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High Birefringence and Low Viscosity Liquid Crystals with Negative Dielectric Anisotropy

Sebastian Gauza[1], Przemysław Kula[2], Xiao Liang[3], Shin-Tson Wu[1], and Roman Dąbrowski[2]
[1]College of Optics and Photonics, University of Central Florida, Orlando, Florida, USA
[2]Institute of Chemistry, Military University of Technology, Warsaw, Poland
[3]Department of Chemistry, Tsinghua University, Beijing, China

Fast response time is critical for reducing the image blurs in LCD TVs. A straightforward approach is to use thin cell with a high birefringence and low viscosity liquid crystal material. We have synthesized and evaluated the physical properties of some high birefringence, laterally difluorinated terphenyl compounds and mixtures. These mixtures exhibit a high birefringence ($\Delta n \sim 0.24$) in the visible spectral range and a relatively low viscosity. When doped in commercial mixtures, the difluoro terphenyl compounds enhance the mixture's birefringence while causing almost no penalty to the rotational viscosity. These mixtures are particularly attractive for thin cell LCDs to achieve fast response time.

Keywords: fluorinated terphenyl; high birefringence; liquid crystals; response time; vertical alignment

1. INTRODUCTION

Nematic liquid crystals (LCs) with a 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 video applications. Besides high contrast ratio, fast response time is very desirable for almost all the LC devices, especially for reducing the motion blurs of liquid crystal display televisions (LCD TVs) and the

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Address correspondence to Shin-Tson Wu, College of Optics and Photonics, 4000 Central Florida Blvd., Orlando 32816, United States. E-mail: swu@mail.ucf.edu

color breakup of color sequential LCDs. For transmissive LCD TVs, [2] a typical cell gap is 3.5 μm and the trend is to go thinner. In color-sequential projection displays using a single reflective liquid-crystal-on-silicon (LCoS) panel, [3] color breakup would be negligible if the LC response time can be reduced to ~ 1 ms. [4] A typical cell gap for LCoS is 2 μm, in which color breakup is still noticeable. Reducing cell gap is a straightforward approach to improve response time because the LC response time is proportional to the LC layer thickness (d) as $\tau_o \sim d^x$, where the exponent x is dependent on the surface anchoring energy; it varies between 2 and 1 from strong to weak anchoring [5–8]. A high birefringence LC material enables a thinner cell gap to be used while keeping the same phase retardation, i.e., $d\Delta n/\lambda$ [9–13].

The rise time and decay time of a VA cell are given as follows [14,15]:

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

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

where V is the turn-on voltage, V_{th} is the threshold voltage, γ_1 is the rotational viscosity, and K_{33} is the bend elastic constant. Therefore, it is important to not only increase birefringence but also maintain low visco-elastic coefficient (γ_1/K_{33}). Elongating the π-electron conjugation of the LC compounds is the most effective way to increase birefringence [9,15–19]. Common functional groups that contribute to the conjugation lengths include unsaturated rings, such as phenyl rings, and unsaturated bonds, such as carbon–carbon double [20–22] or triple bonds [23–25]. Among unsaturated carbon–carbon bonds, stilbene [26,27] and diacetylene [28,29] are not stable under UV illumination and should be avoided. Negative dielectric anisotropy can be achieved by introducing polar groups in the lateral positions of a LC compound. A widely adopted structure is the lateral (2,3) difluoro substitutions on the phenyl ring. As a result, the effective dipole moment is perpendicular to the principal molecular axis. These difluorinated negative $\Delta\varepsilon$ compounds have been employed in many commercial LC mixtures for VA LCDs. [30,31] Inclusion of more (2,3) difluorinated phenyl rings in the rigid core helps to increase the negative $\Delta\varepsilon$ at the expense of increased viscosity [32–34]. Therefore, taking high Δn, negative $\Delta\varepsilon$, and low viscosity into considerations, the 2′,3′-difluoro-4-alkyl-4″alkyl-[1,1′;4′,1″]-terphenyl structure is a promising candidate [30,35].

In this paper, we report the physical properties of some recently synthesized 2′,3′-difluoro-4-alkyl-4″alkyl-[1,1′;4′,1″]-terphenyl LC compounds and mixtures. Such a terphenyl-based mixture is used as dopant in two commercial mixtures for enhancing their figure-of-merit. Potential applications of these mixtures for VA LCDs are addressed.

