

# High Performance Room Temperature Nematic Liquid Crystals Based on Laterally Fluorinated Isothiocyanato-Tolanes

Sebastian Gauza, Shin-Tson Wu, *Fellow, IEEE*, Anna Spadło, and Roman Dabrowski

**Abstract**—High birefringence and low viscosity isothiocyanates liquid crystal single compounds and eutectic mixtures, based solely on laterally fluorinated aromatic rigid core structures, are reported. Extraordinarily high values of figure-of-merit were observed at room temperature and also elevated temperatures for the nematic mixtures we formulated. Potential applications of such mixtures for laser beam steering at  $\lambda = 1.55 \mu\text{m}$  using optical phased arrays are emphasized.

**Index Terms**—Fast response time, high birefringence, high figure-of-merit, low viscosity, nematic liquid crystals.

## I. INTRODUCTION

HIGH birefringence ( $\Delta n > 0.4$ ) and low viscosity nematic liquid crystal (LC) mixtures are critically needed for infrared applications, such as laser beam steering at  $\lambda = 1.55 \mu\text{m}$  [1]. In order to retain a  $2\pi$  phase change  $\delta = 2\pi d\Delta n/\lambda$ , the required optical path length ( $d\Delta n$ ) should increase proportionally as the wavelength increases; here,  $d$  denotes the cell gap of the homogeneous LC cell. Meanwhile, the response time of a LC device is proportional to  $d^2$  and visco-elastic coefficient ( $\gamma_1/K_{11}$ ). To achieve fast response time, low rotational viscosity ( $\gamma_1$ ) LC mixture and thin cell gap are two preferred approaches [2]–[4]. However, high birefringence and low viscosity do not go hand-in-hand. A highly conjugated LC compound usually exhibits a high viscosity because of its increased moment of inertia. Moreover, high birefringence LC compounds usually possess high melting temperatures. To lower the melting temperature, many LC structures need to be developed and eutectic mixtures formulated.

The most effective way to increase birefringence is to elongate the  $\pi$ -electron conjugation lengths of the LC compounds [11]–[13]. Conjugation length can be extended by multiple bonds or unsaturated rings in the rigid core. Four problems associated with highly conjugated LC compounds are high melting temperature, increased viscosity, reduced UV stability, and relatively low resistivity because of ion trapping near the polyimide alignment interfaces. The high melting temperature can be overcome through the use of eutectic mixtures. The

increased viscosity is inherent to all the highly conjugated compounds. Cyano (CN) and isothiocyanato (NCS) are two commonly employed polar groups used for elongating the molecular conjugation. The NCS compounds are less viscous than the CN ones; but on the other hand, they tend to exhibit smectic phases [14]. The CN group has a larger dipole moment ( $\mu = 3.9\text{D}$ ) than NCS ( $\mu = 3.7\text{D}$ ) because of its linear structure. However, due to the very strong polarization of the carbon-nitrogen triple bond, the Huckel charges of carbon and nitrogen are high and well localized [15]. Accordingly, dimmers are formed by strong intermolecular interactions between the nitrile groups. This is the main reason responsible for the observed relatively high viscosity of the cyano-based LC mixtures [16]. In contrast, the dipole moment of the NCS group is  $\sim 30\%$  lower than that of a CN. The NCS compounds do not form dimmers so that their viscosity is lower than the corresponding CN compounds.

Based on the rationales mentioned above, we synthesize some isothiocyanate compounds with totally unsaturated rigid cores. Molecular structures, mesomorphic, and electro-optic properties of the single compounds and eutectic mixtures are reported. Potential applications of these mixtures for laser beam steering using an optical phased array are discussed.

## II. EXPERIMENT

Several measurement techniques are typically involved in characterizing the physical properties of the LC compounds and mixtures in our laboratory. Measuring a birefringence greater than 0.3 (at  $\lambda = 633 \text{ nm}$ ) requires a different setup than the classic refractometric method using Abbe refractometer because the extraordinary refractive index ( $n_e > 1.80$ ) of the LC is beyond the instrument's upper limit. Thus, the electro-optic measurements are needed in order to overcome Abbe's limitation. We prepared homogeneously aligned cells with cell gaps ranging from  $d \sim 4 - 8 \mu\text{m}$  while a linearly polarized He–Ne laser ( $\lambda = 632.8 \text{ nm}$ ) was used as the light source. A linear polarizer was placed at  $45^\circ$  with respect to the LC cell rubbing direction and an analyzer was crossed. 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). An ac voltage with 1-kHz square waves was used to drive the LC cell whose inner surfaces were coated with indium–tin–oxide (ITO) electrodes. On top of the ITO, the substrates were covered with a thin polyimide alignment film. The buffing induced pretilt angle was about  $2^\circ - 3^\circ$ . The cell was held in a Linkam LTS 350 Large

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S. Gauza and S.-T. Wu are with the College of Optics and Photonics, CREOL, Orlando, FL 32816 USA (e-mail: sgauza@creol.ucf.edu).

