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High figure-of-merit nematic mixtures based on totally unsaturated isothiocyanate liquid crystals

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High birefringence and low viscosity isothiocyanate liquid crystal single compounds, and eutectic mixtures based solely on unsaturated rigid core structures, are reported. Extraordinarily high values of figure-of-merit were observed at room temperature for the formulated nematic mixtures. Potential applications of such mixtures for laser beam steering at $\lambda=1.55\,\mu$m using optical phased arrays are emphasized.

1. Introduction

The continuous demand for faster electro-optic response times is the driving force for developing novel high birefringence ($\Delta n>0.4$) nematic liquid crystal (LC) mixtures [1]. Almost all LC-related devices, such as notebook and desktop computers, liquid crystal TVs, spatial light modulators, and optical phased arrays (OPAs) for laser communications, require faster response times. In order to achieve a fast response time, low rotational viscosity (γ_1) LC mixtures are preferred [2–4]. Another straightforward approach is to use a thin cell gap filled with a high birefringence (Δn) and low viscosity LC mixture [5, 6]. High birefringence also enhances the display brightness and contrast ratio of polymer-dispersed liquid crystal (PDLC), holographic PDLC, cholesteric LCD, and LC gels [7–10]. Recently, many manufacturers have reported display devices with reduced cell gaps of below 4 μm in order to achieve fast response time.

The most effective way to increase birefringence is to elongate the π-electron conjugation lengths of the LC compounds [11, 12]. 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 compounds, but they tend to exhibit smectic phases [13]. The CN group has a larger dipole moment ($\mu=3.9$ D) than NCS ($\mu=3.7$ 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 [14]. Accordingly, dimers 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 [15]. In contrast, the dipole moment of the NCS group is ~30% lower than that of CN. Thus, such an LC medium will allow for faster switching times by using a thinner cell gap, allowed by increased optical anisotropy.

Based on the principles mentioned above, we decided to investigate a group of highly polar isothiocyanates with totally unsaturated rigid cores as compounds that would give, potentially, the fastest high birefringence liquid crystal mixtures for photonic applications. Molecular structures, mesomorphic and electro-optical properties of the single compounds and eutectic mixtures are reported. Potential applications for optical phased arrays are discussed.

2. Experimental

Several measurement techniques are typically involved in characterizing the physical properties of the LC compounds and mixtures. For the electro-optic

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measurements, we prepared homogeneously aligned cells with cell gaps ranging from $d \sim 4$–$8\,\mu m$, while a linearly polarized He-Ne laser ($\lambda = 632.8\,nm$) was used as the light source. A linear polarizer was placed at $45°$ with respect to the LC cell rubbing direction and an analyser 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 a.c. 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–$3°$. The cell was held in a Linkam LTS 350 large area heating/ freezing stage equipped with a Linkam TMS94 temperature programmer. The phase retardation (δ) of the homogeneous cells was measured by the LabVIEW system. The LC birefringence (Δn) at wavelength λ and temperature T can be obtained by measuring the phase retardation of the homogeneous cell from the following equation [11]:

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

In addition, we also estimate Δn at $\lambda = 1.55\,\mu m$ using a single band birefringence dispersion model [16]:

$$\Delta n = G \lambda^2 \lambda^{*2} / \left(\lambda^2 - \lambda^{*2} \right) \qquad (2)$$

where G is the proportionality constant and λ is the mean electronic transition wavelength. By measuring the LC birefringence at two visible laser wavelengths, G and λ^* can be obtained. Once these two parameters are determined, the birefringence at any wavelength of interest, e.g. $\lambda = 1.55\,\mu m$, can be extrapolated from equation (2).

