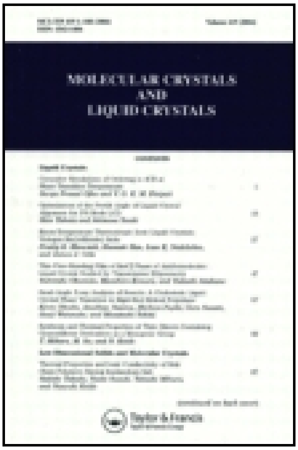

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Electro-Optic Properties of an Unusual Guest-Host Liquid Crystal Mixture: A Mauve Anthraquinone Dye in a Ferroelectric Organosiloxane

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Electro-Optic Properties of an Unusual Guest-Host Liquid Crystal Mixture: A Mauve Anthraquinone Dye in a Ferroelectric Organosiloxane

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We examine here the electro-optic properties of an unusual guest-host liquid crystal mixture of a high contrast anthraquinone dye and a new ferroelectric organosiloxane liquid crystal. From measurements of the transition temperatures, tilt angles, spontaneous polarisations and rotational viscosities, we show that dye concentrations as high as 4% w/w have negligible effect upon the host properties. Furthermore, we show that the mixture, with a constant tilt angle of 36° across its smectic-C* phase range from 50°C down to 10°C, high absorbance and good alignment, produces contrast ratios in the V–V scattering mode of 50:1 or higher, with optical response times of 120 μs or less at 20°C. We argue that the technological implications of mixtures of this type are important, due to their being composed of only two components and having properties surpassing that of commercial optimised mixtures.

Keywords: Ferroelectric, guest-host, organosiloxane, anthraquinone

INTRODUCTION

The surface-stabilised ferroelectric (SSFLC) device is presently the object of much research due to its application to display technology and its potential replacement of the need for TFT (thin-film transistor) technology in many device modes.[1,2] Many of the initial problems of SSFLC displays—related to poor alignment quality, resistance to mechanical shock and temperature variation of many of the key ferroelectric properties—appear to have been overcome in practice. New alignment polymers, compensating addressing schemes and rugged fabrication techniques have all been incorporated into prototype displays.[3] Recently, we announced[4] an unusual new series of room temperature organosiloxane ferroelectric liquid crystals in which the optical tilt angle and spontaneous polarisation were virtually independent of temperature between 10°C and 50°C, and in which the rotational, or projection, viscosity was lower than many commercially available mixtures. These materials would therefore

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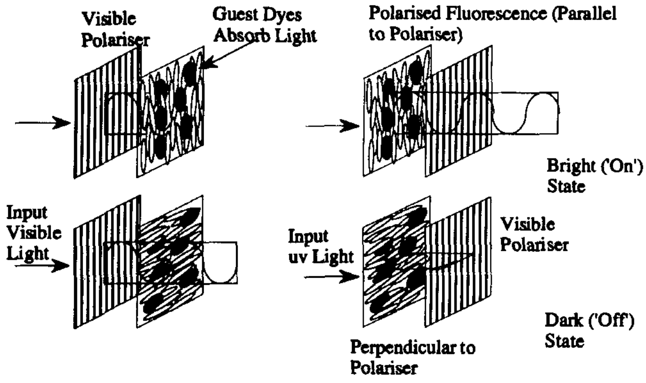
appear to have great potential as an alternative molecular solution to the above driving and fabrication problems.

A further problem that arises, which is particularly important for low power consumption portable displays, is that of low optical efficiency. Most devices to date use a birefringence mode of operation incorporating a crossed polariser-analyser pair to produce a monochrome display.[5] A coloured or polychrome display is then made by overlaying a colour filter matrix onto the device. This, however, leads to a further transmission loss and it is unusual to produce an optical throughput of greater than 20%. Hence such displays require fairly high-powered backlighting. One method of improving the optical throughput, by at least a factor of two, whilst still maintaining the colour feature, is to use a single polariser dye guest-host device as an alternative to the birefringence mode. This has a further advantage that colour can be produced either through subtractive (absorption) or additive (emission/fluorescence) processes.

