

Effect of doping with carbon dots on the alignment and dielectric properties of nematic liquid crystal 4-cyano-4'-pentylbiphenyl in ITO sample cells without conventional alignment layers for low-cost display applications

Priscilla P^a, Michael R. Fisch^b, Harikesh Meena^{a,c}, Srashti Tomar^{a,d}, Arvind K. Gathania^{e,*}, Sandeep Kumar^{f,g}, Jai Prakash^h, Supreetⁱ, Sanjeev Kumar^j, Gautam Singh^{a,*}

^a Department of Applied Physics, Amity Institute of Applied Sciences, Amity University Uttar Pradesh, Noida 201313, India

^b College of Aeronautics and Engineering, Kent State University, Kent, OH 44242, USA

^c Department of Electronics Science, Atma Ram Sanatan Dharam College, University of Delhi, Dhaula Kuan, New Delhi-110021, India

^d Physics Department, Deshbandhu College (University of Delhi), Kalkaji 110019, New Delhi, India

^e Department of Physics and Photonic Science, National Institute of Technology, Hamirpur, Himachal Pradesh 177005, India

^f Raman Research Institute, C.V. Raman Avenue, Sadashivanagar, Bengaluru 560080, India

^g Department of Chemistry, Nitte Meenakshi Institute of Technology, Yelahanka, Bengaluru 560064, India

^h Department of Physics, Aligarh Muslim University, Aligarh 202002, India

ⁱ Department of Physics, Amity School of Applied Sciences, Amity University Haryana 122413, India

^j Department of Physics, Chandigarh University-Gharuan, Mohali 140413, India

ARTICLE INFO

Keywords:

Nematic liquid crystal
Carbon dots
Vertical alignment
Composites

ABSTRACT

The melding of nanomaterials with liquid crystalline materials is at the frontier of scientific research due to the transformative impact of nanoparticles on the functionalities of host liquid crystal materials. Here, we report the effect of doping of carbon dots (CDs) in the nematic liquid crystal (NLC), 5CB (4-cyano-4'-pentylbiphenyl) in indium tin oxide (ITO) sample cells without alignment layers (i.e., unaligned ITO (U-ITO) sample cells) using polarizing optical microscopy and dielectric spectroscopic techniques. Polarizing optical microscopy reveals largely dark optical textures under crossed polarizers confirming vertical alignment of Pure 5CB in U-ITO sample cells. However, defects present in the texture pose severe constraints on the use of induced vertical alignment in U-ITO sample cells for device applications. To improve the quality of vertical alignment, CDs of size 2.8 nm at concentrations of 0.03, 0.05 and 0.1 wt% are doped into 5CB. Optical texture studies show the quality of induced vertical alignment of the 0.03 wt% composite is better than pure 5CB and other composites. Frequency-temperature dependent dielectric studies verify the induced vertical alignment by observation of the short-axis molecular relaxation. The stability of the vertical alignment throughout the nematic phase of 5CB is confirmed through temperature dependent dielectric and optical texture studies. The induced vertical alignment of 5CB in U-ITO sample cells could be attributed to the stronger LC-LC interaction than the ITO-LC interaction. The improvement in the quality of vertical alignment of CDs-5CB composites could be due to the CDs influencing LC-LC and ITO-LC interactions. Finally, the effect of CDs on the increasing dc electrical conductivity of 5CB in U-ITO sample cells is investigated. Our results clearly indicate that CD-5CB composites would be useful in cost-effective display and other photonic devices devoid of alignment layers.

1. Introduction

Nematic liquid crystals (NLCs) are one of the widely known and leveraged classes of liquid crystals. In this phase the molecules have a general tendency of orientating on an average towards a common direction defined as director (\mathbf{n}). NLCs are utilized in a wide spectrum of

applications spanning from display devices, photonics, sensors to optical devices [1–5]. One of the most crucial factors for the employability of these NLCs in devices is their easy molecular alignment by alignment layers and external fields. Generally, the molecular alignment in a sample cell is categorized as either: planar (\mathbf{n} is parallel to the substrates) or vertical (\mathbf{n} is perpendicular to the substrates). Numerous

* Corresponding authors.

E-mail addresses: akgathania@nith.ac.in (A.K. Gathania), gsingh6@amity.edu (G. Singh).

<https://doi.org/10.1016/j.molstruc.2024.139894>

Received 6 June 2024; Received in revised form 28 July 2024; Accepted 31 August 2024

Available online 2 September 2024

0022-2860/© 2024 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

techniques are utilized to achieve a uniform alignment of NLCs including rubbing of polyimides [6], coating alignment layers [7], photoalignment [8], electric and magnetic fields [9,10], modification of the substrate surface [11] and doping of nanoparticles [12]. Polyimide coating is widely used in industry to obtain both planar and vertical alignment in display devices. However, coating a substrate with polymer layers to obtain uniform alignment of molecules is not budget-friendly, produces suboptimal display performance, have complex processing, and require a high curing temperature [13]. Because of these severe drawbacks alternate approaches to obtain consistent alignment have been developed. One such alternative approach, is the doping of nanoparticles (NPs) in NLCs that has emerged as a promising technique and has garnered considerable attention in research circles [12].

It has been shown in the literature that certain cleaning processes performed on glass, oxides, and metals produce vertical alignment of NLCs; however, such induced alignment is not uniform and often shows defects and light leakages which are not suitable for their employment in applications [14–17]. Hence, addition of NPs offers a potential solution to overcome this limitation, as it influences not only the alignment but also the dielectric, electrical, and thermal properties of NLCs [18–27]. Amongst NPs, quantum dots (QDs) have been in the limelight over the last decade due to their relatively small size (size range ~2–10 nm), fluorescence property, quantum confinement effect, etc. [28–30]. Doping of QDs in NLC has enabled the tuning of the properties of the host material significantly which researchers believed can be implemented for device application [31–34]. Some of the works conducted on the addition of QDs in positive dielectric NLC infiltrated in unaligned ITO glass plates or plain glass slides is reported by the Hegmann group [35] in which they doped two different QDs (hexadecylamine-capped CdSe and thioglycolic acid-capped CdTe) in a phenyl pyrimidine NLC and observed the induction of vertical alignment in the host material at concentrations of 1 and 2 wt% of CdSe QDs, and higher than 2 wt% for CdTe QDs. However, the obtained vertical alignment between plain glass slides was not free from defects and showed birefringent stripe patterns and optical textures which posed a hurdle in their utilization for application purposes [35]. Continuing this, in another study they reported doping of three different QDs (QD1, QD2 and QD3) in the same NLC material. Compositionally different Zn doped QD3 showed the induction of vertical alignment at all concentrations (1–5wt%) prepared for the investigation. The vertical alignment in this case also produced birefringent stripe patterns [36]. In recent years, driven by concerns regarding cadmium toxicity levels [37–45], researchers have increasingly prioritized the utilization of eco-friendly QDs. From this perspective, less work has been reported on the doping of eco-friendly QDs in positive dielectric NLCs filled in unaligned LC cells. One such report from Lee and group elucidated the effect of doping CuInS₂ (CIS)–ZnS core-shell QDs in a positive NLC material. They observed that the capillary filling method induced a planar alignment of NLC when filled in an unaligned ITO cell which was explained due to the formation of 1D-chain like structures by the QDs clusters that then guide the LC molecules that are near the QD surface to align parallel to the substrate which gradually gets propagated into the bulk of the sample producing a uniform planar alignment [46].

