

Effect of Perovskite Quantum Dots on the Dielectric Properties of a Nematic Liquid Crystal Material

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Dispersion of quantum dots (QDs) in liquid crystal (LC) medium can effectively modify their dielectric and electro-optical properties which can be useful in LC based display as well as non-display applications. Here, we reported the effect of doping of perovskite quantum dots (PQDs) on the dielectric properties of a nematic liquid crystal (NLC) material namely ZLI-1565 throughout its nematic and isotropic phases. The dielectric parameters of pure NLC and its composites with PQDs (0.1 wt.%, 0.25 wt.% and 0.5 wt. %) were observed in the frequency range of 20 Hz - 2 MHz. The value of dielectric permittivity (ϵ') and dielectric loss (ϵ'') increases in composites as compared to pure NLC in the low frequency region due to the increment in the mobile ion density. The spectral peak of loss factor ($\tan \delta$) of pure NLC shifts towards the high frequency region with the addition of PQDs. Moreover, the temperature dependent dielectric parameters were also evaluated for pure NLC and 0.25 wt.% PQDs-NLC composite (*i.e.* optimum concentration). Moreover, the dielectric anisotropy and threshold voltage were also evaluated for pure sample and 0.25 wt.% composite. A point to be noted here that the clearing temperature (T_{N-I}) of 0.25 wt.% composite is reduced by ~ 4 °C as compared to pure NLC. The results obtained on such PQDs-NLC composites could be utilized in the fabrication of NLC based electrical devices with tunable dielectric features.

Keywords: Nematic liquid crystal; Quantum dots; Dielectric permittivity

1 Introduction

Liquid crystal (LC) nanoscience has shifted towards the dispersion of quantum dots (QDs) in LC material for enhancing its dielectric and electro-optical properties for the fabrication of various devices¹. The LC is the intermediate phase between crystalline solids and isotropic liquids owning anisotropic electrical, magnetic, and optical properties. The molecules of LC transmit light which depends on their molecular orientation. When the light transmits through them after passing from polarizer, it changes the plane of polarization and enters the analyser. Thus, LCs can easily control the light passing through its molecules which is essential for the display devices. In addition, the orientation of LC molecules can be controlled by applying the electric field². They exhibit different phases based on the type of symmetry and order possessed by them such as nematic, smectic and cholesteric. The nematic (N) phase of LC (*i.e.* nematic liquid crystal, NLC) has long range orientational order with the rod-shaped molecules oriented in the preferred direction *i.e.*, director (n)³⁻⁵. It is widely used in display and non-display devices due to its tuneable

characteristics on applying the electric field. NLCs contain some mobile ions which exists during synthesis process or through polymer alignment layer and these ions significantly influence their dielectric properties in the low frequency region that needed to be improved to certain extent⁶.

On the other side, nanotechnology has a wide range of applications in the field of electronics and photonics due to their unique electrical and optical features and thus, it plays an important role in altering the properties of the material⁷. Dispersion of nanostructured materials in LC can enhance their dielectric features due to the guest-host interactions which has proved to be an effective method for optimization of LC properties. Various nanomaterials like metallic nanoparticles (NPs), ferroelectric NPs, semiconducting NPs such as quantum dots and carbon nanomaterials are dispersed in LC material to modify their properties⁸⁻¹⁷. On dispersing these guest entities, they increase or decrease the number of mobile ions in the material which effect their electro-optical properties¹⁸. Among these nanomaterials, QDs emerged has a new dopant for LC matrix due to their tuneable electronic and optical properties, high energy efficiency, strong confinement, and small size¹⁹. The

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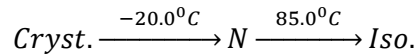
QDs are zero-dimensional nanomaterials with thousands of atoms that manifests high charge transfer properties. The dispersion of CdSe/ZnS QDs into NLC enhances the rotational viscosity due to increment in free ion concentration²⁰. For instance, the dielectric anisotropy and threshold voltage were found to decrease on the addition of CdSe/ZnS QDs in NLC (5CB) due to the trapping of ionic impurities on the surface of QDs²¹. Recently, perovskite QDs (PQDs) have gained immense attention due to their intrinsic superiorities with magnificent luminescence performance and conveniently adjustable emission which make them a suitable for the electro-optical devices²². For instance, Satapathy *et al.*^{23,24} reported the dual anisotropic and electrically switchable emission from the composites of CsPbBr₃ quantum cuboids and NLC using the polarised optical microscopy and fluorescence spectroscopy. Authors pointed out that results on these soft composites would be certainly useful in obtaining (i) backlight sources with narrow full width at half maximum (FWHM) and (ii) polarised emission to achieve high quality low-cost LC display devices. Afterwards, the physical properties of NLC material dispersed with PQDs were evaluated by Liu *et al.*²⁵ and found that the dielectric anisotropy, splay elastic constant and threshold voltage decreases with the increase in the concentration of PQDs due to the interaction between NLC and ligands of PQDs which creates disturbance in their orientation that will be beneficial for display devices with improved optical contrast and lower operating voltage. Recently, Sutar *et al.*²⁶ reported the enhanced photoluminescence intensity of NLCs doped with CsPbBr₃ PQDs and attributed to the significant improvement in the planar alignment of NLC molecules.