To characterize the performance of liquid crystal mixtures, a figure-of-merit (*FoM*) which takes phase change and response time into account has been defined as [17]:
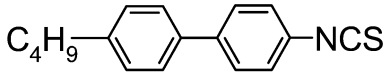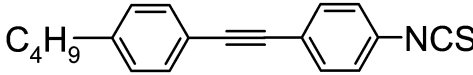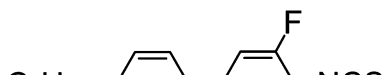
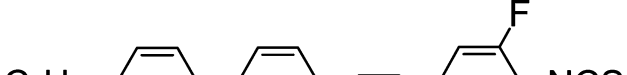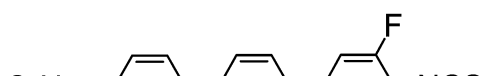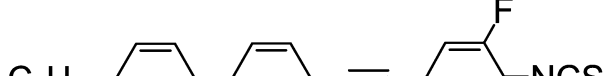$$FoM = K_{11} (\Delta n)^2 / \gamma_1 \qquad (3)$$

where K_{11} is the splay elastic constant, Δn is the birefringence, and γ_1 is the rotational viscosity. All of these parameters are temperature dependent. The dielectric anisotropy ($\Delta \varepsilon$), threshold voltage (V_{th}), and elastic constants (K_{11}, K_{33}) were measured by the LCAS II system from LC Vision. All the measurements were conducted at a room temperature of $23°C$ and the applied a.c. 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 ($\sim 1.5\,mg$) at a $2°C\,min^{-1}$ scanning rate. The observed LC phase transitions were confirmed by polarizing optical microscopy (POM). The UV absorption spectra of the single LC compounds were measured using a dual channel Cary 500 UV/Vis/IR spectrophotometer. To avoid detector saturation, the LC samples were dissolved in cyclohexane with 2×10^{-4} molar concentrations. Standard quartz semimicrocells of 10 mm thickness were used in the sample and reference channels of the spectrophotometer.

3. Single compounds

Our study focuses on thermotropic, rod-like molecular systems with a polar isothiocyanate terminal group. The rigid cores of the molecules and lateral substitutions vary, aiming to get as high as possible a value of the birefringence, while keeping a relatively low viscosity. Therefore, the residues typically used for the rigid core of the nematic LC compounds are phenyl (benzene) and naphthalene rings. Phenyl ring and naphthalene ring systems are unsaturated residues, both rich in π-electrons. Thus, these rings are particularly desirable for elongating π-electron conjugation through the rod-like molecule and increasing the polarizability along the principal molecular axis. Another source of π-electrons, which may contribute to π-electron conjugation through the molecule, is the unsaturated double and triple carbon–carbon bonds, which bridge unsaturated rings of the rigid core. Double carbon–carbon bonds [18] were reported as extremely weak under UV and even daylight conditions [19] so we concentrated on tolane-based rigid cores, as their photochemical stability appears to be higher. Four different groups of high birefringence LC compounds were chosen for discussion.

Scheme 1 lists the compound structures and their phase transition temperatures with respect to the different formations of the rigid core. The biphenyl-isothiocyanate (PP-NCS) compounds exhibit melting temperatures near $84°C$ and $55°C$, respectively for four (C4) and five (C5) carbons in the terminal alkyl chain. The C5 homologue shows a short nematic phase range that ends at $74°C$. The PP-NCS compounds have a strong tendency to form a smectic phase. To avoid this undesirable feature, laterally fluorinated compounds were synthesized, whose melting temperatures are much lower. We measured $32°C$ and $28°C$, respectively for the C5 and C7 homologues. No smectic phase is observed in the fluorinated PP-NCS compounds but the nematic temperature range is rather narrow. Another group of molecules with an NCS terminal group, chosen for these experiments, is based on the terphenyl rigid core, which

No	Structure	No	Structure
1	C₄H₉—⟨phenyl⟩—⟨phenyl⟩—NCS PP4NCS Cr 84 (N 25) Iso	5	C₄H₉—⟨phenyl⟩≡⟨phenyl⟩—NCS PTP4NCS Cr 44 SmK 71 SmE 87 Iso
2	C₅H₁₁—⟨phenyl⟩—⟨phenyl-F⟩—NCS PP(3F)5NCS Cr 32 Iso	6	C₄H₉—⟨phenyl⟩≡⟨phenyl-F⟩—NCS PTP(3F)4NCS Cr1 38 Cr2 41 (N 17) Iso
3	C₄H₉—⟨phenyl⟩—⟨phenyl⟩—⟨phenyl-F⟩—NCS PPP(3F)4NCS Cr 130 N 265 Iso	7	C₄H₉—⟨phenyl⟩—⟨phenyl⟩≡⟨phenyl-F⟩—NCS PPTP(3F)4NCS Cr 140.4 SmB 181.3 N 242.9 Iso
4	C₅H₁₁—⟨phenyl⟩—⟨phenyl⟩—⟨phenyl-2F⟩—NCS PPP(3,5F)5NCS Cr 95 SmA 108 N 187 Iso	8	C₄H₉—⟨phenyl⟩—⟨phenyl⟩≡⟨phenyl-2F⟩—NCS PPTP(3,5F)4NCS Cr 67 SmA 98 N 207 Iso