2. EXPERIMENTAL

Several techniques were used to characterize the physical properties of the single terphenyl compounds and mixtures. Differential Scanning Calorimetry (DSC, TA Instrument Model Q-100) was used to determine the phase transition temperatures. Results were obtained from 3–6 mg samples in the heating and cooling cycles at scanning rate of 2°C/min.

To measure birefringence, we filled a 5-μm homeotropic cell (pretilt angle ~87°) and probed its phase retardation using a He–Ne laser ($\lambda = 633\,\mathrm{nm}$) [36]. At a given temperature, the phase retardation is related to cell gap d, birefringence Δn, and wavelength λ as:

$$\delta = 2\pi d \Delta n / \lambda \tag{3}$$

In this study, we compare the compound performances based on the Figure-of-Merit which is defined as [37]:

$$FoM = K_{33} \Delta n^2 / \gamma_1, \tag{4}$$

where K_{33} is the bend elastic constant and γ_1 is the rotational viscosity. The temperature dependent birefringence of an LC can be described as follows:

$$\Delta n = \Delta n_o S, \tag{5}$$

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

where Δn_o is the birefringence at $T = 0\,\mathrm{K}$), S is the order parameter, β is a material constant, and T_c is the clearing temperature of the LC. By fitting the experimental data using Eqs. (5) and (6), we can obtain Δn_o and β. Once these two parameters are determined, the LC birefringence at any temperature can be extrapolated.

Using Eq. (4) and knowing that $K_{33} \sim S^2$ and $\gamma_1 \sim S \cdot \exp(E/kT)$, we derive FoM as follows [38]:

$$FoM = a(\Delta n_o)^2 \left(1 - \frac{T}{T_c}\right)^{3\beta} \exp\left(\frac{-E}{\kappa T}\right) \tag{7}$$

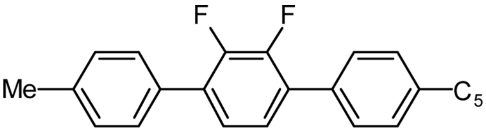
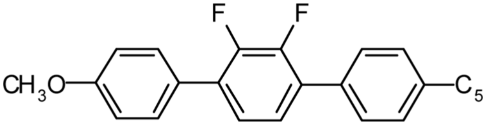
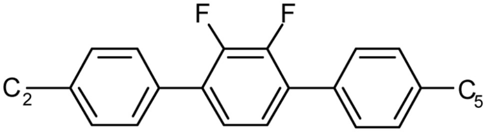
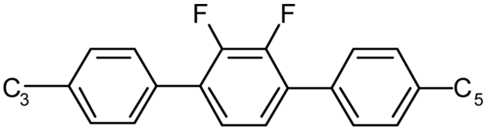
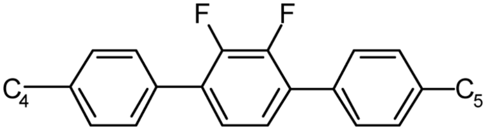
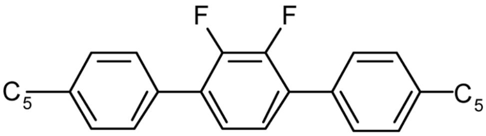
where *a* is a proportionality constant. FoM is commonly used to compare the performance of a LC compound or mixture because it is independent of the cell gap employed. The dielectric and elastic constants of the mixtures were measured by the capacitance method [38,39] of a single homeotropic cell, using a computer controlled LCAS II (LC-Vision) instrument.