In the present article, we have dispersed PQDs (0.1 wt.%, 0.25 wt.% and 0.5 wt.%) in NLC, namely ZLI-1565 and investigated its effect on the dielectric properties of later using the frequency and temperature dependent dielectric spectroscopy. Dielectric parameters (dielectric permittivity, dielectric loss, and loss factor) were measured and found enhancement in these parameters on the dispersion of PQDs in NLC (ZLI-1565). Dielectric anisotropy and threshold voltage were also evaluated for pure NLC and PQDs dispersed NLC composites.

2 Experimental Details

In this study, we used a commercially available NLC material ZLI-1565. It has been procured from

Merck (E. Merck, Darmstadt, Germany) and used as a host material for doping of PQDs in varying concentrations. The phase sequence of the NLC material under investigation is as follows:



Where Cryst. represents crystalline phase, N represents nematic phase and Iso. represents isotropic phase of NLC (ZLI-1565)²⁷.

The dopant was oleic acid and oleylamine coated PQDs dispersed in toluene. The PQD dispersion was procured from Sigma Aldrich. To prepare the composites of PQDs with NLC material, we weighed 7 mg of NLC material in a vial. Thereafter, we added the appropriate amount of dispersion in weighted NLC material. It was again sonicated for an hour at 40 °C to ensure a uniform mixture of PQDs in NLC. Then the mixture was kept in an oven at a temperature, above the boiling point of toluene so that toluene could evaporate from the dispersion, and we obtained the PQDs-NLC composite. To observe the changes in the various dielectric parameters of the NLC material after the dispersion of the PQDs, we used commercially available homogeneously aligned LC cells (Instec Inc., Colorado, Boulder, USA) of 5 μm thickness with an active area of 100 mm². These LC cells consist of indium tin oxide (ITO) coated glass plates for electrode connections and rubbed in the parallel direction for homogeneous alignment. The LC cells were filled with pure and PQDs dispersed NLC composites via the capillary action method for measurements at room temperature. The dielectric parameters (ϵ' , ϵ'' , and $\tan \delta$) of the filled cells were measured using the LCR meter (E4980A, Keysight, USA) in the frequency range of 20 Hz to 2 MHz with an oscillation voltage of 500 mV. For the temperature-dependent dielectric measurements, we connected the LCR to a temperature controller (mk200, C100, INSTEC, USA) and a chiller (C100W, INSTEC, USA).

3 Results and Discussion

3.1 Dielectric measurements

Figure 1 exhibits the variation of dielectric parameters (ϵ' , ϵ'' and $\tan \delta$) of the pure NLC and PQDs doped NLC composites with frequency at 50 °C. The frequency measurements were carried out in the range of 20 Hz – 2 MHz and we observed the ionic effect of LC material, prominent in the low frequency region. Moreover, the instrument which we

have used for the dielectric measurements is operated in the above range. The frequency dependent real part of the complex dielectric permittivity (ϵ') for the pure sample and composites are shown in the Fig. 1(a). The variation in the value of ϵ' with frequency for the pure sample and composites shows the response of charge carriers towards the applied oscillating field²⁸. In the region of low frequency (*i.e.*, below 10^3 Hz), the value of ϵ' increases for the composites as compared to the pure NLC. This increment may be due to the increase in the number of ions after the doping of PQDs in the pure NLC²⁹. When the molecular reorientation follows the electric field, the induced polarization remains constant as observed in the mid regime but at high frequencies, the LC dipoles are no longer in phase with the applied electric field and the net orientational polarization reduces which results in the lower value of dielectric permittivity³⁰. Various LC based devices such as filters, audio wave transmitter such frequency for their operation. Moreover, Fig. 1(b) shows the variation in the imaginary part of the complex dielectric permittivity (ϵ'') with frequency for the pure sample and composites. The value of ϵ'' increases with the doping of PQDs up to the 0.25 wt. % concentration and after that it gets almost saturated. The increment in the value of ϵ'' represents the high

dielectric loss in the composites as compared to the pure NLC sample and could be attributed to the increased number of ions after the doping of PQDs²⁹.

