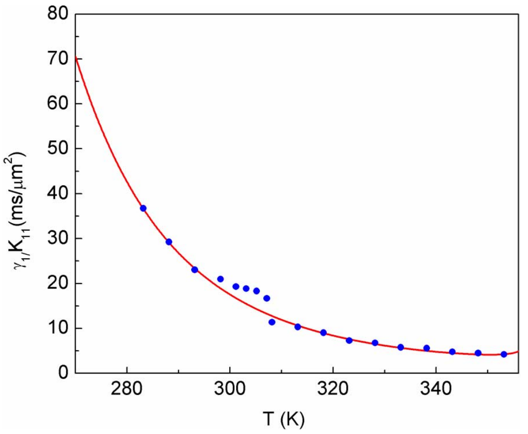

Fig. 3. Temperature dependent visco-elastic constant of M4: dots are experimental data and solid line is fitting with (7).

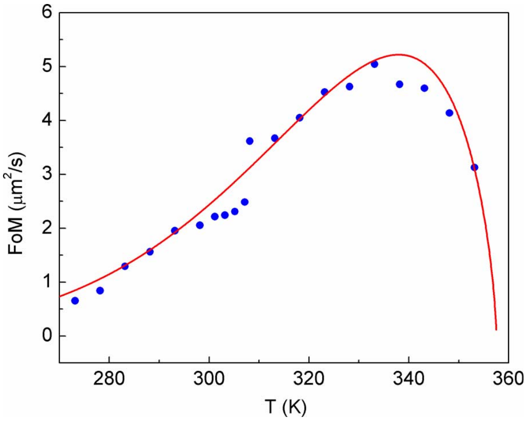

Fig. 4. FoM of M4 versus Temperature. $\lambda = 633$ nm. Dots are experimental data and solid line is fitting with (8).

From the relaxation time of the LC cell, the visco-elastic coefficient $(\gamma_1/\mathrm{K}_{11})$ was calculated according to (2) and (3). We measured γ_1/K_{11} at different temperatures and fitted the experimental results by (7), as shown in Fig. 3

$$\frac{\gamma_1}{K_{11}} = \frac{A \cdot \exp(E/K_B T)}{(1 - T/T_c)^{\beta}} \qquad (7)$$

where A is a proportionality constant, E is the activation energy of the LC mixture, and $K_B = 1.38\cdot 10^{-23}$ J/K is the Boltzmann constant. Here the activation energy is 346.9 meV.

Since K_{11} is proportional to S^2 and γ_1 to $S\cdot\exp(E/K_BT)$, we can rewrite FoM as follows [15]:

$$\mathrm{FoM} = a(\Delta n_o)^2\left(1-\frac{T}{T_c}\right)^{3\beta}\exp\left(\frac{-E}{K_BT}\right) \tag{8}$$

where a is a proportionality constant. As shown in Fig. 4, the blue dots stand for the measured data and the red curve for the fitting results. M4 has best performance at an elevated temperature of ~65 °C. It is worth mentioning that at room temperature, FoM of this mixture is ~2 μm^2/s, which is 9× larger than that of MLC-6815. This indicates that we can improve the response time of the LC cell by using a high Δn and low viscosity LC material.

IV. CONCLUSION

We have demonstrated a fluoro-terphenyl mixture (M1) with high birefringence, which enables thin-cell-gap approach for achieving fast response while keeping sufficient phase retardation. Due to the narrow nematic range, M1 cannot be used alone. By doping M1 into a low birefringence mixture, the performance can be improved by 2×–3×. More importantly, by using M1 mixture instead of individual homologues, the final mixture's properties, especially clearing point, become predictable. Based on this fluoro-terphenyl mixture, we also formulated a eutectic mixture (M4) with wide nematic range from 0 °C to 83.9°C, high birefringence, large dielectric anisotropy, and high resistivity, which could be an attractive candidate for active matrix LCDs.

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Hong Tang, photograph and biography not available at time of publication.