

Nematic Liquid Crystals Dispersed with Multiwalled Carbon Nanotubes: A Perspective Way for Improving the Response Time and Birefringence of Electro-Optical Devices

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Abstract: This study investigated dielectric and electro-optical performance of nematic liquid crystal (LC) dispersed with carboxylic acid functionalized carbon nanotubes (fCNT). The investigation reveals the LC-fCNT composite systems exhibits nearly 60% faster response time as compare to pure LC. The composite system also revealed a reduced rotational viscosity and an enhanced dielectric anisotropy by the ion trapping mechanism at the adsorbing sites of carbon. Dielectric spectra of vertically aligned (VA) LC cells explained a remarkable reduction in relaxation time (about short molecular axis) hence rotational viscosity of LC-fCNT composite systems. The results suggest a specific concentration of fCNT doping in LC decrease the rotational viscosity and hence accelerated the electro-optical response and also does not affect the nematic director called threshold limit of concentration (in our case up to 0.05 wt%). The measurement also confirms that the significant enhancement in nematic-isotropic phase transition temperature (T_{NI}). Consequently, birefringence also enhanced the anchoring energy due to π - π electron stacking between LC and fCNT enhanced the order parameter of LC-fCNT composite systems. These results successfully demonstrate the dielectric and electro-optical operations of LC-fCNT composite systems.

Keywords: Functionalized Carbon Nanotubes; Liquid Crystals; Ion Trapping; Response Time; Birefringence; Order Parameter.

1. Introduction

Liquid crystal (LC) materials are ubiquitous in everyday life. It has a wide range of commercial applications such as economical and reliable displays for the several electronic devices¹, tunable filters and lenses for ophthalmic applications²⁻³, smart windows, various components of medical

equipment⁴, sensors for chemical, biological and satellite applications⁵⁻⁷, just to name a few. Generally, thermotropic liquid crystals (i.e., the phases are formed by change in temperature) are used for such types of applications. The simplest and most common phase of thermotropic LC materials is nematic phase. It has rod like shape, long range orientational order without any positional order.

In recent years, the physical interactions between liquid crystals (LCs) and carbon nanotubes (CNTs) have gained great research interest⁸⁻¹³. Various research groups around the world reported that the small amount of CNT doping in LC exhibit a variety of fascinating phenomena. Prasad et al. demonstrated that doping of a small amount of CNT leads to self-assembly of layered smectic phase and as a consequence re-entrant phase sequence in a host LC exhibiting nematic mesophase only¹⁴. A combined theory of Flory-Huggins and Landau-de Gennes has also been given to support his results. L. Dolgov et al. have observed the irreversible electro-optical response i.e. electro-optical memory of negative dielectric anisotropic LCs doped with CNT¹⁵. Petrov et al. have studied the magnetic field induced orientational transition and influence of magnetic segregation effect on the orientation structure and magneto-optical response as well of CNT doped nematic LC^{12,16}. A detailed study of suppression of field screening in nematic LC by CNT has also been reported by H. Y. Chen and W. Lee¹⁷. They have observed that, the lower transient current in the LC-CNT hybrid system has ability to decrease the moving-ion density and consequently suppressed the undesired field screening effect and hence reduce the driving voltage. Qiao et al. reported that a very low concentration of CNT enhances the boundary layer viscosity of LC in the both nematic and isotropic phase¹⁸. A systematic dielectric study has been explained by S. K. Gupta et al. of single-walled carbon nanotube (SWCNT) in ferroelectric liquid crystal (FLC)¹⁹. Malik et al. reported multi-walled carbon nanotube (MWCNT) in FLC material slightly decrease the nematic-isotropic phase transition temperature (T_{NI}), nearly 80% faster response, improvement in the contrast ratio (CR) and lower threshold voltage²⁰. A series of papers by Basu et al. published in the early 2013s provide a comprehensive overview of LC-CNT composite system including their nematic anchoring on CNT⁹, orientational coupling⁸, field induced nematic switching²¹, electroclinic effect in achiral LC²² and dielectric response as a function of applied AC electric field²³. CNT-doped liquid crystals have been studied in many other researches and have rich literature about their fundamental applications but the ion trapping mechanism LC-fCNT composite system with the variation of fCNT concentration is not systematically discussed yet.

Herein, we investigate the dielectric and electro-optical properties of a pure nematic LC and LC-fCNT composite system at different concentrations. The dielectric spectrum used to calculate dielectric permittivity and anisotropy of pristine and doping LC cells, and these results were used to calculate the splay elastic constant. Present investigation reveals that up to a certain concentration, fCNTs act as an ion catcher with high ion trapping efficiency. Thus, LC-fCNT composite system has lower free ion which enhance the dielectric anisotropy, decrease the rotational viscosity and hence accelerated the electro-optical response of the composite system. The threshold limit of the fCNT concentration has been also optimized after which the LC-fCNT composite system no longer switches faster. This study will certainly be useful for the applications of electro-optical devices. The enhancement in T_{NI} , dielectric anisotropy, electro-optical response time, birefringence, order parameter as a function of fCNT concentration have been well studied and discussed within the scope of this paper.