3. RESULTS AND DISCUSSIONS

Table 1 lists the molecular structures and phase transition temperatures of the laterally fluorinated terphenyl compounds we prepared. Compounds **1-5** have different length in the left and right alkyl terminal chains. Compound **1**, with a methyl terminal group, shows a fairly high melting temperature $T_M \sim 90.1°C$. Replacing methyl group with methoxy (compound **2**) does not change T_M of the compound but increases its clearing point temperature (T_C) by ~ 4 degrees. The heat fusion enthalpy of compounds **1** and **2** is almost the same (~6.1–6.2 kcal/mole) which is the highest among the homologues we investigated in this experiment. On the contrary, compounds **3** (ethyl-pentyl) and **4** (propyl-pentyl) have the lowest T_M which is 44.7°C and 42.9°C, respectively, in the terphenyl series we studied. Moreover, their heat fusion enthalpy is about 30% lower than that of compounds **1** and **2**. Small heat fusion enthalpy is desirable for mixture formulation. The melting temperature gradually increases as the terminal alkyl chains of a compound become shorter (compounds **5–8**). As expected, compound (# **8**) with short and equally long chains exhibits the highest melting point. As shown in Table 1, the melting temperature of a certain compound strongly depends on the length of the two terminal alkyl chains while the rigid terphenyl core remains the same. The more asymmetric compounds tend to have a lower melting point temperature, except for a compound with a methyl group which is too short and too rigid to introduce good mesomorphic properties, see Compound **1**. Based on mesomorphic properties, the most attractive for mixture formulation among the presented structures are Compounds **3** and **5**.

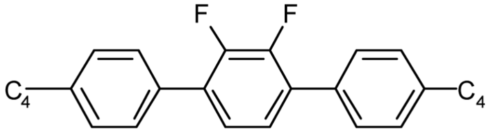
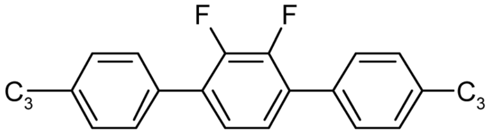
Following single compounds mesomorphic properties we formulated several mixtures based on the compounds shown in Table 1. Representative results are listed in Table 2. Mixture TB-1 consists of solely terphenyl compounds. Its birefringence is 0.247, measured at room temperature and $\lambda = 633$ nm. Although TB-1 exhibits a high birefringence, its melting point remains at 22.4°C. Super cooling effect was observed and it allowed us making measurements at a temperature below 20.0°C. Two commercial negative $\Delta\varepsilon$ LC hosts were chosen for this study: a low birefringence mixture TC-1 with $\Delta n = 0.075$ and a

TABLE 1 Mesomorphic Properties of the Laterally Fluorinated Terphenyl Compounds we Studied

No	Compound	Tm [C]	ΔH [kcal/mol]	T_c [C]
1		90.1	6.1	159.9
2		90.0	6.2	164.2
3		44.7	4.8	110.2
4		42.9	3.9	122.5
5		52.1	5.1	112.4
6		59.9	4.4	119.6

(*Continued*)

TABLE 1 Continued

No	Compound	Tm [C]	ΔH [kcal/mol]	T_c [C]
7		69.4	5.8	103.3
8		95.8	5.3	130.0

relatively high birefringence mixture TC-2 with $\Delta n = 0.145$ at the same experimental conditions. As mentioned above, we concentrate our effort on developing LC material with possibly highest birefringence and Figure-of-Merit value as it will embed fast response time. If a new or modified mixture shows higher Figure-of-Merit, a shorter response time is expected if material is filled into an electro-optical cell with properly adjusted cell gap.

The comparison of the Figure-of-Merit measured for TB-1, TC-1, and TC-2 mixtures indicated the highest FoM value for terphenyl based TB-1 mixture. Measured at the same experimental conditions TB-1 shows about 330% improvement over the FoM value for TC-1 and

TABLE 2 Physical Properties of TB-1 (Terphenyl Mixture) and Two Host Mixtures TC-1 and TC-2. Here Δn was Measured at $\lambda = 633$ nm

Mixture	T_M/T_C [all in °C]	Temp. [°C]	Δn	γ_1/K_{33}	FoM
TB-1	22.41/113.40	25	0.2470	22.81	2.67
		35	0.2300	18.40	2.88
		55	0.2276	8.91	5.82
TC-2	< -50/109.37	25	0.1450	13.58	1.55
		35	0.1400	9.38	2.09
		50	0.1330	5.20	3.40
TC-1	< -50/72.55	25	0.0749	9.06	0.62
		35	0.0722	6.23	0.84
		50	0.0702	4.54	1.09

