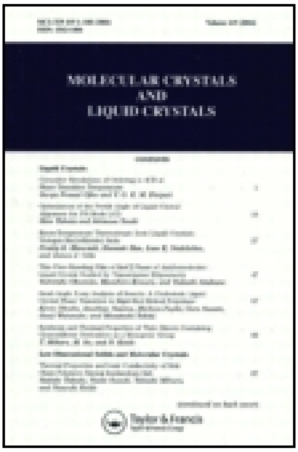

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A Comparative Study of Poly (3,4-ethylenedioxythiophene) (PEDOT) Nanotubes Doped Nematic Liquid Crystal (NLC) System and Carbon Nanotubes (CNT) Doped NLC System for Greater Modification of Electro-Optical Properties of the Host NLC 1770-2

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A Comparative Study of Poly (3,4-ethylenedioxythiophene) (PEDOT) Nanotubes Doped Nematic Liquid Crystal (NLC) System and Carbon Nanotubes (CNT) Doped NLC System for Greater Modification of Electro-Optical Properties of the Host NLC 1770-2

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The aim of this present paper is to compare the effects of conducting polymer, poly (3,4-ethylenedioxythiophene) nanotubes and carbon nanotubes, on the electro-optical properties of a nematic liquid crystal mixture (1770-2). From the optical transmission and capacitance behavior it has been proved that the conducting polymer – nematic liquid crystal system possesses much lower threshold voltage and driving voltage than the carbon nanotube – nematic liquid crystal system which might be very useful in display applications. The effective elastic constant has been also significantly reduced in the conducting polymer – nematic liquid crystal system.

Keywords Conducting polymer nanotubes; electro-optic properties; nematic liquid crystal; threshold voltage

1. Introduction

Blending nanomaterials with nematic liquid crystal (NLC) is considered to be a prospective method to enhance the electro-optical properties of the NLC host. Threshold voltage, driving voltage, residual dc, response time and rotational

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viscosity etc. are found to decrease in nano doped liquid crystal system and in turn the anisotropic order of the liquid crystalline host imparts order in the nano-sized guest particles [1–9]. Proper selection of size, shape and crystallographic phase of nanomaterial is important to achieve desired improvements of the host. It has been observed that the liquid crystal in presence the elongated anisotropic nanoparticles such as nano tubes or nano rods respond dramatically to the applied field due to their inherent dipole moment and cause greater modification than that when doped with the spherical or centrosymmetric nanoparticles.

Among all nanomaterials investigated in this new interdisciplinary field, the carbon nanotubes (CNT) have been proved to be most efficient [1–7] till now. The high electron affinity, mobility of π-electrons along the tubular axis and high anisotropy of polarizability of the CNTs may be the probable reason behind their excellent performance in the nematic liquid crystal host. The density functional calculations have revealed strong anchoring of LC molecules on CNTs which results persistent CNT alignment in LC medium [6]. Furthermore the existence of permanent dipole moment of CNTs easily captures the ionic impurities of the cell and thus reduces the residual DC [4–7]. Here we report another nanomaterial, poly (3,4-ethylenedioxythiophene) (PEDOT) nanotubes which when blended in nematic liquid crystal gives better performance than that obtained in the CNT doped NLC cell. PEDOT is a prototypical conjugated polymer having tunable high electrical conductivity, environmental stability and excellent optical properties in doped conducting state [10–14]. It has π-electron density along the tubular axis similar to that of CNTs. From the optical transmission and capacitance behavior it has been found that PEDOT-NLC system possesses much lower threshold voltage (V_{th}) and driving voltage (V_d) than the CNT-NLC system which might be exploited in display applications. Moreover PEDOT can be easily synthesized by reverse microemulsion technique and can be efficiently doped instead of CNTs in nematic liquid crystal to achieve greater results at much lower cost.

2. Experimental Techniques

The NLC mixture 1770-2 used for present study is synthesized by Dabrowski and co-workers. It possesses high birefringence, large dielectric anisotropy and a wide nematic range. The NLC mixture is consisted of alkyl fluoroisothiocyanatotolanes and alkylphenylfluoroisothiocyanatotolanes. The components and phase sequence of NLC mixture are shown in Figure 1. CNT employed here is multiwalled and commercially available from CheapTubes.com. PEDOT nanotubes are prepared by reverse microemulsion technique. To a 19.12 m mol AOT solution (in n-hexane), 1 ml 10 m mol $FeCl_3$ solution was added on gentle stirring followed by addition of EDOT monomer (3.52 m mol). After 3 hours dark blue-black precipitate was found, separated and washed with methanol prior to drying in vacuum. The precipitate is PEDOT nanotubes and this as-grown sample was directly used without any further purification for this study. The Field emission scanning electron microscopic (FESEM) picture of CNT and PEDOT are shown in Figure 2.

