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**To cite this Article** Coles, H. J. , Lester, G. A. and Owen, H.(1993) 'Fluorescent dye guest-host effects in advanced ferroelectric liquid crystals', Liquid Crystals, 14: 4, 1039 — 1045
**To link to this Article: DOI:** 10.1080/02678299308027811
**URL:** http://dx.doi.org/10.1080/02678299308027811

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LIQUID CRYSTALS, 1993, VOL. 14, NO. 4, 1039–1045

# Fluorescent dye guest–host effects in advanced ferroelectric liquid crystals

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Previous work has shown that guest–host ferroelectric systems incorporating dichroically absorbing dyes are suitable for use in colour display applications. These utilize either the dichroic absorption of a conventional dye, or the emission of a fluorescent dye. We present here the electrooptical properties of several advanced ferroelectric liquid crystals doped with a new fluorescent dye, coloured blue in emission. The data consists of measurements of tilt angle, response time, spontaneous polarization, and rotational viscosity, from which we conclude that certain hosts are not adversely affected by the fluorescent dopants. These results are then discussed in connection with the use of these mixtures in two novel colour display configurations, which are also presented, utilizing either the dichroic absorption or the polarized fluorescence of the fluorophore guests.

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## 1. Introduction

The guest–host effect in liquid crystal displays is now well-researched, after having been first proposed in 1968 [1]; dyes are now being synthesized [2] and used as the basis for commercial colour display devices. However, interest in the use of fluorescent dyes in such devices has declined, due to problems of solubility and degradation of the dye (for example, by light, electric fields, chemical effects). This view is largely based on measurements made in nematic materials [3, 4]. This is a pity, since fluorescent dyes offer distinct advantages over ordinary dyes—very large viewing angle (up to 180°), greater brightness (above ambient visible light levels), and greater perceived contrast [5]. Much of current display research is on ferroelectric materials, which are viewed as being the basis of the next generation of liquid crystal displays. Little research has been done on the behaviour of fluorescent dyes in these materials, but it is likely that the stability of fluorescent dyes in ferroelectrics (and other smectics) will exceed that so far seen in nematics, due to the increased ordering present in these phases—perhaps approaching that of solid polymer materials, in which fluorescent dyes are already known to have lifetimes in excess of 5 years. This paper summarizes an initial study of a commercial blue fluorescent dye in four commercial ferroelectric mixtures, to ascertain whether the properties of the resulting mixtures show any promise regarding the construction of such devices.

## 2. Experimental

### 2.1. *The materials studied*

The guest material used in this study was the strongly fluorescing blue dye, EB501, supplied by Mitsui Toatsu Chemical Co. (manufactured for use in polymer systems).

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This dye has a UV absorption band at 343 nm and 400 nm and has an emission band that peaks at 433 nm and extends to 500 nm. The host used were the ferroelectric mixtures Felix 007, Felix 010/1 (supplied by Hoechst Ltd.), SCE13 and ZLI 4237 (supplied by Merck Ltd.). The dye was not soluble above the 1 per cent w/w level in any host, but was stable at 0·5 per cent, with little recrystallization evident. (These materials are available from the suppliers indicated who may be contacted for further structural information.)

Test cells of 7·5 $\mu$m thickness were used to determine the device characteristics of the guest–host materials, the indium–tin oxide (ITO) electrodes coated with a rubbed polyimide alignment layer, the rubbing directions antiparallel in the assembled device. All the hosts have the phase sequence $S_C^*$–$S_A$–N*–I; planar alignment in the $S_C^*$ phase was achieved by slow cooling from the isotropic regime (2°C min$^{-1}$) into the $S_C^*$ phase, and then cycling between that phase and the $S_A$ phase until good alignment was achieved.