The dye guest-host (DGH) effect was first recognised in nematic liquid crystals many years ago.[6] In this effect a guest dye is dissolved into the liquid crystal matrix such that the dye co-aligns with the host's director. Application of an external electric field causes the director, and hence dye, to realign. Assuming that the dye is dichroic (or more generally pleochroic), the realignment process also induces a change in the macroscopic absorption properties of the DGH mixture, leading to a colour switching device. The DGH effect was recognised more recently in ferroelectric liquid crystals (DGHFLCs).[7] In the latter effect the dye is again aligned along the director, at an angle θ (the tilt angle) to the smectic layer normal. Assuming an SSFLC geometry, application of a polarisation reversing field switches the director and hence the dye molecules from $+\theta$ to $-\theta$. If this dye is chosen such that its direction of maximum absorption is also along the direction of its major geometric axis then this absorption direction will switch through 2θ. The overlaying of an external polariser parallel to either $+\theta$ or $-\theta$ creates a dark to light or light to dark transition in transmitted light intensity, thereby producing a simple, fast absorption or fluorescence mode device (Figure 1).

Such devices have not hitherto been exploited commercially[8] and there are several reasons for this. Firstly, incorporation of the dye at high enough concentration to



(a) Dichroic Absorption Mode **(b) Polarised Fluorescence Mode**

FIGURE 1 Schematic of guest-host device operation in the SSFLC configuration.

produce a good extinction ratio often alters the phase transition temperatures, optical tilt angle and spontaneous polarisation properties of the host FLC. Secondly, optimal contrast ratios require a tilt angle of 45°C as opposed to 22.5° for a birefringence mode device. This high tilt angle leads to difficulties in producing defect-free textures (needed for bistability and low scattering). Most materials that use a compensated chiral nematic-smectic A–smectic C* phase sequence (with a second-order S_A/S_C^* phase transition to give a defect-free bookshelf geometry in the SSFLC configuration) rarely give tilt angles greater than 25° at or near to room temperature. Thirdly, the high tilt angle materials give slower response times than the low tilt (22.5°) systems, due simply to the increased angle swept by the molecules during switching. Finally, dyes with good absorption coefficients, large geometrical anisotropy and high order parameter in the host tend to be elongated structures[9] that increase the viscosity and hence slow down the response times further.

In the present work we have re-examined the DGH effect using our novel organosiloxane materials. As shown previously,[10] these host FLC materials have high tilt angles ($\sim 36°$) which are independent of temperature from well below room temperature up to 50°C. Further, these materials have lower rotational viscosities than many commercially available mixtues, and may be readily aligned, despite their high tilt angle, using an electrohydrodynamic mode[11] at the isotropic-to-smectic phase transition. The anthraquinone guest dye we use was chosen because of its already favourable behaviour in DGHFLC mixtures based on commercially available hosts.[12] Herein we will present data on the alignment procedures, contrast ratio, tilt angles, spontaneous polarisations and rotational viscosities as functions of temperature for these new organosiloxane-based DGHFLC mixtures.

EXPERIMENTAL

The host was doped with 4% (w/w) with the dye CLU503300. The structures of the host organosiloxane FLC and anthraquinone dye are shown below (Figure 2).

The mixture and pure host were studied in electro-optic cells specially made for us (manufactured by EEV Lucid), comprising two Indium-Tin Oxide coated glass surfaces with rubbed polyimide surface alignment layers applied to them. These are then

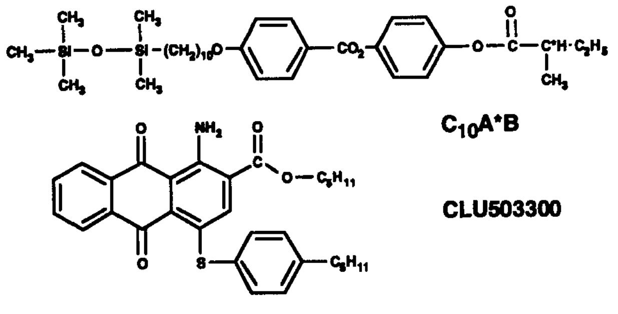


FIGURE 2 Molecular structure of materials used. $C_{10}A^*B$ is the host organosiloxane FLC and CLU503300 is the anthraquinone dye.