A literature review shows that currently no report is available on the doping of carbon dots (CDs) in NLC infiltrated into a U-ITO coated cell [39–44]. Here, we report the effect of doping of varying concentrations of CDs on the induced vertical alignment of positive dielectric 5CB, NLC in the U-ITO sample cell. Optical texture and dielectric studies confirm that uniform and stable vertical alignment (without birefringent stripes or defects) is achieved for a 0.03 wt% CDs-5CB composite. The thermal stability of the alignment and the impact of CDs on the conductivity of 5CB have also been elucidated in this study.

2. Experimental details

2.1. Details of material and preparation method

In the present work, we have employed 5CB (4-cyano-4'-pentylbiphenyl), NLC acquired from Sigma-Aldrich and used without any further purification. The phase sequence of 5CB is Cr 25 °C N 35 °C Iso, where Cr, N and Iso denote Crystal, Nematic and Isotropic phases, respectively. Dopant CDs were synthesized using one pot selective synthesis method and characterized by Kumar et al. [47]. The size and morphology of the CDs were determined through HRTEM and found to be quasi-spherical of uniform size of 2.8 ± 0.72 nm [48]. The U-ITO coated LC sample cells of thickness 4 μ m were purchased from Instec Inc. USA and utilized for optical, dielectric, and electrical investigations. 0.1 w/v% of CDs solution was prepared using chloroform as solvent. For our experiments, initially 5 mg of NLC was weighed in glass vials and 0.03, 0.05 and 0.1 wt% concentrations of CDs solutions were added into them. These mixtures were then ultrasonicated for two hours to attain a homogenous distribution of CDs in the NLC and thereafter the chloroform was evaporated by keeping the composite in a muffle furnace for 1 hour at 65 °C. These composites in the isotropic phase were capillary filled into U-ITO LC cells.

2.2. Apparatus and measurements

Optical studies were conducted on pure 5CB and its composites with CDs using a polarising optical microscope (POM) with crossed polarizers (CENSICO International 13809, India). For dielectric studies, an LCR meter (nF Corp, ZM2376, Japan) with an oscillating voltage maintained at 300 mV was employed in the frequency range of 100 Hz–5.5 MHz. The temperature of the sample cells were controlled using a customized hot stage equipped with a temperature controller integrated with a water bath (Thermotech, AQS-WB-200, India) having a precision control of ± 0.5 °C.

3. Results and discussion

Polarized optical microscope is used to verify the quality of dispersion of nanoparticles in LC materials and the quality of alignment of the LC through observation of optical textures. Fig. 1 illustrates optical micrographs in nematic phase (29 °C) of Pure 5CB and CDs-5CB composites filled in U-ITO sample cells. Fig. 1(a) shows the induced vertical alignment of Pure 5CB in a U-ITO sample cell. However, the presence of numerous defects that cause light leakage, indicated reduced quality of induced vertical alignment. The occurrence of such induced vertical alignment of Pure 5CB when filled in U-ITO substrate can be explained by Friedel–Creagh–Kmetz (FCK) rule [14]. According to this rule, if $\gamma_S < \gamma_{LC}$ (where γ_S is the additional surface energy of the solid substrate, and γ_{LC} is the strength of LC-LC interaction) a vertical alignment will be produced [49]. Here, the intermolecular interaction between the polar “heads” of the 5CB molecules is relatively higher than the van der Waals interaction produced by the ITO substrate leading to the formation of vertical alignment [14,16,46]. To reduce the nonuniformity and light leakages of induced vertical alignment of 5CB in U-ITO sample cells, we doped CDs into 5CB. As seen in Fig. 1(b) and (c), doping of CDs produced better vertical alignment of 5CB with relatively fewer defects and a more uniform texture for the lower concentrations of 0.03 wt% and 0.05 wt% CDs. Since the sample cells employed for this investigation are U-ITO cells (i.e., no rubbed polyimide), it is observed that even the smallest concentration of CDs (0.03wt%) produces good vertical alignment, unlike in our earlier report that used planar aligned sample cells, wherein vertical alignment is achieved for 0.3wt% CDs in 5CB [50]. Interestingly, the absence of an alignment layer proves to be an important factor in the achievement of a uniform vertical alignment at minimal concentrations. Nevertheless, CDs at higher concentrations don't favor an optimal vertical alignment as demonstrated in Fig. 1(d).

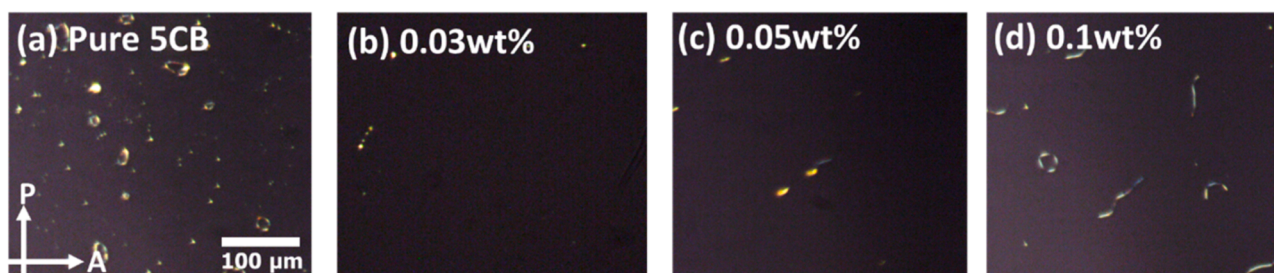


Fig. 1. Optical textures of the nematic phase of (a) Pure 5CB, (b) 0.03 wt%, (c) 0.05 wt% and (d) 0.1 wt% of CDs-5CB composites at 29 °C. Here, P and A denote polarizer and analyzer, respectively. The scale bar is 100 μm . The thickness of U-ITO sample cells is 4 μm .

At 0.1wt%, optical textures reveal the emergence of defects underscoring an undesirable outcome at a higher concentration of CDs. The defects observed in Pure 5CB are significantly reduced with the addition of low concentration CDs. However, once the concentration of CDs is increased to 0.1 wt%, the defects reappeared in the texture. A point to be noted here that such defects have previously been reported in both micro and nano doped LC composites [49,51,52] and termed as, well patterned bright defect structures with four extinction lines [51], or doughnut-shaped birefringent structure [52]. The appearance of such defects could be due to distortion in the uniform vertical alignment of the bulk 5CB caused by doping of CDs of higher concentration.