70% improvement over TC-2. Such a significant increase originates from the birefringence difference between terphenyl base TB-1 mixture and TC-1 and TC-2 host mixtures. Detailed values at different temperatures are listed in Table 2. A drawback of our terphenyl based mixture is a relatively high melting point temperature of 22.4°C. Therefore, we doped TB-1 mixture to TC-1 and TC-2 hosts to enhance their birefringence without severe increase in rotational viscosity. Several mixtures were prepared during the course of our study. Doping as much as 40% by weight of TB-1 did not increase melting temperature, which remains below −50°C for either TC-1b or TC-2b. Further increase of the dopant concentration resulted in a melting temperature increase above −50°C which falls below a minimum requirement for practical applications. A clear advantage of the newly formulated TC-1b and TC-2b mixtures is their higher clearing temperatures: 40°C and 4°C over the host mixtures, respectively, for TC-1 and TC-2. As expected, the birefringence of both TC mixtures was greatly improved while doped with TB-1.

Figures 1(a) and 1(b) show the temperature-dependent birefringence of investigated LC mixtures. Dots represent experimental data and lines are fitting curves using Eq. (5). The two doped mixtures (TC-1b and TC-2b) exhibit a 61% and 23% increase in birefringence over their host mixtures (TC-1: low Δn and TC-2: high Δn) if compared at room temperature. Moreover, we found that doping terphenyl based mixture TB-1 does not increase the visco-elastic coefficient of the whole system in either TC-1 or TC-2, see Figures 2(a) and 2(b). We believe that this phenomenon results from the low rotational viscosity of terphenyl compounds with lateral fluorination on the middle phenyl ring as well as slightly increased value of bend elastic constant K_{33}, see Table 3. Figure-of-Merit puts both birefringence and visco-elastic coefficient together which rules out cell gap as a factor to consider for a switching speed performance. Therefore it visualizes the effect coming from the dopant mixture TB-1 without a need of cell gap correction. The FoM of TC-1 is 0.62 $\mu m^2/s$ at 25°C and $\lambda = 633$ nm. Doping 40 wt% of TB-1 increases FoM to 1.70 $\mu m^2/s$ under the same experimental conditions.

Because of the operating temperature of a direct-view LCD and projection LCD panel is usually in the 35–40°C and 50–55°C range, we also studied the temperature dependent birefringence, visco-elastic coefficient, and FoM. From Figure 3, TC-1b mixture which contains 40% TB-1 in TC-1 base material shows FoM ~ 2.5 and 3.6 at 35°C and 50°C, respectively. This is ~ 3X higher than that of undoped TC-1 mixture at the same temperature. Based on the measured data and Equations (2) and (4) we can estimate the response time of a LC

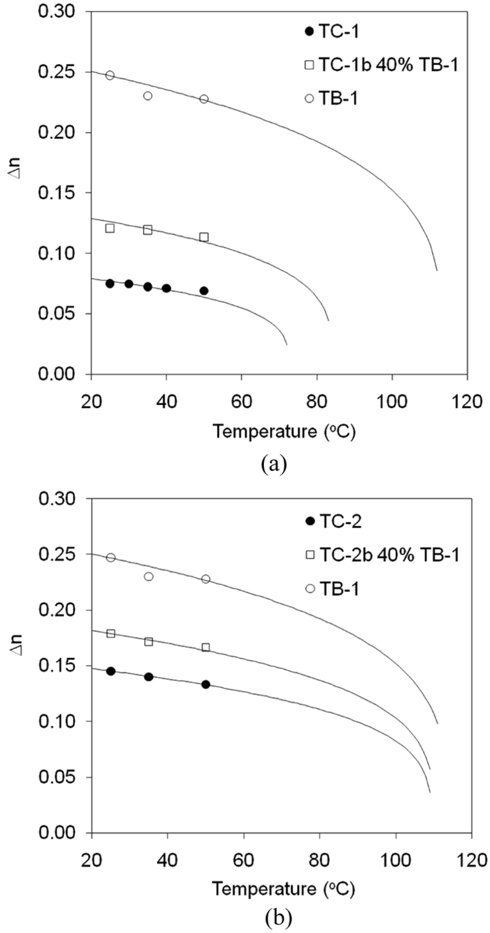
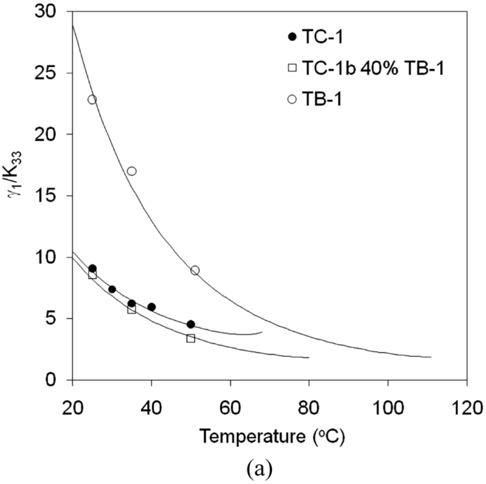


