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A practical liquid crystal mixture for IR applications

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A practical liquid crystal mixture for IR applications

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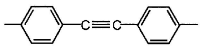
The goal of this work was to formulate an inexpensive room temperature nematic mixture having a large birefringence in the near-IR and good switching properties. It was accomplished by mixing two liquid crystalline compounds that are easy to synthesize with a commercial liquid crystal, E7. In view of the good electro-optical properties of the mixture and the simplicity of the syntheses, it is considered to be a very practical liquid crystal material for applications in the near-IR.

1. Introduction

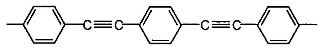
Since the invention of 'twisted nematic' (TN) displays in 1974, progress in liquid crystal (LC) electro-optic devices has been remarkable. At present, LC displays (LCDs) for consumer markets, such as calculators and notebook computer screens, and some advanced applications, such as light switches and modulators, are mainly designed for applications in the visible region of the spectrum. On the other hand, many important industrial operations require devices specially designed to function in the infrared (IR) range. In particular, the important fibre-optic technique of dense wave division multiplexing (DWDM) often operates at or near 1550 nm, and liquid crystal technology development for applications in telecommunication has recently attracted special attention [1]. However, the birefringence (Δn) for most commercial liquid crystals is not high enough for these kinds of application. Therefore, liquid crystals with high birefringence in the near-IR region have been synthesized, and their electro-optic properties studied [2].

Most commercial LCs, including cyanobiphenyls and cyanoterphenyls, do not have a highly conjugated mesogenic core, so that their birefringence is quite low; they are suitable mostly for reflective-mode displays. On the other hand, the phenylacetylene unit, which is conjugated and linear, is very favourable for imparting to a liquid crystal a large Δn extending into the IR. Many of these also have reasonable nematic ranges and low viscosities. Compounds studied include tolanes [3–6], bistolanes [7–9], diphenyldiacetylenes (PTTP) [4, 10, 11], thiophenylacetylenes [12], and dibenzothiophenylacetylenes [13].

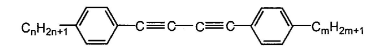
Tolanes



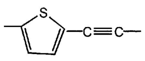
Bistolanes



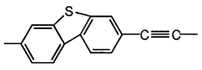
PTTM-nm



Thiophenylacetylenes



Dibenzothiophenylacetylenes



For these types of compounds, each of which contains two or more aromatic rings without lateral substituents, the melting points are usually above room temperature. Therefore, they can only be used as dopants or components in mixtures for room temperature applications. One of the simplest eutectic mixtures is PTTP-24/36 [14], which has been used as a solvent for the formulation of LC mixtures with high Δn. For example, we have reported that several LC mixtures of fluorinated 1-(4-alkylpiperidylphenyl)-2-(4-nitrophenyl)-diazenes dissolved in PTTP-24/36 show very good electro-optic properties [15]. However, the diazenes and many other phenylacetylene compounds, including the eutectic mixture PTTP-24/36, require elaborate syntheses with rather limited yields, rendering them impractical for actual applications. Therefore, we have devoted considerable

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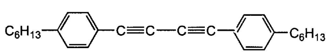
effort to formulate liquid crystal mixtures with high Δn in the near-IR, low threshold voltage, and short switching times, for *practical* applications. The most successful result is reported here.

2. Results and discussion

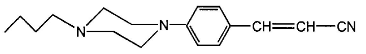
The desired liquid crystal mixture should have large Δn in the near-IR region, high dielectric anisotropy ($\Delta\varepsilon$) for low threshold voltage, and low viscosity for fast switching. It must be nematic at room temperature.

Since PTTPs have large Δn, they can be used as a component in the LC mixture. However, the asymmetrical compounds PTTP-24 and PTTP-36 require many steps to synthesize, and yields are not high. Therefore, we chose a symmetrical compound PTTP-66, which has the lowest melting point (59°C) among all symmetrical PTTPs, as one of the components in the mixture:



PTTP-66

The PTTPs, whether symmetrical or asymmetrical, have very low dielectric anisotropy and therefore high threshold voltage. To overcome this problem, we chose a compound with a large molecular dipole moment as the second component. Compounds containing an electron-donating group at one end of a conjugated system and an electron-accepting group at the other end ('push–pull' structure) have this property. We found that some fluorinated 1-(4-alkylpiperidylphenyl)-2-(4-nitrophenyl)-diazenes have very large $\Delta\varepsilon$ [15, 16], but they require elaborate syntheses and are therefore only suitable for laboratory investigations. Therefore, another type of push–pull compound, alkyl cyanoethenylphenyl piperazines, which have reasonable melting points, was considered. Although these compounds have a shorter conjugated core and a weaker electron-accepting group ($-CN$ instead of $-NO_2$), they are easy to synthesize with high yield [17]. Therefore, we chose one of the homologues, 4CNPP (melting point 61°C), as another component of the mixture.



4CNPP

The melting points of mixtures of PTTP-66 and 4CNPP were studied, showing that the eutectic mixture has a weight ratio of 64 : 36. However, its melting point is 23°C, too high for room temperature applications.

The commercial LC mixture E7 has a wide nematic range, low threshold voltage, and short switching times, and is often used as the solvent to measure the electro-optic properties of other LCs. Therefore, we chose it as the third component to formulate a LC mixture with good overall properties for practical near-IR applications. The mixture contains 4CNPP, PTTP-66 and E7 in weight ratios of 3 : 4 : 3, and has a melting point of 9°C. It is called TF-mixture for the sake of simplicity.

Before we address the electro-optic and viscoelastic properties of the mixture, its chemical and physical properties are briefly discussed.