A. Spadło and R. Dabrowski are with Institute of Chemistry, Military University of Technology, 00-908 Warsaw, Poland.

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Area Heating/Freezing Stage equipped with Linkam TMS94 Temperature Programmer. The phase retardation ( $\delta$ ) of the homogeneous cells was measured by the LabVIEW system. The LC birefringence ( $\Delta n$ ) at wavelength  $\lambda$  and temperature  $T$  can be obtained by measuring the phase retardation ( $\delta$ ) of the homogeneous cell from the following equation [11]:

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

Birefringence results obtained from the electro-optic method are in good agreement to that measured by the Abbe refractometer. Typically, we observed about 1%–2% lower  $\Delta n$  value measured by our electro-optic setup than the one we measured from Abbe refractometer.

The measured data in the visible spectral region allow us to extrapolate the  $\Delta n$  at  $\lambda = 1.55 \mu\text{m}$  by using a single band birefringence dispersion model [17]:  $\Delta n = G\lambda^2\lambda^{*2}/(\lambda^2 - \lambda^{*2})$ , where  $G$  is the proportionality constant and  $\lambda^*$  is the mean electronic transition wavelength. By measuring the LC birefringence at two visible laser wavelengths, we can obtain  $G$  and  $\lambda^*$ . Once these two parameters are determined, the birefringence at any wavelength of interest, e.g.,  $\lambda = 1.55 \mu\text{m}$ , can be extrapolated.

To characterize the performance of liquid crystal mixtures, a figure-of-merit (FoM) which takes optical phase change and response time into account has been defined as [18]:

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

where  $K_{11}$  is the splay elastic constant,  $\Delta n$  is the birefringence, and  $\lambda_1$  is the rotational viscosity. All of these parameters are temperature dependent. The dielectric anisotropy ( $\Delta\epsilon$ ), threshold voltage ( $V_{th}$ ), and elastic constants ( $K_{11}$ ,  $K_{33}$ ) were measured by the LCAS II system purchased from LC Vision. All the measurements were conducted at a room temperature of 23 °C and the applied ac voltage frequency was 1 kHz unless otherwise mentioned. All the thermal analyses were performed using a high sensitivity differential scanning calorimeter (DSC, TA Instrument Model Q-100). Phase transition temperatures were measured using small samples ( $\sim 1.5 \text{ mg}$ ) at a 2 °C/min scanning rate. The observed LC phase transitions were confirmed by the polarizing optical microscopy (POM) method. The UV absorption spectra of the single LC compounds were measured by using a dual channel Cary 500 UV/VIS/IR spectrophotometer. To avoid detector saturation, the LC samples were dissolved in cyclohexane solutions with  $2 \times 10^{-4}$  molar concentrations. Standard quartz semimicrocells with 10-mm thickness were used in the sample and reference channels of the spectrophotometer.

### III. SINGLE COMPOUNDS

Our study focuses on the thermotropic, rod-like molecular systems with a polar isothiocyanate terminal group. The rigid cores of the molecules and lateral substitutions vary, aiming to get a  $\Delta n$  value as high as possible while keeping a relatively low viscosity. Therefore, the residues typically used for the rigid

core of our nematic LC compounds are the aromatic ones like phenyl (benzene) and naphthalene rings. Phenyl ring and naphthalene ring system are unsaturated residues, both are rich in the  $\pi$ -electrons. Thus, these rings are particularly desirable to elongate the  $\pi$ -electrons conjugation through the rod-like molecule and to increase the polarizability along the principal molecular axis. Another source of  $\pi$ -electrons, which may contribute to the  $\pi$ -electron conjugation thru the molecule, is the unsaturated double and triple carbon-carbon bonds, which bridge unsaturated rings of the rigid core. Double carbon-carbon bonds [19] were reported as extremely weak under UV and even daylight conditions [20] so we concentrated on the tolane-based rigid cores because their photochemical stability appears to be better. Four different groups of high birefringence LC compounds were chosen for discussion.