To prepare CNT doped NLC cell at first CNTs are dissolved in chloroform at known concentration. This CNT solution was then added to NLC such that the final concentration of CNT in NLC host is 0.05%. This mixture is then thoroughly sonicated and heated until the CNTs get well dispersed in the NLC medium and the chloroform is completely evaporated. Finally this resultant mixture is filled in a

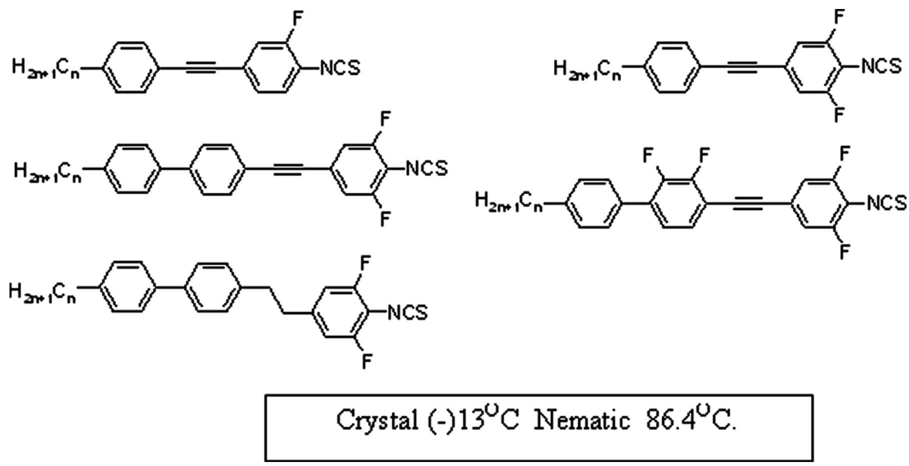

Figure 1. The components and phase sequence of NLC mixture 1770-2.

6.8 μm thick twisted nematic cell at the isotropic temperature of the NLC. PEDOT doped NLC cell is prepared in a similar way. For electro-optic measurement HP33120A signal generator, F10A voltage amplifier, a photomultiplier tube and DL1620 oscilloscope were used. The temperature of the cells was controlled by a Mettler FP52 hot stage attached to a FP5 temperature controller. Dielectric data were recorded in the frequency range from 10 Hz to 13 MHz using a HP4192 Impedance Analyzer.

3. Results and Discussions

We observed the pure LC, CNT doped and PEDOT doped cells under polarizing microscope (Fig. 3). All the three cells show almost same texture when no voltage is applied. The uniformity of the textures assures the homogeneous alignment of the LC molecules as well as the CNT and PEDOT molecules at 0 V. After applying a high bias voltage the LC molecules and the nanotubes orient homeotropically and exhibit a total extinction of polarized light. We observed four lobe patterns in both doped cells above a certain voltage, but the number of the four lobes was much

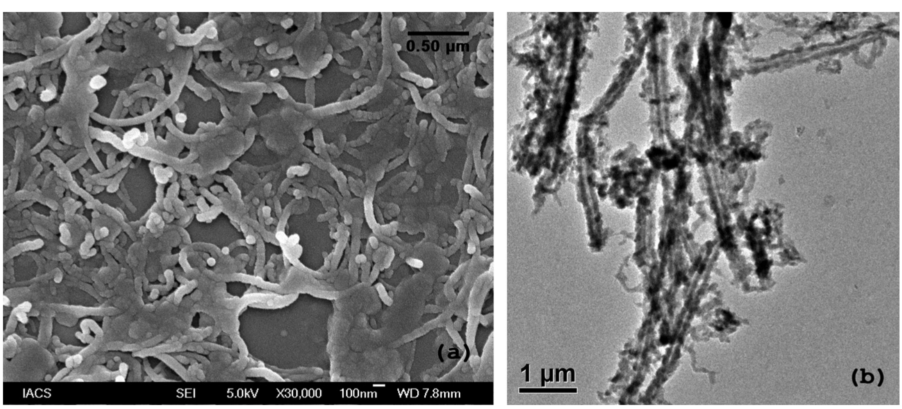

Figure 2. FESEM images of (a) CNT, (b) PEDOT nanotubes.