It is known that PTTP compounds [4, 10, 11] do not have high photo-stability in the UV range. Although this is not critical for IR applications, the new component 4CNPP should be no less stable than the PTTPs. A survey of the literature indicated that the conjugated framework of 4CNPP, *trans*-cinnamonitrile, is quite stable both chemically and photochemically. For example, it survives the attack of strong bases such as sodium ethoxide [18, 19], and adds to ethyl cyanoacetate only at elevated temperatures [20]; photochemically it undergoes cycloaddition only with certain conjugated compounds [21, 22].

Physically, PTTTs are known to have very low solubility in cyanobiphenyl liquid crystals because of complex formation [23]. However, 4CNPP mixes with PTTP-66 completely and possibly prevents the formation of complexes with cyanobiphenyls, so that a large amount of E7 can be added to the eutectic mixture without precipitation. Although the melting point of the TF mixture is higher than that of E7, it is low enough to be suitable for room temperature applications.

The birefringence of the TF-mixture was measured at room temperature as a function of wavelengths (λ), using a home-built instrument [14, 15]. The results are shown in the figure. Like all other systems studied, the birefringence values of the mixture gradually decrease with increase of wavelength. This change can be described using the equation [24]

$$\Delta n(\lambda, T) = G(T)\frac{\lambda^2(\lambda^*)^2}{\lambda^2-(\lambda^*)^2} \qquad (1)$$

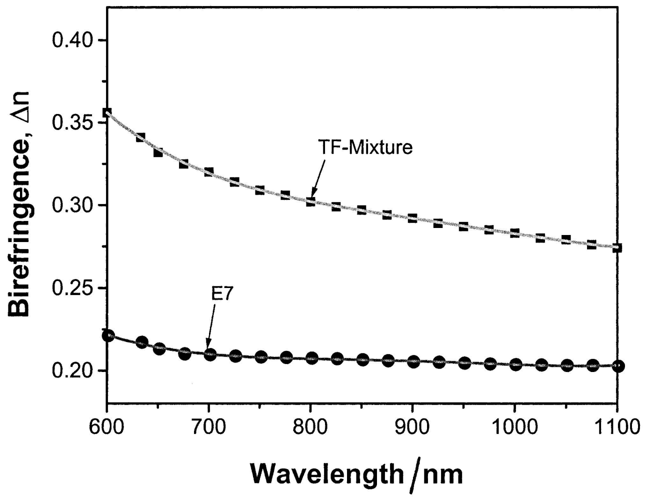


Figure. Wavelength dependence of the birefringence of the TF-mixture and E7.

Table. Dielectric and elastic properties of the TF-mixture (4CNPP/PTTP-66/E7 in ratios of 3:4:3) and E7 alone. The rise time is defined by the change of transmittance from 10% to 90%; a driving voltage of 8.0 V was used in our experiments.

	d / 10^{-6} m	V_{th} / V	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	K_{33}/K_{11}	γ_1/K_{11} / 10^9 m^{-2} s	Rise time / 10^{-3} s
TF-mixture	3.87	1.74	14.18	4.07	10.11	1.53	29.3	19
E7	4.25	1.55	18.95	5.21	13.74	1.41	23.6	15

where $G(T)$ is a function which includes the effect of temperature and is wavelength independent, and λ^* is the mean resonance wavelength. Both $G(T)$ and λ^* can be obtained by fitting the Δn data as a function of λ to equation (1). The best-fit curves are shown in the plot. The value of $G(T)$ for the TF-mixture is equal to 2.34×10^{-6}, and λ^* is 302 nm at room temperature.

For $\lambda \gg \lambda^*$, equation (1) can be simplified to $\Delta n(\infty) = G(\lambda^*)^2$. This is the extrapolated birefringence value in the far infrared region. For commercial liquid crystal mixtures, the values of $\Delta n(\infty)$ are 0.191 for E7, 0.123 for ZLI-1132, and 0.179 for NP-5 [25]. The $\Delta n(\infty)$ value for the TF-mixture is 0.213, which is considerably higher. By substituting the values of $\Delta n(\infty)$ into equation (1), it can be found that at $\lambda = 1550$ nm, the wavelength used for DWDM applications, $\Delta n = 0.222$ for the TF-mixture, compared with 0.198 for E7.

The electro-optic measurements of the TF-mixture were carried out using a Displaytech APT III automatic property tester [15, 16]. The dielectric, switching and elastic properties of the TF-mixture, together with those of E7, are listed in the table. The data show that the TF-mixture has smaller values in $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and $\Delta\varepsilon$, and bigger values in V_{th} and K_{33}/K_{11} than those of E7. This is partly due to the non-polar structure of PTTP-66. The viscoelastic coefficient determines the decay time of the electro-optic response [26]. It can be seen from the table that the TF-mixture has slightly higher γ_1/K_{11} and rise-time values than E7.

3. Conclusion

In conclusion, a new liquid crystal mixture has been formulated. It contains 4CNPP/PTTP-66/E7 with weight ratios 3:4:3, and is called TF-mixture. Its physical properties were measured. The value of Δn is 0.222 at $\lambda = 1550$ nm, the threshold voltage is 1.74 V, and the rise time is 19 ms. Although the birefringence of the TF-mixture is lower than for some of the compounds studied previously [15], and the threshold voltage and the rise time are slightly larger than E7, these parameters are still good enough and suitable for applications in the near-IR. Most importantly, the components 4CNPP and PTTP-66 are quite easy to synthesize with good overall yield (25% and 27%, respectively). Therefore, the TF-mixture is a good candidate for *practical* applications in LC devices operating in the near-IR. If it is tolerable to have a slightly higher threshold voltage and longer switching times, the percentage of PTTP-66 can be increased to give mixtures with even larger Δn values.

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