Table I lists the compound structures and their phase transition temperatures with respect to the different formations of the rigid core. Previous reports by different authors [14], [21], [22] found that the birefringence of NCS-tolane is below 0.4 at  $\lambda = 633 \text{ nm}$  and room temperature. We looked closely on this group of compounds as an attractive base for forming high birefringence eutectic mixtures. Table I lists the compound structures we investigated. The simple, non-fluorinated NCS-tolanes with short alkyl chains (Comp. **1** and **2**) do not show any enantiotropic liquid crystal phase. Instead, highly ordered smectic K and E phases appear during monotropic transition. Elongating the flexible chain lowers the melting temperature so that the enantiotropic smectic phases occur [23]. Single lateral fluorination of the phenyl ring in the direct neighborhood of the NCS group lowers the melting point but these compounds still do not show mesomorphic properties (Compounds **3**, **4**, **5** and **6**). The (3,5) double fluorinations further decrease the melting point but the enantiotropic nematic phase still does not exist if short alkyl or alkoxy chain is in use (Compounds **7**, **8** and **9**). The double laterally fluorinated tolane with pentyloxy flexible chain (Compound **11**) shows a short range of nematic phase without the presence of any highly ordered smectic phase. It suggests that double fluorinated tolane compound may be the right dopant to suppress the highly ordered smectic phases existing in the high  $\Delta n$  LC compounds. We validated this idea by making our two base mixtures (UCF-Base-1 and UCF-Base-2) which differ only by the addition of double fluorinated alkoxy-tolanes. The second group of compounds with an NCS terminal group that we chose for our experiment is based on the terphenyl rigid core, shown in Table II. The terphenyl rigid core has been widely used in commercial high birefringence mixtures. A popular example is 4-cyano-4'-pentyl-terphenyl, also known as 5CT [24]. The phase transition temperatures of 5CT are relatively high, with a melting point at 130 °C and clearing point at 239 °C.

Based on our experience with highly conjugated linear molecular structures, we decided to start from single laterally fluorinated cores and then extend to the double fluorinated ones. The melting point of the single fluorinated compound PPP(3F)3NCS is  $\sim 130 \text{ °C}$  and clearing point  $\sim 265 \text{ °C}$ , which is rather similar to that of 5CT. By introducing another fluoro group to the neighborhood of the NCS group, the melting point of PPP(3,5F)3NCS and PPP(3,5F)5NCS is reduced to 106 °C and 95 °C, respectively. However, the second compound exhibits a smectic phase

TABLE I  
 TOLANE-BASED COMPOUNDS

No	Structure
1	 PTP2NCS Cr 94.4 S <sub>K</sub> 85.8 S <sub>F</sub> 90.5 Iso
2	 PTP4NCS Cr 44.3 S <sub>K</sub> 71.0 S <sub>F</sub> 87.0 Iso
3	 PTP(3F)2NCS Cr 71.3 Iso
4	 PTP(3F)3NCS Cr 76.0 Iso
5	 PTP(3F)4NCS Cr <sub>1</sub> 38.4 Cr <sub>2</sub> 40.5 (N 17) Iso
6	 PTP(3F)5NCS Cr 49.2 Iso
7	 PTP(3,5F)3NCS Cr 51.6 Iso
8	 PTP(3,5F)5NCS Cr 46.5 Iso
9	 PTP(3,5F)O2NCS Cr 95.4 Iso
10	 PTP(3,5F)O4NCS Cr 61.6 (N 59.7) Iso
11	 PTP(3,5F)O5NCS Cr 49.5 N 56.6 Iso

up to 108 °C. The  $\Delta n$  of the mixture based on the above-mentioned terphenyl LCs is  $\sim 0.35$ – $0.38$  depending on the detailed compositions and final clearing temperature.

In order to achieve a higher birefringence, it is necessary to use compounds with longer  $\pi$ -electron conjugation.