Scheme 1. Single compound structures and their phase transition temperatures (°C).

has been widely used in commercial high birefringence mixtures. A popular example is 4-cyano-4″-pentylterphenyl, also known as T15 or 5CT [20]. The phase transition temperatures of 5CT are relatively high, with a melting point at 130°C and clearing point at 239°C. Based on experience with highly linear molecular structures, we decided to start from single laterally fluorinated cores rather than synthesize the double fluorinated ones. The melting point of the single fluorinated compound PPP(3F)-4NCS is ~130°C and its clearing point ~265°C, which is rather similar to that of 5CT. By introducing another fluorine atom into the neighbourhood of the polar NCS group, we were able to reduce the melting point to 107°C and 95°C for the PPP(3,5F)-3NCS and PPP(3,5F)-5NCS compounds, respectively. Unfortunately, the second compound exhibits a smectic phase from 95° to 108°C.

Neither of the mentioned groups of NCS compounds have any bridging group between unsaturated phenyl rings. Further increase of the π-electron conjugation could be obtained by introducing one or two unsaturated linking groups between the phenyl rings. We considered two groups of this kind of single compound. The first group is based on the tolane rigid core (with possible lateral fluorination); the second group is based on the phenyl-tolane core with single or double fluorination. Simple NCS-tolane compounds with relatively short alkyl or alkoxy chains typically do not show an enantiotropic nematic phase [21]. For longer alkyl chain NCS-tolanes, a highly ordered Smectic E (SmE) phase is observed as a monotropic phase. In the case of alkoxy chain analogues, the SmE phase appears in longer chain homologues [22]. The single lateral fluorination lowers the melting temperature and the nematic phase appears, although it is monotropic. The (3,5) double fluorinations further decrease the melting point but an enantiotropic nematic phase still does not appear.

The last group of reported high birefringence compounds is based on the phenyl-tolane rigid core. Working with such a highly conjugated linear structure is particularly difficult. High linearity results in a strong tendency to form smectic phases and high melting point temperatures, well above 100°C (see scheme 1). Phenyl-tolane, 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 the smectic phase; at 221°C the transition to the nematic phase takes place. Finally, the isotropic state occurs at 270°C. The high melting temperature and occurrence of the 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 67°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 98°C, respectively.

Although the mesomorphic properties of the discussed single compounds appear to be far from ideal, and their usability is questionable, these types of molecules exhibit superior electro-optic properties when filled into the LC cell. The birefringence of the isothiocyanato-biphenylates is approximately 0.22–0.24 while that of isothiocyanato-terphenyls is increased to 0.36–0.38. The same level of birefringence is observed for the isothiocyanato-tolanes; but for their phenyl derivatives, the birefringence increases much more, becoming as high as 0.46–0.48. Thus, we favour the tolane rigid cores because of their high birefringence and low viscosity. A disadvantage of the tolane structure is its inadequate UV stability [23]. However, for infrared application the photostability is not a great concern.

