Optimization of the electrical parameters of nematic and discotic liquid crystalline materials due to the dispersion of nano particles, nano tubes and quantum dots for display and photo-voltaic applications

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ABSTRACT

Electro-optical and dielectric parameters of the nano particle and carbon nano tube dispersed room temperature liquid crystalline materials 5CB and 6CHBT have been determined. In the nano-entity dispersed systems, nematic to isotropic transition temperatures are highly affected. Threshold voltage required to switch molecules from bright state to dark state is decreased. Longitudinal and transverse components of the dielectric permittivity are affected in such a way that it improves display properties.

Doping of functionalized nano particles have drastically enhanced conductivities through the columns of the discotic liquid crystals which are very useful in several applications including one dimensional conductor. This includes application of discotic-nano composites in flexible photovoltaic areas as well. Calculations shows that due to the increase electrical conductivity there would be appreciable enhancement in the efficiency due to the doping of the metallic and semi conducting nano-particles.

Keywords: Electro-optical properties, nematic displays, functionalized nano particles, columnar discotics, one dimensional conductor, photovoltaics

1 INTRODUCTION

Study of the influence of nano systems on the properties of liquid crystals has attracted huge attention since the beginning of the last decade [1]. One nano meter (nm), is considered to be a magical point on the dimensional scale. The nano particles doped liquid crystals have been studied due to their very attractive properties and prospective applications in electronic industry by different groups around the world and also for studying the special aspects such as dielectric [2-12], electro-optical [2, 3, 5-11, 13-19], memory effect [3, 14], photoluminescence [13], fluorescence confocal polarizing microscopy [20], one dimensional conductor and above all photovoltaic applications.

The nano particles share their intrinsic properties with the liquid crystals because of the mutual interactions at molecular level due to the similarity of the dimensions. Influence of nano particles, nano tubes or quantum dots on liquid crystalline properties is generally achieved by adding a very low concentration of nano entities into the liquid crystal (LC) matrix. These dilute nano suspensions are stable due to the weak interactions of the particles at low concentrations. The nano particles are so small that they do not disturb the LC ordering and macroscopically identical structures are obtained, i.e. the suspensions appear similar to that of a pure LC without apparent evidence of dissolved nano entities. At the same time the nano entities are sufficiently large to maintain the intrinsic properties of the materials from which they are made (e. g. ferromagnetism or ferroelectricity) and share these properties with the LC materials. In most cases, nano particles reduced threshold voltage (V_{th}) required to switch the molecules from planar to homeotropic configuration [2, 6, 7, 11, 14-19].

The supramolecular assemblies of disc-shaped molecules lead to the formation of discotic liquid crystals [20]. These materials are becoming of increasing interest as self organizing molecular wires through which charge or excitons can migrate rapidly [21, 22]. Because of this property, their potential applications in conducting, photoconducting, optical data storage, light emitting diodes, photovoltaic solar cells and several other devices are being considered [21, 22]. As the charge mobility in the discotic liquid crystals is very high and their processability is convenient and economic, large scale use of photovoltaic devices for electricity generation can be realised. In a seminal report [23], Mende *et al* constructed a *p*/*n*-type photovoltaic solar cell using discotic liquid crystalline hexabenzocoronene (HBC) as the hole-transporting layer and a perylene dye as electron transporting layer. A chloroform solution of crystalline dye perylene *N*,*N*'-*bis*(1-ethylpropyl)-3,4,9,10-perylene*bis*(dicarboximide) and room temperature discotic liquid crystal hexadodecylphenyl-HBC were spin-coated onto indium tin oxide. Photodiodes were prepared by the evaporation of aluminum onto organic semiconducting blend films. The device exhibits external quantum efficiencies (EQEs) up to 34% and power efficiencies of up to ~2%. Efficient photoinduced charge transfer between the hexabenzocoronene and perylene and facile charge transport through vertically segregated perylene and hexabenzocoronene *p*-systems are primarily responsible for these efficiencies.

Here, we present experimental results on effect of nano particles and nanotubes on various display parameters of nematic phases of LC materials. 4'-pentyl-4-cyanobiphenyl (5CB) and 4-(trans-4'-n-hexylcyclohexyl) isothiocyanatobenzene (6CHBT). We also report enhancement of conductivity along the columns due to the doping of nano particles in discotics which is useful for the enhancement of the efficiency of photovoltaic cells.