Extension of the rigid core could be realized either by introducing unsaturated bond(s) or/and unsaturated cyclic structures [25]. However, adding an unsaturated bond right next to the toluene core will result in severe photochemical instability [26], [27]. Replacing a phenyl ring on the flexible chain side by a naphthalene ring will increase conjugation and boost birefringence to 0.46 [22]. However, naphthalene exhibits a lower UV stability and is more viscous than the linear toluene structure. The most preferable choice in this case is to use biphenyl-

 TABLE II  
 TERPHENYL-BASED COMPOUNDS

No	Structure
12	 PPP(3F)4NCS Cr 130.5 N 265 Iso
13	 PPP(3,5F)3NCS Cr 106.4 N 204.8 Iso
14	 PPP(3,5F)5NCS Cr 95.3 S <sub>A</sub> 108.2 N 197.1 Iso

 TABLE III  
 BIPHENYL-TOLANE BASED LC COMPOUNDS

No	Structure
14	 PPTP(3F)2NCS Cr 146.2 N 254.8 Iso
15	 PPTP(3F)4NCS Cr 140.4 S <sub>B</sub> 181.3 N 242.9 Iso
16	 PPTP(3,5F)3NCS Cr 122.0 N 233.6 Iso
17	 PPTP(3F)4NCS Cr 65.3 (S <sub>B</sub> 50.1) N 212.0 Iso
18	 PPTP(3,5F)5NCS Cr 119.0 (S <sub>B</sub> 55.0) N 208.5 Iso

toluene unit in place of toluene as a rigid core. However, such a highly linearly conjugated structure possesses a strong tendency to form smectic phases and high melting point temperatures, well above 100 °C (see Table III). Phenyl-toluene with an NCS terminal group without lateral substitution shows two different crystalline forms with transitions at 169 °C and 207 °C, which is also the transition to smectic phase, then at 221 °C where the transition to nematic phase takes place. Finally, the isotropic state occurs at 270 °C. The high melting temperature and smectic phase limit the usefulness of this compound, especially from the mixture formulation viewpoint. To lower the melting point temperature and avoid smectic phases, we synthesized laterally fluorinated homologues. The melting point drops to 140 °C and 65 °C, respectively, for the single and double fluorinated compounds with four carbons in the alkyl chain. The smectic phase was suppressed below 181 °C and 50.1 °C, respectively; see detailed structures in Table III.

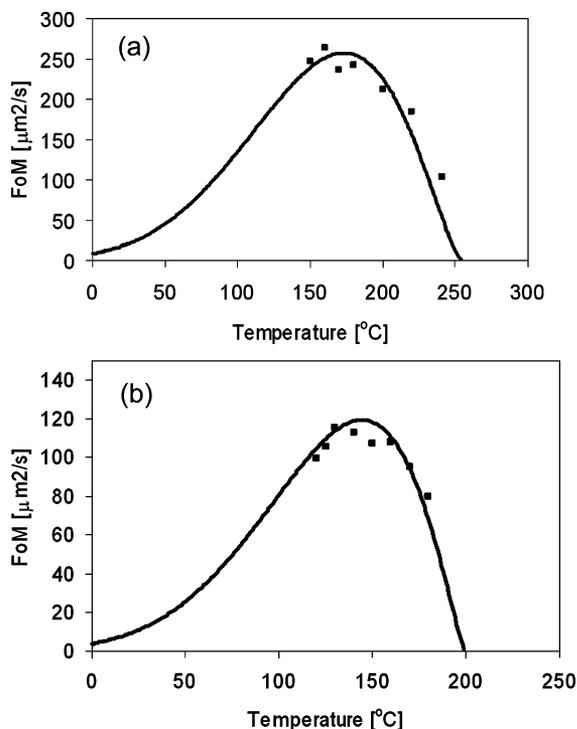


Fig. 1. The temperature dependent FoM of (a) PPTP(3F)2NCS and (b) PPP(3,5F)3NCS. Dots are experimental results and lines are fittings using (3).

Although the mesomorphic properties of the discussed single compounds appear to be far away from ideal, they exhibit superior electro-optic properties when filled into a LC cell. The birefringence of the isothiocyanato-terphenyls is approximately 0.36–0.38. A similar birefringence is observed for the isothiocyanato-tolanes, but for their phenyl derivatives the birefringence is increased to 0.48–0.52. The extrapolated  $\Delta n$  value depends on the host mixture if the guest–host method is used. The clearing temperature ( $T_c$ ) will influence the measured  $\Delta n$  value according to (3)

$$\Delta n = \Delta n_0(1 - T/T_c)^\beta \quad (3)$$

where  $\Delta n_0$  is the birefringence at  $T = 0$  K and  $\beta$  is a material constant. If a guest–host mixture has a higher clearing point, then the extrapolated birefringence value for the guest compound would be higher at room temperature. Thus, the guest–host method provides a quick reference, but its accuracy is limited. For example, in [28] where Comp. **16** has an extrapolated  $\Delta n \sim 0.4838$  at  $\lambda \approx 589$  nm and  $T = 23$  °C based on the 10/90 wt% guest–host system with E44. In our studies, the host mixture we selected (NCS-tolanes and NCS-cyclohexyl-tolane) has similar structure as the guest compounds. The  $\Delta n$  values we report here are extrapolated from the mixtures with a clearing temperature in the range of 140 °C–160 °C. Specifically, we obtained a consistent birefringence value of 0.52 for Comp. **16** at  $\lambda = 633$  nm and  $T = 23$  °C from both 80/20 wt% and 40/60 wt% guest–host systems.