2. Materials and Method

The nematic LC E7 (Merck® KGaA, Darmstadt, Germany, $T_{NI} = 60.5$ °C) used in the experiment (CAS No. 40817-08-1). The intermediate compounds of nematic LC E7 was mainly LC monomers 5CB (51%), 7CB (25%), 8OCB (16%), and 7CT (8%). E7 LC mixture had positive dielectric anisotropy ($\Delta\epsilon$) of 14.1, birefringence (Δn) of 0.22, nematic–isotropic phase transition temperature (T_{NI}) of 60.5 °C, rotational viscosity (γ) of 232.6 mPas, and elastic constants K_{11} , K_{22} , and K_{33} values of 11.1, 5.9, and 17.1 pN, respectively, at 20 °C. A highly purified MWCNTs (carboxylic acid functionalized, thin, extent of labelling: > 8% carboxylic acid functionalized) were obtained from Sigma-Aldrich®, Saint Louis, USA (Product Number: 755125) and had average diameter 9.5 nm, inner diameter 0.5-1 nm and average length 1.5 microns. A LC-fCNT composite was prepared by dispersing the fCNT powder directly in LCs without any solvents; then the mixture was ultrasonically stirred for 20 min at RT.

A 5- μ m-thick empty cell composed of two indium–tin–oxide (ITO) glass substrates was constructed. The detailed process of sample cell fabrication one can finds in our previous reported work²⁴⁻²⁵. The thickness was confirmed by optical interferometric method and found to be $\sim 5.2 \pm 0.05$ μ m. The fCNT concentration was set to 0.001, 0.005, 0.010 and 0.050 wt%. The LC mixtures were heated above the isotropic temperature to fill in the empty cell uniformly via capillary action and successively cooled down to the nematic phase. Notably, the selection of cell thickness and length of

fCNT is very important because at a high electric field across the fCNT can cause a resistance blow-up effect²⁶. Hence in the present investigation we choose fCNT of average length 1.5 micron which is much smaller than the cell gap (~5.3 micron) so that they do not short out the electrode in vertical configuration.

3. Experimental Details and Measurement Techniques

Various instruments and experimental techniques used in the present investigation are discussed below: Polarizing optical microscope (POM) (DM EP, LEICA, Germany) integrated with temperature controller (T95-PE, Linkam, UK) was used to record optical texture and observe T_{NI} of pure E7 and LC-fCNT composite system. The transmission spectra with the variation of wavelength were recorded using computer operated commercial software ISM-Lux® by Isuzu Optics corp. Taiwan integrated with a white light source. The response time was calculated by optical switching technique of pure E7 and LC-fCNT composite system at room temperature (RT). Experimental setup and measurement techniques for voltage dependent transmission curve (V-T curve) and response time were reported in our previously published articles²⁴⁻²⁵. Crystal rotation method²⁷ was used to calculate the pre-tilt angles of homogeneously aligned (HA or ECB) cell and vertically aligned (VA) LC cells of pure E7 and LC-fCNT composite systems and the values are listed in table 1. The polar anchoring energy coefficients W_{polar} of the fCNT-doped LC cells were estimated via the high electric field techniques²⁸. The W_{polar} of the fCNT-doped LC cells slightly increased, as shown in Table 1. The dielectric spectra of the HA and VA of pure E7 and LC-fCNT composite systems were measured using an LCR meter (Hioki 3532-50, Japan) with an applied alternating current (AC) field of 0.01 V/ μ m and the frequency was varied from 42 Hz to 5.5 MHz to obtain the real and imaginary part of dielectric permittivities. The Δn of the LCs was derived with the phase retardation technique^{24,29}.

Table 1. W_{polar} and pretilt angle at various fCNT concentrations.

fCNT concentration (wt%)	0	0.001	0.005	0.010	0.050
W_{polar} (10^{-4} J/m ²)	1.22	1.39	1.50	1.61	1.77
Pretilt angle of ECB cell (Degrees)	2.59	2.38	2.30	2.06	1.98
Pretilt angle of VA cell (Degrees)	88.48	88.58	88.68	88.79	88.92