FIGURE 1 Temperature dependent birefringence of terphenyl (TB-1) doped mixtures: (a) TC-1 and (b) TC-2.

cell filled with TC-1 and TC-2 mixtures and compare with their doped modifications. Depending on the operating principles we assumed $d\Delta n = 320$ and $d\Delta n = 180\,nm$ respectively for transmissive (T) mode and reflective (R) mode. Based on the birefringence of TC-1 mixture, the minimum cell gap for T-mode was calculated to be 4.4, 4.6, and 5.3 μm respectively at 25, 35, and 50°C. Therefore, based on the elastic constant and rotational viscosity values, the calculated total response time was equal to 19.3, 14.8, and 12.0 ms. Following the similar procedures, the response time calculated for TC-1b was significantly shorter



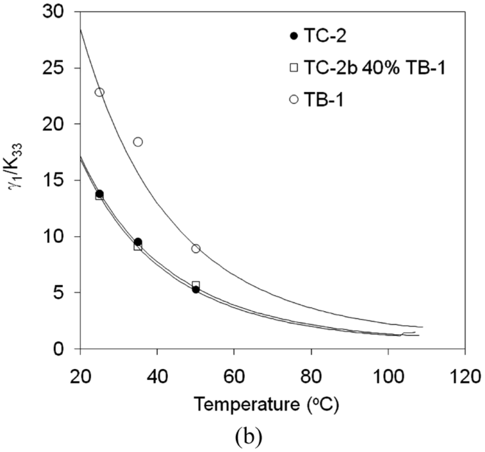
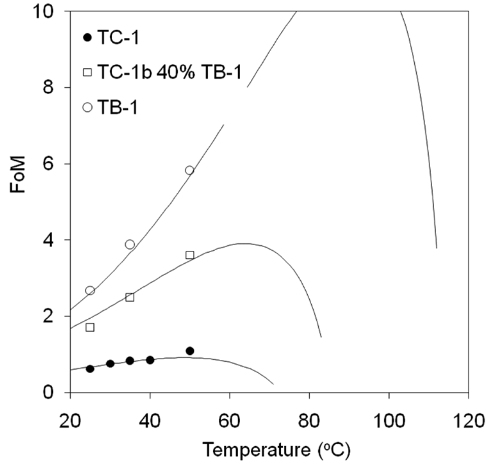


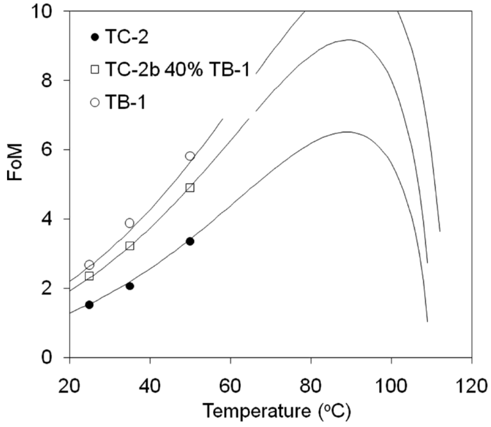
FIGURE 2 Temperature dependent visco-elastic coefficient of terphenyl (TB-1) doped mixtures: (a) TC-1 and (b) TC-2.