Fig. 1(a) and 1(b) plots the temperature dependent FoM for the single fluorinated PPTP(3F)2NCS and double fluorinated PPP(3,5F)3NCS compounds, respectively. Their maximum

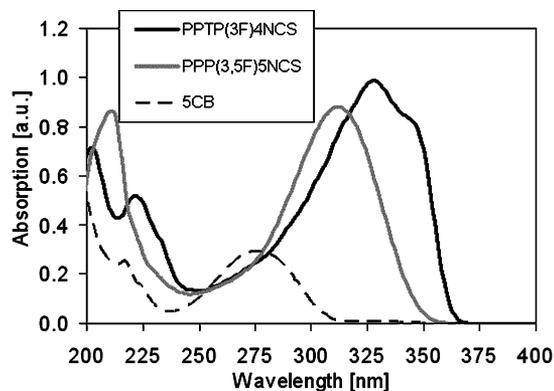


Fig. 2. Measured absorption spectra of four isothiocyanate compounds in comparison to the pentyl-cyano-biphenyl (5CB) compound. Each LC compound was dissolved in cyclohexane solution with  $2 \times 10^{-4}$  molar concentrations. Cell gap is 1 cm.

FoM values (at  $T \sim 150$  °C) reach  $250 \mu\text{m}^2/\text{s}$  and  $120 \mu\text{m}^2/\text{s}$ , respectively. The FoM of PPTP(3F)2NCS is by far the highest we have ever found, although its operating temperature is as high as 150 °C. High temperature operation is quite undesirable because it involves a heat stage. Thus, we extrapolate the FoM of these two compounds to  $T \sim 23$  °C. We fit the data measured at elevated temperatures using (2) and find that the FoM stays  $\sim 20 \mu\text{m}^2/\text{s}$  and  $10 \mu\text{m}^2/\text{s}$  for the phenyl-tolane and terphenyl compounds, respectively, as shown in Fig. 1(a) and 1(b).

Typically, high birefringence compounds are solid at room temperature. Thus, we measured the UV absorption spectra from a cyclohexane solution. Fig. 2 shows the measured UV absorption spectra of some of the single compounds listed in Tables II and III. All of the presented NCS compounds have a longer absorption tail than that of 5CB ( $\lambda = 310$  nm), shown as a benchmark for comparison. This is chiefly because they all have a longer  $\pi$ -electron conjugation than the pentyl-cyano-biphenyl. Due to the extended  $\pi$ -electron conjugation, NCS-phenyl-tolane (Comp. **7**) has an absorption tail as far as  $\lambda \sim 370$  nm. From the terphenyl group, the PP(3,5F)5NCS (Comp. **14**) has absorption tail at  $\lambda = 360$  nm. Overall, this means that all of these compounds absorb the long-wavelength UV light. Extra caution of protecting these high birefringence LC devices from UV ( $\lambda \sim 365$  nm) exposure should be taken. In general, these highly conjugated LC structures are not suitable for the applications that require a UV curing process [29].

We favor the tolane rigid cores because of their high birefringence and low viscosity. A disadvantage of the tolane (biphenyl tolane) structure is its inadequate UV stability [27]. However, for infrared application the photostability is not a big concern.

#### IV. EUTECTIC MIXTURES

Based on the single component results, we formulated some test mixtures. First, two different high birefringence mixtures were formulated. As mentioned before, double lateral fluorination of the tolane rigid core effectively lowers the melting point of the NCS tolans. Thus, these two base mixtures only differ by the amount of the double fluorinated tolans. UCF-Base-1 contains only non-fluorinated or single fluorinated tolans and