### 2.2. *Experimental procedure*

The operation of any guest–host device is in part dependent on the dopant interaction with the host, and whether its effect on the host properties is detrimental or beneficial. The measurements relevant to device properties are phase transition temperatures, optical tilt angle, response times, spontaneous polarization and rotational viscosity. Phase transition temperatures were measured by polarizing microscopy, the dye depressing the phase transition temperatures of Felix 010/1 and ZLI 4237 by 1°C

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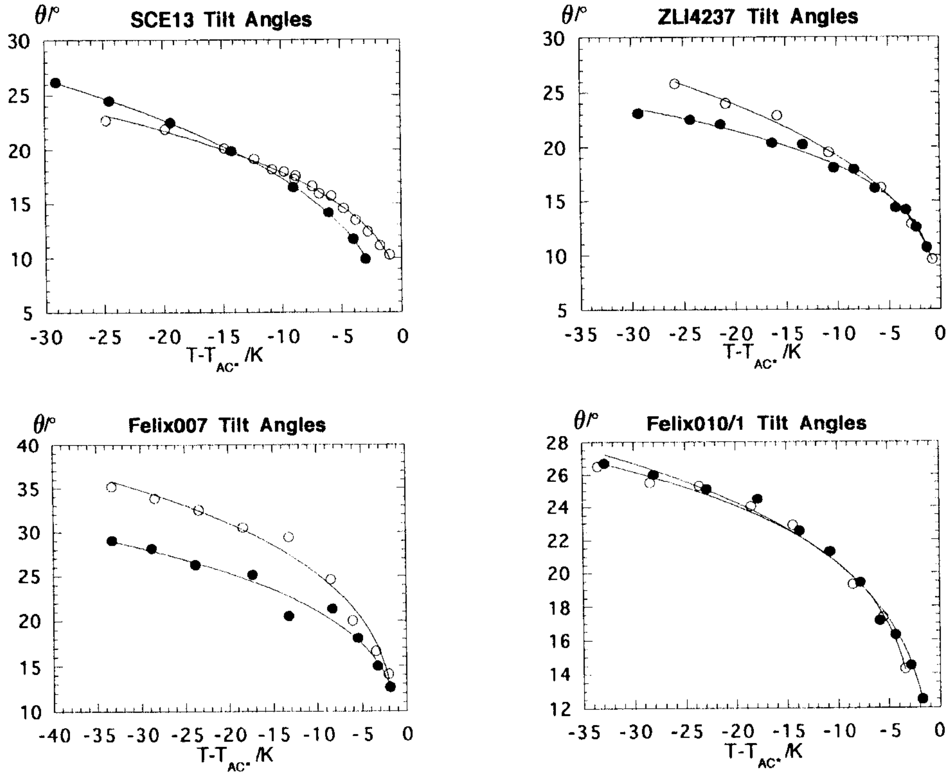


Figure 1. Variation of tilt angle with temperature of doped and pure ferroelectrics. ○, Pure tilt angle; ●, EB501/ferroelectric mixture tilt angle.

on average and by 2°C in SCE 13 (except that the $S_C^*$–$S_A$ transition temperature was depressed by 5·5°C in SCE 13). Felix 007 was left virtually unchanged.

### 2.3. *Tilt angle*

The operation of the single polarizer, dye guest–host, ferroelectric (DGHFE) device relies on the cooperative alignment of the dichroic dye by the ferroelectric host. The orientation of the dye is rotated through twice the tilt angle ($2\theta$) of the guest–host material on changing from one switched state to the other. For maximum contrast, a tilt angle of 45° is ideally required, although a 10–90 per cent change in intensity