4. Results and discussion

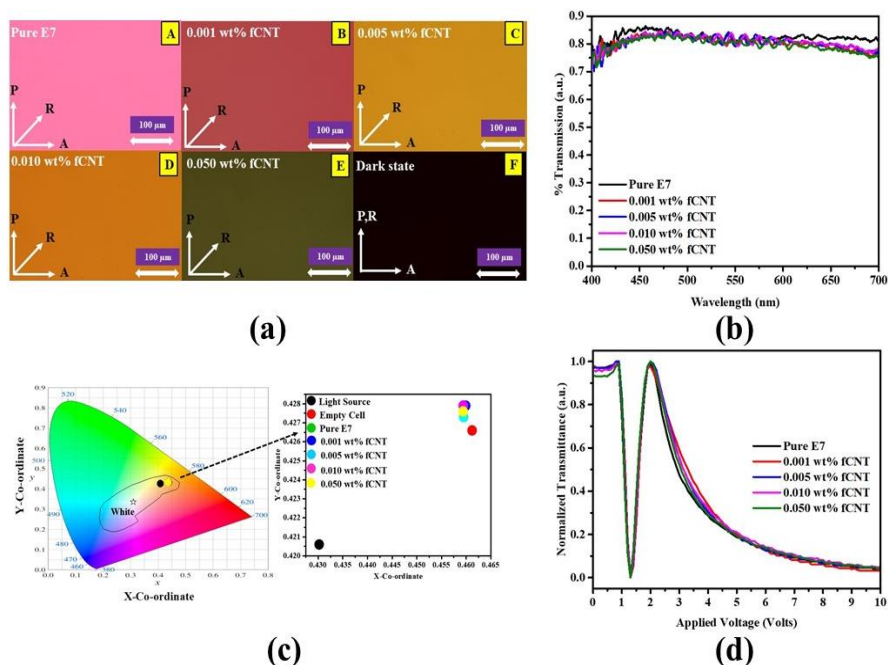


Figure 1. (a) POM Textures, (b) transmission spectra, and (c) CIE 1931 color chromaticity diagram (d) V-T curves of the fCNT-doped LC cells at room temperature (RT).

The solid arrows indicate the rubbing direction (R) and transmission axes of the polarizer (P) and analyzer (A).

Figure 1 (a) shows the POM textures of the fCNT-doped LC cells, where the rubbing direction of the cell was placed at 45° with respect to the transmission axes of the polarizer and the analyzer. POM texture A to E represents the bright state and F represents the dark state of pure E7 and fCNT doped composite systems. Only one dark state texture is represented in the figure because any significant change has been not observed between the dark state of pure and fCNT doped systems. The confirmation of uniformity and similarity of the dark state of pure and fCNT doped system, the POM textures have been processed by ImageJ® software and found approximately similar intensities (~ 6 a.u.). The uniform colors throughout the cell of bright state textures confirm that the LC molecules are aligned homogeneously²⁹⁻³². We have not observed any visible agglomeration or significant defect instead of the color shift indicates fCNT is homogeneously dispersed in the LCs matrix and Δn of LCs has been changed with fCNT doping. Fig. 1(b) shows the transmission spectra of the fCNT-doped LC cells in the visible range between 400 and 700 nm. The

light loss around 11% (85% to 74%) is caused by that fCNT doping changes the refraction index of LC mixture and hence increases the haziness among the surfaces between glass substrates and LC layer. Fig. 1(c) shows the Commission Internationale de l'Éclairage (CIE) 1931 chromatographic coordinates' diagram and corresponding 'x' and 'y' co-ordinates are listed in table-2, which illustrates the stimuli-induced color change. The luminescence properties designate that the intensity and color of the luminescence almost keep at the same position with the increased fCNT concentration, indicating fCNT doping does not cause the color shifts of the LC cell even it has an absorbance for short wavelengths.

Table 2. CIE color coordinates (x, y) of fCNT-doped LC cell at room temperature.

fCNT concertation (wt.%)	x	y
Light source	0.4302	0.4206
Empty cell	0.4612	0.4266
Pure E7	0.4597	0.4279
0.001	0.4599	0.4279
0.005	0.4595	0.4273
0.010	0.4594	0.4279
0.050	0.4594	0.4276

Fig. 1(d) shows the V-T curves of the fCNT-doped LC cells measured at room temperature (RT). It has been observed that there is no significant shift in the V-T curve with the increased fCNT concentration, indicating the petite amount of fCNT dispersion does not affect the threshold voltage (V_{th}) and operation voltage (V_{op}) significantly of the LC cell. A decrease in maximum transmission was also obtained because fCNT doping enhanced the scattering of light or it changed the refractive index of the LC mixture, resulting in refractive index mismatch between the interfaces or absorption of light by the fCNT-doped LC mixture. Four different techniques have been used to analyse the V_{th} ; (i) By V-T curve: V_{th} is defined as the voltage corresponding to which initial transmission of the V-T curve begins to change, but this method is not too accurate because one can confuse between the V_{th} and distortion of transmitted light. (ii) By phase curve: To define the V_{th} of the fCNT-doped LC cell, the V-T curves were transferred to voltage-dependent phase retardations in which V_{th} was defined as the voltage required for the phase retardation changes from 100 % to 90 % of maximum value. (iii) By POM image: The POM images of the fCNT-doped LC cells with various voltages were measured to determine the V_{th} of the LC cell. V_{th} was defined as the voltage at which the color of POM

image began to change, indicating the initial distortion of LCs in the middle of the LC cell and (iv) By C-V curve: The C-V curve of the fCNT doped homogeneously aligned LC cells were measured. V_{th} was defined as the voltage at which capacitance began to increase. The present investigation reveals that in all four techniques we observed approximately the same V_{th} (~ 0.96 Volts) for pure and LC-fCNT composite system at RT.

Contrast ratio (CR) is also an important parameter for any electro-optical display devices. It is defined as $CR=T_{on}/T_{off}$ where T_{on} is maximum transmission and T_{off} is the minimum transmission of pure and fCNT doped homogeneously aligned LC cells³³. The calculation of CR of pure and fCNT doped LC cells has been done by processing the bright (on state) and dark (off state) state POM textures by ImageJ® software. Carefully taking the same scale of bright and dark state textures we have calculated the average value of T_{on} and T_{off} of pure and composite systems and the ratio of it can give the CR. The calculated values of V_{th} , V_{op} , and CR are listed in table 3.