TABLE IV  
PHYSICAL PROPERTIES OF UCF-BASE MIXTURES

Mixture	E44	UCF-Base-1	UCF-Base-2
$T_{mp}$ [°C]	-6.0	-21.8	-54.0
$T_c$ [°C]	100.0	109.8	100.0
$V_{th}$ [ $V_{rms}$ ]	1.4	1.6	1.4
$\epsilon_{11}$	17.8	19.8	21.2
$\epsilon_{\perp}$	4.1	4.2	4.6
$\Delta\epsilon$	13.7	15.6	16.7
$K_{11}$ [pN]	13.3	21.0	16.0
$K_{33}$ [pN]	40.3	32.0	31.0
$K_{33}/K_{11}$	3.03	1.5	1.9
$\Delta n$	0.248	0.38	0.37
$\gamma_1/K_{11}$ [ms/ $\mu\text{m}^2$ ]	22.8	10.5	12.0
FoM [ $\mu\text{m}^2/\text{s}$ ]	<b>2.7</b>	<b>13.8</b>	<b>11.7</b>

UCF-Base-2 has 30% of the double fluorinated tolanes, Compounds **9**, **10**, and **11**. Although, both mixtures have almost the same physical properties, their melting temperatures are significantly different. UCF-BASE-1 melts at  $-21.8$  °C but stays as smectic up to  $-2.0$  °C, and then nematic clears at  $109.8$  °C. On the other hand, UCF-Base-2 melts at  $-54$  °C, stays nematic and clears at  $100$  °C; no smectic phase occurs. Thus, UCF-Base-2 is our natural choice, even its electro-optic performance is slightly worse than that of UCF-Base-1. A commercial high birefringence mixture E44 from Merck is included in Table IV for comparison.

Both UCF-Base mixtures were doped by high birefringence compounds **16**, **17**, and **18**. As expected, when UCF-Base-1 was doped by a small amount of difluoro-biphenyl-tolane (10% of Comp. **17**), smectic phase appears at  $15$  °C above room temperature. Thus, UCF-Base-1 cannot serve as a base mixture for biphenyl NCS-tolanes if the guest compound concentration is higher than 10%. Under such a circumstance, the extrapolated birefringence at room temperature would not exceed 0.4. Second base mixture, UCF-Base-2, shows a much higher tolerance for eutectic composition of compounds **16**, **17** and **18** up to 45% where the melting point stays at  $5$  °C and smectic phase below  $10$  °C. Based on the composition comparison, the laterally difluorinated tolanes are a better choice than the single fluorinated ones. A large amount of biphenyl-tolane dopant and the increased clearing temperature leads to a high birefringence ( $\Delta n \sim 0.43$  measured at  $25$  °C and  $\lambda = 633$  nm). The nematic range was relatively wide with melting point at  $9.8$  °C and clearing point at  $135.8$  °C [UCF-A]. The smectic phase was observed with the phase transition into nematic at  $14.0$  °C. Further increase of biphenyl-tolane-NCS concentration results in increased melting and smectic-nematic phase transition temperatures. The highest concentration of compounds **16** and **15** we were able to mix into UCF-Base-2 was 50%. The mixture's melting point was  $25$  °C and monotropic smectic to nematic transition was  $18$  °C. This mixture (UCF-B) exhibits a  $\sim 10$  °C wide supercooling effect. Unfortunately, we found that the UCF-B system was not thermodynamically stable and the dopant compound was precipitated from the mixture after several hours of storage at room temperature. In this case additional compounds which may effectively destabilize smectic order are necessary to obtain room temperature mixture. To

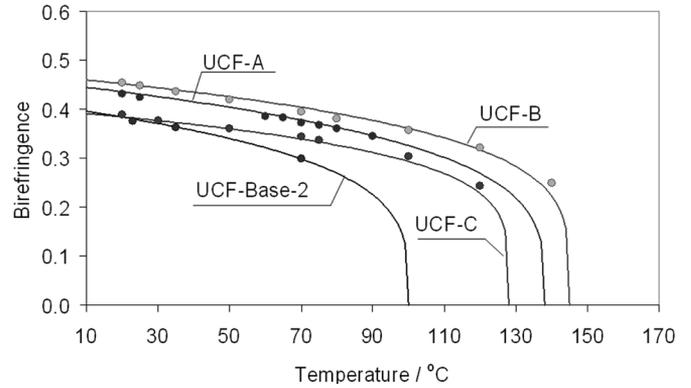


Fig. 3. Temperature dependent birefringence of UCF-Base-2, UCF-A, UCF-B, and UCF-C mixtures.  $\lambda = 633$  nm.