2 EXPERIMENTAL TECHNIQUES

For the study of the Electro-Optical (E-O) properties, polymer-coated and parallel-rubbed Indium tin oxide (ITO)-coated glass plates with a pre-tilt angle of ~1-3° have been used to prepare the cells of electrode spacing ~ 5 μm. In such cells molecules are aligned parallel to the rubbing direction on the glass plates. The same cell has been used to determine static value of the transverse component of relative dielectric permittivity ($\varepsilon'_{\perp}$). However, for the determination of longitudinal component of relative dielectric permittivity ($\varepsilon'_{||}$), gold coated glass plates with the coating of lecithin have been used to prepare the cells. E-O characteristics i.e. transmission voltage (T-V) curves were drawn by using polarized light microscope coupled with a photo-detector. Photo-voltage (which is proportional to the intensity of the transmitted light) obtained from the photo-detector was recorded by using a six and half digit multimeter. V_{th} was determined from the T-V curve. In order to determine other display parameters, dielectric data have been acquired by using the impedance analyzers, in the frequency range 1 Hz to 35 MHz in both planar and homeotropic anchoring of the molecules. The temperature of the sample was controlled with the help of a hot stage having an accuracy of ± 0.1°C. Detailed experimental techniques are already described in previous reports. DC conductivities have been determined with the conductivity plot with frequency as well as with the electrometer.

In the case of dispersive material, the measured dielectric spectrum can be described with the help of generalized Cole-Cole equation:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' = \varepsilon'(\infty) + \frac{(\Delta\varepsilon)}{1+(jf\tau)^{(1-h)}} + \frac{A}{f^n} - j\frac{\sigma_{ion}}{2\pi\varepsilon_0 f^k} - jBf^m \quad (1)$$

where $\Delta\varepsilon$ (=$\varepsilon(0)$-$\varepsilon(\infty)$), τ and h are the dielectric strength, the relaxation time (inverse of relaxation frequency) and the symmetric distribution parameter ($0 \le h \le 1$) of the relaxation mode, respectively. $\varepsilon(0)$ and $\varepsilon(\infty)$, the low and high frequency limiting values of the relative dielectric permittivity. Third and fourth terms in Equation (4), represent the contribution of the electrode polarization capacitance and ionic conductance at low frequencies where A and n are constants. In the case of pure ohmic conductance, constant k is found to be 1. The fifth imaginary term Bf^m is included in Equation (1) to partially account for the high-frequency electrode surface resistance, B and m being constants as long as correction is small and ε_0 (=8.85 pFm^{-1}) is the free space permittivity. Real and imaginary part of Equation (1) can be written as follows:

$$\varepsilon' = \varepsilon'(\infty) + \sum_i \frac{\Delta\varepsilon_i[1+(\omega\tau_i)^{(1-h_i)}\sin(h_i\pi/2)]}{1+(\omega\tau_i)^{2(1-h_i)}+2(\omega\tau_i)^{(1-h_i)}\sin(h_i\pi/2)} + \frac{A}{f^n} \quad (2)$$

and

$$\varepsilon'' = \sum_i \frac{\Delta\varepsilon_i(\omega\tau_i)^{(1-h_i)}\cos(h_i\pi/2)}{1+(\omega\tau_i)^{2(1-h_i)}+2(\omega\tau_i)^{(1-h_i)}\sin(h_i\pi/2)} + \frac{\sigma_{ion}}{2\pi\varepsilon_0 f^k} + Bf^m \quad (3)$$

To explore relaxation mode of the pure as well as dispersed system, the dielectric permittivity and loss data have been fitted with the help of Equations (2) and (3). We have subtracted low frequency correction terms due to electrode polarization capacitance from the measured data to explore relaxation phenomenon in the nematic phase. More so 10 kHz dielectric data have been treated as the 'static' values, as they are free from low and high-frequency artifacts and there is no dispersion mechanism up to this frequency. These data have been used to determine anisotropy of the relative dielectric permittivity $\Delta\varepsilon'$ (=$\varepsilon'_{||}$-$\varepsilon'_{\perp}$) of the various studied materials.