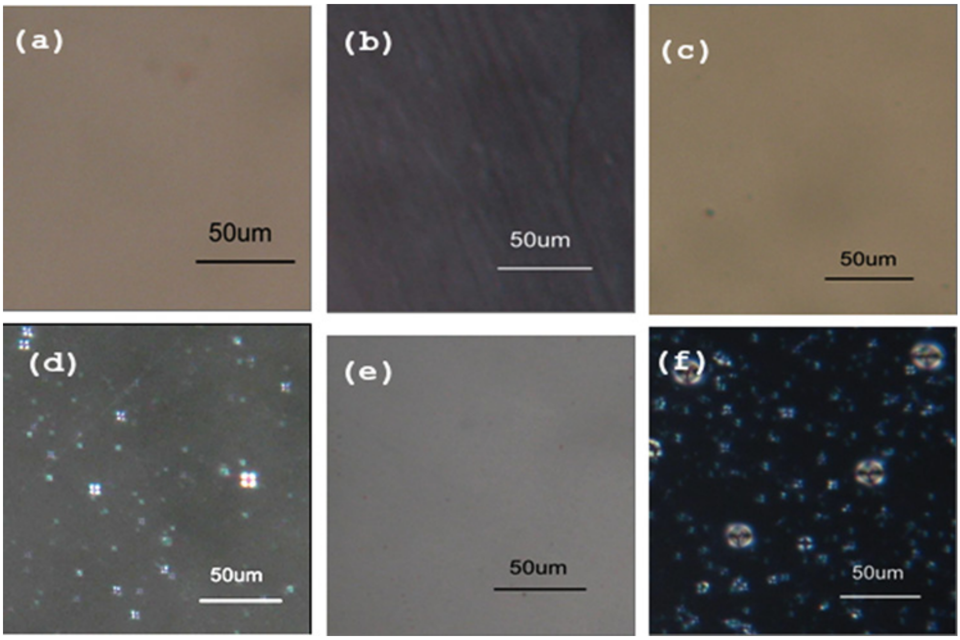

Figure 3. Optical micrographs of (a) undoped, (c) CNT doped, (e) PEDOT doped TN cells under 0 V bias and (b) undoped, (d) CNT doped, (f) PEDOT doped TN cells under 35 V bias. (Figure appears in color online.)

greater in the PEDOT doped cell. Nanotubes with excess charge and a permanent dipole moment possess translational and time dependent orientational motion under external electric field in the LC medium. This translational motion of the nanotubes induces phase retardation of the surrounding LC medium which leads to the leakage of light and thus four lobe patterns appear [15,16]. The net charge of the nanotubes is accumulated either by the charge transfer from adjacent interacting molecules or by trapping ions present in the LC cell. The greater number of the four lobes in PEDOT-doped cell suggests that the net charge of the PEDOT tubes is greater than that of the CNT i.e., they interact more strongly with the LC molecules and also trap the free charges of the LC medium efficiently.

The threshold and driving voltages for Freedericksz transition in a twisted nematic cell in normal white condition (i.e., cell transmits 100% light at zero voltage) are defined as the voltage where the optical transmission gets 90% and 10% of the initial transmission. Here threshold voltage for Freedericksz transition reduces almost 70% in the PEDOT-doped cell whereas it reduces 33% in CNT doped cell as observed in the voltage dependent capacitance (C-V) and transmission (T-V) characteristics (Fig. 4). Also the driving voltage reduces to 49% in CNT doped cell and 72% in the PEDOT doped cell.

As we know the threshold voltage (V_{th}) in a twisted nematic cell may be written as

$$V_{th} = \pi\sqrt{\frac{k_{11} + (k_{33} - 2k_{22})/4}{\varepsilon_0 \Delta\varepsilon}} = \pi\sqrt{\frac{k_{eff}}{\varepsilon_0 \Delta\varepsilon}}$$

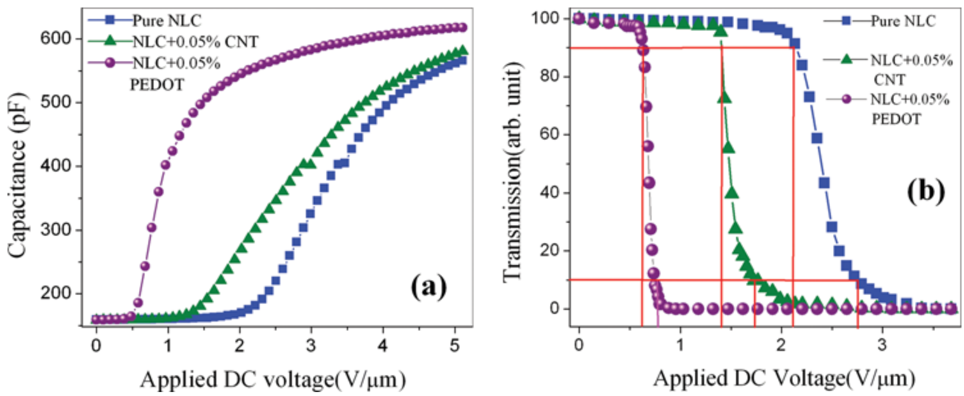

Figure 4. DC voltage dependence of (a) electrical capacitance (C-V) and (b) normalized optical transmission (T-V). (Figure appears in color online.)