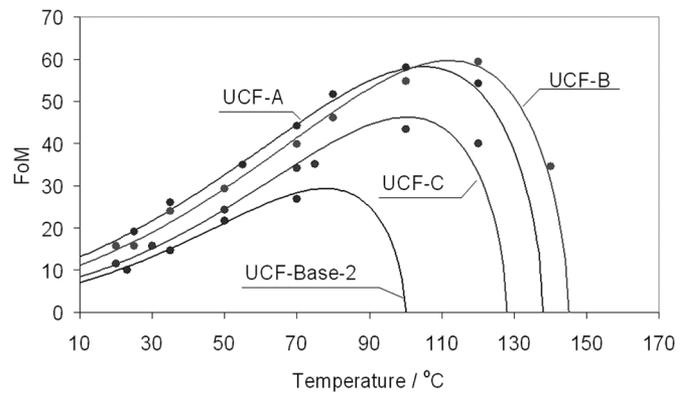


Fig. 4. Temperature dependent FoM of UCF-Base-2, UCF-A, UCF-B, and UCF-C mixtures.  $\lambda = 633$  nm.

enforce usability of the biphenyl-tolane isothiocyanates for high birefringence LC mixtures, we prepared a test mixture (UCF-C) which contains 30% of cyclohexyl-tolane-NCS 4-(trans-2-butylcyclohexyl)-3-fluoro-4-isothiocyanatotolane instead of 30% biphenyl-tolane-NCS, Comp. **17**, to match the clearing point of UCF-A. Doping 30% of cyclohexane compound results in increased melting and clearing temperatures from  $[-54.0$  °C,  $100.0$  °C] to  $[15.1$  °C,  $127.6$  °C], respectively, for UCF-Base-2 and UCF-C. As expected, birefringence is significantly higher for biphenyl-tolane doped UCF-A mixture than for UCF-C. We measured  $\Delta n \sim 0.43$  at  $T = 25$  °C and  $\lambda = 633$  nm. This mixture is thermodynamically stable; there is no sign of mixture recrystallization due to excessive amount of highly conjugated biphenyl-tolanes. For comparison, UCF-B shows  $\Delta n = 0.45$  at the same experimental conditions. Temperature dependent birefringence for the discussed mixtures is shown in Fig. 3. At this stage, UCF-A is the highest birefringence LC mixture with room operation capability.

An interesting phenomenon was observed by comparing the temperature dependent FoM (see Fig. 4) and visco-elastic coefficient (see Fig. 5) of the UCF-A and UCF-B. FoM was higher for UCF-A with a lower concentration of biphenyl tolane compounds (**16**, **17** and **18**) than for UCF-B with larger content of highly conjugated compounds **16** and **17**.

This effect comes from the lower visco-elastic coefficient value in the case using three homologues of biphenyl

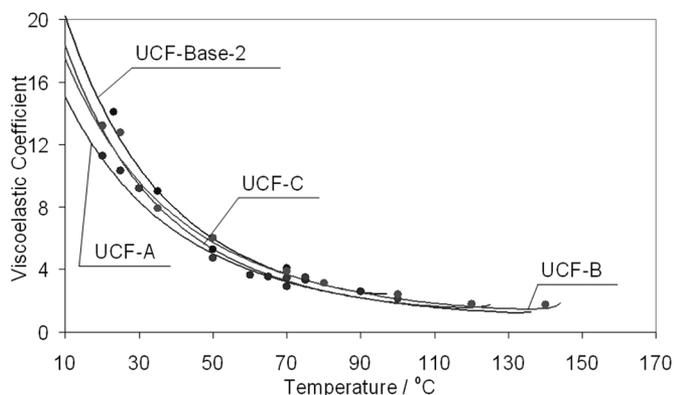


Fig. 5. Temperature dependent viscoelastic coefficient of UCF-Base-2, UCF-A, UCF-B, and UCF-C mixtures.

tolanes than just using Comp. 16 and 17. Higher melting point of UCF-B could also contribute to the observed higher visco-elastic coefficient value.

## V. DISCUSSION

There is a common concern about the reliability of highly polar (CN and NCS) LCs in terms of resistivity, ionic concentration, and voltage holding ratio. Recently it was reported that by introducing one or two fluoro groups at the 3- or (3,5)-positions of the phenyl ring where CN or NCS resides, the voltage holding ratio is improved to better than 95% [15], [30]. Thus, the fluorinated NCS or CN compounds are useful for active matrix displays.