After the confirmation of induced vertical alignment of 5CB, NLC at one temperature deep in the nematic phase, it is critical to assess its stability throughout the nematic phase. Fig. 2 demonstrates the optical

micrographs of Pure 5CB and CDs-5CB composites at higher temperatures in the nematic phase. The induced vertical alignment remains stable over the complete nematic phase of pure and composite samples. This clearly shows that the strong interaction of CDs with LC molecules is not diminishing with rise in temperature. That means the accumulation of CDs on the ITO surface is also stable with temperature. The stability of alignment with changing temperature is one of the crucial parameters for display devices. So, the induced vertical alignment of 5CB by CDs is certainly reliable throughout nematic phase. In other words, the induced vertical alignment is thermally stable throughout nematic phase of 5CB.

The pure and composite samples were examined through dielectric spectroscopic techniques at a constant temperature of 29 °C. Fig. 3 shows the frequency dependent relative real dielectric permittivity (ϵ')

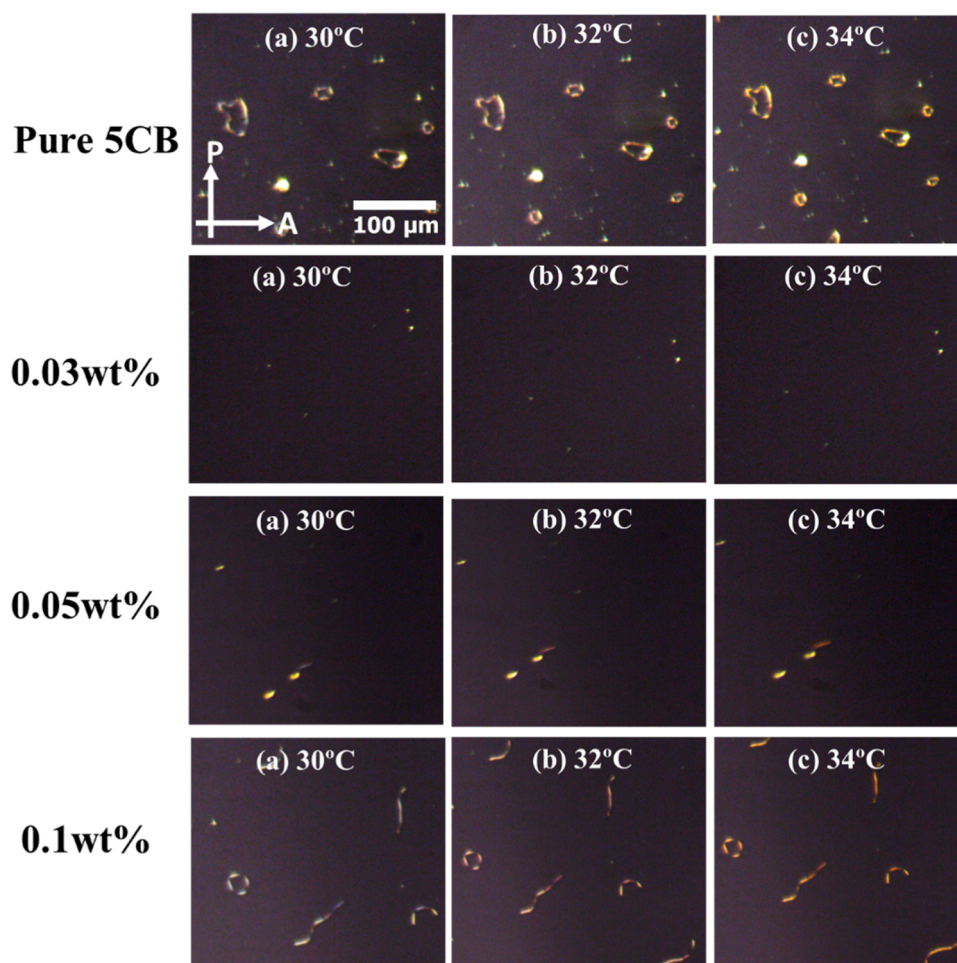


Fig. 2. Temperature dependent optical textures in the nematic phase of Pure 5CB and CDs-5CB composites (0.03, 0.05 and 0.1 wt%) in U-ITO cells. Here, P and A denote polarizer and analyzer, respectively. The scale bar is 100 μm . The thickness of the U-ITO sample cells is 4 μm .

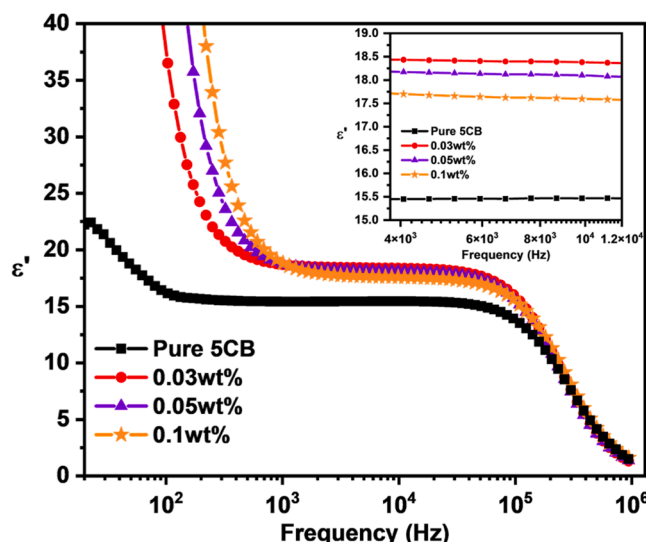


Fig. 3. Frequency dependent relative dielectric permittivity (ϵ') of the nematic phase of pure 5CB and CDs-5CB composites at 29 °C. Inset shows the magnified permittivity graph.

for pure 5CB and CDs-5CB composites. The value of ϵ' in the plateau region is observed to increase initially and thereafter, for higher concentrations, decrease. At a constant frequency of 10 kHz, the value of ϵ' for Pure 5CB is observed to be 15.46 which increased to the maximum value of 18.37 for 0.03 wt% and further increment in the concentration of CDs to 0.05 and 0.1 wt% illustrated a decrease in ϵ' . The increase in the value of ϵ' for lower concentration (i.e., 0.03 wt%) is attributed to the enhanced vertical alignment and reduction of the defects. However, for higher concentration (>0.03 wt%), such induced vertical alignment seems to get disturbed due to strong CD-CD interaction and eventually lead to reduction in the ϵ' . Here, 0.03 wt% can be considered as the optimal concentration that helps in achieving a nearly perfect vertically aligned state. To the best of our knowledge, this is the lowest concentration of NP in LCs leading to induced alignment. The tendency of the ITO coating to vertically align molecules and the absence of alignment layers support the direct interaction of CDs with LC molecules in orientating them to the vertical state. However, higher concentrations of CDs seem to produce undesirable effect which is reflected in the form of decrement in the value of ϵ' .