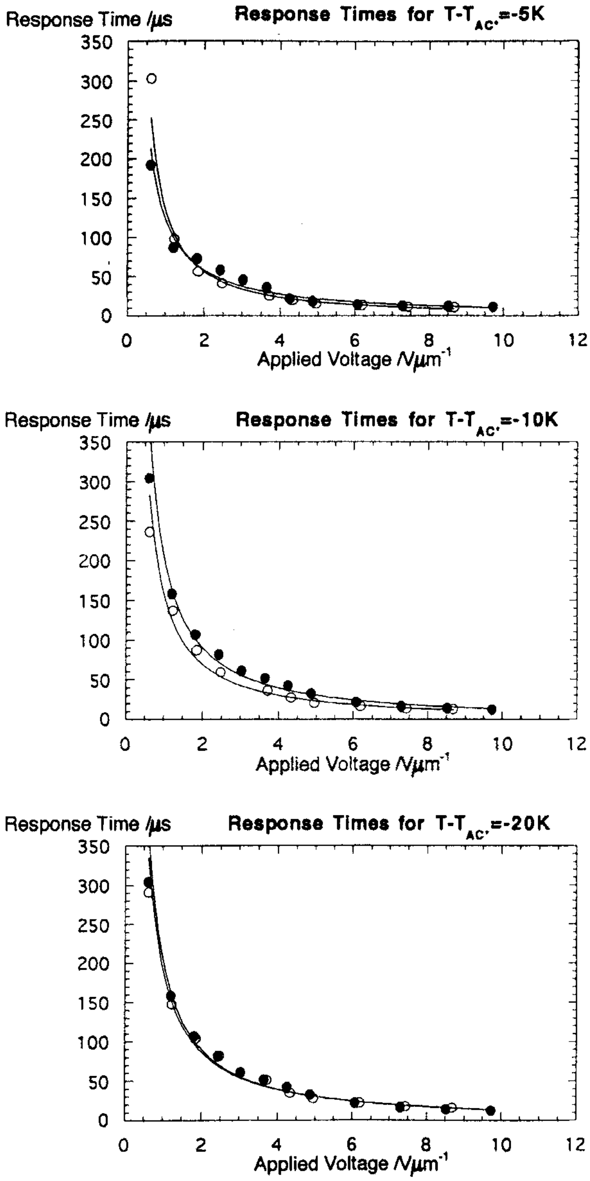


Figure 2. Typical 10–90 per cent response times of doped and pure ferroelectric hosts (SCE13). ○, Pure; ●, doped.

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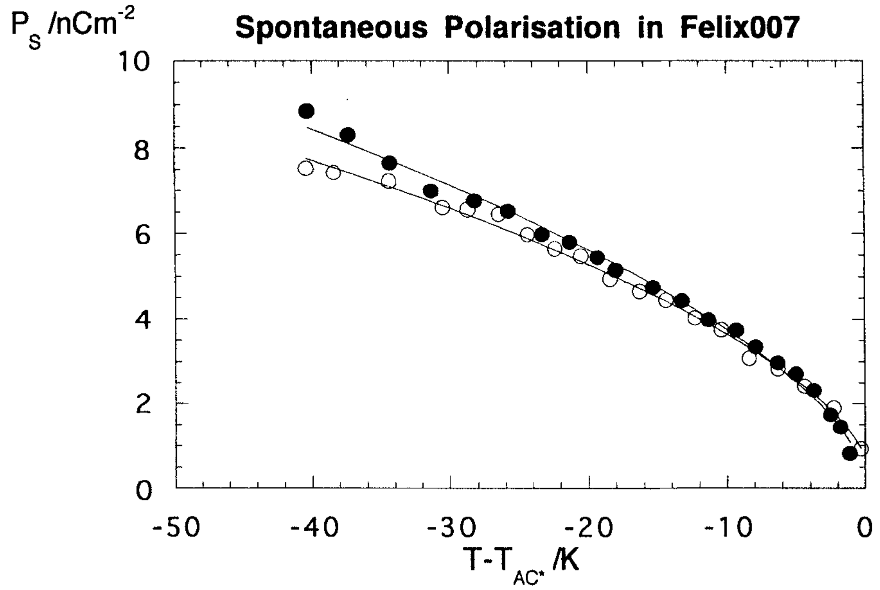


Figure 3. Spontaneous polarization of Felix 007 against temperature, 0·5 per cent w/w of EB501 (●), and pure host (○).

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(cf. the maximum possible) can be obtained with a tilt angle of only 27°. Although good contrast ratios can be obtained with tilt angles as low as 20–25°, it is important to ensure that the addition of dopants do not reduce the tilt angle further. Optical tilt angles were therefore measured, as half the angle between extinction positions with crossed polarizers under opposite applied electric fields. It was found that the tilt angles were reduced by 7° in Felix 007 at room temperature, by 4° in ZLI 4237, with a negligible change in the other two hosts (see figure 1).