Table 3. Calculated values of threshold voltage (V_{th}), operating voltage (V_{op}), and contrast ratio (CR) of homogeneously aligned LC cells with the variation of fCNT concentrations at RT.

fCNT concertation (wt.%)	V_{th} (Volts)	V_{op} (Volts)	CR
Pure E7	0.96	2.01	28.55
0.001	0.96	2.01	26.64
0.005	0.96	2.00	25.78
0.010	0.96	2.00	25.03
0.050	0.96	2.00	24.65

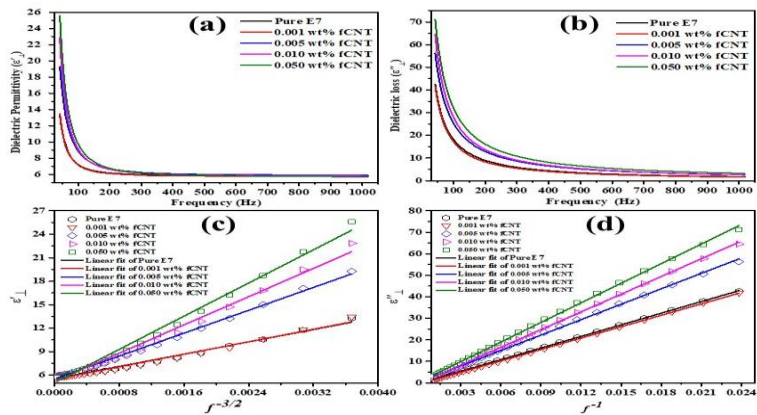


Figure 2. (a) Real and (b) imaginary parts of the complex dielectric permittivity; (c) and (d) represent the linear fitting of the experimental data of the corresponding dielectric permittivity of the NLC at different doping concentrations of fCNTs at room temperature.

Uemura model has been used to analyse the dielectric parameters in the low frequency region. The model can be formulated as follows³⁴⁻³⁵:

$$(4.1) \quad \varepsilon'(f) = A.f^{-\frac{3}{2}} + B,$$

$$(4.2) \quad \varepsilon''(f) = C.f^{-1},$$

where
$$A = \frac{2nq^2D^{\frac{3}{2}}}{\varepsilon_o\sqrt{\pi}dk_BT}, \quad B = \varepsilon_{\infty} \quad \text{and} \quad C = \frac{2nq^2D}{\varepsilon_o k_BT}.$$

From the above-mentioned formula, diffusion coefficient (D) can be calculated as:

$$(4.3) \quad D = \frac{2nA^2d^2}{C^2},$$

The ion concentration (n) can be calculated as-

$$(4.4) \quad n = \frac{C\varepsilon_o k_BT}{2q^2D},$$

where n is the ionic concentration, D is the diffusion constant of the ions, q is the electronic charge, k_B is the Boltzmann constant, T is the absolute temperature and d is the thickness of the LC sample holder. The equations (4.1) and (4.2) do not describe the formation of EDL however; they explain the effect of the space charge polarization. The EDL may strongly be dependent on the adsorption and desorption efficiency of the impurity ions³⁶. The study of dielectric parameters is confined here within the range 50 Hz to 1 kHz. DC conductivity can be described in terms of diffusion constant and ionic concentration according to the well-known equation $\sigma_{dc} = nq^2D/K_BT$; whereas, the AC conductivity is related to the imaginary part of dielectric permittivity $\sigma_{ac} = \varepsilon_o\omega\varepsilon''$. In general, liquid crystals contain a significant amount of free ions, the presence of ions results in an increase in rotational viscosity, slowing down the director's response to an external field. The fCNT in LC media acts as ion catchers with a high ion-trapping constant and the ions are trapped at the adsorbing sites of carbon. Thus, the suspension of adequate amount of fCNTs in LC media, lowers the free ion

concentration, decreasing the rotational viscosity, of the overall system. The enhanced dielectric anisotropy and lower rotational viscosity of the hybrid system shows an accelerated response to the electric field which could be used to develop the faster LCDs. In present study we have also optimise the threshold limit of the fCNT concentration (0.05 wt%) above which the system get disturbed, starts aggregating, starts ion generation instead of ion trapping, no longer switches faster, decreases birefringence and order parameter. In our case we found the best results for 0.05 wt% and the results are listed in table-4.