The variation in the value of dielectric loss factor ($\tan \delta$) with frequency for the pure and composites is shown the Fig. 1(c). The low frequency relaxation peak is only observed for the composites with dopant concentration (≥ 0.25 wt.%) and could be attributed to the space charge polarisation³¹. However, as it appears from the graph that such low frequency relaxation peak is present in the pure sample and composites (< 0.25 wt.%) but not visible due to out of range of our measuring frequency window. Additionally, the value of low frequency relaxation increases with the increase in doping concentration of PQDs in NLC due to the increased number of ions. Moreover, the temperature dependent dielectric parameters as a function of frequency have been also measured for the pure sample and composites. Fig. 2 represents the value of ϵ' with a variation of temperature ranging from 10 °C to 98 °C for the pure NLC and 0.25 wt.% PQDs doped NLC composite. The temperature range is selected according to the phase sequence of LC material used for the experiment so that it can cover the whole LC phase and can provide the information regarding the phase transition from LC to isotropic phase. In the low

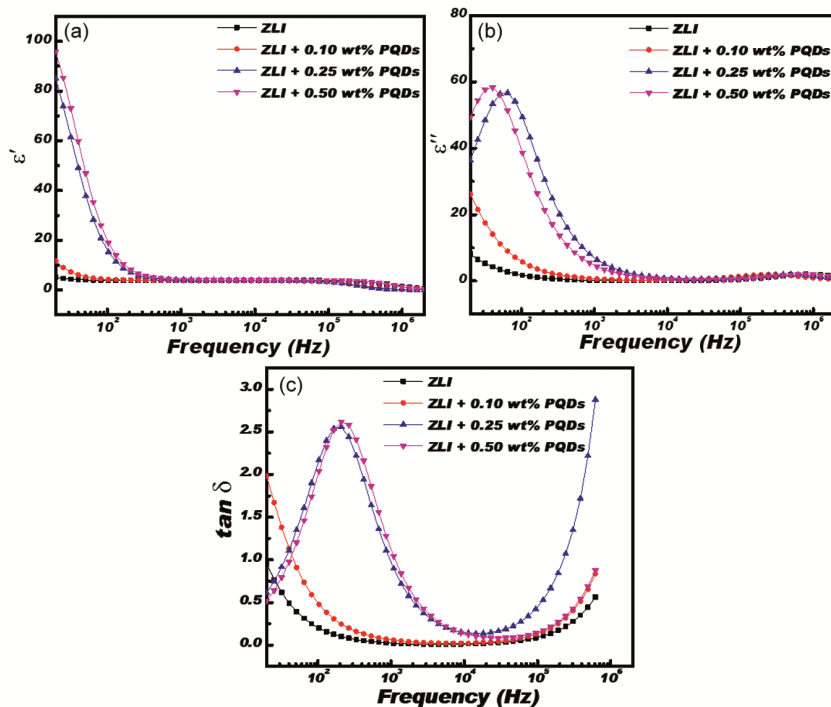


Fig. 1 — Variation of the (a) dielectric permittivity (ϵ'), (b) dielectric loss (ϵ'') and (c) loss factor ($\tan \delta$) as a function of frequency for the pure NLC and PQDs-NLC composite at a temperature of 50 °C.

frequency region, the value of ϵ' increases with the increase in temperature for both the pure NLC and 0.25 wt.% PQDs doped NLC composites. The increment in the value of ϵ' is found to be temperature and dopant concentration dependent. The rotational viscosity of NLC and its composite with PQDs in nematic phase would decrease with increase in temperature and facilitate easy movement of ions towards the electrodes (*i.e.* increase in space charge polarisation) and eventually lead to enhancement in the value of ϵ' ^{28,29,32}.