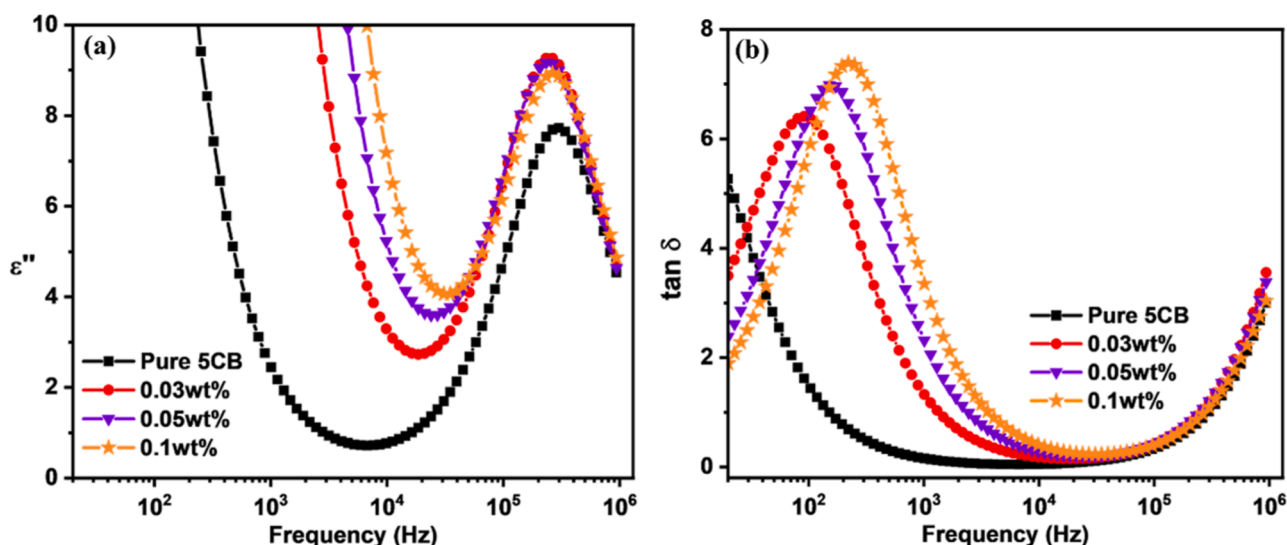


Fig. 4. Frequency dependent (a) dielectric loss (ϵ'') and (b) dielectric loss factor ($\tan \delta$) of the nematic phase of Pure 5CB and CDs-5CB composites at 29 °C.

The frequency dependent dielectric loss (ϵ'') and loss factor ($\tan \delta$) were also studied for pure CD-5CB and composites at 29 °C. Fig. 4(a) demonstrates the observance of a short axis relaxation peak (ν_R) at frequencies above 10^5 Hz in the ϵ'' plot verifying the vertical alignment of pure 5CB and its composites [21]. For Pure 5CB, ν_R is 2.9×10^5 Hz and further decrease to 2.48×10^5 Hz and 2.44×10^5 Hz for 0.03 and 0.05 wt %, respectively. However, for the highest concentration i.e., 0.1 wt%, ν_R increased to 2.61×10^5 Hz. Fig. 4(b) shows the effect of CDs on the ionic relaxation for Pure 5CB and CDs-5CB composites. It is observed that the value of $\tan \delta$ increases with an increase in dopant concentration. A shift in the ionic relaxation peak is also observed in the low frequency region. A point to be noted here is that ionic relaxation for Pure 5CB may be present at very low frequencies and hence not visible in the data shown in Fig. 4(b) as the frequency range was beyond the scope of the employed LCR meter. However, addition of CDs has produced a significant shift towards higher frequency. The ionic relaxation peak frequency for 0.03 wt% was observed to be at 89 Hz that increased to 159 Hz for 0.05 wt% and finally for 0.1 wt% the peak reached a frequency of 223 Hz. For the lowest concentration of 0.03 wt% this could be attributed to the faster relaxation of ions facilitated by the better vertical alignment produced by CDs. Furthermore, for 0.05 and 0.1 wt% the shift appears to be due to the enhanced space charge polarization effect due to increased ion density with concentration.

After probing the effect of CDs in 5CB at 29 °C (nematic phase), temperature dependent dielectric permittivity measurements were performed to examine the stability of the induced vertical alignment throughout the nematic phase. Fig. 5 shows the effect of temperature on ϵ' of Pure 5CB and CDs-5CB composites at a constant frequency of 10 kHz. At 29 °C, the value of ϵ' for Pure 5CB is 15.46 and it increased to 18.37 for 0.03 wt% and thereafter for 0.05 and 0.1 wt% it is reduced to 18.07 and 17.58, respectively. The graph clearly shows a decrease in the value of ϵ' with increasing temperature and could be attributed to the decrease in the orientational order of 5CB, NLC. Although ϵ' is decreasing it maintains the vertical state in the composites thereby illustrating the stability of the induced vertical alignment. The nematic to isotropic transition temperature i.e., clearing temperature (T_{NI}) for Pure 5CB is found to be 35 °C corroborating the reported value [53]. All CDs-5CB composites show the same T_{NI} as that of Pure 5CB demonstrating that in the concentration range studied the addition of CDs does not have any noticeable impact on its clearing temperature.

Further insight on the dielectric properties of the composites can be obtained from conductivity measurements. To analyze the impact of CDs on the conductivity (σ) of 5CB, we have employed the fundamental

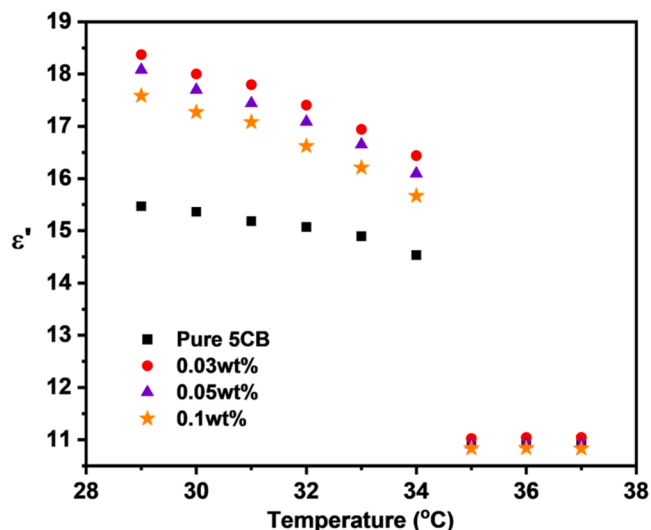


Fig. 5. Temperature dependent relative dielectric permittivity (ϵ') of Pure 5CB and CDs-5CB composites at a constant frequency of 10 kHz.