We also purified NCS-based high birefringence mixtures ( $\Delta n \sim 0.38$ ), with acceptable yield, up to resistivity level of  $10^{+13}$  [31]. In addition, mixtures with birefringence of 0.43–0.45 (at  $\lambda = 633$  nm) allow us to use a relatively thin cell gap at  $\lambda = 1550$  nm to obtain the required  $2\pi$  phase change. According to the single band birefringence dispersion model [17], the birefringence of UCF-B is estimated to be  $\Delta n \sim 0.37$ – $0.38$  at  $\lambda = 1.55$   $\mu\text{m}$ . Thus, we consider our UCF mixture an excellent candidate for laser beam steering using optical phased arrays and light shutters where a high voltage holding ratio is not crucially needed.

## VI. CONCLUSION

We have designed several new, high birefringence, and relatively low viscosity mixtures for applications that require operating conditions at room temperature. By using high birefringence compounds based solely on the unsaturated rigid core structures with highly polar NCS terminal group, we obtained a record-high FoM value in such conditions. For the first time, we formulated a high birefringence of 0.43 ( $\lambda = 633$  nm) and simultaneously high performance nematic mixture with FoM greater than  $15.0 \mu\text{m}^2/\text{s}$  at  $T \sim 23$  °C. It is particularly difficult due to severe rotational viscosity increase with  $\pi$ -electron conjugation increase and multiple lateral substitutions. Previously, to get such performance we would have to operate at an elevated temperature in order to shorten the response time. The best results for commercial high birefringence nematic mixtures

under the same experimental conditions are  $\text{FoM} < 3 \mu\text{m}^2/\text{s}$ . The high birefringence of our UCF mixtures enable the use of a thinner cell gap which efficiently reduces the response time while the required optical phase change is still maintained. The on-off-on switching time obtained for UCF-Base-1 mixture using a 2- $\mu\text{m}$  cell gap was 640  $\mu\text{s}$  at 35 °C, which is the fastest optical modulator driven by simple square waves. The response time could be further reduced if UCF-A or UCF-B mixture will be applied to electro-optical cell with thickness below 2- $\mu\text{m}$ . The applications for various OPA and optical shutter devices are foreseeable. The potential applications for telecommunication industry are also foreseeable.

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**Sebastian Gauza** received the Ph.D. degree in chemistry from the Military University of Technology, Warsaw, Poland, in 2001.

He is currently a research scientist at College of Optics and Photonics/CREOL/FPCE, University of Central Florida, Orlando, FL. His current research is to develop novel high birefringence nematic liquid crystals single compounds and mixtures for photonic applications.



**Shin-Tson Wu** (M'98–SM'99–F'04) received the B.S. degree in physics from National Taiwan University, Taipei, and the Ph.D. degree from the University of Southern California, Los Angeles.

He is currently a PREP professor at College of Optics and Photonics, University of Central Florida, Orlando. His studies at UCF concentrate in foveated imaging, bio-photonics, optical communications, liquid crystal displays, and liquid crystal materials. He has coauthored three books, *Fundamentals of Liquid Crystal Devices* (Wiley, 2006), *Reflective Liquid Crystal Displays* (Wiley, 2001), and *Optics and Nonlinear Optics of Liquid Crystals* (World Scientific, 1993), 4 book chapters, over 300 papers, and 55 issued and pending patents.

Dr. Wu is a Fellow of the Society for Information Display (SID) and Optical Society of America (OSA).



**Ania Spadlo** graduated from the Department of Chemistry, Radom Technical University, Radom, Poland, in polymer technology in 1999, and received the Ph.D. degree in organic chemistry from the Institute of Chemistry, Military University of Technology (MUT), Warsaw, Poland, in 2004. She is a doctorate of organic chemistry.

She is involved in European Research Training Network SAMPA (Synclinic and Aticlinic Mesophases for Photonic Applications) at the Polytechnic of Madrid, Madrid, Spain.



**Roman Dąbrowski** received the Ph.D. degree in polymer technology from Warsaw Technical University, Warsaw, Poland, in 1966, and the Sc.D. degree from the Military University of Technology (MUT), Warsaw, Poland, in organic semiconductors studies in 1970.

He is currently full Professor of organic chemistry and Director of the Institute of Chemistry in the Military University of Technology (MUT). Since 1975, he changed his interest to liquid crystals, searching for new LC materials for displays and photonic applications and investigating relations between the chemical structure of molecules and their mesogenic and physical properties. He has authored over 300 publications and conference presentation.

Dr. Dąbrowski was a member of Scientific and Organizing Committees of International Liquid Crystal Conferences and a recipient of the Frederick's Medal in 2005.

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