The increment in the value of ϵ' in nematic phase of 0.25 wt.% composite (Fig. 2(b)) as compared to pure NLC (Fig. 2(a)) is attributed to the increase in number of ions due to the dopant PQDs. Moreover, in the isotropic phase of pure and composite samples, the molecules are randomly oriented due to the lowering of viscosity and resulting into dominance of thermal agitation over the intermolecular interactions which create randomization of the molecules throughout the LC medium³³. Therefore, the increment in low frequency dielectric permittivity in the isotropic phase

could be attributed to the easy movement of mobile ions in the effect of measuring field as compared to the nematic phase³⁴⁻³⁶. Fig. 3 shows the variation of dielectric loss (ϵ'') with frequency for the pure NLC and 0.25 wt.% PQDs dispersed NLC composite at different temperatures. The magnitude of dielectric loss increases with the increase in temperature in the region of low frequency for both the pure and composite samples. This may be due to the (i) effective role of ions since the movement of ions towards the electrode, in the region of low frequency is faster than the rate of change of polarity of the applied field and (ii) thermal agitation at higher temperature the transportation of ions is more than the low temperature which results the increase in the value of dielectric loss³⁷. The value of low frequency peak in the Fig. 3(b) is found to be shifted towards the higher frequency side with the increase in temperature. This shift may be due to the decrease in the rotational viscosity of the LC sample cell with increase in temperature^{28,38}. The increment in the value of ϵ'' for the composite as compared to the pure

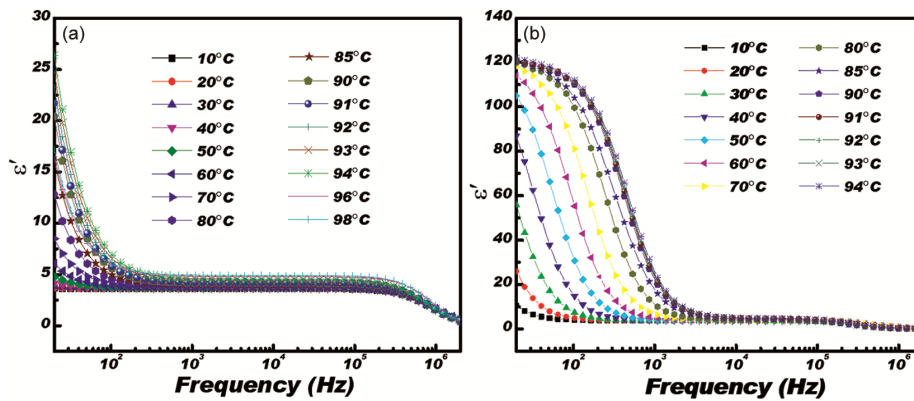


Fig. 2 — Variation of temperature-dependent dielectric permittivity as a function of frequency for (a) pure NLC and (b) 0.25 wt.% PQDs-NLC composite.

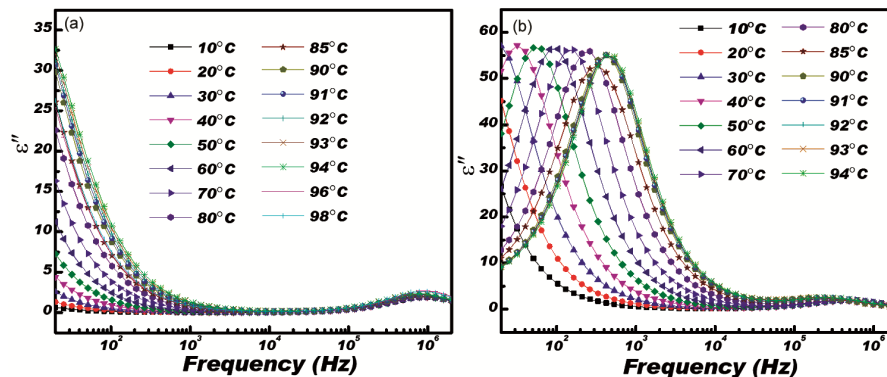


Fig. 3 — Variation of the temperature-dependent dielectric loss as a function of frequency for (a) pure NLC and (b) 0.25 wt.% PQDs-NLC composite.

sample at each value of temperature may be due to the increased ion density after the doping of PQDs²⁹.

Figure 4 shows the frequency dependent variation of $\tan \delta$ for the pure NLC and 0.25 wt.% PQDs doped NLC composite with variation of temperature. The low frequency relaxation peak observed in both the Fig. 4 (a, b) is due to the effect of ion diffusion and space charge polarisation^{28,35}. The magnitude of low frequency peak in the composite is found to be higher as compared to the pure NLC which attributed the higher dissipation of energy in the composite as compared to the pure NLC²⁹. Moreover, the value of low frequency peak is shifted towards the higher frequency side with the increase in temperature which is suggesting the easy transportation of ions with the increase in temperature³⁸.