Table 4. The fitted values of the constants A, B and C and corresponding calculated values of ionic concentration (n), diffusion constant (D), dc

E7 + fCNT	A	B	C	n (m ⁻³)	D (m ² /sec)	σ_{dc} (S/m)	μ (m ² /V.s ec)
Pure E7	1962.41	5.53	1803.37	1.28E+19	1.01E- 10	7.98E- 09	3.89E- 09
0.001 wt.% fCNT	2002.23	5.45	1768.59	1.16E+19	1.09E- 10	7.83E- 09	4.21E- 09
0.005 wt.% fCNT	3653.13	5.51	2393.83	8.66E+18	1.98E- 10	1.06E- 08	7.64E- 09
0.010 wt.% fCNT	4514.48	5.18	2747.96	8.58E+18	2.29E- 10	1.22E- 08	8.86E- 09
0.050 wt.% fCNT	5301.61	5.04	3040.79	8.43E+18	2.58E- 10	1.35E- 08	9.97E- 09

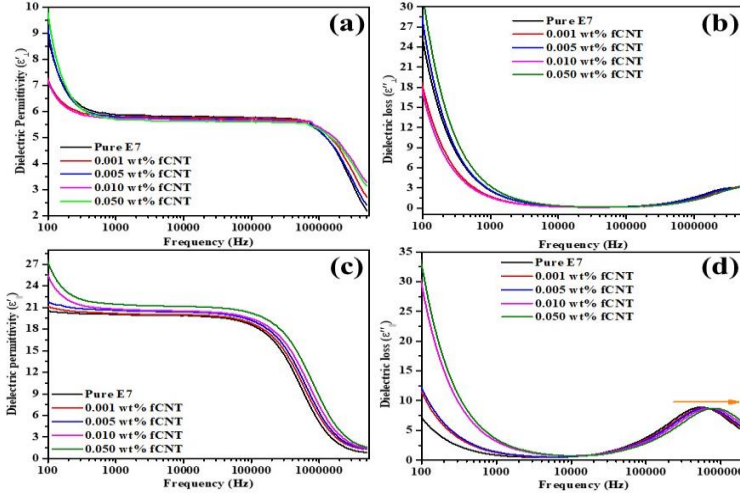


Figure 5. Dielectric spectra of homogeneously aligned (a) dielectric permittivity, (b) dielectric loss and vertically aligned (c) dielectric permittivity, (d) dielectric loss of LC cells with the various fCNT concentrations at room temperature.

Fig. 5 shows the dielectric spectra of homogeneously-aligned (HA) and vertically-aligned (VA) fCNT-doped LC cells. Fig. 5 (a) and (c) shows the variation of perpendicular and parallel component of dielectric permittivities ($\epsilon'_{\perp}$ & $\epsilon'_{\parallel}$) with the function of frequency for pure E7 and doped LC cells at room temperature (RT). Interestingly, the fCNT doping decreases the dielectric permittivity of HA cell ($\epsilon'_{\perp}$) and increases the dielectric permittivity of VA cell ($\epsilon'_{\parallel}$). Consequently, the dielectric anisotropy ($\Delta\epsilon = \epsilon'_{\parallel} - \epsilon'_{\perp}$) appears to increase with the fCNT concentration. For the effective dispersion of fCNTs in LCs we need the strongly polar and highly polarisable LCs because of the fCNTs have strong dipole-dipole interaction among the fCNTs due to greater polarizability along the tube axis. The liquid crystal mixture used in present investigation (E7) follow the same criteria. The LCs with strong dipole moment will enhance the interaction between fCNT and LC molecules. Notably, it has negative sides too, this strong interaction between LC molecules will leads to an antiparallel orientation which will reduce the possibility of dispersion of amount of fCNT effectively. Therefore, the optimization of threshold concentration of fCNT in LC media is also an important factor hence the LC with moderate dipole moment is preferred for the dispersion of fCNTs. Therefore, the orientation of fCNTs can be achieved by imposing the self-organizing capability of LC molecules to CNTs. The intrinsic orientational order of LCs can be easily switched to fCNTs. The free energy of the LC-fCNT composite is minimum when fCNTs are aligned along the director.

Notably, there is one more important phenomenon is also responsible for the strong interaction between fCNTs and LC molecules inside the nematic matrix named π - π stacking. A strong anchoring energy due to electron stacking between LC-fCNT molecules results in an increase in the $\Delta\epsilon$ (listed in table 2) for the hybrid system, indicating a significant enhancement in the orientational order parameter. Only very small concentration (> 0.05 wt%) of fCNTs in LCs is found to be well dispersed and oriented, however higher concentrations (< 0.05 wt%) leads to agglomeration due to the Vander-Waals forces (in case of direct dispersion i.e., without any organic solvent).

As shown in Fig.5 (d), near the frequency of 10^6 Hz, the peak frequency f_p of the vertically aligned cell is slightly decreasing and shifted towards higher frequency region with increasing fCNT concentrations. This relaxation mode is consequently related to the LC reorientation along the short axis. The relaxation time $\tau_{\parallel}$ of LCs is related to the peak frequency f_p of the dielectric loss of the LC mixture, as shown in Equation (4.5).