TABLE I

Transition Temperatures of the Samples

Pure Material	I50.4°C S_C^* ~ 10°C Cryst.
Dyed Material	I51.2°C S_C^* ~ 10°C Cryst.

assembled into the cell with microsphere glass sphere spacers to produce 3.4 μm thick sample cells with the polyimide rubbing directions being antiparallel.

IDENTIFICATION OF THE PHASES

The thermal behaviour of the liquid-crystalline phases was investigated using polarising microscopy observations, X-ray analysis and differential scanning calorimetry (DSC).

Microscopic Observations

The textures and transition temperatures of the mesophases were studied by polarising optical microscopy using a Nikon L-Ke polarising microscope linked to a Mettler FP82 Hot Stage and Mettler FP80 temperature controller. X-ray analysis was also performed,[13] confirming a single enantiotropic smectic-C phase in both the pure and dyed ferroelectric samples, with transition temperatures measured optically as in Table I. In the thin (3.4 μm) cells the mesophase supercools and crystallises at typically less than -5°C. The samples are robust, withstanding large electric fields (more than 30 Vμm^{-1}) without degradation and showing no observable change in properties over several weeks of exposure to normal light and environmental conditions.

FERROELECTRIC PROPERTIES

Alignment

Ferroelectric liquid crystals with first-order transitions into the ferroelectric phase do not generally align well using the same methods as those used for FLC phases underlying orthogonal smectic and chiral nematic phases, due to the multiple formation of Dupin cyclides on cooling into the smectic from the isotropic phase. This results in the natural focal-conic optical texture when viewed by polarising microscopy.

In order to align this material we therefore used the effect of the electrohydrodynamic (EHD) instability, in this case applying a low-frequency (~200 Hz) alternating electric field (~10 V μm^{-1}) to the SSFLC cell at the isotropic/smectic C* transition, causing the Dupin cyclides to align and coalesce, producing a quasi-bookshelf geometry on cooling. Figure 3 shows a typical alignment obtained in $C_{10}A^*B$. This effect is discussed more fully elsewhere.[11]