relationship between ϵ'' and σ as shown in Eq. (1) and obtained σ values for the acquired data.

$$\sigma = 2\pi f \epsilon_0 \epsilon'' \quad (1)$$

The conductivity plots shown in Fig. 6 for Pure 5CB and CDs-5CB composites at a constant temperature of 29 °C clearly demonstrates the significant enhancement in conductivity even at the lowest concentration of CDs i.e., 0.03 wt%. The plots were further fitted using the well-known Jonscher's Power law (JPL) [54,43] which is represented as:

$$\sigma(\omega) = \sigma_{DC} + \sigma_{AC} = \sigma_{DC} + A\omega^n \quad (2)$$

Here $\sigma(\omega)$ denotes the total conductivity of the material as a function of angular frequency, σ_{DC} and σ_{AC} represents the DC and AC conductivity, A is a pre-power-law factor, the exponent n is a constant varying between $0 < n < 1$ for disordered solids. For the samples under investigation, the value for the exponent 'n' lie above the "universal range" observed in disordered solids. Secondly, two regions can be observed in Fig. 6, a low frequency region exhibiting dc conductivity which can be seen as a plateau and secondly a high frequency region where the

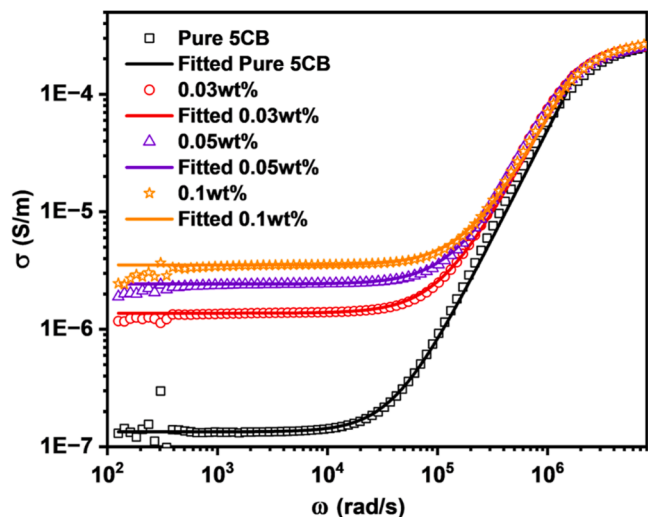


Fig. 6. Angular frequency (ω) dependent conductivity (σ) plots for the nematic phase of Pure 5CB and CDs-5CB composites at 29 °C. The symbols represent the experimental data and the solid lines denote the fitted data using Jonscher's Power Law (JPL).

conductivity shows a dramatic increase with increasing frequency. In our earlier report [55] on planar anchored sample cells, we have obtained three different regions in the conductivity curve which includes an electrode polarization (EP) regime in the low frequency region. In this work, the EP region is not prominent for Pure 5CB and 0.03 wt%, but for higher concentrations 0.05 and 0.1 wt% it is slightly visible, and it doesn't interfere with the dc conductivity regime. The effect of ions seems to be relatively lower in sample cells lacking an alignment layer as compared to cells with a planar polyimide alignment layer. The addition of 0.03 wt% of CDs in 5CB produces a one order of magnitude increase in the DC conductivity compared to Pure 5CB; however, for higher concentrations it exhibits a modest increment. For instance, the value of σ_{DC} for Pure 5CB is found to be $1.34 \times 10^{-7} \text{ S m}^{-1}$ which increased to $1.37 \times 10^{-6} \text{ S m}^{-1}$ for 0.03 wt% (one order of magnitude increment) and for the higher concentrations of 0.05 and 0.1 wt% it exhibited a value of 2.43×10^{-6} and $3.54 \times 10^{-6} \text{ S m}^{-1}$, respectively. Since the doping of CDs was able to induce a better vertical alignment with fewer defects at 0.03 wt%, the mobility of ions gets facilitated thereby portraying the highest increment in conductivity. For 0.05 and 0.1 wt% CDs, the system is seen to become more lossy (Fig. 4b). Formation of defects in the textures i.e. the distortion of alignment may produce more ions in the system thereby causing a marginal increase in the conductivity. The increase in conductivity in the unaligned sample cell is comparatively lower than the increment seen in planar anchored cell which may be attributed to the higher dissociation of ions experienced by CDs when interacting with polyimide alignment layers [55]. The variation of conductivity was explored with varying temperature through Arrhenius plots.

Fig. 7(a) shows the dependency of the longitudinal ($\sigma_{||}$) component of DC conductivity with respect to the inverse of the absolute temperature plotted using the Arrhenius equation [43] given as:

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (3)$$

$$\ln(\sigma_{||}) = \ln(\sigma_0) - \frac{E_a}{k_B T} \quad (4)$$

Here, E_a is the activation energy, σ_0 is a pre-exponential factor, k_B represents the Boltzmann constant and T is the absolute temperature. From Fig. 7(a), where the parameters E_a and σ_0 are obtained from the least squares fit to the data. Note that $\sigma_{||}$ increases with increase in temperature for all samples under investigation. With an increase in temperature the molecules lose their orientational ordering and the nematic becomes less viscous which eventually eases the flow of ions within the material contributing to the rise in conductivity. Additionally, we observed that the variation of dc conductivity as a function of temperature slows down for the CDs-5CB composite as compared to Pure 5CB. This slowing down can be ascribed to the addition of CDs in the Pure 5CB matrix that can cause a slight hindrance in the movement of ions, even though increasing temperature is making the system less viscous. However, it is not devoid of the constraints imparted by higher concentration of CDs (0.1 wt%) in the LC system as compared to Pure 5CB system where the movement of ions remains unhindered. Furthermore, Fig. 7(b) shows the variation of E_a with increasing dopant concentration. The values of fitted σ_{DC} values at $T = 29$ °C and activation energy related to ionic conductivity is summarized in Table 1. For Pure 5CB, E_a is 0.67 eV which is lowered by 21 % to a value of 0.531 eV for 0.03 wt% and for 0.05 wt% it is again reduced to 0.465 eV (31 %). However, for 0.1 wt%, the value is observed to rise back to 0.534 eV. This can be attributed to the observance of defect formation in the optical texture (Fig. 1(d)) and decrease of ϵ' (Fig. 3) which causes a hindrance in the flow of ions leading to the increased E_a .