$$(4.5) \quad \tau_{\parallel} = \frac{1}{2f_p},$$

The addition of fCNTs provides significant shift in the peak frequency of the dielectric loss of the LC mixture, and hence decreases the relaxation time of LCs. Further, Meier and Saupe indicate that the relaxation time τ is related to the potential barrier parameter η in the vertically aligned cell³⁷:

$$(4.6) \quad \eta = \frac{b}{RT},$$

where b is the rotation barrier height of the flip-flops of the molecules around the axis, R is the gas constant, and T is the temperature. The barrier height b impedes the molecular rotations, therefore the relaxation time τ has been slow down in comparison with the situation when the potential $b = 0$. They also introduce the retardation factor g , in which the potential barrier parameter η is proportional to the dielectric relaxation time τ ³⁸,

$$(4.7) \quad g = \frac{\tau}{\tau_0} = \frac{\exp(\eta) - 1}{\eta},$$

where τ_0 corresponds to a hypothetical state with $b = 0$. In Figure 5 (d), fCNT addition significantly decreases the relaxation time of the LC cell,

decreases the rotation barrier height b around the short axes of the LCs and the associated rotational viscosity γ of LC mixture³⁹. The decreased rotational viscosity accelerates the response time of the LC cell with fCNT doping. It is worth mentioning that the accurate relaxation frequencies of LC medium should be higher than those of the measured cells in this experiment, because of the cell relaxation⁴⁰⁻⁴¹. The cell relaxation also causes the measured real part of permittivity to be below the vacuum permittivity at high frequencies. Because of the lack of accurate ITO resistance and inductance of the wire, the exact relaxation frequencies of LCs are not estimated further. However, the effects of fCNTs on LC materials can still be observed and explained.

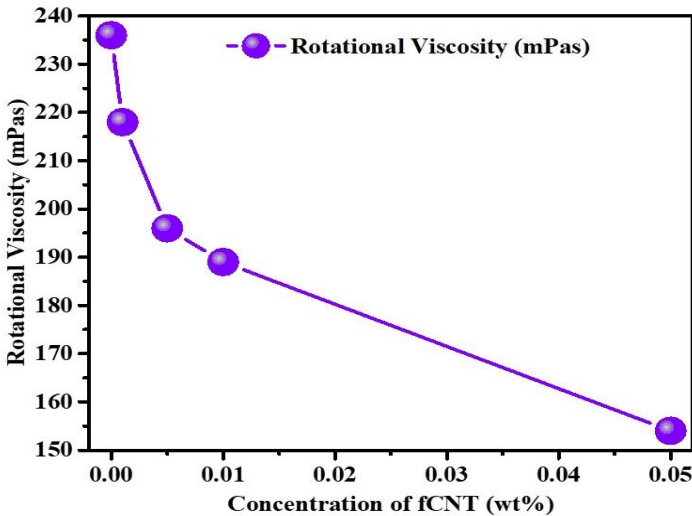


Figure 6. Variation of rotational viscosity of fCNT doped LC cells at various concentrations.

The response times of rotational molecular orientation of pure E7 and LC-fCNT composite systems were acquired through the measurement of transient current induced by a direct-current step voltage and from optical transmission data. In order to understand how fCNTs affect the dynamic response of LC molecules, one would like to first know the change in rotational viscosity in a fCNT-doped cell, which is closely related to the rotational motion of the LC (as discussed in dielectric section). The experimental results in conjunction with the corresponding mathematical analyses suggest that the rotational viscosity of the LC is decreased by doping the fCNT additive ($\sim 38\%$ for 0.05 wt%). Importantly, in our system, we found that the relaxation process is not only determined by the

rotational viscosity but also influenced by the ion concentration. Our observations reveal that the appropriate amount of fCNT (from 0.005 to 0.05 wt%) significantly reduce the ion concentration ($\sim 34.4\%$ for 0.05 wt%) by ion trapping mechanism. The reduced ion concentration reducing the field-screening effect. The reduced ion concentration suppresses the image-sticking effect after removing the applied voltage which, in turn, fasten the relaxation process.

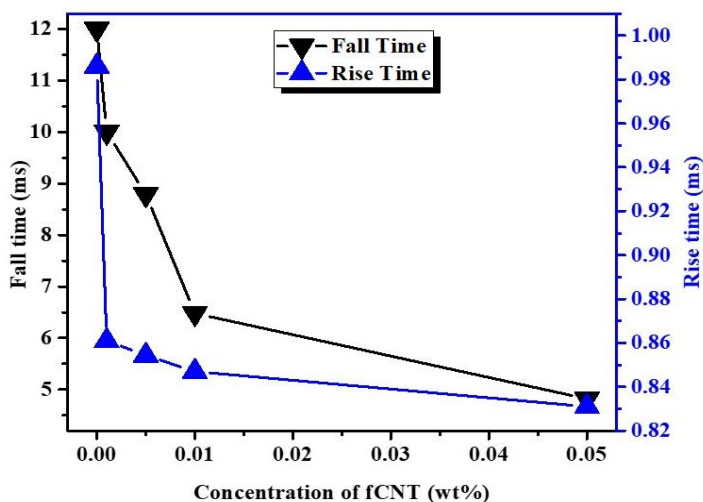


Figure 7. Dynamic response of pure E7 and E7 + fCNT at room temperature.