### 2.4. *Response times*

Response times were measured as the time taken for a change in the optical transmission from 10 to 90 per cent of maximum transmission (or vice versa) under electric field reversal. This was performed using square-wave applied voltages, the transmitted light being detected with a fast photodiode (risetime $< 1\ \mu s$). The dye had little effect on the response time of SCE 13 (no more than 10 per cent change), and lowered the speed of Felix 010/1 (by a factor of two), but raised the speed of both ZLI 4237 and Felix 007 (by about 20 per cent). This may be due in part to the lowering of the rotational viscosity of the host by the inclusion of the dye. We may conclude that the inclusion of the dye EB 501 into certain ferroelectric hosts at low concentrations (0·5 per cent) may have no detrimental effects on response times. A typical set of response times is shown in figure 2.

### 2.5. *Spontaneous polarization and rotational viscosity*

A striking feature of ferroelectric displays is the fast field-induced transition between the two optically different states; the most important physical properties of a material with respect to this response time are its spontaneous polarization, $P_s$, and its rotational viscosity $\gamma$. These were measured using the electric field reversal method [6], $P_s$ measured from the integral of the induced current pulse on switching, and $\gamma$

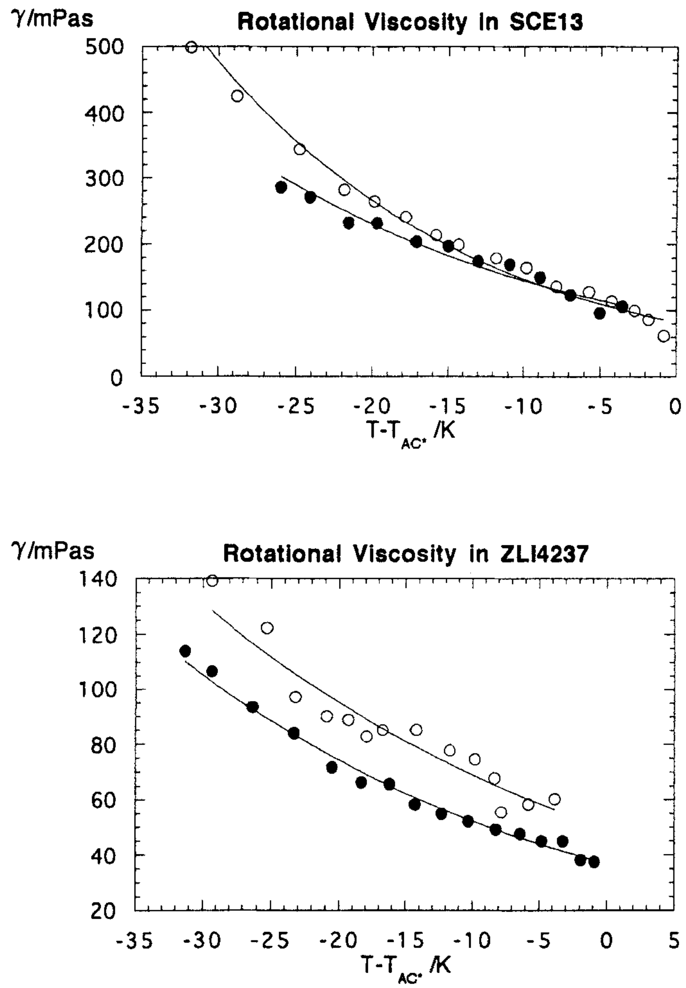


Figure 4. Rotational viscosity in SCE 13 and ZLI 4237 against temperature, 0·5 per cent w/w of EB501 (●) and pure host (○).

measured from the current pulse profile. It was found that the dye had little effect on the spontaneous polarization of SCE 13 and ZLI 4237 (no more than 2 per cent), while that of Felix 007 was raised by 1 nC cm$^{-2}$ (at 30°C: 12 per cent, see figure 3), and lowered in Felix 010/1 by 2 nC cm$^{-2}$ (at 30°C: 15 per cent). The rotational viscosity of Felix 007 was raised by the inclusion of the dye (from 70 to 105 mPa s at 30°C), while it was lowered slightly in Felix 010/1 (from 160 to 150 mPa s at 30°C). Unusually, the inclusion of the dye lowered $\gamma$ in both SCE 13 and ZLI 4237 significantly (from 430 to 350 mPa s and 130 to 100 mPa s at 30°C, respectively, see figure 4). The explanation of this effect is at present unclear.

