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Fluorescent dye doped ferroelectric liquid crystal: An anchoring energy, electro-optical and fluorescence study

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ABSTRACT

In this study anchoring energy parameters, electro-optical (E-O) study along with UV absorption and fluorescence study have been performed for pure ferroelectric liquid crystal (FLC) and three different concentrations i.e. 1%, 3% and 5% of fluorescent dye in pure FLC. The UV absorption has been shifted towards lower frequency side for fluorescent dye doped system in comparison to the pure FLC. Excitation wavelength, emission wavelength and quantum yield have been determined for all the mixtures from fluorescence study. Anchoring energy parameters, spontaneous polarization and response time have been determined by E-O study. The values of these parameters are strongly changed by the concentration of fluorescent dye.

1. Introduction

Ferroelectric liquid crystals (FLCs) are very important in the display and non-display points of view due to low driving voltage and low coercive field. Due to helical structure and ferromagnetism, FLCs can also be used in the memory devices [1–4]. These materials are technologically important due to their considerable characteristics such as high optical contrast, and good switching response [5, 6, 8 & 11]. The incorporation of different types of guest materials into the host material (FLC) is a very practical method for manipulating the properties of host material [9]. The ability to control and direct self-assembly of dye molecules into specific geometries with new efficient dielectric and optical properties, doping of fluorescent dye into FLCs has been introduced. The doping of fluorescent dye is an attractive research endeavor for preserving the original properties of pure FLCs. The doping of fluorescent dye in pure FLC modifies or improves properties of pure FLC [5]. The UV absorbance and fluorescence study [5] along with electro-properties of FLC material doped with different concentration of fluorescent dye have been investigated.

In the present paper, we report a comprehensive study of the dielectric and electro-optical (E-O) properties of a ferroelectric liquid crystal highly doped with fluorescent dye. The present work has a motive to analyze the effect of high concentration of the fluorescent dye on the FLC matrix and also on the E-O and dielectric parameters. In development of less energy consuming displays, use of fluorescent dye seems attractive [10]. The effect of fluorescent dye on dielectric loss factor is also subject of our current interest due to promising tunable materials especially at high frequencies due to lower losses at higher microwave frequencies, as they are flexible and continuously tunable. With growing interest in switchable devices for the high frequency range, there is a strong demand for liquid crystals (LC) exhibiting low absorption. The fluorescent dye doped samples were added in 1, 3 and 5% wt/wt concentrations to the pure FLC 16/100. The results show that the doping of fluorescent dye alters the physical properties of the pure FLC. The results are discussed and explained on the basis of the interactions taking place between the dye and FLC molecules in the composite geometry, effect of high doping of dye on the pure FLC, and molecular dynamics of fluorescent dye and FLC molecules with their dipolar contributions.

2. Materials and methods

The sample cells for the present study consisted of highly conducted (≈10 Ω/square and the visible light transmission is more than 90%) indium tin oxide (ITO) coated glass plates. The ITO patterns which were square of dimension of 5 mm used as electrodes. Such patterns were achieved by photolithographic techniques [11–15]. The thickness between two glass plates was uniformly maintained 10 μm. The planar alignment on the patterned glass plates was obtained by using conventional rubbed polyimide techniques. A commercially mixture Felix 16/100 has been used as host material purchased from Clariant Chemicals Co Ltd. Germany. The phase transition sequence of this FLC sample was given as follows [11].

$$\text{Cryst.} \xrightarrow{-20^\circ C} \text{SmC}^* \xrightarrow{72^\circ C} \text{SmA} \xrightarrow{82^\circ C} \text{N}^* \xrightarrow{90-94^\circ C} \text{Iso.}$$

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The fluorescent dye used for doping is Poly[(4,4′-hexafluoroisopropylidene) diphthalic anhydride-alt-3,6-diaminoacridine hemisulfate] has been used as guest material purchased from Sigma-Aldrich, India. The structure of this fluorescent dye has been shown in Fig. 1.

The fluorescent dye has excitation peak at wavelength 269 nm while it has emission wavelength of 516 nm in DMSO. The three concentrations of fluorescent dye have been prepared by doping of fluorescent dye 1%, 3% and 5% into pure FLC and we call these as mixture 1, mixture 2 and mixture 3 in the whole paper.

The UV visible absorption study has been performed UV–VIS spectrophotometer (Thermo 201) for a wavelength interval 300–600 nm. The fluorescent measurement has been performed fluorescent spectrophotometer (Elico SL-174) in wavelength interval 200–600 nm. During the fluorescent measurement all the parameters like excitation and emission band pass filter have been kept the same for all the mixtures [14]. From fluorescent study we have also evaluated quantum yield for all the mixtures. The conductivity has been determined by using dielectric data measured with the help of impedance/gain phase analyzer HP-4194A in the frequency range 100 Hz to 10 MHz. The temperature of the samples has been maintained with the help of Instec Hot Plate HCS 302.

The spontaneous polarization measurement has been carried out by well known polarization reversal current method [12–15]. The optical response of FLC was performed by square wave method by using a 5 mW He–Ne laser of wavelength 633 nm. The optical response was recorded by photo detector Instec PD02-L1 [13,14]. The triangular and square wave signals (10 Hz frequency and 20 V peak to peak) were applied using a function generator (Tektronix AFG-3021B) for the measurement of spontaneous polarization and response time. The electrical and optical responses of pure and fluorescent dye doped mixtures have been recorded by Textronic TDS-2024C. The output waveform was now used to determine the response time. The response time of FLCs was evaluated using $\tau = t_{90} - t_{10} / 1.8$.

