P-153: High Birefringence Fluoro-terphenyls for Thin-cell-gap LCDs

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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 TFT mixture improves the figure of merit by 2-3X.

1.   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 and sacrifice the response time. Therefore, terphenyl could be an optimal structure. For active matrix LCDs, high resistivity and sufficiently large dielectric anisotropy ($\Delta\varepsilon$) are two more critical requirements. Fluoro group provides an excellent resistivity, modest dipole moment, and low viscosity. Therefore, fluorinated terphenyls seem to meet all the desirable properties abovementioned.

Several fluoro 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 could lead to a large degree of uncertainty.

In this paper, we report the physical properties of two series of fluoro terphenyls. Surprisingly, a binary mixture (designated as M1) exhibits a narrow (~4°) 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. Moreover, 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 2X-3X. More importantly, the final mixture's clearing temperatures can be predicted reliably.

2.   Experiment

We have prepared two series of fluoro terphenyl compounds with their chemical structures shown in Table 1. 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 additional 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% of PP(3F)P-3FFF and 49.66 wt% of PP(3F)P-5FFF. Unexpectedly, M1 shows an enantiotropic nematic phase. Its nematic phase range is from 27.82 °C to 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

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
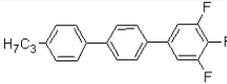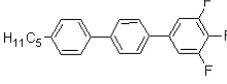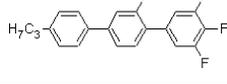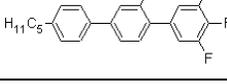
Table 1. Chemical structures and properties of the fluoro terphenyls studied. C stands for crystalline phase, S for smectic phase, and I for isotropic phase.

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 higher. The birefringence 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 $d \sim 5$ 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 an elevated temperature of ~50 °C. The LC director was oriented at 45° with respect to the polarizers' optical 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 the 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 (Δn) at wavelength λ and temperature was obtained from the phase retardation (δ) using the following equation [9]:

$$\delta = 2\pi d \Delta n / \lambda \qquad (1)$$

where d is the cell gap.

3.   Results

3.1.   Birefringence

The birefringence of M1 was measured at different temperature from 30°C to 12°C. Results are plotted in Figure 1. The blue dots represent the measured data and the red solid line is the theoretical fitting curve using following equation [10]:

$$\Delta n = \Delta n_0 (1 - \frac{T}{T_c})^{\beta} \qquad (2)$$

where T is the operating temperature in Kelvin, T_c (=304.21K) is the clearing point of M1, and the fitting parameters are Δn_0=0.309 and β=0.217. Equation (2) fits the experimental data well. Due to low clearing point, the data measured correspond to a reduced temperature $T/T_c \sim 0.97$, where the order parameter is small. Thus, the birefringence is relatively low. However, with a normal operating condition $T/T_c \sim 0.8$, the Δn of M1 is close to 0.22 (λ=633 nm). At λ=550 nm, the expected Δn should be ~0.24. For a 90° TN cell, to satisfy Gooch-Tarry first minimum condition the required $d\Delta n \sim 0.48$ 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.
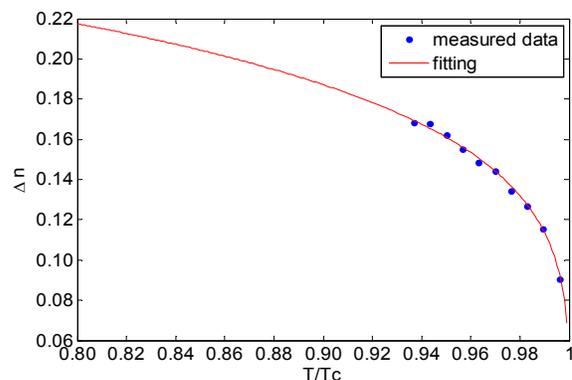

Figure 1. Birefringence of M1: dots stand for measured data and solid line for fitting curve. λ=633 nm.

3.2.   Dopant Effect

To formulate a wide nematic range mixture using entirely terphenyl compounds, we need to develop more compounds with a higher clearing temperature. Here, we use M1 as 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 2. The overall performance of the samples was evaluated based on the FoM defined as [10]:

$$FoM = \frac{(\Delta n)^2}{\gamma_1 / K_{11}} \qquad (3)$$

The MLC-6815 LC host has a relatively low birefringence (Δn=0.0529), measured at λ= 632.8 nm and room temperature. When we mix 30 wt% M1 with 70 wt% MLC-6185 (called M2), the birefringence is increased to 0.0888. Although its γ_1/K_{11} is also increased slightly, the FoM is improved by 2.25X.

For M3 (50% M1 and 50% MLC-6815), Δn is increased to 0.1073. Nevertheless, the FoM is almost 3X 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 threshold voltage.

It deserves mention here is the predictability of M1 while forming eutectic mixtures with MLC-6815. As shown in Table 1, 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

Sample	Compositions		T_c (°C)	Δn	γ_1/K_{11} (ms/μm²)	$\Delta\varepsilon$	FoM (μm²/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

Table 2. Properties of LC host MLC-6185 before and after doping M1.

vs. 60°C, and 50°C vs. 51.8°C, respectively. The small difference is because we simply use the weight percentage in the calculation. To be more precise, we should use molar fractions instead of weight percentages.

4.   Conclusion

With high birefringence, fluoro-terphenyl compounds enable thin-cell-gap approach for achieving fast response while keeping sufficient phase retardation. In addition, the advantages of low viscosity, large dielectric anisotropy, and high resistivity make these compounds attractive for active matrix LCDs. More importantly, by using M1 mixture instead of individual homologues, the final mixture's properties, especially clearing point, become predictable.

5.   References

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