## 3. Display types

There have been many guest–host configurations proposed [7, 8], the simplest of which is shown in figure 5 (*a*) for a fluorescent system. As in an ordinary guest–host device, the configuration relies on the dichroic absorption of the fluorophore giving bright fluorescence over all angles. This requires polarized ultraviolet light, for which

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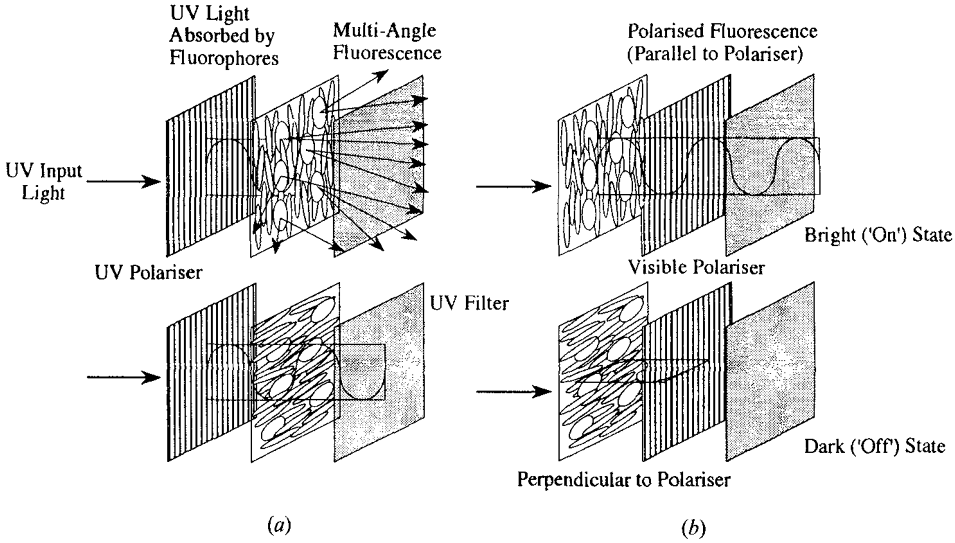


Figure 5. Fluorescent display configurations: (*a*) dichroic absorption mode; (*b*) polarized fluorescence mode.

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the use of a dichroic ultraviolet polarizer is needed, which is comparatively expensive and yields poor dichroic ratios. Instead of this, it may be possible to use a polarizer constructed from a plastic sheet embossed with surfaces at the Brewster angle to polarize the UV. This could conceivably increase contrast ratios in this display mode while reducing cost.

An alternative configuration is shown in figure 5 (*b*), and relies on the polarization in the fluorescence from the guest molecules, and on the selective absorption of the unpolarized incident UV light by the dichroism of the fluorophore. It was thought that the contrast of this device would be low, due to depolarization effects (the fluorophore rotating during the lifetime of the excited state, as in nematic materials), but the increased ordering present in smectic materials results in a reduction in the depolarization, and thus a reasonable contrast. This effect is enhanced by the fact that the fluorescence is bright even in low ambient visible light levels, so that perceived contrast ratios are extremely high.

## 4. Conclusion

In this paper we have described the operation of three modes of fluorescent display operation in ferroelectrics, of which the polarized fluorescence mode is peculiar to this type of guest–host material. We have shown that the inclusion of a fluorescent dye, at a concentration of 0·5 per cent w/w, into a ferroelectric liquid crystal can result in mixtures with properties similar to that of the pure host. Careful selection of the dye and host can result in mixtures where the host properties are enhanced by the dopant. The mixtures presented here can produce displays with very high perceived contrast ratios and brightness above ambient light levels. We conclude that further research on the behaviour of fluorescent dyes in ferroelectric materials holds great potential, and that such combinations are viable and attractive alternatives to the current avenues of display development. Further work on both dyes and hosts should result in commercially useful mixtures.

We thank Mitsui Toatsu Chemical Co., Hoechst Ltd., and Merck Ltd., for the kind provision of materials. We also thank the SERC, for a research studentship (HQ), and the Wolfson Foundation for the funding of this research, and for financial support to attend the 14th International Liquid Crystal Conference.

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