Fig.7 shows the field-induced switching response for both pure E7 and E7 + fCNT hybrid cells at various concentrations. Dynamic response has been measured at a voltage higher than the threshold switching voltage. The electro-optical setup has used for the dynamic response calculations and the data acquisition has been done using LabView® software. The rise and fall time are defined as the time required for the transmission to change from 90% to 10% and 10% to 90% of the maximum transmission when the cell is turned on from 2 to 10 V (turned off from 10 to 2 V). The rise time is significantly smaller than the fall time because of electric torque-driven reorientation, whereas the latter is a free relaxation reorientation. The rise times of the pure E7 and fCNT-doped LC cells are found to be ~ 0.986 ms, 0.861ms, 0.854 ms, 0.847 ms and 0.831 ms at room temperature (RT), due to the different turn-on voltage (driving voltage) 2.12 V to 1.89 V. Notably, the fall time of fCNT-doped LC cell decreases with various fCNT concentration, due to fCNT doping decreases γ of LC mixture. Interestingly, the 0.05 wt% fCNT-doped LC cell emerges the $\sim 60\%$ faster fall time than the pure one at RT. If the applied voltage (V_{app}) is much

higher than V_{th} , the relationships among fall time (τ_{off}), rise time (τ_{on}), V_{th} , and γ can be expressed as follows⁴²,

$$(4.8) \quad \tau_o = \frac{\gamma d^2}{K_{11} \pi^2},$$

$$(4.9) \quad \tau_{on} = \frac{\tau_o}{\left| \left(\frac{V_{app}}{V_{th}} \right)^2 - 1 \right|},$$

$$(4.10) \quad \tau_{off} = \frac{\tau_o}{\left| \left(\frac{V_{bias}}{V_{th}} \right)^2 - 1 \right|},$$

where τ_o is the relaxation time constant when the LC cell is turned off from V_{app} slightly higher than V_{th} , K_{11} is the splay elastic constant, V_{bias} is the bias voltage, and d is the cell thickness. fCNT doping significantly decreased τ_{off} due to the reduced γ and V_{th} . Notably, fCNT doping decreases τ_{off} and K_{11} and hence γ , which confirms the conjecture from Eqns. (4.8) and (4.10). Now the question is: why does the presence of fCNTs significantly reduce the field induce nematic switching time? For a planar aligned LC cell, the director's response to an external field is given by equation (4.8) to (4.10). These equations express field induced nematic switching is not only the optical response. It is the time taken by the nematic director to rotate from planar to homeotropic configuration without any backflow in the LC cell. However, since the optical response is mainly due to the director's rotation when the field is on, one can write $\tau_{on} \propto \tau_o$, neglecting the backflow in the cell. Thus, from equation (6) to (8), for a constant d , V_{app} and V_{th} , the response would be faster for a reduced γ ($\sim 35\%$), an enhanced $\Delta\epsilon$ ($\sim 3.5\%$), and a reduced K_{11} ($\sim 24\%$) for LC-fCNT composite system. Therefore, separate experiments were performed to find γ and $\Delta\epsilon$ for the pure LC and hybrid system.

Table 5. fCNT concentration-dependent birefringence (Δn), nematic-isotropic temperature (T_{NI}), and estimated second order orientational order parameter (S) of pure LC composites at RT.

fCNT concertation (wt%)	Δn	(T_{NI} °C)	S
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0.000	0.216	60.500	0.583
0.001	0.219	61.500	0.592
0.005	0.226	63.000	0.611
0.010	0.232	65.000	0.627
0.050	0.248	66.500	0.670

Table 5 shows that fCNT doping increased the T_{NI} of the LC mixture, measured by POM on heating nematic to isotropic phase at a rate of 0.25 °C/min by using a temperature controller. Moreover, fCNT doping increased the associated order parameter S and Δn of the LC mixture according to Equation (4.1) and (4.5)⁴²⁻⁴⁴.

The concentration dependence of the birefringence (Δn), nematic-isotropic temperature (T_{NI}), and estimated second order orientational order parameter (S) of pure LC composites are listed in table 5. The birefringence increases with the dispersion of fCNT in nematic LC (up to 0.05 wt%). For 0.001 wt%, 0.005 wt%, 0.01 and 0.05 wt%, we observed the increment of 1.38%, 4.63%, 7.1% and 14.82% respectively. This enhancement of birefringence can be attributed to increased T_{NI} , and S of LC-fCNT composite system. Haller's extrapolation method was used to calculate the orientational order parameter⁴⁵⁻⁴⁷.

$$(4.11) \quad \Delta n = \Delta n_0 \left(1 - \frac{T}{T^*} \right)^\beta,$$

where Δn_0 , T^* and β are the adjustable parameters and have been shown in Table 5. Δn is the experimentally calculated temperature dependent birefringence value, Δn_0 is the extrapolated birefringence in the perfectly ordered state (i.e., $T = 0K$), T^* is the temperature which is about 1-4 K higher than the isotropic temperature (T_{NI}) and β is the critical exponent value, which depends upon the molecular structure of the material and its value is close to 0.25. Equation (4.11) is only valid for T sufficiently smaller than T_{NI} ⁴⁸⁻⁴⁹. This technique enables us to deduce Δn at absolute zero temperature and find Δn_0 .

The variation of order parameter can be expressed as follows:

$$(4.12) \quad S = \left(1 - \frac{T}{T_{NI}} \right)^\beta,$$

The validity of above equation is that the ambient temperature (T) is sufficiently lesser than that of anisotropic temperature (T_{NI})⁴⁸⁻⁴⁹. Although, fCNT doping significantly increased the T_{NI} (measured by POM) and hence associated Δn and S of pure and fCNT doped LC cells also increased according to equation (4.11) and (4.12)⁴²⁻⁴⁴.