TABLE 3 Physical Properties of Host and Terphenyl Doped Mixtures

LC Mix.	T_{MP} [°C]	T_C [°C]	V_{th} [Vrms]	ε_{II}	$\varepsilon_{\perp}$	$\Delta\varepsilon$	K_{11} [pN]	K_{22} [pN]	K_{33} [pN]	γ_1 [mPas]
TC-001	<−50	72.6	3.16	3.34	6.59	−3.25	16.8	10.1	17.5	168
TC-001b	<−50	84.9	3.52	3.30	6.14	−2.84	18.2	10.9	20.9	178
TC-002	<−50	109.4	3.35	3.45	7.22	−3.77	22.0	13.2	24.5	338
TC-002b	<−50	110.1	3.64	3.45	6.65	−3.20	22.0	13.2	25.7	350



(a)



(b)

FIGURE 3 Temperature dependent Figure-of-Merit of terphenyl (TB-1) doped mixtures: (a) TC-1 and (b) TC-2.

7.9, 5.3, and 3.5 ms, respectively, at 25, 35, and 50°C. If we consider R-mode operation, the obtained response time is 4.8, 3.7, and 3.0 ms for TC-1 versus 2.0, 1.3, and 0.9 ms for TC-1b, respectively, at 25, 35, and 50°C, which is a 60–70% improvement over the undoped TC-1. These results clearly show the merit of increasing the birefringence by doping TC-1 mixture with TB-1, terphenyl based dopant.

A slightly less significant improvement was observed for TC-2; a relatively high birefringence mixture. The initial birefringence of

TC-2 is 0.145 and TB-1 is 0.247, and their visco-elastic coefficient is similar. A new mixture TC-2b consisting of 60 wt% TC-2 and 40% TB-1 was formulated. Its FoM is increased from 1.52 (for undoped TC-2) to 2.36 at T = 25°C. Increasing the operation temperature 35°C and 50°C, the FoM of TC-2b is boosted to 3.22 and 4.90. Based on the same estimation method as for TC-1, we calculated the response time of TC-1 and TC-1b at 35°C and 50°C. Based on the birefringence of TC-2 mixture, the minimum cell gap for T-mode operation is 2.5, 2.6 and 2.7 μm. While for TC-2b mixture, its cell gap is reduced to 2.0, 2.1, and 2.2 μm respectively at 25, 35 and 50°C. Under these conditions, a response time of 8.6, 6.4 and 3.9 ms was calculated for TC-2 mixture based on Eq. 2. However, TC-2b mixture has a higher birefringence so that its cell gap can be reduced. As a result, its response time is reduced to 5.6, 3.9 and 2.3 ms at 25, 35 and 50°C, respectively. The improvement is 35–40%. Similarly, the calculated response time for R-mode using TC-2 is 2.2, 1.6, and 1.0 ms, respectively, at 25, 35, and 50°C. For TC-2b, the calculated response time is reduced to 1.4, 1.0, and 0.6 ms respectively at 25, 35, and 50°C. Similar to T-mode, the use of TC-2b mixture leads to 35–40% faster response time than using TC-2.

In addition to birefringence and FoM of the prepared mixtures, we also measured their threshold voltage, dielectric and elastic properties. Results are listed in Table 3. The base mixtures doped with TB-1 exhibit a decreased dielectric anisotropy which implies to a slightly higher threshold voltage. This effect becomes important when the cell gap is reduced to around 1 μm [8]. To enhance dielectric anisotropy of the presented material systems, we could add some properly fluorinated biphenyl or terphenyl compounds [30,40]. Rotational viscosity remains basically unchanged for the doped systems. As shown in Table 3, doping with TB-1 leads to an increased bend elastic constant K_{33}.

4. CONCLUSION

We have developed eight laterally fluorinated terphenyl LC compounds and evaluated their mesomorphic and electro-optic properties. Double lateral fluorination in the middle ring of 4-alkyl-4″alkyl-[1,1′;4′,1″]-terphenyl structure was reported previously [30,35] as having the least effect on rotational viscosity. A high birefringence mixture, developed on the reported compounds, shows good miscibility with TC-1 and TC-2 initial mixtures. As a result, TC-1b and TC-2b shows birefringence of 0.1206 and 0.1790, respectively. This is 61% and 23% an increase over the TC-1 and TC-2 mixtures. In addition, there is no significant change to the rotational viscosity for TB-1 doped mixtures. Therefore, the Figure-of-Merit was improved by ~ 3X for TC-1b and ~2X for TC-2 mixtures at room temperature. Further calculation of a possible response time with a cell gap adjusted according to the improved birefringence shows 30–70% improvement on the response time. Applications of these high performance mixtures for direct view LCDs and LCoS projection displays are foreseeable.

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