Figures 1(a) and 1(b) plot the temperature-dependent figure-of-merit for the single fluorinated PPTP(3F)-4NCS and double fluorinated PPP(3,5F)-NCS compounds, respectively. Their maximum FoM values (at $T \sim 150°C$) reach 250 and 120 $\mu m^2 s^{-1}$, respectively. The *FoM* of PPTP(3F)-4NCS 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 hot stage. Thus, we extrapolate the *FoM* of these two compounds at room temperature. We fit the data measured at elevated temperatures using equation (3) and find that the *FoM* stays ~20 and 10 $\mu m^2 s^{-1}$ for the phenyl-tolane and terphenyl compounds, respectively, as shown in figures 1(a) and 1(b), respectively.
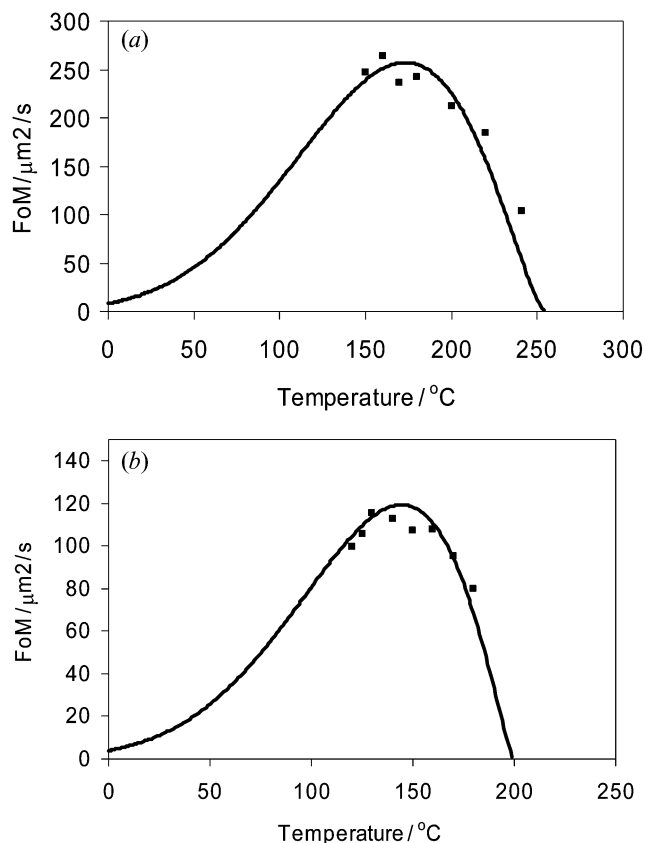

Figure 1. The temperature-dependent figure-of-merit of (a) PPTP(3F)-2NCS and (b) PPP(3,5F)-3NCS. Dots are experimental results and lines are fittings using equation (3).

Typically, high birefringence compounds are solid at room temperature. Thus, we measured the UV absorption spectra from cyclohexane solution. Figure 2 shows
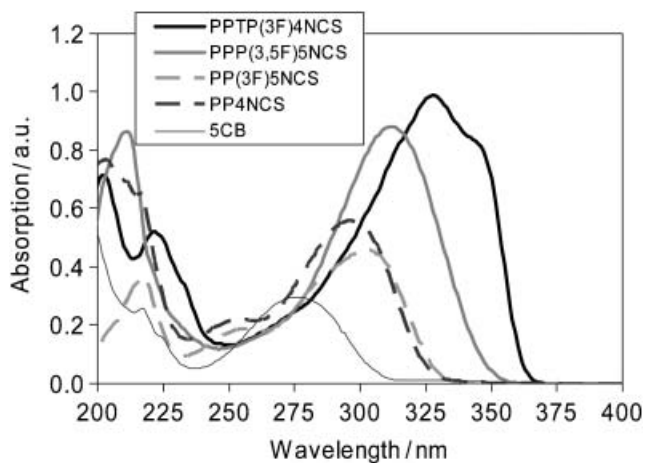

Figure 2. The measured absorption spectra of four isotiocyanate compounds in comparison with the pentylcyanobiphenyl (5CB) compound. Each LC compound was dissolved in cyclohexane solution at 2×10^{-4} molar concentration. Cell gap is 1 cm.

the measured UV absorption spectra of some of the single compounds listed in scheme 1. All of the presented NCS compounds have a longer absorption tail than that of 5CB ($\lambda = 310$ nm), shown as a bench-mark for comparison. This is chiefly because they all have a longer π-electron conjugation than the pentyl-cyanobiphenyl. Due to the extended π-electron con-jugation, NCS-phenyl-tolane (**7**) pushes the absorption tail as far as $\lambda \sim 370$ nm. From the tolane group, the alkyl tolane PTP-4NCS (**5**) has an absorption tail at $\lambda = 343$ nm. Overall, this means that all of these compounds absorb long wavelength UV light. The extra precaution of protecting these high birefringence LC devices from UV ($\lambda \sim 365$ nm) exposure should be taken. In general, highly conjugated LC structures are not suitable for applications that require a UV curing process [24].