4. Conclusion

The effect of doping CDs on the molecular alignment, dielectric, and electrical properties of 5CB, NLC in U-ITO sample cells (i.e., without

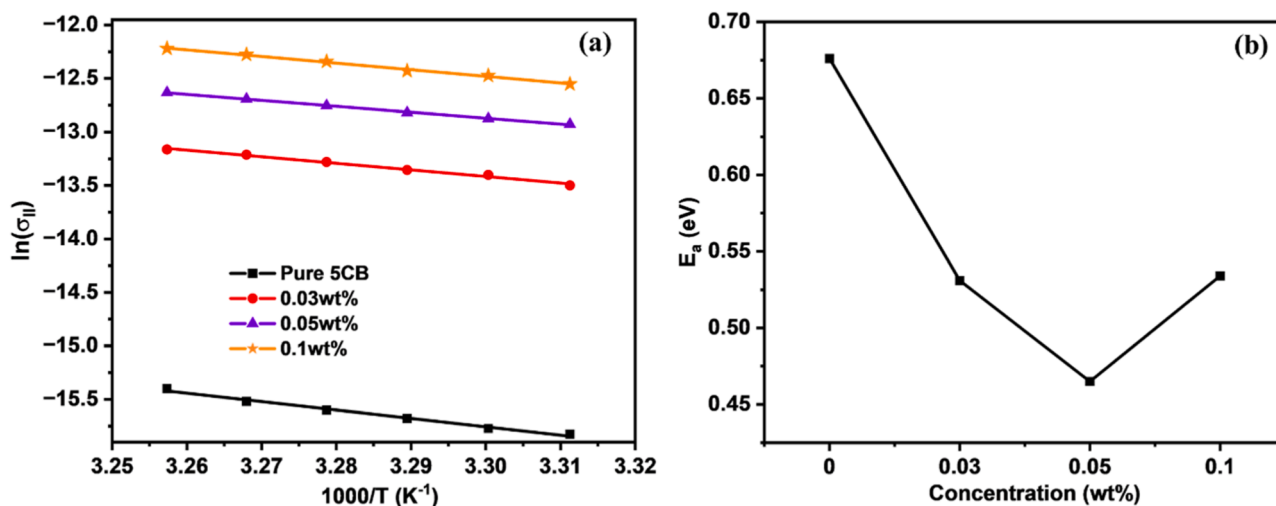


Fig. 7. (a) Variation of the longitudinal ($\sigma_{||}$) component of DC conductivity with inverse of absolute temperature (Arrhenius graph) where the symbols represent the experimental data and the solid lines denotes the fitting employed using Arrhenius equation, and (b) Concentration dependent activation energy for Pure 5CB and CDs-5CB composites. $\sigma_{||}$ denotes the value of conductivity measured along the director (n) of NLC.

Table 1

The fitted σ_{DC} values at $T = 29$ °C and activation energy related to ionic conductivity of Pure 5CB and its composites with CDs.

S. No.	Sample	Fitted σ_{DC} values at $T = 29$ °C (S m ⁻¹)	Activation Energy (eV)
1.	Pure 5CB	1.34×10^{-7}	0.676
2.	0.03 wt% CDs	1.37×10^{-6}	0.531
3.	0.05 wt% CDs	2.43×10^{-6}	0.465
4.	0.1 wt% CDs	3.54×10^{-6}	0.534

alignment layer) has been investigated in detail using optical polarizing microscopy and dielectric spectroscopy techniques. The induced vertical alignment of 5CB is obtained in the U-ITO sample cell and could be attributed to the strong intermolecular interaction between the polar 5CB molecules that lowers the van der Waals forces exhibited by the ITO surface. The quality of such induced vertical alignment is poor due to the presence of several defects. Therefore, to improve the quality of induced vertical alignment, doping of CDs of varying concentration into 5CB was performed. Optical texture and dielectric data confirm that the 0.03 wt% composite shows the best quality vertical alignment as compared to the composites of higher concentration and the pure sample. Interestingly, the thermal stability of vertical alignment is confirmed through temperature dependent optical texture and dielectric studies. The short axis molecular relaxation, a hallmark of vertical alignment, is also affected by the presence of CDs. Moreover, the DC conductivity is found to increase with an increase in the concentration of CDs. The activation energy, evaluated from Arrhenius plots, is also found to vary with dopant concentration. Our results clearly show that the 0.03 wt% CDs-5CB composite demonstrates the most uniform and defect-free vertical alignment as compared to composites of higher concentration and pure the 5CB sample. However, it is worth pointing out here that the electro-optical switching of vertical aligned 5CB in the vertical switching cell is not feasible due to the LC's positive dielectric anisotropy. To exploit the electro-optical switching, one could use either in-plane switching sample cells for positive dielectric NLCs or negative dielectric anisotropic NLCs in vertical switching sample cells. Our results clearly indicate the use of CDs to align 5CB, NLC vertically will pave the way forward to eliminate the requirement of alignment layers. We anticipate the use of such uniform and defect free vertical alignment of NLC, 5CB in sensors, high quality displays and other photonic devices of low cost.

CRediT authorship contribution statement

Priscilla P: Writing – original draft, Validation, Investigation, Formal analysis, Data curation. **Michael R. Fisch:** Writing – review & editing, Visualization, Validation. **Harikesh Meena:** Writing – review & editing, Formal analysis. **Srashti Tomar:** Writing – review & editing, Formal analysis. **Arvind K. Gathania:** Writing – review & editing, Visualization, Validation. **Sandeep Kumar:** Writing – review & editing, Visualization, Validation, Resources. **Jai Prakash:** Writing – review & editing, Visualization, Validation. **Supreet:** Writing – review & editing, Formal analysis. **Sanjeev Kumar:** Writing – review & editing. **Gautam Singh:** Writing – review & editing, Visualization, Validation, Supervision, Methodology, Investigation, Conceptualization.

Declaration of competing interest

No potential conflict of interest was reported by the authors.

Data availability

Data will be made available on request.

Acknowledgements

Authors are thankful to Prof. Sunita Rattan, Director, Amity Institute of Applied Sciences (AIAS), Amity University Uttar Pradesh (AUUP), Noida for her continuous encouragement and interest in the present work. We are also grateful to AUUP, Noida for providing the research facilities to carry out the present research work. Priscilla P would like to thank UGC for the fellowship awarded under the scheme Savitribai Jyotirao Phule Single Girl Child Fellowship (SJSJG 2022–2023). Jai Prakash and Gautam Singh are grateful to the Council of Science and Technology (CST), U. P., India for financial assistance under CST, U. P. funded research project (Project ID: 1960). Supreet, Sanjeev Kumar and Gautam Singh acknowledge the support provided under SERB SURE Grant no. SUR/2022/004020 of Govt. of India. M. Fisch was supported by a grant from the National Science Foundation (USA) under grant DMR-2211347.