3.2 Dielectric anisotropy

Dielectric anisotropy ($\Delta\epsilon$) is an important parameter which defines how effectively a LC molecule reorient in response to the applied field and

also gives information about the nematic to isotropic transition. Fig. 5 shows the variation in the value of ϵ_{\perp} and ϵ_{\parallel} with the temperature at a frequency of 1 kHz for the pure NLC and 0.25 wt.% PQDs doped NLC composite. The value of $\Delta\epsilon$ is calculated by the difference between the parallel (ϵ_{\parallel}) and perpendicular (ϵ_{\perp}) component of dielectric permittivity at 1 kHz. The variation in the value of $\Delta\epsilon$ can be explained by the Maier-Meier theory³⁹.

$$\Delta\epsilon = \frac{NHF}{\epsilon_0} \left[\Delta\alpha - \frac{F}{2KT} \mu^2 (1 - 3\cos^2\beta) \right] S$$

Where N is the number density of molecules, F is the feedback factor, S is the order parameter, $\Delta\alpha$ is the anisotropy of the polarizability, μ is the resultant dipole moment and β is the angle between the dipole moment and long axis of the molecule.

The decrease in the value of dielectric anisotropy with temperature can be understood by the decrease in the value of S. When the temperature increases, the

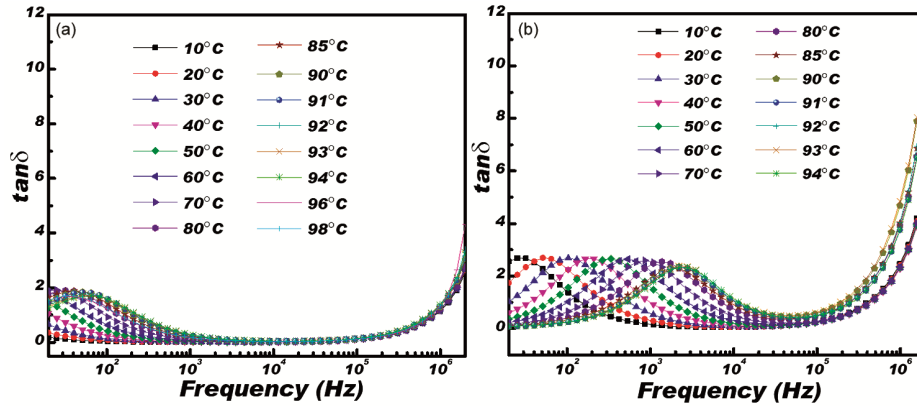


Fig. 4 — Variation of the temperature-dependent dielectric loss factor as a function of frequency for (a) pure NLC and (b) 0.25 wt.% PQDs-NLC composite.

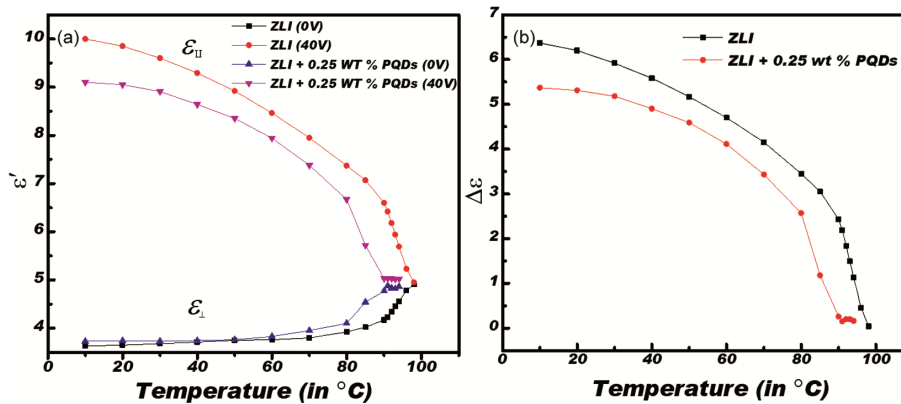


Fig. 5 — Variation of (a) temperature dependent parallel and perpendicular component of ϵ' and (b) $\Delta\epsilon$ with temperature for pure NLC and 0.25 wt.% of PQDs-NLC composite. The 40 V dc bias was applied to change the alignment of sample cell from homogeneous to homeotropic to obtain the parallel component of ϵ' .