4. Eutectic mixtures

Based on the single component results, we formulated some test mixtures for comparison with some commer-cial materials and our previously reported mixtures. Two Merck mixtures were selected for comparison: MLC 10400-000 (a TFT mixture) and E44 (a high birefringence mixture). We prepared two experimental mixtures, UCF-A with moderate birefringence, and UCF-B with high birefringence. As mentioned before, the higher figure-of-merit implies a faster switching speed. Thus, we decided to formulate liquid crystal mixtures using only the unsaturated rigid core isothio-cyanate compounds. The mixtures are thus very different from those in our previously reported studies, where the mixtures were based on hosts containing 4′-alkylcyclohexyltolane-isothiocyanates or laterally fluorinated analogues [25, 26].

The compositions of the reported UCF mixtures are based on, but not limited to, those listed in scheme 1. Detailed physical and electro-optic properties of two UCF and two Merck mixtures are listed in table 1 for comparison; the differences are easily seen. The UCF-B mixture contains only unsaturated (highly conjugated)

rigid core molecules. The UCF-A was doped with molecules containing a saturated cyclohexane ring incorporated into the rigid core. The basic reason for doing this, in the case of UCF-A, was to match the birefringence of the E44 LC mixture. The Cyano based E44 mixture which has a relatively high birefringence is frequently chosen for LC-polymer composites although there are some concerns about the photostability of this mixture [27].

5. 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% [14, 28]. Thus, fluorinated NCS or CN compounds are useful for active matrix displays.

We also purified our NCS-based high birefringence mixtures ($\Delta n \sim 0.38$), with acceptable yield, up to a resistivity level of 10^{+13} [29]. In addition, the birefrin-gence of 0.38 and higher (at $\lambda = 633$ nm) allows the use of a relatively thin cell gap at a $\lambda = 1550$ nm wavelength to obtain the required 2π phase change. According to the single band birefringence dispersion model, equa-tion (2), the birefringence of the UCF-B is estimated to be $\Delta n \sim 0.3$ at $\lambda = 1.55\,\mu$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.

6. 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 unsaturated rigid core structures with a highly polar NCS terminal group, we were able to obtain a record high *FoM* value. For the first time, we formulated a

Table 1. Physical and electro-optic properties of the investigated mixtures.

Mixture	$T_{mp}/$°C	$T_c/$°C	V_{th}/V_{rms}	$\varepsilon_\parallel$	$\varepsilon_\perp$	$\Delta\varepsilon$	$K_{11}/$pN	$K_{33}/$pN	K_{33}/K_{11}	Δn	$\gamma_1/K_{11}/$ ms μm^{-2}	*FoM*/ μm^2 s^{-1}
MLC 10400-000	< -30	98	2.5	7.5	3.4	4.1	13.8	28.0	2.03	0.107	7.1	1.6
E44	-6	100	1.4	17.8	4.1	13.7	13.3	40.3	3.03	0.248	22.8	2.7
UCF-A	-6	89	1.7	13.5	3.0	10.5	15.6	54.9	3.52	0.254	6.4	10.1
UCF-B	13[a]	95	1.6	19.9	4.2	15.7	20.9	40.2	1.92	0.354	6.7	18.7

[a]Smectic phase.

high performance nematic mixture with $FoM \sim 20\,\mu m^2\,s^{-1}$ at $T \sim 23°C$. Previously, to obtain such a performance, an elevated temperature would have been needed in order to shorten the response time. The best results for commercial nematic mixtures under the same experimental conditions are measured to be below $3\,\mu m^2\,s^{-1}$. The high birefringence of our UCF mixtures permit the use of a thinner cell gap which efficiently reduces the response time, while the required optical phase change is maintained. The on-off-on switching time obtained for UCF-B mixture using a $2\,\mu m$ cell gap was $640\,\mu s$ at $35°C$, which is the fastest optical modulator driven by simple square waves. Applications for various OPA and optical shutter devices are foreseeable. The possibility of applications in the telecommunications industry will be determined.

Acknowlededgments

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