The birefringence is related to the order parameter (S) of LC and it can be calculated by the following relation

$$(4.13) \quad S = \frac{\Delta n}{\Delta n_0},$$

Here Δn is the birefringence at particular temperature and Δn_0 is the birefringence at the absolute zero temperature for perfect ordering obtained from Haller's approximation for the order parameter. Our investigation reveals that the $\Delta n_0 = 0.37$ at $\lambda = 633$ nm and RT which is in accordance with the available literature⁵⁰⁻⁵². In the LC-fCNT composite system the inherent order of LC can be transferred to fCNTs dispersed in it. The anisotropic elastic forces of an LC lead to a situation where the minimum free energy for a fCNT in the LC matrix is reached for a configuration where the fCNT points along the director of LC. Other orientations lead to a distortion of the director field and an increase of the free energy of the system thus torque acting to reorient the tube towards the state of lower energy, causing the uniform alignment of fCNTs along the LC director. As expected, the order parameter increases on increasing the concentration of fCNT. The increment in the order parameter is possibly due to the enhanced anchoring effect by π - π interaction between LC-fCNT. Results increment in the $\Delta\epsilon$, enhancing the S of LC-fCNT composite system. It is also worth to mention that, the isotropic-nematic phase transition temperature (T_{NI}) of LC mixture is enhanced by the dispersion of small amount of fCNT also indicating improvement of nematic order and broad nematic range^{8,53}. Since the fCNT used in present investigation is not ferromagnetic in nature so the additional ordering must not be due to the electronic coupling of any permanent dipole moments with the LC dielectric anisotropy⁵⁴. Therefore, enhancement in $\Delta\epsilon$ and consequently improvement in S is attributed due to anisotropic structure of fCNTs and enhanced anchoring energy (since $\Delta\epsilon \propto S$). In the present investigation the enhancement in the order parameter is 1.54%, 4.80%, 7.55% and 14.92% for 0.001 wt%, 0.005 wt%, 0.01 and 0.05 wt% has been found respectively.

Generally, the accurate determination of elastic constants of LCs are less straightforward. The elastic constant is a parameter characterizing the elastic interaction between the LC molecules. When fCNT is dispersed in LCs, the elastic constant (K_{11}) of LC mixture also reflects the interaction between the LC molecules and the fCNT dopant⁵⁵. For the LC-fCNT composite, K_{11} can be roughly estimated by the well-known formula,

$$(4.14) \quad V_{th} = \pi \sqrt{\frac{K_{11}}{\epsilon_0 \Delta \epsilon}},$$

where V_{th} is the reorientation threshold voltage for Fréedericksz transition. The roughly calculated values of K_{11} with the variation of fCNT concentrations are listed in the table. The K_{11} is estimated using the experimentally observed values of V_{th} and $\Delta \epsilon$ by putting it in equation (4.14). Notably, $K_{11} \propto V_{th}^2$ and $\Delta \epsilon$, since dispersion of fCNT does not significantly affect V_{th} , it is approximately constant ($V_{th}^{LC+fCNT} \approx V_{th}^{LC}$), i.e., therefore increasing $\Delta \epsilon$ increases K_{11} of fCNT dispersed composite system i.e. $K_{11}^{LC+fCNT} > K_{11}^{LC}$. It is worth to notice that, $\sqrt{K_{11}^{LC} / \Delta \epsilon^{LC}} \approx \sqrt{K_{11}^{LC+fCNT} / \Delta \epsilon^{LC+fCNT}} = 0.91$, which gives $K_{11}^{LC+fCNT} = 1.11 K_{11}^{LC}$ for 0.05 wt% fCNT. Thus, the surface anchoring may be responsible for the strong elastic interaction between LC molecules and fCNTs which may increase the elastic energy of LC-fCNT composite system and hence increase in K_{11} .

5. Conclusions

The dielectric and electro-optical effects of fCNT dispersed in nematic LCs were demonstrated in this study. In this investigation, the fCNT dopant well-preserved the color performance but slightly reduced the transmission of LC cells due to the scattering of light by CNT. The threshold limit of fCNT concentration (0.05 wt%) also optimized for the direct dispersion of fCNT in LC without any solvent. The fCNT doping significantly reduce the impurity ion (~34.4%), enhanced $\Delta \epsilon$ and K_{11} of LC-fCNT composite system. Consequently, a drastic decrement in the rotational viscosity and hence in electro-optical response about ~60% has been observed. Moreover, the fCNT doping enhanced the S and Δn of the LC-fCNT composite system about ~15% due to the increased T_{NI} and anchoring energy by π - π electron stacking between LC and fCNT. The above results demonstrate a small amount of fCNT dispersion in LC can significantly

enhanced the device parameters which is useful for the development of futuristic device applications. Future work involves the investigation of dielectric and electro-optical performances of LC-fCNT composite systems and optimisation of threshold limit of the concentration by different dispersion methods such as by using different solvents and fine bead mill method for the optimization of best results.

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