References

- [1] M.G. Tomilin, S.A. Povzun, A.F. Kurmashev, E.V. Gribanova, T.A. Efimova, The application of nematic liquid crystals for objective microscopic diagnosis of cancer, *Liq. Cryst. Today* 10 (2001) 3.
- [2] R. Mazur, W. Piecsek, Z. Raszewski, P. Morawiak, K. Garbat, O. Chojnowska, M. Mrukiewicz, M. Oliferczuk, J. Kedzierski, R. Dabrowski, D. Weglowska, Nematic liquid crystal mixtures for 3D active glasses application, *Liq. Cryst.* 44 (2017) 417.
- [3] B.P. Singh, S. Sikarwar, K.K. Pandey, R. Manohar, M. Depriester, D.P. Singh, Carbon nanotubes blended nematic liquid crystal for display and electro-optical applications, *Elect. Mater.* 2 (2021) 466–481.
- [4] K. Wu, J.J. Sun, L. Gao, H. Xing, M. Cai, T. Zhao, C. Yang, W. Ye, X. Kong, Highly sensitive and transparent flexible temperature sensor based on nematic liquid crystals, *Liq. Cryst.* 49 (2022) 372.
- [5] B. Kieser, D. Pauluth, G. Gauglitz, Nematic liquid crystals as sensitive layers for surface plasmon resonance sensors, *Anal. Chim. Acta* 434 (2001) 231.
- [6] L.T. Creagh, A.R. Kmetz, Mechanism of surface alignment in nematic liquid crystals, *Mol. Cryst. Liq. Cryst.* 24 (1973) 59.
- [7] N.A.J.M. van Aerle, A.J.W. Tol, Molecular orientation in rubbed polyimide alignment layers used for liquid-crystal displays, *Macromolecules* 27 (1994) 6520.
- [8] Y. Reznikov, O. Ostroverkhova, K.D. Singer, J.H. Kim, S. Kumar, O. Lavrentovich, B. Wang, J.L. West, Photoalignment of liquid crystals by liquid crystals, *Phys. Rev. Lett.* 84 (2000) 1930.
- [9] K. Ruan, X. Shi, Y. Zhang, Y. Guo, X. Zhong, J. Gu, Electric-field-induced alignment of functionalized carbon nanotubes inside thermally conductive liquid crystalline polyimide composite films, *Angew. Chem. Int. Ed.* 62 (2023) e202309010.
- [10] M.I. Boamfa, S.V. Lazarenko, E.C.M. Vermalen, A. Kirilyuk, T. Rasing, Magnetic Field Alignment of Liquid Crystals for Fast Display Applications, *Adv. Mater.* 17 (2005) 610.
- [11] B. Sivarajini, R. Mangaiyarkarasi, V. Ganesh, S. Umadevi, Vertical alignment of liquid crystals over a functionalized flexible substrate, *Sci. Rep.* 8 (2018) 1.
- [12] H. Qi, T. Hegmann, Formation of periodic stripe patterns in nematic liquid crystals doped with functionalized gold nanoparticles, *J. Mater. Chem.* 16 (2006) 4197.
- [13] I. Son, J.Y. Yoo, J.H. Kim, B. Lee, C. Kim, J.H. Lee, Vertical alignment of liquid crystal using an in situ self-assembled molecular layer on hydrophilic ITO electrodes, *Ferroelectrics* 495 (2016) 174.
- [14] J. Cognard, Alignment of nematic liquid crystals and their mixtures, *Mol. Cryst. Liq. Cryst. Supplement Series* 1 (1982) 1–78.
- [15] M. Macchione, G. De Filipo, F. Emma, F.P. Nicoletta, N. Picci, G. Chidichimo, Characterization and alignment properties of rough substrates, *Mol. Cryst. Liq. Cryst. Sci. Technol. Sec. A. Mol. Cryst. Liq. Cryst.* 363 (2001) 137–147.
- [16] G. Singh, G. Vijaya Prakash, A. Choudhary, A.M. Biradar, Homeotropic alignment of nematic liquid crystals with negative dielectric anisotropy, *Phys. B Condens. Mat.* 405 (2010) 2118–2121.
- [17] L.T. Creagh, A.R. Kmetz, Mechanism of surface alignment in nematic liquid crystals, *Mol. Cryst. Liq. Cryst.* 24 (1973) 59–68.
- [18] H. Qi, T. Hegmann, Multiple alignment modes for nematic liquid crystals doped with alkylthiol-capped gold nanoparticles, *ACS Appl. Mater. Inter.* 1 (2009) 1731.
- [19] H. Qi, T. Hegmann, Impact of nanoscale particles and carbon nanotubes on current and future generations of liquid crystal displays, *J. Mater. Chem.* 18 (2008) 3288.
- [20] S.C. Jeng, C.W. Kuo, H.L. Wang, C.C. Liao, Nanoparticles-induced vertical alignment in liquid crystal cell, *Appl. Phys. Lett.* 91 (2007) 061112.
- [21] P.K. Singh, R. Dhar, R. Dabrowski, Enhancement of dielectric and electro-optical characteristics of liquid crystalline material 4'-octyl-4-cyano-biphenyl with dispersed functionalized and nonfunctionalized multiwalled carbon nanotubes, *Phys. Rev. E* 107 (2023) 044704.
- [22] P. Priscilla, P. Malik, Supreet, A. Kumar, R. Castagna, G. Singh, Recent advances and future perspectives on nanoparticles-controlled alignment of liquid crystals for displays and other photonic devices, *Crit. Rev. Solid State and Mater. Sci.* 48 (2023) 57.
- [23] J. Prakash, A. Kumar, S. Chauhan, Aligning liquid crystal materials through nanoparticles: a review of recent progress, *Liquids* 2 (2022) 50–71.
- [24] D. Varshney, J. Prakash, G. Singh, Indium tin oxide nanoparticles induced tunable dual alignment in nematic liquid crystal, *J. Mol. Liq.* 374 (2023) 121264.
- [25] D. Varshney, J. Prakash, G. Singh, Indium tin oxide nanoparticles induced molecular rearrangement in nematic liquid crystal material, *J. Mol. Liq.* 387 (2023) 122578.
- [26] A. Parveen, J. Prakash, G. Singh, Impact of strontium titanate nanoparticles on the dielectric, electro-optical and electrical response of a nematic liquid crystal, *J. Mol. Liq.* 354 (2022) 118907.
- [27] A. Kumar, G. Singh, Recent advances and future perspectives of photoluminescent liquid crystals and their nanocomposites for emissive displays and other tunable photonic devices, *J. Mol. Liq.* 386 (2023) 122607.
- [28] K. Bourzac, Quantum dots go on display, *Nature* 493 (2013) 283.
- [29] M.A. Cotta, Quantum dots and their applications: what lies ahead? *ACS Appl. Nano Mater* 3 (2020) 4920.
- [30] D. Bimberg, U.W. Pohl, Quantum dots: promises and accomplishments, *Mater. Today* 14 (2011) 388.