3 BRIEF RESULTS AND DISCUSSION

When functionalized Gold Nano Particles (GNPs) of average size 2.4 nm were dispersed (0.1 wt%) in room temperature nematic material 5CB, nematic to isotropic transition temperature increased by about ~3.3 °C against the common observations where it decreases. Electro-optical studies suggested substantial decrease of the threshold voltage (V_{th}) as can be seen from Fig. 1. Threshold voltage is governed by the following equation:

$$V_{th} = \pi(K_{11}/\varepsilon_0\Delta\varepsilon')^{1/2} \quad (4)$$

where K_{11} is the splay elastic constant. In order to find the other parameters of eq. (4), we carried out dielectric measurements. Variations of $\varepsilon'_{||}$ and $\varepsilon'_{\perp}$ (and hence $\Delta\varepsilon' = \varepsilon'_{||} - \varepsilon'_{\perp}$) are shown in Fig. 2 for the pure and GNP dispersed samples. $\Delta\varepsilon'$ of GNP dispersed sample has decreased significantly. Despite decrease of $\Delta\varepsilon'$, V_{th} has decreased which suggests that K_{11} is also decreasing (eq. 4) due to the dispersion of GNPs. Fig. 2 also confirms the increase of T_{NI} for the GNP dispersed sample as compared to that of the pure sample. Detailed results and interpretation can be seen in ref 24. Appreciable increase in the conductivity has been observed due to the presence of GNPs as can be seen in Fig 3. Conductivity has increased by more than an order of magnitude.

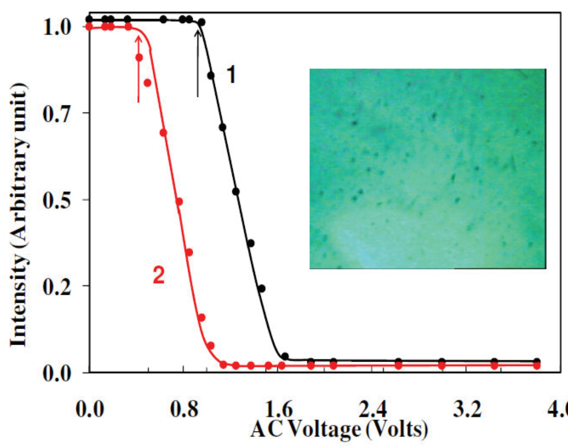

Figure 1: Electro-optical response the pure and GNP dispersed 5CB. Upward arrows represent the threshold voltages. The microphotograph in the inset represents the bright state of the cell with the GNPs dispersed in 5CB. Black spots are GNPs and appear due to molecular distortions around them.

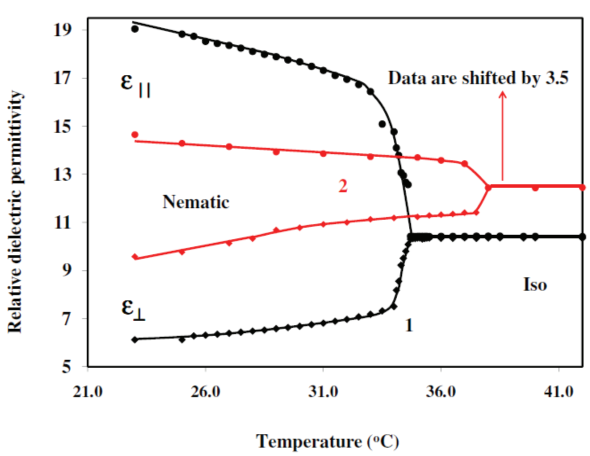

Figure 2: Variations of two components of the dielectric permittivity for the pure and GNPs dispersed 5CB indication that the anisotropy is decreasing due to the presence of GNPs.

When Single-wall carbon nanotubes (SWCNTs) of length~100-300 nm have been dispersed in the nematic matrix of room temperature liquid crystalline material 4-(trans-4'-n-hexylcyclohexyl) isothiocyanatobenzene (6CHBT), again decrease in V_{th} as shown in Fig. 3 has been observed. In this case, presence of SWCNTs in the nematic matrix of 6CHBT, increased dielectric anisotropy and decreases splay elastic constant [11]. These two parameters have been consequently responsible for the substantial decrease in the threshold voltage required to switch molecules from planar (bright state) to homeotropic (dark state) configuration. Nematic matrix supported alignment of the SWCNTs parallel to the nematic director. On the other hand, the presence of SWCNTs improved local orientational ordering of molecules in the nematic phase probably due to intense van der Waals interactions and thereby increasing nematic order parameter. Further details of the results can be seen in ref 11.