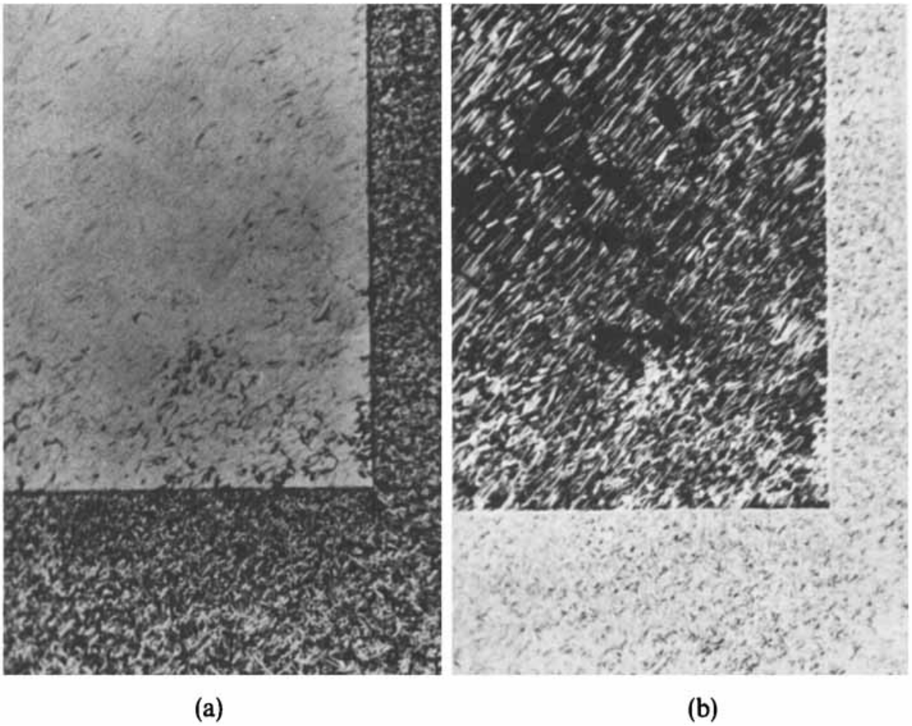


FIGURE 3 Alignment obtained in C_{10}A*B. (a) Shows the dark state, (b) shows the light switched state. The region where the EHD method has been applied is at the top right of each picture. The unaligned regions retain the natural focal-conic texture of the mesophase. Note the almost complete extinction obtained in the aligned area.

Electro-Optic Properties of the Pure and Dyed Organosiloxane

The electro-optic properties of the S_C^* mesophase of this material were studied in the electro-optic cells described above, having been aligned using the EHD process. With no field applied the bookshelf structure induced during alignment relaxes, the director assuming its preferred helical structure (the relaxation seen as birefringent flashes) and producing chevron-type zig-zag defects.[14] The measurements were thus taken in the switched (field applied) states, examining the variation of the properties of the aligned state of the mesophase (tilt angle, spontaneous polarisation and rotational viscosity) as a function of temperature.

Tilt angles were measured as half the angle between extinction positions on electric field reversal (square-wave applied field 10V μm^{-1} at 1Hz) under microscopic observation. These results are summarised in Figure 4.

Spontaneous polarisations were determined by the well-known current-pulse technique,[15] the value being determined directly from the integral of the induced current pulse during polarisation reversal (triangular-wave applied field 10V μm^{-1} at 100Hz).

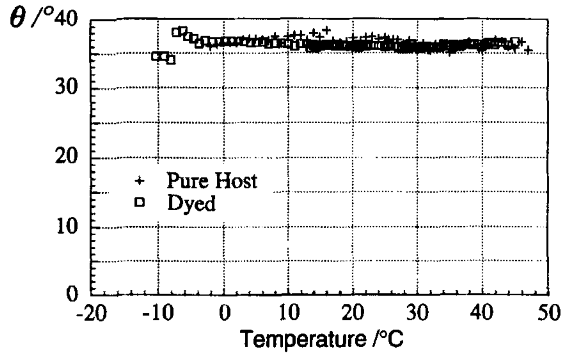


FIGURE 4 Variation of tilt angle with temperature of pure host and 4% (*w*/*w*) dyed mixture.

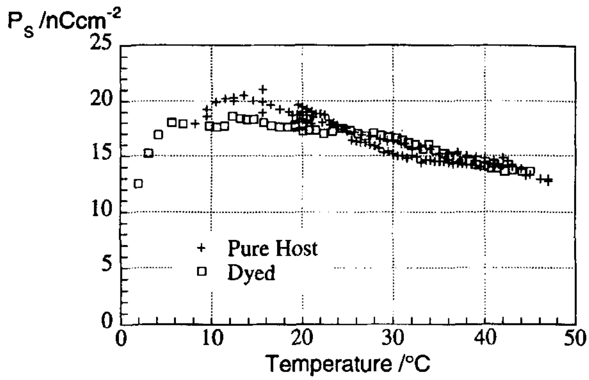


FIGURE 5 Variation of spontaneous polarisation with temperature of pure host and 4% (*w*/*w*) dyed mixture. The fall-off at low temperatures is due to the onset of crystallisation.

These are summarised in Figure 5. Effective viscosities were obtained using this method from the width of the current pulse during switching (Figure 6). Response times were also measured as the time taken for a 10–90% change in transmitted intensity of light at a single wavelength (632.8nm) when the applied electric field reverses polarity (square-wave applied field at 100Hz). This may only be done in the dyed case since contrast reversal occurs in the birefringence mode of the pure material (tilt angle greater than 22.5°). These results are summarised in Figure 7. As a comparison, the characteristic response times τ_C for the two samples as calculated from P_S and γ are shown in Figure 8, using the relationship

$$\tau_C = \frac{\gamma}{P_S E},$$

where the optical 10–90% response time $\tau \approx 1.8\,\tau_C$ (16).