- [31] J. Mirzaei, M. Reznikov, T. Hegmann, Quantum dots as liquid crystal dopants, *J. Mater. Chem.* 22 (2012) 22350.
- [32] G. Singh, M. Fisch, S. Kumar, Emissivity and electrooptical properties of semiconducting quantum dots/rods and liquid crystal composites: a review, *Rep. Prog. Phys.* 79 (2016) 056502.
- [33] N.G. Singh, P. Malik, S. Kumar, P. Malik, A.K. Singh, Supreet, Tunable optical, electro-optical and dielectric properties of eco-friendly graphene quantum dots-nematic liquid crystal composites, *Liq. Cryst.* 50 (2023) 2345–2359.
- [34] A.A. Ansari, J. Prakash, Nidhi, Aafreen, S. Chauhan, G. Singh, Effect of perovskite quantum dots on the dielectric properties of a nematic liquid crystal material, *Indian J. Pure & Appl. Phys.* 62 (2024) 109–115.
- [35] B. Kinhead, T. Hegmann, Effects of size, capping agent, and concentration of CdSe and CdTe quantum dots doped into a nematic liquid crystal on the optical and electro-optic properties of the final colloidal liquid crystal mixture, *J. Mater. Chem.* 20 (2009) 448.
- [36] J. Mirzaei, M. Urbanski, K. Yu, H.S. Kitzerow, T. Hegmann, Nanocomposites of a nematic liquid crystal doped with magic-sized CdSe quantum dots, *J. Mater. Chem.* 21 (2011) 12710.
- [37] Supreet, G. Singh, Recent advances on cadmium free quantum dots-liquid crystal nanocomposites, *Appl. Mater. Today* 21 (2020) 100840.
- [38] A. Kumar, D.P. Singh, G. Singh, Recent progress and future perspectives on carbon-nanomaterial-dispersed liquid crystal composites, *J. Phys. D: Appl. Phys.* 55 (2022) 083002.
- [39] Neha, G. Singh, S. Kumar, P. Malik, Supreet, Recent trends and insights into carbon dots dispersed liquid crystal composites, *J. Mol. Liq.* 384 (2023) 122225.
- [40] M. Urbanski, J. Mirzaei, A. Sharma, D. Hofmann, H.S. Kitzerow, T. Hegmann, Chemically and thermally stable, emissive carbon dots as viable alternatives to semiconductor quantum dots for emissive nematic liquid crystal-nanoparticle mixtures with lower threshold voltage, *Liq. Cryst.* 43 (2) (2016) 183–194.
- [41] H. Eskalen, Influence of carbon quantum dots on electro-optical performance of nematic liquid crystal, *Appl. Phys. A* 126 (2020) 1–10.
- [42] A. Rastogi, G. Hegde, T. Manohar, R. Manohar, Effect of oil palm leaf-based carbon quantum dot on nematic liquid crystal and its electro-optical effects, *Liq. Cryst.* 48 (2021) 812.
- [43] A. Rastogi, F.P. Pandey, A.S. Parmar, S. Singh, G. Hegde, R. Manohar, Effect of carbonaceous oil palm leaf quantum dot dispersion in nematic liquid crystal on zeta potential, optical texture and dielectric properties, *J. Nanostruct. Chem.* 11 (4) (2021) 527.
- [44] P. Priscilla, S. Kumar, A.K. Gathania, A.K. Singh, J. Prakash, Supreet, S. Kumar, P. Malik, R. Castagna, G. Singh, Effect of Carbon dots in tuning molecular alignment, dielectric and electrical properties of a smectogenic cyanobiphenyl-based liquid crystal material, *J. Phys. D: Appl. Phys.* 57 (2024) 355302.
- [45] L.K. Gangwar, A. Kumar, G. Singh, A. Choudhary, Rajesh, S.P. Singh, A.M. Biradar, Probing the impact of carbon quantum dots on partially unwound helical mode in ferroelectric liquid crystals, *J. Appl. Phys.* 125 (2019) 125108.
- [46] W.K. Lee, S.J. Hwang, M.J. Cho, H.G. Park, J.W. Han, S. Song, J.H. Jang, D.S. Seo, CIS-ZnS quantum dots for self-aligned liquid crystal molecules with superior electro-optic properties, *Nanoscale* 5 (2013) 193.
- [47] P. Mahesh, A. Shah, K. Swamynathan, D.P. Singh, R. Douali, S. Kumar, Carbon dot-dispersed hexabutyloxytriphenylene discotic mesogens: structural, morphological and charge transport behavior, *J. Mater. Chem. C* 8 (2020) 9252.
- [48] P. Priscilla, et al., Carbon Dots induced homeotropic alignment in a negative dielectric nematic liquid crystal material [under communication], 2024.
- [49] S.J. Hwang, S.C. Jeng, C.Y. Yang, C.W. Kuo, C.C. Liao, Characteristics of nanoparticle-doped homeotropic liquid crystal devices, *J. Phys. D: Appl. Phys.* 42 (2008) 025102.
- [50] P. Priscilla, D. Varshney, J. Prakash, S. Kumar, A. Singh, P. Malik, Supreet, A. K. Gathania, R. Castagna, D.E. Lucchetta, G. Singh, Eco-friendly carbon dots induced thermally stable vertical alignment in planar anchored nematic liquid crystal, *J. Mol. Liq.* 385 (2023) 122318.
- [51] U.B. Singh, R. Dhar, A.S. Pandey, S. Kumar, R. Dabrowski, M.B. Pandey, Electro-optical and dielectric properties of CdSe quantum dots and 6CHBT liquid crystals composites, *AIP Adv* 4 (2014) 117112.
- [52] M.B. Pandey, T. Porenta, J. Brewer, A. Burkart, S. Čopar, S. Žumer, I.I. Smalyukh, Self-assembly of skyrmion-dressed chiral nematic colloids with tangential anchoring, *Phys. Rev. E Stat. Nonlin. Soft Matter Phys.* 89 (2014) 060502.
- [53] H. Yoshida, K. Kawamoto, H. Kubo, T. Tsuda, A. Fujii, S. Kuwabata, M. Ozaki, Nanoparticle-dispersed liquid crystals fabricated by sputter doping, *Adv. Mater.* 22 (2010) 622.
- [54] S.K. Prasad, M. Vijay Kumar, T. Shilpa, C.V. Yelamaggad, Enhancement of electrical conductivity, dielectric anisotropy and director relaxation frequency in composites of gold nanoparticle and a weakly polar nematic liquid crystal, *RSC Adv* 4 (2013) 4453.
- [55] P. Priscilla, A.K. Singh, P. Malik, S. Kumar, Supreet, A.K. Gathania, J. Prakash, R. Castagna, D.E. Lucchetta, P. Malik, G. Singh, Effect of doping of organo-soluble carbon dots on ionic relaxation and conductivity of planar anchored cyanobiphenyl based nematic liquid crystal, *J. Mol. Struct.* 1301 (2024) 137403.