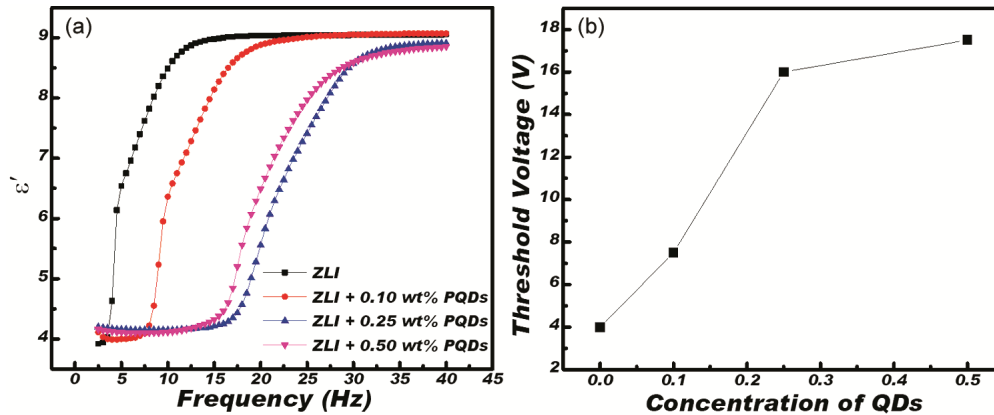


Fig. 6 — Variation of (a) ϵ' with voltage and (b) threshold voltage as a function of concentration of PQDs-NLC composite.

order of LC molecules decreases due to the thermal agitation and on further increasing the temperature, they approach towards the isotropic liquid phase where the long-range interactions no longer exist. Hence, the anisotropies that distinguish LCs disappear and becomes weaker with temperature⁴⁰. The value of dielectric anisotropy decreases for 0.25 wt.% of PQDs doped NLC composite as compared to the pure NLC and could be attributed to the decrease in the orientational ordering of LC molecules. Moreover, the clearing temperature (T_{N-I}) of the composite is reduced by ~ 4 °C as compared to the pure sample and which further corroborates well with the decrease in the order parameter of NLC by the dopant PQDs.

3.3. Threshold Voltage

We have also measured the threshold voltage (V_{th}) for the pure NLC and PQDs doped NLC composites. Fig. 6 (a) shows the variation in the value of real dielectric permittivity (ϵ') with the DC bias voltage at a particular frequency of 1kHz for the pure and PQDs doped NLC composites. The value of V_{th} is calculated by the 10 % change in the initial value of dielectric permittivity. Fig. 6(b) shows that the value of V_{th} increases with the doping of PQDs in NLC up to the optimum concentration (*i.e.*, 0.25 wt.%) and after that it gets almost saturated. The increase in the value of V_{th} is attributed to the increment in screening effect caused by the increased number of ions due to the dopant PQDs⁴¹.

4 Conclusion

We have observed the effects of PQDs on the dielectric properties of NLC (ZLI-1565) material by the measurements of dielectric parameters as function of frequency, DC voltage, temperature, and dopant

concentration. The value of dielectric permittivity (ϵ'), dielectric loss (ϵ'') and dielectric loss factor ($\tan \delta$) are found to be higher for the composites as compared to the pure NLC material. The increment in the magnitude of these dielectric parameters (ϵ' , ϵ'' and $\tan \delta$) clearly indicates the presence of more ions after the doping PQDs in the NLC material. We have obtained 0.25 wt.% as an optimum concentration of dopant PQDs and after that the dielectric parameters get saturated. Moreover, we have observed the shift in the value of low frequency relaxation peak towards the higher frequency side which actually manifests the effects of increased ion density. We have also observed the increment in the value of threshold voltage with the doping of PQDs in the NLC material which confirms the presence of more ions in the composites. The significant reduction in the clearing temperature (T_{N-I}) of investigated NLC after doping of PQDs for the 0.25 wt.% has been observed. It is clear from our results that significant (i) increase in threshold voltage and dielectric anisotropy and (ii) decrease in clearing temperature of 0.25 wt% composite as compared to pure NLC, would not be useful for the display applications. However, we do anticipate that such PQDs doped NLC composites would be useful in the fabrication of NLC based electrical devices with tunable dielectric features and test bed for the understanding the effect of PQDs on the ionic effect of NLC materials.

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Conflict of Interest:

The authors declare that they have no conflict of interest.

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