Here, t_{90} and t_{10} are the time taken by the output waveform to reach 90% and 10% of the maximum of the output waveform. The alignment of all the mixtures has been checked by Radical polarizing microscope. In this method, a square wave of frequency 1 Hz and amplitude 20 V peak to peak is applied to the sample cell.

3. Results and discussion

The UV absorption study has been carried out to observe absorbance of white light by pure FLC and fluorescent dye doped FLC mixtures. The absorbance in arbitrary unit on the wavelength scale in nanometer for the pure and fluorescent dye doped has been plotted in Fig. 2. From Fig. 2 we see that absorbance is higher for fluorescent dye doped FLC mixtures in comparison to the pure FLC, but absorption wavelength is shifted to lower side for fluorescent dye doped FLC. The absorption wavelength for pure FLC is 334 nm, while it decreases for mixture 1, mixture 2 and mixture 3 i.e. 311 nm, 314 nm and 312 nm respectively. In fluorescent dye doped FLC mixtures we see that absorbance is highest for mixture 2 in comparison to the other two mixtures.

The wavelength variation of fluorescent intensity has been plotted for excitation and emission spectra for all the mixtures and shown in

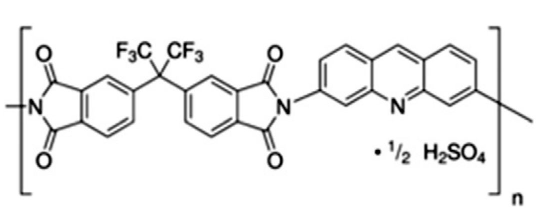

Fig. 1. Structure of fluorescent dye Poly [(4,4′-hexafluoroisopropylidene) diphthalic anhydride-alt-3,6- diaminoacridine hemisulfate].

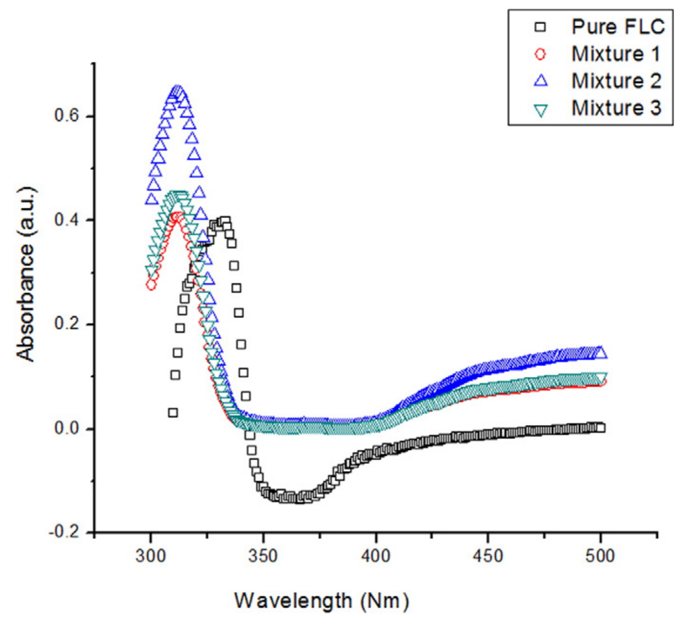

Fig. 2. Wavelength variation of absorbance for pure and fluorescent dye doped FLC mixtures.

Fig. 3(a) and (b). From this figure we see that there is non-linear behavior of fluorescent intensity for all mixtures. The excitation wavelength for pure FLC is 335.5 nm, while it decreases for mixture 1, mixture 2 and mixture 3 i.e. 320 nm, 321 nm and 335 nm respectively. The figure of emission spectra for all the mixtures shows the same trend as for excitation spectra in comparison to all the mixtures. We have also evaluated quantum yield with the help of Elico software using excitation and emission data for all the mixtures. The value of quantum yield 2.58, 2.15, 2.23, and 2.09 for pure FLC, mixture 1, mixture 2 and mixture 3 respectively. The value of quantum yield for mixture 3 is lowest it means that mixture 3 i.e. 5% concentration of fluorescent dye into pure FLC has lesser probability of excited state being deactivated by fluorescence in comparison to the all mixtures. The emission spectra for 5% doping of fluorescent dye (Mixture 3) in pure FLC shows a small neck. The reason for this neck behavior is due to the energy associated with fluorescence emission transitions which is typically less than absorption; therefore, the resulting emitted photons have lesser energy and shifted towards longer wavelengths. This phenomenon occurs due to the rapid decay of excited electrons to the lowest vibrational energy level of excited state in solutions commonly investigated.

The quantum yield can be described by the relative rates of radiative and non-radiative relaxation pathways which deactivate the excited state. In other words quantum yield gives the probability of excited state being deactivated by fluorescence rather than by another non radiative mechanism [16]. An energetically excited state is formed when a fluorophore absorbs a photon of light. The fate of this species is varied, depending upon the exact nature of the fluorophore and its surroundings and end result is deactivation and return to the ground state by fluorescence, internal conversion and vibrational relaxation [16].

The E-O parameters spontaneous polarization, optical response time and anchoring parameters have been evaluated from E-O study and theoretical fitting of the experimental data. Figs. 4, 5, & 6 show variation of spontaneous polarization, optical response time and anchoring parameters with applied voltage for pure FLC and fluorescent dye doped FLC i.e. mixture 1, mixture 2 and mixture 3.

The nature of spontaneous polarization and response time with voltage variation is the same as reported for other FLCs [12–15]. The value of spontaneous polarization increased for mixture 1 and decreased for mixture 2 in comparison to the pure FLC. The value of response time