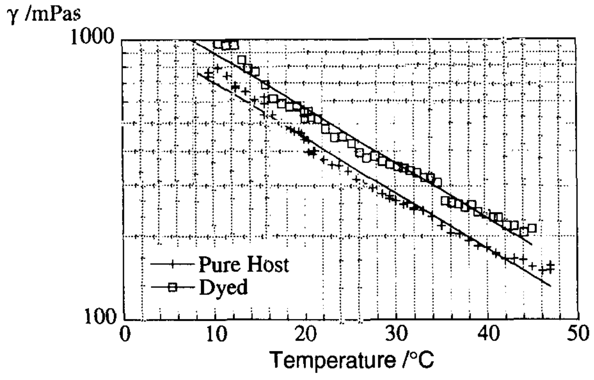


FIGURE 6 Variation of rotational viscosity with temperature of pure host and 4% (*w*/*w*) dyed mixture.

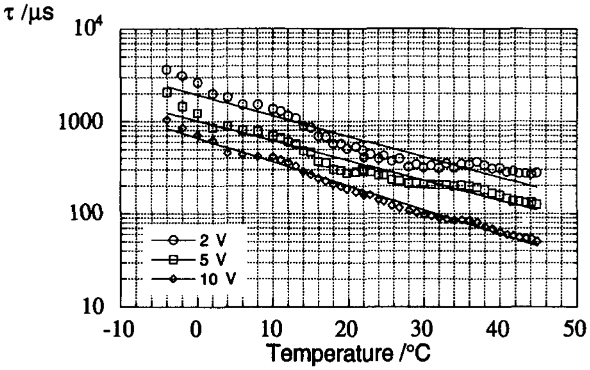


FIGURE 7 Variation of optical response time with temperature of 4% (*w*/*w*) dyed mixture in the dye guest-host mode at 2, 5 and 10 V μm^{-1}.

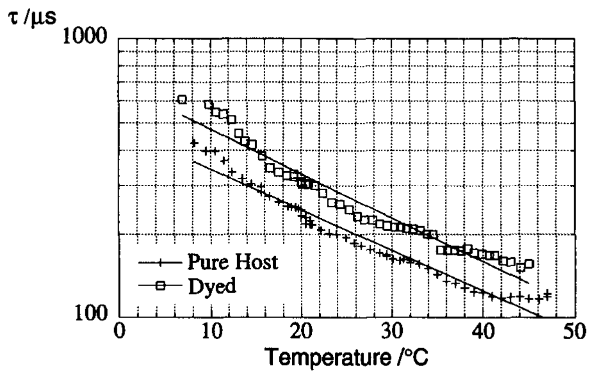


FIGURE 8 Variation of characteristic response times with temperature of pure host and 4% (*w*/*w*) dyed mixtures, as calculated from the switching current-pulse profiles.

TABLE 2

Properties of pure host and mixture with 2% CLU437730 at 20°C.

Property	Host Value	Dyed Mixture Value	Change / %
$\theta/°$	35.8	34.6	−3
P_S/nCcm^{-2}	19.5	18.6	−5
γ/mPas	495	390	−20

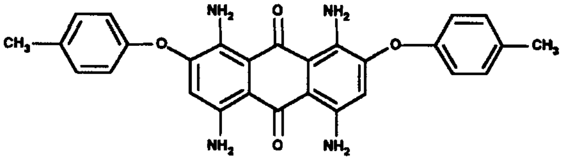


FIGURE 9 Structure of dye CLU437730.