where k_{11}, k_{22} and k_{33} are the Oseen-Frank elastic constants, $k_{eff} = k_{11} + (k_{33} - 2k_{22})/4$ is the effective elastic constant, ε_0 is the permittivity of free space and $\Delta\varepsilon$ is the dielectric anisotropy of the system. The dielectric anisotropy increases in the doped cells and effective elastic constant k_{eff} decreased significantly to 54% in CNT doped cell and 90% in the PEDOT doped cell (Table 1). The addition of CNTs and PEDOT nanotubes perturb the order parameter of the liquid crystal host. As the PEDOT nanotubes interact more strongly with the LC molecules the perturbation in order parameter is higher in the PEDOT doped cell. Again the shape of the nanomaterials also has great impact. Probably the strong anchoring of the LC molecules on the wall of the PEDOT nanotubes helps to reduce the effective elastic constant of the LC cell.

The contrast ratio of the TN cells are defined as the $\frac{\text{MaximumTransmission}}{\text{MiniimumTransmission}}$ in the normally white mode. We have found that contrast ratio is higher in doped cells (Table 1). It increases by nearly 3.7% in CNT doped cell and 6% in PEDOT doped cell respectively.

The dielectric spectrum of the pure and the doped NLC cells are shown in Figure 5. The only absorption peak at high frequency is attributed to the rotation of the LC molecule around their short axis. In CNT and PEDOT doped cells the absorption peak slightly moves towards higher frequency keeping the dielectric strength almost the same.

Table 1. The values of dielectric permittivities ($\varepsilon_{\|}$, $\varepsilon_{\perp}$), dielectric anisotropy ($\Delta\varepsilon$), threshold voltage (V_{th}), driving voltage (V_d), effective elastic constant (k_{eff}) and contrast ratio in pure, CNT-doped and PEDOT-doped NLC mixture (retrieved from the C-V and V-T curves). The values of threshold voltages obtained from both C-V and V-T curves are almost the same

Samples	$\varepsilon_{\|}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	$V_{th}(V/\mu m)$	V_d	K_{eff}(pN)	Contrast ratio
Pure 1770-2	17.36	4.78	12.58	2.12	2.75	50.77	14.48
0.05% CNT + 1770-2	17.72	4.78	12.94	1.41	1.4	23.10	15.03
0.05% PEDOT + 1770-2	18.35	4.68	13.67	0.63	0.77	4.87	15.36

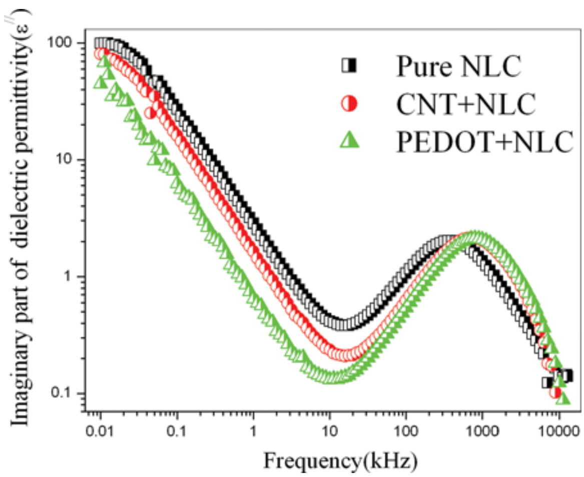

Figure 5. Dielectric spectra of pure, CNT doped and PEDOT doped NLC mixture. (Figure appears in color online.)

4. Conclusion

Electro-optical properties of pure nematic liquid crystal mixture 1770-2 and that by doping it with CNT and PEDOT nanotubes are compared in twisted nematic cells. The threshold and driving voltages and effective elastic constant are much reduced in the PEDOT-doped cell than the CNT-doped and undoped liquid crystal cell. The strong interaction of the PEDOT nanotubes with host nematic liquid crystal molecules is the probable reasons behind such modifications. There is also significant increase in contrast ratio in the PEDOT-doped cell. In this study PEDOT nanotubes have been proved to be much more efficient than the carbon nanotubes to improve the electro-optical properties of the NLC host. Thus we can conclude that TN cell with PEDOT nanotubes makes it possible to construct a bright display with better electro-optical parameters than the TN cell with pure liquid crystal or carbon nanotubes doped liquid crystal.

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