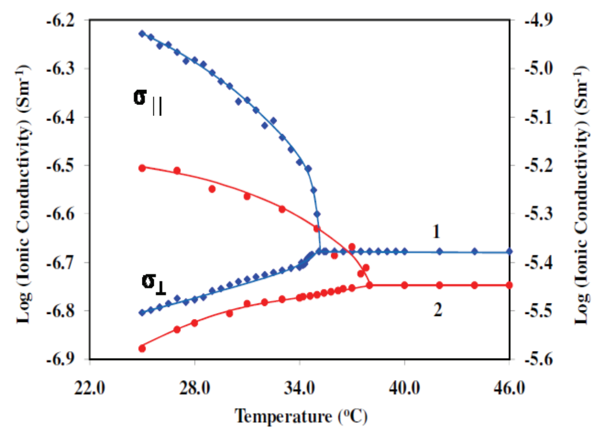

Figure 3: Variation of the ionic conductivity in the direction parallel and perpendicular to the director for (1) pure 5CB-left vertical axis and (2) the GNPs dispersed 5CB- right vertical axis.

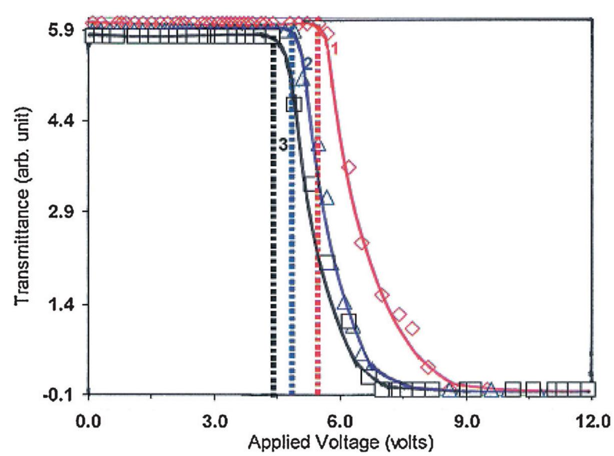

Figure 4: Electro-optical curves for (1) pure (red-dumbles), with (2) 0.01% (blue-triangles) and (3) 0.02% (squares) SWCNTs in 6CHBT. Vertical lines represent threshold voltages.

In another work we have observed drastics increase in the permittivities of 4-Pentylphenyl 4-(Octyloxy) benzoate (4PP4OB) and 6CHBT due to the dispersions of low percentage of CdSe quantum dots. Detailed results are yet to be summarized.

As discussed in the introduction section, photodiodes employing high conductivity along the columns of the discotic liquid crystals (DLCs) are already reported [23]. In order to increase the efficiency of these diodes, doping of metal and semiconducting nano particles and nano tubes seems useful due to as both of these increase conductivity along columns drastically (see Fig 5).

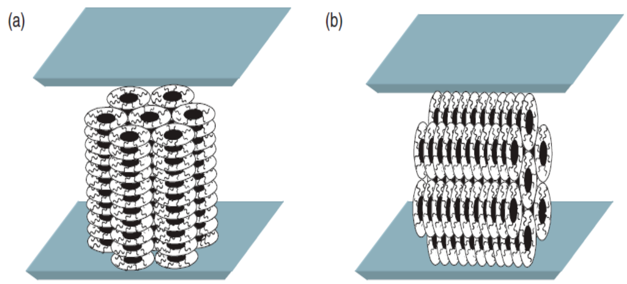

Figure 5: DLCs sandwitched between two parallel electrodes with (a) plane of the discs paralel to the electrodes and (b) plane of the discs normal to the electrodes. When E is applied through electrodes in case (a)- conductivity is measured along the columns. In the case (b) conductivity will be normal to columns.

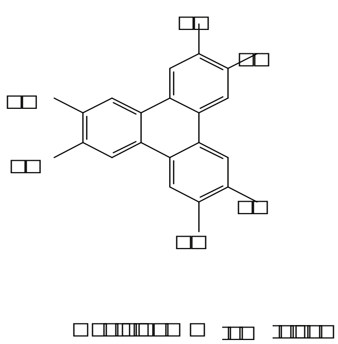

Figure 6: The molecular structure Discotic Liquid Crystal HAT4.

We have measured conductivity of pure as well as GNP dopped in a DLC abbreviated as HAT4 (molecular structure shown in Fig. 6) along the columns and have observed that enhanced dark and photo conductivities as much as by 2-3 order of magnitudes. We are translating such a high increase of photoconductvity in enhancing photodiodes using DLCs.

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