DISCUSSION

As may be seen from the results presented, the inclusion of a significant percentage (4% w/w) of CLU503300 into the organosiloxane FLC produces little effect on its properties. The phase transition temperatures, tilt angles and spontaneous polarisations are essentially unaltered. Both θ and P_S remain independent (or nearly so in the case of P_S) of temperature. The rotational viscosity increases slightly on dye addition although the DGH mixture still has a lower viscosity than the non-dyed commercial mixture SCE13 (Merck Ltd.) despite its high (36°) tilt angle. This lower viscosity is reflected in the fast optical and characteristic response times. Response times (to a square-wave field of 10V μm^{-1}) of the order of 100 μs are readily achieved in the DGH mode at 20°C. In the impulse mode, used for matrix addressing, one would expect the minimum pulse width time to be an order of magnitude faster than this. CLU503300, chosen for its high absorption coefficient and solubility, is not isolated in its minor effect on this host. For instance, the related blue dye CLU437730 (Figure 9) also has a negligible effect on this host (see Table 2) at the 2% (w/w) concentration level. Generally, this group of dyes have a greater effect on host properties when doped into commercial mixtures.[12] The contrast ratios obtained are also promising, being greater than 50:1 in the V–V scattering mode for 3.4 μm thick sample cells. We may thus conclude that overall, this organosiloxane when combined with such anthraquinone dyes produces good materials for use in guest-host mode devices.

CONCLUSION

In fabricating guest-host devices, the current philosophy is to incorporate dyes into complex mixtures with second-order phase transitions to create good alignment on cooling through the transition.[8] However, the process of optimisation for these multiple-component systems is very complicated and haphazard, and results in mixtures with a large variation of material parameters with temperature, requiring temperature compensation and some compromise in the placing of polarisers etc. during fabrication. The use of first-order organosiloxanes obviates the need for all of this as the material parameters are much more constant, meaning that the entire phase range may be utilised, and the use of only two components means that the system may be much more easily optimised for specific applications. This is made feasible by the use of the EHD process to align the liquid crystal. We suggest that the accepted approach may therefore be redundant, as we have shown that it is possible to create systems with commercially usable parameters and high optical throughput. Future work should improve on these materials, but we have shown that these organosiloxane systems are promising for guest-host applications.

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References

1. J. Dijon, in *Liquid Crystals, Applications and Uses* (Vol 1), edited by B. Bahadur (World Scientific, 1990), Chap. 13.
2. S. T. Lagerwall and I. Dahl, *Mol. Cryst. Liq. Cryst.*, **114**, 151 (1984).
3. A. Tsuboyama, Y. Hanyu, S. Yoshihara and J. Kanbe, *Proc. Jap. Display*, **SID**, 53 (1992).
4. H. J. Coles, H. Owen, J. Newton and P. Hodge, *Liq. Cryst.*, **15**, 739 (1993).
5. N. A. Clark, M. A. Handschy and S. T. Lagerwall, *Mol. Cryst, Liq. Cryst.*, **94**, 213 (1983).
6. G. H. Heilmeier and L. A. Zanoni, *Appl. Phys. Lett.*, **13**, 91 (1968).
7. K. Kondo, S. Era, M. Isogai and A. Mukoh, *Jpn. J. Appl. Phys.*, **24**, 1389 (1985).
8. K. Kondo, personal communication.
9. R. J. Cox, *Mol. Cryst. Liq. Cryst.*, **55**, 1 (1979).
10. J. Newton, H. J. Coles, H. Owen and P. Hodge, *Proc. Int. FLC Conf.*, Tokyo, Japan (1993).
11. J. A. Guerst and W. A. Goossens, *Phys. Lett.*, **41**, 369 (1972).
12. J. Kang, Ph.D. Thesis (Manchester University, 1991).
13. M. Ibn-Elhaj, to be published.
14. N. A. Clark and T. P. Rieker, *Phys. Rev. A*, **37**, 1053 (1988).
15. C. Escher, T. Geelhaar and E. Böhm, *Liq. Cryst.*, **3**, 469 (1988).
16. X. Jui-Zhi, M. A. Handschy and N. A. Clark, *Liq. Cryst.*, **2**, 707 (1987).